1. INTRODUCTION

Purpose and Objectives

The current energy system is based on naturally available fossil fuels. As domestic supplies of these fuels dwindle and the energy demand continues to grow, more and more fossil fuels are imported. In the long term, the United States may change its energy system to one that is self-sufficient, based on solar, nuclear, and other nonfossil energy sources. The energy from these sources could be used to make electricity or, as has recently been suggested, could be transformed into a synthetic chemical fuel. This project was undertaken to provide the National Aeronautics and Space Administration with technical and economic information on the possibilities of producing and utilizing just such a synthetic energy carrier — hydrogen.

The objectives of this study were —

- To identify and evaluate all developed processes for the production of hydrogen and to assess any novel or unconventional methods discovered during the study
- To review present and potential uses of hydrogen as a fuel, in residential and industrial applications, and as a chemical feedstock
- To prepare recommendations for a series of research projects to develop the technologies needed to bring about a significant use of hydrogen fuel in the United States
- To provide an estimate of the cost of developing these technologies in a broad R&D program planned for the next 5 years.

This report discusses known processes for the production of hydrogen and the present and future industrial uses of hydrogen as a fuel and as a chemical feedstock. Novel and unconventional hydrogen-production techniques have been evaluated, with emphasis placed on thermochemical and electrolytic processes. Potential uses for hydrogen as a fuel in industrial and residential applications were identified and reviewed in the context of anticipated U.S. energy supplies and demands. A detailed plan for the period from 1975 to 1980 has been prepared for research on and development of hydrogen as an energy carrier.

Scope and Definitions

Included in the scope of this study were all hydrogen-production techniques that have been proposed in the literature; studied in laboratories; or operated on a pilot, demonstration-, or commercial-plant scale. Several processes were selected for more detailed study:

- Hydrogen production by electrolysis of pure and impure water
- Thermochemical hydrogen-production processes
- Hydrogen production from coal and water
- Hydrogen production from sunlight and water by photosynthesis or by electrochemical photolysis.

To survey other hydrogen-production processes, the recent literature was was reviewed; and a search was made of U.S patents granted between 1917 and 1974.

The transmission, storage, and delivery of hydrogen were reported on from information presented in the literature. Data on the industrial and residential uses of hydrogen were gathered both from the literature and from interviews conducted with industry representatives. Hydrogen's role in the manufacture of synthetic hydrocarbon fuels was given special attention and is reported on in a separate section.

The use of hydrogen in transportation – whether for automobiles, aircraft, or ships – was specifically excluded from the scope of the study. The potential hydrogen demand by these fuel markets should be kept in mind as the report is reviewed.

To put in context the concept of hydrogen as an energy carrier, this report includes a review of U.S. energy supplies and demands, presented as two energy "models."

Two energy demand and supply projections (models) are detailed — an optimistic possibility of domestic energy self-sufficiency, as well as a pessimistic possibility of continued dependence on energy imports. The projections are not intended to be models of energy allocation; rather, they are intended to show quantitatively the hypothetical deficits and excesses that could exsist in the future. For certain years, the models show energy deficits that must be filled either by imports or by an energy carrier (such as hydrogen) produced from a previously undedicated energy source.

We have chosen to include in this report our survey of industrial hydrogen that is produced "onsite" from feedstocks such as natural gas. Although this "captive" hydrogen may be recombined into another chemical a few minutes after its production, it represents a demand that could be satisfied by synthetic-fuel hydrogen, should it become available at a competitive cost.

In this report, all figures that refer to a quantity of hydrogen as a number of Btu or that cite a hydrogen price in terms of dollars per million Btu are calculated on the basis of gross (or higher) heating value.

2. POTENTIAL DEMANDS FOR HYDROGEN – J. B. Pangborn and J. C. Gillis

Introduction

Two models have been developed to project the U.S. domestic energy demand and supply for the period from 1975 to 2000. These models show the need for development of more conventional and new (unconventional) energy sources and for the conversion of these sources to useful chemical energy and electricity. These hypothetical models are based on assumed growth rates for energy consumption and energy supply. They are intended to delimit the situation that will actually occur in the future in terms of energy deficits and maximum hypothetical demands for hydrogen.

These models do not predict a "most likely" situation, and they are not intended as recommendations for energy allocation. They have been constructed to estimate the bounds of the energy deficits and/or excesses expected for various domestic market sectors. This allows a prediction of the maximum need for alternative fuels (including hydrogen), synthesized from additional or new energy sources, when energy imports from foreign sources are excluded. Hydrogen could be synthesized from either additional conventional energy sources (including nuclear fission) or new energy sources (including solar energy or nuclear fusion).

The premises on which the two models, denoted Model I and Model II, are based are illustrated below. Model I is the "optimistic" case, requiring the least additional energy and the least hydrogen; and Model II is the "pessimistic" case because of the predicted energy deficits and the huge requirements of additional energy.

	Model I	Model II
Energy Supply	IGT post-1973 energy supply projection: high level of supply with synthesized fuels, in the spirit of Project Independence	IGT pre-1973 energy supply projection: moderate level of supply, including some synthesized fuels using coal and oil shale
Energy Demand	NPC "low level" of demand: low rates of economic growth, expensive energy, and energy conservation	NPC "high level" of demand: high rates of economic growth, cheap energy, and little energy conservation

	Model I	Model II
Energy Deficit	Moderate deficits requiring new (more) energy sources and imported energy, large deficits after 1990, complete self-sufficiency unlikely	Extreme deficits requiring huge amounts of new energy and imports, domestic self-sufficiency impossible

Model I Energy Demand and Supply

The assumptions and bases of the energy demand and supply in Model I are presented below. This model determines the lower bound (the least amount) of hydrogen and of additional synthesized fuels and the additional electricity that will be needed, along with imports, to satisfy the U.S. domestic energy demand for the period from 1975 to 2000. We emphasize that these energy requirements are in addition to the synthetic fuel supplies (e.g., SNG) that are projected (optimistically) within the model to be available from coal and oil shale.

Model I Bases and Information Sources

In the future, all market sectors will receive percentages of the total energy supply that differ somewhat from the present percentages. Market-sector-demand growth rates for 1970 to 1985 are patterned after the "low level of demand" presented in the authoritative NPC report for 1973, U.S. Energy Outlook.[7] For this model and during this period, the annual growth in the total energy demand falls from about 3.5% to about 3.3%. We have extrapolated this low-level-demand projection to the year 2000 and have used an average annual growth rate of 2.8% for the period from 1985 to 2000. The growth rates for individual market sectors are listed in Table 2-1. In this model, the electricity-generating sector grows at a rate necessary to adequately supply the other sectors, but this rate does not exceed 5.5%/yr for the supply of electricity to the residential/commercial sector of 6.0%/yr for that to the industrial sector.

Table 2-1. ANNUAL GROWTH RATE OF DEMAND
(Low Level)

Market Sector	1970-1980	1980-1985	1985-2000
		%/yr	
Residential/Commercial	3.0	2.5	2.8
Industrial	2.1	1.9	2.8
Transportation	3.5	3.0	2.8
Other	4.3	5.5	2.8

For this model, the energy supply levels for the future are patterned after two sources: "A Program for Maximizing U.S. Energy Self-Sufficiency" by H. R. Linden[5] and the IGT feasibility study, "Alternative Fuels for Automotive Transportation," performed for the EPA.[8] This is an optimistic model for a future high-level energy supply. It typifies the goals of Project Independence by assuming the rapid development of domestic sources of fossil energy, synthesized fuels, and nuclear power.[6]

Model I Assumptions

The assumptions for Model I include those in respect to –

- Oil supply:

Oil Supply = Domestic Crude Oil + Condensates +
Natural Gas Liquids + Coal Liquids
(Hydrocarbons and/or Methanol)
After 1980* + Syncrude Products
From Oil Shale After 1980

The transporation sector receives its historic portion, 54.7%, of the oil supply in 1975. After 1975, this market is supplied with all of the shale syncrude plus at least 55% of the remaining oil supply, including coal liquids.

The residential/commercial sector receives its historic portion of the oil supply, excluding shale oil products. This is 21% of the crude and coal liquids.

The industrial sector receives its historic portion of the oil supply, excluding shale oil products. This is 17.5% of the crude and coal liquids.

The other-uses sector receives 0.6% of the supply of crude and coal liquids.

The electricity-generating sector continues, until 1975, to increase its use of oil. Thereafter, this portion remains constant at 6.2% of the 1975 oil supply. Electricity is produced from oil at a 35% efficiency (delivered).

- Gas supply:

Gas Supply = Domestic Natural Gas + SNG
(Coal-Based) After 1980†

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* Coal converted to delivered hydrocarbons at a 65% efficiency. Coal converted to delivered methanol at a 45% efficiency.

† Coal converted to delivered SNG at a 65% efficiency from 1980 to 2000.

The residential/commercial sector receives its historic portion, about 32%, of the natural gas in 1975. Because of priorities and allotments, this percentage grows to more than 36% by the year 2000. About one-half of the SNG produced goes to this market.

The industrial sector receives its historic 35.5% of the gas supply.

The electricity-generating sector does not increase its use of gas after 1970. Its historic portion is 17.4% of the 1970 supply. No SNG goes to this market. Electricity is generated from gas at a 35% efficiency (delivered).

The other-uses sector is supplied with about 15% of the natural gas, plus SNG.

The transportation sector uses negligible natural gas and SNG.

- Coal supply (for direct uses, not chemical fuel synthesis). The electricity-generating sector uses its historic 61.9% of the coal supply from 1970 to 1975 and 64.3% of the supply thereafter. Electricity is generated from coal at a 35% efficiency (delivered).

  The industrial sector uses 35.7% of the coal supply (from 1970 to 2000).

  The residential/commercial sector uses 2.3% of the coal supply from 1970 to 1975 and negligible amounts thereafter.

  Negligible coal is used by the transportation and other-uses sectors.

- Electricity consumption. The residential/commercial sector consumes electricity at a rate that grows by 5.5% annually from 1975 to 2000.

  Consumption by the industrial sector grows but the rate does not exceed 6%. (In many years, the demand is not satisfied.)

  The transportation and other-uses sectors consume relatively small amounts of electricity, although the amount consumed by the transportation sector increases rapidly (more than 6%/year).

- Nuclear heat (heat energy, not power). The electricity-generating sector consumes nuclear heat in generating electricity. The electricity demand is determined by the other market sectors. The total nuclear-heat requirement consists of the product electricity (in heat units) plus the waste heat of generation. For purposes of this model, nuclear heat is not used by any other sector, although the model shows that some would be available to other sectors for process uses in fuel synthesis. Electricity is generated from nuclear heat with an efficiency that is at least 35% after 1985.

- Geothermal heat and hydropower. Geothermal heat is used for electricity generation, and it is included with hydropower (as heat) as an energy supply for the electricity-generating sector. In the case of hydropower, of course, waste heat is not significant, and a fuel supply is not required.

- Hydrogen production. In this model, the total supply of fossil fuels, geothermal heat, and hydropower is consumed. However, some potential surplus nuclear heat (not used for electricity generation) does exist. This heat could be used for hydrogen production as follows:

Nuclear heat converted to delivered hydrogen via electrolysis	30% efficient from 1980 to 1985 35% efficient from 1985 to 2000
Nuclear heat converted to delivered hydrogen via thermochemical processes	45% efficient from 1990 to 2000

Model I Overall Demand and Supply Projections

Using the model bases for projections, the energy demands and supplies can be determined by market sector and by type, respectively. We have calculated the market sector demands, and they are presented in Table 2-2. In this table, the electricity-generation demand is the quantity of waste heat resulting from and required in the generation of electricity. The electricity so produced is matched to and included in the projected demands of the other market sectors. The Model I energy supply is presented in Table 2-3.

It should be noted that although the total energy supply numerically exceeds the total demand (by a small amount) after about 1985, this does not imply domestic self-sufficiency, primarily because some of the energy supply, notably the nuclear heat, would be converted to additional useful fuels (or electricity). The associated waste heat is not utilized as a fuel and is in addition to the heat demand listed in Table 2-2 for the electricity-generating sector. This additional waste heat cannot be used to satisfy the demands of the other market sectors; hence, energy (fuel) shortfalls will occur.

Model I Energy Demand and Supply, by Sector

We have used the Model I assumptions to determine the apportionment of domestic energy supplies to the various market sectors: residential/commercial, industrial, transportation, other uses (miscellaneous and nonenergy uses of fuels such as for petrochemical feedstocks, chemical commodities, fertilizers, and lubricants), and electricity generating. The demand and supply projections for these respective market sectors are presented in Tables 2-4 through 2-8. The unfilled demand (the bottom line in Tables 2-4 through 2-7) is the energy deficit to be filled by development of more of the same energy sources than is predicted by the model, exploitation of new energy sources, and energy imports.

Table 2-2. MODEL I ENERGY DEMAND BY MARKET SECTOR

	1970	1975	1980	1985	1990	1995	2000
Market Sector	10^{15} Btu						
Residential/Commercial	15.8	18.3	21.1	23.9	27.5	31.6	36.3
Industrial	20.0	22.2	24.7	27.1	31.1	35.7	41.0
Transportation	16.3	19.3	23.0	26.7	30.6	35.1	40.3
Electricity Generating*	11.6	12.8	16.7	18.3	23.4	31.6	41.6
Other	4.1	5.1	6.2	8.1	9.3	10.8	12.3
Total	67.8	77.7	91.7	104.1	121.9	144.8	171.5

* Matched to electricity demand in other sectors, This is waste heat only.

Table 2-3. MODEL I DOMESTIC ENERGY SUPPLY

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Crude Oil and Condensates	21.0	22.9	27.2	29.6	28.7	26.4	24.3
Natural Gas	22.4	23.5	23.6	26.7	28.5	26.3	24.1
Coal (Direct Use)	13.1	16.0	18.6	21.5	24.9	28.9	33.3
Coal (SNG)	0.0	0.0	1.0	2.0	4.0	6.0	8.0
Coal (Liquids)	0.0	0.0	0.2	1.1	3.7	6.9	10.2
Shale Syncrude	0.0	0.0	0.6	1.9	4.7	5.5	6.7
Hydro- and Geothermal Power (as Heat)	2.7	3.0	3.5	4.0	4.5	5.0	5.5
Nuclear Heat	0.2	3.5	9.5	21.0	30.0	42.0	60.0
Total	59.4	68.9	84.2	107.8	129.0	147.0	172.1

Table 2-4. MODEL I RESIDENTIAL AND COMMERCIAL ENERGY DEMAND AND SUPPLY (Domestic)

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Demand	15.8	18.3	21.2	23.9	27.5	31.6	36.3
Fossil-Fuel Supply							
Oil (21% of Crude + Coal Liquids)	4.4	4.8	5.8	6.4	6.8	7.0	7.2
Gas (Available Supply)	7.0	7.6	8.1	10.1	12.0	11.8	11.7
Coal (2.3% of Supply)	0.3	0.3	0.0	0.0	0.0	0.0	0.0
Total Fossil	11.7	12.7	13.9	16.5	18.8	18.8	18.9
Electricity Consumption	2.7	3.2	4.2	5.5	7.2	9.4	12.3
Total Supply	14.4	15.9	18.1	22.0	26.0	28.2	31.2
Unfilled Demand	1.4	2.4	3.1	1.9	1.5	3.4	5.1

Table 2-5. MODEL I INDUSTRIAL ENERGY DEMAND AND SUPPLY (Domestic)

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Demand	20.0	22.2	24.7	27.1	31.1	35.7	41.0
Fossil-Fuel Supply							
Oil (17.5% of Crude + Coal Liquids)	3.7	4.0	4.8	5.4	5.7	5.8	6.0
Gas (35.5% of Supply)	7.9	8.3	8.7	10.2	11.5	11.5	11.4
Coal (35.7% of Supply)	4.7	5.7	6.6	7.7	8.9	10.3	11.9
Total Fossil	16.3	18.0	20.1	23.3	26.1	27.6	29.3
Electricity Consumption	2.3	3.0	4.0	3.8	5.0	6.7	9.0
Total Supply	18.6	21.0	24.1	27.1	31.1	34.3	38.3
Unfilled Demand	1.4	1.2	0.6	0.0	0.0	1.4	2.7

Table 2-6. MODEL I TRANSPORTATION ENERGY DEMAND AND SUPPLY
(Domestic)

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Demand	16.3	19.3	23.0	26.7	30.6	35.1	40.3
Fossil-Fuel Supply							
Oil (Shale Syncrude + Balance)	11.5	12.5	15.7	19.2	23.0	24.4	26.3
Gas*		--	--	--	--	--	--
Coal (0.1% of Supply)*	--	--	--	--	--	--	--
Total Fossil	11.5	12.5	15.7	19.2	23.0	24.4	26.3
Electricity Consumption	--*	--*	0.2	0.3	0.4	0.6	0.8
Total Supply	11.5	12.5	15.9	19.5	23.4	25.0	27.1
Unfilled Demand	4.8	6.8	7.1	7.2	7.2	10.1	13.2

* Negligible.

Table 2-7. MODEL I OTHER-USES ENERGY DEMAND AND SUPPLY
(Domestic)

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Demand	4.1	5.1	6.2	8.1	9.3	10.8	12.3
Fossil-Fuel Supply							
Oil (0.6% of Supply)	0.1	0.1	0.2	0.2	0.2	0.2	0.3
Gas (15.8% of Supply)	3.5	3.7	3.9	4.5	5.1	5.1	5.1
Coal (0.0% of Supply)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total Fossil	3.6	3.8	4.1	4.7	5.3	5.3	5.4
Electricity Consumption*	0.1	0.1	0.2	0.2	0.2	0.3	0.3
Total Supply	3.7	3.9	4.3	4.9	5.5	5.6	5.7
Unfilled Demand	0.4	1.2	1.9	3.2	3.8	5.2	6.6

* Expressed as a constant percentage, 2.5% of the total demand.

Table 2-8. MODEL I ELECTRICITY GENERATION

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Demands							
Electricity Produced	5.0	6.3	8.6	9.8	12.8	17.0	22.4
Waste Heat Required	11.3	12.8	16.7	18.3	23.4	31.6	41.6
Total Heat	16.3	19.1	25.3	28.1	36.2	48.6	64.0
Fossil-Fuel Supply							
Oil (6.2% of 1975 Supply)	1.3	1.4	1.4	1.4	1.4	1.4	1.4
Gas (17.4% of 1970 Supply)	3.9	3.9	3.9	3.9	3.9	3.9	3.9
Coal*	8.1	9.9	12.0	13.8	16.0	18.6	21.4
Total Fossil	13.3	15.2	17.3	19.1	21.3	23.9	26.7
Hydro- and Geothermal Power†	2.7	3.0	3.5	4.0	4.5	5.0	5.5
Nuclear Heat Required for Remaining Demand	0.3	0.9	4.5	5.0	10.4	19.7	31.8
Total Heat Supply	16.3	19.1	25.3	28.1	36.2	48.6	64.0

* 61.9% of supply from 1970 to 1975, 64.3% thereafter.

† Heat equivalent of hydropower plus heat required for geothermal power.

Model I Demand and Potentials for Hydrogen Production

The demands of the electricity-generating sector, depicted in Table 2-8, do not use all of the potentially available energy supplies: According to the apportionments in this model, some potential excess nuclear heat remains unused. Alternatively (with different model assumptions), some coal could remain unused, instead of this nuclear heat. This nuclear heat is in excess only in the sense that the electricity-generating sector does not need it, and it is potentially available according to the projections used as a basis for Model I. Other sector deficits, summarized in Table 2-9, could be partially filled with a useful fuel generated from this nuclear heat. If this fuel were hydrogen, the potential quantities generated would be as shown in Table 2-9.

Table 2-9. MODEL I MAXIMUM DEMAND AND POTENTIALS FOR HYDROGEN PRODUCTION

	1975	1980	1985	1990	1995	2000
	10^{15} Btu					
Unfilled Demands per Sector*						
Residential/Commercial	2.4	3.0	1.9	1.5	3.4	5.1
Industrial	1.2	0.6	0.0	0.0	1.4	2.7
Transportation (25% of Total Demand for This Sector)	1.7	1.8	1.8	1.9	2.5	3.3
Other	1.2	1.9	3.2	3.8	5.2	6.6
Potential Hydrogen Demand	6.5	7.3	6.9	7.2	12.5	17.7
Unused Nuclear-Heat Supply	2.6	5.0	16.0	19.6	22.3	28.2
Potential Hydrogen Supply (Nuclear Heat)						
Electrolysis	0.0	1.5	4.8	6.1	6.1	6.1
Thermochemical	0.0	0.0	0.0	0.0	1.2	3.9
Total Hydrogen	0.0	1.5	4.8	6.1	7.3	10.0

* Excluding the electricity-generating sector.

Alternatively, of course, the unfilled demands could be satisfied by importing fuels. Because imports are not included in the Model I assumptions for the energy supply, the potentials for hydrogen demand are a maximum case. The minimum case would be zero demand for fuel hydrogen — i.e., complete importation of fuels and feedstocks to satisfy deficits and no need for hydrogen additional to its conventional production from fossil hydrocarbons (especially natural gas). The extent of future importation of energy supplies depends on economic and political factors not assessed in this study.

In Table 2-9, we have summed the shortfalls of the residential/commercial sector, the industrial sector, the other-uses sector, and 25% of the transportation sector to determine the potential demand for hydrogen. Two recent studies on alternative fuels for transportation, conducted for the Environmental Protection Agency, have revealed that before the year 2000 hydrogen will not be among the top three alternative fuels for automotive transportation (cars, trucks, and buses accounting for about 75% of the energy consumption in this sector). Accordingly, only a portion of the transportation sector shortfall, 25% (for airlines, railroads, and water transport), is a potential market for hydrogen. The potential demand for hydrogen could be satisfied by producing hydrogen from "excess" nuclear heat, from additional fossil resources (i. e., in addition to the supplies listed in Table 2-3), or from "new" energy sources. These new energy sources include solar heat, geothermal heat, waste materials, nuclear fusion, windpower, and ocean thermal gradients.

Model II Energy Demand and Supply

The assumptions and bases for the energy demand and supply in Model II are presented below. These differ from Model I only in the demand-supply data used and in certain assumptions in which Model II data necessitate slight changes. Basically, both models use the same assumptions for energy apportionment. Model II determines the upper bound (the greatest amount) of hydrogen and of additional synthesized fuels and the additional electricity that will be needed, along with imports, to satisfy the U. S. domestic energy demand for the period from 1975 to 2000. As in Model I, imports are not included in the Model II assumptions on energy supply.

Model II Bases and Information Sources

In the future, all market sectors will receive percentages of the total energy supply that differ somewhat from the present percentages. Market-sector-demand growth rates for 1970 to 1985 are patterned after the "high level of demand" presented in the authoritative NPC report for 1973, U.S. Energy Outlook.[7] For this model and during this period, the annual growth in the total energy demand falls from about 4.5% to about 4.3%. We have extrapolated this high-level-demand projection to the year 2000 and have used an average annual growth rate of 3.8% for the period from 1985 to 2000. The growth rates for individual market sectors are given in Table 2-10. The electricity-generating sector grows at a rate necessary to adequately supply the other sectors, but this rate does not exceed 7.0%/yr for supply of electricity to the residential/commercial sector or 7.5% for that to the industrial sector.

In Model II, the energy supply levels for the future are patterned after the pre-1973 projections included in the study, "A Program for Maximizing U.S. Energy Self-Sufficiency," by H. R. Linden.[5] Presented in this study,

Table 2-10. ANNUAL GROWTH RATE OF DEMAND
(High Level)

Market Sector	1970-1980	1980-1985	1985-2000
		%/yr	
Residential/Commercial	4.0	4.0	3.8
Industrial	3.1	3.2	3.8
Transportation	4.1	3.5	3.8
Other	5.3	6.2	3.8

in addition to the case used in Model I, is a less optimistic projection of the energy supply, and this case corresponds to the energy economics prevailing before the 1973 Middle East oil embargo. Reasonable development of domestic natural resources and growth of a synthetic fuel industry are assumed. Large amounts of imported energy are necessary for a demand-supply balance, and the domestic energy supply is necessarily less than that in Model I.

The energy-demand levels are the "high levels" presented in the NPC study, *U.S. Energy Outlook.*[7] The effect of energy conservation in the United States is assumed insignificant (at least from 1975 to 1985); and the demand growth rates continue at high levels, similar to those prevailing before the "energy crisis" began. However, these demand growth rates (except that for electricity) do decrease with time.

Model II Assumptions

The assumptions for Model II include those in respect to —

- Oil supply:

Oil Supply = Domestic Crude Oil + Condensates +
Natural Gas Liquids + Coal Liquids After
1985[*] + Syncrude Products From Oil
Shale After 1980.

The distribution of the oil supply in Model II follows the same pattern as that in Model I.

- Gas supply:

Gas Supply = Domestic Natural Gas + SNG
(Coal-Based) After 1980[†]

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[*] Coal converted to delivered hydrocarbons at a 65% efficiency from 1985 to 2000.

[†] Coal converted to delivered SNG at a 65% efficiency from 1980 to 2000.

In Model II, the electricity-generating sector receives its historic portion, 17.4%, of the natural gas supply (a variable quantity). This is less gas than in Model I, in which this sector continues to receive the fixed quantity of 17.4% of the 1970 supply. Otherwise, the distribution of the gas supply follows the same pattern as that in Model I. This minor change makes slightly more of the limited supply of natural gas available to higher priority market sectors.

- Coal supply (for direct uses, not chemical fuel synthesis). The distribution of the coal supply in Model II follows the same pattern as that in Model I.

- Electricity consumption. The residential/commercial sector consumes electricty at a rate that grows 7.0% annually from 1975 to 2000. Consumption by the industrial sector grows but it does not exceed 7.5%. (In many years, the demand is not satisfied.)

  The transportation and other-uses sectors consume relatively small amounts of electricity, although the amount consumed by the transportation sector increases rapidly (more than 6%/year).

- Nuclear heat, geothermal heat, and hydropower. The distribution of these energy sources in Model II follows the same pattern as that in Model I.

- Hydrogen production. In Model II, the total supply of fossil fuels, geothermal heat, and hydropower is consumed. Relatively small amounts of nuclear heat, potentially in excess of the needs of the electricity-generating sector, would exist from 1975 to 1990. Otherwise, there are nuclear energy deficits. Because of the small nuclear-heat supply and the 15-year time period, a hydrogen-production industry in this model would require significant energy sources other than nuclear fission reactors. For the nuclear (fission) heat that is available, we have assumed the following conversion efficiencies:

Nuclear heat converted to delivered hydrogen via electrolysis	30% efficient from 1980 to 1985 35% efficient from 1985 to 1990

  No thermochemical hydrogen processes based on nuclear (fission) heat will be commercialized because, according to this model, required nuclear heat will not be available after 1990. Thermochemical processes based on new energy sources could be commercialized.

Model II Overall Demand and Supply Projections

As in Model I, we have used the model bases to tabulate the energy demands by market sector and the energy supplies by type. These are presented in Tables 2-11 and 2-12, respectively. The demand of the electricity-generating sector is waste heat only, as in Model I. This prevents double counting of the electricity demand for each market sector.

Table 2-11. MODEL II ENERGY DEMAND BY MARKET SECTOR

Market Sector	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Residential/Commercial	15.8	19.2	23.4	28.5	34.3	41.3	47.9
Industrial	20.0	23.8	27.2	31.9	38.4	46.3	55.8
Transportation	16.3	19.9	24.4	29.0	34.9	42.1	50.7
Electricity-Generating*	11.6	13.2	18.2	24.6	34.2	49.1	69.3
Other	4.1	5.3	6.8	9.2	11.1	13.4	16.1
Total	67.8	81.4	100.0	123.2	152.9	192.2	239.8

* Matched to electricity demands in other sectors assuming certain conversion efficiencies. This is waste heat only.

Table 2-12. MODEL II DOMESTIC ENERGY SUPPLY

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Crude Oil and Condensates	21.0	21.9	24.3	23.9	24.3	22.7	22.9
Natural Gas	22.4	21.2	18.8	17.6	17.1	16.9	16.7
Coal (Direct Use)	13.1	16.0	18.6	21.5	24.9	28.9	33.3
Coal (SNG)	0.0	0.0	0.2	1.1	3.3	6.0	8.5
Coal (Liquids)	0.0	0.0	0.0	0.4	2.4	5.2	8.2
Shale Syncrude	0.0	0.0	0.2	0.6	2.5	4.5	6.4
Hydro- and Geothermal Power (as Heat)	2.7	3.0	3.5	4.0	4.5	5.0	5.5
Nuclear Heat	0.2	3.5	9.5	21.0	30.0	42.0	60.0
Total	59.4	65.6	75.1	90.1	109.0	131.2	161.5

Because of the bases used, the total energy demand and the domestic energy supply are badly out of balance in Model II. New, large-scale energy sources and imports would be required to meet the demands in this model.

Model II Energy Demand and Supply, by Sector

Here, as in Model I, we have used the assumptions to determine the apportionment of domestic energy supplies to the various market sectors. The demand and supply projections for these market sectors are presented in Tables 2-13 through 2-17. The unfilled demand (the bottom line in Tables 2-13 through 2-16) is the energy deficit to be filled by development of more of the same energy sources than is predicted by the model, exploitation of new energy sources, and energy imports.

Table 2-13. MODEL II RESIDENTIAL AND COMMERCIAL ENERGY DEMAND AND SUPPLY (Domestic)

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Demand	15.8	19.2	23.4	28.5	34.3	41.3	47.9
Fossil-Fuel Supply							
Oil (21% Crude and Coal Liquids)	4.4	4.6	5.1	5.1	5.6	5.9	6.5
Gas (Available Supply)	7.0	6.7	6.0	6.0	7.0	8.2	9.4
Coal (2.3% of Supply)	0.3	0.3	0.0	0.0	0.0	0.0	0.0
Total	11.7	11.6	11.1	11.1	12.6	14.1	15.9
Electricity Consumption	2.7	3.3	4.6	6.4	9.0	12.6	17.6
Total Supply	14.4	14.9	15.7	17.5	21.6	26.7	33.5
Unfilled Demand	1.4	4.3	7.7	11.0	12.7	14.6	14.4

Model II Demand and Potentials for Hydrogen Production

The demands of the electricity-generating sector, depicted in Table 2-17, do not require all of the available energy supplies for the years 1975 to 1990. Potentially, relatively small amounts of excess nuclear heat exist during this

Table 2-14. MODEL II INDUSTRIAL ENERGY DEMAND AND SUPPLY (Domestic)

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Demand	20.0	23.8	27.2	31.9	38.4	46.3	55.8
Fossil-Fuel Supply							
Oil (17.5% of Crude and Coal Liquids)	3.7	3.8	4.2	4.3	4.7	4.9	5.4
Gas (35.5% of Supply)	7.9	7.5	6.7	6.6	7.2	8.1	8.9
Coal (35.7% of Supply)	4.7	5.7	6.6	7.7	8.9	10.3	11.9
Total Fossil	16.3	17.0	17.5	18.6	20.8	23.3	26.2
Electricity Consumption	2.3	3.1	4.4	6.3	9.0	12.9	18.5
Total Supply	18.6	20.1	21.9	24.9	29.8	36.2	44.7
Unfilled Demand	1.4	3.7	5.3	7.0	8.6	10.1	11.1

Table 2-15. MODEL II TRANSPORTATION ENERGY DEMAND AND SUPPLY (Domestic)

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Demand	16.3	19.9	24.4	29.0	34.9	42.1	50.7
Fossil-Fuel Supply							
Oil (Shale Syncrude and Balance)	11.5	12.0	13.7	14.0	17.3	20.0	24.0
Gas*	--	--	--	--	--	--	--
Coal (0.1% of Supply)	--	--	--	--	--	--	--
Total Fossil	11.5	12.0	13.7	14.0	17.3	20.0	24.0
Electricity Consumption	--	--	0.2	0.3	0.4	0.6	0.8
Total Supply	11.5	12.0	13.9	14.3	17.7	20.6	24.8
Unfilled Demand	4.8	7.9	10.5	14.7	17.2	21.5	25.9

*Negligible.

Table 2-16. MODEL II OTHER USES OF FUELS DEMAND AND SUPPLY
(Domestic)

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Demand	4.1	5.3	6.8	9.2	11.1	13.4	16.1
Fossil Fuel Supply							
Oil (0.6% of Crude and Coal Liquids)	0.1	0.1	0.1	0.1	0.2	0.2	0.2
Gas (15.8% of Supply)	3.5	3.3	3.0	3.0	3.2	3.6	4.0
Coal	--	--	--	--	--	--	--
Total Fossil	3.6	3.4	3.1	3.1	3.4	3.8	4.2
Electricity Consumption†	0.1	0.1	0.2	0.2	0.3	0.3	0.4
Total Supply	3.7	3.5	3.3	3.3	3.7	4.1	4.6
Unfilled Demand	0.4	1.8	3.5	5.9	7.4	9.3	11.5

Negligible.

†Expressed as a constant percentage, 2.5%, of the total demand.

Table 2-17. MODEL II ELECTRICITY GENERATION

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Demands							
Electricity Produced	5.0	6.5	9.4	13.2	18.7	26.4	37.3
Waste Heat Required	11.3	13.2	18.2	24.6	34.2	49.1	69.3
Total Demand	16.3	19.7	27.6	37.8	52.9	75.5	106.6
Fossil-Fuel Supply							
Oil (6.2% of 1975 Supply)	1.3	1.4	1.4	1.4	1.4	1.4	1.4
Gas (17.4% of N.G. Supply)	3.9	3.7	3.3	3.1	3.0	3.0	2.9
Coal (61.9% of Supply, 64.3% after 1975)	8.1	9.9	12.0	13.8	16.0	18.6	21.4
Total Fossil	13.3	15.0	16.7	18.3	20.4	23.0	25.7
Hydro- and Geothermal Power	2.7	3.0	3.5	4.0	4.5	5.0	5.5
Nuclear Heat Required for Remaining Demand	0.3	1.7	7.4	15.5	28.0	47.5	75.4
(Nuclear Heat Available†)	(0.3)	(3.5)	(9.5)	(21.0)	(30.0)	(42.0)	(60.0)
Total Heat Supply	16.3	19.7	27.6	37.8	52.9	70.0	91.2

Heat required for generation.

†Not included in total.

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period. However, after 1990 there is a shortfall in the energy supply for this sector. According to the assumptions of Model II, the excesses and deficits are nuclear heat; but with different assumptions, these quantities could be expressed as coal energy.

Table 2-18 lists the individual energy shortfalls for each sector and the quantities of hydrogen that are potentially available from the excess nuclear heat. As in Model I, we have calculated the potential demand for hydrogen by summing up the sector deficits (using 25% of the transportation-sector deficit). Although the electricity-generating sector has energy deficits in Model II, we have excluded its demand from the total potential hydrogen demand because it is not considered practical to synthesize hydrogen for use as a fuel to generate electricity. The reasons for this are the large required hydrogen capacity and the capital costs that result from the accumulative energy losses associated with the many consecutive energy-conversion steps.

Table 2-18. MODEL II MAXIMUM DEMAND AND POTENTIALS FOR HYDROGEN PRODUCTION

	1975	1980	1985	1990	1995	2000
	10^{15} Btu					
Unfilled Demands by Sector[*]						
Residential/Commercial	4.3	7.7	11.0	12.7	14.6	14.4
Industrial	3.7	5.3	7.0	8.6	10.1	11.1
Transportation	7.9	10.5	14.7	17.2	21.5	25.9
Other	1.8	3.5	5.9	7.4	9.3	11.5
Potential Hydrogen Demand	11.8	19.1	27.6	33.0	39.4	43.5
Unused Nuclear Heat Supply	1.8	2.1	5.5	2.0	0.0[†]	0.0[†]
Potential Hydrogen Supply (Nuclear Heat)						
Electrolysis	0.0	0.6	1.6	0.7	0.0	0.0

[*] Excluding the electricity.

[†] Actually a deficit.

The potential demand for hydrogen might be satisfied by producing hydrogen from potential excess nuclear heat, from additional fossil resources (i.e., in addition to the supplies listed in Table 2-12), or from new energy sources. These new energy sources include solar heat, waste materials, nuclear fusion, windpower, and ocean thermal gradients. As is the case with Model I, the sector deficits here also might be filled by energy imports. As this model does not include imports, the deficits and the attendant hydrogen demands constitute a maximum case for hydrogen demand.

Summary of Potential Hydrogen Demand

The potential maximum demand for hydrogen is bracketed by using the sector demands (for hydrogen) from each model. The lower bound is the value from Model I, and the upper bound is the value from Model II. We stress that this potential demand could be filled by hydrogen, or by combinations of hydrogen with other synthesized chemical fuels and electricity. Imported energy could also contribute. If domestic energy were to supplement, new and additional energy sources, beyond those included in the models, would be necessary. Assuming, however, that these demands are met solely by hydrogen, then the bounds of the potential hydrogen demand are as presented in Table 2-19.

Table 2-19. BOUNDS OF POTENTIAL MAXIMUM DEMAND FOR HYDROGEN

Market Sector	1975	1980	1985	1990	1995	2000
	10^{15} Btu					
Residential/ Commercial	2.4- 4.3	3.0- 7.7	1.9-11.0	1.5-12.7	3.4-14.6	5.1-14.4
Industrial	1.2- 3.7	0.6- 5.3	0.0- 7.0	0.0- 8.6	1.4-10.1	2.7-11.1
Transportation	1.7- 2.0	1.8- 2.6	1.8- 3.7	1.9- 4.3	2.5- 5.4	3.3- 6.5
Other	1.2- 1.8	1.9- 3.5	3.2- 5.9	3.8- 7.4	5.2- 9.3	6.6-11.5
Total	6.5-11.8	7.3-19.1	6.9-27.6	7.2-33.0	12.5-39.4	17.7-43.5

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Present and Future Demands for Specific Uses of Hydrogen

Models I and II show the limits of the size of the "energy gap" that could be filled by a fuel such as hydrogen. Examination of these two models is useful because it shows that the traditional supplies of domestic energy will be unable to satisfy a large portion of the future energy market; thus there is an opening for a new energy carrier such as hydrogen. In addition, one model shows that some nuclear heat, up to 28.2 quadrillion Btu in the year 2000, could potentially be available for hydrogen synthesis. The question that remains is: In what fashion could the synthesized hydrogen be utilized?

We have surveyed portions of the market for present and future uses of hydrogen to show how some of the "energy gaps" predicted by Models I and II might be filled by hydrogen. The market estimates are not comprehensive, are not taken directly from either Model I or Model II, and should not be compared directly to them without expecting some incongruities. Instead, the estimates are based on the extrapolation of historical data, and model growth rates are used only when necessary.

Extrapolation of Present-Day Hydrogen Demands

Table 2-20 shows the largest present-day uses of hydrogen (as a feedstock or intermediate), the amount of hydrogen so consumed in 1973, and their growth rates, as given by various sources.

Table 2-20. PRESENT-DAY HYDROGEN USES AND GROWTH RATES

Use	1973 Usage, 10^{15} Btu	Annual Growth Rate, %
Ammonia Synthesis[9]	0.340*	4.5
Chemical Methanol Synthesis[2]	0.076*	6.0
Oil Refining[1]		
Hydrotreating	0.176	10.0
Hydrocracking	0.241	<1.0
Others[9]	0.049*	10.0

* U.S. Bureau of Mines, "Hydrogen Commodity Statement 1973," unpublished. Washington, D. C., December 1974.

To estimate the demand for hydrogen from these sources, we have made the following assumptions:

- Ammonia and chemical methanol synthesis will grow at their historical rates.

- Because of recently applied sulfur restrictions, hydrotreating is growing at an accelerated rate. This rate was assumed to continue until 1979, at which point the hydrotreating growth rate would decrease to that of oil refining in general.
- The growth of hydrocracking is currently depressed, primarily by the sudden shortage of natural gas. It is assumed that hydrocracking will begin to grow again at the same rate as oil refining in general, in 1980.
- The rate of growth for oil refining was assumed to be about 2% per year, (as indicated by Model II).
- The "other" uses of hydrogen have been growing at a rate of 10% per year. It was assumed that this growth rate would continue until 1985, then decrease to a rate of 5% per year after that.

Table 2-21 thus shows the estimated hydrogen demand for traditional uses (feedstock or intermediate that could become a feedstock).

Table 2-21. HYDROGEN DEMAND FOR TRADITIONAL USES

Use	1973	1980	1985	1990	1995	2000
	10^{15} Btu/yr					
Ammonia Synthesis	0.340	0.46	0.60	0.7	0.9	1.1
Chemical Methanol Synthesis	0.076	0.11	0.15	0.20	0.30	0.4
Oil Refining						
Hydrotreating	0.176	0.34	0.38	0.41	0.46	0.5
Hydrocracking	0.241	0.26	0.29	0.32	0.35	0.4
Other	0.049	0.10	0.15	0.20	0.25	0.3
Total	0.882	1.27	1.57	1.83	2.26	2.7

Future Uses of Hydrogen as a Chemical Feedstock

In the next few decades, a number of new markets for hydrogen may open up. Hydrogen may be used as a reducing gas in iron ore refining, and estimates have been published showing the quantities of hydrogen that may thus be needed. Table 2-22 gives the estimates of hydrogen usage presented in a report[3] by The Futures Group.

As will be shown in a later section of this report, tremendous amounts of hydrogen will be needed for coal liquefaction and gasification processes. Oil shale processing, while less hydrogen intensive than the production of clean fuels from coal, will also require large amounts of hydrogen. Table 2-23 shows, for each process, the approximate quantity of hydrogen needed per

Table 2-22. DEMAND FOR HYDROGEN BY IRON ORE DIRECT-REDUCTION PROCESSES

Year	Demand, 10^{15} Btu/yr
1980	0.102
1985	0.215
1990	0.357
1995*	0.487
2000	0.650

*Interpolated.

Table 2-23. HYDROGEN DEMAND FOR SYNTHETIC FUEL PROCESSES PER UNIT OF OUTPUT

Process	Demand, SCF of Hydrogen
Coal Gasification	1.3/SCF of methane
Coal Liquefaction	6000/bbl of syncrude
Oil Shale	1100/bbl of 45° API-gravity syncrude

unit of product. These hydrogen demands were calculated from process flow sheets and represent the amount of molecular hydrogen utilized in each process. Hydrogen generated in a process in a manner such that an outside stream of hydrogen could not be substituted for it is not counted. Table 2-24 shows the demand for hydrogen that would be created if the if the synthetic-fuels industry were to grow at the rate predicted by Model II.

Table 2-24. HYDROGEN DEMAND FOR SYNTHETIC FUEL PROCESSES (Model II Growth)

Process	1980	1985	1990	1995	2000
			10^{15} Btu/yr		
Coal Gasification	0.09	0.48	1.45	2.65	3.74
Coal Liquefaction	0.00	0.14	0.84	1.81	2.86
Oil Shale	0.01	0.04	0.16	0.29	0.41
	0.10	0.66	2.45	4.75	7.01

Hydrogen as a Substitute for Natural Gas

Hydrogen may be very useful as a supplementary or gaseous fuel. To estimate this demand, we have used the projections given in "Future Gas Consumption of the United States," by the Future Requirements Committee (FRC) of the American Gas Associstion.[4] This publication presents expectations for the gaseous-fuel market during this century if supply were not a problem.

Table 2-25 shows the gas supply predicted by Model II, the demand estimated by the FRC (excluding all interruptible supplies), and the unfilled demand (the difference between the two amounts).

Table 2-25. GASEOUS FUEL SUPPLY AND DEMAND

	1980	1985	1990	1995	2000*
	10^{15} Btu/yr				
Demand (FRC)	25.3	30.1	34.9	41.6	49.2
Supply (Model II)	20.0	18.7	20.4	22.9	25.2
Unfilled Demand	5.3	11.4	14.5	18.7	24.0

* Extrapolated.

It should be clear from Table 2-21, 2-22, 2-24, and 2-25 that, although there are sizable demands for hydrogen as a chemical, the largest market for hydrogen will be its use as a fuel — if it can be produced and delivered cheaply.

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3. HYDROGEN PRODUCTION BY ELECTROLYSIS – D. P. Gregory

Introduction

The production of hydrogen by the electrolysis of water is, in principle, very simple. The basic electrolysis cell consists of a pair of electrodes immersed in a conducting electrolyte dissolved in water. A direct current is passed through the cell from one electrode to the other. Hydrogen is evolved at one electrode, oxygen is evolved at the other, and water is thus removed from the solution. In a continuously operating electrolysis cell, replacement of the pure water is continuously supplied; and a continuous stream of hydrogen and oxygen may be obtained from the two electrodes. In practice, electrolysis cells are rather more complicated than this, containing various other components that allow them to work efficiently and economically. Because the basic electrolysis cell has no moving parts, it is reliable and trouble-free; and electrolysis represents the least labor-intensive method of producing hydrogen. In addition to the trouble-free operation, electrolysis is the most efficient way of generating hydrogen under pressure. Increasing the pressure of operation of the cell results in a higher theoretical voltage requirement to drive the cell, but electrolysis cells normally work more efficiently at a higher pressure; and the gain in efficiency usually more than offsets the extra electrical energy requirement.

The most important characteristic of electrolysis is not that hydrogen and oxygen are split out from water, but that they are separated at the same time. This benefit is derived at the expense of having to use a high "energy form," namely electric power, as the input to the cell. Electrolysis has traditionally been considered one of the more expensive methods of hydrogen production and electrolyzers have been assumed to be inefficient and expensive. On the contrary, it is the electric-generation step that is expensive and inefficient; and most commercial electrolyzers available today are capable of operating at electricity-to-hydrogen efficiencies above 75%, while their capital-cost potential is far less than that of the power stations that would be required to run them.

In this section, the principles of electrolysis and the energy requirements for production of electrolytic hydrogen are discussed. The various basic designs of electrolyzer cells are described, as are some of the available units. The status of industrial electrolytic hydrogen production is such that this method represents only a small fraction of the total hydrogen-production capacity, but a large number of small electrolysis plants exist in various parts of the world; and the location and size of some of the larger ones are described in this report. The estimated costs of hydrogen produced by various electrolyzers as a function of electric power costs have been calculated and an outline of various research programs, largely aimed at reducing the cost of electrolytic hydrogen production, is given.

Principles of Electrolysis

When a direct current is passed through water between two electrodes, water decomposes according to the reaction —

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

Water is actually a poor conductor of electricity; and in order for this reaction to proceed, a conducting electrolyte must be added to the water. Water essentially dissociates into hydrogen and hydroxyl ions (H^+ and OH^-). The positive hydrogen ions migrate toward the cathode, the negative electrode, where they are discharged by picking up electrons and forming hydrogen molecules:

$$2H^+ + 2e^- \rightarrow H_2$$

The hydrogen molecules accumulate on the surface of the electrode until a bubble forms, breaks away, and rises to the surface of the electrolyte. At the oxygen electrode, a similar process occurs in which hydroxyl ions are discharged by giving up their electrons to the electrode and reacting to form water and oxygen. The oxygen molecules accumulate into gas bubbles and rise to the surface.

Both of these electrode reactions require some intermediate catalytic reaction with a metal surface. It is believed that the hydrogen ions discharge on the metal surface to form an adsorbed layer of hydrogen atoms, which then recombine on the surface to form hydrogen molecules. The ease with which the electrode reactions occur is profoundly affected by both the physical and chemical natures of the surfaces of the electrodes.

A basic electrolyzer cell consists of the following components:

- An electrolyte — a water solution made conductive by mixing a salt or compound with water. The selection of the electrolyte is important because it must have the following characteristics: It must exhibit high ionic conductivity; it must not be chemically decomposed by voltage as large as that applied to the cell (so that only water is decomposed); it must not be volatile enough to be removed with the evolved gas; and, because hydrogen-ion concentrations are being rapidly perturbed at the electrodes, the electrolyte should have a strong resistance to pH changes – i.e., it should be a buffer solution.

For the most practical applications, these criteria can be met by the use of a strong acid, such as sulfuric acid, or a strong alkali, such as potassium hydroxide (KOH). Most salts are themselves decomposed under electrolysis at voltages likely to be encountered in an electrolyzer cell. Acid electrolytes present severe corrosion problems and are not usually selected for electrolyzers. Therefore, most commercial electrolyzers operate with an alkaline electrolyte. Maximum conductivity occurs in KOH solutions at about a 30% concentration, and this is the concentration usually selected. There is one notable exception to this use of alkaline electrolytes – the use of a solid polymeric ion-exchange material that also has good ionic conductivity. Ion-exchange resins having mobile negative ions (in other words, alkaline ion-exchange resins) are notoriously sensitive to chemical degradation at elevated temperatures, and this restricts the choice of ion-exchange electrolytes to acidic systems. The most successful work with ion-exchange electrolytes has been carried out using a polymerized fluorinated polystyrene sulfonic acid.

- Electrodes that have the following characteristics – they must be electronic conductors; they must have a suitable catalytic surface for the discharge of hydrogen or hydroxyl ions; they must provide a large-area interface between the catalyst and the electrolyte; they must provide adequate sites for the nucleation of gas bubbles; and they must provide a reasonable means for the detachment of gas bubbles so that they may separate themselves from the electrolyte at the operating voltage of the cell.

The form of the electrodes varies considerably from one cell design to another. Large surface areas are obtained by the use of sintered structures, finned bodys, screens, perforated plates, and flat plates with electrochemically roughened surfaces. In the alkaline cells, nickel is the most commonly used catalytic surface. Rather than making electrodes out of solid nickel, nickel-plated mild steel is often used. The application of precious-metal catalysts, such as platinum, assists the electrode processes considerably and allows them to proceed more rapidly than on nickel, but the extra cost of the precious metal is not usually considered justified. In the case of the polymeric acid electrolyte, electrodes must be made of more chemically resistant materials than nickel or steel. Tantalum and gold have been used, while the precious metals themselves, platinum, rhodium, iridium, etc., are usually considered necessary as catalysts. When platinum is used, a large surface area can be obtained by the use of so-called platinum black, a finely divided powder of platinum metal particles.

- A separator – required between the two electrodes and serving the following purposes: It prevents the electrodes from touching each other and shorting out, and it prevents the hydrogen and oxygen gases from mixing together inside the cell. To provide this function properly, the separator must consist of a porous diaphragm or matrix through which the electrolyte solution can pass, affording an ionic conducting path from one side of the cell to the other. These pores must remain full of liquid so that gas cannot penetrate them. Additionally, the separator material must not be corroded by the electrolyte in the presence of hydrogen or oxygen gas, and it must remain structurally stable for the entire operating life of the cell so that the pores do not collapse. To keep the ionic resistance of the cell as low as possible, the separator is usually made in the form of a thin sheet, the thickness of which is determined by mechanical strength and gas crossover limitations. In the case of alkaline cells, asbestos has commonly been used for the separator material. Woven asbestos cloth and matted asbestos fibers are both used in commercial cells. Some experimental materials, including potassium titanate, have been used in other alkaline cells. In the case of the polymeric acid ion-exchange resin, this material acts as its own separator; and no additional material is needed.

- A container – required to hold the electrolyte. In some cells, a nickel-plated steel tank with a lid is used, while in others, solid metal sheets are interposed between the electrodes, which are then stacked together with peripheral gaskets used to seal the outer edges. This way, no separate container is required, and current is passed from one electrode to the next through the metal separator plate.

In addition to the basic components of the electrolyzer cell itself, an electrolyzer "system" requires further components. These include power-conditioning equipment to convert ac power to the dc current required by the cell; electrical bus bar equipment to distribute the dc power to the various electrodes in an assembly of electrolyzer cells; gas-exit pipe work to duct the hydrogen and oxygen away from the cell; separation systems to separate the gases from the electrolyte, which may be entrained with the gas or deliberately circulated out of the cell with the gas; cooling systems to remove waste heat from the cell itself; and drying systems to dry the hydrogen and oxygen after they have been generated. Thus, an electrolyzer system may be seen to be far more complex than the simple concept of "two electrodes in an electrolyte" that was presented earlier. Later in this section, options for electrolyzer cell and system designs will be described and discussed in more detail.

Energy Requirements for Electrolysis

The overall process of water decomposition by electrolysis is the reverse of the process of hydrogen combustion. Therefore, the theoretical amount of energy required per unit quantity of hydrogen produced is the same as heat of combustion. Each hydrogen molecule is formed by the addition of two electrons to two hydrogen ions in solution, so that a direct relationship exists between the current passed (the electron flow rate) and the rate of hydrogen production (Faraday's law). Deviations from Faraday's law (which implies that 15.6 SCF[*] of hydrogen is produced per 1000 A-hr) are characterized by the electric-current efficiency of the cell. The current efficiency in most cells approaches 100%. Any lower efficiencies experienced are the result of extraneous electrode reactions during the electrolysis; but, theoretically, no alternative chemical reactions can occur except the recombination of hydrogen and oxygen in solution. A perfectly efficient cell would require 94 kWhr of electrical energy for each 1000 SCF of hydrogen produced. Of these 94 kWhr, only 79 need be supplied as electrical energy; the remainder can be supplied as heat. Because this energy input to the cell is in the form of power (the product of voltage and current), each electrolytic process has a theoretical voltage corresponding to the energy required for the reaction to proceed.

In electrolysis, only the free energy of reaction, ΔG, can be interchanged with electrical energy at constant temperature and pressure. The quantity of electric charge corresponding to the molar quantities indicated in the balanced chemical equation is nF, where n is the number of electrons transferred per molecule and F is the Faraday value. If this quantity of electrical charge is transported through a potential difference of E volts, the amount of work required is given by nFE. Because this electrical change does not involve pressure-volume work and is carried out isothermally, the change in Gibbs free energy is given by —

$$\Delta G = -nFE \tag{3-1}$$

where E is the potential difference, or voltage, which by convention is taken as positive. If ΔG is negative for a spontaneous cell reaction and E is taken as positive for a spontaneously discharging cell, there results a negative sign in Equation 3-1.

The entropy change for an electrolytic-cell reaction may be calculated from the temperature coefficient of the electromotive force because —

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[*] All cubic feet measurements given in this section are at standard conditions, 68°F and 14.7psi.

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = \Delta S$$

Introducing this into Equation 3-1, we have —

$$nF\left(\frac{\partial E}{\partial T}\right)_p = \Delta S \qquad (3\text{-}2)$$

The enthalpy change for the cell reaction may be calculated by substituting Equations 3-1 and 3-2 into —

$$\Delta H = \Delta G + T\Delta S = -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_p \qquad (3\text{-}3)$$

It is apparent from Equation 3-3 that the difference between the free-energy change and the total-energy change (enthalpy) is accounted for by an entropy change in the process. Because the entropy change cannot be converted to electricity, it must be supplied or liberated as heat.

For a water electrolysis cell, we can calculate that the voltage corresponding to the enthalpy change, or the heat of combustion of hydrogen, is 1.47 volts at 25°C (77°F), whereas the cell voltage corresponding to the free-energy change is only 1.23 volts.

In an ideal case, then, 1.47 volts applied to a water electrolysis cell at 25°C (77°F) would generate hydrogen and oxygen isothermally — that is, at 100% thermal efficiency with no waste heat produced. However, a voltage as low as 1.23 volts would still generate hydrogen and oxygen, but the cell would absorb heat from its surroundings. The electrical energy required for the process is only 83.7% of the combustion energy of the hydrogen produced; the other 16.3% is supplied as heat. Another way of expressing this is that the fuel value of the hydrogen produced is 120% of the heating value of the electrical energy input.

In practical cells, there is usually an efficiency loss that is greater than the difference between the free-energy voltage and the enthalpy voltage. In other words, practical cells usually operate at voltages greater than 1.47 volts and liberate heat because of a variety of efficiency losses occurring within the cell. The heat required to supply the entropy of reaction is therefore provided by some of this waste heat, and practical cells do not absorb heat from their surroundings. If an extremely well performing cell could be operated at a voltage below 1.47 volts, it would act as a refrigerator, drawing heat from its surroundings to make up the deficit in the energy input. There seems to be little chance of developing electrolyzer cells that operate so close to the ideal that they do, in fact, act as refrigerators. However, there seems to be a reasonable chance of obtaining cell operation at 1.47 volts, which would represent an apparent 100% conversion of electrical energy to the fuel value of hydrogen. If such a cell performance can be achieved and an apparent cell efficiency of 100% is demonstrated, this would still represent an electrochemical efficiency of only 83%. It is curious, therefore, that a practical device could probably be produced that operates at an apparent efficiency of 100% without violating the basic laws of thermodynamics. This operating voltage of 1.47 volts is a good target to aim for in the development of advanced electrolyzer cells.

The free-energy-change voltage, E, or "reversible" voltage as it is called, varies with temperature as shown in Figure 3-1. As can be seen, raising the temperature lowers the voltage at which water can be decomposed. This factor operates in favor of electrolysis cells because at higher temperatures the electrode processes proceed faster, with less loss, while the required energy input is less. This is in contrast to fuel cells; their available energy output falls as the temperature is raised.

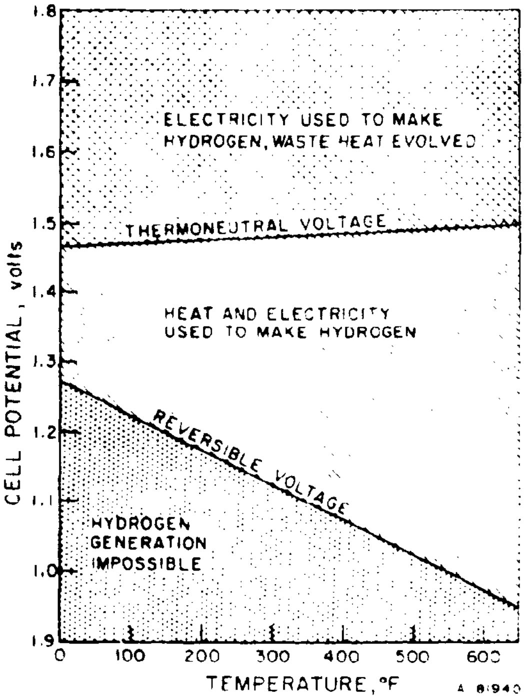


Figure 3-1. IDEALIZED OPERATING CONDITIONS FOR ELECTROLYZER[17]

The voltage corresponding to enthalpy change, or as we shall term it, the "thermoneutral voltage," varies only slightly with temperature, from 1.47 volts at 25° C (77° F) to 1.50 volts at 340° C (644 ° F). This is also shown in Figure 3-1. Three areas, therefore, can be identified: 1) that in which no hydrogen is evolved, 2) that in which hydrogen is made at an apparently greater-than-100% efficiency, and 3) that in which hydrogen is made at an efficiency of less than 100% with the production of waste heat.

Effect of Pressure on the Decomposition Voltage

In considering the theoretical aspects of the effect of pressure on electrolysis, we have to inquire into the effect of pressure on the decomposition voltage and on the efficiency losses within the cell. During electrolysis the free-energy change can be written as –

$$dG = -SdT + VdP \qquad (3\text{-}4)$$

If we apply this at constant temperature we can write –

$$\frac{\partial Gp}{\partial P} - \frac{\partial Gr}{\partial P} = Vp - Vr \qquad (3\text{-}5)$$

where G_r, G_p, V_r, and V_p are the Gibbs free energies and volumes of the reactants and products, respectively. This equation may be written –

$$\frac{\partial \Delta G}{\partial P} = \Delta V \qquad (3\text{-}6)$$

where ΔV is the change in volume during reaction. Substituting ΔG into Equation 3-6 we obtain –

$$\frac{\partial E}{\partial P} = \frac{-\Delta V}{nF} \qquad (3\text{-}7)$$

If we assume that the volume of the liquid water is small compared with that of gaseous products hydrogen (H_2) and oxygen (O_2), and if we further assume the volumes of these gases obey the perfect gas law –

$$PV = ZRT \qquad (3\text{-}8)$$

where Z = number of moles, we derive –

$$dE = \left(\frac{ZRT}{nF} \quad \frac{dP}{P}\right)_{O_2} + \left(\frac{ZRT}{nF} \quad \frac{dP}{P}\right)_{H_2} \qquad (3\text{-}9)$$

By integration between ambient conditions and the operating pressure we obtain –

$$E_p = E_1 + \frac{0.052}{2} \log P_{H_2} + \frac{0.058}{4} \log P_{O_2} \qquad (3\text{-}10)$$

Because during electrolysis $P_{H_2} = P_{O_2}$ –

$$E_p = E_1 + 0.0435 \log P \qquad (P = \text{atm}) \qquad (3\text{-}11)$$

Thus, raising the pressure of operation of a water electrolyzer results in a theoretical increase in the decomposition voltage of 43 mV for every tenfold increase in pressure. The energy required to provide this additional voltage is exactly equal to the potential energy contained in the high-pressure hydrogen. In practice, electrolyzer cells operate slightly closer to the ideal at higher pressures than they do at atmospheric pressure — that is, efficiency losses are less at higher pressures. This is because of a variety of reasons, including the fact that the gas bubbles evolved are smaller and provide less hindrance to the passage of ionic current across the cell. At pressures of up to about 400 psia, the saving in energy due to increased efficiency is greater than the extra energy that has to be expended to overcome the theoretical voltage. Thus, pressurized operation of electrolyzers is an extremely efficient way of generating pressurized hydrogen; and, up to moderate pressure increases, pressure can be developed at "apparent" pumping efficiencies of greater than 100%.

In addition to the energy required to pass current through the electrolyzer cell itself, certain parasitic energy requirements must be met. Most practical electrolyzer systems contain pumps for circulation of the electrolyte, gas, or cooling fluid; and these consume small, but significant, quantities of energy. The power supplied to the cell must be relatively low voltage dc, although power supplies are conventionally high-voltage, 3-phase ac. The conversion of ac line power to dc power is not carried out with 100% efficiency; and the power-conditioning equipment, therefore, represents a further parasitic energy load on the system. These parasitic energy loads amount to somewhat less than 5% of the total energy consumption of an electrolyzer system.

Returning to the electrolyzer cell itself, the energy requirements of a practical cell are always greater than the minimum theoretical energy requirements described above. Efficiency losses occur because of a) the resistance of the electrolyte itself, b) changes in the voltage of the electrodes due to concentration polarization (changes in the concentration of hydrogen ions, oxygen ions, or water in the vicinity of the electrodes), and c) voltage gradients set up at the electrode-electrolyte interface itself due to the slowness of the electrode reactions. Additionally, there are small losses in the electronic conduction of current through the metal parts of the cell.

Because a practical cell operates at a higher voltage than the theoretical value of 1.23 volts (at room temperature and pressure), the difference between the actual applied voltage and the theoretical voltage is commonly called overvoltage. The change in voltage at individual electrodes is often called polarization, and the terms overvoltage and polarization are used synonymously. The voltage efficiency of the cell can be determined by comparing the actual operating voltage with the theoretical voltage at the operating conditions. The operating voltage of a cell varies according to the current that is passed through it. Just as in an ohmic resistance, increasing the current results in an increase in voltage. Thus, the voltage efficiency of an electrolyzer cell is a function of the current passed through it, decreasing as the current is raised. If the operating voltage of the cell is plotted against the current per unit area of electrode, commonly termed the current density, a characteristic curve, commonly called a polarization curve, is obtained. This curve is a vital design parameter for an electrolyzer system because it shows the relationship between voltage for efficiency and the current density for the rate of hydrogen production. Clearly, by doubling the rate of current density, and thus doubling the hydrogen-production rate, the effective capital cost of the cell is halved, although efficiency is penalized. The polarization curve can be used to show a trade-off between capital cost and efficiency in determining an optimum operating point.

The current required to decompose water is determined simply by the fact that two electrons are needed to discharge one molecule of hydrogen. This corresponds to 15.6 SCF of hydrogen produced/1000 A-hr. In practical cells, high current efficiencies, approaching 100%, are usually achieved because there usually is no other path for the current to take. When multiple cells are connected together in series and use a common electrolyte, some current can short-circuit from one end of the cell stack to the other through the electrolyte feed channels. This only occurs with certain cell designs and results in a slight loss of current efficiency. Another source of efficiency loss is the recombination of hydrogen and oxygen because they dissolve to some extent in the electrolyte and crossover into the separator. This loss becomes more pronounced when cells are operated at high pressures because of the increase in solubility. In practical low-pressure cells, current efficiencies in excess of 98% are usually obtained. The energy efficiency, or power efficiency, of a cell is therefore largely dependent upon the voltage losses or polarization of the cell, which remains the most important characteristic in determining the energy requirements for the practical electrolyzer cell.

Basic Designs of Electrolyzer Cells[4]

The oldest form of industrial electrolysis of water uses the tank electrolyzer in which a series of electrodes, anodes and cathodes alternately, are suspended vertically and parallel to one another in a tank partially filled with electrolyte. Alternate electrodes, usually cathodes, are surrounded by diaphragms that prevent the passage of gas from one electrode compartment to another. The diaphgram is impermeable to gas, but permeable to the cell's electrolyte. The whole assembly is hung from a series of gas collectors. A single tank-type cell usually contains a number of electrodes, and all electrodes of the same polarity are connected in parallel, electrically, as pictured in Figure 3-2. This arrangement allows an individual tank to operate across a 1.9 to 2.5 volt dc supply. In general, the cost of electrical conductors increases as the current load increases, but the cost of ac-dc rectification equipment per units of output decreases as the output voltage increases. This is one important consideration in the design of tank-type electrolyzers.

There are two major advantages to tank-type electrolyzers:

1. Relatively few parts are required to build a tank-type electrolyzer, and those parts that are needed are relatively inexpensive. Because of this feature, tank-type electrolyzers tend to optimize at a lower thermal efficiency than do more sophisticated electrolyzer structures. Therefore, tank-type electrolyzers are usually selected when electric-power costs are at their lowest.

2. Individual cells may be isolated for repair or replacement simply by short-circuiting the two adjacent cells with a bus bar. This feature allows maintenance to be carried out with a minimum of downtime for the entire plant.

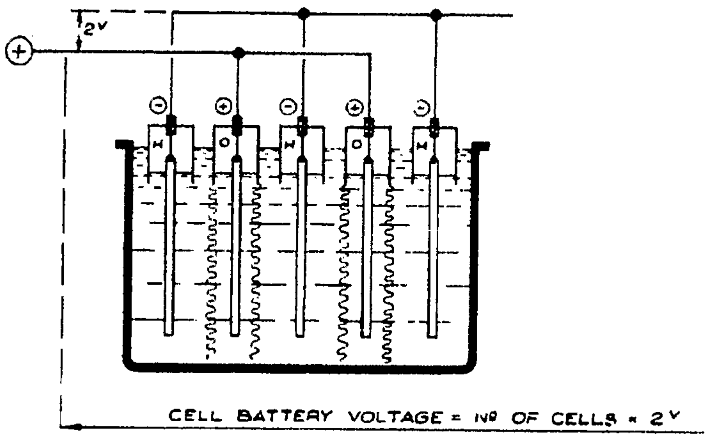


Figure 3-2. SCHEMATIC DIAGRAM OF A UNIPOLAR (Tank-Type) ELECTROLYZER [14]

The major disadvantages of tank-type electrolyzers are a) their inability to operate at high temperatures because of heat losses from the large surface areas; b) their requirements for more floor space than other types of electrolyzers (a point disputed by some proponents of tank-type electrolyzers, who state that tank cells can be accommodated in as small a floor space as the filter-press type), and c) the difficulty of designing the tanks to operate at high pressures.

As an alternative to tank-type electrolyzers, more recent electrolyzer designs use stacks so that the positive electrode of one cell is directly connected to the negative electrode of the next. An assembly of cells has superficial resemblance to a filter press because the electrolyte is manifolded to flow through each cell in parallel while hydrogen and oxygen exit lines are similarly manifolded through the stack.

Figure 3-3 is a schematic of a filter-press cell construction. This type of cell is sometimes called a bipolar cell (in contrast to the monopolar assembly in the tank-type cell) because each electrode is used with one face as the positive electrode of one cell and the opposite face as the negative electrode of the next cell. In practice, filter-press-type cells are usually constructed with separate electrodes in each cell that are electrically connected through a solid metal separator plate that serves to keep the hydrogen cavity of one cell separate from the oxygen cavity of the next. Because the cells of the

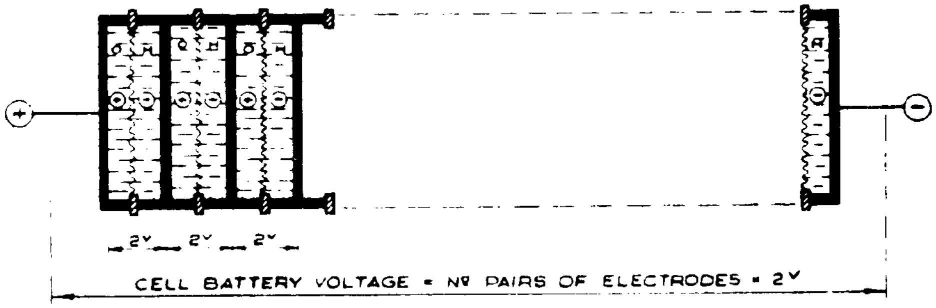


Figure 3-3. FILTER-PRESS (Bipolar) CELL CONSTRUCTION[13]

filter-press-type electrolyzer can be relatively thin, a large gas output can be achieved from a relatively small piece of equipment. It is usually necessary to cool the cells by circulating the electrolyte through them, and the electrolyte exiting from the cell carries with it the gas produced. In many designs, separation of the gas from the electrolyte is accomplished in a separating drum mounted on top of the electrolyzer. The electrolyte, free of gas, is recirculated through the cells. The major advantages of filter-press-type electrolyzers are that a) they take up less floor space than the tank-type design, b) they are more amenable to operation at high pressures, and c) they are more amenable to operation at high temperatures. The major disadvantages are that a) they require a much closer tolerance in construction because of sealing problems, and b) they are more difficult to maintain because if one cell fails, the entire battery has to be dismantled, and production of hydrogen is lost.

Filter-press electrolyzers usually present higher capital costs per unit area than tank-type cells; and, to compensate for this, they are operated at higher current densities.

Cells that use a solid-polymer electrolyte are usually constructed on the filter-press-type design. They do not require electrolyte circulation because the electrolyte is immobilized in the form of an ion-exchange resin. The electrodes are either embedded in the surface of the resin sheets or pressed closely against the two opposing faces of the sheet of resin material. A ribbed or corrugated solid-metal separator plate is interposed between cells, providing electric continuity between one cell and the next while separating the hydrogen from the oxygen in adjacent cells. This type of cell is usually cooled by circulating water through the cavity between the metal separator and the electrode plate. Hydrogen or oxygen evolved into this cavity is swept out by the coolant stream and is separated from the water outside the cell. The advantages of the solid-polymer-type cell are that a) the electrolyte membrane or diaphragm can be made very thin, allowing high conductivity without risk of gas crossover, and b) the electrolyte is immobilized and cannot be leached out of the cell. The disadvantages of the solid-polymer-electrolyte (SPE) cell are that a) the electrolyte costs more than the conventional alkaline solutions and b) the electrolyte is corrosive and requires more expensive metal components to be used in the cell. For these reasons, solid-polymer-electrolyte cells are usually operated at somewhat higher current densities than cells that use a liquid alkaline electrolyte.

Electrolyzer-System Designs

A total electrolyzer system consists of all the equipment necessary for the process, from the input of electrical power to the output of hydrogen and oxygen gas at the appropriate purity and pressure levels. In addition to the electrolyzer cell module itself, which has already been described, three major subsidiary systems can be used in various forms.

Power Supply

For relatively large-scale electrolyzer systems, power is usually supplied from a three-phase, high-voltage line. To convert this into the relatively low voltage dc power needed for the electrolyzer cell, a combination transformer-rectifier unit is usually used. There is a trade-off to be to be made in the design of the transformer-rectifier system, which can provide dc at relatively high or relatively low voltages. By connecting the cells in series, high-voltage dc systems can be used, and this can have some cost advantages in the requirements for transformers and rectifiers. For reasonably large systems, dc voltages of 70 to 100 volts are usually used. Clearly, this is not possible with very small units because a large number of very small cells would be needed.

The cost of a transformer-rectifier system is considerable and can represent as much as 1/3 to 1/2 of the cost of the entire system. If electric power is being generated onsite, some consideration should be given to the direct generation of dc power and to the use of this for electrolysis. There seem to be no examples of this in other electrochemical installations, for example, in chloride-caustic plants or aluminum-smelting installations that use onsite power. However, recent developments in the technology of acyclic or dc generators may make the direct reduction of dc power more promising. Modern, acyclic dc generators operate only at low voltages and this implies the use of very large currents, very large bus bars to distribute the power to the electrolyzer cells, and very complicated switch gear for handling high-current, low-voltage dc. On the other hand, dc generators apparently can be produced for about the same cost as ac generators; and the use of the dc system could considerably reduce capital costs that would otherwise be required in the provision of transformer-rectifier units. At present, not enough information is available to draw any conclusions about the relative merits and disadvantages of the ac versus dc supply systems.

Cooling Systems

Because electrolyzer cells are not, in fact, 100% efficient, a considerable amount of waste heat is generated in the electrolyzers and must be removed from the cells. There are several ways of doing this: a) by circulating electrolyte, b) by circulating hydrogen, c) by circulating water through the cell, and d) by circulating water through a heat exchanger in contact with the cell.

Circulation of electrolyte requires a pump capable of handling a corrosive liquid at relatively high temperatures and possibly at a high pressure. If electrolyte is circulated through a common manifold through a large number of cells connected in series, then a high voltage is applied to it from one end of the manifold to the other. This induces a short circuit through the electrolyte, thus utilizing only the electrodes at either end of the cell stack. There is a trade-off between the reduction of this short-circuit current or "shunt current," which results in low current efficiency of the entire cell stack, and the deliberate introduction of high-resistance paths in the electrolyte circulation loop, which result in a requirement for high circulating pumping power. In some types of cells, notably the tank-type cells in which the electrolyte in each cell is kept entirely separate from that in all others, these shunt currents are not possible. The circulation of electrolyte in these cells is usually provided by the gas-lift effect of the gases being evolved at the electrodes. Thus, very little parasitic energy is required, and no electrolyte circulating pump is needed. However, the circulation rates achieved by this means are not usually sufficient to remove the generated heat from the cell, but simply serve to stir up the electrolyte to reduce concentration gradients resulting from the removal and replacement of water.

Hydrogen itself can be used as a heat transfer material by circulating it repeatedly through the cell. Again, a circulating pump is required that can handle hydrogen, sometimes in the presence of traces of electrolyte. Hydrogen is withdrawn from the circulating loop at the rate at which it is produced at the electrode, and the circulating loop contains the heat exchanger by which the waste heat of the cell is removed.

In the SPE-type cell, it is possible to circulate water through the cell, in contact with the electrolye, without leaching out the electrolyte itself. This approach is not possible in a cell that uses an aqueous electrolyte solution; and, in this case, a separate water compartment must be used. This is easier to achieve in a tank-type cell than in a filter-press type, although water-cooled plates can be built into stack-type cells. In some tank cells, a water chest, to act as a heat-removing mechanism, is incorporated into the design of the tank itself.

One of the problems of operating electrolyzer cells at very high pressures is that the auxiliary equipment, including the cooling system, would also have to be operated at high pressures; and thus the cost of even electrolyte and feedwater pumps, which in an atmospheric system would be insignificant, can become considerable.

Gas-Removal Systems

Once gas has been generated at the electrodes, it must be removed from the electrolyzer cell and conditioned to the temperatures, pressures, and purity levels required by the customer. There are two ways of removing the gas from the cell: One is to allow it to be entrained in the flowing stream of electrolyte, bring both out from the cell together, and pass the stream through an external separator. This usually makes the design of the electrolyzer cell itself more simple, but requires extra equipment for the separation of electrolyte from the gas. Clearly, two separator systems would be required — one for hydrogen and one for oxygen. The second method is to allow the gas to separate itself from the electrolyte within the cell and then remove it as a gas stream only. In this case, it is likely to carry over a spray of electrolyte, and a spray trap of some sort is needed. Once hydrogen and oxygen have been removed from the cell, they must be dried because they are produced from the cell saturated with water vapor. After drying, they must be compressed if the cell is not operating at the required delivery pressure. This need for an external compressor increases the parasitic load or energy requirement of the overall cell system. The removal of small traces of oxygen from the hydrogen stream can be accomplished by use of a so-called "deoxo" catalyst. This catalyst is usually a high-surface-area palladium catalyst, supported on asbestos, that has the effect of causing the traces of oxygen to combine with hydrogen to form water. Because oxygen and water vapor are the only major impurities likely to be found in electrolytic hydrogen, drying and oxygen removal are the only purification steps necessary for obtaining very high purity hydrogen.

Survey of Types of Industrial Electrolyzers

The Electrolyser Corporation

The Electrolyser Corporation Ltd., of Toronto, Canada, produces tank-type electrolyzers that use potassium hydroxide as the electrolyte. Their cell designs are known as Stuart cells and are sold in many parts of the world. A Stuart cell consists of a nickel-plated steel cell tank with positive and negative electrodes arranged alternatively and suspended from the cell cover. Electrodes in a single-cell tank are connected in parallel, and the cell tanks are connected in series to form a cell battery and to promote a higher overall voltage. consequently lowering rectification costs. This arrangement results in an operating voltage of approximately 2 volts dc, even in large cells.

Electrodes used in these cells are made of high-conductivity, high-surface-area, sand-blasted steel; the anodes are nickel plated to prevent corrosion. As in most tank electrolyzers, each anode is surrounded by a woven asbestos cloth diaphragm that prevents the mixing of hydrogen and oxygen. It also channels the oxygen generated toward a storage chamber beneath the cell cover. Hydrogen formed at the cathodes rises between the diaphragm to the hydrogen compartment under the cover. It is not uncommon for these diaphragms to last well over 20 years without replacement.

According to A. K. Stuart, the unique and proprietary construction of the Stuart-cell electrodes provides a large surface for electrolysis in a minimum of space. Because of the large active surfaces of the electrodes, Stuart says the cells are able to operate at a high total current with the surfaces exhibiting low current densities. Details of electrode construction are not publicly available.

The low cell-operating voltage and the physical separation of each cell tank simplifies electrical insulation within each cell and enables efficient sealing against loss of the electrolyte and gas product. The electrolyte is circulated independently within the cell by means of the lifting effect of the rising gas bubbles. This method requires no moving parts and avoids the hazards and complexity associated with external electrolyte pumping systems. A 10 to 15 year or more life span is customary before the electrolyte needs to be replaced. A 28% potassium hydroxide solution is the recommended electrolyte for the Stuart cell.

Each of the Stuart cells is automatically supplied with feedwater through individual valves set to maintain correct electrolye levels and concentrations. A cooling-water header passes along the rear of the cell tank, supplying individual hydrogen and oxygen scrubbers at the cell's gas outlets and a cooling jacket on the back of each cell. The water flow is adjusted to maintain optimum cell temperature; the effluent water is suitable for recycling. As is common with many tank electrolyzers, the Stuart cell operates at a rather low temperature, 158° F (70° C), and low current density, which minimizes waste-heat production. Under these conditions, overall cell efficiency is higher at all levels of hydrogen output than it would be if the cell were operated at high current densities.

The Stuart cell is rugged and simple to assemble and maintain, and the component parts are inexpensively fabricated. Hydrogen is produced at a 99.9% purity. Because the Stuart cell is contained in a closed system (not exposed to the atmosphere), the problem of formation of potassium carbonate from combination with the carbon dioxide in the air is not experienced.

The basic Stuart hydrogen plant is of modular construction in that an unlimited number of cells may be connected in series. Thus, hydrogen production capacity may be increased by simply adding more cells.[14] Plants consist of assemblies of cells, each 44 inches long and 49 inches high, ranging in width from 12 to 33 inches according to the number of electrodes and output capacity. Standard cells produce from 63.6 to 350 CF of hydrogen per hour and weigh from 1665 to 5135 pounds. Standard production rates for these cells, per 1000 amperes of current, are 15.9 CF of hydrogen per hour and 7.95 CF of oxygen per hour. The dc power consumption is 128 kWhr/1000 CF of hydrogen. Maximum gas production pressure is slightly above atmospheric (10 inches, water column).

Typical Stuart hydrogen plants produce hydrogen at the rate of tens of thousands of cubic feet per hour. The utility requirements of a typical Stuart electrolyzer plant are as follows: For 1000 CF of hydrogen and 500 CF of oxygen, electric power consumption (ac) is 133 to 145 kWhr; the demineralized feedwater required is 0.895 CF; and the cell cooling water required is 38.77 CF.

Some uses for hydrogen outputs in the tens of thousands of cubic feet per hour include the manufacture of semiconductor materials; that of hydrogen coolant at thermal and nuclear power stations; the synthesis of chemical intermediates for long-chain polymer production; the hydrogenation of oils and fats in margarine, shortening, and soap production; the direct reduction of metal oxides; the annealing of stainless and electrical steels; and that in float-glass manufacture.

Electrolyser Corporation makes a smaller unit known as the Stuart Packaged Hydrogen Generator. The generator is a self-contained, factory-assembled unit capable of producing pure hydrogen in quantities of from 20 to 1000 CF/hr.

Some applications for these smaller units include hydrogen for laboratories, the inflation of meteorological balloons, hydrogen and oxygen for cutting and welding, and the sintering of metal powders.

According to Stuart, both cell improvements and total hydrogen plant development are necessary to improve Stuart-cell hydrogen production. An increase in cell operating temperatures (a 2-year goal), from the current 158° to 194°F, is expected to increase the overall thermal efficiency by lowering the operating voltage. Stuart's 2 to 3 year goals for electrolyzer development include an electric-power consumption of 22.9 to 24.6 kWhr/lb of hydrogen produced, an operating voltage of 1.9 to 2.04 volts, and a thermal efficiency of 77%.

Stuart feels that some exploration of advanced diaphragm materials, to handle the higher temperatures of operation, will be necessary. Present asbestos diaphragms can possibly handle these temperatures, but the upper limits consistent with a satisfactory life span are not yet known. Life testing is now being performed. Continued development of electrodes has the potential of lowering cell overvoltage.

Some scale-up of present cells is expected; however, overall plant development is necessary to provide the best economics. The economic conversion of shaft power to high dc current is considered by Stuart to provide the best opportunity for improved operation of his cells. Acyclic generators rated at 250,000 amperes (dc) would be connected directly to high-current cells. Acyclic generators would not require the switchgear or transformers needed with the more conventional ac-dc rectification equipment. The capital costs for conventional ac-dc conversion are approximately $40/kW, whereas capital costs for an acyclic generator are expected to be about $10/kW.

According to Stuart, no heat-transfer problem is expected when his cells operate from a 250,000-ampere dc source. Heat transfer associated with Stuart-cell scale-up has not posed any problem in a series of scale-ups. Stuart cells operate at a current density of 125 A/sq ft and have gone up to 500 A/sq ft without evident heat difficulty.[13]

Teledyne Isotopes, Inc.[4,5,16]

Teledyne Isotopes, of Baltimore, Md., acquired the fuel-cell and electrolyzer R&D technology that had been developed by Allis-Chalmers Corp. up until 1967. Teledyne manufactures, or can build to suit a user's requirements, three families of hydrogen producing electrolyzers: 1) generators that produce from 0.177 to 0.353 CF/min, 2) systems that produce from 0.177 to 7.06 CF/min, and 3) plants that produce several tons/day.[4] Plants in categories 1 and 2 have been sold commercially, but plants in category 3 have yet to be ordered and built.

The current Teledyne Electra cell systems are of filter-press type and, in general, consist of modules made of multiple electrolysis cells connected in series, electrically, by common bipolar plates. The electrodes are separated by a matrix saturated with electrolyte. The matrix prevents mixing of the gases and provides a conductive path for the electrode current. As the hydrogen and oxygen are formed, they are kept apart; and the gases from each cell are ducted internally, through manifolds, to storage containers.

The electrolyzer uses a potassium hydroxide-water solution (25% by weight) electrolyte with advanced-design, porous nickel electrodes and operates at moderate temperatures, 100° to 200°F. The cell contains no precious-metal catalysts.

Various subsystems support the electrolysis module by recirculating and cooling the electrolyte, adding water, conditioning the product gases, and supplying electricity.

Small hydrogen generators that produce from 0.177 to 0.353 CF of hydrogen/min are used for such applications as producing carrier gases for gas chromatographs and fuel for flame-ionization instruments, primarily in the pollution-control and monitoring industry. These small generator units operate from a standard 110 volt (ac) power source and delivery hydrogen at from 0 to 35 psig with a purity of better than 99.99%.

A schematic diagram of the generator system is provided in Figure 3-4. The electrolyte is recirculated on the oxygen side of the module to supply each cell with water and to remove heat. The generation of oxygen gas in the cell provides a gas-lift effect for convective circulation, thereby eliminating the need for a pump. While auxiliaries are available to provide for con-

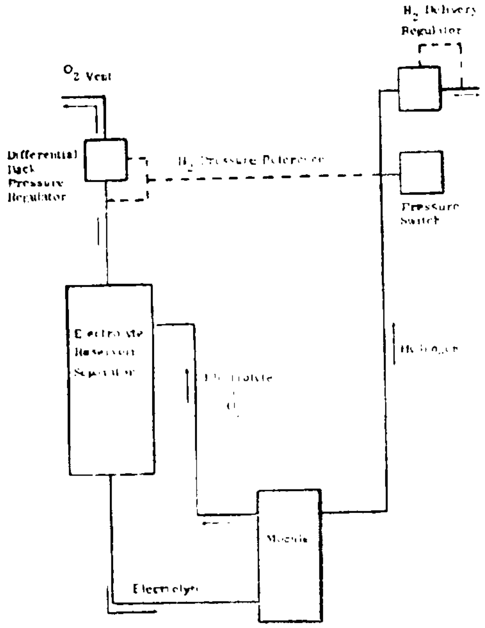


Figure 3-4. SMALLEST TELEDYNE HYDROGEN GENERATOR[7]

tinuous water replacement, the basic system operates on a batch-feedwater refill technique. In most cases, heat is removed at the electrolyte reservoir by natural convection to the ambient air, allowing the system to operate at less than 130°F.

Larger quantities of hydrogen are produced with the Teledyne intermediate-size electrolysis systems. Where larger quantities of hydrogen are needed for industrial processing, such as in the production and sintering of metal powders of iron, nickel, cobalt, and molybdenum, for the bright annealing of stainless steels, or in electrical-utility use, Teledyne electrolysis units have been sized to provide from 0.177 to 7.06 CF of hydrogen/min. Increased capacity and optimum equipment utilization can be provided by using multiple units.

This system differs from the smaller generator in that the electrolyte is recirculated on the oxygen side of the module by a centrifugal pump. This arrangement resupplies each cell with water, removes heat, and carries away generated oxygen. A tube-and-shell type heat exchanger is provided to transfer heat to a water cooling loop. Usual system operating temperatures are less than 185°F. Oxygen is separated from the electrolyte in the electrolyte reservoir, where the supply of water is also renewed. The separated oxygen flows through a condenser to remove excess moisture and then flows to a pressure-control device to regulate and control the oxygen and electrolyte loop pressure. Hydrogen generated in the module is manifolded and is piped directly to a condenser for removal of most of the water vapor and then to a molecular sieve dryer.

These larger systems weigh from 1000 to 2000 pounds per cabinet and have dimensions of 33 x 74 x 64 inches. Facilities to supply 460-volt (ac), three-phase electricity, cooling water, feedwater, and a small amount of inert gas are the only other facilities required. This system requires a minimum of maintenance. The electrolyte is sampled once a month to determine its specific gravity. After the initial electrolyte change at the end of the first month of operation, the electrolyte is changed only semiannually. Semiannual changing of the electrolyte filter, water-flushing of the solenoid valves, and calibration of the pressure switches are recommended.

When quite large quantities, several tons per day, of hydrogen are required, Teledyne recommends a considerably different system of hydrogen production. A schematic diagram of this system is shown in Figure 3-5. In this system, the electrolyte circulates to both sides of the electrolysis module, which allows for more efficient heat removal and simplifies the pressure-control function. The electrolyte is recirculated by a single pump to both the hydrogen and oxygen cavities of the module. Each gas and electrolyte mixture is then returned to a different reservoir and separator where the gas and liquid phases are separated. The electrolyte is cooled in a heat exchanger and then mixed with electrolyte from the opposite portion of the system. Replacement water is continuously added at the mixing chamber. The gases are piped through condensers to remove excess moisture and then through a pressure-control device and are finally delivered for use. With this system of "double flooding" the gas-collection chambers, there is a) no pressure differential across the diaphragm or pushing away of the electrodes, which may occur with a large enough pressure differential, b) no concentration gradient across the cell, and c) a more economical production of hydrogen because more hydrogen is

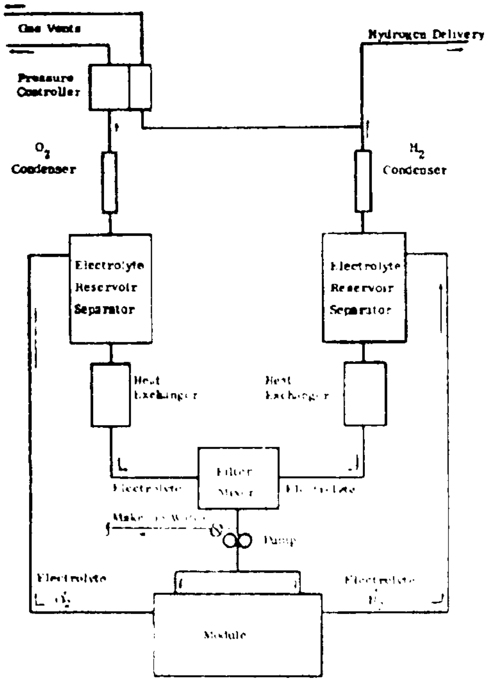


Figure 3-5. LARGER-MODEL TELEDYNE HYDROGEN GENERATOR[7]

being produced while the costs and requirements of auxiliary equipment remain the same. Simple pressure-control devices are incorporated in this cell system to allow an operation of up to approximately 100 psig.

These systems can be controlled to provide constant gas-production rates and a specified level of gas purity. Multiple-system packages can be installed to supply virtually an unlimited quantity of hydrogen. Each system occupies approximately 260 cu ft of floor space and will generate hydrogen at an efficiency of 140 kWhr/1000 SCF.

Although none have been built, Mr. W. C. Kincaide of Teledyne states that the hydrogen plants producing 1 to 4 tons of hydrogen/day would operate at an electrical-conditioning efficiency of 95% and at an electrolysis efficiency of 82%.

Future expectations for 2 to 5-year developments include electrolyzer cells consuming 19-22 kWhr/lb at an operating voltage of between 1.6 and 1.8 volts and an overall thermal efficiency of between 82 and 92%. Ultimate goals project the development of a cell that consumes 15 kWhr/lb of hydrogen and has an operating voltage of 1.24 volts at a 118% thermal efficiency, which is almost congruous with the thermodynamic limit.

Teledyne mentions certain goals yet to be attained. Increased operating efficiencies can be achieved by the use of noble-metal catalysts on the electrodes in the modules; but, in some cases, the additional increase in capital costs can more than offset any advantage gained. Teledyne is currently engaged in continuing the development of low-cost catalysts that would lower overvoltages.

Teledyne states that improvements in cell operating-temperature capability are expected within the next 2 years and should produce operating-efficiency improvements of 15%. Improvements in cell materials must also be developed to withstand the increased temperatures. It is expected that present asbestos diaphragms or gas separators will not be able to withstand increased temperatures of operation, and research is being undertaken to alleviate this problem.

Teledyne revealed that it has had problems in obtaining good commercially manufactured parts for its electrolyzers. In many instances it has developed its own system parts to meet close tolerances and specifications.

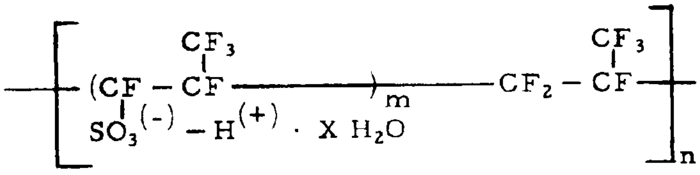
All Teledyne systems currently operate at pressures higher than ambient. An insignificant power penalty (0.431 kWhr/lb of hydrogen at 100 psia) is realized when compared with conventional compressors. Teledyne realizes the importance of the generation of hydrogen at high pressure to storing and transmitting large amounts of the gas. The operating pressures of present systems are limited by structural features. One specific question being reviewed by Teledyne is whether to design a cell stack to withstand pressure or to place a pressurized tank around an existing stack. Studies are being performed to determine the demand and cost effectiveness of high-pressure systems in commercial applications. Teledyne is building, for the U.S. Navy, electrolytic gas generators that operate at pressures of up to 3000 psig. Power penalties for generating gas directly at this pressure are less than 1.197 kWhr/lb.

General Electric Company[2, 11, 18, 19, 20]

General Electric Co. of Lynn, Mass., has been developing a water-electrolysis system based on solid-polymer-electrolyte (SPE) fuel cell technology. SPE fuel cells were first used in space during the Gemini Program, in which they provided primary on-board power for seven of the spacecraft flights.

According to staff at GE certain technological advances in the design of the SPE have resulted in a water-electrolysis unit of considerable simplicity in design and operation that can maintain stable and efficient use of relatively expensive electricity supplies.

The SPE is a thin, solid, plastic sheet of perfluorinated sulfonic acid polymer, which has many of the physical characteristics of Teflon. Chemically, the polymer approximates[20] –



$$-\left[(\underset{\substack{|\\ SO_3^{(-)}-H^{(+)}\cdot X\,H_2O}}{CF}-\overset{\substack{CF_3\\ |}}{CF}\text{———})_m\text{———}CF_2-\overset{\substack{CF_3\\ |}}{CF}\right]_n-$$

Unlike Teflon, however, when a thin sheet of this material is saturated with water, the polymer becomes an excellent ionic conductor, providing low electrical resistance. Used in an electrolysis cell, it is the only electrolyte required; there are no free acids or alkalis in the system. Ionic conductivity is provided by the mobility of the hydrated hydrogen ions ($H^+ XH_2O$), which move through the sheet of electrolyte by passing from one sulfonic acid group to another. Because the system is solid, the sulfonic acid groups are fixed, keeping the acid concentration within the electrolyte constant.

An important feature of the SPE system is the simplicity of the electrodes. Because the electrolyte is a solid, the catalytic electrodes are not required either to retain or support the electrolyte, and can therefore be optimized for catalytic activity at minimum cost. Currently, a thin layer of high-catalytic-activity platinum black is attached to the SPE surface to form the hydrogen electrode. A similar layer of a proprietary precious-metal-alloy catalyst forms the oxygen electrode. Additional metal current collectors are pressed against the catalytic layers. To date, the system has incorporated the use of niobium or titanium as the current-collector and separator-sheet material. Figure 3-6 is a schematic diagram of the SPE electrolysis cell.

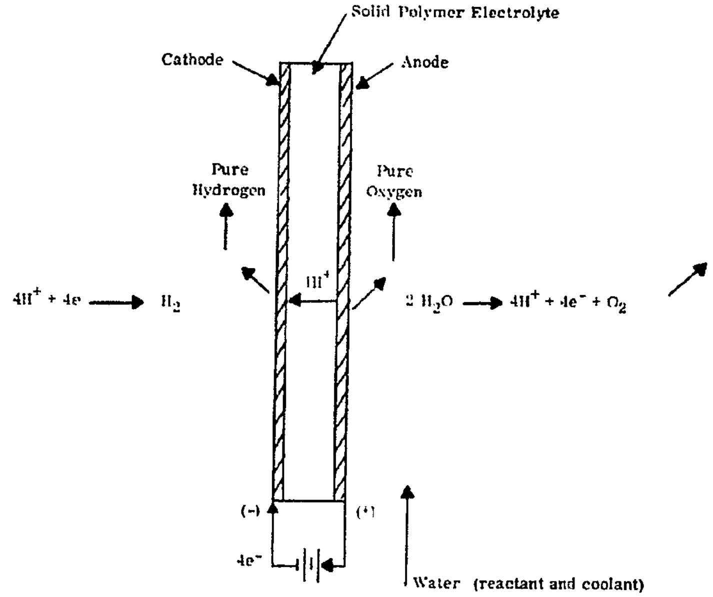


Figure 3-6. SCHEMATIC DIAGRAM OF AN SPE ELECTROLYSIS CELL[11]

In this configuration, water is supplied to the oxygen-evolving electrode (the anode), where it is electrochemically decomposed to provide oxygen, hydrogen ions, and electrons. The hydrogen ions move to the hydrogen-evolving electrode (the cathode) by migrating through the SPE. The electrons pass through the external circuit and to the hydrogen electrode. At the hydrogen electrode, the hydrogen ions and electrons recombine electrochemically and produce hydrogen gas. An excess of water is usually supplied to the system and is recirculated to remove any waste heat.

The gases produced by the SPE are generated, at any pressure, in the stoichiometric ratio of hydrogen to oxygen. The electrolyte sheet can withstand pressure differences of up to 1000 psi, as well as high generating pressures (up to 3000 psi), simply by back-pressuring the system. The high generating pressures may be useful in solving transmission and storage problems.

According to staff at GE, use of the SPE results in the following advantages[18, 20]:

- The cell can operate with high differential pressures (>1000 psia) in addition to high gas-generating pressures.
- The concentration of the electrolyte is fixed, and the electrolyte is not mobile.
- There is no possibility of acid carry-over into the effluent gas.
- There are no corrosive electrolytes to control or that can leak in the system.
- The electrolyte is essentially invariant in operation.
- The acid-SPE electrolysis unit results in a minimum power requirement per unit of gas generated.
- High-current-density capability can result in an optimum design for low capital cost, as well as for low operating cost.

Although most of the SPE development was done for the space program and for aircraft applications, GE now produces two smaller hydrogen generators for commercial applications. Applications for these generators include the production of hydrogen for gas chromatographs and for flame-ionization detectors. At present, 22 kWhr of power are absorbed per pound of hydrogen produced at an operating voltage of 2.00 volts and a thermal efficiency of 74%.

The future of the GE cell seems to lie in operations at very high efficiencies, thus minimizing power costs and justifying the relatively high capital costs. Because these cells will also operate at higher current densities, a greater hydrogen-production rate per unit cost will be achieved. GE's objectives are to further improve the thermal efficiency of the SPE-cell system

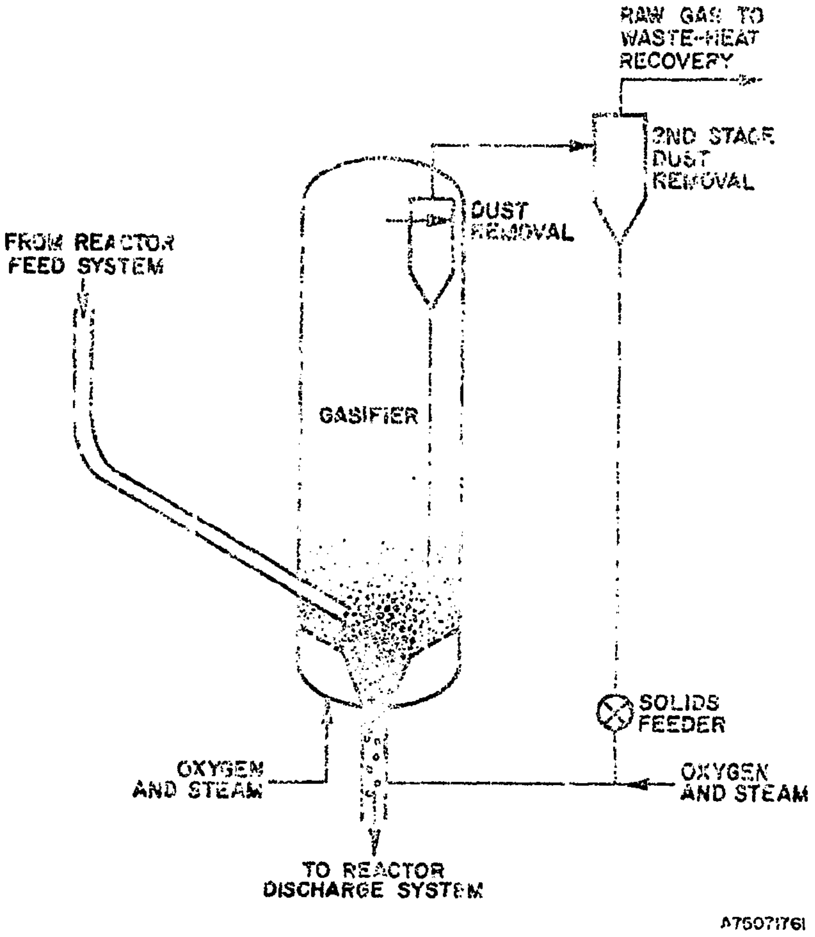


Figure 5-4. SIMPLIFIED DIAGRAM OF THE GASIFIER TO BE USED IN THE IGT U-GAS SYSTEM WHEN PRETREATMENT IS NOT REQUIRED

[illegible], the cost of the boiler is less; and, more importantly, the plant is more [illegible] by from 3% to 7%, again depending on the type of high-temperature [illegible] system used as a comparison.

The low-temperature shift catalyst cannot be used with a gas that contains [illegible]. Because the acid-gases (hydrogen sulfide and carbon dioxide) must be removed at some stage of the process, it is desirable in our design to remove [illegible] hydrogen sulfide prior to, the carbon dioxide after, the carbon monoxide

Table 5-8. U-GAS HYDROGEN-FROM-COAL PLANT
(Based on the Use of Montana Subbituminous Coal)

	Gasifier Raw-Gas Composition	Product-Gas Composition
	mol % (dry basis)	
Carbon Monoxide	50.1	0.1
Carbon Dioxide*	11.5	--
Hydrogen	35.3	94.3
Methane	2.1	4.8
Nitrogen and Argon	0.7	0.8
Hydrogen Sulfide	0.3	--
Total	100.0	100.0

*50.0 ppm

Prior to hydrogen sulfide removal, the gas is compressed to 700 psig. [illegible] facilitates acid-gas removal because a physical absorption system has [illegible] chosen for the plant, and higher partial pressures are favorable for [illegible]. The unit selected for acid-gas removal is a two-stage Rectisol [illegible] that is similar to units that have been successful in commercial opera[illegible]. The hydrogen sulfide absorption system produces hydrogen sulfide-rich [illegible] that yields 76.1 long tons of molten sulfur per day in the sulfur-recovery [illegible], with 250 ppm of sulfur remaining in the gas vented to the atmosphere.

After shifting, the carbon dioxide is removed in the second stage of the [illegible] unit. This carbon dioxide-rich stream is vented to the atmosphere. [illegible] sulfur content is claimed to be less than 5 ppm.) A methanation unit is [illegible] to reduce the carbon monoxide content of the product gas from 1.5% to [illegible]. This is more economical than using the shift reaction to convert all of [illegible] monoxide. The unit is a single-stage, adiabatic reactor similar to [illegible] used in ammonia plants in removing carbon oxides. Water is removed and to develop lower cost materials and manufacturing processes to achieve an overall cost for large-scale electrolytic hydrogen production of $2 to $3/million Btu (based on 1974 costs), assuming electrical-power costs in the range of 5 to 10 mills/kWhr.

W. A. Titterington lists four specific elements to be included in a long-range development program: 1) electrolysis-module development, 2) system definition, 3) demonstration of a 5-MW prototype, and 4) incorporation of advanced technology.

SPE electrolysis-module technology is limited mainly by the cell operating temperature and by the lack of suitable cell-component materials. The importance of cell operating temperature is reflected by the fact than an increase in temperature from 80° to 220°F decreases power consumption by 10% with the same amount of hydrogen produced. At 300°F, if cell operating temperatures as high as this can be attained, the theoretical decomposition voltage of water decreases from 1.18 volts (at 180°F) to 1.12 volts. However, at 300°F the cell-sealing techniques or gasket materials may be a problem because they cannot withstand high temperatures and wet environments.

Experience has also been obtained at hydrogen gas generation pressures of up to 3000 psia. The resulting effect on performance is shown in Figure 3-7.

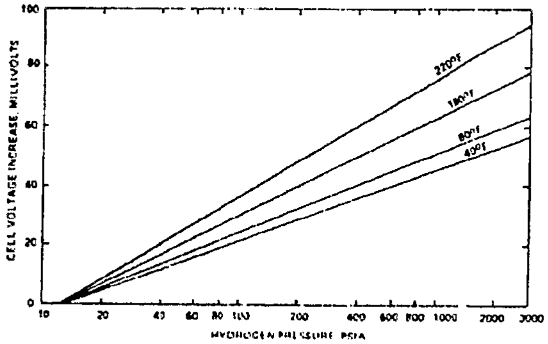


Figure 3-7. EFFECT OF HYDROGEN PRESSURE ON GE-CELL VOLTAGE[20]

To date, the SPE electrolysis systems have used niobium or titanium as the collector and separator-sheet material, in spite of statements that the SPE is noncorrosive. Niobium is quite expensive, $40 to $50/lb; titanium, however, has a more desirable price, $8/lb. GE states that alternative materials, including molybdenum, zirconium, and various alloys of these materials, should be tested for compatibility in high-temperature SPE electrolysis cells.

The SPE in the currrently manufactured cells is 12 mils thick. Considerable voltage reductions could be attained by halving this thickness. Representatives from GE have suggested that minor modifications in both the cell-fabrication technique and the hardware design would then be required. Further reduction in the thickness of the SPE could further lower the electrical resistances; therefore, more experiments are to be conducted along this line. It must also be remembered that as the SPE's thickness is decreased, its cost is also decreased. Alternative, lower cost SPE's (at as low as $2/sq ft) are currently under development.

Two other areas of research that may provide economic advantages for the SPE cell are decreases in the catalyst loadings on the electrodes and advancement of the catalytic electrodes. Progress in these areas could result in lower capital costs for the entire cell and in lower overvoltages at both the anode and the cathode. The present cathode catalyst is platinum black, with loadings of 4 mg/sq cm. A proprietary metal-alloy catalyst is applied to the anode, also at a loading of 4 mg/sq cm. Expectations of catalyst loadings as low as 1 mg/sq cm on each electrode are not unreasonable.

Life Systems, Inc.[3, 12]

The static feedwater electrolysis system developed by Life Systems, Inc., under NASA sponsorship, has potential applicability for terrestrial hydrogen production. Developed for the space program, the static water electrolysis system uses a) an alkaline electrolyte; b) a method whereby the electrolyte is retained in a thin, porous matrix, eliminating bulk electrolyte; and c) a static water feed mechanism (depending on distillation of water inside the cell) to prevent electrode and electrolyte contamination and to eliminate the need for very pure feedwater.

In the static water feed system, the water to be electrolyzed is supplied to the cell electrolyte as a vapor. Each cell is divided into three main compartments: a water-feed compartment, a hydrogen-gas compartment, and an oxygen-gas compartment. Compartment separation and liquid-vapor phase separation are achieved by the capillary action provided by liquid-filled asbestos sheets. Catalyzed porous-nickel plaques support the cell matrix, forming a composite electrolysis site. Plastic screens similarly support the water feed matrix. The cell configuration is given in schematic form in Figure 3-8, and Figure 3-9 shows the principle of cell operation. The latter figure represents a thermally insulated box enclosing two bowls of electrolyte. When power is applied to the electrodes, water in the cell electrolyte is consumed. As a result, the concentration of the cell electrolyte increases, causing its vapor pressure to drop below that of the feed-compartment electrolyte. This difference in vapor pressure is the driving force that causes the water vapor to diffuse across the hydrogen cavity to the cell matrix.

Two major advantages to this cell system are apparent: 1) the product gases need not be separated from the feedwater or electrolyte, and 2) semipure water may be used because contaminants rarely lower the vapor pressure of the feedwater. The electrodes and electrolyte remain uncontaminated because the water comes to the hydrogen electrode as pure vapor. The only factor limiting impurities is the eventual blockage of the feedwater-matrix pores. The amount of water transferred is direrctly proportional to the difference in water vapor pressures of the cell and feed electrolyte.

The cell design utilized in the static feed system includes a bipolar-plate, filter-press construction with welded bus bars providing intercell current connection. The hydrogen electrode is placed directly on the cathodic current collector. Current then flows from the cathode, through the matrix, and to the oxygen electrode. An expanded nickel screen is placed on the back of the anode, .providing both a path for the current and a space for oxygen evolution. A major portion of the cell's inefficiency in the electrolysis of water occurs at the anode, and this inefficiency results in waste heat that must be removed. The cell coolant passages were placed directly over the bipolar plate opposite the oxygen cavity. If air cooling is desired, this plate is extended out past the cell frame, forming external fins for convection or forced air cooling.[3]

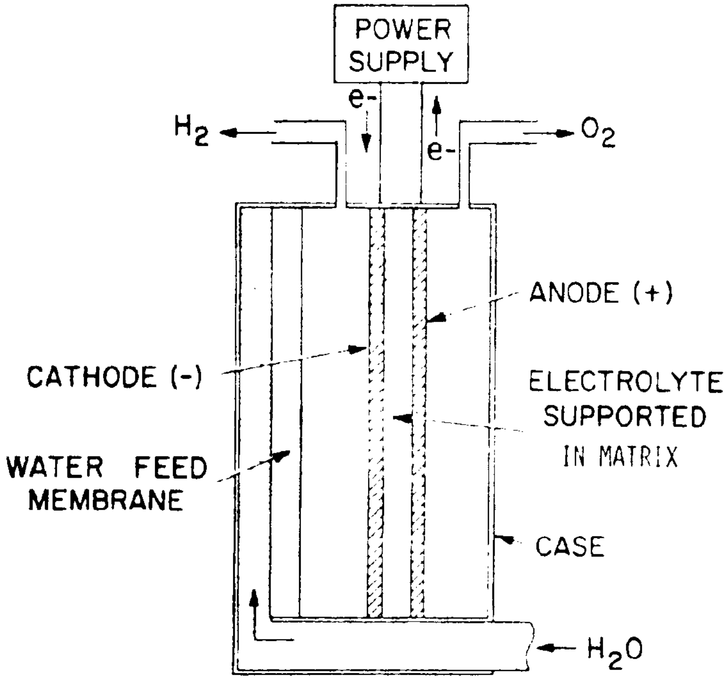


Figure 3-8. LIFE SYSTEMS CELL CONFIGURATION[3]

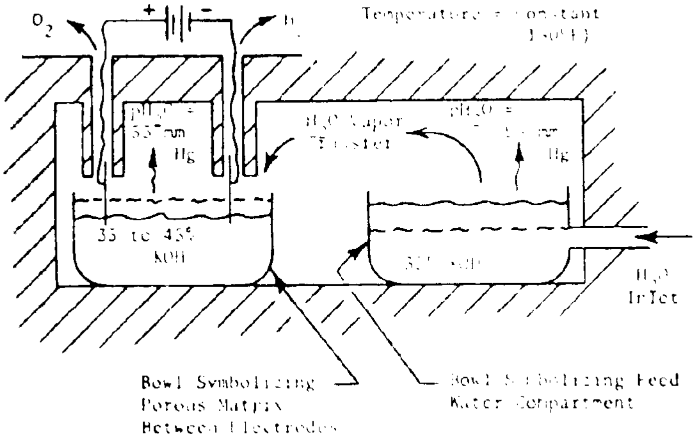


Figure 3-9. LIFE SYSTEMS CELL OPERATION[3]

Because Life System's electrolysis designs were developed for the space program, expensive materials were utilized to provide reliability and efficiency. The system cell frames are injection-molded from flame-resistant plastic. All metallic parts are made from nickel alloy, which is then gold-plated. Both the feedwater matrix and the cell matrix are made of Life System's reconstituted asbestos. Other cell materials include stainless-steel end plates and polypropylene screens used to provide structural support for the matrices.

The electrolyte used is a 35% potassium hydroxide-water solution instead of the more electrically conductive 25% to 28% solution.[3] At higher electrolyte concentrations and at higher temperatures, differences in the concentrations of the water feed and all the cell-matrix electrolyte result in greater water vapor partial-pressure differences. Because this difference is the driving force for the amount of water transferred, this phenomenon is accelerated.

The projected 1975 capabilities for Life Systems's cells are –

- Maximum pressure, 2000 psi
- Maximum temperature, 300 °F (for short periods)
- Maximum current density, 1500 A/sq ft
- Power requirement, 129 kWhr/1000 SCF of hydrogen at 1500 A/sq ft
- Single-cell area, 0.10 sq ft.

At Life Systems, studies are under way on an alternative diaphragm material suitable for high-temperature (>200 °F) electrolysis. Potassium titanate has shown some excellent high-temperature and long-life stability capabilities. Additional studies are also being conducted on the availability of alternative structural materials suitable for high-temperature applications and enabling cell operation with lower electrolysis power requirements. Advanced designs, using zirconia and yttria-thoria ceramics for solid electrolytes, are being evaluated. These electrolytes conduct only at temperatures above about 1490 °F. Advanced catalyst development is also being performed to increase electrode performance and to lower costs. This work is being conducted in parallel with the high-temperature research in order to develop high-pressure, large-scale hydrogen generation.[3]

Lurgi GmbH [8,22]

Of the many electrolyzers produced in other countries, the Zdansky-Lonza electrolyzers, manufactured by Lurgi GmbH, Germany, are particularly noteworthy because these electrolyzers, working under a pressure of 30 atmospheres, are very economical, compact, and reliable. The Lurgi electrolyzer is basically of the filter-press type.

In each cell of the electrolyzer, between two round, nickel-plated discs pressed in nickel-plated gaskets, are pressed-metal screen electrodes, pressed-asbestos diaphragms, and sealing and insulating gaskets. The gas manifolds are located within the cells and are formed of Teflon rings: The holes in these provide passages from the inner space of the cells to the gas channels. The cells are very narrow, making it possible to connect several hundred cells (up to 500 cells in the largest electrolyzer) in one single apparatus.

Forced electrolyte circulation is used in the Lurgi electrolyzer. A pump forces cool electrolyte through an asbestos filter and into the lower manifold of the cell bundle. The electrolyte is cooled in the gas separators by means of coils built into storage drums through which the coolant and condensate circulate. The condensate is pumped through a closed loop and is cooled in an adiabatic heat exchanger. The total volume of condensate in the cooling system of an electrolyzer consisting of 250 cells with a capacity of 10,543 CF/hr of hydrogen is 28.25 CF.

Hydrogen and oxygen are manifolded into separate collection chambers. A floating valve is installed in the oxygen gas separator to regulate the escape of oxygen and to maintain a constant electrolyte level in the gas separator. Desalinated feedwater is provided to the cells by means of a variable-ratio pump, the capacity of which is adjusted manually, depending on the electrolyzer load.

If the level of the electrolyte in any of the gas-separator drums drops, the corresponding safety floating valve is opened; and the gas, the pressure of which was too high, is vented into the atmosphere. If the electrolyte level in one of the gas separators continues to drop, a magnetic relay shuts the electrolyzer down.

Lurgi produces only one size of electrolyzer, circular in shape and about 5 feet in diameter. Electrolyzer cells are assembled, at the factory, in blocks of from 70 to 139 cells. These preassembled cell blocks can be installed at the operation site. Each block is pressed together by end plates coupled with tie rods. The pressure exerted by the tie rods is so great that totally reliable sealing is obtained in all the cells. A typical electrolyzer unit has an output capacity of from 110 to 750 standard cubic meters (or 4100 to 28,300 SCF) of hydrogen per hour. The delivery pressure is 30 kg/sq cm (or 440 psig). The electrolyte is 25% KOH, and the specific power consumption is from 4.3 to 4.6 kWhr per standard cubic meter of hydrogen (or 116 to 124 kWhr/1000 SCF of hydrogen). A typical plot of specific power consumption versus current for a cell with a diameter of 1.6-meter is shown in Figure 3-10.

According to staff at Lurgi, improvements in performance can be expected if they can find a way to increase the operating temperature of the cell. They believe that the factor limiting the temperature increase is the asbestos diaphragm. Researchers at Lurgi are also working on improved catalysts for the electrode structures, but information on these remains proprietary.

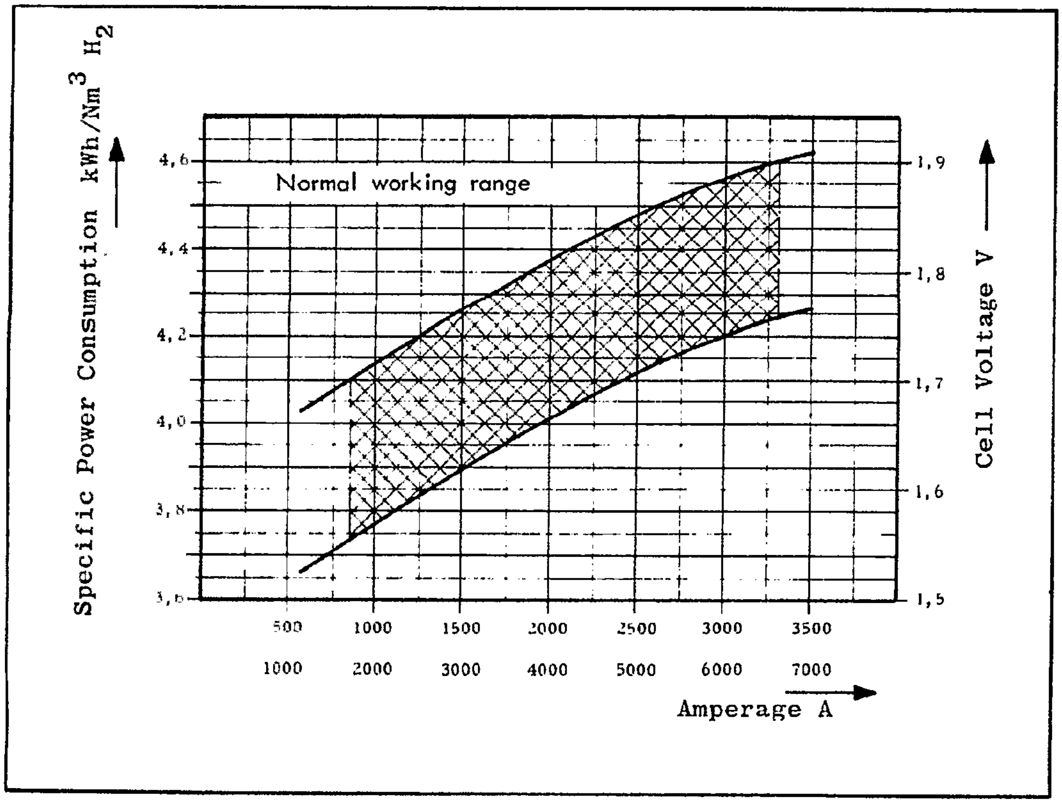


Figure 3-10. OPERATING CHARACTERISTICS OF ELECTROLYZER

A typical Lurgi high-pressure electrolyzer is shown in Figure 3-11.

Cominco, Ltd.[9, 10]

One of the largest hydrogen plants in the world is located in Trail, British Columbia, Canada. Although it has been shut down for over a year now because of rising power costs, this plant represents the first North American attempt at large-scale hydrogen production.

Individual cells are of Cominco patented design. The characteristic feature of this tank-type cell is a concrete top that supports the electrodes, asbestos diaphragms, asbestos collecting skirt, feedwater pipes, bus bar, and gas-main connections. In this concrete cover also are the two gas chambers for hydrogen and oxygen and the narrow, inverted-trough-like collecting bins. The cell tank is made of iron, and the electrodes are made of mild steel plates. The anode is nickel-plated and has a current density of 67 A/sq ft.[15]

This hydrogen plant contains 3229 individual cells and has a total theoretical hydrogen-producing capacity of 41 tons of hydrogen/day. The cells operate at about 2.1 volts, the current efficiency is close to 100% at atmospheric operating pressure, ac-dc rectification is provided, and the overall ac power consumption is about 60,000 kWhr/ton of hydrogen.[10] At a usual operating temperature of 140°F, some cells have life spans of over 20 years.

De Nora, S.p.A.[1]

De Nora, S.p.A., of Milan, Italy, manufactures large, industrial, electrochemical processing plants that include the electrolysis of water in their range of applications. Of the three large electrolysis installations built since 1945, De Nora built the 1,059,300 CF/hr plant at Nangal, India. (The other two are a 2,118,600 CF/hr plant in Raikon, Norway, with its own Zdansky-type electrolyzers, and a 1,412,400 CF/hr plant at Kima, Egypt, built by Demag of Germany.) All these units are of bipolar, filter-press construction.

The standard De Nora electrolyzer[1] consists of rectangular cells 16.4 feet wide by 5.25 feet high. These are stacked in series on either side of a cooling chamber and are surmounted by an electrolyte gas separation unit. Figure 3-12 is a photograph of a typical cell stack.

A unique feature of the De Nora design is the use of a double diaphragm. Two distinct layers of woven asbestos are used. These are in physical contact with each other, but the space between them is vented to the atmosphere.

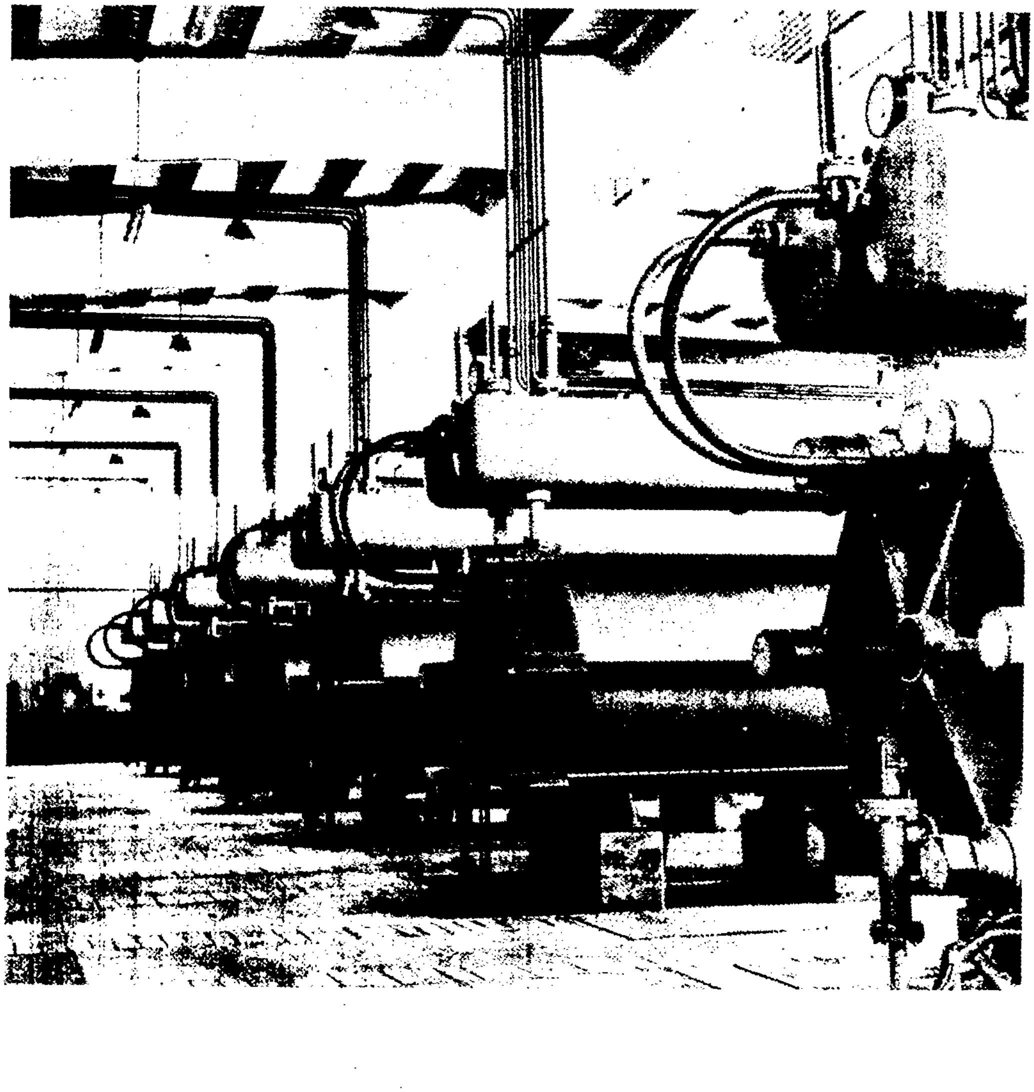


Figure 3-11. LURGI HIGH-PRESSURE ELECTROLYSIS PLANT (5100 Standard cu m of Hydrogen and 2550 Standard cu m of Oxygen per Hour)[8]

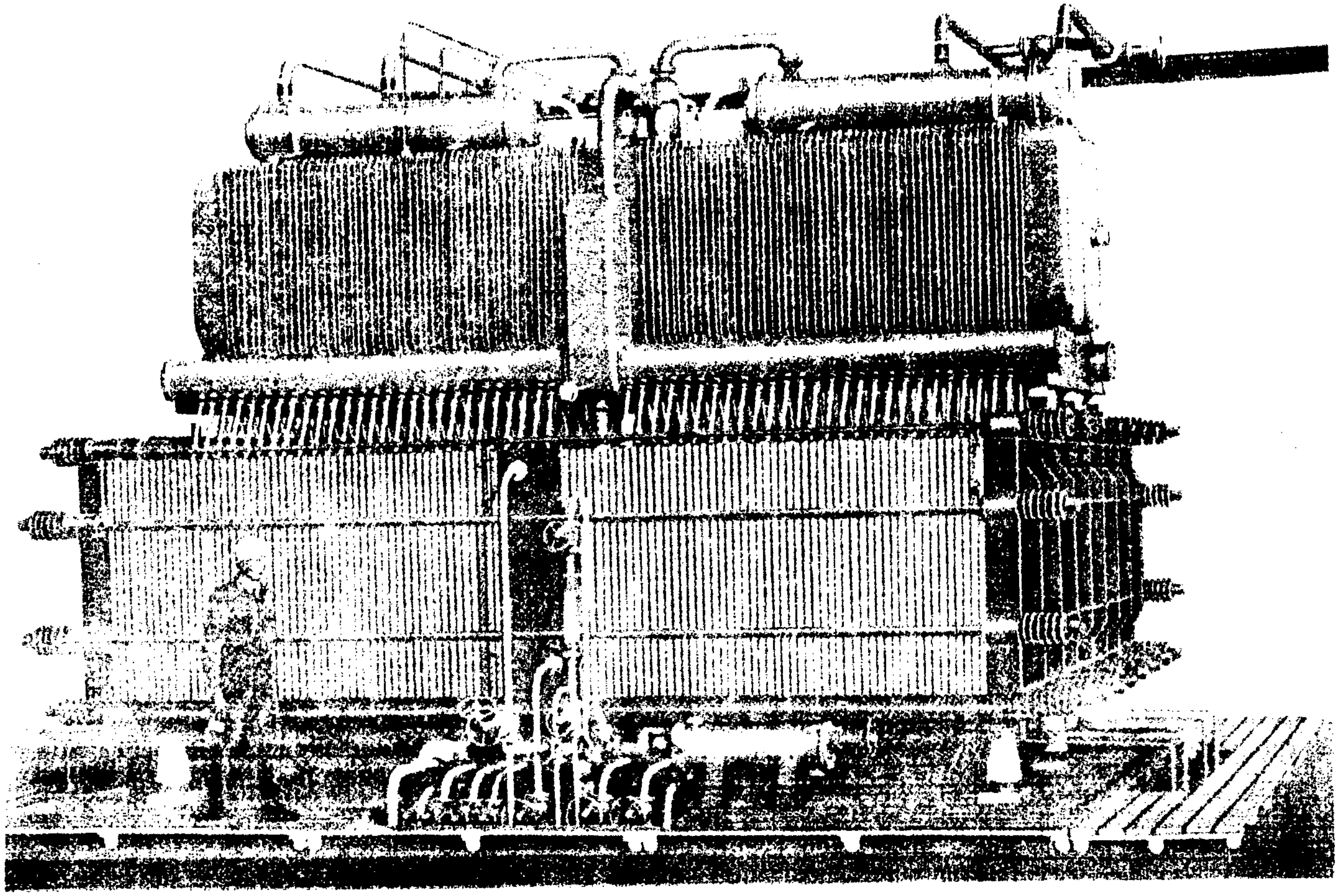


Figure 3-12. DE NORA WATER ELECTROLYZER[1]

During normal operation, the diaphragms are pressed against one another; but any penetration of gas bubbles results in the formation of a larger bubble between the diaphragms, which is then vented to the outside, and thus cannot intermix with the opposing gas.

The electrodes are single-layer sheet metal,perforated to allow gas to exit, and have a proprietary electrolytic surface treatment that creates a large surface area. No precious-metal catalysts are used. The electrodes are of low-carbon steel, and the anode is nickel-plated. The electrolyte is 25% KOH.

The Nangal plant consists of 60 units, each with 108 cells. Each cell stack is 16.4 x 5.25 x 49.2 feet in size and consumes 12,000 amperes at from 2.2 to 2.3 volts per cell (250 volts or 3 MW per unit). Thus, the entire plant consumes 180 MW (dc).

De Nora's standard cell sizes are 2500, 4500 and 10,000 ampere capacity and operate at about 180 to 200/sq ft. The Nangal plant, built in 1960, had a guaranteed performance of 2.1 volts per cell at 10,000 amperes. Any new plant delivered today would have a guaranteed performance of 1.85 volts at 12,000 amperes,[21] made possible by better activation treatment of the electrode. A performance of 1.80 volts at 18,000 amperes (300 A/sq ft) might be made possible by dissolving a homogeneous catalyst in the electrolyte, an approach that seems to be unique to De Nora.

Comparative Evaluation of Various Electrolyzers

Figure 3-13 is a comparison of the cell operating performances of various electrolyzers. These data are meant to give only a technological comparison of cell types, not a comparison of the economics; but a cell comparison based on voltage-current relationships is meaningless unless cell cost is included.

Interestingly, data for some advanced cell types are shown near and below the 1.47-volt point at current densities as high as 50 A/sq ft. Under these conditions, the cell operates "thermoneutrally," and the apparent thermal efficiency is 100%. This gives some reassurance that electrolyzer efficiencies approaching 100% can be achieved in practical units. At present, however,

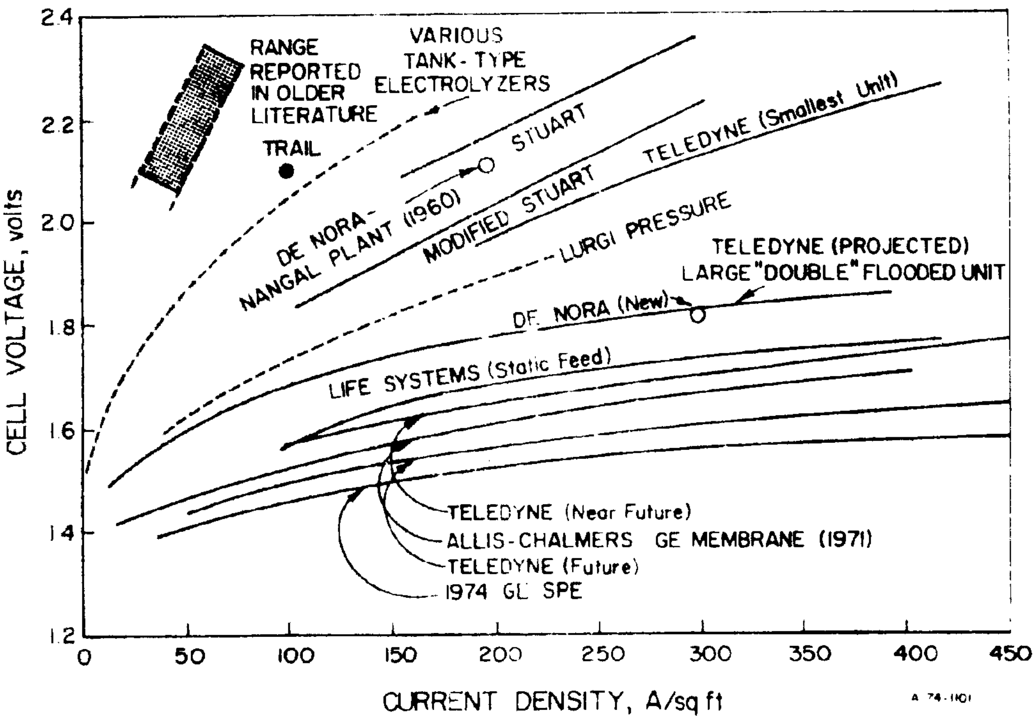


Figure 3-13. COMPARATIVE PERFORMANCE OF ELECTROLYZER SYSTEMS

operation of the GE cell at current densities below 1000 A/sq ft will cause proportionate increases in the effective capital cost.

Survey of Electrolyzer Manufacturers

Seven commercial manufacturers of fuel cells were contacted through either personal visits or correspondence. In addition, two chemical companies that manufacture and operate their own cells supplied limited information for the survey, as did one company that makes electrolyzers for space applications. (See Table 3-1). Manufacturers were asked to describe their systems, to provide data on cell performance and efficiency, and to provide enough cost information to enable us to derive the cost of hydrogen produced as a function of the amount of electric power supplied. It is noteworthy that a) manufacturers of the larger installations of electrolyzers are located in Europe, not in North America, b) very few of the manufacturers produce cells capable of delivering hydrogen at pressure, and c) most of the manufacturers prefer the stack or filter-press design to the tank type.

Table 3-1. MANUFACTURERS SURVEYED

Name	Location	Type	Pressure, psig
Electrolyser Corp.	Canada	Tank	0.4
Teledyne Isotopes, Inc.	U.S.A.	Stack	35-3000
De Nora, S.p.A.	Italy	Stack	1
Lurgi GmbH	W. Germany	Stack	440
Construction John Brown, Ltd.	U.K.	Stack	440-3000
Brown-Boveri	Switzerland	Stack	0.4
General Electric Co.	U.S.A.	Stack	2-3000
Norsk-Hydro	Norway	Tank	1
Cominco, Ltd.	Canada	Tank	0.1
Life Systems, Inc.	U.S.A.	Stack	600

Status of Industrial Electrolytic Hydrogen Production

Five large industrial electrolyzer plants (none in the United States) are currently producing hydrogen, for use in ammonia production, from hydroelectric power. In addition, many smaller units are located in almost every country in the world. These smaller units are used in applications in which high-purity hydrogen is required and in which operational manpower has to be kept to a minimum (See Table 3-2). Electrolytic hydrogen production is by no means the major way of producing hydrogen; but, on the other hand, it does represent a technology that is used to a significant extent in industry.

Electrolytic processes are widely used in industry, for other than hydrogen production; for example, most of the chlorine, caustic soda, and aluminum produced today are made by electrolytic processes. Process electrochemistry is thus a major arm of chemical technology.

Hydrogen Production by the Electrolysis of Impure Water

Electrolysis of Seawater

Seawater contains about 3.5% sodium chloride and smaller quantities of other dissolved salts. When a dilute sodium chloride solution is electrolyzed, various reactions are possible, including the following:

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

and

$$2H_2O + 2NaCl \rightarrow 2NaOH + Cl_2 + H_2$$

Table 3-2. STATUS OF ELECTROLYTIC HYDROGEN PRODUCTION

Large Units

Location	Manufacturer	Hydrogen Output, 10^6 CF/hr	Power Input, MW	Year Built
Rjakon, Norway	Norsk-Hydro	2.2	250	1965
Kima, Egypt	Demag (BBC)	1.4(0.5)	170(60)	1960(1972?)
Nangal, India	De Nora, S.p.A.	1.1	125	1958
Trail, Canada	Cominco, Ltd.	0.7	90	1939
Curco, Peru	Lurgi GmbH	0.2	25	1958

Smaller Units

Many units in service used for —

Fats and soaps
Metallurgy
Semiconductors
Float glass
Generator cooling
Chemical feedstocks
Meteorological stations

In practice, both reactions occur together; and, while hydrogen is evolved at the cathode, a mixture of oxygen and chlorine is evolved at the anode. This presents severely corrosive conditions at the anode and makes the selection of anode materials very critical. Moreover, the chlorine evolved presents a severe disposal problem, unless means of utilizing the chlorine can be found.

The conductivity of seawater is very low; and therefore, the resistance of the seawater electrolysis cell is too high for the process to be considered as a commercial means of hydrogen production. There are two potential ways of overcoming this problem. One is to concentrate the seawater into brine. The other is to add a supporting electrolyte, such as sodium hydroxide. In the first case, the partial dehydration of seawater to concentrated sodium chloride will result in the almost-complete suppression of the first, oxygen-evolving reaction and in the complete domination of the second, chlorine-producing reaction. Indeed, this is the process used in industry to produce chlorine and caustic soda in large quantities. In a chlorine-producing cell, means must be provided for removing the sodium hydroxide produced and for replacing the sodium chloride. Although this type of cell does, in fact, produce large quantities of hydrogen, its use as a primarily hydrogen-producing cell is not feasible because of the large amounts of byproducts. If hydrogen is to be produced in the quantities that are of interest for large-scale chemical feedstocks and fuels, then the disposal of both the sodium hydroxide and the chlorine presents serious problems.

The other alternative, the addition of sodium hydroxide as a supporting electrolyte, is only slightly more attractive. As the cell is operated, it produces its own sodium hydroxide; therefore the concentration of this electrolyte will automatically increase to a point at which the sodium hydroxide itself must be dumped from the cell. If the concentration of sodium chloride can be kept low, the evolution of chlorine can be kept to a minimum and, in principle, the cell could be retained as a hydrogen-oxygen cell. However, because the cell is only expelling hydrogen and oxygen with an intermediate purging of sodium hydroxide and because it is constantly being fed a sodium chloride solution, the chloride-ion concentration inevitably builds up in the cell. This ultimately results in an increase in chlorine evolution, resulting in the same problems as have previously been discussed.

We conclude that the electrolysis of seawater to produce hydrogen alone is not a practical proposition, and research in this area does not appear to be justified.

Electrolysis of Unpurified Water

The electrolysis of water that contains only small levels of impurities results in the production of hydrogen and oxygen, but also in the continual accumulation of the impurities in the cell. This occurs because the cell is only able to produce hydrogen and oxygen; and if even the smallest amounts of impurities are present in the water fed to the cell, these impurities cannot escape from the cell and ultimately reach a high degree of concentration. The results of the accumulation of impurities include: 1) corrosion of the electrodes, 2) the onset of side reactions that give rise to undesirable byproducts, and 3) contamination of the ion-exchange membrane in the SPE-type cell. Inhibiting the accumulation of impurities by purging the electrolyte in the cell does not appear to be an attractive solution because of the cost of the continual replenishment of the KOH electrolyte. Thus, there does not seem to be a reasonable prospect for the economic electrolysis of impure water as long as water-purification costs remain reasonably low.

Electrolyzer-Feedwater Quality Standards

Most electrolyzer manufacturers stipulate feedwater quality in their specifications. In general, feedwater must be purified to a level approximating that of boiler-feedwater quality or "distilled-water" standards. Most electrolyzers have demineralizers in the feedwater stream that remove the last traces of dissolved salts. Thus the electrolyzer can be fed replacement water continuously for periods of up to 6 months. Lurgi specifies feedwater of an initial purity equivalent to that of heating-steam condensate, the feedwater then being passed through an active carbon filter and through a demineralization unit containing a mixed-bed ion exchanger that provides the water with a minimum specific resistance of 1 megohm-centimeter. Usually, the purity of the feedwater is monitored by a conductivity meter installed in the system.

Energy Required for Water Purification

Upon first consideration, the requirements for a pure-water feed may appear to be prohibitively expensive. However, the amount of water required to feed an electrolyzer is relatively small compared with the amount of hydrogen produced. For example, the electrolysis of 1000 gallons of water will produce 166,000 SCF of hydrogen. Thus both the energy cost and the dollar cost of treating 1000 gallons of water should be debited from the selling price of the 166,000 SCF of hydrogen produced. The latent heat of vaporization (or the energy required for straight distillation) is 9.8 kcal/mole, while typical water desalting methods appear to use between 1 and 10 kcal/mole.* This is to be compared with the typical electrical input, 93 kcal/mole, to the commercial electrolyzer operating at 2 volts. Thus the energy required for water purification is 10% or less of the electrical energy required for the electrolysis itself. The energy required to desalt water is of a far lower grade than that needed to run an electrolysis plant, which of course has to be in the form of electricity. Relatively low grade heat, possibly available from the power station supplying the electricity, could be used to purify the electrolyzer feedwater.

The cost of desalting seawater to irrigation standards was earlier estimated at approximately $0.80/1000 gal. The 1000 gallons would, in turn, produce 166,000 SCF of hydrogen; thus the ratio of the water desalting cost to the heating value of the hydrogen produced would be about 1.4¢/million Btu. This is considerably less than 1% of the expected selling price of the hydrogen. It is likely that the full treatment of seawater to the 1 megohm-centimeter standard required by an electrolyzer will in fact cost more than $0.80/1000 gal; but in any event, the overall cost of purifying the water is likely to be less than 2% or 3% of the anticipated overall cost of producing the hydrogen.

We conclude, then, that rather than embarking on a research program to solve the difficult problems of electrolyzing sewater or brackish water, it is better to suffer the small energy and cost penalties involved in purifying the water to acceptable standards.

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* Recent technology indicates[6] that a multiple-effect distillation system has an energy requirement of 1 million Btu/1000 gal, or approximately 1.2 kcal/g-mole.

Note that any process that converts water to hydrogen and oxygen is likely to require the same consideration of feedwater standards. Any process that splits water into hydrogen and oxygen will deposit feedwater impurities, thus contaminating the plant. It is therefore anticipated that thermochemical processes, as well as electrochemical processes, will require water-treatment plants and therein incur a similar expense.

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4. COST OF ELECTROLYTIC HYDROGEN – K. G. Darrow, Jr.

The basis for the costs contained in this section is information supplied by three major vendors of electrolysis systems. We contacted several such companies by mail and/or in person and requested technical and economic data regarding capital costs, operating parameters, scale-up factors, and polarization curves. The General Electric Co., Lurgi Apparate-Technik of Germany, and Teledyne Isotopes each supplied us with enough information to allow for an estimate of overall capital and operating costs.

Factors Considered in Overall Hydrogen-Cost Calculations

With the data provided by the manufacturers, we were able to calculate the cost of electrolytic hydrogen production as a function of electric power. Such curves for electrolysis systems have appeared in much of the recent literature concerning hydrogen, but there has been no uniform base for determining these costs. Different financial assumptions can lead to very different figures for the cost of hydrogen, even when utilizing the same equipment. Some vendors include more equipment within their quoted costs than do others. At the same time, certain systems need more auxiliary equipment than do others. Although the information received from the vendors was not complete in all cases, we have attempted the analysis of a standard-sized plant producing 10 million SCF/day of hydrogen. Respecting the proprietary nature of the information provided and market position of the respondents, we have elected to somewhat limit the degree of detail presented in this section.

To provide a clear idea of all that is involved in building a large-scale electrolysis plant, the equipment and auxiliary facilities of a typical alkaline-electrolyte, "filter-press" design system are given below. The major equipment components of such a system are –

- Electrolyzer modules
- Gas separators
- Gas cooling system
- Electrolyte cooling system
- Feedwater supply system
- Electrolyte preparation and storage tank
- Nitrogen tank and purge system.

Also required, and generally included by the vendor as part of the equipment cost, are —

- Pumps and pump motors
- Instrumentation and control facilities
- Maintenance equipment
- Valves and piping.

If any of these items are not included as part of the quoted equipment costs, they must be added to the overall plant costs.

In addition to the cost of plant equipment, the costs of the following items and services must be added to the investment to derive the cost of a complete facility:

- An electrical plant consisting of ac-to-dc rectification and transformers
- Packing, shipping, and installation of the equipment
- Additional electrical equipment and its installation, (e.g., bus bars, switches, cables)
- A building, foundation, and other support structures, including lighting and painting
- Facilities for services such as water treatment, water distribution, air compression, communications, and fire protection
- Engineering and supervision during construction and start-up
- Contractors
- Land, site preparation and yard improvements, and administrative facilities.

Finally, compression, transmission, and storage costs, which are developed separately in this report, must be included. This section, however, is devoted solely to production costs.

To indicate the magnitude of the additional costs that must be added to the equipment costs, we have developed factors for these other items based on percentages of equipment costs reasonable for chemical processes in general and for specific electrolytic plants. Table 4-1 presents two cost work-ups — one for a pressurized alkaline cell that represents a composite of Lurgi and Teledyne information for currently available equipment and the other for the

Table 4-1. CAPITAL COSTS FOR ELECTROLYSIS PLANTS

Equipment Costs	Alkaline Pressure Electrolyzer \$/kW (out)*	Projected GE 1980 Commercial \$/kW (out)
Electrolyzer and Auxiliary	255	84
Power Conditioning ($45/kW ac in)	60	57
Total	315	141
Installed Plant Cost		
Equipment X 1.5	472/kW (out)	212/kW (out)

*$/kW (out) = dollars per kilowatt of product hydrogen, converted on the basis of higher heating value; i. e.—

$$\frac{\text{Capital Cost}}{\text{SCF/hr} \times 325\ \text{Btu/SCF} \div 3413\ \text{Btu/kWhr}}$$

The fact that the GE cell will operate at about 10 times the current density of the alkaline cell explains its relatively low cost (on an equivalent output basis), in spite of the fact that the GE cell actually uses more expensive materials than the alkaline cell.

reported GE Solid-Polymer Electrolyte (SPE) system that is to be developed by 1977 and commercialized by 1980. The percentages quoted for GE installations are higher (that is, the auxiliary-equipment costs for the GE system are a greater percentage of the total capital cost) because GE's cells are expected to be cheaper (on a unit-output basis) than currently available cells, but the costs of their auxiliary equipment will be about the same as for present-day cells.

The accuracy of this kind of cost projection is on the order of plus or minus 30%. However, the information on overall costs for large-scale water electrolysis systems is scanty, at best. Although such systems have been built, typically they are few in number; were built as many as, or more than, 20 years ago; and were built in nonindustrial areas, and cost breakdowns were never published.

Table 4-2 summarizes the system operating characteristics reported by the three responding companies. Where information was lacking, we were forced to make assumptions, often based on information supplied by other vendors. Because the cost of electric power is the most important operating cost, we have assigned fixed values to all other operating costs and have computed the hydrogen costs parametrically as a function of electrical costs. Other operating costs are shown below in order of their importance:

1. Maintenance, 2% of total investment
2. Cooling-tower water, 15¢/1000 gal
3. Direct labor (2 persons per shift), 8.4 person-years at $6.00/hr
4. Overhead, 50% of direct labor
5. Demineralized feedwater, 1 megohm-cm minimum resistance, $1.90/1000 gal.

In addition to these operating costs, capital charges representing depreciation, income taxes, interest on debt, return on equity, and ad valorem taxes and insurance must be taken into account. We adopted a straightforward financing method in an attempt to represent an average utility situation. The parameters we used are as follows:

- 60:40 debt-to-equity ratio
- 4% interest on debt

Table 4-2. OPERATING CHARACTERISTICS OF THREE ELECTROLYZERS

	Teledyne	Lurgi	GE (Projected)
Size of System Compared, MW equivalent of hydrogen	39.9	53.3	51.6
Million SCF of Hydrogen/ Stream Day	10	13.44	13.0
DC Electric Input (Max.), kW	58,400	69,000	65,300
Specific Cell Efficiency	68%-70%	77%	82.2
AC-DC Converter Efficiency	86%	97%	97%
Auxiliary-System Efficiency		NA	99%
Overall Efficiency	58.7-60.4	74.7	78.9
Operating Pressure	100 psig	440 psia	Pressure vessel designed for operating pressures of up to 3000 psig
Cooling Water, gal/hr	NA	184,940	Closed cycle, dry cooling tower
Feedwater, gal/1000 SCF	6.36	6.36	6.36
Nitrogen per Start-up	Yes	74,640 SCF	No
Caustic-Potash Initial Charge, lbs	NA	344,000	None
Labor, men/shift	NA	2	NA
Mode of Operation	Fully automatic	Fully automatic	Fully automatic

Note: NA = not available.

- 15%, after tax, return on equity
- 48% income-tax rate with no investment tax credits
- 20 years' sum of year's digits depreciation on total plant investment, for taxes, and 20 years' straight-line depreciation, for cost accounting. (Note that all three vendors specified a 20-year life.)

The weighted average cost of capital for this capital structure is 11.4%. The annual fixed-charge rate that would exactly yield this return for the overall firm was computed to be 18.6%, the sum of a capital-recovery factor of 12.8%, an income-tax factor of 3.8%, and an allowance of 2% for ad valorem taxes and insurance.

We then developed a unit hydrogen cost that satisfies the minimum revenue requirements of the firm — i.e., it covers all operating costs and yields a return on investment equivalent to the cost of capital. Figures 4-1 and 4-2 show hydrogen costs (as a function of electricity rates) for systems functioning at a 90% plant-operation factor — 10% of the total possible operating time having been set aside from the otherwise continuously run system to allow for downtime for scheduled maintenance. (Note that Figure 4-1 is based on present-day cells while Figure 4-2 is a projection based on the expected 1980 technology.)

Optimization of Operating Characteristics

It should be pointed out that the operating characteristics of a given electrolyzer can be "tuned" to provide hydrogen at the minimum cost possible under a given set of economic conditions. This is one reason for some vendors' reluctance to make generalized cost statements.

The hydrogen output of a given electrolyzer varies directly with the current applied to the cell (based on the relationship of 15.6 SCF of hydrogen/1000 A-hr). However, as the current density on the electrodes is increased, efficiency decreases. Hence, as current density is increased, unit capital costs decrease and electric power requirements increase. At some current density, hydrogen costs will be minimized.

The point of minimum cost is determine by describing capital costs and efficiency as functions of current density and by then substituting these functions into the overall cost equation. The partial derivative of the cost equation with respect to current density is then used to find the point of minimum cost.

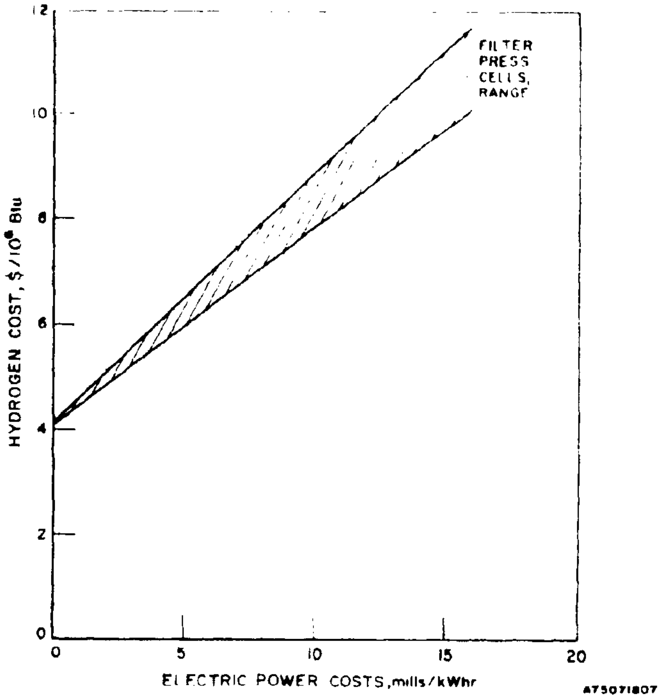

Figure 4-1. HYDROGEN COSTS VS. ELECTRICITY RATES FOR PRESENT-DAY CELLS

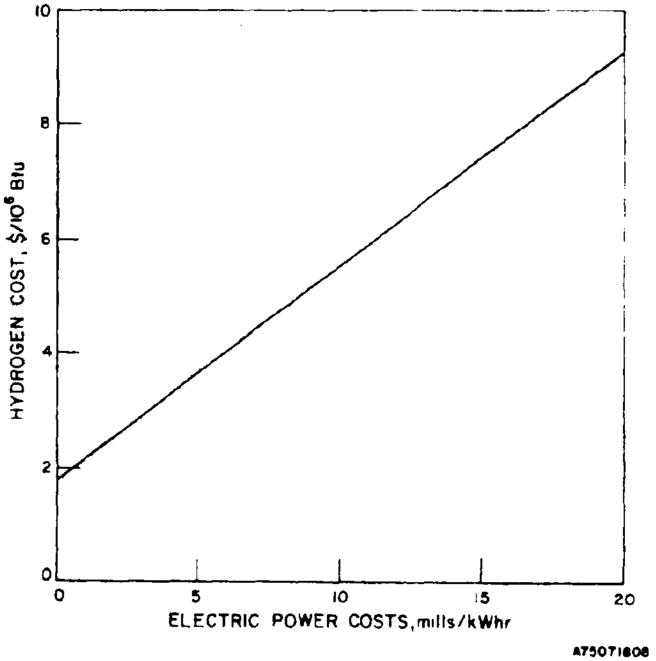

Figure 4-2. HYDROGEN COSTS VS. ELECTRICITY RATES FOR GE ELECTROLYZER (1980 Projection)

Plant life, however, is also a function of current density. In our analysis, plant life was assumed constant, with the added constraint that current density not exceed the manufacturer's recommended maximum value.

Any conclusions drawn from an inspection of Figure 4-1 and 4-2 are true only for the situation described by our technical and economic assumptions. Any other assumptions could conceivably change the relative positions of these curves.

It should be noted that comparatively large industrial units are, today, available for purchase from some manufacturuers while others represented in this figure are, at present, unable to meet large industrial orders. Thus, in some cases this figure compares current selling prices with projected prices.

5. THE MANUFACTURE OF HYDROGEN FROM COAL – C. L. Tsaros, J. Arora, and K. B. Burnham

As part of the NASA-Langley Research Center project being conducted by IGT, process flow diagrams for the conversion of coal to high-purity hydrogen were prepared and are herein presented. The process flow diagrams, energy balances, and efficiencies reported herein are preliminary, and the reader is referred to the NASA-LRC report* for finalized information. Plant capacities that would yield total product heating values of 250 billion Btu/day were established. Because of small variations in product heating value, production rates range from 698 to 767 million SCF/day. This capacity is typical for the standard methane- or pipeline-gas-from-coal plant and is considered to be beyond the point at which economy of scale is significant. It also meets the supply required by a major airport for aircraft fueling.

Processes were selected purposely to represent different technologies. Process designs have been made in sufficient detail to allow determination of overall plant efficiencies on a comparable basis. In addition, capital and operating costs for one of the processes were estimated for comparison with the costs of methane and kerosene produced from coal, as estimated in other phases of the project. The processes selected are –

- The Koppers-Totzek Process – a commercially available process based on the suspension gasification of pulverized coal by steam and oxygen at essentially atmospheric pressure under slagging conditions in excess of 3000°F. Since the first commercial installation of the Koppers-Totzek Process in Oulu, Finland, in 1952, 20 plants have been ordered that use a total of 52 Koppers-Totzek gasifiers. Four of these plants were ordered after 1970. The most common use of the product gas has been for ammonia synthesis. A hydrogen-production facility would utilize the same gasifying principles as an ammonia plant, but would require different downstream process operations, which are described in this report. A complete list of the 20 commercial installations, none of which is in the United States, is presented in Table 5-1.

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* Tsaros, C. L., Arora, J. and Burnham, K. B., "Study of Conversion of Coal to Hydrogen, Methane, and Liquid Fuels," IGT Project 8963, Contract NAS 1-13620, Chicago, 1975.

Table 5-1. COMMERCIAL PLANTS FOR GASIFICATION OF ALL KINDS OF FUELS BY THE KOPPERS-TOTZEK PROCESS

Plant	Fuel	Number of Gasifier Units	Capacity (Carbon Monoxide and Hydrogen in 24 hr) standard cu m	SCF	Use of Synthesis Gas	of Order
African Explosives and Chemical Industries Ltd., Johannesburg, Modderfontein Plant, South Africa	Coal dust	6	2,150,000	80,025,000	Ammonia synthesis	1972
Amoniaco Português S.A.R.L., Lisbon, Estarreja Plant Portugal	Heavy gasoline, plant extendable to lignite- and anthracite-dust gasification	2	169,000	6,300,000	Ammonia synthesis	1956
Azot Sanayii T.A.S., Ankara, Kütahya Works, Turkey	Lignite dust	4	775,000	28,850,000	Ammonia synthesis	1966
Charbonnages de France, Paris, Mazingarbe Works (P.d.C.) France	Coal dust, coke-oven gas, tail gas	1	75,000- 150,000	2,790,000- 5,580,000	Methanol and ammonia synthesis	1949
Chemical Fertilizer Company Ltd., Thailand, Synthetic Fertilizer Plant at Mae Moh, Lampang, Thailand	Lignite dust	1	217,000	8,070,000	Ammonia synthesis	1963
Chemieanlagen Export-Import GmbH, Berlin für VEB Germania, Chemieanlagen und Apparatebau Karl-Marx-Stadt VEB Zeitz Works	Vacuum residue and/or fuel oil	2	360,000	13,400,000	Raw gas to produce hydrogen for hydrogenation	1966
Empresa Nacional "Calvo Sotelo" de Combustibles Liquidos y Lubricantes, S.A., Madrid, Nitrogen Works in Puentes de Garcia Rodriguez, Coruña, Spain	Lignite dust	3	242,000	9,000,000	Ammonia synthesis	1954
Empresa Nacional "Calvo Sotelo" de Combustibles Liquidos y Lubricantes, S.A., Madrid, Nitrogen Works in Puentes de Garcia Rodriguez, Coruña, Spain	Lignite dust or naphtha	1	175,000	6,500,000	Ammonia synthesis	1961
Kobe Steel Ltd., Kobe Japan for Industrial Development Corp., Zambia, at Kafue Near Lusaka Zambia, Africa	Coal dust	1	214,320	7,980,000	Ammonia synthesis	1967
Nihon Soiso Kogyo Kaisha, Ltd., Tokyo, Japan	Coal dust	3	210,000	7,820,000	Ammonia synthesis	1954
Nitrogenous Fertilizers Industry S.A., Athens, Nitrogenous Fertilizers Plant Ptolemais, Greece	Lignite dust	1	165,000	6,150,000	Ammonia synthesis	1969
Nitrogenous Fertilizers Industry S.A., Athens, Nitrogenous Fertilizers Plant Ptolemais, Greece	Lignite dust	1	242,000	9,009,000	Ammonia synthesis	1970
S.A. Union Chimique Belge, Brussels, Zandvoorde Works Belgium	Bunker-C oil, plant convertible for coal-dust gasification	2	176,000	6,550,000	Ammonia synthesis	1955
The Fertilizer Corporation of India Ltd., New Delhi, Korba Plant, India	Coal dust	4 (One as standby)	2,000,000	74,450,000	Ammonia synthesis	1972
The Fertilizer Corporation of India Ltd., New Delhi, Ramagundam Plant, India	Coal dust	4 (One as standby)	2,000,000	74,450,000	Ammonia synthesis	1969
The Fertilizer Corporation of India Ltd., New Delhi, Talcher Plant, India	Coal dust	4 (One as standby)	2,000,000	74,450,000	Ammonia synthesis	1970
The General Organization for Excuting the Five Year Industrial Plan, Cairo, Nitrogen Works of Société el Nasr d'Engrais et d'Industries Chimiques, Attaka, Suez, United Arabian Republique	Refinery off-gas, LPG, and light naphtha	3	778,000	28,950,000	Ammonia synthesis	1963
The Government of the Kingdom of Greece, The Ministry of Coordination, Athens: Nitrogenous Fertilizers Plant, Ptolemais, Greece	Lignite dust, bunker-C oil	4	629,000	23,450,000	Ammonia synthesis	1959
Typpi Oy Oulu, Finland	Coal dust, oil, and peat	1	140,000	5,210,000	Ammonia synthesis	1950
Typpi Oy Oulu, Finland	Coal dust, oil and peat	2	140,000	5,210,000	Ammonia synthesis	[illegible]

- The U-GAS™ Process — currently undergoing process development on a fluidized-bed gasifier. The operating pressure is substantially above atmospheric, 300 psig being typical. Gasification occurs in the presence of steam and oxygen, but under nonslagging conditions at 1900° F. The U-GAS Process is primarily intended to produce a low-Btu fuel gas. A 4-foot-diameter gasifying reactor is now in operation. The project is jointly funded by the Energy Research and Development Administration and the American Gas Association as part of the IGT HYGAS program.

- The Steam-Iron Process — a modern, continuous version of the old batch method of generating hydrogen. To make a producer gas, coal is gasified by steam and air in a fluidized bed at 1900°F. This gas is used to regenerate iron oxide, which, in the reduced state, decomposes steam in a separate vessel to provide the hydrogen. The iron oxide is circulated between the oxidizer (hydrogen-generation vessel) and the reductor. Because the hydrogen is not derived from the producer gas, the nitrogen introduced in the use of air does not contaminate the product. The new process is designed to operate at a pressure of 350 psi, which allows for smaller reactors than does the old, atmospheric-pressure batch process. This modern system is being developed at IGT to supply hydrogen for the HYGAS Process. Construction of a continuous steam-iron pilot plant has begun.

The above processes produce hydrogen ranging in purity from 93% to 96%, the impurities being nitrogen and methane (produced in the gasifier). Because of variations in the methane/nitrogen proportions, there are small variations in heating value.

250 Billion Btu of Hydrogen per Day From Montana Subbituminous Coal by the Koppers-Totzek Process

The Koppers-Totzek Process involves the partial oxidation of pulverized coal in suspension with oxygen and steam. (This design is based on the gasification of Montana subbituminous coal.) The conversion of coal to hydrogen is a complex process that requires many operations. These may be grouped under three major headings:

1. Coal storage and preparation
2. Coal gasification for production of synthesis gas
3. Upgrading of the raw synthesis gas to produce hydrogen.

Figure 5-1 is a flow diagram of the processing steps required for this plant.

Coal Storage and Preparation

The hydrogen plant is assumed to be located near a coal mine that will provide coal for at least 25 years. Raw coal is brought, by truck, from the

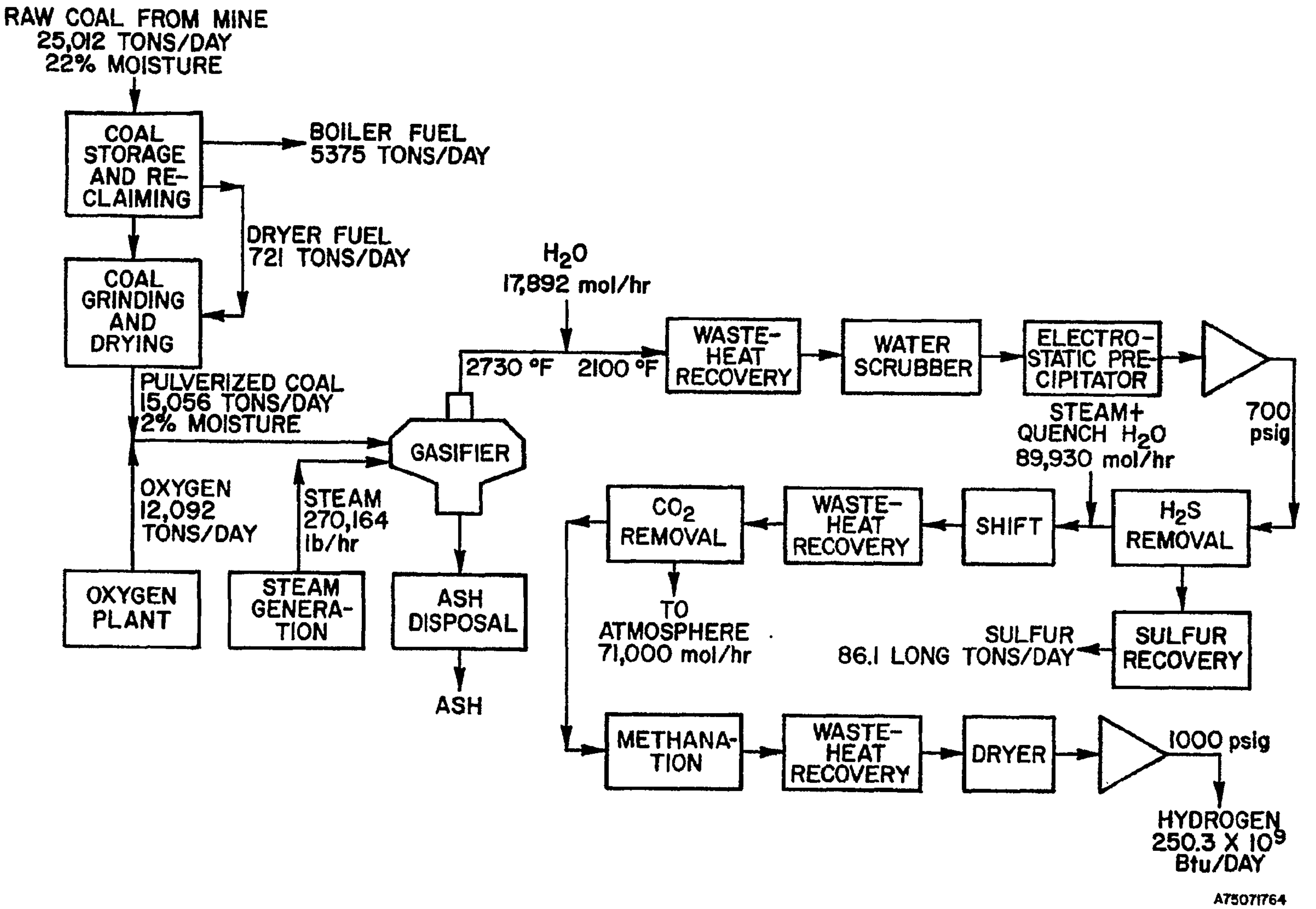

Figure 5-1. KOPPERS-TOTZEK GASIFICATION FOR A 250 X 10^9 Btu/DAY HYDROGEN PLANT THAT USES MONTANA SUBBITUMINOUS COAL

mine to a storage area where a 60-day supply of coal (broken to 1-1/2-inch x 0 size — i.e., very small to 1-1/2-inch-diameter pieces) is accumulated. The plant requires a continuous flow of 25,012 tons of raw coal (22% moisture) per day from the mine. Provision is made to store the coal in such a way that it is uniformly distributed in the storage pile; and the reclaimed coal fed to the gasifiers approaches a uniform composition, even though the run composition of the coal varies. About 24.4% of the feed coal is used as boiler and dryer fuel.

In combination grinder-dryer mills, coal is dried to 2% moisture and is pulverized so that 70% of the mass passes through 200 mesh (74-micron opening). The pulverized coal is conveyed to the storage bins before being fed to the gasifiers.

Coal Gasification for Production of Synthesis Gas

Figure 5-2 is a sketch of the Koppers-Totzek gasifier. The pulverized coal is continuously discharged into a mixing nozzle in which it is entrained in oxygen and low-pressure steam. Moderate temperature and high burner velocity prevent reaction of the coal with the oxygen until entry into the gasification zone. The quantities of coal, steam, and oxygen required for the gasifier are shown in Table 5-2.

Table 5-2. KOPPERS-TOTZEK GASIFIER FEED QUANTITIES
(For a 250 X 10^9 Btu/Day Hydrogen Plant That Uses Montana Subbituminous Coal)

	Amount
Coal, lb/hr (dry basis)	1,229,590
Steam, lb/hr	270,164
Oxygen, tons/day (98% pure)	12,092

The oxygen, steam, and coal react at a pressure slightly above atmospheric and at 3300°F in a refractory-lined, horizontal cylindrical vessel with conical ends. The fixed carbon and volatile matter in the coal are gasified to produce raw synthesis gas and molten slag at 2730°F. About 50% of the molten slag drops into a water-filled quench pot, thus forming a 200°F slag-water slurry. This slurry is cooled to 125°F and is sent to a slag-settling pond. The water is recycled to the slag quench pot. The composition of the raw gas from the gasifier is shown in Table 5-3.

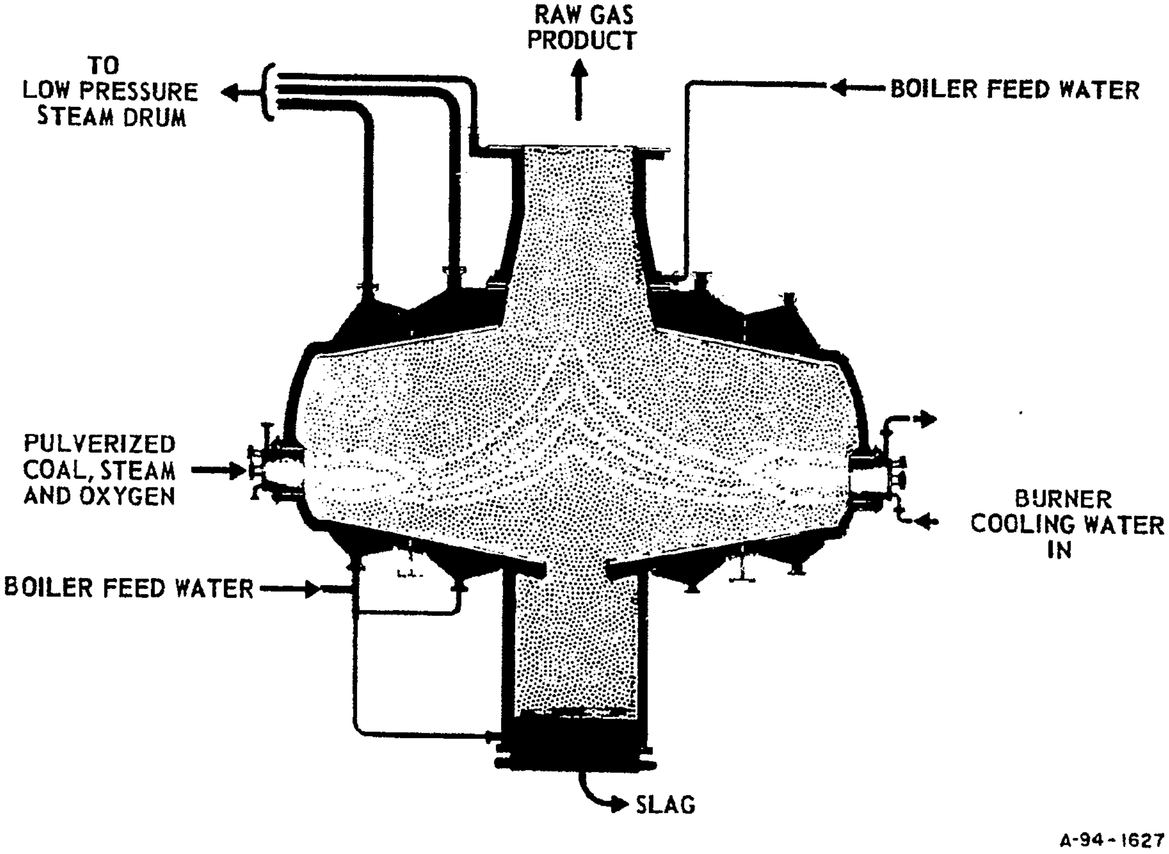

Figure 5-2. KOPPERS-TOTZEK GASIFIER

Table 5-3. COMPOSITION OF THE RAW GAS FROM A KOPPERS-TOTZEK GASIFIER
(Pressure, 6.2 psig; Temperature, 2730°F)

	Actual	Dry Basis
	mole %	
Carbon Monoxide	51.3	58.3
Carbon Dioxide	8.8	10.0
Hydrogen	26.8	30.4
Water Vapor	12.0	--
Methane	--	--
Nitrogen and Argon	0.9	1.0
Hydrogen Sulfide and Carbonyl Sulfide	0.2	0.3
Total	100.0	100.0

Upgrading of the Raw Gas to Produce Hydrogen

The synthesis gas leaving the gasifier is cooled to 2100°F by direct quenching with water, which also helps to solidify the entrained slag droplets. The quenched gas is cooled to 180°F in the waste-heat recovery boiler where a significant portion of the 1200-psig, 900°F, superheated steam for driving the turbines is generated. The cooled gas is washed with water in a venturi scrubber to reduce entrained solids to a concentration of between 0.002 and 0.005 grains/SCF. The gas is cleaned further, in electrostatic precipitators, before it is compressed to 700 psig. The slag and fine particles removed in the venturi scrubber are disposed of.

In order to upgrade the gas to the desired hydrogen product, the dust-free compressed gas undergoes hydrogen sulfide removal, carbon monoxide shift, carbon dioxide removal, methanation and drying, and final compression. To increase the hydrogen yield, the carbon monoxide and water in the gas are converted to carbon dioxide and hydrogen by the well-known carbon monoxide shift reaction performed with a shift catalyst:

$$CO + H_2O \underset{\text{catalyst}}{\rightleftarrows} CO_2 + H_2$$

Commercial catalysts for reactions in two temperature ranges (from 350° to 500°F and from 600° to 950°F) are available. The use of a low-temperature shift catalyst requires much less steam than does use of a high-temperature shift system because of the more favorable equilibrium and greater catalyst activity with the former. The lower steam requirement increases the plant thermal efficiency and reduces the boiler cost. However, the low-temperature shift catalyst cannot be used with gases that contain sulfur. Because the acid gases (hydrogen sulfide and carbon dioxide) must be removed at some stage of the process, it is desirable to remove the hydrogen sulfide prior to, and the carbon dioxide after, the carbon monoxide shift.

In this design, the carbon monoxide concentration is shifted from 59% in the feed to 3% in the effluent. This is less expensive than shifting to an even lower carbon monoxide level and still results in a 93% hydrogen product gas. A total of 53,938 moles of carbon monoxide/hr are shifted in four seven-stage reactors, with a steam-to-dry gas ratio of 0.3 for each stage. The total gas flow is divided into four parallel trains to minimize the pressure drop through the seven stages. Quench water and steam are added between the stages to cool the previous stage effluent to 370°F and to bring the steam-to-dry gas ratio to 0.3. A total of 44,826 moles of steam/hr and 45,104 moles of quench water/hr is required.

Prior to the carbon monoxide shift, hydrogen sulfide is removed in the first stage of a two-stage Rectisol system, which has been successfully demonstrated in commercial operations (e.g., in the Sasol plant of the South African Coal, Oil, and Gas Corp.). The sulfur compounds are removed completely by washing the gas with methanol that has been charged with carbon dioxide at 115°F and 700 psig. The higher operating pressure of the Rectisol system favors the physical absorption of acid gas by methanol. The regeneration of this solvent yields a 25.5% hydrogen sulfide-rich gas that yields 86.1 long tons of sulfur/day in the sulfur-recovery plant, with 250 ppm of sulfur remaining in the gas vented to the atmosphere.

After the carbon monoxide shift, and before going to the second-stage of the Rectisol system for carbon dioxide removal, the effluent is cooled to 115°F by waste-heat recovery and water cooling. The carbon dioxide-rich stream is vented to the atmosphere because it contains less than 5 ppm sulfur.

To achieve a pipeline-gas standard of a maximum of 0.1% carbon monoxide,* the effluent from the second stage of the Rectisol system, which contain 4.8% carbon monoxide, is methanated. A single-stage, recycle-quench methanation

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*Because the pipeline gas, which contains toxic carbon monoxide, will eventually be delivered to individual residences, the maximum carbon monoxide level must be this low.

system with a feed temperature of 550°F and an effluent temperature of 900°F is used. The methanation effluent is cooled to 125°F, with a portion of the gas being used as the recycle quench stream. The product gas is dried in a standard glycol drying unit to 7 lb of water/million SCF of gas.

The dried gas is compressed to 1000 psig in a single-stage, product-gas compressor and is sent to the pipeline. Because the heating value of hydrogen is approximately one-third that of methane, per SCF of gas, the volume of the hydrogen product gas is approximately three times that of SNG for a comparable 250 X 10^9 Btu/day plant, or 698 million SCF of hydrogen/day. Table 5-4 shows the composition of the hydrogen product gas.

Table 5-4. COMPOSITION OF THE GAS PRODUCED BY KOPPERS-TOTZEK GASIFICATION
(For a 250 X 10^9 Btu/Day Hydrogen Plant, Operating at 140°F and 1000 psig, That Uses Montana Subbituminous Coal)

	Amount, %
Carbon Monoxide	0.1
Carbon Dioxide*	--
Hydrogen	93.1
Methane	5.5
Nitrogen and Argon	1.3
Total	100.0

* 50 ppm

Table 5-5 shows the process thermal efficiency. Approximately 56.8% of the higher heating value of the feed coal is converted to higher heating value in the product gas, and 0.2% of the feed coal is product sulfur. The other major heat losses are shown in Table 5-6. The remaining 3.3% loss is attributable to waste-heat recovery, the venting of carbon dioxide to the atmosphere, reactor ash, etc.

In summary, production of 250 X 10^9 Btu of hydrogen/day from Montana subbituminous coal, using a Koppers-Totzek gasifier operating at 6 to 7 psig and at 2700° to 3300°F, requires 25,012 tons of 22%-moisture coal per day, thus converting 56.8% of the HHV of the coal to HHV in the product hydrogen.

Table 5-5. KOPPERS-TOTZEK PROCESS EFFICIENCY
(For a 250 X 10^9 Btu/Day Hydrogen Plant That Uses
Montana Subbituminous Coal)

	Amount
Reactor Coal, lb/hr (dry basis)	1,229,590
Boiler Coal, lb/hr (dry basis)	396,218
Total Coal, lb/hr (dry basis)	1,625,808
HHV* of the Total Coal, 10^6 Btu/hr (at 11,290 Btu/lb)	18,355
HHV of the Product Gas, 10^6 Btu/hr	10,429
% Converted to Product Gas	56.8
% Converted to Sulfur	0.2
Total % Converted to Products	57.0

*High heating value.

Table 5-6. HEAT-LOSS SUMMARY FOR THE KOPPERS-TOTZEK PROCESS

	Amounts, 10^6 Btu/hr	% of HHV of Total Coal
Air-Cooling Units	58.3	0.3
Rejected by Cooling Water	6113.2	33.3
Boiler Losses	591.7	3.2
Coal Drying	529.1	2.9
Total	7292.3	39.7

Description of a 250 Billion Btu/Day Plant Producing Hydrogen From Montana Subbituminous Coal by the U-GAS Process

The U-GAS Process utilizes single-stage, fluidized-bed gasifiers. The major advantages of this type of operation include—

- High reaction rates because of good gas-solids contact
- A uniform and easily controlled bed temperature
- A high concentration of carbon in the fluid bed, thus ensuring reducing conditions; giving good product gas; and ensuring that sulfur is converted to hydrogen sulfide, which is readily removed
- An ash-removal system that is unique because it allows for the recycling and subsequent gasification of fines and for removal of only low-carbon ash. This system results in high carbon conversion and, hence, is highly efficient.

Our process designs for hydrogen production are based on the use of Montana subbituminous coal, which is noncaking and thus needs no pretreatment. Coal (22% moisture) is received from the nearby mine at the rate of 21,443 tons/day. For the coal-drying system, 16,760 tons of process coal (22% moisture) per day are required, and the boiler requires 4148 tons of coal (22% moisture) per day. (See Figure 5-3.)

Coal is simultaneously crushed to 1/4-inch x 0 size and dried to a moisture content of 10% before being conveyed to the reactor feed system. Lock hoppers have been chosen for this feed system because they have been commercially proved in systems operating at this reactor pressure (335 psig). Coal is dropped from a feed bin into an open lock hopper. After being isolated by the lock hopper valves, the lock hopper is pressurized (with nitrogen from a recycle nitrogen compressor) to the reactor pressure. The lock hopper discharge valve is then opened; and the contents of the lock hopper flow, by gravity, into a continuous reactor feed bin. The pressure in the lock hopper is then released to a surge drum upstream of the recycle compressor, and the cycle begins again.

Generation of Synthesis Gas

This plant requires two gasifiers, each with an inside diameter of 31 feet and a 68-1/2-foot straight shell. These two units consume 8631 tons of 98% oxygen per day, combined with 375,776 lb of steam/hr. The steam and oxygen serve as a fluidizing-gasifying medium for the 14,525 ton/day gasifier coal feed. Table 5-7 shows the gasifier feed quantities and the steam required for the carbon monoxide shift.

Table 5-7. U-GAS GASIFIER FEED QUANTITIES
(For a 250 X 10^9 Btu/Day Plant That Uses Montana Subbituminous Coal)

	Amount
Coal, lb/hr (dry basis)	1,089,399
Steam, lb/hr	375,776
Oxygen, tons/day	8,631
Steam for the Shift, lb/hr	790,758

The coal is gasified in a single-stage fluidized bed at 1900°F and 335 psig. Reactor residence time is 80 minutes, and the fluidizing velocity is 1.5 ft/s. Because the coal is injected below the surface of the fludidized bed, methane

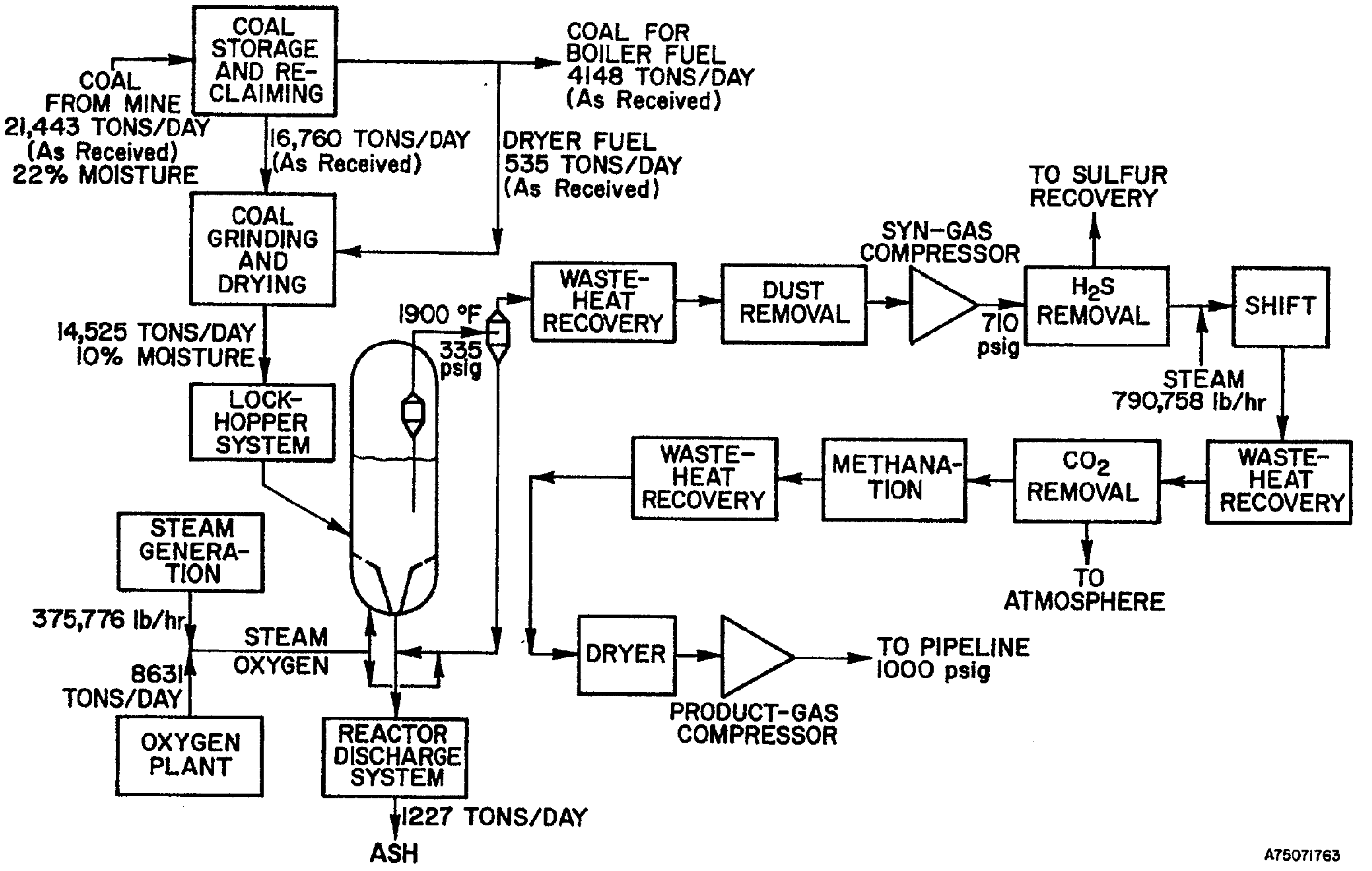

Figure 5-3. U-GAS GASIFIER FOR HYDROGEN

formation is minimized; and, because of the high temperature, devolatilization products are decomposed. The gasifier is unique in its method of ash removal and fines handling. (See Figure 5-4.) Simultaneous with the gasification of the coal, the ash is agglomerated into larger, heavier particles that eventually fall out of the bed.

The ash agglomerates fall into a water-filled quench pot, thus forming a slurry that is cooled and then depressurized across a valve before being channeled to one of two slurry-settling ponds. The water is recycled to the slurry quench pot. The ash is reclaimed from the unused pond and is disposed of in the mining area.

The raw gasifier product is cooled from 1900° to 300°F in a waste-heat recovery boiler that generates about 90% of the required process steam (the remaining process steam required being generated in the carbon monoxide-shift waste-heat recovery unit).

Small dust particles (less than 5 microns in diameter) carried over from the cyclones are removed in a jet venturi scrubber that has a high removal efficiency for particles of from 1 to 2 microns in size. This completely removes particulate matter from the gas before it is compressed.

The Manufacture of Hydrogen From Synthesis Gas

Table 5-8 shows the composition of raw synthesis gas and product gas. To increase the hydrogen yield, the carbon monoxide and water in the gas are converted to carbon dioxide and hydrogen by the well-known shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) performed in a catalytic reactor. Commercial catalysts for reactions in two temperature ranges (from 350° to 500°F and from 600° to 950°F) are available. The use of a low-temperature shift catalyst requires much less steam than does use of a high-temperature shift system because of the more favorable equilibrium with the former. In this case, 45,275 lb-mol of carbon monoxide/hr are being shifted. The low-temperature shift system saves either 1.2 million or 2 million lb of shift steam/hr, depending on whether the system used as a comparison is a) an all-high-temperature shift catalyst with no water quench between stages or b) a combination high temperature-low temperature shift catalyst with a water quench between each stage. Also, because the low-temperature shift system decreases steam

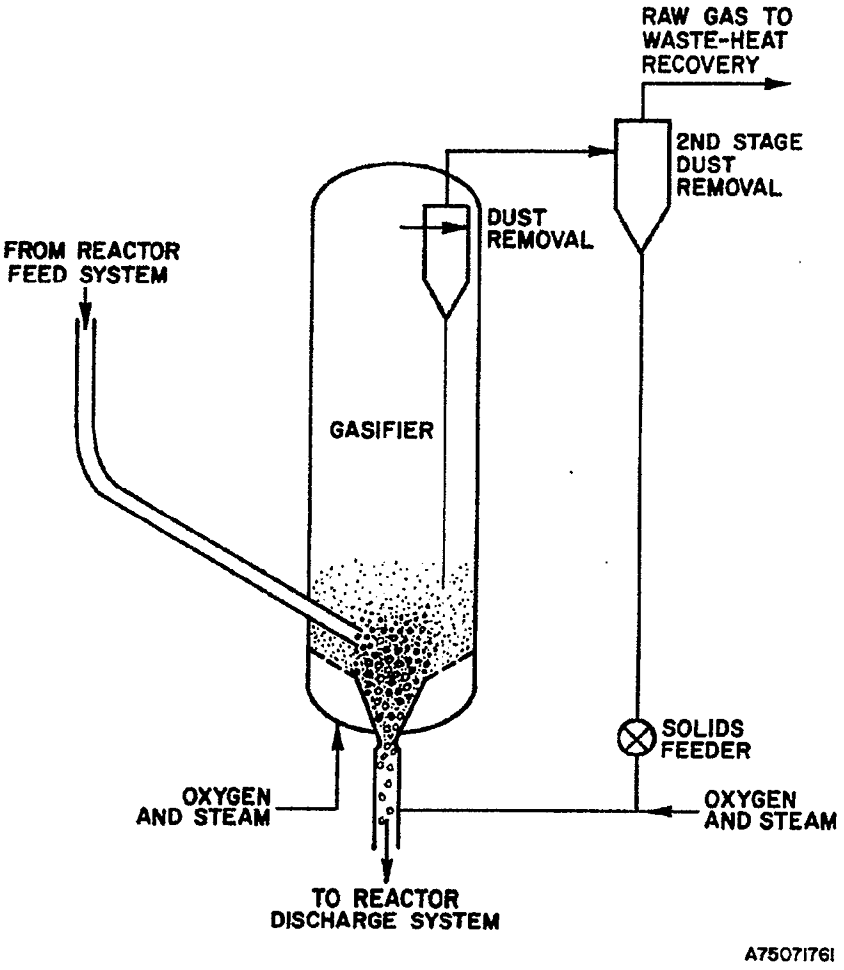

Figure 5-4. SIMPLIFIED DIAGRAM OF THE GASIFIER TO BE USED IN THE IGT U-GAS SYSTEM WHEN PRETREATMENT IS NOT REQUIRED

usage, the cost of the boiler is less; and, more importantly, the plant is more efficient by from 3% to 7%, again depending on the type of high-temperature shift system used as a comparison.

The low-temperature shift catalyst cannot be used with a gas that contains sulfur. Because the acid-gases (hydrogen sulfide and carbon dioxide) must be removed at some stage of the process, it is desirable in our design to remove the hydrogen sulfide prior to, the carbon dioxide after, the carbon monoxide shift.

Table 5-8. U-GAS HYDROGEN-FROM-COAL PLANT
(Based on the Use of Montana Subbituminous Coal)

	Gasifier Raw-Gas Composition	Product-Gas Composition
	mol % (dry basis)	
Carbon Monoxide	50.1	0.1
Carbon Dioxide*	11.5	--
Hydrogen	35.3	94.3
Methane	2.1	4.8
Nitrogen and Argon	0.7	0.8
Hydrogen Sulfide	0.3	--
Total	100.0	100.0

*50.0 ppm

Prior to hydrogen sulfide removal, the gas is compressed to 700 psig. This facilitates acid-gas removal because a physical absorption system has been chosen for the plant, and higher partial pressures are favorable for absorption. The unit selected for acid-gas removal is a two-stage Rectisol plant that is similar to units that have been successful in commercial operations. The hydrogen sulfide absorption system produces hydrogen sulfide-rich gas that yields 76.1 long tons of molten sulfur per day in the sulfur-recovery unit, with 250 ppm of sulfur remaining in the gas vented to the atmosphere.

After shifting, the carbon dioxide is removed in the second stage of the Rectisol unit. This carbon dioxide-rich stream is vented to the atmosphere. (The sulfur content is claimed to be less than 5 ppm.) A methanation unit is used to reduce the carbon monoxide content of the product gas from 1.5% to 0.1%. This is more economical than using the shift reaction to convert all of the carbon monoxide. The unit is a single-stage, adiabatic reactor similar to those used in ammonia plants in removing carbon oxides. Water is removed from the gas exiting the methanator by a standard glycol drying unit. The dried gas is compressed to 1000 psig by the product-gas compressor and is sent to the pipeline.

In terms of volumes of gas handled, this plant is larger than the standard-sized 250 billion Btu/day SNG plant. This plant produces 705 million SCF of hydrogen/day, whereas an SNG plant produces only about 250 million SCF of hydrogen/day.

The plant capital investment has been estimated in terms of mid-1974 costs, and the hydrogen cost has been calculated by the discounted cash flow (DCF) method used in the Final Report of the Supply-Technical Advisory Task Force, Synthetic Gas-Coal prepared for the Supply-Technical Advisory Committee for the National Gas Survey by the Federal Power Commission. The capital cost breakdown is shown in Table 5-9.

Table 5-9. CAPITAL-COST BREAKDOWN
(Mid-1974 Basis)

	$\$ 10^6$
Process Units	151.1
Utilities and Offsites	158.4
Installed-Plant Cost (Excluding Contingency)	309.5
Contingency at 15%	46.4
Total Bare Cost	355.9
Contractors' Overhead and Profit at 15%	53.4
Total Plant Investment	409.3
Return on Investment During Construction	92.1
Start-Up Costs	20.5
Working Capital	17.9
Total Capital Required	539.8

The largest costs are for the hydrogen sulfide and carbon dioxide removal unit and for the oxygen plant. These two plants together comprise 44% of the installed-plant cost. Based on a 16% DCF rate of return with coal costing \$0.30/million Btu, the cost of the product hydrogen is \$2.17/million Btu. Figure 5-5 shows the calculated price of hydrogen as a function of the price of coal.

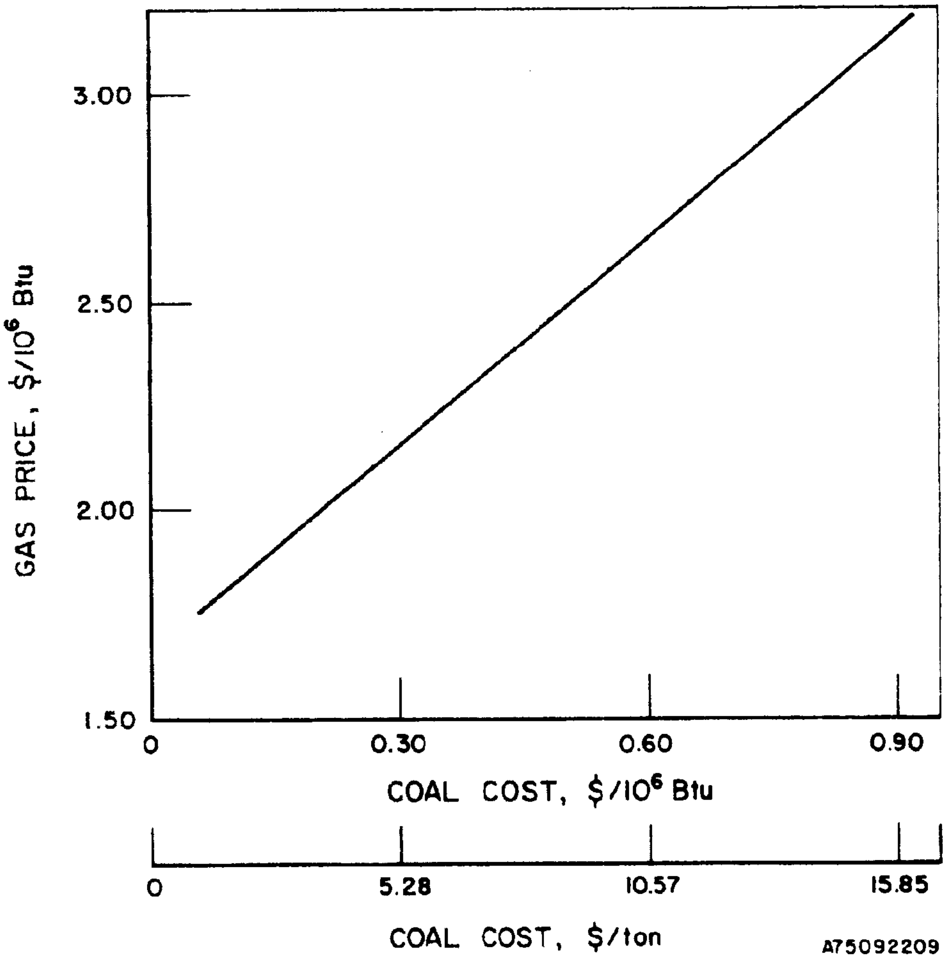

Figure 5-5. GAS PRICE VERSUS COAL COST (250 X 10^9 Btu/Day Hydrogen Plant, U-GAS Gasification of Montana Subbituminous Coal)

The process-efficiency calculation is shown in Table 5-10. About 66.2% of the high heating value (HHV) in the coal is converted to HHV in the product gas. Waste-heat recovery units, which reduce the amount of heat lost to the cooling media, have been used to the maximum extent practicable. The total HHV of the coal used in this process is 15,736 million Btu/hr, of which 1972 million Btu/hr (12.5%) is recovered by waste-heat recovery units. The product gas has a total HHV of 10,425 million Btu/hr (66.2% of the total HHV of the coal). Other major heat losses are shown in Table 5-11.

Table 5-10. U-GAS PROCESS EFFICIENCY

	Amount
Reactor Coal, lb/hr (dry basis, 11,290 Btu/lb)	1,089,399
Boiler Coal and Dryer Fuel, lb/hr (dry basis)	304,363
Total Coal, lb/hr (dry basis)	1,393,762
HHV of the Coal Used, 10^6 Btu/hr	15,736
HHV of the Product Gas, 10^6 Btu/hr	10,425
% Converted to Product Gas	66.2

Table 5-11. SOURCES OF HEAT LOSS IN THE U-GAS PROCESS

	Heat Loss, 10^6 Btu/hr	% of Total HHV of Coal
Air-Cooling Units	898.8	5.7
Rejected by Cooling Tower	3050.9	19.4
Boiler Losses	456.6	2.9

The remaining losses are each less than 2% of the total HHV of the coal consumed and are attributable to such things as the venting of carbon dioxide to the atmosphere, the coal dryer, the combustion-gas vent, by-product sulfur, and reactor ash.

In conclusion, the U-GAS Process, which involves operation of a single-stage, fluidized-bed gasifier at 335 psig and 1900°F, will produce hydrogen from Montana subbituminous coal in an environmentally acceptable manner. The efficiency of conversion of the total coal HHV to product gas HHV is 66.2%. The plant capacity is 250 billion Btu of product gas (94.3% hydrogen) per day and the total capital investment is $528 million.

250 Billion Btu of Hydrogen per Day From Montana Subbituminous Coal by the Steam-Iron Process

In this process, the crushed and dried coal is reacted with steam and air to make producer gas, which is used to reduce the oxidized iron from the steam-iron reactor. Hydrogen is derived from water according to the reactions discussed in a later portion of this report section. The advantages of this process include —

- Production of high-purity hydrogen
- No need for an oxygen plant because air is used directly
- No need for a carbon monoxide shift
- Production of a large amount of by-product electric power.

Any type of coal from bituminous to lignite can be gasified in this process. For the caking coals, pretreatment with air at 700° to 800°F is required to reduce the agglomerating tendency. For this design, Montana subbituminous coal was gasified, so no pretreatment was necessary. The steps required in the conversion of coal to hydrogen by this process are shown in Figure 5-6. These steps may be grouped under the following major headings:

- Coal storage and preparation
- Functions of the producer-gas generator and steam-iron reactor
- Upgrading of the oxidizer effluent to the desired hydrogen product
- Power generation from reductor off-gas using a combined power cycle.

Coal Storage and Preparation

The hydrogen plant is assumed to be located near a coal mine that will provide coal for at least 25 years. Raw coal is brought, by truck, from the mine to a storage area where a 60-day supply is maintained. The plant requires a continuous flow of 31,583 tons of the raw coal (22% moisture) per day from the mine. About 3.2% of the feed coal is used as dryer fuel.

The plant feed is ground so that 80% of the mass is below No. 10 U.S. Sieve Series size (2.00-millimeter opening) and is dried to a moisture content of 5.77% in combination grinder-dryer mills. A lock-hopper feed system, which has been used successfully at 300 to 400 psig in commercial Lurgi

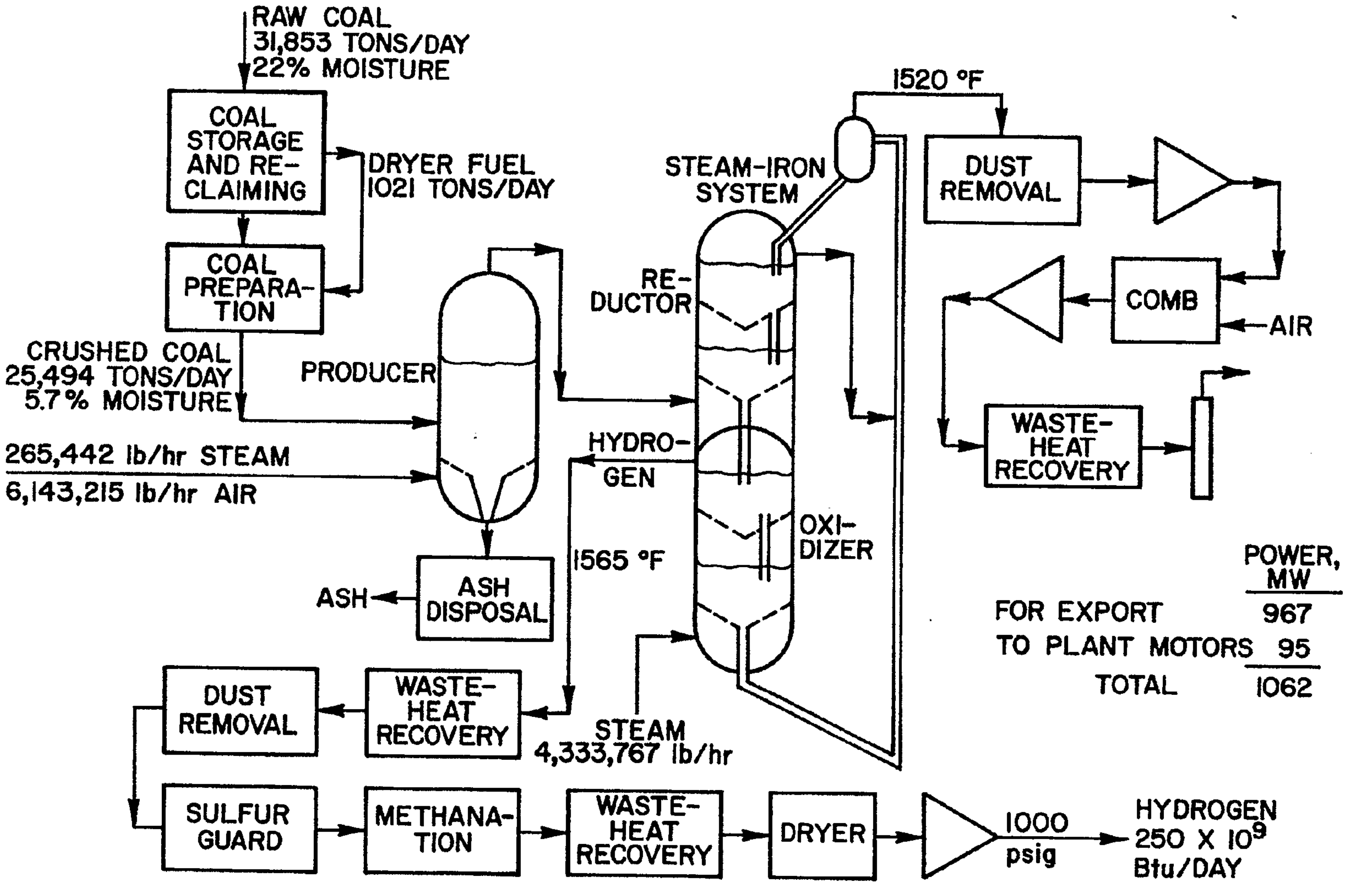

Figure 5-6. STEAM-IRON GASIFICATION FOR HYDROGEN
(For 250 X 10^9 Btu of Product Gas per Day Using Montana Subbituminous Coal)

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plants, is used to feed coal to the producer-gas generator. Coal is fed to a lock hopper from a storage bin. After the lock hopper valves are closed, the vessel is pressurized with an inert gas (plant stack gas) to the reactor pressure level. The lock-hopper discharge valve is then opened; and the contents of the lock hopper flow, by gravity, into a continuous producer-gas generator feed bin. The lock hopper is then depressurized, and the cycle is repeated. The inert gas is recovered, recompressed, and recycled.

Producer-Gas Generator and Steam-Iron Reactor

The steam-iron gasification system is shown in Figure 5-7. The ground and dried coal is continuously discharged to the fluidized-bed producer-gas generator, which is operated at 1950°F and 355 psig. A high percentage of the carbon is gasified in the producer-gas generator. The following gasification reactions take place in the producer:

$$C + H_2O \rightarrow CO + H_2 - \text{Heat}$$

$$C + \underset{\text{(air)}}{1/2O_2 + 2N_2} \rightarrow CO + 2N_2 + \text{Heat}$$

Small quantities of carbon dioxide, methane, and hydrogen sulfide are also formed.

The quantities of coal, steam, and air required for the producer-gas generator are shown in Table 5-12. Table 5-13 shows the composition of the raw producer gas. The residue from the producer-gas generator is cooled to 200°F in a water-filled quench tank. The residue-water slurry is further cooled to 125°F, is depressurized, and is sent to a slurry-settling pond. The water is recycled to the quench pot, and the residue in the pond is disposed of.

Table 5-12. STEAM-IRON GASIFICATION FEED QUANTITIES
(For a 250 Billion Btu/Day Hydrogen Plant That Uses
Montana Subbituminous Coal)

	Coal (Dry Basis)	Steam	Air
	lb/hr		
Producer-Gas Generator	2,004,079	265,442	6,143,215
Steam-Iron Reactor	--	4,333,767	149,572
Total	2,004,079	4,599,209	6,292,787

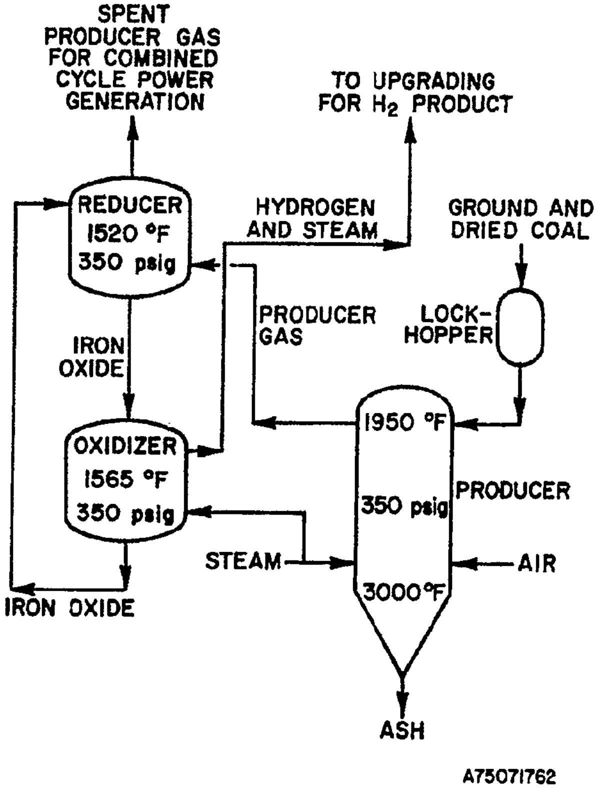

Figure 5-7. STEAM-IRON REACTOR SYSTEM FLOW SCHEME

Table 5-13. STEAM-IRON PRODUCER GAS COMPOSITION (For a 250 X 10^9 Btu/Day Hydrogen Plant, Operating at 1950°F and 355 psig, That Uses Montana Subbituminous Coal)

	mole %
Carbon Monoxide	27.4
Carbon Dioxide	3.9
Hydrogen	14.3
Water Vapor	4.3
Methane	0.4
Hydrogen Sulfide	0.1
Nitrogen	49.6
Total	100.0

The steam-iron reactor consists of an oxidizer and a reductor. A stream of iron oxide is cyclically reduced with producer gas in the reductor and is reoxidized by decomposition of steam, the hydrogen-forming reactor, in the oxidizer. The following reactions take place in the steam-iron reactor:

Reductor	$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$
	$Fe_3O_4 + H_2 \rightarrow 3FeO + H_2O$
Oxidizer	$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$

In addition to producer gas, the steam-iron reactor requires additional amounts of steam and air, the quantities of which are shown in Table 5-12. Two effluent streams, one from the oxidizer and one from the reductor, are available for further processing. The compositions of both streams are shown in Table 5-14.

The oxidizer effluent contains primarily hydrogen and steam and is thus upgraded to the desired hydrogen product, whereas the reductor off-gas (spent producer gas) is used for power generation.

Table 5-14. STEAM-IRON REACTOR RAW-GAS COMPOSITIONS
(For a 250 Billion Btu/Day Hydrogen Plant That Uses Montana Subbituminous Coal)

	Reductor Off Gas (at 1520°F and 350 psig)		Oxidizer Effluent (at 1565°F and 350 psig)	
	Actual	Dry	Actual	Dry
	mole %			
Carbon Monoxide	8.8	10.4	0.5	1.4
Carbon Dioxide	20.7	24.7	0.1	0.2
Hydrogen	6.2	7.4	37.1	95.9
Water Vapor	16.0	--	61.3	--
Methane	0.4	0.5	--	--
Nitrogen and Argon	47.8	56.9	1.0	2.5
Hydrogen Sulfide and Carbonyl Sulfide	0.1	0.1	--	--
Total	100.0	100.0	100.0	100.0

Oxidizer-Effluent Upgrading

The oxidizer effluent contains very small quantities of carbon monoxide and carbon dioxide, but no hydrogen sulfide. This eliminates the need for a carbon monoxide shift and acid-gas removal, so only methanation is required to upgrade the gas to the desired hydrogen product. Because a temperature of 550°F is desirable for the methanation-reactor feed, the effluent is cooled to 500°F in a waste-heat boiler; and thusly generates about 50% of the steam required for the steam-iron reactor. Before methanation, dust particles are removed by cyclone separators and electrostatic precipitators. The gas passes through a zinc oxide bed as a precautionary step against methanation-catalyst poisoning by any sulfur compound that may have been carried from the reductor to the oxidizer by the iron oxide.

The amounts of carbon monoxide and carbon dioxide methanated are such that the final hydrogen product contains a maximum of 0.1% of both carbon monoxide and carbon dioxide. The methanation reactor is a single-stage adiabatic reactor. The effluent (at 615°F) is used in waste-heat recovery, is cooled to 100°F, is dried in a glycol dryer to 7 pounds of water per million SCF of gas, is compressed to 1000 psig in a product-gas compressor, and is sent to pipeline. The composition of the product gas is given in Table 5-15. The product-gas rate is 768 million SCF/day.

Table 5-15. STEAM-IRON GASIFICATION PRODUCT GAS COMPOSITION (For a 250 Billion Btu/Day Hydrogen Plant, Operating at 140°F and 1000 psig, That Uses Montana Subbituminous Coal)

	Amount, mol %
Carbon Monoxide	0.1
Carbon Dioxide	0.1
Hydrogen	95.7
Methane	1.5
Nitrogen and Argon	2.6
Total	100.0

Power Generation From Reductor Off-Gas Using a Combined Power Cycle

To extract maximum power, the system incorporates the use of a gas turbine, an expander, compressors, and a steam turbine. The amount of hydrogen sulfide in the reductor off-gas is so low that the pounds of sulfur dioxide per million Btu of total coal to the plant is below the specified limit. Thus, no sulfur-removal system is specified. After the removal of dust by cyclone separators and electrostatic precipitators, the effluent is expanded to 125 psig and 1165°F, recovering power to drive the producer air compressor. The expanded gas is burned with air, in a combustor, at 125 psig and 2400°F. The effluent from the combustor is expanded, in a gas turbine, to

20 psig and 1690°F. A portion of the expansion power is used to drive combustor and producer air compressors that are on the same shaft. The remaining power is converted, in a generator, to 690 MW of electric power. The current maximum temperature range is approximately from 1800° to 2000°F, but gas turbines with an inlet temperature of 2400°F are expected to be available by the time this process is commercialized.

The expanded gas is used in a steam-power cycle to generate 372 MW of electric power from 1200-psig, 900°F steam (generated in a waste-heat boiler) and to generate a portion of the process steam required for the oxidizer. The cooled combustor gas leaves the waste-heat boiler at 350°F. A total of 1062 MW of power is generated, in addition to shaft power used for air compression. Of this amount, 95 MW is used within the plant for motor drives, etc., leaving 967 MW of power as a by-product.

Table 5-16 shows the thermal efficiency of this process. Approximately 44.6% of the higher heating value of the feed coal is converted to higher heating value in the product gas, and 14.1% becomes by-product power (taken at the value of 3413 Btu/kWhr). The other major heat losses are shown in Table 5-17.

Table 5-16. STEAM-IRON-GASIFICATION PROCESS EFFICIENCY
(For a 250 Billion Btu/Day Hydrogen Plant That Uses
Montana Subbituminous Coal)

	Amount
Reactor Coal, lb/hr (dry basis)	2,004,079
Boiler and Dryer Coal, lb/hr (dry basis)	66,347
Total Coal, lb/hr (dry basis)	2,070,426
HHV of the Total Coal, 10^6 Btu/hr (at 11,290 Btu/lb)	23,375
HHV of the Product Gas, 10^6 Btu/hr	10,425
% Converted to Product Gas	44.6
By-Product Power, kW	967,000
By-Product Power, 10^6 Btu/hr (at 3413 Btu/kWhr)	3,300
% Converted to By-Product Power	14.1
Total Products, 10^6 Btu/hr	13,725
Total % Converted to Products	58.7

Table 5-17. HEAT-LOSS SUMMARY FOR THE STEAM-IRON PROCESS
(For a 250 Billion Btu/Day Hydrogen Plant That Uses
Montana Subbituminous Coal)

	Amount, 10^6 Btu/hr	% of HHV of Total Coal
Air-Cooling Units	1798.9	7.7
Rejected by Cooling Water	3051.3	13.1
Cooled Combustor Off-Gas	2474.6	10.6
With Producer Char	1204.2	5.2
Dryer Off-Gas	536.6	2.3
Total	9065.6	38.9

The remaining 2.4% loss is attributable to waste-heat recovery and sensible heat losses associated with various plant streams.

In summary, a 250 billion Btu/day hydrogen plant that uses Montana subbituminous coal and the steam-iron gasification process requires 31,853 tons of raw coal (22% moisture) per day. Of the HHV of the coal, 44.6% is converted to HHV in the hydrogen product, and 14.1% becomes by-product power.