

HYDROGEN AND SYNTHETIC FUELS FOR THE FUTURE*

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INTRODUCTION

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

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

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

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

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

PRODUCTION OF FUELS

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

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Table 1. Comparative characteristics of synthetic fuels

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

^aDensity of hydrogen in the fuel.

^bRelative ranking.

^cIncluded for reference only.

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

Water Electrolysis

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

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

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

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

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

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

Thermochemical Processes

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

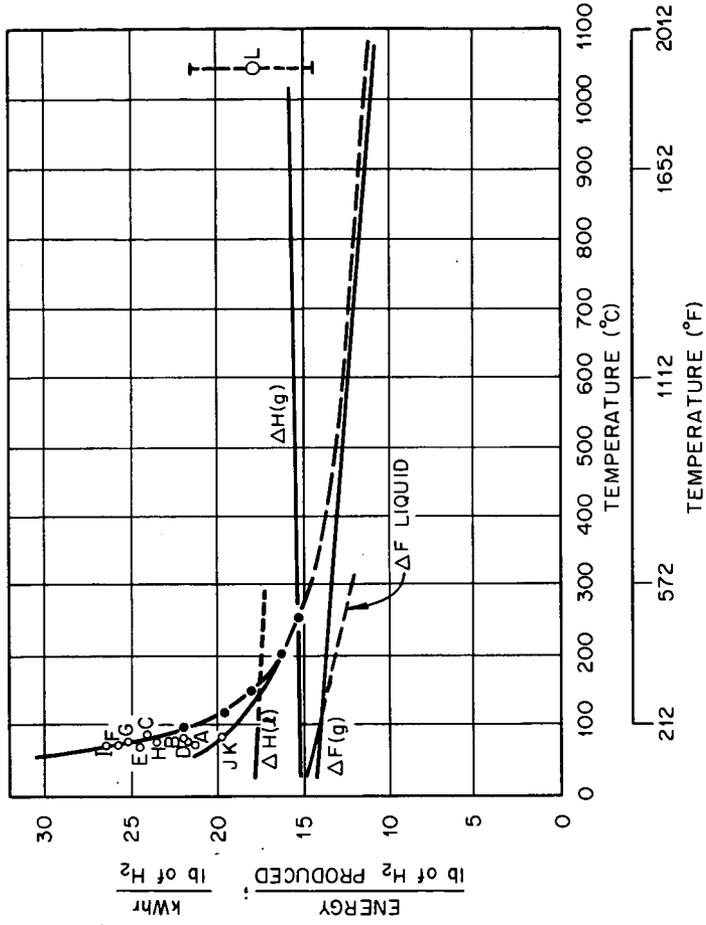


Fig. 1. Performance of water electrolysis cells compared to theoretical relationships. (See Table 2 for identification of A to L.)

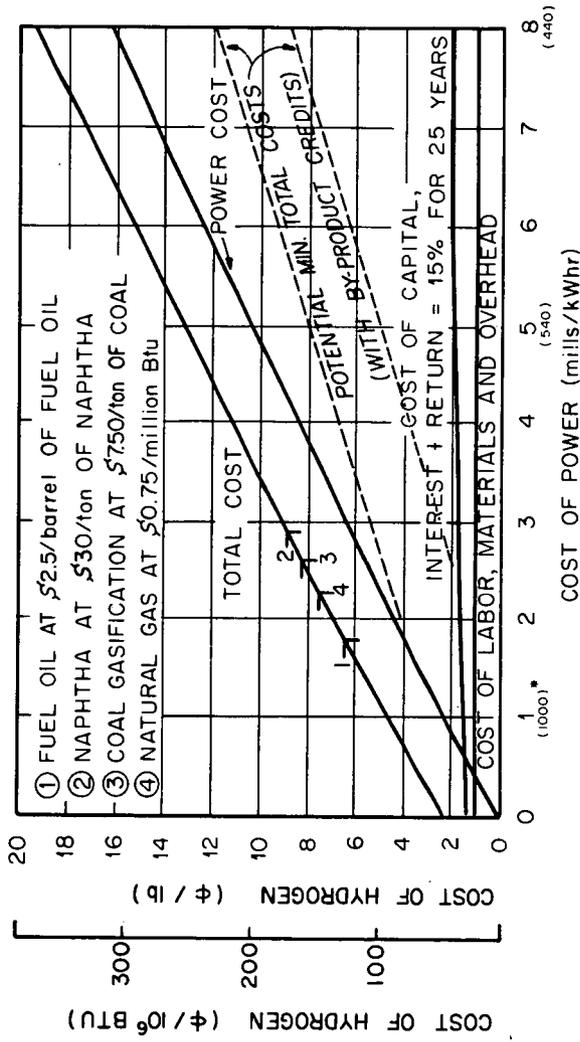
Table 2. Summary of electrolytic hydrogen plant equipment

Company/location	Cell name	Type	Cell Design				Experience			
			Current (A/cell)	Operating Voltage (V/cell)	Module (lb H ₂ /day)	Pipework (ft)	Number of plants	Largest plant (lb H ₂ /day)	Earliest plant (year)	Best Atom plant (year)
A. Norsk Hydro Bodden, Norway	Hydro-Fuehranz	Filter press	140	1.778	1880	1	3	284,000	1927	Rjukan, Norway 1965
B. Lurgi Frankfurt, Germany	Zdanusky-Loma	Filter press	200	1.832	4200	440	32	22,000	1955 ^a	Cuzco, Peru 1958
C. DeSore Italy	DeSore	Filter press	280	2.00 ^b	4100	1	2	110,600	1958	Madag, India 1958
D. Pilsch-Baag Germany	Baag	Filter press	230	1.788	2600	13.5	200	UNK	1935	UNK
E. Electrolyser Corp. Canada	Stuart	Tank	200	2.04	40	0.03	1000	1,130	1930	Teleyne Wash Chang, Alabama, USA, 1971
F. Cominco Canada	Trail	Tank	80	2.142	38	0.1	1	77,000	1939	Trail, Canada 1939
G. Teledyne Isotopes USA	EGGS	Filter press	400	2.1	65	70	2	50	1968	Teledyne isotopes, USA, 1972
H. Demag Elektro- metallurgie ORH Duisburg, Germany	Demag	Filter press	82 to 175- 280	1.75- 1.95	900	1	57	177,000	1945	Awana Dm, Egypt 1960
I. Electric Heating Equipment Co. USA	Kent	Tank	115	2.2	28	0.1	100	1,610	1920	Hobart, Tasmania 1949
Cells being developed										
J. Teledyne Isotopes USA		Filter press	400	1.65	13	2000				Designed for military aircraft application
K. Teledyne Isotopes		Filter press	250	1.64	94	3000				Designed for nuclear submarine application
L. General Electric		Solid electro- lytic	360	1.2- 1.8		1				2000 ^o F, not now under development
M. Westinghouse		Solid electro- lytic	900	0.5 ^c		1				Used for CO ₂ electrolysis in spacecraft atmosphere control system

^aFirst Zdanusky-Loma plant.

^bBefore has indicated an ability to achieve 1.61 V on new cells.

^cAssumes a fuel depolarized mode of operation, i.e., coal. Does not expect cell to be used as water electrolyser.



* Cell current density, amps/ft²

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

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

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

Biological and Other Processes

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

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

The technologies and costs for the production of other synthetic fuels, specifically NH_3 , CH_3OH , and N_2H_4 , were shown to be well developed commercial processes. The long-range potential problem of a source of carbon (as CO or CO_2) for methanol synthesis was believed to be available from the atmosphere, limestone, seawater or combustion of waste organic matter.

Waste Processes

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

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

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

Agricultural Processes

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

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

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

USE OF COAL

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

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

Two methods for producing hydrogen from coal were reviewed: steam-oxygen (Synthane) and CO₂-acceptor. These processes give similar production costs; those for the CO₂-acceptor process are shown in Fig. 3 as a function of the cost of the raw material. While these processes appear to be commercially viable, they have not been used in the U.S. due to the relatively lower cost of hydrogen available from natural gas and various petroleum fractions. In comparison to the production of methane from coal, hydrogen appears to offer a simplified flow sheet since no methanation step is required.

Methanol has been produced from coal in some parts of the world but not in the U.S. A two-step analysis of the manufacturing costs of (1) coal gasification and synthesis gas (H₂, CO) purification and (2) methanol synthesis is summarized in Table 3. The cost of

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

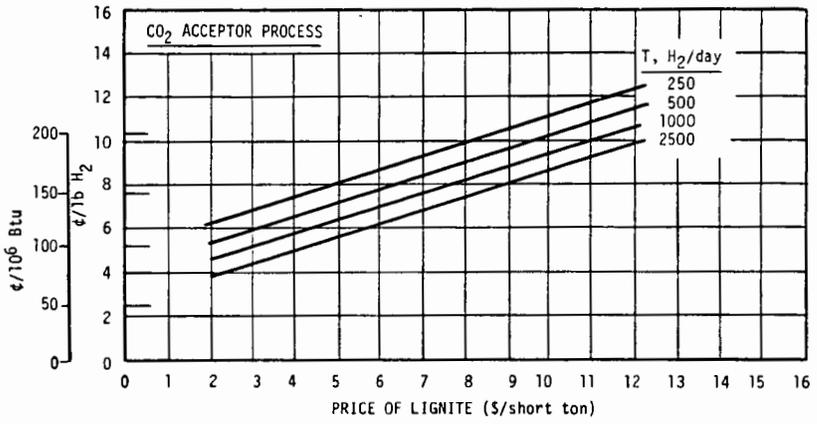


Fig. 3. Cost of producing hydrogen from coal.

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

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

^aCombined raw material and fuel.

^bPurge gas from synthesis gas plant.

producing the synthesis gas is seen to be the dominant cost and this, in turn, is largely dependent on the cost of coal. If lignite at \$2/ton were used, the total cost would decrease to 6.4¢/lb (\$110/10⁶ Btu). The costs of the various fuels are summarized in Table 4.

STORAGE AND TRANSPORTATION OF SYNTHETIC FUELS

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

Storage of Fuels

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

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

The cost of a compression and/or liquefaction system should be added to the cost of storage in assessing the utility of hydrogen energy systems. The cost of hydrogen gas compression might typically be 15 to 50¢ per 10⁶ Btu (.8 to 2.6¢/lb) for a wide range of delivery pressures and equipment utilization factors. The cost of hydrogen liquefaction might typically be \$1 to \$2 per 10⁶ Btu (5.2 to 10.4¢/lb) for a wide range of system capacities and utilization factors. The electrical power requirement alone is about 5 kWhr/lb H₂. These costs are usually more significant than tankage costs and must be considered in the design and evaluation of liquid H₂ storage systems.

Evaporation losses from large LH₂ tanks (~10⁶ gal) are typically 0.03%/day while small mobile tanks may be from 1 to 10%/day. A possibility for circumventing some of the above costs and storage losses is the use of hydrides or compounds of hydrogen. Several hydride storage systems have been investigated and indicate that a large number of binary and tertiary metal systems are available for this use. Magnesium and alloys of Mg and Cu or Ni⁽¹¹⁾ will release H₂ at 1 atm at temperatures of from 440°F to 540°F. Also some intermetallic compounds of the composition AB₅,⁽¹²⁾ where A is a rare-earth metal and B is nickel or cobalt, are reported to absorb and desorb large quantities of hydrogen at near room temperature. Some compounds such as ammonia and hydrazine can be readily decomposed to yield H₂. The hydrogen density in these compounds is from 1.5 to 2.0 times that of liquid hydrogen. Still lower effective heating values would, however, result since the heat of dissociation must be supplied, although in some applications waste heat may be utilized for this purpose.

Table 4. Summary of synthetic fuels production cost^a

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

^aCosts are based on 15% fixed charge rate and large plant capacities.

^bWater electrolysis plant operated at a 0.3 load factor.

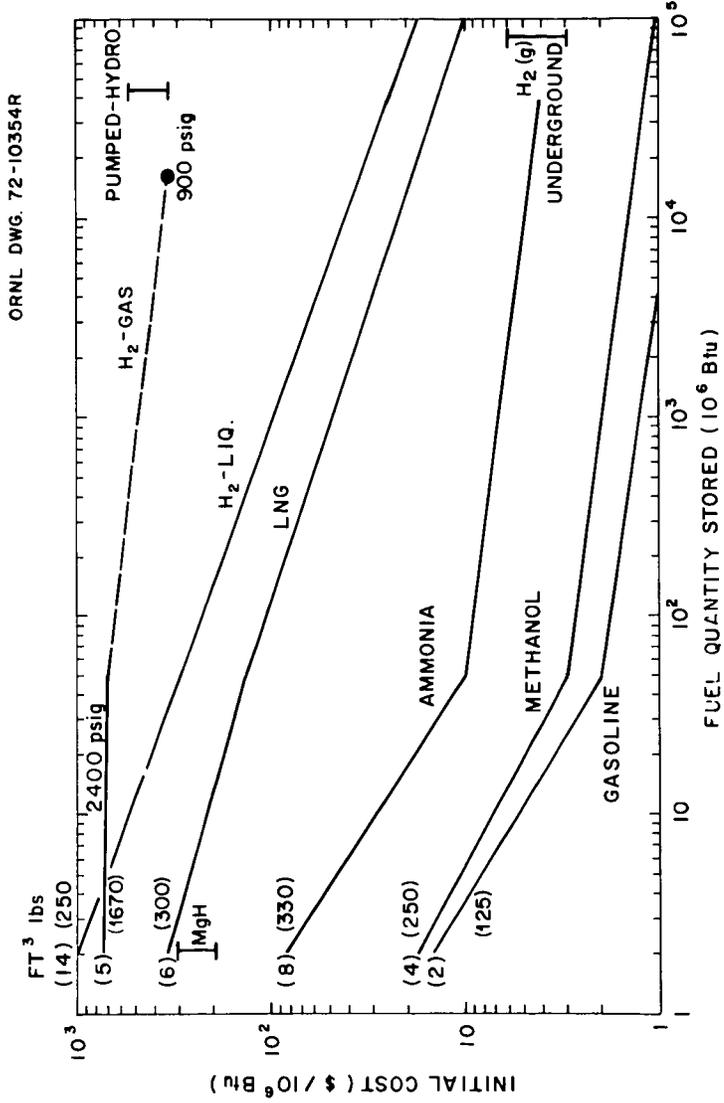


Fig. 4. Investments costs for storage of energy.

Fuels Transportation

The costs of transporting various forms of energy in a near-urban environment are summarized in Table 5. An average cross-country cost for natural gas transmission today is reported to be 1.5 to 1.7¢/10⁶ Btu per 100 miles.⁽¹³⁾ Hydrogen transmission cost would be 2.6 times this cost since compressor size and horsepower must be considerably increased and a more expensive fuel (hydrogen) used to power the compressors. By increasing the pipeline operating pressure from the "usual" 750 psia to 2000 psia, this factor could be reduced to about 1.5. Further, the average pipeline distance for hydrogen is likely to be less than for natural gas so that the total costs of delivery may be nearly equal.

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

USE OF SYNTHETIC FUELS

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

Industrial

Industrial uses for H₂ are mainly as a chemical as in ammonia production and in petroleum refining. Iron ore reduction could potentially require large amounts of hydrogen as will most coal processing schemes. Its use as an industrial fuel appears, technically, to be unlimited. Further, if a dual pipe (hydrogen and oxygen) system were available, or as dictated by economic tradeoffs, with oxygen from an air liquefaction plant, process steam could be produced directly. With this arrangement, a simple pipe-combustor-attenuator (as a closed system) would be substituted for the current massive water tube steam generators.

Of the other synthetic fuels methanol appears the easiest to adapt to industrial fuel uses - in fact, is already (as "methyl-fuel")⁽¹⁴⁾ being evaluated as a boiler fuel. Because of its toxicity and poor combustion properties, ammonia would be less suitable for this use. It may, however, be readily dissociated to H₂ and N₂ which for many applications would be an attractive fuel.

Urban

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

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

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

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

^bReported pipeline costs can vary by as much as a factor of 4, depending on terrain, congestion, etc.

^cFor cross-country straight lines, 50% reduction is likely.

^dNo reliquefaction included.

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

Transportation

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

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

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

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

Electricity Generation

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

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

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

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

Fuel cells have also been proposed for supplying utility peak power needs using hydrogen fuel (and oxygen) produced electrolytically during low demand periods. Overall efficiencies (electricity in/electricity out) with today's technologies will probably be under 30%, but with possible future technologies the efficiency could approach 50%. As an alternative to pumped hydro storage, it does offer a flexibility of location and a compact plant which may become an important consideration for peaking facilities. Other fuels, e.g., NH_3 , N_2H_4 , CH_3OH , have been used to a limited extent in fuel cells, both directly and after dissociation.

SYSTEMS ANALYSIS

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

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

It was estimated that the amount of available off-peak power in the year 2000 could satisfy: (a) 50% of the automotive, (b) 50% of the aircraft, or (c) all of the diesel fuel requirements. In one case where the off-peak fossil-generated power (for the production of H_2) was shifted to nuclear (part base load), a decrease of over 20% in petroleum imports was projected. The impact of this change on environmental factors is illustrated in Fig. 5 showing a decrease in chemical pollutants with an increase in radioactive wastes.

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

* Team to Advance Research for Gas Energy Transformation.

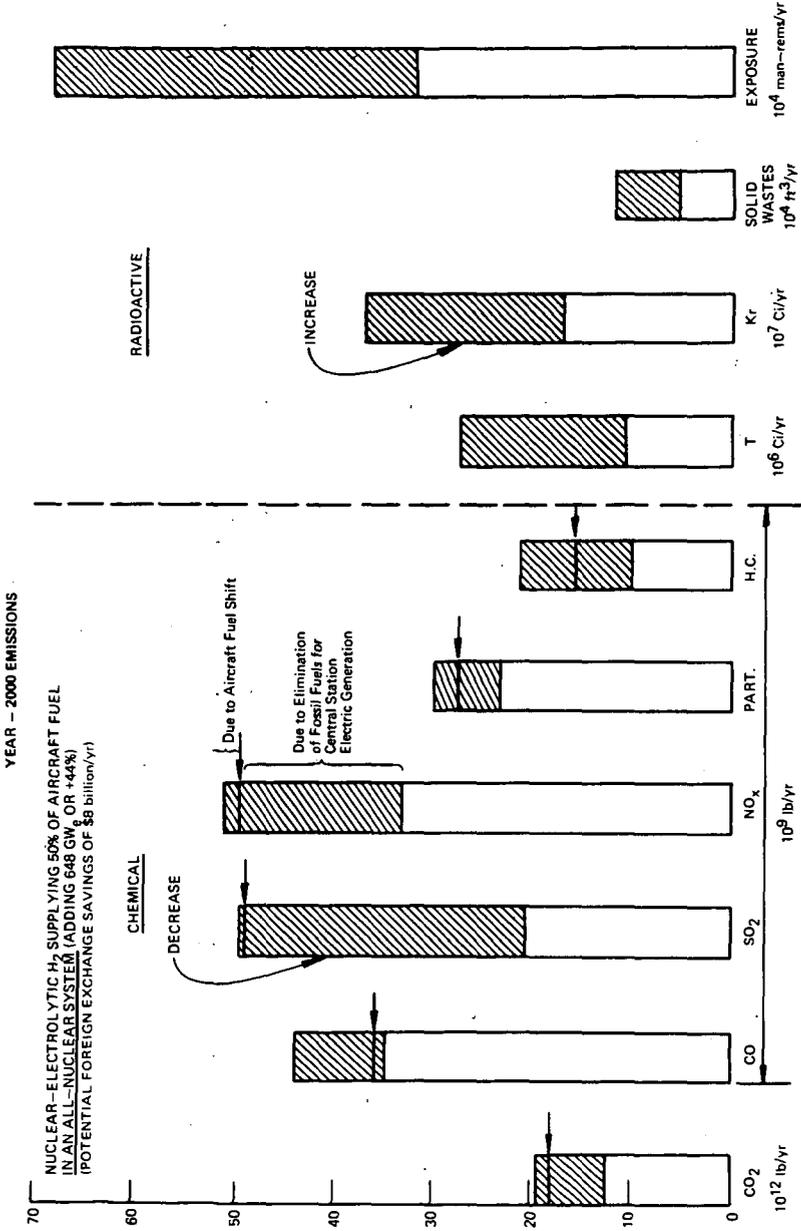


Fig. 5. Systems analysis - emission tradeoffs.

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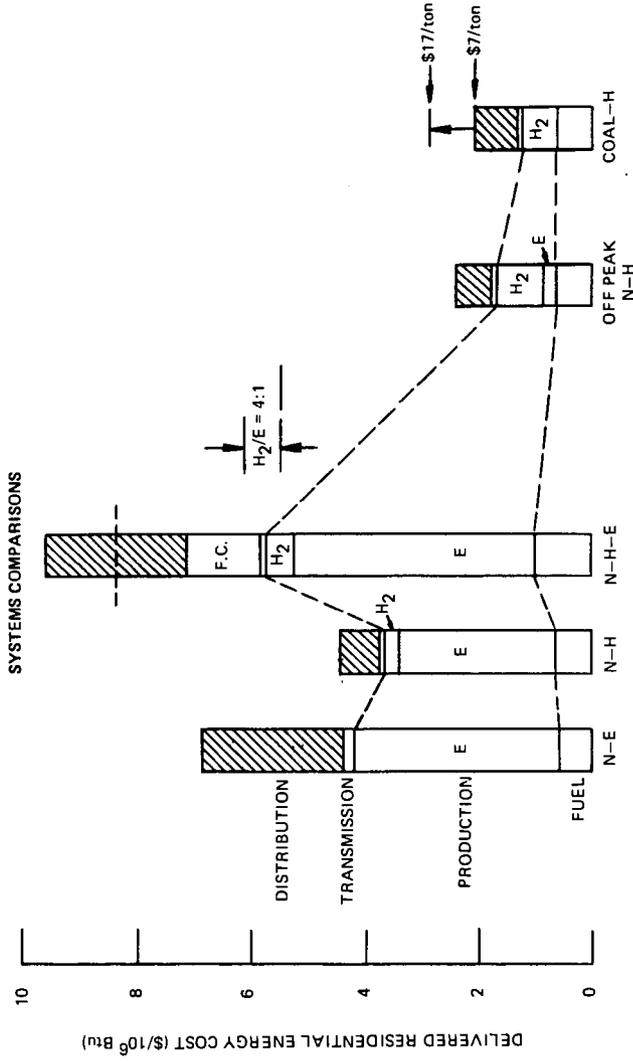


Fig. 6. Cost of delivered energy.

CONCLUSIONS AND RECOMMENDATIONS

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

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

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

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

1. Development and demonstration of methanol from coal as an automotive fuel.
2. Development and demonstration of H₂ as an energy storage medium for electric utilities use in supplying peak power demands.
4. Development and demonstration of the production of gaseous and liquid fuels from urban and agricultural waste products.

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

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

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

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

5. Overall systems analyses.

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

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

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

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

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

APPENDIX

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

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REFERENCES

1. Hydrogen and Other Synthetic Fuels - A Summary of the Work of the Synthetic Fuels Panel, USAEC Report TID 26136 (Sept. 1972).
2. J. E. Mrochek, J. M. Holmes, and J. W. Michel, "The Role of Electricity-Intensive Industries in the Economics of Nuclear Power," pp. 639-52 in Proceedings of Symposium on Nuclear Energy Costs and Economic Development, Istanbul, Turkey, Oct. 20-24, 1969, IAEA, Vienna (1970).
3. J. W. Michel, Status and Recent Developments in Agro-Industrial Complex Studies, ORNL-TM-3019 (June 1, 1970).
4. J. E. Funk, "Thermodynamics of Multistep Water Decomposition Processes," paper presented at the 163d National Meeting of the American Chemical Society, Boston, Mass., Apr. 9-14, 1972.
5. G. DeBenedi and C. Marchetti, "A Chemical Process to Decompose Water Using Nuclear Heat," paper presented at the 163d National Meeting of the American Chemical Society, Boston, Mass., Apr. 9-14, 1972.
6. H. F. Feldmann, "Pipeline Gas from Solid Wastes," paper presented at AIChE 69th Annual Meeting, Cincinnati, Ohio, 1971.
7. G. E. Johnson et al., "The Production of Methane by the Anaerobic Decomposition of Garbage and Waste Materials," Pittsburgh Energy Research Center, Bureau of Mines, USDI, presented at the 163d National Meeting of the American Chemical Society, Boston, Mass., Apr. 9-14, 1972.
8. G. A. Azego, A. A. Fox, and D. R. Eaton, "The Energy Plantation," pp. 1131-34 in Proceedings of 1972 Intersociety Energy Conversion Engineering Conference, San Diego, Calif., Sept. 25-29, 1972.
9. C. G. Golueke and W. J. Oswald, "Power from Solar Energy - via Algae-Produced Methane," Solar Energy 7(3) (1963).
10. Paul Averitt, "Coal Resources of the United States, Jan. 1, 1967," U.S. Geological Survey Bull. 1275.
11. K. C. Hoffman et al., "Metal Hydrides as a Source of Fuel for Vehicular Propulsion," SAE International Auto Engineering Conference, Detroit, Mich., Jan. 13-17, 1969.
12. J.H.N. van Vucht, F. A. Kuijpers, and H.C.A.M. Bruning, "Reversible Room Temperature Absorption of Large Quantities of Hydrogen by Intermetallic Compounds," Phillips Res. Rep. 25, 133-40 (1970).
13. D. P. Gregory and J. Wurm, "Production and Distribution of Hydrogen as a Universal Fuel," pp. 1329-34 in Proceedings of 1972 Intersociety Energy Conversion Engineering Conference, San Diego, Calif., Sept. 25-29, 1972.
14. Letter of Apr. 3, 1972, from David Garrett, Vulcan Cincinnati, Inc., to T. S. Mackey, ORNL.
15. A. M. Squires, I. Steelmaking in an Industrial Complex, ORNL-4294 (November 1968).
16. W. A. Sevian, F. J. Salzano and K. C. Hoffman, Analysis of Hydrogen Energy Systems (to be published).

HYDROGEN GENERATION BY SOLID POLYMER ELECTROLYTE WATER ELECTROLYSIS

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

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

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

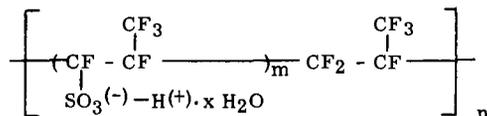
SOLID POLYMER ELECTROLYTE TECHNOLOGY

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

Solid Polymer Electrolyte

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

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



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

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

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

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

The use of the SPE results in the following advantages:

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

Catalytic Electrodes

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

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

Stack and Hardware Design

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

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

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

Present SPE Water Electrolysis Capability

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

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

Projected SPE Water Electrolysis Capability

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

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

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

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

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

APPLICATION OF WATER ELECTROLYSIS IN FUTURE POWER SYSTEMS

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

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

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

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

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

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

All of the present studies assume electrolysis energy requirements in the area of 22 to 28 KWH/lb H₂ and capital costs in the range of \$785/lb H₂/hr output capacity.

Based on the projected performance and cost estimates discussed previously, we see energy requirements of 18 to 20 KWH/lb H₂ in the 1985 - 1990 time period, dropping as low as 15 KWH/lb H₂ by the year 2000. A capital cost of \$785/lb H₂/hr capacity is reasonable for the 1985 time period with reduction to \$250 - 350/lb H₂/hr capacity by the year 2000.

Conceptual Hydrogen Utility System

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

In the electrolysis plant the water is electrolyzed into hydrogen and oxygen. The hydrogen can be stored in sub-surface tanks, either under pressure or as liquid H₂, in sufficient quantity to compensate for load fluctuations while allowing the power plant and electrolysis plants to operate at full capacity at all times. The hydrogen, which can be generated under pressure, is then transmitted through sub-surface pipe lines to local distribution points where it can be 1) distributed and used directly as fuel by domestic and industrial customers, 2) re-converted to electricity via either gas turbine generators or fuel cells, or 3) liquified and distributed in the liquid form for automotive or aircraft use.

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

Hydrogen as a Fuel

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

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

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

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

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

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

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

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

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

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

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

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

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

Energy Transmission by Hydrogen Pipe Line

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

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

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

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

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

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

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

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

	<u>1985</u>	<u>2000</u>
$\$/KW_{out}$	\$120/KW	\$120/KW
η	55%	70%

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

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

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

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

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

Energy Storage - In Hydrogen Energy Transmission

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

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

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

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

Liquid hydrogen dewars as large as 0.9 million gallons have been built at costs of approximately \$2 per gallon capacity (11). This is approximately a \$55.40/10⁶ Btu or 189 mils/KWH storage capacity. Large-size tanks have boil-off rates as low as 0.03 to 0.05% per day. Boil-off, as such, has minimal effect on storage costs since any boil-off can be returned to the main supply and does not necessarily represent waste. The heat required to reheat the liquid hydrogen for transmission as a gas would be readily available from the waste heat of the electrical generation plant.

Assuming 1% of the annual output is stored, storage dewars amortized over 35 years, and a liquification cost of \$0.70/MBtu stored, leads to an additional cost on delivered energy of \$0.023/10⁶ Btu (or 0.08 mil/KWH). This small cost could be greatly overshadowed by the savings in capital equipment costs due to being able to size the plant for nominal load rather than peak load.

Energy Storage - As Part of Existing Electrical Power System

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

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

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

Future Applicability

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

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

REFERENCES

- (1) W. Hausz, G. Leeth, C. Meyer, "ECO-ENERGY", conference proceedings - 7th Intersociety Energy Conversion Engineering Conference, 1972.
- (2) L. Lessing, "The Coming Hydrogen Economy", Fortune, November 1972.
- (3) L. O. Williams, "The Cleaning of America", Astronautics and Aeronautics, February 1972.
- (4) Business Week, "When Hydrogen Becomes the World's Chief Fuel", September 23, 1972.
- (5) C and EN, "Hydrogen: Likely Fuel of the Future", June 26, 1972.
- (6) C and EN, "Energy: The Squeeze Begins", November 13, 1972.
- (7) D. P. Gregory, J. Wurm, "Production and Distribution of Hydrogen as a Universal Fuel", conference proceedings - 7th Intersociety Energy Conversion Engineering Conference, 1972.

- (8) E. C. Tanner, R. A. Huse, "A Hydrogen-Electric Utility System with Particular Reference to Fusion as the Energy Source", conference proceedings - 7th Intersociety Energy Conversion Engineering Conference, 1972.
- (9) P. H. Sager, J. M. Kruse, "Combined Nuclear Gas Turbine Power and Desalination Plant", conference proceedings - 7th Intersociety Energy Conversion Engineering Conference, 1972.
- (10) W. E. Winsche, K. C. Hoffman, F. J. Salzano, "Economics of Hydrogen Fuel for Transportation and Other Residential Applications", conference proceedings - 7th Intersociety Energy Conversion Engineering Conference, 1972.
- (11) J. R. Bartlet, F. J. Edeskuty and K. D. Williamson, Jr., "Experience in Handling, Transport and Storage of Liquid Hydrogen - The Recyclable Fuel", conference proceedings - 7th Intersociety Energy Conversion Engineering Conference, 1972.
- (12) W. A. Titterington, A. P. Fickett, "Electrolytic Hydrogen Fuel Production with Solid Polymer Electrolyte Technology", presented at 8th Intersociety Energy Conversion Conference, Philadelphia, August 13, 1973.
- (13) Chem Eng News, Vol 46, No. 47, 1968.
- (14) H. S. Spacil and C. S. Tedman, Jr., "Electrochemical Dissociation of Water Vapor in Solid Oxide Electrolyte Cells", Journal of Electrochem. Soc., Vol 116, No. 12, 1969.

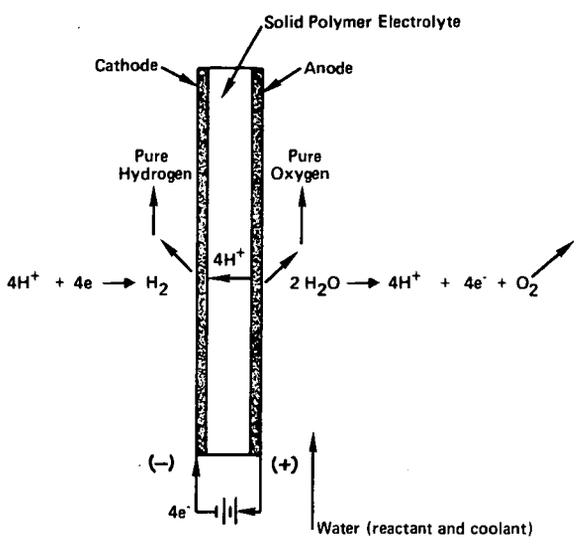


Figure 1. SPE Electrolysis Cell Schematic

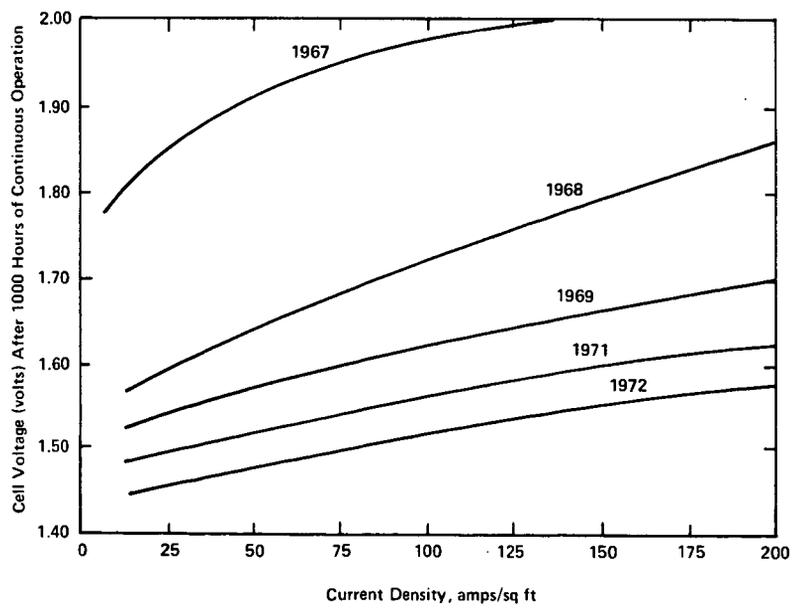


Figure 2. SPE Electrolysis Performance at 120°F and Ambient Pressure

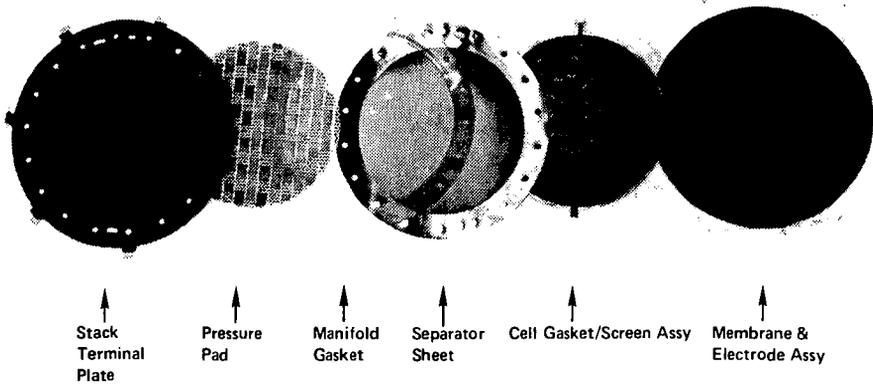


Figure 3. Electrolysis Cell Component Parts

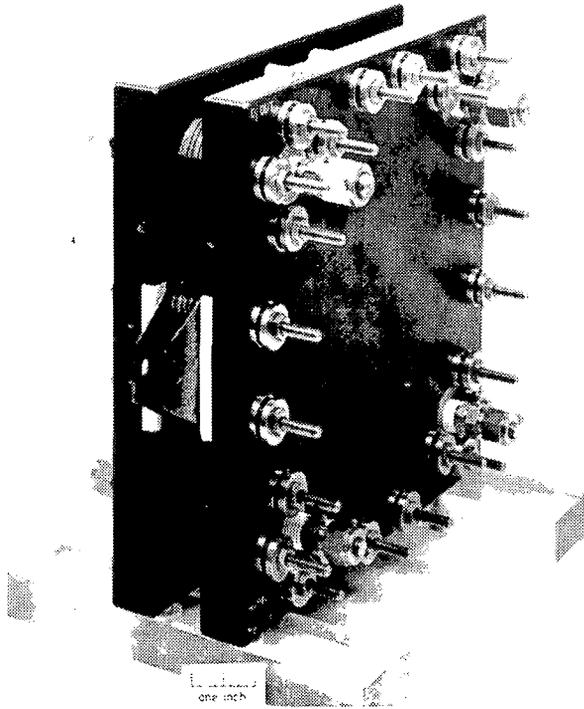


Figure 4. Seven-Cell NASA/LRC Electrolysis Stack

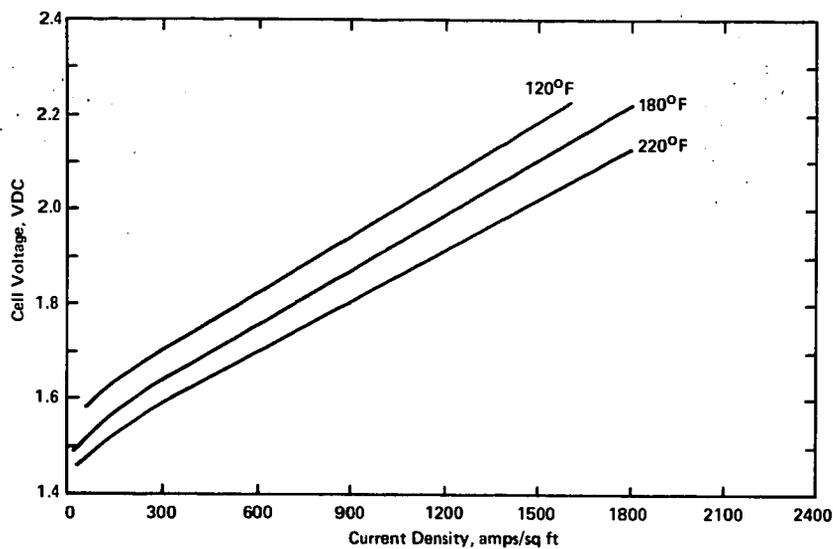


Figure 5. 1972 SPE Water Electrolysis Capability

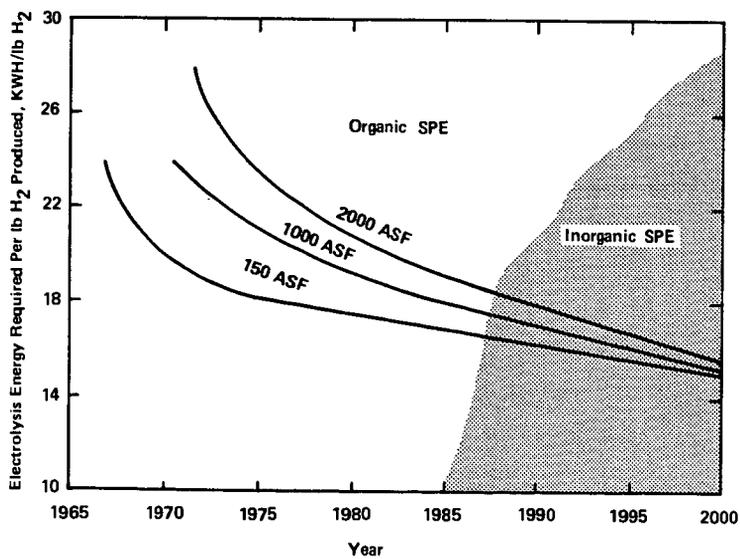


Figure 6. Energy Requirements for SPE Electrolysis

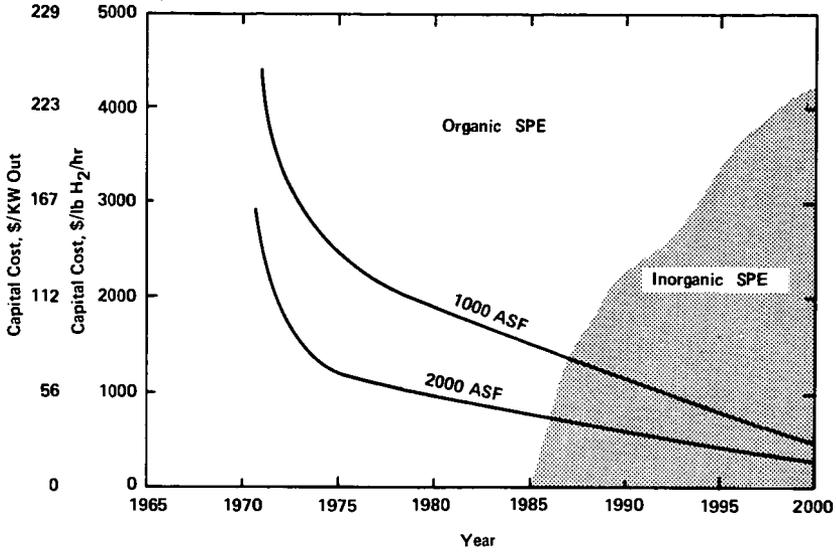


Figure 7. Capital Cost Requirements for SPE Electrolysis

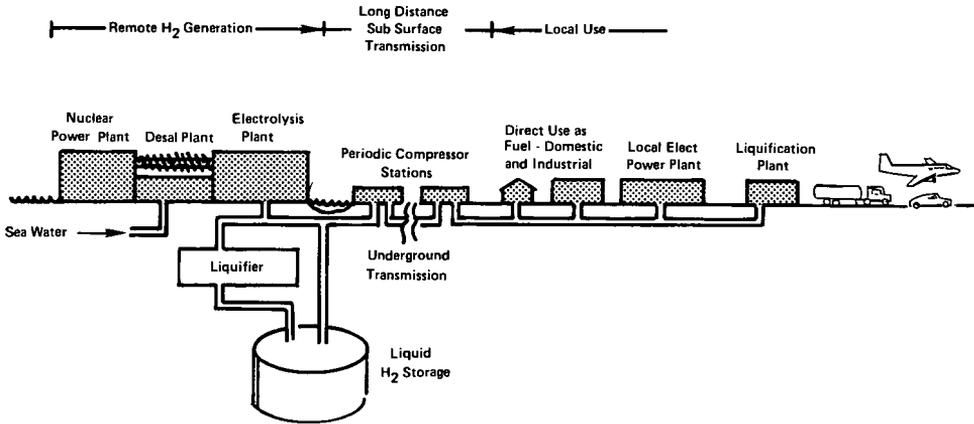


Figure 8. Conceptual Hydrogen Utility System

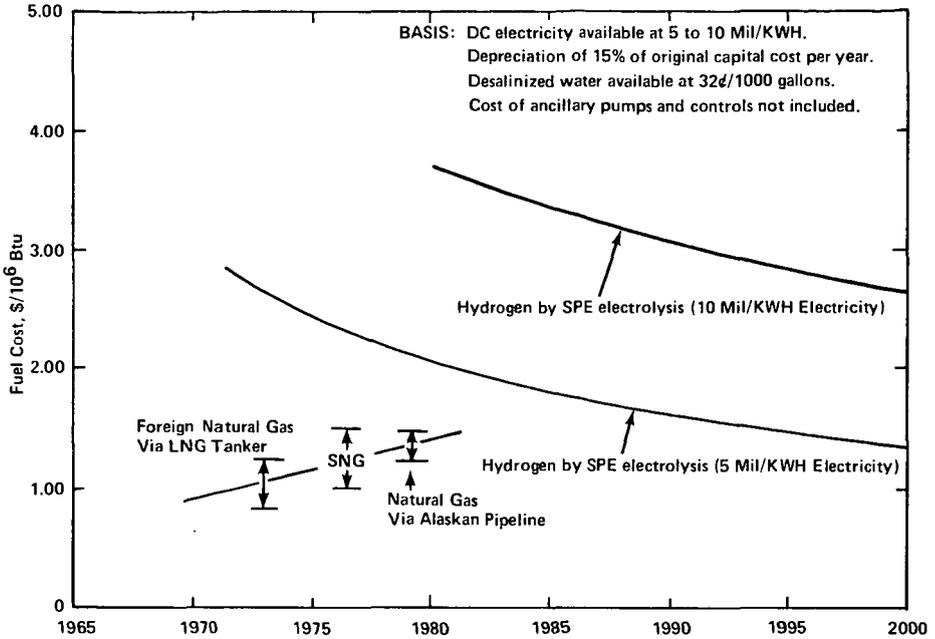


Figure 9. Projected Cost of Hydrogen Production by SPE Electrolysis

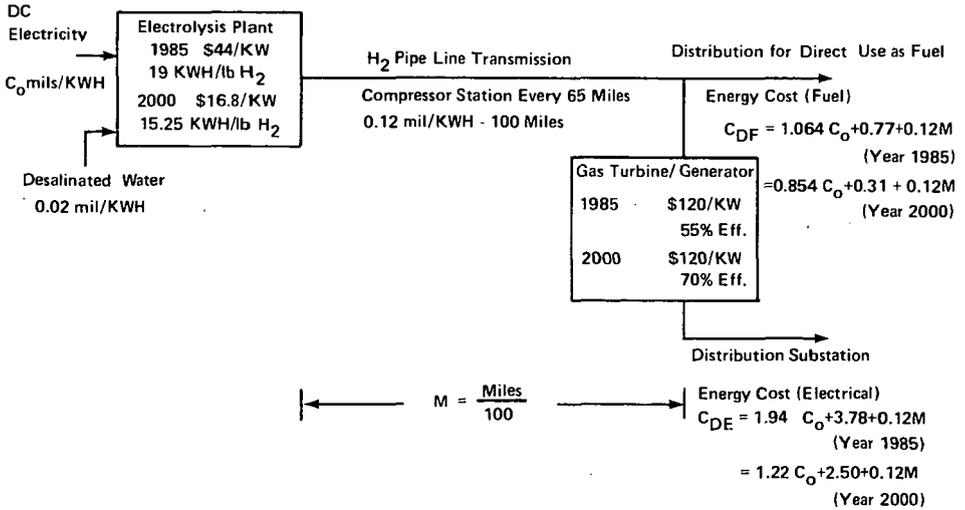


Figure 10. Model of Hydrogen Pipe Line Energy Transmission

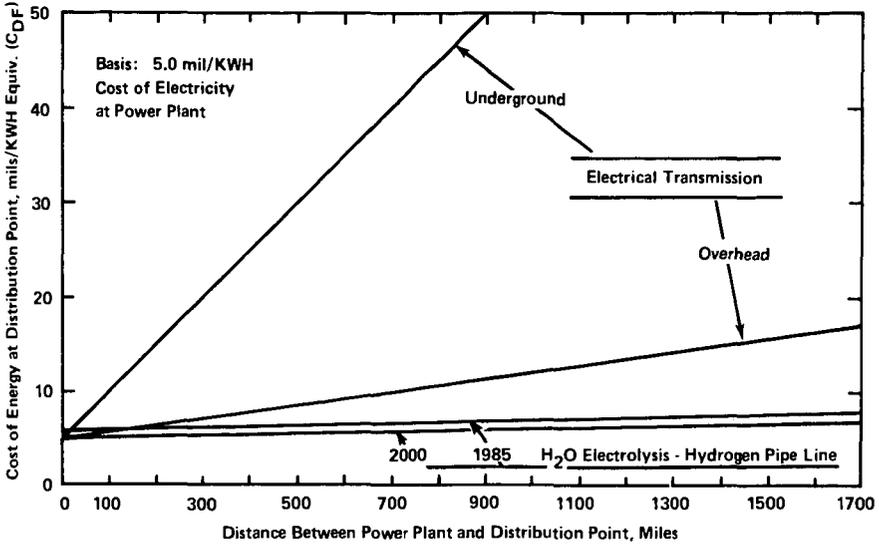


Figure 11. Comparison of Cost of Energy at Distribution Point for Electrical vs. Hydrogen Pipe Line Transmission

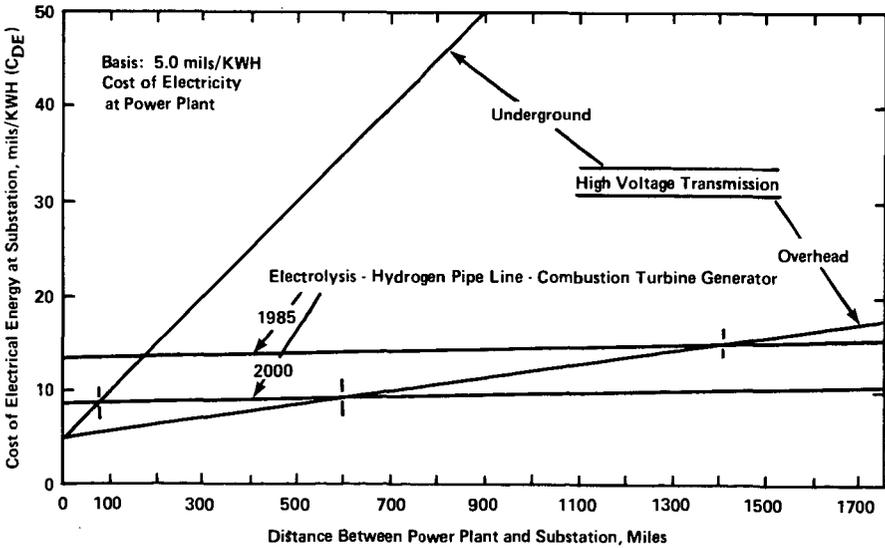
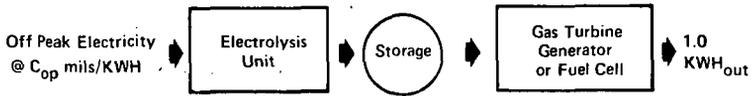
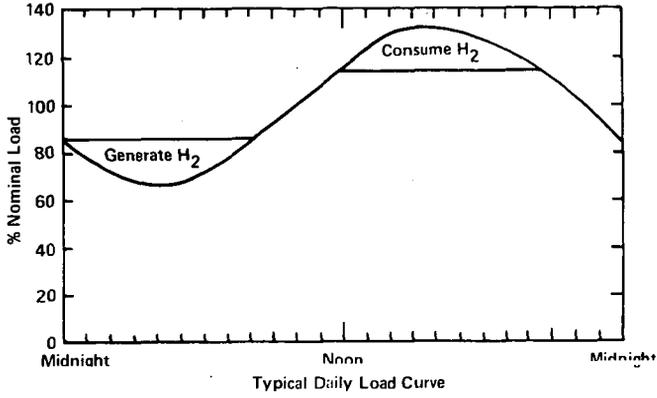


Figure 12. Comparison of Cost of Electrical Energy at Distribution Substation for Electrical Transmission vs. Hydrogen Pipe Line



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

COST RELATIONSHIPS

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

Figure 13. Typical Bulk Storage System

THERMOCHEMICAL SYSTEMS FOR HYDROGEN GENERATION. R. E. Hanneman and R. H. Wentorf, Jr.
Corporate Research and Development, General Electric Company, P. O. Box 8,
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Closed-cycle thermochemical hydrogen production, using water and heat as input ingredients and yielding hydrogen, oxygen and degraded heat as products, through multi-step reactions with cycled chemical intermediates will be treated. The approaches, criteria and limitations for identification of potentially viable closed-cycle methods of water splitting will be described. Key features of a new closed-cycle process developed in our laboratory will be presented in terms of the above factors. Practical overall thermal efficiencies based on hydrogen combustion energy produced relative to endothermic nuclear heat supplied can range from less than 20 percent to more than 60 percent with maximum input temperatures of 750°C for the various systems analyzed in our study. Limitations due to corrosion, reaction kinetics, system complexity, ecological and economic factors will be briefly outlined. Closed-cycle approaches will be compared to evolving open-cycle methods of hydrogen production with a fossil fuel, such as coal, wherein water and heat are input ingredients and hydrogen, CO₂ and degraded heat are the idealized exit products. Other methods of hydrogen generation including electrolysis, mixed-cycle, photolysis, and biological means will be briefly discussed.

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

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INTRODUCTION

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

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

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

The growing shortage of gas and oil in the US clearly points to the need for major emphasis to be placed on the gasification and liquefaction of coal. Most of the heat requirements of oil refineries for operations such as cracking and distillation are in the range of 300 to 550°C and could be met by adaptation of existing nuclear reactors although this will not be economically attractive until the price of petroleum products is higher. However, the use of nuclear heat to reduce consumption of coal as a source of energy in the gasification process has attracted interest. A key reaction in many of the processes being considered for that purpose is the endothermic reaction between C and H₂O to produce CO and H₂. The temperature required for this reaction is in the range of 1050-1150°C and the required heat is produced at the expense of coal. If the energy requirements for gasification were met by nuclear energy, the consumption of coal could be limited to supplying the carbon atoms required for the hydrocarbon synthesis. In view of the limitations of the world's coal and the huge rate of hydrocarbon consumption that exists, the saving could be very significant.

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

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

TABLE 1

PROJECTED HEAT CONSUMPTION BY
U.S. MANUFACTURING INDUSTRIES IN 1967^a

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

^aAfter Tarrice (1)

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

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

fuel temperature and the temperature imparted to the process materials.

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

Water-Cooled Reactors

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

Following development of the PWR for submarine propulsion, the first commercial electric power plant was put in operation at Shippingport in 1957. This reactor was followed by many others which have incorporated improvements, mostly notably an increase in burn-up from about 8000 to about 33000 MWd/t. The fuel material is usually slightly enriched UO_2 ($\sim 3\%$ ^{235}U) clad in zircalloy or stainless steel which presents a barrier to escape of fission products. Problems which tend to limit the performance of PWR fuel include fuel swelling and fission gas pressure, irradiation effects on fuel and cladding, stress corrosion of stainless steel cladding and oxidation and hydriding of zircalloy cladding. The output temperature is modest, falling in the range 260° to 350°C , though pressures are high, up to 2500 psia to prevent boiling. Useful heat is extracted from the primary hot water coolant loop through a heat exchanger located inside the reactor containment vessel. In the usual case where electricity is desired, steam is generated in the heat exchanger and supplied to a turbine. If process heat were desired, the steam, usually at $\sim 260^\circ\text{C}$ and ~ 720 psi could be used to transport heat to the desired process. Alternatively, in some instances, it might be desirable to transfer heat directly from the primary pressurized water core coolant loop through a heat exchanger to one or more of the materials to be processed. Safety considerations would probably determine whether such direct heat transfer was acceptable or whether instead a secondary heat transfer loop between the primary heat exchanger and the desired heat sink was preferable.

The BWR power reactor prototype was built at Vallecitos and put in operation in 1957. The fuel material of reactors of this type is usually UO_2 with zircalloy cladding. The output saturated steam temperature is 250° to 300°C at steam pressure of about 1000 psia and burnup is of the order of 30,000 MWd/t.

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

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

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

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

CO₂ Cooled Reactors

The British and French nuclear power reactor programs are based on CO₂ cooled, graphite moderated reactors using metallic natural uranium fuel with a magnesium alloy cladding, Magnox. This is a Mg alloy containing 0.8% Al, 0.008% Ca, 0.002%-0.05% Be, and 0.006% Fe. The British Calder Hall reactors began operation in 1956 and a total of about 35 such reactors have been built. Reactors of this type are conservative in design and have operated with very low fuel element failure rate. An inherent and important limitation is that the practical limit of reactor output temperature is about 500°C, because of oxidation of the cladding by CO₂. The core output temperatures of this and other types of reactor are compared⁽²⁾ in Fig. 1. Indeed, the melting point of the cladding is about 645°C and, in addition, uranium undergoes a phase change from α to the lower density β at about 665°C. Problems with the fuel have been mainly;

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

In 1963 the British Advanced Gas Reactor (AGR) at Windscale began operation. This is a higher temperature modification of the CO₂ gas cooled reactor leading to more efficient power generation. The fuel element temperature limitations of the Calder Hall reactor were significantly relieved by the substitution of UO₂ for uranium metal and of stainless steel cladding for the magnesium alloy. The stainless steel alloy, containing 20% Cr, 25% Ni, resists oxidation by CO₂. However, stainless steels and nickel alloys undergo loss of ductility as a result of neutron irradiation. The output gas temperature of this type of reactor has been in the range 500° to 575°C and burnup typically 10000 MWd/t. For electric power generation, heat is transferred through a heat exchanger to steam for turbine operation. If it were desired to use the output heat for process purposes, the considerations would resemble those applying to the PWR.

Na Cooled Moderated Reactors

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

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

Breeder Reactors

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

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

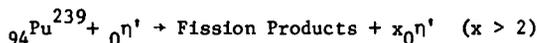
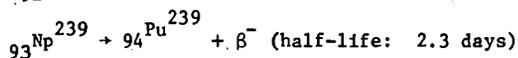
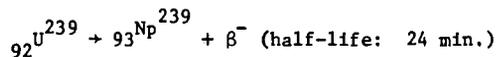
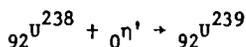
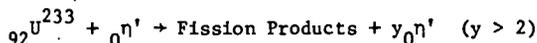
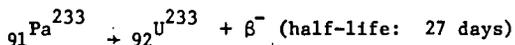
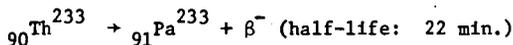
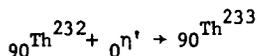
TABLE 2

<u>Price of Uranium Concentrates</u> <u>\$/pound U_3O_8</u>	<u>Tons of Uranium Resources</u> <u>at this or Lower Price^a</u>
8	594,000
10	940,000
15	1,450,000
30	2,240,000
50	10,000,000
100	25,000,000

^aAEC Report WASH 1098 (3)

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

TABLE 3

THE PRINCIPAL FUEL BREEDING REACTIONSUranium Breeding CycleThorium Breeding Cycle

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

The breeder fuel generally contains initially about 85 wt% U and 15 wt% plutonium to provide a fissionable fuel for startup. A variety of fuel compositions has been considered, including metal alloys of U and Pu, as well as $\text{UO}_2\text{-PuO}_2$, UC-PuC and UN-PuN. Of these, $\text{UO}_2\text{-PuO}_2$ has been the principal choice, in part because of its high melting point and good compatibility with cladding and coolants, good fission product retention and relative tolerance of irradiation. Several cladding materials have been considered including mainly stainless steels as well as nickel alloys and zirconium alloys. If the reactor is operated at a useful power density, the low thermal conductivity of UO_2 results in approach to the melting point of UO_2 at the fuel element centerline and this limits reactor operating temperature. Carbide fuels have higher thermal conductivity and greater metal atom density and reactors using them would be expected to have shorter Pu doubling time. There is, however, less experience with high irradiation of carbide fuels than with oxide fuels.

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

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

Gas Cooled Moderated Reactors

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

This type of thermal neutron reactor employs graphite as moderator and a graphite fuel element with fissionable fuel particles dispersed in it. Use of the chemically inert helium as coolant avoids problems of chemical reaction of coolant with fuel and to a large extent with structural materials in the core. The comparative absence of neutron absorbers in the core, which essentially contains only fuel and moderator, permits high specific power and very high burnup. The burnup in reactors of this class, 10⁵ MWD/t in the case of Ft. St. Vrain, promises fuel economy.

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

With variations of detailed structure, the fuel elements of HTGR's are based on the use of coated fuel particles contained in graphite. A great deal of effort has been expended in developing particle coatings and measuring their performance. The basic reason for coating the fuel is to impede the release of fission products to the coolant gas stream. Although at the highest operating temperatures it is not possible to completely retain fission products, the ratio of fission product atoms released to those born has been improved a great deal. The particles used in the Ft. St. Vrain reactor are called TRISO particles.⁽⁴⁾ The core of a fissile particle is about 200 μm in diameter and consists of (Th,U)C₂ in an atom ratio of 4.25 Th to 1 U. It is covered first with a low density layer of pyrocarbon about 50 μm thick which provides void volume to accommodate gaseous fission products, furnishes a cushion to allow for thermal expansion mismatch of core and coating, and protects the outer layers of coating substantially from damage by recoiling fission fragments. A 20 μm layer of higher density isotropic pyrocarbon greatly slows the release of iodine, tellurium and noble gas fission products. A third layer of pyrolytically deposited SiC about 20 μm thick acts as a very effective diffusion barrier, greatly improving the retention of metal fission products, notably Cs, Ba and Sr. The coating is completed by an outer layer of isotropic pyrocarbon about 20 μm in thickness. Fertile particles for this reactor contain 400 μm diameter cores of ThC₂ with the same coatings as fuel particles.

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

The Ultra High Temperature Reactor Experiment (UHTREX) yielded an output gas temperature of 1300°C which is several hundred degrees higher than any other reactor of the HTGR type, Fig. 1. The purpose of the reactor was to demonstrate the capability of this type of reactor for producing power and high temperature process heat. The fuel elements were unclad graphite containing coated UC_2 particles. This reactor had the unique capability of permitting refueling without interruption of full power operation. There was some fission product escape from the fuel and this was continuously removed by a coolant gas purification system. The UHTREX project was terminated in 1970 because of stringent budget limitations.

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

Economic Considerations

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

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

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

*with SO₂ scrubbers.

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

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

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

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

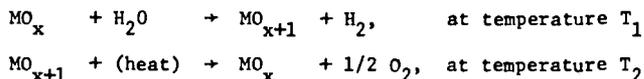
The Question of Plant Size

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

Hydrogen as an Energy Distribution Medium

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

then distribute this go-between energy to its multitudinous end users. Hydrogen is a very attractive medium to consider for this distribution system. It has a high heat content, is readily available (in H_2O), easily transportable, and ecologically attractive. It can readily be used in various industries such as ammonia synthesis, plywood drying, glass making, coal hydrogasification, metal ore reduction, petroleum refining, as well as for primary heating. The central problem is how best to make use of heat energy from a nuclear reactor for the decomposition of water. Although the indirect electrical generation/electrolysis route is technically feasible it is inefficient (28% presently, 40% ultimately may be possible). A more attractive approach from the thermodynamic viewpoint is the use of a dual temperature thermochemical cycle shown schematically by: (M stands for metal or compound and, in fact, four or more actual reactions may be necessary.)



The maximum cyclic efficiency of this process, from H_2O back to H_2O , is given simply by the Carnot relation, $(T_2 - T_1)/T_2$. The advantage of a process using a high temperature heat source is evident. If suitable reactants can be found in the temperature range of 1000°C to 1300°C, and if 80% of Carnot efficiency can be realized, then an efficiency of 60 to 65% will be achievable. These are two big ifs, but the incentive is sufficient to warrant a thorough search.

References:

1. R. R. TARRICE, "Nuclear Energy for Industrial Heat," A. Conf. 15/P/443, Second U.N. International Conference on Peaceful Uses of Atomic Energy (1958).
2. M. T. SIMNAD, Fuel Element Experience in Nuclear Power Reactors, Gordon and Breach Science Publishers, New York (1971).
3. "Potential Nuclear Power Growth Patterns," U.S. Atomic Energy Commission, Report WASH-1098 (Dec. 1970).
4. "Summary Report on the use of TRISO-Coated Particles in the PSC Reactor Plant", USAEC Report GA-8467, January 1968.

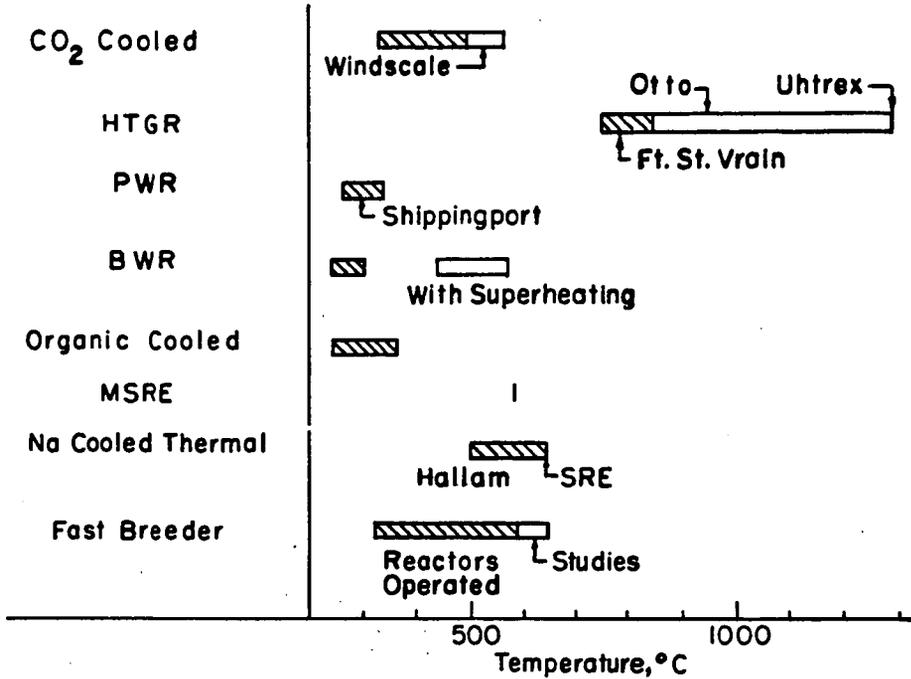


Fig.1 Output Temperature From Core of Various Types of Reactor

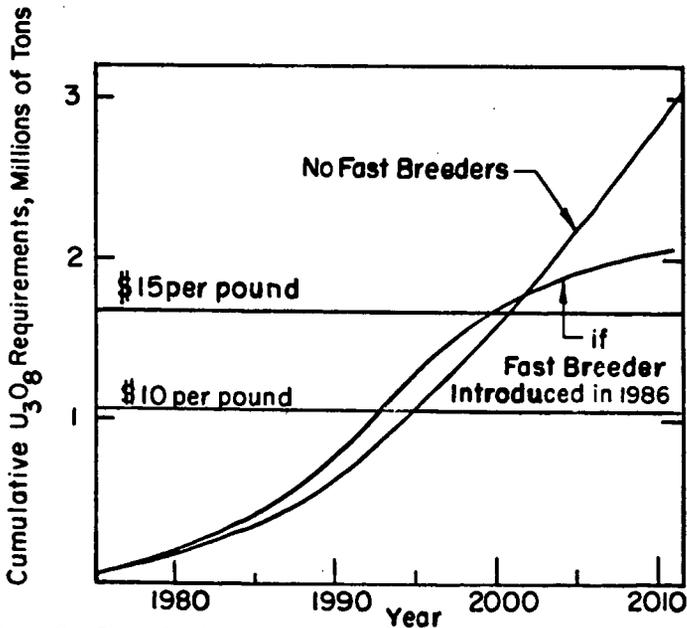


Fig.2 U.S. Cumulative Uranium Requirements

IRON TITANIUM HYDRIDE: ITS FORMATION,
PROPERTIES, AND APPLICATION

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Iron and titanium form two known stable intermetallic compounds, FeTi and Fe₂Ti.¹ It is also generally accepted that a third compound, FeTi₂,² exists above 1000°C, decomposing to FeTi and Ti below that temperature. We have briefly noted previously^{3,4} that one of these compounds, FeTi, will react directly with hydrogen to form an easily decomposed hydride which may be useful as a hydrogen storage medium. Our primary purpose here is to discuss the Fe-Ti-H system in some detail with particular emphasis on the reaction of FeTi with hydrogen and the formation and properties of two ternary hydrides, FeTiH_{~1} and FeTiH_{~2}. A further, though secondary, purpose is to discuss the application of iron titanium hydride as a storage medium for hydrogen fuel.

I. FORMATION AND PROPERTIES

Experimental

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

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

Our procedure for hydriding metals which form unstable hydrides, as in this instance, has also been described,⁶ and only a brief synopsis will be given here. The reactor was loaded with the granular alloy samples, sealed, evacuated and then heated to 400-450°C while outgassing continuously. Upon reaching the cited temperature range, hydrogen was admitted to the reactor until the pressure was ~100 psia. After ~30 minutes the reactor was evacuated and cooled to room temperature and H₂ was admitted to the reactor until the pressure was ~950 psia. Usually the metal-hydrogen reaction proceeded immediately with the evolution of heat. If no reaction took place over a course of ~15 minutes the above procedure was repeated. It should be noted that if the alloy is in ingot form, rather than granular, the initiation of the reaction is somewhat more difficult and may require several such treatments. In order to obtain a highly active metal substrate, the sample was hydrided and dehydrided several times. Dehydriding was accomplished by outgassing and heating to ~200°C.

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

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

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

Results and Discussion

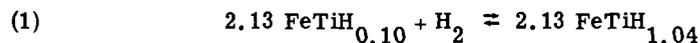
The Fe-Ti-H system was explored between the approximate limits, by weight, of 70% Fe-30% Ti and 37% Fe-63% Ti, corresponding to the atomic proportions Fe_2Ti and FeTi_2 . At the iron-rich end of this range no hydrogen was absorbed, but all compositions richer in Ti than Fe_2Ti did take up hydrogen to some extent. The stable intermetallic compound, FeTi, reacted readily, and a series of pressure-composition isotherms for the FeTi-H system is shown in Figure 1. The composition of the starting alloy was 53.6% Fe and 46.7% Ti. The metal phase present should be only that of FeTi, which was confirmed by an x-ray diffraction pattern taken of the sample. In the graphs the equilibrium dissociation pressure of the hydride is plotted against the hydrogen content of the alloy expressed as the ratio of hydrogen atoms to that of the total number of metal atoms ($\text{H}/(\text{Fe} + \text{Ti})$ or simply H/M). The shape of the isotherms can be interpreted as follows: on the left, where the isotherms rise steeply as the hydrogen content of solid increases, is the region of solid solution of hydrogen in the FeTi metal lattice. This solid solubility region may be designated as the α phase of the FeTi-H system. As the hydrogen

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

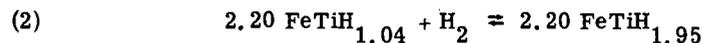
The effect of hysteresis in the FeTi-H system is illustrated in Figure 3. It is worth noting that the system almost forms two loops, the reason being that in the region of the pure β phase hysteresis is reduced substantially, which is the usual case in single phase regions. The loops are not closed since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

isotherms at H/M 0.5 does not occur in the absorption isotherm. This situation appears to be analogous to that occurring in the uranium-hydrogen system below 400°C, where a similar dip in the desorption isotherm was noted by Spedding et al.⁷ and by Wicke and Otto.⁸ Our results indicate that at higher temperatures the dip is less pronounced and finally disappears altogether in the 70° isotherm. This behavior is, again, similar to that of the uranium-hydrogen system, where Libowitz and Gibb⁹ found no dips in isotherms determined at high temperatures (450°+). Wicke and Otto have suggested that the phenomenon is due to the supersaturation of hydrogen vacancies in the hydride phase, while Flotow et al.¹⁰ have proposed that it is an effect caused by the state of subdivision of the solid.

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



which is followed by



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

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

The existence of the ternary compound TiFeH_1 is strongly supported by evidence gathered from x-ray diffraction patterns of material whose composition lies in the lower plateau region of the P-C isotherm. In order to obtain a suitable sample for x-ray analysis, an amount of $\text{FeTiH}_{\sim 1}$ was cooled to -70° and the hydrogen remaining in the gas phase was quickly evacuated; the sample was then contacted with air and allowed to warm to room temperature. This, in effect, "froze" the hydrogen content of the solid at a high level since such a procedure deactivates the hydride by air contact, thus preventing its rapid decomposition even at relatively high temperatures under conditions far removed from equilibrium. A portion of this material was taken and its x-ray diffraction pattern determined. The remaining material was analyzed for hydrogen by heating and decomposing it. While it is quite possible that the x-ray sample was not of the same composition as the bulk of material, or suffered some subsequent decomposition after sampling, as long as its composition

was within the lower plateau region, the pattern due to the β hydride phase should be discernible. We have followed this technique with material of a composition corresponding to $\text{FeTiH}_{0.89}$. Upon subtracting the lines due to FeTi (α phase), the ternary hydride phase FeTiH_1 was indexed as having tetragonal symmetry with $a = 3.18^\circ\text{A}$ and $c = 8.73^\circ\text{A}$, giving a c/a ratio of 2.74. The observed and calculated d lines are given in Table II.

In addition, the density of another sample having composition corresponding to $\text{TiFeH}_{0.80}$ was measured under benzene and found to be 6.003. Since this is a mixture of two phases, hydrogen saturated TiFe and TiFeH_1 , and the density of TiFe is known (6.50), the density of TiFeH_1 was calculated to be 5.88. Knowing the density and using the lattice parameters given above, the number of molecules in a unit cell were calculated to be 2.99 or 3. That the calculated value is so very close to an integral number is substantial evidence that the indexing treatment is correct.

The situation with solids of higher hydrogen contents, i.e. in the β - γ region is more complex and has not been resolved. A sample of the higher hydride was treated the same as outlined above; however, this material is more unstable than the lower hydride and decomposes more rapidly. We have taken an x-ray pattern at room temperature of material whose bulk composition was $\text{FeTiH}_{1.75}$, but it is quite possible that some decomposition took place in the process of obtaining the diffraction pattern. Only 5 lines were observed, which are listed in Table III. Three of these (2, 3, 4) are lines which are also observed with FeTiH_1 and one (5) is a line observed with unhydrided FeTi . On this basis no identification can be made. However, it does appear that the crystal structure is quite similar to that of the monohydride phase; a presumption which is supported by the low critical temperature of β - γ two phase region.

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

The FeTi phase is homogeneous in the composition region extending from 45.9% Ti to 48.2% Ti. The equiatomic composition is 46.17% Ti; thus an appreciable amount of Ti can be dissolved in the intermetallic phase. This fact may be responsible for the behavior illustrated in Figure 5, in which the starting alloy was enriched in Ti to the extent that its initial composition, 49.3 wt/% Ti and 50.7 wt/% Fe, was slightly above that corresponding to the single phase region. The isotherm (B) has been significantly distorted, the equilibrium dissociation pressure markedly decreased and the boundary between the lower and higher hydride almost indistinguishable. Such a situation is not without precedent and a somewhat similar effect occurs in the LaNi_5 -hydrogen system when excess nickel is added to the starting alloy,¹¹ i.e. the dissociation pressure of the hydride is increased by a factor of over three upon increasing the nickel content of the alloy from $\text{LaNi}_{4.90}$ to $\text{LaNi}_{5.5}$. Thus, in order to obtain reproducible behavior it is advisable to control the intermetallic composition as closely as possible. Upon increasing the Ti content to 63.2 wt/%, the pressure-composition isotherm (C) is greatly distorted as also shown in Figure 5. This alloy was annealed at 1000° for 12 hours, and then quenched in an unsuccessful attempt to prepare metastable FeTi_2 ; but only FeTi and Ti were produced. After hydriding, an x-ray diffraction pattern of the product indicated the presence of $\text{FeTiH}_{\sim 2}$, $\text{TiH}_{\sim 2}$, TiFe and Ti. The increased amount of residual hydrogen in the solid is undoubtedly due to the presence of the stable titanium hydride.

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

a reduction in the amount of hydrogen sorbed as shown in Figure 5. The starting alloy was a two-phase mixture, Fe_2Ti and FeTi , having an overall composition of 60.5 wt/% Fe and 39.5% Ti. The isotherm (A) is essentially congruent with that obtained with FeTi , indicating little interaction between the two phases or solid solubility of Fe in TiFe ; an observation which is in accord with the known homogeneity range of FeTi . The amount of hydrogen actually sorbed is somewhat less than that expected from the proportionate amount of FeTi present in the alloy, which may be due to the mere physical presence of Fe_2Ti .

II. APPLICATION TO HYDROGEN STORAGE

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

A simplified diagram in Fig. 6 shows a hydrogen storage reservoir of $\text{FeTiH}_{\sim 2}$ integrated with a hydrogen burning energy converter. The heat of decomposition is supplied from the waste heat of the energy converter by circulating its coolant through a heat exchanger in contact with the metal hydride. The heat, of course, must be supplied at a rate consistent with the fuel demand of the converter. For example, if the reservoir temperature can be maintained at $\sim 25^\circ\text{C}$ by the waste heat, the hydride is readily capable of delivering H_2 fuel continuously, at high flow rates and at pressures in excess of one atmosphere. If the heat supply is insufficient the bed will progressively cool and the H_2 flow will decrease until a balance is struck between the decomposition rate and the available heat. When the bed is exhausted it can be regenerated by following the opposite procedure, i. e. , the bed is contacted with hydrogen at

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

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

We have previously noted the performance of the Wankel engine using hydrogen fuel⁴; our purpose here is merely to demonstrate the application of iron titanium hydride as the hydrogen storage medium. We did not optimize the storage system in any way or quantitatively weigh such factors as kinetics,

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

The FeTi alloy was activated by the procedure outlined in Section 1. Following activation and several hydriding-dehydriding cycles, a composition corresponding to $\text{FeTiH}_{\sim 1.8}$ could readily be attained. During the hydriding step, the reservoirs were exposed to hydrogen at a pressure of 60 atm and were cooled by immersion in an ice bath. After hydriding, the ice bath was replaced with hot water ($\sim 50^\circ\text{C}$) and the reservoirs were connected to the engine intake manifold through the intermediate H_2 flow control and monitoring devices. The hydrogen delivery pressure was regulated at about 25 psia which insured good throttling capability. The pressure at the engine intake manifold was slightly below atmospheric and no air regulation or supercharging was required. Lubricating oil, normally mixed with the gasoline fuel, was aspirated into the engine by the gaseous fuel mixture.

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

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

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

Acknowledgment

The authors wish to express their thanks to Messrs. J. Hughes and A. Holtz for their expert assistance in the laboratory.

References

1. R. P. Elliott, "Constitution of Binary Alloys, First Supplement." McGraw-Hill, New York, 1965.
2. D. H. Polanis and J. G. Parr, Journ. of Metals Trans. AIME, 1148, Oct. 1954.
3. K. C. Hoffman et al., "Int. Automotive Eng. Congress," Jan. 1969, S.A.E.
4. R. H. Wiswall, Jr. and J. J. Reilly, "Metal Hydrides for Energy Storage," Intersociety Energy Conversion Eng. Conf., San Diego, Sept. 1972.
5. J. J. Reilly and R. H. Wiswall, Jr., Inorg. Chem. 6, 2220 (1967).
6. J. J. Reilly and R. H. Wiswall, Jr., Inorg. Chem. 9, 1678 (1970).
7. F. H. Spedding et al., Nucleonics 4, 4 (1949).
8. E. Wicke and K. Otto, Z. Phys. Chem. (Frankfurt) 31, 222 (1962).
9. G. G. Libowitz and T. R. P. Gibb, J. Phys. Chem. 61, 793 (1957).
10. H. E. Flotow et al., J. Amer. Chem. Soc. 81, 3529 (1959).
11. K. H. J. Buschow and H. H. Van Mal, J. Less-Common Metals 29, 203 (1972).
12. J. J. Reilly and R. H. Wiswall, Jr., "Metal Hydrides as a Source of Hydrogen Fuel," ACS Meeting, Chicago, Ill., Sept. 1970.

Table 1

Relative Partial Molal Quantities Per Gram Atom of Hydrogen

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

Table II

d Spacings for FeTiH_1

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

* by visual inspection

Table III

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

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

* by visual inspection

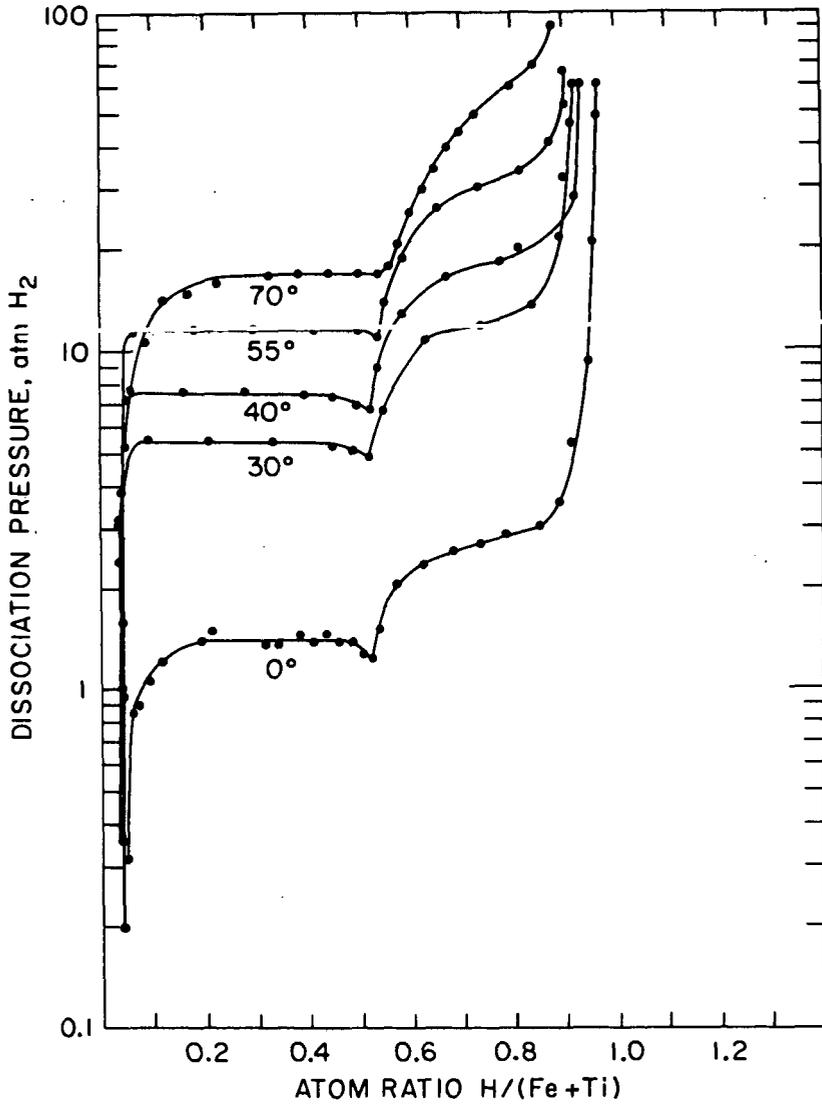


Figure 1 - Pressure-composition isotherm for the FeTi-H system. The initial alloy composition was 53.6% Fe and 46.7% Ti.

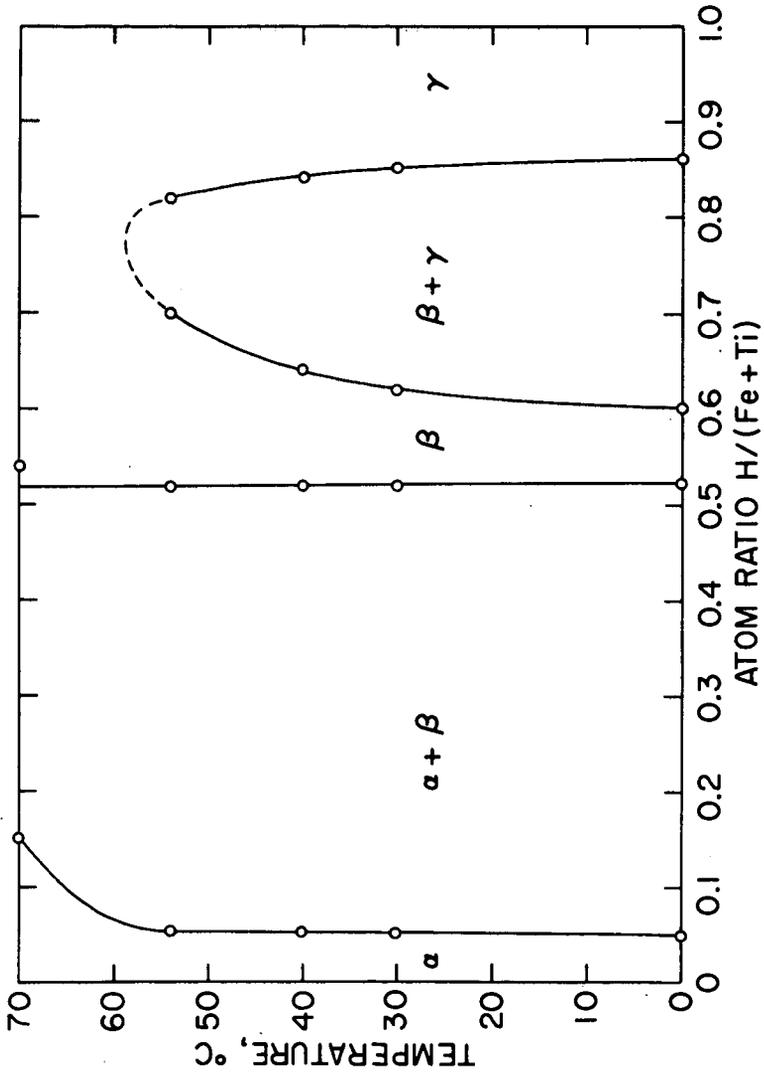


Figure 2 - Phase diagram of the FeTi-H system.

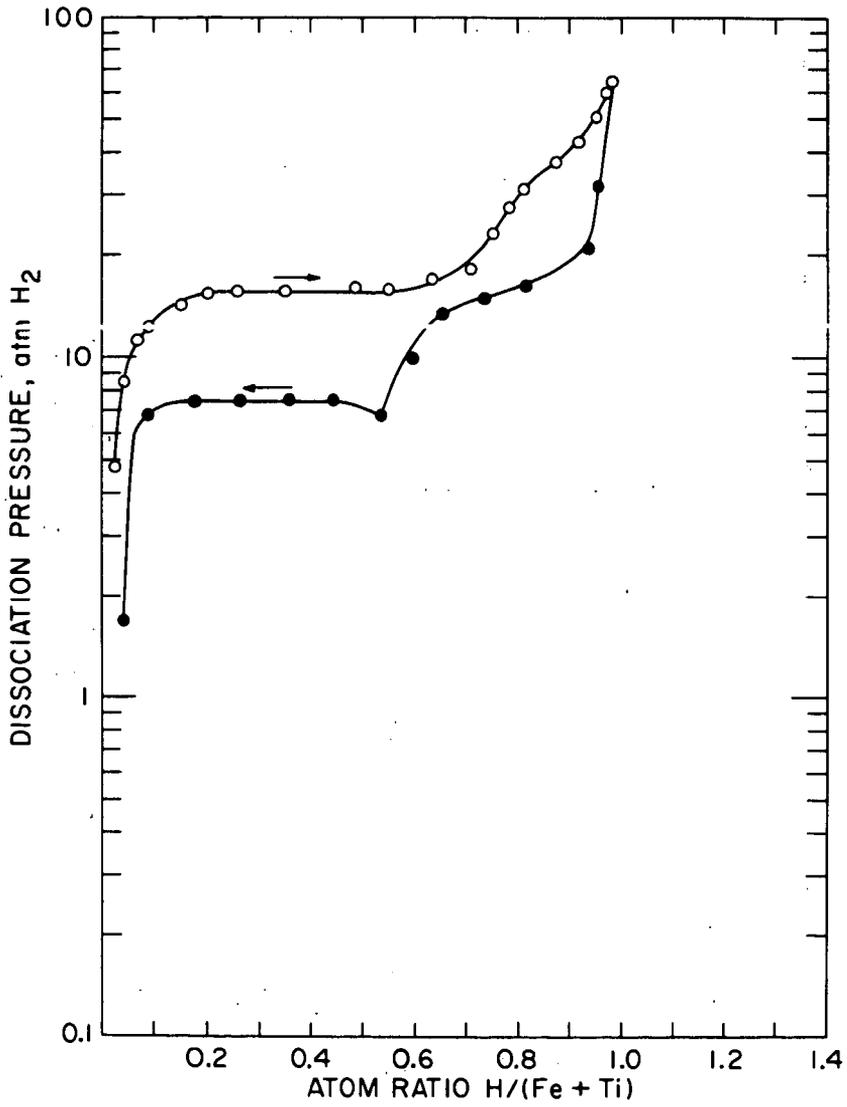


Figure 3 - Hysteresis in the FeTi-H system.

40°C

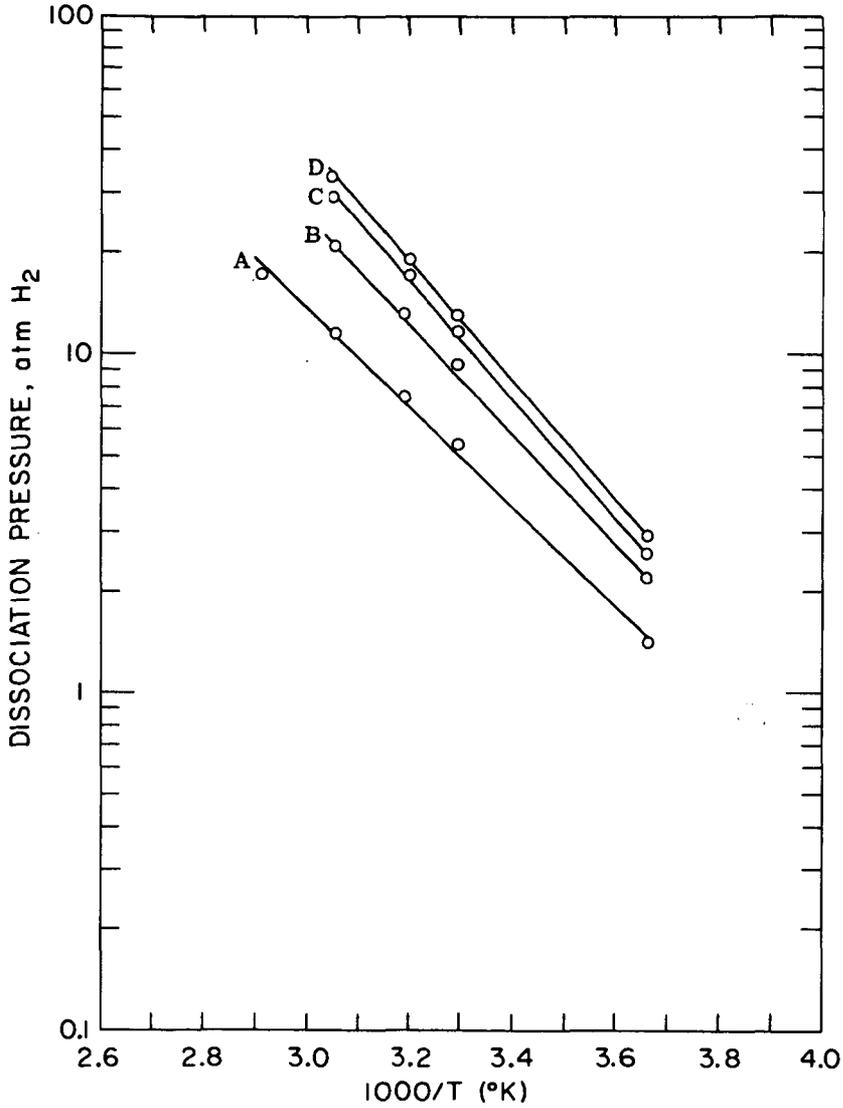


Figure 4 - Equilibrium dissociation pressure vs. reciprocal temperature for FeTiH_x .
 A) $\text{FeTiH}_{0.1}$ - FeTiH_1 ; B) $\text{FeTiH}_{1.2}$;
 C) $\text{FeTiH}_{1.4}$; D) $\text{FeTiH}_{1.6}$.

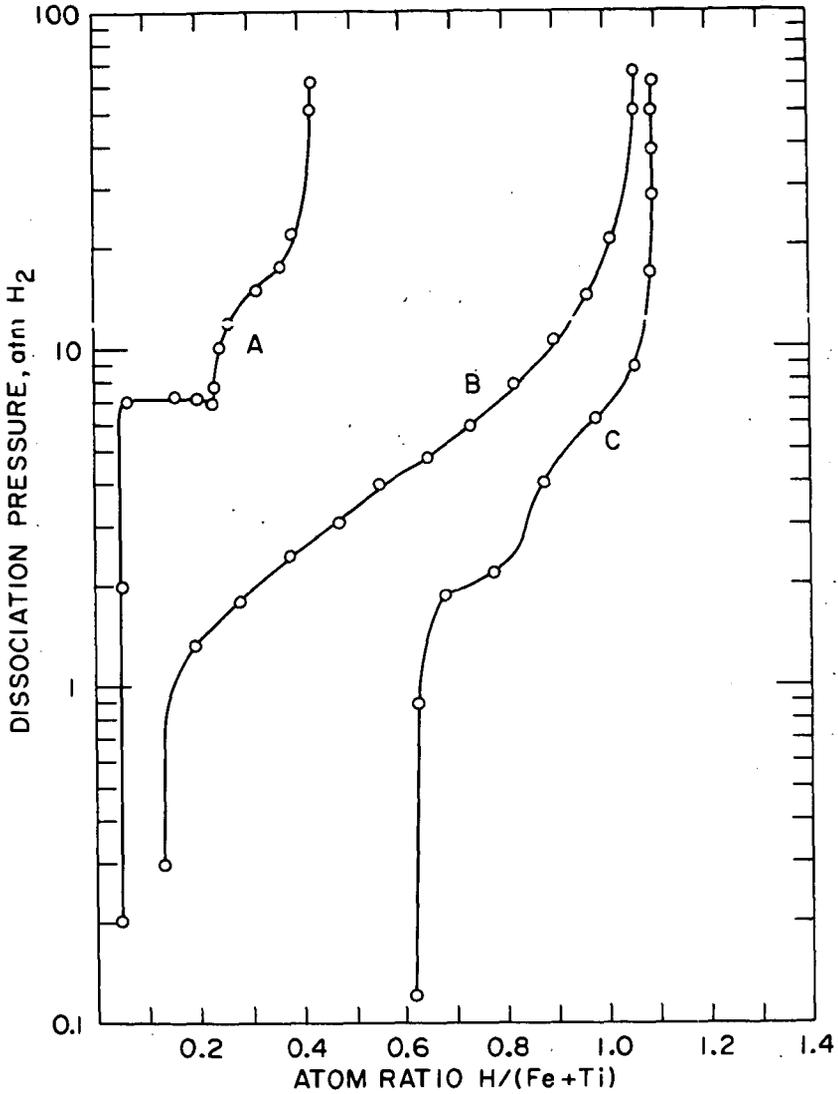


Figure 5 - Pressure-composition isotherms for alloys of various Fe/Ti ratios at 40°C.
 A) 60.5 wt % Fe, 39.5 wt % Ti; B) 50.5 wt % Fe, 49.2 wt % Ti; C) 36.7 wt % Fe, 63.2 wt % Ti.

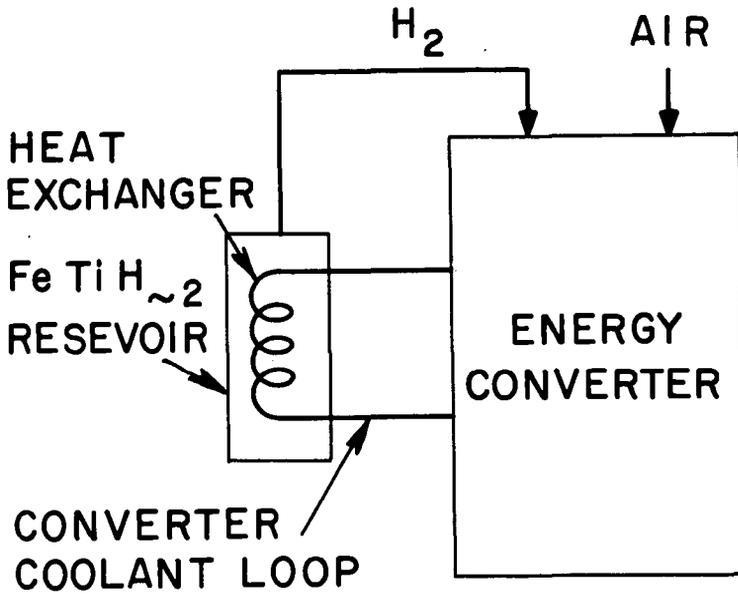


Figure 6 - Schematic of an Integrated Metal Hydride-Energy Converter System.

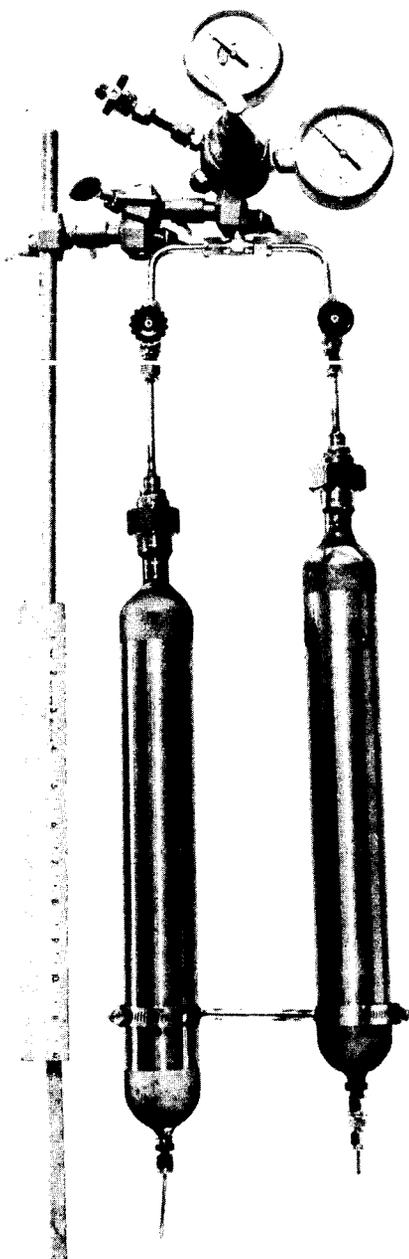


Figure 7 - Metal Hydride Reservoirs - Each Reservoir Contains 1.5 Kg of $\text{FeTiH}_{\sim 1.8}$

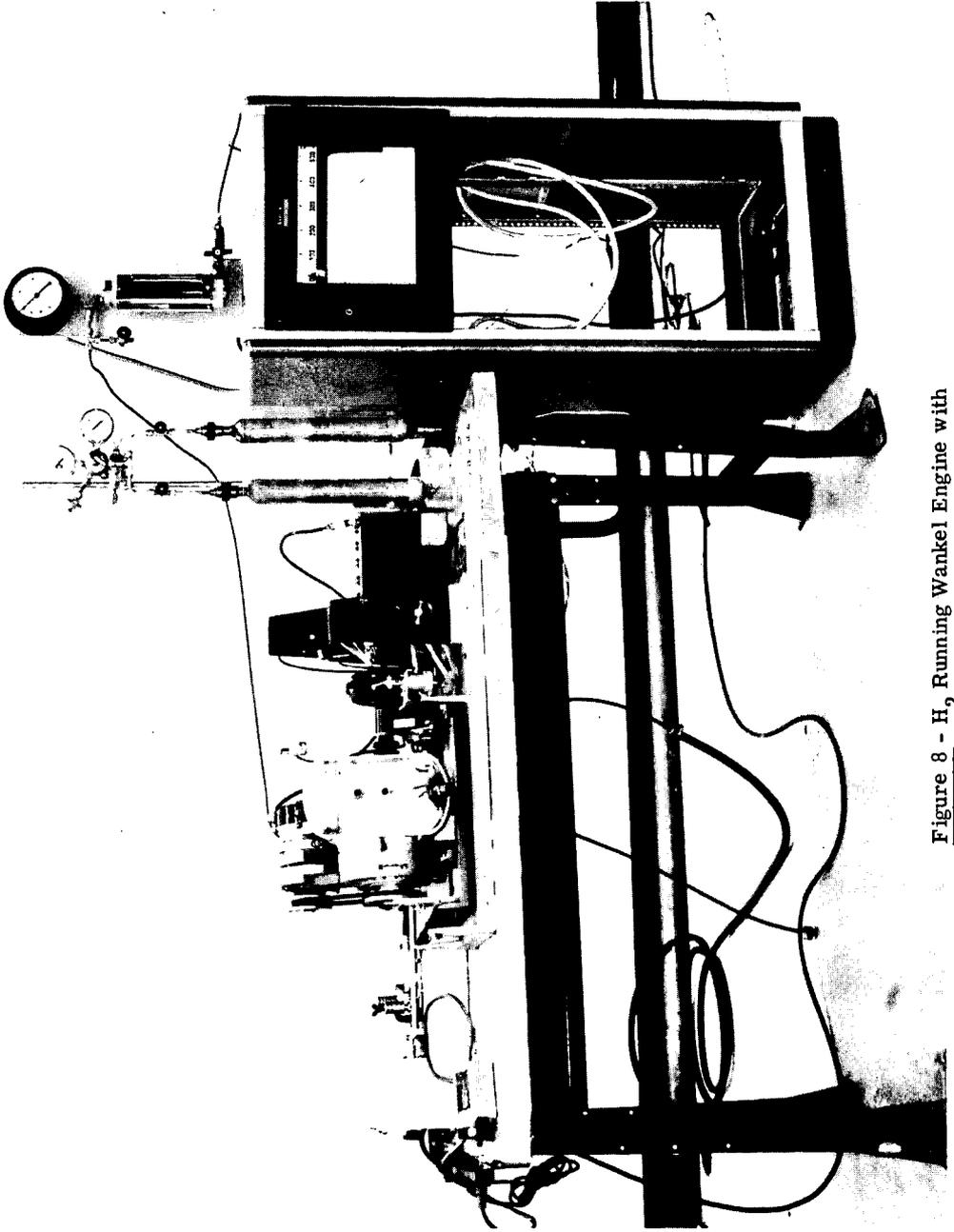


Figure 8 - H₂ Running Wankel Engine with Hydride Reservoirs.

CARBON MONOXIDE AS A FUEL

D. G. Walker

Tenneco Chemicals, Inc., Intermediates Division, Pasadena, Texas

The purpose of this talk is twofold. First, to familiarize you with a process for the separation of CO from gaseous mixtures which is called COSORB. COSORB cheaply and efficiently produces pure carbon monoxide from an ambient temperature and pressure gaseous mixture. Second, to discuss a coal gasification process which would produce pure CO for transmission and use as a fuel. This coal gasification process consists of (1) a slagging-ash gas producer using compressed air as oxidant, (2) gas processing units to extract the sensible heat of the producer gas as steam, isolate the tar and benzols produced and separate the sulfur, dust, and nitrogen containing compound from the gas, (3) COSORB which separates the CO from the rest of the purified producer gas (mostly nitrogen).

R. M. Jameson, at the recent Dallas meeting of this division, outlined at length why a coal refining industry needs to evolve in the immediate future. 85% of the total chemical fuel reserves of this country are coal. Yet coal is dirty. In addition to smoke problems, the sulfur and nitrogen content of coal go out the stack during its combustion in a boiler plant. Environmental problems will not allow future expansion of raw coal burning. Yet scrubbing stack gases for environmental clean-up is very expensive and only partially effective. The proposed process to be discussed here hopefully is an economically sensible way to use coal as an energy source. It refines the coal by gasification near the mine, purifies the gas, removes sulfur and nitrogen containing impurities, and then transports the pure CO by pipeline to the energy consumer. Pollution problems faced by the consumer would be practically nil.

It is to be emphasized that this process is completely unthinkable without an efficient, cheap separation of CO from nitrogen by a process such as Tenneco's COSORB. No such process has even been proposed before because COSORB did not exist before.

On the first slide, a diagram of COSORB is shown. The process has two packed towers, an absorber and a stripper. A copper containing solvent is circulated through the absorber where the solvent is contacted with a gaseous mixture, for illustrative purposes, a mixture of N_2 and CO. The copper cation in the solvent "coordinately" complexes the CO and absorbs it into the solvent. N_2 is untouched and dissolves in the solvent only by physical forces. It is quite easy to get the CO content of the nitrogen down to less than 1000 ppm. The CO rich solvent flows from the bottom of the absorber to a heat exchanger where it gives up a large fraction of the dissolved CO to the gas phase. In the stripper, a boiling aromatic compound drives the CO quantitatively out of the solvent. The hot lean solvent flows through the heat exchanger where it is cooled and then fed into the absorber to complete the circuit. A turbine compressor is shown in the diagram that may be used to compress the CO by letting down the nitrogen from its pressure in the absorber to one atmosphere. The stripper is run at some 5 psig or so pressure.

The entire apparatus for COSORB is built of simple mild steel. No corrosion problems exist.

Packed towers no taller than thirty feet are more than adequate to allow the quantitative separation at million lb/day carbon monoxide rates. The only utilities necessary are cooling water, low pressure steam, and electricity sufficient to pump the solvent from the stripper column to the absorber.

Having acquainted you with the COSORB process, I now turn to discuss a coal to CO energy complex.

Figure 5 is a diagram of a slagging-ash producer. The coal entering the top is mixed with a flux (limestone) and the residual ash from burning the coal exits the producer as a liquid. These producers can be built in very large units (the blast furnace, a prototype of this producer, is built in standard sizes of 1000 tons coke

per day). Under pressure, they also can be run at very high specific rates of production. These producers have a specific production rate fourfold that of the Lurgi process oxygen gasifiers. With pure carbon, the gas exit temperature is from 1000 to 1200C. The gases exiting a coal fed producer will be at a lower temperature because part of the sensible heat arising from the reaction of C to CO will be used to distill the tar, benzol, and moisture in the coal out of the coal on top of the very hot reaction zone. 72% of the energy of the carbon reacted will exit the producer as latent heat of combustion of CO while the remaining 28% will be sensible heat in the gas.

On slide 2, a line diagram of the coal to CO complex is shown. The heated producer gas goes to a steam generation unit where all possible sensible heat is transformed to steam. This steam is used as the driver in the succeeding units and also in the COSORB process to separate CO from the producer gas.

Tar and benzol are made in quantities similar to those obtained by low temperature coking of the coal in question.

One of the several developed efficient processes is then used to desulfurize the gas.

An activated carbon unit is then used for final clean-up to remove all heavier organics and nitrogen and sulfur from the gas.

A drying step (very probably a glycol-solvent absorber and stripper) is then used to finally prepare the gas for feed to COSORB. At this stage, the dry producer gas will be 33% CO with small amounts of H₂, CH₄, and CO₂ and the balance nitrogen.

This dry gas is then fed to COSORB (Fig. 1). In the absorber at 100 psig and ambient temperature, the CO is quantitatively absorbed in the solvent while the nitrogen goes overhead. A turbine lets down the pressurized nitrogen and compresses the pure CO. Considerable excess energy is available here and would be used to compress part of the air needed in Fig. 2 for the gas producer.

This energy complex would be at the mine. The product CO could be transported up to 400 miles to power generation stations or industrial complexes for use as fuel.

On slide 3, I have put down some salient points of interest about CO as a fuel. Its fuel value per unit volume is only 1/3 that of methane. This is a disadvantage for transport by pipeline, but not a severe one as long as the distances are reasonable. CO may be transported 400 miles by pipeline at an energy cost of only 13% of its fuel value.

As fuel, CO is superior to methane. It contains no water in its combustion gas. Its gross and net heat of combustion are the same. Methane uses only 90% of its gross heat of combustion in almost all of its fuel uses. CO has a higher octane number than methane. In a gas engine, fully 25% more horsepower can be delivered with CO than with methane as fuel.

CO can produce a completely dry hot gas if the combustion air is dried. This might be of great practical use in places where a very hot, but completely dry gas product is needed.

Engineering estimates for a COSORB based process and summarized on Fig. 4 for a very large CO producing complex, the complex size is 668 x 10⁶ SCF/day CO. This is equivalent in delivered BTU's to a 250 million SCF/day rate of methane.

The unit gasifies 10,800 tons of carbon per day. The tons coal would be larger than this by the amount of tar and benzol distilled in the gas producer. Twenty-eight percent of the heat value of carbon would appear as sensible heat in the producer gas upon oxidation to CO. This heat is equivalent to 3.5 million pounds of steam per hour. About 2.2 million pounds of steam is enough to drive all the purification units for the gas feed and also to operate a COSORB unit for the separation of CO from nitrogen.

One primary process driver (100,000 H.P.) operates from exhausting nitrogen. A second process driver is used (112,000 H.P.) for air compressing. Only the latter would need fuel. This fuel in a turbine would be about 14% of the heating value of the CO produced.

It is my opinion that the process discussed is a much more promising economical method of coal gasification than any method which uses oxygen as oxidant and which synthesizes methane as product.

CO does not have the BTU per SCF to substitute for methane in the present gas network. However, it needs emphasis that two-thirds of the present use of methane is in industrial or electricity use. Only 1/3 of the methane presently used goes to homes or other non-industrial usage.

Industrial and electrical generating uses of methane could be switched from methane to CO without great problems. This would conserve methane, so that an ample supply could be assured to continue home heating.

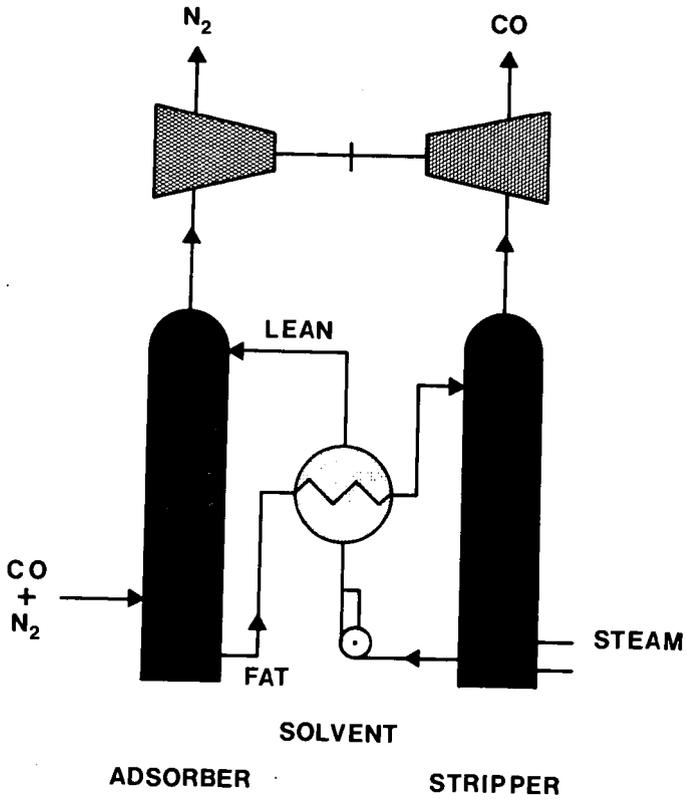


FIG. 1 - COSORB UNIT

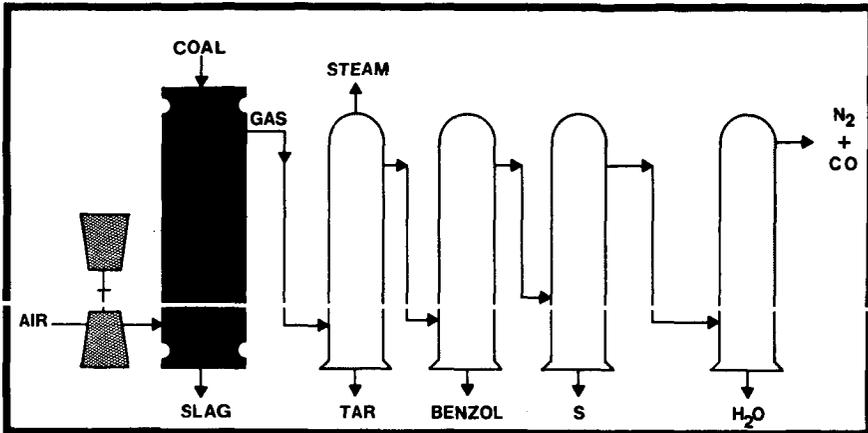


FIG. 2 - ENERGY COMPLEX: COAL - CO

CARBON MONOXIDE AS FUEL

HEATING VALUE: 340 BTU/SCF

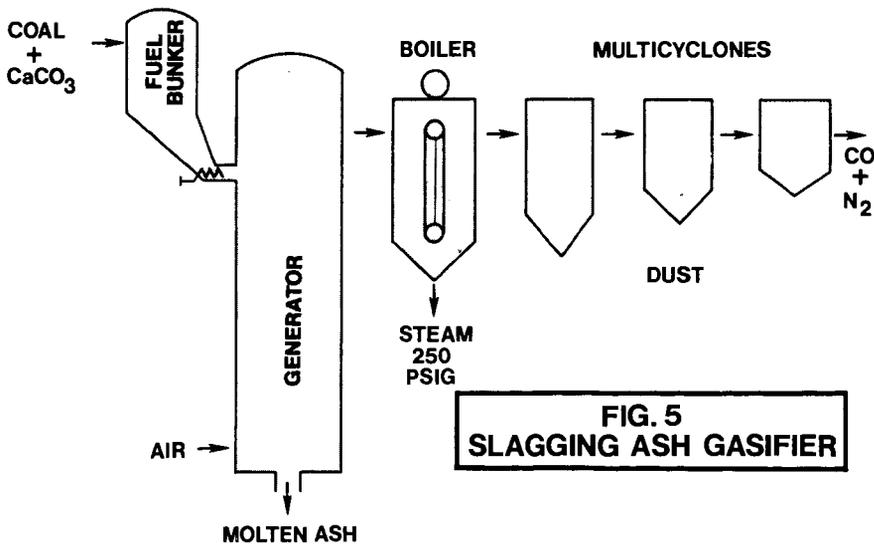
COMBUSTION EQN: $\text{CO} + \frac{1}{2}\text{O}_2 + 2\text{N}_2 \rightarrow \text{CO}_2 + 2\text{N}_2$

CO/CH₄ RELATIVE ENERGY DENSITY: 1.25/1

USEABLE COMPRESSION RATIO
IN OTTO CYCLE ENGINE: >9

COAL-CO ENERGY COMPLEX

- SIZE: 668×10^6 SCF CO/DAY
- GASIFIER P: 115 PSIG
- CO P: 100 PSIG
- CARBON GASIFIED: 10,800 TONS/DAY
- DRIVE: TRANSFER TURBINE 100,000 H.P.
AIR COMPRESSION 112,000 H.P.
- COSORB SOLVENT: 67,000 GPM
- STEAM USED: 2.23×10^6 #/HR.
- STEAM EQUIVALENT
OF GAS SENSIBLE HEAT: 3.56×10^6 #/H.R.



Very Large Steam Reformers

B M Blythe *
R W Sampson **

* Davy Powergas Inc
Box 2436 Lakeland
Florida 33803
USA

** Davy Powergas Ltd
8 Baker Street
London W1M 1DA
ENGLAND

INTRODUCTION

Recent forecasts of future natural gas requirements in the United States indicate that demand will exceed locally utilised production by 6,800,000,000,000 cubic feet during the year 1980 - (a 18,600,000,000 CFD deficit) (Reference - The Economist Intelligence Unit Ltd).

Japan similarly will have a deficit by 1980 for which estimates vary widely. The Economist Intelligence Unit forecast the figure for the year 1980 as 600,000,000,000 cubic feet (1,640,000,000 CFD).

Trans-oceanic transportation of natural gas in the liquid form (LNG) from countries with surplus supplies has been seen as one means of making up these deficits.

A major problem associated with the LNG scheme is the provision of transportation vessels. Cryogenic tankers are required which at present are on a 5 to 7 year delivery schedule and their costs are extremely high and still escalating rapidly.

An alternative means of transporting "natural gas" is now being studied in great detail. The idea is to convert the natural gas at its source to fuel quality methanol (or Liquid Chemical L.C.F) and to ship the methanol in conventional tankers for burning direct as fuel at the user location, or convert the methanol to SNG (Substitute Natural Gas) to supplement the locally produced natural gas.

Economic comparisons between the two schemes have been discussed elsewhere and the general opinion is that both types of plant will be built.

The plants to produce "methanol fuel" in economic quantities will be far larger than the methanol plants now being built for "chemical quality methanol".

LARGE PLANT

Contractors in the process industry and equipment vendors are being continually asked to supply larger plants in order that the chemical producer, refinery operator and fuel supplier, can keep pace with the ever increasing demand for more and cheaper product. For example, single stream ammonia plants have increased in size from 150 TPD of ammonia to 1,500 TPD in about one decade. The industry now faces a much larger increase in the size of methanol plants when the "fuel quality methanol" schemes proceed.

In a period from 1968 until 1975 we are expecting to see an increase in capacity of a methanol plant from 150 TPD to 25,000 TPD. In order to achieve the minimum production costs, this 25,000 TPD plant should be made up from the minimum number of single streams.

PROCESS ROUTE TO METHANOL FUEL

The natural gas which is currently being or that will be flared in areas such as the Middle East can be converted to methanol by the following process route. (See Fig. I).

The process consists of three basic steps:-

Steam reforming of desulphurised natural gas.
Compression to, and synthesis at, 100 atmospheres.
Dehydration to the required calorific value quality by distillation.

1 Reforming

Desulphurised natural gas is mixed with steam, reformed under optimised conditions in a tubular reformer, and then cooled.

2 Compression and Synthesis

Cold synthesis gas is fed by centrifugal compression to the synthesis loop where the methanol is formed.

Excess hydrogen is purged directly from the loop and burned in the reforming furnace, thus maintaining the overall plant efficiency at a high level.

3 Dehydration

Separation of water and dissolved gases from the L.C.F is achieved in a simple single-column distillation system.

THE STEAM REFORMER IS THE MAJOR PIECE OF EQUIPMENT IN THE METHANOL PLANT

The steam reformer is the most important and expensive single item of equipment in the methanol plant. It is therefore important to optimise the size and number of steam reformers required to produce 25,000 TPD of methanol within technical limitations. To date, the largest steam reformer is operating in a methanol plant at Clear Lake Texas (Celanese Chemicals Co) and contains 600 reforming tubes. This plant can produce 1,500 TPD of methanol by a similar route to that described above, or 1,800 TPD by slightly modified process route.

The following table shows the number of reforming tubes required for the range of methanol plants discussed.

Methanol Output TPD	Reformer Tubes (approx)	
	4" I.D; 40' heated length	
150	60	
1,500	600	
5,000	2,000	
25,000	10,000	

OPTIMUM PLANT SIZE

The basis of this paper is that a single stream methanol plant can be built to produce 5,000 TPD of methanol. Five such identical plants will be required to produce 25,000 TPD. We are thus talking of a reforming furnace containing approximately 2,000 tubes, which is in excess of three times the world's largest operating single stream furnace.

Improvement to catalysts and reformer equipment are continually being implemented. Increases in output from these improvements are disregarded in this paper because they are insignificant with respect to the magnitude of the increase in output required for the economic production of L.C.F.

The reasons for selecting 5,000 TPD methanol plant are two fold:

- 1 Equipment other than the reformer is proven commercially at this sizing.
- 2 The increasing size of reformers over the years projected to 1976 show a progression to approximately 2,000 reforming tubes. (Figure II).

This paper continues with the description of a single stream 2,000 tube reformer.

STEAM REFORMER

A steam reformer contains a number of reforming tubes which are basically heat transfer tubes filled with catalyst. The process reactants, (steam and hydrocarbon) are passed through the tube where they react endothermically. These tubes are held vertically in a direct fired furnace box. The output of the plant is dependent on the following:

- 1 The number of tubes.
- 2 The physical dimension of the tubes.
- 3 The operating conditions.
- 4 The analysis of the total feed to the reformer.
- 5 The activity of the catalyst.

TUBE DESIGN PARAMETERS

Some of the important design parameters of the reforming tubes and the limitations imposed upon them are as follows:

Tube Length

It is possible to increase the output of a furnace by lengthening a given number of reformer tubes and thereby increasing the volume available for catalyst.

Actual costs prove it is more economical to increase the length of a given number of tubes than to maintain tube dimensions and increase the number of tubes. Benefits from increasing the length are available until limited by one of the following factors.

a Pressure Drop through the catalyst packed tube.

In order to limit the pressure drops through the plant to an acceptable level, the maximum heated length of a tube, currently being considered, is 50 feet giving a pressure drop through the tube in the order of 70 psi.

b Thermal Expansion.

As the reformer tubes operate at elevated temperatures, the tubes expand when heated from the ambient to operating temperatures. This expansion has to be taken up by the adjoining pipework, making its design rather cumbersome.

c Compression Load at elevated temperatures.

It is necessary, due to the length and relative small diameters of the tubes, to minimize the self weight compressive load on the tube. This is done by partially supporting the tube at the top by either counter-weights or by tensioning springs. Whichever method is used, a tube length from 40-50 feet seems to be the optimum.

Tube Diameter

Increasing the diameter of the tube achieves a larger volume available for catalyst for a given number of furnace fittings, as does lengthening the tube. Although in increasing this dimension consideration must be given to the following:

a Increasing the hoop stress in the tube.

This will increase the thickness of the tube wall, offering a higher resistivity to heat transfer, resulting in higher tube wall temperatures. The higher tube wall temperature again increases the wall thickness and therefore an economic optimum diameter must be chosen.

b Decreasing the tubes' heat transfer surface area for a given volume of catalyst.

This increases the tube wall metal temperatures and hence the tube wall thickness resulting from the higher heat fluxes required to pass the heat of reaction.

c Reduction in the gas side heat transfer coefficient.

Resulting again in higher tube wall temperatures and hence thicker tube walls.

The cost of tube material in its fabricated form is approximately \$1.25 per pound weight (compared with \$0.25 per pound for carbon steel), the need for optimisation then is critical on reformers containing 2,000 tubes.

Taking into account the above, also the heat flux and catalyst loading limitations imposed by the catalyst suppliers, the economical diameters for reformer tubes vary between 3½" and 4½" ID dependent upon operating conditions.

Tube Pitch

Take one row of tubes firstly it is necessary to select the tube pitch. This choice is governed by mechanical limitations of how close together tubes can be placed and an economic evaluation of tube wall thickness against the pitch selected. In general terms, the closer the tubes are together, the hotter the tubes will be for a given set of operating conditions. As the metal thickness of the tube is highly dependent upon the metal temperature of the tube an economic tube pitch is essential on large furnaces. Tube pitches of 9 to 11 inches are normally chosen after economic optimisation.

Other Variables

Consideration must also be given to catalysts and their activity, the temperature and pressure of the reaction, the steam to hydrocarbon ratio, of the catalysts' loading: all of which can be optimised to give the best possible output from a given number of tubes.

The above considerations leads the designer to the dimensions of the tube and the proximity of the tubes to each other within a single row.

TYPE OF FURNACE

Secondly we must consider the basic type of furnace which is best suited to large steam reformers.

Furnaces are generally classified into two types:

- i Vertically fired multirow furnaces.
- ii Side fired furnaces.

Side Fired

The side-fired furnace relies upon the tube being bounded on two sides by a refractory wall. The heat is received by the tubes from the radiating refractory wall. This, in fact, limits a dimensional freedom when trying to increase the size of the furnace. As we have already discussed, the heated length of a tube is fixed at say 40'-50' and each tube must be bounded on two sides by a refractory wall : this leaves just one dimension for expansion.

Vertically Fired Furnaces

Conversely on an up-fired or down-fired furnace the heat to the tubes is supplied by the radiating products of combustion and not radiating refractory. This means that we can have more than one row of tubes within the furnace box. This then allows for two dimensions of freedom. (See Figure III).

Single cell multi-row steam reformer furnaces have been operating for many years. In fact the majority of reformers outside the United States are of this type. The choice between up and down firing of the multi-row furnace generally breaks in favour of down firing when the size of the furnace and its convection section is large enough to require an induced draught fan to ensure good operation. This breakpoint is generally a furnace containing about 10 tubes.

The fundamental difference between a side-fired and vertically fired furnace is that the former requires refractory wall to effect heat supply to the tubes whilst the latter relies upon radiant heat transfer from the combustion gases. Thus multirow vertically fired furnaces are constructed without inter-row refractory walls.

Side Fired or Top Fired Furnaces for very large Steam Reformers

The maximum number of tubes than can be satisfactorily contained within a single cell side-fired furnace is approximately 150. This means about 13 radiant boxes would be required to produce 5,000 TPD of methanol and 65 boxes to produce 25,000 TPD.

The largest multi-row furnace now operating contains 600 tubes* which reduces the radiant box requirements to 4 and 16 for the 5,000 TPD and 25,000 TPD plants respectively.

Furnaces of the multi-row type containing 2,000 tubes will reduce the radiant box requirement to only 1 and 5 respectively.

*This 600 tube furnace was designed on the Modular concept (detailed description to follow) such that by repeating proven modules any number of tubes can be accommodated.

Summary of Number of Radiant boxes required by the different furnaces.

Number of Radiant Boxes.			
Output (Methanol)	Side Fired. 150 tubes per radiant box	Top Fired. 600 tubes per radiant box	Top Fired. 2,000 tubes per radiant box
5,000 TPD	13	4	1
25,000 TPD	65	16	5

This table shows the magnitude of the variance in designs when applied to very large reformed gas requirements.

The economic and operational advantages of selecting a low number of radiant boxes are considerable. Each radiant box will have its own piping, valving, instrumentation, burners and flue gas exhaust fan and all will require attention from plant operators.

MODULAR FURNACE

A radiant box containing approximately 2,000 tubes is the economic design for the proposed 5,000 TPD methanol plant, we now describe the Davy Powergas Modular Steam Reformer. The "MODULAR" concept that allows for an almost limitless expansion of the reformers.

This design has been developed over many years and is based upon the experience gained by our company in supplying over 170 steam reformers.

PRIMARY REFORMER (RADIANT SECTION)

General (See Figure IV)

The modular reformer is basically a box shaped refractory lined chamber, encasing the tubes.

The reformer tubes are supported vertically in straight rows and are connected to the feed stock header and reformed gas header systems by means of small bore tubes called pig tails. These pig tails protrude from the top and bottom of the furnace respectively.

The feedstock and steam flow downwards inside the catalyst filled reformer tubes. The heat for reaction is supplied by the products of combustion passing co-currently down the furnace outside the tubes.

The flue gases from the furnace flow into flue gas coffins or chambers of firebrick construction which run the entire width of the furnace. These are situated between the rows of tubes. The openings or ports in these coffins offer a resistance to flow which ensures even distribution of the flue gases within the furnace box.

The flue gas coffins empty into a refractory lined collecting duct which is located along the entire length of the furnace. This duct transfers the flue gases to the Convection section. See Figure IV.

MODULAR CONCEPT

The MODULAR concept entails the detailed design of a standard module or section of the steam reformer which is repeated until the reformer is of the required size. The module consists of 2 rows of reforming tubes and their associated burners. It can contain up to 74 tubes and is designed such that it may be repeated with respect to process, mechanical, and structural considerations. It is the prime requirement of the concept that extrapolation of the basic design is eliminated.

Reformer Tube

The reformer tubes packed with catalyst are simply guided and part supported on steel work below the furnace hearth plate.

The tubes are generally centrifugally cast 25% Cr - 20% Ni - 0.4% Carbon alloy steel. 24% Cr - 24% Ni - 1.5% Niobium steel which has a higher stress value may be used in place of the above material but the economics must be calculated on a case by case basis.

Burners

The burners are arranged in rows on each side of the tube lines and are fired vertically downwards. The burners can be designed to fire either liquid, or gaseous fuels or combinations of both. Normally forced draught combustion air (either ambient or heated) is used. With gaseous fuels the burners can be designed to be self inspirating.

Inlet and Outlet Header System

The inlet and outlet header systems consist of a number of subheaders arranged symmetrically about the furnace and these headers are connected to the tubes by inlet and outlet pigtailed.

Each inlet header is connected to one row of tubes by small bore pipes called pig tails. These pigtails are designed to absorb, the horizontal expansion of the headers, the vertical expansion of reformer tubes and self expansion. These small bore pipes also assist even feedstock distribution to all reformer tubes by having a significant pressure drop through them.

Each outlet header is connected to two rows of tubes by small bore tubes called outlet pigtails made from 32% Ni - 20% Cr (Alloy 800). These pigtails are designed to accommodate both vertical and horizontal expansions of outlet headers and self expansion of the pigtail.

The reactants outlet sub-headers are fabricated from 32% Ni - 20% Cr material. Each subheader has a central tee connection and transition piece to the refractory lined main which transfers the product to the next process unit downstream of the reformer.

CONVECTION SECTIONS FOR LARGE REFORMERS

With increasing capacities of reforming furnaces the convection section duties have increased proportionately. The steam generation on a 5,000 Te/day Methanol plant can be as much as 1,500,000 lb/hour.

During the last decade, maximum steam pressures on reforming plants have increased from 400 to 1500 psig. Due to the above factors, convection sections have changed and are now in design similar to conventional type of power station boiler plant.

Convection sections must be "purpose" designed to meet the individual mechanical requirements and operational flexibility of the individual plant.

In determining the performances of convection sections the following factors must be considered.

i Thermal Design

Correct thermal design is most important, operational problems are encountered with oversurfacing while undersurfacing means a lack of performance.

ii Cavity Radiation

Cavity Radiation emitted by the furnace refractory and the flue gases coming from the radiant box are directed at the first heat transfer unit in the convection section. This radiation is dependant upon the flue gas temperature and the volume of the cavity upstream of the first unit, but is independent of the output of the plant. It is then necessary to safeguard convection units with varying operating duties from this constant source of cavity radiation.

If the first unit in the convection section was a process steam superheater, this unit would have a varying heat load dependant upon the process requirement. When the plant is operating at reduced loads or a plant start-up it would be subjected to the full radiation causing high metal temperatures. This results in the choice of higher alloy for the fabrication of the unit which increases the cost and may introduce metallurgical problems not experienced with the lower temperatures and alloys.

Radiant Shield Water Tube Boilers are therefore installed to absorb cavity radiation, and their purpose is:

- a To absorb high radiant loads providing the flexibility to include auxiliary firing within the furnace collecting duct. This is sometimes necessary for steam raising and/or process control.
- b Protection of downstream units.

iii Flue Gas Distribution

Natural draught furnaces have known problems of gas distribution in furnace "bridging" sections due to relative low gas velocities. With the MODULAR furnaces induced draught is provided, giving higher gas velocities which offer ideal gas distribution and the elimination of unbalanced gas temperature streams.

iv Induced Draught

Higher rates of heat transfer are achieved with an induced draught system offering more compact designs. Convection sections need not conform to the radiant box dimensions, and can be designed to suit the individual plant requirements.

In the Modular furnace waste gases are collected in a separate duct, elsewhere and the convection section is independent of main point.

v Compact Tube Banks

Economic use of tube configurations and pressure drop evens out irregular flow patterns or irregular firing of auxiliary burners in modular furnace collecting duct.

This is a particular problem area in side-fired furnaces. Normally their design constraints result in the supply of units that are both long and narrow, and have large bore heat transfer tubing which can give maldistribution of flue gases and uneven metal temperatures.

vi Circulation

Boiler Water circulation is a most important factor. Usually failures of boiler systems can be attributed in one form or other to circulation problems eg:

- a Pump failure in forced circulation systems.
- b Dry-out caused by water loss.
- c Interference with circulation by extraneous matter.
- d Water chemistry causing build up of deposits, or corrosion in high flux zones with subsequent failures.

Circulation can be either Natural or Forced.

Natural Circulation Systems are preferred as they do not require any "prime movers", circulation is maintained by the "thermodynamics" of the system. Higher circulation rates exist with Natural Circulation Systems than with Forced circulation Systems.

With modular designed furnaces, the natural circulation systems is always offered.

vii Materials

Careful selection of materials to cater for all conditions of operation and start up duties. As stated in this text the design of the Modular furnaces convection section assist in reducing the severity of the various operating conditions and makes for safer designed units.

viii Steam Drums

Steam drums must be adequately sized, not only to provide steam of high quality demanded by modern chemical plant, but, also to provide a sufficient reserve of water "hold up" to maintain circulation to "radiant" steam generators during emergency conditions.

ix Air Preheat

Combustion air preheaters improve the overall efficiency of the units, and these are becoming increasingly important as fuel prices continue to rise. For large reforming furnaces, rotary regenerative airheaters are economically more attractive than the conventional shell and tube types.

x Flexibility of Operation & Control

Controlled supplementary firing in furnace collecting ducts can be incorporated to produce additional steam which may be required to obtain the optimum steam/power balance.

The control of steam superheat is by adjustments of firing rates and/or the use of spray water attemperators at an intermediate stage in the steam superheater.

The facility for bypassing flue gases around heat transfer units is incorporated in the design.

Further supplementary firing at intermediate points in recovery duct is a further method of control which is sometimes incorporated.

Manufacture

Where possible, units should be designed to minimise field erection. During shop manufacture more stringent control can be applied to material identification, workmanship, inspection and non-destructive testing. Field erection costs are usually more expensive than "shop" charges.

STRUCTURAL DESIGN OF LARGE STEAM REFORMING FURNACES

Radiant Section

The structure forming the radiant section of the Modular Reforming Furnace can be considered in three separate parts :-

- 1 Top Housing - supporting and providing weather protection to the process pipework the burners and to the suspended refractory brickwork.
- 2 Casing - supporting the refractory brickwork, burners and reforming tubes, and providing weather protection to the brickwork forming the walls.
- 3 Sub-frame - supporting the casing and providing a rigid "table" over which the casing is free to thermally expand. This thermal expansion takes place radially from an anchor point and movement is guided on the rectangular axes of the furnace.

All the design methods and fabrication techniques used for the structural steelwork of the radiant section are as specified in standard structural codes.

In accordance with the modular concept the major part of the structural steelwork of the radiant section is formed by assembling a series of standard designed and shop fabricated units. Included in this category are all hearth frames, side and end casing panels, intermediate columns, beams supporting the suspended refractory roof and the top housing members. By using standardised units, fabrication time and erection periods are minimised and the possibility of fabrication errors reduced.

The maximum size of the radiant section is not governed by steelwork design, considerations. The modular concept has eliminated almost all the structural design problems which are encountered in designing large conventional furnaces.

Convection Section

The structural steelwork of the convection section duct is of similar construction to that of the radiant section although it is purpose designed. Prefabrication is maximised to reduce the erection period.

When designing the structural steelwork arrangement for the duct, consideration is given to the initial installation of boiler and superheater units; also to their removal and replacement should there be a failure during operation.

Sections of steelwork are provided which can be easily removed, normally complete with the refractory insulation.

As with the radiant section, thermal expansion of the steelwork of the duct is catered for by the provision of expansion joints at strategic places and PTFE sliding bearings in the case of a horizontal duct. Spring suspension systems are installed where the convection section is a vertical duct.

Conclusion

The energy shortage in certain areas of the world is leading the suppliers to investigate various methods of transporting the readily available natural gas from areas such as the Middle East to these areas in need of energy.

One method that is gaining interest and support is to produce and transport "fuel quality methanol".

Economic studies indicate that 5,000 TPD methanol plants are the optimum size. The critical item in these plants is the steam reformer and this paper discusses the various types of reformer available. Side fired furnaces are considered unsatisfactory for this duty due to their basic design precluding this type of furnace from increasing in physical size.

The vertically fired modular type furnace as developed by Davy Powergas, has the design capability to increase in size. The worlds largest furnace is designed to this concept, and from the design, erection and operating experience gained from this furnace we describe a steam reformer satisfactory in all aspects to meet the new requirements in the production of fuel quality methanol.

STEAM REFORMING SECTION

ASSOCIATED EQUIPMENT

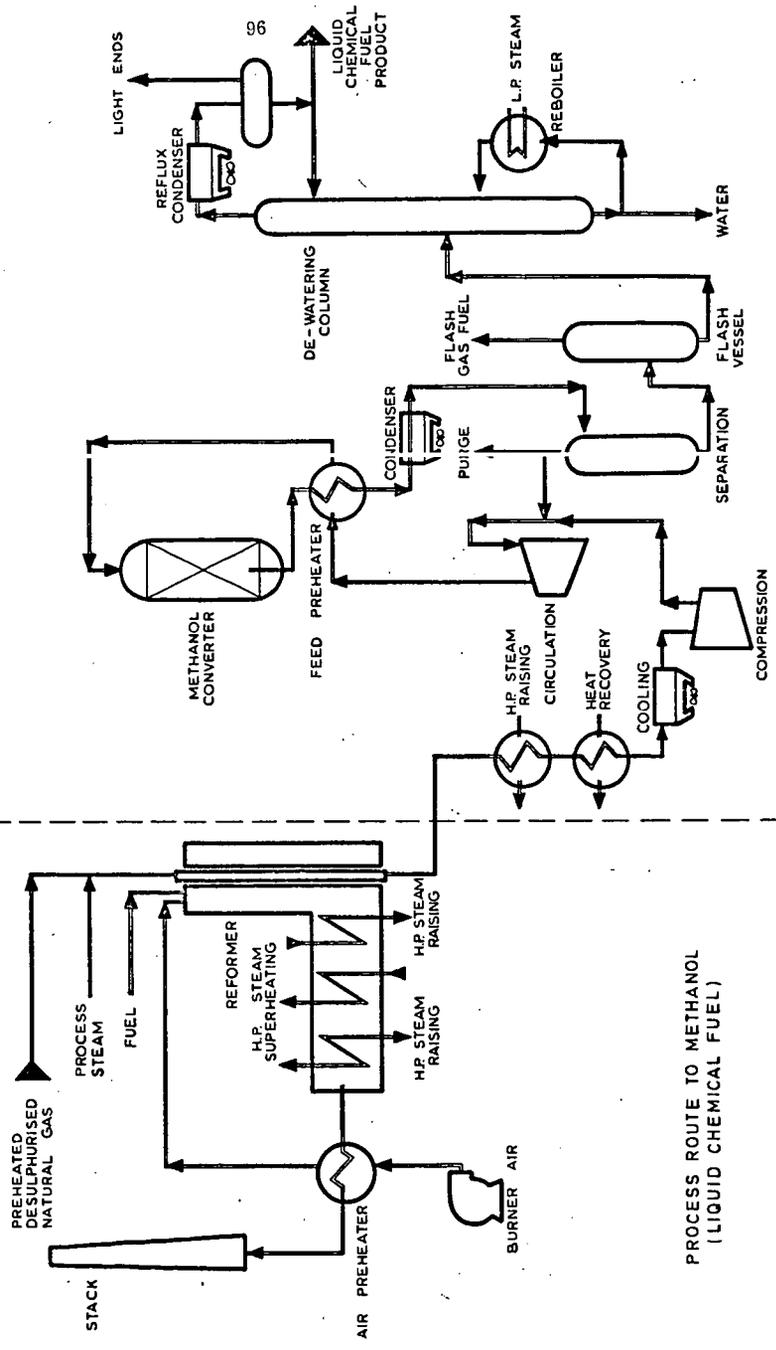


Figure I

PLOT SHOWING NUMBER OF TUBES
VERSUS THE YEAR OF DESIGN

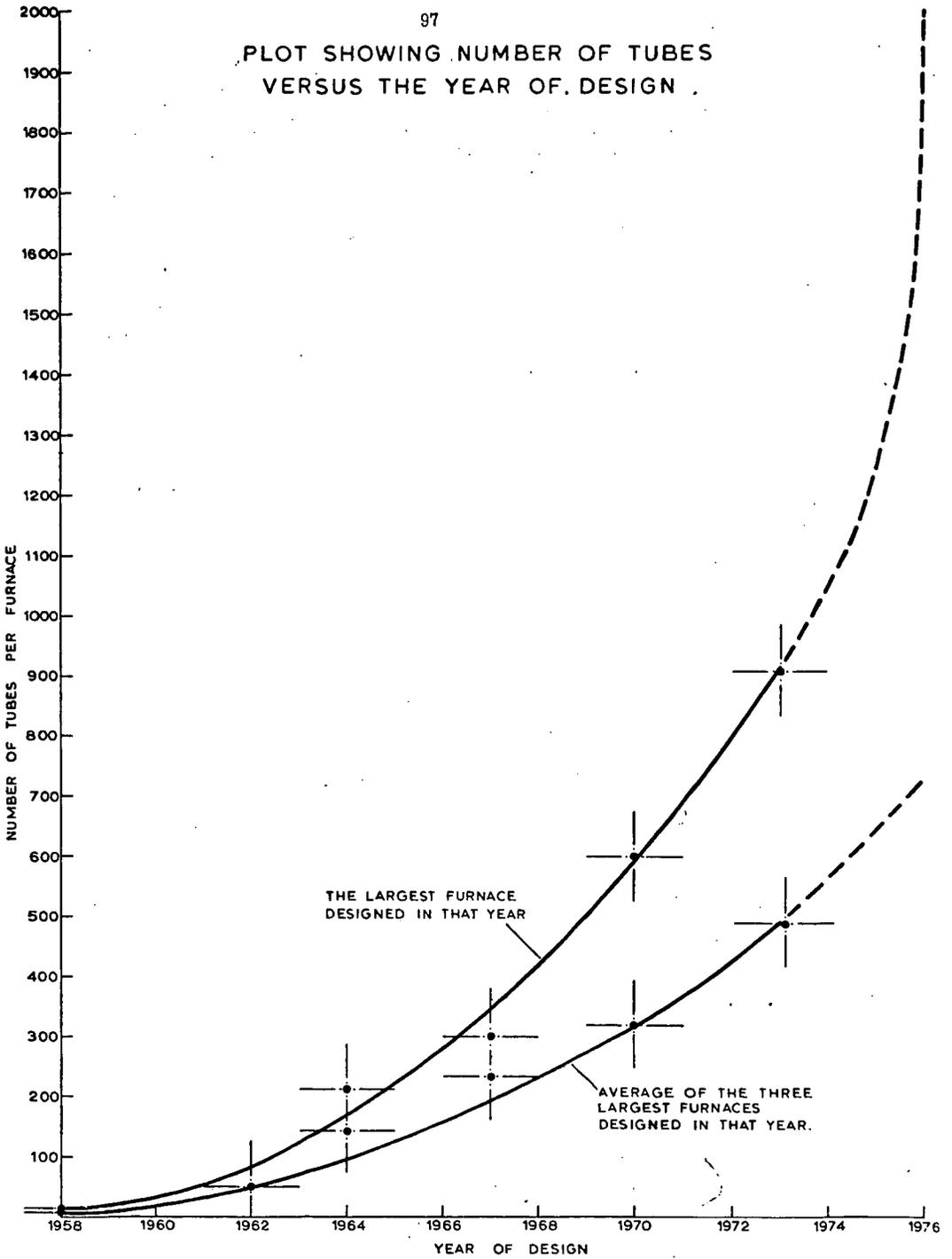
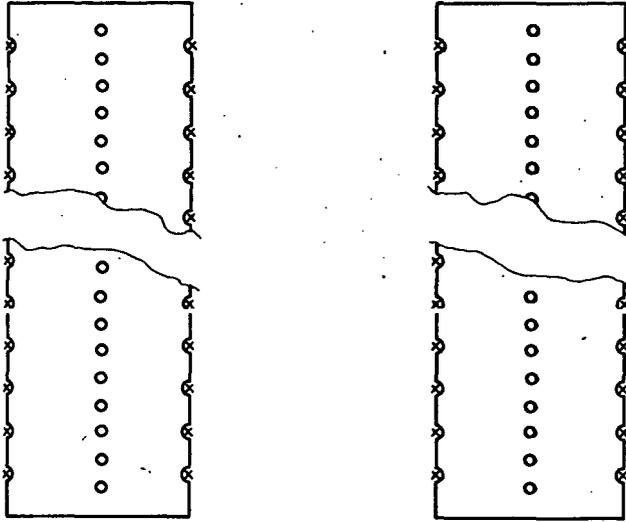
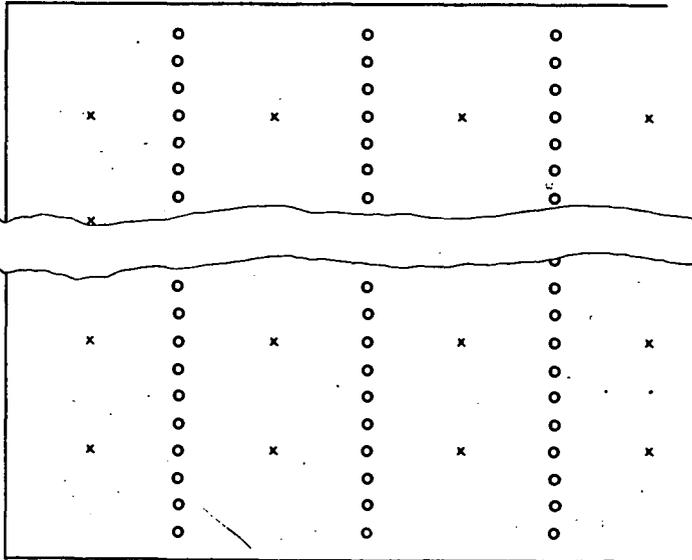


Figure II

PLAN VIEW OF SIDE FIRED FURNACES
 SHOWING NEED FOR 2 REFRACTORY SIDE WALLS
 FOR EACH ROW OF TUBES

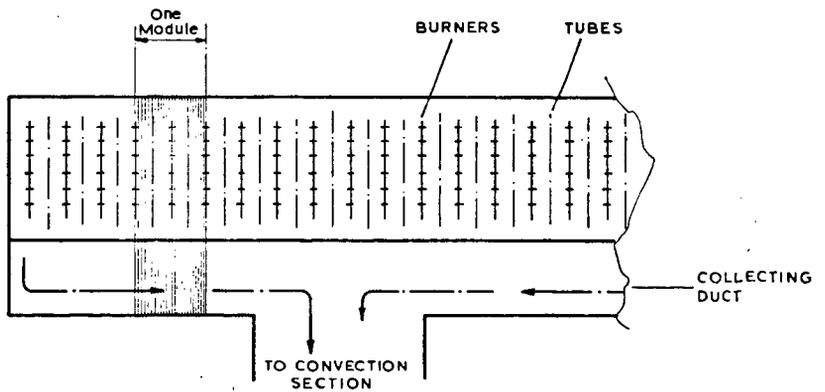
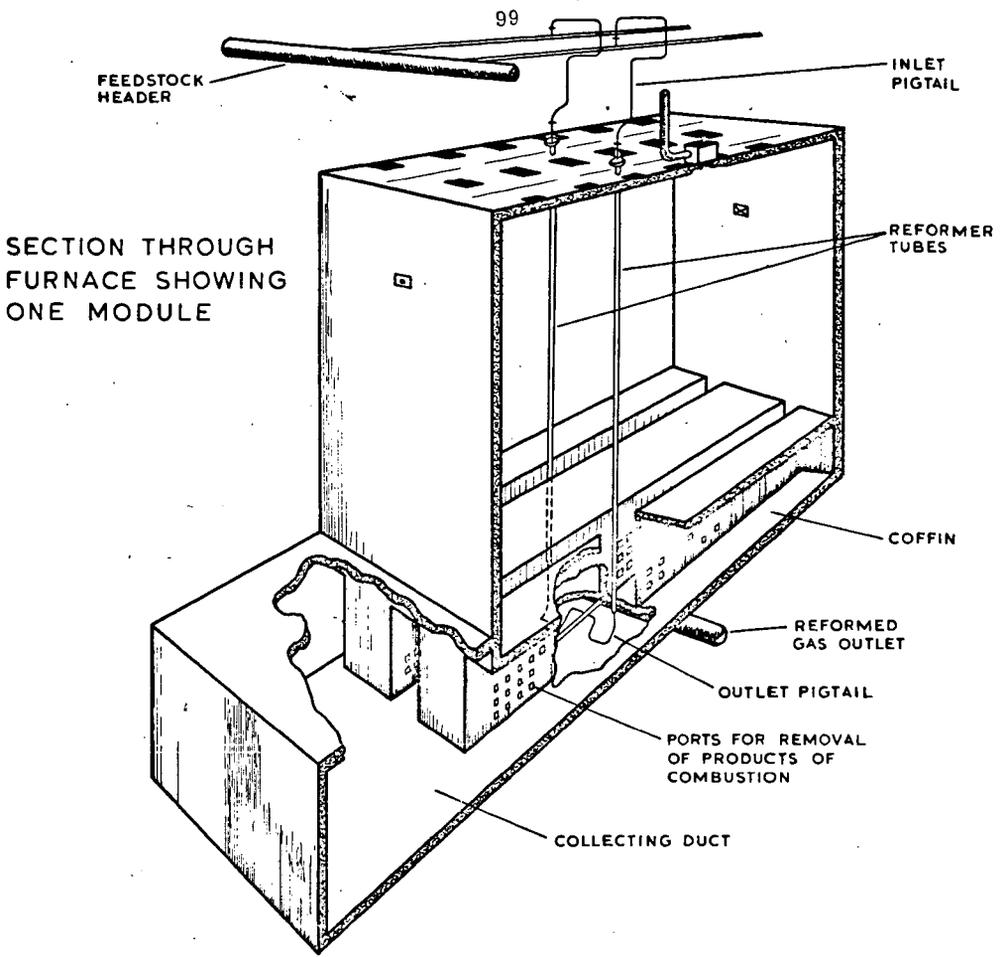


X BURNERS
 O REFORMER TUBES



PLAN VIEW OF A VERTICALLY FIRED FURNACE
 INTERMEDIATE REFRACTORY WALLS BETWEEN TUBE ROWS
 ARE ABSENT FROM THE DESIGN

Figure III



PLAN VIEW

Figure IV

CLEAN FUELS FROM COAL - AN ALTERNATIVE TO SNG

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Alliance Research Center
Alliance, OhioINTRODUCTION

A major portion of current coal gasification research is directed toward processes for production of substitute natural gas (SNG). These processes rely typically on relatively low temperature, high pressure gasification to enhance methane yield in the gasifier, followed by extensive water gas shifting and acid gas removal, and finally a catalytic methanation step. Those portions of the SNG processes most critical to their success—high pressure gasification and methanation—are farthest from being proven technology.

The Methyl Fuel process, however, produces a clean liquid fuel, primarily methanol, from synthesis gas produced at medium pressures bypassing the problems of high pressure gasification. The process, shown schematically in Figure 1, is composed of operations each of which has been proven in commercial applications.

PROCESS DESCRIPTION

Synthesis begins with steam/oxygen gasification at 22 atm. or below and at temperatures well above 1500K (2240F). These conditions insure rapid reaction rates and high carbon utilization, with minimal problems in coal handling and feed. Steam gasification is accomplished in the upper chamber of a two-stage suspension gasifier, with heat being provided by combustion with oxygen of ungasified char recycled to the lower chamber. The resulting synthesis gas is virtually methane-free, consisting principally of hydrogen, steam and carbon oxides. Gasifiers of this type have been available commercially for many years. One example is the Belle, W. Va., gasifier built by B&W for duPont in the early 1950's.

Particulate removal is achieved by a cyclone system, which recycles the bulk of the unburned char back to the combustion zone of the gasifier, followed by a venturi-water scrub system which also cools the "make" gas.

Gaseous sulfur compounds are removed by a conventional hot carbonate scrubbing system, which also removes a portion of the CO_2 produced in the gasifier. Elemental sulfur is recovered as a salable byproduct in a conventional Claus plant. The sweetened synthesis gas is then reacted catalytically with steam in a water gas shift reactor to adjust the relative concentrations of hydrogen and carbon monoxide for Methyl Fuel synthesis. Shift requirements are about two-thirds of those needed for methanation.

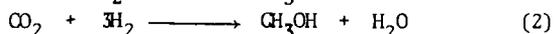
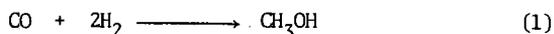
A second hot carbonate scrubber removes most of the remaining CO_2 , which is vented to the atmosphere. Hot carbonate systems were chosen here because of their well-known commercial acceptance and economy for removal of large quantities of acid gas, although other systems, such as the Rectisol system could also be used. In the latter case, methane absorption would be no problem in the Methyl Fuel process.

The sweet synthesis gas is then dewatered and compressed for alcohol synthesis, the degree of compression depending on the synthesis process used. In this study, we have chosen the Vulcan-Cincinnati, Inc. high pressure process partly because of the rugged nature and regenerability of its zinc-based catalyst.

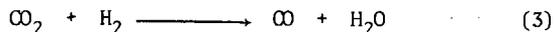
Composition of the gas at this point is hydrogen and carbon monoxide in about a two-to-one ratio, with small amounts of CO_2 , water, nitrogen, and methane. The carbon oxides react with hydrogen over a catalyst to form methanol and small amounts of higher alcohols and water. A condenser removes liquid products, which pass to a small refinery operation for purification. The finished product, trademarked Methyl Fuel, is a clean, sulfur and nitrogen-free liquid fuel suitable as a blending agent for gasoline and a substitute for light fuel oils. The fuel has a gross heating value just over 5500 kcal/kg (10,000 Btu/lb), and burns cleaner than natural gas.

A preliminary process study has shown that for suspension gasification without char recycle, where carbon losses are about 12 percent, we can expect an overall thermal efficiency of about 63.5 percent for the process. These figures are based on actual performance of the B&W Morgantown gasifier built for the Bureau of Mines in the early 1950's⁽¹⁾.

The above thermal efficiency seems low compared to efficiencies of 65-70 percent now being reported for competitive SNG processes, suggesting that some means may be available for improving process efficiency. Because of the nature of the high temperature gasification process, only a small number of products (CO, CO₂, H₂ and H₂O) are formed in significant quantities in the gasifier; and these are related through a mass balance and shift equilibrium. Thus a very simple expression can be derived to show the effects of certain gasification variables on Methyl Fuel production and thermal efficiency. Methyl alcohol is formed through the reactions:



which are related through the water gas shift reaction,



A simple molar balance based on these reactions shows that the maximum production of methyl alcohol is directly proportional to the moles of carbon monoxide and hydrogen formed in the gasifier, assuming that a shift converter is available to optimize the relative concentrations of CO and hydrogen, and that reactions (1) and (2) go to completion:

$$[\text{CH}_3\text{OH}] = 1/3 ([\text{CO}] + [\text{H}_2]) \quad (4)$$

If gasification is complete and methane and tar formation are negligible,

$$[\text{CO}] = [\text{C}]_f - [\text{CO}_2] \quad (5)$$

$$[\text{H}_2] = [\text{H}_2]_f - [\text{H}_2\text{O}] \quad (6)$$

$$[\text{O}_2]_f = [\text{CO}_2] + 1/2 [\text{CO}] + 1/2 [\text{H}_2\text{O}] \quad (7)$$

where $[C]_f$, $[H_2]_f$ and $[O_2]_f$ are the moles of carbon, hydrogen and oxygen fed to the gasifier, excluding char recycle since it is already included in the coal feed, but including hydrogen and oxygen in the coal and steam feeds; and $[CO]$, $[CO_2]$, $[H_2]$ and $[H_2O]$ are the moles of carbon oxides, hydrogen, and steam in the synthesis gas leaving the cyclone separators. Substituting and rearranging,

$$[CO] + [H_2] = 2([CO]_f - [O_2]_f) + [H_2]_f \quad (8)$$

From equation (4), then, recognizing that neither carbon gasification nor methyl alcohol formation may go to completion, and that side reactions occur

$$[CH_3OH] = n_M \frac{2(n_G [C]_f - [O_2]_f) + [H_2]_f}{3} \quad (9)$$

where $[CH_3OH]$ is the maximum number of moles of methyl alcohol produced, n_M and n_G represent the conversion efficiencies of methyl alcohol synthesis and gasification, respectively. Then $n_G [C]_f$ represents the number of moles of carbon leaving the gasifier as gaseous carbon oxides. For the purpose of this paper, we will assume complete conversion in the Methyl Fuel synthesis loop.

EFFECT OF CHAR RECYCLE

Using Equation (9), one can determine the effects of char recycle, CO_2 recycle, and steam addition on overall product yield and thermal efficiency. The B&W Morgantown gasifier may be used as a reference, producing 2.641 kmoles of Methyl Fuel for each 100 kg of West Virginia coal. Addition of char recycle raised the carbon utilization efficiency to 95 percent, the production of Methyl Fuel to 2.894 kmoles, and the overall thermal efficiency to 69.3 percent.

EFFECT OF CO_2 SUBSTITUTION

Substitution of CO_2 for oxygen represents one method for reducing oxygen costs. Off-gas from the hot carbonate scrubbers could be compressed and

recycled back to the gasifier to take advantage of the Boudouard reaction:



Treating CO_2 as totally gasified carbon and oxygen, equation (9) shows that, with char recycle, a 10 percent molar substitution of CO_2 for oxygen increases the methanol yield to 3.048 moles/100 kg of coal, and the thermal efficiency of the synthesis process to 73.4 percent.

In actual practice, this efficiency would not be achieved since the Boudouard reaction places a heat penalty on the gasifier reducing the amount of process steam available for the remainder of the process. If this heat penalty is made up by combustion of coal in an auxiliary boiler, the overall process thermal efficiency is reduced to 70.6 percent as shown in Figure 2. Further substitution of CO_2 continues to improve the thermal efficiency of the process at the expense of gasification temperature until carbon utilization efficiency decreases, and methane and tars begin to form. At this point, equation (9) no longer holds, and gasification is not suitable for Methyl Fuel production.

EFFECT OF STEAM/OXYGEN RATIO

The effect of altering the steam/oxygen ratio may also be shown by equation (9). Steam substitution has the beneficial effect of increasing the hydrogen yield of the gasifier while decreasing the production of CO_2 . Again using char recycle, a 10 percent molar substitution of steam for oxygen also increases the methanol yield to 3.048 moles/100 kg coal, and the apparent thermal efficiency to 73.4 percent. The steam gasification reaction



is also endothermic and places a heat penalty on the system. This reaction is less endothermic than the Boudouard reaction, however, resulting in a practical thermal efficiency of 70.8 percent.

The thermal penalties produced by CO₂ recycle and steam substitution are shown in Figure 3, expressed as percent of process heat available compared to that of the Morgantown gasifier. The thermal advantage of steam substitution is quite evident, especially at higher steam/oxygen ratios.

EFFECTS ON GAS TREATMENT

If it is assumed that the feed to the Methyl Fuel synthesis loop is balanced— i.e., in a two-to-one ratio of hydrogen to equivalent CO— then all excess carbon will leave the system as CO₂ via the carbonate scrubbers. Equation (9) and a simple carbon balance

$$[\text{CO}_2]_{\text{scrubbed}} = n_G [\text{C}]_f - [\text{CH}_3\text{OH}] \quad (12)$$

will then show the effects of char recycle, CO₂ recycle and steam substitution on acid gas scrubbing load. Figure 4 illustrates these effects clearly, showing CO₂ absorber load as a percent of that required for the Morgantown gasifier case.

Raising carbon utilization efficiency to 95 percent by char recycle increases the ratio of CO to CO₂ in the gasifier and enhances the production of hydrogen. More usable carbon is produced, and the CO₂ absorber load drops to 91.7 percent of its original value. Since acid gas removal represents about 15 percent of the capital cost in a Methyl Fuel plant, and is one of the major users of process steam and electric power, the cost savings are significant.

CO₂ recycle has the effect of increasing the amount of CO₂ that must be absorbed. For every three moles of CO₂ recycled, one additional mole of CO₂ is absorbed. In a practical system, then, the cost of CO₂ compressors, added CO₂ absorber capacity, and additional process steam capacity would tend to offset any advantages due to an increase in overall process thermal efficiency.

Steam substitution has the reverse effect, reducing the amount of CO₂ discarded. For every three moles of steam substituted, two moles of CO₂ do not have to be absorbed. In addition to the capital cost savings, this route represents a more economical use of the process steam, since a typical hot carbonate stripper requires about three moles of steam for each mole of CO₂ absorbed. Operating with char recycle, a 10 percent steam substitution would reduce CO₂ absorber load by about 6 percent.

CONCLUSIONS

With few exceptions, today's SNG processes are years from commercialization or even demonstration. The Methyl-Fuel process, on the other hand, consists of components each of which has been demonstrated commercially, and thus could be readily commercialized. Overall process thermal efficiency is comparable to present SNG processes.

Because of the simplicity of the process and the gasification products produced, a simple expression relates gasifier feeds to Methyl Fuel output. This expression shows that char recycle, CO₂ recycle and steam substitution can all improve thermal efficiency, but all impose a heat penalty on the system. The combination of char recycle and steam substitution has been found most advantageous, since it maximizes thermal efficiency while minimizing the gasifier heat penalty and reducing capital costs and process steam requirements.

REFERENCES

1. P.R. Grossman and R.W. Curtis, "Pulverized-Coal-Fired Gasifier for Production of Carbon Monoxide and Hydrogen," Trans. ASME 76, pp. 689-95 (1954).

FIGURE 1

METHYL FUEL PROCESS FLOWSHEET

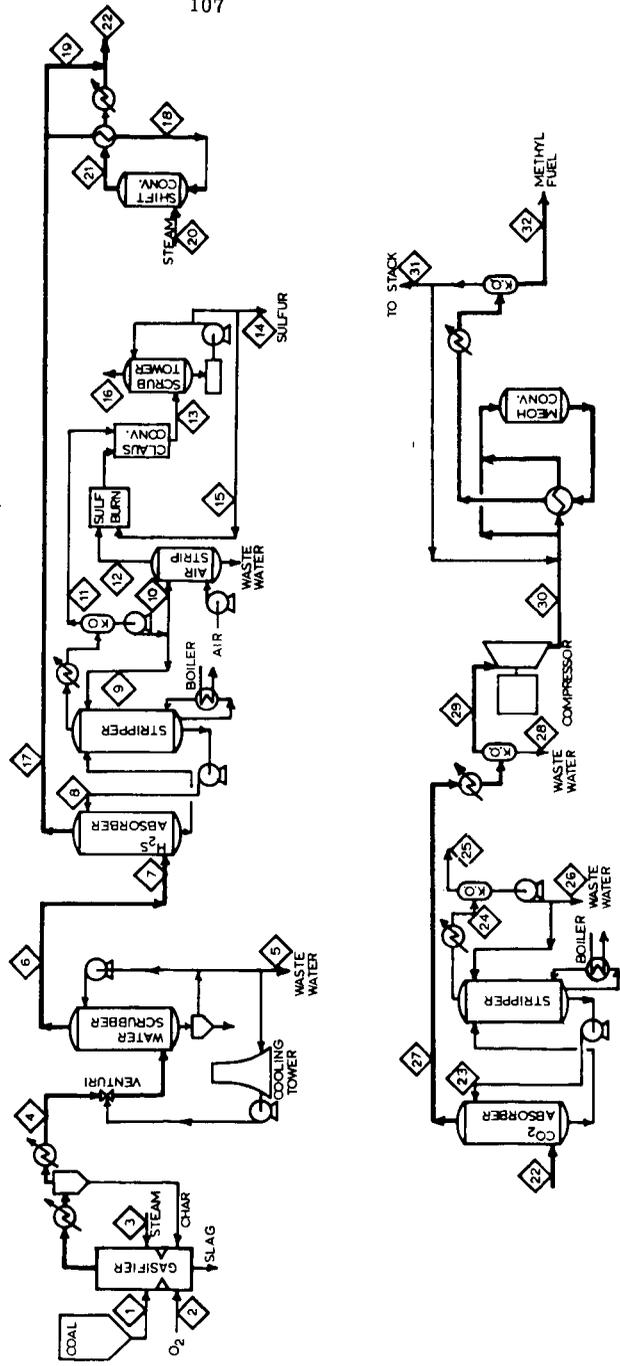


FIGURE 2

EFFECTS OF MODIFICATIONS IN
GASIFIER OPERATION-
THERMAL EFFICIENCY

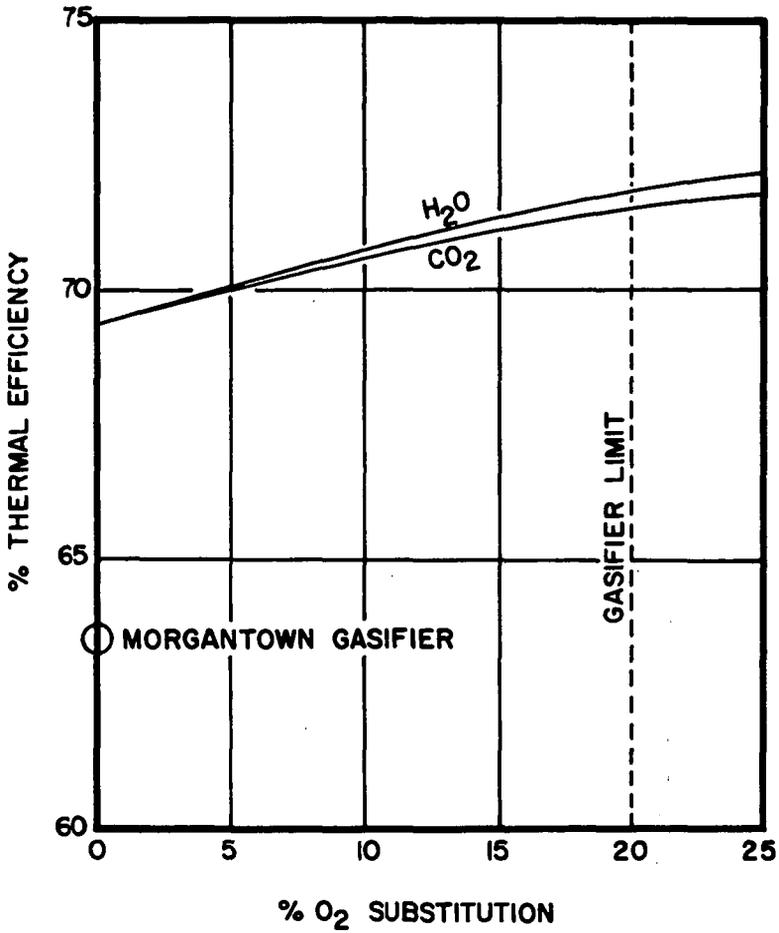


FIGURE 3
EFFECTS OF MODIFICATIONS IN
GASIFIER OPERATION -
ACID GAS REMOVAL

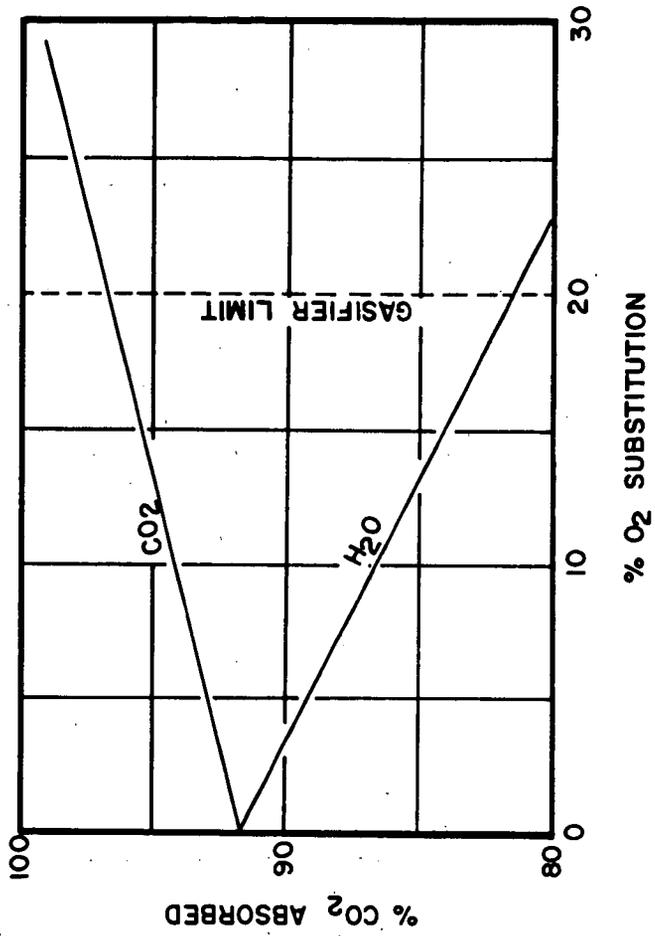
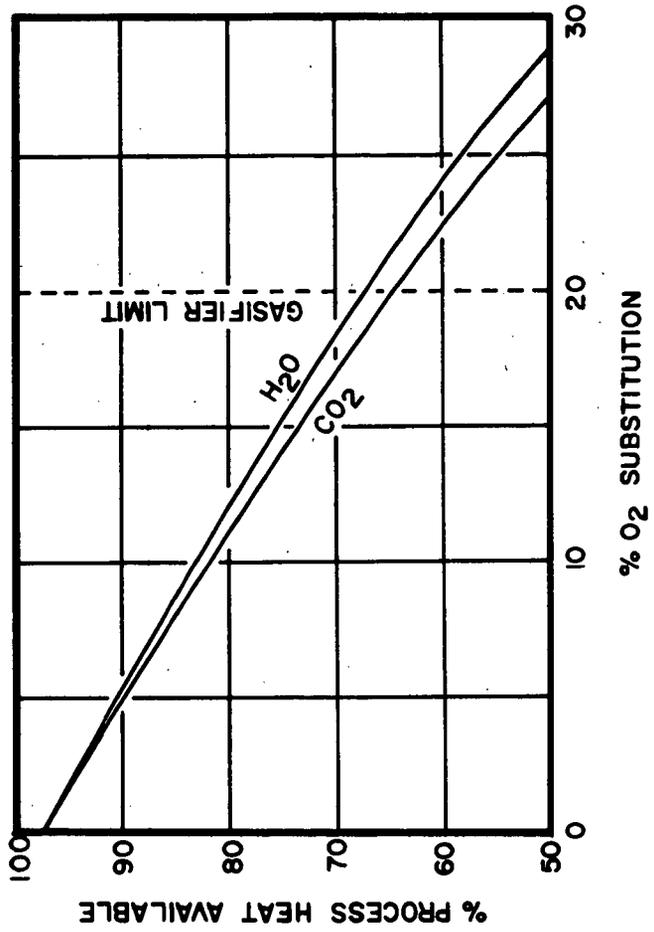


FIGURE 4
EFFECTS OF MODIFICATIONS IN
GASIFIER OPERATION -
STEAM GENERATION



Methyl-Fuel — A New Clean Source of Energy, David Garrett, T. O. Wentworth, Vulcan-Cincinnati, Inc., 1329 Arlington, Cincinnati, Ohio 45225

A new liquid fuel has been developed with all the advantages of natural gas or fuel oil, but which is actually less polluting than natural gas. This liquid fuel, designed for use in power plants, large industrial furnaces and boilers and for gas turbines, is a mixture of predominately methanol with controlled percentages of higher alcohols. The fuel has been named METHYL-FUEL, a trademark registered for Vulcan-Cincinnati, Inc. The METHYL-FUEL process produces liquid fuel with essentially zero sulfur, nitrogen and metals content, at costs competitive with very low sulfur fuel oils and with imported LNG on a "Btu delivered to burner" basis. Actual combustion tests showed NO_x emissions in flue gas are lower than that for natural gas. METHYL-FUEL may be regasified to methane if desired, at costs competitive with naphtha gasification. METHYL-FUEL may also be added to gasoline as an effective octane improver and gasoline extender replacing lead additives for this purpose. The technology for METHYL-FUEL production and regasification is reviewed and results from combustion tests are discussed.

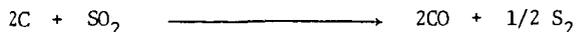
GASIFICATION OF CHAR WITH SULFUR DIOXIDE

N.J. Kertamus, M.A. Paisley, W.L. Sage

Babcock & Wilcox Research Center, Alliance, Ohio

1.0 INTRODUCTION

The preliminary experiments summarized here were aimed initially at determining optimum conditions for reducing sulfur dioxide to elemental sulfur with char. However, an important secondary objective followed when we found that carbon monoxide (CO) was the main oxidized product generated in the reduction. In other words, this second objective was focused on the possibility of defining a novel gasification system based on the reaction:



Finally, supporting experiments were made using Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) to better understand the gasification of char with SO_2 .

2.0 BACKGROUND

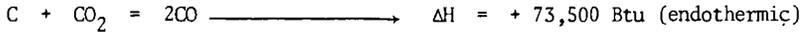
Because of current environmental considerations, many regenerative processes are being proposed to remove sulfur-containing products from the tail gases of coal burning systems. Some of these processes generate a concentrated SO_2 stream at some point. The SO_2 concentration may vary for the particular process; however, it is generally agreed that the most desirable end product is free sulfur. For example, one such process described in two previous papers,^(1,2) is the hot iron/iron oxide desulfurization concept developed by the Babcock and Wilcox Company. Briefly, in this concept, hydrogen sulfide (H_2S) is removed from a fuel gas generated by air-blown suspension gasification of coal. Two overall steps are involved in the desulfurization concept:



After all of the available iron oxide surface scale has reacted to form iron sulfide, regeneration or recovery of the iron oxide is necessary. In practice, this regeneration is accomplished by purging the iron sulfide scale with air to recover iron oxide and a regenerant gas that contains from 10 to 13 vol. percent SO_2 in nitrogen. The overall process concentrates sulfur from less than 1.0 vol. percent in the fuel gas to 10-13 vol. percent SO_2 in the regenerant gas.

In a coal burning process, one readily obtainable reductant is a hot char produced by partial combustion of the coal feed.

The major difference between present-day and earlier coal gasification to medium Btu gas ($CO + H_2$) is the direct use of oxygen in the gasification process. Today, oxygen is used to burn part of the carbon to supply the endothermic heat necessary to drive the gasification reactions. For example, considering coal to be carbon at 1300F, the following reactions occur during oxygen or air gasification:



The sum, $2C + O_2 = 2CO$, $\Delta H = -96,400$ Btu (exothermic), represents overall gasification with oxygen to yield carbon monoxide and recoverable heat.

Depending on the type of gasifier, the upper temperature level during gasification is of prime concern from the standpoint of reaction rates or kinetics. For example, in air-blown entrainment gasification, the short residence time in the high-temperature zone determines gas quality and the fraction of coal gasified.⁽³⁾ In other words, any variable that reduces temperature, such as a heat loss or the presence of steam, detracts from gas quality. Using oxygen instead of air, however, generates such extreme temperatures that some steam addition is necessary to moderate gasification temperature. With steam addition, a second heat consuming reaction occurs, $C + H_2O + CO + H_2$, $\Delta H = +58,500$ Btu (endothermic).

The disadvantage of oxygen-blown gasification relates to the necessity and expense of providing an associated oxygen plant. However, using air as the oxygen source dilutes the gas produced with nitrogen to reduce its heating value to the range of 100 Btu/Scf as opposed to a theoretical 320 Btu/Scf for pure oxygen gasification. Moreover, nitrogen cannot be economically removed from the produced gas.

3.0 POSSIBLE CONCEPT

A second possible route for producing non-nitrogen diluted CO involves the use of SO_2 as the gasification agent. Sulfur dioxide can be separated from N_2 . The following steps might constitute a possible concept for accomplishing this process:

- (1) Sulfur is burned in air to produce a gas containing 19-21% SO_2 .
- (2) Using an acid gas scrubbing system, SO_2 is separated from the inert nitrogen diluent and fed, together with hot char, to a gasifier.
- (3) Undiluted SO_2 reacts with hot char to yield CO and elemental sulfur, $2C + SO_2 \longrightarrow 2CO + 1/2 S_2$.
- (4) Product gases from the gasifier are quenched to separate sulfur from the product CO.

4.0 MAJOR CONCERN

From the standpoint of the basic chemistry involved, the area of greatest concern centers around the calculated endothermic gasification of carbon with SO_2 . For example, the reaction $2C + SO_2 = 2CO + 1/2 S_2$ at 2200F is endothermic to the extent of 880 Btu/lb of SO_2 reduced (50,400 Btu/mole). This calculation is based on the reaction of carbon in the standard state. The carbon in char may, of course, yield slightly different thermodynamics than carbon in the standard state; however, char may contain other constituents like ash that react with SO_2 . These reactions may provide additional heat.

In considering char gasification with SO_2 , one logical question to be addressed is "What differences exist between SO_2 and CO_2 ?" On the surface, CO_2 gasification of carbon is more endothermic to the extent of 1600 Btu/lb of CO_2 reduced (70,400 Btu/mole). Other differences, as we shall see, center around the kinetics or reaction rates involved.

5.0 EQUIPMENT AND PROCEDURE

Basically, two test rigs were used. For the initial tests, a small (1-inch I.D.) externally heated mullite tube served as the reactor sketched in Figure 1. The feed gases (N₂ + SO₂) were metered and fed to a preheating section where the gas temperature was increased to about 900F. The hot char temperature was in the range of 1600 to 2000F where reaction occurred. As the products exited the reactor, quenching was accomplished by a device designed to condense sulfur by contact with water in a container filled with glass beads. Product gases were analyzed by gas chromatography.

Later tests were made in a 5-inch diameter tube using a fluidized bed of char. This reactor (sketched in Figure 2) consisted of a 36-inch long silicon carbide tube heated by an outer annular furnace firing natural gas. Bed temperatures of 2200F were easily attained in this furnace. Product gas samples were drawn through a water-cooled stainless-steel probe to quench temperature. As before, gases were analyzed by gas chromatography.

Thermal analysis (DTA and TGA) was performed on an instrument manufactured by Tracor. Kinetic measurements of the carbon, SO₂, and CO₂ reaction were made at constant temperature with a modified Tracor TGA balance. For the kinetic measurements, a 15 mg sample of graphite was placed in an inert gas while the system was heated to reactant temperature. At the desired temperature, SO₂ or CO₂ was substituted for the inert gas and the weight loss was monitored.

6.0 CARBON SOURCES

Carbon sources were as follows:

- (1) Metallurgical coke (-16 + 30 mesh) with the following analysis:

<u>Proximate Analysis, % of wt.</u>	<u>Ultimate Analysis (Dry), % of wt.</u>
Volatile Matter 0.5	C - 90.8
Fixed Carbon 92.0	H - 0.2
Ash 7.5	S - 0.7
	N - 0.8
	Ash - 7.5

- (2) Coal char from FMC
 (3) Pulverized graphite.

7.0 RESULTS

For discussion, the experimental results are broken down into three areas; each area represents a different approach at understanding the gasification step.

1. Bench scale test reactors
2. Differential Thermal Analysis (DTA)
3. Kinetic measurements

7.1 BENCH SCALE TEST REACTOR

Our bench scale test reactors ranged from a small fixed bed to a larger fluidized bed. In the fluidized bed reactor, provision was also made for air addition. The reason of course, for the scale up was to answer questions unanswered by the small reactor.

7.1.1 Fixed Bed Tests

Table 1 illustrates initial test results obtained with the 1-inch I.D. fixed bed reactor. The first two tests illustrated were made with 13 vol. percent SO_2 in nitrogen or a simulated regenerate gas from our hot Fe/FeO_x desulfurization process to determine whether SO_2 could be reduced with hot carbon. The results with both the simulated regenerant gas and pure SO_2 clearly illustrate that carbon was an excellent reductant at temperatures around 2200F and space velocities from 700 to 800. No SO_2 survived the reduction.

The second tests also showed that a significant amount of CO was formed. Unfortunately in the tests with pure SO_2 , a significant amount of COS was produced. We felt that COS probably was formed from the gas phase reaction $\text{CO} + 1/2 \text{S}_2 \rightarrow \text{COS}$ as the gases slowly cooled while exiting the reactor. In other words, it was not possible to reduce temperature rapidly from 2200F in the small reactor.

7.1.2 Fluidized Bed Test

To quench the product gases rapidly, we switched to the water-cooled sample probe and the 5-inch diameter fluidized bed reactor. The objective, of course, was to reduce the time CO and S_2 were in contact with each other at temperatures from 1800F down to the condensation point of sulfur.

Results from the fluidized bed tests with coke were tabulated in Table 2. No SO_2 survived the reduction; all of the SO_2 fed to the char bed was reduced to elemental sulfur or COS. In comparison to the previous tests, quick quenching the product gases reduced the COS level. With simulated regenerant gas (13 vol. percent SO_2) only a trace of COS survived; however, with pure SO_2 the COS level was still quite high or at least 7 vol. percent.

7.1.3 Air Addition

Since the reduction was calculated to be endothermic, several experiments were made to see how much we could back off the external heat and still maintain the SO_2 - char gasification. This was done by decreasing the heat (natural gas) input to the outer annular furnace. Two other changes were made; i.e.,

- (1) Some air was added to the SO_2 but not enough to compensate for the calculated heat uptake of the reaction.
- (2) The bed consisted of coal char instead of metallurgical coke.

Results from part of the tests are found in Table 3. The SO_2 -to-air ratio varied from 2 to 10 vol. SO_2 per vol. of air. Although the tests were not designated to give quantitative information, we were surprised to find that once the reduction started, it maintained itself without the addition of external heat. In other words, the char - SO_2 gasification approached a heat balanced reaction with some air addition.

7.2 DIFFERENTIAL THERMAL ANALYSIS (DTA)

To better define the relative heat uptake of the char/coke reaction with SO_2 and CO_2 , differential thermograms were obtained using the two reactant gases with pulverized metallurgical coke. We found that, because of the highly endothermic fusion of the ash constituents in the coke at 1800 to 2000F, it was necessary to preheat the coke sample blanketed with inert nitrogen to reactant temperature (2350F). Once the preheated ash had been heated and cooled back to ambient temperature, a second heating cycle in inert gas did not reveal the endothermic fusion of the ash. After one cycle in nitrogen, SO_2 or CO_2 was substituted for the DTA measurements. Two typical curves obtained with CO_2 and SO_2 are illustrated in Figure 3. Negative peaks represented endothermic or heat consuming reactions.

Although the differential thermograms were not quantitative, the results (Figure 3) presented a comparative picture of coke gasification with SO_2 and CO_2 . The curves suggested that the CO_2 - coke reaction was far more endothermic at about 2000F where gasification occurs than was the corresponding reaction with SO_2 . In fact, the coke - SO_2 reaction was nearly heat balanced.

7.3 KINETIC MEASUREMENTS

The last series of measurements made involved a comparison of the kinetics, or the rate of weight loss versus time of pulverized graphite in SO_2 and CO_2 . For these measurements, graphite served as the source of carbon instead of metallurgical coke or coal char. The latter sources of carbon proved to be too reactive for accurate kinetic measurements.

For the weight loss-time measurements, a strip chart recorder was added to the basic X-Y recorder in the TGA apparatus to measure sample weight versus time. The weight loss was plotted as a function of time at constant temperature. Figure 4 illustrates a plot of the fractional weight loss versus time curve for graphite gasification with SO_2 at 2100F.

The simplified model used to interpret the weight loss-time curves assumes:

- that the heterogeneous graphite particle mix can be approximated by spheres with an average diameter, initially of r_0 , and at some time later as r . The fractional weight loss, fw , is given by

$$fw = 1 - \frac{r^3}{r_0^3}; \quad (1)$$

- that the reaction of carbon is first order with respect to available carbon atoms; and
- that the concentration of SO_2 or CO_2 in a flowing system is constant,

$$\frac{dc}{dt} = -k Ca, \quad (2)$$

where (dc/dt) represents the rate of carbon atom gasification and 'Ca' is the concentration of available carbon atoms on the surface of the graphite particle being gasified. The rate of decrease of the particle radius is constant, or

$$\frac{dr}{dt} = -k' \quad (3)$$

Differentiating equation (1), substituting for 'r' and integrating gives the following expression that relates the fraction reacted (fw) to time (t) by the temperature function of the reaction (k').

$$1 - (1-fw)^{1/3} = k't \quad (4)$$

The use of equation (4) to fit the experimental data is illustrated in Figure 4 by the dashed line. Similar fits are obtained for the other experimental weight loss-time curves.

The spherical model represents only a crude approach at defining the temperature function of the reaction. The Arrhenius expression for the rate constant k' is:

$$k' = Ae^{-E/RT} \quad (5)$$

The utility, however, of the simplified approach is that it gives us a means of estimating the temperature-time performance of graphite gasification with SO₂ or CO₂.

From the rate constants, Figure 5 was constructed. These curves represented the time-temperature relationship to gasify 50, 75, and 90 wt. percent of graphite with SO₂ and CO₂. Several points were indicated:

1. The rate of gasification is faster at a given temperature with SO₂ than CO₂. For example, the time required to gasify 50 wt. percent of the graphite at 2300F ranges from 15 minutes for SO₂ to 60 minutes for CO₂ (no thermodynamic limitation at 2300F).
2. The predicted rates apply only for pulverized graphite. Char gasification would give a more rapid rate because of a higher specific surface area.
3. A few seconds at 3000F is worth tens of minutes at lower temperatures for equivalent gasification.

8.0 CONCLUSIONS

From this process oriented study, our conclusions are as follows:

- (1) SO₂ in a nitrogen containing regenerant gas can be converted primarily to CO and sulfur by reaction with carbon (char) at temperatures in excess of 2000F.
- (2) The gasification of char with SO₂ may proceed along several paths. Some of these may be exothermic such that the overall reaction is nearly heat balanced.
- (3) The burning of sulfur in an air atmosphere and the subsequent separation to produce a highly concentrated SO₂ gas may prove to be an economical means of producing a high CO content gas without requiring an oxygen plant.
- (4) SO₂ gasification of carbon proceeds at a faster rate at a given temperature than the CO₂-carbon reaction.

In terms of our initial objectives, SO_2 can be completely reduced to elemental sulfur by reaction with hot char. Further, aside from free sulfur, CO is the primary product formed from the reduction.

REFERENCES

1. Bhada, R.K. and Sage, W.L., Preprints, Div. of Fuel Chemistry, A.C.S., 14, No. 4, (101) 1970.
2. Kertamus, N.J., *ibid*, 18, No. 2 (131) 1973.
3. Sage, W.L., *ibid*, (211).

TABLE 1 FIXED BED (COKE)

Input Gas Flow Ft ³ /hr	GHSV*	Input% SO ₂	Avg. Temp. °F	%CO ₂	%N ₂	Output %CO	%COS	Test Length Min.
6.80	773	13	2230	5	77	18	-----	60
4.384	813	100	2100	32.5	---	43.0	24.5	30
4.384	776	100	2220	11.0	---	42.0	47.0	60

Ft³ of gas/hr @60F

*Gaseous hourly space velocity =

Ft³ of bed (initial)

TABLE 2 FLUIDIZED BED (COKE)

Input Gas Flow Ft ³ /min	GHSV	Input% SO ₂	N ₂	Avg. Temp. °F	%CO ₂	Output %N ₂	%CO	%COS	Test Length Min.
0.56	1.93	100	--	2240 -	< 1	4	80	7	15
0.9	391	100	--	2100	< 1	5	76	7	35
				2250					
0.9	315	100	--	2250	6	1	68	22	25
1.9	813	13	87	2000 -	< 1	80	18	1	60
				2100					

TABLE 3 AIR ADDITION TO SO₂ (CHAR)

Input Gas Flow Ft ³ /min	GHSV	Input SO ₂	Gas% N ₂	Gas% O ₂	Avg. Temp. °F	CO ₂	Output Gas% N ₂	CO	COS	Test Length Min.
1.13	276	13	87	----	1800	1	69	24	2.7	85
1.1	264	14.2	84.9	.903	1900	< 1	84	17	1	250
0.683	252	15.6	83.5	.945	2060	< 1	62	35	2.0	300
0.379	138	89.2	8.5	2.3	2210	< 1	3.7	87.0	9.2	153
0.45	164	100	----	----	2240	11.6	---	79.7	8.6	153

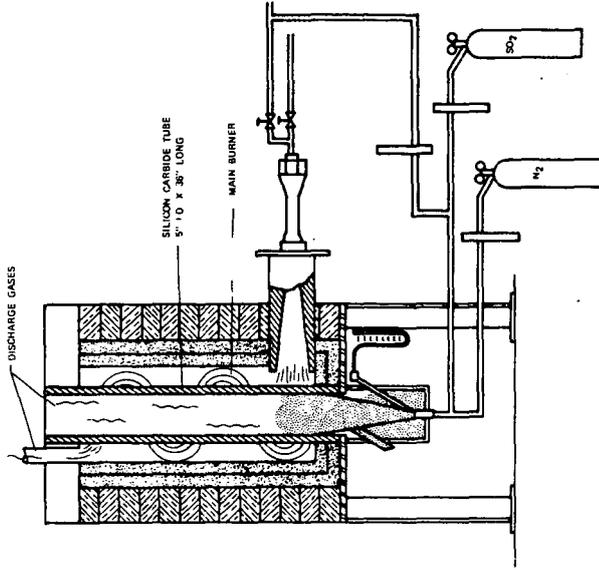


FIGURE 2. 5-INCH FLUIDIZED BED REACTOR

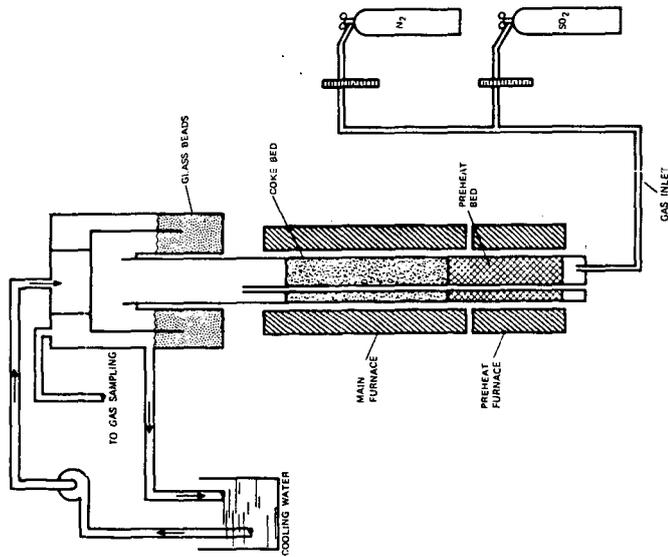


FIGURE 1. FIXED BED GASIFIER

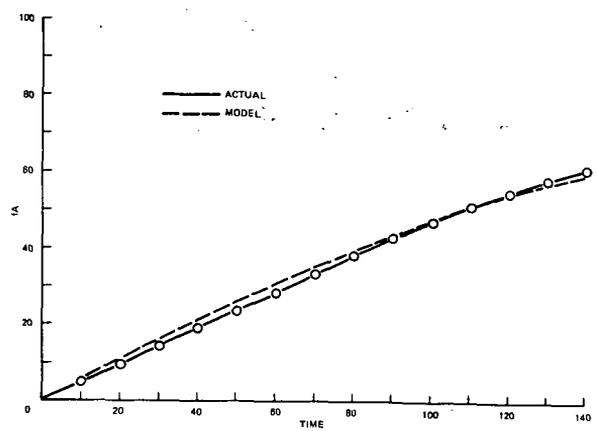
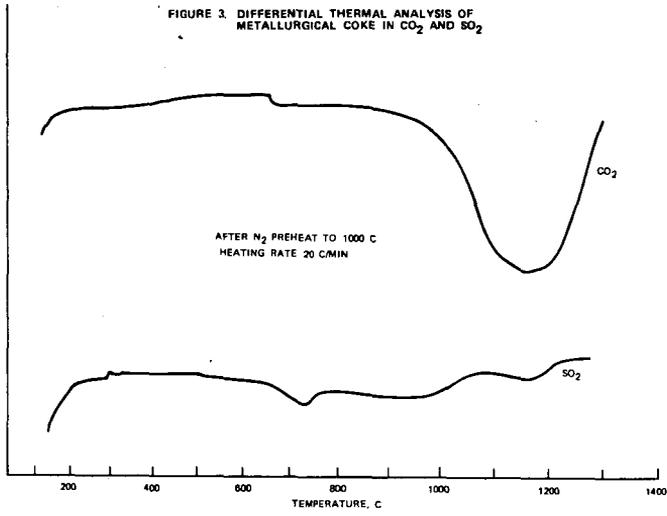
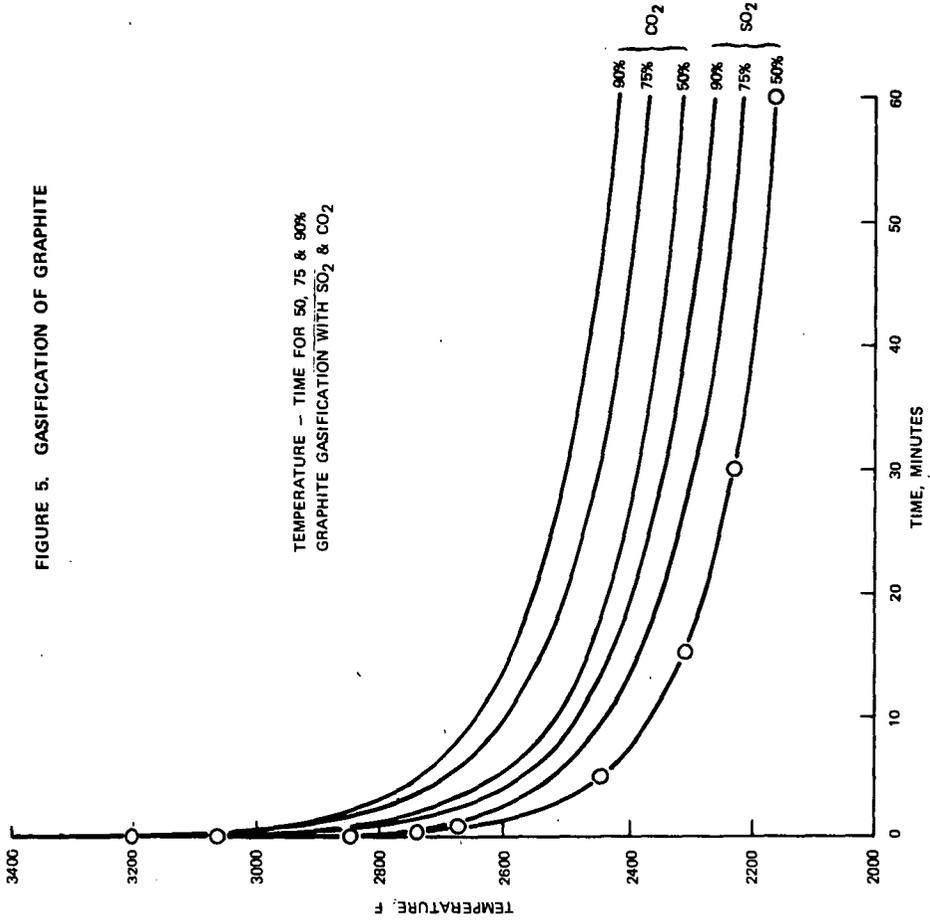


FIGURE 4. FRACTIONAL WEIGHT LOSS VS. TIME GRAPHITE + SO₂ AT 2100 F

FIGURE 5. GASIFICATION OF GRAPHITE



MAJOR MINING RESEARCH PROGRAMS CONDUCTED BY BITUMINOUS COAL RESEARCH, INC., FOR THE UNITED STATES BUREAU OF MINES. R. D. Saltsman, Bituminous Coal Research, Inc., 350 Hochberg Road, Monroeville, Pa. 15146; Joseph Grumer, U.S. Bureau of Mines, 4800 Forbes Ave., Pittsburgh, Pa. 15213; Kelly Strebis, U.S. Bureau of Mines, Twin Cities, Minnesota 55111.

Enough rock dusting prevents a coal dust explosion from propagating by absorbing heat from the otherwise possible flame. Theoretical calculations are presented which compare adiabatic flame temperatures for coal and coal plus rock dust with adiabatic flame temperatures of gas flames at their lean limits of flammability; these calculations show that concentrations of rock dust in mine dust determined empirically to be necessary to inert coal dust are reasonable. Based on this, United States mines are equipped to maintain certain incombustible levels in the settled dust, created during the mining process, by applying rock dust to the surfaces created when the coal is removed. Monitoring and enforcing these requirements are time-consuming and expensive. Results of a data gathering and statistical study to find methods and procedures for reducing the number and quantity of samples required are described. The present respirable dust standards that American coal producers have to meet require new developments. Optimizing the conventional use of air and water to control the respirable dust will not be sufficient. One promising method involves the flushing of the cutting bits with water while the bits are cutting coal. The water flushing concept, pioneered in England for longwall machines, has been adapted to American continuous miners. The problems encountered and the results obtained to date, will be described.

APPLICATION OF ENGINEERING FUNDAMENTALS
TO EVALUATION OF DUST COLLECTION DEVICES

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One consequence of the high degree of mechanization of modern coal mining techniques is the production of a large amount of coal dust during the process of bringing the coal from seam to surface. Wide-spread use of the continuous mining machine has contributed substantially to coal production figures, but it has also added to the level of coal dust in the air the miner breathes. Dust control techniques for the area around a continuous mining machine are relatively ineffective up to the present, compared to other dust sources in the mining operation.

One of the possible approaches to this problem is to collect the dust at or near the mining face as it is generated. In late 1969 a one year contract was awarded by the U.S. Bureau of Mines to Garrett Research and Development Company to evaluate those types of commercially available dust collection equipment which might be applicable to this purpose.

In retrospect, the work done in performance of this contract provides a clear example of how engineering fundamentals can be applied toward solving problems of industrial significance. Two such problems which arose during the planning of this work were: first, what is respirable dust, and what efficiency would be required of a collection device in the underground mining environment? -- and second, how could we evaluate representative dust collection devices with only a small amount of time-consuming experimental work, and yet obtain results which would be general enough to apply to devices and operating conditions other than those specifically investigated?

Details of this work such as experimental procedures are discussed in earlier papers (1,2) and in the final contract report (3).

RESPIRABLE DUST

Mine dust control regulations currently in effect are based on allowable loadings of respirable dust in the mine atmosphere. From the legal point of view, respirable dust is that part of the total dust which is collected by certain portable sampling devices after the dust passes through sections of those devices intended to simulate the dust-collecting abilities of the nose and throat. In order to specify the performance required of a dust collector in a coal mine entry, it is necessary to do the following:

1. Define the size distribution of the "total dust," i.e., the dust generated by a continuous mining machine at a working face.
2. Compute the size distribution of respirable dust, i.e., the part of the total dust which would pass the pre-classifier ("nose and throat") of a portable sampler.
3. From an estimate of the respirable dust loading in a mine, determine the respirable dust collection efficiency required to reduce the respirable dust loading to a legal level.

Three sources of data on dust from continuous coal mining operations were used: the U.S. Bureau of Mines (4), publications of E.J. Baier (5), and mine samples taken as part of this work. With the assumption that the total dust size distribution was logarithmic-normal, and after resolving some inconsistencies in the available data, it was concluded that a conservative (i.e. small) estimate of the size distribution of the total dust near the working face is a mass mean diameter of 15 microns with a standard deviation of 3.0. The size distribution of the respirable dust fraction was then calculated by combining the total dust size distribution with collection efficiency data for the respirable dust sampler. The resulting size distribution for the respirable dust fraction based on the AEC sampler collection efficiency data is a mass mean diameter of 2.55 microns with a standard deviation of 1.7.

The loading of respirable dust in the mine atmosphere near a continuous mining machine has been estimated at 5 to 10 mg/m³, based on the AEC personal sampler. The current maximum allowable respirable dust loading to which a miner may be exposed is 2 mg/m³. However, this limit is based on measurement with the MRE portable sampler which, because its pre-classifier operates on a different principle, measures dust loadings differently from the AEC sampler (6,7). An approximate relationship between the dust loadings measured by the two samplers is

$$\text{MRE} = 1.63 \text{ AEC} + 0.67 \quad 1)$$

Thus, the legal limit of 2 mg/m³ (MRE) corresponds to an AEC-measured loading of 0.81 mg/m³. Accepting a conservative (high) 10 mg/m³ estimate for the loading of respirable dust from the continuous miner, the collection efficiency of a device must be

$$\frac{10 - 0.8}{10} = 92\%$$

on respirable dust in order to achieve compliance.

The problem now is, given experimental measurements on the performance characteristics of a dust collection device, how can this information be related to that collector's efficiency on respirable dust? Obviously it is impractical to attempt to use sample dust with the exact size distribution of respirable dust for performance tests on collection equipment. The overall efficiencies measured, therefore, will pertain to the size distribution of the sample dust, rather than respirable dust. The solution is to use a testing procedure which determines the collection efficiency as a function of particle size, so that the primary result of each test is a penetration function $P(D_p)$, the fraction of particles of diameter D_p which penetrates (is not collected by) the collector. (Efficiency and penetration are related by $E \equiv 1 - P$.)

The size distribution of a dust is defined by $f(D_p)$, where $f(D_p)dD_p$ is the mass fraction of particles having a diameter in the range D_p to $D_p + dD_p$, and

$$\int_0^{\infty} f(D_p) dD_p \equiv 1 \quad 2)$$

The gross penetration for any dust through any collection device can be calculated from

$$P = \int_0^{\infty} P(D_p) f(D_p) dD_p \quad 3)$$

where $P(D_p)$ is the penetration function of the collection device and $f(D_p)$ is the size distribution frequency of the dust. Thus, if the penetration function can be measured or calculated for a given collection device, it is possible to calculate the gross penetration of any dust of known size distribution.

A numerical integration computer program was written to perform the integration of Equation 3, so that the effect of any penetration function and size distribution on gross penetration could rapidly be calculated.

It was implied earlier that the size distribution and loading of respirable dust in a coal mine are not well known. This means Equation 3 is a particularly valuable tool, because it separates the effects of the dust size distribution and the penetration function of the collection device. Hence, experimental results expressed in the form of a penetration function for a given device have complete generality and are applicable to any dust whose size distribution is known.

DUST COLLECTION MECHANISMS

Several basic mechanisms can be used for particle collection, including gravity, inertia, diffusion, electrostatic attraction,

fabric filtration, radiation, magnetism, and agglomeration. Most of these are either impractical or dangerous for use in the control of coal dust underground (3). Only inertia and fabric filtration appear to be technically feasible mechanisms in an underground mine, and because of space limitations, inertia is the more promising. Accordingly, this work was limited to investigation of collection devices operating by one or more inertial mechanisms.

Since the intent of the program was not simply to test several commercial dust collection devices but rather to determine what collection mechanisms could best be applied to the problem of coal mine dust, the strategy adopted was to select or develop a mathematical model for each potentially applicable mechanism and to test collection devices which used these mechanisms in order to confirm or disprove the models. With the ultimate goal of evaluating each inertial mechanism for application to coal dust, the immediate goal of the modelling and testing program was to determine for each inertial mechanism the penetration function $P(D_p)$ under various operating conditions. Once this was done, the penetration function could be applied using the technique described in the previous section.

Cyclone

In a cyclone separator, rotary motion of the entire gas stream throws dust particles to the outer wall under the influence of centrifugal force. The particles then fall through the bottom of the cyclone or are otherwise removed. The cyclone separator tested in this work was a multiple cyclone collector consisting of a bank of 46 small cylindrical cyclones in parallel. The dusty air inlet flow was parallel to the axis of the cyclone, and a tangential motion was imparted to the air by fixed vanes set at an angle to the axis. Each cyclone had a hub occupying the central part of its volume. This device was modelled by adapting equations given in Strauss (8) for more conventional cyclones. In this model it was assumed that if a particle reaches the outer wall at any time before leaving the cyclone with the gas, it is collected. No consideration was given to re-entrainment by the gas. The resulting penetration

function is given by

$$P(D_p) = 1 - \frac{1 - \sqrt{1 - (D_p/C)^2}}{1 - (D_{hub}/D_{shell})^2} \quad 4)$$

where C is a constant characteristic of the cyclone geometry and the air and dust properties. The observed dust penetration through the multiple cyclone as a function of particle size is shown in Figure 1. The curve was calculated from Equation 4. (The value of C in Equation 4 was calculated from the model, not fitted empirically.) The observed gross penetration of the test dust was 76%, and the gross penetration calculated using Equation 4 with Equation 3 was 79%.

It was concluded that within the precision of the experimental techniques used, the penetration function of Equation 4 is an adequate representation of the penetration function of the multiple cyclone which was tested. Equation 4 was then used again as the penetration function in Equation 3 to predict that the gross penetration of respirable dust through this device would be 53% at the test conditions. This is to be compared with the estimated 92% efficiency (8% gross penetration) required to achieve a legal respirable dust loading.

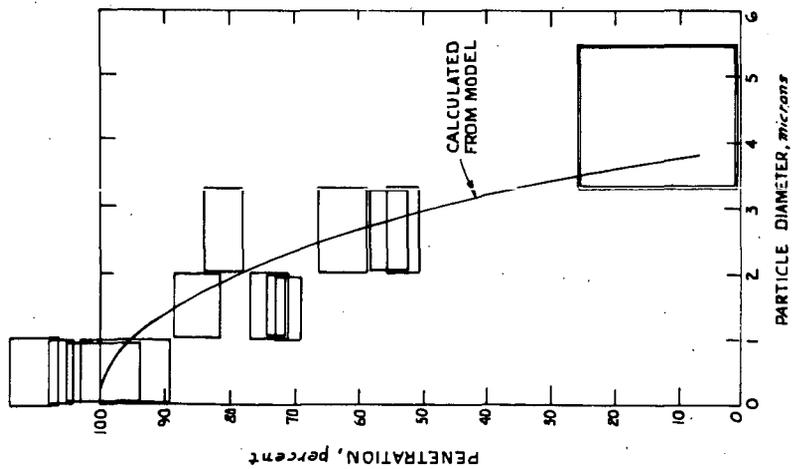
Curved Passages

Many dust collectors use essentially the same principle as the cyclone separator, but the gas is caused to turn by curved passages of some sort. This type of collector includes those with louvers, deflectors, or corrugated passages, and packed beds. In these devices, dust particles are spun out against solid or liquid surfaces by centrifugal force as the gas stream flows through a multitude of curved paths.

A simple packed bed scrubber was fabricated in-house to represent this collection mechanism. For a packed bed, the penetration function can be expressed (9) as

$$P(D_p) = \exp \left[-C \frac{Z}{D_t} K \right] \quad 5)$$

MULTIPLE CYCLONE
PENETRATION AS FUNCTION OF PARTICLE DIAMETER



where K is the inertial impaction parameter, $U_0 D_p^2 / 9 \mu D_t$, and C is an empirical constant (9) which depends on the packing geometry. The test results for the packed bed scrubber are shown in Figure 2. The curve was calculated from Equation 5 using a value of $C = 12$ for 1-1/2 inch Pall rings. The observed gross penetration of the test dust was 39%, and the gross penetration calculated using Equation 5 with Equation 3 was 41%.

Impaction Targets

Cylindrical objects such as rods, wires, and fibers are used in a large number of collection devices. As the gas stream flows around the target, the inertia of the dust particle tends to make it impact on the target instead of passing around it. The factors influencing the collection efficiency of such a device are the gas velocity relative to the impaction target, the size of the target, the gas viscosity, the number of targets the gas stream must pass, and the particle density and size. All of these effects except the number of targets are included in the inertial impaction parameter K . An empirical penetration function based on past experimental results for impaction on cylinders and on spheres is

$$P(D_p) = 1 - \left(\frac{K}{K+0.7} \right)^2 \quad 6)$$

(Impaction on spheres is one of the mechanisms involved in a venturi scrubber, discussed below.)

A wetted screen device was tested which employed the impaction target mechanism. An accordion pleated screen constituted the impaction targets, and the screen was continuously wetted to keep the collected particles from blinding it. The screen was followed by a horizontal cyclone functioning as an entrainment separator. The test results are shown in Figure 3. The higher of the two penetration curves was calculated from Equation 6 directly. However, since the total area of the screen wires was about twice the cross sectional area of the scrubber, it was hypothesized that the scrubber might comprise two impaction stages. The penetration

**PARTICLE COLLECTION EFFICIENCY
VS IMPACTION PARAMETER
FOR IMPINGEMENT OF JETS ON
LIQUID OR SOLID SURFACES**

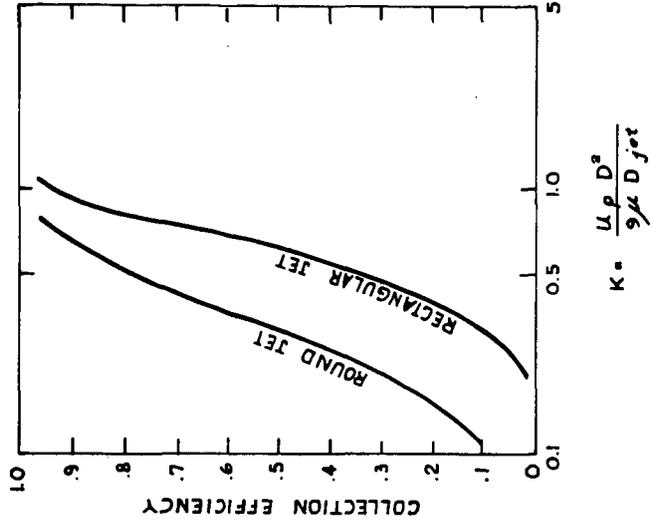


FIGURE 4

**WETTED SCREEN SCRUBBER
PENETRATION AS FUNCTION OF PARTICLE DIAMETER**

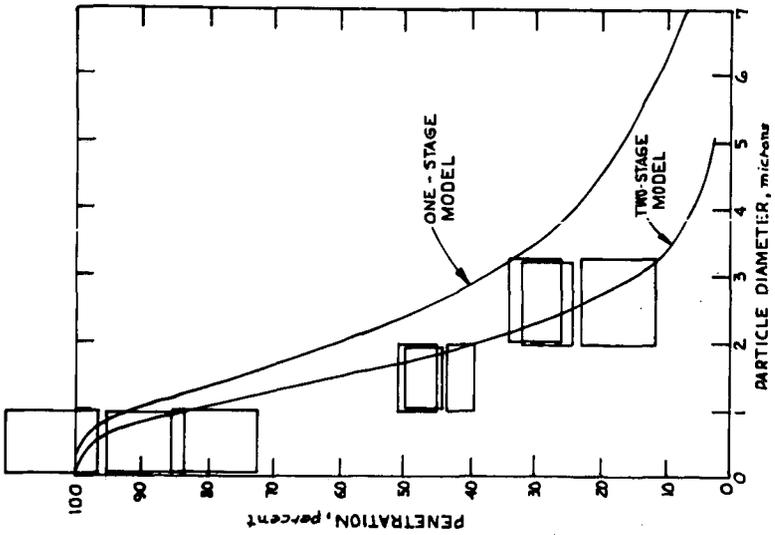


FIGURE 3

function indicated by the lower curve is just the square of the penetration calculated from Equation 6. The observed gross penetration of the test dust through the wetted screen was 54%, and the gross penetration calculated from the two-stage penetration function and Equation 3 was 56%. The same two-stage penetration function applied to the estimated size distribution for respirable dust using Equation 3 gave a gross penetration of 35%.

Jet Impingement

Some dust collection devices are based on impingement of a jet of the gas stream on a solid or liquid surface, a mechanism quite similar to impaction on targets. In this case, however, the space through which the gas stream must pass is much smaller, and the gas flow characteristics are thus different from the case where the flow is around relatively isolated bodies. The common examples of the impingement mechanism are sieve tray and ballast tray scrubbers. When the gas jet impinges on a surface, the inertia of the particles prevents them from following the sharp change of direction taken by the gas. Again, the collection efficiency is affected mainly by the variables included in K , the inertial impaction parameter. Past experimental data are correlated in Figure 4, which gives the penetration function indirectly by showing the efficiency as a function of K , for impingement of round and rectangular jets on surfaces.

The collection device tested to represent the jet impingement mechanism was an impingement scrubber consisting of a cylindrical tower containing water spray nozzles and baffle plates. The test results are shown in Figure 5. The penetration function curve shown was calculated by assuming the collection mechanism was two stages of impingement of round air jets on flat plates, with each stage having a penetration function obtained from Figure 4. Using this penetration function with Equation 3 and the estimated size distribution, a gross penetration of 27% was predicted for respirable dust through this device.

**VENTURI SCRUBBER
PENETRATION AS FUNCTION OF PARTICLE DIAMETER**

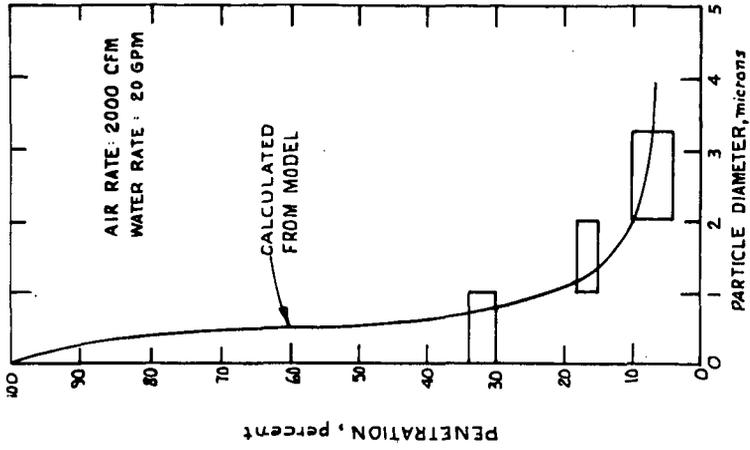


FIGURE 6

**IMPINGEMENT SCRUBBER
PENETRATION AS FUNCTION OF PARTICLE DIAMETER**

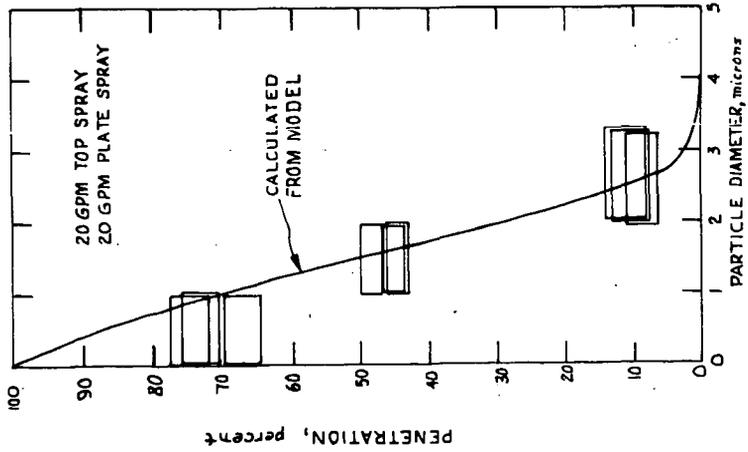


FIGURE 5

Venturi

In venturi devices, the gas stream is forced through an orifice or a narrow throat. A scrubbing liquid is introduced at or upstream of the throat, and is atomized at the throat due to the high gas velocity. The dust particles are collected by impaction on the atomized droplets. The penetration function for the venturi mechanism is given (9) as

$$P(D_p) = \exp [-2 \times 10^{-5} (1 - P_s) (13,500 L + 1.2 UL^{2.5})] \quad 7)$$

for the air-water system at room temperature and atmospheric pressure. P_s is the penetration calculated from Equation 6 for impaction on spheres. The spheres which are the impaction targets are the droplets atomized in the venturi throat. Their diameter (for calculating the inertial impaction parameter K) is estimated from the Nukiyama-Tanasawa correlation, which can be written as

$$D_t = \frac{16500}{U} + 1.45 L^{1.5} \quad 8)$$

for air and water at room temperature and atmospheric pressure. Equation 8 is applicable when the air velocity is greater than 200 ft/sec.

In the experimental program, a simple venturi collector was tested, as well as two commercial devices operating primarily by the venturi mechanism. Partial test results for the simple venturi are shown in Figure 6. The observed gross penetration of the test dust was 19%, and the gross penetration calculated by using the penetration function given by Equations 7 and 8, in Equation 3 was 19%. The same penetration function applied to the estimated respirable dust size distribution gave a gross penetration of 6%. The test results for the two commercial venturi scrubbers also confirmed the venturi mechanism model.

DISCUSSION

A major conclusion from the contract program was that currently available knowledge of dust collection mechanisms is adequate both to explain the performance of a wide variety of dust collection devices and to provide a basis for the design of dust collection systems.

Potential dust collection mechanisms cannot fairly be evaluated only on the basis of the test results reported, because the tests on the various collectors were not always run at comparable conditions. Indeed, little in the way of useful conclusions could have been achieved if the program had been confined to testing various devices, even if the testing had been more extensive. But the purpose of the tests was to confirm the available models, and based on the application of those models, some general conclusions can be offered about the applicability of the different collection mechanisms to the coal mine dust problem.

1. A dry centrifugal collector cannot perform adequately for this application.

2. None of the "wet dynamic" mechanisms -- curved passages, impaction targets, jet impingement -- could meet current standards based on the respirable dust loading (10 mg/m^3) assumed in this work. However, if the respirable dust loading could be lowered, for instance by redesigning the air system in the mine entry, these mechanisms would be worth reconsidering, particularly in view of their relatively low energy and water requirements and potentially small size of the collection device.

3. The required collection efficiency could be achieved with a high energy scrubber using a venturi mechanism. The disadvantages of such a device are high pressure drop (i.e. high energy requirement) and a large water requirement. Also, there is at present no commercially available high energy scrubber which could fit in a coal mine entry.

NOMENCLATURE

(Any consistent units may be used, except in cases noted.)

D_{hub}	diameter of cyclone hub
D_p	particle diameter
D_{shell}	inside diameter of cyclone
D_t	target size: sphere - diameter (microns in Equation 8) cylinder - diameter round jet - diameter rectangular jet - width packing - nominal size
f	size distribution frequency
K	$\equiv \frac{\rho U D_p^2}{9\mu D_t}$, inertial impaction parameter
L	liquid rate, gallons/thousand cubic feet of air
P	penetration
U	air velocity (ft/sec in Equations 7 and 8)
Z	packed height
μ	gas viscosity
ρ	particle density

REFERENCES

1. Legatski, L.K. and Clavert, S., "Scrubbers for Control of Coal Mining Dust," presented at A.I.Ch.E. meeting, Chicago, December, 1970.
2. Preston, G.T., "Dust Control in Underground Mines," Proceedings of the Conference on the Underground Mining Environment, University of Missouri at Rolla, October, 1971.
3. Calvert, S. and Legatski, L.K., "A Comprehensive State-of-the-Art Evaluation for All Types of Dust Collection Equipment That May Be Applicable in Underground Coal Mines," National Technical Information Service, U.S. Department of Commerce, Document No. PB 197 739, \$3.00.
4. U.S. Bureau of Mines, private communication.
5. Baier, E.J. and Diakun, R., J.Am.Industr.Hygiene Assoc. 25, 476 (1964).
6. "Sampling and Evaluation of Respirable Coal Mine Dust," Mineral Industry Health Program Training Course 100.
7. "Proceedings of the Symposium on Respirable Coal Mine Dust," USBM Information Circular 8458, 1970.
8. Strauss, W., "Industrial Gas Cleaning," Pergamon Press, New York, 1966.
9. Calvert, S., in "Air Pollution," ed. A.C. Stern, Academic Press, New York, 1968, vol. 3, pp. 457-496.

THE U.S. BUREAU OF MINES PROGRAM
TO CONTROL RESPIRABLE DUST IN COAL MINES

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INTRODUCTION

Inhalation of dust has long been recognized as a health hazard leading to pulmonary diseases. In the 16th century, Agricola, the father of mining, discussed dust inhalation during mining and called it a "widow maker." In the 19th century the "black lungs" of autopsied coal miners were recorded. The 11th Edition of Encyclopaedia Britannica, some 60 years ago, described fibroid changes and included a graphic photomicrograph of a cross section of a coal miner's lung.

The Federal Coal Mine Health and Safety Act of 1969 (PL 91-178, December 30, 1969) established health standards in underground coal mines for the first time in the United States. The Act specifically stated that the working conditions in each underground coal mine should be sufficiently free of respirable dust to allow each miner to work underground without incurring any disability from coal workers' pneumoconiosis (CWP) or other occupation-related disease during his working life. Based largely upon British studies, the Act specified that the maximum allowable concentration of airborne respirable dust particles (nominally less than $7.1 \mu\text{m}$ in diameter) in bituminous coal mines should be $3 \text{ mg}/\text{m}^3$ by June 30, 1971 and $2 \text{ mg}/\text{m}^3$ by December 30, 1972. The maximum permitted dust level is decreased if the silica content of the dust is greater than 5 weight percent so that the Threshold Limit Value (TLV) of $100 \mu\text{g}/\text{m}^3$ of silica for an eight hour exposure will not be exceeded.

CWP is the most severe health and safety problem facing the coal mining industry today.

1. The number of permanent disabilities and deaths of coal miners due to CWP is 3.5 times the disabilities and deaths due to all other mine accidents (1964-1970 Pennsylvania data). (1)
2. About 30 percent of the present working miners have CWP (1972).
3. About 165,000 claims for CWP have been approved and some 100,000 additional claims are currently under review.

The cost to Government and industry for CWP compensation has been estimated to be \$1 billion per year.

However, it has been estimated that coal production must double by the year 2000 in order to meet the energy requirements of the nation. The necessity for society to devise methods for mining coal at a rapid and economical rate while maintaining a healthful mining environment is apparent.

The 1969 Act directed that the Departments of the Interior and Health, Education and Welfare shall "develop new or improved means and methods of reducing the concentrations of respirable dust in the mine atmospheres of active workings of the coal mines." The Bureau of Mines was assigned the responsibility for planning and implementing a research and development (R&D) program to provide the advanced technology for reducing the amount of respirable dust in coal mines. This advanced

technology would assist the mine operator to meet the stringent dust limits imposed by the Act.

The present problem of dust control during coal mining operations is considerably different from the problems normally encountered during industrial operations. For example, coal is often mined underground using continuous (mechanical) mining methods,* where coal is removed by cutting bits on a rotating wheel or chain. Dust is formed by the cutting action of the bits, and also at nearby locations by secondary handling operations. Water sprays are used to suppress the dust being formed by the cutting action. Also, air is passed over the machine to the face and then back behind a brattice cloth (usually) to "push" the dust away from nearby personnel. However, dust control during actual coal mining operations is not so clear-cut. An analogy to a typical industrial operation would be to devise ways to control a hazardous impurity in a chemical processing plant where:

1. the sources of the impurity (dust) are imperfectly known;
2. laboratory and pilot plant information is of limited usefulness (it is almost impossible to simulate the underground mining situation in the laboratory);
3. the amounts of the impurity are variable (cutting bits become broken, cutting rate varies with machine operator);
4. the flows in the plant are ill-defined and highly variable, e.g., a pipe (spray nozzle) plugs, the flow through a main pipe changes intermittently and irregularly (the distance of the brattice cloth to the face changes);
5. the chemical process varies (variety of coal seams, variation of coal structure in a seam and in a given mine, variety of mining machines);
6. imperfect operating equipment (numerous equipment malfunctions in the rugged mine environment);
7. inadequate sampling equipment (long-duration dust samplers to determine transient dust concentrations);
8. erratic sampling equipment (difficult to scientifically sample airborne dust);
9. hostile environment (a 30-inch-high seam, roof falls down).

The Bureau's program has been divided into four general categories: dust control, personal protection, instrumentation, and chemical analysis. Expenditures are summarized as follows:

	<u>FY 70</u>	<u>FY 71</u>	<u>FY 72</u>	<u>FY 73 (estimated)</u>
	(\$1,000)			
Dust control	1,168	2,176	1,639	1,523
Personal protection	32	90	106	-
Instrumentation	270	447	253	379
Chemical analysis	<u>168</u>	<u>227</u>	<u>347</u>	<u>135</u>
	1,638	2,940	2,345	2,037 (estimated)

*About 50 percent of the coal mined underground in the United States is obtained by continuous (mechanical) mining, 47 percent by conventional (blasting) mining, and 3 percent by longwall (mechanical) mining. This paper is limited to dust control by the first mining technique.

The program involves inhouse work at two Bureau research facilities, Twin Cities Mining Research Center and Pittsburgh Mining and Safety Research Center, and also an assortment of contracts and grants with outside organizations.

This paper briefly describes the major items in the Bureau program and their status.

DUST CONTROL

Continuous mining machines were designed to mine coal at a fast rate. They are very efficient mining machines. However, by using blunt high-speed bits, they probably are the best machines for forming dust that could be invented, except for a grinding stone.

Bureau research has shown that continuous mining forms approximately 5,000 grams of respirable dust at the face per ton of mined coal. About 2 grams of this dust becomes airborne at the face; the remainder remains adhering to the run-of-face broken coal.

An exploratory statistical study indicated that the same mining occupations in different seams often had significantly different dust exposures. For example, the continuous miner operator in the Pittsburgh and Pocahontas seams is exposed to more dust than the same man in the Kittanning seam, but curiously, the Kittanning seam gives more dust along a haulage road than the other seams. Such information suggests basic differences in the dust-forming characteristics of different coal seams, but the explanation for these differences is not presently known.

Dust control techniques at the face include:

- available technology
- machine cutting parameters
- supplementary ventilation; dust collector
- water sprays
- wetting agents
- pick flushing
- foam
- infusion

These items are described and are followed by a concluding section discussing secondary dust:

Available Technology. Considerable technology is already available, but it is often not effectively used because of inconvenience or expense. For example, while water sprays provide a valuable dust control technique, their practical usefulness underground is limited because they frequently clog in the rugged mine environment. Cleaning or replacement of a clogged nozzle is expensive to the mine operator in terms of time and cost. The development of a non-clogging spray nozzle system would reduce operator expense and inconvenience and therefore would increase the actual effectiveness of water sprays as a dust suppression technique. A contract to develop a non-clogging nozzle is expected to be awarded in late FY 73.

Machine Cutting Parameters. The British conducted pioneering work examining the effect of machine parameters on the formation of airborne dust and concluded that sharp, slow-moving, deep-cutting bits produce less dust. The problem now is to obtain quantitative information on the amount of airborne dust versus machine parameters with American coal and mining methods, along with cost and other engineering information. Improvement in cutting parameters is estimated to offer a 50-percent decrease in airborne dust.

A full-scale machine which permits varying of the machine parameters (rpm, sump and shear rate, bit geometry and array) is being constructed by Ingersoll-Rand under Bureau contract. The machine will be automatically controlled to avoid operator variables and will be used in full-scale underground tests to obtain the desired information on the effect of the machine parameters versus dust formation. Also, a research mining machine having a single full-scale cutting wheel was designed and constructed. This research machine permits the machine parameters to be varied over a wider range than the full-scale machine and will be used as a "pilot plant" to further investigate the effect of cutting parameters on the formation of respirable dust. Finally, several laboratory programs are investigating dust formation during cutting in order to better understand the fragmentation process. Such studies hopefully will lead to new bit designs and the selection of machine parameters that reduce dust production.

Supplementary Ventilation. Air flow at a mining face is normally controlled by line brattice or by extensible tubing, occasionally in conjunction with an auxiliary fan. However, supplementary ventilation techniques that involve machine-mounted fans to draw or exhaust the dusty air from the vicinity of the face appear very attractive for dust control because they reduce the recirculation of face dust back to nearby personnel and can in principle be applied to various kinds of continuous mining machines and local mining situations. A disadvantage of this local exhaust approach is that the dusty air must either be discharged into the return via a duct or be passed through a machine-mounted dust collector with the partly cleaned effluent air being discharged at the mining machine.

A current program is examining the exhaust approach with an auger-type mining machine in low coal. A machine-mounted dust collector is used, but the effluent air is ducted into the return. The unit is presently being tested underground. Initial results are encouraging, but additional testing is required.

A severe problem in coal mines, especially in low coal, is the space limitation. For example, the available high-cfm fans were too large to install on the low-coal auger machine and two small-cfm fans had to be used in parallel. This was undesirable from an engineering viewpoint but was the only alternative at the time. It has since been established that technology is indeed available to fabricate a high-cfm, small-diameter fan suitable for operation in low coal, and a prototype unit is being constructed inhouse. The availability of such a fan would expedite the use of supplemental ventilation techniques in low coal and other areas where space limitations are critical.

Passing the exhaust dusty air through a machine-mounted dust collector has mushroomed in popularity during the past year. This approach has the distinct advantage of avoiding ducting from the machine to the return. However, the dust collector must be very efficient because any effluent dust may bathe the machine operator and nearby personnel and could even increase their dust exposure. Available dust collectors tested in 1970, comprising a large assortment, were all found unsatisfactory because of a low collection efficiency for respirable size dust or because of bulk or safety problems. The Bureau has fabricated an above-ground facility to evaluate the collection efficiencies of new full-scale collectors as they become available. For example, the collection efficiency of a typical scrubber designed for mounting on the boom of a continuous miner ranged from 80 percent for 1 micron dust to 99 percent for 5 micron dust. While surprisingly high, these efficiencies are still too low to scrub anticipated incoming dust levels to a 2 mg/m³ level.

A venturi wet-collection approach appears to be the most attractive mechanical approach for achieving high collection efficiency. A Bureau-designed research-type venturi collector will be used to investigate collection efficiency versus power input, water flowrate, and other engineering parameters. Results will provide

guidance for the design of dust collectors for specific situations and can assist a mine operator to determine whether a mechanical collector will bring him into compliance. In the interim, the Bureau is fabricating a new, simpler, low-cost, venturi collector that is especially designed for use in coal mines.

An alternative and new approach for a respirable dust collector is to use plastic surfaces such as polystyrene and polyethylene. Such materials usually have "islands" of electrical charge that rapidly collect airborne coal dust if the dust has an electrical charge. Exploratory inhouse underground tests have shown that mine dust often has an electrical charge and that an appreciable collection can be obtained merely by passing the dusty air through a plastic tube. In principle, such collection should be especially effective for smaller particles because of their higher mobility. In view of the difficulty of collecting very small particles, the feasibility of a plastic-type dust collector for coal mine use is being explored.

In general, the air flow pattern in the vicinity of the mining machine and at the face is crucially important in affecting the transport of face dust back to the machine operator and nearby personnel in exhaust ventilation. However, local flow patterns are largely unknown. Since the machines usually occupy a large fraction of the cross section of an entry, their presence would be expected to significantly influence flow patterns. Recent inhouse work confirmed this expectation and also found that the motion of the cutting wheels influences the local flow pattern.

A 1/10-scale laboratory model of a low-coal entry including the auger-type mining machine is being used in an inhouse study of local flow patterns and the effect of these patterns on the transport of respirable dust. This work supports the low-coal field contract. Results to date indicate that drawing about half of the incoming ventilating air through the machine leads to a drastic reduction of the dust levels at typical personnel locations. Modeling appears very attractive as an inexpensive technique for screening proposed auxiliary ventilation techniques before underground testing is initiated. Underground measurements are currently being made to verify the modeling concept.

Water Sprays. One of the main dust control techniques presently in use is water sprays. Sprays are reported to reduce the respirable dust level 20 to 60 percent, although 30 percent is a typical number. The type and placement of spray nozzles is currently selected in an arbitrary manner because guidelines are not available; a typical approach seems to be to merely add more nozzles in the hope of reducing more dust. Techniques seemingly could be devised which would make a more effective use of the sprays, e.g., either greater dust suppression with the existing water flow or sufficient suppression with a smaller water flow rate.

British laboratory studies indicated that the capture of airborne respirable-size particles with water drops is dependent upon the size, concentration, and velocity of the drops, although optimum spray parameters to be used to achieve maximum dust suppression for underground spray systems were not determined.

A Bureau program to determine these optimum parameters for a spray system was undertaken. A theoretical model for the capture of airborne dust was developed and verified in the laboratory. Capture efficiencies of up to 75 percent were obtained. The theory can be used to select an optimum spray nozzle which gives the maximum collection efficiency of airborne dust at a specific spray-nozzle location in a mine for the water flowrate, line pressure, and geometry at that location. In practice, of course, the water spray drops can also impact and moisten the surface of coal and thereby suppress the formation of airborne dust by interfering with the dust-forming cutting process or by enhancing the adhesion of newly-formed particles. The development of a theoretical impaction model is being studied inhouse. Combination of the impaction and airborne models will then be attempted.

In the interim, the usefulness of the above airborne theory for improved dust suppression at the front end of a continuous mining machine was tested underground. In one test series, dust suppression was about equal with all spray nozzles, although the "good" sprays used about one-third less water than other sprays. In another less extensive series, the good sprays also gave one-third less dust. The use of one-third less water is a major accomplishment because many mines already have excessive moisture. Additional underground testing is required to obtain definitive data regarding dust suppression.

Another Bureau program indicated that steam and water spray were about equal in effectiveness for suppressing the formation of airborne dust or for collecting airborne dust. The use of steam underground would involve difficult logistics and is not recommended.

Wetting Agents. The usefulness of wetting agents for increasing the effectiveness of water sprays as a dust control technique is controversial. Some workers state that they are worthless, others state they are helpful, and there is little published data to support either statement. Clarification is warranted in view of the expense and inconvenience associated with using such agents. The Bureau had a contractor measure the wetting behavior of 16 wetting agents on coal from six different seams. All agents essentially wetted all the coals. At present, another contractor is measuring the drop size and velocity of the sprays from several nozzles with several wetting agents. Underground tests will be conducted to establish the usefulness of wetting agents as a dust suppression technique.

Bit Flushing. British studies indicated that a 75 percent reduction in dust is obtainable by directly flushing the cutting bits with water. However, internal plugging of the orifices and seal leakage have prevented this technique from being widely used in the United States. Although approximately 40 such "wet-head" machines are underground, only two are reported to be using the wet-head mode. A contractor has designed an improved seal with one type of wet-head ripper machine and is presently conducting underground tests.

Foam. The use of foam for dust suppression is based on the concept of using a high-expansion foam to "blanket" the cutting site and thus physically prevent any dust from becoming airborne. Several studies to establish the merit of foam have been attempted over the past 10 years, but results were inconclusive because of insufficient underground testing. The Bureau therefore initiated a new, more detailed effort in order to obtain definitive results on the usefulness of foam. Brief underground tests in FY 72 established that the foam broke rapidly, that there were no slip hazards, and that the foam was well received by mine personnel. However, the underground testing regarding dust suppression was inconclusive, and the program is being continued to obtain sufficient data in order to be statistically significant.

Infusion. Water infusion has been useful in Europe for reducing dust formation during subsequent mining. German mining regulations require water infusion wherever possible as a dust control technique, but implementation seemingly is left to the discretion of individual mines. About 15 percent of the collieries in England are using infusion to control dust but are having problems due to the low permeability of English coal beds.

Infusion has received only limited attention in the United States owing to engineering-type equipment problems. The Bureau initiated an infusion program with the dual objectives of controlling methane and reducing the formation of the dust. To date, significant methane control has been achieved and dust seemingly is reduced by about 50 percent. However, considerable additional field work is required to obtain definitive results.

Secondary Dust Generation. Points of secondary dust generation include the gathering arms on the continuous mining machine or loader, dumping of material into the shuttle car, operation of the shuttle car along the roadway, belt operation, belt transfer points, etc.

Inhouse Bureau work has shown that enough respirable-size coal dust adheres to 20 pounds of ordinary run-of-face broken coal to contaminate approximately 1 million cu ft of air up to the 2 mg/m^3 level if it should become airborne. The potential danger of secondary hauling as a dust source is obvious. The magnitude of the forces involved in physical adhesion of coal particles to massive substrates was measured and found to approximately agree with expected adhesion forces.

Laboratory work indicates that only about 10 percent of the dust adhering to the run-of-face coal is dislodged and becomes airborne during a typical drop operation. Dust generation can be reduced only somewhat by changing the belt parameters, e.g., the dust would be reduced by about 30 percent by decreasing the drop height or slowing the belt by a factor of 2. A 70-percent reduction of dust should be obtainable by passing the broken coal down an inclined chute instead of a vertical drop or by using water sprays along the belt somewhat upstream of the drop point. These laboratory conclusions have not yet been tested in a full-scale operation.

At an underground belt transfer point, water sprays or a low-expansion foam injected directly into the falling coal reduced the formation of airborne dust by about 50 percent. Additional application of water sprays onto the underside of the belt reduced airborne dust by 60 percent, while foam on the underside of the belt reduced dust by 90 percent.

Laboratory research indicates that the formation of new dust due to secondary breakage during dropping is insignificant compared to the dislodgment of adhering dust.

PERSONAL PROTECTION

While the Bureau does not consider personal protective devices such as face masks as a primary approach for reducing the miner's exposure to dust, such personal protection can be visualized as an interim measure and also as a "last alternative" for certain dusty operations in case remedial measures are unsuccessful. The present filter-type face mask is undesirable because of (1) a high-pressure drop when clean and an excessive pressure drop during use due to plugging, (2) an imperfect match to the facial contour, (3) poor day-to-day refit in the field, (4) irritation due to dust at the mask-face juncture, and (5) interference with voice communication, spitting, etc.

A personal device employing the air curtain concept is presently being developed under Bureau contract. Dusty air from the environment is filtered and an air curtain of dust-free air is passed from the hat brim down over the miner's face, thereby shielding him from the dusty environment. Such a unit requires considerable power and therefore is limited to machine operators but hopefully will be of interest to industry in general.

INSTRUMENTATION

Improved dust samplers for monitoring the eight-hour exposure of miners and also for research purposes are required. The state-of-the-art in dust sampling is aptly summarized in an International Labor Organization report (1967), which concludes that "No evaluation or comparison of dust content has any significance... unless the type of equipment, the method of sampling, and the nature of the dust are precisely known."

The dust hazard in United States mines currently is assessed gravimetrically with a personal sampler continually worn by the miner during his working shift. The sampler uses a battery-powered pump to draw 2 l/min of dusty air through a cyclone, which collects the nonrespirable dust, and then through a membrane filter, which collects the respirable fraction. The filter is weighed in the laboratory to determine the total mg/m^3 of dust exposure; 2 mg of weighed dust approximately corresponds to $2 \text{ mg}/\text{m}^3$ exposure for eight hours.

Although this system functions, the weight and size of the personal sampler is burdensome to the miner, the sampler is subject to mischief, the entire approach is expensive, and the accuracy of the system has been questioned.

Bureau research has indicated that about half of the 1 to $2 \mu\text{m}$ underground airborne particles are agglomerated to large nonrespirable airborne particles. This means, unfortunately, that a size classifier must be used with any sampler, i.e., the sampler merely cannot collect all the dust and the respirable fraction measured in the laboratory, for the respirable dust concentration then would be overestimated.

Respirable dust nominally involves $7.1 \mu\text{m}$ -diameter or smaller particles and is specifically defined by the Act in terms of the size classifier of the British MRE dust sampler. However, medical authorities are seriously considering revising the TLV standard for silica to emphasize the smaller size particles. Also, some medical workers feel that dust particles somewhat larger than the respirable fraction may lead to some respiratory diseases, while others feel that the submicron particles are especially dangerous to human health. Furthermore, medical authorities are becoming increasingly concerned that short exposures to high dust levels may be more hazardous than the eight-hour time-averaged value of the dust exposure, which is the present basis of the dust standard.

Research purposes require a short-duration, fast-response field sampler to test the effectiveness of a dust control technique and to assist the identification of dust sources. The present midget impinger unit requires about 10 minutes to obtain sufficient dust for analysis by the Coulter counter. This technique is reasonably satisfactory for screening, comparison-type purposes. However, a 10-minute sample time is excessive for monitoring many mining operations owing to the short duration of the operation.

Light scattering is attractive because response time is rapid and the electrical output signal can be readily measured and could be telemetered or used in control circuitry. However, light scattering is related to the area of the particles in a dust cloud, and results must be converted to mass concentration (mg/m^3). With laboratory dust, this conversion is reasonably reproducible. With mine dust, the size distribution varies, and variable amounts of noncoal materials that have different densities and indexes of refraction are often present. Such variations will lead to a variable (and unknown) conversion factor. Despite the potential uncertainty in the conversion factor, a prototype unit was fabricated by a contractor. The unit has a fast response time (5 seconds) and already has been valuable in underground work as a "screening" tool.

CHEMICAL ANALYSIS

The 1969 Act specifies a maximum exposure to respirable coal mine dust of $2 \text{ mg}/\text{m}^3$ but also stipulates that the permitted level is reduced below the $2 \text{ mg}/\text{m}^3$ standard to the value given by the expression $10/(\text{percent quartz})$ to match the TLV of $100 \mu\text{g}/\text{m}^3$ quartz for an eight-hour exposure. All the silica in a coal-mine dust sample is assumed to be quartz.

At present, the Bureau analyzes the quartz content in mine dust by removing the dust from about 10 personal respirable dust samples, combining the dusts, ashing the combined dust, making a KBr pellet of the ashed dust, and measuring the amount of silica in the pellet with infrared (IR) techniques. This approach is time consuming and expensive and, by combining the silica content of the several samples, does not give the eight-hour exposure of an individual.

A technique for analyzing the silica content of a single field filter sample was recently developed by the Bureau wherein the dust was removed and redeposited onto a new filter and then analyzed by IR and X-ray techniques. Results obtained by both techniques agreed, giving support to the values obtained by both techniques. However, the true accuracy of any of the mentioned methods is exceedingly difficult to determine. Also, the effect of particle size, the occurrence of other SiO_2 polymorphs, and perhaps surface effects must be examined.

Direct measurement of the silica in the mine dust as collected on the field filter sample would greatly expedite analysis and is being explored by the Bureau and a contractor using IR techniques and by another contractor using a new soft X-ray approach.

Recent work in West Germany indicates that silica dusts from different coal mines have significantly different toxicities despite similar particle sizes and concentrations. Considerable clarification of the hazards associated with silica by medical authorities appears necessary.

Medical researchers have become increasingly concerned that small quantities of inorganic and other materials in the coal mine dust may add to the health hazard. The Bureau initiated several programs to develop laboratory analytical methods to measure the concentrations of assorted materials in anticipation that standards may be established. In addition, techniques were developed for measuring the surface areas and density of different size fractions in the respirable dust, in anticipation that such information would be of medical value. However, medical authorities have been hesitant to promulgate new standards in these areas, and only one program examining carcinogenic organic compounds in respirable dust has been continued.

CONCLUSION

The final objective of the present Bureau program is to provide advanced technology to control airborne respirable dust in coal mines by 1975 and preferably earlier. An assortment of approaches is being explored, for it is unlikely that a single technique will be equally suitable for the diverse mining operations. The present respirable dust problem is almost unique in industry because controlled experiments are difficult to perform, dust samplers are imperfect, and the environment is exceedingly hostile.

REFERENCES

1. P. Dessauer, et al, Annals of the New York Academy of Sciences, v. 200, 1972, p. 220.

INVESTIGATION OF MATERIALS FOR USE AS A MINE SEALANT/COATING, J. R. Carlson and W. P. Banks, Continental Oil Company, P. O. Box 1267, Ponca City, Oklahoma 74601.

The deterioration of rib-roof surfaces in coal mine entries which must be maintained for many years is a serious problem. A coating of sprayed urethane foam is known to effectively control deterioration in many cases, but at the same time poses a fire hazard. This paper presents an overview of recent work done with Consolidation Coal Company to find an effective, non-hazardous coating. Performance criteria are summarized for various mine conditions and are related to desired basic material properties. Results of laboratory and field tests on several types of materials using varied approaches to the problem are discussed. Comparisons are made on the safety, performance and economics of these materials.

THE EXTINCTION LIMITS OF AN ESTABLISHED FLAME

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INTRODUCTION

Many coal mine explosions originate when the methane-air mixture at the working face is ignited. The air motion resulting from the initial combustion causes the coal dust layer on the walls to become stirred into the air ahead of the propagating flame. The explosion process then becomes one of a propagating coal dust methane flame. Therefore, any device which is designed to extinguish the flame by adding some sort of suppressant to the unburned air must be effective with coal dust methane flames of varying proportions. It is, therefore, essential to have a knowledge of the effectiveness of various suppressants and the mechanism by which they work.

In this project, we are developing a technique to study both the effectiveness and suppression mechanism for various solid and gaseous suppressants in methane coal dust air flames. In this paper, we are reporting some initial results dealing with the effect of gaseous suppressants on a gaseous methane air flame.

Traditionally, the flammability of such fuel-air suppressant mixtures has been determined by observing the upward or downward propagation of a flame over a fixed distance in a relatively large diameter tube after ignition at the open end of the tube (1). There is, however, some question as to the applicability of this type of data to the case where a flame propagates from a fully flammable region into a region that contains a suppressant.

This paper describes a new technique for determining flammability limits using a large steady flow burner in which the suppressant mixture is placed in contact with a flame propagating through a mixture devoid of suppressant in an attempt to more realistically model the mine situation.

THE BURNER

In order to investigate the problem of direct extinguishment, a special steady flow burner was constructed. Provisions have been made for the use of coal dust as a fuel and solids as suppressants although they were not used to obtain the results discussed in this report. The basic objective of the burner design was to obtain two relatively large area streams, one of which will support a steady oblique flame sheet such that the flame can be made to propagate from this fully flammable region into another region containing suppressant. This was accomplished by dividing the flow areas at the burner head in the manner shown in Figure 1.

The two inner rectangular regions of this burner are fed by flows that contain only a fuel-air mixture for the larger annular shaped

rectangular region and fuel-air suppressant mixtures for the central rectangular region. The outer of these two regions therefore provides a typical non-suppressed premixed laminar flame as an ignition flame while the inner region contains a flow in which a suppressant may be added to the mixture to test for flammability limit behavior. The flow rates and composition of each region may be varied and measured independently using rotameters. The nitrogen flows along the two short edges of the burner prevent flame attachment at the end of the burner and facilitate end-on observation of the flame (i.e., observation along the major axis of the burner). The air channels along the longer outer edges of the burner shield the outer edges of the flame from external disturbances and can be used to stabilize large diffusion flames in the annular rectangular flow regime. Flow diffusers have been placed in all of the flow streams below the burner head in order to obtain a uniform flow velocity in each outlet region of the burner. The final exit plane of the burner is filled with over 2000 closely packed 1/8 inch stainless steel tubes which are long enough to develop and stabilize a fully laminar flow at the burner head. These tubes also serve to quench the flame and prevent flash back into the body of the burner at low flow velocities. In addition, as shown in Figure 1, the burner head contains a number of parallel stainless steel shim stock spacers which help stabilize both the flow and the flame.

THE TECHNIQUE

The flame shapes that are observed in this burner are actually quite complex and, in general, depend upon the stoichiometry of both the surrounding ignition stream and the central suppressant stream as well as their velocities.

It has been found that in the ignition stream a single large tent flame, open at both ends, may be easily stabilized on the rich side even though on the lean side it is easier to stabilize a flame which attaches to most of the shim spacers and thereby producing a shorter height multiple tent flame which is also open at the ends. In all these cases, the inner test stream, which may contain suppressant, is contacted on four sides by a hot product stream issuing from the ignition region.

In the experiments on flammability, we are interested in how this central stream behaves as its composition passes through the flammability limit of the mixture. Preliminary observations showed that for suppressant and ignition stream equivalence ratios which were lean-rich or rich-lean and for a flammable mixture in the suppressant stream the burner always exhibited a central tent flame in the suppressant stream which was anchored at the rectangular stream divider edges. However, for a rich-rich or lean-lean interface, the flame did not attach at the interface divider edge but instead propagated across the interface to produce a flame which, in general, situated itself at a different oblique angle than that which existed in the ignition stream. These two behaviors are illustrated for a section of the flame in Figure 2.

It was observed that if one viewed the flame along the major axis of the burner as one altered the suppressant stream composition from flammable to inflammable, the included angle of the central tent flame at first rapidly approached an angle which was near zero and then remained at or near that small angle with further changes in composi-

tion. Interestingly enough, this type of distinct limit behavior was observed for either of the interface geometries described in Figure 2.

Based on the above observations, the following procedure for determining flammability limits was developed. A premixed laminar flame was established in the outer (non-suppressed) stream, while the mixture in the inner (suppressant) stream was set well beyond the flammability limit in order to prevent flashback. The flows were adjusted so that the inner stream velocity always remained close to that of the outer stream.

During an experimental run the composition of the inner (suppressant) stream was changed systematically so that its composition varied in steps from a completely non-flammable to a completely flammable mixture. This was done by either changing the percentage of fuel (methane) or the percentage of suppressant depending upon the region of the flammability curve that was to be investigated in that particular run. Observations of the flame angle were made through a transparent plexiglass window located approximately three feet from the burner head. For each of the flow settings (i.e., for each of the compositions of the suppressant stream) the operator placed his eye in line with each flame tent edge and drew lines parallel to each side of the flame sheet as it existed just inside of the suppressant stream. A transparent plastic sheet was mounted on the plexiglass window for this purpose. In this way an accurate measurement of the included flame angle was obtained for that particular set of rotameter settings. This included angle between the two flame sheets was divided by two to obtain the oblique flame angle α . Since this operation was performed for a number of points during a systematic change in composition, the technique in effect involves titrating the flame for an end point corresponding to the flammable limit of that particular mixture. Figure 3 illustrates the experimentally obtained relationship between the included flame half angle, α , and the fuel concentration in the suppressant stream for three different suppressant percentages. In this case the percent methane was the titration variable. Observe the decrease of α towards zero with a distinct change in the slope of the alpha-fuel composition curve when the angle becomes close to zero. In some cases, the stream lines were slightly divergent or convergent so that the maximum inflection in the curve (end point) was observed for values of alpha slightly less than or slightly greater than zero. In actual practice, the flammable limit composition was chosen as the point at which the flammable and inflammable branches of the alpha, percent composition curves intersected as indicated by the smooth extrapolation of these curves. It should be noted that it was still possible to observe an "apparent flame sheet" in our burner even though the suppressant stream composition was well outside the flammability limit. This can be attributed to reactions occurring as the fuel in the suppressant stream encounters hot combustion gases from the ignition stream due to diffusional processes. Thus, some observable reactions were occurring although under these conditions they were not of sufficient magnitude to support a propagating flame in the suppressant stream.

ACCURACY AND REPRODUCIBILITY OF THE TECHNIQUE

In order to check on accuracy and reproducibility, a few titration runs were repeated at different suppressant flow velocities and on different days. A comparison of the α versus CH_4 percent for these cases is shown in Figure 4.

Both of these curves illustrate that the reproducibility of the data is $\pm 1/2$ percent CH_4 and that the location of the inflection point is relatively insensitive to the flow velocity. However, sensitivity of the technique is determined by the flow velocity to some extent because at high flow velocity and at high suppressant concentrations, the maximum value of α becomes very small, as is shown in Figure 3. Therefore, the experiments were always performed with the lowest possible suppressant flow velocity for the particular desired titration.

We feel that the equivalence ratio of the external ignition stream may possibly have an effect on the end point, i.e., on the measured flammability limit. However to date all the data has been taken with a lean surrounding ignition stream. This is the reason why the rich end of the α curves in Figure 4 all have inflexible branches whose value of α is greater than zero degrees. Under these conditions the rich branch of the flammability curve is always measured from an attached flame and flow divergence does not occur easily. The lean branch, on the other hand, is always oriented as shown in Figure 2b and under these conditions central stream divergence occurs relatively easily. Thus, some of the lean end points occur for relatively large negative values of α .

RESULTS

The effects of four suppressants (Ar , N_2 , CO_2 , and Halon 1301) on the flammability limits of a methane-air flame are shown in Figure 5. The flammability limits determined by this technique were generally found to be wider than those determined by standard vessel propagation techniques. The lean limits obtained tended to be about 1 percent CH_4 leaner than vessel propagation limits and conversely, the rich limits were about 1 percent CH_4 richer than vessel propagation limits for a given percentage of suppressant. The only exception noted was the case of Halon 1301 in which the rich flammability limits were approximately 2 percent CH_4 richer than those from vessel propagation limits (2).

It was observed that the rich limits for N_2 and Ar were indistinguishable and that the lean limits were very close, although the N_2 lean limits were 10 percent higher than the values of Ar lean limits. The results of other investigators (1) show a substantial difference between N_2 and Ar limits. The reason for the differences in the results is not clear at this time. One of the features of the new technique which may have a bearing on the comparison with other techniques is the lack of a heat sink for the suppressed gases. Thus, the thermal conductivity of the gases may have a stronger influence in one system than in the other. In addition, since the new technique involves the use of a forced-flow system, the physical properties of the gases could also have varying degrees of influence in the different techniques.

CONCLUSIONS

A technique has been developed for the measurement of the extinction limits of well-established flames by gaseous suppressants. The results of this technique are similar to the results of conventional techniques, although the flammability limits are wider for this technique than those obtained for conventional techniques.

ACKNOWLEDGMENT

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REFERENCES

1. Coward, H.F. and Jones, G.W. "Limits of Flammability of Gases and Vapors" Bulletin 503, U.S. Bureau of Mines, 1952.
2. Kuchta, J.M. and Burgess, D.S. "Effectiveness of Halogenated Agents Against Gaseous Explosions and Propellant Fires" Proceedings of Symposium on an Appraisal of Halogenated Fire Extinguishing Agents, National Academy of Sciences, p. 257, 1972.

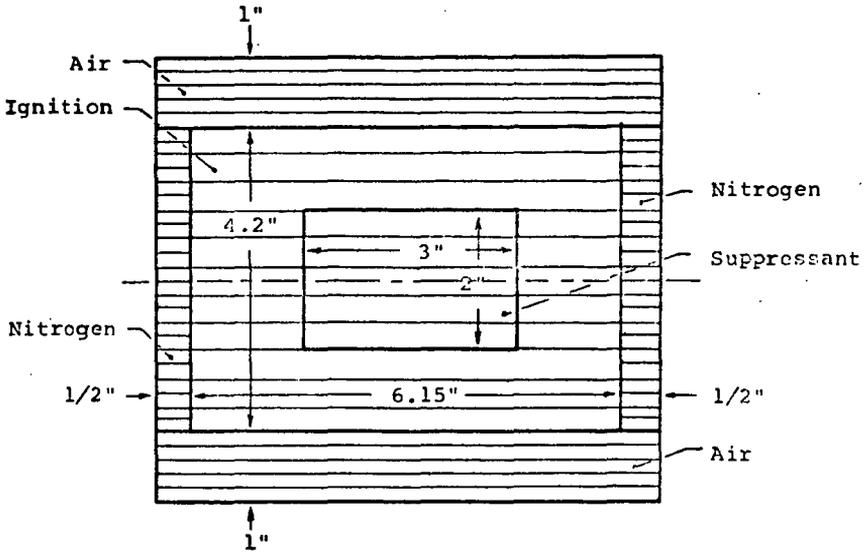


Figure 1. The burner head showing the different flow regions and the shim stock sheets (thin lines) used as flow straighteners and flame holders.

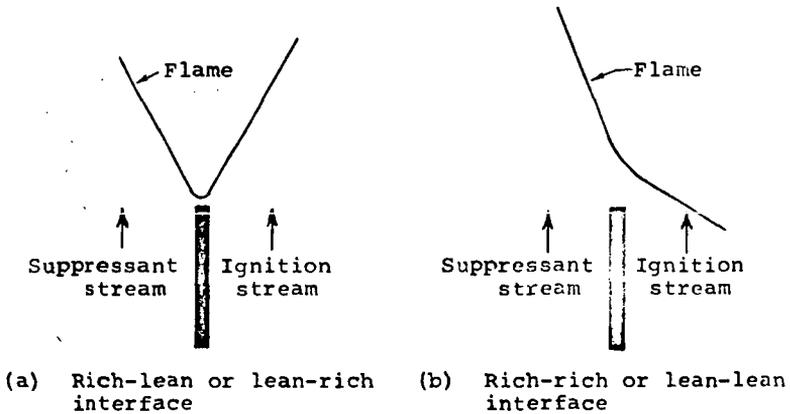


Figure 2. Flame geometries as determined by relative equivalence ratios at the interface.

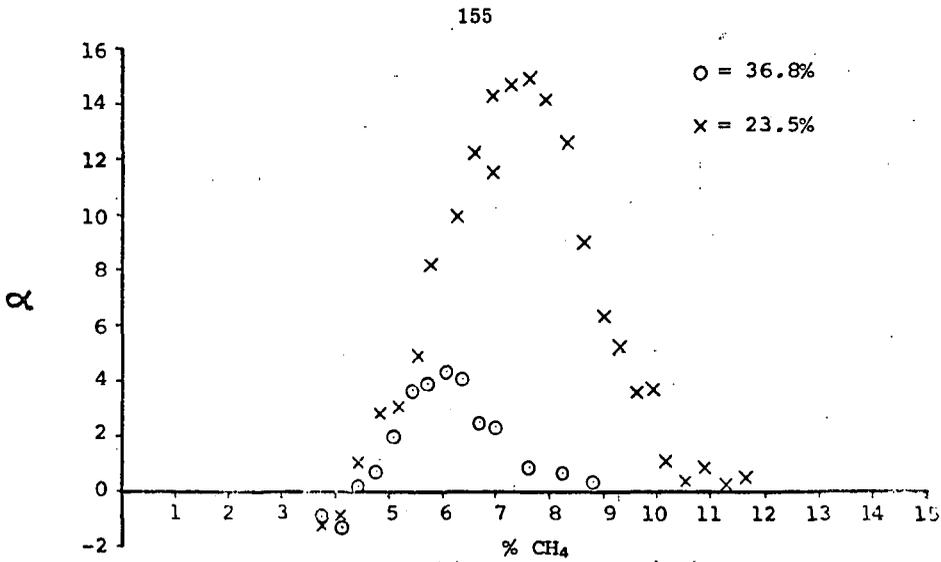


Figure 3. Effect of fuel concentration on flame angle.

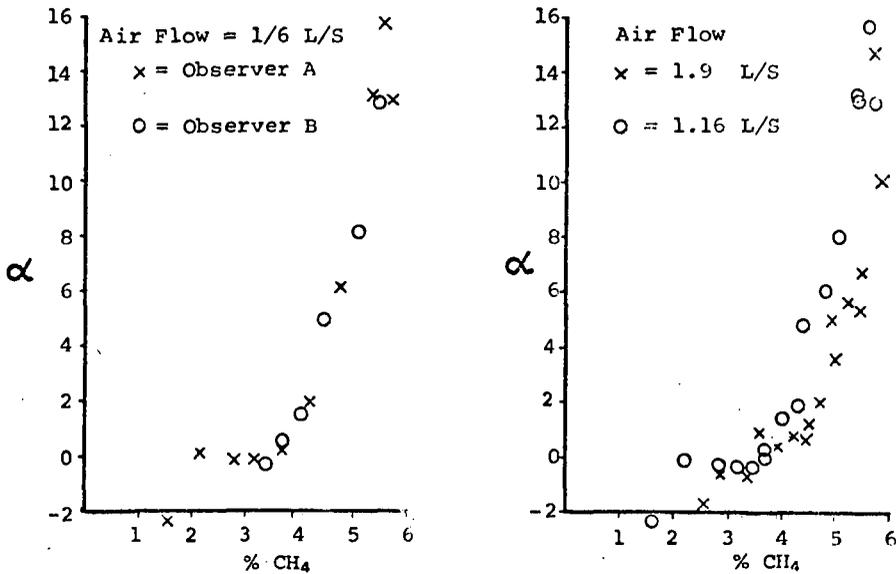


Figure 4. Effect of observer and flow velocity on end point.

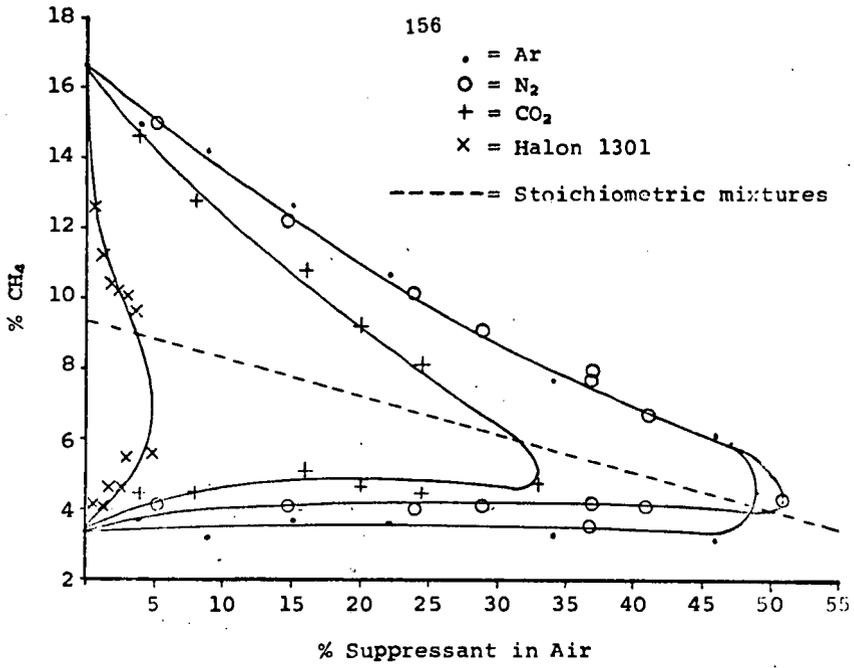


Figure 5. Flammability limits for methane-air suppressant mixtures.

THE USE OF GEOLOGICAL INFORMATION TO DESCRIBE COAL MINE ROOF CONDITIONS.

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Since bad mine-roof conditions directly affect mine production and safety, it is important to be able to detect or identify the location of areas where such conditions are likely to be encountered in undeveloped portions of coal reserves. From our studies of the geology associated with the coal seams in our Cambria Division mines in central Pennsylvania as well as from discussions with our coal mine operators, we worked out a model based on geological variables that will make it possible to identify areas of potentially bad mine-roof conditions prior to mining. The geological factors in this model are: the intensity, direction and extent of surface fractures as determined from aerial photographs; the nature and thickness of the strata immediately above the coal seam; the thickness of the overburden; and the presence and extent of ancient stream-channel deposits. Taken together, these geological factors in a conventional mine-development plan should make it possible to assign a relative ranking of the roof conditions that are likely to be found as mining progresses over the extent of the coal reserve. Of course, quantification of this ranking will require a thorough knowledge of the independent role of each of the geological variables in mine-roof conditions, and this will be accomplished as mining advances over a larger portion of the area under study. Once the required information is obtained, the model will not only enable us to pinpoint the location of bad mine roof in coal reserves but should ultimately provide the guidelines for working out mine-development plans that will result in optimum productivity and maximum safety throughout the life of the coal reserve.

ENGINEERING ASPECTS OF COAL MINE VENTILATION SYSTEMS

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INTRODUCTION

The single most critical factor affecting the health and safety of workers engaged in the coal-winning process is the mine environment; which is broadly defined as the space in which man works when underground and includes the physical and chemical conditions of the surrounding enclosure and the nearby mining equipment. A fundamental objective of a mine ventilation system is to supply this environment with an adequate and sufficient quantity of uncontaminated fresh air. It is the largest single logistics application in health and safety for underground coal mining operations. It is sometimes necessary to course intake air through several miles of underground airways in order to achieve this purpose. Leakages will be severe and yet an adequate supply of fresh air must be delivered to the last open cross-cut outby of the active face. This process is identified as quantity control. Equally important, if not more crucial, is the quality control process dealing with the control of respirable contaminants liberated during mining operations.

The Federal Coal Mine Health and Safety Act of 1969, Sec. 303(b), stipulates that the primary ventilation system must deliver at least 9,000 cfm of uncontaminated fresh air to the last open cross-cut. Auxiliary ventilation systems are required to supply 3,000 cfm to the coal face. Sec. 202(b), (2), of the 1969 Act states that each mine operator shall continuously maintain an average concentration of respirable dust in the mine environment during each shift at or below 2.0 mg/m³. Respirable dust can be defined as solid coal particles in the minus 10 micron range which become airborne and do not settle easily.

With respect to gaseous concentration, the 1969 Act states that no working section of the mine shall contain more than 0.5 percent carbon dioxide and no harmful quantities of other noxious or poisonous gases such as the oxides of nitrogen. The concentration of methane should at all times be maintained below one percent. A split of air returning from any working section shall contain no more than 1.5 percent of methane and air that has passed by an opening of any abandoned area shall not be used to ventilate any working place in the coal mine if such air contains more than 0.25 percent methane. Methane concentration in the returns from the bleeder entries should not exceed 2.0 percent, and no air that has passed through an opening which is inaccessible for examination shall be used to ventilate any active areas. While the air quantity requirements alone can easily be met, the governing condition in most mines is the dilution requirements for quality control. A sufficient quantity of air is required to render harmless and carry away noxious and respirable pollutants.

Good ventilation is essential for efficient mine operation. On one hand, available ventilation facilities place certain limitations on production level. On the other hand, ventilation possibilities and requirements cannot be defined other than in relation to a production plan. Thus, ventilation and production planning are interdependent. Experience

in the last decade has shown that the development of larger and more powerful machines for higher production rates calls for increased sophistication in ventilation planning. Over the last twenty years, ventilation standards have risen steadily and stringent regulations have been enacted. It is also evident that in the near future, ventilation requirements will become increasingly more demanding. The trend is a consequence of change in both mining conditions and equipment. These changing conditions, such as higher production from fewer mines, extraction of thinner seams, increasing depth of workings and additional installed horsepower, influence the planning and design of ventilation systems. It is, therefore, becoming increasingly important that ventilation requirements should be adequately assessed at the planning stage.

COMPUTERS IN MINE VENTILATION STUDIES

The role which computers can play in evaluating ventilation parameters and processes is tremendous. During the past decade, the role of the digital computer has expanded in an unprecedented manner from purely commercial applications to problems involving the design, maintenance, and control of technical systems. Major development of computer applications for mine ventilation has been in the field of ventilation planning. When an enormous amount of data has been collected, a computer can be used advantageously to relieve the ventilation engineer from the tedium of routine repetitive calculations. In addition, digital data processing has both short and long term significance. Long range data processing involves such observations which are routine and are being continually recorded. An accumulation of such data could be tested for statistically significant trends (6). This information could then be used in planning the ventilation of new sections or adjacent mining operations. Short term data processing involves spot testing and checking of such parameters as fan performance, optimum roadway sizes, air horsepower losses, and statistical examination of information surveys.

Development of computerized methods of calculations is only one aspect of the use of digital machines by research personnel. An example of ventilation research which is completely computer dependent is the theoretical investigations to study the patterns of methane flows and rates into the mine openings from the roof, sides, and floor. Mathematical models have been developed which enable the computer to simulate gas flow rates while varying such parameters as the position and emissivity of the gas sources, boundary pressures, and the permeabilities of the intervening strata.

The application of energy and mass transport phenomena, or more appropriately, physico-chemical principles, to quantify mining engineering parameters for quality and quantity control of the mine environment has taken an unprecedented outlook since the advent of digital computers. These machines enable complex problems in ventilation to be modeled and solved numerically. It is, therefore, not surprising that solution of problems of temperature and humidity, fluid flow dynamics, and toxic emission dilution in the mine environment are being attempted through mathematical models and computers. The parameters obtained from such numerical estimation can then be utilized in engineering and process control.

Today, more than ever, much attention is being focused on the development of a system of remote monitoring and control of environmental parameters. Significant progress is being reported in remote sensing

and monitoring of environment. Some work has already been done in the United Kingdom on automatic monitoring of a methane drainage system. Such automatic controls can be extended to other environmental parameters such as heat and humidity, temperature and dust levels. As studies are perfected in the determination of suitable parameters for control, their range of operation and choice of monitoring sites, these advances can eventually be used to develop on-line computer control systems of the complete mine environment.

VENTILATION NETWORK ANALYSIS

The theory of network analysis has long played an important role in many branches of engineering sciences. Transportation and other distribution problems have been solved by applying tools of network analysis. Literature review reveals that the application of this theory to mine ventilation planning and network analysis is a recent development. There has, however, been a growing awareness in recent years that certain concepts of network theory can be successfully applied in many other fields as well. It is, therefore, not surprising that in the last ten years, these tools have found increasing application in mine ventilation network analysis.

The major advance in ventilation network analysis in the last decade has been, therefore, the development of computer programs capable of developing and solving the systems of equations defined by the junction and pressure laws. Ever since Hardy-Cross iterative technique (4) was adapted and modified by Scott and Hinsley (13) for the solution of ventilation network problems, several programs have been developed to solve for mine ventilation parameters. A brief description of most of the quantity flow mine ventilation programs is presented by Geiger (5).

METHANE GENERATOR MODELS

The quantity of methane emitted into the mine atmosphere and the movement of gas through solid coal and the adjoining country rock are dependent on gas emissivity, boundary conditions, and the initial gas distribution pressures and the combination of natural and mining factors. Functional relationships between these factors are not yet known. Consequently, the development of rigorous mathematical equations to simulate methane flow into the mine air is difficult, and to date, no model has been reported which is capable of such a function. Several researchers in many parts of the world have attempted to quantitatively describe the pattern of gas emission in mines as functions of seam characteristics and the confining gas pressure (1,2,9), none with complete success.

Thus far, empirical formulas available for the calculation of gas released from underground sources appear amenable to analytical computation. These estimations are at best only crudely approximate. The numerical methods available have not been made practical enough for use in the industry. Therefore, a relationship amenable to numerical analysis and practical enough for application in the industry would provide the flexibility lacking in analytical approaches. The mathematical model developed and presented by Owill-Eger (10) is yet another attempt to correlate as many flow governing parameters in a single equation. This model solves gas flow-rates into mine workings from coal seams and intervening layers of rocks and is designed to handle only two dimensional steady state flow systems. It represents a modified gas diffusion system

for flow through porous media. Mathematical considerations and derivation of the flow equation are presented in the reference.

Various investigators have shown that temperature also affects the rate of gas flow. However, at temperatures usually encountered in mines, methane has a very low rate of diffusion. As long as shallow deposits are being extracted, the effect of temperature on the rate of gas flow will remain insignificant. At great depth where rock temperature will be high, temperature will affect flowrate of gas and has to be considered. The chemistry of multi-component multi-phase systems has also been considered in a recent report on methane flow modelling (12). It has been pointed out that the presence of water affects the migration characteristics of methane in coal seams even though the two fluids are said to be chemically unreactive.

HEAT AND HUMIDITY CONTROL

Temperature and humidity control is important in the face area, or more generally, any active section of the mine where men are exposed to the environment for as long as a shift. Factors that affect the temperature of the ventilating air in such areas are the presence of men and machines, the temperature of the incoming air, chemical oxidation of coal, evaporation of water which may extract part of the latent heat from the air and the heat transfer from the surrounding strata. This last factor is very significant especially in deep mines where wall rock temperature is much higher than that of the incoming ventilation stream. In the U.S. coal mines today, rise in temperature and humidity as a result of heat transfer from the wall rock is not significant because coal seams being mined presently are very shallow - less than 1500 feet. However, these coal reserves are being depleted at a very fast rate. It is only logical to say that operation at great depth in the near future is inevitable. In deep metal mines, heat transfer from the enclosing strata can be significant and, consequently, techniques for predicting air temperatures have been developed. The first requirement in mathematically formulating heat transfer problems is knowledge of the thermal properties of the strata surrounding the roadway or model area. Jones (7), Jordan (8), and Paulin (11) have presented details of mathematical considerations which can be taken to estimate such parameters if the thermal history of the region is unknown. Extensive work in this area is reported in South Africa and in Japan, Amano and Shigeno (3) and Vance and Kathage (15).

DUST IN COAL MINES

Coal dust is defined as any solid coal particles smaller than 100 microns (1 micron = 10^{-4} cm) which become airborne when disseminated. During the coal winning process, dust is inevitably generated by the mining machines. Transfer points and transport systems, and high air velocities, contribute to the dust problem in the mine roadways. Inadequate suppression of coal dust can lead to explosion hazards and the coal workers' pneumoconiosis. Pneumoconiosis is supposed to be caused by the inhalation of respirable coal dust (~ 10 micron) for extended periods of time.

In addition to the human suffering, cost of compensating pneumoconiosis victims is high. For example, in the fiscal year 1972, the Department of HEW provided \$384 million for this cause which marked an increase of \$142 million over the 1971 budget (14). This cost is expected

to rise even more steeply in the next few years as more and more coal workers become eligible for compensation benefits.

In the light of economics of remedial actions due to dust hazards, the prediction of dust content in air is very necessary from health and safety points of view. The amount of coal dust deposited along the mine roadways is of paramount importance because it serves as the assessment of the dust explosion hazard, and it can be used to calculate the amount of incombustible dust required for rock-dusting. Mechanisms of dust deposition and quantity estimations have been discussed at length (5). Two processes have been employed to control dust levels at the working face. These are 1) water sprays, and 2) face ventilation to reduce the concentration of respirable coal dust. Although water sprays reduce dust load handled by ventilation systems, the current spray techniques are not effective in the control of respirable dust (5). Currently, face ventilation is the most commonly used procedure.

A dust control program should, therefore, be able to deal effectively with both the fine and ultra-fine dust sizes. Work in the area of dust characterization, particularly with respect to the size-consist, chemical properties is reported (14). Under the Coal Mine Health and Safety Act of 1969, research on dust control has accelerated.

HAZARDS FROM DIESEL EQUIPMENT

The principal hazards of using diesels underground have been identified as:

- 1) The transportation and storage of a highly flammable and volatile fuel with resultant hazards of fire and/or explosions.
- 2) Unhealthy conditions caused by the discharge of toxic substances from the engine exhaust.
- 3) Ignition of flammable atmospheres by hot surfaces of the engine, such as exhaust manifold or by burning particles of carbon from the exhaust gas.

It has been long established from engineering tests that diesel exhaust quantities are related to displacement and speed characteristics of the engine, the design of the engine, and the fuel-air ratio needed to produce useful power. It has also been recognized that diesels under proper control produce only minor amounts of toxic and noxious fumes although there is an irreducible limit for the exhaust gases. The contaminants that are released into the mine atmosphere must be diluted immediately to minimize local concentrations. Furthermore, since multiple units usually will be operating in the same air stream, there is a cumulative effect on contaminant concentrations. The rate of contamination, therefore, is related to the volume and velocity of the ventilating air, frequency and duration of engine operations, and engine load and location. Ventilation, in addition, affects the rate at which the contamination moves through the workings. Because of Threshold Limit Values (TLVs) and excursion rates allowed on some of the contaminants, the calculations for ventilation requirements must take into account the time variant characteristics of the contaminant concentrations and average them over the entire operating period of the mine. The objective of a research program at Penn State is the development of a digital simulation model to study the effect of using diesels underground on mine ventilation systems (16).

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SUMMARY

In its most elementary form, coal mining is materials handling and consists of removing in-situ coal from multiple mine origins to final destinations. There are certain special environmental considerations peculiar to underground mining. These include the problems of toxic, noxious, and explosive atmospheres caused by gases and dust. A fundamental objective of a mine ventilation system is to supply the mine environment with an adequate quantity of uncontaminated fresh air to deal with the control of respirable and explosive contaminants and to provide for the health and safety of the workmen. This paper has briefly reviewed some recent research programs presently underway in the mine ventilation area.

It is difficult to quote an average cubic feet per minute ventilation figure for coal mines. The weighted figure is unknown and really has no significance. However, in a modern coal mine, for each ton of coal produced each day, on an average, 4-6 tons of air is circulated. Similarly, cost figures are very difficult to obtain from the industry because of the concern for releasing proprietary information. Also, accounting principles vary from one mine to another to make comparisons less meaningful. However, as a typical figure for a group of mines, operating costs are 15¢ per ton and capital costs 25¢ per ton, accounting for about 6% of the total costs. However, the indirect costs of mine ventilation, though difficult to ascertain, can be quite high. Severe disruption of work and losses in production cannot be ruled out. In any case, the end results of inadequate control in mine ventilation can be sudden and catastrophic e.g., explosions, ignitions, fires, suffocations, etc.

Much research - theoretical, empirical, laboratory, and field studies - has been done and is being done toward the identification and quantification of the hazards posed by inadequate ventilation. Model studies of gas and heat flow problems provide the necessary input parameters to sophisticated quantity and quality control models. Research efforts are also aimed at the determination of suitable parameters for process control, their range of operations, the development of remote sensing and monitoring equipment, choice of monitoring sites, etc. In the future, it is not difficult to foresee a highly sensitive monitoring system coupled to computers that are programmed for automatic corrective action.

REFERENCES

1. Airey, E. M., 1968, "Gas Emission from Broken Coal - An Experimental and Theoretical Investigation", Int. J. Rock Mech. Min. Sci., Vol. 5.
2. _____, January 1969, "Diffusion of Firedamp in Mine Airways", The Mng. Engr., No. 100, Vol. 128.
3. Amano, K., and Shigeno, S., 1969, "An Underground Ventilation Network Analysis and Estimation of Temperature of Air Current", A Decade of Digital Computing in the Mineral Industry, edited by A. Weiss.
4. Cross, H., 1936, "Analysis of Flows in Networks of Conduits or Conductors", Bull. Engrg. Exp. Sta., Univ. Ill., No. 286.
5. Geiger, G. E., September 1, 1972, "Development of an Air Quality Simulator for Coal Mines", U.S.B.M. Project No. Go101478 (MIN-35).

6. Jolliffe, G. V., February 1970, "The Emission of Methane from Rapidly Advancing Coalfaces", *The Mng. Engr.*, Vol. 129, No. 113.
7. Jones, C., June 1964, "Air Temperature Along a Main Intake Roadway", *Coll. Guard.*, Vol. 208.
8. Jordan, D. W., 1965, "The Numerical Solution of Underground Heat Transfer Problems - I. Methods Relating to Dry Roadways", *Int. J. Rock Mech. Min. Sci.*, Vol. 2, pp. 247-270, Pergamon Press Ltd., London.
9. Lidin, G. D., Airuni, A. T., Klebanov, F. S., and Matrienko, N. G., 1964, Control of Methane in Coal Mines (Translated from Russian), Israel Program for Scientific Translation, Jerusalem.
10. Owili-Eger, A. S. C., March 1973, "Simulation of Quantity and Quality Control in Mine Ventilation", M.S. Thesis, The Pennsylvania State University, University Park, Pennsylvania.
11. Paulin, A., 1970, "Thermal Conductivity of Porous Materials", *Mining and Metallurgy Quarterly*, No. 1, NOLIT Publishing House, Belgrade, Yugoslavia.
12. Price, H. S., and Abdalla, A. A., 1972, "Mathematical Model Simulating Flow of Methane and Water in Coal Mine Systems", U.S.B.M. Project Contract No. S0110752, PMSRC, Int. Comp. Appl., Houston, Texas.
13. Scott, D. R., and Hinsley, F. B., December 1951, "Ventilation Network Theory", *Coll. Engrg. Parts 1-4*, February, April, June, and December, 1951.
14. Thakur, P. C., September 1971, "Mass Distribution, Percent Yield, Non-Settling Size and Aerodynamic Shape Factor of Respirable Coal Dust Particles", M.S. Thesis, The Pennsylvania State University, University Park, Pennsylvania.
15. Vance, W. E., and Kathage, B. A., March 1967, "A Model Experiment to Determine Ventilation Cooling Occurring Around Underground Roadways", *J. Mine Vent. Soc. of S. Africa*, Vol. 20, No. 3.
16. Stefanko, R., and Ramani, R. V., January 1973, "The Effect of Diesel Equipment on Mine Ventilation Systems", Paper presented at the U.S. Bureau of Mines' Diesel Symposium, Pittsburgh, Pennsylvania.

Respiratory Protection and Respirable Dust
in Underground Coal Mines

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I. INTRODUCTION

During the past several years, and especially as a result of the enactment of the Federal Coal Mine Health and Safety Act of 1969, much attention has been focused on respirable coal dust and various means of preventing the inhalation of such dust, including the use of dust respirators.

The use of respirators in coal mines is certainly not new and, in fact, almost 40 years ago the Bureau of Mines first established performance requirements under Schedule 21(1).^{*} However, there was little information available about the usage of respirators in the field and, importantly, there was no information on how effective are dust respirators under actual working conditions. Consequently, the National Institute for Occupational Safety and Health sponsored a research project with Eastern Associated Coal Corp., with the Harvard School of Public Health acting as a subcontractor. The three major objectives of this project were:

- a. To determine, by means of a field survey, the current status of respirator usage with regard to duration and frequency of use, types, and maintenance levels.
- b. To determine protection factors provided by respirators worn by working miners.
- c. To make recommendations on ways to improve existing units, or on research needed to develop new types of respiratory protective devices for coal miners.

II. FIELD SURVEY

A field survey (2), which was carried out in 1970 and 1971, involved visits to 47 mines and interviews with 511 supervisory and underground mining personnel; personnel interviewed included representation of all of the major job classifications found in underground mining operations.

Results from this survey showed not only was there rather widespread possession and usage of dust respirators (a small percentage of which, incidentally, were not Bureau of Mines approved) but the working miners expressed strong sentiments for the need for use of respirators, Table I.

*Underlined numbers in parentheses refer to references at the end of this paper.

TABLE I. Need for Use of Respirators in Coal Mines

	Percent of Underground Work Force*
Generally Needed	42
Used Whenever Dust is Present	45
Used Only When Necessary	4
Needed, but are Hard to Wear	8
Prevent Dust to Make Usage Unnecessary	1

*428 people in various job classifications,
plus 17 Section Foremen

It was also found that virtually all coal miners use respirators on an intermittent basis, i.e., putting the respirator on and taking it off a varying number of times during a work shift. Based on intermittent use, a significant number of miners found the presently available, approved respirators to be only marginally acceptable or unacceptable, Table II.

TABLE II. Respirator Acceptability Based on Intermittent Use

	Percent of Underground Work Force*
Completed	2
Generally	64
Marginally	24
Unacceptable	10

*See Note on Table I.

Major complaints about current dust respirators in use could be placed in two categories, namely, breathing difficulties and physical discomfort, Table III, and, consequently, the miners want respirators that are more comfortable and provide easier breathing, Table IV.

TABLE III. Problems Associated with Respirator Use

	Percent of Underground Work Force*
Cause Breathing Difficulties	37
Physical Discomfort	55
Generally Cumbersome and Uncomfortable	13
Cause Perspiration	9
Interfere with Tobacco Chewing	9
Troublesome Head Harness	7
Respirator Too Large	6
Facepiece Troublesome	5
Dust Inside Mask	5
Improper Fit	1
Interference with Work	9
Restricts Vision or Interferes with Wearing Glasses	5
Exhalation Valve Troublesome	2
Interferes with Communications	1
Difficult to Carry	1

*See note on Table I.

TABLE IV. Improvements in Respirators Desired by Mining Personnel

<u>Improvements</u>	<u>Percent</u>	
	<u>of Underground Work Force*</u>	
	<u>A</u>	<u>B**</u>
Easier Breathing	19	28
Comfortable Facepiece	12	18
Smaller Unit	11	16
Comfortable Head Harness	11	16
Lighter Unit	6	9
Better Filter	5	7
Better Valves	2	4
Easier to Carry	1	2
Educate Men to Use Them	3	-
Cannot Be Improved	2	-
Do Not Know	<u>28</u>	<u>-</u>
	100	100

* See Note on Table I.

** Percentage Recomputed from Part A by eliminating last three items in Part A.

Further information on results of the field survey have been reported elsewhere.(2)

III. PROTECTION FACTORS

1. General

As mentioned previously, the field survey revealed that virtually all underground miners wear respirators only on an intermittent basis. This, coupled with the fact that the accumulated exposure of miners to respirable coal dust is considered to be of importance with respect to the incidence of coal workers pneumoconiosis, indicated two protection factors should be determined. One protection factor, entitled "Effective Protection Factor (EPF)", represents the amount of protection obtained by working coal miners over the entire work shift when the respirators are used intermittently and worn according to the miner's training and work habits. Therefore, EPF was determined, in the field, by sampling separately, but concurrently, the ambient air and the air inside the respirator facepiece; over the entire working shift the concentration of respirable dust was determined for each sample. EPF was calculated as follows:

$$EPF = \frac{DC_A}{DC_M} \quad 1)$$

where:

EPF = Effective Protection Factor

DC_A = Dust Concentration in the mine air

DC_M = Dust Concentration in the air in the respirator mask.

Since sampling was done over the entire working shift both DC_A and DC_M are time weighted average concentrations of respirable dust.

While EPF represents the protection provided to the working coal miner, it does not tell how much protection is provided by the half-mask respirator when the respirator is actually worn. Consequently, True Protection Factor (TPF), which is defined as the amount of protection the user receives when he is actually wearing the respirator and in accordance with the manufacturer's instructions, was determined by sampling separately but concurrently the ambient air and air inside the facepiece only when the respirator was worn; respirable dust concentrations were determined for both samples. TPF was calculated as follows:

$$TPF = \frac{DC_S}{DC_R} \quad 2)$$

where:

TPF = True Protection Factor

DC_S = Dust Concentration in the Mine Air in the Vicinity of Miner wearing the respirator

DC_R = Dust Concentration in the air inside the respirator facepiece.

2. Equipment and Procedure:

a. Equipment

For determining EPF's, mine air sampling was done with conventional personal mass respirable sampling equipment (3) in use throughout the coal industry. Air inside the facepiece of the respirator was sampled using the same mass respirable sampling equipment, Figure 1, with the cyclone mounted on the respirator and connected to a sampling port inside the respirator (4). Also, located inside the facepiece, Figure 2, was a thermistor which is a part of a time-of-wearing device (4) that was used to determine the amount of time the respirator was actually worn.

In the case of TPF, sampling of the mine air and the air in the mask was done using two GCA RDM-101 Respirable Dust Monitors (5) both equipped with the same 10mm AEC Cyclone as used with the personal samplers. Figure 3 shows the sampling equipment in actual use underground.



FIGURE 1 - TEST SUBJECT WEARING SAMPLING EQUIPMENT

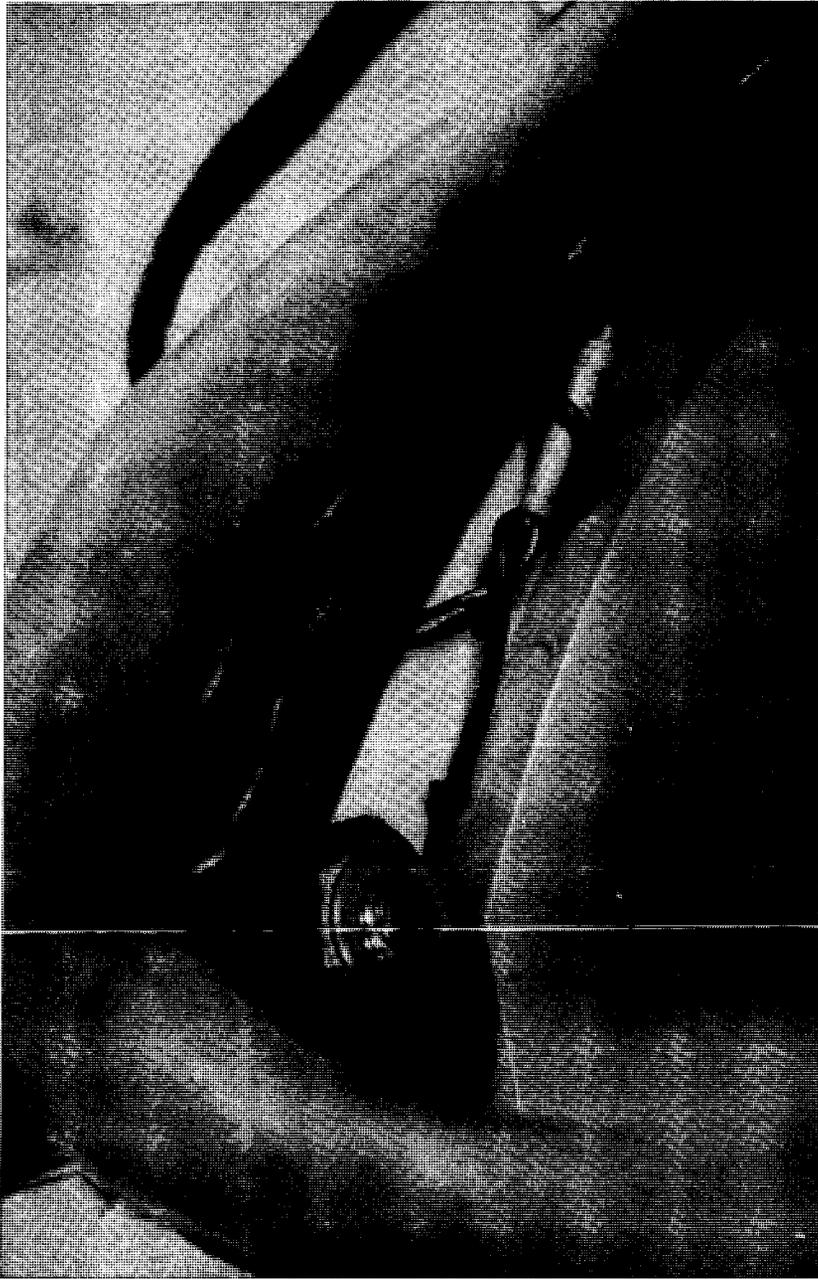


FIGURE 2 - INSIDE OF RESPIRATOR FACEPIECE SHOWING THERMISTOR

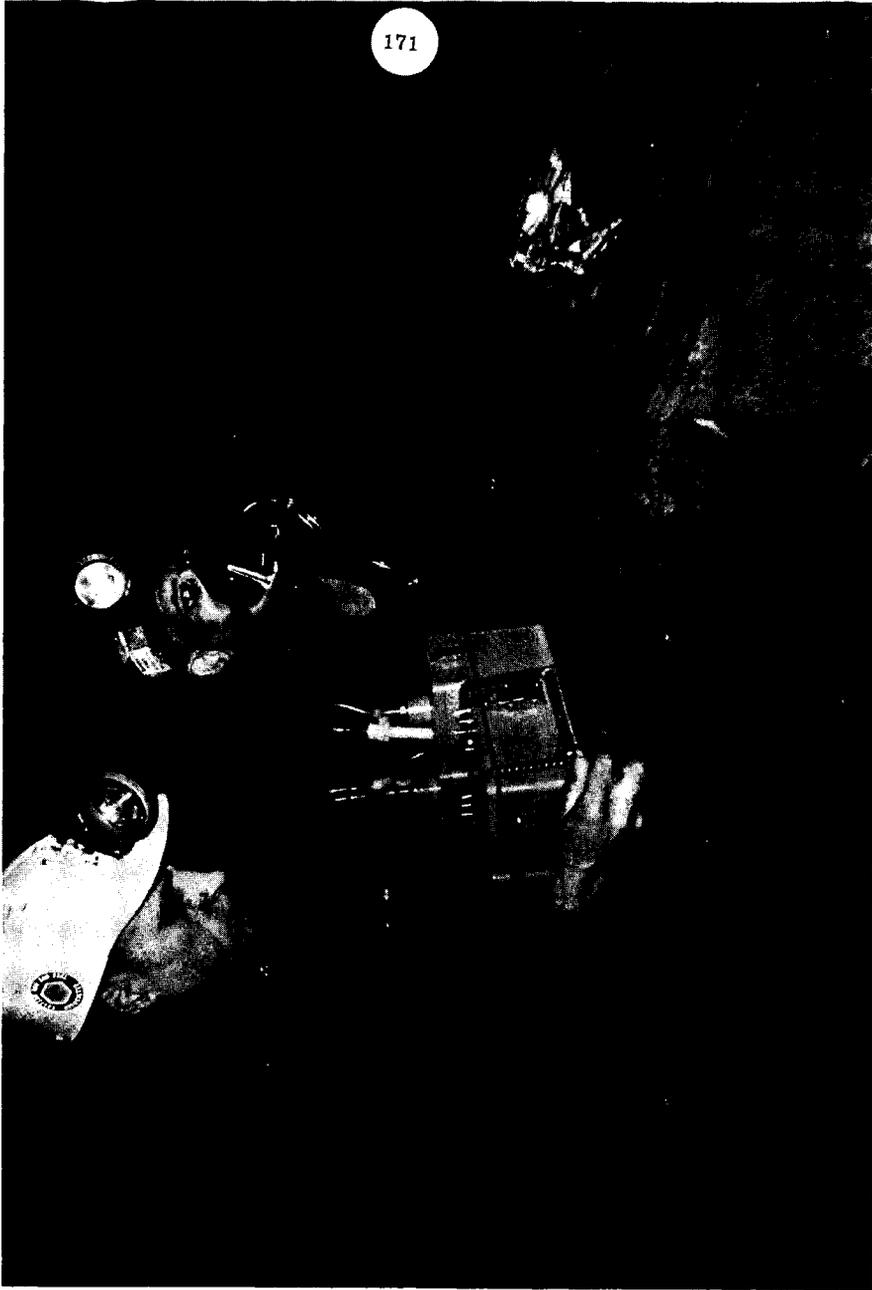


FIGURE 3 - TRUE PROTECTION FACTORS SAMPLING EQUIPMENT

b. Procedures

For EPF's, air and in mask sampling was done from the time each test subject miner started work until work ceased at the end of the shift, except for the lunch period. As shown in Table V, testing was done in five different mines and involved 208 man shifts and 13 different job classifications, mostly those at the working face. Five different models of respirators were used.

TABLE V. Scope of Testing - Effective Protection Factor

No. of Mines	5
Days of Testing	26
Man Shifts of Testing	208
<u>Test Subjects (by job classification)</u>	
Continuous Mining Machine Operator	5
Continuous Mining Machine Helper	1
Loading Machine Operator	6
Roof Bolter	3
Shuttle Car Operator	7
Bratticeman	2
Cutting Machine Operator	2
Coal Driller	2
Longwall Machine Headgate Operator	1
Longwall Machine Tail Operator	1
Longwall Machine Jack Machine Operator	2
Safety Technician	4
Rock Duster	8
Research Investigator	1
Total	45

For the TPF, 8 different face miners and one research engineer were used as test subjects. These people, which included 6 different job classifications of face miners, represented 8 different facial sizes as classified by the system set forth by Hyatt, et al (6); a diagram of this system is shown in Figure 4. Each of the test subjects wore 5 different respirator models over a 3 day period. During the period each respirator was worn, four sampling runs, each of four minutes duration, were made in which the mine air in test subjects' breathing zones and the air inside the respirator facepiece were sampled concurrently.

3. Results

While all of the data have been obtained, the analyses of the data had not been completed at the time this manuscript was prepared; consequently this should be considered in the nature of a progress report.

The distribution of EPF's for all the test subjects who were face miners is shown in Figure 5 and, similarly, the distribution for TPF's is shown in Figure 6. Some interesting differences can be observed.

Figure 4

Facial Size Classification Diagram
 (Job Classification of Test Subjects put in
 appropriate block according to facial measurements)
 Face Width, mm

		129 - 139	140 - 145	146 - 155
F A C E L E N G T H mm	136 126-	A Roof Bolter	B Cutting Machine Operator	C Continuous Miner Operator
	125 116-	D Bratticeman	E Timberman Loading Machine Operator	F Roof Bolter
	115 105-	G Research Engineer	H Loading Machine Operator	I None

DISTRIBUTION OF PROTECTION FACTORS

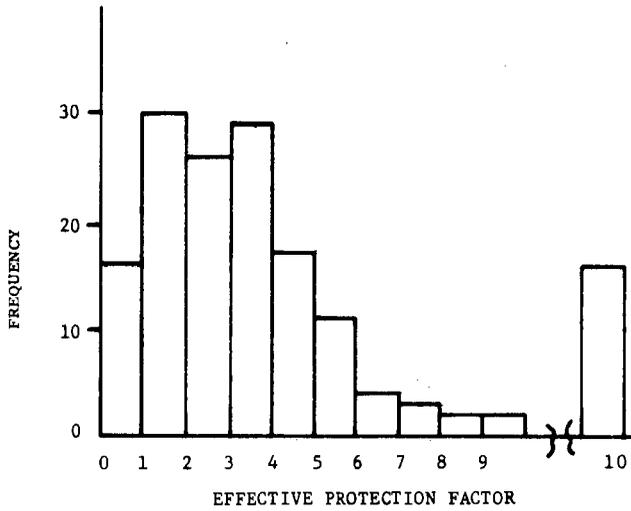


FIGURE 5

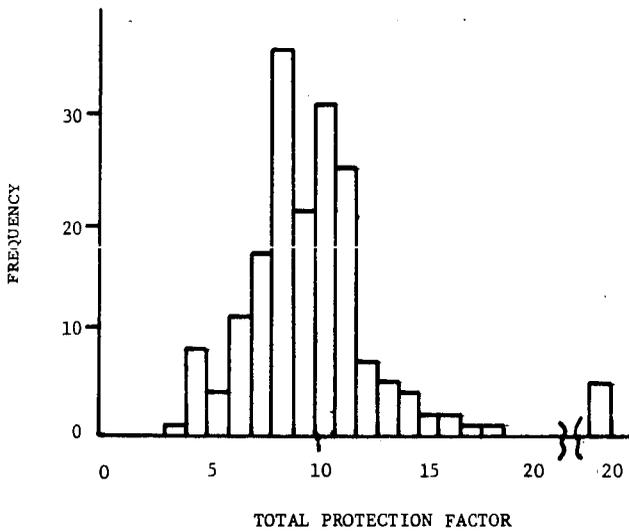


FIGURE 6

For the EPF's, values ranged from less than one to as high as 40 and above; however, most of the values were in the one to four range. Of the 151 values obtained, 16, were less than 1.0. While it may seem surprising that on occasion a respirator user is, either getting no protection at all or is possibly inhaling more respirable dust than is present in the ambient air, field observations indicate such is the case. For example, it is quite possible that respirable dust collected on the miner's clothes could be brushed off or knocked loose and be collected in the mask, which was worn hanging loose on the wearer's chest, thereby creating the higher dust concentrations found in the mask.

Unlike the EPF's, the TPF's showed a reasonably normal distribution and with little difference between mean and median values.

As shown in Figure 7, during the EPF test work the time the respirators were actually worn during the work period by the test subjects varied from a low of about 10 percent of the time to almost 90 percent; the mean average was about 46 percent of the time. It might be expected that a relationship should exist between the length of time the respirator is actually worn and the level, or effectiveness, of the protection obtained; in other words, the longer the respirator is worn, the better the protection (higher EPF) obtained. However, so far we have found no relationship to exist between the time the respirator was worn and the protection obtained. This suggests there are probably other factors that obviate the effect of time of wearing.

Test results for the five different models of respirators tested (for EPF) is shown in Table VI. It should be noted that the data shown include some very high values and values, as mentioned previously, where the EPF is less than 1.0. Both can, of course, influence the mean average and, consequently, the median value is also shown. Although we have not completed a statistical analyses of the data, it does appear there are differences among the respirators tested with respirators B and E being less effective than the others.

TABLE VI. Comparison of Different Respirator Types Tested

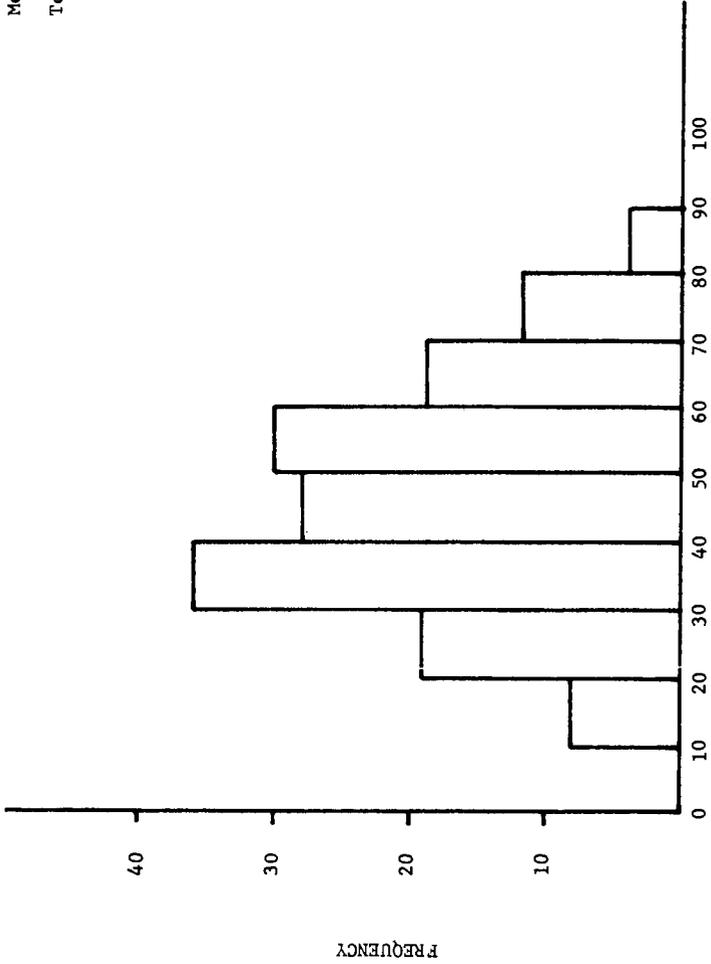
<u>Respirator</u>	<u>No. of Test Subjects</u>	<u>Effective Protection Factor</u>	
		<u>(EPF)</u>	
<u>Model</u>		<u>Mean Avg.</u>	<u>Median</u>
A	8	4.9	3.4
B	11	5.0	2.6
C	11	6.8	3.7
D	6*	8.5	3.9
E	4	3.2	2.0

* Actually 3 different test subjects.

The TPF's obtained for the same five respirators is given in Table VII. While, in each case, the TPF obtained was substantially higher than the EPF, the TPF is still somewhat less than that theoretically possible based on filter efficiencies.

PORTION OF WORK PERIOD THAT RESPIRATORS WERE WORN

Mean Average 46.8 Percent
Total Work Period \approx 6.7 hours



PERCENT OF TIME WORN

FIGURE 7

TABLE VII. Comparison of Different Respirator Models

<u>Respirator</u>	<u>No. of Test Subjects</u>	<u>True Protection Factor (TPF)</u>	
		<u>Mean Avg.</u>	<u>Median Avg.</u>
A	9	11.1	10.6
B	9	9.2	8.9
C	9	11.4	10.8
D	9	8.7	8.4
E	9	8.7	8.5

(Penetration of filter media by particles 0.8 to 1.0 micron in size is usually less than 4 percent.) We feel this loss in respirator effectiveness is primarily caused by the lack of an ideal fit or seal between the facepiece and the subject's face. Not only is a proper face seal disturbed by facial and body movement, but undoubtedly the facial size and shape affects the seal obtained. This is indicated by the range of values obtained for the different test subjects, Table VIII, each of whom wore all the different respirators.

TABLE VIII. Range of TPF's

<u>Test Subject</u>	<u>TPF*</u>	
	<u>High</u>	<u>Low</u>
1	12.3	6.6
2	13.5	5.8
3	14.2	4.0
4	11.4	8.2
5	15.4	7.2
6	19.5	8.3
7	10.2	6.6
8	11.9	9.6
9	10.0	5.9

* Average of four values obtained for one respirator worn.

It is probably this difficulty of easily achieving and maintaining a good fit and face seal that accounts for much of the difference between EPF and TPF. In this connection and in the case of EPF the fit problem becomes more difficult because miners find it impractical to wear a two-strap respirator head harness in the prescribed manner. Therefore, the miners wear the two straps in a single-strap configuration below the ears. The development of a more appropriate head harness is an area wherein research is much needed. In addition, there is need for better materials of construction and better designs which will provide both a more comfortable respirator and better face seal.

V. CONCLUSIONS

1. Half-mask dust respirators are in general use in underground coal mines and working miners feel there is a definite need for respiratory protective devices.
2. Most miners feel presently available approved respirators are acceptable for intermittent use but over a third of the miners feel the current units are unacceptable or marginally acceptable.
3. Discomfort to wear and breathing resistance are cited by miners as the major disadvantages of present day half-mask respirators.
4. As used in the field, presently available respirators provide the working miners a reasonable level of protection against the inhalation of respirable dust. However, the level of protection obtained is significantly lower than possible under ideal conditions. Difficulty in maintaining the proper seal between facepiece and face is one of the major reasons for reduced protection levels under actual working conditions.
5. There is a need for more comfortable respirators with reduced resistance to breathing. Likewise, there is a need for better materials of construction and better designs so that a good fit between facepiece and face can be secured and maintained with half-mask type respirators.
6. In the development of improved respiratory protective devices for coal miners a systems approach should be used.

VI. FURTHER OBSERVATIONS

It is evident that improved respiratory protective devices for underground coal miners are needed. In the development and design of such devices, a systems approach should be used because of the need to integrate protection requirements of different kinds with the constraints of the work requirements and work environment. In the case of the coal miner, there is, as a minimum, a need, all or part of the time, for the following, each of which can be considered a system:

- a. head protection
- b. illumination
- c. eye protection
- d. noise protection
- e. others, e.g., carrying of special equipment
or tools

At the same time, the miner needs to have the maximum amount of mobility and the work environment often imposes severe constraints in terms of space and size and weight limitations. Consequently, it will be necessary, for example, when developing and designing improved respiratory equipment to take into account the miner's need for such things as head, eye, and noise protection and illumination, and to integrate these systems.

An example of the lack of systems approach are the present difficulties associated with respirators with the two-strap head harness and the miner's use of the hard hat (7). Clearly, such difficulties must be eliminated in newer and improved designs.

REFERENCES

1. Schutz, R. H., "The Dust Respirator Problem", Proceedings of the Symposium on Respirable Coal Mine Dust, Washington, D. C. November 3-4, 1969.
2. DeSieghardt, W. C., H. E. Harris, W. A. Burgess, and P. C. Reist, "Respirator Usage in Underground Bituminous Coal Mines", Mining Congress Journal, pp 43-48, August 1971.
3. IC 8503, "Sampling and Evaluating Respirable Coal Mine Dust," U. S. Bureau of Mines, February 1971.
4. Harris, H. E., W. C. DeSieghardt, W. A. Burgess and P. C. Reist, "Respirator Usage and Effectiveness in Bituminous Coal Mining Operations." American Industrial Hygiene Conference, San Francisco, Calif. May 18, 1972.
5. Lilienfeld, P. and J. Dulchinos, "Portable Instantaneous Mass Monitor for Coal Mine Dust," AIHA Journal, Vol. 33, No. 3, pp 136-145 (1972)
6. Hyatt, C. C., A. L. Hack, T. O. Moore, and C. P. Richards, "LASL Respirator Test Panel - Representative of U. S. Male Facial Sizes.
7. Harris, H. E., W. A. Burgess, and W. C. DeSieghardt, "Effectiveness of Dust Respirators in Underground Coal Mines", AIME Annual Meeting, Feb. 25 - Mar. 2, 1973, Chicago, Ill.

EQUIPMENT MODIFICATION
FOR INCREASED SAFETY

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INTRODUCTION

This paper is a progress report on the work performed to date under the Federal Bureau of Mines "Inherently Safe Mining Systems" contract.

The concept of initiating a large action-oriented contract, directed towards obtaining coal-mining systems with greatly improved safety characteristics, was conceived by the Bureau in January 1971.

The concept of working demonstrable systems, rather than just a conceptual study, was felt to be necessary for two significant reasons. In the development of any new system, the translation from concept to working hardware is usually a costly and time-consuming process that acts as a deterrent to implementation. Second, many decisions in the mining community to change equipment or systems are based on first-hand observation of the new system, in operational practice, an attitude which is certainly understandable in view of the high capital costs of equipment.

Based on a competitive procurement process, the Inherently Safe Mining Systems contract was awarded to the FMC Corp., San Jose, Calif., on June 18, 1971. The major goal of this contract is to develop and demonstrate safer mining equipment and procedures that can be developed using existing state-of-the-art technology.

This program is aimed at demonstrating improved safety of operations in the area from the working face to the first point of coal transfer in underground bituminous coal mines with seam heights of 4 to 8 feet, with emphasis placed on the prevention of fatal and nonfatal accidents

by avoiding, warning, or protecting against the physical hazards of machinery and against falls of roof and rib. Long-term health problems and catastrophes (for example, explosions) are not being directly addressed, although procedures and equipment developed for this project will be evaluated to verify that they do not aggravate these problems.

The program is being conducted in three phases. Phase I, which has been completed, involved data accumulation and analysis leading to problem definition and the development of concepts to alleviate these problems. We are currently well into Phase II of the program, in which all the basic equipment elements are to be procured and modified and new equipment fabrications completed. Subsequent portions of this paper present the status of these major equipment developments. Phase III, the 1-year operational demonstration, is scheduled to begin in August of this year for the conventional section and later for the continuous section.

PROBLEM DEFINITION

A brief review of the magnitude of the safety problem associated with those activities within the scope of this program is of interest. This work in problem definition was performed during the first phase of the program and has been reported in detail in a report entitled "Accident Analysis by Functional Classification for Bituminous Coal Mines in 4-Foot to 8-Foot Seam Heights." This report was completed on

September 11, 1972, and has been placed with the National Technical Information Service.

Data on fatal and nonfatal accidents in underground bituminous coal mines operating in 4- to 8-foot seams was gathered to evaluate the problem and to assist designers in developing designs for equipment and procedures, which will reduce the incidence of these accidents. The data was structured in a form that would identify --

The types of accidents that are occurring

The causes of these accidents

The aspects of the job or equipment that contribute to these accidents

The nature and duration of the hazards to which workers are exposed.

The fatal accident data base consisted of 283 accidents resulting in 302 fatalities.

Nonfatal accident data was gathered in the field from company records on file at various mining company offices. The specific accident information sources have been masked to preserve their identities. Information on 65 conventional mining sections and 155 continuous-mining sections is contained in the data base. This sample represents 10,907,757 total annual man-hours in 4- to 8-foot seams, which is about 14% of the industry wide total annual labor hours in 4- to 8-foot seams.

Table 1 is an overall summary of the frequency and severity of nonfatal accidents, the incidence of fatal accidents, and the industry-wide expectation of lost man-days per year by system function.

Worthy of notice is the total of 220,500 estimated man-days lost each year as a result of compensable and noncompensable accidents. This is equivalent to a labor force of approximately 890 men, enough men to mine coal in 75 to 90 underground mining sections.

Table 2 provides information on the principle causes of injury for each of the major system functions.

Based on the results of accident studies and unit operation analysis, criteria for concepts to improve the safety of the conventional and continuous mining systems were developed. These criteria were made available to design personnel through accident study conclusions, operation analysis study conclusions, and recommended design approaches.

CONVENTIONAL MINING SYSTEM CONCEPTS

Work is progressing on the modification of equipment for use in the conventional mining section demonstration. The specific modifications planned or underway are described in the following sections. The major common features in these modifications are all-around protective suspended cabs and improved and standardized controls. The cab suspension feature, incorporated in a variety of unique ways on the section equipment, has two advantages: first, in the event of a major fall the cab can deflect in a controlled manner to enable the machine frame to pick

Table 1 INDUSTRY IMPACT — ACCIDENT SURVEY SUMMARY

Underground Bituminous Coal Mines -Inby The Face
Seam Height 4 - 8 Feet

SYSTEM FUNCTIONS	NON-FATAL										FATAL	
	Compensible					Non-Compensible					Estimated Man-Days Lost Per Year	Five Year Total Accidents
	One Accident for Every X Man-Years	Estimated Accidents per Year	Severity: Man-Days per Accident	Estimated Man-Days Lost per Year	One Accident for Every X Man-Years	Estimated Accidents per Year	Severity: Man-Days per Accident	Estimated Man-Days Lost Per Year				
4.0.0 Support Roof Roof Bolter	5.7	1114	53.7	60000	3.8	1621	1.6	2600		50		
52.0.0 Load Coal Loader	6.1	293	70.4	21000	2.6	673	1.5	1000		47		
1.0.0 Extract Coal Continuous Miner	16.5	447	56.1	25000	10.9	671	1.7	1100		43		
3.0.0 Move & Load Coal Shuttle Car	25.8	320	51.0	16000	11.7	799	1.8	1400		38		
9.0.0 Maintenance All Maintenance	10.6	468	48.8	23000	3.1	1560	1.4	2200		20		
51.1.0 Cut Face Cutter	12.9	158	115.3	18000	7.7	252	1.7	400		14		
			Sub-Total	163000			Sub-Total	8700		212		
All Other Functions (At Face)	-	952	48.4	46000	-	1842	1.5	2800		71		
Totals	Totals	3752	-	209000	Totals	7418	-	11500		283		

Table 2 ACCIDENT MATRIX

System Function Unit	Location	Analysis Factors	Source of Injury													
			Roof Falls	Free & Riv Falls	Falling and Flying Objects	Handing Material	Head Trauma	Striking on Object	Striking or Clamping	Electricity	Machinery	Burns - (Pressure)				
1.0.0 EXTRACT COAL (Continuous Miner)	Worker Controls	% of Accidents 17.1 % Man-Days Lost 26.4 Average Severity 35.9	6.2	7.5						4.1			14.4			
	Worker in Support	% of Accidents 3.4 % Man-Days Lost 8.1 Average Severity 21.7	2.0	4.2						4.7			13.2			
	Worker at Controls	% of Accidents 48.0 % Man-Days Lost 34.6 Average Severity 21.7	4.1	5.1	11.6	7.1							15.1			
51.1.0 CUT FACE (Cutter)	Worker Controls	% of Accidents 73.2 % Man-Days Lost 21.6 Average Severity 23.3	14.3	10.7						7.1			16.1			
	Worker in Support	% of Accidents 26.8 % Man-Days Lost 25.2 Average Severity 47.0	1.6	2.2	13.7	5.4							8.9			
	Worker at Controls	% of Accidents 75.0 % Man-Days Lost 14.3 Average Severity 19.0	12.5	8.1	12.0	24.3				44.5			35.7			
51.2.0 DRILL FACE (Drill)	Worker Controls	% of Accidents 35.0 % Man-Days Lost 13.5 Average Severity 10.3														
	Worker in Support	% of Accidents 89.0 % Man-Days Lost 77.6 Average Severity 19.7	8.1	35.3						2.9			18.4			
	Worker at Controls	% of Accidents 11.0 % Man-Days Lost 22.5 Average Severity 25.2	6.0	6.5	3.7	14.2				0.6			37.5			
52.0.0 LOAD COAL (Loader)	Worker Controls	% of Accidents 15.3 % Man-Days Lost 19.2 Average Severity 20.2	3.6	15.0						26.5			19.4			
	Worker in Support	% of Accidents 18.4 % Man-Days Lost 39.1 Average Severity 25.1	3.7	9.1						27.1			11.1			
	Worker at Controls	% of Accidents 12.0 % Man-Days Lost 23.0 Average Severity 25.1	2.4	3.6	6.5	2.4							9.8			
3.0.0 MOVE & LOAD COAL (Shuttle Car)	Worker Controls	% of Accidents 12.0 % Man-Days Lost 23.0 Average Severity 25.1	2.4	3.6												
	Worker in Support	% of Accidents 25.1 % Man-Days Lost 40.1 Average Severity 40.1	4.1	13.1									4.1			
	Worker at Controls	% of Accidents 7.1 % Man-Days Lost 13.1 Average Severity 13.1	1.0	1.0	1.0	1.0							32.2			
4.0.0 SUPPORT ROOF (Roof Bolt)	Worker Controls	% of Accidents 2.4 % Man-Days Lost 13.1 Average Severity 13.1	0.2	0.3									25.2			
	Worker in Support	% of Accidents 2.4 % Man-Days Lost 13.1 Average Severity 13.1	0.2	0.3									25.2			
	Worker at Controls	% of Accidents 2.4 % Man-Days Lost 13.1 Average Severity 13.1	0.2	0.3									25.2			
TOTAL																

Summary of Analysis
By System Function
And Source Of Injury

Notes: Percentages will not add to 100
because only major sources are
listed.

up a portion of the load; and secondly, the elevation can be adjusted to obtain the maximum visibility allowable under existing seam height and roof conditions.

Controls on all section equipment have been examined from a human engineering control function and consistency viewpoint and similar motions and locations have been established to the maximum extent possible. This was considered to be of importance in view of the learning experience required when an operator is new to a piece of equipment or is called upon to operate temporarily a different equipment element. It has been shown that this learning experience is often attendant with a higher accident rate.

All section equipment with the exception of the DC shuttle cars will employ 950-volt power. This permits the utilization of shielded cable with safety grounds without any increase in cable size or weight.

SHUTTLE CAR

Two National Mine Service Lokar's have been procured and are being identically modified for this program. To a large degree, the modifications being performed identify what can be accomplished when sufficient space is available on the basic machine. The basic modification is a human engineered swing-around suspended cab. This cab will elevate or depress under power from a nominal 6-inch to a maximum of 16-inch ground clearance. In the event of a fall, the cab will deflect to the floor in a controlled fashion.

The operator is not required to leave the cab when the direction of shuttle car travel is reversed. This is accomplished by the release of an underseat latch, powered rotation of the cab about an axis near the operator's center of gravity, and latch reengagement when rotation is complete. The controls travel with the operator and are automatically reversed when the new position is reached. Steering by means of an automotive-type wheel is always consistent with the direction of travel. Tram and brake controls are also consistent with automotive practice and rotate with the cab.

Cab side clearance in the 90° rotated position is 31 inches beyond the outer edge of the existing machine structure. In the fore and aft position, cab side extension is 4 inches. This was required in the interest of additional operator comfort.

FACE DRILL

The face drill procured for this program was a Long Airdox model TDF-24C. Control modifications will consist of a reduction in the number of control valves by means of combined joystick controls. The drill frame swing and elevate controls will be combined as will the drill arm swing and elevate functions thus reducing the number of levers in the operators compartment. Additionally, automotive wheel-type steering will be utilized, the tram and brake controls will remain unchanged. An operators cab similar to that employed for the shuttle cars will be used with a 10-inch nominal adjustable height.

UNDERCUTTER

The cutting machine employed in this system will be a Joy model 15RU-6B. Joystick boom and bar controls and wheel steering similar to the face drill will be used. Since insufficient space for a suitable cab existed on the standard machine, it was modified by relocation of the hydraulic tram motor in order to provide leg room for the operator.

The machine will be equipped with forced air to the end of the cutter bar for slot ventilation and water spray nozzles for dust control.

LOADING MACHINE

The loading machine will be a Joy model 14BU10. Some of the special features of this machine are an oblique mounted operator's cab with limited reel cable storage and simplified cab mounted controls. The existing standard loading machine does not provide sufficient space for installation of a cab of adequate dimensions. The availability of this space to provide a comfortable cab is felt to be important since this is the one location where a worker can be protected, and everything possible should be done to make it desirable and practical for the operator to remain in the cab.

The cab, as configured, will elevate and depress about a horizontal pivot at the operator's feet. The additional side clearance was required because of oblique mounting of the cab to facilitate the operators view of the tail boom during the loading operation.

Cable reel storage for approximately 100 feet of cable will be provided in the rear of the operator's cab. The reel, which will be controlled by a cab-mounted, foot-operated valve, should ease the cable handling requirements.

AUTOMATED TEMPORARY ROOF SUPPORT BOLTER

A piece of equipment that will be built in two versions, one for use in the conventional section and one in the continuous section, is an automated roof bolter incorporating temporary roof support. The basic machine chassis will be a Galis model 3510. The key features of this machine will be an automated magazine supplied bolter that can be remotely operated by the worker from the protective cab position to bolt a 20-foot-wide place without local repositioning of the machine.

In the remote-control operational mode, the capability will exist to drill holes and install bolts with a length of from 5 to 6 feet, depending on the machine version. The machine can also be utilized with the operator working at the head end under the remotely actuated temporary support canopy. In this mode, the capability will exist to drill holes and install bolts of whatever length required.

For tramping, the bolts and drill steel are removed from the magazine and the protective canopy is then collapsed to a maximum height of approximately 3 feet.

CONTINUOUS-MINING SYSTEM CONCEPTS

The scheduled start date for the underground demonstration of the continuous-mining system is about 4 months later than for the conventional section. The equipment development is, therefore, not as far advanced as in that discussed for the conventional section.

The principle thrust for this equipment is to develop the capability to install a full bolting pattern automatically from the continuous-mining machine in order to obtain permanent support installation as rapidly as possible and allow the convenient utilization of continuous-belt haulage systems. The benefits of success in this development are apparent, but the problems encountered are also quite significant. The major obstacle is, of course, the space constraints. Existing continuous-mining machines are large and encumbered with considerable necessary machinery components, and the dimensions of the working space are, of course, limited. The on-board space available to accommodate equipment to drill and bolt a full three- or four-bolt pattern without restricting equipment maneuverability or effecting complete machine redesign is, therefore, extremely limited.

What has been developed through the preliminary design phase is illustrated by the sketch in figure 1. The basic machine to be employed is a Joy 12CM1-15B full-face miner capable of driving a 15-1/2-foot entry. Four on-board bolters are shown which would permit the installation of a four bolt pattern with a maximum center-to-center spacing of 4-1/2 feet. The bolting machine would employ a single drilling bolting

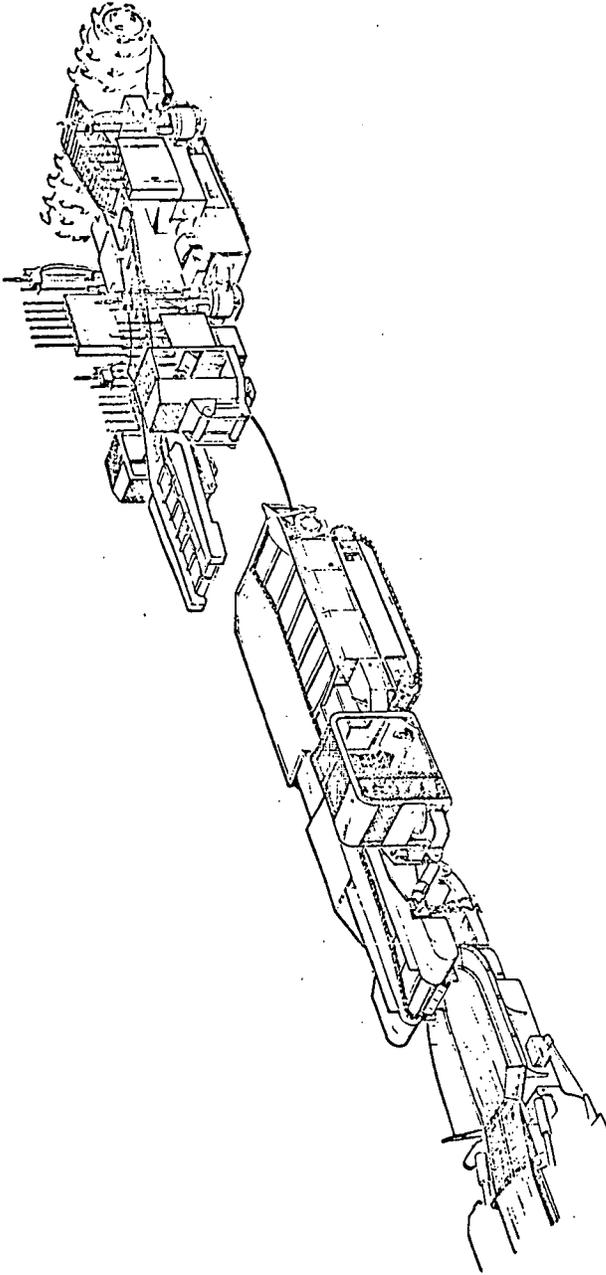


Figure 1
CONTINUOUS MINING SYSTEM

head with magazine storage and should be able to install a bolt approximately 2 feet less than the seam height.

In order to accommodate the rear bolters, the operators compartment has been removed, the conveyor extended, and the tailboom hinge pin moved forward. Two cabs have been added to the tailboom, one for the miner operator and one for the roof bolter. With the hinge pin relocation, the maneuverability of the machine is essentially the same as with the unmodified version.

Operation of the drilling bolting cycle is completely automated, and all four bolters are controlled from the operator's cab. All bolters are jack stabilized, and bolting should be possible during the shearing portion of the cycle. However, no slide-through capability is incorporated, and no drilling or bolting can be done during sumping. It is presently planned that the front bolters will have an eight-bolt magazine and the rear bolters, a four-bolt magazine. Reloading, which is a simple insertion process, would be required after about a 20-foot advance of the face. Bolting, in turn, is felt to be possible, although this will require some repositioning of the machine to accommodate bolt-spacing constraints. Some pick up bolting will be required when the machine is pulled out of a place since the forward bolts can be placed no closer than 12 feet from the face. This pick up bolting will be accomplished by means of a TRS bolter described previously.

The extensible belt haulage system to be used will be the Lee Norse system with one tram car and several drive storage units. Each drive

storage unit will accommodate a maximum length of 150 feet of belt, which can be extended or retrieved at a rate of 140 feet per minute. System capacity is on the order of 12 tons per minute. Modifications to the extensible belt system include the addition of protective cabs or canopies to all units and revisions to the steering and tram controls.

ANCILLARY SYSTEMS

Given the time duration and extent of the demonstration phase of this program, it was considered desirable to integrate to the maximum extent all research and development results that could be incorporated in this phase. The additional items to be incorporated are those developed from the efforts of mining research, which is conducted both in-house and under contract programs other than the "Inherently Safe Mining Systems" contract. The following indicates some of the equipment and/or systems that will be incorporated in the areas of roof control, communications, illumination, dust control, and monitoring systems. The incorporation of these elements will include both demonstration, in those cases where the technology has already been proven, and test and evaluation where concepts are still under development.

The items under consideration for incorporation are as follows:

Roof Monitoring

1. Horizontal Roof Strain Indicator (HORSI) system
2. 3-in-1 roof deformation and failure warning device
3. U-type bolt tension indicator

Roof Monitoring (continued)

4. Micro seismic roof-fall warning system
5. Helix pressure gage
6. Hand held infrared scanner for detection of loose material
7. Mobile shield -- during experimental phases of system development in SRCM, Bruceton, and at ISMS mine, if applicable.

Monitoring, Communications, Lighting

1. Automatic monitoring of methane, air velocity, temperature, and CO
2. Advanced carrier phone systems and portable pocket paging equipment for section personnel
3. New lighting systems including wide-angle incandescent, mercury vapor, and, as development permits, polarized and/or fluorescent for face area illumination and electroluminescent for machine identification. Hardware includes machine-mounted, portable, and personal units.

Dust Control and Monitoring

1. Application of foam in both coal cutting and handling
2. Air curtain respiratory device for personnel protection
3. Wet-drilling for automated roof drills
4. Continuous miner equipped with integral respirable dust scrubber and water sprays at cutter bits
5. Portable dust meters
6. Portable rock dust/coal dust analyzer, development permitting.

IN-MINE DEMONSTRATION

The precise demonstration start dates and location are currently under review and cannot be specifically identified at this time. As planned, the conventional section will be demonstrated in a seam of about 4 feet in height and the continuous section, in about 8 foot coal. Since both of these sections are to be operated for a years duration each, and numerous visitors are anticipated it is important that easy access to the sections be available both in a geographic and in-mine sense. Another important consideration is, of course, the cost of obtaining and operating these demonstration facilities over this time-frame desired.

A number of locations in West Virginia, Virginia, Illinois, and Kentucky have been examined and are currently being evaluated and it is anticipated that this question will be resolved shortly.