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MIDWEST RESEARCH INSTITUTE

MRI REPORT

RESEARCH AND DEVELOPMENT ON MEMBRANE PROCESSES FOR REMOVAL OF ACID GASES DURING COAL GASIFICATION

Report No. FE-2008-5

FINAL REPORT
June 20, 1975, through October 19, 1976

Contract No. E(49-18)-2008
MRI Project No. 4121-N

For

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
Fossil Energy Program
20 Massachusetts Avenue, N.W.
Washington, D.C. 20545

MRI—NORTH STAR DIVISION 10701 Red Circle Drive, Minnetonka, Minnesota 55343 • 612 933-7880

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MIDWEST RESEARCH INSTITUTE 425 VOLKER BOULEVARD, KANSAS CITY, MISSOURI 64110 • 816 753-7600

MRI WASHINGTON, D.C. 20005—1522 K STREET, N.W. • 202 293-3800

RESEARCH AND DEVELOPMENT ON MEMBRANE PROCESSES FOR REMOVAL OF ACID GASES DURING COAL GASIFICATION

By

R. J. Petersen
J. E. Cadotte
E. J. Conway
R. H. Forester
M. J. Steuck

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PREFACE

This report contains the results of research activities in the program "Research and Development on Membrane Processes for Removal of Acid Gases During Coal Gasification," Contract No. E(49-18)-2008.

This study was conducted for Fossil Energy Research, Energy Research and Development Administration. Dr. Fred Witmer was the Technical Program Officer.

The project leader for the MRI team was Dr. Robert J. Petersen. Major participants in the program effort were John E. Cadotte, Edward J. Conway, Ralph Forester, and Michael J. Steuck.

North Star Division
MIDWEST RESEARCH INSTITUTE

Robert J. Reid, Manager
Environmental Studies

Approved:

Arsen Darnay
Arsen J. Darnay, Director
North Star Division

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ABSTRACT

The object of this program was to develop novel and unique membranes for separating acid gases from coal gasification streams. Many candidate membranes, including cationic, hydrophilic, and silicone, were tested. Optimum separation properties were possessed by membranes formulated from crosslinked methyl cellulose coated on polysulfone support films. The observed separation properties were explained theoretically by the solubility of the various gases in the water contained within the membranes rather than by activated transport. The optimum membrane compositions were not economical for the proposed separations but they may be economical for other applications.

SUMMARY

The objective of this research and development program was to develop novel and unique polymer membranes and apply them to the removal of acid gases from raw gas streams in coal gasification processes. Initially, this objective was to be accomplished through development of weakly cationic membranes, such as crosslinked polyethylenimine, deposited as very thin films on porous support media. Later program efforts included evaluation of various other hydrophilic polymer membranes.

The following tasks were completed during this program: 1) an initial critical assessment of the economics of current acid gas removal systems, including estimates for membrane processes; 2) screening of potential membrane compositions; 3) selection and optimization of the most promising membrane composition; 4) thorough characterization of the final membrane formulation for gas separations; and 5) an evaluation of the feasibility and economics of this final membrane system in a gas purification train of a coal gasification plant.

The membranes developed during this program did not perform well enough at high pressures to be useful in a coal gasification application. In addition they were less economical than the conventional processes now in use. These formulations, however, are still promising for applications at lower pressures, such as removal of sulfur containing gases from small biogas converters for which conventional processes may be unusable or uneconomic.

INTRODUCTION

Objective

The objective of this research and development program was to develop novel and unique polymer membranes and apply them to the removal of acid gases from raw gas streams in coal gasification processes. In particular, membranes were sought that would demonstrate selective removal of carbon dioxide, hydrogen sulfide, and other sulfur-bearing gases from the feed gas. Since the raw gases exit from coal gasifiers at high pressures, membrane purification of these raw gases could potentially be carried out at very low operating costs, with no cost input for gas compressors.

In previous research programs, the North Star Division of Midwest Research Institute had developed a unique composite membrane technology for high performance reverse osmosis membranes. The basis for this technology was the *in situ* condensation of polymeric materials on the surface of microporous polysulfone support materials.(1) This approach gave exceptionally thin barrier films of almost any chemical composition desired, but in a form easily handled and applied. The ability to achieve high gas fluxes through these composite films appeared well suited for application in the purification of raw gas from coal gasifiers.

Scope of the Program

The scope of this program involved the following specific tasks:

- Exploratory screening of membrane candidates for gas selectivity and flux;
- Optimization of promising membranes for maximum performance;
- Thorough characterization of a final, optimized membrane;
- Critical assessment of the economics of current acid gas removal processes;
- Evaluation of the economic feasibility of experimental gas separation membranes vis-a-vis current processes.

If gas separation membranes were demonstrated to be economically attractive in coal gasification applications, a second phase was planned for this program. This second phase would have involved the scale-up of membrane development to devices such as 33-square-foot-membrane-area spiral wrap modules for characterization and field testing. Results of this research program did not warrant continuation into the second phase.

EXPERIMENTAL METHODS

Membrane Fabrication Techniques

Experimental membranes were fabricated for testing by a thin film composite membrane technology previously developed in research on reverse osmosis membranes. These composite films consisted of ultrathin (one- to three-micron-thick) barrier layers cast onto asymmetric, microporous polymer support films. The microporous support layer contributed strength and handling qualities, while the extreme thinness of the barrier layer allowed for rapid permeation characteristics.

Two types of microporous supports were used in this work: Celgard microporous polypropylene film (Celanese Corporation) having elliptical pore dimensions of about 300 x 1000 angstroms, and polysulfone supports having circular pore dimensions of about 25 to 125 angstroms. The polysulfone supports were hand-cast at MRI for most of the experimental membrane fabrication studies, but commercially available microporous polysulfone samples were also evaluated. Hand-made support films were prepared by casting a seven-mil-thick layer of 15 percent polysulfone (P-3500, Union Carbide Corporation) solution in dimethylformamide onto a smooth glass plate, then quenching the liquid film in water. These films had a shiny surface (air side) with a 125 angstrom or less pore size; the back side was dull and contained pore dimensions of 30,000 to 40,000 angstroms (3 to 4 microns).

Membranes for acid gas separations were fabricated by coating the microporous films with dilute solutions of polymers compounded with reactive crosslinking agents and catalysts. Usually, microporous polysulfone was used in these studies. In some cases similar films of polyacrylonitrile were used. Coatings were applied to the upper, microporous surface of the polysulfone films which had the 125 angstrom pores. The coated sheets were then heat-cured to form thin, crosslinked, semipermeable barrier films on this upper surface. Applicable coating solvents were water, heptane, or the lower alcohols. Any other solvents would swell and seal off the 125 angstrom pores in the polysulfone substrates. Where other solvents were required, microporous polypropylene (Celgard) supports were sometimes used, although Celgard was not as effective as microporous polysulfone in this application. In some cases, such as cellulose acetate, it was useful to float-cast an ultrathin film of the polymer on a water surface using water-soluble solvents. The pre-formed ultrathin membrane was then laminated to the microporous polysulfone substrate.

The above techniques were largely developed during earlier research work on reverse osmosis membranes under sponsorship of the former Office of Saline Water, U.S. Department of the Interior. Such compositions were repeatedly shown to perform satisfactorily at 1500 psig in reverse osmosis applications. Variability due to pinhole leakage can occur in these membrane systems, but can be eliminated by judicious choice of coating weight and care in the fabrication of microporous polysulfone substrates.

Membrane Test Procedures

Experimental membranes were evaluated by testing their permeabilities to selected, humidified gases, either separately or as mixtures. Most test data were generated at 200 psig, but some test data were also obtained at higher pressures.

A membrane test apparatus was specifically designed and assembled for this research program. Figure 1 is a schematic diagram showing the various components in the test apparatus. The test line was designed so that gases from two high pressure cylinders could be fed through control valves to mass flowmeters, then mixed and humidified before entering the membrane test cells. Typically, three test cells were on-line at one time, but each cell could be individually isolated from the system if desired. A back pressure regulator controlled the system pressure. Quick disconnects were provided for removing the test cells and for sampling the high pressure feed gas. Figure 2 contains photographs of the test line in operation.

Specific components of this test line included the following: two Airco high pressure gas regulators; two Nupro "S" series very fine metering valves for gas entry into the system; two Thermo Systems Model 1352-2G mass flowmeters (with filter screens installed upstream); electronics for powering and reading the mass flowmeters, including Thermo-Systems Models 1050 and 1051-6 and a Fairchild Model 7050 digital multimeter; a Whitey Model ORF-2 valve plus quick disconnect for feed gas sampling; a one-liter steel tank humidification chamber (filled with wet glass wool) having a check valve at the inlet to protect the mass flowmeters from backwash; a U.S. Gauge Superfrunt stainless steel gauge with a 1000 psi dial; three Whitey Model SS-43-YF2 two-way valves; three stainless steel test cells; and a Tescom 1500 psig back pressure regulator Model 25-1725-2Y. Stainless steel tubing and connectors were used throughout.

The membrane test cells consisted of Millipore 47-mm-diameter pressure filters (Cat. No. XX4504700) which were modified by drilling and threading a second hole in the top-half of each cell. The gas inlet and outlet on the top of each cell were both fitted with quick disconnects to facilitate removal of cells from the test line for membrane changes. The single outlet on the permeate side of each cell was fitted with nylon capillary tubing which led to a gas flowmeter. The three cells were immersed during operation in a constant temperature water bath equipped with a Sargent Heater/Circulator and a Sargent Thermonitor Model ST.

The mass flowmeters were calibrated for each test gas used in the system. This was accomplished by means of a wet test gas flowmeter at the system outlet.

A gas chromatograph was installed near the test apparatus to be used for analysis of gas mixtures. This was a Hewlett-Packard Model 5710A equipped with

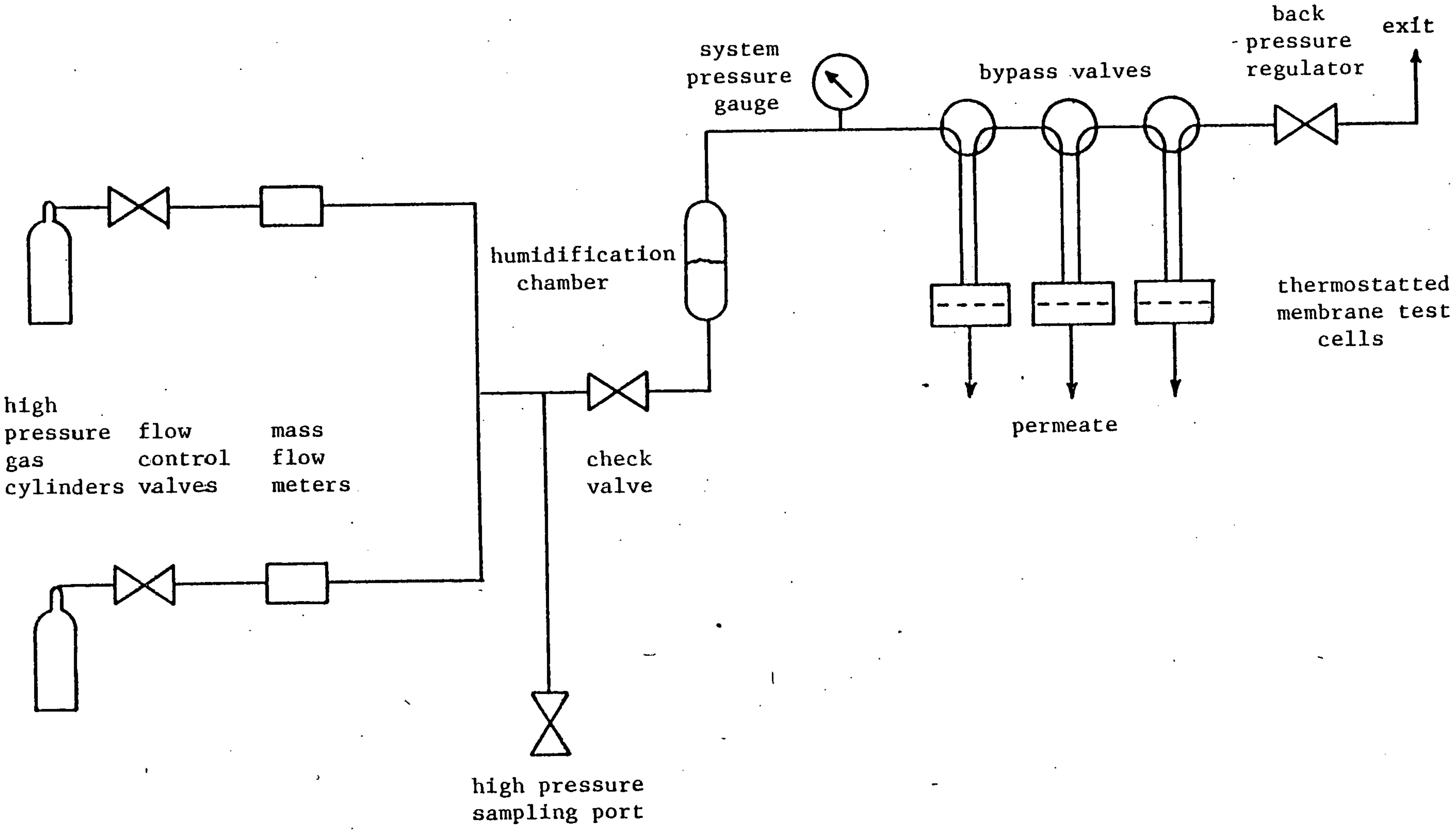
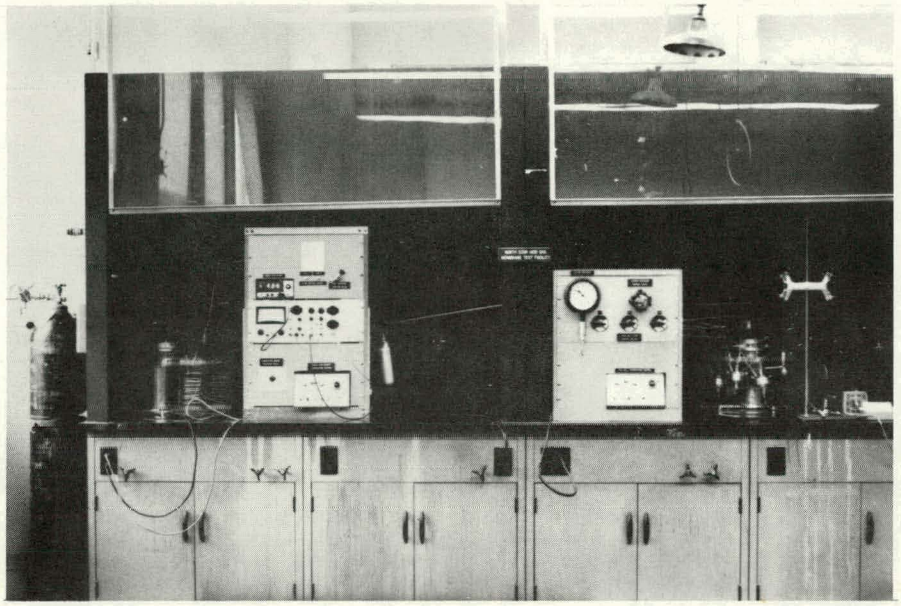
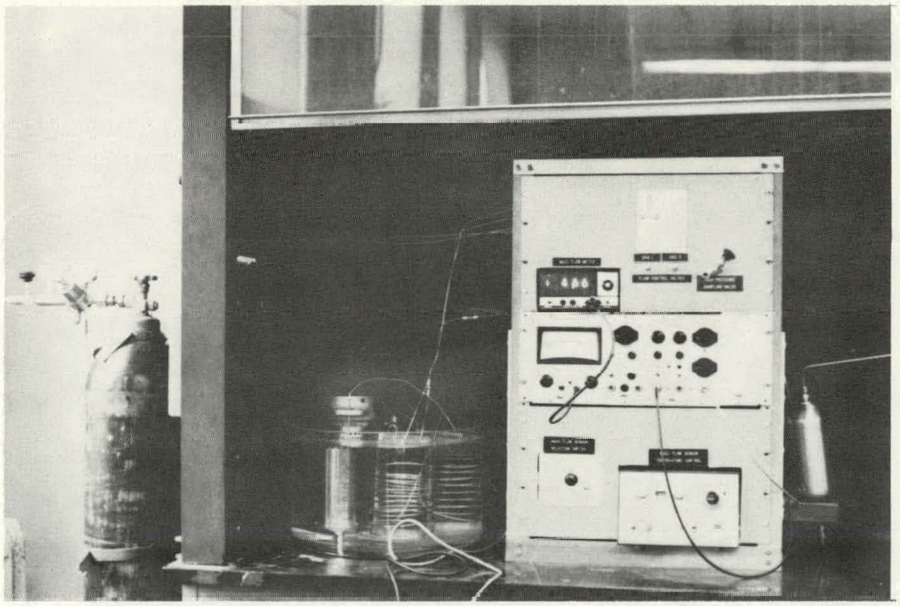


Figure 1. Schematic Drawing of the Membrane Permeability Test System

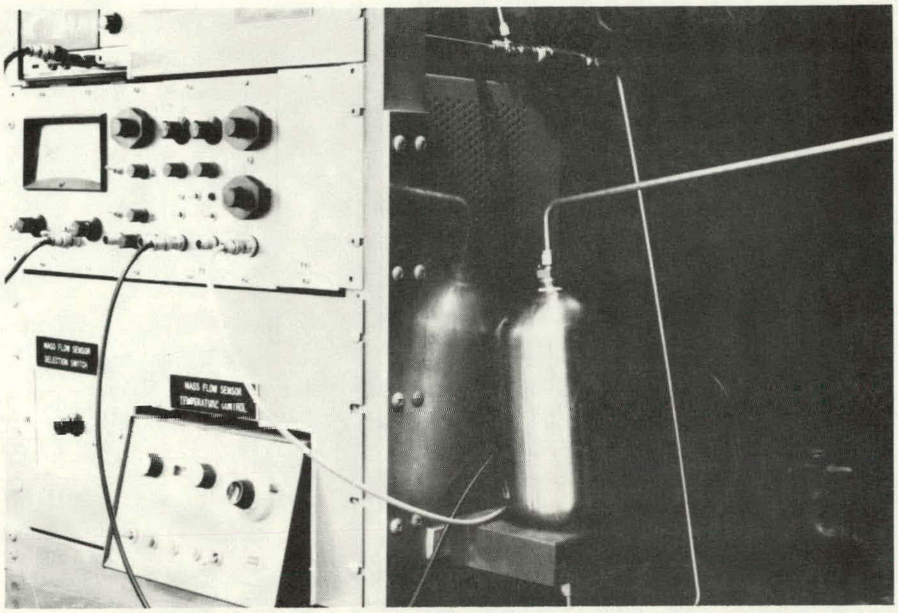


a. Entire Test Line

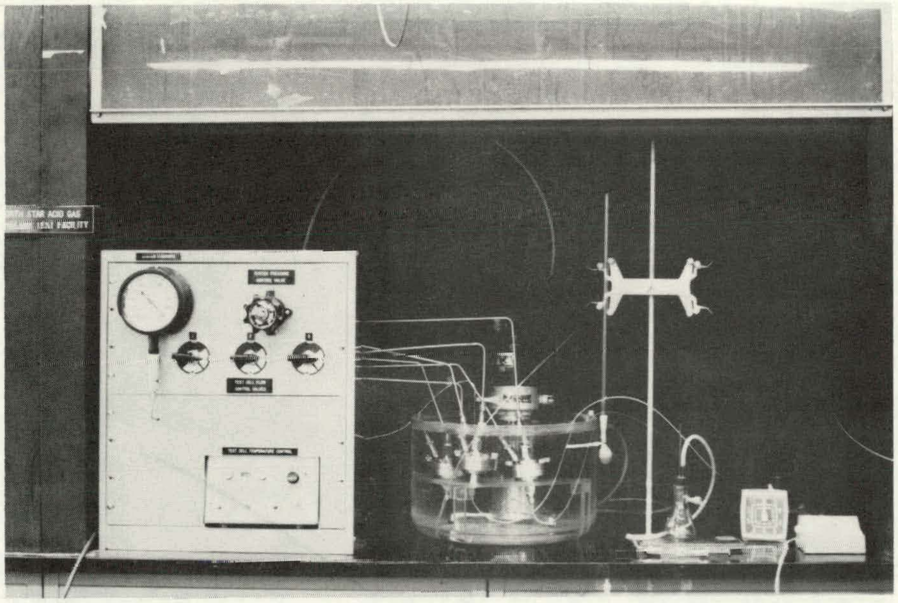


b. Gas Cylinder, Constant Temperature Bath and Controls, Flow Control Valves, Mass Flow Meter Controls and Readout, High Pressure Sampling Port, and Humidification Chamber

Figure 2. Photographs of the Test Line in Operation

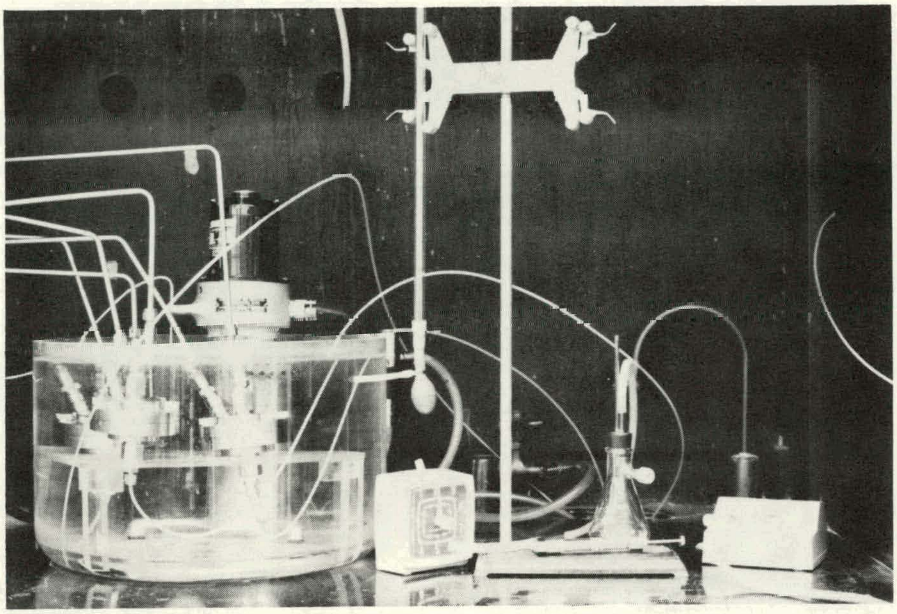


c. Mass Flow Meter Controls and Readout, Constant Temperature Bath Controls, Check Valve, and Humidification Chamber

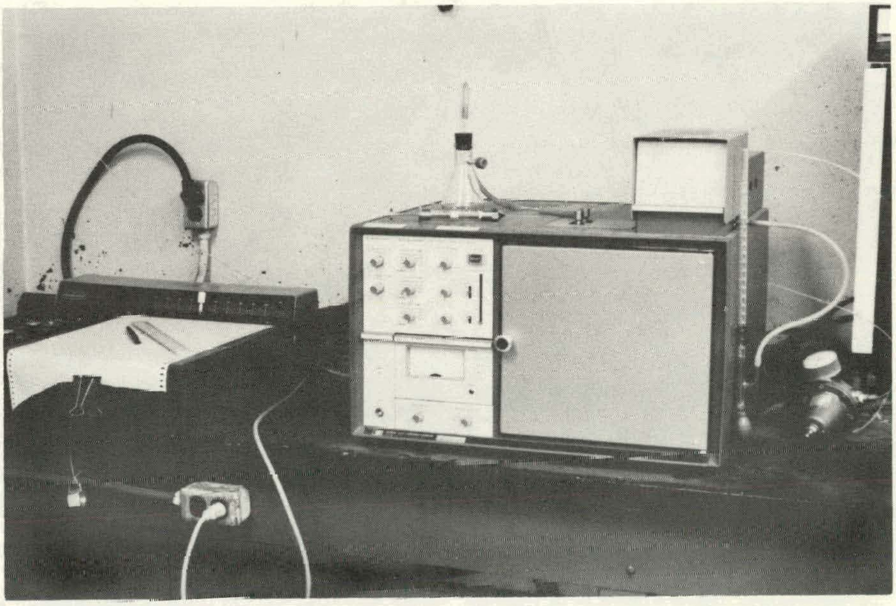


d. System Pressure Gauge, Back Pressure Regulator, Bypass Valves, Constant Temperature Bath Controls, Membrane Test Cells in Constant Temperature Bath, and Permeate Sampling Equipment

Figure 2. Photographs of the Test Line in Operation (Continued)

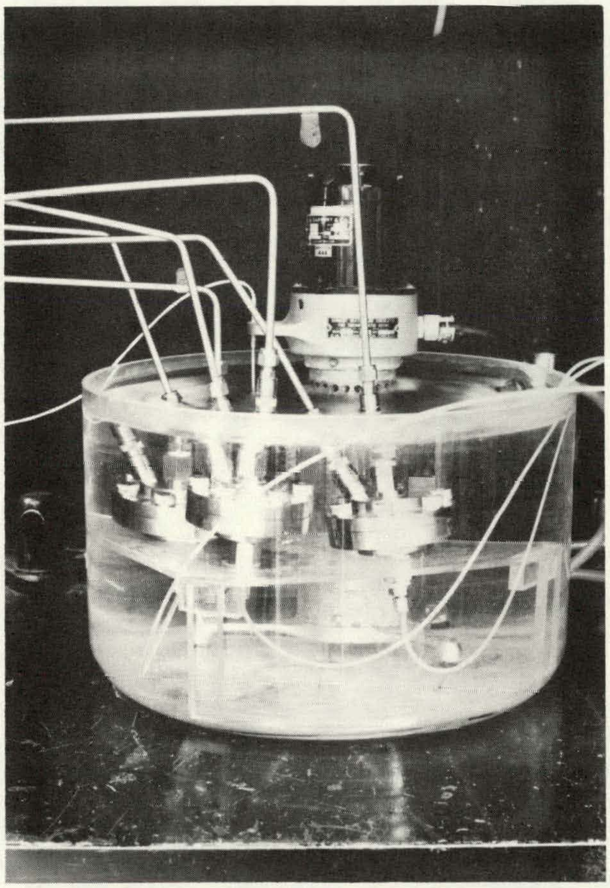


f. Membrane Test Cells in Constant Temperature Bath, and Permeate Sampling Equipment



g. Gas Chromatograph, Recorder, and Permeate Sampling Equipment

Figure 2. Photographs of the Test Line in Operation (Concluded)



e. Membrane Test Cells in Constant Temperature Bath

Figure 2. Photographs of the Test Line in Operation (Continued)

a Poropak N column for gas fractionation. It employed a thermal conductivity detector. It was calibrated for each gas individually. For hydrogen-containing gases, the carrier gas consisted of helium containing 8.5 percent hydrogen, available from Matheson Gas Products.

Permeation rates of gases through the membranes were measured by the soap bubble column technique. Movement of a soap bubble upward through a buret attached to the low pressure side of a membrane test cell was timed. For pure gas feedstreams, these data were directly converted into membrane flux values. For mixed gas feedstreams the permeate gas was first analyzed by gas chromatography to determine its composition.

The method of converting the gas chromatograph peaks into membrane fluxes was straightforward. For the particular column and detector it was observed that the peak height multiplied by the attenuation was a linear function of the mass of the gas injected. This relationship was observed for all four pure gases (hydrogen, carbon dioxide, methane, and hydrogen sulfide) in the gas mixtures employed in this program. The same relationship was observed for each component of several standard mixtures of these components. Thus it was possible from the size of the gas chromatograph peaks to obtain the mass fraction of each component in a gas mixture. Because the molecular weight of each component was known, the mole fractions of each component in the mixture could also be determined. In order to calculate the flux of each component the pressure on each side of the membrane and the rate at which the mixed gases were permeating the membrane must also be known. The high pressure was read from a pressure gauge and the low pressure was assumed to be the average barometric pressure at this altitude, 74 cm Hg. The rate at which mixed gases permeated the membrane was measured with a soap bubble flowmeter and a timer. From the mole fractions and the pressures, the partial pressures of each gas component on each side of the membrane could be calculated. From the rate at which mixed gas permeated the membrane and the mole fractions, the amount of each component permeating the membrane could be calculated. Then the flux for each component is given by:

$$\text{flux of "i"} = \frac{\text{rate at which "i" is permeating}}{\text{(driving force for "i")} \times \text{area}}$$

$$= \frac{\text{rate at which "i" is permeating}}{\text{(difference in partial pressures of "i")} \times \text{area}}$$

$$= \frac{\text{rate at which "i" is permeating}}{\begin{array}{l}\text{(partial pressure of "i" on high pressure side} \\ \text{minus partial pressure of "i" on low pressure} \\ \text{side)} \times \text{area}\end{array}}$$

The permeation rates were usually measured in ml/min, the pressures in psig or cm Hg and areas as sq mm. These were converted to ft^3/hr for permeation rates, ft^2 for area and 100's of psi for partial pressure difference. The fluxes have been tabulated as ft^3/ft^2-hr-100 psi of difference in this report. In all cases the gas volumes used in calculating fluxes have been normalized to a standard condition of 60°F and 30.0 in Hg by means of the ideal gas law. This allows convenient comparison on the same basis for experiments run under different conditions.

The ratio of any two fluxes, especially of CO_2 to H_2, is called the selectivity in this report.

The computer program MEMPER which performed the flux calculations is given in Table B-2 of the Appendix.

The entire system was assembled and operated within a large fume hood because of the presence of hydrogen sulfide as one of the test gases.

Choice of Gases for Permeability Tests

The molar composition of the raw gas stream from a coal gasifier can vary widely depending upon the type of gasifier employed. For a Hygas process operating on a high sulfur coal, the gas composition on a dry basis was estimated to comprise approximately 29 percent hydrogen (H_2), 26 percent carbon monoxide (CO), 25 percent methane (CH_4) (and some ethane), 17.5 percent carbon dioxide (CO_2), 2.5 percent hydrogen sulfide (H_2S), and small amounts of carbon oxysulfide (COS), methyl mercaptan (CH_3SH), and thiophene. Naphtha, ammonia, particulates and other materials would be present as well.

By shift conversion and gas purification processes, this raw gas stream was to be rendered suitable for methanation to produce a pipeline quality, high Btu product stream. The primary objective of this research program was to develop membrane processes for removal of all sulfur-bearing gases before methanation. Most of the CO_2 was also to be removed; a residual of two mole percent or less in the purified gas before methanation was set as a target in this program for CO_2 removal.

Preliminary work at MRI had indicated the following gas permeation rates for the principal gas feed components, expressed as ratios based on methane:

carbon monoxide	0.6
methane	1.0
hydrogen	3.0
carbon dioxide	15
hydrogen sulfide	45

These rates were measured for crosslinked polyethylenimine membranes using humidified gas streams at 5 to 80 psig transmembrane pressure difference. It was apparent that the crucial separation was the H_2/CO_2 separation. Under conditions of good carbon dioxide flux, removal of H_2S (and other sulfur-bearing gases) would be effectively achieved. Membrane research had to concentrate on achieving the highest possible CO_2/H_2 selectivity so that hydrogen losses would be minimized.

Initially therefore, membrane permeability tests were conducted with CO_2 and H_2 separately or as mixtures. These two gases were used in screening a variety of individual membrane compositions with minimum expenditure of time. Later, as program efforts concentrated on the most promising membrane compositions, sulfur-bearing gases and complex gas mixtures were also utilized in membrane permeability tests.

To simulate the complex gas mixture that would be encountered from a coal gasifier, a special order gas mixture was obtained from Matheson Gas Products which contained hydrogen (H_2), carbon dioxide (CO_2), methane (CH_4), and hydrogen sulfide (H_2S) in a mole ratio of 56.5:25.2:15.7:2.6 respectively. This composition,if mixed with a proper proportion of carbon monoxide (CO) from a second tank, could give a five-component gas mixture that simulated raw synthetic gas from a coal gasifier.

SCREENING OF EXPERIMENTAL MEMBRANES

The membrane approach to the cleanup of raw synthetic gas from coal gasification processes was based on earlier work on reverse osmosis membranes. A reverse osmosis membrane called NS-100, which was developed at the North Star Division of MRI, appeared to show selectivity for acid gases in preliminary gas permeability experiments. The NS-100 membrane was based on crosslinked polyamines supported on microporous polysulfone sheeting. These compositions were weakly cationic. The theory seemed plausible that weakly cationic membranes would selectively pass acidic gases such as carbon dioxide, hydrogen sulfide, carbon oxysulfide, and carbon disulfide.

Beginning efforts on the program centered on various crosslinked polyamine membrane compositions, mostly based on polyethylenimine (Tydex, Dow Chemical Company). Later efforts shifted to hydrophilic membrane systems in general when it was found that water content of the membranes was a controlling factor on acid gas transport, not the presence of weakly cationic groups. Of the various compositions that were examined, membranes based on methylcellulose proved to have the best combination of selectivity and permeability for acid gases.

Cationic Membranes

The first series of membranes fabricated and tested in this program consisted of thin coatings of polyethylenimine (Tydex 12, Dow Chemical Company) coated onto microporous polysulfone support sheets and insolubilized by various cure methods. Representative data for selected examples of these membranes are listed in Table 1. Many formulations in addition to those in Table 1 were fabricated but gave poor results or were too fragile, and so are not included. Two such examples were a polyethylenimine-Gantrez polysalt coating and a polyethylenimine-formaldehyde coating that was not heat-cured.

In general, carbon dioxide fluxes for polyethylenimine-based compositions were in the range of 1 to 2 ft^3/ft^2-hr-100 psi. Hydrogen permeabilities were naturally lower in all cases except those where membranes proved defective. The CO_2/H_2 selectivity ratios of the membranes typically ranged from 5 to 12, with occasional examples of up to 14. There was no particular advantage gained in terms of coating concentration or crosslinking agent. Room temperature cures for aldehyde-crosslinked membranes gave defective membranes, and compositions cured at 135°C and higher often exhibited little or no selectivity for CO_2 versus H_2.

Coating weights were varied by coating the polysulfone substrate with various concentrations of polyethylenimine in aqueous solution. Typically, 0.67 and 3.3 percent by weight solutions were used. In some cases, polysulfone supports were coated twice or three times to assess the effect of multiple layers on CO_2/H_2 selectivity. No consistent trend was noted in these experiments.

Table 1. Gas Permeability Data for Polyethylenimine-Based Membranes

Membrane	Composition (All on Polysulfone Backing)	Type of Test	Ratio of CO_2/H_2 Fluxes	Flux (ft^3/ft^2-hr-100 psi)*	
				CO_2	H_2
1B	0.67% Polyethylenimine, 1% CH_2O, 110°C cure	Pure Gases	5.7 - 6.7	1.8 - 4.3	0.26 - 0.75
1C	Same as above, but triple-coated	Pure Gases	12.5 - 14.1	1.2 - 1.5	0.10 - 0.11
1C (repeat)	0.67% Polyethylenimine, 1% formaldehyde pre-reacted, triple-coated, 110°C cure	Pure Gases	1.6 - 5.9	1.1 - 1.6	0.20 - 0.94
1D	NS-101 reverse osmosis membrane	Pure Gases	5.7 - 6.8	0.71 - 0.78	0.10 - 0.14
2A	3.3% Polythylenimine, 110°C cure	Pure Gases	13.4 - 13.5	0.97 - 1.4	0.077 - 0.10
2C	3.3% Polyethylenimine, 3.3% formaldehyde, pre-reacted, 110°C cure	Pure Gases	7.8 - 9.3	0.47 - 0.56	0.061 - 0.062
2E	3.3% Polyethylenimine, 4% glyoxal, pre-reacted, 110°C cure	Pure Gases	4.4 - 8.7	0.26 - 0.40	0.046 - 0.060
2G	3.3% Polyethylenimine, 4% glyoxal, not pre-reacted, 110°C cure	Pure Gases	7 - 7.8	0.33 - 0.35	0.044 - 0.047
3A	3.3% Polyethylenimine, 4% glyoxal, not pre-reacted, 135°C cure	Pure Gases	5.2	0.25	0.049
3D	0.67% Polyethylenimine, 1% CH_2O, not pre-reacted, double coating, 135°C cure	Pure Gases	7.9 - 8.2	0.51 - 0.58	0.065 - 0.070
4A	0.67% Polyethylenimine, 3.3% epichlorohydrin, pre-reacted, 110°C cure	Pure Gases	2.2 - 5.1	1.2 - 2.2	0.24 - 0.82
4B	0.67% Polyethylenimine, 3.3% epichlorohydrin, 1% piperazine, pre-reacted, 110°C cure	Pure Gases	1.8 - 4.5	1.7 - 2.2	0.51 - 0.014
6A	3.3% Polyethylenimine, 2% polyvinyl alcohol [illegible] 1.1% formaldehyde, pre-reacted, 135°C cure	Pure Gases	7.4	0.38	0.051
6C	6A saturated with arsenic trioxide	Pure Gases	8.4 - 12.2	1.0 - 1.2	0.074 - 0.11
7C	2% Ethylcellulose (G-50), 2% polyethylenimine, 135°C cure, in 2-methoxyethanol	Pure Gases	5.6 - 6.0	1.1 - 1.4	0.18 - 0.25
8C	Repeat of 2A	Pure Gases	4 - 12.1	2.2 - 2.6	0.20 - 0.55
14E	3.3% Polyethylenimine, 3.3% acrolein bisulfite, 135°C cure	Pure Gases	8.7 - 8.9	1.1 - 1.4	0.12 - 0.16
47D	Repeat of 2A	CO_2/H_2 Mixture	7.4 - 7.6	0.81 - 1.2	0.11 - 0.16
107D	0.67% Polyethylenimine, 2% 5-formyl-2-furansulfonic acid NA salt, 110°C cure	Pure Gases	4.3 - 4.9	1.6 - 1.7	0.34 - 0.37
104B	0.67% Polyethylenimine, 2% dichloroacetic acid, 2% 1,2-dichloroethane, 140°C cure	Pure Gases	7.6 - 13.5	0.94 - 1.9	0.07 - 0.26
107E	0.67% Polyethylenimine, 2% dichloroacetic acid, 140°C cure	Pure Gases	3.8 - 12.2	1.4 - 1.7	0.10 - 0.40

*Test Conditions: Humidified gas feed at 200 psig, test cells at 25°C and 200 psig, permeate at atmospheric pressure and room temperature (about 74 cm Hg and 20 to 25°C). Flux normalized to 60°F and 30.0 in Hg.

Insolubilization of the polyethylenimine was achieved simply by heating at a minimum temperature of 110°C in air for 15 minutes. Condensation reactions between polyethylenimine segments with evolution of ammonia occur at this temperature. In other cases, reaction with aldehydes was utilized for insolubilization. Aldehydes that were used included formaldehyde, glyoxal, and acrolein bisulfite. In some cases, aldehydes were pre-reacted with polyethylenimine in the coating solution, producing soluble prepolymers with N-methylol groups; in other cases, aldehydes were mixed into the coating solution, and reaction took place *in situ* in the coating during heating in an oven. Again, no advantage was gained by any particular choice of these conditions.

Example 1D consisted of an NS-101 reverse osmosis membrane in which the surface of the polyethylenimine coating is interfacially reacted with isophthaloylchloride/hexane solution to provide an ultrathin crosslinked polyamide barrier layer on the surface. This was then given a heat cure at 110°C in an oven. Its CO_2/H_2 selectivity and CO_2 flux were below the average.

Examples 4A, 4B, 104B, and 107E represented instances in which quaternary ammonium salts would be present in the membranes. In the case of dichloroacetic acid incorporation (Examples 104B and 107E) some high CO_2/H_2 selectivities were achieved at CO_2 fluxes above the average.

Example 6C represented a case in which arsenic trioxide was incorporated into the membrane. Arsenic ion acts as a catalyst for carbon dioxide conversion to carbonic acid in aqueous media.(2) It would thus promote increased absorption rates for CO_2 into membranes at the interface. Example 6C did show higher CO_2/H_2 selectivities and higher flux than the control, Example 6A, but these results were not above the overall average.

Lack of reproducibility was a problem throughout the series of tests on polyethylenimine membrane systems. The simplest formulation, represented by Example 2A which involved only polyethylenimine in the coating and a 110°C heat-cure for insolubilization, was fairly reproducible, however. This is shown by later repeat experiments with Examples 8C and 47D.

Table 2 contains results of two miscellaneous cationic membranes made with alternative polyamines. The first membrane, Example 3B, was made by coating microporous polysulfone with an aqueous solution of meta-phenylenediamine (neutralized with sulfuric acid), and reacting this with formaldehyde vapors to produce a polymeric coating. The second membrane, Example 3C, was made with polyepiamine(3) (the reaction product of ethylenediamine with polyepichlorohydrin) and formaldehyde. Both membranes gave average to below average CO_2/H_2 selectivities compared to polyethylenimine compositions. The polyepiamine composition showed twice the flux of polyethylenimine compositions, however.

Table 2. Gas Permeability Data for Other Cationic Membranes

Membrane	Composition	Ratio of CO_2/H_2 Fluxes	Flux (ft^3/ft^2-hr-100 psi)*	
			CO_2	H_2
3B	2% Metaphenylenediamine sulfate, formaldehyde, 110°C cure	1.5 - 6.6	1.1 - 1.3	0.17 - 0.88
3C	2% Epiamine Resin, 2% formaldehyde, coated twice, 110°C cure	4.6 - 7.2	2.0 - 4.3	0.33 - 0.63

*Test Conditions: Humidified gas feed at 200 psig, test cells at 25°C and 200 psig, permeate at atmospheric pressure and room temperature (about 74 cm Hg and 20 to 25°C). Pure gases used. Flux normalized to 60°F and 20.0 in Hg.

Various Hydrophilic Membranes

During the fabrication and testing of polyethylenimine membranes, it became apparent that the presence of water in the membranes and/or the feed gas affected the gas flux and selectivity characteristics. In recognition of this behavior, similar membranes were fabricated from other polymers that were water-sensitive. It became quickly apparent that some of these hydrophilic membranes were capable of matching or exceeding the cationic membranes in terms of both gas flux and CO_2/H_2 selectivity. A variety of different hydrophilic polymers was thus examined, and results of this screening effort are described below.

Experimental Methylcellulose Compositions

Table 3 contains screening data for several experimental methylcellulose membranes. Composite membranes containing methylcellulose exhibited CO_2 fluxes of 1.5 to 3.8 ft^3/ft^2-hr-100 psi. Typical fluxes were about twice the level experienced for polyethylenimine membranes. The CO_2/H_2 selectivities varied from 2 to 12, with several membrane compositions showing ratios at around 10. The best example was a membrane consisting of microporous polysulfone coated with an aqueous solution of 2 percent w/v methylcellulose and 2 percent w/v glyoxal (Example 16B). W/V refers to a percentage calculated on the basis of weight of solute per volume of solvent, in grams/100 milliliters. The coated membrane was drained, air-dried, then heated to 135°C for 15 minutes to insolubilize the coating. Carbon dioxide fluxes were 3.5 to 3.8 ft^3/ft^2-hr-100 psi at CO_2/H_2 selectivities of 9.9 to 12.2. While this result was not matched in any of the other exploratory methylcellulose membranes, including one repeat case (Example 17E), optimization efforts on methylcellulose membranes would presumably improve on this situation.

Experimental Polyvinyl Alcohol Membranes

Table 4 contains gas permeability data for exploratory polyvinyl alcohol composite membranes. This hydrophilic polymer gave highly variable results, with CO_2/H_2 selectivities occasionally above 10. The CO_2 fluxes were generally less than 1 ft^3/ft^2-hr-100 psi, although a polyvinyl alcohol/polyvinyl pyrrolidone blend exhibited a CO_2 flux of 2 ft^3/ft^2-hr-100 psi at a CO_2/H_2 selectivity of 8 to 8.6. In general, polyvinyl alcohol membranes are possible that would match the performance of polyethylenimine membranes, but average performance would be lower.

Experimental Cellulose Acetate Membranes

Table 5 contains gas permeability data for exploratory membranes based on cellulose acetate coatings. The first example in Table 5 consisted of an ultrathin cellulose acetate (39.8 percent acetyl content) membrane prepared by float-casting a film of the polymer on the water surface from its solution in cyclohexanone, then laminating it to a microporous polysulfone support.

Table 3. Gas Permeability Data for Exploratory Methylcellulose Membranes

Membrane	Composition	Ratio of CO_2/H_2 Permeabilities	Flux (ft^3/ft^2-hr-100 psi)	
			CO_2	H_2
14B	2% Methylcellulose, 2% glyoxal, 135° cure	7.1 - 8.1	2.3 - 2.4	0.28 - 0.33
15C	2% Methylcellulose, 2% acrolein, 1% hydrochloric acid, 135°C cure	3.1 - 4.3	2.3 - 2.5	0.54 - 0.75
16A	2% Methylcellulose, 2% glyoxal, 2% hydrochloric acid, 135°C cure	7.7 - 8.4	1.6 - 1.8	0.20 - 0.22
16B	2% Methylcellulose, 2% glyoxal, air-dried, 135°C cure	9.9 - 12.2	3.5 - 3.8	0.31 - 0.36
16C	2% Methylcellulose, 2% glyoxal, 5% ammonium hydroxide, solution allowed to stand 16 hrs and filtered, 135°C cure	6.7 - 10.1	1.7 - 1.9	0.17 - 0.36
16D	2% Methylcellulose, 2% formaldehyde, 135°C cure	9.4 - 10.1	1.9 - 2.4	0.21 - 0.24
16E	2% Methylcellulose, 2% glyoxal, 1% sodium sulfite, 135°C cure	8.8	2.1	0.24
17A	Membrane 16B saturated with 10% sodium arsenite solution	2.9 - 11.3	1.5 - 1.8	0.13 - 0.50
17B	1-mil-thick methylcellulose without support film, crosslinked with glyoxal, 150°C cure	18?	Very slow	Very slow
17C-1	Repeat of 14B	5.6 - 7.3	1.7 - 2.0	0.24 - 0.32
17C-2	Membrane 17C-1 saturated with 5% sodium arsenite solution	4.7 - 7.0	1.3 - 1.7	0.24 - 0.29
17D	2% Methylcellulose, 2% epichlorohydrin, 1% sodium hydroxide, 135°C cure	6.1 - 7.5	2.2 - 2.5	0.23 - 0.34
17E	Repeat of 16B	4.4 - 8.3	2.2 - 2.9	0.33 - 0.63
18A	1% Methylcellulose, 1% glyoxal, 135°C cure	5.0 - 7.8	2.2 - 2.4	0.29 - 0.46
21D	2% Methylcellulose, 2% glutaraldehyde/sulfur dioxide, air-dried, 135°C cure	About 2	Not Calculated	Not Calculated

Test Conditions: Humidified gas feed at 200 psig, test cells at 25°C and 200 psig, permeate at atmospheric pressure and room temperature (about 74 cm Hg and 20 to 25°C). Pure gases used. Flux normalized to 60°F and 30.0 in Hg.

Table 4. Gas Permeability Data for Exploratory Polyvinyl Alcohol Membranes

Membrane	Composition	Type of Test	Ratio of CO_2/H_2 Fluxes	Flux (ft^3/ft^2-hr-100 psi)*	
				CO_2	H_2
6B	Polyvinyl acohol	Pure Gases	10.7 - 11.2	0.85 - 0.86	0.078 - 0.080
11D	Polyvinyl alcohol, glycidol	Pure Gases	6.8 - 8.5	0.61 - 0.63	0.071 - 0.096
12A	Polyvinyl alcohol, acrolein bisulfite	Pure Gases	4.1 - 4.6	0.075 - 0.13	0.018 - 0.028
12B	Polyvinyl alcohol, acrolein bisulfite, higher ratio	Pure Gases	5.4 - 5.9	0.32 - 0.38	0.054 - 0.071
12C	Polyvinyl alcohol, acrolein bisulfite, even higher ratio	Pure Gases	2.6 - 3.5	0.96 - 1.0	0.29 - 0.37
22A	1% Polyvinyl alcohol crosslinked with acrolein bisulfite, formaldehyde and sulfuric acid	CO_2/H_2 Mixture	2 - 3.5	not calculated	not calculated
22B	1% Polyvinyl alcohol, 2% glutaraldehyde	CO_2/H_2 Mixture	about 1.5	not calculated	not calculated
42B	2% Polyvinyl alcohol, 0.4% glyoxal, 0.4% hydrochloric acid, 135°C cure	CO_2/H_2 Mixture	3.9 - 5.5	not calculated	not calculated
43B	1% Polyvinyl alcohol, 0.2% sodium hydroxide, 1% divinyl sulfone, 135°C cure	Four Gas Mixture	10.8 - 13.0	0.39 - 1.3	0.03 - 0.12
43C	2% Polyvinyl alcohol, 0.4% glyoxal, 0.4% hydrochloric acid, 50% isopropanol, 135°C cure	CO_2/H_2 Mixture	3.3 - 4.5	0.35 - 0.69	0.079 - 0.18
44B	Repeat of 43C, 1% Carbowax 20M added to the coating solution	CO_2/H_2 Mixture	6.9 - 9.1	0.38 - 0.57	0.050 - 0.062
49A	2% Polyvinyl alcohol, 2% polyvinyl pyrrolidone, 2% hydrochloric acid, 4% formaldehyde, 135°C cure	CO_2/H_2 Mixture	8 - 8.6	2	0.23 - 0.26
49B	2% Polyvinyl alcohol, 2% triethanolamine 4% glyoxal, 135°C cure	CO_2/H_2 Mixture	5.9 - 7.7	1.4 - 1.9	0.21 - 0.25

*Test Conditions: Humidified gas feed at 200 psig, test cells at 25°C and 200 psig, permeat at atmospheric pressure and room temperature (about 74 cm Hg and 20 to 25°C). Flux normalized to 60°F and 30.0 in Hg.

Table 5. Gas Permeability Data for Exploratory Cellulose Acetate Membranes

Membrane	Composition	Ratio of CO_2/H_2 Permeabilities	Flux (ft^3/ft^2-hr-100 psi)*	
			CO_2	H_2
--	Ultrathin cellulose acetate membrane float cast on water from cyclohexanone solution	8.1	5.4**	0.67**
18B-1	2% Cellulose acetate in glacial acetic acid, air-dried	4.1 - 4.5	0.73 - 0.88	0.17 - 0.20
18B-2	Cellulose membrane made by hydrolysis of 18B-1 in NH_4OH	5.3 - 5.4	0.63 - 0.88	0.12 - 0.16
18C	Cellulose triacetate, made by *in situ* acetylation of 18B-1 with acetic anhydride and hydrochloric acid	1.2 - 1.9	0.63 - 1.5	0.46 - 0.88
18D	2% Cellulose acetate in glacial acetic acid, 1% paraformaldehyde, 135°C cure	2.9 - 3.3	0.50 - 0.60	0.17 - 0.20
18E	Cellulose acetate (36% acetyl content), prepared as in 18B-1	3.5 - 5.4	0.34 - 0.83	0.067 - 0.21

*Test Conditions: Humidified feed at room temperature and 200 psig, cells at 25°C and 200 psig, permeate at room temperature and atmospheric pressure (about 25°C and 74 cm Hg). Pure gases used. Flux normalized to 60°F and 30.0 in Hg.

**140 psig test pressure.

This membrane, which was approximately 200 angstroms thick, exhibited very good CO_2 flux (5 ft^3/ft^2-hr-100 psi at 140 psig), and the CO_2/H_2 selectivity ratio was promising at 8.

When cellulose acetate was dissolved in glacial acetic acid and coated directly onto microporous polysulfone substrates, selectivities were lower, and CO_2 flux was typically less than 1 ft^3/ft^2-hr-100 psi. In Example 18B-2, the cellulose acetate coating was hydrolyzed to cellulose by soaking in concentrated ammonium hydroxide overnight. No significant improvement in flux or selectivity over the cellulose acetate control (Example 18B-1) was noted in this test.

Experimental Polyacrylamide Membranes

Table 6 contains gas permeability data for exploratory membranes made from polyacrylamide and acrylamide copolymers. Examples 13A through 14D all consisted of polyacrylamide coated onto microporous polysulfone and crosslinked by various means. In this series, little or no CO_2/H_2 selectivity was achieved. Thus, though polyacrylamide is a hydrophilic polymer, it produced membranes with poor separation characteristics for CO_2 versus H_2.

In Example 19A, the copolymer of acrylamide with vinyl acetate was synthesized in our laboratory and fabricated into a membrane. It exhibited a CO_2/H_2 selectivity that met the low average value for polyethylenimine membranes; its CO_2 flux was good, however, at 2.9 to 3.2 ft^3/ft^2-hr-100 psi. Similarly, acrylamide-vinyl pyrrolidone copolymer was synthesized, but its CO_2/H_2 selectivity was not as favorable.

In Example 48B, an emulsion was prepared containing the crosslinked copolymer of acrylamide, with N,N'-methylene-bis-acrylamide. Membranes made by coating this emulsion on microporous polysulfone gave high CO_2 fluxes, but CO_2/H_2 selectivity was poor.

Miscellaneous Hydrophilic Polymer Membranes

Table 7 contains gas permeability data for a number of miscellaneous exploratory hydrophilic membranes.

Example 7B represents a non-hydrophilic membrane prepared from ethylcellulose, which exhibited selectivity for H_2 versus CO_2. When the ethylcellulose was pre-reacted with acrolein, giving a more hydrophilic membrane, the selectivity was shown to reverse and favor CO_2 by a factor of 3 to 4.

Two membranes were tested that contained crosslinked carboxymethyl hydroxyethyl cellulose coatings. One gave fair CO_2 flux and selectivity; the other behaved poorly.

A commercial sample of vinyl pyrrolidone-vinyl acetate copolymer gave membranes with a CO_2/H_2 selectivity ratio as high as 12 at a CO_2 flux of

Table 6. Gas Permeability Data for Membranes from Acrylamide Polymers

Membrane	Composition	Type of Test	Ratio of CO_2/H_2 Fluxes	Flux (ft^3/ft^2-hr-100 psi)	
				CO_2	H_2
13A	2% Polyacrylamide, 2% formaldehyde, pre-reacted, 135°C cure	Pure Gases	<1	very high	very high
13B	Same as 13A, sulfuric acid catalyst	Pure Gases	<1	very high	very high
13C	2% Polyacrylamide, 1% formaldehyde, 2% hydrochloric acid, 135°C cure	Pure Gases	1.4	0.68	0.47
13D	2% Polyacrylamide, 1% formaldehyde, 1% glyoxylic acid, 135°C cure	Pure Gases	1.2	2.8	2.3
13E	2% Polyacrylamide, 2% glyoxal, 135°C cure	Pure Gases	<1	---	---
13F	2% Polyacrylamide, 2% glyoxal, 2% hydrochloric acid, 135°C cure	Pure Gases	2.0	1.7	0.83
14A	2% Polyacrylamide, 2% glyoxal, 1% piperazine, 2% hydrochloric acid, 135°C cure	Pure Gases	<1	---	---
14C	2% Polyacrylamide, 2% acrolein bisulfite, 135°C cure	Pure Gases	1.6	1.8	1.1
14D	4% Polyacrylamide, 2% acrolein bisulfite, 3% sulfuric acid, 135°C cure	Pure Gases	1.8	0.78	0.44
19A	2% Acrylamide-vinyl acetate copolymer, 2% formaldehyde, pre-reacted, 135°C cure	Pure Gases	6.1 - 6.9	2.9 - 3.2	0.45 - 0.53
19B	Same as 19A but with 2% sulfuric acid	Pure Gases	2.6 - 2.9	5.5 - 5.8	2.0 - 2.2
20D	4% Acrylamide-vinyl pyrrolidone copolymer, 2% formaldehyde, 135°C cure	CO_2/H_2 Mixture	3.5 - 4.2	1.6 - 2.5	0.40 - 0.69
48B	2% Acrylamide/methylene-bis-acrylamide copolymer emulsion, 2% formaldehyde, 2% hydrochloric acid, 135°C cure	CO_2/H_2 Mixture	1.1 - 3.7	3.2 - 12.2	0.85 - 10.6

Test Conditions: Humidified gas feed at 200 psig, test cells at 25°C and 200 psig, permeate at atmospheric pressure and room temperature (about 74 cm Hg and 20 to 25°C). Flux normalized to 60°F and 30.0 in Hg.

Table 7. Gas Permeability Data for Miscellaneous Hydrophilic Membranes

Membrane	Composition	Type of Test	Ratio of CO_2/H_2 Permeabilities	Flux (ft^3/ft^2-hr-100 psi)	
				CO_2	H_2
7B	2% Ethylcellulose coated from 2-methoxyethanol, air-dried	Pure Gases	0.24 - 0.42	1.1 - 1.3	2.7 - 5.3
11C	2% Ethylcellulose pre-reacted with 2% acrolein in t-butanol, 2% hydrochloric acid, 135°C cure	Pure Gases	3.0 - 4.1	1.1 - 1.6	0.25 - 0.50
9D	2% Carboxymethyl hydroxyethyl cellulose, 2% glyoxal, 2% hydrochloric acid, 135°C cure	Pure Gases	5.0	1.5	0.30
11A	2% Carboxymethyl hydroxyethyl cellulose, 2% acrolein bisulfite, 2% hydrochloric acid, 135°C cure	Pure Gases	0.76 - 0.80	2.1 - 3.2	2.8 - 4.3
10D	5% Vinyl pyrrolidone-vinyl acetate copolymer, 2-1/2% H_2SO_4, 2% formaldehyde, 135°C cure	Pure Gases	7.8 - 12.1	1.8 - 2.0	0.17 - 0.23
19D	2% Vinyl pyrrolidone-vinyl acetate copolymer, 2% formaldehyde, 2% H_2SO_4, pre-reacted, 135°C cure	Pure Gases	2.8 - 3.8	3.5 - 3.8	0.96 - 1.3
20B	2% Vinyl pyrrolidone-vinyl acetate copolymer, 2% acrolein bisulfite, 3% H_2SO_4, 135°C cure	Pure Gases	3.6 - 4.2	1.8 - 2.3	0.42 - 0.63
10E	5% Carboset 525, 2-1/2% NH_4OH, 135°C cure	Pure Gases	5.0 - 5.8	0.50 - 0.79	0.083 - 0.16
18F	2% Polyvinyl acetate in glacial acetic acid, air-dried	Pure Gases	3.4 - 7.1	0.83 - 1.0	0.15 - 0.28
23B-1	2.5% Sulfonated polysulfone, coated on poly-acrylonitrile support from $CHCl_3$, air-dried	CO_2/H_2 Mixture	1.8 - 3.7	not calculated	not calculated
23B-2	Same as 23B-1, morpholine salt	CO_2/H_2 Mixture	4.0 - 13.8	1.2 - 1.3	0.093 - 0.31
28C-1	Repeat of 23B-2	CO_2/H_2 Mixture	4.8 - 8.2	1.6 - 1.7	0.20 - 0.35
--	Block copolymer of poly(ethylene oxide) and polycarbonate, commercial membrane	Pure Gases	12.0 - 16.2	0.66 - 0.70	0.04 - 0.056
42A	5% Block copolymer of poly(ethylene oxide) and polycarbonate coated on polyacrylonitrile support from chloroform, air-dried	CO_2/H_2 Mixture	21	0.23 - 0.24	0.011 - 0.012
45C	Ultrathin film of block copolymer of poly (ethylene oxide) and polycarbonate cast on glass plate from 5% w/v chloroform, air-dried	CO_2/H_2 Mixture	14.2	0.083 - 0.10	0.0059 - 0.0071
46B-1	Ultrathin film cast from solution of 45C with 4% w/v sulfolane added, not dried before testing	CO_2/H_2 Mixture	7.7 - 8.8	0.44 - 0.83	0.061 - 0.095
46B-2	Same as 46B except air-dried before testing	CO_2/H_2 Mixture	3.4 - 4.2	0.13 - 0.25	0.038 - 0.059
40C	Poly(ethylene oxide)-poly(ethylene terephthalate) block copolymer (70% PEO) dense membrane cast on glass from 10% w/v in DMF	CO_2/H_2 Mixture	6.0 - 12.1	0.22	0.018 - 0.052
47A	5% Polyvinylformal from glacial acetic acid, air-dried	CO_2/H_2 Mixture	3.9 - 5.4	0.061 - 0.075	0.011 - 0.019
47B	5% Poly(ethyl methacrylate) in cyclohexanone, float-cast on water, air-dried	CO_2/H_2 Mixture	2.7 - 5.7 0.91 - 0.03 (500 psig)	0.90 - 1.2 17 - 32 (500 psig)	0.16 - 0.43 19 - 34 (500 psig)
47C	Same as 47B, heat-cured at 135°C	CO_2/H_2 Mixture	1.0 - 1.1	0.79 - 1.1	0.80 - 1.1

*Test Conditions: humidified feed gas at room temperature and 200 psig, test cells at 25°C and 200 psig, permeate at room temperature and atmospheric pressure (about 20°C and 74 cm Hg). Flux normalized to 60°F and 30.0 in Hg.

approximately 2 ft^3/ft^2-hr-100 psi. Low to moderate CO_2/H_2 selectivities were seen for Carboset (a commercial, self-crosslinking hydrophilic polymer), polyvinyl acetate, sulfonated polysulfone (synthesized in our laboratory), and polyvinyl formal. A membrane made from morpholine salt of sulfonated polysulfone gave CO_2/H_2 selectivities of as high as 13.8 at CO_2 fluxes of 1.2 to 1.3 ft^3/ft^2-hr-100 psi, but this high selectivity was not easily reproduced.

Excellent CO_2/H_2 selectivity was shown by a commercial hemodialysis membrane made from the block copolymer of polyethylene oxide and polycarbonate, when tested directly as received. When a portion of this membrane was dried, dissolved in chloroform, and cast into a thin film on glass or coated onto a microporous polyacrylonitrile support, its high CO_2/H_2 selectivity was easily reproduced. However, its measured CO_2 fluxes were uniformly low--less than 1 ft^3/ft^2-hr-100 psi--and improvements in its permeability were not readily obtained.

A 70/30 block copolymer of polyethylene oxide and polyethylene terephthalate, synthesized in our laboratory, was also tried as a thin, dense film. It also showed good to excellent CO_2/H_2 selectivity, but again at low CO_2 flux.

A poly(ethyl methacrylate) coating on polysulfone was tested because of information that it showed very high CO_2 fluxes at high pressures.[4] This membrane exhibited a CO_2 flux of about 1 ft^3/ft^2-hr-100 psi at 200 psig feed gas pressure. Its CO_2 flux indeed increased by a factor of 15 to 25 at 500 psig pressure. However, comparison tests with H_2 showed similar large increases and loss of membrane selectivity. The poly(ethyl methacrylate) coating apparently deformed and opened up pinholes at the 500 psig test pressure. Although its glass transition temperature is listed as 65°C, it behaves somewhat like a rubber at room temperature.

Conclusions from the Membrane Screening Effort

The gas permeability test results in Tables 1 through 7 showed that a variety of membrane compositions were capable of selectively passing CO_2 versus H_2. The permeation rates were not dependent on the presence of cationic groups in the coating. Rather, hydrophilicity of the coating and the presence of water in the membrane were important to the selective permeation of CO_2 and rejection of H_2.

However, the nature of the polymer also played a role. While polyacrylamide is basically a very hydrophilic polymer for example, its membranes routinely showed very low CO_2/H_2 selectivity.

The highest CO_2 fluxes at favorable CO_2 selectivities were shown by methylcellulose compositions. Apparently, the rather rigid backbone of the methylcellulose polymer results in an open structure for CO_2 permeation that does not collapse under pressure.

The highest overall CO_2 selectivities were shown by the polyethylene oxide-polycarbonate block copolymer. However, CO_2 fluxes were low, presumably because the flexible rubbery polyethylene oxide segments undergo compaction at the high test pressures.

Considering these various factors, selection of methylcellulose as a membrane material for optimization seemed appropriate, based on its superior combination of flux and selectivity in these exploratory trials.

MEMBRANE OPTIMIZATION STUDIES

The goal of this task was the optimization of the membrane composition judged to be best as found in the screening tests reported in the previous section of this report. Methycellulose was chosen on the basis of its superior gas flux properties relative to other membrane compositions. On the basis of gas selectivity for CO_2 versus H_2, it also showed good behavior, often giving CO_2/H_2 selectivity ratios of 10 to 12. Optimization studies on the methylcellulose membranes covered several variables, including molecular weight (viscosity grade), concentration, nature of the solvent system, nature and concentration of crosslinking agents and catalysts, the type of microporous support film, the degree of heat cure, and the casting technique.

Highest Fluxes Achieved with Methylcellulose Membranes

High carbon dioxide fluxes, up to 7 ft^3/ft^2-hr-100 psi, at good CO_2/H_2 selectivity (α = 7 to 11) were achieved in gas mixtures using crosslinked methylcellulose membranes. These high-flux formulations are listed in Table 8. A few lower flux membranes are also listed for comparison to facilitate discussion of the optimum fabrication variables. The parameter α represents the CO_2/H_2 selectivity in this report.

The methycellulose membranes that provide the maximum observed CO_2 flux were made by coating a polysulfone support film with a water solution containing equal weights each of 100 cps methylcellulose and glyoxal. A heat-cure at 135° was used to force reaction of the glyoxal with unsubstituted hydroxyl groups of methylcellulose.

It is notable in Table 8 data that either the addition of isopropanol to the coating solution or the soaking of the membrane in water for several hours gave excellent CO_2 fluxes of about 5 to 7 ft^3/ft^2-hr-100 psi at high separation ratios. Either 1 or 2 percent methylcellulose may be used. Membranes cast without use of isopropanol appeared quite hydrophobic when first immersed in water. However, after 24 hours in water, the crosslinked methylcellulose coating absorbed water with substantial swelling. The membrane in the water-swollen state exhibited its maximum flux of about 7 ft^3/ft^2-hr-100 psi.

If the membrane was not first saturated with water, the separation ratio was about the same, but the flux was generally lower and more variable. This is illustrated by the Examples 34A-1 and 34A-2 in Table 8.

The degree of swelling of the film in water was reduced by addition of a volatile acid catalyst (hydrochloric acid), which probably increased the degree of crosslinking. (A non-volatile acid catalyst such as sulfuric acid could not be used because it hydrolyzed the methylcellulose.) Addition of 0.4 percent hydrochloric acid to the methylcellulose coating solution served this purpose. The tighter membranes that resulted were characterized by 50 percent lower flux, as illustrated by Example 35F in Table 8.

Table 8. Examples of High Flux Methylcellulose Membranes

Membrane	Composition	CO_2 Flux*	Approximate CO_2/H_2 Flux Ratio
31D	2% methylcellulose, 2% glyoxal, 25% isopropanol, heat cured	5.3-6.2	7-8
32E	1% methylcellulose, 1% glyoxal, 20% isopropanol, heat cured in humidified oven.	4.7-6.9	9-11
34A-1	1% methylcellulose, 1% glyoxal, heat cured at high humidity, soaked in water for a few minutes	3.2-5.6	9-13
34A-2	Same as 34A-1 but soaked for 21 hours.	5.8-7.0	10.5
34C	1% methylcellulose, 1% glyoxal, 20% isopropanol, on wet support, heat cured in humidified oven	5.4-7.0	6-9.5
35A	1% methylcellulose, 1% glyoxal, 0.4% hydrochloric acid, 50% isopropanol, on wet support, heat cured in humidified oven	2.0-2.6	13
39B	1% Dow F-50, 1.2% glyoxal, 50% isopropanol, 0.4% hydrochloric acid, heat cured in humidified oven	2.5-3.3	9-12
47E	1% Dow F-50, 2% glyoxal, 50% isopropanol, heat cured in humidified oven	2.0-5.1	8.5
51E	0.85 methylcellulose, 1.3% glyoxal, 26% isopropanol, filtered, 0.6% hydrochloric acid, heat cured in humidified oven.	4.7-4.9	7.5-10

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*Ft^3/ft^2-hr-100 psi, normalized to 60°F, and 30.0 in. Hg.

The use of hydroxypropyl derivatives of methylcellulose rather than methylcellulose itself yielded membranes with lower fluxes. The best of these, Dow F-50, had a flux of up to 5 ft^2/ft^2-hr-100 psi at a CO_2/H_2 separation ratio of 8.5. Again, as shown by Example 39B in Table 8, the flux was lowered by the addition of hydrochloric acid.

Example 51E of Table 8 showed that the flux of methylcellulose membranes could still be quite respectable even if the formulation was not quite optimum. Flux appeared to be broadly rather than sharply related to key fabrication parameters such as concentration, heat-cure temperatures and crosslinking aids. In Example 51E, the low ratio of methylcellulose to glyoxal and the presence of hydrochloric acid should both tend to reduce the membrane flux. Both agents would lead to a tighter membrane network less likely to absorb water and to permeate gases. Despite these factors, a very respectable flux of 5 ft^2/ft^2-hr-100 psi was still achieved.

Other Methylcellulose Membrane Test Results

Many other tests of methylcellulose membranes were made as part of this optimization study. Test data on these are compiled in Table 9. Many of these membranes gave very good separation ratios but none approached the high CO_2 fluxes of those in Table 8. Example 46C in Table 9 was interesting in that it was a dynamically formed methylcellulose membrane. It was fabricated by exposing polysulfone supports to dissolved methylcellulose (4000 cps) in a reverse osmosis line under pressure. It exhibited good gas separation properties but low flux.

Results on Related Cellulose Derivatives

In addition to crosslinked methylcellulose membranes, tests were made on other closely related derivatives of cellulose and, for comparison, upon cellulose itself. This was considered a necessary part of the optimization effort, since standard methylcellulose was not necessarily the perfect cellulose derivative for this application. Results of these investigations are shown in Table 10.

Methylcellulose derivatives modified by reaction with propylene oxide were commercially available. Two products were selected that contained a low and a high degree of hydroxypropoxyl substitution:

Methocel F-50, 1.7-1.9 methoxyl D.S., 0.1-0.2 hydroxypropoxyl M.S.,
Methocel 5JMS, 1.1-1.6 methoxyl D.S., 0.7-1.0 hydroxypropoxyl M.S.,
(D.S. = degree of substitution, M.S. = molar substitution.)

Membranes made from these derivatives, Examples 39B and 39C were similar in flux to a methylcellulose control (39A), but had better selectivities, as illustrated in Table 10. The advantages of these modified polymers were in their ease of solution and the greater physical strength of the resulting membranes in the water-swollen condition.

Table 9. Variation in Methylcellulose Membrane Fabrication Conditions and Resulting Gas Permeability Data

Membrane	Composition	Type of Test	Ratio of CO_2/H_2 Permeabilities	Flux (ft^3/ft^2-hr-100 psi)*	
				CO_2	H_2
24A	2% methylcellulose (15 cps), 0.4% glyoxal, coated on wet polysulfone support film, 135°C cure	CO_2/H_2 mixture	3.5 - 5.5	Not calculated	Not calculated
24B	Same as 24A, glyoxal 1%	CO_2/H_2 mixture	4.2 - 6.2	1.7 - 2.2	0.34 - 0.41
24C	Same as 24A, glyoxal 2%	CO_2/H_2 mixture	4.6 - 7.6	2.4 - 2.7	0.34 - 0.57
24D	Same as 24C but coated onto dry polysulfone support film	CO_2/H_2 mixture	8.0 - 9.2	2.0 - 2.5	0.25 - 0.28
28A	0.5% methylcellulose (4000 cps), 0.4% glyoxal, 135°C cure	CO_2/H_2 mixture	1.3 - 1.4	3.6 - 7.0	2.7 - 5.0
28B	Same as 28A, 0.7% benzenedisulfonic acid catalyst added	CO_2/H_2 mixture	2.2	6.7	3.0
29A	2% methylcellulose (15 cps), 2% glyoxal, 135°C cure in humidified oven	CO_2/H_2 mixture	3.8 - 18.6	1.9 - 2.2	0.10 - 0.57
29B	Same as 29A, coating solution aged 24 hours.	Pure Gases	1.9 - 2.7	2.0 - 2.2	0.80 - 1.1
29C	Same as 28B, 5% calcium chloride catalyst added	Pure Gases	6.1 - 6.7	3.0 - 3.1	0.44 - 0.51
30A	2% methylcellulose (15 cps), 2% glyoxal, 135°C cure in an aluminum tray	Pure Gases	2.4 - 2.7	3.1 - 3.6	1.21 - 1.5

Table 9, Variation in Methylcellulose Membrane Fabrication [illegible] and Resulting Gas Permeability (Continued)

Membrane	Composition	Type of Test	Ratio of CO_2/H_2 Permeabilities	Flux (ft^3/ft^2-hr-100 psi) CO_2	Flux (ft^3/ft^2-hr-100 psi) H_2
30B	2% methylcellulose (15 cps) 2% glyoxal, excess wiped off with a rubber roller, 135°C cure	Pure Gases	5.7 - 7.7	2.6 - 3.1	0.34 - 0.37
30C	Same as 30B except used a glass rod	Pure Gases	6.3 - 7.4	2.2 - 2.8	0.41 - 0.48
31A	2% methylcellulose (15 cps), 2% glyoxal, 1% glycerol, 135°C cure in aluminum tray (very hydrophilic)	Pure Gases	3.2 - 8.8	3.0 - 3.2	0.33 - 0.99
31B	Same as 31A, 1% magnesium chloride catalyst added	Pure Gases	8.4 - 11.6	2.9 - 3.5	0.24 - 0.42
31C	2% methylcellulose (15 cps) 2% glyoxal, 20% isopropanol, 135°C cure in aluminum tray	Pure Gases	1.4 - 10.4	1.9 - 2.7	0.19 - 1.9
32A	Same as 31C but no tray	Pure Gases	6.4 - 14.5	2.6 - 3.1	0.21 - 0.41
32C	1% methylcellulose (100 cps) 1% glyoxal, 135°C cure	CO_2/H_2 mixture	8.4 - 15.5	3.2 - 5.2	0.20 - 0.51
32D	Same as 32C, humidified oven	Pure Gases	5.7 - 9.3	2.6 - 4.1	0.28 - 0.63
33A	Same as 32D, 135°C cure at very high humidity	Pure Gases	6.7 - 8.4	1.8 - 2.6	0.22 - 0.38
33B	Same as 32D, 135°C cure in dry oven	Pure Gases	6.4 - 7.6	1.8 - 2.2	0.23 - 0.30

Table 9. Variation in Methylcellulose Membrane Fabrication Conditions and Resulting Gas Permeability (Continued)

Membrane	Composition	Type of Test	Ratio of CO_2/H_2 Permeabilities	Flux (ft^3/ft^2-hr-100 psi)	
				CO_2	H_2
34B	1% methylcellulose (100 cps) 1% glyoxal, 20% isopropanol, coated onto dry polysulfone support film, 135°C cure, humidified oven	Pure Gases	7 - 8.4	1.6 - 20.	0.23 - 0.24
36D	1% methylcellulose (100 cps), 2% glutaraldehyde, 50% isopropanol, 0.4% hydrochloric acid, 135°C cure, humidified oven	Pure Gases	4.6 - 6.4	0.69 - 2.6	0.15 - 0.42
38A	Repeat of 36D	Pure Gases	8.7 - 11.3	1.6 - 2.0	0.14 - 0.19
39A	1% Dow A15 methylcellulose, 1% glyoxal, 50% isopropanol, 135°C cure, humidified oven	Pure Gases	2.1 - 2.6	2.3 - 2.5	0.90 - 1.2
43A	2% methylcellulose (100 cps), 0.2% sodium hydroxide, 1% divinyl sulfone, 135°C cure (very soft when wet)	CO_2/H_2 mixture	3.2 - 11.6	0.16 - 0.19	0.014-0.058
46C	4000 cps methylcellulose membrane formed dynamically in a reverse osmosis system	CO_2/H_2 mixture	5.7 - 9.9	0.056 - 0.15	0.0056-0.026
51A	0.85% methylcellulose (100 cps), 26% isopropanol, 1.3% glyoxal, filtered, 115°C cure	CO_2/H_2 mixture	8.3 - 11.6	1.6 - 2.2	0.19 - 0.20
51C	0.85% methylcellulose (100 cps) 1.3% glyoxal, 1.3% Petro BA (sodium xylene sulfonate solution), 120°C cure	CO_2/H_2 mixture	1.9 - 2.8	1.8 - 3.2	0.65 - 1.7

Table 9. Variation in Methylcellulose Membrane Fabrication Conditions and Resulting Gas Permeability (Continued)

Membrane	Composition	Type of Test	Ratio of CO_2/H_2 Permeabilities	Flux (ft^3/ft^2-hr-100 psi)*	
				CO_2	H_2
51D	0.85% methylcellulose (100 cps), 1.3% glyoxal, 135°C cure	CO_2/H_2 mixture	4.8 - 9.2	2.5 - 3.2	0.27 - 0.67
51F	Same as 51D, 0.75% hydrochloric acid added, 135°C cure	CO_2/H_2 mixture	3.9 - 8.4	2.6 - 3.7	0.31 - 0.45
51G	Same as 51C, 0.5% hydrochloric acid added, 135°C cure	CO_2/H_2 mixture	3.1 - 5.8	1.8 - 2.3	0.53 - 0.58

*Test conditions: Humidified feed gas at room temperature and 200 psig, test cells at 25°C and 200 psig, permeate at room temperature and atmospheric pressure (about 20°C and 74 cm Hg). Flux normalized to 60°F and 30.0 in. Hg.

Table 10. Membrane Permeability Test Results on Related Cellulose Derivatives

Membrane	Composition	Type of Test	Ratio of CO_2/H_2 Permeabilities	Flux (ft^3/ft^2-hr-100 psi)*	
				CO_2	H_2
39A	1% Dow A15 (standard methylcellulose, methoxyl D.S. 1.6 to 1.9), 1% glyoxal, 50% isopropanol, 0.4% hydrochloric acid, 135°C cure, humidified oven.	Pure Gases	2.1 - 2.6	2.3 - 2.5	0.90 - 1.2
39B	Same as 39A but used Methocel F50	Pure Gases	9.2 - 11	2.5 - 3.3	0.27 - 0.28
39C	Same as 39B except used Methocel J5MS	CO_2/H_2 mixture	6.6 - 14	1.9 - 2.1	0.15 - 0.28
41A	Cellulose (2% CA 398-10 in formic acid coated on polysulfone, air-dried and hydrolyzed with ammonium hydroxide), air dried.	CO_2/H_2 mixture	10.3 - 11.4	0.38 - 0.50	0.037-0.043
41B	Same as 41A but after air drying cured in oven at 135°C	CO_2/H_2 mixture	6.2 - 6.8	0.52 - 0.53	0.076-0.086
41C	Same as 41B but used 2% glyoxal, 0.4% hydrochloric acid, 2-methoxyethanol as solvent	CO_2/H_2 mixture	4.6 - 9.4	0.35 - 0.51	0.038-0.092
41D	Same as 41B but used 2% glyoxal alone (as crosslinking agent)	CO_2/H_2 mixture	4.3 - 10.3	0.35 - 0.51	0.049 - 0.082
47E	1% Methocel F50, 50% isopropanol, 2% glyoxal, 135°C cure, humidified oven	CO_2/H_2 mixture	8.5 - 8.6	2.0 - 5.1	0.23 - 0.60
48A	1% Methocel J5MS, 2% glyoxal, a few drops of concentrated ammonium hydroxide, 135°C cure, humidified oven	CO_2/H_2 mixture	7.1 - 8.8	1.3 - 1.8	0.18 - 0.21

Table 10. Membrane Permeability Test Results on Related Cellulose Derivatives (continued)

Membrane	Composition	Type of Test	Ratio of CO_2/H_2 Permeabilities	Flux (ft^3/ft^2-hr-100 psi)*	
				CO_2	H_2
48C	Same as 48A except 1% hydrochloric acid added	CO_2/H_2 mixture	7.7 - 10.2	2.7 - 3.0	0.29 - 0.40
44D	0.25% ethyl hydroxyethyl cellulose (EHEC-75H), 50% isopropanol, 0.8% glyoxal, 0.4% hydrochloric acid cured at 135°C, humidified oven	CO_2/H_2 mixture	3.4 - 4.7	5.1 - 7.9	1.5 - 1.7
29D	Ultrathin membrane of methylcellulose acetate cast from cyclohexanone	Pure Gases	11 - 12	3.0 - 4.8	0.26 - 0.44
32F	Methylcellulose acetate coated on a polysulfone support from a t-butanol solution	Pure Gases	3.2 - 5.2	0.72 - 2.7	0.21 - 0.73
36A	Thick methylcellulose acetate membrane	Pure Gases	40	0.1	0.0025

*Test Conditions: Humidified feed gas at room temperature and 200 psig, cells at 25°C and 200 psig, permeate at room temperature and atmospheric pressure (about 20°C at 74 cm Hg). Flux normalized to 60°F and 30.0 in. Hg.

In later tests with these methylcellulose derivatives, the addition of isopropanol increased the flux of a Dow F-50 membrane, as shown by Example 47E, to about 5 ft^3/ft^2-hr-100 psi, almost the level attained by the optimized methylcellulose membrane. Considering their other useful properties these substituted methylcellulose membranes showed promise for acid gas cleanup applications.

Pure, unsubstituted cellulose membranes (Examples 41A through 41C) were also examined for comparison. They were made by hydrolyzing cellulose acetate membranes with ammonium hydroxide. They gave selectivities as high as 9 to 11, but at quite low fluxes (such as 0.5 ft^3/ft^2-hr-100 psi). These formulations were not promising in this application.

A membrane was made from a sample of ethyl hydroxyethyl cellulose obtained from Hercules, Inc. This membrane gave a high flux, almost 8 ft^3/ft^2-hr-100 psi, albeit at a somewhat low CO_2/H_2 selectivity of about 4.

Methylcellulose acetate was of interest because it was not water soluble (thus, required no crosslinking treatment), was nevertheless hydrophilic, and could potentially be fabricated into asymmetric membranes (unlike methylcellulose itself).

A thick film of methylcellulose acetate, Example 36A, was prepared and gave an apparently very high selectivity of 40, albeit at a very low CO_2 flux of 0.1 ft^3/ft^2-hr-100 psi. An ultrathin film of the polymer float-cast on a water surface from cyclohexanone also showed good selectivity (Example 29D, CO_2/H_2 selectivity = 11-12), and at a relatively good CO_2 flux of 3.0 to 4.8 ft^3/ft^2-hr-100 psi. When the polymer was deposited directly on a porous polysulfone support from a t-butanol solution, both selectivity and flux were lower.

Asymmetric Methylcellulose Acetate Membranes

Earlier in the program, an asymmetric dialysis membrane composed of a block copolymer of polyethylene oxide and polycarbonate had been tested for gas separation properties. It exhibited CO_2/H_2 selectivities that were consistent from one sample to the next, and approached the theoretical limits for water-mediated CO_2/H_2 selectivity. Its flux, however, was too low for economic use. Nevertheless, it served to indicate the potentially high performance of asymmetric membranes in this application, if high flux membranes could be developed. Microporous supports would not be necessary in this approach.

Methylcellulose acetate was of interest because of the promising results shown by it in Table 10. Because methylcellulose acetate was also insoluble in water, it could be cast as an asymmetric membrane. A series of methylcellulose acetate membranes were fabricated and tested during this period.

Synthesis of methylcellulose acetate in substantial quantities proved not to be straightforward. The reaction between methylcellulose and acetic anhydride required an acid catalyst. But acids also very readily split the cellulose backbone, especially at higher temperatures. Traces of perchloric acid as the acetylation catalyst, for example, caused extensive depolymerization of the methylcellulose at 35°C. Eventually, use of sulfuric acid under tightly controlled temperature conditions led to good polymer product, as follows.

A solvent composed of three parts by weight of acetic acid to one of acetic anhydride was preheated to 65 to 70°C, but no higher. One to three drops of 94 percent sulfuric acid were added for each 100 grams of solvent. The methylcellulose, 15 percent of the total weight, was added in small portions with vigorous stirring. Initially, the acetylation reaction was very exothermic. It was important to maintain the temperature in the range of 65 to 70°C to avoid cellulosic chain scission. Later additions of the methylcellulose were characterized by slower reaction and by build-up of unreacted, gelatinous particles in suspension. After the methylcellulose had all been added, the mixture was heated in an oven at 70 to 100°C until the solution became clear and free of gel. The solution was then poured into vigorously stirred water. The polymer was recovered for washing and purification by reprecipitation from acetone.

To form an asymmetric membrane, it was necessary to find a suitable solvent system. A combination of at least one each of a solvent and a nonsolvent was required. By necessity, the best solvent formulation would be the most volatile. The composition of the casting solution would be chosen so that evaporation of a small amount of solvent would gel a thin layer on the surface in contact with air. The bulk of the polymer solution would gel later by a phase inversion process. The thin upper layer would be dense and would have the properties of a barrier film while the thick porous lower layer would provide support and permit the rapid escape of the gas permeating the upper layer.

Data were gathered on the solubility of methylcellulose acetate in various liquids. Results are listed in Table 11. Of the liquids tested, only water and alcohols did not dissolve the methylcellulose acetate. Dioxane, isopropyl alcohol, morpholine, and propylene carbonate were intermediate, behaving as poor solvents. All of the others behaved as true solvents, and could be used as the primary polymer solvent in a casting solution, depending upon the suitability of their evaporation rates. The broad solubility of methylcellulose acetate in water miscible solvents represented a drawback in the formulation of asymmetric membranes. Typical casting dope recipes for cellulose acetate could not be borrowed and applied to methylcellulose acetate.

To make an asymmetric membrane, a quantity of the polymer solution was poured onto a glass casting plate and then drawn out to a uniform thickness with a doctor blade. The film of solution was exposed to the air long

Table 11. Water-Miscible Solvents and Nonsolvents for Methylcellulose Acetate

True Solvents

Acetic acid
Acetone
Acetonitrile
Bis-(2-methoxyethyl)ether
Butyl cellosolve
Dimethylformamide
Ethyl lactate
Formamide
Formic Acid
Furfuryl alcohol
Methyl cellosolve
2-butanone
2-methoxyethyl acetate
Nitromethane
Tetrahydrofuran
Tetramethylurea
Triethylphosphate

Intermediate Solvents (gave hazy solutions)

Dioxane
Isopropyl alcohol
Morpholine
Propylene carbonate

Nonsolvents

Water
Ethanol
Methanol
Tert-butyl alcohol

enough to allow the upper surface of the solution to gel. The plate was then submerged in water until the membrane floated free. The casting technique and the exposure time to the air were as important to the properties of the membrane as the composition of the solvent.

The separation ratio and flux data obtained from the asymmetric membranes as well as their compositions are listed in Table 12. In general the results were below expectation. Selectivities for CO_2/H_2 of as high as 8 to 11 were seen, but in only a few instances. Fluxes of CO_2 for these instances were typically in the range 0.2 to 0.4 ft^3/ft^2-hr-100 psi, i.e., very low. It was difficult to obtain asymmetric membranes free of defects. The low selectivities observed in most of the tests probably reflected this factor.

A thick film of methylcellulose acetate cast from acetone exhibited a carbon dioxide flux of 0.07 to 0.08 ft^3/ft^2-hr-100 psi. Since this film was 0.9 to 1.0 mils thick and flux was inversely proportional to thickness, it was concluded that the active layers of the asymmetric membranes were probably one-fourth to one-tenth of a mil thick. High-flux asymmetric cellulose acetate membranes for reverse osmosis, by comparison, have an active layer about 0.01 mil thick. Any further work on these methylcellulose acetate compositions would have to be directed toward achieving a thin upper layer.

Several of the asymmetric membranes were air-dried before testing. The CO_2/H_2 selectivities of the air-dried membranes were always lower than those of the membranes kept wet until tested. The air-dried membranes were also quite variable in flux compared to those kept wet. Opening up of micropores in the membranes certainly occurred in some cases, as indicated by CO_2/H_2 selectivities of less than one.

Test on Membranes Using Commercial Supports

Most of the methylcellulose membranes were formed *in situ* on hand cast sheets of microporous polysulfone or polyacrylonitrile support films. Eventual development of this membrane into a spiral wrap module would be facilitated if commercially produced support films could be used. Various membrane formulations coated on different commercial supports were therefore tested. The results are listed in Table 13.

Of primary interest in this table are results for four identical methylcellulose membranes coated on commercial polysulfone-on-cloth backings. These were tested and compared to the same formulation coated on a hand-cast polysulfone support film. Support films tested with crosslinked methylcellulose coatings were:

35A	Hand-cast polysulfone support film
35B	UOP polysulfone support on sailcloth
35C	Envirogenics polysulfone support on sailcloth
35E	Osmonics polysulfone support on sailcloth
35D	Osmonics polysulfone support on nonwoven fabric

Table 12. Gas Permeability Data for Asymmetric Methylcellulose Acetate Membranes

Membrane	Composition	Ratio of CO_2/H_2 Permeabilities	Flux (ft^3/ft^2-hr-100 psi)†	
			CO_2	H_2
55E	20% methylcellulose acetate in 1:1:1 acetone : isopropanol : formamide, filtered	0.97 - 2.4	0.79 - 1.8	0.34 - 1.8
55G	Same as 55E but exposed to air longer	4.5 - 11 3.7 - 4.4††	0.30 - 0.33 0.38 - 0.39	0.03 - 0.07 0.09 - 0.11
55H	Same as 55E	8.5 - 9.5 2.6 - 5.2 ††	0.38 - 0.58 2.1 - 3.9	0.04 - 0.06 0.41 - 1.5
58-A	20% methylcellulose acetate (from 400 cps methylcellulose), 20% dioxane, 60% acetone (very cloudy membrane)	1.4 - 1.5 0.27 - 0.43††	0.16 - 0.19 0.49 - 4.0	0.11 - 0.13 1.2 - 14
59-B	20% methylcellulose acetate, 10% dioxane, 50% acetone, 20% isopropanol (very clear membrane)	7.8 - 9.4 0.22 - 0.41††	0.32 - 0.35 0.54 - 3.4	0.03 - 0.04 2.5 - 8.3
59-C	One-to-one mixture by weight of 58-A and 58-B (made intermediate membrane)	0.49 - 1.7	0.39 - 1.1	0.23 - 2.2
58-D	25% methylcellulose acetate, 19% dioxane, 50% acetone, 6% isopropanol	0.18 - 2.7 2.4 - 3.8††	0.16 - 0.87 0.10 - 0.11	0.06 - 3.4 0.03 - 0.05
58-E	22% methylcellulose acetate, 17% dioxane, 44% acetone, 17% isopropanol	4.6 - 11 1.6 - 2.3††	0.29 - 0.34 0.17 - 0.24	0.03 - 0.06 0.10 - 0.11
58-F	21% methylcellulose acetate, 16% dioxane, 51% acetone, 5% isopropanol, 7% formamide	1.3 - 6.5††	0.19 - 0.21	0.03 - 0.17
58-G	20% methylcellulose acetate, 15% dioxane, 50% acetone, 15% isopropanol	0.59 - 6.2††	0.16 - 0.23	0.03 - 0.39
58-H	Thick film of methylcellulose acetate cast from acetone, one mil thick.	4.2 - 4.6††	0.07 - 0.07	0.02

Table 12. Gas Permeability Data for Asymmetric Methylcellulose Acetate Membranes (Continued)

Membrane	Composition	Ration of CO_2/H_2 Permeabilities	Flux (ft^3/ft^2-hr-100 psi)†	
			CO_2	H_2
58-I	15% methylcellulose acetate, 18% dioxane, 37% acetone, 30% acetonitrile (hazy, greyish white membrane)	5.9 - 7.7	0.11 - 0.13	0.01 - 0.02
		0.33 - 4.3††	0.14 - 3.2	0.03 - 0.86

† Test Conditions: Humidified feed gas at room temperature and 200 psig, test cells at 25°C and 200 psig, permeate at room temperature and atmospheric pressure (about 20°C and 74 cm Hg). Pure gases used. Flux was normalized to 60°F and 30.0 in. Hg.

†† These samples were air dried before testing. All others were kept wet until tested.

Table 13. Gas Permeability Data for Methylcellulose Membranes on Commercial Supports

Membrane	Composition	Type of Test	Ratio of CO_2/H_2 Permeabilities	Flux (ft^3/ft^2-hr-100 psi)*	
				CO_2	H_2
28C-1	Sulfonated polysulfone, morpholine salt, hand-cast polyacrylonitrile support film	CO_2/H_2 mixture	4.8 - 8.2	1.6 - 1.7	0.20 - 0.35
28C-2	Solution from 28C-1 coated on an Acropor AN-450 polyacrylonitrile support	CO_2/H_2 mixture	No separation properties		
35A	Methylcellulose membrane on hand-cast polysulfone, See Table	Pure gases	10.7 - 13.5	2.4 - 2.7	0.19 - 0.24
35B	Same as 35A but UOP polysulfone support used	Pure gases	9.4 - 14.4	1.4 - 1.9	0.0093-0.20
35C	Same as 35A but Envirogenics polysulfone support used	Pure gases	3.3 - 3.8	2.5 - 3.2	0.70 - 0.94
35D	Same as 35A but Osmonics polysulfone support on a non-woven backing was used	Pure gases	1.6 - 6.5	2.1 - 3.1	0.32 - 2.0
35E	Same as 35A but Osmonics polysulfone support on sailcloth backing was used	CO_2/H_2 mixture	1.8 - 2.9	1.6 - 2.8	0.85 - 1.0
44C	1% methylcellulose (100 cps) 50% isopropanol, 2% glyoxal, 0.4% hydrochloric acid on Abcor support film, cured at 135°C, humidified oven	CO_2/H_2 mixture	Progressive failure of membrane observed		
45A	2% Dow Methocel F-50, 1.3% glyoxal, 1.3% hydrochloric acid on UOP polysulfone support, 135°C cure, humidified oven	CO_2/H_2	1.8 - 8.9	0.78 - 2.0	0.088 - 1.1

Table 13. Gas Permeability Data for Methylcellulose Membranes on Commercial Supports (Continued)

Membrane	Composition	Type of Test	Ratio of CO_2/H_2 Permeabilities	Flux (ft^3/ft^2-hr-100 psi)*	
				CO_2	H_2
45C	Ultrathin film of block copolymer of polycarbonate and polyethylene oxide cast from 5% w/v chloroform, air-dried	CO_2/H_2 mixture	14.2	0.083 - 0.10	0.0059 - 0.0071
45D	Solution of 45C coated on Gelman Acropor AN-450, air dried	CO_2/H_2 mixture	No separation properties		
47A	Polyvinylformal on UOP polysulfone support, air-dried	CO_2/H_2 mixture	3.9 - 5.4	0.061-0.075	0.011 - 0.019

*Test Conditions: humidified feed gas at room temperature and 200 psig, test cells at 25°C and 200 psig, permeate at room temperature and atmospheric pressure (about 20°C and 74 cmHg). Flux normalized to 60°F and 30.0 in. Hg.

Reference to Table 13 shows that only the UOP support proved functional for the methylcellulose coating. Compared to Example 35A, using a hand-cast polysulfone support, all of the other three commercial supports gave membranes that leaked. This can be seen from the much lower selectivities in Table 13. These support films had visible pinholes and defects when inspected against strong backlighting. The UOP commercial polysulfone support maintained the same overall selectivities as Example 35A but exhibited gas fluxes that were lower by 30 to 50 percent. This would result in greater membrane area and higher costs for gas cleanup.

Later tests with the UOP backing, Examples 45A and 47A, reconfirmed these conclusions.

Two other commercial supports were obtained. One was Acropor AN 450 from Gelman Instrument Company; the other, an ultrafiltration membrane from Abcor, Inc. Membranes were formed on these films and compared to similar membranes fromed on laboratory microporous sheets. Results included in Table 13 on these examples indicated that these latter two supports were totally inadequate. These two supports always led to defective membranes.

In conclusion, UOP microporous polysulfone support films could be used in the fabrication of these gas separation membranes. However, they led to lower fluxes than observed with laboratory test materials. These flux values would have to be entered into economic feasibility calculations if this support material were used.

CHARACTERIZATION OF OPTIMIZED MEMBRANE COMPOSITIONS

During the screening and optimization of gas separation membranes, most of the test measurements were made with carbon dioxide and hydrogen at 200 psig pressure and room temperature. An important part of the program was to test the best membrane systems under a variety of conditions to characterize their performance. These test data would be necessary to predict their performance in the field and to properly assess the economic feasibility of these membranes.

As part of this effort, membrane flux and gas separation properties were tested at temperatures of 25 to 70°C, at pressures of 200 to 700 psig, and in contact with various gases that included pure methyl mercaptan and a quaternary mixture of H_2, CO_2, CH_4, and H_2S.

Four membrane formulations were examined in this work. These are listed in Table 14. They consisted of two hydroxypropoxylated methylcellulose membranes, a commercial hemodialysis membrane, and, for comparison, a polyethylenimine membrane.

Table 14. Composition of Membranes Chosen for Various Characterization Tests

Membrane	Composition
47D	3.3% Tydex 12, 110°C cure in an aluminum tray
47E	1% Methocel F50, 50% isopropanol, 2% glyoxal, 135°C cure, humidified oven
48A	1% Methocel 5JMs, 2% glyoxal, a few drops of concentrated ammonium hydroxide, 135°C cure, humidified oven
Dialysis Membrane	Block copolymer of polycarbonate and poly(ethylene oxide) (commercial asymmetric membrane)

Tests with Four-Component Gas Mixtures

The four membrane compositions were tested at 25°C and 200 psig with a quaternary gas mixture that contained, by volume: 56.5 percent hydrogen, 25.2 percent carbon dioxide, 15.7 percent methane, and 2.6 percent hydrogen sulfide.

The total gas flux through each of the membranes was measured using soap bubble flowmeters. The product gases were analyzed for composition by gas chromatography. From these data, the individual flux and permeability of each of the four gases was calculated.

The results, listed in Table 15, confirmed in general previous test results with individual gases, though fluxes were not quite up to expectation. Generally, the hydrogen flux was slightly higher and the carbon dioxide flux significantly lower than in the runs with the binary carbon dioxide-hydrogen mixtures. The hydrogen sulfide flux was about two to three times the carbon dioxide flux. The methane flux was lower than the hydrogen flux, as expected.

Tests with Methyl Mercaptan

These four membrane compositions were also tested with pure methyl mercaptan at 5 psig and room temperature. The results are presented in Table 16. The fluxes attained were generally equivalent to those for H_2S in gas mixtures. The result on Example 48A appears to be erroneously high, however, and the result for Example 47E to be somewhat low.

Methyl mercaptan is an easily condensable gas and should exhibit high solubility in the membrane compositions. This high solubility would counterbalance its lower diffisivity based on molecular size, leading to favorable permeation rates through membranes.

No evidence of facilitated transport of methyl mercaptan through the polyamine membrane was evident. Thus, the concept of facilitated transport due to acid-base affinities was not operative with the weakly acidic methyl mercaptan. This agrees with the lack of such interactions already noted for CO_2 and H_2S in contact with the polyamine membrane.

Table 15. Membrane Permeability Test Results Using Four-Component Gas Mixtures

Membrane	Type of Test	Flux (ft^3/ft^2-hr-100 psi)*			
		H_2	CO_2	H_2S	CH_4
47D (polyethylenimine)	CO_2/H_2 mixture	0.11 - 0.16	0.81 - 1.2	--	--
	four gas mixture	0.16 - 0.18	0.64 - 0.78	1.2 - 1.6	0.066 - 0.080
47E (Methocel F 50)	CO_2/H_2 mixture	0.23 - 0.60	2.0 - 5.1	--	--
	four gas mixture	0.28 - 0.65	1.3 - 2.7	2.9 - 5.0	0.13 - 0.27
48A (Methocel 5JMS)	CO_2/H_2 mixture	0.18 - 0.21	1.3 - 1.8	--	--
	four gas mixture	0.18 - 0.20	1.0 - 1.2	1.9 - 2.6	0.10 - 0.12
Dialysis Machine	CO_2/H_2 mixture	0.054 - 0.064	0.55 - 0.66	--	--
	four gas mixture	0.054 - 0.068	0.45 - 0.55	1.1 - 1.4	0.04 - 0.05

*Test conditions: humidified feed gas at room temperature and 200 psig, cells at 25°C and 200 psig, permeate at room temperature and atmospheric pressure (about 20°C and 74 cm Hg). Flux normalized to 60°F and 30.0 in. Hg.

For CO_2/H_2 mixture the feed composition was 33% CO_2; for four gas mixture the feed composition was 56.5% H_2, 25.16% CO_2, 2.60% H_2S, and 15.74% CH_4.

Table 16. Membrane Permeability Test Results Using Methyl Mercaptan

Membrane	Flux (ft^3/ft^2-hr-100 psi)*
47D (polyethylenimine)	2.9
47E (Methocel F-50)	0.77
48A (Methocel 5JMS)	15
Dialysis Membrane	2.6

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*Test Conditions: humidified feed gas, cell at room temperature and 5 psig, permeate at room temperature and atmospheric pressure (about 20°C and 74 cm Hg). Flux normalized to 60°F and 30.0 in Hg.

Tests of the Effect of Temperature

The four membrane compositions were also tested with CO_2/H_2 mixtures at 25°C, 50°C, and about 70°C. The results are reported in Table 17. As a general statement, selectivity dropped as temperature increased. The selectivity at about 70°C was much lower than that at 25°C. In the cases of the 47D (the polyethylenimine membrane) and the asymmetric dialysis film, there was a small drop in the CO_2/H_2 selectivity at 50°C and a larger one at 70°C. However, for the two methylcellulose derivatives (membranes 47E and 48A), the drop in selectivity was rather large, even at 50°C. In all cases the CO_2 flux dropped at 70°C. The propoxylated methylcellulose membranes behaved poorly in that hydrogen fluxes became quite high at 70°C.

These results indicated in general that one must operate at or below 50°C to maintain good selectivities at 200 psig for these gases.

Tests of the Effect of Pressure

The four membrane compositions were also tested at 600 to 700 psig at room temperature. These tests were compared to standard tests at 200 psig. Results are shown in Table 18. In all cases there was a decrease of the CO_2/H_2 selectivity at the higher pressure. An increase in CO_2 flux with pressure was observed in only two of the membranes, and did not meet expectations in this regard.

Table 17. Membrane Permeability Test Results as a Function of Temperature

Membrane	Temperature	Ratio of CO_2/H_2 Permeabilities	Flux (ft^3/ft^2-hr-100 psi)*	
			CO_2	H_2
47D (polyethylenimine)	25°C	7.4 - 7.6	0.81 - 1.2	0.11 - 0.16
	50°C	5.6 - 6.1	0.88 - 1.3	0.16 - 0.23
	68°C	1.8 - 4.9	0.19 - 0.32	0.04 - 0.18
47E (Methocel F-50)	25°C	8.5 - 8.6	2.0 - 5.1	0.23 - 0.60
	50°C	0.88 - 3.5	0.93 - 1.6	0.44 - 1.1
	70°C	0.64 - 1.2	1.6 - 3.3	1.3 - 3.9
48A (Methocel 5JMS)	25°C	7.1 - 8.8	1.3 - 1.8	0.18 - 0.21
	50°C	1.3 - 1.4	0.82 - 1.1	0.61 - 0.84
	72 - 73°C	0.74 - 0.81	1.0 - 1.8	1.3 - 2.5
Dialysis Membrane	25°C	10.1 - 10.7	0.55 - 0.66	0.054 - 0.064
	50°C	7.0 - 7.9	0.54 - 0.65	0.077 - 0.084
	about 70°C	2.3 - 4.7	0.11 - 0.32	0.024 - 0.11

*Test Conditions: humidified feed gas at 200 psig, test cells at 200 psig, permeate at room temperature and atmospheric pressure (about 20°C and 74 cm Hg). Mixed 33:67 CO_2/H_2 gas feed used. Flux normalized to 60°F and 30.0 in. Hg.

Table 18. Membrane Permeability Test Results as a Function of Pressure

Membrane	Pressure	Ratio of CO_2/H_2 Permeabilities	Flux (ft^3/ft^2-hr-100 psi)*	
			CO_2	H_2
47D (polyethylenimine)	200 psig	7.4 - 7.6	0.81 - 1.2	0.01 - 0.16
	700 psig	1.5 - 1.8	1.2 - 1.5	0.79 - 0.88
47E (Methocel F-50)	200 psig	8.5 - 8.6	2.0 - 5.1	0.23 - 0.60
	700 psig	3.1 - 5.6	1.2 - 2.1	0.22 - 0.65
48A (Methocel 5JMS)	200 psig	7.1 - 8.8	1.3 - 1.8	0.18 - 0.21
	600 psig	3.8 - 6.8	1.7 - 2.0	0.26 - 0.54
Dialysis Membrane	200 psig	10.1 - 10.7	0.55 - 0.66	0.054 - 0.064
	700 psig	7.5 - 8.7	0.23 - 0.27	0.031

*Test Conditions: humidified feed gas at room temperature, cell at 25°C, permeate at room temperature and atmospheric pressure (about 20°C and 74 cm Hg). Mixed 33:67 CO_2/H_2 Flux normalized to 60°F and 30.0 in. Hg.

The best overall behavior was exhibited by the commercial dialysis membrane, a block copolymer of poly(ethylene oxide) with polycarbonate. The CO_2/H_2 selectivity decreased only moderately from about 10 to about 8. Its CO_2 flux dropped by 60 percent, however. Combined with its initially low flux, this drop in flux ruled out this membrane for coal gasification applications on the basis of economic infeasibility.

The propoxylated methylcellulose derivatives showed mixed behavior, in that CO_2 flux alone changed on one (decreased), and hydrogen flux increased on the other. Each showed about a 40 percent drop in the selectivity for CO_2/H_2.

The polyethylenimine membrane exhibited a severe drop in selectivity as hydrogen flux rose very significantly.

A second series of tests was later run to examine further the effects of operating pressure on these gas separation membranes. These later tests were run with methylcellulose rather than propoxylated methylcellulose membranes, and tests were conducted with the quaternary gas mixture.

Membranes were prepared duplicating Example 51E of Table 8 and Example 51F of Table 9. In the preparation of the 51E membranes, a 0.85-percent solution of methylcellulose (100 cps) in 75:25 water : isopropanol was prepared. Just before use, it was modified by addition of 1.3 percent by weight of glyoxal, filtered, and further modified with 0.6 percent hydrochloric acid by weight. A wet polysulfone substrate was immersed in this solution for two minutes, then was drained for two minutes. It was then heat-cured in an oven at 135°C for 15 minutes. The glyoxal and hydrochloric acid served to crosslink the methylcellulose A coating thickness corresponding to approximately 1.5 micron of crosslinked methylcellulose (dry) was achieved in this process.

The preparation of the 51F membranes was essentially the same except that use of isopropanol (used as a co-solvent for the methylcellulose) was eliminated. The function of the isopropanol was primarily to achieve a more true solution of methylcellulose (a solution thereby containing less colloidal matter) to hopefully achieve thinner, more uniform deposits on the polysulfone substrate surface.

The above membranes, obtained in the dry state from this preparative procedure, were wetted in water before insertion into test cells. They were mounted in the test cells, maintained at 25°C, and exposed to a humidified stream of the quaternary gas mixture. Each sample of membrane was tested nine times: at 200,400, 600, 800, 1000, 800, 600, 400 and 200 psig, in that order. The first five tests at increasing pressures were conducted to determine if there were any differences in gas fluxes or selectivities at different pressures. The last four tests at decreasing pressures were conducted to see if short term exposure of a methylcellulose membrane to a high pressure such as 1000 psig would have any effect on the gas flux or the selectivity.

Two of the membrane specimens (Type 51E) partially failed at 800 to 1000 psig. Data from the remaining four specimens were combined and graphed as shown in Figure 3. The data indicated substantial flux decline for the water-interacting gases (CO_2 and H_2S), but not for the water-insensitive gases (H_2 and CH_4).

The membranes did not behave as expected in this test. First, H_2 and CH_4 fluxes did not increase in proportion to increases in pressure; fluxes of the acid gases actually declined. Second, the original fluxes of the membranes were below the normal range for these membranes. The data would seem to be consistent with a progressive drying out and densification of the membrane during the test series. These results indicate that the membranes behaved best at low pressures (200 to 400 psig), and that they may not be applicable for operating pressures exceeding 400 psig.

Long Term Performance Tests

The performance of the optimized methylcellulose membranes in short-term (half day) tests had been determined under a variety of conditions. The question remained as to whether short-term test data would accurately reflect longer term performance under operating conditions of high pressure (1000 psig). A long-term, high-pressure test was performed on crosslinked methylcellulose membranes.

The membranes chosen for the test were of two crosslinked methylcellulose coatings which in previous tests had given high carbon dioxide flux at high CO_2/H_2 selectivities (Examples 31D and 51E). The compositions of these membranes were as follows:

Membrane	Composition
31D Type	1.5% methylcellulose (100 cps), 1.5% glyoxal, 19% isopropanol coated on a wet polysulfone support saturated with 80:20 water : isopropanol, oven-cured at 135°C.
51E Type	0.8% methylcellulose (100 cps), 1.3% glyoxal, 0.6% hydrochloric acid, 25% isopropanol, filtered, coated on a dry polysulfone support, oven-cured at 135°C.

Two samples of each were tested. The high pressure was supplied by 1000 psig nitrogen (humidified) throughout the test period. The CO_2 flux of the membrane was periodically monitored by purging the test system with CO_2, then measuring its permeation rate at 500 psig. At the beginning and end of the long term tests, H_2 fluxes were also measured to determine the CO_2/H_2 selectivity. All gases were humidified. The average temperature during these tests was about 30°C.

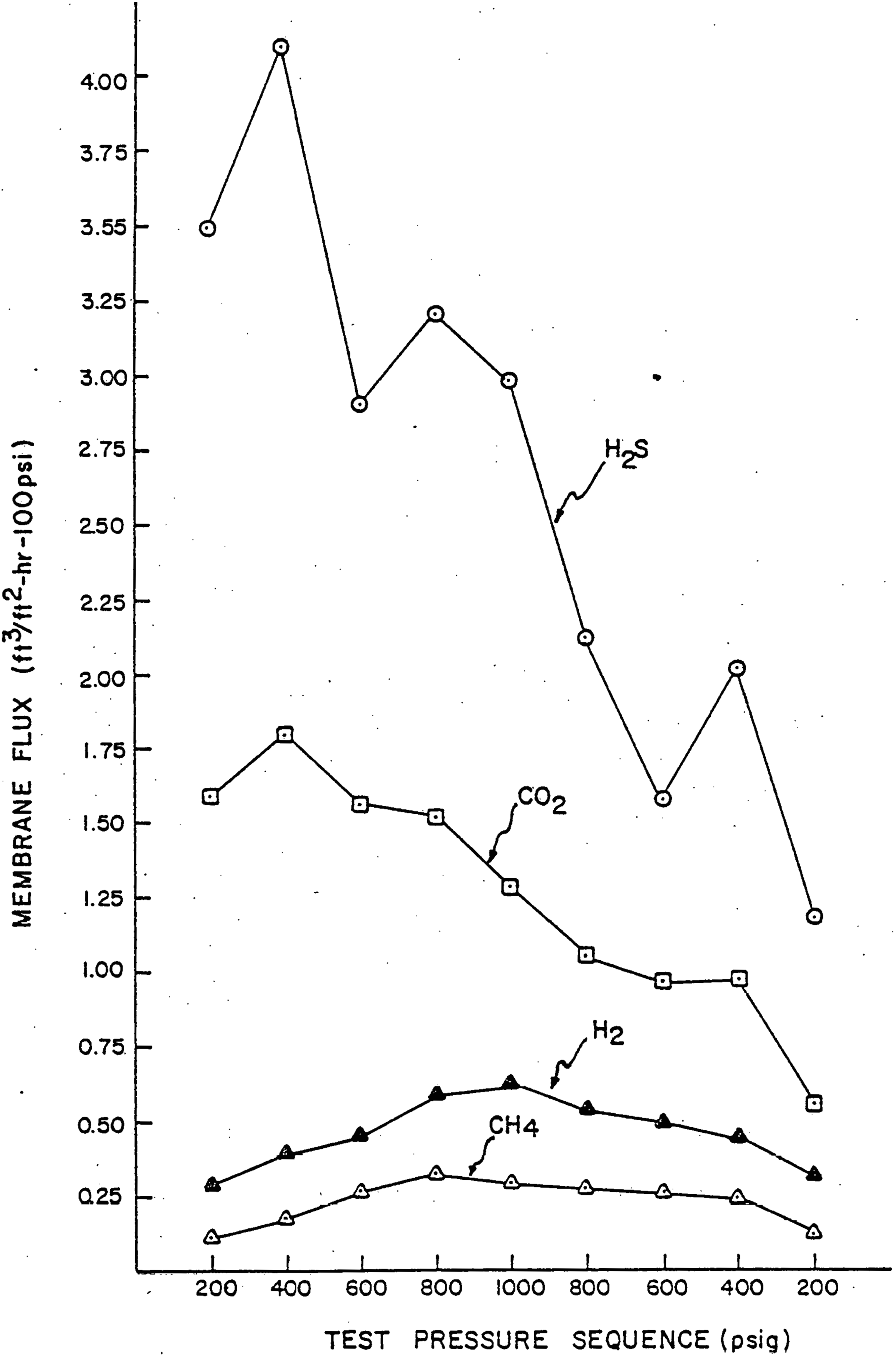

Figure 3. Pressure Effects on Fluxes of Various Gases Through Methylcellulose Membranes

Data from this test are shown in Table 19. Rapid initial flux declines were evident during the first day. Beyond one day the CO_2 flux of the Type 31D membranes approached 1.9 ft^3/ft^2-hr-100 psi as a stable flux plateau. This is further illustrated by the graph in Figure 4. One of the Type 51E membranes showed continual flux decline through the 140 hour test period; the other one failed after 50 hours at 1000 psig.

Table 19. Methylcellulose Membrane Flux Data for 140-Hour High Pressure Test

Time of Exposure to 1000 psig	Carbon Dioxide Flux* (ft^3/ft^2-hr-100 psi) Cell 1 31D	Cell 2 31D	Cell 3 51E	Cell 4 51E
Initial	1.3	4.0	4.6	2.6
25 hours	1.4	2.1	2.5	1.8
50 hours	1.5	1.8	1.7	1.6
80 hours	1.9	2.1	†	1.4
115 hours	1.8	1.7	---	1.1
140 hours	1.8	1.9	---	1.2

*Test Conditions: humidified carbon dioxide feed and cells at room temperature and 500 psig, permeate at room temperature and atmospheric pressure (about 30°C and 74 cm Hg for this test). Flux normalized to 60°F and 30.0 in. Hg.

† Membrane failed.

The selectivity of the membranes to CO_2 versus H_2 also dropped during the 140-hour test period. The H_2 flux essentially doubled during this time, while the CO_2 flux was dropping by 50 percent and more. Resulting selectivities at 140 hours were in the 3.4 to 4.0 range. Selectivity data are shown in Table 20.

Compressibility of the hydrophilic membranes at high pressure, presumably combined with water elimination from the membrane structure, very likely occurred, leading to the observed results.

Long term testing was repeated in approximately the same manner, but for a longer period (360 hours), and with membranes of the following composition:

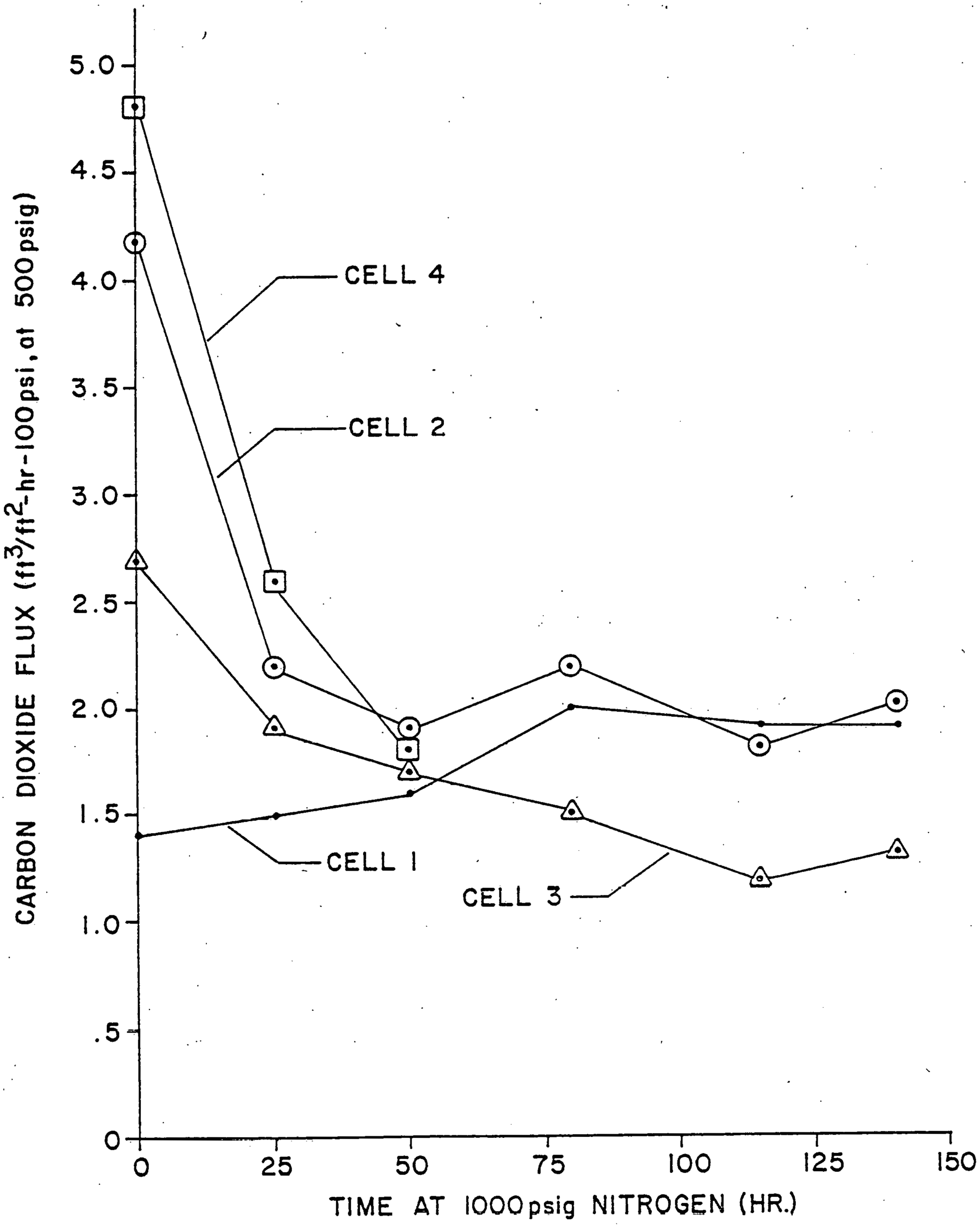

Figure 4. Carbon Dioxide Flux Decline Curves for Methylcellulose Membranes

Membrane	Composition
108C	1.5% methylcellulose (100 cps), 1.5% glyoxal, 19% isopropanol, coated onto both surfaces of a wet polysulfone support film, oven cured at 150°C.

The carbon dioxide was measured at 500 psig at intervals throughout the test. The nitrogen flux was also measured at different pressures several times during the test. The hydrogen flux was measured at the end of the test.

Table 20. Membrane Flux and Selectivity Before and After 140 Hours at High Pressure

State	Pressure	Parameter	Cell 1 31D	Cell 2 31D	Cell 3 51E	Cell 4 51E
Before Long-Term Test	500 psig	CO_2 flux	1.3	4.0	4.6	2.6
	200 psig	H_2 flux	0.10	0.20	0.26	0.15
	--	CO_2/H_2 ratio	13.4	19.7	18.2	17.2
After Long-Term Test	200 psig	CO_2 flux	1.7	1.6	†	1.0
	200 psig	H_2 flux	0.45	0.40	†	0.31
	200 psig	CO_2/H_2 ratio	3.8	4.0	†	3.4

Test Conditions: humidified feed gas and cells at room temperature and 1000 psig except when tested at the specified pressure, permeate at room temperature and atmospheric pressure (about 30°C and 74 cm Hg for this test). Data reported in ft^3/ft^2-hr-100 psi normalized to 60°F and 30.0 in. Hg.

† Membrane had failed during test.

The carbon dioxide flux throughout the test is shown in Table 21. It will be seen that the general trend in all three cells was a decrease of the carbon dioxide flux. Smooth representations of the carbon dioxide flux decline may be found in Figure 5. From the graph it appears that membrane was still undergoing a decline in flux after 360 hours. The plateau for this membrane formulation appears to be 0.2 to 0.4 ft^3/ft^2-hr-100 psi.

Table 21. Carbon Dioxide Flux During 360-Hour High Pressure Test

Time into Test (Hours)	CO_2 Flux, (ft^3/ft^2-hr-100 psi)		
	Cell 1	Cell 2	Cell 3
0	1.85	2.16	1.26
6.0	1.27	--	0.785
11.2	--	1.46	--
17.4	1.05	--	0.682
35.8	--	2.20	--
42.1	0.863	--	0.477
54.2	--	0.834	--
60.7	6.4	--	0.661
77.3	--	0.749	--
83.6	0.759	--	0.524
146.1	--	0.664	--
151.4	0.702	--	1.18
175.2	--	1.71	--
181.5	0.651	--	1.01
198.9	--	0.600	--
205.2	0.623	--	1.07
221.0	--	0.589	--
227.4	0.626	--	--
292.4	--	0.536	--
298.7	0.426	--	0.498
335.7	--	0.529	--
342.0	0.429	--	0.476
354.3	--	0.508	--
360.6	0.093	--	0.337

Flux normalized to 60°F, 30.0 in. Hg.

Table 22 shows the CO_2/N_2 selectivity during the test and the CO_2/H_2 selectivity at the end. The CO_2/N_2 separation ratio dropped to one-third its initial value during the first 80 hours but there is only a small decline after that. The CO_2/H_2 separation ratio at the end of the test was about five, lower than usual for a methylcellulose formulation, but far better than in the previous 140 hour test. It was presumed to have decreased throughout the test in the same way that the CO_2/N_2 selectivity decreased. This test showed that a highly crosslinked methylcellulose having a low carbon dioxide flux initially will still suffer a flux and selectivity decline when exposed to high pressure. The flux decline probably occurred because the pressure compacted the active methylcellulose layer and the gas stream tended to dry the membrane out. Because this membrane was more highly crosslinked than those tested for 140

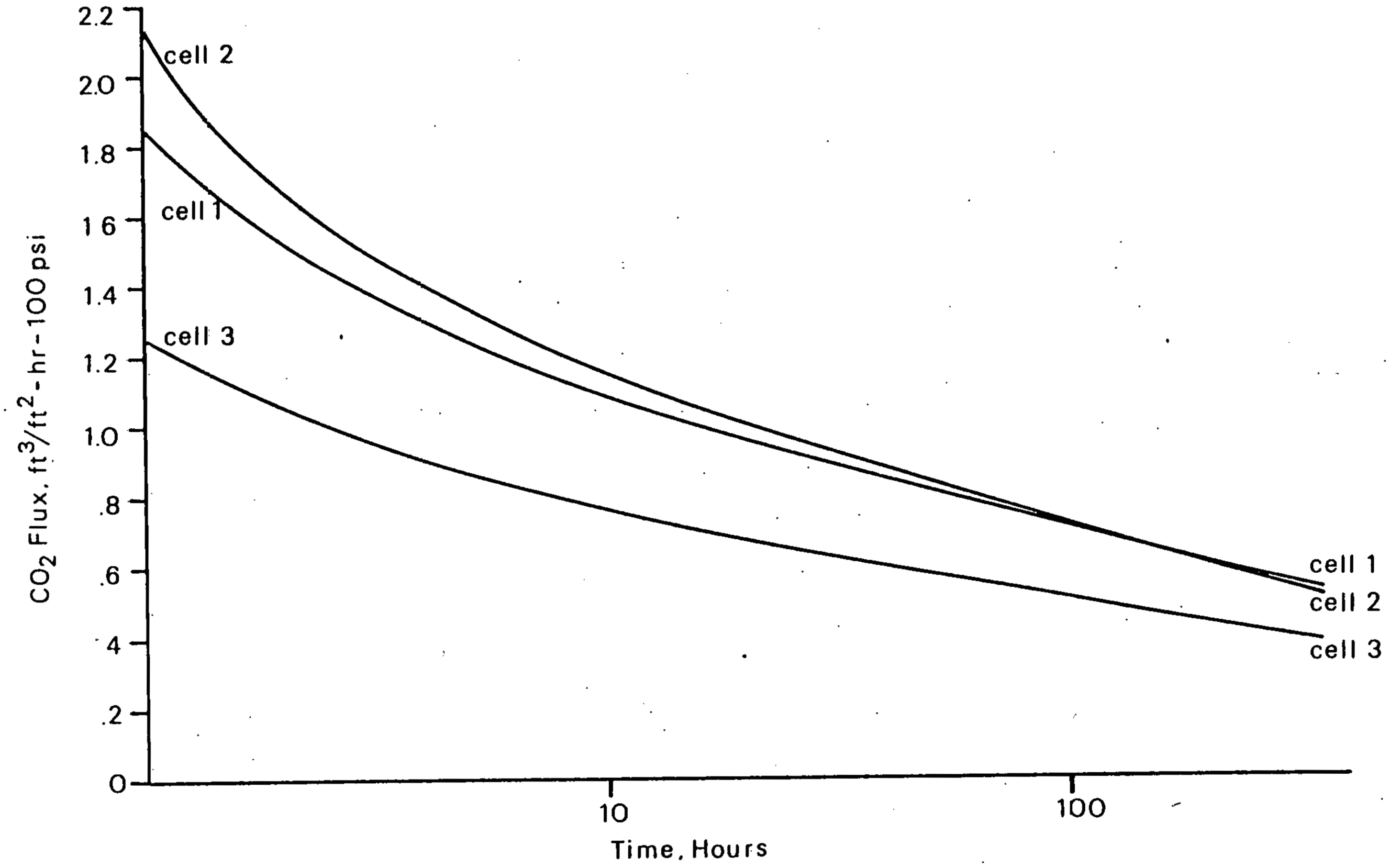

Figure 5. Long-Term Flux Decline Test

hours, these effects took longer. Methylcellulose membrane formulations thus appear to be unsuitable for use at high pressures.

Table 22. Membrane Selectivity Data During 360-Hour High Pressure Test

Time Into Test (Hours)	Components	Pressure (psig)	Flux Ratio (Selectivity)		
			Cell 1	Cell 2	Cell 3
0	CO_2/N_2	200	70.1	--	77.4
77.3*, 83.6**	CO_2/N_2	200	25.5	23.6	31.5
		500	33.0	23.7	26.5
354.3*, 360.6**	CO_2/N_2	200	19.4	35.8	17.7
		500	25.2	35.3	23.4
	CO_2/H_2	200	4.72	5.33	3.57
		500	5.45	5.70	6.50

* Time for Cell 2

** Time for Cells 1 and 3

ATTEMPTS AT IMPROVED MEMBRANES THROUGH SILICONE-BASED COMPOSITIONS

Very high carbon dioxide permeabilities are listed in the technical literature for silicone rubber membranes.(4,5) These membranes were generally reported to have selectivities for CO_2/H_2 of 4 or 5 to 1.

If this separation ratio could be improved while maintaining the high flux characteristic of silicone rubber, a very attractive membrane system could be developed. One possible way of improving the separation ratio was to modify the silicone rubber to possess hydrophilic character. Another possible approach was to use silicone rubber-impregnated support films as high flux, pinhole-free support layers for ultrathin hydrophilic membranes. These membranes could be coated on top of the silicone layer (top coatings) or formed *in situ* on the silicone membrane surface by gas plasma polymerization techniques.

Development of methylcellulose membranes would be facilitated if an adequate commercially-available support film were available. However all commercial support films previously tested had leaked through visible pinholes with the possible exception of a polysulfone-on-sailcloth support obtained from UOP. A coating of a silicone rubber having a high carbon dioxide flux could plug the pinholes in an inexpensive commercial film such as Celgard, which by itself is an inadequate support. The resulting composite support film would have a high carbon dioxide flux and appreciable separation properties, and could further be overcoated with a hydrophilic polymer. The final hydrophilic topcoating would give the membrane the high separation ratio desirable for an economic gas cleanup system.

Silicone and Topcoated Silicone Membranes

The silicone rubber selected for the first tests was General Electric Company's RTV-108, a commercial unpigmented moisture-cure silicone rubber adhesive. A listing of the membranes fabricated from RTV-108 and the data obtained may be found in Table 23. The selectivity of CO_2/H_2 was about 4 in the first two sets of tests (Examples 60 and 62A).

The RTV silicone rubber material that was used in these first tests was about three years old. Some advancement in the cure state seemed evident. New stock was obtained and used in Example 66A. Results were not significantly different using the new material.

The use of UOP polysulfone-on-cloth as a support film (Example 62F) rather than our hand-cast polysulfone raised the selectivity slightly but cut the carbon dioxide flux by 30 to 50 percent. Nevertheless, fluxes were an order of magnitude higher than with methylcellulose in most of the examples.

Table 23. Gas Permeability Test Data for Exploratory Silicone Membranes

Membrane	Composition	Ratio of CO_2/H_2 Permeabilities	Flux (ft^3/ft^2-hr-100 psi)*	
			CO_2	H_2
60	5% RTV-108 in hexane on polysulfone	3.2 - 4.8	19 - 33	4.6 - 7.2
62A	5% RTV-108 in heptane on polysulfone (thinner coating)	2.6 - 4.4	50 - 65	12 - 25
66A	5% RTV-108 (new sample) in heptane on polysulfone	2.4 - 4.0	39 - 43	10 - 18
62F	Same as 62A except used UOP polysulfone-on-cloth support film	4.2 - 4.7	28 - 45	6.8 - 9.6
62B	5% RTV-108 and 2.5% A-1100 in heptane on polysulfone, air dried overnight, dipped in 0.9% hydrochloric acid for 1/2 minute and cured at 100°C oven for 20 minutes	4.5 - 5.6	33 - 34	5.9 - 7.5
62C	5% RTV-108, 2.5% A-186 in heptane on polysulfone, air dried overnight, dipped in 0.9% hydrochloric acid for 40 seconds and cured in 100°C oven for 20 minutes	0.55 - 1.2	0.58 - 1.0	0.46 - 1.9
62H	Same as 62C except used UOP polysulfone-on-cloth support film and dipped in acid for only 1/2 minute.	3.6 - 5.0	2.0 - 3.4	0.40 - 0.95

*Test Conditions: humidified feed gas at room temperature and 200 psig, test cells at 25°C and 200 psig, permeate at room temperature and atmospheric pressure (about 20°C and 74 cm Hg). Pure gases were used. Flux was normalized to 60°F and 30.0 in. Hg.

An attempt was made to obtain a higher selectivity by incorporating hydrophilic silane modifiers into the RTV-108 coatings. Two silane adhesion promotors obtained from Union Carbide Corporation were used: 3-aminopropyltriethoxysilane (A-1100) and 2-(3,4-epoxycyclohexyl)-ethyltrimethoxysilane (A-186). Hydrolysis of the A-186 by acid should give a hydrophilic glycol.

Both A-1100 and A-186 were incorporated into solutions of RTV-108 silicone rubber and coated on supports. A film containing A-1100 in silicone deposited on polysulfone gave a slightly higher selectivity than the unmodified RTV-108 film. The flux was 30 to 50 percent lower, but still high in comparison to nonsilicone membrane systems. None of the other combinations was as good as the straight RTV-108. Neither of the silane-modified membranes seemed to be wettable by water or to be demonstrably hydrophilic. Acid treatment of the membrane modified with A-186 did not observably increase hydrophilic character or gas separation performance.

Other silicones were examined that involved elevated-temperature, peroxide-cure systems rather than room-temperature, moisture-cure mechanisms. A vinyl-modified silicone gum rubber obtained from Union Carbide Corporation, labeled W-984, gave good results. A gum rubber without vinyl functionality did not work. A silicone pressure sensitive adhesive composition (Dow Corning #282) was also briefly examined.

Table 24 contains the results of studies with silicone rubber compositions on two commercial support films--Celgard 2400 and UOP polysulfone-on-sailcloth. These studies were made to determine the minimum required coating weights for pinhole-free performance. Celgard 2400 proved difficult to use as a support for RTV-108 coatings. Gel particles in the RTV coating solutions (5 to 25 percent in heptane) were apparently at fault.

Dicumyl peroxide-cured W-984 silicone gave more consistent results on Celgard 2400 at low coating weights than RTV-108. The DC #282 silicone adhesive was not effective as a coating.

Much higher fluxes were obtainable with RTV silicone-coated polysulfone support films, as shown in Table 24. A thick film of RTV-108 silicone rubber itself showed a good CO_2/H_2 selectivity of 5.7, somewhat higher in this case than literature values which range from 4 to 5.

The concept of using these silicone membranes as support materials for ultrathin hydrophilic polymer membranes was explored. The silicone coatings on polysulfone or Celgard 2400 would provide a pore-free support for hydrophilic membranes. Gas flux through the silicone layers would be high enough so as not to affect gas flux through the less permeable topcoatings. Several membrane systems were prepared and tested. Results are shown in Table 25.

Table 24. Gas Permeability Data for Silicone Membranes on Commercial Support Films

Composition	Coating Weight ($g/cm^2 \times 10^4$)	Ratio of CO2/H2 Permeabilities	Flux (ft^3/ft^2-hr-100-psi)*	
			CO_2	H_2
RTV-108 on Celgard 2400	2.9	1.6	8.5	5.4
	2.1	3.3 - 5.1	2.0 - 3.2	0.4 - 0.95
	9.9	0.38	6.2	16
	11.7	1.3	3.1	2.3
	26.3	4.5	0.99	0.22
W-984 on Celgard 2400	3.3	3.7	36	9.8
	4.0	3.9	62	16
Dow Corning #282 on Celgard 2400	2.6	1.8	28	15
RTV-108 on UOP polysulfone support	41.5	2.7	6.5	2.4
RTV-108 thick film (0.11 cm), no support	--	5.7	0.14	0.024

* Test Conditions: humidified feed at room temperature and 200 psig, cells at 25°C and 200 psig, permeate at room temperature and atmospheric pressure (about 20°C and 74 cm Hg). Pure gases used. Flux normalized to 60°F and 30.0 in. Hg.

Table 25. Gas Permeability Data for Silicone Membranes Topcoated with Hydrophilic Polymers

Membrane	Composition	Ratio of CO_2/H_2 Permeabilities	Flux (ft^3/ft^2-hr-100 psi)*	
			CO_2	H_2
66C	RTV-108 on polysulfone, overcoated with methylcellulose acetate (2% in CH_3CN)	0.22 - 0.92	11 - 34	26 - 52
66E-2	RTV-108 on polysulfone, methylcellulose acetate (2% in 2:1 ethanol : acetone)	2.9 - 3.8	1.4 - 4.0	0.37 - 1.4
66E-3	Same as 66E-2, soaked for 69 hours in water	5.6 - 15.6	0.18 - 0.37	0.020-0.065
112DC	W-984 on Celgard 2400, overcoated with methylcellulose from 2:4:94 MeCell : A-1100 : H_2O	5.1 - 15	0.41 - 3.3	0.036 - 0.54
112EC	Same as 112DC except 1% methylcellulose	3.4 - 4.2	12 - 35	3.5 - 8.2
105A	Celgard; 2% methylcellulose acetate in acetone	0.30 - 0.35	230 - 260	760
105B	Same as 105A, except two coats of 2% methylcellulose acetate in acetone	4.80 - 5.1	1.5 - 1.8	0.30 - 0.39
118	W-984 on Celgard 2400, overcoated with ethylhydroxyethylcellulose from 0.5% in morpholine	7.6 - 10.3 4.6†	0.91 - 2.2 1.0†	0.09 - 0.71 0.22†

* Test Conditions: Humidified feed gas at room temperature and 200 psig, cells at 25°C and 200 psig, permeate at room temperature and atmospheric pressure (about 20°C and 74 cm Hg). Pure gases were used. Flux normalized to 60°F and 30.0 in. Hg.

† This sample was tested dry.

Ultrathin hydrophilic topcoatings of methylcellulose, methylcellulose acetate, and ethyl hydroxyethyl cellulose were tried. Results were mixed in that some examples leaked, some gave good selectivities, and some gave poor selectivity. Selectivities for CO_2/H_2 of up to 15:1 were achieved, but at very low flow rates. Best results were obtained with an ethyl hydroxyethyl cellulose coating. It gave CO_2/H_2 selectivities of 7:1 to 10:1 at CO_2 fluxes of 1 to 2 ft^3/ft^2-hr-100 psig. This approach appeared to show some promise.

Application of smooth, adherent, ultrathin topcoatings onto the silicone surfaces proved to be rather difficult, and may have contributed to the mixed results. A technique that appears promising in this application would be the formation of exceptionally thin, hydrophilic coatings on silicone surfaces via gas plasma polymerization conditions. Deposition of polymer from monomer plasmas would give a very complete coverage of the silicone surfaces at very low thicknesses, and the polymer coating would be tightly bound. Plasma-formed membranes have been proven effective for reverse osmosis by Yasuda et al(6) and Bell et al.(7)

Gas Plasma-Modified Silicone Membranes

In our experiments a radio frequency (RF) gas plasma was generated in an argon atmospher at 10^{-3} torr in an evacuated bell jar. Different monomers were fed into the RF plasma at this level of pressure to produce different types of coatings. Resulting membranes were soaked in water, then tested for CO_2 and H_2 permeabilities at 200 psig.

Initial experiments established that the microporous polysulfone used in this work was unaffected by RF gas plasma conditions. Then, silicone-coated polysulfone films were exposed to different, simple gas plasmas to determine effects of plasma modification of the silicone surface. Results are shown in Table 26 for the argon plasma and for argon modified with nitrogen, oxygen, or water. This initial series indicated that argon and argon/nitrogen plasmas did not affect the gas selectivity toward CO_2/H_2 and tended not to change membrane flux. Oxygen-containing plasmas (O_2, H_2O in argon) caused a severe drop in flux, and a somewhat lowered gas selectivity.

Emphasis was then shifted to plasma polymerizations of gaseous monomers on membrane surfaces. Table 27 contains results for a series of organic monomers that were plasma-polymerized onto silicone composite membranes or onto polysulfone directly. Both unsaturated monomers (acrylic acid, acryloyl chloride, methyl acrylate) and saturated monomers (morpholine, pyridine, ethylenediamine) were used. Best results were achieved with ethylenediamine and acryloyl chloride individually applied to silicone-coated polysulfone supports. Both gave CO_2 fluxes that were typically above 5, and reached as high as 21.6 ft^3/ft^2-hr-100 psig. However, CO_2/H_2 selectivity was only moderately improved (10 to 15 percent) over that of silicone rubber composite membranes. Plasma-deposited polymers applied to uncoated polysulfone gave low-flux, hydrogen-selective membranes.

Table 26. Effect of Gas Plasma Treatments on Silicone Membrane Gas Permeabilities

Membrane	Composition	Ratio of CO_2/H_2 Permeabilities	Flux (ft^3/ft^2 hr-100 psi)* CO_2	H_2
67D	RTV-108 on polysulfone (control)	4.5	22.7	5.1
67B	RTV-108 on polysulfone, treated in an argon plasma	4.7	5.1	1.1
71A	W-984 on polysulfone, treated in an argon plasma	4.4	24.5	5.6
83D	RTV-108 on polysulfone, treated in a nitrogen plasma	4.6	24.9	5.4
84A	RTV-108 on polysulfone, treated in an oxygen plasma	3.4	0.1	0.03
92B	RTV-108 on polysulfone, treated in a water plasma	3.4	0.36	0.10

*Test Conditions: Humidified feed gas at room temperature and 200 psig, test cells at 25°C and 200 psig, permeate at room temperature and atmospheric pressure (about 25°C and 74 cm Hg). Pure gases were used. Flux normalized to 60°F and 30.0 in. Hg.

Table 27. Gas Permeability Data for Plasma-Polymerized Membranes

Membrane	Composition	Ratio of CO_2/H_2 Permeabilities	Flux (ft^3/ft^2-hr-100 psi)*	
			CO_2	H_2
77C	Acrylic acid plasma on a polysulfone support	0.70 - 1.53	0.14 - 0.90	0.21 - 0.59
77D	Acrylic acid plasma on RTV-108 silicone-coated polysulfone support	1.74 - 3.65	0.99 - 1.44	0.30 - 0.57
78B	Acryloyl chloride plasma on a W-984 silicone-coated polysulfone support	4.17 - 5.67	5.79 - 10.00	1.14 - 2.36
83B	Methyl acrylate plasma on RTV-108 silicone-coated UOP polysulfone support	1.50 - 3.22	1.9 - 7.1	0.89 - 2.31
79A	Morpholine plasma on RTV-108 silicone-coated polysulfone support	0.01 - 0.62	0.02 - 0.94	0.04 - 46.
79E	Pyridine plasma on a polysulfone support	0.04 - 0.09	0.05 - 0.45	0.57 - 1.41
79F	Pyridine plasma on RTV-108 silicone-coated polysulfone support	1.22 - 1.39	0.071 - 0.085	0.047 - 0.061
82B	Ethylenediamine plasma on RTV-108 silicone-coated polysulfone support	4.82 - 5.50	8.1 - 21.6	1.71 - 3.93

* Test conditions: Humidified feed gas at room temperature and 200 psig, test cells at 25°C and 200 psig, permeate at room temperature and atmospheric pressure (about 25°C and 74 cm Hg.) Pure gases were used. Flux normalized to 60°F and 30.0 in. Hg.

These experimental membranes did not achieve the goals that were expected of them. In particular, very low flux membranes were obtained in several cases despite the extreme thinness of the plasma-deposited coating. This probably reflected a tight, highly-crosslinked coating. The high flux membranes that were achieved represented only a slight advantage over untreated silicone composite membranes, which would not justify the added membrane processing cost.

Theoretical Explanation of the Observed Test Results

Examination of the data obtained in this program led to the theory that water immobilized in the membrane surface controlled the gas permeation rates. The role of water was examined as a possible source of explanation for the observed decreases in CO_2/H_2 separation at higher temperatures and pressures.

It is known that the permeability of a gas through a membrane is proportional to the product of its solubility (S) in the membrane and its diffusivity (D) through the membrane (P = k DS). Table 28 contains data comparing the solubility (S) of six gases in water from 25°C to 70°C. These data were normalized to hydrogen at 25°C. Also shown in Table 28 are the diffusivities (D) of three of the gases in water at 25°C. Data were not readily available for higher temperatures, but diffusivities increase with temperature. When the normalized solubilities in Table 28 are multiplied by the respective diffusivities, estimates for the theoretical permeability ratio CO_2/H_2 through a pure water membrane can be made. This was done, and results are shown below:

Temperature	CO_2/H_2 Permeability Ratio
25°C	14
50°C	9
60°C	7

For a pure water membrane, therefore, a theoretical maximum CO_2/H_2 separation ratio at 25°C would be approximately 14 to 1. As temperature is increased, this theoretical ratio would decrease because of the rapid decrease in the CO_2 solubility in water relative to H_2 solubility. Diffusivities would increase with temperature, but probably not sufficiently to counteract the solubility decreases.

This concept was explored further by calculating theoretical flux data for H_2 and CO_2 through hypothetical water films. Objectives in this approach were: 1) to determine what the maximum attainable gas fluxes would be through a water film, comparing these with the current level of attainment by our experimental membranes, and 2) to outline the effects that might be expected as temperature and pressure were varied in the system.

The permeability of water to gases was calculated by the formula:

$$P = S \cdot D/\Delta p$$

Where P = intrinsic "Barrer" permeability of the gas through the film (cm^3-cm/cm^2-sec-cm Hg),

S = solubility of the gas in the water film (cm^3/gas/cm^3 H_2O),

Table 28. Solubilities and Diffusivities of Various Gases in Water

Solubilities of Various Gases in Water
(Volume/Volume) at Low Pressure Based
on Hydrogen at 25°C(8)

	H_2	O_2	CO	CH_4	CO_2	H_2S
25°C	1.00	1.61	1.22	1.71	43	130
50°C	0.92	1.19	0.92	1.22	25	80
60°C	0.91	1.11	0.85	1.11	20	68
70°C	0.91	1.05	0.82	1.04	--	58

Diffusivities of Various Gases
in Water at 25°C(9)

	D(10^{-5} cm^2/sec)
H_2	5.95
CO_2	1.96
H_2S	1.61

D = diffusivity of the gas in water (cm^2/sec),

Δp = partial pressure difference in the gas across the film (cm Hg).

The Barrer permeabilities were converted to ft^3/ft^2-hr-100 psi and normalized to 60°F and 30.0 inches Hg for this report. Calculations were made only for H_2 and CO_2 since the separation attainable between these two gases was the primary controlling factor in the economic feasibility of a membrane purification process.

Solubility data for CO_2 and H_2 in water at various temperatures and pressures were taken from the chemical literature.(10,11,12,13,14) The diffusitivites of these gases in water at 25°C and low pressures were similarly available.(15) Diffusivities at higher temperatures were estimated via the standard formula:

$$D\mu/T = \text{constant}$$

Where D = diffusivity in the liquid,

μ = viscosity of the liquid at temperature T,

T = temperature (°K)

Viscosity data on water at various temperatures were readily available.(16)

Figure 6 illustrates the theoretical CO_2 flux through a water film plotted against film thickness. Conditions of 25°C and a pressure drop from 25 atmospheres to one atmosphere across the hypothetical water membrane were used in preparing this graph. A straight line relationship was evident when the data were plotted on a log-log basis. Thus, a 200 μm (0.008 inch) thickness of water would allow a CO_2 flux of about 5.2 ft^3/ft^2-hr-100 psi. A 2 μm water film, which would correspond approximately to the thickness of the active layer in our gas separation membranes, would give a flux of 520 ft^3/ft^2-hr-100-psi. Since our experimental membranes have produced fluxes for CO_2 of only about 5 ft^3/ft^2-hr-100 psi, considerable leeway for higher fluxes still exists.

The solubility of H_2 in water increases as a linear function of pressure through 140 atmospheres. The solubility of CO_2 in water, by contrast, increases in a nonlinear fashion through the 10 to 30 atmosphere pressure range. Above 30 atmospheres, its solubility increases at only 30 percent the rate of H_2 as a function of pressure. The solubilities of both gases in water decrease with increasing temperature. These factors combine to give differently shaped curves for CO_2 and H_2 in graphs of flux versus pressure.

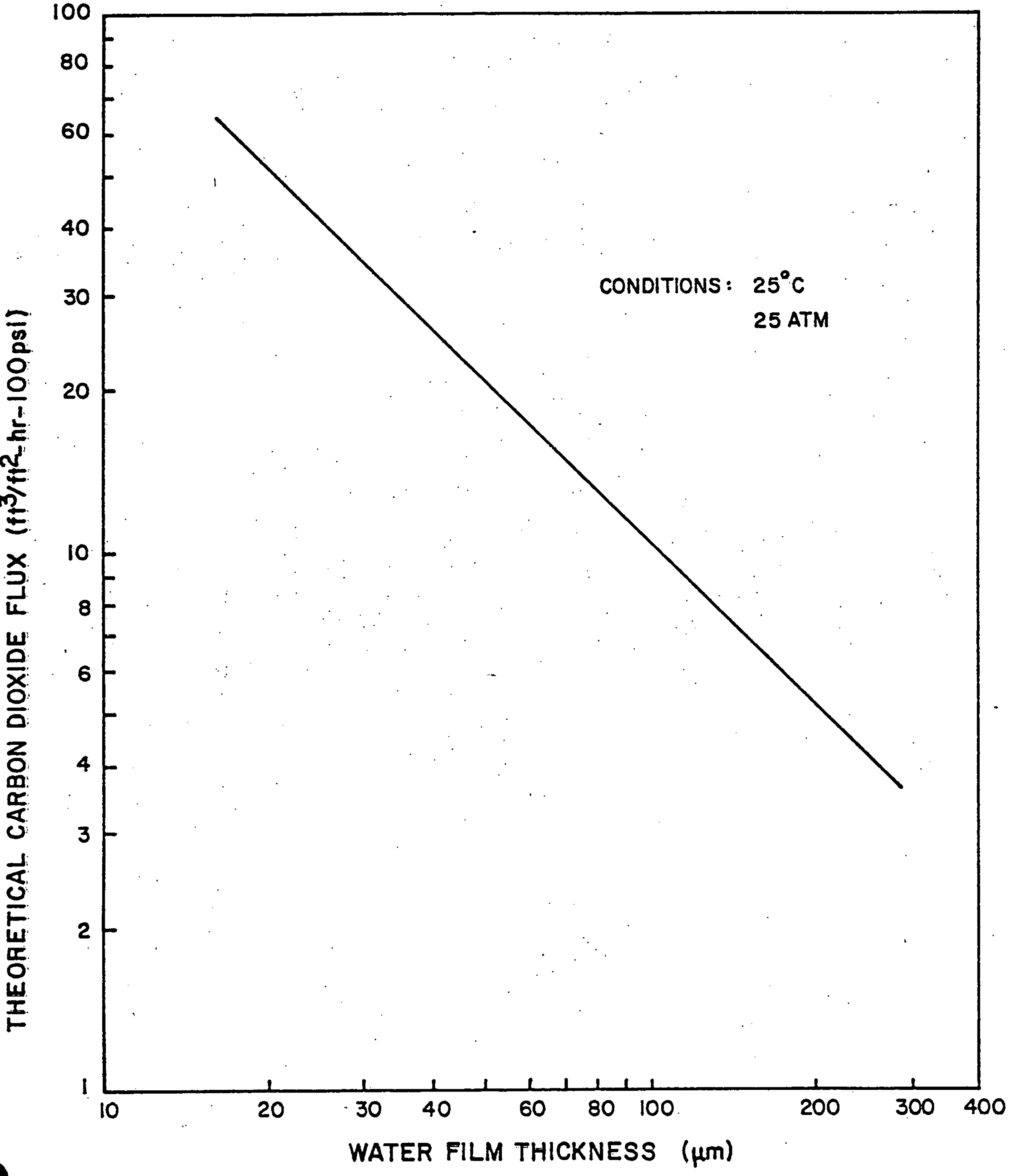

Figure 6. Theoretical Flux of Carbon Dioxide through a Water Film as a Function of Film Thickness

Figure 7 illustrates the differences between these two gases. Curvilinear plots were seen for the CO_2 flux as a function of pressure; a family of curves was derived corresponding to a family of selected temperatures. A similar plot of H_2 flux versus pressure gave a series of essentially straight lines, one for each selected temperature.

The significance of the curves in Figure 7 was that the CO_2/H_2 selectivity changed with both temperature and pressure. This was calculated for an equimolar mixture from the pure gas fluxes and is illustrated graphically in Figure 8. The selectivity for CO_2 versus H_2 was particularly influenced by temperature. A large theoretical drop in the CO_2/H_2 selectivity occurred with an increase in temperature from 25°C to 50°C, for example.

Pressure effects on the CO_2/H_2 separation ratio were also present, although not to a particularly significant degree. At 25°C, for example, the CO_2/H_2 separation ratio was 15.7 at 1 atm partial pressure for each gas, and it edged downward to 12.8 at 25 atm partial pressure for each gas. Greater effects were noted at high pressures. However, anticipated operating conditions in a coal gasification plant should not exceed the 25 atm level for CO_2 and 35 atm for H_2.

Program efforts have heretofore concentrated on test conditions involving temperatures of 25 to 75°C. Emphasis was placed on determining the maximum feasible operating temperature. These calculations illustrated the fact that the lowest possible operating temperature would result in the best membrane selectivity. Membrane selectivity could presumably be improved by operating at temperatures below 25°C. The information at 0°C in Figures 7 and 8 amply demonstrate this factor. The quantitative prediction at a carbon dioxide partial pressure of one atmosphere was as follows:

	25°C	0°C	Percent Increase (0° versus 25°C)
CO_2 Flux*	1227	1250	1.9
CO_2/H_2 selectivity	14.5	26.5	83

*ft^3-100 Å/ft^2-hr-100 psi

The gas transport properties of a composite polysulfone-silicone-methylcellulose membrane were measured at 0° and 25°C in order to test this theoretical prediction.

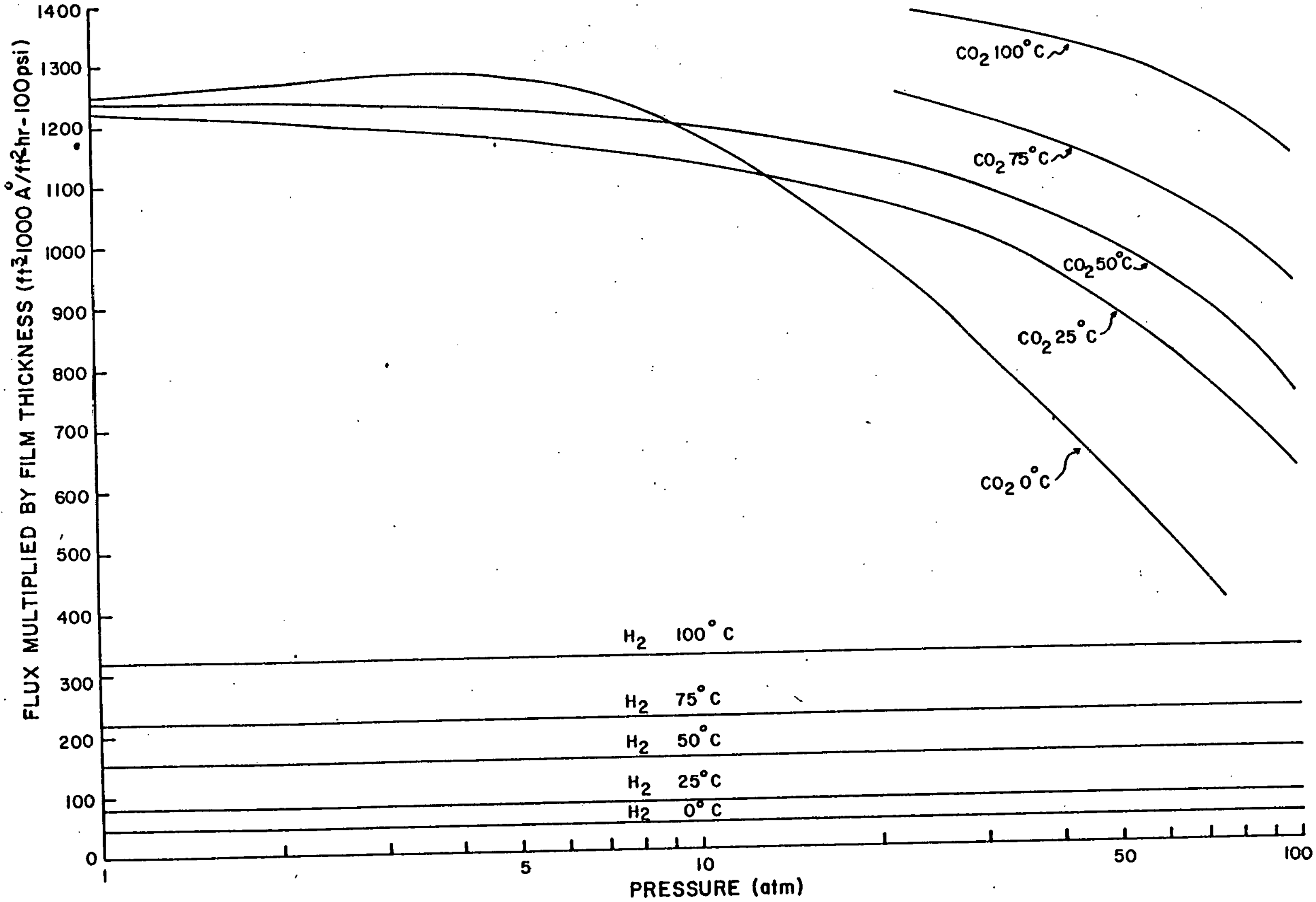

Figure 7. Theoretical Gas Flux through Water Membranes as a Function of Temperature and Pressure

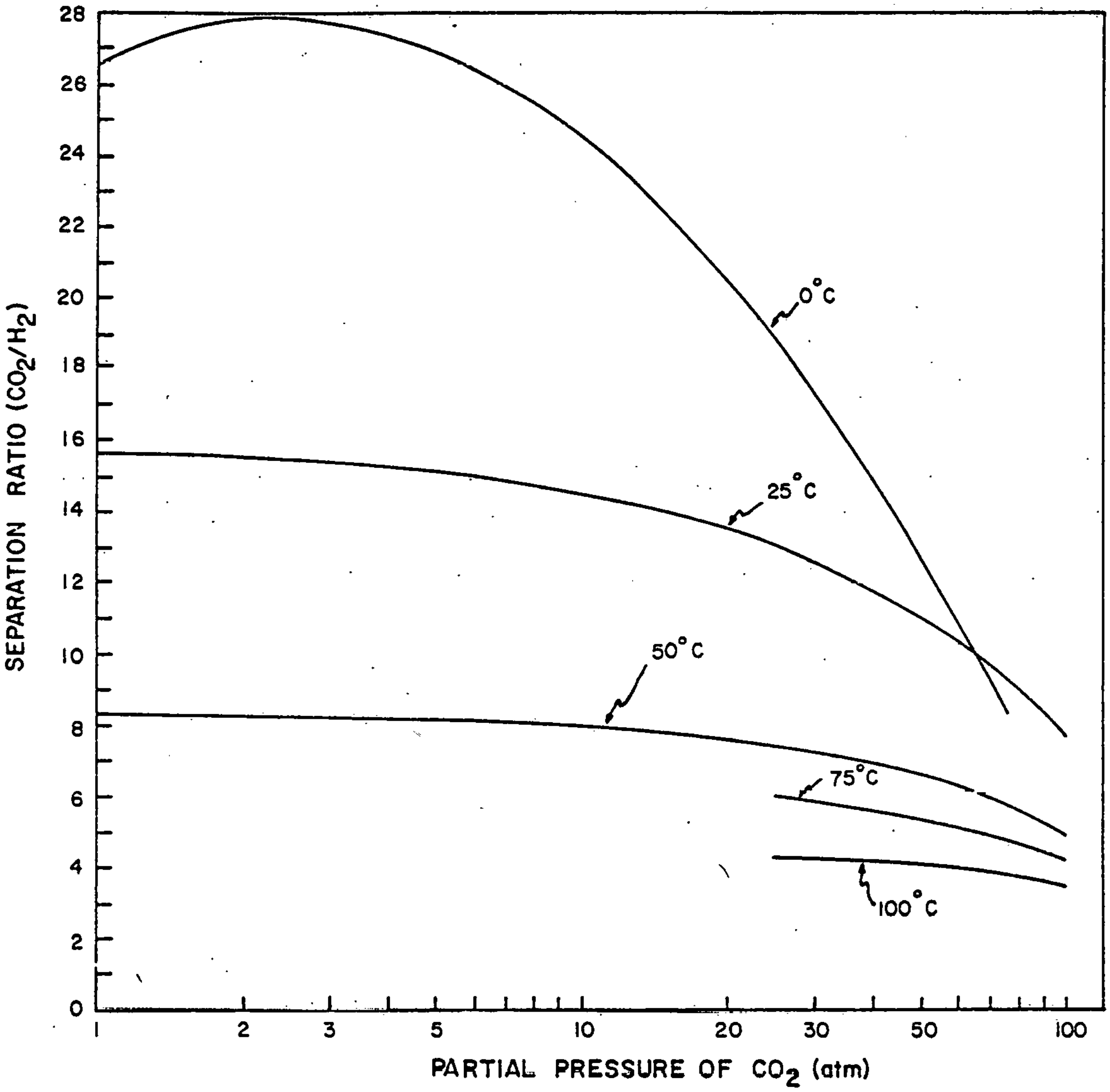

Figure 8. Theoretical Separation Ratio of Equimolar CO_2/H_2 Gas Mixtures as a Function of Pressure and Temperature

Three sets of membranes were made as follows. A dry sheet of 2-mil-thick, hand-cast, microporous polysulfone was coated with a heptane solution of Union Carbide W-984 vinyl-modified silicone resin. This was cured *in situ* with dicumyl peroxide in an oven at 150°C. The silicone composite membrane was then coated with an ultrathin layer of methylcellulose (100 cps grade) by dipping into an aqueous solution containing 1 percent methylcellulose, 1 percent hydrochloric acid, 2 percent glyoxal, 40 percent isopropanol, 0.1 percent Triton X-100, and 0.1 percent Fluorad FC-170 fluorosurfactant. The hydrochloric acid and glyoxal served to crosslink the methylcellulose topcoating. The isopropanol and the two surfactants were necessary to achieve a uniform deposit of methylcellulose on the low-energy surface of the silicone.

Two of the three sheets proved defective, but the third sheet behaved well, giving a combination of flux and CO_2/H_2 selectivity that exceeded all previous membrane data for topcoated silicone composite membranes. These data, shown in Table 29, indicate CO_2/H_2 selectivities approaching the theoretical limit of about 14.5 at 25°C and CO_2 fluxes of about 2 ft^3/ft^2-hr-100 psi.

It was predicted that the same membranes, tested at 0°C, would exhibit a slightly improved CO_2 flux, and that the CO_2/H_2 separation ratio should increase by 83 percent, rising from 14.5 to 26.5. Actual data in Table 29 showed a 50 percent increase, with CO_2 gas flux essentially unchanged.

There was no assurance that the membrane surfaces were actually operating at 0°C, because the gases were at room temperature as they entered into the refrigerated test cells. Cooling of the gases completely to 0°C was certainly not fully achieved. Thus, the full 83 percent increase in CO_2/H_2 selectivity might still be achievable under tighter control of gas temperatures. Nevertheless, these results strongly supported the theory.

Table 29. Permeability Comparison Test at 0 and 25°C

Temperature	Selectivities	Flux (ft^3/ft^2-hr-100 psi)*	
		CO_2	H_2
25°C	8.3 - 14.5 Average = 11.3	1.3 - 2.7	0.09 - 0.24
0°C	14.5 - 18.9 Average = 17.0 Increase = 50%	1.2 - 2.5	0.08 - 0.14

*Test Conditions: Pure feed gases and cells at 200 psig, permeate at room temperature and ambient pressure (about 30°C and 74 cm Hg). Flux normalized to 60°F and 30.0 in. Hg.

It appears, therefore, that water absorbed by these hydrophilic membranes was vital to the effective separations of the acid gases from H_2 , CO, and CH_4. The absorbed water, in turn, absorbs soluble gases (CO_2, H_2S, CH_3SH), allowing their penetration through the membrane structure. This same water excludes the water-insoluble gases (H_2, CO, CH_4), promoting their rejection.

The separation ratios observed for CH_4, H_2, CO_2, H_2S and CH_3SH are all consistent with the water mechanism. The loss of separation effectiveness with increasing temperature and pressure are also consistent with this theory. This theory explains why CO_2/H_2 separations in this research effort have often exceeded 10 but almost never exceeded 14. Ratios greater than 14, which have been observed on rare occasions at 25°C, probably involved erroneous data.

Apparently, therefore, membrane purification of raw SNG from coal gasifiers will have limitations as to operating temperature and pressure.

ECONOMIC REVIEW OF ACID GAS REMOVAL PROCESSES

Our goal in the economic analysis was to obtain the significant costs of competitive acid gas clean-up processes using a reasonable flow scheme and typical operating conditions. The earliest economic analysis pointed out the membrane properties having a significant effect on costs. These membrane properties were investigated in the membrane development phases which followed. The later cost analysis, presented here, shows how well the membrane process can compete with the conventional processes now being used.

Summary of Conventional and Membrane Process Acid Gas Clean-Up Costs

Reliable estimates have been obtained of costs of four acid gas clean-up processes, for final sulfur removal, for a guard chamber, and for one sulfur recovery process. Standard engineering cost estimating procedures were used. The costs are reported on the basis of cents per thousand standard cubic feet of pipeline quality gas producted (¢/Mscf). The cost of conventional acid gas clean-up processes is about 40 cents per MSCF of gas produced. There was relatively little difference in the economics between the various gas scrubbing processes (35 to 42 cents per Mscf). These processes are known to be competitive in other applications, and this is confirmed in our cost analysis.

The cost of acid gas clean-up with the best performing membranes developed during this project appeared to be about 52 cents per Mscf of gas produced. These calculations were based on reasonable assumptions outlined later in this report. The range of costs for these best membranes was 43 to 62 cents per Mscf as shown in Figure 10 (page 93). This is more than conventional processes and includes additional costs required for membranes such as product gas losses peculiar to membrane processes. The selectivity of carbon dioxide relative to hydrogen rather than that of hydrogen sulfide to methane or carbon monoxide control the economics for the membrane process. The experimental program provided data for estimating the additional membrane costs which depend on the performance characteristics.

In addition to the costs for separating the acid gases by one of these processes, the cost for final sulfur cleanup is 0.3 to 0.5 cents per Mscf of gas produced for conventional processes and about 3 cents for membranes, the cost for a guard chamber is 1.5 cents per Mscf of gas produced and the cost for recovering sulfur from the separated acid gas by a variant of the Claus process is about 5 cents per Mscf of gas produced.

When these additional costs are included in the cost for acid gas clean-up, the cost of the conventional processes is raised to about 47 cents per Mscf of gas produced (range 43 to 49 cents) while the cost of the membrane process is raised to 62 cents per Mscf of gas produced (range 43 to 75 cents). The cost disadvantage for the membrane process of 15 cents per Mscf of gas produced cannot be overcome without a shift in some of the component costs. A decrease in the cost of the electricity used for gas compression relative to the cost of fuel or steam would improve the competitiveness of membranes. A decrease in the cost of membranes relative to the cost of conventional scrubbing equipment would likewise improve the competitiveness of membranes. Finally less stringent residual sulfur requirement in the methanator would improve the competitiveness of the membrane process. The economics of the membrane process might also be greatly changed if gases of different compositions or pressures were considered. For example the membrane process would probably be economical for removing sulfur containing gases from a low pressure biogas mixture.

Credit for the amount of sulfur produced would be substantial but was not included in this analysis. It would not affect the cost disadvantage of the membrane process compared to the conventional processes.

Comparison of the Economics of Gas Scrubbing Processes

Table 30 summarizes investment and operating costs estimated for several competing processes for removal of acid gases from coal gasification streams. Data are presented for the Rectisol process (a refrigerated physical solvent system using methanol at -40°C),the Benfield process (a hot carbonate chemical solvent system), and the Sulfinol process (an ambient system using both a chemical reactant and a physical solvent). Data are also presented for the solid absorbent system, fluidized dolomite.

As seen in Table 30, the costs of the various acid gas removal processes are grouped rather closely at around 40¢ per Mscf of gas produced. The processes appear competitive in this respect.

The costs given above were estimated through information obtained from the process licensors and from the technical literature. Various assumptions were made in the treatment of data, and these are described below.

We chose for a standard case a 785-MMscfd stream at 1000 psig with a dry basis composition (the gas is actually saturated with water vapor) of 36.7 percent H_2, 12.0 percent CO, 22.1 percent CH_4, 27.0 percent CO_2, 2.2 percent H_2S. This approximates the product expected from a shift reactor in a 250-MMscfd Hygas coal gasification plant under certain conditions. Requirements for purified gas were one to two percent CO_2 and .02 to .2 ppm total sulfur compounds (to avoid poisoning of methanation catalysts), with little or no loss of the valuable gas components (CH_4, CO, and H_2). In developing comparative cost data, we permitted for scrubbing processes a residual of two percent CO_2, 1 to 4 ppm H_2S (4 ppm is the current "pipeline specification"), and the loss of less than one percent of the other components. It was assumed that an additional solid absorbent (zinc oxide) would be used for final sulfur removal but the additional cost is estimated separately and not included in this section. For a membrane process we permitted two percent CO_2, about 50 ppm H_2S, and losses of less than one percent H_2. This assumed that the use of a second clean-up step with a solid absorbent would be required before the final sulfur removal which would be similar to that required for a scrubbing system. The cost of this extra clean-up step is estimated separately.

Table 30. Summary of Estimated Investment and Operating Costs for Various Acid Gas Clean-Up Processes, Mid-1976.

	Fixed Investment (Installed Plant) $Million	Total Investment $Million	Operating Cost $Million/ Year	Total Annual Cost $Million	Cost Based on Gas Produced ¢/Mscf
Rectisol, 1 train	38.1	52.1	21.4	30.5	34.8
Rectisol, 3 trains	56.1	72.1	22.3	34.8	39.8
Benfield HiPure "high"	19.8	36.7	30.4	37.0	42.3
Benfield HiPure "low"	12.6	28.7	30.0	35.3	40.3
Sulfinol	20.0	34.6	25.6	31.8	36.3
Fluidized dolomite (H_2S only)	19.4	23.2	4.2	9.2	10.5
Fluidized dolomite (H_2S + CO_2)	--	--	--	--	40.6*
Final sulfur clean-up from 50 ppm, zinc oxide	1.8	3.1	2.3	2.9	3.34
Final sulfur clean-up from 4 ppm, zinc oxide	0.5	0.69	0.29	0.42	0.48
Final sulfur clean-up from 1 ppm, zinc oxide	0.24	0.34	0.21	0.27	0.31
Gaurd chamber, zinc oxide	5.1	5.8	0.98	1.3	1.53
Liquid phase Claus, Consolidation Coal Company	11.4	13.36	1.94	4.24	4.84

*See discussion of this process for details.

We also made several economic assumptions in this study as follows. To calculate investment, we included: 1) fixed investment (the mid-1976 installed cost of the plant, but not including investment in offsite utilities outside the battery limits or interest on the cash flow during construction and startup), 2) amortized investment (research, development, and engineering at 10 percent of the installed cost of the plant, plus startup cost of three months of labor and utilities), and 3) recoverable investment (working capital equal to three months of labor, utilities and maintenance).

Not included in the calculation of clean-up process costs were the costs of a quench step, of demisting, of dust removal, or of the land, as all of these are basically the same for each acid gas clean-up process considered. The costs of additional sulfur removal, of a guard chamber, and of sulfur recovery have been obtained separately for comparison with the cost of acid gas clean-up. We estimated the cost of capital at 11.6 percent based on 70 percent debt financing at 8.0 percent plus 30 percent equity at 20 percent. To obtain the annual costs of the investment we assumed five years to recover the capital of the amortized investment and 20 years to recover the capital of the fixed investment. Other annual charges on investment were insurance, administrative and general costs, and property taxes (respectively 0.5, 1.0, and 1.5 percent of the fixed investment) and interest alone on the recoverable investment. Operating costs included labor; utilities (fuel at $1.00 MM Btu and a boiler efficiency of 40 percent for making steam; electricity at 1.5¢/kw-hr, and a motor efficiency of 85 percent; cooling water at 20¢/Mgal, and a rise of 35°F, unless otherwise noted; the boiler feed quality water at 40¢/Mgal), and maintenance at five percent per year of the installed plant cost. Other economic assumptions are peculiar to one process and will be noted in the particular discussion of that process.

Discussion of Rectisol Process Economics

The Rectisol process of Lurgi-Linde is a physical solvent process using methanol at about -40°C. It is the only process that has been widely used for acid gas clean-up in coal gasification plants particularly in systems with the Lurgi gasifier. Its great disadvantage is the large investment required for the plant. The low operating cost, particularly in the low consumption of steam, partially offsets this. Another advantage of Rectisol is that the gas is automatically dried to a low dew point suitable for a pipeline. As indicated in Table 31, the installed cost of a single-train Rectisol plant large enough for this application is $38.1 million. This is so much larger than any present Rectisol plant that several trains may be required. The installed cost of a three-train Rectisol plant is $56.06 million. We considered both of these cases in Table 31. For the one train plant the fixed investment is $38.1 million, the total investment $52.1 million, the operating cost $21.4 million per year, and the total annual cost $30.5 million, equivalent to 34.8¢ per Mscf of gas produced. For a three-train plant these become respectively $56.1, $72.1, $22.2, and $34.8 million, and 39.8¢. Rectisol's investment is very high but the operating costs are low enough to keep it

Table 31. Economics of the Rectisol Process, Mid-1976

	1 Train	3 Trains
Investment - $ Millions		
Fixed	38.1	56.06
Amortized	8.67	10.47
Recoverable	5.34	5.56
Total Investment	52.11	72.09
Annual Costs - $ Millions		
Investment	9.13	17.56
Operating Costs		
Utilities		
Refrigeration	7.63	7.63
Steam	1.44	1.44
(18°F rise) Cooling Water	6.64	6.64
Electricity	2.70	2.70
Makeup Solvent	.734	.734
Total Utilities	19.14	19.14
Maintenance	1.905	2.803
Labor	.3	.3
Total Operating	21.35	22.25
Total Annual	30.48	34.80
Cost based on gas produced - ¢/Mscf	34.8	39.8

competitive in total cost. Reference to Table 31 shows that the cost of the Rectisol process is not highly sensitive to fuel costs, but a change in the interest rate or the availability of capital would have a large effect on the annual costs.[17]

Discussion of Benfield Process Economics

The Benfield process of the Benfield Corporation uses a chemical reactant, hot potassium carbonate, and a proprietary activator dissolved in water. A modification called the HiPure process uses two solvents of differing compositions. The investment is 5 to 10 percent higher for the latter, but the steam requirement is the same or lower. The purification is much better, about 1 ppm of H_2S, in some cases down to 0.1 ppm. The temperature in the absorption tower bottoms (the hottest point in the towers) must be lower than 95°C to prevent the CO present in coal gasification streams from reacting with the active potassium to form inactive potassium formate. This considerably cuts the advantage of a "hot" process. The presence in the gas of light oils, such as those used to slurry the coal in the Hygas process causes foaming problems. As indicated in Table 32, a Benfield plant in the present application would consist of three trains, each $4 to $6 million, with an additional 5 to 10 percent for HiPure. This is the erected plant cost, but does not include the investment for utilities. We have included two cases for the high and low investment estimates in Table 32, but we consider the "high" case more realistic. For this case, the fixed investment is $19.8 million, the total investment $36.7 million, the operating costs $30.4 million per year, and the total annual cost $37.0 million, equivalent to a cost of 42.3¢ per Mscf of gas produced. The costs in the "low" case are $12.6, $28.7, $30.0, $35.3 million, and 40.3¢, respectively. Reference to Table 32 will show that the cost of steam to strip the solvent is $22.3 million per year, or over 60 percent of the annual cost. The cost of this process is very sensitive to fuel prices.[18]

Discussion of Sulfinol Process Economics

The Sulfinol process of Shell Oil combines a physical solvent, tetrahydrothiophene-1,1-dioxide (also called sulfolane), a chemical reactant (di-isopropanolamine), and water. Like physical solvents, this mixture works best at high pressure. Like chemical reactants, it achieves very good acid gas removals. For our case, Shell provided a utilities summary and a mass balance on the gas stream but no plant investment data.[19] For the plant investment we assumed $20 million.[20] As indicated in Table 33, the fixed investment is $20 million, the total investment is $34.6 million, the operating cost is $25.6 million per year, and the annual cost is $31.8 million equivalent to 36.3¢ per Mscf of gas produced. Reference to Table 33 shows that stripping steam costs $16.5 million per year, or over 50 percent of the total annual cost. The cost of this process is very sensitive to fuel prices.

Table 32. Economics of the Benfield-HiPure Process, Mid-1976

	"High" Case	"Low" Case
Investment - $ Millions		
Normal Benfield Plant	18.0	12.0
Additional for HiPure	1.8	.6
Total Fixed Investment	19.8	12.6
Amortized	9.32	8.6
Recoverable	7.59	7.5
Total Investment	36.71	28.7
Annual Costs - $ Millions		
Investment	6.63	5.26
Operating Costs		
Utilities		
Steam	22.3	22.3
Cooling Water	5.55	5.55
Electricity	1.16	1.16
Makeup Solvent	.064	.064
Total Utilities	29.07	29.07
Maintenance	.99	.63
Labor	.3	.3
Total Operating	30.36	30.0
Total Annual	36.99	35.26
Cost based on gas produced - ¢/Mscf	42.3	40.3

Table 33. Economics of the Sulfinol Process, Mid-1976

Investment - $ Millions	
Fixed	20.0*
Amortized	8.2*
Recoverable	6.2*
Total Investment	34.6
Annual Costs - $ Millions	
Investment	6.2*
Operating Costs	
Utilities	
Steam	16.5
Cooling Water	4.3
Electricity	3.2
Makeup Solvent	.327
Total Utilities	24.3
Maintenance	1.0*
Labor	.3
Total Operating	25.6
Total Annual	31.8
Cost based on gas produced - ¢/Mscf	36.3

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*Estimated

Discussion of the Fluidized Dolomite Process Economics

The fluidized dolomite process under development by Consolidation Coal Company differs from the CO_2 Acceptor coal gasification process in that the H_2S clean-up is separate from the gasification. About 97 percent of the initial H_2S may be removed, for example, from 0.65 percent to 2000 ppm. An additional clean-up step is required before methanation. For removal of only the H_2S, as indicated in Table 34, the fixed investment is $19.4 million, the total investment is $23.22 million, the operating cost $4.23 million per year, and the annual cost $9.17 million per year, equivalent to 10.5¢ per Mscf of gas produced. Although this is a very low cost, only gross H_2S is being removed.[21] This process can also remove CO_2 just like the CO_2 Acceptor coal gasification process. However it is very difficult to estimate the cost for this removal. Additional equipment or much larger equipment would be necessary if CO_2 removal were required from this process in addition to H_2S removal. We are unable to estimate how large this additional equipment would be or how much investment cost this would involve. However it is possible to estimate a large portion of the increased operating cost. It is clear that a large increase in the operating cost would be entailed by the heat needed to regenerate the used dolomite that has absorbed the CO_2. In lime-making kilns, the net heat required is about 5 x 10^6 Btu/ton CaO produced.[22] If the regenerator ran this efficiently, the cost of the additional heat required in a CO_2 removal system would be $26.3 million per year or 40.6¢ per Mscf of gas produced as shown in Table 34. This is a minimum cost which does not include most of the equipment investment or operating costs other than heat. However, this heat requirement appears to be the largest operating expense in this process and its cost should be very sensitive to fuel prices.

Economics of the Membrane Process for Acid Gas Removal

The intent of this cost analysis was to determine costs of removing carbon dioxide and hydrogen sulfide from a shifted coal gasification stream by membranes. Two important membrane parameters were varied and the costs determined for several different cases. The parameters were the CO_2 flux and the CO_2/H_2 selectivity (α). Early in this project it was found that these two parameters rather than the fluxes of CH_4, CO, and H_2S controlled the process economics.

A high CO_2 flux allows use of a smaller membrane area and therefore lower cost. For all membranes tested the H_2S flux was higher than the CO_2 flux and the CH_4 and CO fluxes were lower than the H_2 flux. The CO_2/H_2 separation was therefore the most difficult. A successful separation of these two would likely assure the simultaneous separation of all the acid gases from all the product gases. A low CO_2/H_2 selectivity would permit a large amount of hydrogen to escape by permeation through the membrane. This raised the cost in three ways. There were two additional costs for recovering hydrogen. One of these was the greater investment required for the larger membrane area necessary to recover the hydrogen via recycle loops. The other was the greater operating cost required to recompress the permeate gas back to high pressure for this recovery. A third additional cost was the value of the hydrogen not recovered from the last recycle

Table 34. Economics of the Fluidized Dolomite Process for H_2S Removal, Mid-1976*

Investment - $ Millions	
Fixed	19.4
Amortized	2.76
Recoverable	1.06
Total Investment	23.22
Annual Costs - $ Millions	
Investment	4.94
Operating Costs	
Utilities	
Steam	.63
Cooling Water	.76
Electricity	.18
Makeup Absorbant	1.39
Total Utilities	2.96
Maintenance	.97
Labor	.3
Total Operating	4.23
Total Annual	9.17
Cost based on gas produced - ¢/Mscf	10.5

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*Additional cost for CO_2 clean-up:

- gross heat for regenerating dolomite (without heat recovery)	$54.3 Million per year 62.2¢ per Mscf of gas produced
- net heat for regenerating dolomite (with heat recovery as in lime kilns)	$26.3 Million per year 30.1¢ per Mscf of gas produced
- possible cost for H_2S + CO_2 clean-up ignoring additional investment and operating costs	$35.5 Million per year 40.6¢ per Mscf of gas produced

permeator in a train of one or more recycle loops. In this study no cost was assigned to the value of the hydrogen lost from conventional processes because this loss is very low. However the costs reported for the membrane process do include the value of the hydrogen lost. For the membrane process, cost estimates were made using the same method as used for the conventional processes. Costs are reported for various CO_2 fluxes, CO_2/H_2 selectivities, hydrogen losses, and a product gas CO_2 concentration of 1 to 2 percent.

In the membrane process the various membrane units, which are called permeators, can be combined in different ways. The gas which passes through the membrane, mostly acid gas, is called the permeate. The gas which is retained on the high pressure side of the membrane is called the retentate. Figure 9 illustrates in a schematic the flow diagram for gases through a membrane process. In this figure, the retentate of the first permeator, at 1000 psig, forms the major part of the product gas. The permeate, at 14.7 psia, is recompressed to 1000 psig and is fed into the second permeator for hydrogen recovery. The retentate of the second permeator is recycled with the untreated gas to become the feed of the first permeator. The permeate of this second permeator may be fed to the third permeator for additional hydrogen recovery. The retentate of this and subsequent permeators are fed forward and combined with the retentate of the first permeator to become the final product gas. Permeate from the third permeator is fed into the fourth permeator, and so forth, until the hydrogen content of the permeate from the final permeator is approximately one percent. This ultimate permeate is then sent to sulfur recovery, for example, a Claus process plant. Each permeator would be smaller than the previous one and would handle less gas.

In developing cost calculations on the membrane process, the selectivity of carbon dioxide relative to hydrogen was the key variable parameter because, as noted previously, this separation was the most difficult to achieve for the membranes studied. The selectivity ratios of $H_2S:CO_2$, $H_2:CH_4$ and $H_2:CO$ were each set at 2:1. Based on the experimental data obtained in this program, this was a reasonable approximation. The second variable for the parametric study of process economics was the CO_2 flux, which greatly influenced the required membrane area. A third parameter was the percent of the hydrogen originally present which was lost through the membrane process. The price of hydrogen was taken to be $2.00 per Mscf and methane to be $4.00 per Mscf. Most of the lost product gas would be hydrogen and very little would be methane.

The first step in the economic analysis, once the CO_2 flux and CO_2/H_2 selectivity were set, was to perform a mass balance on each permeator and on the complete system. Calculation of the mass balance of a permeator was accomplished by using a computer program previously developed at North Star. This program, called NGASLAM, assumed no axial mixing on each side of the membrane. This assumption would be correct for a very large permeator and nearly correct for a series of small, completely mixed permeators.

If the concentrations entering the permeator were known the program calculated, by means of a numerical integration technique, compositions on

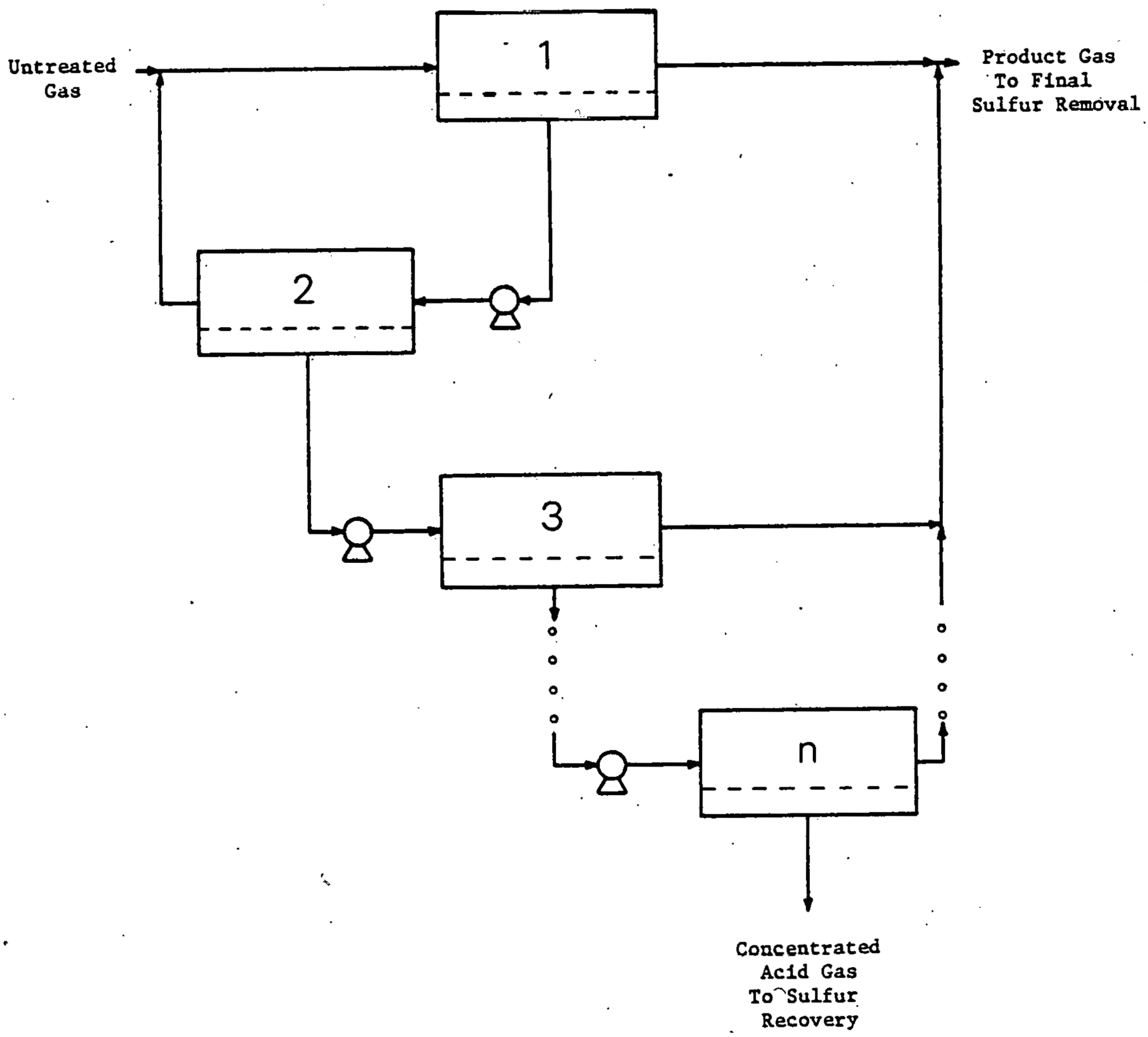

Figure 9. General Flow Diagram of the Membrane Process for Acid Gas Removal

both sides of the membrane and the percentage of the feed appearing in the permeate at incremental area values. The calculation proceeded until a desired concentration of a specific component in the retentate or permeate was reached. At this point, the computer program generated the volumes and mole fractions of gases in the permeate and retentate.

The gas feed to be treated by the membrane process was assumed to have the composition stated as a "standard case" at the beginning of this section. However, because of the recycle of an unknown amount and composition of gas from the first recycle permeator (see Figure 9), the exact composition of the feed gas entering the first permeator would not be known. It would consist of a blend of the raw feed and the recycle feed. Therefore, an iteration procedure must be used for the first and second permeators in these calculations. The amount of the recycle and its composition was assumed. The carbon dioxide content of the recycle stream was set at 27 percent in all cases. This was the same level as the carbon dioxide content of the initial feed. A new feed composition was then calculated and the program run for the first two permeators. The feed composition was next calculated using the values for the recycle stream generated by the program. If each component content was within one percent of the feed levels in the previous iteration, then the iteration procedure was terminated. Otherwise, another feed composition was determined and the procedure repeated. Calculation of the mass balances for the other permeators was simpler because of the feed forward system employed in those subsequent permeators.

The costs of the process can be determined from the membrane area, the gas volume to be recompressed, and the loss of hydrogen and methane. The installed permeator cost was taken to be \$8.50 per square foot and membrane replacement as \$4.00 per square foot with a one-year service life.[23] Of course, it was impossible to predict an exact service life without field tests. Compressor installation cost was calculated from literature data.[24,25] The amortized investment was the same as for the other processes. Recoverable investment, or working capital, was taken to be three months of labor and utilities plus replacement of the membranes. Labor costs were set at \$0.16 MM per year. The cost of utilities was the same as for the other processes. The utilities for the membrane process consisted of electricity to power the compressors and cooling water for interstage cooling of the multistage compressors. The horsepower required for compression was calculated for an ideal gas mixture undergoing a six stage adiabatic compression from 14.7 psia to 1014.7 psia.[25,27] It was assumed that gas mixtures of these compositions would not depart greatly from ideality at these pressures although the individual gases do.[28]

A sample cost calculation is presented in Table 35 for the case where the CO_2/H_2 selectivity ratio (α) is 15, the carbon dioxide flux is 7.5 ft^3/ft^2-hr-100 psi and the hydrogen loss is 3.5 percent. This case, which represents the maximum flux obtained with methylcellulose membranes at the maximum theoretical separation rate at room temperature, led to a purification cost of 34¢/Mscf.

Table 35. Sample Calculation of the Economics of a Membrane Process, Mid-1976.

Membrane Case: CO_2/H_2 Selectivity, $\alpha = 15$
CO_2 flux = 7.5 ft^3/ft^2- hr-100 psi
hydrogen loss = 3.5%

<u>Investment - $ Millions</u>	
2 permeators	14.75
1 compressor	2.05
Fixed	16.08
Amortized	4.06
Recoverable	9.34
Total Investment	30.2
<u>Annual Costs - $ Millions</u>	
Investment	4.89
Operating Costs	
Utilities	
Cooling Water	1.01
Electricity	8.28
Total Utilities	9.38
Labor	0.16
Replacement of Membranes	6.95
Gas lost	8.35
Total Operating	24.84
Total Annual	29.73
Cost based on gas produced - ¢/Mscf	34.0

Several cases with various selectivities, CO_2 fluxes, and hydrogen losses were considered. Information from the cases studied was plotted and is shown in Figure 10. The inverse of the flux was chosen for the ordinate because flux was inversely proportional to the area which is directly proportional to cost. The cost is shown in ¢/Mscf without reporting the investment or operating costs separately. The straight line relationship between cost and the inverse of flux was indicative of the fact that a change in CO_2 flux caused a change only in the required membrane area, not a change in compression costs. The cost axis corresponded to infinite flux or no membrane area investment costs. On this axis the costs were wholly attributable to the selectivity rather than the CO_2 flux. At low selectivity the costs were high even at infinite flux. There were several groups of cost lines generated in this parametric economic analysis. Each group represented the cost effects of a specific selectivity. Each line within the particular group represented the cost of a membrane system having a particular CO_2/H_2 selectivity and a particular hydrogen loss. The hydrogen loss could be lowered by recovering hydrogen through additional permeators. The investment cost for addition permeators and compressors and the operating cost for additional compression eventually would become higher than the value of the recovered hydrogen. The operating cost would reach a minimum at a specific percentage of hydrogen lost for any particular CO_2 flux and selectivity. This is shown in Figure 11. Figure 11 also shows that the minimum cost occurred at lower degrees of hydrogen loss when the CO_2/H_2 selectivity was raised. All of the lines shown in Figure 10 were near the minimum cost for the particular CO_2/H_2 separation ratio.

In examining the data in Figure 10, it was apparent that membranes developed in this program were uneconomic. To achieve a treatment cost of 40¢/Mscf, a membrane with a selectivity of 10 had to exhibit a CO_2 flux in excess of 10 ft^3/ft^2-hr-100 psi. Similarly, membranes with a CO_2 flux of only 5 ft^3/ft^2-hr-100 psi were required to exhibit a selectivity of 15 (the theoretical maximum at room temperature).

Actually, the membrane process economics had to be better than this level (40¢/Mscf) for two reasons. First, additional sulfur cleanup costs would be required because of the H_2S residual. Data on the additional sulfur removal costs are presented in the next subsection. Second, a potential cost advantage must be shown by the membrane process to justify its development. The membrane process did not demonstrate a potential cost advantage in this application. However, as noted before, relatively cheaper membranes, releatively cheaper electrcity, less stringent sulfur requirements, or different compositions or pressures might make the membrane process cheaper than conventional processes and justify its development.

Discussion of Residual Sulfur Removal Economics

The various processes previously discussed can not consistently achieve the low sulfur levels required to prevent sulfur poisoning of the methanation catalyst. The Rectisol and Benfield HiPure processes can attain 1 ppm H_2S or less.[17,18] The Sulfinol process can attain 4 ppm H_2S in this application.[19]

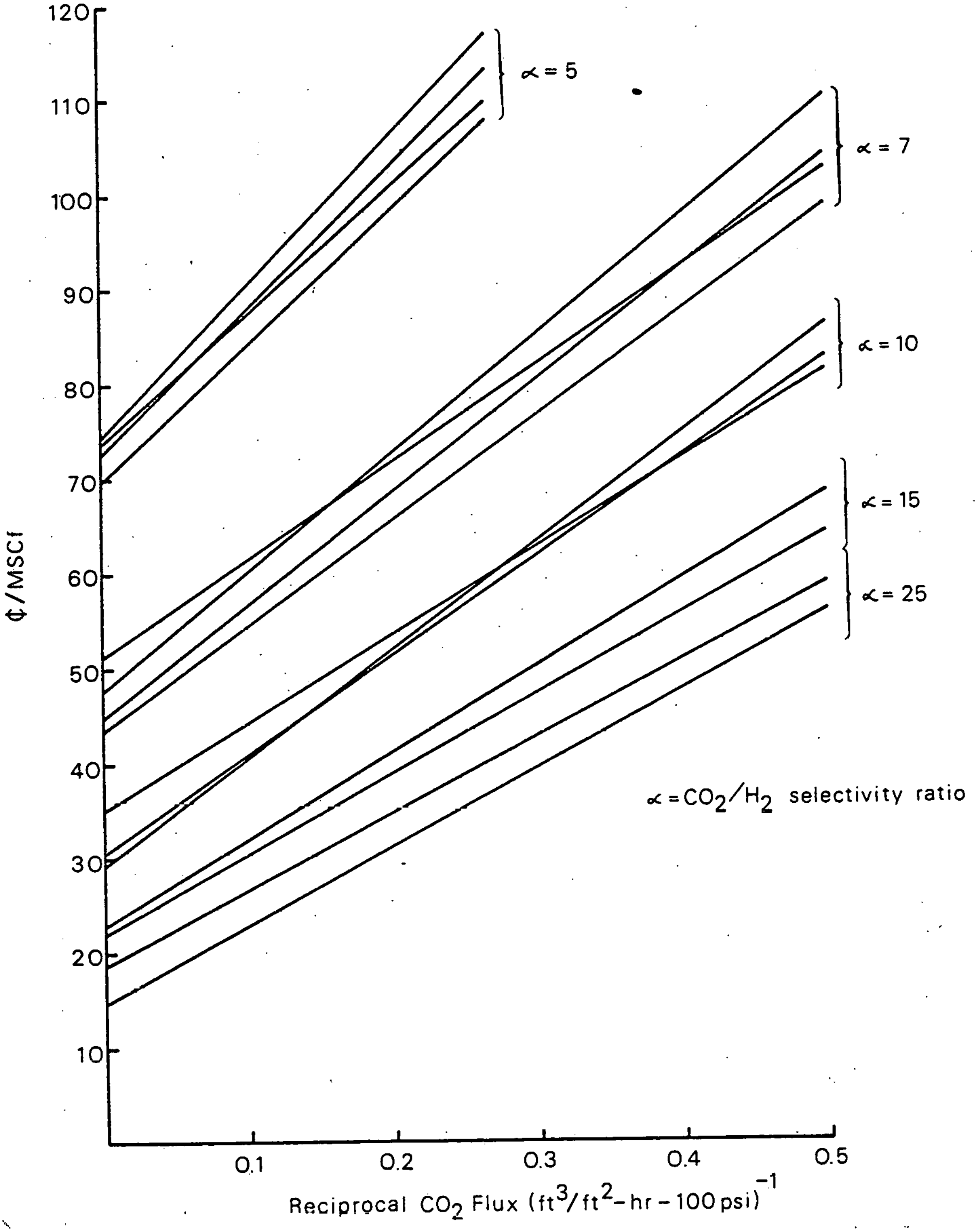

Figure 10. Mid-1976 Membrane Process Costs as a Function of Membrane Selectivity and Flux

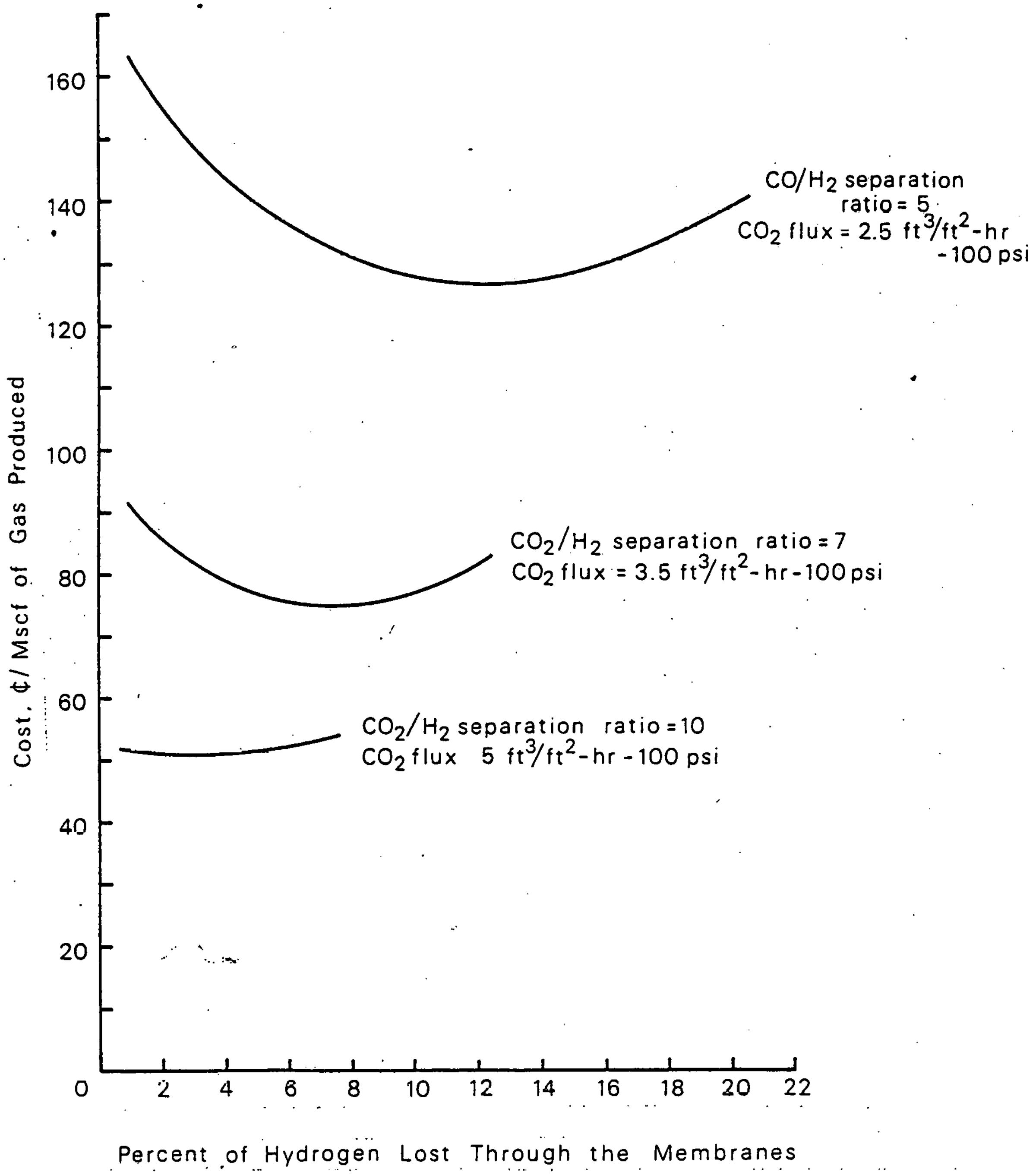

Figure 11. Mid-1976 Membrane Process Cost Minimums Related to Hydrogen Loss Through Permeators

The fluidized dolomite process should result in about 600 to 700 ppm residual H_2S content.[21] Our membrane calculations showed that 50 ppm H_2S or less could be attained whenever the residual CO_2 content was reduced to one to two percent by membrane processing. According to an industrial source, an H_2S concentration of 0.02 to 0.2 ppm was low enough to assure a lifetime of two to three years for the methanation catalyst. For this study we assumed that 0.1 ppm of H_2S was suitable for methanation. Absorption of residual H_2S such as by zinc oxide was required to attain this level.

The costs of treating gases containing 50 ppm, 4 ppm, and 1 ppm H_2S with zinc oxide are shown in Table 36. The costs for 600 to 700 ppm H_2S were not calculated but would be much higher than any of those shown in the table. The cost based on the amount of gas produced is about 1/3 cent per Mscf at the 1 ppm level and about 1/2 cent per Mscf at the 4 ppm level. These are insignificant additions to the costs of the scrubbing processes. The cost at the 50 ppm level (i.e., for membranes) is 3.34 cents per Mscf, a significant additional cost. In this case the fixed investment is $1.8 million, the total investment $3.1 million, the operating cost $2.3 million per year, and the total annual cost $2.9 million. Over 70 percent of the annual cost is for replacing the spent zinc oxide absorbent.

Discussion of Guard Chamber Economics

Because the methanation catalyst is very susceptible to poisoning by sulfur and is very expensive to replace, it must be protected from process upsets upstream. The simplest way to protect this catalyst has been through use of a "guard chamber" of zinc oxide which absorbs hydrogen sulfide. Costs were obtained for a pair of guard chambers, each capable of protecting against one percent H_2S for one day, and are shown in Table 37. The fixed investment was $5.1 million, the total investment, $5.8 million, and the operating cost, $0.36 million per year. The total annual cost was $1.3 million, equivalent to 1.5 cents per Mscf of gas produced. The investment cost accounted for almost 75 percent of the annual cost. In this calculation the cost of the replacement of the spent zinc oxide absorbent was not included. It was not known how often such an incident would occur, but it should be infrequent in a well-operated plant. However, replacing all the zinc oxide in one of the guard chambers would result in an operating cost of $1.2 million. If this happened only once a year the cost would be 1.4 cents per Mscf of gas produced.

Discussion of Claus Process Economics

There are other processes necessarily related to acid gas clean-up, such as sulfur removal and sulfur recovery. Of these processes the only one for which we have cost data is a liquid-phase Claus process for sulfur recovery. In this process, part of an H_2S stream is oxidized to SO_2. Then the H_2S and SO_2 are reacted to make sulfur and steam. In our standard case, about 700 long tons per day were recovered. The recovered sulfur may be sold, but we have not included this credit in our cost. We converted the published costs for

Table 36. Economics of Residual Sulfur Removal with Zinc Oxide, Mid-1976

	50 ppm H_2S	4 ppm H_2S	1 ppm H_2S
Investment - $ Millions			
Fixed	1.8	0.5	0.24
Amortized	0.725	0.121	0.0583
Recoverable	0.568	0.0715	0.0373
Total Investment	3.09	0.692	0.336
Annual Costs - $ Millions			
Investment	0.645	0.133	0.059
Operating Costs			
Makeys Absorbant	2.08	0.161	0.037
Maintenance	0.09	0.025	0.012
Labor	0.1	0.1	0.1
Total Operating	2.28	0.286	0.208
Total Investment	2.92	0.419	0.267
Cost based on gas produced - ¢/Mscf	3.34	0.48	0.31

Table 37. Economics of a Guard Chamber for Final Sulfur Removal, Mid-1976

Investment - $ Millions	
Vessels	2.75
Absorbant	2.39
Total Fixed Investment	5.14
Amortized	0.539
Recoverable	0.089
Total Investment	5.77

Annual Costs - $ Millions	
Investment	0.985
Operating Costs	
Utilities	0*
Maintenance	0.257
Labor	0.1
Total Operating	0.357
Total Annual	1.34
Cost based on gas produced, ¢/Mscf	1.53

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*Additional operating cost each time the zinc oxide in one of the two guard chambers has to be replaced is $1.2 million or 1.37¢/Mscf of gas produced.

a liquid-phase Claus process (under development by Consolidation Coal Company) to our own basis. The resulting investment and costs are in Table 38. These costs include clean-up of the Claus tail gas. The fixed investment was $11.4 million, the total investment, $13.4 million, and the operating cost, $1.94 million per year. The total annual cost was $4.24 million, equivalent to 4.84¢ per Mscf of gas produced. The charges on investment were $2.3 million per year, or 54 percent of the total annual charges. The costs of this process were therefore sensitive primarily to the interest rate and the availability of capital.[21]

Summary Comparison of Overall Gas Clean-Up Economics

Each of the acid gas clean-up processes considered in this report required additional sulfur clean-up, a guard chamber, and a Claus plant for recovering sulfur. These additional costs were calculated in the previous sections and were added to the base costs for acid gas removal from the raw SNG. The results are presented in Table 39. When the additional costs were added to the costs of the Rectisol, Benfield, Sulfinol, and fluidized dolomite processes the total costs ranged from 43 to 49¢/Mscf. For the membrane process the additional sulfur removal costs were about 3.3¢/Mscf to be added to the base costs for acid gas removal. The best membrane composition found during this program, one which exhibited a CO_2/H_2 selectivity of 13 at a CO_2 flux of 6 ft^3/ft^2-hr-100 psi, would entail a process cost of about 53¢/Mscf with these additions. This is about 7¢/Mscf more than for the average of the other processes.

No better membrane performance is predicted on the basis of the experiments performed during this project. Without a shift in several cost factors, membranes cannot be competitive in large scale acid gas removal from coal gasification streams. These cost factors whose shift could lead to an economical membrane process have been enumerated previously. The possibility that reduced energy availability could lead to such shifts should not be discounted but are not foreseen in the near future.

Table 38. Economics of Liquid Phase Claus Process (Consolidation Coal Company), Mid-1976

Investment - $ Millions	
Fixed	11.4
Amortized	1.48
Recoverable	0.485
Total Investment	13.36
Annual Costs - $ Millions	
Investment	2.30
Operating Costs	
Utilities	
Electricity	0.607
Cooling Water	0.428
Boiler Feed Quality Water	0.101
Total Utilities	1.14
Maintenance	0.57
Labor	0.23
Total Operating	1.94
Total Annual	4.24
Cost based on gas produced - ¢/Mscf	4.84

Table 39. Comparison of Overall Mid-1976 Costs for Several Acid Gas Clean-Up Processes

	Rectisol (3 trains)	Benfield (High Case)	Sulfinol	Dolomite	Membrane (α = 13, CO_2 flux = 6)
Main Process	39.8	42.3	36.3	c.a. 40.6	c.a. 43
Final S	0.3	0.3	0.5	>>0.5	3.3
Guard	1.5	1.5	1.5	1.5	1.5
Claus	4.8	4.8	4.8	4.8	4.8
TOTAL	46.4	48.9	43.1	>46.9	52.6

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APPENDIX A

Table A-1. List of Raw Materials and Suppliers

Table A-1. List of Raw Materials and Suppliers

1. Polymers

Raw Material	Trade Name	Supplier
Acrylamide-methylene bisacrylamide copolymer	---	synthesized
Acrylamide-vinyl acetate copolymer	---	synthesized
Acrylamide-vinyl pyrrolidone copolymer	---	synthesized
Aromatic amine resin	Epicure 8494	Celanese Resins
Carboxymethyl hydroxyethyl cellulose	CMHEC	Hercules, Incorporated
Cellulose	---	synthesized
Cellulose acetate	E 398-10 and E 360-60	Eastman Chemical Products Inc.
Cellulose triacetate	---	synthesized
Epiamine resin	XD 8278.1	The Dow Chemical Company
Ethyl cellulose	G-50	Hercules, Incorporated
Ethyl hydroxymethyl cellulose	EHEC-75H	Hercules, Incorporated
Hydroxypropyl methylcellulose	Methocel J5MS and F 50	The Dow Chemical Company
Maleic anhydride-methyl vinyl ether copolymer	Gantrez AN-119	GAF Corporation
Methyl cellulose (15 cps, 100 cps, 4000 cps)	---	Fisher Scientific Company
Methylcellulose	Methocel A15	The Dow Chemical Company

Table A-1. List of Raw Materials and Suppliers (continued)

1. Polymers (continued)

Raw Material	Trade Name	Supplier
Methylcellulose acetate	---	synthesized
Polyacrylamide	---	synthesized
Polyacrylic ester emulsion	Rhoplex AG33	Rohm and Haas Company
Polyacrylonitrile	---	synthesized
Polycarbonate	Lexan 112	General Electric Company
Polyethylenimine (PEI)	Tydex 12	The Dow Chemical Company
Polyethylene oxide	Carbowax 20M	Union Carbide Corp.
Poly(ethylene oxide)(ethylene terephthalate) block copolymer	---	synthesized
Polyethylene oxide polycarbonate block copolymer dialysis membrane	---	American Membrane Company
Polyethyl methacrylate	---	synthesized
Polysulfone	P-3500	Union Carbide Corp.
Polyvinyl acetate	Vinac B-100	Air Products and Chemicals, Inc.
Polyvinyl alcohol	Lemol 5-88	Borden Chemical Company
Polyvinyl formal	---	synthesized
Self-crosslinking vinyl polymer	Carboset 525	B. F. Goodrich Chemical Company

Table A-1. List of Raw Materials and Suppliers (continued)

1. Polymers (continued)

Raw Materials	Trade Name	Supplier
Silicone adhesive	RTV-108	General Electric Co.
Sulfonated polysulfone	---	synthesized
Vinyl pyrrolidone-vinyl acetate copolymer	PVP-VA S-630	GAF Corporation

2. Support Films

Raw Materials	Trade Name	Supplier
Microporous polypropylene support film	Celgard 2400	Celanese
Polyacrylonitrile support film	Acropor AN 450	Gelman Instrument Company
Polysulfone support on sailcloth	---	Envirogenics, Inc.
Polysulfone support on sailcloth	---	Osmonics, Inc.
Polysulfone support on sailcloth	---	UOP
Polysulfone support on non-woven fabric	---	Osmonics, Inc.
Ultrafiltration membrane	---	Abcor

Table A-1. List of Raw Materials and Suppliers (continued)

3. Adhesion Promotors and Wetting Agents

Raw Materials	Trade Name	Supplier
Beta 3,4 (epoxycyclohexyl) ethyltrimethoxysilane	A-186 silane	Union Carbide Corp.
Gamma aminopropyltrimethoxysilane	A-1100 silane	Union Carbide Corp.
Silicone gum-rubber with vinyl groups curable by peroxides	W-984 silicone	Union Carbide Corp.
Silicone pressure sensitive adhesive	282 Adhesive	Dow Corning Corp.

APPENDIX B

Table B-1. NGASLAM Computer Program
Table B-2. MEMPER Computer Program

Table B-1. NGASLAM Computer Program

NGASLAM calculates the membrane areas required to perform specified separations.

```
NAM !    LAM
100 DIM Y(10),X(10),W(10),Z(10,4),Q(10),A(10),B(10),C(10),N(4),D(10)
110 PRINT 'INPUT ALL PARAMETERS IN CONSISTENT UNITS.'
120 PRINT
130 PRINT !INPUT NUMBER OF GAS CONSTITUENTS (LIMIT = 10)';
140 INPUT N
150 PRINT
160 PRINT 'INPUT HIGH PRESSURE, LOW PRESSURE IN ABSOLUTE UNITS';
170 INPUT P1,P2
180 PRINT
190 PRINT 'INPUT INITIAL MOLE OR VOLUME FRACTION AND PERMEABILITY FOR EACH CONSTITUENT.'
200 PRINT
210 S=0
220 FOR I=1 TO N
230 PRINT 'CONSTITUENT ';I;'    ';
240 INPUT Y(I),Q(I)
250 S=S+Y(I)
260 NEXT I
270 IF S<.99999 THEN 300
280 IF S>1.00001 THEN 300
290 GO TO 320
300 PRINT 'SUM OF MOLE OR VOLUME FRACTIONS = ';S;' ,WHICH SHOULD BE 1. RE-ENTER SETS OF VALUES.'
310 GO TO 200
320 PRINT
330 PRINT 'USE PROGRAM INTEGRATION INCREMENT (Y OR N)';
340 INPUT A$
350 IF A$≠'Y' THEN 390
360 D=1E-4
370 PRINT 'PROGRAM AREA INCREMENT,1E-4, WILL BE USED.'
380 GO TO 410
390 PRINT 'INPUT INTEGRATION INCREMENT';
400 INPUT D
410 PRINT
420 PRINT 'INPUT HOW OFTEN TO PRINT RESULTS';
430 INPUT M
440 FOR I=1 TO N
450 C(I)=P1*Q(I)
460 B(I)=P2*Q(I)
470 A(I)=C(I)-B(I)
480 NEXT I
490 A=0               !AREA
500 N0=1              !OLD VALUE OF DIMENSIONLESS FLOW RATE ABOVE MEMBRANE
510 FOR I=1 TO N
520 W(I)=Y(I)
530 NEXT I
540 :   DN/DA     AREA       N         1
550 :##.####!!!! #.####!!!! #.####!!!!
560 : #.####!!!!
```

```
570                 ""
580 .                          6B
590 PRI
600 PRINT
610 PRINT USING 540;
620 FOR I=2 TO N
630 PRINT USING 570,I;
640 NEXT I
650 PRINT
660 FOR K1=1 TO M
670 G0=0
680 FOR I=1 TO N
690 D(I)=C(I)*W(I)
700 G0=G0-D(I)        !INITIAL GUESS FOR G
710 NEXT I
720 GOSUB 1280        !SUBROUTINE TO FIND ROOT G
730 N(1)=G1*D
740 FOR I=1 TO N
750 Z(I,1)=(A(I)+G1)*G1*W(I)*D/(N0*(B(I)-G1))
760 NEXT I
770 FOR L=2 TO 4
780 G0=0
790 IF L=4 THEN 850
800 FOR I=1 TO N
810 D(I)=C(I)*(W(I)+.5*Z(I,L-1))
820 G0=G0-D(I)
830 NEXT I
840 GO TO 890
850 FOR I=1 TO N
860 D(I)=C(I)*(W(I)+Z(I,L-1))
870 G0=G0-D(I)
880 NEXT I
890 GOSUB 1280
900 N(L)=G1*D
910 IF L=4 THEN 960
920 FOR I=1 TO N
930 Z(I,L)=(A(I)+G1)*G1*(W(I)+.5*Z(I,L-1))*D/((B(I)-G1)*(N0+.5*N(L-1)))
940 NEXT I
950 GO TO 990
960 FOR I=1 TO N
970 Z(I,L)=(A(I)+G1)*G1*(W(I)+Z(I,L-1))*D/((B(I)-G1)*(N0+N(L-1)))
980 NEXT I
990 NEXT L
1000 N0=N0+(N(1)+2*N(2)+2*N(3)+N(4))/6
1010 FOR I=1 TO N
1020 W(I)=W(I)+(Z(I,1)+2*Z(I,2)+2*Z(I,3)+Z(I,4))/6
1030 NEXT I
1040 A=A+D
1050 NEXT K1
1060 N1=1-N0          !TOTAL FLOW BELOW MEMBRANE
```

```
10   [illegible]     O N
1080 X [illegible](Y(I)-N0*W(I))/N1
1090 N [illegible] I
1100 G0=0
1110 FOR I=1 TO N
1120 D(I)=C(I)*W(I)
1130 G0=G0-D(I)
1140 NEXT I
1150 GOSUB 1280      !RETURNS CURRENT VALUE CF DN/DA
1160 PRINT USING 550,G1,A,N0;
1170 FOR I=1 TO N
1180 PRINT USING 560,W(I);
1190 NEXT I
1200 PRINT
1210 PRINT USING 580,0;
1220 PRINT USING 560,N1;
1230 FOR I=1 TO N
1240 PRINT USING 560,X(I);
1250 NEXT I
1260 PRINT
1270 GO TO 660
1280 S1=-1            !SUM TO FIND F
1290 S2=0             !SUM TO FIND F'
1300 FOR I=1 TO N
1310 R=B(I)-G0
1320 S1=S1+D(I)/R
1330 S2=S2+D(I)/(R*R)
1340 NEXT I
1350 G1=G0-S1/S2
1360 IF ABS(G1/G0-1)<.001 THEN 1390
1370 G0=G1
1380 GO TO 1280
1390 RETURN           !G1=FINAL ROOT
1400 END
```

Table B-2. MEMPER Computer Program

MEMPER calculates the permeabilities (proportional to fluxes for each component in a multigas test).

```
CLE
ENT BAS
NAM MEMPER
100 DIM A(20),A$(20),B(20,3),C(20,3),B$(20),D(20,41)
110 M1=8             !NUMBER OF CONSTITUENTS THAT HAVE BEEN CODED BELOW
120 DATA 'HYDROGEN',2.016,'CARBON DIOXIDE',44.01,'HYDROGEN SULFIDE',34.08,'METHANE',16.04,'CARBON MONOXIDE',28.01
130 DATA 'WATER VAPOR',18.016,'METHYL MERCAPTAN',48.1,'NITROGEN',28.02
140 FOR I=1 TO M1
150 READ A$(I),A(I)
160 NEXT I
170 DATA 7
180 DATA 2,1,.6667,2,.3333
190 DATA 4,1,.5067,2,.2857,3,.029,4,.1786
200 DATA 4,1,.565,2,.2516,3,.026,4,.1574
210 DATA 4,1,.526,2,.2713,3,.0291,4,.1736
220 DATA 4,1,.522,2,.274,3,.0284,4,.1756
230 DATA 4,1,.5157,2,.2797,3,.0282,4,.1764
240 DATA 5,1,.4603,2,.2302,3,.0256,4,.1535,5,.1304
250 READ N1
260 FOR I=1 TO N1
270 READ D(I,1)
280 FOR J=1 TO D(I,1)
290 READ D(I,2*J),D(I,2*J+1)
300 NEXT J
310 NEXT I
320 PRINT 'DO YOU WISH TO USE ONE OF THE STANDARD COMPOSITIONS ABOVE THE MEMBRANE (Y OR N)';
330 INPUT Z$
340 IF Z$≠'Y' THEN 620
350 PRINT
360 PRINT 'INPUT THE STANDARD COMPOSITION NUMBER CODE';
370 INPUT C1
380 N=D(C1,1)
390 FOR I=1 TO N
400 C(I,1),B(I,1)=D(C1,2*I)    !CONSTITUENT CODE
410 C(I,2)=D(C1,2*I+1)         !MOLE FRACTION ABOVE MEMB.
420 B$(I)=A$(C(I,1))
430 NEXT I
440 PRINT 'FOR EACH CONSTITUENT CODE LISTED BELOW, INPUT THE MASS FRACTION BELOW THE MEMBRANE.'
450 PRINT
460 U1=0
470 FOR I=1 TO N
480 PRINT B(I,1);
490 INPUT B(I,3)
500 U1=U1+B(I,3)
510 NEXT I
520 IF U1=1 THEN 540
530 PRINT 'SUM OF MASS FRACTIONS ≠ 1.'
```

```
54[illegible]
550 FO [illegible] TO N
560 S=S+B(I,3)/A(B(I,1))
570 NEXT I
580 FOR I=1 TO N
590 C(I,3)=B(I,3)/(A(B(I,1))*S)
600 NEXT I
610 GO TO 900
620 PRINT 'HOW MANY CONSTITLENT GASES IN YOUR DATA';
630 INPUT N
640 PRINT
650 PRINT 'AFTER EACH QUESTION MARK, INPUT GAS CONSTITUENT NUMBER, MASS FRACTION ABOVE MEMBRANE, AND MASS FRACTION BELOW MEMBRANE!
660 PRINT
670 PRINT 'FOR EXAMPLE ----- 3,.602,.475'
680 PRINT
690 U1,U2=0
700 S1,S2=0
710 FOR I=1 TO N
720 INPUT B(I,1),B(I,2),B(I,3)
730 U1=U1+B(I,2)
740 U2=U2+B(I,3)
750 C(I,1)=B(I,1)
760 B=B(I,1)
770 S1=S1+B(I,2)/A(B)
780 S2=S2+B(I,3)/A(B)
790 NEXT I
800 IF U1≠1 THEN 830
810 IF U2≠1 THEN 830
820 GO TO 840
830 PRINT 'SUM OF MASS FRACTIONS ≠ 1.'
840 FOR I=1 TO N
850 B$(I)=A$(C(I,1))
860 B=A(B(I,1))
870 C(I,2)=B(I,2)/(B*S1)
880 C(I,3)=B(I,3)/(B*S2)
890 NEXT I
900 PRINT
910 PRINT 'DO YOU WISH TO USE THE STANDARD MEMBRANE THICKNESS - AREA COMBINATION (Y OR N)';
920 INPUT Y$
930 IF Y$≠'Y' THEN 960
940 K1=5.73842E-6
950 GO TO 1000
960 PRINT
970 PRINT 'INPUT MEMBRANE THICKNESS AND AREA IN CM. AND SQUARE CM.';
980 INPUT T,A
990 K1=T/(60*A)
1000 PRINT
1010 PRINT 'DO YOU WISH TO USE THE STANDARD HIGH AND LOW PRESSURES (Y OR N)';
```

```
1020 INPUT X$
1030 IF X$≠'Y' THEN 1070
1040 P1=1110        !HIGH PRESS.=200 PSIG = 1110 CM.HG.ABS.
1050 P2=74                    !LOW PRESS.=74 CM.HG.ABS.
1060 GO TO 1110
1070 PRINT
1080 PRINT 'INPUT HIGH PRESSURE (PSIG) AND LOW PRESSURE (CM.HG.ABS.)';
1090 INPUT P0,P2
1100 P1=5.17144*(P0+14.7)
1110 PRINT
1120 PRINT 'INPUT TOTAL FLOW THROUGH MEMBRANE (CC/MIN)';
1130 INPUT Q
1140 PRINT
1150 PRINT
1160 PRINT 'SUMMARY OF CALCULATIONS'
1170 PRINT
1180 PRINT 'GAS COMPOSITION: ';
1190 IF Z$='Y' THEN 1220
1200 PRINT 'NON-STANDARD'
1210 GO TO 1230
1220 PRINT 'STANDARD COMPOSITION NUMBER ';C1
1230 PRINT 'MEMBRANE PARAMETERS: ';
1240 IF Y$='Y' THEN 1280
1250 PRINT USING 1260,T,A
1260 :THICKNESS = #.#### CM.   AREA = ###.### SQUARE CM.
1270 GO TO 1290
1280 PRINT 'STANDARD VALUES'
1290 PRINT 'PRESSURE VALUES: ';
1300 IF X$='Y' THEN 1340
1310 PRINT USING 1320,P0,P2
1320 :HIGH PRESSURE = ###.# PSIG    LOW PRESSURE = ###.# CM.HG.ABS.
1330 GO TO 1350
1340 PRINT 'STANDARD'
1350 PRINT USING 1360,Q
1360 :TOTAL FLOW RATE THRCUGH MEMBRANE = ###.### CC/MIN.
1370 PRINT
1380 :-------------------------------------------------------
1390 :|                   |             |      BARRER       |
1400 :| GAS CONSTITUENT   |MOLE FRACTION|   PERMEABILITY    |
1410 :|                   |-------------|   (CM**3)(CM)/    |
1420 :|                   |ABOVE |BELOW |(CM**2)(SEC)(CM.HG)|
1430 :|###################|#.####|#.####|   ##.####!!!!     |
1440 PRINT USING 1380
1450 PRINT USING 1390
1460 PRINT USING 1400
1470 PRINT USING 1410
1480 PRINT USING 1420
1490 PRINT USING 1380
1500 FOR I=1 TO N
1510 PRINT USING 1430,B$(I),C(I,2),C(I,3),K1*Q*C(I,3)/(P1*C(I,2)-P2*C(I,3))
```

```
1520 NEXT I
1530 PRINT USING 1380
1540 PRINT
1550 PRINT
1560 PRINT
1570 PRINT
1580 PRINT 'DO YOU WISH TO COMPUTE MORE CASES (Y OR N)';
1590 INPUT C$
1600 IF C$='Y' THEN 320
1610 END
```