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Review of Membrane Technology for Methane Recovery From Mining Operations

By F. Garcia and J. Cervik

**UNITED STATES DEPARTMENT OF THE INTERIOR
Donald Paul Hodel, Secretary**

**BUREAU OF MINES
David S. Brown, Acting Director**

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm	centimeter	lb/in ²	pound (force) per square inch
ft	foot		
ft ³	cubic foot	lb/in ² (ga)	pound (force) per square inch, gauge
gal	gallon	m	meter
hp	horsepower	m ³	cubic meter
in	inch	pct	percent
kPa	kilopascal	st	short ton
kW	kilowatt	vol pct	volume percent
lb	pound		

REVIEW OF MEMBRANE TECHNOLOGY FOR METHANE RECOVERY FROM MINING OPERATIONS

By F. Garcia¹ and J. Cervik²

ABSTRACT

Recent advances in the commercial separation of gases using membranes have renewed interest in the possibility of applying this technology to the recovery of methane (CH_4) from mining operations. This Bureau of Mines report briefly reviews the history of the development of membranes for gas separation, the theory of how they work, and their application to the separation of methane from air and associated problems.

However, methane-air mixtures are difficult to separate with membranes because the pertinent gas couples, $\text{O}_2\text{-N}_2$, $\text{O}_2\text{-CH}_4$, and $\text{N}_2\text{-CH}_4$, have poor separation characteristics, as indicated by their separation factors of about 3 or less. Even if these separation factors were substantially higher, there is doubt that methane could be recovered economically from the low concentrations in mine ventilation exhaust (2 vol pct or less). The exhaust pressures are not sufficient for adequate separation. The power cost of compressing these mixtures would far exceed the value of the methane recovered.

New discoveries could make separation of gob hole methane-air mixtures practical. These mixtures have much higher concentrations of methane (from 30 to 100 vol pct); however, for safety reasons, treatment would be limited to gob gas with 60 vol pct CH_4 or more.

¹Mining engineer.

²Supervisory geophysicist.

Pittsburgh Research Center, Bureau of Mines, Pittsburgh, PA.

INTRODUCTION

A Bureau of Mines study showed that in 1985 coal mines in the United States emitted 304 million ft^3 (8.6 million m^3) of methane daily (1).³ This reflects an increase of about 48 million ft^3 (1.4 million m^3) since 1980 (2). Factors contributing to this increase were the opening of new mines in deeper and gassier coal beds in the last ten years and these mines are now larger mines.

Ventilation is the primary method of controlling methane in coal mines. At an active coal face, the methane must be diluted with air to 1 vol pct CH_4 or less

for safety reasons. In return airways and bleeders, the maximum allowable methane concentration is 2 vol pct. The methane in gas vented from coal mines cannot be recovered economically with present technology such as distillation, absorption, and adsorption (3).

Cryogenic distillation has always been the system of choice for large-scale separation of gases as well as liquids (4). However, advances in membrane technology in the past 6 yr have spurred interest in and wide industrial use of membranes for gas separation.

HISTORY OF MEMBRANE TECHNOLOGY

A simple approach to separating a gas mixture is to construct a barrier that permits molecules of one kind to pass through it while excluding others. Such a barrier in the form of a membrane was first reported in 1831 (5). Thirty-five years later, the mechanism of permeation through a membrane was discussed and demonstrated by using a rubber membrane to separate a gas mixture.

Polymer membranes were introduced in the late 1940's. These were composite membranes that consisted of a very porous but inert substrate covered by a polymer layer that separated components. Certain uses of these membranes are well established, and many improvements in the performance of these membranes have been achieved (6). For example, large-scale water-desalination plants can process more than 600 million gal (2.3 million m^3) of water daily; the dairy industry uses membrane technology to process whey proteins; and hemodialyses, a standard treatment for patients with kidney failure, depends upon membrane technology.

The possibility of using membranes for industrial gas separation became evident in the 1950's with the development of new polymeric materials. Many industrial gas separation processes were examined to determine if the use of membranes could

be applied to them. These processes included separation of O_2 from air, He from natural gas, H_2 from coal-hydrogenation tail gas and refinery gas, NH_4 from mixtures containing N_2 and H_2 , and CO_2 from various gas mixtures. The use of membranes in these industrial processes was limited severely by low permeation rates through the membrane and the poor membrane durability under operational conditions.

A major breakthrough in membrane technology occurred in 1960 with the development of asymmetric membranes (7). These membranes are porous throughout, but have a thin, relatively dense skin near one surface, which generally accounts for a very small fraction (0.1 to 1 pct) of the total membrane thickness (4). These membranes have proportionally higher permeation rates than the dense membranes of equivalent thickness because the effective separating layer (the dense skin) is so thin. However, they contain pores that are substantially larger than gas molecules, and as a result, they make poor gas separators.

In the mid-1970's, a new process developed by Monsanto Co., St. Louis, MO, overcame the problem of surface porosity in asymmetric membranes by applying a high-permeability coating to the porous membrane. The coating plugged surface pores and also served to protect the substrate from damage due to abrasion and normal handling (7). Because of the

³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

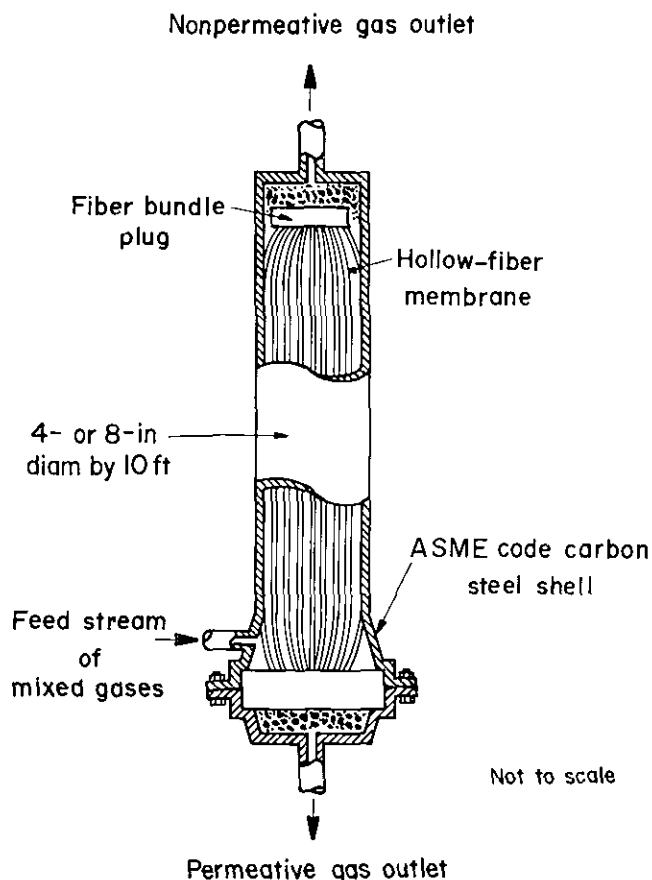


FIGURE 1.—Hollow-fiber membrane.

coating, the gas-separating layer can be made thin without concern regarding pore problems and consequently, gas flow rates through the substrate are 1,000 to 10,000 times faster than through other types of membranes.

The Monsanto membrane⁴ can be manufactured in flat sheets or as a hollow-fiber membrane (8). The two membrane types have different configurations. Hollow-fiber membranes are slender, spun

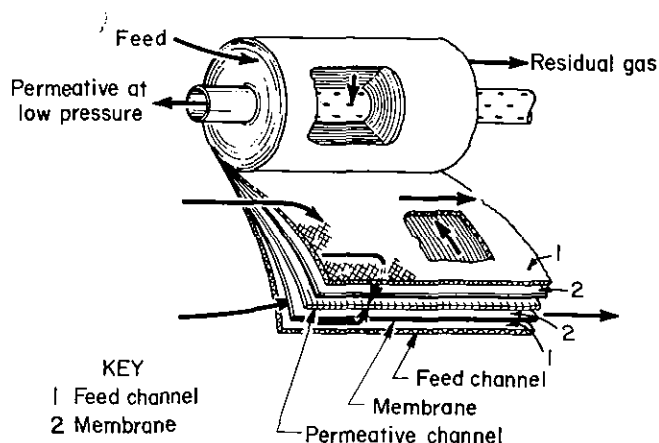


FIGURE 2.—Spiral-wound membrane.

filaments several hundred microns in diameter. Typically, they are packaged in parallel in a 4- or 8-in-diam (10.2- or 20.3-cm) steel tube (module) into which the gas mixture is forced. The gas to be separated permeates from the outside to the inside of the hollow fibers (or vice versa) and is collected at one end of the tube (fig. 1). To obtain a spiral-wound configuration, several flat sheets are separated by spacers to create a turbulent flow path for the feed gas, and then rolled up on a central tube and inserted into a steel shell (module) (fig. 2). Both hollow-fiber and spiral-wound modules are arranged into various interconnected banks to constitute a separation system.

Monsanto-type members are used commercially for the separation of H_2 and He from gases such as N_2 , CO, and CH_4 (4). Potential applications for these membranes include H_2 recovery from purge gases in ammonia synthesis and the recovery and recycling of CO_2 in enhanced oil recovery processes.

GAS TRANSPORT THROUGH MEMBRANES

Gas transport through a membrane is controlled by Fick's law of diffusion and Henry's law relating solubility of a gas in the polymeric membrane (4, 9). By Fick's law, diffusion through the membrane is

$$Q = \frac{D_a A \Delta C_a}{L}, \quad (1)$$

where Q = flow of component a through membrane,

D_a = diffusion coefficient for component a,

⁴Reference to specific products does not imply endorsement by the Bureau of Mines.

ΔC_a = concentration difference
across the membrane,

A = membrane surface area,

and L = membrane thickness.

Henry's law relates the concentration of gas a to the partial pressure of gas a in contact with the polymer:

$$C_a = S_a P_a, \quad (2)$$

where S_a = solubility constant

and P_a = partial pressure in contact
with membrane.

Substituting equation 2 into equation 1 yields

$$Q = \frac{K_a A \Delta P_a}{L}, \quad (3)$$

where $K_a = S_a D_a$ = permeability
coefficient.

An equation of this form can be written for each component in the gas stream. Equation 3 shows that where the partial pressure differentials for two gases in a mixture are the same, the ratio of the flow rates of each gas through the membrane may be expressed as

$$\frac{Q_a}{Q_b} = \frac{K_a}{K_b} = \alpha, \quad (4)$$

where α = selectivity or separation
factor.

The separation factor indicates the ability of the polymer to separate two gases in a given mixture.

Equation 3 shows that high gas flows through a membrane can be obtained by increasing the permeation coefficient (K), or increasing the surface area of the membrane (A), or increasing gas pressure (P). The problems associated with the control of the physical and separation properties (K) of polymers can be almost as great as those associated with making working membranes (4). Consequently, commercial membrane separation systems are based on available polymers developed

for other applications. Increasing the surface area of a membrane increases the size and cost of the system and at some point, which is specific for each application, use of additional surface area makes the system uneconomical. Gas flow through a membrane requires a driving force; this force is represented in equation 3 by the partial pressure differential across the membrane (ΔP_a). Gas flow through the membrane can be increased by increasing gas pressure. However, compression consumes energy; and the increased cost of pressure vessels, compressors, and energy associated with compression makes this approach unattractive. In addition, higher operating pressures require a membrane of much greater strength. Thus, practical and economic problems limit the degree to which the permeation coefficient, membrane surface area, and gas pressure can be changed.

Equation 3 shows that gas flow rates through a membrane are inversely proportional to the thickness (L) of the membrane. Thus, the development of thinner polymer membranes made possible the production of high-gas-flow systems that satisfy the demands of the commercial gas separating industry. For example, the overall thickness of the Monsanto membrane ranges from 1 by 10^{-3} to 10 by 10^{-3} in (2.5 by 10^{-3} to 25 by 10^{-3} cm). Its dense skin, which actually accomplishes the gas separation, is 0.004 by 10^{-3} to 0.04 by 10^{-3} in (0.01 by 10^{-3} to 0.1 by 10^{-3} cm) thick (4).

The selectivity or separation factor (α in equation 4) should be at least 20 and often must be more than 40 for the gases to be separated (4). The separation factors for various gas couples follow:

H ₂ O (vapor)-CH ₄	200-400
H ₂ -CH ₄	40-55
CO ₂ -CH ₄	20-30
H ₂ S-C ₃ H ₈	75-110
He-CH ₄	60-85
O ₂ -N ₂	4-5

The O₂-N₂ separation factor is of an order of magnitude less than the separation factors of the other gas couples because of the small differences between

O₂ and N₂ molecular size and solubility (10). This low separation factor makes O₂ enrichment difficult to accomplish.

POSSIBILITIES FOR APPLYING MEMBRANE TECHNOLOGY TO MINING

Methane is exhausted from coal mines through the ventilation system and through surface gob holes. In some mines, long horizontal holes are drilled into the coalbed to drain methane. These holes are connected to an underground pipeline that transports the gas to the surface. Because the methane content of the drained gas is 90 vol pct or greater, it usually requires no remedial treatment and can be compressed and pumped into a commercial gas transmission pipeline. However, the gas exhausted through the ventilation system and produced from gob requires remedial treatment before it can be pumped into commercial pipelines.

The main gas components of a CH₄-air mixture are O₂, N₂, and CH₄. The following tabulation gives the permeation rates of these gases at 750 lb/in² (5,170 kPa), in standard cubic feet per hour per square foot times 100 lb/in²:

CH ₄	0.18
N ₂	0.16
O ₂	0.59

The permeation rates for N₂ and CH₄ are practically the same, while the rate for O₂ is almost three times greater than either CH₄ or N₂ (11). Consequently, the use of membranes to upgrade coal mine exhaust ventilation systems does not appear to be feasible with existing membrane systems. Even if a membrane system existed that would separate the methane from the exhaust ventilation gas with 100 vol pct efficiency, only 2 ft³ (0.06 m³) of methane at most would be obtained for every 100 ft³ (2.8 m³) of exhaust gas treated. Because membrane systems operate at pressures of 2,000 lb/in² (13,790 kPa) or more (4), the cost of energy required to sufficiently compress the exhaust gas far exceeds the value of the

CH₄ recovered. For example, if the exhaust gas is compressed to 2,000 lb/in², and 1 million ft³ (0.028 million m³) of gas were treated daily, a 700-hp (522 kW) compressor would be required. Electrical power to operate the compressor would cost about \$525 daily, while the value of the recovered methane would be only about \$130 based on a sale price of \$6.50 per 1,000 ft³ (\$6.50 per 28.8 m³), a price that is higher than you can now get.

Gob gas is generally mixed with mine air, and its composition varies from nearly 100 vol pct CH₄ when production first starts to 30 vol pct over a period of months. Because the separation factors for the gas couples in the mixture are less than about 3, membrane technology does not appear applicable to upgrade gob gas to a saleable product. There are safety factors to consider when compressing gob gas. Methane-air mixtures are explosive in the range from 5 to 15 vol pct CH₄ at atmospheric conditions. Methane is almost always the major constituent of natural gas. Consequently, methane and natural gas have similar limits of flammability (table 1). At pressures of 2,000 lb/in² the lower limit of flammability decreases to 3.60 vol pct and the upper limit increases to 59.0 vol pct. Thus, if appropriate

TABLE 1. - Flammability limits of natural gas-air mixtures

Pressure, lb/in ² (ga)	Limits, vol pct natural gas	
	Lower	Upper
0 (atmospheric).....	4.50	14.20
500.....	4.45	44.2
1,000.....	4.00	52.9
2,000.....	3.60	59.0
3,000.....	3.15	^e 60.0

^e Estimated.

Source: Jones (12, p. 7).

membrane technology were available, only gob gas that contained more than 60 vol pct CH_4 could be treated. The remainder would have to be vented.

The gases N_2 , O_2 , and CH_4 tend to have low permeabilities in most polymers and are therefore difficult to separate. New

discoveries will be needed to make such separations practical with membranes. Many new developments in both membranes and the process design of new applications are expected in the next several years (4).

CONCLUSIONS

The present state of membrane technology precludes the use of membranes for separation of methane from exhaust ventilation or gob gas.

Because methane concentration in exhaust ventilation is 2 vol pct or less, it is doubtful that this methane could be recovered economically even if membrane technology were available. The power cost of gas compression far exceeds the

value of the methane that could be recovered. For gob gas, treatment would be limited to methane concentrations of 60 vol pct or more because of the explosive nature of compressed methane-air mixtures.

Membrane technology for gas separation is still developing. New membranes yet to be developed could make upgrading of gob gas feasible.

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