

HIGH PERFORMANCE CONTAMINANT RESISTANT MEMBRANES MINIMIZE PRETREATMENT AND IMPROVE CO₂ REMOVAL ECONOMICS

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ABSTRACT

For most of the 20 years in which gas separation membranes have been commercially available, their application in natural gas processing has been limited primarily to carbon dioxide (CO₂) removal. Traditional membranes are susceptible to common contaminants found in wellhead natural gas and require extensive pretreatment. This limits the potential uses of membranes, especially for applications where unattended operation is required or where space and weight restrictions are significant.

The recent development and commercial application of membranes based on Teflon chemistry promises significantly reduced pretreatment requirements for CO₂ removal applications. Efficient packaging, ease of installation and an innovative process design will extend the reach of membranes to an even wider range of CO₂ removal applications. The combination of lower installed and operating costs, higher total Btu recovery, and ease in moving the systems from one field location to another will make the more widespread use of membrane units possible, resulting in increased exploitation of currently shut-in natural gas production.

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Introduction

The first membrane systems for CO₂ removal were installed in the early 1980s. The use of membranes in this area has steadily grown, especially in the area of bulk removal of CO₂ from natural gas. Membrane units have now been deployed in CO₂ processing of streams as large as 300-500 MMSCFD of gas. While use of membranes has expanded significantly, the need for multi-step pre-treatment of the incoming feed to protect the membranes has limited their more widespread use.

In recent years, significant improvements in the way membranes are manufactured have resulted in advances that promise to mitigate these issues. One breakthrough is the commercialization of composite membrane structures. Each layer of the composite can be individually tailored to achieve optimal properties.

The use of these new membranes and processes incorporating them has addressed a key concern of the industry—membrane stability—and has reduced the need for significant pretreatment to protect membranes from plugging, fouling, and failing chemically or mechanically. Membrane Technology and Research, Inc. (MTR) and ABB Lummus Global have signed an exclusive agreement for the use of these membranes in natural gas processing, especially in the area of acid gas separation.

Membrane Background

Traditional membranes used for CO₂ removal are made from a single polymer, such as cellulose acetate, cellulose triacetate or polyimide. These membranes, known as asymmetric membranes, are cast in such a way as to form a thin, dense skin on a sponge-like porous substructure. The underlying porous layer provides mechanical strength; the thin skin layer is responsible for the separation properties. Both these layers are made of the same polymeric material. Polymers that exhibit good CO₂/CH₄ separation performance (selectivity and flux) may not be ideally suited for providing mechanical support and long-term chemical stability. Therefore, a compromise has to be made, usually resulting in a membrane that is either a very good separation membrane or sufficiently robust, but not both.

Better membranes can be made if the performance and strength properties are uncoupled. The technology to uncouple these two intrinsic membrane requirements has

now been developed and perfected, and MTR is now developing a series of them specifically for the natural gas market. The cross-section of one of these membranes is shown in Figure 1. The membrane consists of three layers: a nonwoven fabric that serves as the membrane substrate (the support web); a tough, durable, solvent-resistant microporous layer that provides mechanical support without mass transfer resistance; and a nonporous, defect-free selective layer that performs the separation.

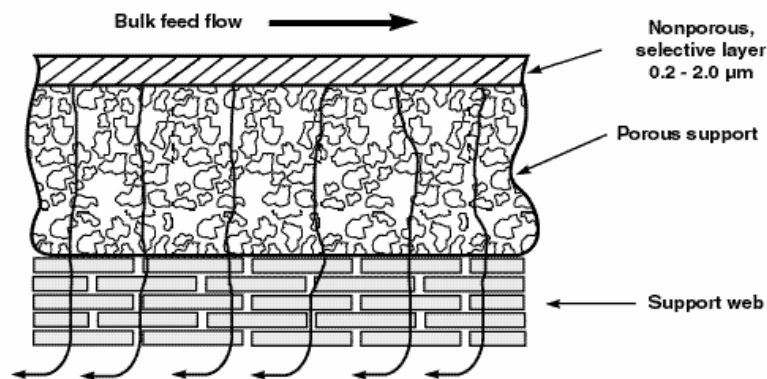


Figure 1. Cross-section of an MTR composite membrane.

This configuration allows each of the layers to be independently chosen to optimize their function: the selective layer for high flux and selectivity, and the support layers for mechanical and chemical stability that will not influence the separation. Specific selective layers may be chosen for specific separations, opening up exciting new applications, such as separation of heavy hydrocarbons from light hydrocarbons and nitrogen, separation of CO₂ and H₂S from methane, and dehydration.

Technology Status – Current And Future

Until recently, the types of membrane used for CO₂ separation could be broadly classified into two categories: cellulosic membranes (cellulose acetate and cellulose triacetate or blends thereof) and polyimide membranes (of various structures – some proprietary). Virtually all these types of membranes are asymmetric membranes; that is, the polymer used to make the selective layer (in which the CO₂ and CH₄ are separated) is the same material as the strength-providing layer. Single-polymer membranes present key potential trade-off issues:

- First, the polymeric material that has the ideal properties for separating CO₂ from CH₄ by virtue of differential permeation rates of these molecules, may not be mechanically strong or chemically resistant.
- Alternatively, the polymeric material that meets the strength and chemical stability requirements may not have good permeation characteristics; that is, it may either have too low a CO₂/CH₄ selectivity or too low a permeation flux.

Therefore, identifying that ideal material is always a compromise between stability, selectivity and manufacturability of the polymer to make a commercially viable membrane.

MTR has developed a unique and proven approach to decouple these wide ranging requirements for membrane performance. The membranes manufactured in this manner are called composite membranes.

Common Gas Contaminants: Effects On New And Traditional Membranes

Table 1 shows the effect of common contaminants on the membranes discussed in this paper. The last column shows the effect of these contaminants on traditional glassy membranes used in the gas patch. As Table 1 (attached at the end) indicates, the new membranes show enhanced stability against common contaminants, and mitigate the need for extensive pretreatment trains. When traditional membranes for CO₂ removal are used, heavy components, such as aromatics, BTEX, and heavy aliphatic hydrocarbons do not permeate the membrane. As the CO₂ is removed, the concentration of these components can build up along the feed channel. If the concentration reaches a level such that the phase envelope is crossed, hydrocarbons can condense on the surface of the membrane. Since these organic liquids are often solvents for the membrane materials, such condensation is potentially devastating. It can literally dissolve the membranes. Significant pretreatment of the feed gas is usually required to prevent hydrocarbon condensation. The simplest treatment is to heat the gas above the highest expected dewpoint, but in many cases adsorption beds or refrigeration are required upstream to lower the hydrocarbon content.

The composite membranes described above can be structured to use materials that are impervious to hydrocarbon exposure. These new membranes for CO₂ removal behave in the same manner as traditional membranes insofar as they selectively permeate CO₂ and reject hydrocarbons. However, the chemistry of the membrane has been carefully designed so that aromatics and other hydrocarbons are *not* solvents for the membrane materials. Therefore, even if briefly exposed to liquid hydrocarbon condensates, the membranes are not permanently affected. After removal of the liquids, the membranes continue to function normally.

Further, the chemical structure of the new membrane materials, and their packaging configuration as spiral-wound elements, allow them to be cleaned and reused. This results in lowered operating costs and reduced disruption to production.

Membrane Packaging

Composite membranes are made in flat-sheet form and can be packaged in a spiral-wound module configuration, as shown in Figure 2. Spacers on the feed and permeate sides of the membrane create flow channels. The feed gas enters the module

and flows between the membrane sheets. The faster permeating component permeates the membrane preferentially, and flows inward to a central collection pipe. Slower permeating components are rejected and exit as the high pressure residue stream.

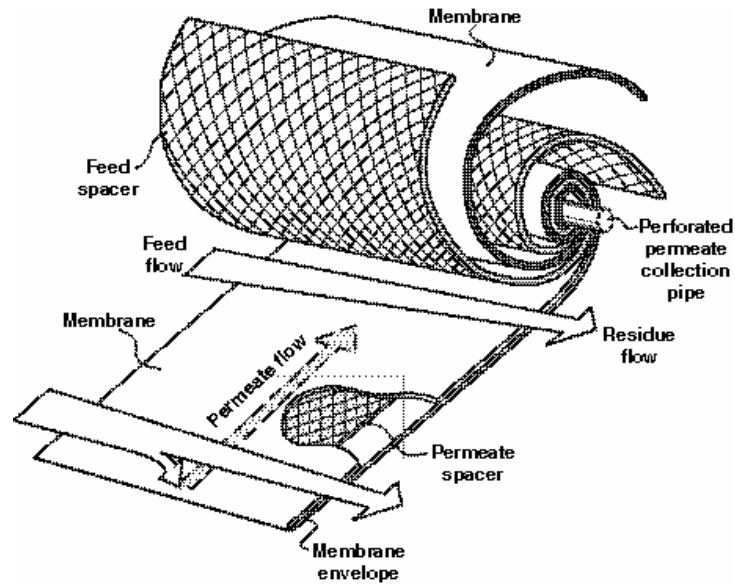


Figure 2. Schematic diagram showing components and gas flow patterns of a spiral-wound module.

The spiral-wound modules are manifolded and placed in pressure vessels made from commercial steel pipe. The membrane elements are configured in series and parallel flow combinations to meet the requirements of particular applications. A picture of a typical skid-mounted membrane system containing 16 pressure tubes is shown in Figure 3.



Figure 3. A typical membrane skid; sixteen carbon steel pressure tubes house the membrane modules.

CO₂ Removal Process

The removal of CO₂ has been the predominant traditional application of membranes in the natural gas industry. Numerous small plants and several larger plants processing up to 500 MMSCFD of gas or more have been installed using cellulose acetate, cellulose triacetate or polyimide membranes. These polymer materials show good separation performance but are known to be susceptible to damage due to exposure to aromatics, other organics liquids or water, any of which can cause irreversible damage to the membranes. To mitigate the risk of damage, membrane processes utilize significant pretreatment steps to remove offending components down to acceptable levels. This increases capital and operating costs, and adds complexity to an otherwise simple process. Additionally, any upsets in the pretreatment train may still expose the membranes to harmful contaminants, resulting in the need to replace the membrane inserts.

More intrinsically robust composite membranes developed recently can operate safely with minimal pretreatment of the feed gas, and are more forgiving of accidental exposure to high levels of contaminants. The membranes are based on polymer chemistry similar to that of Teflon[®], the well known non-stick material. These polymers do not dissolve or disintegrate in aromatics like other conventional polymers, and retain performance even after limited accidental exposure to such components.

MTR/ABB have combined their resources to work with Dominion Field Services and address the market for processing high-CO₂ natural gas by reducing the CO₂ content

to required pipeline specifications, thus bringing additional gas to market. The approach has been to develop a complete standardized process and equipment solution including inlet piping, compression, and pretreatment to provide a one-stop solution for independent producers who may not have the engineering resources to develop the entire package in a timely and cost-effective manner. This has been accomplished by focusing on several key engineering aspects which are discussed below in more detail.



Figure 4. A standard CO₂ treatment skid with pretreatment filter/separators on adjacent skid to left.

Standardization Of Skids

Two different, but standardized size membrane skids are being sold to Dominion. One skid is 50 percent larger than the other, and differs mainly in the use of longer membrane vessels.

Standardization of skids allows reuse of detailed design. Standardization lowers cost and provides the end user a proven full-feature equipment package. The use of different combinations of skids creates easy scalability for a variety of projects. It also makes installed capacity flexible for production rates that change over time.

Limited Pretreatment

Figure 4 shows the pretreatment filter separators mounted on a separate skid to the left of the membrane skid. Pretreatment consists of using filter/separators and managing temperatures to control hydrocarbon dew point. The gas from the recycle compressor requires only a filter/separator to remove lube oil and trace contaminants. The feed is

conditioned to remove water, thus avoiding free water formation that would cause corrosion. For gases rich in heavy hydrocarbons, the feed is also superheated in a field heater to avoid hydrocarbon condensation.

Wide Range Of Applicability

The standard CO₂ membrane skid was designed with contract CO₂ treating on the U.S. Gulf Coast in mind. Dominion Field Services offers a broad array of services to gas producers; among these services is a membrane-based CO₂ treatment service. Dominion's membrane treatment unit is designed to be flexible and superior to an amine-based solution. The golf term "fairway" is often used to describe the targeted range of gas treating applications. The CO₂ treatment fairway ranges from 3-11 mol% CO₂, and from 2-10 MMSCFD flow. The membrane system is designed for wide turndown. Nominal performance for the larger model standard skid is 7 MMSCFD of feed containing 7 percent CO₂, with 2 percent CO₂ in the sales product. The CO₂ sales specification in proposed applications has varied from 1.25 percent to 4 percent, with a 2 percent pipeline spec being the most common sales specification. With slight modifications to the design, the application range can be expanded to accommodate higher percentages of CO₂ in the feed.

The design can also accommodate feeds with a range of NGL content. The feed can be very lean coal seam type gas or associated gas with a few g/1000scf NGL.

High Btu Recovery

Minimal gas shrinkage, high Btu recovery was a prime objective in the CO₂ process development we are describing. In order to compete with amine units, gas shrinkage must be small. Historically, gas shrinkage of membrane systems was competitive at higher CO₂ concentrations, but suffered particularly high methane losses with 3-11 percent CO₂ in the feed. This new patent pending process has multiple membrane stages for high recovery mated with a single three-stage reciprocating compressor typically found in gathering systems. For this membrane process, gas shrinkage depends on vent losses and the amount used as compressor fuel. For many applications, gas shrinkage is less than 2 percent of the inlet gas.

Scope Of Facility

The facility was designed with minimal field construction in mind. The membrane system and filter separator are supplied as skid mounted systems. The system includes a complete PLC-based control system. Figure 5 is a picture of the Alverstone unit being unloaded. It only takes a few hours to unload and set the skid mounted equipment. The equipment came off the truck in the afternoon, and the installation team was ready to start interconnecting piping the next day.



Figure 5. A standard membrane-based CO₂ treatment unit is lifted from the truck.

A few additional considerations include the following:

- **Ease of Installation.** All major equipment is skid mounted. No equipment requires foundations. Normally, soil is compacted and equipment is placed on pads topped with gravel. The relatively light and small equipment is easy transported and unloaded on-site. The membrane skid is similar in size to the direct fired reboiler used on a comparable amine system.
- **Number of skids.** A typical installation has the membrane skid, the membrane filter/separator skid, a skid mounted recycle compressor, a skid for auxiliary equipment, and a portable building. The portable building is a converted shipping container which is used for controls, storage and field shelter.
- **Rapidity of deployment.** Dominion is building an inventory of membrane units and other equipment for rapid deployment. This allows the producer to begin production ASAP. It also makes the project schedule for installing this membrane solution very competitive with the reinstallation of an existing amine system.

Performance Test Data

Dominion's Alverstone unit near Sheridan, Texas, has been in operation since April 2006. Extensive data were collected during the performance test and some spot tests were taken in the subsequent months. Although the Alverstone unit was originally sold to process a feed at 975 psig containing 5.125 percent CO₂, it was placed in service

at 710 psig and 6.4 percent CO₂. Initially, the membrane skid was only half loaded because available gas volumes were low. The membrane unit lowered the CO₂ in the sales gas stream to 1.83 percent during the performance test. The vent stream averaged 78.4 pct CO₂; this allowed 98.8 percent retention of the inlet Btu value in the sales gas stream.

Long-Term Data

Spot samples were taken at the Alverstone unit over the summer. When the unit was running steadily, variations between subsequent samples and initial start-of-run data could be attributed to changes in field conditions rather than changes in membrane performance. Dominion Exploration uses CO₂ to stimulate wells, resulting in a feed volume and composition that can change every few minutes, making steady state observations impossible. During these dynamic operating days, the membrane unit performance was favorable. Surges of CO₂ in the feed resulted in surges of CO₂ in the vent.

Dominion has now elected to fully load all of the membrane cartridges into the service unit at Alverstone. Analyzers on the inlet and sales gas were also installed. Fully loaded, the membrane skid has excess capacity, and irregularities in the feed composition and flow are easily filtered out of the gas. Figure 6 below shows data taken with field instrumentation after the membrane skid was fully loaded with membrane. The graph shows very little change in the sales gas CO₂ content, while the inlet gas composition changes. The sales gas is held well below the 2 percent CO₂ specification (But the amount of CO₂ in the sales gas can be adjusted to run closer to 2 percent if so desired).

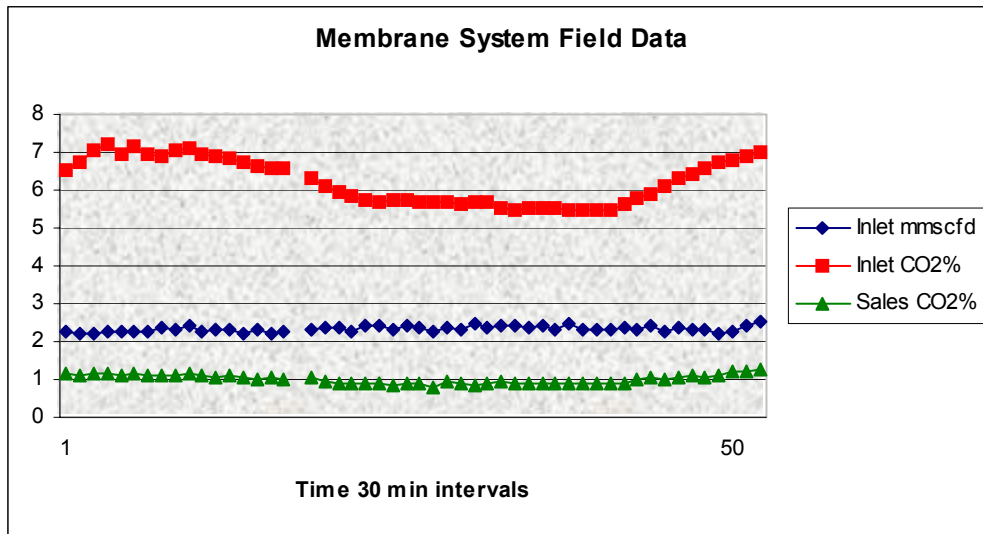


Figure 6. Field performance data for operation of a membrane CO₂ removal system (Dominion's Alverstone unit near Sheridan, Texas).

Potential Issues To Consider In Membrane System Design

During the design, construction, and operation of this project, several important issues were considered and worked through by the project team. Some of these issues are summarized below.

Dew Point Management

Before proceeding with a project, information regarding gas temperature, pressure and composition should be known. The membrane system performance and check dew point conditions in the membrane unit can then be simulated. Typically, 30 degrees of super heat is applied to the gas before being processed through the membranes. The membrane itself is tolerant of NGL liquids, but two-phase flow must be avoided. Crossing over into the dew point region has been observed in the field. The presence of liquids reduces mass transfer. When proper temperature is restored, the membrane dries out in a few minutes and performance fully recovers.

Safe Purging

A membrane system must be safely purged to remove air before start-up. Reverse pressurization on the membrane modules during purging can cause mechanical damage to membrane modules. The membrane include a PLC program to assist the operator during purging. The PLC provides instructions and opens and closes automated valves during purging.

Safe Shutdown

A safe and systematic shutdown of the membrane system is performed by the PLC. The system is isolated and blown down on shutdown. The membrane system includes special blow-down valves designed to prevent condensation of NGLs that can occur during shutdown.

Automated Operation

The membrane system is controlled from the PLC screen. The PLC screen has a graphical user interface for easy operation. Start-up and normal operation of the unit can be achieved without opening or closing any manual isolation valves on the membrane skid. The PLC system has been successfully interfaced with a SCADA system for remote monitoring.

Startup Time

Routine start-up of the membrane system can be achieved in a few minutes. Membranes are a fast responding system. The PLC helps automate start-up, providing instructions to the operator and automatically ramping set points during start-up. A single operator can start the unit. If auxiliary equipment is ready for service, startups typically take only 15-30 minutes.

Pretreatment

Although the membranes for this system are engineered to be tolerant of contaminants, contaminants should be avoided. A good upstream operation to remove dirt, oil, TEG, and so forth, helps protect the membrane system. The filter coalescer elements before the membrane unit are “last line of defense.” The filter coalescer used in this project removes several quarts a day of lube oil from the recycle gas stream. The filter coalescer on the inlet stream is downstream of a TEG unit.

Upstream Environment

The membrane system needs to be able to tolerate changes in the upstream environment. Frequent changes in gas volume composition and availability are possible due to normal field operations. The automation of the membrane unit keeps it online through most changes in field conditions. The ability to easily restart is a benefit when gas flow is discontinued due to field compression or well problems.

Summary

In order to address a large need of natural gas producers to monetize high-CO₂ gas in the US and Canada, MTR/ABB and Dominion Field Services have combined their individual strengths to come up with a completely packaged membrane solution for acid gas reduction in natural gas. Robust membranes that require a minimal amount of pretreatment, using standardized skids and very high Btu recovery processes, have been developed and demonstrated commercially.

TABLE 1. Common Contaminant in Natural Gas and Their Potential effects on CO₂ Membranes and Traditional Amines

Contaminant	Occurrence	MTR/ABB Blend membrane	Traditional Glassy Membranes	Traditional Amine Systems
		Comments	Comments	
Mercury Elemental and/or organic	Uncommon	No chemical interaction. No effect expected	Unknown – Some membranes have limitation on HG concentration allowable in feed gas	Potential Accumulation in Column – Disposal Hazard Issue
Inorganic salt	Uncommon	Chemical reactions not expected. Upstream filtration required to remove gross particulate matter to avoid pressure drop increase	Filter Separator removes all salt particles > 0.3 microns. Hollow fibers can be fouled leading to higher pressure drops	Can lead to foaming in Amine systems
Asphaltenes	Rare	May cause flux decline over time if deposited on membrane towards the residue end	Causes flux decline over time. In some cases severe flux declines observed	Fouls system
Paraffinic waxes	Rare	No chemical interaction expected. May cause flux decline over time if deposited on membrane. Membrane can be washed with hydrocarbon solvent to remove	Will deposit on membrane surface and lower fluxes. Cannot be washed away with liquid solvents	Fouls system often combines with particles in system, can contribute to foaming
Water	Common	No effect. Permeates the membrane resulting in gas dehydration	Significant flux decline in some membranes. No effect on some other glassy membranes	None
Elemental sulfur	Rare	No chemical reaction expected. But if coated on membrane flux decline could occur over time	Unknown	Sulfur dust forms a sulfur scum when combined with water, can foul the system and contribute to foaming
Mercaptans	Common	Smaller mercaptans expected to behave like H ₂ S. Larger mercaptans will be rejected to product stream	Unknown	None
Oxygen	Uncommon	No effect	Unknown	Oxidation issues – Corrosion issues in high loading environments
Aromatics	Common	Lab data suggests membrane swells to some extent, but is resistant to BTEX (and other hydrocarbons) Hydrocarbons will be rejected to residue stream and build up from feed to residue end of modules	Aromatics are solvents for many conventional glassy membranes. Accidental exposure to aromatics can result in severe irreversible damage requiring complete membrane change out. Upset conditions needs to be evaluated.	Surfactant can lead to foaming
Ethylene glycol	Common	May cause flux decline over time if deposited on membrane especially if CO ₂ concentration changes are high	May cause flux decline over time if deposited on membrane	Foaming enhancer
BTEX	Common	No interaction of liquid BTEX with membrane. Once liquid BTEX is removed, membrane regains original performance	BTEX are Solvents for the membrane. Exposure will result in destruction of membrane.	Surfactant can lead to foaming
Methanol	Common	No effect	Unknown	None
TEG	Common	TEG aerosols will be removed in the filter separator. No chemical interaction with membrane	If gas heated, TEG may break down and products will deposit on membrane	Unknown
Amine	Common	Amine aerosols will be removed in the filter separator. No chemical interaction with membrane. May accumulate on surface over time, can be washed away	If gas heated, amines may break down to products that are harmful to membrane	-
Wellhead treatment chemicals	Uncommon	Filter separator removes any aerosols. No interaction with chemicals expected	Unknown	Wellhead chemicals can deactivate amines and cause foaming and pressure drops
Compressor oil	Common	Oil deposition on membrane over time will result in flux decline. A well designed coalescing filter will eliminate 99.99% of oil aerosols	Oil deposition on membrane over time will result in flux decline. A well designed coalescing filter will eliminate 99.99% of oil aerosols	Forms third phase floats on amine phase. Needs to be skimmed out. Contributes to foaming