Recent Developments in CO_2 Removal Membrane Technology

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Abstract

Membrane systems have become a tried and accepted natural gas treating technology with distinct advantages in a variety of processing applications. From the earliest units producing below 10 MM SCFD treated gas, systems are now in place to produce upward of 250 MM SCFD. Plans for plants producing 500 MM SCFD and higher are in the works. Although most units have been installed onshore, some offshore facilities do exist, and many more are planned. These systems, as well as those in the Middle East and elsewhere, exploit the reliability and minimum manpower requirements of membranes.

Some early installations highlighted the need for suitable preprocessing prior to membrane treatment. This need has led to the development of a robust and comprehensive pretreatment scheme that ensures extended membrane life. This pretreatment, in combination with the continuing development of advanced membranes, has even further enhanced the reliability and performance of membrane technology and made it the CO_2 removal technology of choice in a variety of processing conditions.

This paper describes operating experiences and design philosophy for larger membrane-based CO_2 removal plants.

Introduction

Membranes have become an established technology for carbon dioxide (CO_2) removal since their first use in this application in 1981. Initial acceptance was slow and limited to smaller streams, mostly because of the economic risks involved in treating larger streams, but also because many process design parameters were largely unknown. A further factor was the general downturn in the oil and gas industry in the 1980s.

The multiple benefits of membrane technology promised by early innovators have since been proven in a wide variety of installations in many locations around the world, and vendors of traditional CO_2 removal technologies have been quick to acquire or develop membrane-based processes to supplement their older processing routes. Such companies have been able to achieve the best of both worlds: hybrid systems. In some cases, the most economical approach is to combine membranes with existing technologies or use membranes to debottleneck existing solvent-based plants.

Membrane companies have had to allocate significant portions of their revenues to research and design efforts. This investment has been necessary to fully understand the dynamics of membrane system operation over time and also to further enhance membrane performance. The latter has been achieved by modifying existing membrane materials and investigating alternative membrane materials. Of equal importance have been improvements in membrane element configuration, pretreatment design, and optimization of the system's mechanical design.

This paper summarizes the principles involved in CO_2 removal by membranes, design considerations, UOP's experiences in larger plants, and recent innovations by UOP's Gas Processing group, both in membrane and membrane pretreatment design.

The Need for CO_2 Removal

Carbon dioxide, which falls into the category of acid gases (as does hydrogen sulfide, for example) is commonly found in natural gas streams at levels as high as 80%. In combination with water, it is highly corrosive and rapidly destroys pipelines and equipment unless it is partially removed or exotic and expensive construction materials are used. Carbon dioxide also reduces the heating value of a natural gas stream and wastes pipeline capacity. In LNG plants, CO_2 must be removed to prevent freezing in the low-temperature chillers.

A wide variety of acid gas removal technologies are available. They include absorption processes, such as the Benfield™ process (hot potassium carbonate solutions) and Amine Guard-FS™ process (formulated solvents); cryogenic processes; adsorption processes, such as pressure swing adsorption (PSA), thermal swing adsorption (TSA) and iron sponge; and membranes.

Each process has its own advantages and disadvantages, but membranes increasingly are being selected for newer projects, especially for applications that have large flows, have high CO_2 contents, or are in remote locations. The reasons for this choice are described later in the paper.

Membranes have been widely used in two main CO_2 removal applications:

- Natural gas sweetening
- Enhanced oil recovery (EOR), where CO_2 is removed from an associated natural gas stream and reinjected into the oil well to enhance oil recovery

Other applications also exist, for example landfill gas purification, but these applications are far fewer in number.

Membranes

Membranes are thin semipermeable barriers that selectively separate some compounds from others. This definition is necessarily broad because of the large variety of membrane materials separating an equally vast number of compounds in all phases. Applications include:

- Ceramic membranes for gas purification in the semiconductor industry
- Palladium-based metallic membranes for hydrogen extraction
- Silicon rubber membranes for organic vapor recovery from air
- Polyvinyl alcohol-based membranes for ethanol dehydration

Membrane Materials for CO_2 Removal

Currently, the only commercially viable membranes used for CO_2 removal are polymer based, for example, cellulose acetate, polyimides, polyamides, polysulfone, polycarbonates, and polyetherimide. The most widely used and tested material is cellulose acetate as used in UOP's membrane systems. Polyimide has some potential in certain CO_2 removal applications, but it has not received sufficient testing to be used in large applications.

The properties of polyimides and other polymers can be modified to enhance performance. For example, polyimide membranes were initially used for hydrogen recovery but were then modified for CO_2 removal. Cellulose acetate membranes were initially developed for reverse osmosis but are now the most rugged CO_2 removal membrane available.

Membrane Permeation

The membranes used for CO_2 removal do not operate as filters, where small molecules are separated from larger ones through a medium with pores. Instead, they operate on the principle of solution-diffusion through a *nonporous* membrane. The CO_2 first dissolves into the membrane and then diffuses through it. Because the membrane does not have pores, it does not separate on the basis of molecular size. Rather, it separates based on how well different compounds dissolve into the membrane and then diffuse through it.

Because carbon dioxide, hydrogen, helium, hydrogen sulfide, and water vapor, for example, permeate quickly, they are called “fast” gases. Carbon monoxide, nitrogen, methane, ethane and other hydrocarbons permeate less quickly and so are called “slow” gases. The membranes allow selective removal of fast gases from slow gases. For example, as CO_2 is removed from a natural gas stream, water and H_2S are removed at the same time; but methane, ethane, and higher hydrocarbons are removed at a much lower rate.

Fick’s law, shown below, is widely used to approximate the solution-diffusion process:

$$J = \frac{k \times D \times \Delta\rho}{\ell}$$

J is the membrane flux of CO_2, that is, the molar flow of CO_2 through the membrane per unit area of membrane.

k is the solubility of CO_2 in the membrane.

D is the diffusion coefficient of CO_2 through the membrane.

$\Delta\rho$ is the partial pressure difference of CO_2 between the feed (high pressure) and permeate (low pressure) side of the membrane.

ℓ is the membrane thickness.

To simplify matters further, the solubility and diffusion coefficients are usually combined into a new variable called *permeability* (P). Fick’s law can therefore be split into two portions: a membrane-dependent portion (P/ℓ) and a process-dependent portion (Δp). To achieve a high flux, the correct membrane material and the correct processing conditions are needed. P/ℓ is not a constant; it is sensitive to a variety of operating conditions such as temperature and pressure.

The Fick’s law equation can be equally written for methane or any other component in the stream. This set of equations leads to the definition of a second important variable called *selectivity* (α). Selectivity is the ratio of the permeabilities of CO_2 to other components in the stream and is a measure of how much better the membrane permeates CO_2 compared to the compound in question. For example, most CO_2 membranes provide a CO_2-to-methane selectivity anywhere between 5 and 30, meaning that CO_2 permeates the membrane 5 to 30 times faster than methane.

Both permeability and selectivity are important considerations when selecting a membrane. The higher the permeability, the less membrane area is required for a given separation and therefore the lower the system cost. The higher the selectivity, the lower the losses of hydrocarbons as CO_2 is removed and therefore the higher the volume of salable product.

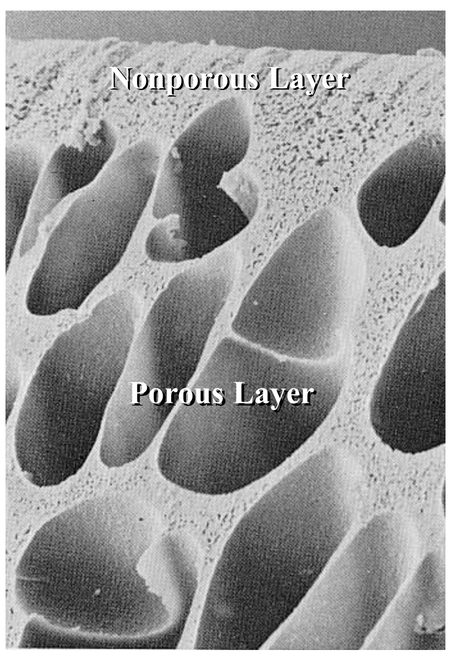
Unfortunately, high CO_2 permeability does not correspond to high selectivity, though achieving this combination is a constant goal for membrane scientists. Instead, they have to settle for a highly selective *or* permeable membrane *or* somewhere in-between on both parameters. The usual choice is to use a highly selective material then make it as thin as possible to increase the permeability. However, this reduced thickness makes the membrane extremely fragile and therefore unusable. For many years, membrane systems were not a viable process because the membrane thickness required to provide the necessary mechanical strength was so high that the permeability was minimal. An ingenious solution to this problem allowed membranes to break this limitation.

Membrane Structure

The solution was to produce a membrane consisting of an extremely thin nonporous layer mounted on a much thicker and highly porous layer of the same material. This membrane structure is referred to as asymmetric, as opposed to an homogenous structure, where membrane porosity is more-or-less uniform throughout. An example of an asymmetric membrane is shown in Figure 1.

Figure 1

Asymmetric Membrane Structure



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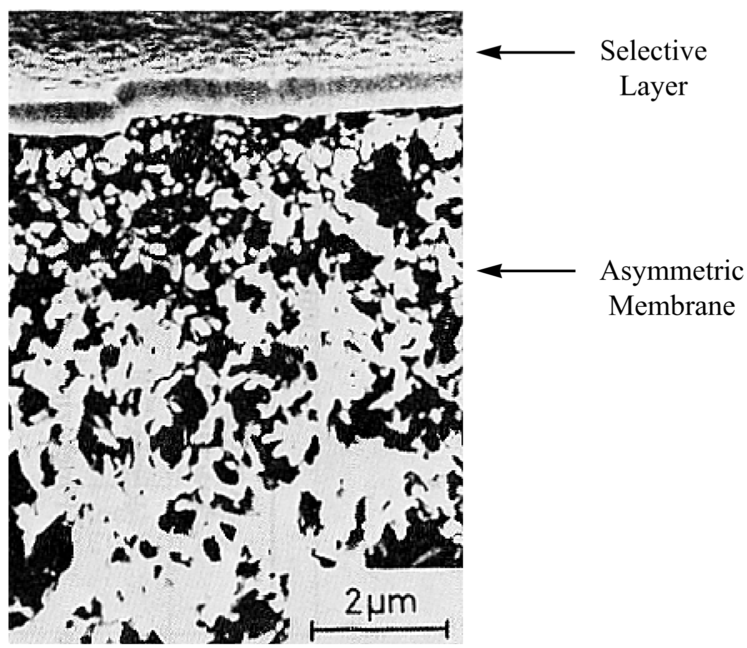
The nonporous layer meets the requirements of the ideal membrane, that is, it is highly selective and also thin. The porous layer provides mechanical support and allows the free flow of compounds that permeate through the nonporous layer.

Although asymmetric membranes are a vast improvement on homogenous membranes, they do have one drawback. Because they are composed of only one material, they are costly to make out of exotic, highly customized polymers, which often can be produced only in small amounts. This difficulty is overcome by producing a composite membrane, which consists of a thin selective layer made of one polymer mounted on an asymmetric membrane, which is composed of another polymer. This composite structure allows membrane manufacturers to use readily available materials for the asymmetric portion of the membrane and specially developed polymers, which are highly optimized for the required separation, for the selective layer. An example of this structure is shown in Figure 2.

Figure 2
Composite Membrane Structure



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Composite structures are being used in most of the newer advanced CO_2 removal membranes because the properties of the selective layer can be adjusted readily without increasing membrane cost too significantly.

Membrane Elements

Gas separation membranes are manufactured in one of two forms: flat sheet or hollow fiber. The flat sheets are typically combined into a spiral-wound element, and the hollow fibers are combined into a bundle similar to a shell and tube heat exchanger. Figures 3 and 4 illustrate these element types.

In the spiral-wound arrangement, two flat sheets of membrane with a permeate spacer in between are glued along three of their sides to form an envelope (or *leaf*, as it is called in the membrane industry) that is open at one end. Many of these envelopes are separated by feed spacers and wrapped around a permeate tube with their open ends facing the permeate tube.

Feed gas enters along the side of the membrane and passes through the feed spacers separating the envelopes. As the gas travels between the envelopes, CO_2, H_2S, and other highly permeable compounds permeate into the envelope. These permeated components have only one outlet: they must travel within the envelope to the permeate tube. The driving force for transport is the low-permeate and high-feed pressures. The permeate gas enters the permeate tube through holes drilled in the tube. From there, it travels down the tube to join the permeate from other tubes. Any gas on the feed side that does not get a chance to permeate leaves through the side of the element opposite the feed position.

Figure 3

Spiral Wound Membrane Element

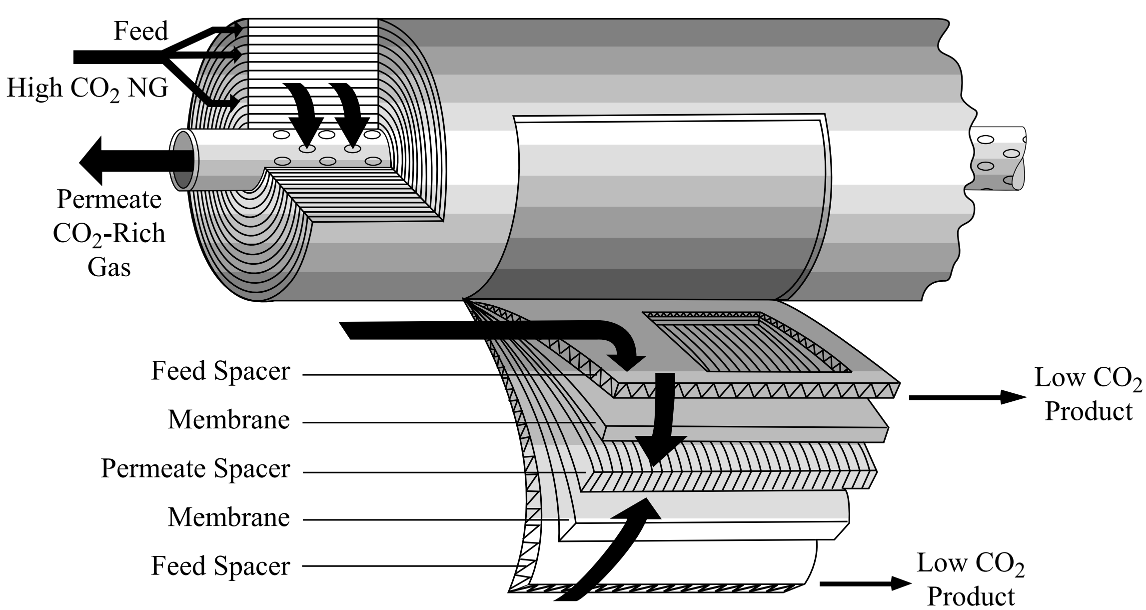

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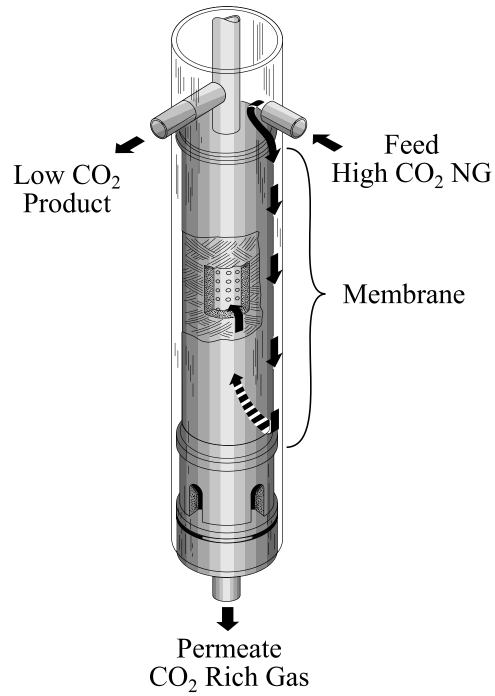
Figure 4

Hollow-Fiber Membrane Element



Possible optimizations for spiral-wound elements include the number of envelopes and element diameter. The permeate gas has to travel the length of each envelope, so having many shorter envelopes makes more sense than a few longer ones because pressure drop is greatly reduced in the former case. Larger-bundle diameters allow better packing densities but increase the element tube size and therefore cost. They also increase the element weight, which makes the elements more difficult to handle during installation and replacement.

In hollow-fiber elements, very fine hollow fibers are wrapped around a central tube in a highly dense pattern. In this wrapping pattern, both open ends of the fiber end up at a permeate pot on one side of the element. Feed gas flows over and between the fibers, and some components permeate into them. The permeated gas then travels within the fibers until it reaches the permeate pot, where it mixes with the permeates from other fibers. The total permeate exits the element through a permeate pipe.

The gas that does not permeate eventually reaches the element's center tube, which is perforated in a way similar to that of the spiral-wound permeate tube. In this case, however, the central tube is for residual collection, not permeate collection.

Many optimizations are possible for hollow-fiber elements. They include adjusting fiber diameters: finer fibers give higher packing density but larger fibers have lower permeate pressure drops and so use the pressure driving force more efficiently. Another optimization is the sleeve design, which forces the feed to flow countercurrent to the permeate instead of the more-usual and less-efficient cocurrent flow pattern.

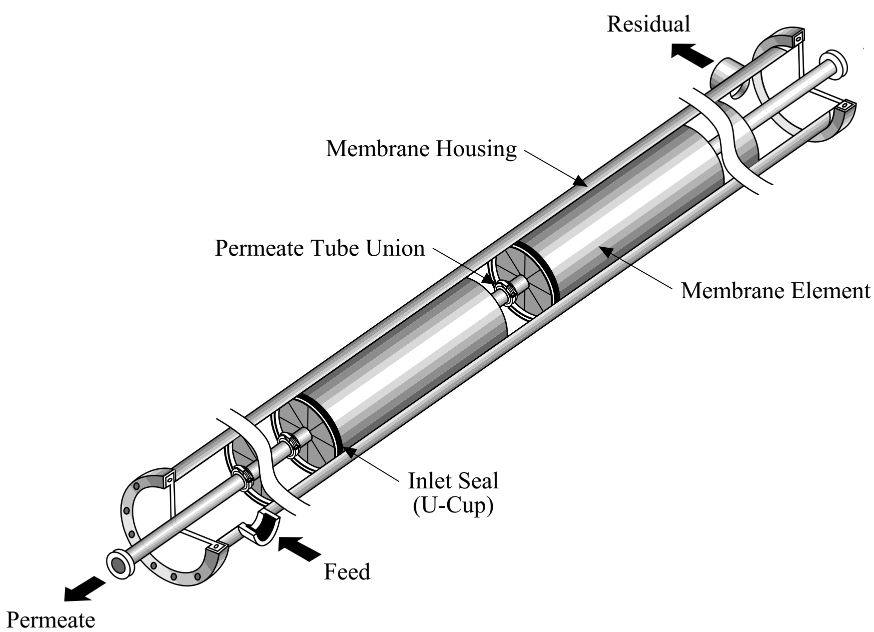
Each element type has its own advantages. Spiral-wound elements can handle higher pressure, are more resistant to fouling, and have a long history of service in natural gas sweetening. Hollow-fiber elements have a higher packing density, and so hollow fiber-based plants are typically smaller than spiral wound-based plants. Those vendors that supply both types of elements can provide objective reasons for choosing one type over the other.

Membrane Modules and Skids

Once the membranes have been manufactured into elements, they are joined together and inserted into a tube (Figure 5).

Figure 5

Membrane Module with Elements



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Multiple tubes are then mounted on skids in either a horizontal or vertical orientation, depending on the membrane company. A skid with horizontal tubes is shown in Figure 6.

Figure 6
Membrane Skid

Advanced Membrane Development

UOP has an ongoing effort to produce novel and enhanced polymers for membranes. These compounds are initially tested in the laboratory followed by pilot testing on slipstreams of actual gas plants and then installed in full-scale plants. Extensive testing on a wide variety of gas streams is imperative to ensuring the long-term, stable, and efficient operation of membrane systems. New membranes cannot be considered truly reliable until this testing is done because different membranes are affected differently by different compounds and operating conditions. For example, because polyimide membranes are much more sensitive to heavy hydrocarbons than cellulose acetate, more-rigorous pretreatment is required.

UOP is developing both advanced spiral-wound and hollow-fiber membranes. UOP's advanced polyimide-based hollow-fiber membranes have already been used in a major plant and have also been installed on slipstreams in other plants already using UOP's current membranes. These advanced membranes have significantly higher selectivities than current membranes, but have lower permeabilities. The permeability can be increased by adjusting operating conditions, such as temperature.

The advanced spiral-wound membranes are not as commercially developed as the hollow-fiber product but show even more promise. These spiral-wound membranes are based on a proprietary polymer that provides significantly higher selectivities at similar permeabilities to current products. These membranes are currently completing extended pilot-plant trials.

When advanced membranes are retrofitted into existing membrane tubes, they reduce hydrocarbon losses, reduce recycle compressor power consumption, and increase the plant's production capacity.

Design Considerations

Many process parameters can be adjusted to optimize performance depending on the customer and application needs. Optimization is most critical for larger systems where small improvements can bring large rewards. Some typical requirements are:

- Low cost
- High reliability
- High on-stream time
- Easy operation
- High hydrocarbon recovery
- Low maintenance
- Low energy consumption
- Low weight and space requirement

Many of these requirements work against one another: for example, a high-recovery system usually requires a compressor, which increases maintenance costs. The design engineer must therefore balance the requirements against one another to achieve an overall optimum system. The process variables affecting the design are described in the rest of this section.

Flow Scheme

The simplest membrane processing scheme is a one-stage flow scheme (Figure 7). A feed gas is separated into a permeate stream rich in CO_2 and a hydrocarbon-rich residual stream.

In high CO_2 removal applications, a significant amount of hydrocarbons permeate the membrane and are lost. Multistage systems attempt to recover a portion of these hydrocarbons. The two-step design shown in Figure 8 allows only a portion of the first-stage permeate to be lost. The rest is recycled to the feed of the first stage.

The portion of first-stage permeate that is lost is usually taken from the first membrane modules, where feed CO_2, hence permeate CO_2, is highest and hydrocarbons are lowest. The permeate that is recycled is at low pressure and must be repressurized before it can be combined with the feed gas.

Figure 7

One-Stage Flow Scheme

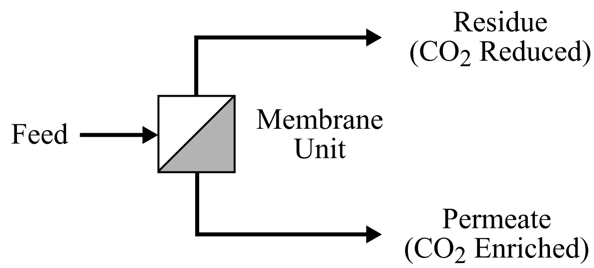

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Figure 8

Two-Step Flow Scheme

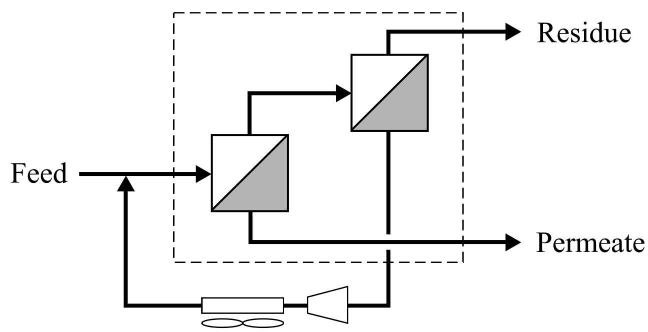

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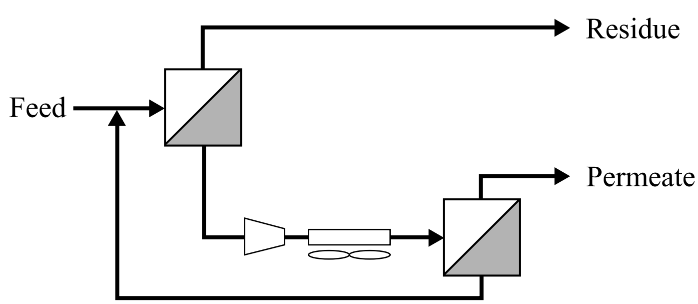
Figure 9

Two-Stage Flow Scheme



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Two-stage designs process the first-stage permeate in a second membrane stage, as shown in Figure 9.

The permeate from the second stage, which has typically twice the CO_2 content as the first-stage permeate, is vented. The residue is either recycled and combined with the feed gas. A compressor is required to repressurize the first-stage permeate before it is processed in the second stage. Two-stage designs provide higher hydrocarbon recoveries than two-step or one-stage designs but require more compressor power (because more gas must be compressed to be treated).

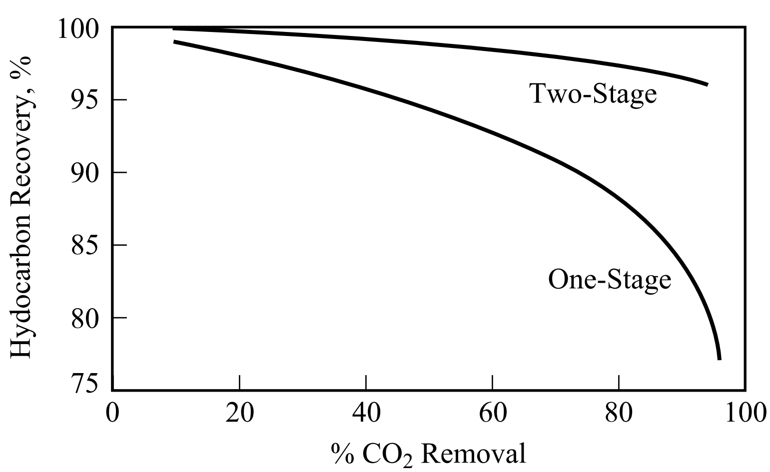
Other flow schemes are also possible though rarely used. One exception is the two-stage with premembrane flow scheme, where a single-stage system provides bulk CO_2 removal, followed by a two-stage system for final CO_2 removal. This scheme uses a much smaller recycle compressor than that required by a standard two-stage system, although hydrocarbon losses are higher because of the single-stage portion of the system.

When deciding whether to use a single-stage or multistage system, many factors must be considered. An economic analysis must be completed to ensure that the cost of installing and operating a recycle compressor does not exceed the savings in hydrocarbon recovery. Figure 10 illustrates this issue.

The percentage hydrocarbon recovery is plotted versus percentage CO_2 removal for one- and two-stage systems at certain process conditions. The *percentage hydrocarbon recovery* is defined as the percentage of hydrocarbons recovered to the sales gas versus the hydrocarbons in the feed gas.

Figure 10

Effect of Number of Stages



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The hydrocarbon recovery of a two-stage system is significantly better than that for a single-stage system. However, when deciding whether to use a single or multistage approach, the designer must also consider the impact of the recycle compressor. This impact includes the additional hydrocarbons used as fuel, which increases the overall hydrocarbon losses, as well as the significant capital cost of compressors and the difficulty of maintaining them in remote locations. For moderate CO_2 removal applications, that is, below approximately 50%, single-stage membrane systems usually provide better economic returns than do multistage systems.

Flow Rate

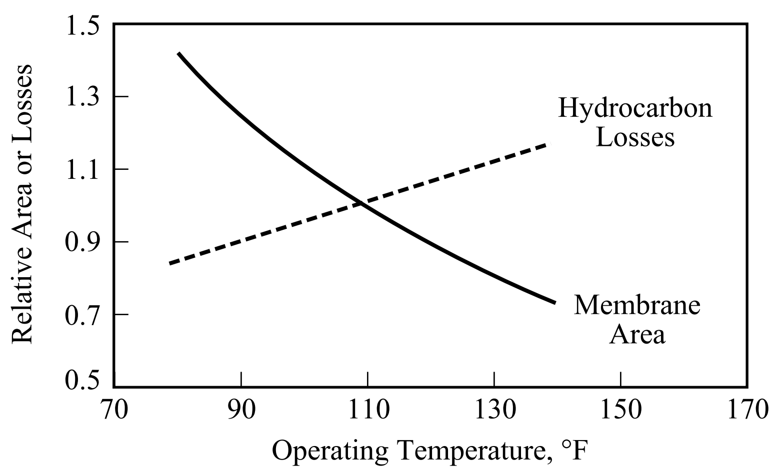
Because membrane systems are modular, an increase in flow rate causes a directly proportional increase in membrane area requirement, for a given separation. Hydrocarbon losses, that is, the flow rate of hydrocarbons lost to vent, also increases proportionally, but the percentage hydrocarbon losses (hydrocarbon losses ÷ feed hydrocarbons) stay constant.

Operating Temperature

An increase in feed temperature increases membrane permeability and decreases selectivity. The membrane area requirement is therefore decreased, but hydrocarbon losses and the recycle compressor power for multistage systems are increased, as shown in Figure 11.

Figure 11

Effect of Operating Temperature



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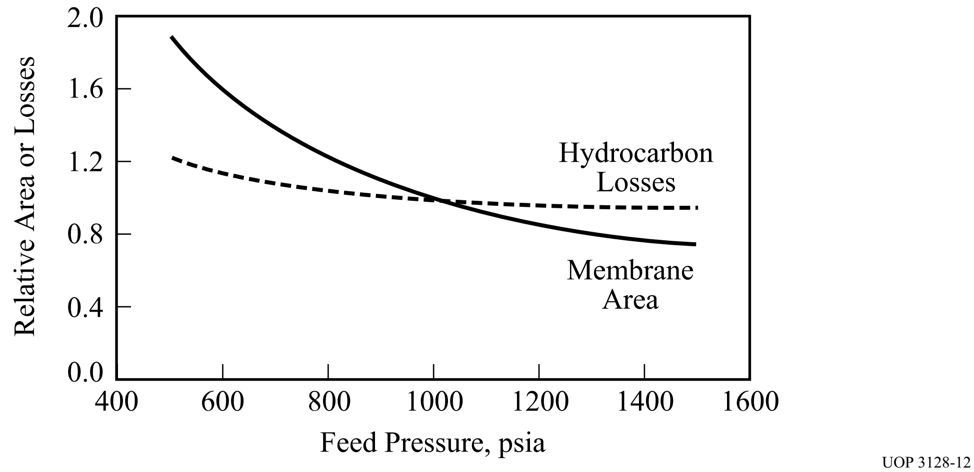
Feed Pressure

An increase in feed pressure decreases both membrane permeability and selectivity. However, the increased pressure creates a greater driving force across the membrane. A net increase in permeation through the membrane results and the membrane area requirement therefore drops. Compressor power increases slightly, and hydrocarbon losses decrease slightly (Figure 12).

Figure 12

Effect of Feed Pressure



Because the membrane area requirement is so affected by pressure, while other variables are not, designers attempt to use the maximum operating pressure possible to achieve a cheaper and smaller system. A limiting factor is the maximum pressure limit for the membrane elements and the cost and weight of equipment at a higher-pressure rating.

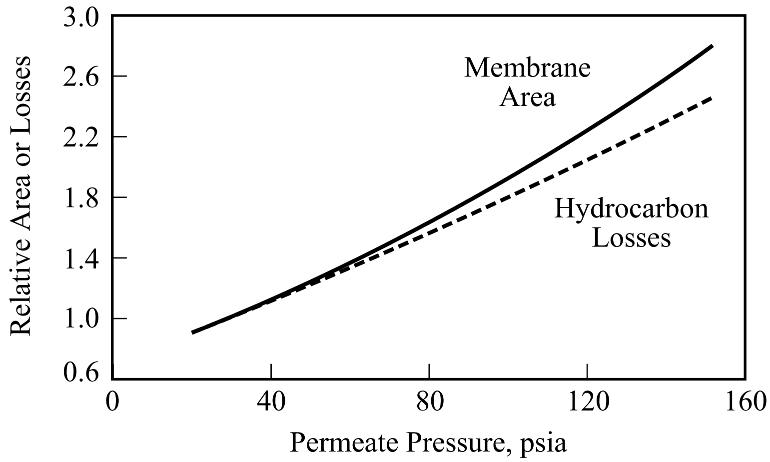
Permeate Pressure

The effect of permeate pressure is the opposite of the effect of feed pressure. The lower the permeate pressure, the higher the driving force and therefore the lower the membrane area requirement. Unlike feed pressure, however, permeate pressure has a strong effect on hydrocarbon losses (Figure 13).

The pressure difference across the membrane is not the only consideration. Detailed analysis shows that an equally important factor in system design is the pressure *ratio* across the membrane. This ratio is strongly affected by the permeate pressure. For example, a feed pressure of 90 bar and a permeate pressure of 3 bar produce a pressure ratio of 30. Decreasing the permeate pressure to 1 bar increases the pressure ratio to 90 and has a dramatic effect on system performance. For this reason, membrane design engineers try to achieve the lowest-possible permeate pressure. This need is an important consideration in deciding how to further process the permeate stream. For example, if it must be flared, then flare design must be optimized for low pressure drop. If the permeate gas is to be compressed, for example, to feed it to a second membrane

Figure 13

Effect of Permeate Pressure



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stage or reinject it into a well, the increased compressor power and size at low permeate pressures must be balanced against the reduced membrane area requirements.

CO_2 Removal

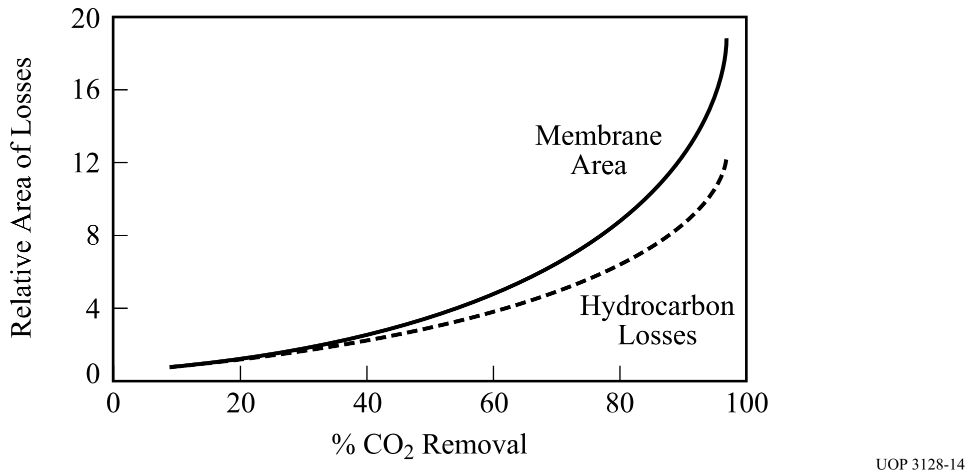
For a given sales-gas CO_2 specification, an increase in feed CO_2 increases membrane area requirement as well as hydrocarbon losses (more CO_2 must permeate, and so more hydrocarbons permeate). This is shown in Figure 14.

The membrane area requirement is determined by the percentage of CO_2 removal rather than the feed or sales-gas CO_2 specifications themselves. For example, a system for reducing a feed CO_2 content from 10 to 5% is similar in size to one reducing a feed from 50 to 30% or one reducing a feed from 1 to 0.5% ñ all have a CO_2 removal requirement of about 55%. This behavior is different from the way in which traditional CO_2 removal technologies operate. For these operations, a reduction in CO_2 from 3 to 0.1% does not require a much larger system than that required for a reduction from 3 to 1%. For a membrane system, the large difference in CO_2 removal (97 versus 70%) means that the system for 0.1% sales gas is about three times the size of the 1% system.

Traditional solvent- or adsorbent-based CO_2 removal technologies have the opposite limitation, that is, their size is driven by the absolute amount of CO_2 that must be removed. So a system for CO_2 removal from 50 to 30% is substantially larger than one reducing CO2 from 1.0 to 0.5%. For this reason, using membranes for bulk CO_2 removal and traditional technologies for meeting low CO_2 specifications makes a lot of sense. Depending on the application, either one or both of the technologies could be used.

Figure 14

Effect of CO_2 Removal



Changes in the feed CO_2 content of an existing membrane plant can be handled in a number of ways. The existing system can be used to produce a sales gas with higher CO_2 content. Alternatively, additional membrane area can be installed to meet the sales-gas CO_2 content, although with increased hydrocarbon losses. If heater capacity is available, the membranes can be operated at a higher temperature to also increase capacity. If an existing nonmembrane system must be debottlenecked, installing a bulk removal CO_2 removal system upstream of it makes good sense.

Other Design Considerations

Process conditions are not the only variables affecting the membrane system design. A variety of site-, country-, and company-specific factors also must be considered. Some of these factors are:

- **Location:** The location of the membrane system dictates a number of issues such as space and weight restrictions, level of automation, level of spares that should be available, and single versus multistage operation. Also, design codes for offshore and onshore locations are different and must be taken into account.
- **Environmental regulations:** These regulations dictate, for example, what can be done with the permeate gas. In some locations the permeate gas may be vented to the atmosphere. In other cases, the permeate may need to be flared either directly or catalytically.
- **Fuel requirements:** Fuel can be obtained upstream of the membrane system, downstream of the pretreatment system, downstream of the membrane, or from the recycle loop in multistage systems.

- **Design standards:** Design codes and standards vary from company to company. Some companies may require duplex lines, where others allow carbon steel. Some may specify maximum pipe velocities of 0.5 psi/100 ft, while others may allow up to 1.5. Even supposedly simple issues such as painting specifications can vary greatly from company to company and can add significant unexpected cost. All such items must be predetermined during the bidding stage to prevent costly modifications later.

Membrane Pretreatment

Proper pretreatment design is critical to the performance of all membrane systems. Improper pretreatment generally leads to performance decline rather than complete nonperformance.

Substances commonly found in natural gas streams that will lower the performance of CO_2 removal membranes include:

- **Liquids:** Liquids cause swelling of the membranes and destruction of membrane integrity.
- **Heavy hydrocarbons, approximately > C_{15}:** Significant levels of these compounds slowly coat the membrane surface, thus decreasing permeation rate.
- **Particulate material:** Particles can block the membrane flow area. The possibility of blockage is much lower for spiral-wound membranes than for hollow-fiber membranes, which have a low flow area. However, a long-term particle flow into any membrane could eventually block it.
- **Certain corrosion inhibitors and well additives:** Some corrosion inhibitors and well additives are destructive to the membrane, but others are safe. Membrane vendors should be consulted before either of these groups of compounds is introduced.

The pretreatment system must remove these compounds and must also ensure that liquids will not form within the membranes themselves.

Two effects may allow condensation within the membrane. First, the gas cools down, as a result of the Joule-Thomson effect, as it passes through the membrane. Second, because CO_2 and the lighter hydrocarbons permeate faster than the heavy hydrocarbons, the gas becomes heavier and therefore its dew point increases through the membrane. Condensation is prevented by achieving a predetermined dewpoint before the membrane and then heating the gas to provide a sufficient margin of superheat.

The pretreatment system must have a wide safety margin and be highly flexible to cope with unexpected circumstances. UOP's experience has shown that the heavy hydrocarbon content of a feed gas can vary widely from initial pre-start-up estimates and also from month to month during the plant's life. Large variations are seen even between different wells in the same area. A reliable pretreatment system must take this variation into account and must be able to protect the membranes against a wide range of contaminants.

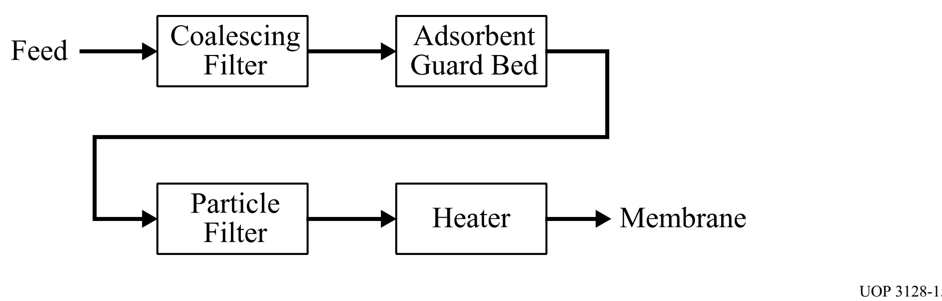
Traditional Pretreatment

The traditional pretreatment scheme for membrane systems used in CO_2 removal consists of the following equipment (Figure 15):

- Coalescing filter for liquid and mist elimination
- Nonregenerable adsorbent guard bed for trace contaminant removal
- Particle filter for dust removal after the adsorbent bed
- Heater for providing sufficient superheat to the gas

Figure 15

Traditional Membrane Pretreatment



Although this scheme is adequate for light, stable composition gases, it has the following limitations:

- The adsorbent bed is the only item removing heavy hydrocarbons. A sudden surge in heavy hydrocarbon content or heavier than initially estimated feed gas can saturate the adsorbent bed within days and render it useless. Because these beds are typically nonregenerable, they can become functional again only after the adsorbent has been replaced.
- Problems with the heater require that the whole membrane system be taken off-line, because the heater is the only item of equipment providing superheat.

Additions to Traditional Pretreatment

Various items of equipment are commonly added to the traditional pretreatment scheme to enhance its performance. The more common items are:

Chiller

A chiller may be included to reduce the dew point of the gas and also the heavy hydrocarbon content. However, because chilling does not completely remove heavy hydrocarbons, an adsorbent guard bed is still required. Furthermore, if deep chilling is necessary, then steps have to be taken to prevent hydrates from forming either by dehydrating the gas upstream or adding hydrate formation inhibitors. If inhibitors are added, then they may need to be removed downstream of the chiller because some inhibitors are damaging to the membrane.

Turboexpander

A turboexpander serves the same purpose as a chiller, but has the benefit of being a dry system. Turboexpanders are also smaller and lighter than a mechanical refrigeration system. A disadvantage is the net pressure loss, which must be taken up by the export compressor.

Glycol Unit

Glycol units are typically added upstream of a chiller to prevent hydrate formation or freeze-up. An adsorbent guard bed is still required for removing heavy hydrocarbons. This bed must be even larger than it would normally be because it must also remove the glycol carried over from the absorber vessels.

Need for Enhanced Pretreatment

For many membrane systems, traditional pretreatment is adequate. However, UOP's experience with a number of membrane systems has indicated the need for developing an enhanced pretreatment system that can better handle higher or fluctuating heavy-hydrocarbon levels.

A large Separex™ membrane system was installed in 1995 to process what was expected to be a light gas. The client had supplied an extended gas analysis, which has been verified by external test agencies. Based on this analysis, the system was supplied with a traditional pretreatment system, which consists of a coalescing filter, adsorbent guard bed, particle filter, and preheater.

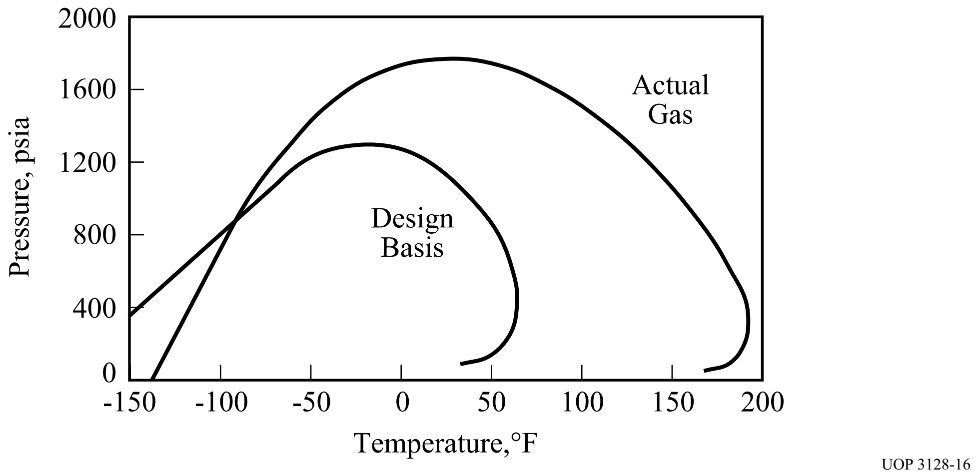
A short while after the system was started up, however, deterioration in membrane performance was observed, and UOP determined that the gas was significantly heavier than originally anticipated. Figure 16 shows phase envelopes for the design and actual gas analysis.

The pretreatment system did not have sufficient flexibility to handle such a wide departure from the design conditions. First, the adsorbent bed was fully saturated within a short time, leading to performance degradation. Second, the preheaters were not large enough to achieve feed temperatures that were much higher than designed. A standard way to handle a gas that is heavier than expected is to operate the membranes at a higher temperature. This temperature increase increases the margin between the gas dew point and operating temperature and thus prevents condensation in the membrane. In this case, the high temperature required could not be achieved by the installed heaters.

UOP proposed retrofitting with an enhanced pretreatment system. The client has this system under consideration but has not implemented it yet because well production is lower than expected. As a result, the heaters can raise the gas temperature enough to allow satisfactory performance.

Figure 16

Expected and Actual Phase Envelopes



ENHANCED PRETREATMENT

After considering a wide variety of options, UOP has devised an enhanced pretreatment scheme that is more suitable for cases where one or more of the following is expected:

- Wide variation in the feed gas content
- Significant amount of heavy hydrocarbons or other contaminants
- Feed gas that may be heavier than analyzed, based on the known information from nearby wells or other locations

UOP's enhanced pretreatment scheme is shown in Figure 17.

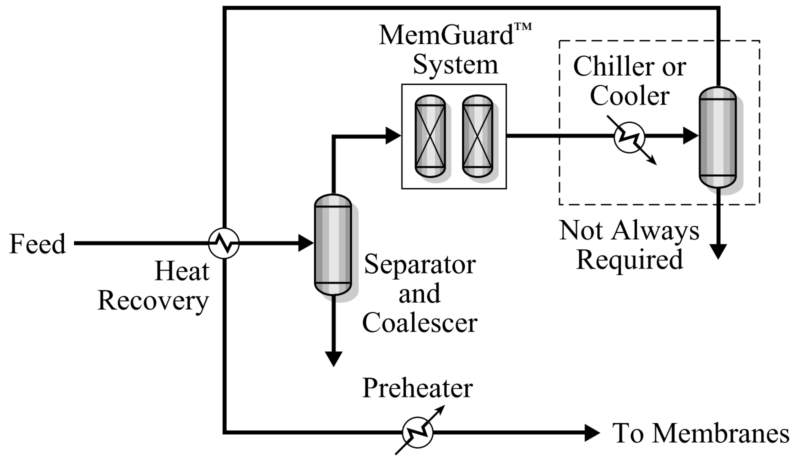
The feed gas is first cooled down in a heat recovery exchanger, and any condensate formed is removed in a separator and coalescer. The liquid-free gas then enters a regenerable adsorbent-based MemGuard™ system, where heavy hydrocarbon and other harmful components are *completely* removed. The contaminant-free gas passes through a particle filter before leaving the MemGuard system.

The MemGuard system has a major advantage in that water is removed along with the heavy hydrocarbons, and so no upstream dehydration is required. Mercury and other contaminants can also be removed in the MemGuard system.

In some cases, the MemGuard product gas is then cooled down in a cooler or chiller whose main purpose is to reduce the hydrocarbon dew point of the feed gas. Any condensate formed in

Figure 17

Enhanced Pretreatment Scheme



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the chiller is removed in a separator and the separator-outlet gas is routed to the feed cross exchanger. Here the gas cools down the system-feed gas and also obtains necessary superheat. Further superheat and control of membrane feed temperature are provided by a preheater.

The key benefits of UOP's enhanced pretreatment scheme are:

- **Complete removal of heavy hydrocarbons:** Unlike other pretreatment schemes, the absolute cutoff of heavy hydrocarbons is possible.
- **Regenerative system:** Because the MemGuard unit is a regenerative system, it is better able to handle fluctuations in the heavy hydrocarbon content of the feed gas than are traditional guard beds, which require frequent replacement of adsorbent material.
- **Reliability:** The MemGuard unit can be designed to operate satisfactorily even if one of its vessels is taken off-line. Critical items in the pretreatment system are usually spared so they can be serviced or maintained without shutting the system down.
- **Ability to cope with varying feed composition:** The cycle time of the MemGuard unit can be adjusted to provide efficient treatment of a wide variety of feed compositions and heavy hydrocarbon contents.
- **Efficiency:** A single MemGuard unit is able to provide a number of functions, such as removal of water, heavy hydrocarbons, and mercury, that would normally be provided by separate pieces of equipment. Heat recovery is implemented in the pretreatment scheme as well as within the MemGuard system itself.

UOP believes this enhanced pretreatment scheme is the most suitable one for the pretreatment requirements of large gas streams containing heavy hydrocarbons in the C_{10} to C_{35} range. Even though membrane systems cost only a fraction of the cost of a complete natural gas plant, they are the heart of the system. If pretreatment is inadequate, the membrane deteriorates and production declines.

Extensive testing has proven the enhanced pretreatment concept, and it is currently operating in two different customer locations. A third unit is currently under construction at an offshore location and is expected to start up in the fourth quarter of 1998.

Because the pretreatment system already includes many unit operations that are ordinarily included in a gas plant, for example dehydration and dew-point control, membrane companies must be brought into a project early in its design. This collaboration prevents unnecessary reworking of the flow scheme later on and may also allow significant cost savings on the part of the gas production company.

Advantages of Membrane Systems

Membrane systems have major advantages over more-traditional methods of CO_2 removal:

- **Lower capital cost:** Membrane systems are skid mounted, except for the larger pretreatment vessels, and so the scope, cost, and time taken for site preparation are minimal. Therefore, installation costs are significantly lower than alternative technologies, especially for remote areas. Furthermore, membrane units do not require the additional facilities, such as solvent storage and water treatment, needed by other processes.
- **Lower operating costs:** The only major operating cost for single-stage membrane systems is membrane replacement. This cost is significantly lower than the solvent replacement and energy costs associated with traditional technologies. The improvements in membrane and pretreatment design allow a longer useful membrane life, which further reduces operating costs. The energy costs of multistage systems with large recycle compressors are usually comparable to those for traditional technologies.
- **Deferred capital investment:** Often, contracted sales-gas flow rates increase over time, as more wells are brought on-line. With traditional technologies, the system design needs to take this later production into account immediately, and so the majority of the equipment is installed before it is even needed. The modular nature of membrane systems means that only the membranes that are needed at start-up need be installed. The rest can be added, either into existing tubes or in new skids, only when they are required. Even on offshore platforms, where all space requirements must be accounted for, space can be left for expansion skids rather than having to install them at the start of the project.
- **Operational simplicity and high reliability:** Because single-stage membrane systems have no moving parts, they have almost no unscheduled downtime and are extremely

simple to operate. They can operate unattended for long periods, provided that external upsets, such as well shutdowns, do not occur. Items in the pretreatment system that could cause downtime, such as filter coalescers, are usually spared so that production can continue while the item is under maintenance. The addition of a recycle compressor adds some complexity to the system but still much less than with a solvent or adsorbent-based technology. Multistage systems can be operated at full capacity as single-stage systems when the recycle compressor is down, although hydrocarbon losses will increase. The start-up, operation, and shutdown of a complex multistage membrane system can be automated so that all important functions are initiated from a control room with minimal staffing.

- **Good weight and space efficiency:** Skid construction can be optimized to the space available, and multiple elements can be inserted into tubes to increase packing density. This space efficiency is especially important for offshore environments, where deck area is at a premium, and is the reason why so many new offshore developments have chosen to use membranes for acid gas removal. Figure 18 illustrates the space efficiency of membrane systems. The membrane unit in the lower left corner replaced all the amine and glycol plant equipment shown in the rest of the picture.

- **Adaptability:** Because membrane area is dictated by the percentage of CO_2 removal rather than absolute CO_2 removal, small variations in feed CO_2 content hardly change the sales-gas CO_2 specification. For example, a system designed for 10% down to 3% CO_2 removal produces a 3.5% product from a 12% feed gas, and a 5% product from a 15% feed gas. By adjusting process parameters such as operating temperature, the designer can further reduce the sales-gas CO_2 content.

- **High turndown:** The modular nature of membrane systems means that low turndown ratios, to 10% of the design capacity or lower, can be achieved. Turnup and turndown increments can be set at whatever level is required during the design phase.

- **Design efficiency:** The membrane and pretreatment systems integrate a number of operations, such as dehydration, CO_2 and H_2S removal, dew-point control, and mercury removal. Traditional CO_2 removal technologies require all of these operations as separate processes and may also require additional dehydration because some technologies saturate the product stream with water.

- **Power generation:** The permeate gas from membrane systems can be used to provide fuel gas for power generation, either for a recycle compressor or other equipment. This virtually free fuel production is especially useful in membrane-amine hybrid systems, where the membrane system provides all the energy needs of the amine system.

- **Ideal for debottlenecking:** Because expanding solvent or adsorbent-based CO_2 removal plants without adding additional trains is difficult, an ideal solution is to use membranes for bulk acid gas removal and leave the existing plant for final cleanup. An additional advantage is that the permeate gas from the membrane system can often be used as fuel for the existing plant, thus avoiding significant increase in hydrocarbon losses.

- **Environmentally friendly:** Membrane systems do not involve the periodic removal and handling of spent solvents or adsorbents. Permeate gases can be flared, used as fuel, or reinjected into the well. Items that do need disposal, such as spent membrane elements, can be incinerated.
- **Ideal for remote locations:** Many of the factors mentioned above make membrane systems a highly desirable technology for remote locations, where spare parts are rare and labor unskilled. Furthermore, solvents storage and trucking, water supply, power generation (unless a multistage system is installed), or extensive infrastructure are not required.

Figure 18

Size Comparison of Membrane and Amine Systems

Experience

UOP's membrane systems have been in commercial use for more than 17 years in the natural gas and petroleum refining industries. More than 80 membrane units have been installed by UOP during this time.

Pakistan

The two largest CO_2 removal membrane systems in the world are the Separex™ units installed in Qadirpur and Kadanwari, in Pakistan. Both of these plants specified membranes as the CO_2 removal technology to be used, because of their simplicity, ease of use, and high reliability, essential attributes for remotely located plants. These criteria have all been met, and significant lessons have been learned. For example, a major impetus in the development of UOP's advanced pretreatment system came from experiences with the Kadanwari unit.

Kadanwari

When this facility started up in 1995, it was the largest membrane-based natural gas processing plant in the world. It has been in operation for more than three years using UOP's Separex cellulose acetate membranes.

The Kadanwari system is a two-stage unit designed to treat 210 MM SCFD of feed gas at 90 bar. The CO_2 content is reduced from 12 to less than 3%.

The pretreatment system for this plant was designed for a light gas with minimal C_{10}+ content and a dew point about 50°F, as provided in a customer-supplied gas analysis. After start-up, an analysis of the feed stream indicated a significant heavy hydrocarbon content, including C_{30}s, with a dew point above 125°F. As a result, UOP proposed enhanced pretreatment. Installation has been delayed because well production has been lower than expected. However, because production is expected to soon increase, the client has the enhanced pretreatment design under consideration.

Qadirpur

The Separex membrane system in Qadirpur, Pakistan, is the largest membrane-based natural gas plant in the world. It is designed to process 265 MM SCFD of natural gas at 59 bar. The CO_2 content is reduced from 6.5% to less than 2%. The unit was designed to also provide gas dehydration to pipeline specifications. The owner has plans to expand the system to approximately 400 MM SCFD of processing capacity within the next year.

The Qadirpur membrane system was designed and constructed in two 50% membrane trains. Each membrane train consists of a conventional pretreatment section and a membrane section. The pretreatment section has filter coalescers, guard vessels, and particle filters. Membrane feed heaters are also included in this design to maintain stable membrane process conditions. Figure 19 shows a view of the Qadirpur system. To give an idea of the size of the system, a person in the upper left corner of the picture is circled.

This plant started up in 1995 and has been in operation for almost three years. UOP provided on site assistance from the loading of the membrane elements through start-up and remained until the customer was fully comfortable with the equipment. The plant continues to operate routinely, processing all gas available unless limited by pipeline demand.

The Qadirpur system is proof of the ruggedness of UOP's Separex membrane systems and cellulose acetate membranes. The feed gas contains a significant heavy hydrocarbon content as well as polynuclear aromatics, which are known to damage other membranes. In spite of these contaminants, the unit is operating at design capacity.

Figure 19

Qadirpur Membrane System

Taiwan

UOP installed a membrane system in Taiwan in 1996 with great success. This unit was the first membrane system that used UOP's enhanced pretreatment technology for removal of C_{10}+ heavy hydrocarbons. The feed gas flow rate is 30 MM SCFD at 42 bar. The CO_2 is reduced from 12 to 3%. This system also uses UOP's polyimide-based hollow-fiber elements, instead of the more widely used cellulose acetate spiral-wound membranes.

Mexico

UOP recently installed a membrane system in an enhanced oil recovery (EOR) facility in Mexico. The system processes 120 MM SCFD of inlet gas containing 70% CO_2. The purified CO_2 gas stream contains 93% CO_2 and is reinjected. The hydrocarbon product contains 5% CO_2 and is transported to a nearby gas plant for further processing. Figure 20 shows the membrane system with the pretreatment vessels in the foreground and membrane skids behind them.

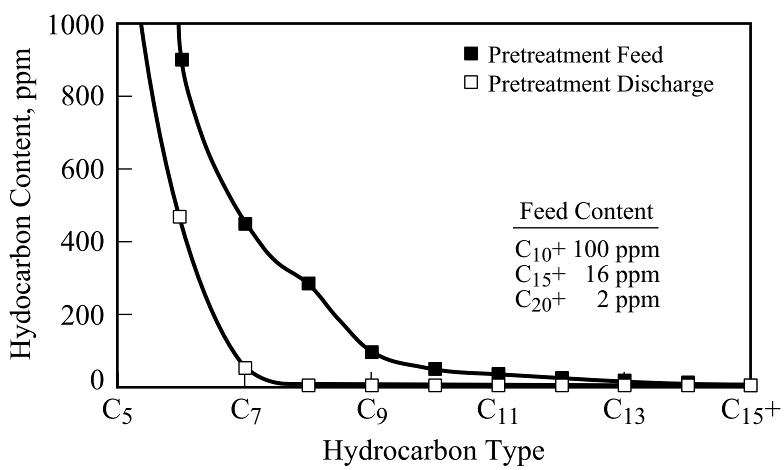
The membrane system uses a version of UOP's advanced pretreatment system and was successfully started up in July 1997. It continues to meet product specifications. Recent gas analysis has shown that the pretreatment system continues to exceed expectations. Figure 21 illustrates recent

Figure 20

Mexico System

Figure 21

Pretreatment Performance



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gas analyses before and after the pretreatment system. The feed gas contained 934 ppm C_7+ compounds, which were reduced to 55 ppm after the pretreatment. The C_9+ content was completely removed.

Salam & Tarek, Egypt

Separex membrane systems soon will be installed in the remote areas of Salam and Tarek, Egypt. These systems consist of three identical units, two for Salam and one for Tarek. Each system is a two-stage unit treating about 100 MM SCFD of natural gas at 65 bar. The CO_2 content will be reduced from about 6 to less than 3%.

Because this application requires about 50% CO_2 removal, it is on the borderline between requiring a one- or two-stage process. The decision was swayed by the client's requirement that the membrane system produce fuel for the whole plant. The fuel source is the first-stage permeate gas, which must be compressed to fuel-supply pressure. Because only marginally more power is needed to compress the rest of the permeate gas, treating this portion in a second stage and recycling it to the first stage makes economic sense.

Reciprocating units were selected for the recycle compressors because they are less expensive, are easier to maintain, and have more readily available spare parts than centrifugal compressors. These features are essential considering the remote location of the plants.

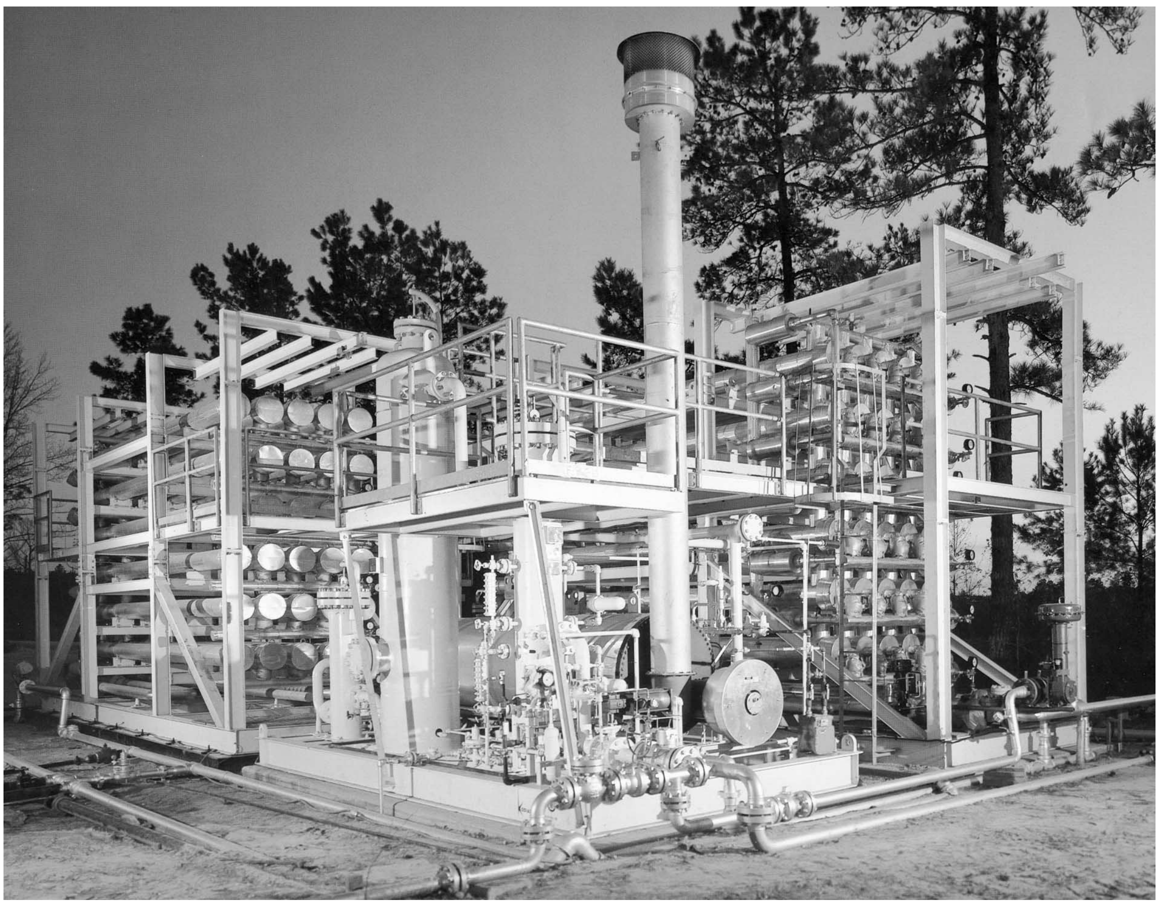
The membrane units are provided with standard pretreatment only because the gas passes through dehydration and dew-point control units before entering the membrane system pretreatment. Therefore, a heavy hydrocarbon content or condensation in the membranes is not a danger. This arrangement came about because UOP was involved in the project in the early developmental stages. As a result, UOP could advise the client on how to arrange their process to best suit all involved. This predesign communication did not occur for the Kadanwari system. As a result, dew-point control was installed downstream of the membrane and so could not be used to protect the membrane.

West Texas, USA

Another example of UOP's broad capabilities is a unit that UOP recently installed in West Texas. This membrane system processes 30 MM SCFD of 30% CO_2 feed gas at an operating pressure of 42 bar. The product CO_2 specification is 10%. The membrane system product gas provides fuel for overall plant operations. This system is similar to the second membrane stage designed for both the Salam and Tarek locations.

Conclusions

Membrane systems are a solid and proven addition to the range of technologies for the removal of CO_2. With correct pretreatment design, they are extremely reliable, efficient, and ideally suited to installation in remote regions. Continuing enhancements in membranes, membrane systems, and membrane pretreatment makes membranes an even more natural choice in the future, especially for applications requiring higher levels of CO_2 removal.



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