CONTINUED DEVELOPMENT OF GAS SEPARATION MEMBRANES FOR HIGHLY SOUR SERVICE

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INTRODUCTION

The traditional gas processing approach for sour gas is to utilize solvent systems for natural gas cleanup and Claus technology for H₂S conversion to elemental sulfur. While this technology is well known and proven, it can be difficult to operate and uneconomic for highly sour gasses as the operating costs are directly related to the amount of sulfur in the feed gas. Moreover, the production of sulfur is a nuisance as there are insufficient market resources to absorb the large volumes of elemental sulfur now on the market from natural gas treating applications. Today major sour gas production areas are building ever-larger sulfur mountains. New technologies that envisage a more sustainable future are needed.

Membranes have become an established technology for carbon dioxide removal since their first use in this application in 1981. This technology is widely practiced for the treating of pipeline gas, enhanced oil recovery (EOR), bulk removal of CO₂ on offshore platforms, and for upgrading of biogas for commercial sale. Membranes are used for the co-removal of CO₂ and H₂S, but only when the sulfur levels are relatively low. 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 CO₂ removal technologies have been quick to acquire or develop membrane-based processes to supplement their older processing routes. In some cases, the most-economical approach is to combine membranes with existing technologies. Membranes are also used to debottleneck existing solvent-based plants.

UOP has developed polymeric membranes that can be used for bulk removal of H₂S from natural gas even at very high H₂S concentrations and at high operating pressures. This approach allows for more sustainable development of new sour gas fields or for retrofitting into existing applications. The membrane system can be used to make a large bulk cut of the acid gases, typically in the 70-90% reduction range, then final pipeline specifications

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can be met in a traditional amine process. The permeate gas from the membrane system can ideally be re-injected, as opposed to being converted to elemental sulfur and stored onsite. Significant reductions in capital and operating costs, as well as sulfur production costs, can be achieved through this new approach.

This paper summarizes the principles involved in CO₂ and bulk H₂S removal by membranes, design considerations, UOP’s experiences in large natural gas processing plants, and the recent innovations by UOP’s Gas Processing group on H₂S removal in natural gas sweetening.

THE NEED FOR CO₂ AND H₂S REMOVAL

Carbon dioxide and hydrogen sulfide, which fall into the category of acid gases, are commonly found in natural gas streams at levels as high as 80%. In combination with water, they are highly corrosive and can rapidly destroy pipelines and equipment unless they are partially removed or exotic and expensive materials of construction are used. Hydrogen sulfide is toxic and at relatively modest levels can be life threatening. Carbon dioxide also reduces the heating value of a natural gas stream and wastes pipeline capacity. In LNG plants, CO₂ 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 UOP’s Benfield™ process (hot potassium carbonate solutions) and UOP’s Amine Guard-FS™ process (formulated solvents); cryogenic processes; adsorption processes, such as pressure swing adsorption (PSA), thermal swing adsorption (TSA) and sulfur scavengers; 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, high H₂S and CO₂ contents, or are in remote locations. Membranes have been widely used in two main CO₂ removal applications: natural gas sweetening and enhanced oil recovery (EOR). 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. Currently, the only commercially viable membranes used for CO₂ removal are polymer based, for example, cellulose acetate, polyimides, polyamides, polysulfone, polycarbonates, and polyetherimide. The membrane does not operate as a filter, where small molecules are separated from larger ones through a medium with pores, rather, it separates based on how well different compounds dissolve into the membrane and diffuse through it.
The membranes are manufactured in flat sheets consisting of an extremely thin nonporous layer mounted on a much-thicker and highly porous layer of the same material, providing mechanical strength. The flat sheets are combined into a spiral-wound element (Figure 1). Feed gas enters along the side of the membrane and passes through the feed spacers. As the gas travels between membrane sheets, CO₂, H₂S, and H₂O permeate through the membrane and are collected in the permeate tube. The driving force for transport is the high-feed and low-permeate pressures. The gas on the feed side that does not permeate leaves through the side of the element opposite the feed position. Once the membranes have been manufactured into elements, six to 12 elements are joined together and inserted into a tube. Multiple tubes are mounted on skids in a horizontal orientation (Figure 2).

In high H₂S applications, most polymers have been shown to have very little resistance to H₂S plasticization (“softening” of the membrane) and as a consequence can only be used at very low H₂S partial pressure limits. UOP’s cellulose acetate membranes in contrast, have been shown to be applicable at extreme H₂S partial pressure conditions. It is these membranes that have been utilized in the testing to determine the limits of membrane performance in high H₂S applications.

**Figure 1 - Spiral Wound Membrane Element**
PROCESSING SCHEME

The simplest membrane processing scheme is a one-stage flow scheme: A feed gas is separated into a permeate stream rich in acid gas and a hydrocarbon-rich residual stream (Figure 3). In high H₂S removal applications, hydrocarbons permeating with the acid gases may be re-injected and therefore are not lost to future gas sales. If re-injection is not possible then multistage systems can be used to achieve higher hydrocarbon recoveries. Figure 4 shows a two-stage design where the first-stage permeate is compressed and processed in a second membrane stage.
**Membrane Pretreatment**

Proper pretreatment design is critical to the performance of all membrane systems. Substances commonly found in natural gas streams that will lower the performance of CO₂ and H₂S removal membranes include liquids, heavy hydrocarbons (approximately > C₁₅), particulates, as well as certain corrosion inhibitors and well additives.

The traditional pretreatment scheme for membrane systems used in acid gas removal is shown in Figure 5. For many membrane systems, traditional pretreatment is adequate.

![Figure 5 - Traditional Membrane Pretreatment](image)

For systems with higher or fluctuating heavy-hydrocarbon levels in the feed gas, UOP has developed an enhanced pretreatment system. The UOP MemGuard™ system is a regenerative system that can provide an absolute cutoff of heavy hydrocarbons. It is better able to handle fluctuations in heavy hydrocarbon content and has a major advantage in that water is removed along with the heavy hydrocarbons, so no upstream dehydration is required. Mercury and other contaminants can also be removed in this system.

UOP believes this enhanced pretreatment scheme is the most suitable one for the pretreatment requirements of large gas streams containing heavy hydrocarbons in the C₁₀ to C₃₅ range. Extensive testing has proven the enhanced pretreatment concept. Currently, 12 world scale commercial installations are in operation with two more units under construction. MemGuard pretreatment systems have been used both at onshore and offshore installations.

**Advantages of Membrane Systems**

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

- **Lower capital cost:** Membrane systems are skid mounted and so the scope, cost, and time taken for site preparation are minimal. Installation costs are significantly lower than alternative technologies, especially for remote areas. Furthermore, no additional facilities for solvent storage and water treatment, needed by other processes, are required.
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.

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 of time. 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.

Good weight and space efficiency: Skid construction can be optimized to the space available. 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 6 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 acid gas removal rather than absolute acid gas removal, small variations in feed acid gas content hardly change the sales-gas acid gas specification. For example, a system designed for 10% down to 3% acid gas removal produces a 3.5% product from a 12% feed gas, and a 5% product from a 15% feed gas.

High turndown: The modular nature of membrane systems means that low turndown ratios, to 10% of the design capacity or lower, can be achieved.

Design efficiency: The membrane and pretreatment systems integrate a number of operations, such as dehydration, CO₂ and H₂S removal, dew-point control and mercury removal. Traditional acid gas 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.

- **Ideal for debottlenecking**: Because expanding solvent- or adsorbent-based acid gas 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 re-injected 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, or extensive infrastructure, are not required.

- **Re-injection optimizations**: Since the permeate stream from the membrane system can be operated at elevated pressures, it is possible to further optimize the capex/opex parameters surrounding the re-injection compression train.

**Figure 6 - Size Comparison of Membrane and Amine Systems**
EXPERIENCE

UOP’s membrane systems have been in commercial use for more than 20 years in the natural gas and petroleum refining industries. More than 90 membrane units have been installed by UOP during that time.

PAKISTAN

Two of the largest land-based CO₂ removal membrane systems in the world are the UOP membrane units installed in Qadirpur and Kadanwari, Pakistan. Both of these plants specified membranes as the CO₂ removal technology after a rigorous comparison against solvent technologies because of their simplicity, ease of use, and high reliability – essential attributes for remotely located plants.

Kadanwari

When this facility started up in 1995, it was the largest membrane-based natural gas processing plant in the world. It has now been in operation for more than twelve years using UOP cellulose acetate membranes. The system uses a two-stage flow scheme designed to treat 210MMscfd of feed gas at 1305psia. The CO₂ content is reduced from 12% to less than 3%.

The system was originally designed for a light feed gas with standard pretreatment. After start up, the feed gas deviated significantly from the original design specification. After seven years of operation using standard pretreatment, the membrane system was retrofitted with a MemGuard pretreatment system to shift the phase envelope and allow operating temperatures at or below the initial design. Along with the regenerative pretreatment system, new elements were installed and since then, the plant production exceeds the design production capacity of 210MMscfd feed gas by 15%.

Qadirpur

The UOP membrane system in Qadirpur, Pakistan, is currently the largest land-based membrane natural gas plant in the world. It was originally designed to treat 265MMscfd of natural gas at 855psia. The CO₂ content is reduced from 6.5% to less than 2%. The original Qadirpur membrane system was designed in two 50% membrane trains, each train consisting of a conventional pretreatment section and a membrane section.

This plant started up in 1995 and has been in operation continuously for twelve years. The Qadirpur system is proof of the ruggedness of UOP membrane systems and cellulose acetate membranes. The feed gas contained a significant heavy hydrocarbon content as well as polynuclear aromatics, which are known to damage other membranes. In spite of these contaminants, the unit has been operating at design capacity.

An upgrade of the Qadirpur plant was successfully started up in 2003. The plant capacity was increased from 265MMscfd to 545MMscfd feed gas. The Qadirpur membrane plant was retrofitted with a chiller system and a regenerative MemGuard pretreatment system to
allow colder operation. The compression system was revamped and high performance membrane elements installed in the existing membrane skids. The result was an expansion of the plant that more than doubled its capacity without the requirement of additional recycle compressors and only 30% additional membrane tube area. UOP’s continued development of advanced membranes allowed very significant cost savings to the customer for this expansion.

Currently, the plant is being expanded to increase its treating capacity to 694MMscfd.

**MEXICO**

UOP installed a membrane system in an EOR facility in Mexico in 1997. The system is designed to treat 120MMscfd of inlet gas containing 80% CO₂. The purified CO₂ gas stream contains 93% CO₂ and is re-injected. The hydrocarbon product contains 5% CO₂ and is transported to a nearby gas plant for further processing.

Figure 8 shows the membrane system with the MemGuard pretreatment system in the foreground and membrane skids behind them. MemGuard pretreatment is essential because the feed gas is oil-associated, so has significant heavy hydrocarbon content. Regular gas analysis has shown that the pretreatment system exceeds expectations, removing the C₉₊ content completely.

**SALAM & TAREK, EGYPT**

UOP’s Separex™ membrane systems were installed in the remote areas of Salam and Tarek, Egypt in 1999. These systems consist of three identical units, two for Salam and one for Tarek. Each system is a two-stage unit treating about 100MMscfd of natural gas at 700psia. The CO₂ content is reduced from about 6% to less than 3%.

Currently, the Salam plant is being expanded with two additional trains treating a feed gas with 9 to 12% CO₂ to less than 3% CO₂. This expansion will bring the total treating capacity for the Salam and Tarek plants to 564MMscfd feed gas.

**WEST TEXAS, U.S.A**

Another example of UOP’s broad capabilities is a unit that UOP installed in West Texas in 1993. Although it processes a relatively small amount of gas (10MMscfd), both the CO₂ content and operating pressure are relatively high at 60% and 1100 psia respectively. This system is the highest CO₂ partial pressure operating membrane system in the world and is proof that UOP’s membranes can withstand high acid gas concentrations. Furthermore, element life has been very good with less than one membrane load change out since 1993.
**RECENT PROJECTS**

The three most recent UOP membrane systems are:

**Indonesia**

A hybrid system operating at 750psia, processing 245MMscfd of 40% CO₂ gas down to 20% in the membrane and then down to 8% in a traditional solvent system. The unit was successfully started up in 2006.

**Offshore Thailand**

This will be an offshore unit in Thailand processing 530MMscfd of 34% CO₂ gas down to 12% at 860psia. This unit is under construction, start-up in 2008.

**Offshore Malaysia**

Lastly, the world’s largest membrane unit, either offshore or onshore, is installed offshore Malaysia, processing 680MMscfd of gas from 45% down to 6%. It incorporates production of NGLs downstream of the membrane to reduce refrigeration duty and stabilization equipment size. The use of UOP’s advanced membranes and pretreatment system allowed for significant cost, weight and layout savings versus competitor offerings. First gas in the unit was in March 2007.

**Figure 7 - Kadanwari Membrane System**  **Figure 8 - Mexico System**
COMMERCIAL H₂S EXPERIENCE

Membrane systems in natural gas service are currently used for the co-removal of CO₂ and H₂S, when the sulfur levels are relatively low. The above references have low to medium H₂S concentrations in the feed gas:

- Pakistan, Kadanwari: 24vppm H₂S
- Pakistan Qadirpur: 60vppm H₂S
- Mexico: 4600vppm H₂S
- USA, West Texas: 2.8% H₂S

UOP H₂S MEMBRANES

UOP LLC has been developing membranes for the large scale treatment of highly sour natural gas streams. Existing membrane materials in some cases can be used for high partial pressures of H₂S, though care must be taken to make sure that all components in the membrane system are compatible with the application.

Pilot plant testing has successfully been completed for the UOP membranes for a very wide range of operating conditions:

- Feed Pressure: 500 - 1300psig
- Permeate pressure: 32psig
- Temperature: 72 - 140°F
- CO₂: 4.8 - 9.5%
- H₂S: 7.6 - 18.9%

The pilot plant testing has allowed to identify the best suited membrane material and to demonstrate that the membrane properties are stable in H₂S service. The membrane properties, permeability and selectivity have been accurately measured.

CASE STUDY

One of the cases that UOP has investigated extensively is an offshore gas reservoir with about 500MMscfd, 15% H₂S, 4% CO₂ and 1350psia feed pressure.

Traditional Gas Processing would be to send the highly sour gas onshore, use a solvent system to remove the H₂S and then a Claus plant to convert the H₂S into elemental sulfur. Dehydration to pipeline specification is then required, and possibly the use of turbo/expander technology for ethane/LPG recovery. The production of sulfur (10⁶ tons S/year) is a nuisance as there is insufficient market resource to adsorb the large volume of elemental sulfur.

A more suitable approach for today would be to place an offshore membrane unit in front of the traditional equipment (onshore). The membrane system can be used to make a large
bulk cut of the acid gases, typically in the 90% reduction range, then final pipeline specifications can be met in a traditional amine process. The permeate gas from the membrane system is ideally re-injected, as opposed to converted to elemental sulfur and stored onsite. The load on the amine and Claus plants is reduced by a factor of ten which eliminates the need for multiple amine and Claus trains. The membrane system is smaller in size and significantly less costly than the additional amine/Claus equipment. Finally, the cost of the pipeline is reduced. Significant reductions in capex, opex and coincidental sulfur production can be achieved through this new approach.

Figure 9 provides some details on the bulk H₂S removal case. At H₂S removal ratios of 70 to 90%, the graph indicates hydrocarbon slippage of less than 10% (the hydrocarbon slippage is not considered a loss if the acid gas is re-injected into the same formation), the membrane permeate is high in H₂S (50-60%), while the membrane system size expressed in relative area is low (1).
CONCLUSIONS

Membrane systems are a solid and proven addition to the range of technologies for the removal of acid gases. 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 H₂S removal. Pilot plant testing has been completed at levels approaching 1400psia (100 bar) and 20% H₂S.

This new approach will allow asset owners to develop highly sour gas fields at lower cost and will minimize the production of elemental sulfur where permeate re-injection is possible. This new technology from UOP is the largest change to sour gas treating in many years.