MEMBRANE BASED CO, REMOVAL FOR OIL AND GAS APPLICATIONS

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INTRODUCTION

Although membrane separation is perceived as new technology, membrane based CO_2 removal has been commercially practiced for more than 15 years. The first commercial membrane based CO, removal system was the SACROC facility in west Texas. The system was commissioned in 1983. Over several expansions, the capacity of the facility has quadrupled and continues to provide a cost effective solution. This installation represents a true success story for membranes. Slowly but surely, membranes are becoming the preferred technology for CO, recovery in EOR applications and for bulk removal of CO, for offshore natural gas treating,. This is largely because of their operational simplicity, lower capital cost, and environmental benefits relative to competitive technologies for acid gas removal.

BASIC MEMBRANE TECHNOLOGY

A membrane is defined as a barrier, which separates two phases and restricts the transport of various components in a selective manner (Figure 1). A membrane separation system separates an influent stream into two effluent streams known as the permeate and the non-permeate. In this case, the non-permeate is a C02-depleted hydrocarbon product and the permeate is a CO2-enriched stream. For penetrants to traverse the membrane, a gradient in chemical potential must exist. For gases, the chemical potential gradient is often approximated as a difference in partial pressure between the feed (high partial pressure) and the permeate (low partial pressure). For liquids, the concentration difference between the feed stream and the permeate stream is most often used to approximate the chemical potential gradient.

Independent of whether the components are a gas or a liquid, transport (permeation) through a solution diffusion membrane consists of three consecutive steps:

1. Sorption (both absorption and adsorption) of the component from the liquid feed into the membrane material.
2. Diffusion of the dissolved component down the chemical potential gradient through the membrane matrix.
3. Desorption of the component from the membrane into the permeate stream.

The permeation rate for solution-diffusion membrane is the product of the solubility related term and a mobility related term. Very simply, the solubility term is related to the amount of the penetrant is in the membrane while the mobility term is related to how fast the penetrant moves through the membrane matrix. The product of these two parameters is the amount that gets through the membrane (permeates). Figure 2 shows relative permeation rates for various molecules encountered in oil and gas applications

For ideal systems, the solubility related term is a constant solubility coefficient and the mobility related term is a constant diffusion coefficient. For these systems the permeability is a constant and is the product of the solubility coefficient and the diffusion coefficient.

To a first approximation the solubility coefficient is determined by the condensability of the sorbate. Simple physical measures of condensability such as normal boiling point, critical temperature or lenard–jones potential well depth correlate well with the solubility coefficient. More condensable components have higher solubility coefficients than less condensable components. For solution-diffusion membranes, diffusion occurs by the activated jump of the penetrant from one molecular scale berth within the dense polymer matrix to another. The larger the molecule the higher the activation energy required for the diffusional jump and the less probable the jump will occur. The diffusivity is highly correlated with the molecular size of the penetrant. Larger molecules have lower diffusion coefficients than small molecules.

DESCRIPTION OF MEMBRANE ELEMENT AND APPLICATION IN GAS SEPARATION

The heart of the membrane module is an asymmetric hollow fiber (Figure 3). The geometry of the fiber is similar to that of a long, thin straw. The fiber is integrally skinned with an asymmetric density gradient across the wall of the hollow fiber. The outside wall of the fiber (0.05 –0.10 um) is dense polymer. A density gradient of porous polymer extends from the

outer skin to the inner wall. Porosity of the fiber increases from the outside wall to the lumen. The inner wall of the fiber is porous.

The dense skin of the hollow fiber performs the separation. Separation performance is an intrinsic property of the polymer used to fabricate the hollow fiber. While the polymer used to fabricate the fiber determines the intrinsic permeability and selectivity of the fiber, permeance (productivity) of the fiber is inversely proportional to the thickness of the dense outer layer. The porous sublayer extending to the inner wall determines the ability of the fiber to withstand the large pressure differentials that exist between the feed and permeate streams. Ideally, this region has negligible impact on separation performance.

Figure 4 shows the incorporation of the asymmetric hollow fiber membrane into a typical membrane module. The membrane module is manufactured by grouping thousands of fibers together in a cylindrical arrangement around a central core tube. Each end of the cylindrical fiber element is sealed with an epoxy resin ring. This tubesheet provides a gas tight seal between the outside wall of the fibers (feed) and the fiber bore (permeate). This arrangement is analogous to a shell and tube heat exchanger.

For this module, the gas or liquid feed is placed under pressure on the shell side or outside portion of the fiber. The bore of the hollow fiber is controlled at a lower pressure. The difference in partial pressure between the exterior feed stream and the interior permeate gas drives components across the membrane wall. Because CO, has a higher permeability than the hydrocarbon components, CO, is selectively removed from the feed stream as the feed travels radially inward across the fiber bundle into the core tube-. CO,-depleted product gas is collected in the central core tube. **A** low pressure, CO2-rich permeate stream is collected in the bore of the fiber. Using o-ring seals, the permeate stream is collected at each end of the module.

In may applications, there is a potential for the hydrocarbon dewpoint to be reached due to C02 removal. Certain membrane manufacturers require the feed to be superheated to a temperature where no condensation occurs. This can be a function of either the module configuration (spiral wound module vs. hollow fiber) or membrane material consideration membranes (hydrophobic vs. hydrophilic membrane material). Vertically mounted hollow fiber based separators readily shed hydrocarbon liquids produced as a result of C02 removal. Liquid hydrocarbons tend to accumulate in the narrow passages of spiral flat sheet spiral wound modules. Even is the module configuration is capable of handling produced liquids, selection of membrane materials is also important. In general, hydrophilic membranes are largely unaffected by the presence of aliphatic hydrocarbons/carbon dioxide mixtures. The combination of liquid hydrocarbons and C02 negatively impact the performance of hydrophobic membrane materials.

MEMBRANE MODULE OPERATION AND PERFORMANCE

Figure 4 illustrates a radial crossflow membrane element. In this idealized element, the composition varies from the feed composition to the non-permeat composition. In addition, a pressure gradient and a composition gradient exists down the bore of the fiber. To accurately model the performance of the device, a model that incorporates the impact of the pressure and compositional changes on local component flux though the membrane element is required. Finite element simulations, which subdivide the module into a multitude of radial and the longitudinal segments, are used for this purpose. Details of these models are beyond the scope of this article; however, results from these simulations are useful for illustrating the operational aspects of membrane separators.

Figure 5 illustrate the simulated performance of a radial crossflow module. For this simulation it is assumed that the feedstream contains 40% CO,. The CO_2/hydrocarbon separation factor of the membrane is 30. The pressure ratio (feed pressure divided by permeate-pressure) is 20. This figure shows the impact of increasing theta (permeate flow divided by feed flow) on permeate purity, non-permeate purity and capacity of the element.

The figure clearly shows that the membrane separator is not a perfect separator. Even when a vanishingly low percentage of the feed is removed as permeate, the permeate stream is not pure. For the condition listed above, a maximum permeate purity of –94% is achievable. This value is determined by the CO_2/hydrocarbon selectivity of the membrane. **A** higher selectivity would produce higher CO, purity and a lower selectivity would produce a lower purity permeate stream. Commercial application of the membrane would occur at higher permeate to feed flow (theta) conditions. For example, at a theta of 0.3 (30% of the feed collected as permeate), the permeate stream is 89.9% CO, and the hydrocarbon rich stream is 27.1% CO_2. This represents 67.4 % removal of the inlet CO, from the feed stream. The hydrocarbon in the permeate stream represents a loss. For these conditions, the hydrocarbon losses are 5.0%.

By increasing the operating theta of the membrane, the CO, content of the non-permeate stream can be further reduced. At a 0.5 theta (50% of the feed is collected as permeate), the CO_2 content of the non-permeate stream is reduced to 2.1%. CO, removal is increased to 97.4%. This is at the expense of permeate purity (77.9% CO,) and hydrocarbon losses (18.4%.)

These above results are simple illustrations of single pass membrane operation with constant membrane flux and separation performance. In reality, membrane performance is a complicated function of feed composition, temperature pressure and differential pressure across the membrane. These performance characteristics are proprietary information of the supplier. In addition, there are very few membrane systems where the feed gas passes through a single stage of membranes. Multiple stages and permeate recycle are often utilized the minimize hydrocarbon loss. **A** properly designed membrane system is much more complex than simply placing a membrane in line with the feed stream. A properly designed system will take into account detailed performance characteristics of the membrane into and overall system design to minimize system cost and maximize performance for the each application.

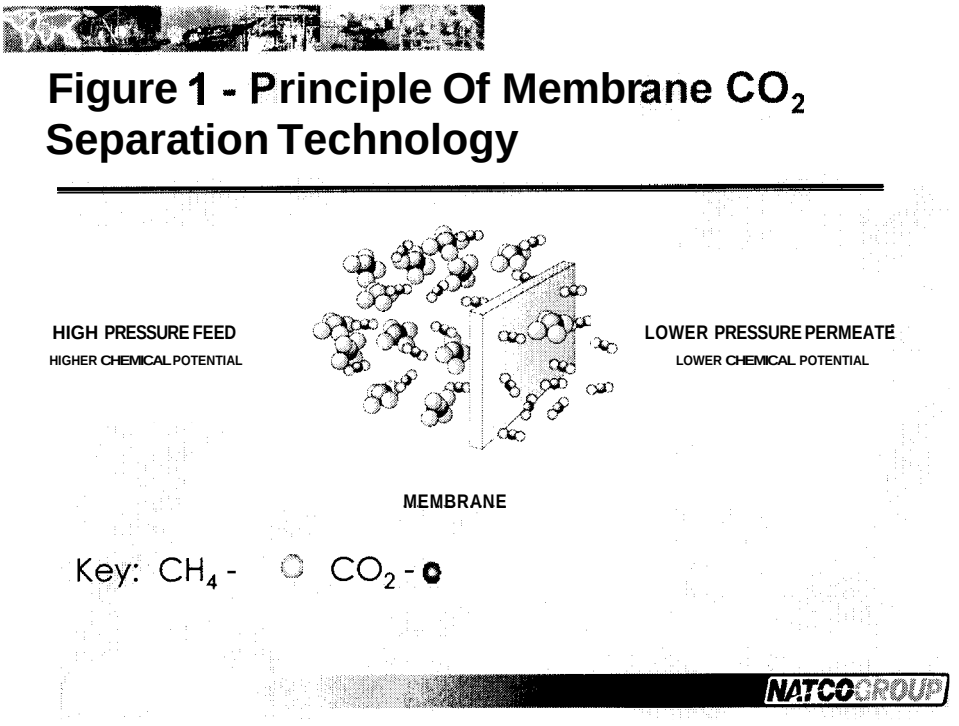
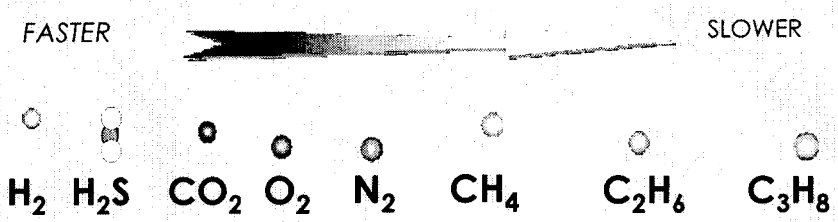


Figure 1 - Principle Of Membrane CO_2 Separation Technology

Figure 2 - RELATIVE TRANSPORT RATES OF GASES THROUGH CYNARA MEMBRANES



Transport is determined by the product of solubility and diffusivity

- Diffusivity- Related to size
- Solubility- Concentration in membrane

Molecular size and relative concentration determine component flux

Membrane chemical composition effects the absolute and relative permeation of each molecule

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Figure 3 - ASYMMETRIC HOLLOW FIBER MEMBRANE TECHNOLOGY

- Gases selectively permeate the membranes
- CO_2 permeates faster than CH_4
- Partial pressure is driving force
- **Result**: CO_2 rich permeate stream
  CO_2 lean non-permeate stream

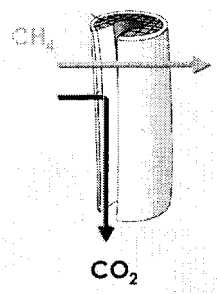

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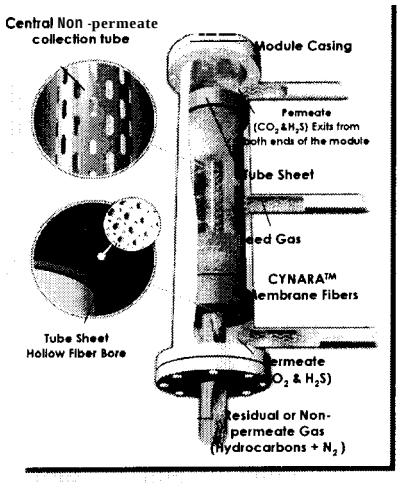
Figure 4 – CYNARA MEMBRANE ELEMENT



Efficient removal of condensing hydrocarbons

- Vertical mounting
- Central non-permeate collection

Double-ended permeate collection to maximize performance

Hollow fiber technology provides decreased footprint & weight relative to competing technology

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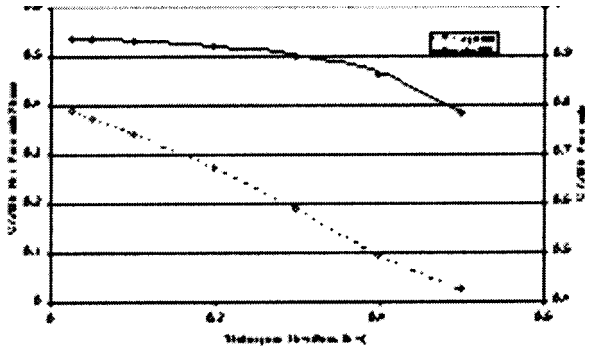
Figure 5 - SIMULATED PERFORMANCE OF RADIAL CROSSFLOW SEPARATOR



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