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Evolution of Natural Gas Treatment with Membrane Systems

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15.1 Introduction

The first commercial membrane system for carbon dioxide removal from natural gas was reported operational in 1983, utilizing cellulose acetate membranes [1,2]. Installations are now worldwide and systems continue to expand in size and scope. In keeping membrane treatment competitive with other separation technologies there have been incremental improvements in membranes, module designs and system performance. With the recent swings in energy prices the demand for natural gas treatment continues to grow. Although the membrane itself has attracted the most research efforts, there are many steps between the identification of a working membrane to the development of a commercially viable process. New generations of cellulose acetate membranes packaged as spiral wound modules are improving the economics and utility in natural gas treatment.

Membranes for natural gas treatment have been employed since the 1980s, with the earlier critical discoveries that cellulose acetate membranes for reverse osmosis (RO) could be transformed into gas separation membranes [3,4]. Since membranes for treatment of water have a high affinity for water transport, a molecule with unique polar properties, there is also an affinity for other polar molecules such as carbon dioxide and hydrogen sulfide. Water, CO₂ and H₂S are impurities in natural gas (methane) termed 'acid gases' that can promote corrosion of steel. Since pipelines are used in the transport

of natural gas from the well-head to the consumer, the control of acid gases is critical. Typical specifications for pipeline quality natural gas call for amounts of less than 2% CO₂, 120 ppm water and 4 ppm H₂S [5].

Early formulations of reverse osmosis membranes called for mixtures of cellulose diacetate and/or cellulose triacetate that were prepared as flat sheet membranes [6,7]. Typically RO membranes are treated with a conditioning agent such as glycerol to allow membranes to be handled as dry sheets. These sheets are assembled into spiral-wound modules for commercial installation. Glycerol allows for easy rewetting with water and physically holds open the pores of the asymmetric microporous membrane structure. But glycerol also physically inhibits the passage of gases and therefore is not appropriate for use in gas separation membranes.

In order to convert RO membranes to gas separations, various techniques such as freeze drying and solvent exchange of water wet cellulose acetate (CA) membranes have been utilized [3,4,8]. When water is directly evaporated capillary forces collapse the microporous membrane structure leading to a denser active surface layer and loss of flux. Freeze drying is a technique that protects the microporous structure with cold temperature. Solvent exchange uses a polar solvent such as alcohol to first wash out and replace water, followed by a low surface tension solvent such as hydrocarbons to wash out the first solvent. This second solvent with low surface tension can then be evaporated while maintaining the pore structure. Another drying technique that has been reported is addition of a low surface tension hydrophobic organic compound such as n-octane that protects the pore walls from the interfacial tension of water and allows direct drying of the membrane structure [9]. n-Octane is preferably incorporated as part of the original dope formulation from which the membrane is formed by the phase inversion process.

Many of the design philosophies required for successful operation of a reverse osmosis system are transferable to natural gas treatment. Reverse osmosis systems can operate at high pressures, even above 172 bar (2500 psi), to overcome solutions with high osmotic forces. Natural gas streams can also be at high pressure, up to 138 bar (2000 psi), with increased productivity possible at higher pressures. In both applications better economics are achieved by employing modules with multi-year service life. Both water and natural gas are natural resources which can be contaminated with materials that can harm long-term membrane performance. Pre-treatment systems to control the quality of the feedstock are therefore a critical component for both in commercial applications.

Early designs for spiral wound modules or hollow fibre bundles came from the RO industry. Modules for treatment of natural gas have also borrowed from these technologies. A skid containing spiral wound modules built in the 1980s for gas treatment is shown in Figure 15.1. This early array had six high pressure housings while current installations for natural gas treatment can have hundreds of tubes.

This chapter will describe some of the market forces driving membrane growth in natural gas treatment, explore some of the competing technologies to CA membranes, examine membrane compaction and the implication to long-term performance, report both recent laboratory and field studies with CA membranes and comment on some of the technical challenges and trends existing today in natural gas treatment with membrane systems that would benefit from future research and development activities.

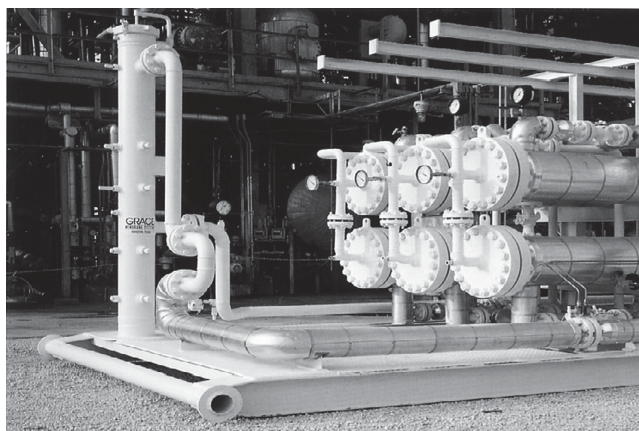


Figure 15.1 A gas treatment skid for hydrogen recovery from the 1980's containing cellulose acetate membranes as spiral wound modules. Image courtesy of W. R. Grace, Copyright (1988) W. R. Grace

15.2 Market for Natural Gas Treatment

Natural gas prices have tripled since 2002, which increases the incentive for treatment by producers to improve the quality and increase supply. The top 20 countries for proven gas reserves are listed in Table 15.1. This list is dominated by the top three of Russia, Iran and Qatar. The three top natural gas producing countries are the combined Russia and former Soviet Union states, the United States and Canada. Worldwide in 2007 there were 15 new gas plants, expansions and modifications scheduled and this number jumped to 24 for 2008 [10]. Opportunities for new membrane installations have been expanding.

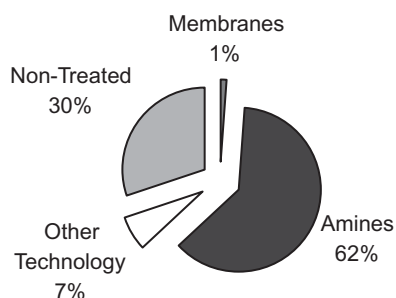
Figure 15.2 breaks down the major technologies in use in 2001 for control of acid gases in natural gas. A good percentage of natural gases are not treated, but the dominant technology in use is amine treaters. In amine treaters aqueous solutions of various alkanolamines are contacted with natural gas in order to scrub out the acid gases. The 'other technology' includes various solid adsorbent systems and cryogenics. In 2001 only 1% by volume of natural gas was treated by membranes, indicating that substantial new opportunities for membranes are available.

Natural gas comes from a variety of sources which influences the composition of the gas streams.

- Natural gas from crude oil wells, termed 'associated gas', which has been in the presence of crude oil. Heavy hydrocarbons will likely be present.
- Natural gas from gas wells or condensate wells is termed 'unassociated gas'. Gas wells produce raw natural gas while the condensate wells also contain light hydrocarbons known as natural gas condensate or natural gasoline.
- Coalbed gas coming from methane deposits in coal seams.

Table 15.1 Top 20 of the major natural gas reserves worldwide in trillions of cubic feet (tcf, $35.3 \text{ ft}^3 = 1 \text{ m}^3$), % share of the total volume and number of production units [10]

Rank	Country	Proven gas reserves (tcf)	% share	Number of plants
1	Russia	1680.0	27.2	24
2	Iran	948.2	15.3	22
3	Qatar	905.3	14.6	2
4	Saudi Arabia	252.6	4.1	10
5	USA	211.1	3.4	572
6	Abu Dhabi	198.5	3.2	
7	Nigeria	184.0	3.0	4
8	Venezuela	166.3	2.7	14
9	Algeria	159.0	2.6	4
10	Iraq	112.0	1.8	4
11	Kazakhstan	100.0	1.6	4
12	Turkmenistan	100.0	1.6	
13	Indonesia	94.0	1.5	13
14	Malaysia	83.0	1.3	5
15	China	80.0	1.3	
16	Norway	79.1	1.3	4
17	Uzbekistan	65.0	1.1	2
18	Egypt	58.5	0.9	19
19	Canada	58.2	0.9	967
20	Kuwait	55.5	0.9	4

**Figure 15.2** Estimate in 2001 of percentage of natural gas treated by various technologies to remove acid gases

- Town gas from gasification of coal.
- Biogas from the anaerobic decay of organic matter or biomass. Biogas is at low pressure and contains mostly methane and CO_2 .
- Landfill gas from the decomposition of waste in landfills is also mostly methane and CO_2 , again at low pressure.
- Enhanced oil recovery (EOR) where liquefied CO_2 is injected into the ground under high pressure to force out oil and natural gas. High CO_2 content is present in the natural

gas recovered and increases with the age of the field. In addition to methane recovery, the CO₂ can be recovered for recycling into the EOR operation.

- Off-shore platforms where space is a premium and the locations can be remote. Partial treatment of natural gas is used to protect pipelines to shore.
- On-shore treatment of natural gas produced off-shore.

Landfill and biogas are often small and localized operations where the methane is at low pressure and requires compression for membrane treatment. The methane gathered in these operations is often locally consumed. Both coal gasification and natural gas from Marcellus Shale on the East Coast have recently been championed in the United States as additional sources of fuels to help in the transition from a dependence on foreign oil to alternative energy sources.

Separex (now part of UOP) reported in 1985 an early membrane system as a trailer mounted skid. This skid treated 3.5 MMSCFD (105 000 m³/day) at an EOR application [11]. The trailer allowed for moving this small system to other sites when a project was completed. MMSCFD are millions of standard cubic feet per day and are common engineering units used in this industry's literature.

A 1989 report by Grace [12] compared the economics of amine and membrane processes for natural gas treating for 3, 10, 30, 37, 60, 100, 104, 140 and 148 MMSCFD (90 000 to 4 440 000 m³/day) scale systems. Costs for membrane/amine hybrid systems were also considered. The median system size in this collection of proposed applications is 60 MMSCFD (1 800 000 m³/day).

UOP offers a report [13] that illustrates the expanding scale of membrane treatment systems. In 1994 a plant was installed in Michigan (USA) that processed 40 MMSCFD (1 200 000 m³/day) to take CO₂ at 11% to less than 2% using spiral wound modules. In 1997 a membrane system was installed at an EOR facility in Mexico. The system processes 120 MMSCFD (3 600 000 m³/day) of inlet gas containing 70% CO₂. The enriched CO₂ permeate stream at 93% CO₂ was reinjected into the EOR process, while the product methane stream was at 5% CO₂. A plant in Pakistan was started up in 1995 at a scale of 235 MMSCFD (7 050 000 m³/day) of natural gas. An upgrade in 2003 increased plant capacity to 500 MMSCFD (15 000 000 m³/day). Critical to these systems is pre-treatment to remove water, heavy hydrocarbons and other contaminants from the inlet natural gas.

NATCO reports the use of hollow fibre bundles of cellulose triacetate in an EOR application in Texas (USA) at a scale 100 MMSCFD (3 000 000 m³/day) of gas since 1994 [14]. Pre-treatment includes chilling to remove heavy hydrocarbons and then dehydration by silica gel beds. An expansion of this facility to 200 MMSCFD (6 000 000 m³/day) was planned in 2005.

Air Liquide and ConocoPhillips report that a membrane system in Indonesia installed in 1998 processed 310 MMSCFD (9 300 000 m³/day) of natural gas, reducing CO₂ from 30% to 15% [15]. The polyimide hollow fibres are protected from heavy hydrocarbons through pre-treatment of the inlet gas with a thermal swing adsorption unit utilizing silica gel.

Another NATCO installation is an off-shore CO₂ removal facility in the Gulf of Thailand commissioned in December 2004 [16]. The feed gas volume is 700 MMSCFD (2 000 000 m³/day) at a CO₂ concentration of 37% and pressure of 43.4 bar (630 psi). A

plot of flux and separation factor from April 2006 through October 2006 shows stable operation with very little if any performance decline.

This history shows that there has been a steady progression to larger plant sizes. Current proposals for membrane treatment of natural gas exceed one billion SCFD (30 000 000 m³/day). With the expanding scale of these projects, membrane penetration into natural gas in 2008 was approaching 5% of the volume treated. These global market forces have been favourable to increased module sales over recent years.

15.3 Amine Treaters

Amine treaters are in essence a small chemical plant operation where an aqueous amine solution is used to scrub out from natural gas the acid gases of CO₂ and H₂S with an absorber column. Typical amines in use are monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), diisopropylamine (DIPA) and diglycolamine (DGA). The various amines are chosen on the basis of cost, capacity for acid gases, solubility, vapour pressure, regeneration conditions, chemical stability and corrosion resistance. The absorber column can be run up to 200 bar, requiring high pressure vessels. In order to release the acid gases and recovery the amine solution for recycle a regenerator tower is used. This regenerator runs at low pressure but is hot, in the temperature range of 115 to 126 °C.

One cost in running an amine system is the continuous slow loss of amine as natural gas is treated, requiring replacement of the chemicals. This is due to solubility of the amine in the product natural gas, the volatility of the amine, chemical degradation and operational problems such as foaming. Additional concerns in operating an amine plant are failure to meet product specification, corrosion, emulsions/carryovers, excessive amine solution losses, formation of heat-stable salts, degradation products and high filter replacement rates [17]. Spillage of amines is also an environmental concern.

As with membrane systems, installation of a good filtration system for pre-treatment of the inlet gas has become one of the key components of amine system design. They can remove particulates and take out heavy hydrocarbons that enter with the feed gas. The cleaner an amine system is the better it operates. This should be coupled with regular chemical analysis of the amine solution to ensure proper control of the plant operation and resolve operational problems before they impact performance [17].

Amine systems are established technology that is readily available with a proven track record. Incremental improvements over the years in the amine chemistry, design of the contactors and improved process schemes have raised the bar for membrane systems to compete. But higher CO₂ concentrations favour membrane systems since in amine treaters in order to remove more CO₂ one needs more amine solution. In contrast, when membranes see higher CO₂ contents they permeate higher CO₂ content. This joins with simpler (even unattended) operations, lower maintenance and operating costs, and smaller foot prints as factors in favour of membrane systems.

Membrane systems do not have to compete with amine treaters but instead can complement them by cutting high CO₂ levels down to levels more compatible with amine treaters. The long-term operations of combined membrane and amine systems by NATCO [14] and Air Liquide [15] are examples of this hybrid process.

15.4 Contaminants and Membrane Performance

The conundrum in designing membranes for high CO₂ permeability is that the separation is enhanced by the solubility of CO₂ in the polymer and that the polymer needs to be dissolved in solvents in order for the phase inversion process to occur and form the asymmetric structure. Properties that enhance CO₂ performance also can make the structure sensitive to contaminants that over the long term can hurt performance and in worst case scenarios completely shut down performance.

Liquid water collapses dried CA membrane structures, requiring in the field that natural gas streams be treated to reduce water content before they are introduced into the membrane. Simple droplet tests on the surface of flat sheet membranes also show that numerous solvents will also damage or dissolve these CA membranes. A partial listing includes acetone, 1,4-dioxane, acetonitrile, dichloromethane, chloroform, propyl acetate, ethyl acetate, 2-butanone, tetrahydrofuran and nitroethane.

Solubility parameters are a methodology that can be used to qualitatively characterize solvent and polymer interactions [18]. Hansen's 1971 Parameters provide tabulations of solvents broken into dispersive (d), polar (p) and hydrogen bonding (h) contributions. Following the conventions of Klein [19], plotting these p and h values for various compounds reported as solvents for cellulose diacetate and triacetate generates a solubility map (Figure 15.3). When a CA blend is used to make CA membranes the area covered in this map expands to an area larger than the contribution from a single polymer. A mixed CA structure may provide better performance but could also have a differing response to some contaminants.

In addition to the hydrocarbons that can be expected with a natural gas stream other organics can find their way into the system, both volatile and non-volatile. A leak in a

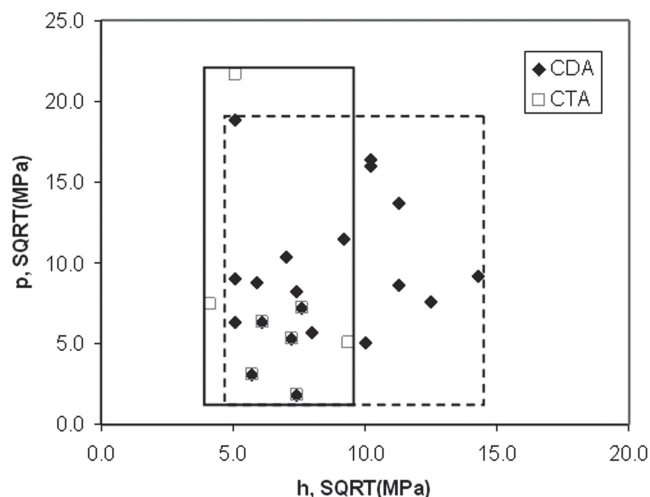


Figure 15.3 Solubility map using Hansen's 1971 Parameters for reported solvents of cellulose diacetate (CDA) and/or cellulose triacetate (CTA). Image courtesy of W. R. Grace, Copyright (2008) W. R. Grace

heat exchanger can introduce glycols or other heat exchange fluids. Gas compressors can leak oil. The high gas velocities that can be present can create and transport aerosols that can coat the membrane surface.

Glycol dehydrators are used to scrub water from natural gas to meet pipeline specifications but also pose a potential hazard to membrane systems. An upset in dehydrator operations can flood membrane modules with triethylene glycol (TEG), commonly employed as the working fluid.

Operations for oil and natural gas recovery can also introduce drilling additives, fracturing fluids and other processing liquids into the ground from which natural gas is extracted. These are low cost and sometimes proprietary mixtures for which the composition can be unknown and/or unreported [20]. There are many potential chemical hazards to a membrane operation so a proper pre-treatment system is recommended for successful long-term operations.

Funk *et al.* reported that high concentrations of water and H₂S can combine to deacetylate cellulose acetate membranes [21]. This report also shows that high relative humidity promoted increased thickness of the dense skin of the membrane with loss of flux. The conclusion was that water levels in the feed gas need to be controlled in these applications.

15.5 Cellulose Acetate versus Polyimide

Although CA is the focus of this study, there are other polymers available of which the most widely reported are the polyimides [22]. Reported values of even 100 for CO₂/CH₄ separation factors (α) are not uncommon with polyimides. This compares with reported pure gas dense film CA α values listed in Table 15.2 of about 32 depending on the acetyl content [23]. The higher acetyl content polymers have higher CO₂ permeability. A commercially available polyimide, Matrimid, has attracted much interest and had a pure gas α reported between 43 and 58 depending on how the membrane was prepared and tested [24]. Chemical structures of these two polymers are illustrated in Figure 15.4.

Table 15.2 Permeability, $P \times 10^{10} \text{ cm}^3(\text{STP}).\text{cm}/(\text{sec}.\text{cm}^2.\text{cm}(\text{Hg}))$ and α for CA dense films 76–127 μm (3–5 mils) thick prepared from Tennessee Eastman, Co. powders and tested at 1 atm (1.01 bar) and 35°C (23). CDA corresponds to 39.8% acetyl content and CTA to 43.5%

Eastman ID weight % acetyl	CA 320S 32.0	CA 398-30 39.8	CA 435-75 43.5
He	9.34	16.0	19.6
H ₂	6.05	12.0	15.5
CO ₂	1.84	4.75	6.56
O ₂	0.32	0.82	1.46
N ₂	0.057	0.15	0.23
CH ₄	0.052	0.15	0.20
CO ₂ /CH ₄ , α	35.6	31.1	32.8
H ₂ /CH ₄ , α	116	80	78

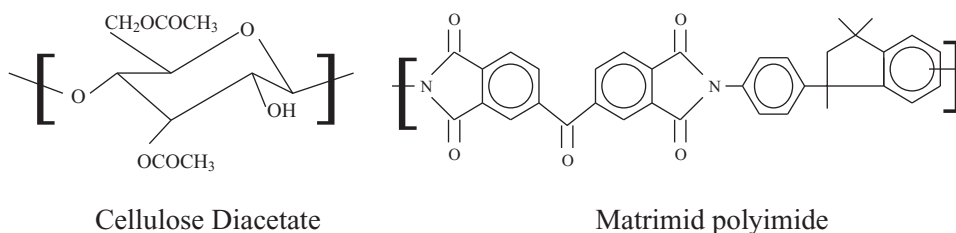


Figure 15.4 Chemical structures of two polymers investigated for use in natural gas separation membranes

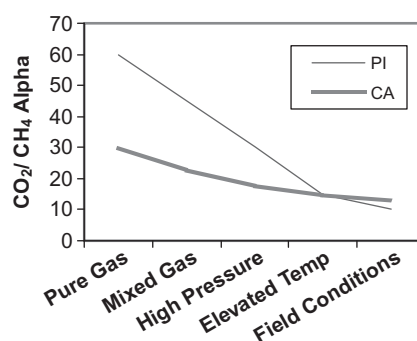


Figure 15.5 Illustration that polyimides and CA have changing α on going from pure gas measurements to field conditions

Both CA and polyimides are susceptible to plasticization by CO_2 [25–27]. When CO_2 solubilizes in the polymer matrix the polymer chains become more flexible and allow faster transport of CO_2 molecules. If other gas molecules such as methane or nitrogen are present they also increase their transport rate often even more so than CO_2 . This means that mixed gas measurements often generate lower α than pure gas. Also, if pure gas measurements are done then methane is usually measured before CO_2 since the polymer ‘remembers’ exposure to CO_2 and needs time to relax the extra free volume that has been created. Various studies have documented the response of CA permeation rates to temperature, pressure and CO_2 concentration [28–31]. When pressure is increased more CO_2 solubilizes in the polymer matrix increasing this plasticization. Going up in temperature also softens the polymer and causes loss of α . In addition, common heavy hydrocarbons in gas fields such as hexane or toluene can negatively impact performance of polyimides in treating natural gas [32–34].

Polyimides would appear to have a clear advantage over CA but in practice other considerations need to be taken into account. Figure 15.5 illustrates how changing process conditions can impact polymer performance. Pure gas measurements are typically reported for dense films at 7 bar (100 psi) or less and 35 °C. Converting from thick dense films to asymmetric structures with thin active layers can introduce a loss of selectivity. Polyimides

are also susceptible to plasticization by CO₂ so therefore on switching to mixed gas there is a drop in α . Increasing in pressure and temperature further plasticizes and softens the polymer structure, resulting in further loss of selectivity. Finally, in going to field conditions the trace contaminants that are very likely to be present can further soften the polymer. What initially looks like a promising and highly selective polyimide polymer has converted into a system with α in the single digits.

Why do polyimides appear to be more impacted than CA on going into field conditions? We have suggested [32] that the polyimides have a more ordered structure giving higher contributions to the diffusivity factor than CA. Therefore the polyimides are more susceptible to structural changes induced by plasticization by CO₂ or higher hydrocarbons.

Although CA was the original polymer system commercialized for natural gas treatment, CA still sets the bench mark against which other polymers can be compared. But if the natural gas stream is clean enough there are applications where the higher selectivities obtained by polyimides offer an advantage.

15.6 Compaction in Gas Separations

Compaction refers to a long-term densification of the active membrane layer which lowers flux over the commercial lifetime of a membrane. It is a difficult property to study experimentally since lab conditions are almost impossible to match with field conditions. Similar difficulties are found in reverse osmosis since it is a technical challenge to distinguish physical compaction from trace impurities in the water that promote fouling during long-term tests. In gas separation the treatment of natural gas is an exception to other gas separations in that CO₂ is a plasticizing agent especially for the more highly selective membrane materials.

There are relatively few reports of compaction of asymmetric gas separation membranes in the scientific literature. Reinsch *et al.* used ultrasonic time-domain reflectometry to look at the very first hour of compaction with a commercial CA membrane [35]. The 13.2% collapse of the membrane thickness in the first seconds probably comes from compression of the membrane sub-structure and/or the fabric support. The roughly 10% flux decline over this first hour was at a much slower rate, which may be an indication of the true compaction process.

In addition, the contaminants in natural gas present in the field can be poorly defined. If the pre-treatment of the feed stream is insufficient then even ppm levels of contaminants at these large gas volumes can collect over time on the membrane surface in large quantities and promote either surface fouling or enhanced compaction rates [36].

Another complication is that thin dense membrane films have been shown to decline in permeation properties over extended periods of time (10 000 hours) even without external stresses. The rate of ageing effect becomes greater the thinner the film [37]. This loss over extended time is presumably due to cast membrane films slowly reorienting polymer chains to achieve equilibrium properties with reduced free volume. The thin dense films used in these studies (0.4–25 μm) approach the same order of thickness as the active layer of cast asymmetric films at less than 2000 Å (0.2 μm). The property appears common in that it was reported in this paper with polysulfone, polyphenylene oxide and polyimide

(Matrimid) dense films. Therefore compaction may be driven not only by physical compressive forces but also by thermodynamic considerations.

15.7 Experimental

Data in this report are generated from both commercial and developmental flat-sheet CA membranes. CA membranes are prepared by dissolving commercial grades of CA polymers into a solvent/non-solvent mixture to give a highly viscous dope solution. After microfiltration a knife blade is used to spread the dope onto a woven nylon substrate. The commercial equipment utilized allows for a 1-m width to be cast. The thin dope film is quenched into a water bath to form the microporous structure by the phase inversion process. Membrane is washed with water and post-treated to give finished product in dry state as roll stock.

Figure 15.6 shows a typical scanning electron microscopy view of the finished membrane structure. The instrument used was a Hitachi 4500 Cold Field Emission Scanning Electron Microscope which allowed for sensitive structures to be examined at high magnification. Overall thickness of the CA layer is about 50 μm . The finely microporous structure helps resist the high pressures required in field applications. The active separation layer is at the very top of the structure. The 20000 magnification is at the highest resolution that could be achieved with this instrument since the polymer structure distorts under the heat generated by the electron beam. Even at this high magnification the thickness of the active layer is not clear although it is believed to be well under 2000 $\text{\AA}$.

Laboratory studies were done with flat-sheet membrane. Membrane coupons were mounted as disks in high pressure test cells. With safety considerations CO_2 in nitrogen (instead of methane) was used as feed in order to avoid the explosion potential with

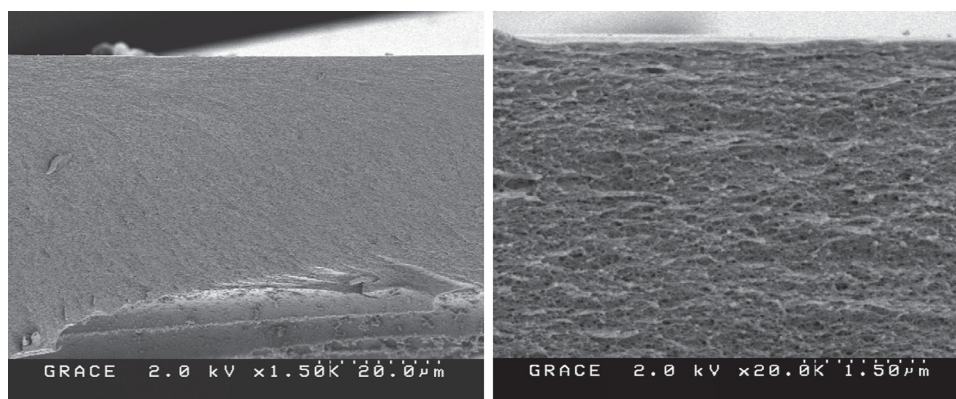


Figure 15.6 Scanning electron microscopy of the cross-section of a commercial CA membrane. The left view at 1500 times magnification is the overall cross-section with the backing layer removed; the right view at 20000 times magnification includes the top active layer. The sample was prepared by freeze fracturing in liquid nitrogen and then electro sputtering with AuPd

methane. Nitrogen and methane have similar permeation rates: with these CA membranes methane averages about 10% higher rate than nitrogen. The feed manifold can be connected to as many as 20 cells in parallel. The feed gas was flowed over the surface of the membrane at a rate so that the retentate gas is at a 12:1 ratio to permeate flow. Flow rates were measured with an electronic bubble meter and gas chromatography was used to monitor CO₂ and N₂ levels in the feed, retentate and permeate. The test equipment could be left under pressure for months in order to follow long-term compaction rates. Flux is a measure of the productivity of an asymmetric membrane and is the polymer permeability (P) divided by the thickness of the active layer. Flux (J) is normalized to standard conditions for permeate volume, membrane area and applied pressure. Units for J are therefore volume/area/pressure for both CO₂ and N₂. The separation factor α is the ratio of CO₂ permeability (or flux) over methane or nitrogen permeability (or flux).

Field studies were done with commercial-scale spiral wound modules. Membrane, spacers and adhesives were wound around the central permeate pipe to form the module. Modules were both vacuum and high pressure tested to insure integrity.

15.8 Laboratory Tests of Cellulose Acetate Membranes

Varying the retentate to permeate balance (R:P ratio) impacts membrane performance because at low values the membrane surface becomes starved of the highly permeable CO₂. Figure 15.7 shows the average result from five coupons of a developmental CA membrane. At higher R:P ratio the % CO₂ in the permeate increases and the total feed flow to the coupon increases. This means smaller stage cut and higher CO₂ in the retentate. At the R:P ratio of 12:1 the mass balance calculates as a stage cut where 7.7 volume % of the feed is collected as permeate. Therefore the test results offer slightly conservative estimates of membrane performance.

A sample of commercial CA membrane was tested against two different sets of feed conditions with one at 38 °C and 69 bar (1000 psi) and the other at 54 °C and 90 bar (1300 psi). Both were with 10 mol.% CO₂ in nitrogen and relative fluxes are reported in Figure 15.8. The curve shapes are typical compaction curves where initial decline in flux

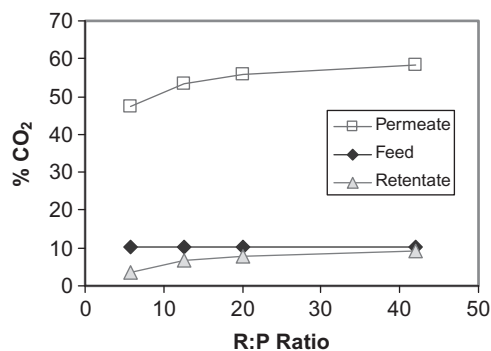


Figure 15.7 Variation of retentate to permeate ratio for a coupon test of a developmental CA membrane under 10% CO₂ in nitrogen at 69 bar and 38 °C

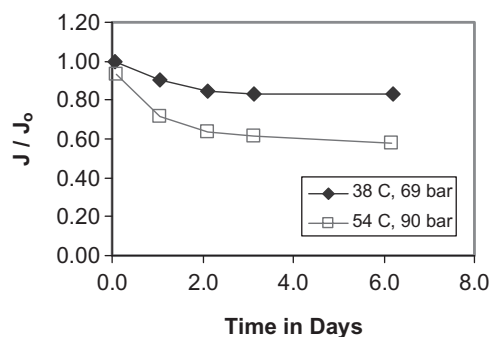


Figure 15.8 Relative CO₂ flux (J/J_0) (against the initial 38°C reading for CA membrane) under 10% CO₂ in nitrogen for commercial CA membrane. Two separate trials are reported, one at each condition of temperature and pressure

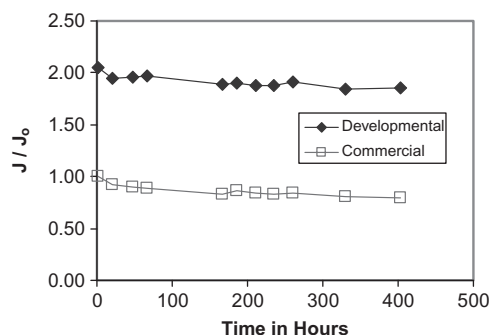


Figure 15.9 Relative CO₂ flux (J/J_0) (based on initial reading for commercial membrane) of two CA membranes under 6% CO₂ in nitrogen at 55 bar and 27°C

is fairly rapid and then flux declines much more slowly over time. On day 6 the 38°C trial was at 83% of the initial reading while the 54°C trial was at only 62% of the initial reading and still visibly declining. Higher pressure and temperature have accelerated the compaction rate.

Literature [28–31] suggests that both the higher pressure and temperature in Figure 15.8 should have increased the initial CO₂ rate through the membrane at 54°C and 90 bar (1300 psi) to be well above (perhaps 50%) of that for 38°C and 69 bar (1000 psi). This was not observed, so during the initial few hours when the test equipment was being allowed to equilibrate the flux must have taken a substantial hit. This high decline rate would not be favourable to long-term applications.

Permeation tests are the primary method to evaluate alternative membrane formulations. Figure 15.9 shows a head-to-head test of commercial CA membrane coupons against a developmental CA membrane. Test conditions were set at 55 bar (800 psi) and 27°C with 6 mol.% CO₂ in nitrogen. These conditions were chosen to simulate an upcoming field

trial at a natural gas production facility. The lower operating pressure and temperature compared to Figure 15.8 results in reduced compaction rates and decline in flux over time. This developmental membrane is at almost twice the flux of the commercial CA membrane. The next question is whether these promising lab results would translate to real field conditions.

15.9 Field Trials of Cellulose Acetate Membranes

A large-scale natural gas producer made available a test skid that would allow for membrane products to be demonstrated under real field conditions. Commercial CA membranes from both Grace and another supplier and the developmental membrane were delivered to the field as full-scale 20 cm (8 inch) diameter spiral wound modules.

The feed gas contained about 6% CO₂ with about 50 ppm H₂S. The bulk of the gas was about 81% methane, with the major other components being about 12% nitrogen and 1% ethane. Target specifications for the sales gas (retentate) were to reduce CO₂ to less than 2% and H₂S content to less than 15 ppm. Feedstock conditions were relatively mild at 55 bar (800 psi) and 27 °C. The three trials were run sequentially over a period of months. One set of analysis was reported for each day of the trials.

The permeate fluxes for the three membrane systems over 30+ days are reported in Figure 15.10. CA membranes can be prepared at different points of the trade-off curve for flux and selectivity and these two commercial CA membranes are at slightly different flux. But the developmental membrane is substantially higher in permeate flow indicating a more productive membrane compared to the commercial CA membranes.

Although there is day-to-day variation as the feed flow rate to the test unit and gas composition varies slightly, none of the three products are showing discernible signs of compaction. This is consistent with the relatively mild process conditions employed in this trial. These results also confirm that laboratory tests – where a developmental membrane was also notably higher in flux than the commercial CA membrane (Figure 15.9) – can be predictive of field performance.

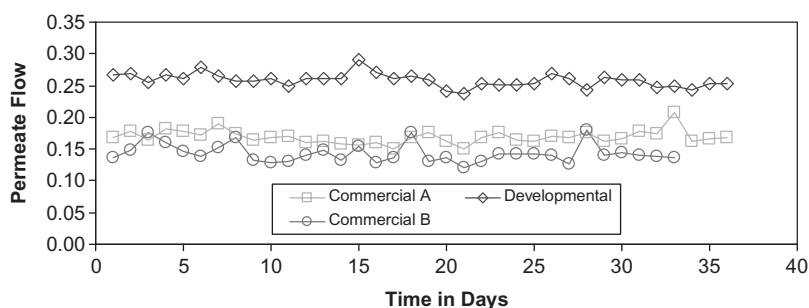


Figure 15.10 Permeate flow for two commercial CA spiral wound modules and a developmental module during natural gas field trials. Process conditions are 6% CO₂ at 55 bar and 27 °C

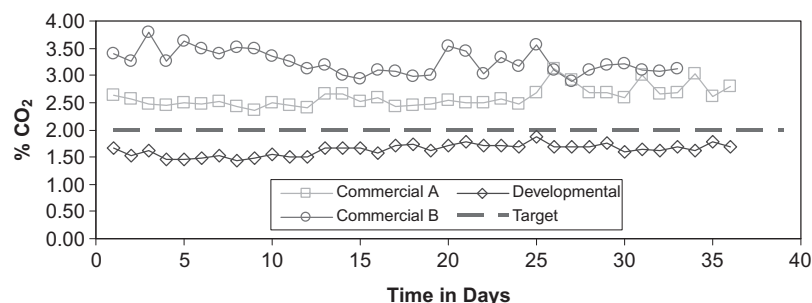


Figure 15.11 Amount of CO₂ in the retentate during the field trials of spiral wound modules at a natural gas plant. Target was less than 2% CO₂

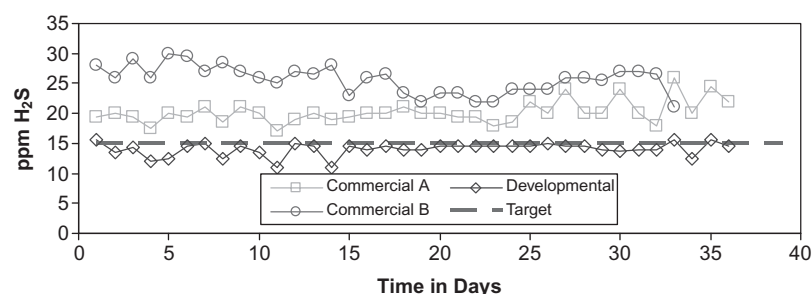


Figure 15.12 H₂S levels in the retentate during the field trials of spiral wound modules at a natural gas plant. Target was less than 15 ppm H₂S

Figures 15.11 and 15.12 report the CO₂ and H₂S levels of the retentate stream. All three products reduce the levels of these impurities in the product gas and are showing stable performance. But with the higher permeate flow from the developmental modules more CO₂ and H₂S are removed and therefore bring the retentate gas stream to the target levels of purity for both CO₂ and H₂S. The developmental membrane has demonstrated in the field substantially better performance and productivity than the two commercial CA membrane products that were also tested.

15.10 Strategies for Reduced Size of Large-scale Membrane Systems

Membrane, module and system performance are interdependent on each other. The membranes have to meet flux and selectivity requirements for a given application. There is a trade-off curve available between flux and selectivity so a preferred strategy is to supply a membrane that meets minimum selectivity and then boost the flux. But meeting the requirements in the lab for flux and selectivity are only the initial step since the membrane has to be designed and engineered into a working installation.

Only perhaps 20% of the cost of a membrane system is in the cost of the modules; since these are high-pressure systems with hazardous gases they require steel construction. Spiral wound modules are typically loaded end-to-end into housings made from piping 8 m in length. Standard industry size is 20 cm (8 inch) diameter modules and every high pressure flange or valve increases the system cost.

Reducing the number of modules required for a system therefore has a 4-fold multiplier in reducing the steel and construction costs going into an installation. Membrane area per spiral wound module has improved over the years with a more refined selection of feed and permeate spacers. This then allows for more functional membrane area to be packaged into every module. This reduces the total number of required modules in large-scale installations.

These techniques for improvements in membrane area have to be balanced against developing a pressure increase on the permeate side as the module attempts to evacuate the permeate gas and the pressure drop on the feed side from end-to-end of the modules as feed gas is forced through for treatment. Too high a permeate pressure increase will negatively impact both flux and selectivity. And since the membranes are highly selective to CO₂, the concentration of CO₂ can build up in the permeate channels and reverse permeate at the tail end of module leaves and contaminates the cleaned retentate gas. Too high a pressure drop on the feed side steals from the driving force for the separation and is exacerbated when modules are in multiple strings. Of concern is that a severe pressure drop can 'telescope' a module and cause complete failure. Anti-telescoping devices are built as end caps on spiral wound modules in order to provide protection against flow surges.

Another strategy to reduce the number of modules is to increase the dimension of the steel housing to handle larger modules. NATCO [5,14] has been successful in increasing the dimensions of hollow fibre bundles to greatly reduce system costs. The earlier modules were 13 cm (5 inch) diameter and 1 m (40 inch) length. This was boosted to 30 cm (12 inch) diameter, then to 41 cm (16 inch) and twice the length, and then to a mega-module at 76 cm (30 inch) diameter. These are potentially equivalent to 72 of the original modules. This represents a substantial decrease in foot print and required pressure housings for a large-scale installation.

For new system builds the same strategy can be done with spiral wound modules designed for natural gas treatment. Grace has constructed a 30-cm (12-inch) diameter module versus the standard 20-cm (8-inch) diameter module. Since membrane area is a squared function of diameter, the ratio of 144 to 64 means a 225% increase in membrane area per module. Although the larger diameter modules and pressure housings each cost more there is potential for reduction in total system cost.

And, of course, higher flux for a membrane would increase the volume of permeate output from the full-scale module. If selectivity is maintained then the total number of modules required is reduced.

The dependence on R:P ratio for coupon performance shown in Figure 15.7 also applies to module performance. In system design the module strings need to be supplied with a sufficient feed rate to promote top membrane performance. Supplying these high feed flow rates needs to be balanced against increasing end-to-end pressure drop. The design of an appropriate module can improve system performance or allow retrofit into existing systems. Figure 15.13 shows a variety of modules built for specific applications (some



Figure 15.13 A variety of module designs from lab-scale to commercial size for multiple applications including natural gas treatment. Courtesy of W.R. Grace

experimental) where different couplings, membrane area or overall dimensions have been incorporated. For example, reducing the diameter of a module increases feed velocity for the same given volume of feed and improves the R:P ratio.

15.11 Research Directions

Of high interest would seem to be improved flux and selectivity through a better polymer. Materials are reported every year with good permeability properties but many studies are carried out with relatively thick dense films on the order of 5 to 50 μm . In addition, with CO_2 any study with pure gas results has to be discounted until mixed gas results are reported because of CO_2 plasticization. Also, thin film permeation properties have been demonstrated as different than those of thick films [37].

For commercial membranes to be competitive in natural gas treatment they must be reliably manufactured with an active separation layer on the order of 0.1 μm . They also have to be resistant to warm and high pressure operating conditions and mechanically resistant to assembly into modules. These are all significant tasks to engineer and inherent permeability of the polymer is only one of the factors involved.

As gas fields age around the world they increase in contaminants that can potentially harm long-term membrane performance. Better chemical resistance for the membrane polymer would be beneficial. Whether highly selective polymers for CO_2 transport (see e.g. Chapters 10–13 of this book) that also have resistance to CO_2 plasticization can be developed remains an open question. Membrane structures with improved resistance to elevated process conditions of temperature and pressure are also desired. Converting new materials into working systems requires attention to preparing high productivity membranes with sub-micrometer active layers. These membranes need to be packaged into modules and then delivered as an engineered system that optimally enhances the original polymer performance.

The observations that very thin cast films lose permeability over time even without external stress is of interest since the active layers of commercial membranes are also thin films. Our commercial modules are pre-stressed with a pressure test to check integrity and can take months to get from the production floor to the customer. How does this thin

dense film behaviour observed in the lab for other polymers relate to the asymmetric thin film structure of commercial CA membranes?

The material science of long-term membrane compaction in asymmetric membranes is not well reported. This phenomenon has been observed in gas separations including this report, but also in reverse osmosis [6] and organic solvent nanofiltration [38]. How to accurately predict multi-year performance in the field with short-term lab tests is a continuing challenge.

Since installed membrane systems for natural gas treatment are continuing to increase in scale, strategies that reduce the number of required modules and therefore total system cost continue to be of interest.

15.12 Summary

Natural gas separations are unusual in that not only is CO₂ highly permeable but that CO₂ and other contaminants can also plasticize the most selective polymer structures. Although cellulose acetate structures are sensitive to solvents and chemicals, effective pre-treatment schemes in the field can allow for stable long-term operations.

New installations in natural gas treatment are increasingly favourable to membrane systems as they expand in scale and treat streams higher in CO₂ content. In systems with large volumes of CO₂ a membrane system can be employed to make the bulk cut and then an amine system can provide the finishing treatment. This is especially applicable in fields employing CO₂ injection for enhanced oil recovery.

Long-term compaction and decline in flux with asymmetric membranes under gases that plasticize the polymer in use are rarely reported. These experiments confirm that higher pressure and temperature can increase compaction levels to unacceptable levels. Conversely, milder process conditions can allow for stable long-term performance in treatment of natural gas.

The developmental membranes reported here that have improved productivity and performance over conventional commercial cellulose acetate membranes indicate that there are avenues for improvement with new and future technologies.

Membrane materials that offer improved resistance to temperature, pressure, high CO₂ content, water and other chemical contaminants are all areas that offer gains in long-term performance desired in commercial applications.

Membrane systems for natural gas treatment are now approaching 30 years of service to the industry and continue to evolve toward better performance. Further advances in the technology should be expected.

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The personnel at Grace Davison Membranes located in Littleton, Colorado (USA) delivered the membranes, modules and experimental results described in this report. This team has included Jerry T. Barnett, Anthony P. Lippl, Craig Paulaha, Samantha K. Stewart and Craig R. Wildemuth. In September 2009 this business was acquired by UOP LLC based in Des Plaines, Illinois (USA).

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