



Power plant post-combustion carbon dioxide capture: An opportunity for membranes

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ABSTRACT

Carbon dioxide capture from power plant flue gas and subsequent sequestration is expected to play a key role in mitigating global climate change. Conventional amine technologies being considered for separating CO₂ from flue gas are costly, energy intensive, and if implemented, would result in large increases in the cost of producing electricity. Membranes offer potential as an energy-efficient, low-cost CO₂ capture option. Recently, working with the U.S. Department of Energy (DOE), we have developed membranes with CO₂ permeances of greater than 1000 gpu and a CO₂/N₂ selectivity of 50 at 30 °C. This permeance is ten times higher than commercial CO₂ membranes and the selectivity is among the highest reported for non-facilitated transport materials. These membranes, in combination with a novel process design that uses incoming combustion air as a sweep gas to generate driving force, could meet DOE CO₂ capture cost targets. Under these conditions, improving membrane permeance is more important than increasing selectivity to further reduce the cost of CO₂ capture from flue gas. Membrane cost and reliability issues will be key to the eventual competitiveness of this technology for flue gas treatment.

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1. Introduction

Carbon dioxide (CO₂) produced as a result of fossil fuel combustion is primarily responsible for human-induced climate change. During the last century, the concentration of CO₂ in the atmosphere increased from 275 to 387 ppm. The higher CO₂ concentration has already produced measurable increases in global temperatures. Climate models indicate that continuation of this trend will dramatically change the global climate by 2100 [1].

Coal-fired power plants generate more than 50% of the electricity in the United States and produce about 40% of the country's CO₂ emissions. Because of the relatively low-cost and large domestic supply of coal, power production from this fuel is expected to increase over the next 20 years [2,3]. According to the Energy Information Agency, growing power demands will result in a 50% increase in installed coal-fired electricity generating capacity by 2030 [4].

Worldwide, the situation is similar. Compared to oil and gas, coal is the lowest cost method of producing electric power and it is relatively abundant in large energy-consuming nations, such as China. For these reasons, it is clear that coal will continue to be used to produce a large percentage of the world's electric power. In fact, a recent MIT study concluded that under any foreseeable scenario, coal use will increase between now and 2050 [2]. The same study predicts that under a business-as-usual scenario (no CO₂ emission mitigation), global CO₂ emissions from coal combustion will increase from 9 Gton/year in 2000 to 32 Gton/year in 2050 [2]. This 2050 value will be 55% of projected global CO₂ emissions at that time.

One way to reduce CO₂ emissions to the atmosphere is carbon capture and sequestration (CCS). In this scheme, CO₂ is captured from power plant emissions, and sequestered underground in geological structures for long periods of time. The U.S. Department of Energy (DOE) is considering three ways to capture CO₂ generated in coal-based power production [3]:

1. post-combustion CO₂ capture from power plant flue gas,
2. pre-combustion CO₂ capture from gasified coal synthesis gas, and
3. oxy-combustion, which separates oxygen from air prior to combustion and produces a nearly sequestration-ready CO₂ effluent [3].

Abbreviations: CCS, Carbon capture and sequestration; COE, Cost of electricity; ESP, Electrostatic precipitation; FGD, Flue gas desulfurization; MMscfd, Million standard cubic feet per day; MMm², Million square meters; bar, 1 bar = 100 kiloPascals (kPa); gpu, Gas permeation unit ($=10^{-6} \text{ cm}^3 \text{ (STP)} / (\text{cm}^2 \text{ s cmHg})$).

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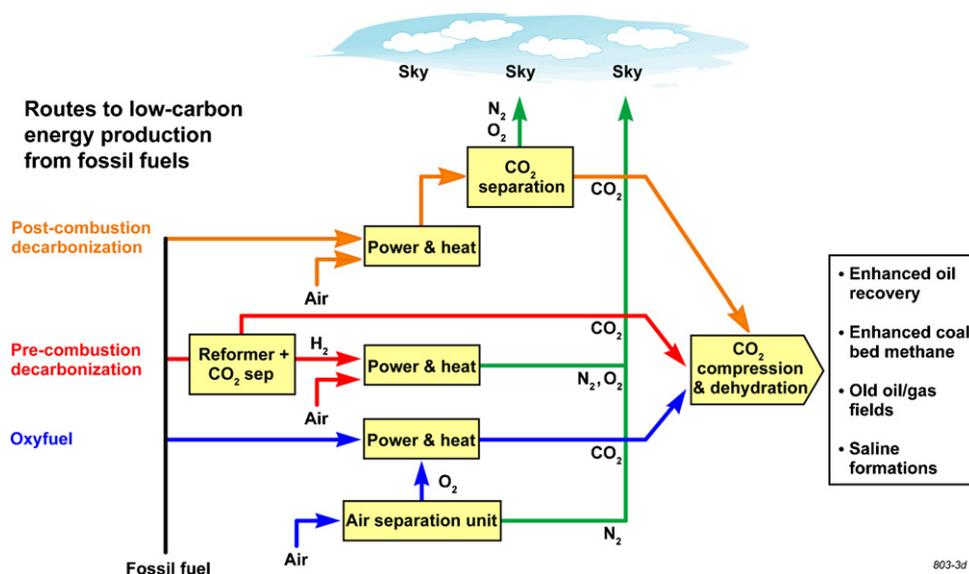


Fig. 1. Approaches to power generation with fossil fuels (coal, oil and natural gas) that include carbon dioxide capture and sequestration (CCS). Adapted from Mikus and Melien [29].

These approaches are shown schematically in Fig. 1. For each case, a different method of capturing CO₂ produced as a by-product of energy production is used. For post-combustion capture, CO₂ at low partial pressure must be separated from flue gas (mostly nitrogen) after the fuel has been completely burned for energy conversion. In the case of pre-combustion capture, CO₂ at much higher pressure will be separated from gasified coal syngas (largely H₂ and CO) prior to the gas going to a combustion turbine. Finally, for oxy-combustion, oxygen is separated from air, and coal is then burned in nearly pure oxygen to generate a flue gas that has a high concentration of CO₂ and is almost ready for sequestration.

While gasification and oxy-fuel processes show future promise for clean, efficient energy production, virtually all coal-fired electricity is currently produced by direct combustion of coal with air in a boiler. In the U.S., there are more than 600 of these pulverized coal combustion power plants. Worldwide, there are more than 5000. New power plants will continue to be of this type for at least the next few decades [2]. Consequently, to address current CO₂ emission concerns, capture technology must be applied to these standard air combustion systems. For this reason, in this study, we will focus on CO₂ capture from post-combustion coal-derived flue gas.

2. CO₂ capture from coal-fired power plants

The main reasons for the high cost of separating CO₂ from power plant flue gas are the low partial pressure of CO₂ and the enormous volume of gas emitted from a typical power plant. An average 600 MW_e coal-fired power plant emits 500 m³/s (1540 MMscfd) of flue gas containing 13% CO₂, which amounts to about 11,000 ton CO₂/day (here and throughout this paper, gas compositions are given in volume percent). This flue gas flowrate is 5–10 times larger than typical streams treated for CO₂ removal with conventional absorption technology in the natural gas and chemical industries. In addition, the flue gas is at atmospheric pressure, so the CO₂ partial pressure is only ~0.13 bar. This means that there is very little driving force available for separation. Finally, the gas to be treated contains a wide variety of contaminants including fly ash, SO₂, NO_x, water, and trace metals. These factors combine to make CO₂ separation from flue gas a costly proposition with existing technologies.

Fig. 2 shows a simplified schematic of the flue gas cleanup train for a coal-fired power plant. After leaving the boiler, the hot flue gas is sent to an electrostatic precipitator (ESP) that removes the bulk of the large particulate matter. Depending on the coal type and local regulations, additional particulates may be removed in a baghouse or wet scrubber. At most plants, the gas is then sent to a flue gas desulfurization (FGD) unit. In this operation, a limestone slurry contactor is used to remove SO₂ from the gas down to levels that meet local emission limits (typically <100 ppm). Most CO₂ capture technologies are being designed to treat the flue gas after it leaves the FGD. At this point, the flue gas is saturated with water at about 50 °C, and contains 10–14% CO₂ in mostly nitrogen. Currently, this entire flue gas stream containing CO₂ is vented to the atmosphere.

Post-combustion capture of CO₂ from power plant flue gas has been the subject of many studies. Useful reviews include a recent IEA Greenhouse Gas Program Report [5], MIT's *The Future of Coal* [2], and a DOE NETL overview paper [3]. Currently, CO₂ capture with amine absorption seems to be the leading candidate technology. There are a number of relatively large CCS demonstration projects under way that use amine absorption to capture CO₂ from power plant flue gas. Amine absorption is being considered for this application because it is a proven technology used successfully to treat industrial gas streams for decades. However, a number of studies

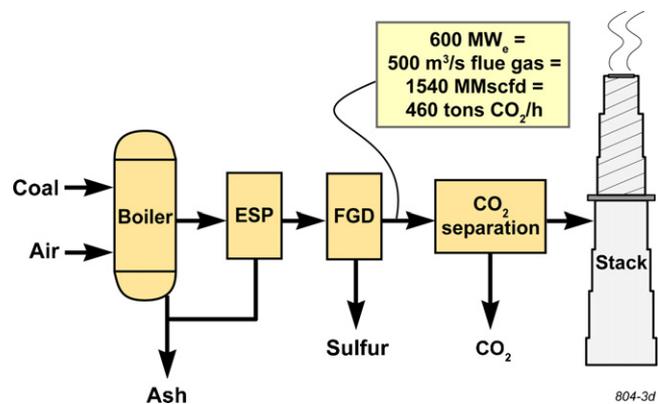


Fig. 2. Simplified schematic of a flue gas cleanup train for a coal-fired power plant.

have shown that amine absorption, when applied to flue gas CO₂ capture, is going to be costly and energy intensive [3,6]. Reports predict that an amine system used to capture 90% of the CO₂ in flue gas will require about 30% of the power produced by the plant and result in a CO₂ capture cost of \$40–100/ton CO₂. This translates to an increase in the cost of electricity (COE) of 50–90% if amines are used to remove 90% of the CO₂ from flue gas. These values are well above the DOE target of less than a 35% increase in COE for 90% CO₂ capture [3]. Because amine absorption is a mature technology, there are unlikely to be significant future improvements in this process.

Membrane processes have been suggested previously for CO₂ capture from flue gas. For example, Hendricks et al. [7,8] reported as early as 1989 that commercial gas separation membranes available at the time were not competitive with absorption techniques for flue gas treatment. Subsequent researchers have largely focused on improving membrane CO₂/N₂ selectivity, often by using facilitated transport mechanisms, to increase the purity of CO₂ produced by a membrane [9–12]. Recently, feasibility studies by Favre and co-workers have rekindled interest in using membranes for CO₂ capture from flue gas [13–17].

For the most part, these studies tried to accomplish the CO₂ separation in a single membrane stage or in a simple multi-stage operation. As a consequence, membranes with very high selectivities were required to make membranes an attractive process; even then, energy costs were very high. In this study, we will show that recently developed membranes with high CO₂ permeance and more modest CO₂/N₂ selectivity can meet DOE CO₂ capture targets using innovative process designs. Furthermore, for real-world system designs, increases in membrane permeance are more important than increases in selectivity to enhance the competitiveness of membranes for flue gas CO₂ capture.

3. Design considerations for post-combustion CO₂ capture with membranes

Separation of CO₂ from flue gas streams is a difficult application for any separation technology. The problems are the low CO₂ concentration and low pressure of the feed gas, coupled with huge gas flows. The enormous volumetric flowrate of a power plant flue gas stream means plants with very large membrane areas are required. However, producing membranes for this application is not the principal problem preventing adoption of post-combustion membrane systems for CO₂ treatment. Separating CO₂ from N₂ is an easy separation for membranes, and membranes with high permeances and high CO₂/N₂ selectivities have been developed. The more difficult problems to overcome are the scale of the process and the very large, expensive, and energy-consuming compression equipment needed.

In the remainder of the section that follows, we will outline some general process design issues that affect the selection of the optimum membrane and module for this application. The final section of the paper will show how these various design issues can be reconciled to produce an efficient and economical CO₂ capture process.

3.1. The pressure ratio issue

To date, most designers of membrane processes for post-combustion CO₂ capture have suggested using a single membrane stage to perform the separation. The energy cost of generating the required pressure difference across the membrane is a key issue. For one-stage separations, compression of the flue gas to more than 10 bar or use of vacuum pumps on the permeate to achieve pressures of less than 0.1 bar or some combination of compression and

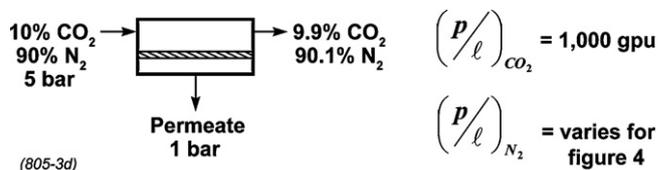


Fig. 3. Single-step membrane separation demonstrating pressure ratio effects. The stage-cut is set at 1% to maintain the feed concentration as constant as possible.

vacuum are needed. The compression equipment required for such designs uses the majority of the energy produced by the power plant. Our calculations show that a pressure ratio (feed pressure divided by permeate pressure) of 5, to perhaps a maximum of 10, is all that can be afforded in this application.

The importance of pressure ratio in the separation of gas mixtures can be illustrated by considering the separation of a gas mixture with component concentration (mol%) of n_{i0} at feed pressure p_0 . A flow of component i across the membrane can only occur if the partial pressure of component i on the feed side of the membrane ($n_{i0}p_0$) is greater than the partial pressure of the component on the permeate side of the membrane ($n_{i\ell}p_{\ell}$) [18]; that is,

$$n_{i0}p_0 \geq n_{i\ell}p_{\ell} \quad (1)$$

It follows that the maximum separation achieved by the membrane can be expressed as

$$\frac{p_0}{p_{\ell}} \geq \frac{n_{i\ell}}{n_{i0}} \quad (2)$$

That is, the enrichment achieved in the permeate relative to the feed ($n_{i\ell}/n_{i0}$) is always smaller than the feed-to-permeate pressure ratio (p_0/p_{ℓ}), no matter how selective the membrane. In practical separation applications, the pressure ratio across the membrane is usually between 5 and 15 [18]. Higher pressure ratios can be achieved by using larger compressors on the feed gas or larger vacuum pumps on the permeate, but the capital and energy costs of this equipment limit the practical range of such approaches.

A sample calculation illustrating the pressure ratio issue is shown in Fig. 3. In this calculation, the feed gas contains 10% CO₂ at a pressure of 5 bar. The permeate pressure is maintained at 1 bar, so the pressure ratio is 5. The CO₂ permeance of the membrane is set at 1000 gpu. The membrane selectivity is varied from 1 to 10,000 by changing the nitrogen permeance as shown in Fig. 4(a). In these calculations, to maintain as constant a feed concentration as possible, only a small fraction of the CO₂ is removed through the membrane (stage-cut is set to 1%). At a membrane selectivity of one, the permeate gas has the same concentration as the feed: 10% CO₂. Membranes with higher selectivities achieve a better separation and the CO₂ concentration in the permeate approaches the maximum value of 50% determined by Eq. (2) at very high selectivities. It is important to note that even when the membrane selectivity is very high, at least half of the permeate gas is nitrogen. At a selectivity of 1000, the nitrogen permeance is only 1.0 gpu. This implies that a very large membrane area is required to process the gas. This point is illustrated in Fig. 4(b).

Fig. 4(b) shows the membrane area required to produce the same volume of permeate gas for membranes of increasing CO₂/N₂ selectivity (constant CO₂ permeance, decreasing N₂ permeance). Although very high selectivities produce the highest purity permeate, the membrane area required is then very large. A trade-off exists between membrane area and permeate CO₂ concentration. Inspection of Fig. 4(a) and (b) suggests that at a pressure ratio of 5, the optimum selectivity for this separation is between 20 and 40 (4–8 times the pressure ratio). A lower selectivity does not produce a good separation; a higher selectivity uses much more membrane area with little additional improvement in CO₂ purity.

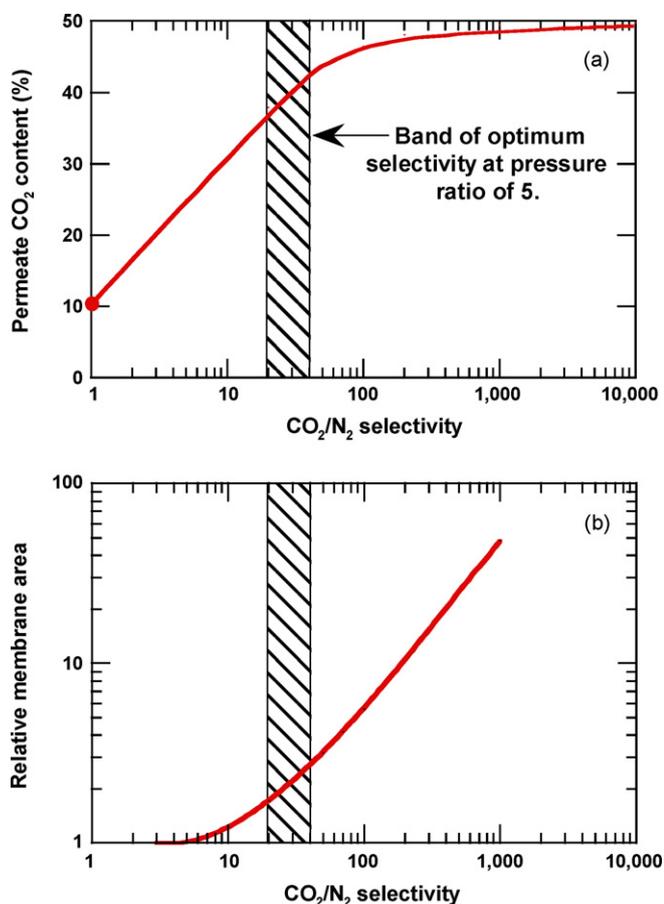


Fig. 4. Effect of CO₂/N₂ selectivity on permeate CO₂ concentration (a) and relative membrane area (b). For the pressure ratio shown in Fig. 3, optimum CO₂/N₂ selectivity falls in a band between 20 and 40.

These calculations and those that follow in this paper were performed with a computer process simulation program (ChemCad 5.6, ChemStations, Houston, TX). The computer package has been modified with differential element subroutines written at MTR for the membrane separation steps.

The curves in Fig. 4(a) and (b) could be changed by increasing the pressure ratio, but as noted earlier, a pressure ratio of 5 is already near the top end of what is economically affordable for this application. In the discussion that follows, we will show that the way around this problem is to use multi-step and multi-stage designs incorporating counter-flow/sweep membrane modules.

3.2. Feed compression versus permeate vacuum design

The pressure ratio required to drive a membrane process can be provided either by compressing the feed gas or drawing a vacuum on the permeate. To date, essentially all of the membrane gas separation equipment installed in the natural gas and petrochemical industry has used feed gas compression because the membrane area needed is much less than when a permeate vacuum is used [18]. Compression is also preferred because the capital cost of compression equipment is two-thirds to half of the cost of vacuum equipment of the same power rating. Nonetheless, as shown below, vacuum equipment will be needed for this flue gas application.

Fig. 5 shows two one-stage membrane processes treating a simplified model flue gas from a 600 MW_e power plant (13% CO₂, 87% N₂, no O₂, no H₂O). Both processes remove 90% of the CO₂ from the

gas and both use the same membranes operating at the same pressure ratio. The difference is that one process uses feed compression, and the other permeate vacuum.

When feed compression is used, recovery of a portion of the energy of compression is possible by means of a turboexpander and this is shown in the figure. When a permeate vacuum is used, a blower is still required to push the gas through the membrane modules and this is also shown. In these illustrative calculations, the efficiency of the vacuum pumps, compressors, blowers and expanders are all taken at 80%.

Even though feed compression uses less than a quarter of the membrane area of the vacuum system, vacuum operation is still favored because of its lower energy consumption. Calculations show that feed compression, even to only 5 bar, uses 20% of the energy production of the power plant. This large energy drain is required because a feed compressor must pump a large volume of gas that is mostly nitrogen. In contrast, the vacuum process only needs to pump the much smaller volume of gas that permeates the membrane.

Although the lower energy cost of vacuum operation is a compelling argument in its favor, there are other issues that must be addressed when using the permeate vacuum approach. Large-scale industrial vacuum equipment is not commonplace, and a vacuum pressure of 0.2 bar is probably the lowest vacuum pressure that can be considered practical for flue gas CO₂ capture. Lower pressures result in equipment size, cost, and energy requirements that are too large to be economical. Furthermore, even if such equipment were affordable, the pressure on the permeate side of the membrane will be higher than that at the suction of the vacuum equipment due to pressure drop in the module permeate channels and to leaks in permeate-side tubing and vessels. For these reasons, research studies that use unrealistically low permeate pressures of 0.1 bar or even lower in experiments and design calculations are not helpful in evaluating the real potential of a membrane CO₂ capture system.

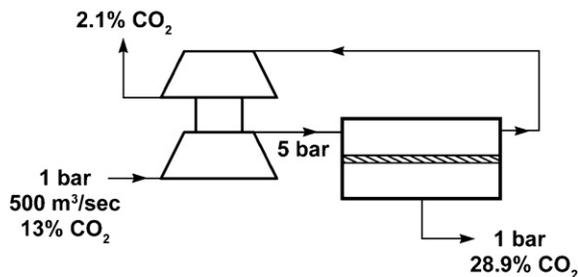
3.3. Cross-flow or counter-flow modules

The membranes shown in Figs. 3–5 all used cross-flow membrane modules. The benefits of counter-flow operation are well known [18,19], but to date, these advantages have not been sufficient to persuade membrane plant designers to deal with the problems of greater complexity, flow distribution and permeate-side pressure drops associated with counter-flow modules. Some authors have also suggested that concentration polarization on the permeate side of the membrane could reduce the benefit of counter-flow [20]. For the reasons given above, counter-flow modules are currently limited to use in air dehydration and some nitrogen-from-air modules. The majority of the installed membrane base uses cross-flow modules. However, the separation of CO₂ from power plant flue gas is an application where counter-flow modules are likely to be used.

The advantage of counter-flow modules for flue gas separation is illustrated in Fig. 6. The separation performed and the membranes used are as previously described in Fig. 5. The only difference is the mode of module operation – cross-flow or counter-flow. Counter-flow operation is clearly superior: the permeate CO₂ concentration increases from 29% to 41%, the membrane area required is reduced by 38%, and the power consumption decreases from 56 MW to 46 MW – an 18% energy saving.

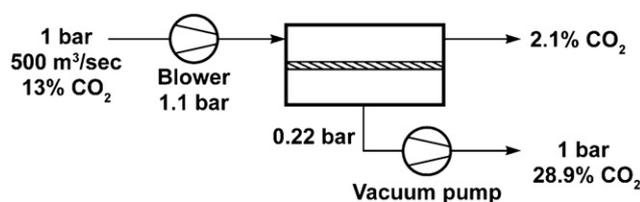
Although cross-flow hollow-fiber and spiral-wound membrane modules are the norm, a number of practical counter-flow module designs are described in the patent literature, so no insurmountable technical problems are foreseen in using this module design.

(a) Single-step membrane process with feed compression



| | |
|---------------|-------------------------------|
| Compressor | 151.3 MW |
| Turboexpander | (-36.6 MW) |
| Total energy | 114.7 MW |
| Membrane area | $2.4 \times 10^6 \text{ m}^2$ |

(b) Single-step membrane process with a permeate vacuum



| | |
|---------------|--------------------------------|
| Blower | 7.2 MW |
| Vacuum pump | 56.3 MW |
| Total energy | 63.5 MW |
| Membrane area | $11.0 \times 10^6 \text{ m}^2$ |

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Fig. 5. A comparison of feed compression versus permeate vacuum as the source of pressure difference across the membrane. The membrane has a CO_2 permeance of 1000 gpu and a N_2 permeance of 20 gpu. At the same pressure ratio, both designs produce the same separation. Feed compression uses less membrane area; vacuum operation uses less energy.

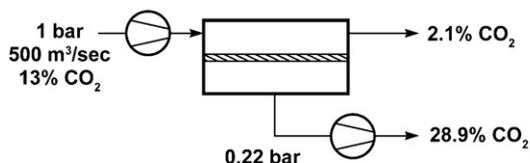
3.4. Sweep modules

The availability of counter-flow modules also means that permeate-side sweep processes can be considered. Performance of a sweep module is compared to a counter-flow module for the target flue gas application in Fig. 7. As in Fig. 6, the feed is a $500 \text{ m}^3/\text{s}$ stream containing 13% CO_2 . The membrane step reduces the CO_2 concentration in the treated flue gas to 2.1% CO_2 and produces a CO_2 -enriched permeate. Fig. 7 modules are of a counter-flow design. However, in the sweep module (Fig. 7(b)), a small portion of the CO_2 -stripped residue gas is reduced in pressure and then introduced to the permeate side at the residue end of the module. The separation obtained depends on how much gas is used as a sweep. In the example shown, the sweep is about 6% of the feed gas flow. The effect is dramatic; the concentration of CO_2 in the permeate remains almost the same, but the membrane area required to perform the separation is reduced almost 40%. Mixing separated residue gas with the permeate gas actually improves the separa-

tion! This paradoxical result is related to the pressure ratio issue described earlier. At the residue end of the module, the feed gas concentration is only 2–3% CO_2 . This means the maximum concentration of CO_2 in the permeate at this end of the module is 10–15% CO_2 (from Eq. (2)). Therefore, 85–90% of the gas must be nitrogen. At this end of the module, it is slow permeation of nitrogen across the membrane that is limiting the rate of CO_2 removal from the feed. When nitrogen is added as a sweep (even if it contains 2.1% CO_2), it reduces CO_2 concentration in the permeate, thus increasing the CO_2 partial pressure difference across the membrane, and allowing CO_2 to more rapidly permeate across the membrane. This in turn reduces the membrane area needed for the separation. This type of sweep result is discussed in more detail elsewhere [18,19].

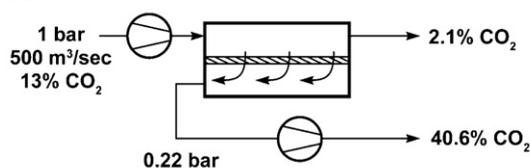
In the example calculations described to this point (Figs. 4–7), the feed gas to the membrane system is assumed to be 13% CO_2 and 87% nitrogen. But real coal-derived flue gas is more complex, containing some oxygen, SO_x and NO_x compounds, other minor contaminants, and in particular, it is saturated with water vapor. At

(a) Cross-flow module



| | |
|---------------|--------------------------------|
| Blower | 7.2 MW |
| Vacuum pump | 56.3 MW |
| Total energy | 63.5 MW |
| Membrane area | $11.0 \times 10^6 \text{ m}^2$ |

(b) Counter-flow module



| | |
|---------------|-------------------------------|
| Blower | 7.2 MW |
| Vacuum pump | 38.8 MW |
| Total energy | 46.0 MW |
| Membrane area | $6.8 \times 10^6 \text{ m}^2$ |

801-3d

Fig. 6. Advantages of (b) counter-flow modules compared to (a) cross-flow modules for flue gas separation. Counter-flow operation increases CO_2 concentration in the permeate, and at the same time it uses less energy and less membrane area. The membrane used in these calculations has a CO_2 permeance of 1000 gpu and a N_2 permeance of 20 gpu.

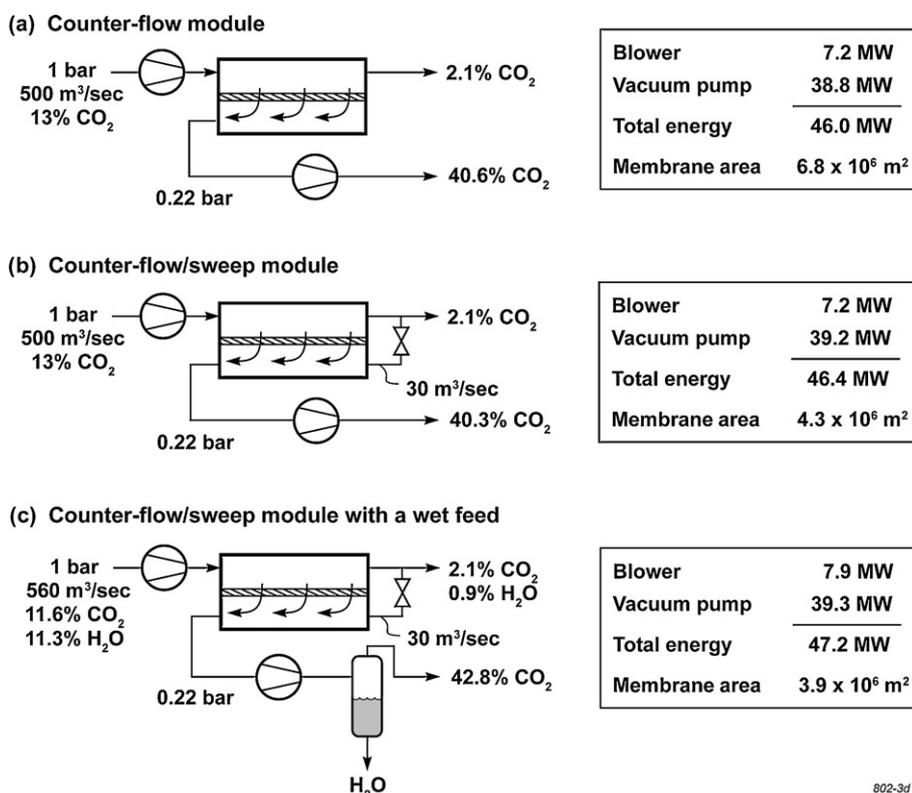


Fig. 7. The impact of sweep on counter-flow module performance in a flue gas application. With sweep, permeate CO₂ concentration remains almost the same, and the membrane area required is almost 40% less. The membrane used in these calculations has a CO₂ permeance of 1000 gpu and a N₂ permeance of 20 gpu.

50 °C, the water content of the fuel gas is about 11%. Water vapor is even more permeable than CO₂ in membranes, and so, the presence of water in the feed has the beneficial effect of providing an internal sweep that dilutes the permeate. As a result, water vapor in the permeate increases the driving force for CO₂ permeation through the membrane. The water in the permeate can then be condensed when the permeate is cooled after leaving the vacuum pump. The net result is to provide a slightly CO₂-enriched permeate gas and to reduce the membrane area required by about 10%. Removing water vapor from the flue gas going to the stack also has some beneficial effects. The impact of a wet flue gas feed is illustrated in Fig. 7(c).

4. Membrane considerations for post-combustion CO₂ capture

A variety of membranes have been considered previously for flue gas CO₂ capture. For example, the early studies of Hendricks et al. [7,8] considered commercial polymer membranes available at the time. The authors concluded that existing membrane systems were not competitive with absorption technologies and that higher CO₂/N₂ selectivities than those commercially available were required. More recently, numerous researchers have examined membranes with much higher CO₂/N₂ selectivities, typically achieved through facilitated transport of CO₂ [9–11,21–23]. Facilitated membranes of this type have been studied for decades [24,25], but they have never been used commercially due to cost and reliability issues [18]. Fig. 8 shows a Robeson-type trade-off plot of CO₂/N₂ selectivity versus CO₂ permeance for membranes reported in the literature as useful for flue gas treatment. Included in this figure are data for a new membrane developed by MTR called Polaris™. Compared to other membranes considered for CO₂/N₂ separation, Polaris™ has modest selectivity but much higher CO₂ permeance. For example, Polaris™ membranes are 10–50 times more permeable than conventional cellulose acetate membranes

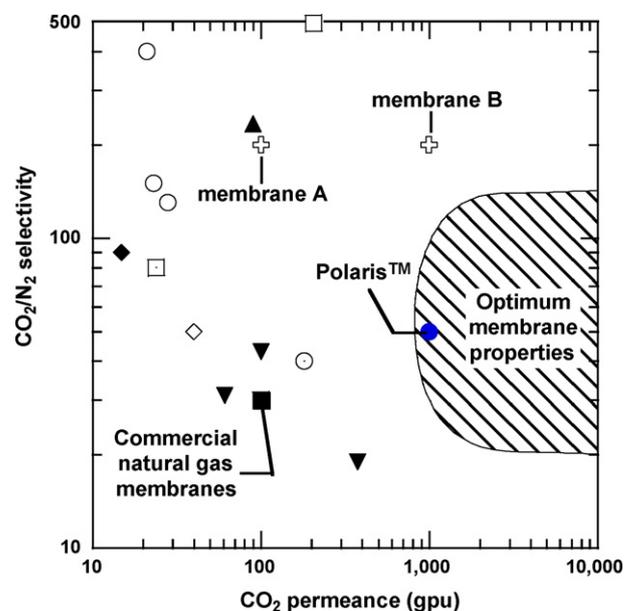


Fig. 8. CO₂/N₂ selectivity versus CO₂ permeance trade-off plot comparing the performance of MTR Polaris™ membrane with commercial natural gas membranes and various developmental membranes reported in the literature. The shaded area shows the region of optimum membrane properties for the separation of CO₂ from flue gas. Open circles (○) are data points for Kia et al. [9] and Duan et al. [22]; the filled triangle (▲) is reported by Bao and Trachtenberg [10]; the open square (□) is data of Zou and Ho [30]; the filled diamond (◆) is data of Deng et al. [11]; the open square with a dot (◻) is data of Cai et al. [31]; the open diamond (◇) is data of Hanioka et al. [32]; the open circle with a dot (⊙) is data from Zhao et al. [33]; the inverted triangles (▼) are data from Hendricks et al. [8]; membranes A and B are described in the text and Table 1.

Table 1
Comparison of membrane area, required power, and CO₂ permeate concentration for three membranes.

| Membrane | CO ₂ permeance (gpu) | CO ₂ /N ₂ selectivity | Membrane area (MM m ²) | CO ₂ concentration in the permeate (%) | Total compression power (MW) ^a |
|------------|---------------------------------|---|------------------------------------|---|---|
| Base case | 1000 | 50 | 2.1 | 46 | 76 |
| Membrane A | 100 | 200 | 59 | 54 | 70 |
| Membrane B | 1000 | 200 | 5.7 | 55 | 70 |

In these calculations, the feed and permeate pressures are 2.0 and 0.2 bar, respectively.

^a Total compression power = feed compressor + permeate vacuum – residue turboexpander.

used for CO₂ removal from natural gas, combined with similar selectivities. As we will demonstrate, because flue gas CO₂ capture is pressure-ratio-limited, high permeance membranes such as Polaris™ are much more economical than high selectivity, but low-permeance membranes. For the remainder of this paper, we will use Polaris™ as the base-case membrane in design calculations, and refer to it as the base-case membrane.

The impact of membrane selectivity and permeance on the CO₂ permeate purity produced by a membrane CO₂ capture process is illustrated in Fig. 9. Two membranes are used to treat flue gas from a 600 MW_e coal-fired power plant in a single step. The membranes compared in this figure are the base-case membrane with a CO₂/N₂ selectivity of 50 and a CO₂ permeance of 1000 gpu and a hypothetical membrane with a CO₂/N₂ selectivity of 200 and a CO₂ permeance of 100 gpu (membrane A). These properties were selected for membrane A because a number of studies have suggested that 200 should be a selectivity target for a flue gas membrane [8,13]. Moreover, the membrane permeance and selectivity are rough averages of the properties of the best high-selectivity membranes in Fig. 8. For Fig. 9 calculations, a single-step membrane process was used with 90% CO₂ removal from the feed. The feed was wet flue gas containing 11.6% CO₂, 11% H₂O, and 4.2% O₂ in nitrogen. The feed pressure was set at 2.0 bar and the permeate pressure was varied. The simulations show that at the lowest practical permeate pressure of 0.2 bar, the difference in CO₂ purity in the permeate is relatively small for the two membranes. Only at very high vacuum conditions where pressure ratio limitations are reduced does highly selective membrane A produce a significantly

purer permeate stream. Unfortunately, as described earlier, such high vacuums are economically and energetically impractical.

The membrane area required by the base-case membrane and membrane A to capture 90% CO₂ is shown in Fig. 10 as a function of permeate pressure. At the lowest practical permeate pressure of 0.2 bar, 2.1 million m² of the base-case membrane are required for 90% CO₂ capture from a 600 MW_e power plant. For the same CO₂ removal, 59 million m² of membrane A are required. Thus, while the high-selectivity membrane gives a slightly higher permeate CO₂ purity, the enormous difference in membrane area (and capital cost) clearly favors a high permeance, moderate selectivity membrane.

The need to optimize membrane selectivity for process operating conditions is further illustrated in Table 1. The table compares the performance of the base-case membrane with membrane A and another hypothetical membrane with the same CO₂ permeance as the base case, combined with a CO₂/N₂ selectivity of 200 (membrane B). Of the three membranes, the base-case membrane uses the least membrane area and is favored economically over even the high permeance, high-selectivity membrane B. This counterintuitive result occurs because pressure ratio limitations require that a significant fraction of the permeate must be nitrogen. The high selectivity of membrane B means that this membrane has lower N₂ permeance than the base-case membrane. Consequently, even though membrane B has the same CO₂ permeance as the base-case membrane and is four times more selective, membrane B requires more membrane area to perform the same separation. This makes membrane B a less desirable membrane for flue gas CO₂ capture.

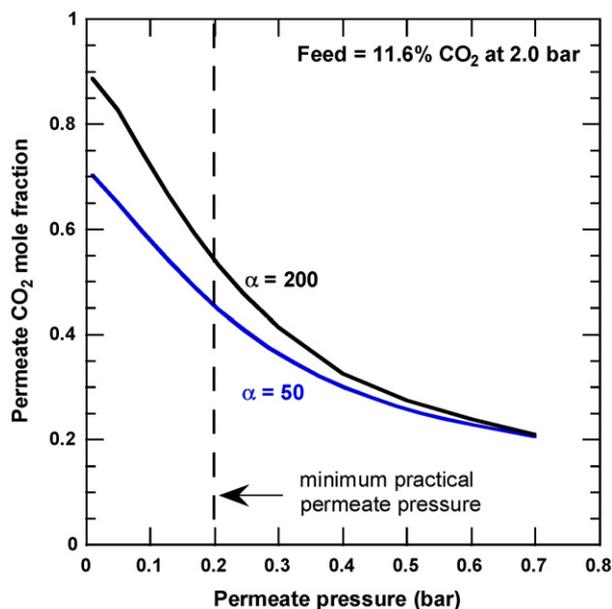


Fig. 9. Effect of permeate pressure on permeate CO₂ concentration for membranes with CO₂/N₂ selectivities of 50 (base case) and 200 (membrane A). The CO₂ permeances for these membranes were 1000 gpu and 100 gpu, respectively. For these calculations, the CO₂ recovery was fixed at 90%.

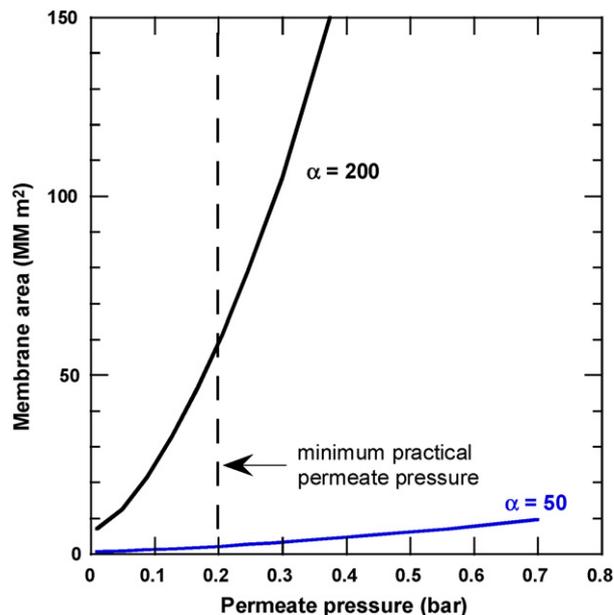


Fig. 10. Effect of permeate pressure on the membrane area required to capture 90% CO₂ for membranes with a CO₂/N₂ selectivity of 50 (base case) and 200 (membrane A). The CO₂ permeances for these membranes were 1000 gpu and 100 gpu, respectively. For these calculations, the feed pressure was 2.0 bar.

In the comparative calculations shown in Table 1, a pressure ratio of 10 was achieved by compressing the feed to 2 bar and using a vacuum of 0.2 bar on the permeate. From an energy standpoint, this is probably the largest pressure ratio that can be tolerated for flue gas CO₂ capture. Table 1 shows that already 70 MW or nearly 13% of the power plant energy has been used by the membrane process regardless of the type of membrane used. Significant additional energy will be needed to further purify and compress the CO₂ in the permeate so that it can be sequestered. Typical targets for capture technologies to produce sequestration-ready CO₂ streams are 95+% CO₂. A one stage process cannot meet this target at an affordable pressure ratio.

The shaded area of Fig. 8 shows the target performance of membranes with properties useful for CO₂ capture from flue gas. High CO₂ permeance membranes are required (≥ 1000 gpu). Membranes with lower CO₂ permeances will simply require too much membrane area. In addition, membranes with a selectivity of less than 20 are unlikely to be selective enough, no matter what their permeance. On the other hand, membranes with a selectivity of much more than 100 are likely to be too selective and require too much membrane area because of the pressure ratio issues described earlier.

The shaded area shown in Fig. 8 is a rough rule of thumb and there are caveats. Firstly, the data points shown in the figure are mostly based on pure-gas measurements, but the shaded area represents the properties required in an actual flue gas separation process (mixed-gas, low CO₂ partial pressure, 40–50 °C, saturated with water). It is possible that membranes that are in the optimum area based on their pure-gas properties may drop out based on their performance under actual operating conditions. Also, the shaded optimum properties are based on the performance of standard cross-flow modules, operated at pressure ratios of 5–10. The optimum area will change, depending on the pressure ratio and the specific design of the final separation process. Furthermore, the optimum membrane properties can be different for membranes used in different portions of the separation plant.

5. Multi-step or multi-stage process designs

The calculations discussed thus far all demonstrate that a single-stage membrane process cannot capture 90% of the CO₂ in flue gas and produce a high-purity CO₂ permeate stream, regardless of the membrane type used. This is because the system performance is restricted by the pressure ratio across the membrane. Because of this limitation, treatment of flue gas requires a multi-step or multi-stage membrane design to achieve the desired CO₂ recovery and purity.

Many different membrane process designs can be considered to improve the performance of a membrane system for flue gas CO₂ capture. To compare the relative merits of different CO₂ capture designs, it is necessary to calculate figures of merit such as the capital cost of the capture equipment, the energy requirement for capture, the increase in the cost of electricity due to capture, and the overall cost of capture per ton of CO₂ sequestered. Estimating the values for these measures of capture efficiency are always subject to a number of assumptions. As a consequence, values quoted in literature sources can vary considerably. We choose to calculate the cost of CO₂ separation, liquefaction, and compression to 140 bar as our figure of merit. The assumptions used in our calculations are summarized in Table 2.

Calculating the cost of capturing CO₂ can be a complicated exercise and the DOE has published reports listing all the factors that should be considered (site works, labor costs, maintenance, engineering hours, and so on [26]). For the purposes of range finding calculations that compare membrane processes, nothing so

Table 2

Assumptions used in base case design calculations.

| Category | Value | Units |
|--|-------|-------------------|
| Compressor, turbo expander, and vacuum pump efficiency | 0.80 | – |
| Compressor and turbo expander cost | 500 | \$/kW |
| Membrane CO ₂ permeance | 1000 | gpu |
| Membrane CO ₂ /N ₂ selectivity | 50 | – |
| Membrane skid cost | 50 | \$/m ² |
| Membrane equipment installation factor | 1.6 | – |
| Capital depreciation/interest | 20 | %/year |
| Cost of power | 0.04 | \$/kW |
| Capacity factor | 85 | % |
| Power plant lifetime | 25 | Years |
| Power plant size | 600 | MW _e |
| Flue gas flowrate | 500 | m ³ /s |
| Flue gas composition (wet gas): 11.6% CO ₂ ; 11% H ₂ O; 73% N ₂ ; 4.4% O ₂ | | |

elaborate is required. The compressor, vacuum pump, and turboexpander efficiencies and cost factors shown in Table 2 are average current values for large gas processing systems. The base-case membrane skid cost of \$50/m² (including membrane modules, housings, frame, valves and piping) is significantly lower than the range for today's commercial gas separation membrane skids (\$500–750/m²). However, industrial gas separation systems operate at high pressures with flammable, corrosive gases. Consequently, expensive steel housings, valves and piping are used. Industrial gas separation systems are also up to an order of magnitude smaller than the proposed flue gas CO₂ capture system. A more relevant comparison is large, commercial reverse osmosis (RO) systems. Several RO plants with a membrane area of more than 1 million m² have been built. These plants are of a similar size to the membrane systems needed to capture CO₂ from a 600 MW_e coal-fired power plant. RO systems benefit from economies of scale and low-pressure plastic components (housing, valves, tubing, etc.), and accordingly, the average membrane skid cost is less than \$50/m². Because flue gas membrane systems will operate at low pressures and can also use low-cost components, we believe low membrane skid costs, equivalent to those found in the RO industry, can be achieved.

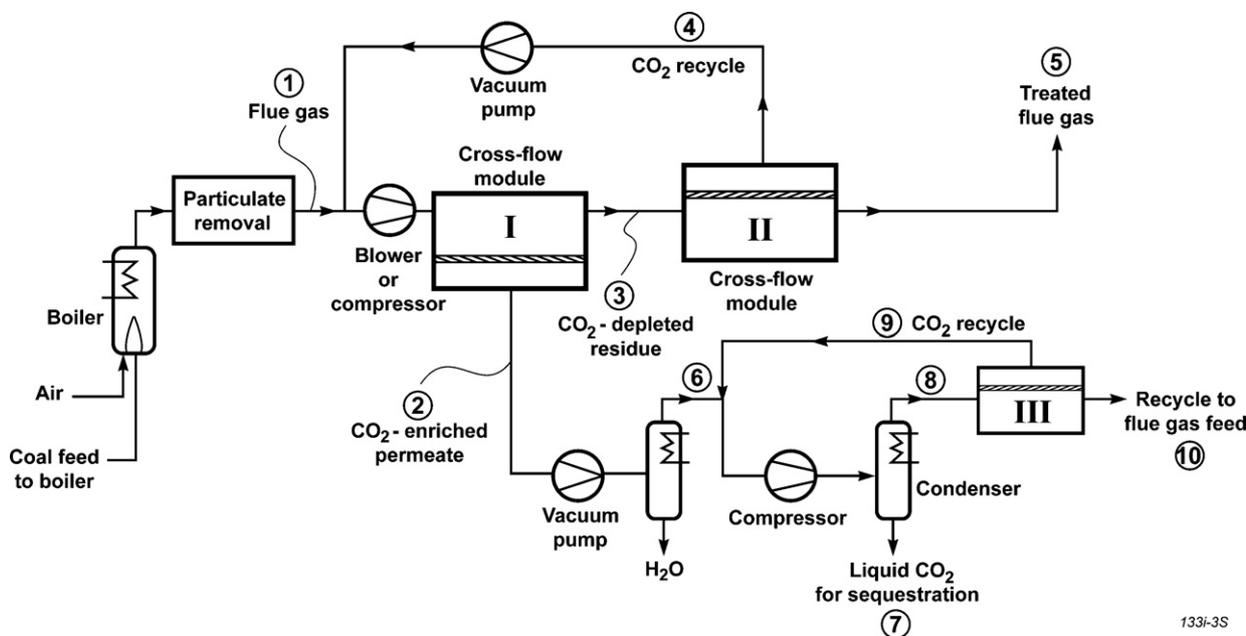
The capital cost of a membrane CO₂ capture system is split roughly equally between the cost of the membrane skids and the cost of vacuum pumps, blowers and associated equipment. The two largest items contributing to the operating cost of a membrane capture system are

- the cost of the power used in the separation process and
- the interest and depreciation charge for the capital used to build the membrane plant.

Calculating the power consumption is straightforward using the assumptions listed in Table 2. The cost of this power is taken as \$0.04/kWh. The power cost may seem low, but it is for electricity produced and used at the plant. There are no distribution and selling costs. For the annual capital charge, we have used 20% of the total membrane plant cost, which should be enough to cover depreciation, interest, and normal labor and maintenance. In equation form, the cost of capture (CC) in \$/ton CO₂ can be expressed as

$$CC = \frac{(P \times T \times E) + (0.2 \times C)}{F_{CO_2} \times T} \quad (3)$$

where P is the power required for CO₂ capture equipment (kW), T is the plant capacity factor (annual operating time in h/year), E is the cost of electricity to run the capture equipment (\$/kWh), C is the capital cost of the capture equipment (\$), and F_{CO_2} is the



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Fig. 11. Simplified flow diagram of a two-step vacuum membrane process to capture and sequester CO₂ in flue gas from a coal-fired power plant. The base-case membrane with a CO₂ permeance of 1000 gpu and a CO₂/N₂ selectivity of 50 was used in the calculations.

mass flow rate of captured CO₂ (ton/h). Typical cost of capture values for conventional flue gas CO₂ capture technologies, such as amine scrubbing, are in the \$40–100/ton CO₂ range. For the membrane process calculations described below, the cost of capture values include compression to supercritical CO₂, but not transport to sequestration sites. The transport cost is relatively small and is usually estimated at \$2–5/ton CO₂ [26].

5.1. Two-step vacuum design

Fig. 11 shows a two-step vacuum design for treating power plant flue gas that we considered in our development program. This design can achieve 90% CO₂ capture and produce 95+% supercritical CO₂ ready for sequestration. In this scheme, two membrane steps are used to reduce the CO₂ concentration of the flue gas (stream ①) from 11.6 to 1.8% CO₂ (stream ⑤). Here and in subsequent designs, the CO₂ concentration in the feed is lower than in earlier calculations because we include water in the feed. The composition assumed for wet flue gas feed is summarized in Table 2. The first membrane step (unit I) produces a permeate (stream ②) containing 50% CO₂ and 29% water. The CO₂-depleted residue (stream ③) leaving this membrane unit is sent to a second membrane step (unit II). The permeate from the second membrane step (stream ④) contains 24% CO₂. This is too dilute to be mixed with the first-step permeate, so this gas is recompressed and recycled to the front of the membrane process. After treatment, the flue gas (stream ⑤) is sent to the stack to be discharged to the atmosphere.

The CO₂-enriched permeate from the first membrane step (stream ②) is compressed in stages to 25 bar and cooled to room temperature, which removes the bulk of the water in the gas. The CO₂ content in the dry gas (stream ⑥) is then 70%. Final traces of water can be removed with a silica bed dryer (not shown). The dry gas is then cooled to –20 °C and sent to a short fractionating condenser column that produces high-purity CO₂ liquid as a bottoms product (stream ⑦). The liquid CO₂ can then be pumped to 140 bar and sent for sequestration as a supercritical fluid. The overhead gas from the column contains the non-condensable gases (mostly nitrogen) and some uncondensed CO₂ (stream ⑧). This gas could be sent to the front of the membrane process. However, a better solution is to use a third small membrane unit to recycle the bulk

of the CO₂ in the overhead gas to the front of the condensing column as shown (stream ⑨). Only the residue stream (stream ⑩) is then recycled to the flue gas feed. Overall, this process achieves 90% CO₂ capture using 131 MW of net compression/pumping power and 14 MW of refrigeration. The total energy use is about 24% of the power plant output. In addition, about 3.0 million m² of the base-case membrane would be used, which combined with the power usage, results in a capture cost of about \$39/ton CO₂.

By way of example, the capture cost for Fig. 11 design is calculated in the following manner. Membrane area of 3.0 million m² at \$50/m² equals \$150 million for the membrane skids. The 200 MW of compression/pump/turboexpander equipment at \$500/kW costs an additional \$100 million. Adding these values and multiplying by an installation factor of 1.6 gives a total capital cost of \$400 million. For operating expenses, the cost of power for 131 MW net at \$0.04/kWh assuming an 85% capacity factor equals \$118 million/year. Interest, depreciation, labor, and maintenance at 20% of the total capital cost come to \$80 million/year. The total operating cost is then \$198 million/year. Assuming 90% CO₂ capture and using Eq. (3), the CO₂ capture cost for this membrane design amounts to about \$39/ton CO₂.

The membrane design shown in Fig. 11 is a substantial improvement over the single-step membrane process described earlier. Other multi-step/stage membrane designs can be envisioned, some of which might yield slightly better CO₂ capture performance. However, the energy required in these membrane separation schemes is only marginally better than an amine absorption process and clearly not a game changer.

5.2. Two-step counter-flow/sweep design

A radically different approach that shows promise for flue gas CO₂ capture is to use counter-flow/sweep to improve the partial pressure driving force across the membrane without changing the flue gas pressure [27,28]. This design is shown in Fig. 12. In this scheme, a vacuum pump is used on the permeate side of the first membrane step (unit I). As discussed above, because the volume of the permeate gas (stream ②) passing through the vacuum pump is only a fraction of the volume of the flue gas (stream ①), the

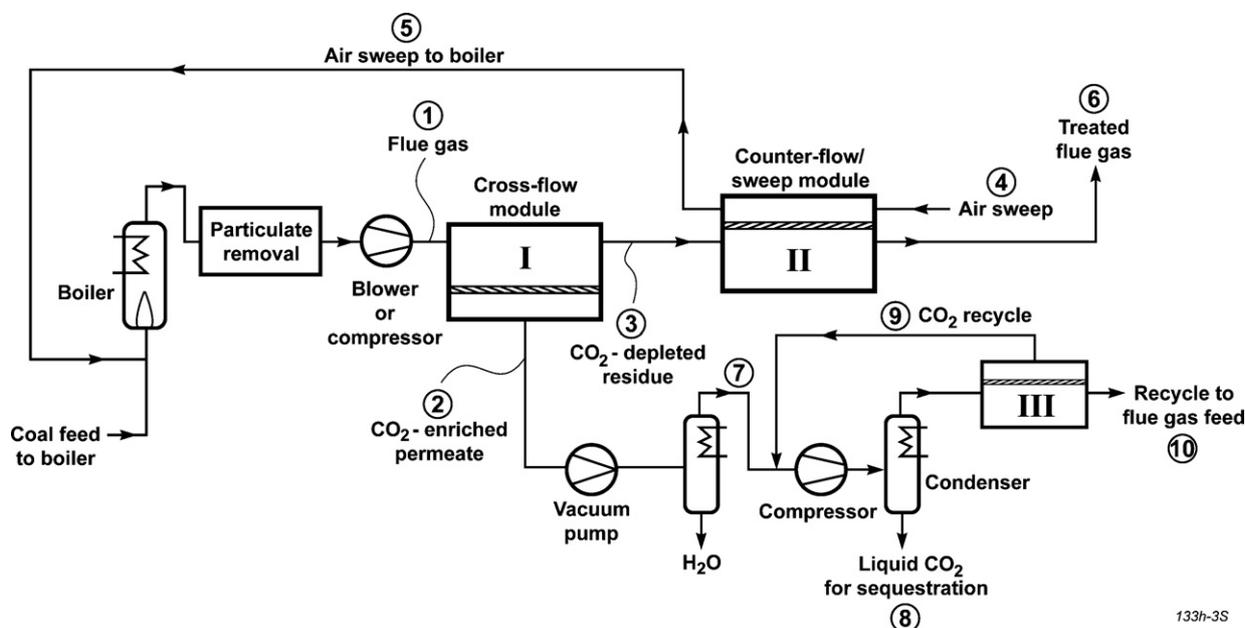


Fig. 12. Simplified flow diagram of a two-step counter-flow/sweep membrane process to capture and sequester CO₂ in flue gas from a coal-fired power plant. The base-case membrane with a CO₂ permeance of 1000 gpu and a CO₂/N₂ selectivity of 50 was used in the calculations.

power used by the vacuum pump is much smaller than the power consumed by compressing the feed gas. This cross-flow membrane unit only removes a portion of the CO₂ in flue gas in a single pass, in order to reduce the membrane area and energy required in this step. The residue gas leaving the cross-flow membrane step (stream ③) still contains about 7% CO₂. This gas passes on one side of a second membrane (unit II) that has a counter-flow/sweep configuration. All or a portion of the feed air to the boiler (stream ④) passes on the permeate side of this membrane as a sweep stream. Because of the low CO₂ concentration in the air sweep, some CO₂ permeates through the membrane and is recycled with the feed air to the boiler (stream ⑤). The treated flue gas (stream ⑥) leaving the counter-flow membrane unit contains 1.8% CO₂ and is vented – 90% CO₂ removal is achieved.

After the bulk of the water has been removed by condensation, the permeate gas from the first-step membrane module (stream ②) contains about 83% CO₂. This gas (stream ⑦) is sent to a compression-condensation-membrane loop similar to that described in the previous design. This liquefaction section uses about 6% of the electric power made by the plant to deliver high-pressure supercritical CO₂ to the pipeline for sequestration (stream ⑧). The permeate of the small liquefaction membrane (unit III) contains mostly CO₂ (stream ⑨) and is recycled to the front of the compressor/condenser train. The residue recycle (stream ⑩) is blended with stream ① after the feed blower. Overall, at 90% CO₂ capture, the membrane process uses 16% of power generated by the plant to produce supercritical CO₂ ready for sequestration. About 1.3 million m² of the base-case membrane is used, which combined with the power usage, results in a capture cost of about \$23/ton CO₂.

Table 3

Comparison of membrane designs for 90% CO₂ capture from a 600 MW_e coal-fired power plant. In these calculations, the feed and permeate pressures are 2.0 and 0.2 bar, respectively, and base-case membrane properties are used.

| Membrane design | Membrane area (MM m ²) | Total power use (MW) ^a | Fraction of power plant energy used (%) | Cost of capture (\$/ton CO ₂) | CO ₂ product concentration (%) |
|-------------------------------|------------------------------------|-----------------------------------|---|---|---|
| Two-step/two-stage | 3.0 | 145 | 24 | 39 | 95+ |
| Two-step countercurrent sweep | 1.3 | 97 | 16 | 23 | 95+ |

^a Total power use = compressors + pumps – turboexpander + refrigeration.

Table 3 compares the key parameters of the two-step vacuum design with the new two-step counter-flow/sweep scheme. The two-step process with counter-flow/sweep offers two key benefits:

- Low-energy use because the counter-flow module design uses incoming combustion air as a sweep to generate driving force for CO₂ separation. In this way, the sweep module avoids the energy penalty of compression or vacuum treatment and provides an essentially “free” separation.
- Low membrane area because the CO₂ recycled in the combustion air stream increases the CO₂ concentration (and permeation driving force) in the feed to the first membrane step.

The use of incoming boiler air as a sweep stream has clear benefits from a separations standpoint. However, the impact of increased CO₂ content in the air sent to a conventional pulverized coal boiler is not clear at this time. In Fig. 12 design, the air going to the boiler (stream ⑤) contains 8.7% CO₂ and 18% O₂. Without some changes to boiler operating conditions, this recycle stream has the potential to lower performance of the boiler. Nevertheless, much larger CO₂ recycle streams are being considered for oxy-fuel boilers, so no insurmountable obstacles are foreseen for the air sweep design.

6. Process sensitivity studies

A number of sensitivity studies were conducted to optimize the performance of the counter-flow/sweep design (Fig. 12) for flue gas CO₂ capture. The base-case process conditions and performance are given in Table 3.

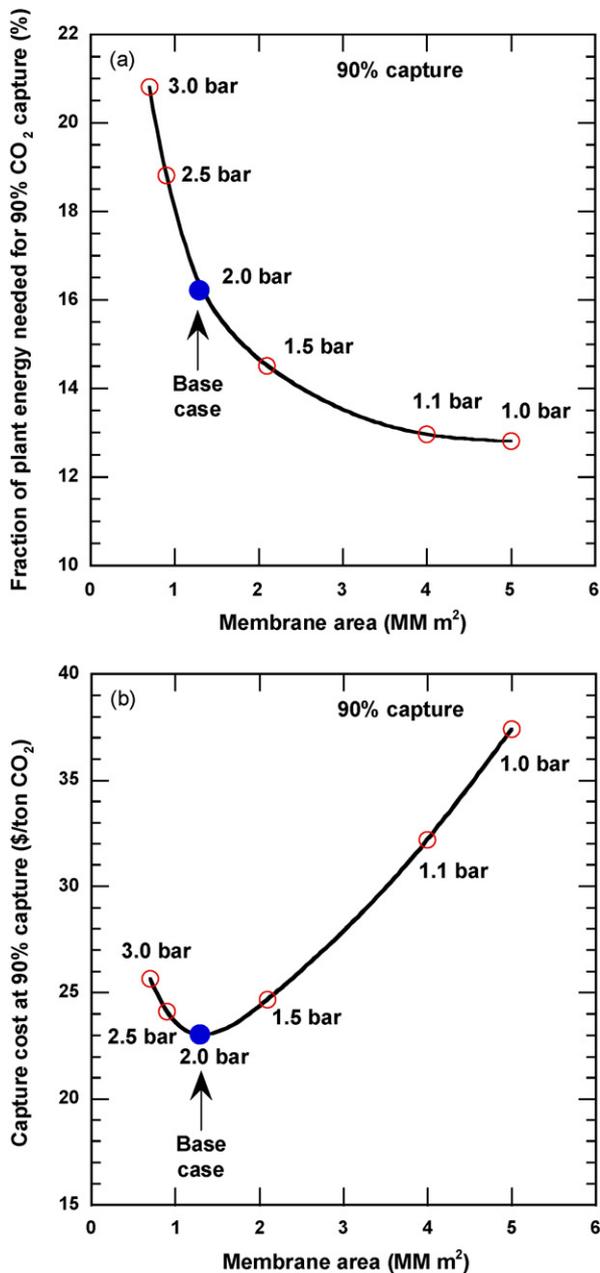


Fig. 13. Trade-offs in membrane area and feed compression for CO₂ capture from flue gas. For these calculations, Fig. 12 plant design was used with a fixed permeate pressure of 0.2 bar and the feed pressure was varied from 1.0 to 3.0 bar as shown in the figure. The base-case membrane properties (CO₂ permeance of 1000 gpu and CO₂/N₂ selectivity of 50) were used. The optimum balance of low-energy use (a) and low capture cost (b) occurs at pressure ratios of 5–10 (feed pressures of 1.0–2.0 bar).

In Fig. 12 design, there is a balance between the energy used to achieve the required pressure ratio and the membrane area employed. Higher pressure ratios reduce membrane area but increase the energy use. This trade-off is illustrated in Fig. 13(a). In these calculations, the permeate pressure is fixed at 0.2 bar, the feed pressure is varied from 1.0 bar (a pressure ratio of 5.0) to 3.0 bar (a pressure ratio of 15), and the CO₂ recovery is fixed at 90%. Little or no feed compression is clearly the low-energy option. For example, as the feed pressure increases from 1.0 to 3.0 bar, the fraction of plant energy used to achieve 90% CO₂ capture increases from 12.8% to 20.8%. Fig. 13(b) shows the effect of pressure ratio and membrane area on the CO₂ capture cost. The total cost of capture goes through a minimum at about 2.0 bar of feed pressure. Above 2.0 bar,

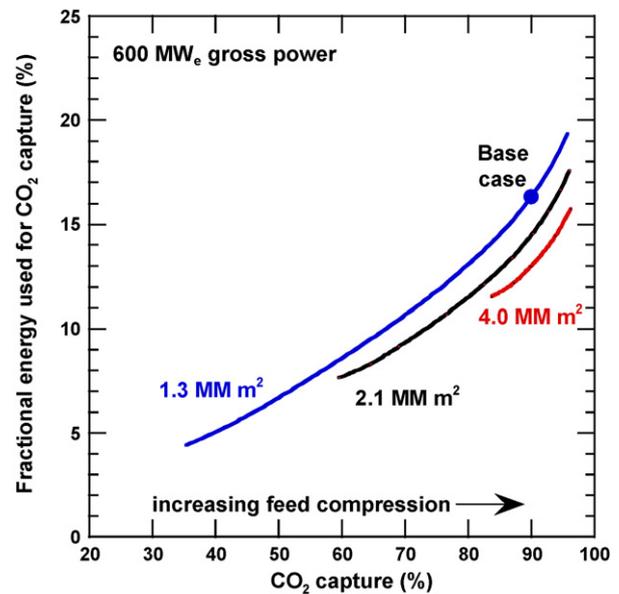


Fig. 14. Percentage of power plant energy used to capture CO₂ as a function of the CO₂ capture amount for the two-step counter-flow/sweep membrane process. Each of the curves represents a fixed total membrane area where the feed compression was varied from 1.0 bar to the pressure needed to achieve >95% CO₂ capture. The solid circle is the 90% capture base case (1.3 million m² of membrane; 2.0 bar feed).

the capture cost rises because of an excessive energy charge. Below 2.0 bar, the capture cost rises because of excessive membrane area. Taken together, the information in Fig. 13 suggests that the optimum balance of low-energy use and low capture cost occurs with a pressure ratio of 5–10 (feed pressure of 1.0–2.0 bar). If membrane permeance can be increased or membrane cost reduced, this will push the optimum toward lower feed pressures.

The DOE has set a capture and sequestration target of 90% CO₂ capture from power plants for its development program. However, many power plant operators believe that initial regulations may require lower capture percentages, and so it is worthwhile to look at the economics of capture over a range of mitigation scenarios. Fig. 14 shows the impact of the CO₂ capture percentage on the energy used for the counter-flow/sweep membrane design. The energy use shown includes the energy required to compress the CO₂ to a supercritical state. In these calculations, the permeate pressure was held constant at 0.2 bar and the feed pressure was varied from 1.1 bar (a blower) to the pressure required to achieve >95% CO₂ capture (by using a compressor). Three different membrane areas were used for comparison (1.3, 2.1 and 4.0 million m²). The energy required for capture increases linearly with increasing percentage of CO₂ captured, up to about 70% capture. At high capture rates (>80%), the energy required begins to increase rapidly, so optimum percent capture based on energy considerations alone is about 70–80%.

The total CO₂ capture cost, including a charge for the capital cost of the capture equipment and the energy consumption, is given in Fig. 15. The capture cost initially decreases with increasing CO₂ recovery, reaches a shallow minimum between 70 and 85% recovery, and then increases sharply at higher recovery rates. At low recoveries, the amount of CO₂ captured (the denominator in Eq. (3)) is relatively small, while the capital investment for a capture system (membrane area and compression equipment) has already been made. Consequently, while the operating costs (power) are also relatively low, the installed capture equipment is not used efficiently, and the overall capture cost is high. As CO₂ recovery increases, the membrane area or power requirements increase, but more slowly than the increasing amount of CO₂ captured. As a

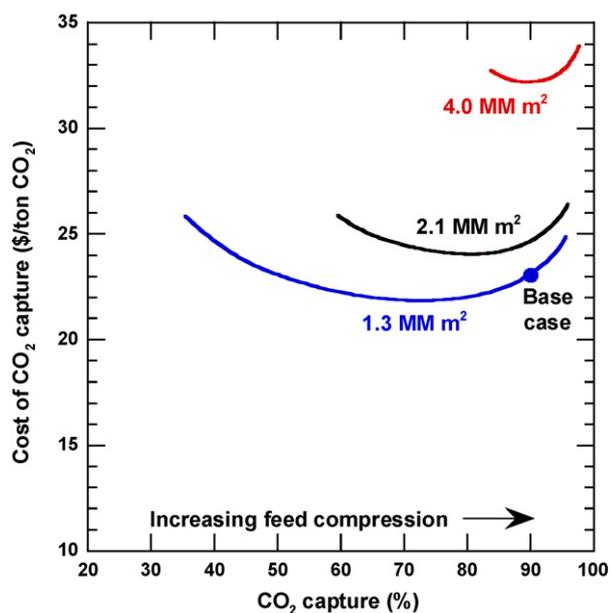


Fig. 15. Cost of capture as a function of the CO₂ capture percent for the two-step counter-flow/sweep membrane process. Each of the curves represents a fixed total membrane area where the feed compression was varied from 1.0 bar to the pressure needed to achieve >95% CO₂ capture. The solid circle is the 90% capture base case (1.3 million m² of membrane; 2.0 bar feed).

result, the cost of capture decreases. At high CO₂ recoveries (>85%), relatively large increases in power or membrane area are required to obtain only incremental increases in the amount of CO₂ captured. Consequently, the cost of capture increases at these high CO₂ recoveries. It appears that the lowest capture cost is at a CO₂ recovery level of 70–85% depending on the amount of membrane area used.

The key energy-saving aspect of Fig. 12 membrane design is the use of an existing process stream (boiler air) as a sweep to generate driving force to separate CO₂ from flue gas. The fraction of the boiler feed air used as a sweep gas affects the efficiency of the process. This is shown in Fig. 16. In this figure, 100% on the x-axis corresponds to all of the air required for combustion being used to sweep the membrane unit. Lesser amounts signify that a portion of the combustion air goes straight to the boiler in the conventional manner. If all of the combustion air going to the boiler is used to sweep the membrane unit, the energy used to capture 90% of the flue gas CO₂ is about 16% of the plant output for the base case (1.3 MM m² of membrane). In contrast, if only 30% of the air going to the boiler is used to sweep the membrane unit, the energy use increases to 20%. For a 600 MW_e power plant, the difference between these two cases is 24 MW_e! If higher membrane area, and less feed compression than the base case is used, the effect of sweep is even greater. Clearly, sweep can result in dramatic energy savings, and from a separations efficiency standpoint, maximum sweep air is preferred.

The preceding sensitivity studies illustrated the effect of operating conditions (feed compression, membrane area, and sweep flowrate) on system performance. Fig. 17 illustrates the impact of membrane properties (CO₂ permeance and CO₂/N₂ selectivity) on the CO₂ capture cost. In these calculations, Fig. 12 sweep design was used with a pressure ratio of 5.5. This pressure ratio corresponds to a feed pressure of 1.1 bar generated by a blower and a permeate vacuum of 0.2 bar. The membrane selectivity was varied for membranes with CO₂ permeances of 1000, 2000, and 4000 gpu. At CO₂/N₂ selectivities of less than 30, the capture cost is a strong function of membrane selectivity. For example, as the membrane CO₂/N₂ selectivity increases from 10 to 30, the capture cost decreases from \$55 to \$33/ton CO₂ for a 1000 gpu CO₂ membrane. However, at selectivities above 30, the capture cost remains

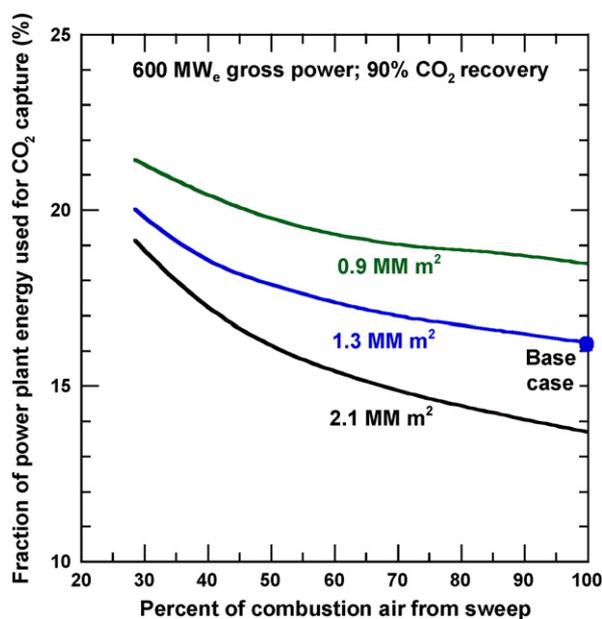


Fig. 16. Effect of sweep flowrate on the percentage of power plant energy used to capture 90% of the CO₂ in flue gas with the counter-flow/sweep membrane process. The solid circle is the 90% capture base case (1.3 million m² of membrane; 2.0 bar feed).

essentially constant for this membrane. This is related to the pressure ratio effect described earlier. In contrast, at a fixed selectivity, increasing membrane permeance has a significant effect on the capture cost by reducing the required membrane area (capital cost). For example, at a selectivity of 50, doubling the membrane permeance from 1000 to 2000 gpu reduces the cost of capture from \$32 to \$21/ton CO₂. If the CO₂ permeance can be doubled again to 4000 gpu, the capture cost drops to \$15/ton CO₂.

In summary, at CO₂/N₂ selectivities above 30, increases in membrane CO₂ permeance are more important than further increases in selectivity. This is because in a real-world membrane process designed to treat flue gas, such as that shown in Fig. 12, the mem-

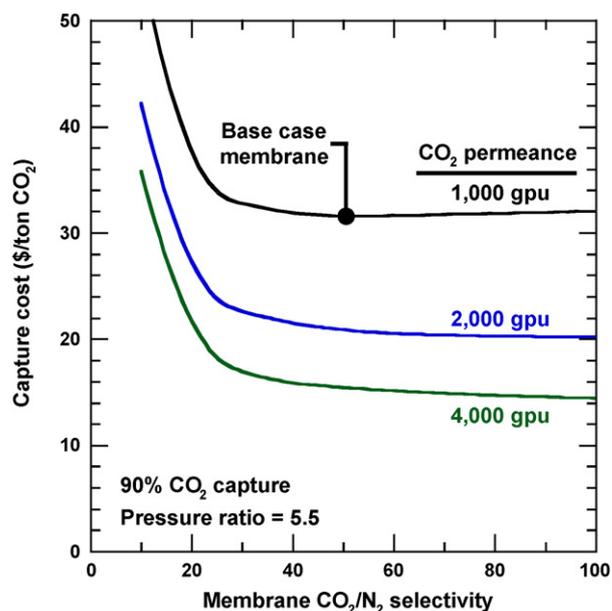


Fig. 17. Effect of membrane CO₂/N₂ selectivity on the cost of capturing 90% of the CO₂ in flue gas for membranes with a CO₂ permeance of 1000, 2000, and 4000 gpu at a fixed pressure ratio of 5.5.

brane operates in a pressure-ratio-limited regime. Under these conditions, increasing membrane permeance will help reduce the required membrane area (and capital cost), but increasing selectivity has only a small impact on product purity (which affects power requirements and operating costs).

As a final aside, Fig. 17 also illustrates the sensitivity of CO₂ capture costs to the cost of the membrane skid. The capital cost of the membrane plant can be changed by varying the CO₂ permeance as described above (base case 1000 gpu) or by changing the membrane skid cost (base case \$50/m²). It follows that being able to produce low-cost (as well as high permeance) membrane skids is a critical element of applying membrane technology to flue gas CO₂ capture.

This paper highlights the potential of membrane processes to cost-effectively capture CO₂ from power plant flue gas. There are, of course, many challenges to realizing this potential. Here, we have focused on the challenges of minimizing energy use through novel process designs, and optimizing membrane properties to reduce cost, taking into account the constraints imposed by practical operating conditions. Other challenges, only alluded to, include the lifetime of membranes operating in a challenging environment (particulate matter, SO_x and NO_x, and trace metals), the need to reduce membrane cost, and the lack of membrane field data treating real power plant flue gas. A future publication describing the results of field demonstrations of MTR's Polaris™ membrane systems will address these issues.

7. Conclusions

There is a growing consensus that man-made CO₂ emissions to the atmosphere must be cut drastically to prevent the damaging effects of global climate change. To make such large reductions in CO₂ emissions while still using coal combustion as a low-cost means of generating power is a significant challenge. Currently, a variety of technologies are being evaluated for their ability to capture CO₂ from power plant flue gas. None of the capture options is a clear winner at this point. The most commercial-ready technology – amine absorption – is costly, energy intensive, and if implemented, would result in large increases in the cost of producing electricity.

Membranes have a significant opportunity to be a low-cost, low-energy solution for flue gas CO₂ capture. However, when evaluating membranes for this application, it is important to recognize the constraints imposed by practical operating conditions. Cost and energy considerations will limit the maximum pressure ratio attainable by feed compression and/or permeate vacuum to about 10. Under these conditions, high membrane permeance is much more important than high CO₂/N₂ selectivity.

Recently, we have developed membranes with CO₂ permeances of greater than 1000 gpu and a CO₂/N₂ selectivity of 50. This permeance is 10-fold higher than commercial CO₂ membranes and the selectivity is among the highest reported for non-facilitated transport materials. These membranes, in combination with a novel process design that uses incoming combustion air as a sweep gas to generate driving force, show promise for meeting DOE CO₂ capture cost targets. Preliminary estimates indicate this membrane process can capture 90% of CO₂ in flue gas as a sequestration-ready supercritical fluid using about 16% of plant energy at a cost as low as \$23/ton CO₂. Further improvements are possible if membrane permeance can be increased or cost reduced.

Process sensitivity studies show that for membrane-based flue gas CO₂ capture:

- Processes using a vacuum on the permeate require significantly less energy than processes using compression of the feed gas.
- Some feed compression lowers the required membrane area and, combined with a partial permeate vacuum, may be the low-

cost capture option (depending on capital cost assumptions); however, no feed compression (blower only), while requiring maximum membrane area, is the low-energy option.

- If high permeance membranes can be developed (~4000 gpu or more) or membrane skid costs can be reduced below \$50/m², no feed compression will be the preferred approach from an energy and cost standpoint.
- Increasing membrane CO₂/N₂ selectivity above ~30 has little benefit; membrane materials research for this application should be focused on identifying highly permeable polymers.
- Sweep operation has the potential to lower the CO₂ capture energy penalty significantly (perhaps by 5% of the total plant output or more). More than 50% of combustion air should be used as sweep to maximize energy savings.

Ultimately, the competitiveness of a membrane flue gas CO₂ capture process will hinge on membrane cost and reliability issues, demonstration and acceptance of large vacuum/compression equipment, and efficient integration with power facility systems. These issues will require close collaboration between membrane developers and the power industry, as well as successful demonstrations of membrane plants of progressively larger size in the field.

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