Extended flue gas trials with a membrane-based pilot plant at a one-ton-per-day carbon capture rate

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Graphical Abstract

Abstract

A membrane-based pilot plant for carbon dioxide capture from the flue gas of a coal-fired power plant has been installed and operated at the National Carbon Capture Center in Wilsonville, Alabama, USA. The membrane system is sized to treat flue gas containing one ton per day of carbon dioxide. Stable operations for three extended runs conducted over a period of two years have been achieved with both pulverized coal and simulated natural gas flue gas. Carbon capture rates up to and over 90% were achieved with full-scale Polaris™ modules in individual trials that ran up to 1800 hours. Both cross-flow and countercurrent sweep spiral-wound modules demonstrated effective and stable carbon capture performance. This paper describes the experimental correlations that were developed, and summarizes the observed performance envelopes resulting from the combination of selected operating process conditions, equipment, and modules.

Keywords: Polaris membrane; flue gas trials; CO₂ capture; spiral-wound modules; two-step pilot plant.

1. Introduction

The U.S. Department of Energy (DOE) is supporting a substantial development effort to demonstrate that separation systems can be used to cost-effectively recover carbon dioxide (CO₂) from power plant flue gas. Current U.S. policy is calling for a variety of technology approaches to mitigate climate change, including development of new processes for carbon capture and sequestration (CCS). A membrane process proposed by Membrane Technology and Research, Inc. (MTR) [1, 2] has been used in extensive field trials at the DOE's National Carbon Capture Center (NCCC), with slipstream flue gas supplied by the Alabama Power E.C. Gaston plant that is fueled with pulverized coal. The membrane unit has been operating at NCCC since 2012, following prior development stages begun as early as the mid-2000s, including smaller field tests at coal and natural gas-fired power plants in 2009 and 2010.

It takes a significant and concerted effort to advance an experimental membrane from lab scale to use in a pilot plant with a one ton/day (TPD) carbon capture capacity operating in the field with real flue gas. There are technical milestones that need to be achieved, each of which requires an order-of-magnitude increase in resources to accomplish. To begin the scale-up process, the membrane chemistry has to be robust enough to transfer to commercial production equipment capable of reproducibly making large quantities of defect-free membrane. Full-scale modules must then be developed for a set of unexplored process conditions and an unconfirmed response of the membranes to performance in real flue gas. Simultaneously, the hardware for the pilot plant has to be designed, specified, and built. With funding from DOE, MTR has followed this development path to bring a new carbon capture membrane to the field trial stage. This paper describes experimental results obtained at a membrane-based pilot plant, which is now operating at the NCCC [3] treating coal-derived flue gas.

Research programs around the world have been operating field trials with carbon capture or related membrane systems [4-11]. For example, as part of a European Union project, small membrane modules developed by NTNU in Norway were recently tested at a coal power plant in Portugal. Such trials are an important step in demonstrating the viability of advanced carbon capture technologies like membranes. Ultimately, if membranes are to be a part of a cost-effective carbon capture solution, they will have to show long-term, stable operation of large module arrays. A full-scale CO₂ capture system at an average power plant will need hundreds of thousands or even millions of square meters of membrane, and the economics are likely to require an average module lifetime of several years. Commercial installations are expected to require tens of thousands of modules and would be on the scale of a large reverse osmosis plant. To start addressing these scale-up issues, this report describes the operation of a pilot plant using full-scale membrane modules treating real coal-derived flue gas over a period of two years.

2. Process designs for carbon capture with membrane systems

MTR has proposed a two-step process design for a membrane system to recover CO₂ from flue gas (Fig. 1). Because of the large volumes of low-pressure flue gas generated by power plants, creating an affordable pressure ratio to drive a membrane separation is a challenge in this application. The MTR process scheme uses a combination of a small amount of feed compression and permeate vacuum in a first membrane step to efficiently generate a pressure ratio and capture around 50% of the inlet CO₂. This is followed by a second membrane step that utilizes a sweep gas of combustion air to drive CO₂ recovery up to 90%. The advantages of this design are:

- It uses a vacuum in the first step to process the smaller permeate stream (compared to compressing the much larger feed stream). This creates a pressure ratio [12] while minimizing power consumption.
- Because it is a two-step design, all of the flue gas CO₂ does not have to be removed in a single step. This allows the first step membrane to operate efficiently at low stage-cut with a relatively high partial pressure of CO₂ on the feed side.
- The second membrane step performs the difficult task of removing CO₂ to very low levels (i.e., to reach 90% capture). This step uses an air sweep stream to maintain separation driving force by keeping a relatively low partial pressure of CO₂ on the permeate side. Because the air stream is already being blown into the boiler as the oxidant for combustion, this sweep gas provides an essentially free separation (i.e., no compressors or vacuum pumps are used in this step).
- Finally, because CO₂ is recycled to the boiler with the air sweep stream, the concentration of CO₂ in the flue gas leaving the boiler is increased (for example, from 12% to 20% CO₂). This enrichment makes CO₂ capture in the first membrane step easier due to the higher CO₂ partial pressure.

While this membrane CO₂ capture design has many advantages, the preferred process for use in practice will depend on many factors including the source of the flue gas, the desired capture rate, and the disposition of the captured CO₂. For the pilot field test described in this paper, both membrane steps of the Fig. 1 process were studied.

Fig. 1. Proposed two-step membrane system for CO₂ capture from flue gas.

A typical 600 MW_e capacity coal-fired power plant generates 500 m³/s of flue gas (1540 MMscfd) containing about 460 tons/hour (11,000 TPD) of CO₂. This test program at 1 TPD is only a small fraction (0.01%) of a commercial plant. If membranes are to capture CO₂ cost effectively from such a large stream, they must be very permeable. The pilot plant operation described in this paper uses a membrane specifically developed by MTR for this application (called PolarisTM), with pure-gas CO₂ permeance values = 1000-2000 gpu (50 psig, 23°C) and CO₂/N₂ selectivity = 50-60. A major objective of this test program was to demonstrate that Polaris membranes could be produced on commercial production equipment at 1 meter width and that this membrane could then be constructed as full-scale modules that function under field conditions. Even with these high permeance membranes, a full-scale carbon capture system will only be viable if the membranes demonstrate stable operation during continuous exposure to flue gas streams.

3. Equipment description

A membrane-based pilot plant system was constructed and installed at NCCC in Wilsonville, Alabama, USA in October 2011 (see Fig. 1 for process schematic diagram). The flue gas used for testing of MTR membrane technology and other third-party developer technologies is drawn from Gaston Unit 5, a base-loaded, 880 MW_e gross supercritical pulverized coal boiler fired with Alabama medium-sulfur bituminous coal and outfitted with selective catalytic reduction (SCR) technology for NO_x control, and a wet flue gas desulfurization (FGD) unit. The flue gas that is sent to PC4 is taken downstream of the FGD unit, and typically contains less than 4 ppm SO₃ and 0.5 ppm NH₃.

The membrane pilot unit was scaled to treat flue gas containing 1 TPD of CO₂, which is approximately the amount of CO₂ generated by a 0.05 MW_e coal power plant. The pilot plant uses cross-flow modules in the first step and countercurrent sweep modules in the second step. The modules used in this system are full-scale commercial modules with a diameter of 20 cm (8 in) and a length of 1 meter. The first step cross-flow modules were installed in two pressure vessels, so it was possible to shut off half of these modules for some of the trials. In front of the membrane modules, there is a condenser to remove excess water vapor, and a filter to remove particulates from the flue gas. A compressor is used to bring feed gas up to 20-30 psig and a vacuum pump is installed on the first step to bring permeate vacuum down to between 1 and 3 psia. This combination of feed pressure and vacuum allows for a pressure ratio of 10 or so to be generated in the first step. The second step uses sweep air provided by a blower. Because the system is treating a slipstream of flue gas, the sweep air containing CO₂ that leaves the membrane is not recycled to the boiler as in the Fig. 1 design, but rather is simply returned to flue gas return header. For the recycle to have an impact on the boiler flue gas composition, the

boiler and membrane would have to be appropriately sized. As a result, the flue gas feed to the membrane unit is not enriched as it would be in the Fig. 1 design. Nevertheless, the membrane unit does test both steps of the Fig. 1 design with real flue gas. A photograph of the equipment on site at NCCC is shown in Fig. 2. The system is located outdoors, which means that the system temperature typically increases during the day and cools down at night, and varies throughout the seasons.

Fig. 2. Photograph of 1 TPD carbon capture membrane system installed at NCCC.

When fully operational, the pilot plant ran 24 hours/day although there were occasional shutdowns – with some for extended time periods – due to power plant outages, mechanical failures, extreme weather, and holidays. The flue gas contained 12 vol % CO₂ – typical of a power plant flue gas from pulverized coal (PCFG) – although there were also campaigns in

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4 which the flue gas was diluted with air to 4% CO₂, to simulate the exhaust for a power plant
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6 fueled with natural gas. A typical flue gas fed into the modules had a dry molar composition of
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8 12% CO₂, 7% O₂, and 81% N₂.
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12 With NCCC's assistance, the membrane system was outfitted with a data collection
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14 system that reported results every 10 minutes; a separate handwritten log was recorded every 12
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16 hours. An auto-sampling non-dispersive infrared sensor (NDIR) determined CO₂ and O₂ in feed,
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18 permeate, and residue concentrations for both steps; and on-line instrument gauges were
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20 provided to record the associated flow rates and pressures.
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29 *3.1 Pilot plant mass balance*

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32 Mass balance for CO₂ was generally less than +/- 10% deviation from ideal which we
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34 consider to be acceptable for data collected from a pilot plant in field operations. Contributing
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36 factors to this variability are that the feed compressor resets about every half hour giving regular
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38 pulses in feed flow, the pilot plant is subject to ambient weather and is not isothermal, and the
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40 gas velocities between the feed and permeate sides of the module are different. Since it takes
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42 time for gases to transport through the multiple modules, and the velocities are different between
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44 feed and permeate sides, it is not possible except by chance to collect a set of data that has
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46 perfect mass balance. Fig. 5 found later in this report illustrates the observed variation in
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48 reported gas flow rates for both the feed and permeate streams over a time period of 1800 hours.
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50 Fig. 7 reports tons/day of CO₂ captured and also shows this variability because the calculation is
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52 based on the volume of gas delivered to the system. The variations in gas concentrations
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reported by the NDIR system were less than the gas flow rate variations, so Figs. 4 and 13 that show %CO₂ versus time have less variability than those Figs. dependent on flow rates.

3.2. A performance example for the two-step pilot plant

Typical point-in-time stream flows through the modules are shown in Fig. 3 for a trial with 12.4% CO₂ in the feed gas. The first step is operating at 13.7% stage-cut and enriched the permeate to 62.6% CO₂, corresponding to an enrichment factor of 5.1 compared to the feed. The sweep modules in the second step reduce the CO₂ content in the exhaust gas by over half, from 5.9% to 2.8%. This data set is from October 2013 after 1091 hours of run time with this set of modules.

Fig. 3. Performance data for 1 TPD carbon capture membrane system installed at NCCC at a single point in time.

The values reported in Fig. 3 are used to calculate mass balance differences at this single point in time. If lbs of CO₂ delivered into step one are compared with lbs of CO₂ recovered as combined residual plus permeate for step one, then the difference is 8.4%. This same calculation with step two yields -7.0% discrepancy. If step one and two are combined then when the feed to the system is compared to the combined output streams (first-step permeate + second-step sweep out + second-step residue) the CO₂ mass balance difference is 5.6%. If total gas flow rates (kscfd) are instead used the discrepancy is -2.6% for step one, -4.0% for step two, and -5.2% for the combined steps (feed + sweep air in versus first-step permeate + sweep out + second-step residue). In all of these scenarios, the difference from ideal mass balance is less than the stated window of +/- 10%.

3.3. *Test program overview*

The spiral-wound modules were changed out as improvements were made in the production and performance of the Polaris membrane, and module designs were refined to lower internal pressure drops and increase the active membrane area. The module designs for the data generated in this report are simply identified as A, B, or C.

Data sets generated during three test campaigns covering the time periods of December 2012 to July 2013, September to October 2013, and January to April 2014 are described in this report. Different sets of modules were used in each campaign. Each run generated over 1000 hours of separation data using flue gas feed, although each of the campaigns had to survive numerous shutdowns and restarts, most of which were not related to operation of the membrane system.

4. Results and discussion

Various strategies can be used to analyze large data sets collected from pilot plants with good instrumentation. In this paper, we start by examining the various measured system data as a function of time. These data illustrate the overall stability of system operation, as well as the variability of individual parameters inherent in field measurements. From these measured variables, key system performance values, including capture rate and CO₂ enrichment are calculated and reported versus time. This is followed by a discussion of the impact on system performance of changing various parameters, including membrane area, feed flow rate, and temperature. A section then discusses a number of correlations describing observed system operating envelopes. Finally, performance results for the air sweep step of the Fig. 1 design are reviewed.

4.1. *Steady state system performance*

In January 2014, an extended run of Polaris modules fed with pulverized coal flue gas was launched. The run sequence totaled 1800 hours (from January 22 to April 7). Fig. 4 shows the measured CO₂ concentration in the feed, permeate, and residue for the first step cross-flow modules. The CO₂ content in the feed was consistently about 12% CO₂, except for a brief period after about 1460 hours, when the feed CO₂ concentration was intentionally dropped to 4%. The maximum observed CO₂ in the first step permeate was 63%. The first-step residue was generally under 5% CO₂. Fig. 5 shows the feed and permeate flow rates for the first step cross-flow modules. Between run hours 480 to 786, the first step was restricted to running just one of the two housings, and alternating between them, so that only half the cross-flow modules were on-

line. This is reflected in the reduced permeate flow rate from the first step, since only half the membrane area was being used. This topic is further addressed in Table 1 later in this narrative.

Fig. 4. Data for flue gas trials from January 22 to April 7, 2014, showing first-step CO₂ levels with 12% CO₂ flue gas as feed (except for a period at 1460 hours with 4% CO₂ flue gas).

The breaks in Figs. 4 and 5 are periods where flue gas was not available for the test system, and the pilot plant would be shutdown. Upon restart, the performance remained steady. This is seen in the %CO₂ of the first-step residue, where at 220 hours the value is slightly under 5%, and at the end of the run after 1700 hours (and after 4 more shutdown periods) where the value is again just under 5%. The permeate flow rates also average around 25 kscfd from start to end of the run. There are periods of extended uninterrupted operations over 300 to 400 hours

where constant performance is observed. Shutdown and restarts place stress onto the modules with possible abrupt changes in flow rates and pressures. For commercial systems, the modules must be designed and constructed to withstand these upsets. In general, the data shows no decline in system performance from the start to the end of this test campaign.

One of the remarkable features observed in running full-scale modules was that even though the system was running under ambient conditions outdoors at NCCC, some of the observed outputs (such as residual CO₂ content) were consistent from day-to-day in both the first and second steps. This behavior reflects that the membrane system, when in operation, demonstrates self-leveling features. "Self-leveling" results from the concept that in a complex system with multiple linked variables, some of the performance functions respond in opposite directions, leading to more constant performance than might first be expected.

Fig. 5. Field data from January 22 to April 7, 2014, showing first-step flow rates with 12% CO₂ flue gas as feed (except for a period at 1460 hours with 4% CO₂ flue gas).

4.1.1. Carbon capture rate

Fig. 6 shows an expanded time frame for results reported in the period from March 1 to March 17, near the end of the run, with all modules running in the first step and providing stable operation. Looking at shorter times allows for more details to be seen. Over this period of almost 400 hours of uninterrupted operation, the feed was at 12% CO₂, the first-step permeate was generally greater than 50% CO₂, the first-step residue was less than 5% CO₂, and the second-step residue was less than 3% CO₂. These measured concentrations were further used, together with pressures and flow rates, to calculate some of the important performance parameters for this application. Among these parameters are

- the carbon capture rate, defined as the mass of CO₂ removed in the membrane permeates (first and second steps) divided by the mass of CO₂ in the feed gas, and
- the enrichment factor, defined as the ratio of CO₂ concentration in the first-step permeate to that in the feed.

As shown in Fig. 6, the carbon capture rate ranges between 83-91% during this test period with the pilot plant. This level of CO₂ removal is consistent with the DOE target for carbon capture from a pulverized coal power plant. The CO₂ enrichment factor for step one ranges between 4 and 5 over the course of the test campaign. This value is important because ultimately the captured CO₂ will need to be purified and compressed for use in enhanced oil recovery or sequestration. The higher the membrane enrichment factor, the lower the cost of subsequent purification/compression. An enrichment factor of greater than 4 is consistent with our expectation for these operating conditions, and when combined with selective recycle as shown in Fig. 1 to bring the feed CO₂ concentration to near 20%, it would produce a CO₂-enriched permeate stream of sufficient purity to make final purification/compression cost

effective. Both sets of data in Fig. 6 are flat and stable over these 400 hours of operation with extension of the total run time now up to 1300 hours.

Fig. 6. Expanded time scale from March 1-17, 2014, showing total carbon capture rate; and the enrichment factor for first-step CO₂ capture.

Another performance value of importance to this program is the carbon capture rate, in tons/day, which is shown as a function of time in Fig. 7. The system was designed to treat a flue gas slipstream containing 1 TPD of CO₂ and capture up to 90% of this CO₂. This is precisely what happens at the beginning of the test period when 0.9 TPD was captured. The slight decline in the TPD of CO₂ captured over this time frame occurs because the CO₂ content in the flue gas feed stream dropped from 12.2% to 11.0%. This meant that progressively less CO₂ was being

supplied to the membrane system, and therefore less mass of CO₂ was captured, although the percentage CO₂ capture rate remained constant at about 90%. Fig. 7 also shows that for this particular arrangement of modules, the bulk of the carbon capture occurs in step one with the cross-flow modules. In step two, the sweep modules capture fewer tons of CO₂ because most of the CO₂ has already been removed from the gas fed to these modules.

Fig. 7. Expanded time scale from March 1-17, 2014, showing the tons/day of CO₂ captured from the step one modules, the step two modules, and the combined total. The slow decline that is observed is because the feed fell from 12.2% to 11.0% CO₂ over this time period.

4.1.2. Effect of different module configurations on performance

One of the parameters that could be changed during this field test was the membrane modules themselves. Over this test period, Polaris membranes with different permeation characteristics, as well as modules with different packing configurations were studied. Table 1 reports data for six cases in which different modules were tested during the 2013 and 2014 campaigns. Cases 1 and 2 were taken from October 2013 trials, Cases 3 and 4 correspond to data taken before and after the test system was switched to operation with half the cross-flow modules in early 2014, and Cases 5 and 6 are data points from two time periods when only half the cross-flow modules were in operation in 2014.

Table 1. Average performance values for the membrane process first step over six selected time periods with steady state operations at NCCC.

Case	Modules used	Flow rate (L/min)		Temperature (°F)	Vacuum pressure (psia)	Stage-cut (%)	CO ₂ concentration (%)		
		Feed	Permeate				Feed	Permeate	Residue
1	A	2104	360	68.4	1.5	17.1	12.09	58.10	4.64
2	A	2851	397	70.3	1.7	13.9	11.95	61.05	5.65
3	B + C	2902	558	68.5	2.4	19.2	12.47	49.25	4.27
4	B + C	3066	533	67.7	2.2	17.4	12.35	50.84	4.65
5	only B	2768	352	62.9	1.6	12.7	12.12	59.20	6.37
6	only C	2760	421	73.4	1.9	15.3	12.00	54.26	5.55

Cases 1 and 2 from October 2013 used baseline Polaris modules. Cases 3 to 6 from 2014 used higher permeance 2nd generation Polaris modules. As a result, Case 6, which uses only half the number of modules, shows a higher permeate rate than Cases 1 and 2 operating at full module capacity. In relative terms, the permeance of the modules follow the order: C > B >> A.

Fig. 8 uses the six cases to show that with increasing stage-cut, both the CO₂ content in the first-step permeate and residue decrease. At low stage-cuts, the average CO₂ concentration on the feed side is higher, so the average permeate concentration is also higher. As the stage-cut increases, the CO₂ in the residue decreases (and CO₂ capture rate increases), but CO₂ purity in the permeate decreases because there is no longer sufficient CO₂ in the feed to sustain a high permeate CO₂ concentration. This is an example of the typical recovery/purity tradeoff observed for membrane systems. You can have either high CO₂ purity or high recovery (capture rate) in the permeate, but not both without multiple stages or steps.

The Fig. 8 data also show that the lower flux modules used in Cases 1 and 2 have higher CO₂/N₂ selectivity than the modules used for Cases 3-6. This is illustrated by the observation that, at the same stage-cut, the CO₂ permeate concentrations for Cases 1 and 2 are higher in comparison with the trend line for Cases 3-6. While the module selectivity has some impact on CO₂ purity, it has a lesser effect on residue CO₂ concentration (a proxy for CO₂ removal). As stage-cut increases, the residue CO₂ concentrations decrease, with all six cases positioned near a single trend line.

Fig. 8. Average stream content data for six selected cases with 12% CO₂ flue gas illustrate that increasing stage-cut decreases the CO₂ concentration of both the first-step permeate and residue (see Table 1 for case details).

Fig. 9. Average performance data from six selected cases illustrate that higher first-step permeate flow rates weaken (i.e., increase) the available first-step vacuum pressure (see Table 1 for case details).

During the course of these module tests, an example of the impact of system design on performance was observed. Fig. 9 shows the vacuum generated in the first step permeate as a function of permeate flow rate for the six cases described in Table 1. As permeate flow rates increase due to installation of higher flux modules, the first-step permeate pressure increases (i.e., a weaker vacuum is generated). Weaker vacuum means higher partial pressures of CO₂ in the permeate channel and thus lower pressure ratio, which limits the potential enrichment factor. These two factors of flux and vacuum work against each other and provided self-leveling performance. Because of this constraint, placing high-flux membranes in this test system did not greatly improve overall performance, even though the modules installed in 2014 provided better CO₂ permeance. This is an example of how engineering design and balance-of-plant equipment can impact membrane system performance. To take full advantage of the higher permeance modules, a higher capacity vacuum pump would need to be installed, and additional flue gas would need to be supplied along with a larger compressor in order to maintain the ~90% capture rate.

4.1.3. Effect of system temperature on performance

The average system temperatures reported in Table 1 are in the range of 63-73 °F. Fig. 10 uses data from January 2013 to show that the temperature swings over each day can be much larger. These data are from Polaris modules that operated between December 2012 and July 2013, providing over 1200 hours of run time, but including some long periods of shutdown – up to three months. The largest direct impact of temperature is on the first-step permeate flow rate, which correlates strongly as shown in Fig. 11(a). Here, the data are plotted as $\ln$ (permeate rate)

versus inverse temperature, fashioned to illustrate the Arrhenius temperature dependence of permeation in the membrane modules. Using the NDIR data, the individual temperature responses for the three main flue gas constituents (CO_2 , O_2 , and N_2) can be determined as shown in Fig. 11(b). The lowest curve is for O_2 since it is present at the lowest feed concentration (7%) although the inherent permeability is more than 2X that of N_2 . From the slope of these curves, the order of the mixed-gas permeation activation energies is as follows: $\text{CO}_2 \ll \text{O}_2 < \text{N}_2$. This order is consistent with Polaris being a solubility selective polymer membrane. While these temperature effects are to be expected for polymer membranes, it is rare that they are reported for full-scale modules operating in a pilot plant.

Fig. 10. Temperature swings in the flue gas feed to the first step from January 8-28, 2013, showing impact on observed first-step permeate flow rate (ksbfd).

Fig. 11. First-step permeate flow rate [ln (kscfd)] versus recorded temperature (1/°K) for data from January 8-28, 2013. a) Combined gas flow; b) individual gas flows.

The impact of temperature on the overall system performance is shown in Fig. 12, which plots CO₂ purity in the first step permeate and overall carbon capture rate against system temperature. As temperature increases, the carbon capture rate increases because the CO₂ permeance of the modules is higher at higher temperature. On the other hand, the purity of the captured CO₂ decreases at higher temperatures, partly because the CO₂/N₂ selectivity of the modules decreases as temperature increases but also since higher stage-cut at higher temperature also lowers CO₂ purity. Considering the relatively large temperature range of 30 °F, the variations in capture rate are quite modest, even though the permeate CO₂ ranged from 56 to 74%. This is another example of self-leveling performance since almost doubling the permeate rate (from about 17 to 31 kscfd) only marginally increased the total carbon capture rate. In the

future a large capture system could compensate for temperature change by taking membrane area on or off-line to control product rate, adjusting the pressure ratio, or the system could be simply built and insulated for operation at constant temperature.

Fig. 12. Carbon capture rate and %CO₂ in first-step permeate as a function of system operating temperature for data from January 8-28, 2013.

Running the pilot plant relatively cold also allowed for the higher carbon capture rates in Fig. 12 at levels from 93-97%. These modules were constructed with membranes that had high selectivity for CO₂/N₂ which is further enhanced by operating at the colder temperatures. These are the highest carbon capture rates observed over these two years of the project.

4.1.4. *Effect of a step change in feed flow rate on performance*

In addition to temperature, another operating condition that periodically changed during the field test was feed flow rate. Fig. 13 shows the impact on various system parameters of an intentional step change in the feed flow rate from 105 kscfd to 150 kscfd. There are small but significant increases in the first step for CO₂ content in the permeate, permeate flow (kscfd), and CO₂ content in the residue immediately after the feed flow increase. The CO₂ content in the first-step permeate increased from just under 60% CO₂ to just over 60% CO₂. Similarly, the permeate flow increased from less than 20 kscfd to just over 20 kscfd, and the CO₂ content in the first-step residue jumped from less than 5% CO₂ to greater than 5% CO₂. These effects are all consistent with a decrease in stage-cut, which increases CO₂ permeation driving force, causing permeate flow and CO₂ content in the permeate to increase. Although there was a one-third increase in feed flow rate, the impact on performance was relatively modest for all these variables, again showing the inherent self-leveling constraints in running this pilot plant.

Fig. 13 also illustrates some of the practical issues encountered in using data reported in field trials. There was a brief shutdown around 1040 hours. When there is a process change, the modules typically take a few minutes to flush gases out of the feed and permeate channels and equilibrate with the new process conditions, producing some transient data that do not reflect true performance. Fig. 13 demonstrates that the variability in the collected data is small enough that even small changes in performance due to feed flow change can still be identified. In addition, Fig. 13 shows flat and steady state performance for key parameters near the end of an extended run with flue gas. The point-in-time example in Fig. 3 was sampled from this run at 1091 hours.

Fig. 13. Expanded time scale from October 10-16, 2013, with a one-third increase in feed flow rate on October 15 for the first step. The two-headed arrows indicate two time periods (Cases 1 and 2 in Table 1) which are considered to represent steady state performance.

4.2. Global overview of performance

It is unusual to collect detailed performance data from commercial membrane plants for gas separations because instrumentation is expensive to install and monitor, and does not necessarily improve the quality of the product delivered from the plant to a customer. In contrast, the research installation at NCCC used for these flue gas trials recorded performance data from numerous flow streams every ten minutes over thousands of hours of operations.

We have found it useful to plot these larger data sets to illustrate the potential performance range and limits for the 1 TPD pilot system. Figs. 14 and 15 contain all of the raw data logged by the data collection system for selected streams when the plant was up and running

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4 during the time periods indicated. None of the data have been removed, but because large data
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6 sets were collected, the overall trends are apparent even though some data recorded during
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8 transitions from one condition to another are included. The fact that all of the data can be
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10 utilized and clear trends can still be identified is again a testament to the robustness of the
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12 membrane modules over months of on-line operations. Commercial systems need to withstand
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14 upsets, and this global data includes the multiple shutdowns and restarts experienced at NCCC.
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23 *4.2.1. Global temperature effects*

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26 Figs. 14(a) and (b) show the effect of operating temperature on the first step residue and
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28 permeate CO₂ concentrations, respectively. In these figures, data for different feeds (coal or
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30 natural gas flue gas) and different module arrangements (full or half capacity) are summarized.
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32 Similarly to the results shown earlier in Fig. 12 for a more limited data set, as temperature
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34 increases, the CO₂ content in the residue decreases (CO₂ capture rate increases) and the CO₂
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36 purity in the permeate decreases. These results are consistent with increased membrane
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38 permeance and reduced CO₂/N₂ selectivity at higher temperatures. At a fixed temperature, full
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40 module capacity will remove more CO₂ and produce a lower purity permeate than half module
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42 capacity, due to higher stage-cut operation when all modules are used. The natural gas data
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44 clusters separately in Figs. 14(a) and (b), which is to be expected because of the different CO₂
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46 content compared to coal flue gas.
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Fig. 14. Data from January 31 to April 7, 2014, showing that the CO₂ content of the first-step (a) residue and (b) permeate is dependent on process feed and configuration, as well as feed temperature.

4.2.2. Mass balance constraints

Fig. 15 shows a correlation between the permeate and residue concentrations of CO₂ in the first step. Because this is a closed system, the values are linked by mass balance and cannot be decoupled. Again, distinct regions of the performance levels achieved are evident. For all cases, as the CO₂ content in the first-step residue increases, so do the permeate CO₂ concentrations. This reflects that the lower stage-cut conditions that produce a high residue CO₂ content also yield relatively high permeate CO₂ composition. An example of a lower stage-cut condition that produces higher CO₂ content in both the permeate and residue streams occurred when only half the modules were operated.

During the brief period of operation with simulated flue gas from natural gas shown in Figs. 14 and 15, the first step was operated at full module capacity. In this case, the flue gas CO₂ concentration was reduced from 4% in the feed stream to 2% CO₂ in the first-step residue, while the permeate was enriched to between 23-29% CO₂. The natural gas data fit visually on the curve in Fig. 15 already defined by the pulverized coal trials. Carbon capture rates ranged from 80-86% during this period with simulated natural gas. The system was not specifically designed to treat the lower CO₂ content of natural gas, yet still managed a significant capture rate.

Fig. 15. Data from January 31 to April 7, 2014, showing that the CO₂ content of the first-step permeate directly correlates with the CO₂ content of the first-step residue over a range of process configurations and feed conditions.

4.3. Sweep modules in step two

During these field tests, the bulk of the CO₂ removal occurred in the first step with the cross-flow modules. Nevertheless, the second step in the Fig. 1 design is important in order to achieve high levels of CO₂ capture (90%) in an energy-efficient manner. Spiral-wound modules were modified to allow air sweep (as required in step two of the Fig. 1 design) and installed on the 1 TPD system. The sweep modules use the residue gas from the first step that is still under pressure as feed, and air on the permeate side as a sweep gas.

Fig. 16 shows the CO₂ concentrations for the feed, residue, and permeate (sweep out) streams for the second-step sweep modules during the 2014 campaign. CO₂ preferentially permeates the membrane and is enriched in the air sweep gas. For example, while the air sweep stream entering the modules has only atmospheric concentrations of CO₂ (400 ppm), the air leaving the module (second-step permeate) contains between 3.5-6% CO₂. At the same time, the CO₂ content of the feed (first-step residue stream) is reduced from 4-7% CO₂ to only 2-3.5% CO₂ in the second-step residue via the sweep modules. The net effect is that approximately 50% of the CO₂ remaining in the flue gas after the first step is removed by these sweep modules.

Fig. 16. Data from February 11 to March 17, 2014, showing %CO₂ in the second step for both feed and sweep streams. The first-step residue is the feed stream for the second step. Air is used as sweep gas.

Fig. 17 shows the good correlation between CO₂ content of the residue streams from the first and second steps. With about 50% CO₂ removal the residue has half the CO₂ content of the feed into the sweep modules. The data set again separates into two regions depending upon whether all or half the modules are operated in the first step. The band with the feed content of 5-7% CO₂ occurs when the first step is operated at half capacity, leaving more CO₂ content in the first-step residue. The band with the feed content of 4-5.5% CO₂ occurs when all modules are running in the first step. The fraction of CO₂ removed by the sweep modules is slightly higher when the first step operates with half capacity and when higher CO₂ concentrations are entering the sweep modules, which should generate higher driving force. This increase is reflected in Fig.

17 which shows that the data when 50% of the modules are operating in step one is shifted slightly to the right of the “all modules” data. Although the flow dynamics within these modified spiral-wound modules are still under study, these sweep modules are successful in providing for additional CO₂ recovery.

Fig. 17. Data from January 23 to March 17, 2014, showing that the %CO₂ of the step-two residue is about one-half of the step-one residue. The number of modules (50% or all) refers to the step one with cross-flow modules where the residue is the feed stream for step two. The number of sweep modules in step two remained constant. The diagonal line represents exactly 50% reduction in CO₂ concentration.

4.4. *Future systems*

In future systems using the Fig. 1 design, the membrane will be integrated with the power plant, so the air sweep gas containing CO₂ will be recycled to the boiler, increasing the CO₂ content of flue gas that is fed to the membrane system to an estimated 20%. With more CO₂ in the feed gas, the first-step permeate will be further enriched in CO₂, making it easier to condense and sequester. We believe the lessons learned with 12% CO₂ flue gas will translate to the 20% CO₂ levels expected in a large-scale membrane system when integrated with a commercial-scale power plant. The balance between the membrane areas for the first step versus the second step will depend on the target rates for carbon capture and allowable oxygen dilution in the sweep gas. These designs can be further tuned by the choice between either higher flux or higher selectivity modules available with the Polaris membrane system. In most pressure-ratio-limited flue gas scenarios, we expect economic benefits with the higher flux modules because they will reduce the quantity of membrane area required and therefore the capital cost.

5. **Summary and conclusions**

During 2012-2014, three extended pilot plant campaigns, each over 1000 hours in length, showed that stable Polaris membrane module performance for carbon capture from real flue gas can be achieved. Full-scale spiral-wound cross-flow and sweep modules were developed for this project and were shown to operate effectively. Important for multi-year operations, the modules also demonstrated stable performance over multiple shutdowns and restarts of the pilot plant.

Carbon capture rates of better than 90% were achieved with coal-derived flue gas. The pilot plant also generated data for simulated flue gas derived from natural gas; although the unit

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4 was not designed for high recoveries from this alternative flue gas, capture rates of greater than
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6 80% were observed.
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10 Although clear differences in the separation performance of the various module designs
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12 were observed, the impact on overall pilot plant performance was less than might have been
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14 expected. This was due in part to mass balance requirements linking the CO₂ concentrations in
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16 the first-step permeate and residue streams, and the observation that high permeate flows
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18 weakened the permeate vacuum, and therefore lowered the available pressure ratio of the system.
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20 These competing factors made the pilot plant performance self-leveling in some respects and led
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22 to clearly defined bands of available performance ranges, depending on system feed and module
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24 set-up.
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30 Significant responses to various operating conditions have been noted, particularly with
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32 respect to the choice of membrane and the number of operating modules, the system temperature,
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34 the available vacuum, and the stage-cut. The choice of module configuration sets clear
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36 boundaries on the performance envelope that can be expected. Another major influence is the
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38 system operating temperature since warmer temperatures increase permeation rates (with
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40 concurrent loss in selectivity), but this result is convoluted because higher permeation rates mean
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42 both larger stage-cuts and less available vacuum. Another constraint is that the low CO₂ content
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44 of flue gas sets limits to performance that can be achieved in an operating membrane plant.
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50 Lessons learned from this 1 TPD pilot plant have now been applied to the design and
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52 construction of a 20 TPD demonstration plant, which has been installed at NCCC and began
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54 operating in early 2015. Results from this new demonstration plant containing multiple
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56 commercial-scale modules will be a topic of future reports.
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Nomenclature

KSCFD	thousand standard cubic feet per day
MMscfd	million standard cubic feet per day
MW _e	megawatt electrical
PCFG	pulverized coal flue gas
Polaris TM	Polaris is a trademark of MTR
scfd	based on oil and gas industry standard values of 60 °F and 1 atm
ton	2000 lbs

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Figure Captions

Fig. 1. Proposed two-step membrane system for CO₂ capture from flue gas.

Fig. 2. Photograph of 1 TPD carbon capture membrane system installed at NCCC.

Fig. 3. Performance data for 1 TPD carbon capture membrane system installed at NCCC at a single point in time.

Fig. 4. Data for flue gas trials from January 22 to April 7, 2014, showing first-step CO₂ levels with 12% CO₂ flue gas as feed (except for a period at 1460 hours with 4% CO₂ flue gas).

Fig. 5. Field data from January 22 to April 7, 2014, showing first-step flow rates with 12% CO₂ flue gas as feed (except for a period at 1460 hours with 4% CO₂ flue gas).

Fig. 6. Expanded time scale from March 1-17, 2014, showing total carbon capture rate; and the enrichment factor for first-step CO₂ capture.

Fig. 7. Expanded time scale from March 1-17, 2014, showing the tons/day of CO₂ captured from the step one modules, the step two modules, and the combined total. The slow decline that is observed is because the feed fell from 12.2% to 11.0% CO₂ over this time period.

Fig. 8. Average stream content data for six selected cases with 12% CO₂ flue gas illustrate that increasing stage-cut decreases the CO₂ concentration of both the first-step permeate and residue (see Table 1 for case details).

Fig. 9. Average performance data from six selected cases illustrate that higher first-step permeate flow rates weaken (i.e., increase) the available first-step vacuum pressure (see Table 1 for case details).

Fig. 10. Temperature swings in the flue gas feed to the first step from January 8-28, 2013, showing impact on observed first-step permeate flow rate (kscfd).

Fig. 11. First-step permeate flow rate [$\ln$ (kscfd)] versus recorded temperature (1/°K) for data from January 8-28, 2013. a) Combined gas flow; b) individual gas flows.

Fig. 12. Carbon capture rate and %CO₂ in first-step permeate as a function of system operating temperature for data from January 8-28, 2013.

Fig. 13. Expanded time scale from October 10-16, 2013, with a one-third increase in feed flow rate on October 15 for the first-step. The two-headed arrows indicate two time periods (Cases 1 and 2 in Table 1) which are considered to represent steady state performance.

Fig. 14. Data from January 31 to April 7, 2014, showing that the CO₂ content of the first-step (a) residue and (b) permeate is dependent on process feed and configuration, as well as feed temperature.

Fig. 15. Data from January 31 to April 7, 2014, showing that the CO₂ content of the first-step permeate directly correlates with the CO₂ content of the first-step residue over a range of process configurations and feed conditions.

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