FIELD TESTING OF A MEMBRANE SYSTEM FOR POST-COMBUSTION CO_2 CAPTURE

Operational History at NCCC for the 1 TPD Bench-Scale System
November 2011 to August 2015

submitted by

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This report discusses operational experience and performance results for the MTR 1 ton/day (TPD) membrane CO_2 capture system that was tested at the National Carbon Capture Center (NCCC). The system was originally installed at NCCC in late 2011, and commissioned in early 2012. Overall, the system accumulated about 11,000 hours of operation until final retirement in July 2015. The objective of the field demonstration was to investigate membrane and module performance with coal-fired power plant flue gas, and gain system operating experience.

Initial Operation of the 1 TPD system with a dry screw compressor

As shown by the process diagram in Figure 1, the 1 TPD system removes CO_2 from flue gas in two steps. The first step uses cross-flow modules with a vacuum on the permeate for CO_2 enrichment, and the second step uses counter-current sweep modules to remove additional CO_2 in the feed gas to meet the overall CO_2 capture target of 90%. Before entering membrane modules, the gas is compressed to generate the necessary pressure ratio for a parametric study of membranes installed on the system. For operation in 2012, an Atlas Copco dry screw compressor was used for feed gas compression. Figure 2 shows a picture of the 1 TPD system installed at the NCCC PC4 site.

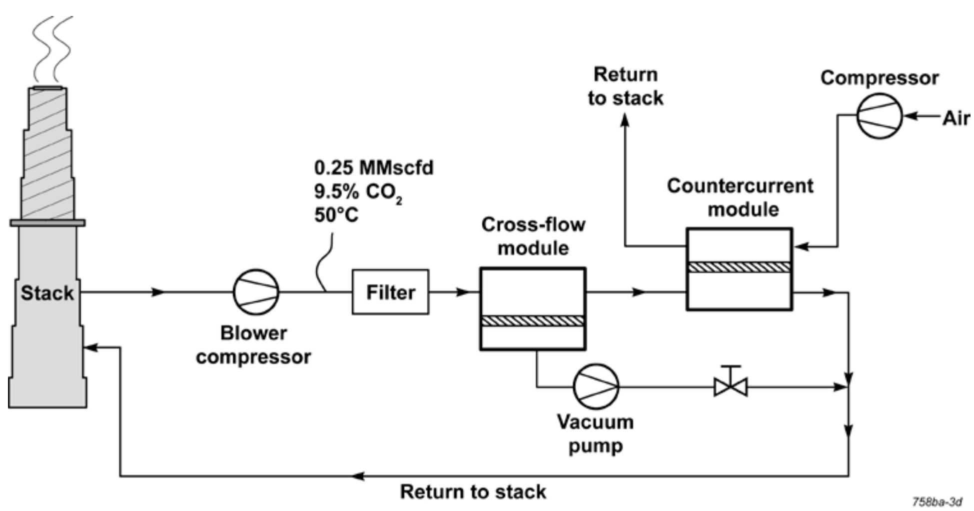

Figure 1. Process flow diagram of the 1 TPD membrane system at NCCC.

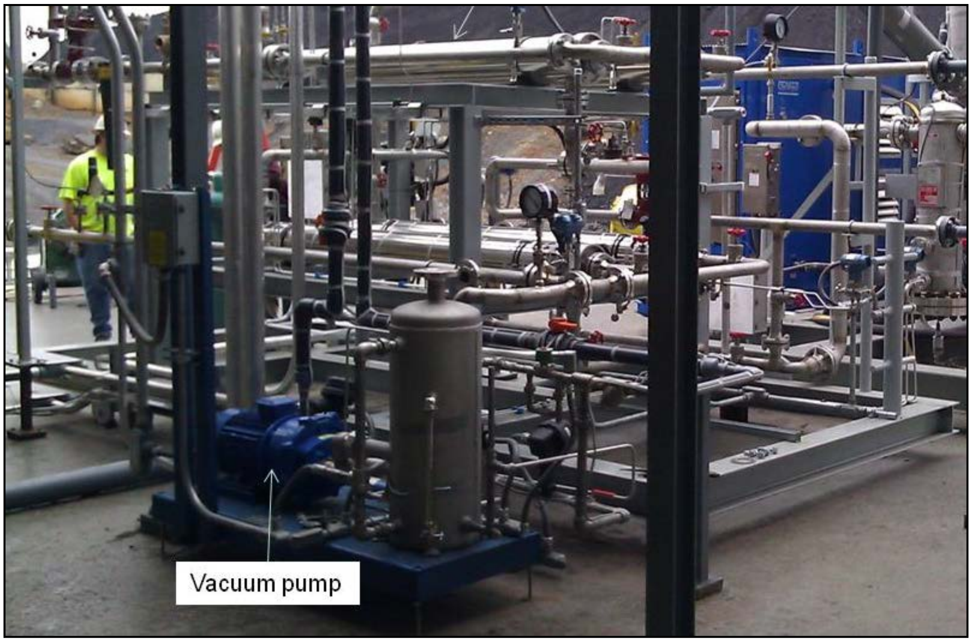

Figure 2. 1 TPD MTR membrane system at the NCCC PC4 site.

Polaris modules were installed on the system prior to the startup in January 2012. After about 1500 hours of operation with flue gas, Polaris modules 6114 and 6419 were returned to MTR for analysis. As shown in Figure 3, no particles appear to have collected on either end of the module. Module 6419 was stripped and cut open. No deposition of particles was observed inside the membrane envelopes. Overall, the membrane modules were in excellent condition after extended operation with flue gas.

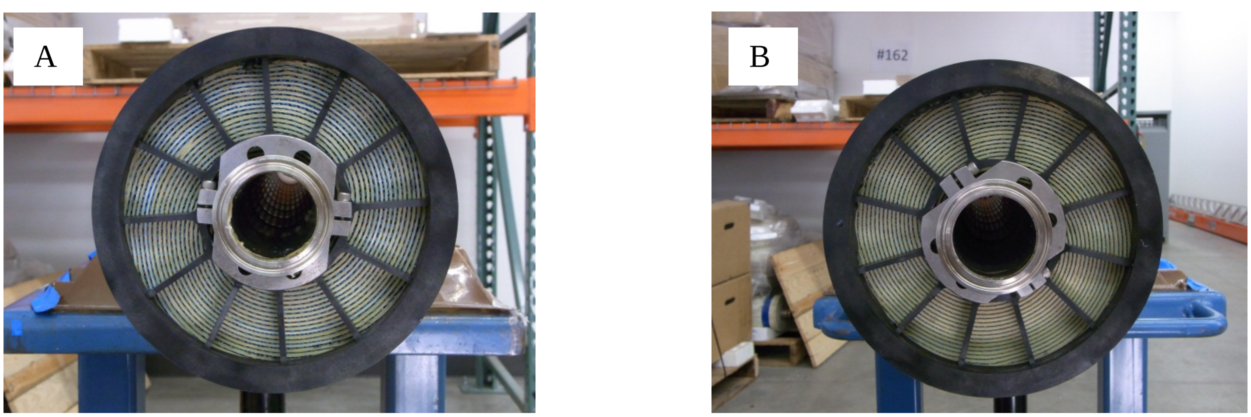

Figure 3. Pictures of feed gas inlet (A) and residue gas outlet (B) of module 6419. The module was tested on the 1 TPD system at NCCC from April to August of 2012.

Operation of the 1 TPD system using a liquid ring compressor

In 2013, the Atlas Copco dry screw feed compressor was replaced with a Gardner Denver Nash liquid ring compressor to improve the overall reliability of the system operation with flue gas. During the system modification, new Polaris modules were rotated into the system. Overall, these modules again demonstrated stable performance at expected levels of separation, even after remaining idle in the membrane system several times during system repair/maintenance and flue gas/cooling water outages at NCCC.

Modules that were tested on the 1 TPD system between December 2012 and July 2013 were brought back to MTR for post-test analysis. Table 1 shows the operating history of these modules. Table 1 shows the pure-gas performance of these modules after testing on the 1 TPD system relative to their original performance before the test. Both CO_2 permeance and CO_2/N_2 selectivity remained almost unchanged (within the error range of the pure gas module testing system), even after going through many cycles of system restart and shutdown, and staying idle in the membrane system for over three months during the flue gas outage at NCCC from February to April 2013.

Table 1. Relative performance of cross-flow modules before and after testing on the 1 TPD system from December 2012 to July 2013.

Module	Normalized CO_2 Permeance	Normalized CO_2/N_2 Selectivity
6704	87%	94%
6706	111%	130%

Starting in July 2013, NCCC sent diluted flue gas with air to simulate the CO_2 content in the flue gas for a natural gas combined cycle (NGCC) power plant to the 1 TPD system. At the same time, new modules were rotated into the 1 TPD system for performance validation. The new modules were made of membranes that were produced using an optimized membrane fabrication process. The process combines multiple fabrication steps into one single step, which allowed for a reduction in manufacturing time, as well as labor and materials costs.

When treating the air-diluted flue gas, the membrane system removed approximately 80% of the CO_2 from flue gas, and enriched it by a factor of 7-8 in the permeate stream. The 1 TPD system was originally designed to capture ~90% CO_2 from regular coal-fired flue gas at a total flow rate of approximately 550 lb/hr. Diluting the flue gas with air caused the CO_2 content to drop from 12% to 4%, resulting in a significant reduction in the CO_2 partial pressure of the feed gas. Separation of CO_2 by membrane technology is primarily driven by the differential in the CO_2 partial pressure. Therefore, without changing the feed gas flow rate or other operating conditions, less CO_2 (percentage-basis and mass-basis) is removed from the feed gas when air-diluted flue gas is used. Nevertheless, the system still achieved more than 80% CO_2 capture and an almost 8-fold CO_2 enrichment in the permeate stream.

Testing the second generation Polaris membrane on the 1 TPD system

Testing on the system in 2014 focused on validating the performance improvement of Polaris membranes in the field. The 1 TPD system has two pressure vessels in parallel in the cross-flow (first) step, which allows for testing of multiple cross-flow modules under the same conditions. In January 2014, MTR rotated modules made of advanced generation 2 (Gen 2) Polaris membranes into one of the vessels for the validation of membrane performance improvement. Meanwhile, old modules that were tested in 2013 were kept in the other vessel for long-term stability monitoring.

The new modules made using Gen 2 Polaris membranes had at least 70% higher CO_2 permeance than that of the base-case Polaris membranes under standard test conditions at MTR. Therefore, the modules were expected to have higher CO_2 removal capacity than the base-case modules that were tested in 2013. This is confirmed by the results shown in Figure 4. Under similar operating conditions, the advanced membrane module showed nearly double the CO_2 removal rate of the base-case module.

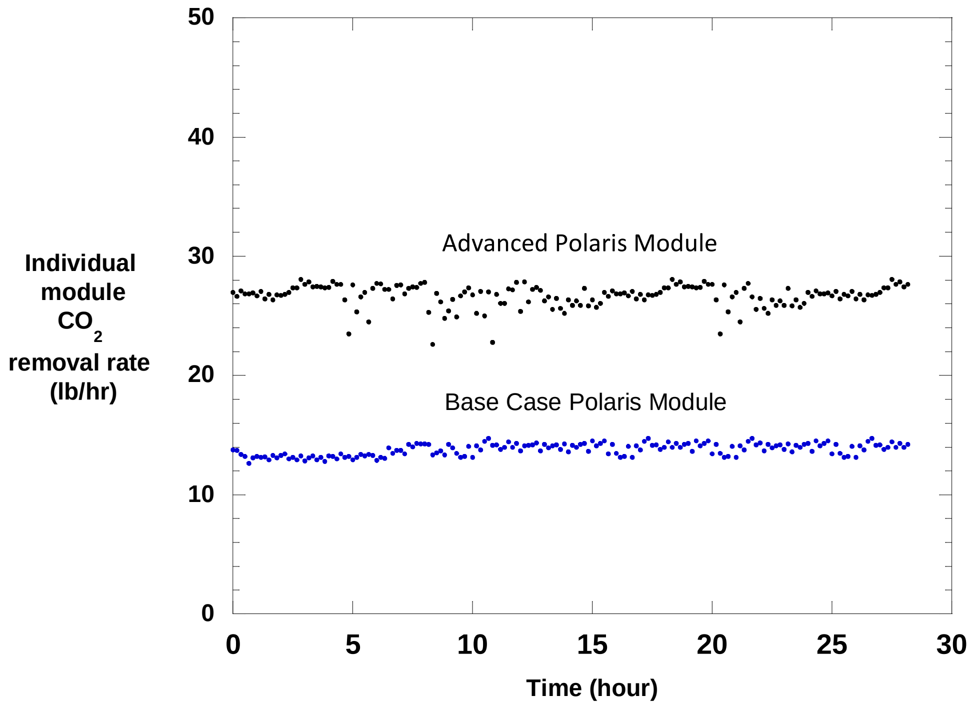

Figure 4. Comparison of the individual module CO_2 removal rates of an advanced Gen 2 Polaris module and a base-case Polaris module. The results were calculated based on the system performance data recorded during February 11 to 13, 2014.

Effect of system temperature on performance

The impact of temperature on the overall system performance is shown in Figure 5, which plots CO_2 purity in the first step permeate and overall carbon capture rate against system temperature. As the temperature increases, the carbon capture rate increases because the CO_2 permeance of the modules is higher at higher temperature. On the other hand, the purity of the captured CO_2 decreases at higher temperatures, partly because the CO_2/N_2 selectivity of the modules decreases as temperature increases but also because higher stage-cut at higher temperature lowers CO_2 purity. Considering the relatively large temperature range of 30 °F, the variations in capture rate are quite modest, while the permeate purity varied over a slightly larger range of 56 to 74% CO_2. In the future, a large capture system could compensate for temperature change by taking membrane area on or off-line or adjusting the pressure ratio to control the capture rate.

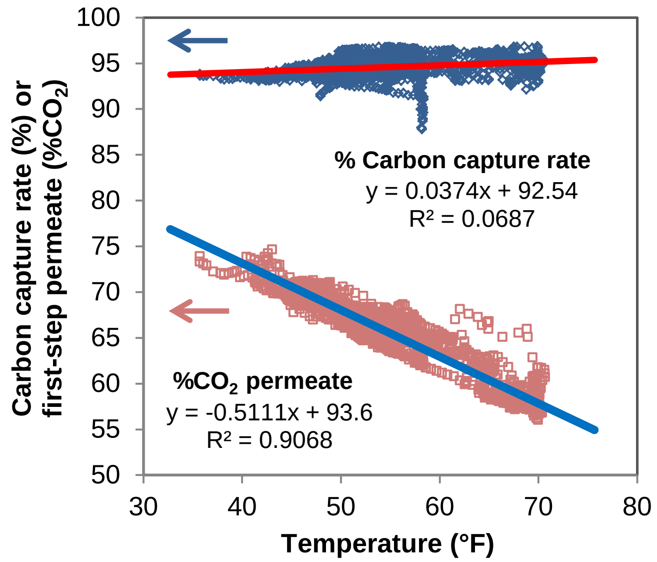

Figure 5. Carbon capture rate and CO_2 concentration in the first-step permeate as a function of system operating temperature for data from January 8-28, 2013.

Carbon capture rate and enrichment factor steady over time

Figure 6 shows an expanded time frame for performance results reported in the period from March 1 to March 17, 2014. Over this period of almost 400 hours of uninterrupted operation, the feed was at 12% CO_2, the first-step permeate was generally greater than 50% CO_2, the first-step residue was less than 5% CO_2, and the second-step residue was less than 3% CO_2. 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 CO_2 removed in the membrane permeates (first and second steps) divided by the mass of CO_2 in the feed gas, and

- the enrichment factor, defined as the ratio of CO_2 concentration in the first-step permeate to that in the feed.

As shown in Figure 6, the carbon capture rate ranges between 83-91% during this test period. This level of CO_2 removal is consistent with the DOE target for carbon capture from a pulverized coal power plant. The CO_2 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 CO_2 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 equipment. An enrichment factor of greater than 4 is consistent with our expectation for these operating conditions, and when combined with selective recycle to the boiler to bring the feed CO_2 concentration to near 20%, it would produce a CO_2-enriched permeate stream of sufficient purity to make final purification/compression cost effective. Both sets of data in Figure 6 are flat and stable over these 400 hours of operation.

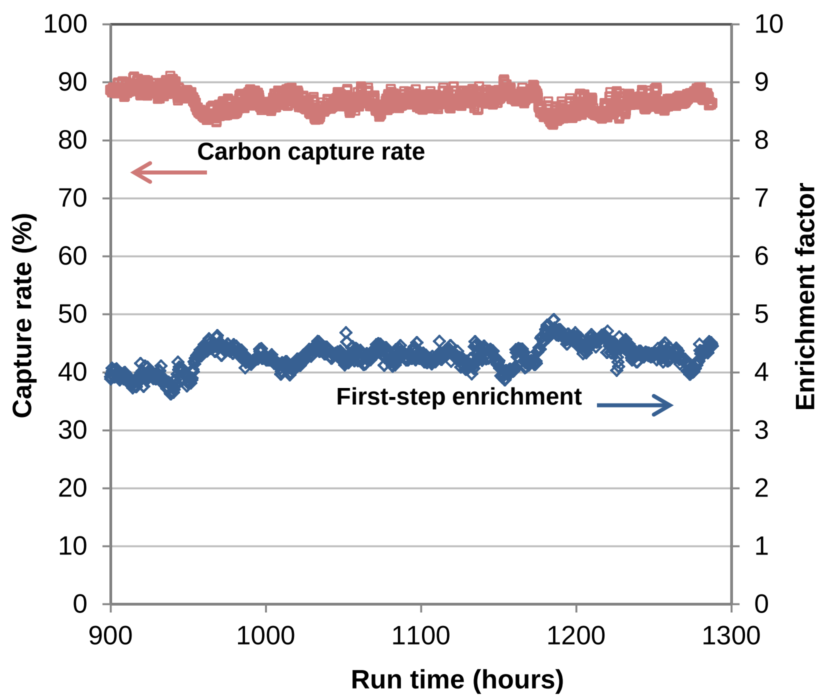

Figure 6. Expanded time scale from March 1-17, 2014, showing total carbon capture rate; and the enrichment factor for first-step CO_2 capture.

Lessons learned from system operation

Dry screw compressor

The selection of a dry-screw compressor for the 1 TPD system to pressurize the flue gas feed was based on previous operation experience at APS Cholla Power Plant. The system tested at Cholla in 2010 used an oil-flooded screw compressor that suffered from severe corrosion issues caused by water condensation from flue gas. We hoped that this issue could be avoided with a dry-screw compressor because it usually operates at very high temperature (360-380°F) where condensation of corrosive species will not occur. In addition, the casing and screw of the Atlas Copco compressor were coated with Teflon® and epoxy, respectively, in an attempt to protect the compressor from corrosion.

Initial experience in 2012 showed that the dry screw compressor had better resistance to corrosion than the oil flooded compressor. However, after three-months of relatively smooth operation, corrosion issues started to surface. Rust and black particles were found inside the dry screw compressor. Figure 7 shows pictures of some components after they were dissembled from the compressor in August 2012. It appears that the corrosion–resistant coating layer does not protect against long-term exposure to flue gas. Presumably, after the coating layer was worn out, the compressor elements were in direct contact with flue gas, and corrosion started to occur gradually. In addition, without the sealing fluid, the compressor has a tight-fit screw-casing design, which reduces the tolerance to particles, dust and rust. These findings indicate that a dry screw compressor is not suitable for long-term operation with flue gas.

Figure 7. Pictures of the feed compressor components showing particulate buildup and corrosion.

Liquid ring compressor

In light of the re-occurring feed compressor issues, we replaced the Atlas Copco dry screw compressor with a Gardner Denver Nash liquid ring compressor. Liquid ring compressors are used in the petrochemical industry to handle toxic, corrosive, and explosive gases, and can be ordered with stainless steel internals. With a liquid ring as the sealing media, these compressors have a greater tolerance for solids in the feed. When operated with the liquid ring compressor in 2013, the overall reliability of the 1 TPD system was significantly improved. Some initial interruptions in operation were caused by mechanical issues due to inappropriate system assembly and handling, and not related to working with flue gas. The compressor was thoroughly inspected by the Nash representative after one month of operation with flue gas. Nash confirmed that all the key components of the compressor were in "good condition." With no pitting or erosion observed. Subsequently, the system was operated periodically for several years with no feed compressor issues.

Summary and Conclusions

From 2012 to 2015, periodic testing of Polaris modules on the MTR 1 TPD system accumulated a total of 11,466 hours of operation with 9,100 hours on flue gas and 2,366 hours on air when flue gas was not available. Out of the 9,100 hours of testing on flue gas, 1,933 hours were on diluted flue gas during a natural gas simulation test, while the remainder was with regular coal flue gas. Throughout these tests, full-scale Polaris spiral-wound modules were shown to operate effectively. Important for multi-year operations, the modules also demonstrated stable performance over multiple shutdowns and restarts of the test system.

Carbon capture rates of better than 90% were achieved with coal-derived flue gas. The system also generated data for simulated flue gas derived from natural gas; although the unit was not designed for high recoveries from this alternative flue gas, capture rates of greater than 80% were observed.

Significant responses to various operating conditions have been noted, particularly with respect to the choice of membrane (base case or Gen 2 Polaris) and the flue gas temperature. Tests on the 1 TPD system confirmed that Gen 2 Polaris modules have nearly double the CO_2 removal capacity of base case (Gen 1) modules. Higher operating temperatures were shown to increase permeation rates (and thus CO_2 capture rates), while reducing the permeate CO_2 purity (due to a combination of reduced membrane selectivity and higher module stage cut).

The most important lessons learned from this 1 TPD bench-scale system centered on selection of durable feed compression equipment capable of operation with real coal flue gas containing corrosive species. This and other learnings from the 1 TPD system were applied to the design and construction of a 20 TPD small pilot plant, which was installed at the NCCC and operated successfully in the first half of 2015. Smooth operation of the 20 TPD system would not have been possible without the experience gained from the 1 TPD system testing. Both MTR systems were shut down in July 2015 for decommissioning and removal from NCCC.