Bench Scale Testing of Next Generation Hollow Fiber Membrane Modules

Field Test Summary Report:
0.3 MWe Field Test at the National Carbon Capture Center

Project Period: October 1, 2015 to December 30, 2019

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Disclaimer

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Abbreviations

AL	Air Liquide
BAHX	Brazed Aluminum Heat Exchanger
BFW	Boiler Feed Water
DOE	Department of Energy
D.I.C	Delaware Innovation Campus
EOR	Enhanced Oil Recovery
FGD	Flue Gas Desulfurization
FTU	Field Test Unit
HMI	Human Machine Interface
JSA	Job Safety Analysis
L/D	Length-to-Diameter (ratio)
Nm^3	Normal cubic meter
PC	Pulverized Coal
PI	Polyimide
PO	Post-combustion (referring to scheduled test windows)
PPE	Personal Protective Equipment
ppm	parts per million (volume)
ALAS	Air Liquide Advanced Separations
NETL	National Energy Technology Laboratory
NCCC	National Carbon Capture Center
μg	microgram (10^{-6} g)
SCR	Selective Catalytic Reduction
TEA	Techno Economic Analysis
TRL	Technology Readiness Level

List of Exhibits

Executive Summary

Air Liquide has developed cost effective post combustion CO_2 capture technology at TRL 5 based on the hollow fiber cold membrane process followed by liquefaction. The CO_2 from flue gas is pre-concentrated in the cold membrane to >58% followed by further purification to EOR grade in a liquefaction step. The objective of this report is to summarize the 0.3 MWe field testing at the National Carbon Capture Center (NCCC) under NETL funded project, DE-FE0026422. The field testing was focused on validating and testing Air Liquide membrane with coal-fired power plant flue gas. Liquefaction was excluded in the field testing due to Air Liquide's extensive experience in cryogenic based gas separations, specifically with CRYOCAP technology for CO_2 capture from oxy-combustion power plants in Callide, Australia and Ciuden, Spain.

The field test unit (FTU) was delivered, installed and commissioned under the previous DOE sponsored project of DE-FE0013163 in 2015. It was re-commissioned under the current project of DE-FE0026422 in October 2017 and was tested until September 2019. The total operating time for the FTU is approximately 5000 hours.

The following membrane bundles have been tested at NCCC with the below listed studies:

Bundle type	Testing type	Duration of test
4" PI-2 Bundle	System performance verification	400 hours
6" PI-2 Bundle (PI2-6IN-01)	Long-term test, Parametric test (CO_2 capture rate, Permeate pressure, Feed temperature, feed flow rates, CO_2 feed concentration)	3000 hours
6" PI-2 Bundle (PI2-6IN-02)	Parametric test (CO_2 capture rate, Permeate pressure, Feed temperature, feed flow rates)	800 hours
12" PI-1 bundle	Parametric test with higher CO_2 (>18%) feed concentration	400 hours
6" PI-1 bundle	Parametric test with higher CO_2 (>18%) feed concentration	400 hours

1. 6" PI-2 Membrane Bundle Performance:

The range of experimental conditions and the 6" PI-2 membrane bundle performance metrics during the continuous operational testing at NCCC are shown in Exhibit 1. The bundle was tested at -30 and -45°C, 11.3 and 14.8 bara, and over a range of feed flow rates. At both temperatures, the bundle met the target success criteria in terms of performance. The test conditions for which the success criteria was exceeded are boxed in the figure.

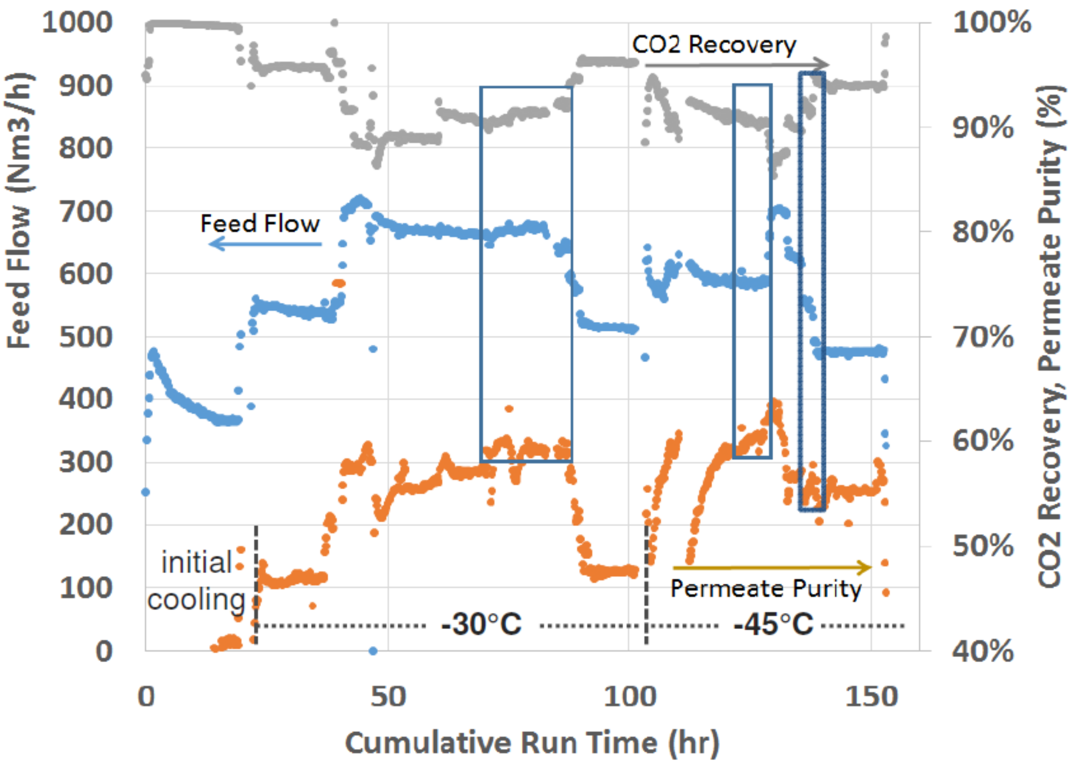


Exhibit 1. 6" PI-2 membrane bundle performance at NCCC test (Performance target: >400 Nm^3/h feed @ 90% CO_2 recovery, >58% CO_2 purity).

2. Long-term steady state test:

As shown in Exhibit 2, testing at NCCC in 2019 showed stable bundle performance for over 700 hours. This total period was achieved over 2 long-term stability test periods (Feb-March and April-May), broken by both plant trips and a parametric testing period. The parametric testing involved feed temperatures down to -60 °C. It was known that the low-temperature testing was potentially destructive; it seems to have resulted in a slight loss of bundle productivity accompanied by a gain in selectivity. It is speculated that the activity of the CO_2 during the -60 °C testing was sufficient to plasticize the polymer, with the resulting thickening of the fiber skin.

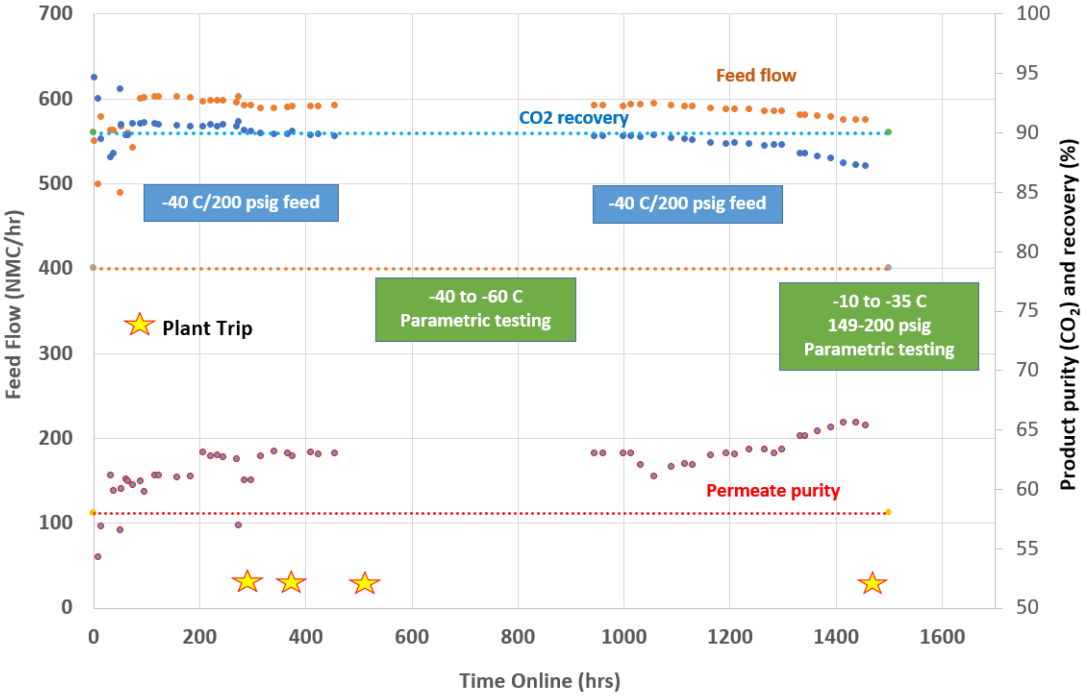


Exhibit 2. 6" PI-2 membrane bundle long-term steady state test at NCCC

<u>Key findings from the test:</u>

- Both of Air Liquide's 6" PI-2 membrane bundles: PI2-6IN-01 and PI2-6IN-02, significantly exceeded the success criteria during the field test at NCCC. The performance target for a 6" PI-2 membrane bundle is to be capable of 90% CO_2 recovery from a 400 Nm^3/hr flue gas feed with a permeate composition greater than 58% CO_2. Field tests demonstrated that Air Liquide bundles are capable of processing > 650 Nm^3/hr of flue gas at 90% CO_2 recovery and providing 59+% permeate purity.
- Extensive parametric testing was performed on the 6" PI-2 bundles. Parametric testing showed that the CO_2 capture cost can be further lowered by operating the membranes at milder temperature of -30°C and lower feed pressure of 11.3 bara (baseline performance at -45°C and 14.8 bara).
- The PI-2 bundle exhibited stable performance during long-term testing. The bundle returned to full performance after events associated with power plant or system trips; however, the bundle performance seemed to have dropped after being exposed to high CO_2 activity (18% CO_2 at 14.8 bar and -60 °C).

1. Introduction

Air Liquide (AL) has developed a post combustion carbon capture technology based on a hybrid cold membrane and liquefaction. In the current project, DE-FE0026422, this technology was advanced to TRL5 (approximately 600 - 1,000 Nm^3/h flue gas, 350 - 600 scfm, 0.2 - 0.3 MWe equivalent) by testing with real Pulverized Coal (PC) flue gas at the National Carbon Capture Center (NCCC) in Wilsonville, Alabama. The slipstream of flue gas was provided from Alabama Power, Plant E.C. Gaston, Unit 5. The 0.3 MWe, approximately 6 tonne/day of CO_2, Field Test Unit (FTU) was located in the Pilot Bay 3 area of the NCCC. Flue gas from plant Gaston was pretreated in a SOx polishing pre-scrubber by the NCCC to reduce SOx down below 1ppm before it was sent to the Air Liquide FTU. The FTU was delivered, installed and commissioned under the previous DOE sponsored project of DE-FE0013163 in 2015. It was re-commissioned under the current project in October 2017 and was tested until September 2019.

The purpose of the 0.3 MWe FTU was to test AL hollow fiber, polyimide (PI) based, membrane bundles for CO_2 capture at cold temperature (-30 to -45°C) and to validate the superior performance observed during previous tests at Air Liquide Delaware Innovation Campus (D.I.C). The FTU was designed to pre-treat and compress the flue gas with an oil-flooded screw compressor followed by additional pre-treatment, and CO_2 separation with a membrane. The previous field test program (DE-FE0013163) showed promising results for the hybrid process utilizing an existing commercial AL membrane fabricated from PI-1 material. Recent AL studies discovered the potential for significant improvements through initial laboratory tests with the novel material (PI-2). The initial PI-2 results showed a step-change in membrane permeance. This will enable further reduction in the cost of CO_2 capture by reducing the number of membrane modules and the size of associated equipments in the system. In order to capture this value, however, the new material needs to be validated by field testing of large bundles (representative of commercial production). Air Liquide has extensive experience in liquefaction through our field testing in Callide, Australia and Ciuden, Spain. The field test at NCCC focused on membrane performance validation and excluded liquefaction testing.

Exhibit 3 below lists the membrane bundles that were tested at NCCC. The total operating time for the FTU is approximately 5000 hours.

Exhibit 3. List of Membrane Bundles Tested at NCCC

Bundle type	Testing type	Duration of test
4" PI-2 Bundle	System performance verification	400 hours
6" PI-2 Bundle (PI2-6IN-01)	Long-term test, Parametric test (CO_2 capture rate, Permeate pressure, Feed temperature, feed flow rates, CO_2 feed concentration)	3000 hours
6" PI-2 Bundle (PI2-6IN-02)	Parametric test (CO_2 capture rate, Permeate pressure, Feed temperature, feed flow rates)	800 hours
12" PI-1 bundle	Parametric test with higher CO_2 (>18%) feed concentration	400 hours
6" PI-1 bundle	Parametric test with higher CO_2 (>18%) feed concentration	400 hours

In this report, section 2 provides a description of the Air Liquide hybrid capture technology and a description of the FTU at NCCC. Section 3 describes the FTU re-commissioning. Section 4 describes the membrane bundle testing results. Section 5 describes the challenges faced with the operation of this novel technology and finally Section 6 summarizes the major conclusions and future steps.

2. Air Liquide Carbon Capture Technology

2.1 Hybrid cold membrane process

The Air Liquide hybrid CO_2 capture process combines a cold temperature membrane operation with partial CO_2 liquefaction as shown in Exhibit 4. The PI-1 and PI-2 membranes, operated at temperatures below -20ºC, were shown to have 2 – 4 times higher CO_2/N_2 selectivity, with similar CO_2 permeance, as compared to ambient temperature operation. This improved membrane performance is the enabling factor for the hybrid membrane and partial condensation process designed by Air Liquide. This process enables over 90% CO_2 recovery from air-fired, PC flue gas at a capture cost lower than $40/tonne, and with greater than 98% CO_2 purity.

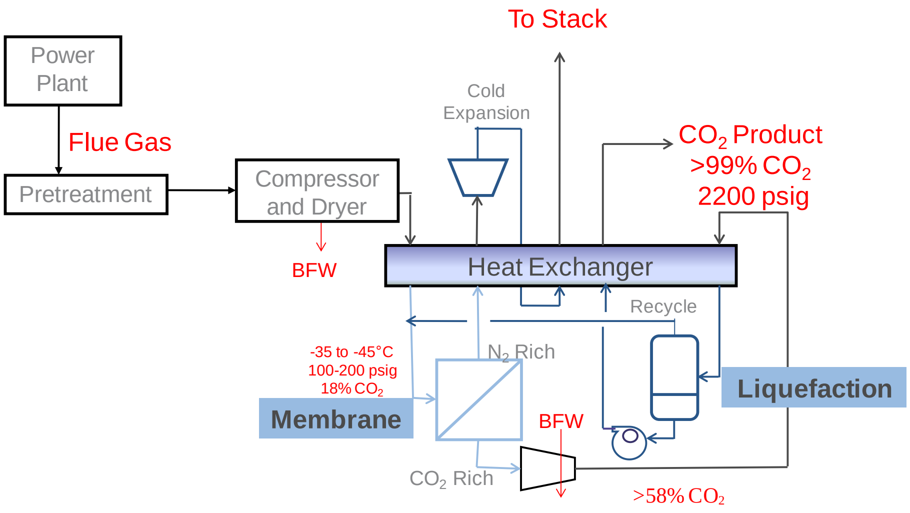


Exhibit 4. Air Liquide CO_2 Capture Process Schematic

The full scale hybrid process is designed to pre-treat the flue gas by removal of NOx, dust, SOx, and compress to 16 bar. In this process, compression is necessary to increase the partial pressure of CO_2 in the membrane feed. An oil free axial compressor is used to compress the flue gas. Inter-stage cooling is minimized to maximize the waste heat generated by the compression. The waste heat from the flue gas compression is used to heat make up water from the condenser in the power plant steam cycle and generate Boiler Feed Water (BFW). The flue gas is further cooled with water in a shell and tube heat exchanger.

The flue gas is then dried to remove moisture and avoid ice formation at cold temperature. The dryer beds eliminate moisture in the flue gas down below 1 ppm. The compressed dried flue gas is then sent to the Brazed-Aluminum Heat Exchanger (BAHX) to cool the membrane feed gas down to the desired temperature. Flue gas at high pressure, 16 bar, and low temperature, -45ºC, is fed to the hollow fiber membrane. The CO_2 selectively permeates through the membrane, producing a CO_2 rich permeate stream (greater than 58%) at low pressure. The CO_2 depleted retentate gas exits the membrane at high pressure. A small portion (3 - 5%) of the retentate gas is delivered back to the permeate-side of the membrane to act as a sweep gas. The remainder of the retentate gas is expanded in a turbo-expander to cool the incoming flue gas and the liquefier feed in the BAHX.

The permeate stream is compressed in a centrifugal compressor with waste heat recovery for BFW generation. The compressed permeate stream is sent to the BAHX for partial liquefaction and to the liquefier column. Liquid CO_2 condensed from the liquefier column is further purified in a distillation column to meet the oxygen specification for Enhanced Oil Recovery (EOR). The CO_2 product from the distillation column is pumped to the desired pressure, 152 bar. The off-gas from the partial condensation column with 30% CO_2 is recycled back to the membrane feed to increase the CO_2 capture rate.

2.2 Description of 0.3 MWe field test unit

The 0.3 MWe FTU was designed to exhibit the superior performance of Air Liquide hollow fiber membranes. Exhibit 5 shows the block flow diagram of the FTU.

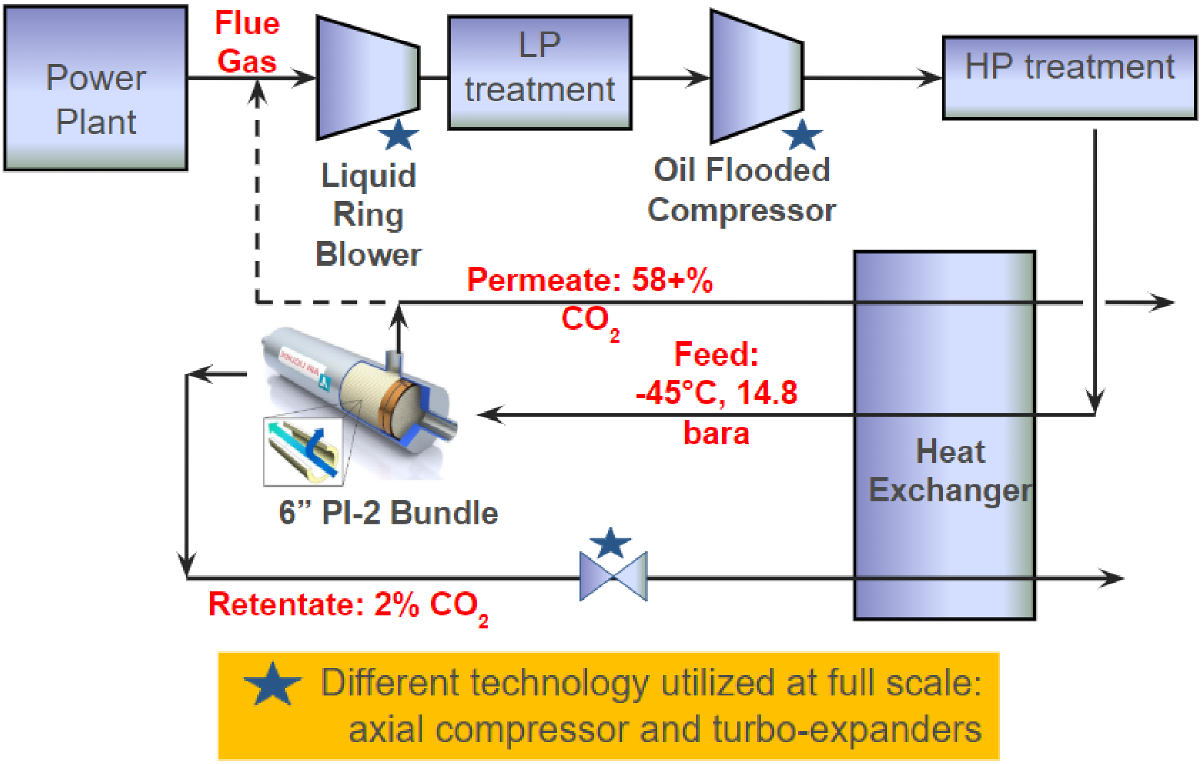


Exhibit 5. Block Flow Diagram of FTU

Flue gas was received from the Alabama Power, Plant E.C. Gaston, Unit 5 coal fired power plant. The flue gas was treated with Selective Catalytic Reduction (SCR) to remove NOx followed by a bag house and Flue Gas Desulphurization (FGD) to subsequently remove particulates and SOx. The flue gas was further treated in a pre-scrubber at the NCCC to reduce SOx down to 1 ppm.

The Air Liquide 0.3 MWe FTU consisted of the following:

Liquid ring blower: The flue gas was sent to the liquid ring blower to boost the pressure to 1.7 bar.

Low pressure treatment: The flue gas underwent low-pressure treatment to remove water in a knock-out vessel and particulates in a dust filter.

Compression: The flue gas was compressed to 16 bar in an oil flooded screw compressor. The oil was separated from the flue gas and recycled back to the compressor after cooling and filtering.

High pressure treatment: The flue gas was treated at high pressure to remove moisture in a dryer bed and hydrocarbon (oil residue) in an activated alumina bed. The flue gas was cleaned in a fine dust filter to remove any particulates.

Brazed Aluminum Heat Exchanger (BAHX): The flue gas was sent to the BAHX to cool the membrane feed gas to -45°C. The membrane feed gas at high pressure, 14.8 bar, and cold temperature, was sent to the hollow fiber membrane to selectively permeate CO_2 on the low pressure permeate side. The high pressure N_2 rich retentate gas was expanded in a Joule-Thomson valve and sent to the BAHX to cool the incoming feed gas. The low pressure permeate gas was also sent back to the BAHX to cool the feed gas.

Membrane: Two membrane materials (PI-1 and PI-2) were tested at the NCCC. Commercial 6” PI-2 and 6” & 12” PI-1 bundles from ALAS’s existing product line were tested for flue gas separation.

Permeate recycle: A portion of the permeate gas was recycled back to the inlet of the blower to increase the CO_2 feed concentration to 18%. This recycle stream was used to mimic the hybrid cold membrane and liquefaction process where off-gas from the liquefier would be recycled back to the membrane feed.

The equipment such as the liquid ring blower, the oil flooded screw compressor, and the Joule-Thomson valve will not be used in the full scale plant due to their low efficiency. Oil free compressors and turbines will be used at large scale.

3. 0.3 MWe Field Test Unit re-Commissioning

The 0.3 MWe FTU was delivered, installed and commissioned in the Pilot Bay 3 area under the previous DOE sponsored project of DE-FE0013163 in 2015. It was re-commissioned under the current project in October 2017. To better accommodate the skid to the current project, the following preparations/upgrades were completed:

- Removed the tarp and wooden roof covering the skid
- All PRVs being re-calibrated
- Refilled the compressor oil
- Replaced the alumina adsorbent
- Replaced all coalescing elements
- Install a dryer bed bypass line, including the pneumatic actuated and gate valves
- Checked the liquid ring blower alignment
- Changed air filter pads for chiller condenser
- O_2 and CO_2 analyzers sent for maintenance

A picture of the 0.3 MWe FTU is shown in Exhibit 6. In Exhibit 6, Label 1 indicates the compressor skid, Label 2 indicates the pre-treatment skid, and Label 3 indicates the membrane skid.

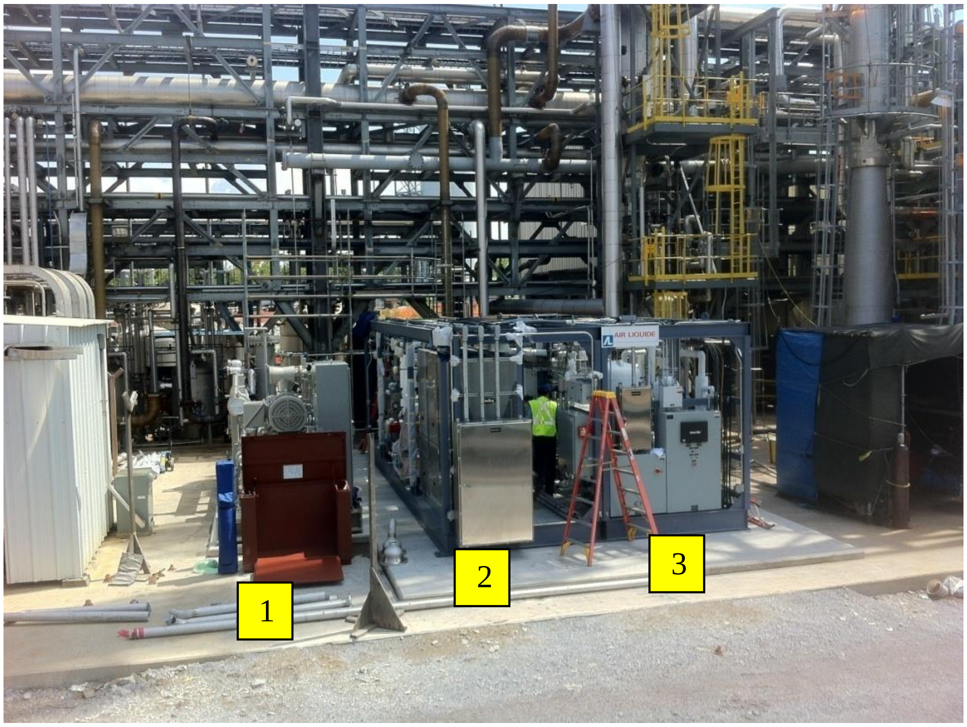


Exhibit 6. Air Liquide Field-Test Unit Installed at the NCCC

Re-commissioning was conducted with a 4” PI-2 prototype bundle installed. Air was fed as the process gas to check the functioning of each piece of equipment sequentially. Once the issues were identified and resolved, all of the process equipment and instrumentation was operated for several hours continuously. Once all of the issues were resolved, the system was run continuously for over 325 hours without issues.

4. Membrane Bundle Testing

4.1 6” PI-2 Bundle Parametric Tests

Two 6” PI-2 bundles, PI2-6IN-01 and PI2-6IN-02, were tested in the FTU at the NCCC for cold temperature performance validation and long-term testing.

4.1.1 PI2-6IN-01

The PI2-6IN-01 bundle, fabricated in Q2-2017, was installed in the 0.3 MWe FTU. The bundle was tested at -30 and -45°C, 11.3 and 14.8 bara, and over a range of feed flow rates. At both temperatures the bundle met the target success criteria in terms of performance. The range of experimental conditions and bundle performance metrics during the continuous operational testing period at NCCC are shown in Exhibit 7.

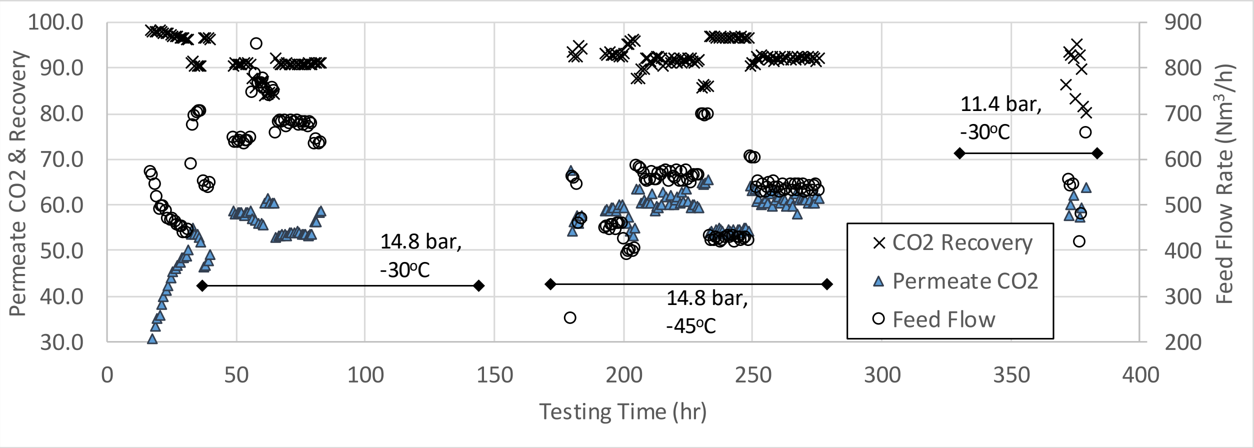


Exhibit 7. Operating conditions and performance metrics for the 6" bundle PI2-6IN-01, tested at NCCC between 12/10/17 - 12/20/17.

The first series of experimental states were taken at -30°C. These states were limited by the high permeance of the PI-2 fiber. The overall productivity of the 6" PI-2 bundle was slightly higher than a 12" PI-1 bundle. The permeate blower, used to control the permeate pressure, has a design flow rate very close to this value. At -30°C and lower recoveries, less than 85%, the blower could not maintain 1.1 bar back pressure. Thus, data was taken at a range of permeate pressures corresponding to capabilities of the system. The two most relevant data points are shown in Exhibit 8.

Exhibit 8. Test Results at -30 ºC. Permeance normalized to PI-1 performance.

Bundle #	**6IN-PI-2-01**			**Success Criteria**
Conditions	17.5% CO_2, 14.8 bara, -30°C, P_{perm}: 1.1 bar	18.4% CO_2, 14.8 bara, -45°C, P_{perm}: 1.1 bar	18.1% CO_2, 11.4 bara, -31°C, P_{perm}: 1.1 bar	
Normalized CO_2 Permeance	8.4	7.3	9.2	
CO_2/N_2 Selectivity	50.6	51.5	50.2	
CO_2 Recovery	91%	91%	90%	90%
Productivity, Feed (Nm³/h)	657	577	473	400
Permeate CO_2 Purity	59%	62%	59%	58%

At -30 C, the bundle exceeded the milestone: 6" PI-2 commercial bundle flue gas testing to reach a target of >400 Nm³/hr productivity from a feed containing 18% CO_2, achieving 90% capture and >58% CO_2 permeate purity. The feed gas is at slightly less than 18% and the permeate pressure is slightly higher than optimal, both these factors would only improve the performance if corrected for.

A series of experimental conditions were evaluated at -45°C. The increased selectivity lowered the permeate flow such that the permeate blower could be fully utilized to reach the target 1.1 bara permeate pressure. At -45°C, performance also exceeded the DOE targets, as listed in Exhibit 8. The feed flow and permeate purity achieved at each temperature for 90.5-91.0% CO_2 recovery is plotted in Exhibit 9.

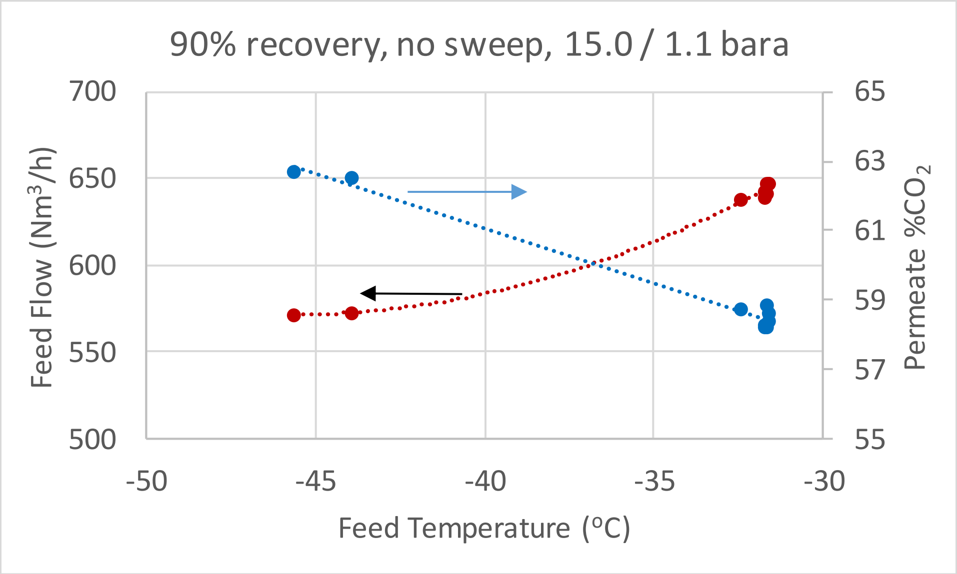


Exhibit 9. Feed flow and permeate purity as a function of feed temperature for PI2-6IN-01 at 14.8 bar, 1.1 bar permeate pressure, and 90% CO_2 recovery.

A recovery curve at this temperature is also shown in Figure Exhibit 10, showing the expected tradeoff between feed flow and permeate purity with varying CO_2 recovery.

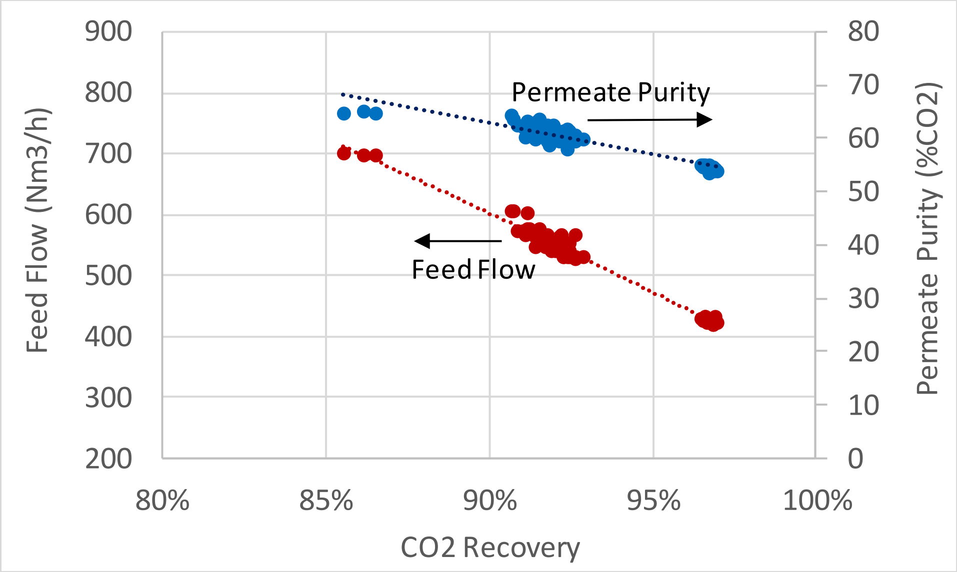


Exhibit 10. Feed flow and permeate purity as a function of CO_2 recovery for PI2-6IN-01 at 14.8 bar, -45°C, and 1.1 bar permeate pressure.

The calculated fiber performance was extrapolated from the data and is shown in Exhibit 11. The permeance is reported as a multiple of that of PI-1. The normalized fiber permeance shows a loss of performance at high recovery, as has been seen before.

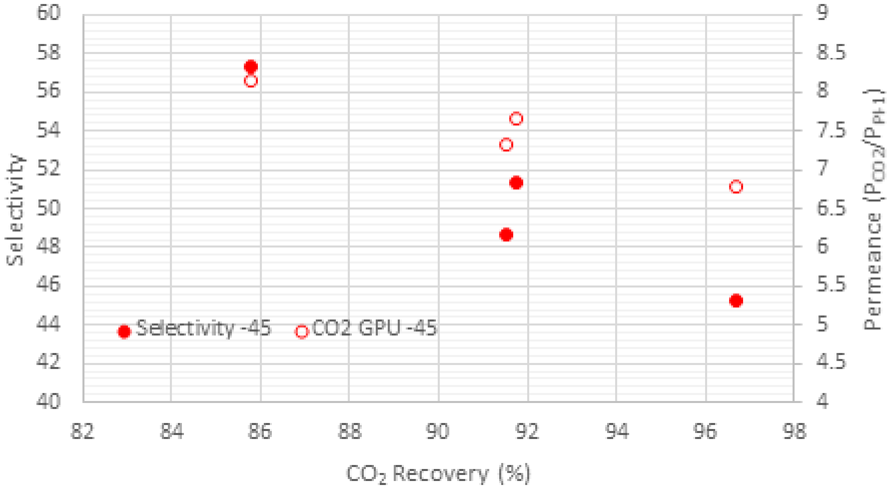


Exhibit 11. Calculated fiber performance as a function of recovery for PI2-6IN-01 at 14.8 bara and -45°C.

A secondary test was performed where the permeate back pressure was changed to determine the optimal operating point. The results are shown in Exhibit 12.

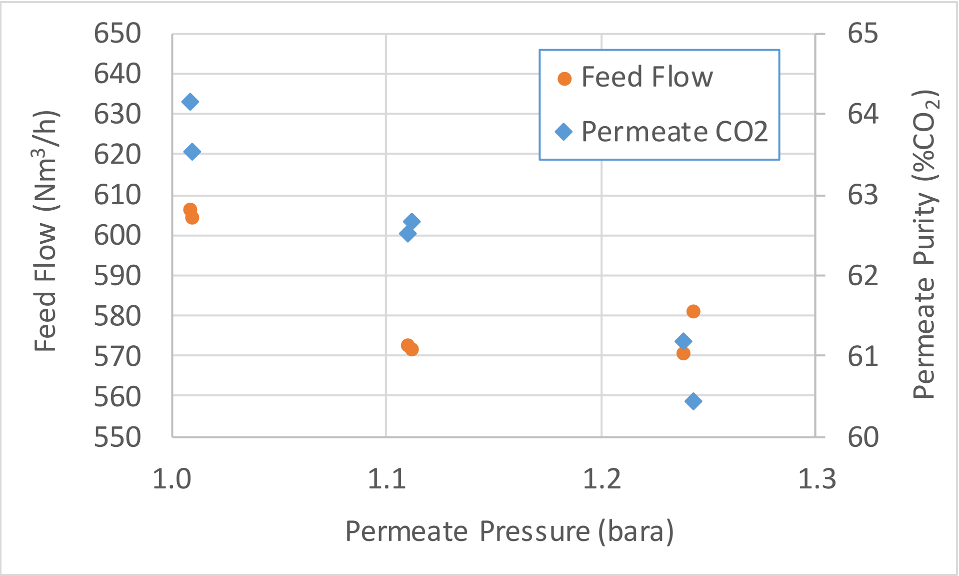


Exhibit 12. Effect of permeate back pressure on PI2-6IN-01 bundle performance at 14.8 bar and -45°C.

While the lower permeate pressure gives an expected advantage in terms of driving force for CO_2 permeation, our previous studies have demonstrated that it also improves counter-current flow. For both of these reasons, the bundle performance was better at lower permeate pressure. Finally, an additional set of test data was collected at a lower operating pressure of 11.4 bara and feed temperature of -31°C. The results are plotted in Exhibit 13.

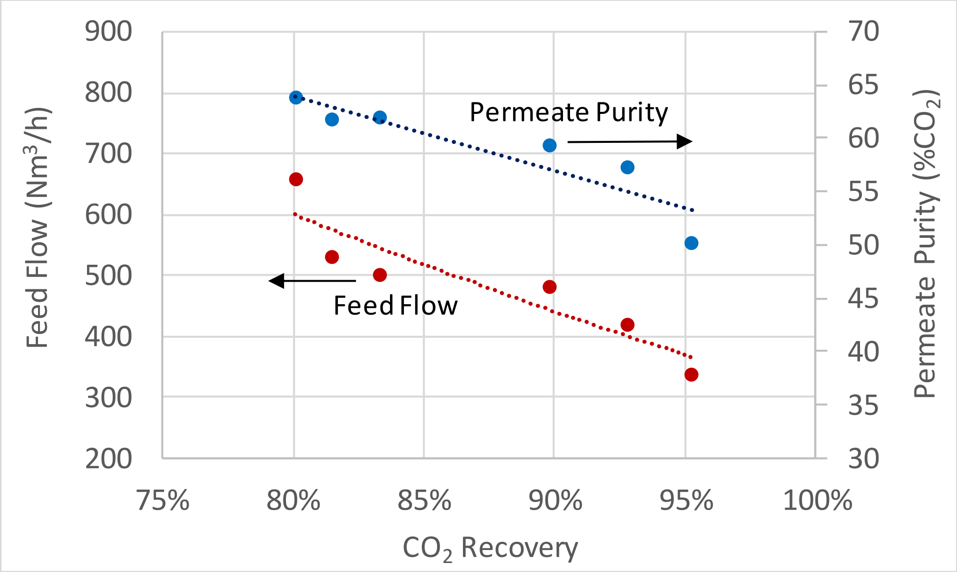


Exhibit 13. Bundle feed flow and permeate purity performance as a function of recovery at 11.4 bar, -30°C, and 1.1 bar permeate pressure.

Even at the lower operating pressure of 11.4 bara and the relatively warmer -31°C, the membrane bundle exhibited performance also exceeding the success criteria as detailed in Exhibit 8.

It should be noted that system limitations due to the high membrane flux prevent operation over the fully intended test window. The extent of the recovery curve at -45°C was limited due to the sizing of the permeate blower. Testing down to 70% CO_2 recovery was desirable, but the actual limit was 85%. At -30°C, the lowest possible recovery was limited to approximately 90%. Testing with a sweep was also not practical since the sweep would have further limited the CO_2 recovery range at either temperature.

4.1.2 PI2-6IN-02

The PI2-6IN-02 bundle was installed in the 0.3 MWe FTU. The bundle was tested at -30 and -45°C, 11.3 and 14.8 bara, and over a range of feed flow rates. At both temperatures the bundle met the target success criteria in terms of performance. The range of experimental conditions and bundle performance metrics during the continuous operational testing period at NCCC are shown in Exhibit 14. The test conditions for which the success criteria were exceeded are boxed in the Exhibit.

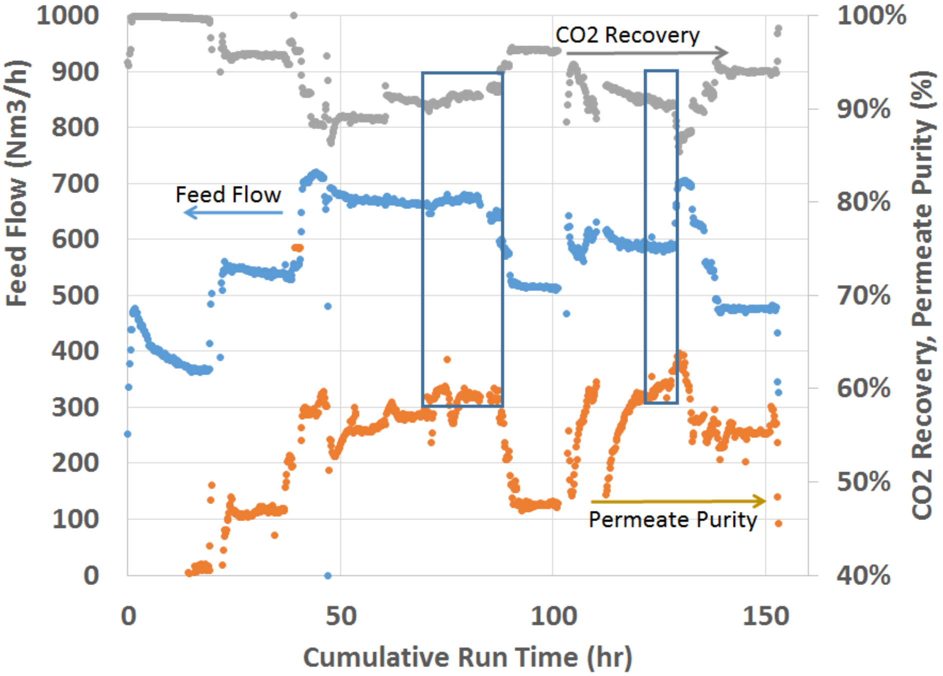


Exhibit 14. Operating conditions and performance metrics for the 6" bundle PI2-6IN-02, tested at NCCC between 1/9/18 – 2/28/18.

The bundle PI2-6IN-02 exhibited even higher performance than the previous module PI2-6IN-01 such that it significantly exceeded the success criteria. A comparison of the bundle performances to the relevant success criteria is given in Exhibit 15.

Exhibit 15. Test results for the bundle PI2-6IN-02 tested at NCCC. Note that the permeance was normalized to a multiple of the PI-1 performance.

Bundle #	**6IN-PI-2-01**	**6IN-PI-2-02**	**Success Criteria**
Conditions	18.4% CO_2, 14.8 bara, -45°C, P_{perm}: 1.1 bar	18.0% CO_2, 13.1 bara, -45°C, P_{perm}: 1.2 bar	
Normalized CO_2 Permeance	7.3	10.6	
CO_2/N_2 Selectivity	51.5	55.8	
CO_2 Recovery	91%	90%	90%
Productivity, Feed (Nm^3/h)	577	646	400
Permeate CO_2 Purity	62%	60%	58%

The second 6" bundle had exceptionally high CO_2 permeance and selectivity, both moderately exceeding the first bundle. These excellent performance metrics resulted in a real bundle productivity significantly exceeding the target success criteria. Moreover, as the membrane was operated at a lower operating pressure than the design 14.8 bar, an implied energy savings can also be realized over the baseline case. The second bundle was manufactured from fiber that had moderately higher permeance and selectivity than the first bundle such that a better overall performance was expected. In both cases, the bundle forming operation was completed without complication such that the good fiber performance directly resulted in a good overall bundle performance.

Unfortunately, the FTU system flow was limited by our main compressor capacity and the C80 permeate blower capacity. These restrictions prevented us from either operating below 90% recovery or maintaining our design 1.1 bar permeate pressure. In the next forming campaign, at least one bundle will be fabricated with less fiber (5" approximate fiber diameter) such that a lower productivity is targeted. While this may seem counterproductive, it will allow us to test over a wider range of CO_2 recovery and gain a better understanding of the non-ideal flow effects present in the bundle.

4.2 6" PI-2 Bundle Long-term Stability Test

In Q1-2019, we initiated the long-term stability test at NCCC on the PI-2 6'' bundle. Testing was progressed with the PI2-6IN-01 bundle, which was the first commercial scale PI-2 bundle fabricated. It has ~ 20-30% lower flux than subsequent bundle PI2-6IN-02, principally because of less fiber area. The NCCC test skid was designed for PI-1 testing, and the compression system does not have the flow capacity to fully test PI-2 bundles over a large parametric range. A slightly larger performance testing range is possible with PI2-6IN-01 compared to its sister bundle. A depiction of the test program (Feb - June 2019) is shown below in Exhibit 16.

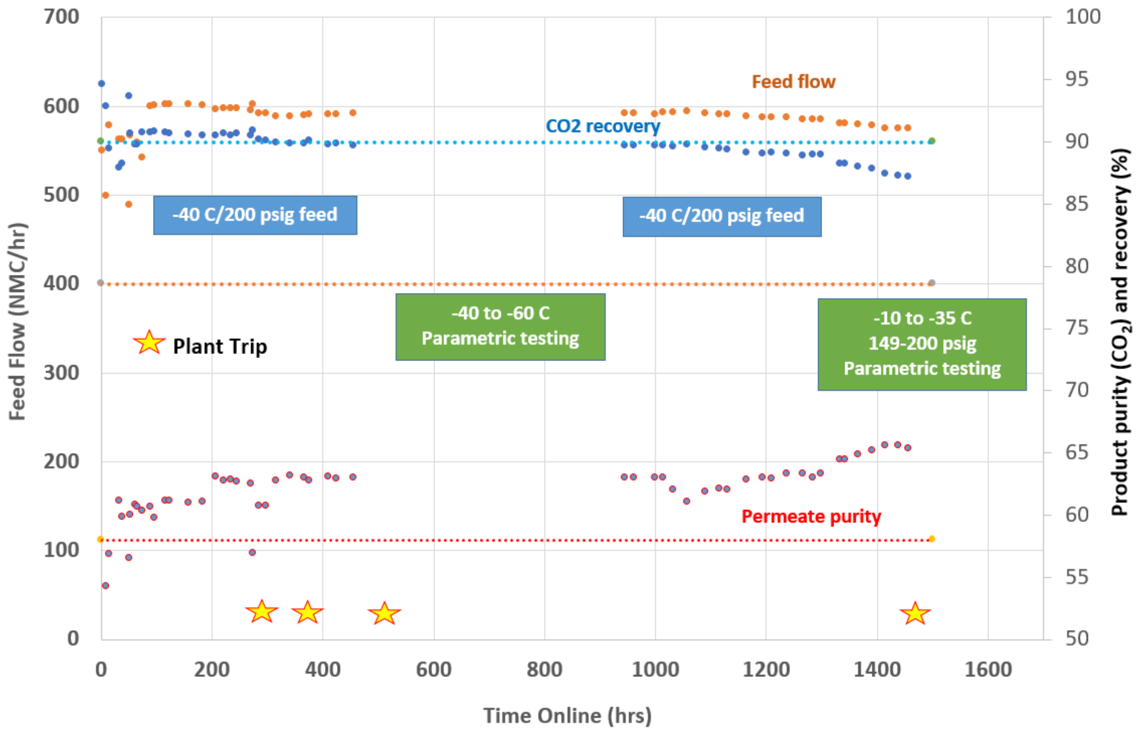
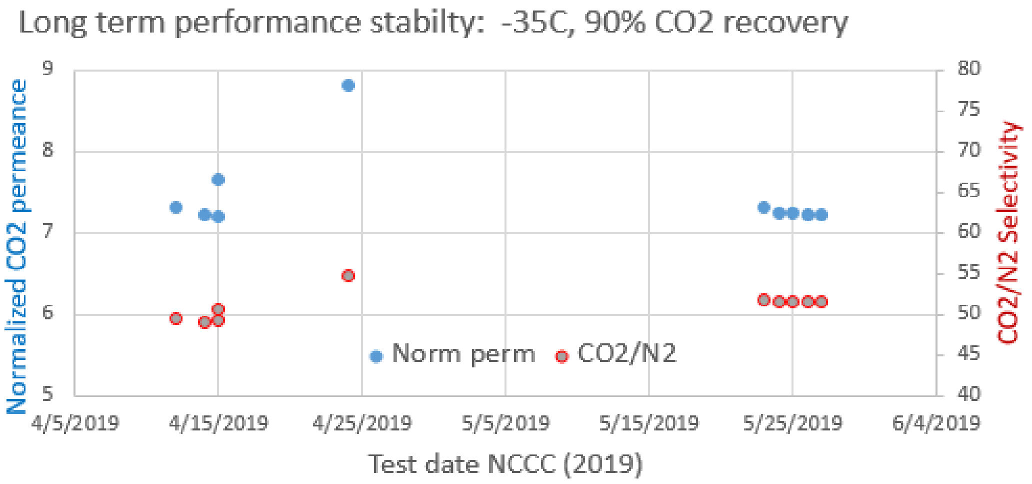


Exhibit 16. PI2-6IN-01 bundle data: Feed flow, CO_2 recovery and permeate purity are shown as a function of on-line time (not counting plant trips). The data were obtained between Feb-May 2019 and correspond to 18% CO_2 feed, ~ 14.8 bar feed pressure, 1.1- 1.3 bar permeate pressure and 87-95% CO_2 recovery.

As shown in Exhibit 16, testing at NCCC in 2019 showed stable bundle performance for over 700 hours. This total period was achieved over 2 long term stability test periods (Feb-March and April-May), broken by both plant trips and a parametric testing period. The parametric testing involved feed temperatures down to -60 °C. It was known that the low temperature testing was potentially destructive; it seems to have resulted in a slight loss of bundle productivity accompanied by a gain in selectivity. We speculate that the activity of the CO_2 during the -60 °C testing was sufficient to plasticize the polymer, with the resulting thickening of the fiber skin. CO_2 thermodynamic activity triples between -45 and -60 °C, and the CO_2 is very close to liquefaction during this portion of the test.

A better visualization of the membrane stability is given by plotting the perm-selectivity measured over constant operating conditions. This is shown in Exhibit 17 for constant conditions at -35 °C (April- May 2019) and at -40 °C (2017 -2019). This performance loss is not unreasonable for hollow fiber membranes and has already been accounted for in the techno-economic evaluations.



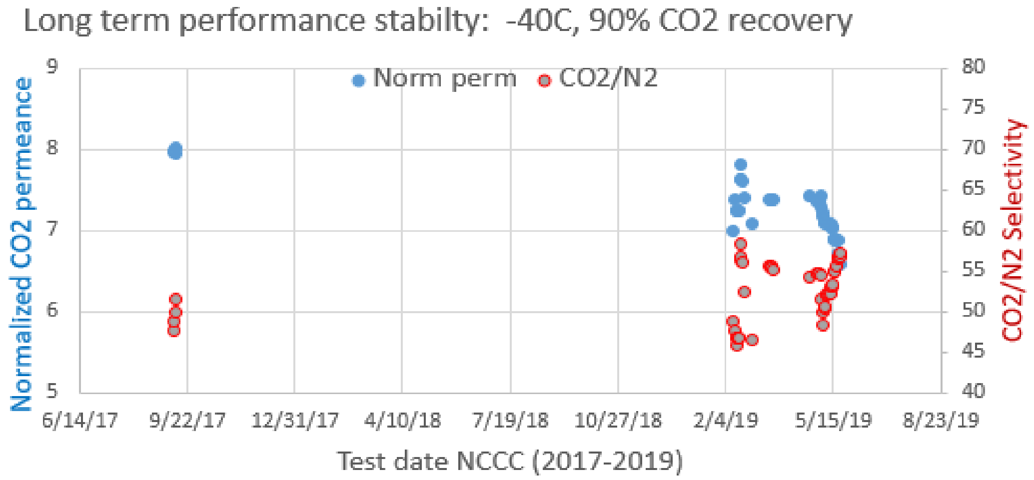


Exhibit 17. PI2-6IN-01 bundle data: long-term perm-selectivity data. The data correspond to 18% CO_2 feed, ~ 14.8 bar feed pressure, 1.1 bar permeate pressure and 90% CO_2 recovery.

During the above-mentioned parametric testing window, CO_2 recovery, feed and permeate pressure, as well as feed temperature were varied:

- Feed pressure: 5.8 to 14.8 bar
- Permeate pressure: 1.1 to 1.3 bar
- CO_2 recovery: 80 to 98%
- Feed temperature: +5 to -60 ^{o}C

The main variable studied was the feed temperature. Results of the parametric test, shown as an Arrhenius plot, can be seen in Exhibit 18.

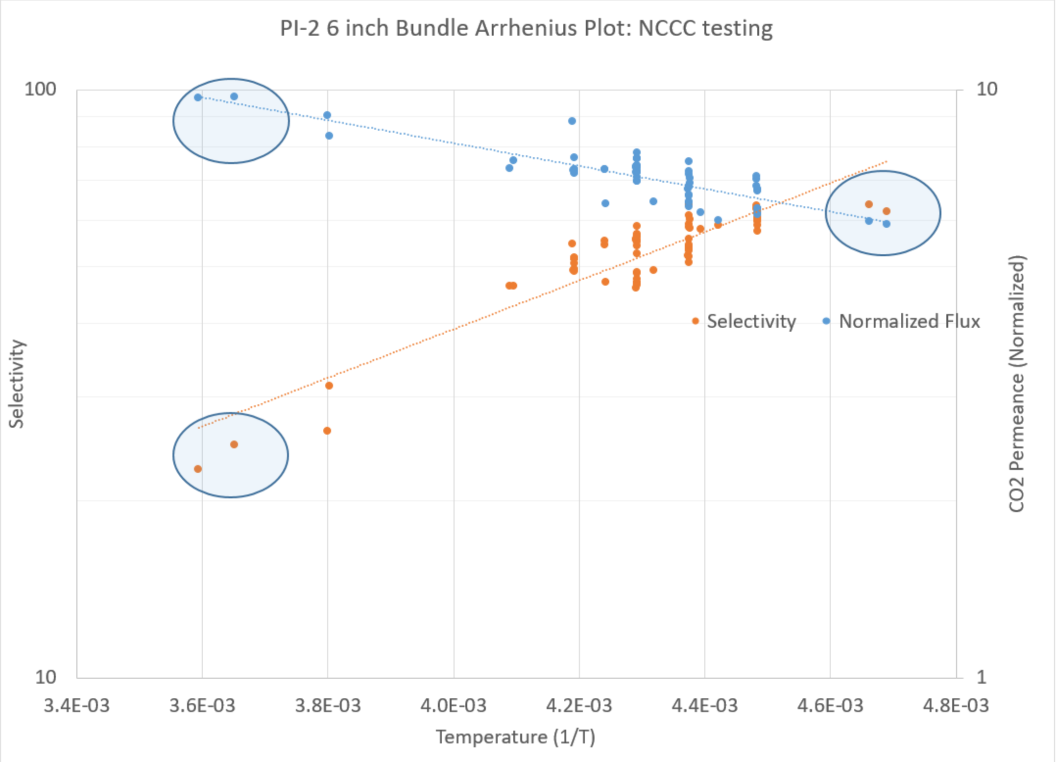


Exhibit 18. Arrhenius Plot of PI2-6IN-01 CO_2/N_2 selectivity and normalized CO_2 permeance. RT and low temperature points are shaded. Data plotted corresponds to 18% CO_2 feed, ~ 14.8 bar feed pressure, 1.1 to 1.3 bar permeate pressure and 80-94% CO_2 recovery.

The impact of cold temperature on PI-2 performance is somewhat different from what previously observed with PI-1. PI-1 showed a flatter permeance profile and increasing selectivity as temperature decreases. The optimum use temperature for PI-1 was approximately -45 to -50 ^{o}C. In contrast, PI-2 selectivity shows marginal increase in selectivity at temperatures < -45 ^{o}C. The optimum temperature for PI-2 may thus be warmer (-30 to -40 ^{o}C) than was the case for PI-1. This distinction may be related either to the greater CO_2 plasticizability of the PI-2 material or the membrane skin morphology differences.

4.3 Extended Tests on AL PI Membrane Bundles

By the end of Q2-2019, AL concluded all originally planned flue gas testing of PI-2 6 inch bundles at NCCC. The testings have been completed are listed in exhibit 19. The total operating time for the skid is approximately 5000 hours.

Exhibit 19: The cold membrane testings completed in NCCC.

Bundle type	Testing type	Duration of test
4" PI-2 Bundle	System performance verification	400 hours
6" PI-2 Bundle (PI2-6IN-01)	Long-term test, Parametric test (CO_2 capture rate, Permeate pressure, Feed temperature, feed flow rates, CO_2 feed concentration)	3000 hours
6" PI-2 Bundle (PI2-6IN-02)	Parametric test (CO_2 capture rate, Permeate pressure, Feed temperature, feed flow rates)	800 hours
12" PI-1 bundle	Parametric test with higher CO_2 (>18%) feed concentration	400 hours
6" PI-1 bundle	Parametric test with higher CO_2 (>18%) feed concentration	400 hours

Apart from flue gas CO_2 capture application, AL is also interested in evaluating membrane performance with higher concentration CO_2 feed, such as would be seen in cement, steam methane reforming or steel processing. For these applications, the membrane must operate under a higher feed of CO_2. The objectives of the extended testing were to test three membrane types at higher CO_2 feed concentrations:

- 6" PI-2
- 12" PI-1
- 6" PI-1

The high CO_2 feed concentration was planned to be met by a simple permeate recycle scheme as shown in Exhibit 20.

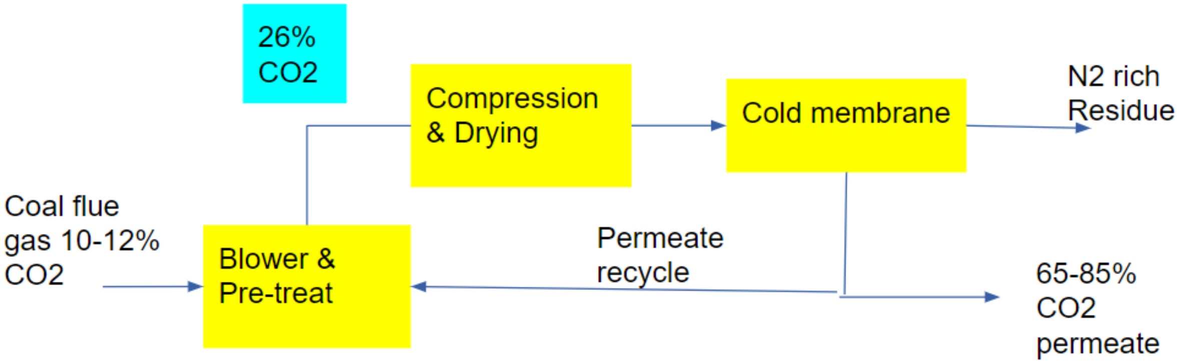


Exhibit 20. Permeate recycle scheme to increase CO_2 concentration in membrane feed.

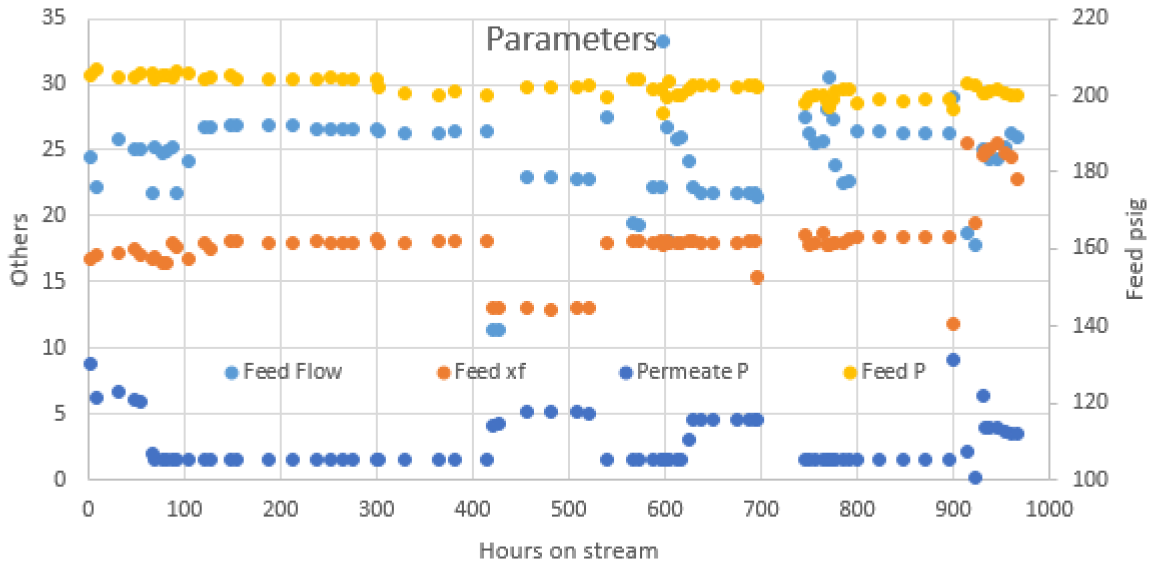
This scheme is in fact the same way we adjust the feed concentration from 13% (supplied by power plant) to 18%, which is the condition that has been used in the bulk of our testing at NCCC (to mimic the effect of the liquefier vent recycle to a 13% CO_2 coal flue gas in the cold membrane process). Preliminary mass balance calculations showed that we should be able to achieve 28% feed concentrations with this scheme; however in reality, some control valve issues, hidden permeate side leaks (e.g PRV to exhaust) and varying feed flue gas concentrations only enabled us to test up to ~ 25-26% CO_2. As a result, the general test conditions conducted in this quarter are:

- 25-26% CO_2, 6 - 8% O_2
- 14.8 bar feed pressure with 1.1 to 1.3 bar permeate pressure
- 0 to -40 ^oC feed temperature
- 70 – 90% CO_2 recovery

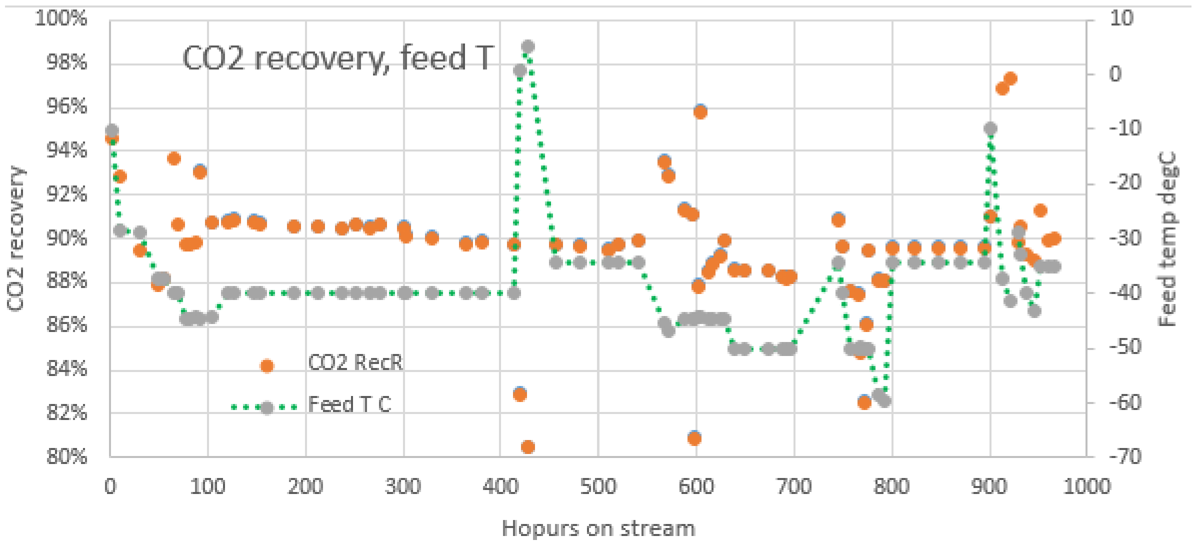
The key lessons we leant from this extended testing are summarized below:

4.3.1 6” PI-2 testing

The extended testing conditions for 6” PI-2 are demonstrated in Exhibit 21. Apart from operation at ~ 25% CO_2 feeding concentration, the test conditions were essentially the same as the long term tests. The skid was run at close to full flow capacity to achieve 90% CO_2 recovery at this higher CO_2 feed concentration. One unavoidable consequence was that the permeate pressure could not be maintained at 1.1 bar as this high flow overwhelmed the permeate blower capacity.



(a)



(b)

Exhibit 21. Complete test conditions assessed for 6" PI-2 bundle (PI2-6IN-01) showing extended test conditions: (a) feed flow, feed concentration, feed pressure, permeate pressure, (b) CO2 recovery and feed temperature.

Since PI-2 is a high free-volume morphology polymer, it was suspected that high CO_2 activity may cause plasticization, leading to lower selectivity when operated at 25% CO_2. Exhibit 22 shows CO_2 perm-selectivity as a function of feed temperature, from which we can see PI-2 continued to maintain the same perm-selectivity. Perm-selectivity calculated from the 25% CO_2 extended testing period (920+ hours) is compared with the previous 800-920 hours period at lower CO_2

concentration. The overlay of this data indicates that the flux profiles developed for PI-2 in previous testing can be extended to the higher (25%) CO_2 range as well.

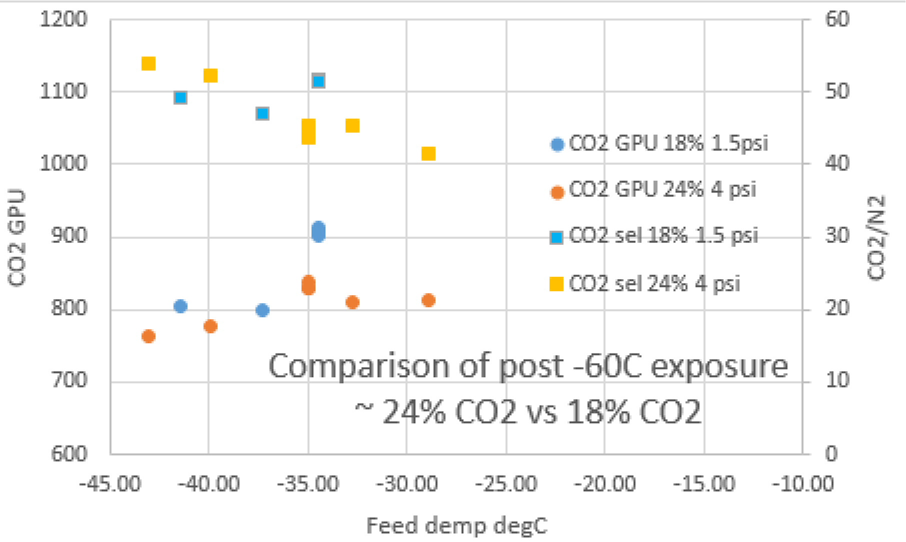


Exhibit 22. Comparison of CO2 /N2 perm-selectivity for extended 900+ hour testing at 25% CO2 vs earlier data in 800-900 hour period.

4.3.2 12” PI-1 testing

A 12” PI-1 bundle was tested to verify the mechanical integrity of a certain method of bundle construction when exposed to high CO_2 activity (sufficiently high CO_2 concentration coupling with cold temperature). Previous testing has shown that this construction technique is completely safe at 18% CO_2 with temperature being as low as -55 ^{o}C.; however, there are doubts about its integrity at high CO_2 concentration. The bundle was tested over ~ 140 hours at 25% CO_2, 14.8 bar and temperature down to -30 ^{o}C. The separation performance is shown in Exhibit 23. Although the permeate purity decreased by only 3% and stayed above 65% CO_2, there was a noticeable decrease in this value over time. The loss in separation ability is clearly seen by comparing the initial and final purity at warmer conditions. The test was aborted. This bundle was shipped back to AL laboratories to examine the root cause: e.g. O-ring slippage, stress crack etc.

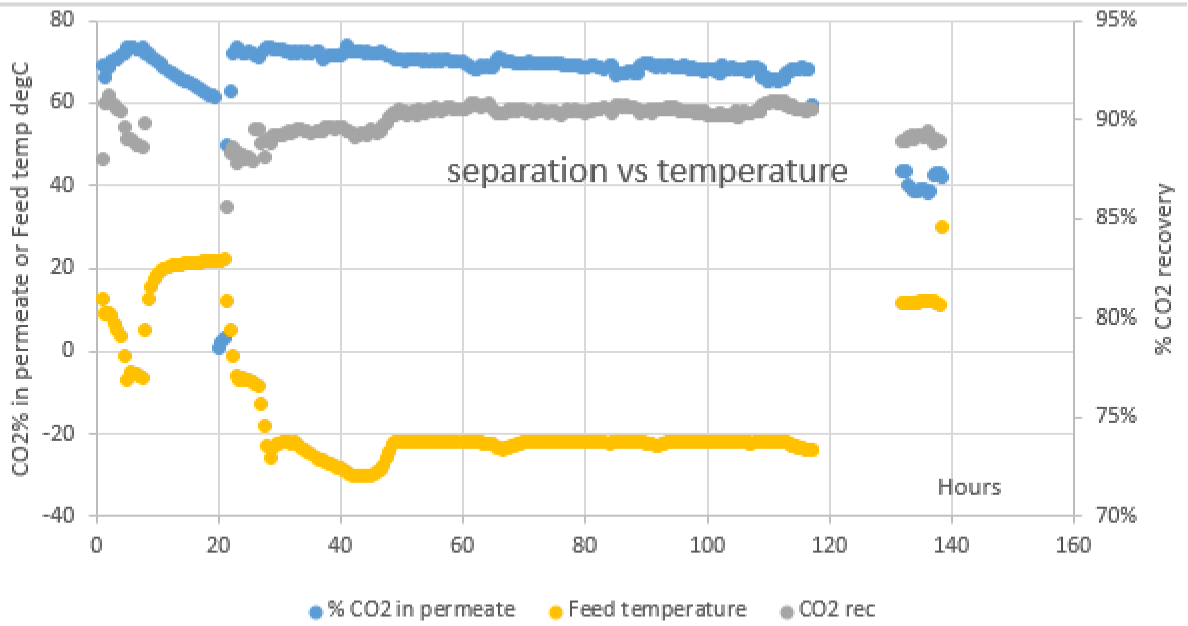


Exhibit 23. CO_2 permeate purity, CO_2 recovery and feed temperature for 12" PI-1 bundle tested at 14.8/1.2 bar feed/permeate pressures, 25% CO_2 feed concentration. Loss of data at ~ 120 hours is due to a computer mishap. The bundle leak appears to be initiated at ~ 40 hours.

4.3.3 6" PI-1 testing

A 6" PI-1 bundle was tested for ~ 300 hours at 14.8 bar, -22 °C and CO_2 feed concentration at 20-26%. As shown in Exhibit 24, after ~ 170 hours, the ability to maintain membrane feed concentration at 25% was lost and subsequent feed concentrations declined to 22% (day) and 19% (night). This may be related to air infiltration as Gaston was under load-shed conditions during this period. The bundle performance (recovery/purity) stayed constant as also verified by perm-selectivity calculations.

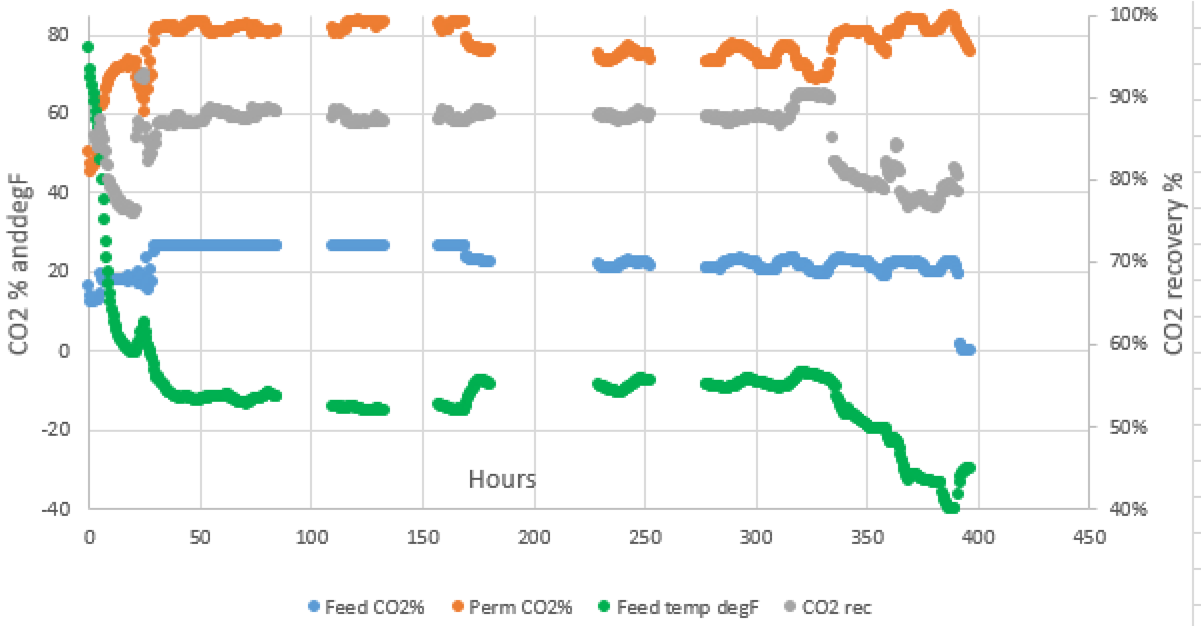


Exhibit 24. Feed and permeate CO_2 concentrations, feed temperature and CO_2 recovery for testing of 6" PI-1 bundle. Feed/permeate pressures were 14.8/1.1 bar.

Over the last ~ 3 days of operation, the feed temperature was decreased to -40 °C, before Gaston shutting down. The bundle performance over the entire period is shown as an Arrhenius plot in Exhibit 25, which follows expected performance at these conditions.

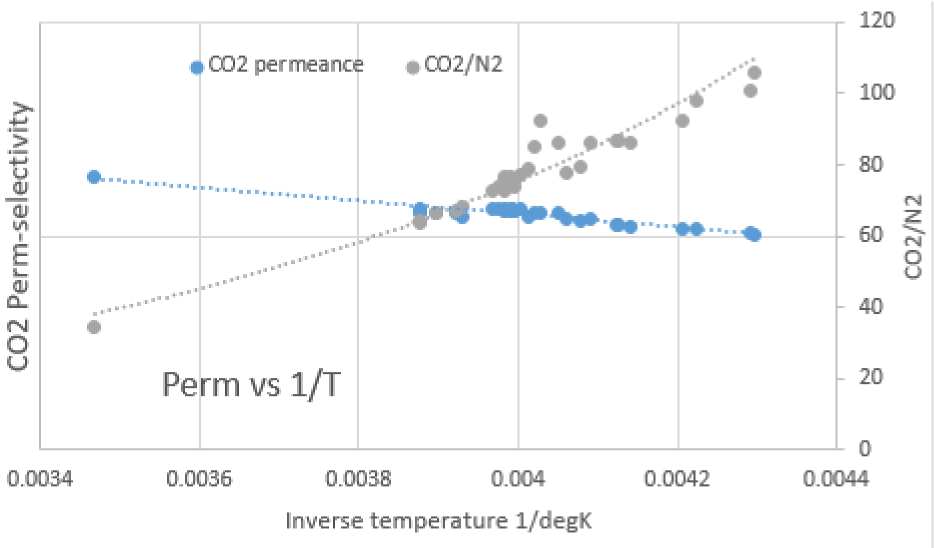


Exhibit 25. CO_2 perm-selectivity as a function of inverse temperature for 6" PI-1 bundle. The dashed lines are fits to the Arrhenius relation.

5. Challenges in the Field and Mitigation Steps

This section lists the challenges faced in the testing campaigns during which membrane bundles were tested with flue gas. The challenges were mitigated by cooperation of the NCCC staff and contractors and Air Liquide on-site staff.

5.1 FTU automation

The FTU was programmed to operate autonomously. However, the complexity of the system hindered the auto-start sequence in many instances. In the future, the skid programming will be further tuned to improve automation and ease of start-up.

5.2 Equipment issues

Several minor equipment related issues were encountered such as a faulty HMI screen, faulty pneumatic valve, loose electrical connection, faulty flow meter, etc. None of these issues were especially significant and were resolved by Air Liquide staff with support from the NCCC.

Several major equipment related issues, listed as below, were encountered which caused testing delay and rescheduling.

Pentair coalescing elements

During Q1-2018, the FTU experienced an unacceptable pressure drop between the C10 blower and the compressor, which limited the maximum capacity of the system. First, it was believed to be caused by the development of scale (lime) in the heat exchanger. The heat exchanger was then removed and cleaned, but little or no lime buildup was observed. The same high pressure drop between C10 blower and compressor resumed upon restart. After further investigation, an increased pressure drop was identified across the Pentair coalescing elements. New elements were installed and the problem solved.

Pentair coalescing elements are a pleated layered material, as shown in Exhibit 26. The spent elements show a significant orange color that is generally assumed to be rust. This discoloration continues through the layers of the media. SEM (Scanning Electron Microscopy) examination of the media shows accumulation of fine material fouling the filter surface. The foulant was further examined with Energy Dispersive X Ray analysis (EDX), which provides an elemental composition difference between the virgin and spent samples. The primary differences were small increases (~2%) in silicon, and the presence of significant amounts (~9%) of iron in the spent samples. This layer of accumulated foulant could potentially block gas flow and results in increased pressure drop.

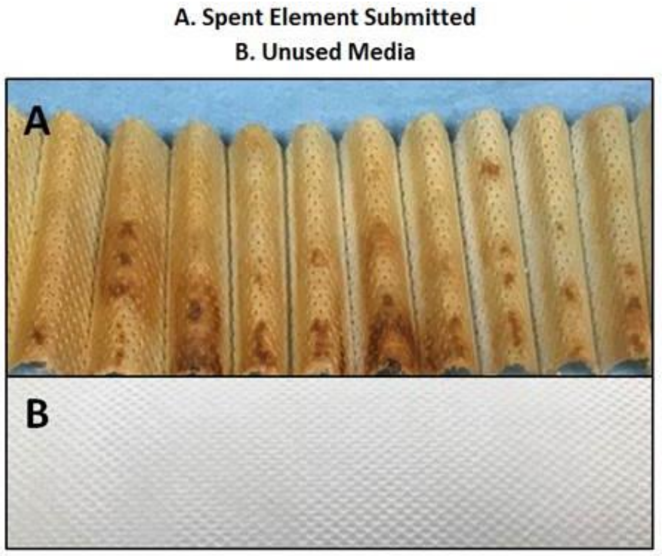


Exhibit 26. Spent and unused media showing rust buildup.

Desaturation heater

The temperature probe of desaturation heater was in direct contact with the heater, as a result, the probe was compromised due to corrosion, as can be seen in Exhibit 27. The cause was suspected to be a combination of vibration, which damaged the stainless steel sheath, and corrosion at that spot. The probe was replaced and the heater was back to normal operation.

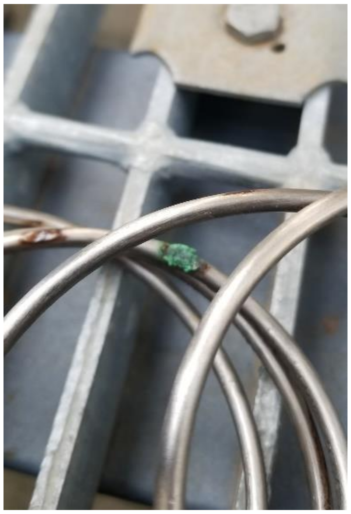


Exhibit 27. Corrosion on temperature probe.

C10 blower

C10 blower is a water flooded Nash blower, and we experienced a malfunctioning bearing on the motor. The failure was likely due to either vibration of the system or misalignment of the motor caused by vibration of the system. The motor was shipped to a NASH certified repairing site, repaired, and put back into service.

Compressor rebuilt

The 0.3 MWe FTU main feed compressor exhibited some control issues resulting in periodic system trips. A service technician conducted an inspection of the unit and discovered that the slide valve was mechanically binding against the main rotor. The possible causes of this binding were likely either wear/corrosion of the main rotor bearing or wear of the slide valve assembly itself. The solution for either case required a partial rebuild of the compressor, conducted at a machine shop. The compressor block was removed from the system and shipped to a licensed repair facility for a partial rebuild.

With the compressor rebuild beginning in July 2018, the 500-hour steady-state test cannot be completed by the scheduled late summer shut-down of Plant Gaston. Plant Gaston is not scheduled to re-start until late Fall of 2018 such that the 500-hour test and de-commissioning could not be completed before the December 31, 2018 project end date. As a result, a project modification was agreed to with NETL. The overall project end date was extended to December 30, 2019.

6. FTU Decommissioning

With all the testing activities concluded, the 0.3 MWe FTU was decommissioned in October 2019. NCCC personnel assisted AL with the removal of hazardous materials from the skids for disposal. The hazardous materials include oil from the compressors, Freon from the chiller, and propylene glycol mixture from the cooling water lines. NCCC assisted AL with the disconnection of process lines, cooling water and electric. The skids were moved off the site at the end of October, and currently being stored at AL contracted storage location for future testing purposes.

All AL activity concluded by the end of October. Below Exhibit 28 shows a picture of AL researcher working on site during decommissioning.

Exhibit 28. AL researcher on site with skids being removed.

7. Conclusions and Future Steps

Air Liquide participated in the testing campaigns from 2017 to 2019. The field test unit had been operated for approximately 5000 hours. The NCCC testing enabled Air Liquide to:

1. Validate the superior performance of commercial 6” PI-2 membrane bundles under cold temperature with actual flue gas.
2. Confirm the long-term stability of the commercial 6” PI-2 commercial bundles under cold temperature with actual flue gas
3. Evaluate the performance of both commercial PI-1 and PI-2 membrane bundles at extended conditions: including extra cold temperature and higher CO_2 feed concentration.

The NCCC staff contributed to the project success from the initial hazardous operability study through the final decommissioning. The NCCC’s assistance and support are gratefully acknowledged.

Currently the FTU is being stored at AL contracted storage location for future testing purposes upon DOE’s assessment and approval.