CO_2 Capture by Cold Membrane Operation with Actual Power Plant Flue Gas

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

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Lead Author:

Trapti Chaubey

Contributing Coauthors:

Sudhir Kulkarni, David Hasse, Monaca McNall, Alex Augustine

Submitted by
American Air Liquide Inc.
200 GBC Drive
Newark, DE 19702

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DOE Program Manager

José D. Figueroa

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Disclaimer

TABLE OF CONTENTS

Abbreviations

AL	Air Liquide
BAHX	Brazed Aluminum Heat Exchanger
BFW	Boiler Feed Water
DOE	Department of Energy
DRTC	Delaware Research and Technology Center
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)
MEDAL	Membranes DuPont Air Liquide (Founded as a joint venture, fully acquired by AL in 1992)
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 is developing a novel, cost-effective post-combustion CO_2 capture technology based on pre-concentrating flue gas in a cold membrane step to 60% CO_2 followed by further purification to Enhanced Oil Recovery (EOR) grade in a liquefaction step. The liquefaction step is well understood due to Air Liquide's extensive experience in cryogenic based gas separations, specifically with the CRYOCAP technology for CO_2 capture from oxy-combustion power plants in Callide, Australia and Ciuden, Spain. The technology development to TRL 5 involved testing the cold membrane step at 0.3 MWe scale with actual flue gas at the National Carbon Capture Center (NCCC) under the NETL funded project DE-FE0013163 (CO_2 Capture by Cold Membrane Operation with Actual Power Plant Flue Gas).

Air Liquide participated in two campaigns:

- PO-4 campaign from October to December 2015
- PO-5 campaign from May to November 2016

The equipment was delivered, installed, and commissioned at the beginning of the PO-4 campaign. The Field Test Unit (FTU) was operated for over 3,200 hours during the two campaigns. After completion of testing, the FTU was weatherized for later use in an alternate NETL funded project, DE-FE0026422.

The NCCC testing enabled Air Liquide to:

1. Confirm **long-term stability** of PI-1 commercial bundles with pre-treated actual flue gas
2. Evaluate the **optimum PI-1 configuration** for CO_2 capture
3. Verify contaminant (NOx, metals) emissions **co-reduction**
4. Confirm the potential of novel PI-2 membranes to **reduce membrane** area

The membrane bundles described in the following table were tested at the NCCC with stable long-term performance. Various sized PI-1 bundles were tested to understand the effect of the geometry parameters on the separation performance. PI-2 is an exploratory membrane material with exceptionally high CO_2 permeance.

Bundle type	Testing type	Duration of test
12" PI-1 bundle	Long-term single bundle test and 2 bundles in series configuration	640 hours (PO-4)
6" PI-1 bundle	Long-term test and parametric test (CO_2 capture rate, permeate pressure, feed temperature, and sweep rate)	900 hours (PO-5)
1" PI-1 bundle	Long-term test, parametric test (CO_2 capture rate)	350 hours (PO-5)
1" PI-2 permeator	Long-term test	700 hours (PO-4)
1" PI-2 bundle	Long-term test and parametric test (CO_2 capture rate)	1,400 hours (PO-5)

In addition to the bundle testing, analytical campaigns were conducted during both the PO-4 and PO-5 campaigns to measure the contaminants Hg, As, Se, NOx and SOx at selected locations throughout the process.

The NCCC staff contributed to the project success from the initial hazardous operability study through the final shutdown and storage in place. The NCCC contribution included spot checks of the FTU, contractor-provided maintenance, remote data monitoring, and analytical measurements ranging from routine gas analyzer calibrations to assistance with trace analyses. The NCCC's assistance and support is gratefully acknowledged.

Various technical challenges were mitigated by cooperation of the NCCC staff and contractors with Air Liquide staff. A few issues, mainly related to flue gas contaminants, such as water slugs in incoming flue gas, need to be mitigated in a more robust manner. A separate "lessons-learned" document has been prepared at the NETL's request, and will be issued shortly.

<u>Key Results</u>

- The PO-4 campaign was devoted mainly to the long-term performance stability verification of a 12" PI-1 bundle. Exhibit 1 shows the 500 hour long-term test of the 12" PI-1 bundle tested at 90% CO_2 capture, 200 psig, and -45°C. The measured bundle productivity exceeded the target of 455 Nm^3/hr by more than 30%, with an actual productivity of approximately 610 Nm^3/hr. The permeate CO_2 purity also exceeded the 60% target.

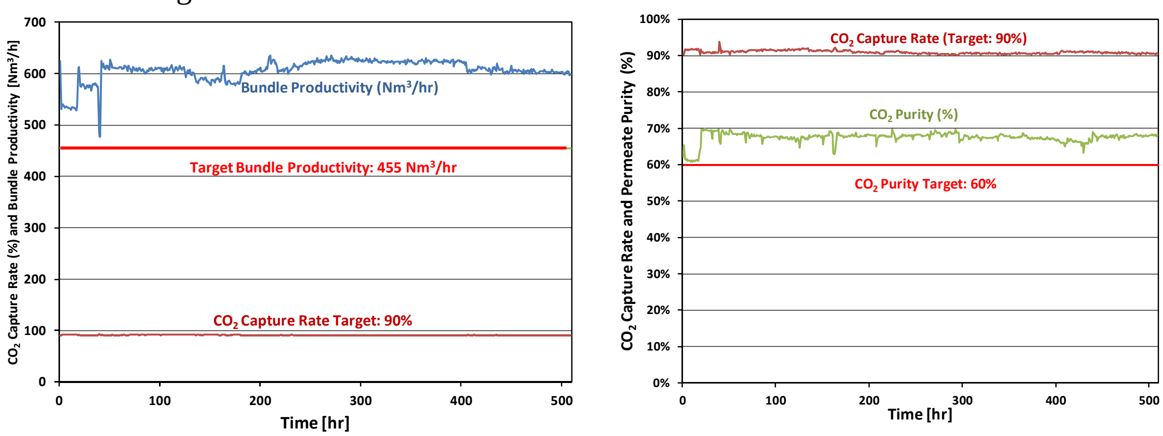


Exhibit 1. Long-term Steady-State Test for 12" PI-1 Bundle at NCCC

- All bundles tested generally exhibited stable performance during long-term testing. There were however, specific events, associated with hydrocarbon and/or moisture contamination, which caused a couple of bundles to lose up to 30% permeance. Bundles experiencing moisture contamination recovered full performance after warm-up. The bundle with hydrocarbon contamination could not be recovered; this appeared to be related to improper oil filling of the compressor, but the investigation is ongoing.
- The separation performance of 1", 6" and 12" PI-1 bundles is compared in Exhibit 2. The exhibit also includes data from a 1" PI-2 module. The 6" PI-1 bundle exhibited superior performance, compared to the 12" bundle, the higher performance is attributed to the higher length-to-diameter ratio, which allowed for an ideal counter-current flow. The 1" bundle exhibited the worst performance due to a different bundle manufacturing technique, which did not allow for an ideal counter-current flow.

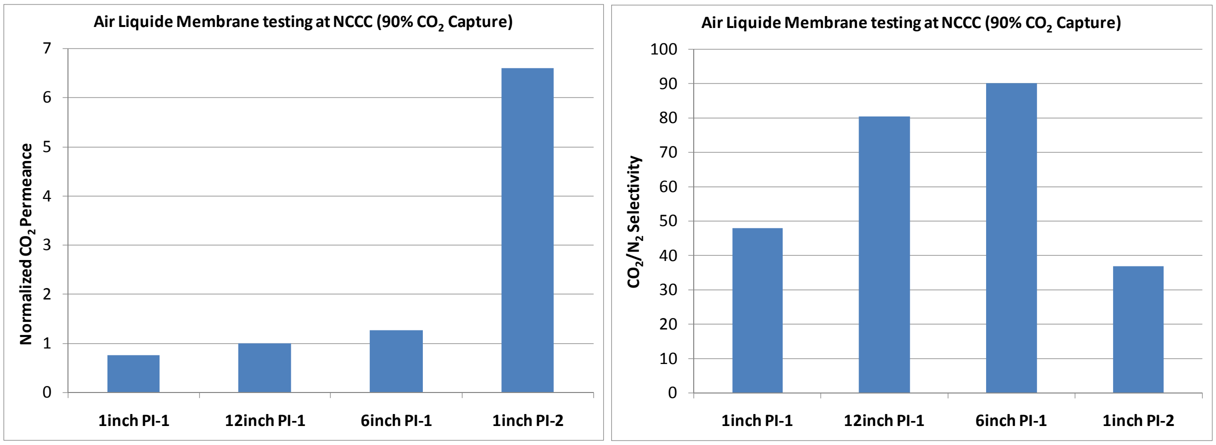


Exhibit 2. Membrane Bundle Performance Comparison at NCCC

- Extensive parametric testing was performed with a 6" PI-1 bundle, mainly during PO-5. An interesting observation during the parametric testing was that the bundle performance improved even further when operated at -50°C (beyond the baseline performance at -45°C).
- Testing of two 12" PI-1 bundles in series configuration did not show superior performance compared to the single bundle configuration.
- The PI-2 bundle exhibited more than 7 times the normalized CO_2 permeance compared to the PI-1 bundle. The projected 12" PI-2 bundle productivity was 4 to 5.5 times greater than that of the 12" PI-1 bundle, but with slightly lower CO_2 permeate purity (ranging from 61 - 64%). The 1" PI-2 bundle projections are approximate due to the highly non-ideal flow and permeate back pressure associated with the smaller bundle design used in the NCCC test.
- The analytical campaign confirmed that impurities such as Hg, Se, and NOx were reduced to levels below detection limits in the membrane feed, due to removal in the pre-treatment condensates, dryer bed, and activated alumina bed. These contaminants were mainly removed in the pre-treatment steps as detailed in Exhibit 3.

Exhibit 3. Contaminant Distribution Based on Analytical Results

Sample Point	Hg	Se	NOx
Low Pressure Condensate	40-60%	80-85%	0%
High Pressure Condensate	<10%	<10%	50-70%
Regen Gas or Dryer bed	40-60%	10%	10-20%
Activated Alumina feed	0%	0%	10-30%

Arsenic was below the detection limit in all the samples tested. The flue gas was treated by both Flue Gas Desulfurization (FGD) and pre-scrubber such that SOx levels in the incoming feed were negligible.

1. Introduction

Air Liquide has developed a post combustion carbon capture technology based on a hybrid cold membrane and liquefaction. In the current project, DE-FE0013163, this technology was advanced to TRL5 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 to 2 ppm before it was sent to the Air Liquide FTU. Air Liquide participated in the PO-4 campaign from October to December 2015 and the PO-5 campaign from May to December 2016 with over 3,200 hours of testing.

The purpose of the 0.3 MWe FTU was to test Air Liquide hollow fiber, polyimide 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 Research and Technology Center (DRTC). 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 testing was conducted with commercial bundles based on the PI-1 polyimide fiber and exploratory membrane bundles based on the highly permeable PI-2 polyimide fiber. The feed stream was split so that 95% of the flue gas was sent to the commercial PI-1 bundle and a slipstream went to the novel PI-2 bundle. The residue from the PI-1 bundle was expanded to generate cold for the process. 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. Analytical campaigns were conducted to trace the impurities in flue gas through the FTU.

Exhibit 4 lists the membrane bundles that were tested at the NCCC with stable long-term performance.

Exhibit 4. List of Membrane Bundles Tested at the NCCC

Bundle type	Testing type	Duration of test
12” PI-1 bundle	Long-term single bundle test and 2 bundles in series configuration	640 hours
6” PI-1 bundle	Long-term test and parametric test (CO_2 capture rate, permeate pressure, feed temperature, and sweep rate)	900 hours
1” PI-1 bundle	Long-term test, parametric test (CO_2 capture rate)	350 hours
1” PI-2 permeator	Long-term test	700 hours
1” PI-2 bundle	Long-term test and parametric test (CO_2 capture rate)	1400 hours

All of the above bundles were tested at 90% CO_2 capture from the PC power plant flue gas along with parametric testing. In addition to the bundle testing, two analytical campaigns were conducted to measure the contaminants mercury, arsenic, selenium, NOx, and SOx in the gas and liquid samples.

Section 2 provides a description of the Air Liquide hybrid capture technology and a description of the FTU at the NCCC. Section 3 describes the FTU acceptance testing, installation, and commissioning. Section 4 describes the membrane bundle testing results. Section 5 describes the analytical campaign to track the contaminants in the FTU. Finally, Section 6 describes the challenges faced with the operation of this novel technology and makes recommendations for future design.

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 5. The commercial AL 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 approaching $40/tonne, and with greater than 98% CO_2 purity.

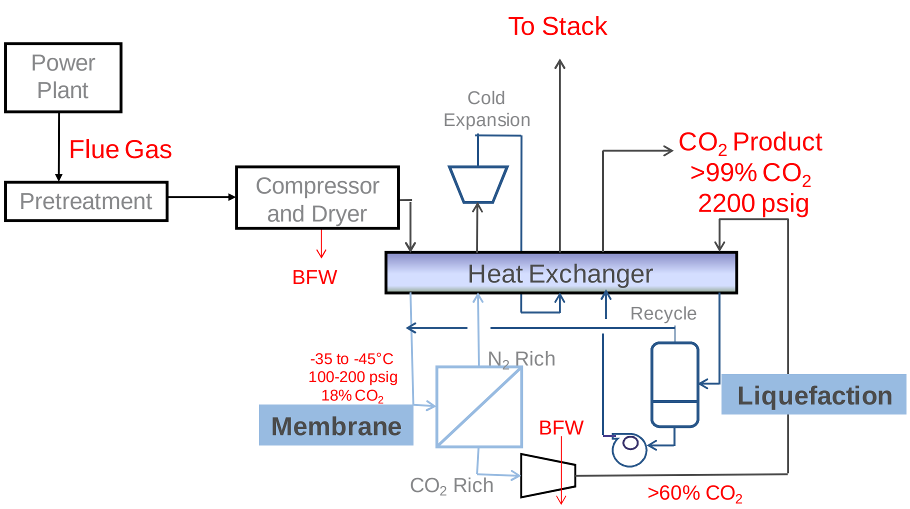


Exhibit 5. Air Liquide CO_2 Capture Process Schematic

The full scale hybrid process is designed to pre-treat the flue gas by removal of NOx, dust, SOx, and compression to 216 psig (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 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, 216 psig (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 62%) 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, 2,200 psig (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 6 shows the block flow diagram of the FTU.

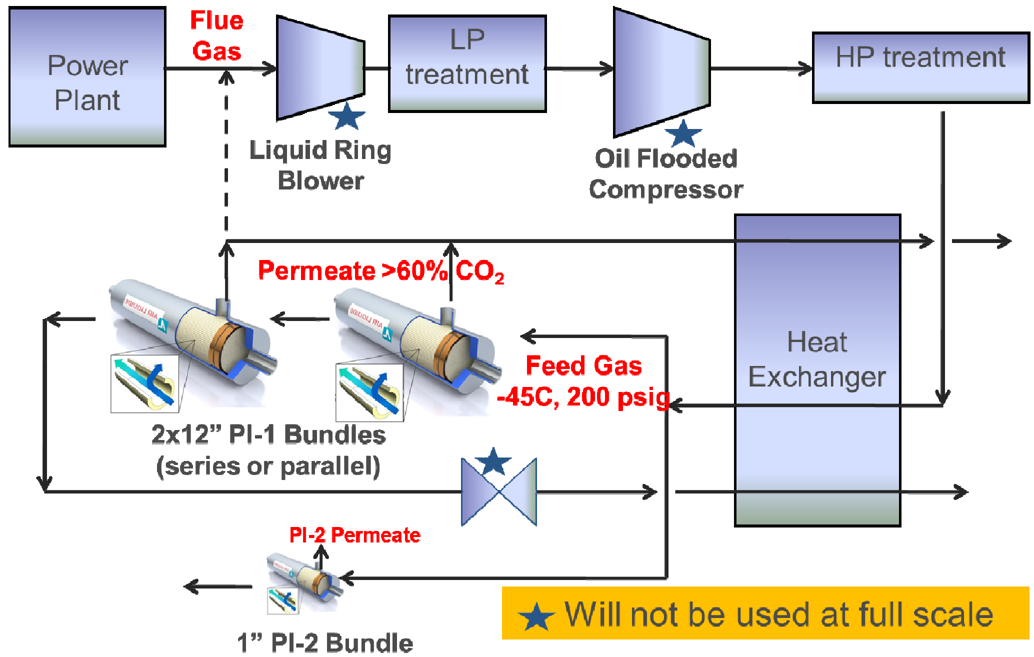


Exhibit 6. Block Flow Diagram of FTU

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 2 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 10 psig.

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 200 psig 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, 200 psig, 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 12”, 6” and 1” PI-1 bundles from MEDAL’s existing product line were tested for flue gas separation. In addition, PI-2, a novel material with 4 to 5 times the projected bundle productivity, was tested in a 1” module. Commercial scale (6”) PI-2 bundles are being developed under a separate DOE funded project, DE-FE0026422, for testing at the NCCC in 2017 - 2018. The bundles were arranged so that two PI-1 bundles could be tested in series or parallel or single bundle configuration. A slipstream of flue gas was sent to the PI-2 bundle for testing.

Permeate recycle: A portion of the permeate gas from the PI-1 bundle 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 Installation and Commissioning

The 0.3 MWe FTU was designed, constructed, and acceptance tested in Newark, DE over the Budget Period 1. The FTU was transported to the NCCC as three skids and installed in the Pilot Bay 3 area. The unit was commissioned using air as the process fluid such that the majority of start-up issues could be identified and addressed before the flue gas was available. All major equipment was successfully operated and no major set-backs were encountered.

3.1 Equipment delivery and installation at the NCCC

The skids were prepared for shipment by careful packaging. Any pieces that extended out past the approximate 30’L, 8.5’W, and 10.5’H boundaries were removed and packaged on the skids. All exposed glass and electronic components were bubble wrapped to protect against road debris. Crates were mounted on the skids so that ancillary equipment (tools, PPE, and spare parts) could accompany the transport. Lastly, custom plastic tarps were secured to the skids. Transportation was scheduled with a freight shipping service and both the pick-up from the fabrication shop and the delivery to the NCCC site were witnessed by Air Liquide personnel. A picture of the membrane skid being lifted onto the trailer-truck is shown in Exhibit 7.

Exhibit 7. Membrane Skid Being Lifted onto the Trailer-truck at the Fabrication Shop.

As part of the technology collaboration agreement with NCCC, a detailed scope of work was prepared for the installation and commissioning with regard to NCCC and Air Liquide's respective responsibilities. The installation proceeded smoothly and with good communication between NCCC and Air Liquide. A picture of the Air Liquide 0.3 MWe FTU installed at the NCCC Pilot Bay 3 is shown in Exhibit 8.

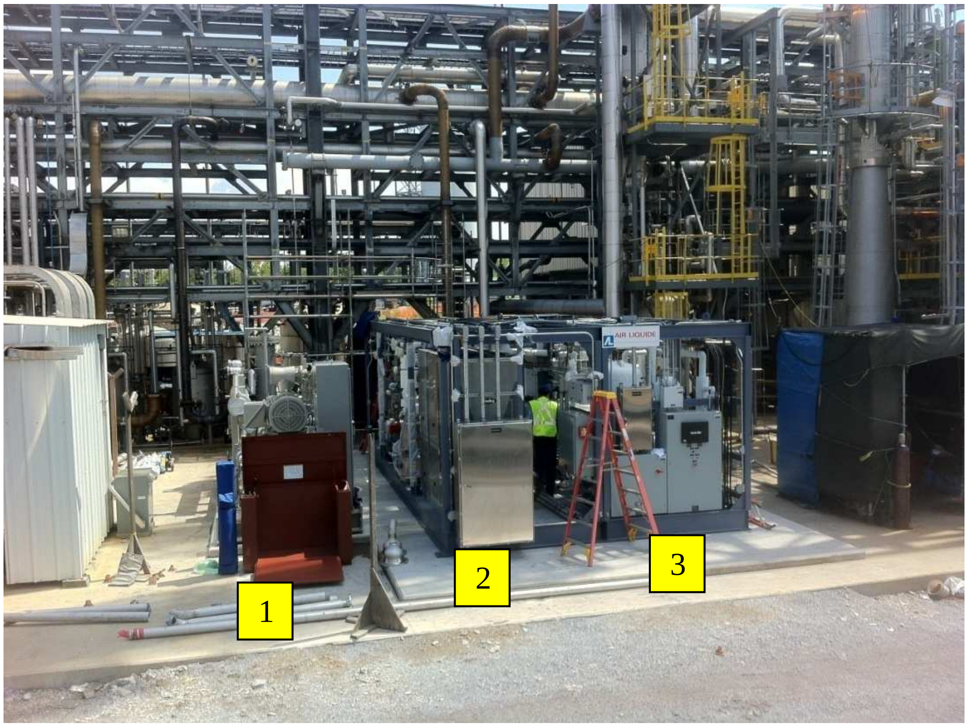


Exhibit 8. Air Liquide Field-Test Unit Installed at the NCCC

In Exhibit 8, Label 1 indicates the compressor skid, Label 2 indicates the pre-treatment skid, and Label 3 indicates the membrane skid.

3.2 Commissioning and shakedown of the FTU

A commissioning checklist was drafted based on the acceptance testing at the skid fabrication shop and on the best practices of MEDAL engineers with regard to commercial membrane packages. The checklist directed the commissioning team as to the instrumentation that must be checked, the appropriate method for first-time start-up of each piece of equipment, and how to confirm proper function.

A Job Safety Analysis (JSA) was conducted prior to any hands-on work. A JSA is a systematic method of identifying potential hazards and aligning risk mitigation practices. Required PPE and risk mitigating practices were agreed to with the NCCC team. The work was executed safely, and no safety related issues occurred.

Commissioning was conducted with air 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. Commissioning continued after the flue gas was made available by the NCCC. Additional equipment issues related to the blower and compressor were identified and addressed.

The pre-treatment skid and compressor skid were commissioned initially with the membrane skid in by-pass mode. Flue gas was analyzed for mercury downstream of the dryer to ensure low mercury content before sending the gas to the BAHX to avoid corrosion and embrittlement issues. The mercury concentration was below the detection and corrosion limits. The flue gas was then sent to the membrane skid, allowing for the final commission step. Two 12" PI-1 commercial membranes were used for commissioning. Both the bundles were previously qualified in the 0.1 MWe DRTC bench scale skid, meeting the performance target. The bundles exhibited superior performance in the FTU compared to the DRTC testing. This completed the commissioning of the FTU.

Once all of the issues were resolved, 24/7 automated operation was possible. The system was run continuously for over 450 hours with no alarms or trips (over 850 hours of total operation, initially interrupted by process trips and Plant Gaston outages). Lastly, data logging and limited remote access were successfully achieved.

4. Membrane Bundle Testing

4.1 12" PI-bundle test

A 12" PI-1 bundle was tested in the FTU at the NCCC for cold temperature performance validation, long-term testing, and a two bundle in series testing. This section describes the 12" PI-1 bundle testing at NCCC.

4.1.1 Cold temperature performance validation

The cold membrane test was conducted mainly with CO_2-enriched flue gas (18% CO_2, 9% O_2, balance N_2), at -45°C, 200 psig, and 1.5 psig permeate pressure based on the optimum conditions identified from bench scale testing at DRTC. A blower on the permeate line allowed the permeate pressure to be adjusted in the range of 1.5 - 8 psig. The effect of sweep was also examined by delivering a small fraction (up to 4%) of the residue stream to the permeate side of the membrane bundle. A portion of the permeate gas from the membrane was recycled back to the inlet of the blower to increase the CO_2 feed concentration to 18%.

Exhibit 9 shows a summary of the bundle productivity and CO_2 purity for the Bundle E tested at DRTC with higher permeate pressure (7 psig) as well as the predicted performance at 1.5 psig permeate pressure. It is beneficial to operate the membranes at lower permeate pressure to increase the driving force across the membranes. However, the design of the DRTC test skid, which recycles the expanded residue and permeate streams to the compressor suction, limited the permeate pressure. The membrane performance at low permeate pressure, 1.5 psig, was therefore estimated, using a membrane model for the NCCC test condition. The NCCC skid was designed to overcome this limitation with a blower on the permeate line.

Exhibit 9 shows the actual performance of Bundle E from the NCCC field test, which was even higher than the estimated performance at 90% CO_2 capture and 1.5 psig permeate pressure. This result suggested that non-ideal flow patterns within the bundle can be reduced by operating the bundle at lower permeate pressure (non-ideal flow effects were not considered by the simulation model used to predict the NCCC performance).

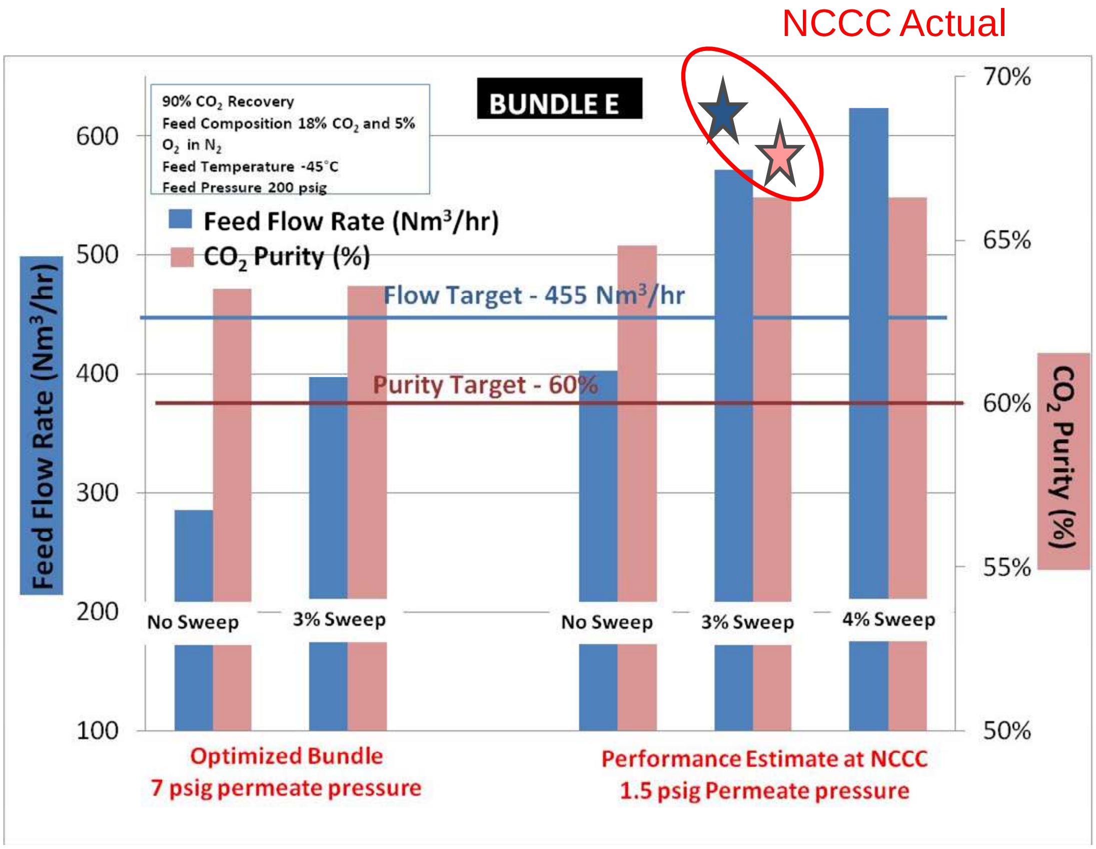


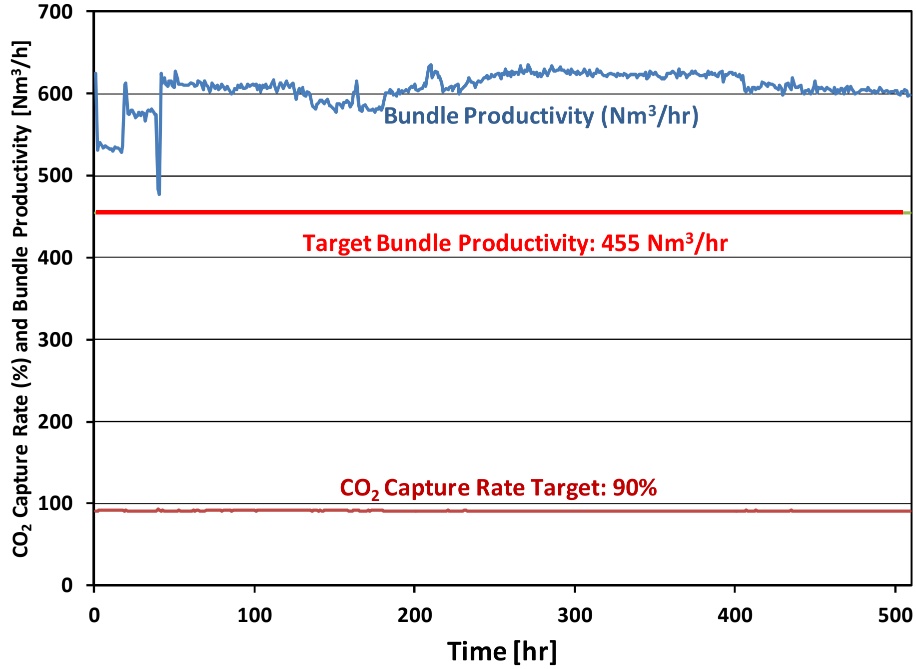
Exhibit 9. Bundle E Productivity and CO_2 Purity for the 12" Membrane Bundle Tested at DRTC (7 psig permeate pressure) and NCCC (1.5 psig permeate pressure estimated and actual).

The bundle performance in the field exceeded the project target. The bundle productivity target (set 30% higher compared to the previous baseline performance) was 455 Nm^3/hr and the CO_2 permeate purity requirement was 60% (to be followed by further purification in the liquefaction unit, not part of the field testing). The membrane Bundle E exceeded the performance target with a productivity of 610 Nm^3/hr, and 68% CO_2 purity, at 90% CO_2 capture.

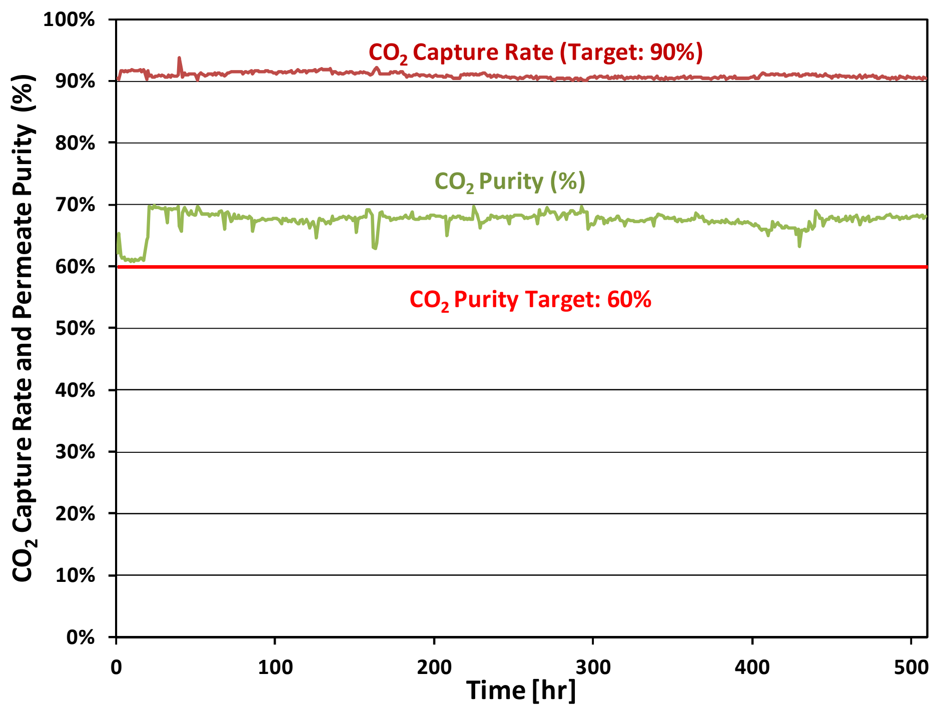
4.1.2 12" PI-1 bundle steady state test

Steady state testing was conducted for 500 hours, as shown in the Exhibit 10, with consistent membrane performance. The test was interrupted a few times due to compressor related shutdowns. The cold box was maintained at cold temperature (-20°C) to prevent the membranes from warming up and to reduce the restart time for the FTU. The operating conditions were 18% CO_2, 9% O_2, balance N_2, at -45°C, 200 psig, and 1.5 psig permeate pressure.

The achievement of this important milestone is shown in Exhibit 10a and 10b. The data shows that over the 500 hour test duration, Bundle F was operated at 90% CO_2 capture, with both productivity and purity exceeding the target values. No degradation in the membrane performance was seen over the entire run.



(10a). Bundle Productivity Over Time



(10b). CO_2 Capture Rate and Permeate Purity Over Time

Exhibit 10. Steady State Test of Bundle F at NCCC

4.1.3 Two bundles in series configuration test

Two bundles in series configuration were tested with the 12” Bundle F as the first stage and the 12” Bundle E as the second stage as shown in Exhibit 11. Note that the Bundle E had similar performance to Bundle F, based on previous testing in the DRTC. The retentate stream (R1) from first bundle was sent to the feed side of the second bundle. The permeate streams from both bundles were combined to form the total permeate stream (P mix). The feed gas was 18% CO_2, 9% O_2, balance N_2, at -45°C, and 200 psig. The permeate blower could not be operated due to the design limitations, resulting in a higher permeate pressure of 7.5 psig. The Stage 1 bundle was operated at approximately 70% CO_2 capture and the Stage 2 operated at 60% CO_2 capture to achieve an overall 90% CO_2 capture. The total productivity was 679 Nm^3/hr with 60% permeate CO_2 purity. The productivity per bundle was 339 Nm^3/hr.

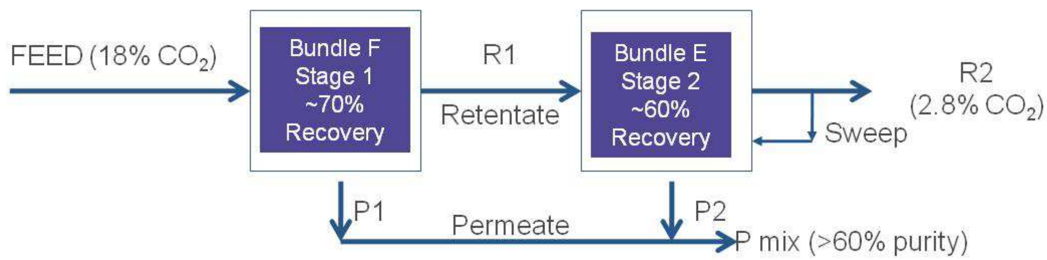


Exhibit 11. Two Bundles in Series Operation at NCCC

Exhibit 12 shows that the single bundle productivity was higher than the two bundles in series (productivity per bundle) at the same operating conditions. Based on simulation, the two bundles in series were predicted to meet the performance target at lower permeate pressure. Still, their use in series was inferior to the single bundle performance.

Exhibit 12. Preliminary Comparison of Single-Bundle Versus Two Bundles in Series

Bundle configuration	Productivity per bundle	CO_2 purity
Single Bundle	450 Nm^3/hr	60%
Two Bundles in Series	339 Nm^3/hr (679 Nm^3/hr overall)	60%

4.2 6” PI-1 bundle test

A PI-1 6” bundle (Bundle G) was tested at the 0.3 MWe FTU at NCCC. Both parametric and long-term testing was conducted on this bundle to provide an engineering design estimate for membrane separation performance at cold temperature.

4.2.1 6” PI-1 bundle long-term and parametric test

Long-term testing was conducted by measuring performance over 900 hours with 18% CO_2, 7% O_2, balance N_2, at -35°C, 200 psig, 1.5 psig permeate pressure, and at 90% CO_2 recovery. Exhibit 13 shows stable bundle productivity over 900 hours of testing at 90% recovery. The bundle productivity at 90% capture was approximately 240 Nm^3/hr, versus 610 Nm^3/hr for the 12" bundle. Thus, the productivity for the 12" bundle was only 2.5 times that of the 6" bundle even though it has approximately 3.7 times more surface area. This is one of the indicators of more ideal bundle performance with the 6" bundle.

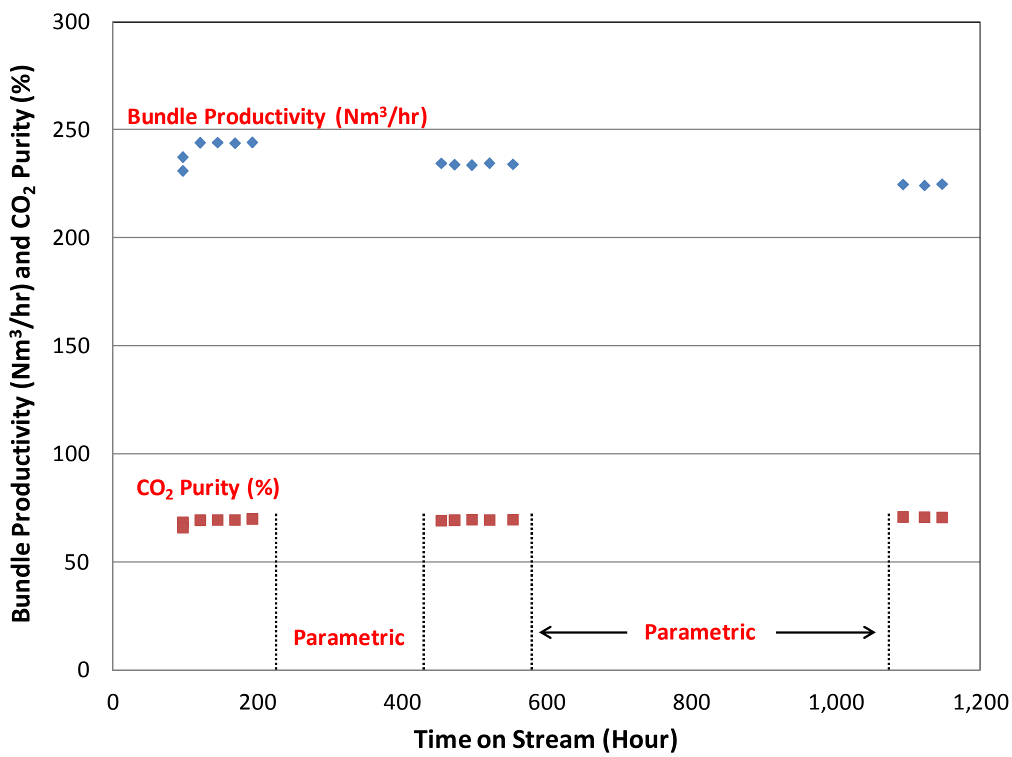


Exhibit 13. 6" PI-1 Bundle G Performance Stability Over Time

4.2.2 6" PI-1 bundle, effect of feed temperature

Parametric testing was continued on the 6" PI-1 bundle with varying feed temperature. The 6" PI-1 bundle was tested with 18% CO_2, 7% O_2, balance N_2, at 200 psig feed pressure, 1.5 - 3 psig permeate pressure, and 70% CO_2 recovery. Exhibit 14 shows the CO_2/N_2 selectivity and normalized CO_2 permeance at varying feed temperature. The CO_2/N_2 selectivity increases with decreasing feed temperature, due to higher CO_2 solubility and conditioning effect at high CO_2 activity. The normalized CO_2 permeance shows a minor drop and then increases with decreasing feed temperature due to the high CO_2 activity. This is the first time an Air Liquide membrane bundle was tested below -45°C for several days. The membrane bundle showed superior separation performance at -50°C. The techno-economic analysis was conducted with the CO_2 permeance and CO_2/N_2 selectivity at -45°C. The carbon capture cost will be improved further with membrane operation at -50°C due to the better membrane performance. This option will be evaluated further with future studies.

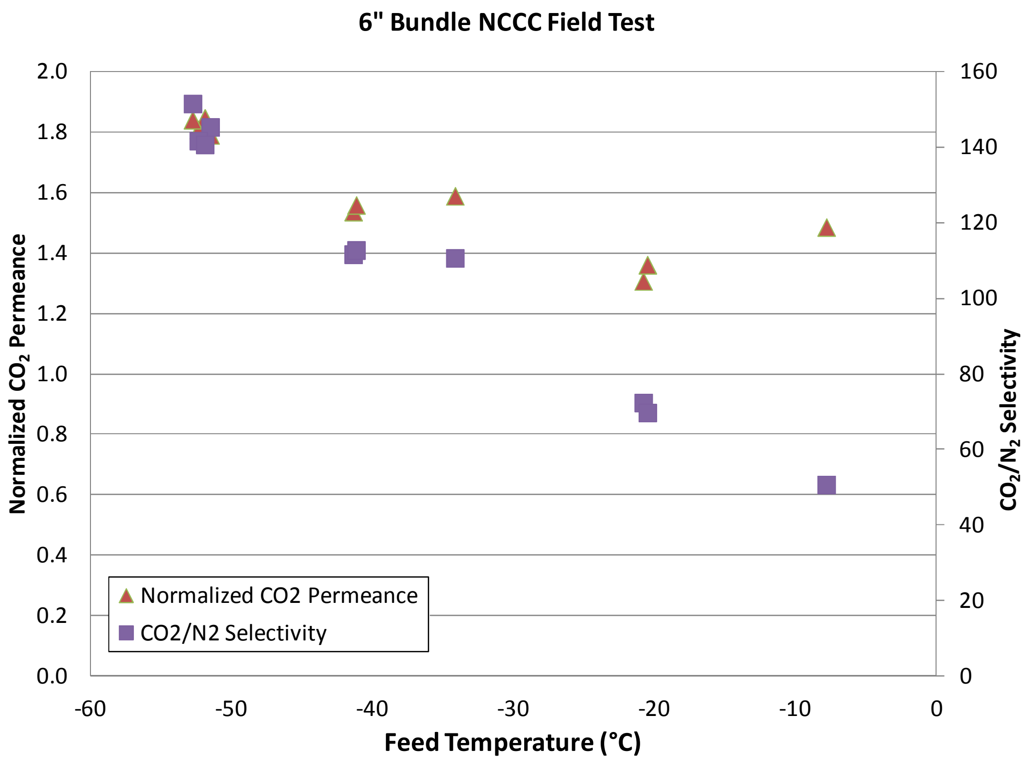


Exhibit 14. 6" PI-1 Bundle Parametric Test

Additional parametric tests were conducted to study the 6" bundle performance with the feed pressure from 100 to 200 psig, permeate pressure from 0.1 to 7 psig and sweep rate from 0 to 5% of the retentate stream. The 6" bundle exhibited excellent membrane performance in all of these test conditions, indicating ideal counter-current flow behavior. These test results gave a better understanding of the bundle behavior for CO_2 capture.

4.3 1" PI-1 bundle test

A 1" PI-1 bundle was tested in the FTU to compare membrane separation performance between 1", 6" and 12" bundles. This information was useful for projecting the performance of larger PI-2 bundles from the actual 1" PI-2 bundle data.

Parametric testing was conducted by changing the CO_2 recovery rate and feed flow rate on the bundle after it was stabilized at cold temperature. The 1" PI-1 bundle was tested with 18% CO_2, 7% O_2, balance N_2, at -40°C, 190 psig feed, and 1.6 - 3 psig permeate pressure. Exhibit 15 shows the CO_2/N_2 selectivity and normalized CO_2 permeance versus CO_2 capture rate. The CO_2/N_2 selectivity and normalized CO_2 permeance dropped by more than 20% as the capture rate was raised from 70% to 90%. This indicated that the 1" bundle had less ideal flow than the 6" or 12" bundles, due to different membrane manufacturing techniques and a lower length-to-diameter (L/D) ratio.

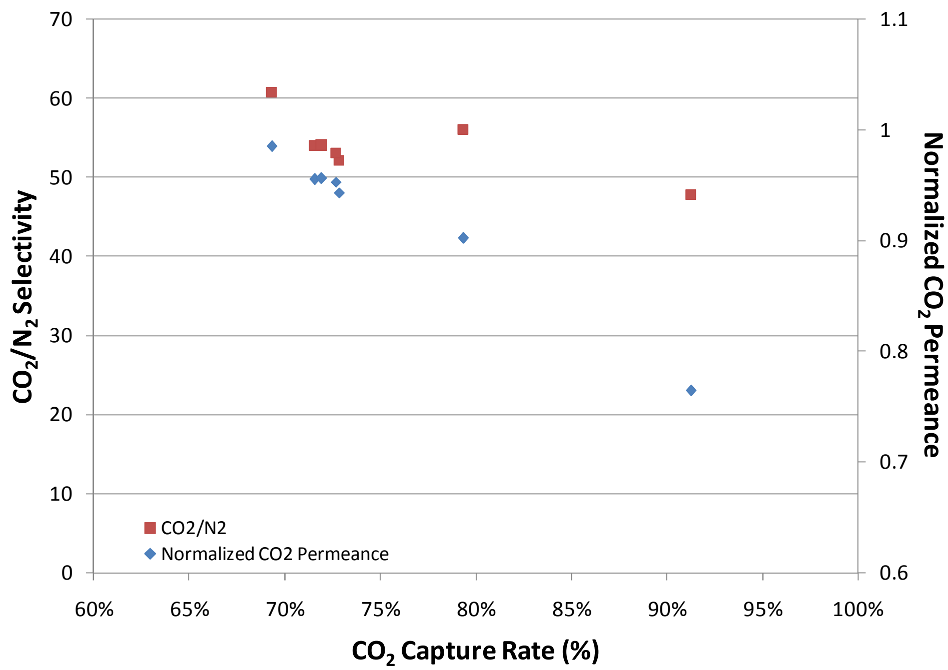


Exhibit 15. 1" PI-1 Bundle Parametric Test

Long-term and parametric testing was conducted by measuring the performance at 18% CO_2, 7% O_2, balance N_2, at -7 to -42°C, 190 psig feed pressure, and 1.5 - 5 psig permeate pressure, for different CO_2 capture rates. Exhibit 16 shows stable bundle performance over the 350 hours of testing at a 70% capture rate. The membrane conditioning effect can be seen by the gradual increase in the CO_2/N_2 selectivity and the normalized permeance over the 350 hours.

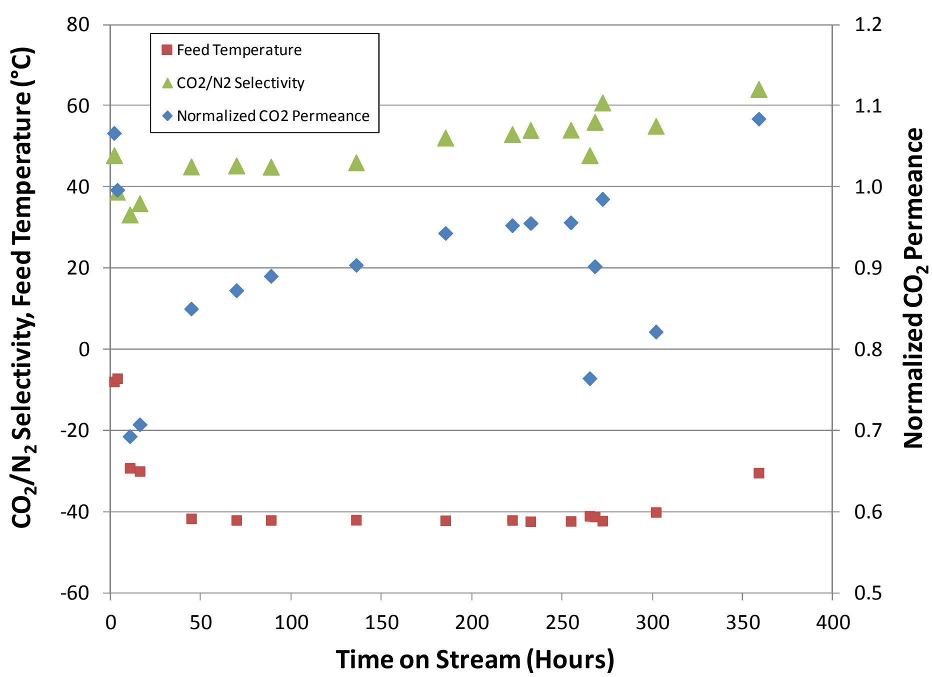


Exhibit 16. 1" PI-1 Bundle Parametric and Long-term Test

4.4 1" PI-2 permeator test

The PI-2 fiber was initially synthesized at a lab scale and fabricated into a module called a 'permeator' by hand. This permeator had a low packing density of fiber such that it could only process small flow rates of gas (less than 10 Nm^3/h). The 1" PI-2 permeator was tested at the NCCC in the PO-4 campaign. The 1" PI-2 permeator was installed in parallel to the PI-1 bundles and tested with a slipstream of the feed. The purpose of this test was to explore the robustness of the PI-2 fiber when exposed to the treated flue gas.

The PI-2 permeator was tested for over 800 hours at cold temperature. The feed to the PI-2 permeator was similar to PI-1 (18% CO_2, 9% O_2, balance N_2, at -41°C, and 200 psig feed). The test was conducted at 50 - 55% CO_2 capture rate and 1.6 psig permeate pressure. The PI-2 permeator had inefficient counter current flow due to the limited number of fibers and lower packing density. Therefore, the permeator was operated at a lower CO_2 capture rate to obtain meaningful data. The CO_2 permeance and selectivity were calculated based on a cross flow model due to the lower packing density. At a low capture rate, the choice of the membrane model (cross-flow versus counter-current flow) was not critical.

Exhibit 17 shows the CO_2 capture rate and CO_2 permeate purity during the long-term test. The PI-2 permeator experienced feed temperature variation in the initial 210 hours due to temperature control loop tuning, manifesting in the CO_2 purity variation between 50% and 80%. After this initial adjustment period, the permeate CO_2 purity was stable at 80% for the remainder of the test.

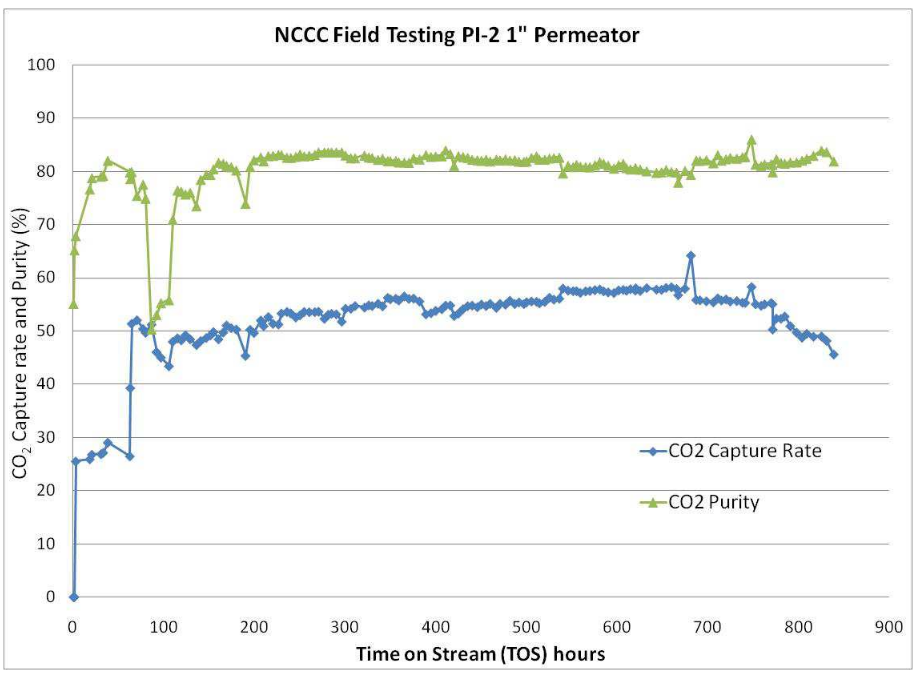


Exhibit 17. 1" PI-2 Permeator Long-term Test

An increase in CO_2 permeance and CO_2/N_2 selectivity was observed during the initial 210 hours due to the conditioning effect as shown in Exhibit 18. The normalized PI-2 permeance was approximately 8.5 times that of the PI-1 permeance from 210 to 750 hours on stream. The CO_2/N_2 selectivity varied between 67 - 82 during the same period. The fluctuation in permeance and selectivity from 200 to 800 hours is potentially due to drift of the CO_2 analyzer. Unfortunately, the analyzer calibration schedule lapsed during that period. The membrane performance calculation was very sensitive to slight changes in the gas composition or flow rate. There was an apparent drop in the CO_2 permeance and an increase in CO_2/N_2 selectivity after 750 hours. This drop in permeance was noticed after a shutdown, suggesting a likely correlation.

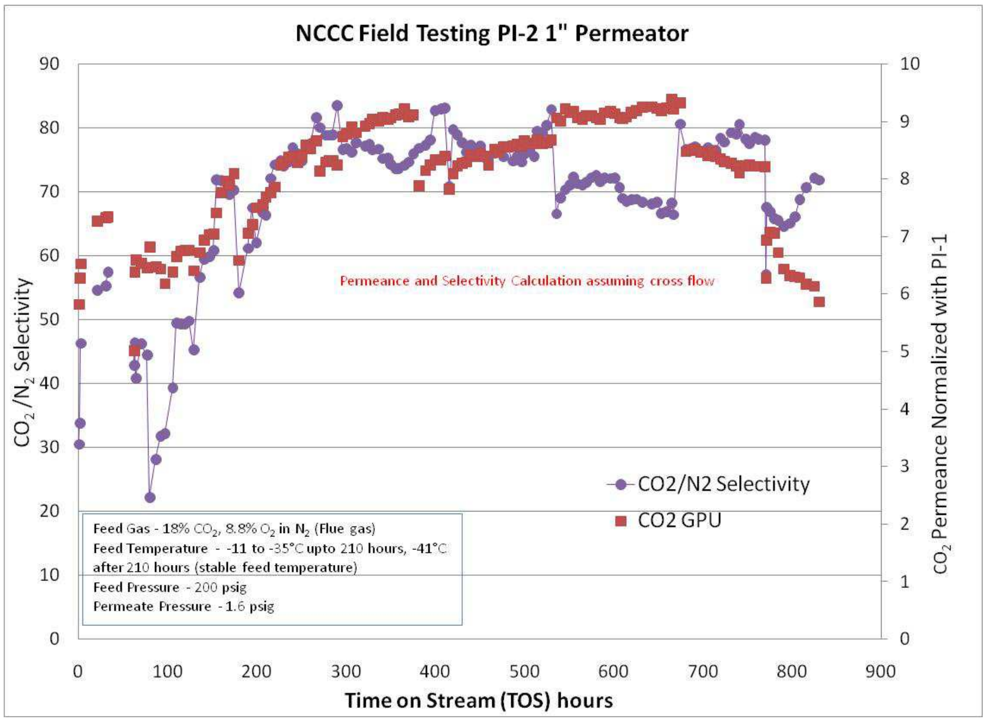


Exhibit 18. CO_2/N_2 Selectivity and Normalized CO_2 Permeance Versus Time on Stream for the 1" PI-2 Permeator

After completion of the PO-4 campaign, the 1” PI-2 permeator from the field was shipped back to DRTC and tested to confirm the performance drop. The permeance had decreased by 30% after testing at NCCC, but with no deterioration of the CO_2/N_2 selectivity. The drop in permeance was attributed to the potential feed contamination to the membrane, as discussed in Section 6.1.

4.5 1” PI-2 bundle testing

By mid-2016, synthesis of the PI-2 fiber had been scaled up such that small (1”) commercial type modules were manufactured. These modules are referred to as ‘bundles’. A 1” PI-2 bundle (#3-2) was tested at the NCCC. Parametric and long-term testing was conducted to assess the PI-2 membrane separation performance at the cold temperature. The parametric testing was conducted with flue gas composed of 18% CO_2, 7% O_2, balance N_2, at -41°C, 180 psig feed, and with varying CO_2 capture rates. The test conditions were replicated several times over the 1,400 hours test period to assess long-term stability.

For this bundle, the performance was strongly dependent on the CO_2 capture rate. Exhibit 19 shows the normalized CO_2 permeance and CO_2/N_2 selectivity declining with increasing CO_2 capture rate. This indicated significant non-ideal flow within the bundle. The PI-2 CO_2 permeance was normalized with the PI-1 CO_2 permeance at room temperature. A similar decrease in the back-calculated permeance and selectivity versus the CO_2 capture rate was noticed with another PI-2 bundle when tested with 11% CO_2 feed (not reported on here).

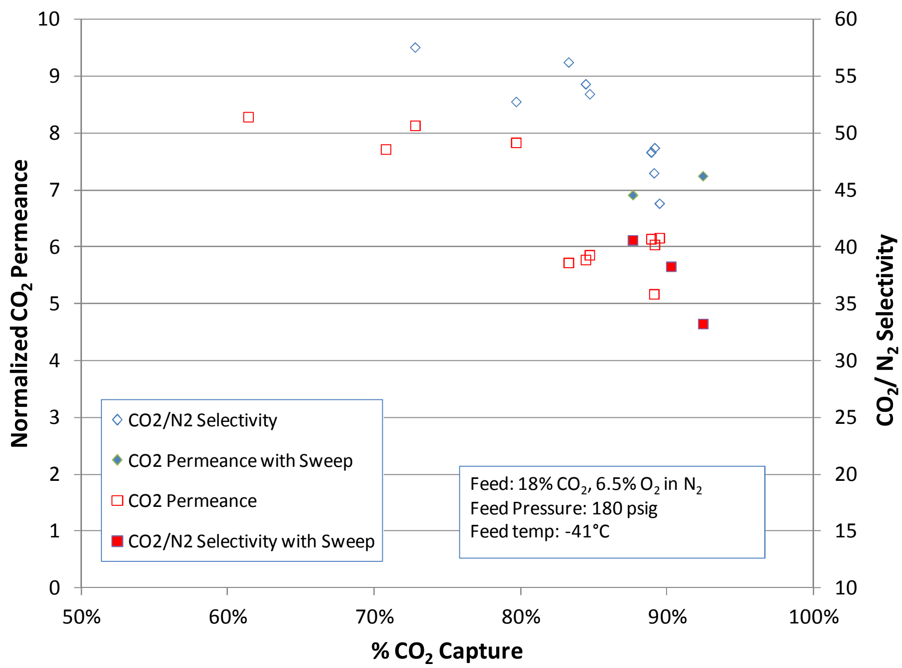


Exhibit 19. PI-2 Bundle (#3-2) Parametric Test

It was noted that the permeate pressure was higher than expected due to the limited port size of the module. The permeate port size was limited by the dimensions of the shell and collar which make up the 1" bundle. Previous 1" PI-1 bundle testing in Section 4.3 demonstrated a drop in membrane performance at higher capture rate due to non-ideal flow within the bundle. Due to the method of construction, the 1" bundle #3-2 also had relatively low packing density (compared to the 6" or 12" PI-1 bundles). The lower pack density caused higher cross flow in the bundle, resulting in a deviation from the back-calculated permeance and selectivity.

This characteristic of the 1" PI-2 bundle design can lead to an underestimation of the projected PI-2 bundle performance at full scale. Two cases of the techno-economic analysis were conducted with PI-2 membranes, using the performance at 90% and 70% CO_2 capture from the field data. The 70% capture data is considered to be more representative of the full scale bundle performance because the non-ideal flow issues can be addressed during manufacturing scale up.

Long-term testing was conducted on the 1" PI-2 bundle (#3-2) to assess the performance stability. The long-term test was conducted with flue gas, 18% CO_2, 7% O_2, balance N_2, at -34 to -42°C, 180 to 200 psig, and with 90% CO_2 capture rate. It should be noted that there was some temperature and pressure variation between the data sets due to the PI-1 testing in parallel, discussed previously in Sections 4.1 – 4.3. The CO_2 permeance was normalized with the PI-1 CO_2 permeance at room temperature. As shown in Exhibits 20 and 21, the CO_2 permeance and CO_2/N_2 selectivity were stable over 1,400 hours. The CO_2 permeance was approximately 7 times the PI-1 permeance and the CO_2/N_2 selectivity varied from 30 to 40. It is important to improve the selectivity of PI-2 membrane bundles in the future in order to improve the efficiency of the overall process. Some improvement is expected immediately as the bundle manufacturing method changes.

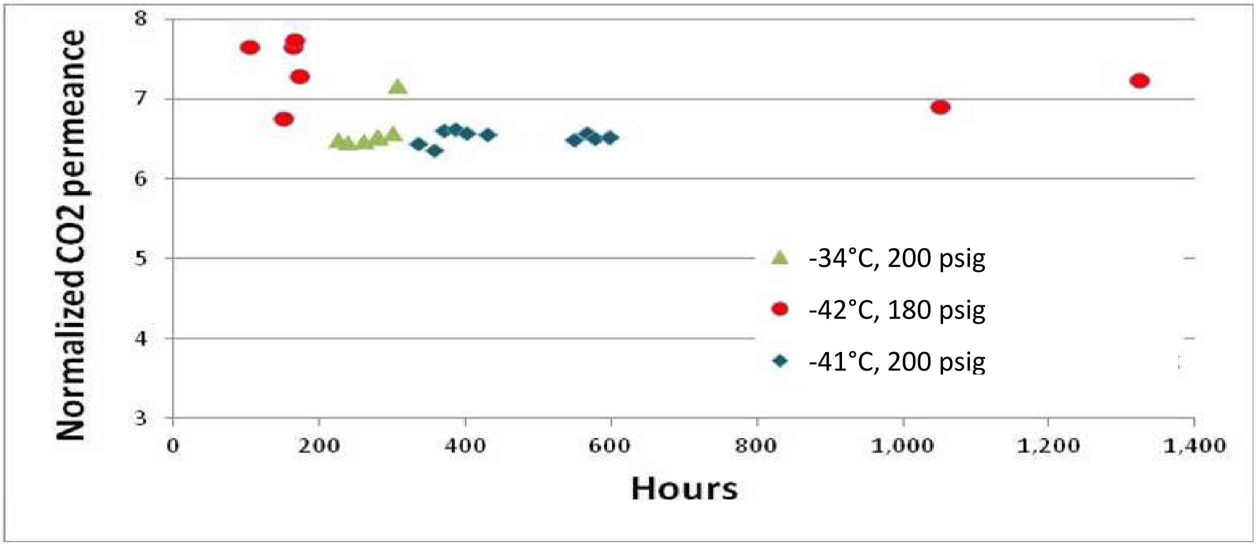


Exhibit 20. Normalized CO_2 Permeance over Time for the PI-2 Bundle

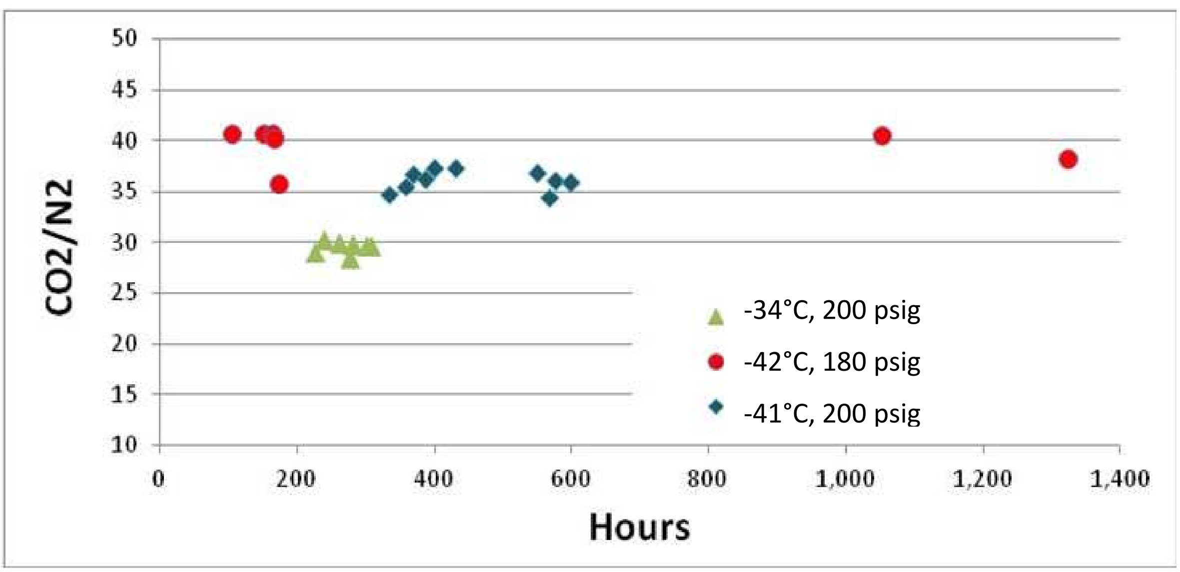


Exhibit 21. CO_2/N_2 Selectivity over Time for the PI-2 Bundle

Exhibit 22 shows the projected 12" PI-2 bundle performance at 90% CO_2 capture using the 1" PI-2 bundle test results from the field. The projection was made using Air Liquide's proprietary bundle simulation software. Field data at 90% and 70% CO_2 capture were used to project to the 12" bundle performance with 4 to 5.5 times the PI-1 bundle productivity and 64% CO_2 permeate purity. The PI-1 bundle productivity for the 12” bundle was 600 Nm^3/hr with 69% CO_2 purity as shown in Exhibits 9 and 10.

Exhibit 22. PI-2 Projected Performance for 12” bundle

	Normalized CO_2 permeance	CO_2/N_2 selectivity	Projected 12” PI-2 bundle productivity*	CO_2 purity*
90% Capture Field Data (TEA Case 1)	6.6	37	2,500 Nm^3/hr (4 times PI-1)	62%
70% Capture Field Data (Ideal case – TEA Case 2)	10	51	3,300 Nm^3/hr (5.5 times PI-1)	64%

*Projected 90% CO_2 capture performance, target performance was greater than 4 times bundle productivity improvement and greater than 60% permeate purity at 90% capture.

4.6 Bundle comparison

A summary comparison was made between the different bundles tested at the NCCC with similar feed conditions. The comparison was made for flue gas composed of 18% CO_2, 7% O_2, balance N_2, at -40 to -45°C, 190 to 215 psig feed pressure, 1.5 to 3 psig permeate pressure, and at 90% CO_2 recovery. Exhibits 23 and 24 show normalized CO_2 permeance and CO_2/N_2 selectivity for the different bundles tested at the NCCC. The CO_2 permeance was normalized with CO_2 permeance for PI-1 at room temperature. The CO_2 permeance and CO_2/N_2 selectivity decreased in the order from 6” PI-1 bundle, 12” PI-1 bundle and 1” PI-1 bundle. This shows that the 6” bundle is more ideal compared to the 12” and 1” bundle. The 1” bundle exhibited the worst performance due to the different bundle manufacturing technique, low L/D ratio, lower packing density, and high permeate pressure. As expected, the 1” PI-2 bundle showed superior CO_2 permeance (more than 6.5 times PI-1) with higher bundle productivity. However the CO_2/N_2 selectivity for the PI-2 bundle was lower than all of the PI-1 bundles as shown in Exhibit 24.

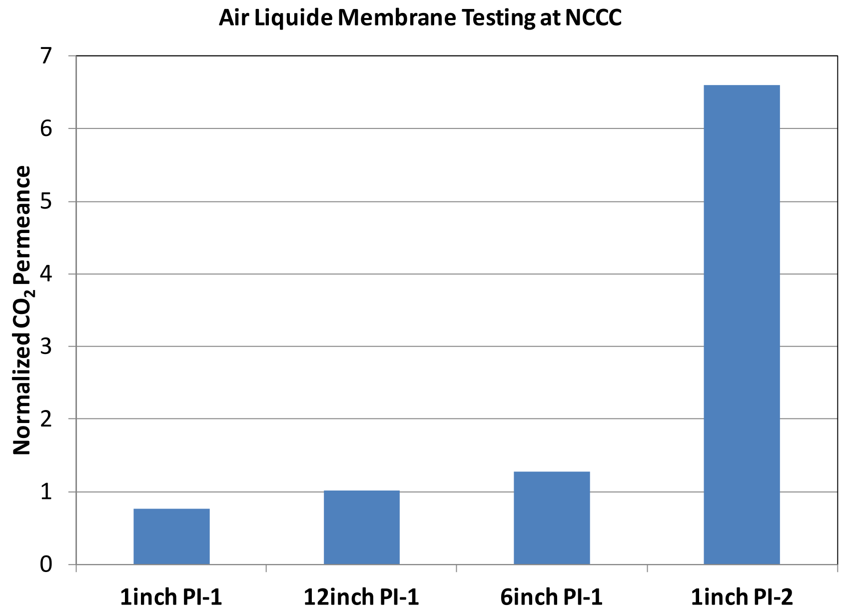


Exhibit 23. Normalized CO_2 Permeance for Membrane Bundles Tested at 90% CO_2 Capture

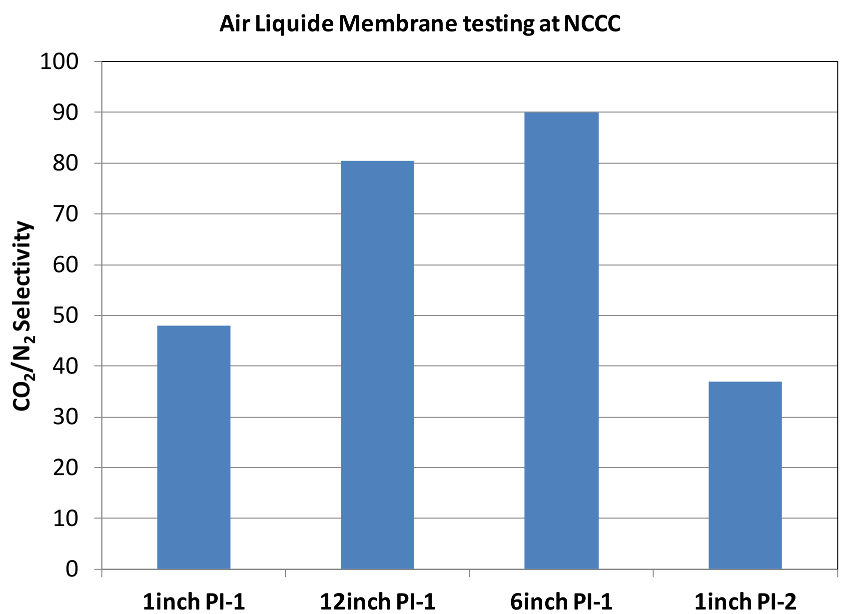


Exhibit 24. CO_2/N_2 Selectivity for Membrane Bundles Tested at 90% CO_2 Capture

The relatively poor performance of the 1” PI-1 bundle compared to the 6” and 12” bundles suggests that the bundle performance can be improved for PI-2 bundles by using a different manufacturing technique, called forming, and a higher L/D ratio. The techno-economic analysis was justified by the two different cases of PI-2 bundle, with Case 1 from actual field performance at 90% capture rate and Case 2 extrapolated from the more representative PI-2 performance at a 70% capture rate.

5. Analytical Campaign

Analytical campaigns were conducted at the NCCC in the PO-4 and PO-5 test campaigns to measure trace impurities in the gas and liquid streams at various points in the FTU. The samples were collected and shipped off-site for metals and liquid analysis.

PO-4 Campaign: Flue gas samples at various locations were digested, prepared, and analyzed according to the Method 29 protocol[1]. Liquid samples were collected and shipped to Element One Laboratory for analysis of mercury, arsenic, selenium, nitrates and sulfates.

PO-5 Campaign: A carbon injection bag house was installed on Plant E.C. Gaston Unit 5 before the PO-5 campaign to mitigate mercury in the flue gas. In the PO-5 campaign, the method of analysis for metal impurities was improved to increase the detection limit by 10 times. MEST-M Sorbent traps were used for collecting gas samples for metal analysis based on recommendation from EPRI[2]. The trap for the flue gas inlet was heated to avoid condensation of moisture in the stream. All other traps were at ambient conditions. After sample collection, the traps were shipped to the Energy & Environmental Research Center for analysis of mercury, selenium and arsenic. Each trap contained two sections of sorbent material. Results were provided by the sum of these two sections. Additional sampling points were added to improve the understanding of impurities fractionation.

NO and NO_2 were analyzed using a X-Stream X2GP Gas Analyzer owned by NCCC during both the test campaigns PO-4 and PO-5. A Nafion dryer was used to dry wet sample streams before sending them to the analyzer.

Exhibit 25 shows the simplified block flow diagram of the FTU, indicating the locations of the various analytical points. Flue gas was compressed and pre-treated before going into the cold membrane for CO_2 separation. Sample point 1 represents the low pressure flue gas from NCCC provided to Air Liquide's FTU. Sample point 2 was the low pressure condensate liquid sampled from the knock-out vessel downstream of the liquid ring blower. Sample point 3 was the flue gas downstream of the blower knock-out. Sample point 4 was liquid sampled from the knock-out vessel downstream of the oil flooded screw compressor. Sample point 5 was the compressed flue gas entering the dryer. Sample point 6 was the regeneration gas exiting the dryer bed during the regeneration cycle. Sample point 7 was the dry flue gas fed to the activated alumina bed. Sample point 8 was the dry flue gas fed to the membrane.

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[1] US Environmental Protection Agency, "Method 29 – Metals Emissions from Stationary Sources", http://www3.epa.gov/ttnemc01/methods/method29.html

[2] C. Dene, N. Goodman, "Evaluation of Sorbent Materials for Flue Gas Mercury Measurement", EPRI Technical Update, Dec-2007, #1014046.

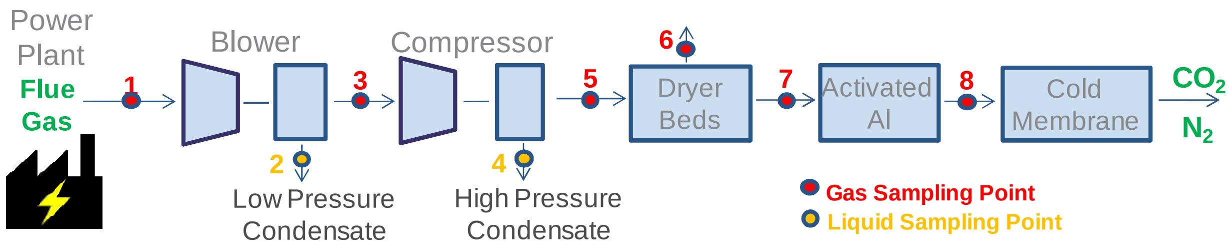

Exhibit 25. Simplified Block Flow Diagram of 0.3 MWe FTU with Analysis Sampling Points

Exhibits 26 and 27 summarize the analytical results from gas and liquid samples, respectively, for the PO-4 and PO-5 campaigns. Exhibit 26 shows the metal impurities, Hg, As, and Se in micrograms per normal cubic meter (µg/Nm^3), in the gas samples along with NO and NO_2 levels in ppmv. Exhibit 27 shows Hg, As, Se, nitrates and sulfates in milligrams per liter (mg/L) in the liquid samples. The metal impurities were lower in the PO-5 campaign after the bag house installation upstream compared to the PO-4 campaign.

Exhibit 26. Analytical Results from Gas Samples

Sample Point	Hg (µg/Nm³)	As (µg/Nm³)	Se (µg/Nm³)	NO (ppm)	NO_2 (ppm)
1: Flue Gas Inlet (P04) (P05)	0.94 0.53	0.19 <0.02	2.1 1.7	30–50 17-21	0.6–1.2 2-4
3: Comp Inlet (P05)	0.07-0.20		0.1-0.30	20 - 42	2 - 7
5: Compressor Outlet (P04) (P05)	<0.17 0.10-0.34	<0.04 <0.02	0.08 0.06-0.14	13 – 15 0	17 – 20 13
6: Regen Gas (P05)	-	-	-	0 - 360	3 - 80
7: Dryer Outlet (P05)	<0.001	<0.02	<0.02	0	9
8: Membrane Inlet (P04) (P05)	<0.17 <0.001	<0.04 <0.02	<0.04 <0.02	1 0	<0.25 1

Measurements reported with the less than symbol (<) were below detection limit and the detection limit has been reported instead. In the PO-5 campaign metals samples for Points 3 & 5 were collected one month apart. In several cases NOx measurements varied over the 30 minute duration of sampling at that location.

Exhibit 27. Analytical Results from Liquid Samples

Sample Point	Hg (mg/L)	As (mg/L)	Se (mg/L)	Nitrates (mg/L)	Sulfates (mg/L)
2: Low Pressure Condensate (P04) (P05)	<0.01	<0.01	0.01	1.2 0.02 – 1.5	246 2.4 - 210
4: High Pressure Condensate (P04) (P05)	0.001 -0.0025	<0.01	<0.01	85 216-514	4.3 32.5 - 39
Blank – Skid Water (P05)	<0.01	<0.01	<0.01	3.6 - 20	364 - 400

Measurements reported with the less than symbol (<) were below detection limit and the detection limit has been reported instead. In the PO-5 campaign liquid samples were taken multiple times, one month apart.

One of the challenges faced in the analytical campaign was that the incoming contaminant levels varied over the sampling duration. Only two of the five sample points could be analyzed each day due to the long sample collection time. Because of this variation, an accurate mass balance for any of the particular species was not achievable. The ranges reported in Exhibits 26 and 27 for metal impurities represents samples taken at different points in time, one month apart in campaign PO-5. These levels varied by as much as 240% The values reported for NOx also varied widely over the 30 minute measurement duration. Exhibit 28 shows the approximate contaminant distribution based on the analytical results of gas and liquid samples presented in Exhibits 26 and 27. Arsenic was below the detection limit in all of the condensate streams.

Exhibit 28. Estimated Assessment of Contaminant Distribution Based on Analytical Results

Sample Point	Hg	Se	NOx
2: Low Pressure Condensate	40-60%	80-85%	0%
4: High Pressure Condensate	<10%	<10%	50-70%
6: Regen Gas or Dryer bed	40-60%	10%	10-20%
7. Activated Alumina feed	0%	0%	10-30%

Metal Impurities – All the metal impurities, mercury (<0.001 μg/Nm^3), arsenic (<0.02 μg/Nm^3) and selenium (<0.02 μg/Nm^3) were below the detection limits at the dryer outlet and membrane feed. Arsenic was undetectable at all sample points in the PO-5 campaign, after the bag house installation. Mercury and selenium were removed by the pretreatment processes moisture condensation and dryer beds. Based on the gas sample analysis, approximately half of the mercury was removed in the low pressure condensate and half was removed by the dryer beds. The majority of selenium, approximately 85%, was removed in the low pressure condensate while the remainder was removed in the high pressure condensate and dryer beds.

Total Suspended Solids - The low pressure condensate streams were evaluated for total suspended solids (TSS). These were found to be below the detection limit (<0.40 mg/L). This low level was attributed to the efficiency of the new bag house installed at Plant Gaston before the PO-5 campaign.

NOx – NOx was mitigated in the gas phase by the flue gas processing. NO was higher than NO_2 in the flue gas inlet (sample point 1). However, NO reacts with O_2 at high pressure to form NO_2, resulting in higher NO_2 and lower NO levels after the compressor (sample point 5). NOx was also accumulated in the dryer bed and was released to the flue gas return during the regeneration period as shown in Exhibit 29. The dryer regeneration was at low pressure where NO_2 was converted back to NO. As the bed was regenerated, NO was released with a maximum concentration of 350 ppmv in the regeneration gas. The NO_2 was more gradually released, with a maximum concentration of 80 ppm. The overall NOx concentration of the dryer regeneration gas peaked at 400 ppmv. After mixing with the exhaust gas, this corresponded to less than 100 ppmv as the regeneration gas was 20% of the entire exhaust gas of the test unit. NO and NO_2 concentrations were very low at the membrane feed, indicating NOx adsorption in the dryer and activated alumina bed.

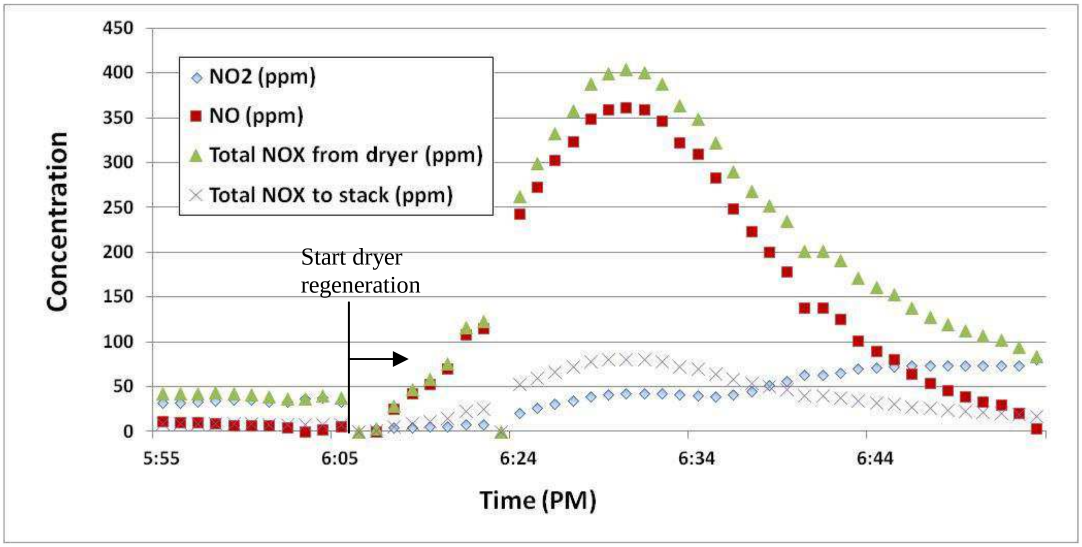

Exhibit 29. Dryer Regeneration NOx Analysis

The nitrate concentration was low at the low pressure knock-out (sample point 2) and high at the compressor knock-out (Sample 4), indicating that the NO_2 formed at high pressure reacted with H_2O and O_2 to form nitric acid. The pH of sample point 2 was 6, while the pH of sample point 4 was 0, confirming the nitric acid formation at that location.

It is estimated that 60% of the NOx was mitigated in the cold membrane pre-treatment and compression process with NOx leaving the system in the compressor knock-out (sample point 4) as nitric acid. An additional 15% of the NOx was adsorbed on the dryer and removed in the regeneration step. Finally, 20% was removed by the activated alumina bed. Air emissions were based on the maximum NOx concentration measured in the regeneration gas. Since NOx was mitigated in the process during compression and pre-treatment, SCR elimination should be evaluated with co-mitigation of CO_2 and NOx in the full scale carbon capture process.

Sulfates – Sulfate was measured at lower levels than the blank water sample (process water provided to the skid, as reported in Exhibit 27) indicating the flue gas contained little or no sulfur species. This was unsurprising considering the presence of the upstream FGD and pre-scrubber units.

6. Challenges in the Field and Mitigation Steps

This section lists the challenges faced in the PO-4 and PO-5 campaign during membrane bundle testing with flue gas. The challenges were mitigated by cooperation of the NCCC staff and contractors and Air Liquide on-site staff.

6.1 Incidents of membrane bundle performance decline

Specific events caused membrane bundles to decline in the CO_2 permeance and CO_2/N_2 selectivity. The decline in performance was due to potential hydrocarbon, oil, or moisture breakthrough reaching the membrane.

Hydrocarbon or oil contamination - After 3 weeks of testing in the PO-5 campaign both the 12" PI-1 and 1" PI-2 bundles experienced a 20% decline in the membrane performance. The performance decline was due to contamination of the membrane, possibly arising from overfilling of oil in the compressor. Visible oil residue was noticed as far downstream of the compressor as the dryer inlet. The test was stopped and the decision was made to replace the coalescing filter elements and adsorbent media. With the support of NCCC contractors, the elements and adsorbent media were expediently replaced. Exhibit 30 shows the pictures of knock-out vessel and the filter element during the change-out process.

Exhibit 30. Photographs of Compressor Knock-out Vessel (left) and Coalescing Filter Element (right)

For the FTU at NCCC, an oil-flooded screw compressor was the chosen compression technology. At larger scale, an oil free compressor will be used and this issue would not apply. The compressor oil separator removed over 99% of the oil followed by further removal in the knock-out vessel. The pressurized flue gas entered the bottom chamber of the knock-out vessel and exited the top chamber through a coalescing filter. Most of the remaining oil was intended to be removed in the bottom chamber of the knock-out vessel with less than 0.001 ppm exiting the top chamber with flue gas. Instead, a high level of oil was observed in the top chamber. It was suspected that the coalescing element had broken or somehow degraded. The coalescing elements from both the oil separator and the knock-out vessel were replaced. A compressor manufacturer representative also made several site visits to inspect the machine and optimize the lubricating oil parameters.

The FTU included an additional coalescing filter and alumina adsorbent media downstream of the compressor. Liquid oil residue was noticed at the inlet of the dryer. The additional filter element downstream of the compressor knock-out was also replaced and the adsorbent media was replaced due to possible oil breakthrough.

It is well known that efficient oil removal after compression is essential to maintain membrane performance. In addition to the above described equipment replacements, bi-weekly measurements of the oil mist levels were conducted with Sensidyne tubes. These tubes broadly detect "hydrocarbons" based on a Cr^{6+} to Cr^{3+} redox reaction. The quantitative accuracy of the hydrocarbon levels (ppm) depends on calibration of the tubes with the specific hydrocarbon species. This was not possible for the proprietary compressor oil. Discussion with Sensidyne indicated that the measurements would be semi-quantitative, such that the reported levels in Exhibit 31 are approximate.

Exhibit 31 shows the expected and measured oil levels at various locations shortly after re-start. The oil level was slightly higher than expected downstream of the compressor and coalescing filter, but was below the detection limit after the final activated alumina adsorbent step. It was crucial that oil was below the detection limit in the membrane feed, downstream of the activated alumina bed. The test was restarted and the gas was sent to the membrane bundle after validating that the oil was below the detection limit at the membrane feed.

Exhibit 31. Oil Level Measurement Using Sensidyne Tubes

Location	Expected oil level	Actual oil level
Sample point 5 (downstream of compressor)	0.001 ppm	~0.25 ppm
Downstream of coalescing filter	Below Detection limit	~0.15 ppm
Sample point 8 (downstream of alumina)	Below Detection limit	Below Detection limit

Moisture contamination - A 12" PI-1 bundle was tested during PO-5 with 18% CO_2, 7% O_2, balance N_2, 200 psig feed pressure, and 1.5 psig permeate pressure. The bundle was purged at 8°C, before starting the test. The bundle experienced a 40% loss in CO_2 permeance during the cool down phase, as shown in Exhibit 32, when the temperature of bundle dropped to -45°C. The CO_2/N_2 selectivity of bundle increased from 49 to 80 during the bundle cool down phase. The increase in CO_2/N_2 selectivity was expected due to the cold temperature performance enhancement effect. The decline in bundle permeance during cool down was attributed to moisture breakthrough during start-up or insufficient bundle purge time. When the bundle was warmed up and purged at higher temperature, the CO_2 permeance recovered to the previous condition as indicated by the arrow in Exhibit 32. The CO_2/N_2 selectivity drop during warm up was expected and similar to the previous values. Additional testing was planned with this bundle at low temperature but the test plan was aborted due to the Plant E.C. Gaston, Unit 5 outage at the end of the PO-5 campaign.

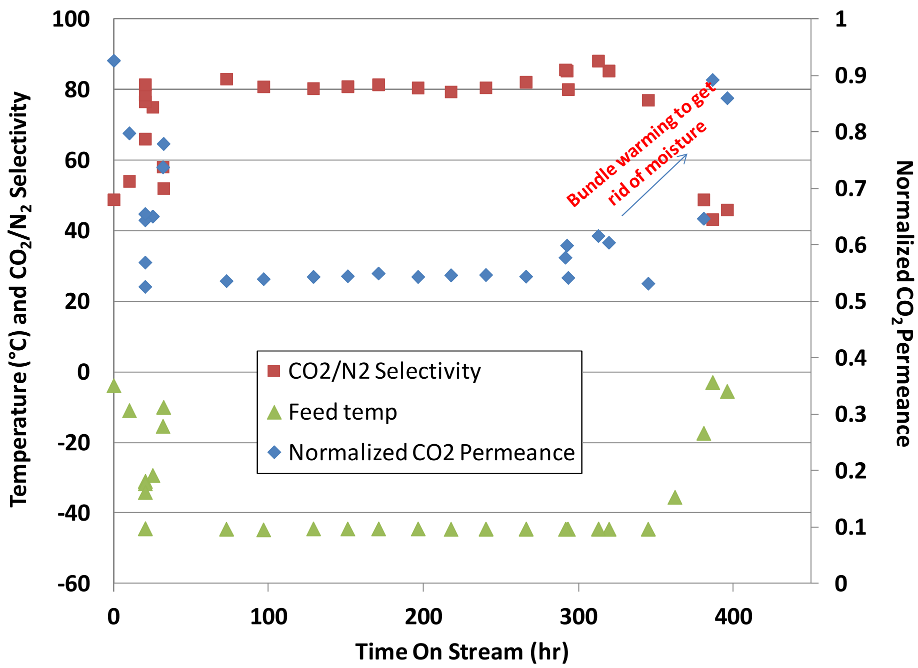

Exhibit 32. 12" PI-1 Bundle Test Showing Likely Moisture Contamination

A similar event occurred with the 1" PI-2 permeator towards the end of the 700 hour test during PO-4. The permeator lost 25% permeance after a re-start at 600 hours testing time. The permeator was returned to DRTC where the performance loss was confirmed. Similar to the previous case, when this permeator was purged overnight at 50°C with dry N_2, the permeance was recovered.

6.2 Compressor oil

6.2.1 PO-4 campaign

A sample of compressor oil was sent for analysis to an analytical lab after 850 hours of field testing with flue gas at the end of the PO-4 campaign. Testing indicated the oil had a high acid number, so the compressor vendor recommended a change-out. Normally, an oil change-out is performed once a year or less, however, NOx in the flue gas can react with oil to form by-products. This issue is specific to the oil-flooded screw compressor installed in the FTU. It will not impact the full-scale process technology, which would use an axial-radial compression technology.

Virgin and used oil samples were collected and shipped to DRTC for analysis. The following analysis was conducted on the samples:
Visual appearance – Exhibit 33 shows appearance of virgin and used oil. The fresh sample looked yellow. The used oil had a darker appearance, most likely resulting from oxidation. There was minor corrosion in the coalescing filter element as shown in Exhibit 33.

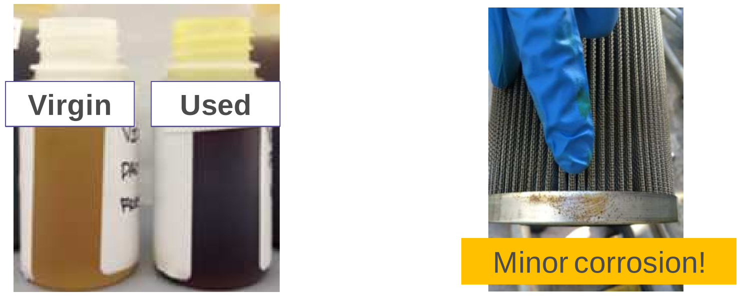

Exhibit 33. Compressor Oil Samples and Coallescing Element Corrosion

pH measurement
The oil samples were extracted for two days with deionized water. The pH of the extracted water was measured and found to be considerably more acidic (pH 4.2) than the fresh oil (pH 6).

FTIR spectra

The oil samples were analyzed with FTIR (PerkinElmer Frontier IR Spectrometer). Used oil showed three additional peaks compared to virgin oil. It is possible that NOx in the feed stream reacted with the paraffinic oil to form nitro compounds.

IC and ICP-MS analysis
IC analysis of the used oil did not show inorganic nitrite or nitrate compounds. ICP-MS analysis of used oil showed sodium and potassium slightly higher and zinc lower than that of the virgin oil. These slightly altered levels were not thought to be a concern.

6.2.2 PO-5 campaign

Based on the oil analysis it was clear that there was unwanted by-product formation due to the nitration reaction between flue gas and oil. An alternative oil, with a higher level of antioxidant additive, was used in the PO-5 campaign with regular oil sampling and analysis to monitor the acid number. At the end of the PO-5 campaign the used oil acid number was still in the acceptable range. The used oil was analyzed with FTIR and there were no new compounds detected. The new oil was judged suitable for the flue gas application and will continue to be used in future campaigns under DE-FE0026422.

6.3 Equipment issues

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

6.4 Flue gas contamination

The field test was interrupted a few times in both the PO-4 and PO-5 campaigns due to the potential flue gas contamination. This section includes the issues encountered due to contamination.

6.4.1 Water

When first started in PO-4, the FTU experienced frequent shutdowns due to slugs of water in the incoming flue gas causing disruption to the suction pressure and blower water level. As a short term solution, a vent valve at the bottom of a U bend on the NCCC feed pipe was opened to release any water build-up. In the future, modification of the flue gas piping should be considered for effective drainage of all low points where water can collect.

6.4.2 Particulate

The pre-treatment section of the FTU experienced higher pressure drop due to plate and frame heat exchanger fouling as shown in Exhibit 34. The heat exchanger was cleaned to remove the debris along with the filter media change-out as a precautionary measure. The ion chromatography analysis of the deposited material showed mainly sulfate and chloride salts. Additional plates were added to the heat exchanger to allow longer operating time between cleanings.

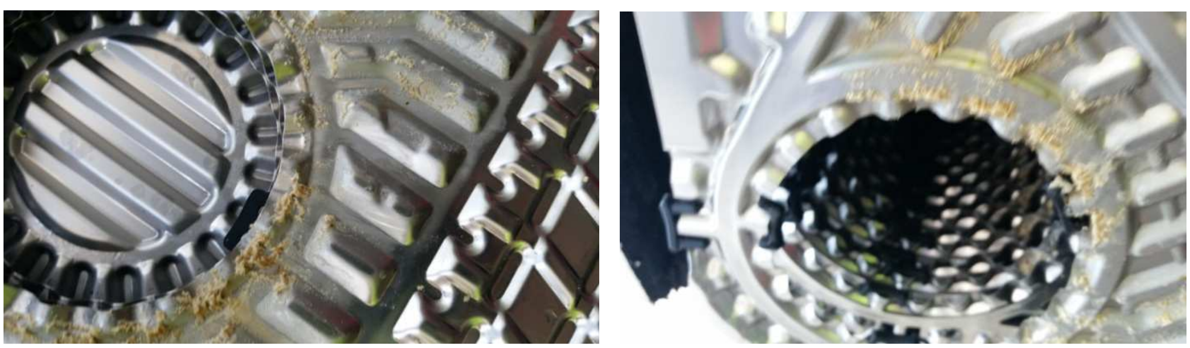

Exhibit 34. Picture of Heat Exchanger Fouling

6.4.3 Hydrocarbon

Hydrocarbon analysis was conducted with Sensidyne tubes at regular intervals to monitor the oil and hydrocarbon breakthrough from the activated alumina bed to the membrane feed. Flue gas was analyzed for hydrocarbons at various points in the FTU. Exhibit 35 shows the hydrocarbon levels measured in June and July 2016 after replacing the activated alumina bed versus those measured in November 2016. The sample points correspond to the schematic in Exhibit 25. The hydrocarbon levels were higher in November at sample points 5 and 8 indicating breakthrough of hydrocarbon from the activated alumina bed. Sample points 1 and 3 were analyzed for hydrocarbon due to high levels measured downstream. Surprisingly, hydrocarbon was also detected at the inlet flue gas from NCCC. The specific species has not yet been identified.

Exhibit 35. Hydrocarbon Analysis

Sample point	Hydrocarbon level: June - July 2016	Hydrocarbon level: November 2016
1 – Flue gas inlet	Not measured	>5 mg/m^3
3 – Compressor inlet	Not measured	8.5 mg/m^3
5 – Compressor outlet	8-10 mg/m^3	23 mg/m^3
7 – Dryer outlet	<5 mg/m^3	3.5 mg/m^3
8 – Membrane inlet	Below Detection Limit	0.3 – 0.5 mg/m^3

It is important to understand the hydrocarbon source and nature of the compound for future test campaigns in the project DE-FE0026422. Hydrocarbon compounds generally have an adverse impact on the Air Liquide membrane bundle separation performance.

6.5 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.

7. Conclusions and Action Items

Air Liquide participated in the PO-4 and PO-5 campaigns during 2015 and 2016. The field test unit was operated for over 3,200 hours during the two campaigns. The NCCC testing enabled Air Liquide to:

1. Confirm long-term stability of the PI-1 commercial bundles with actual flue gas
2. Evaluate the optimum PI-1 configuration for CO_2 capture
3. Verify contaminant emissions co-reduction (NOx, metals)
4. Confirm the potential of the novel PI-2 membranes to reduce membrane area

The NCCC staff contributed to the project success from the initial hazardous operability study through the final shutdown and store-in-place. The NCCC contribution included spot checks of the FTU, contractor-provided maintenance, remote data monitoring, and analytical measurements ranging from routine gas analyzer calibrations to assistance with trace analyses. The NCCC's assistance and support is gratefully acknowledged.

Various technical challenges were mitigated by cooperation of the NCCC staff and contractors with Air Liquide on-site staff. A few issues, mainly related to flue gas contaminants, such as water slugs in incoming flue gas, need to be mitigated in a more robust manner. A separate "lessons-learned" document has been prepared at the request of the NETL, and will be issued shortly.