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

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Abstract

The main objective of the project was to develop a post-combustion CO_2 capture process based on the hybrid cold temperature membrane operation. The CO_2 in the flue gas from coal fired power plant is pre-concentrated to >60% CO_2 in the first stage membrane operation followed by further liquefaction of permeate stream to achieve >99% CO_2 purity. The aim of the project was based on DOE program goal of 90% CO_2 capture with >95% CO_2 purity from Pulverized Coal (PC) fired power plants with $40/tonne of carbon capture cost by 2025. The project moves the technology from TRL 4 to TRL 5. The project involved optimization of Air Liquide commercial 12” PI-1 bundle to improve the bundle productivity by >30% compared to the previous baseline (DE-FE0004278) using computational fluid dynamics (CFD) modeling and bundle testing with synthetic flue gas at 0.1 MWe bench scale skid located at Delaware Research and Technology Center (DRTC). In parallel, the next generation polyimide based novel PI-2 membrane was developed with 10 times CO_2 permeance compared to the commercial PI-1 membrane. The novel PI-2 membrane was scaled from mini-permeator to 1” permeator and 1” bundle for testing. Bundle development was conducted with a Development Spin Unit (DSU) installed at MEDAL.

Air Liquide’s cold membrane technology was demonstrated with real coal fired flue gas at the National Carbon Capture Center (NCCC) with a 0.3 MWe field-test unit (FTU). The FTU was designed to incorporate testing of two PI-1 commercial membrane bundles (12” or 6” diameter) in parallel or series. A slip stream was sent to the next generation PI-2 membrane for testing with real flue gas. The system exceeded performance targets with stable PI-1 membrane operation for over 500 hours of single bundle, steady state testing. The 12” PI-1 bundle exceeded the productivity target by achieving ~600 Nm^3/hr, where the target was set at ~455 Nm^3/hr at 90% capture rate. The cost of 90% CO_2 capture from a 550 MWe net coal power plant was estimated between 40 and $45/tonne. A 6” PI-1 bundle exhibited superior bundle performance compared to the 12” PI-1 bundle. However, the carbon capture cost was not lower with the 6” PI-1 bundle due to the higher bundle installed cost. A 1” PI-1 bundle was tested to compare bundles with different length / diameter ratios. This bundle exhibited the lowest performance due to the different fiber winding pattern and increased bundle non-ideality. Several long-term and parametric tests were conducted with 3,200 hours of total run-time at NCCC.

Finally, the new PI-2 membrane fiber was tested at a small scale (1” modules) in real flue gas and exhibited up to 10 times the CO_2 permeance and slightly lower CO_2/N_2 selectivity as the commercial PI-1 fiber. This corresponded to a projected 4 - 5 times increase in the productivity per bundle and a potential cost reduction of $3/tonne for CO_2 capture, as compared with PI-1.

An analytical campaign was conducted to trace different impurities such as NOx, mercury, Arsenic, Selenium in gas and liquid samples through the carbon capture system. An Environmental, Health and Safety (EH&S) analysis was completed to estimate emissions from a 550 MWe net power plant with carbon capture using cold membrane.

A preliminary design and cost analysis was completed for 550 tpd (~25 MWe) plant to assess the capital investment and carbon capture cost for PI-1 and PI-2 membrane solutions from coal fired flue gas. A comparison was made with an amine based solution with significant cost advantage for the membrane at this scale. Additional preliminary design and cost analysis was completed between coal, natural gas and SMR flue gas for carbon capture at 550 tpd (~25 MWe) plant.

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1. EXECUTIVE SUMMARY

Air Liquide has developed a cost effective, post combustion CO_2 capture technology at TRL 5 based on the hybrid, hollow fiber cold membrane process followed by liquefaction. The CO_2 from flue gas is pre-concentrated in the cold membrane at >60% followed by further purification to EOR grade in a liquefaction step. The objective of this final scientific report is to present the development work of Air Liquide's hybrid cold membrane technology conducted under DE-FE0013163 over a three year program. The project was performed over two budget periods.

Bundle testing:

Air Liquide's hollow fiber polyimide (PI) membrane possesses unique properties when operated at low temperatures (<-20C), exhibiting 2-4x higher CO_2//N_2 selectivity with comparable CO_2 permeance as ambient temperature performance. PI-1 bundle optimization for commercial 6" and 12" bundles was completed with the iterative combination of Computational Fluid Dynamics (CFD) simulation and experiments using 0.1 MWe bench scale skid, resulting in >30% improvement in bundle productivity. Next generation high permeance PI-2 fiber was developed and scaled up from laboratory scale to 1" prototype bundle. PI-2 membranes showed potential to reduce bundle count significantly with 4-5X projected bundle productivity compared to PI-1. The optimized bundles were tested at the National Carbon Capture Center (NCCC) with 0.3 MWe field test unit (FTU). The FTU was operated for approximately 3600 hours during the PO4 and PO5 campaigns. The field testing at NCCC was focused on validating and testing Air Liquide's membranes with coal fired power plant flue gas. Liquefaction was excluded in the field testing due to Air Liquide's extensive experience in cryogenic purification of CO_2 streams.

Exhibit 1 shows the membrane bundles tested at NCCC with stable long term performance:

Exhibit 1. Bundle test at 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, Parametric test (CO_2 capture rate, Permeate pressure, Feed temperature, sweep rate)	900 hours
1" PI-1 Bundle	Long term test, parametric test by changing 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 by changing the CO_2 capture rate	1400 hours

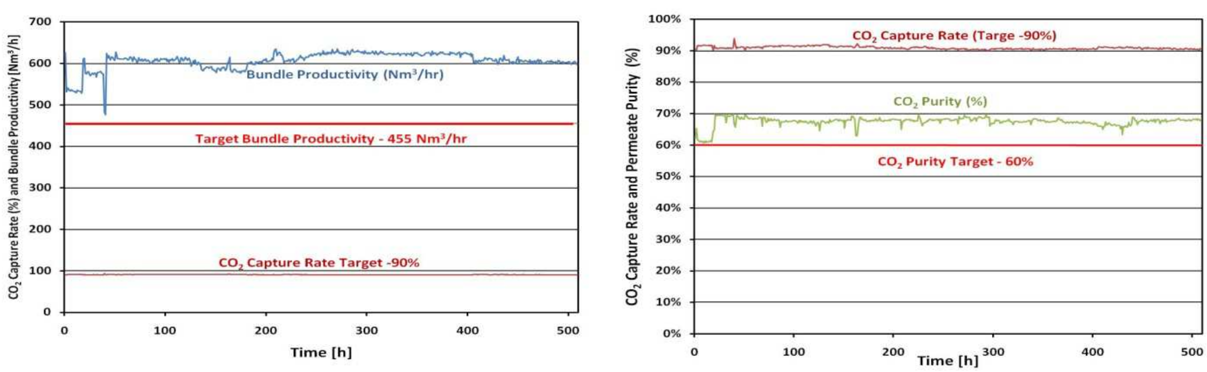


Exhibit 2. Long term steady state test for 12" PI-1 bundle at NCCC

Exhibit 2 shows results of the 500 hours, long-term test of the 12" PI-1 bundle tested at 90% CO_2 capture. Bundle productivity exceeded the baseline target of 455 Nm^3/hr by >30%, with actual productivity at ~610 Nm^3/hr. CO_2 purity in the permeate also exceeded the purity target.

A 6” PI-1 bundle exhibited superior bundle performance compared to the 12” bundle. A 1” PI-1 bundle was also tested to compare bundles with different length / diameter ratios and manufacturing techniques. The 1” bundle was found to demonstrate the lowest performance due to different fiber winding pattern and increased bundle non-ideality.

Techno-economic Analysis:

A final techno-economic analysis (TEA) for a 550 MW_e coal power plant with CO_2 capture was performed upon the completion of the field test with optimized membrane bundles. The TEA study included four cases utilizing Air Liquide’s commercial 12” and 6” PI-1 membrane bundles and next generation, PI-2 membrane case 1 (90% capture field data) and PI-2 case 2 (70% capture field data – ideal performance). All cases were conducted at 90% CO_2 capture with different membrane permeance and CO_2/N_2 selectivity based on the field test data. Predicted CO_2 capture costs are shown in Exhibit 3:

- 12” and 6” PI-1 bundle TEA cases resulted in the capture cost of $41-46/tonne for first of a kind (FOAK) estimate and **$40-45/tonne** for nth of a kind (NOAK) estimate
- PI-2 was projected to result in $2-3/tonne lower capture cost than PI-1 at **$38-42/tonne** due to reduced membrane cost, meeting DOE target of $40/tonne by 2025. Case 12 amine capture was calculated at $55/tonne excluding transportation at 2011$.

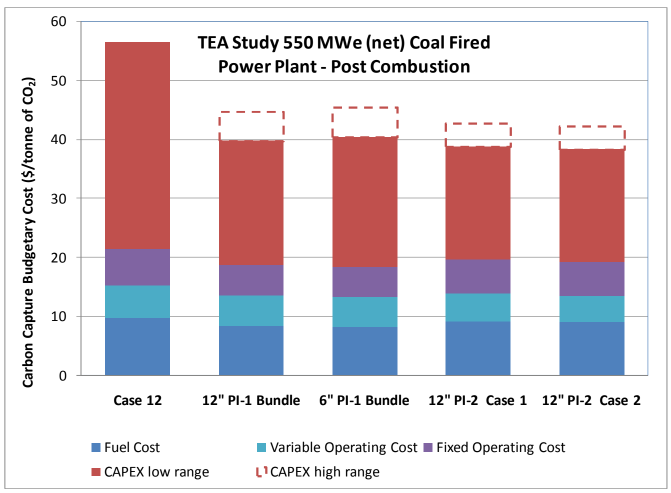


Exhibit 3. Carbon Capture Cost in 2011$ excluding transportation and storage

In addition to the bundle testing, an analytical campaign was conducted to measure contaminants such as mercury, arsenic, selenium, NOx and sulfate in the gas and liquid samples. These analyses demonstrated significant co-reductions of contaminants from the flue gas. An environmental health and safety (EHS) study was performed, showing reduced emissions from cold membrane process compared to Case 12 (amine capture).

Results from testing at the NCCC were used to develop a preliminary design package for scale-up to 550 tpd (~25MWe) for the next phase of cold membrane technology. With the promising aspects of PI-2 membrane and potential to reduce the membrane cost significantly, a separate DE-FE0026422 study is ongoing to produce commercial-scale PI-2 bundles for testing at NCCC. The field test unit was prepared for storage for further use in DE-FE0026422.

2. Air Liquide Carbon Capture Technology

Air Liquide's hybrid CO_2 capture process combines cold temperature membrane operation with partial CO_2 liquefaction as shown in Exhibit 4. The commercial Air Liquide 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 capture from air-fired pulverized coal (AFPC) flue gas at a capture cost approaching $40/tonne, and with greater than 95% CO_2 purity.

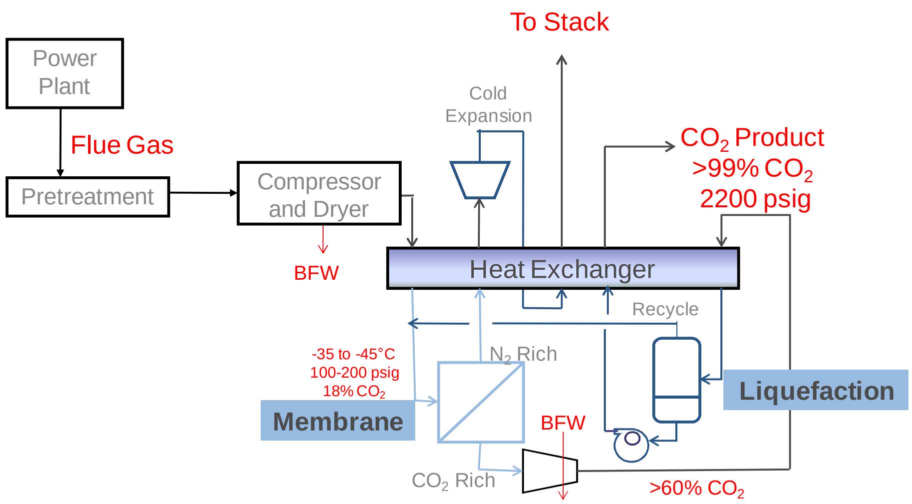


Exhibit 4. Air Liquide CO_2 Capture Process Schematic

The full scale hybrid process was designed to pre-treat the flue gas by removal of NOx, dust, SOx, and compression to 216 psig. 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 the 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. A two-bed regenerating dryer is used, with thermal swing adsorption (TSA) cycle. The two beds will switch between adsorption and regeneration modes. The compressed, dried flue gas is then sent to a brazed-aluminum heat exchanger (BAHX) to cool the membrane feed gas down to the desired temperature. Flue gas at high pressure, 216 psig, 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 the 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. 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.

3. PROJECT ACCOMPLISHMENTS

3.1. Task Summary Table –

Exhibit 5 shows task summary table for the entire project.

Exhibit 5. Task Summary Table

Task #	Title	Accomplishment	Issue	Percent Complete
1	Project Management and Planning	• Conducted Project Kick-off meeting and completed SOPO and PMP • Submitted Quarterly Research reports and invoices to NETL • Presented project update in the CO_2 Capture Technology meetings in 2014 and 2015 • Presented project update at the NCCC bi-annual review • Sub-contract for Project Partner (Parsons) and Technology Collaboration Agreement with NCCC was executed. • Audit by 3rd party was conducted every year with no findings	No issue to report	100%
2	PI-1 CO_2 Membrane Bundle Optimization	• CFD simulations were conducted with different packing density, variation in the fiber performance, sweep addition, permeate back pressure varying permeate opening size and variation in the pressure resistance to assess impact on overall bundle performance. The results from CFD were used to fabricate the optimized bundle. • New membrane vessel was installed with sweep line and oxygen injection line.	No issue to report	100%
3	PI-1 Optimized CO_2 Membrane Bundle Testing on Simulated Flue Gas	• Four 12” PI-1 bundles met the performance target with 0.1 MWe Bench scale unit test using simulated flue gas with the combination of simulation and experiments. More than 30% improvement in bundle productivity was noticed with the addition of sweep and optimization of bundles. • 2 stage configuration was tested with simulated flue gas using single stage bundle with different feed gas composition	No issue to report	100%
4	PI-2 High CO_2 Permeance Fiber Bundle Preparation	• PI-2 permeators tested at cold temperature with >5X flux compared to PI-1, meeting the success criteria in terms of performance. • PI-2 mini-permeators were successfully fabricated and tested for >500 hours at low temperature (-45°C) and high pressure 100-200 psig. • 1” PI-2 permeators were fabricated and successfully tested at cold temperature	No issue to report	100%

5	Optimized High CO_2 Permeance PI-2 Fiber Bundle Testing on Simulated Flue Gas	• PI-2 1" permeator was tested at different feed pressure and temperature • PI-2 1" permeator was tested for >500 hours long term testing	No issue to report	100%
6	Design, Procurement and Fabrication of a CO_2 Membrane Field Test Unit at 0.3 MWe	• Detailed engineering of the field test unit was completed. All major equipments were procured and installed. • Skids installation and acceptance testing to check for components functionality, control programming was completed. Control programming and valve tuning with compressed air was completed.	No issue to report	100%
7	Project Management and Planning	• Submitted Quarterly Research reports and invoices to NETL • Presented project update in the CO_2 Capture Technology meetings in 2016 • Presented project update at the NCCC bi-annual reviews • Submitted topical reports to DOE on TEA, EH&S and Next phase design study • Submitted summary report to NCCC on the field testing in PO4 and PO5 compaign	No issue to report	100%
8	Installation and Testing of a CO_2 Membrane Field Test Unit at 0.3 MWe	• Participated in two Post-combustion campaigns PO4 and PO5 for 3200 hours of testing • Conducted long term and parametric test on 12", 6" and 1" PI-1 bundles and 1" PI-2 permeator/bundle • Successfully conducted long term 500 hour steady state test with stable bundle performance for 12" PI-1 bundle • Conducted two bundles in series test with 12" PI-1 bundles • Conducted analytical campaign to trace impurities such as Hg, As, Se, NOx throughout the process	No issue to report	100%
9	Final Techno-Economic Analysis and EH&S Report	• TEA study was completed to calculate carbon capture cost for 12" PI-1 bundle, 6" PI-1 bundle and projected 12" PI-2 bundle solution • Sensitivity analysis was conducted to assess impact of operating parameters on the carbon capture cost • Cost target of $40/tonne is achieved using PI-2 bundle solution and was $3/tonne higher for PI-1 based solution. • Additional $3/tonne saving could be envisioned if the bundle is operated at lower temperature (~-52C). • EH&S analysis was conducted to assess environmental impact from cold	No issue to report	100%

		membrane CO_2 capture solution at 550 MWe net power plant and a topical report was submitted.		
10	Preliminary Design of Optimized CO_2 Membrane Field Test Unit	• Budgetary cost estimation and design was completed for 550 tpd CO_2 plant (~25 MWe) for CO_2 capture from coal fired flue gas, natural gas fired flue gas and SMR flue gas • Cost comparison was conducted between PI-1, PI-2 and amine based solution for coal fired flue gas • NETL methodology was used to conduct the cost analysis	No issue to report	100%
11	Final De-commissioning	• The skid was weatherized and stored in place for future use in project DE-FE0026422 • Upgraded insulation was installed to protect the skid for long term outdoor storage and use	No issue to report	100%
12	Optimized High CO_2 Permeance PI-2 Fiber Bundle Fabrication and Testing on Simulated Flue Gas	• Development Spin Unit (DSU) was installed to spin multiple fibers simultaneously for making 1” bundles • 1” bundles were fabricated and tested using synthetic flue gas • 0.1 MWe bench scale skid was modified to add a permeate blower and conduct synthetic flue gas test.	No issue to report	100%

3.2. Success Criteria Summary

Exhibit 6 shows success criteria summary table over two budget periods.

Exhibit 6. Success Criteria Summary table

Budget Period	**Success Criteria**	**Accomplishments**	**Percent Complete**
Budget Period 1 (Oct 2013 to March 2015)	A 12" PI-1 membrane bundle configuration capable of 90% CO_2 recovery from a 455 Nm3/hr simulated flue gas feed containing 18% CO_2 at 216 psig pressure with a permeate composition greater than 60% CO_2. This represents a 30% increase in membrane bundle capacity compared to the present performance of 350 Nm3/hr feed / bundle at the same operating conditions.	Four 12" Bundles met the performance target with 0.1 MWe Bench scale test using simulated flue gas with the combination of simulation and experiments. More than 30% improvement in bundle productivity was noticed with the addition of sweep and optimization of bundles.	100%
	A 12" equivalent PI-2 membrane permeator (1" in actual diameter) capable of 90% CO_2 recovery with a projected 5X simulated flue gas feed flow relative to PI-1 containing 18% CO_2 at 216 psig pressure and greater than 60% CO_2	PI-2 fiber met the performance target with >10X permeance compared to PI-1 with mini-permeators and 1" permeators. Process simulation using intrinsic fiber performance showed 4-5X bundle productivity for 12" PI-2 bundle compared to PI-1 bundle at 90% CO_2 recovery with >60% CO_2 in the permeate stream.	100%
	A completed specification list for the CO_2 membrane field test unit at 0.3 MWe detailing major equipment sizing with mass and energy balances that serves as a blueprint for engineering design. The specification list will demonstrate that the proposed design is within the approved budget. The design will be submitted to NETL and NCCC for review of the CO_2 membrane field test unit at 0.3 MWe.	Specification list for the CO_2 membrane field test unit was completed. The proposed design was within the approved budget and was reviewed by NETL and NCCC.	100%
	A final detailed engineering process design package including pre-treatment, compression and drying equipment upstream of the cold membrane bundle field test unit within the project budget (± 10% estimate)	Detailed drawings of major equipment, line & valve sizing, electrical drawings, arrangement drawings were completed and was within the project budget.	100%
	Written confirmation from Southern Company Services (SCS) that the NCCC will be the host site for the location of the CO_2 membrane field test unit and related equipment at 0.3 MWe during BP2. Confirmation is inclusive of the host utility agreement to provide accommodation of the proposed platform area, tie-ins with electrical and water utilities. Confirmation will include acceptance of the final field test unit design prior to fabrication.	Written confirmation was received from NCCC to host the AL cold membrane technology. The proposed design met the NCCC standard.	100%

	High Permeance (PI-2) CO_2 membrane hollow fiber permeator testing with simulated gas will be performed. Optimized CO_2 membrane bundle(s) (PI-1 and PI-2) identifying the configuration(s) for field test unit will be provided. The configuration comparison will include a predicted performance comparison between the two membranes (PI-1 and PI-2).	Four optimized PI-1 bundles were tested and qualified for field testing. PI-1 bundles were tested in two stage series or parallel or single bundle configurations at NCCC. PI-2 permeators were tested at NCCC in parallel to the PI-1 bundles. Projected PI-2 12” bundle productivity was predicted at 4-5X PI-1.	100%
Budget Period 2 (July 2015 to Dec 2016)	A completed test matrix plan for the CO_2 membrane unit field test campaign at 0.3 MWe to achieve the program objectives and success criteria.	A completed test matrix was provided to NETL and NCCC detailing campaign 1 and campaign 2 testing.	100%
	Operational procedures and safety protocols for the CO_2 membrane field test unit at 0.3 MWe will be completed and accepted by the NCCC.	Operational procedures and safety protocols were completed and accepted by NCCC.	100%
	Installation, start-up, parametric testing and continuous steady-state operation of the 0.3 MW_e CO_2 membrane field test unit with the baseline PI-1 membrane bundle and the high permeance PI-2 membrane bundle. A minimum of 500 hours of steady state testing in addition to shakedown and parametric testing for each membrane material and bundle type will be conducted.	Field installation and commissioning with flue gas was completed. PI-1 membrane bundle was tested in single bundle and 2 bundles in series configuration. 500 hours of steady state testing was completed for PI-1 bundle. 1” PI-2 bundle was tested for >1300 hours. Parametric testing was conducted on 12” PI-1 bundle, 6” PI-1 bundle, 1” PI-1 bundle and 1” PI-2 bundle.	100%
	CO_2 membrane bundle field testing at 0.3 MW_e scale with treated flue gas at NCCC in accordance with the approved test plan. Verification of process operability by processing actual treated flue gas and identification of issues with gas contaminants and particulates.	Field testing with flue gas was completed for PI-1 commercial bundle (12”, 6” and 1”) and 1” PI-2 bundle in accordance with the test plan. Contaminants such as oil and moisture removal are critical to avoid membrane performance decline.	100%
	A completed preliminary technical and economic analysis of the proposed process concept for a 550 MW_e power plant that shows a pathway to achieving carbon capture up to 90%, with a capture cost approaching $40/tonne. The proposed cold membrane technology will be compared to NETL case 12 to determine performance advantages. Success for the proposed approach will be defined by the projected ability of the cold membrane technology to reach $40/tonne capture cost on an n^{th} of a kind design basis.	TEA study was completed on four cases by Air Liquide and validated by Parsons. PI-2 membrane hybrid process meets the DOE cost target of $40/tonne by 2025. PI-1 membrane hybrid process was 2-3$/tonne higher than the PI-2 membrane based process. Addition carbon capture cost saving can be achieved by operating the membrane at colder temperature (-52°C) or lower capture rate (80%).	100%
	Complete a preliminary design for scale-up of AL’s CO_2 capture membrane system with an integrated CO_2 compression and purification	Budgetary cost and design of 550 tpd CO_2 plant (~25 MWe) was completed. A carbon capture cost comparison was	100%

	unit (CPU) process for field testing with actual flue gas at a minimum 1 MW_e scale.	made between PI-1 solution, PI-2 solution and Amine (Case 12) from coal fired flue gas. Additional comparison was made between carbon capture cost from coal flue gas, natural gas flue gas and SMR flue gas.	
	Test results of a 1" PI-2 bundle in actual treated flue gas corresponding to projected PI-2 12" module capable of 90% CO_2 recovery from 4-5X flue gas feed flow relative to PI-1 containing 18% CO_2 at 216 psig pressure and > 60% CO_2 permeate purity.	Field data at 90% CO_2 capture and 70% CO_2 capture (ideal) was used to project 12" PI-2 bundle performance with 4 - 5.5X PI-1 bundle productivity and 62-64% CO_2 permeate purity from a flue gas containing 18% CO_2 at 216 psig pressure.	100%

4. EXPERIMENTAL METHODS AND PROCEDURES

4.1. Bundle Development and Qualification

4.1.1. PI-1 Bundle Optimization

Prior bench scale testing from project DE-FE0004278 showed that the large 12" membrane bundles were not well optimized for the high intrinsic membrane permeance-selectivity, and showed lower performance compared to the 6" bundles and mini-permeators. Membrane costs are a significant contributor to the total cost of carbon capture for the commercial scale plant. Therefore, it was deemed essential to optimize the bundle performance in order to reduce the overall capture cost. Bundle design optimization was aimed at improving the membrane bundle counter-current efficiency for larger 12" PI-1 bundles.

Ideal bundle behavior assumes perfect counter-current flow of the feed-side and permeate-side streams. The actual flows are affected by the bundle geometry, entry and exit locations / sizes, pressure drops through the bundle, fiber permeance, etc. As bundle diameter increases, the ratio of radial to axial pressure drop increases and radial flow patterns become more relevant. The direct impact of these effects is difficult, if not impossible to measure experimentally as the required instrumentation can itself perturb the flow pattern. There were two important aspects to the PI-1 bundle optimization: 1) Computational fluid dynamics (CFD) to predict the possible improvements in membrane bundle design and 2) Fabrication and testing of optimized PI-1 bundle using synthetic flue gas at the 0.1 MWe bench scale skid located at Delaware Research and Technology Laboratory (DRTC).

A two dimensional, axi-symmetric CFD model of bore-fed bundles was created in ANSYS Fluent, a commercial, computational fluid dynamics software package. For a given feed and operating pressure, the CFD model predicts the corresponding bundle permeate and residue streams. Our technique was to treat these results as a virtual field test, and back calculate the performance of an ideal bundle (one-dimensional counter-current mode) with the same product streams as the CFD model. Comparison of the results of these two calculation modes allowed an estimation of bundle non-ideality.

A number of bundle issues were explored for the cold membrane CO_2 separation, using CFD. CFD analysis was conducted to examine various effects on bundle ideality: (i) variation in bundle packing density, (ii) variation in fiber performance, (iii) fiber OD/ID variation (iv) sweep addition and location (v) permeate pressure, (vi) varying permeate opening size and (vii) variation in pressure resistance. Using CFD, digital experiments were performed on systems where it was impossible to make physical measurements.

A series of experiments was conducted with 12” PI-1 bundles using synthetic flue gas mix of CO_2/N_2 at different test conditions: (i) varying sweep rate, (ii) varying permeate pressure, (iii) varying permeate opening size etc. The test results from the 0.1 MWe bench scale skid in combination of CFD model results allowed us to understand and predict the reasons for non-ideality resulting in optimized PI-1 12” bundle. The bundle optimization was performed by an iterative combination of CFD analysis, bundle modifications, and bundle testing with synthetic flue gas.

4.1.2. PI-2 Bundle Development

Polymer Qualification

PI-2 polymer is a specialty polymer produced in small batches by a USA-based speciality polymer manufacturer. Air Liquide worked with the supplier to define specifications to qualify uniform polymer batches for fiber spinning. Various batches of PI-2 polymer were characterized using analytical techniques to help establish supplier specifications. This was an iterative process where batch consistency and specifications were evaluated in terms of the polymer analytical parameters and spinning trials.

The PI-2 polymer characterization included following parameters:

- **Shape and Form**: The shape and form were visually evaluated. Small uniform pieces of polymer were desired for easy dissolution in the solvent.
- **Residual moisture and solvent**: Thermo-gravimetric Analysis was used to measure the residual moisture and solvent in the polymer. Volatiles in the temperature range from 100 to 250°C were predominantly solvent (~≤0.5 wt %). Volatile content below 100°C was predominantly moisture (~ ≤1.5 wt %)
- **Solubility**: PI-2 polymer was dissolved in a solvent at 70°C to measure solubility. Complete solubility is essential to transform a polymer into a spinning dope solution.
- **Viscosity**: Viscosity of a 15% polymer solution was measured using a Brookfield viscometer.
- **Molecular weight**: Gel Permeation Chromotography (GPC) was used to measure molecular weight distribution.
- **Spectroscopy**: Fourier Transform Infrared (FTIR) and Nuclear Magnetic Resonance (NMR) were used to characterize the chemical structure.
- **Hydrolytic stability**: PI-2 polymer was boiled in water to determine hydrolytic stability of the polymer. Polymer inherent viscosity (IV) was measured to assess hydrolytic stability.

Commercially viable PI-2 membrane production requires scaling up current laboratory synthesis of the polymer to a consistent high-quality, mass production process. Collaboration is ongoing under the new DOE funded project DE-FE0026422 with the polymer supplier to scale up PI-2 polymer in a cost effective manner and provide batches meeting the quality control necessary for a robust fiber spinning process.

<u>PI-2 membrane development</u>

The goal of this task was to develop spinning techniques for novel high permeance PI-2 membranes with >5X bundle productivity for a 12” PI-2 bundle compared to PI-1. Fiber spinning formulations and post-spin processing steps were developed at the laboratory scale. Exhibit 7 shows the PI-2 membrane scale-up from mini-permeator to 1” permeator and 1” bundle where the number of fibers were increased to allow testing at higher flow rates.

Exhibit 7. Fiber counts in permeators versus bundle

	Fiber Count	# of Modules	Test
Mini-Permeator	1X	>10	Synthetic flue gas
1” Permeator	25X – 45X	6	Synthetic flue gas and real flue gas
1” Bundle	250X – 350X	6	Synthetic flue gas and real flue gas

- **Mini-permeator development**

Several laboratory trials were conducted to develop spinning techniques for the PI-2 mini-permeators. The mini-permeators faced high pressure failures due to the potting issues. An alternative method of permeator construction (shell feed configuration) was used to allow fiber perm-selectivity characterization.

- **1” permeator development**

Once the PI-2 fiber intrinsic perm-selectivity was confirmed via mini-permeator tests, considerable effort was spent in learning how to construct 1” permeators. 1” PI-2 permeators were fabricated with 25X flow capacity compared to the mini-permeators using the MEDAL 1” prototype bundle design. The shell and potting methods and hardware were similar to the prototype 1” bundles; with some modifications for the limited number of fibers with the lab spun samples. The main difference between 1” permeator and 1” bundle is lower fiber count. These permeators used the same construction techniques as prototype 1” bundles but risked only ~ 10% of the final fiber area per trial. Six permeators were fabricated with different spin formulations to assess cold temperature membrane performance with synthetic and real flue gas.

- **1” prototype bundle development – DSU**

PI-2 permeator was scaled to the full 1” prototype bundle with 250X flow capacity compared to the mini-permeator. The Development Spin Unit (DSU) as shown in Exhibit 8 was installed to simultaneously spin multiple fibers and fabricate bundle with large quantities of fiber as opposed to laboratory spun single fiber. DSU is representative of MEDAL’s commercial spin line. The DSU was designed to minimize wastage of expensive PI-2 polymer. Three batches of fiber were spun using DSU to fabricate six 1" PI-2 bundles for cold temperature testing. The final two batches possessed the desired fiber properties for conversion to bundle form.

Exhibit 8. Picture of DSU installed at MEDAL

4.2. Synthetic flue gas test – 0.1 MWe bench scale skid at DRTC

PI-1 bundle optimization and pre-qualification for field testing was conducted in the 0.1 MWe bench scale skid located at the Delaware Research and Technology Center (DRTC) as shown in Exhibit 9. The bench scale skid was fabricated in project DE-FE0004278.[1,2] A new 12" membrane vessel was installed with sweep configuration and with the ability to recycle a portion of retentate to the permeate side of the membrane bundle as sweep gas

The unit was designed to operate in a full recycle mode with make-up from CO_2 and N_2 gas lines equipped with mass flow controllers in order to save operating cost. The synthetic flue gas mix (CO_2/N_2) was compressed in an oil-free reciprocating compressor to the desired membrane feed pressure ~200 psig. The feed gas was cooled in a brazed aluminum heat exchanger (BAHX) to the desired feed temperature and sent to the hollow fiber membrane bundle for CO_2 separation. The CO_2 rich gas exits the bundle at low pressure on the permeate side and N_2 rich gas exits the bundle at high pressure on the retentate side. The expanded retentate and permeate gas was mixed together and recycled back to the inlet of the compressor. The CO_2 concentrations of all three streams (feed, retentate and permeate) were continuously measured by an on-line IR analyzer skid. The cold box contained the heat-exchanger, membrane and the Joule Thompson (J-T) expansion valve. Though the membrane was located in a cold box, the energy for cooling the feed stream mainly comes from Joule-Thomson expansion of the pressurized residue gas. This 'self-refrigeration" scheme with expansion of the residue stream was found effective, even after using relatively inefficient J-T cooling across the residue expansion valve.

Tests were conducted with 12" and 6" MEDAL commercial PI-1 membrane bundles. Several parametric and long term tests were conducted with PI-1 bundles.

Exhibit 9. 0.1 MWe Bench scale skid at DRTC

PI-2 membrane mini-permeators and 1" permeators were tested in a separate laboratory test setup with synthetic flue gas. The 1" PI-2 bundles were fabricated using the DSU and subsequently qualified for field testing using the 0.1 MWe bench scale skid. The 0.1 MWe bench scale skid was modified to add a slip stream for testing of 1" PI-2 bundles with synthetic flue gas inside the cold box.

Additionally the 0.1 MWe bench scale skid was modified by adding a permeate blower and after cooler to improve the test operation and flexibility. The permeate blower and after cooler was added on the permeate return line to the compressor. Exhibit 10 shows a picture of permeate blower and after-cooler installed in the 0.1 MWe bench scale skid at DRTC. The addition of permeate blower allows testing at lower permeate pressure which is desired for better membrane separation performance.

Exhibit 10. Picture of permeate blower installed at 0.1 MWe bench scale skid

4.3. Real flue gas test – 0.3 MWe Field Test Unit (FTU) at NCCC

Air Liquide's hollow fiber membrane bundles were tested with real flue gas at the National Carbon Capture Center (NCCC) located in Wilsonville, AL. Flue gas was received from the Southern Company 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 before delivery to NCCC. The flue gas was further treated in a pre-scrubber at the NCCC to reduce SOx down to 2 ppm.

The 0.3 MWe FTU was designed to demonstrate the superior CO_2 separation performance of Air Liquide's hollow fiber membranes with real flue gas. Exhibit 11 shows the block flow diagram of the FTU.

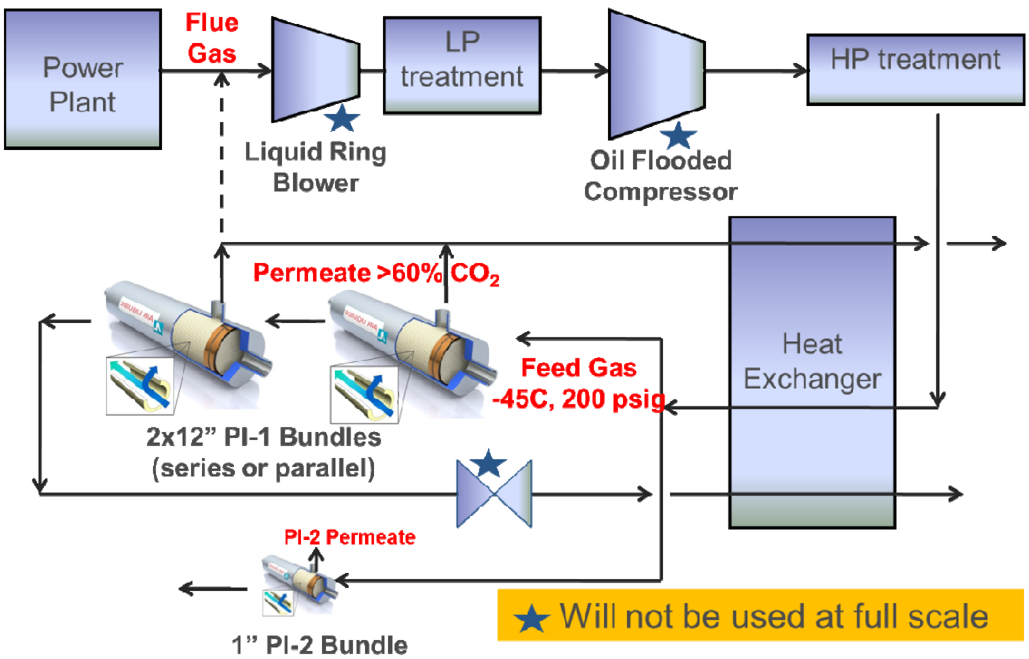


Exhibit 11. Block Flow Diagram of FTU

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 further 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: Both membrane materials (PI-1 and PI-2) were tested at the NCCC. Commercial 12", 6" and prototype 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 1" 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.

Some of the field test 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.

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 so 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. A picture of the Air Liquide 0.3 MWe FTU installed at the NCCC Pilot Bay 3 is shown in Exhibit 12.

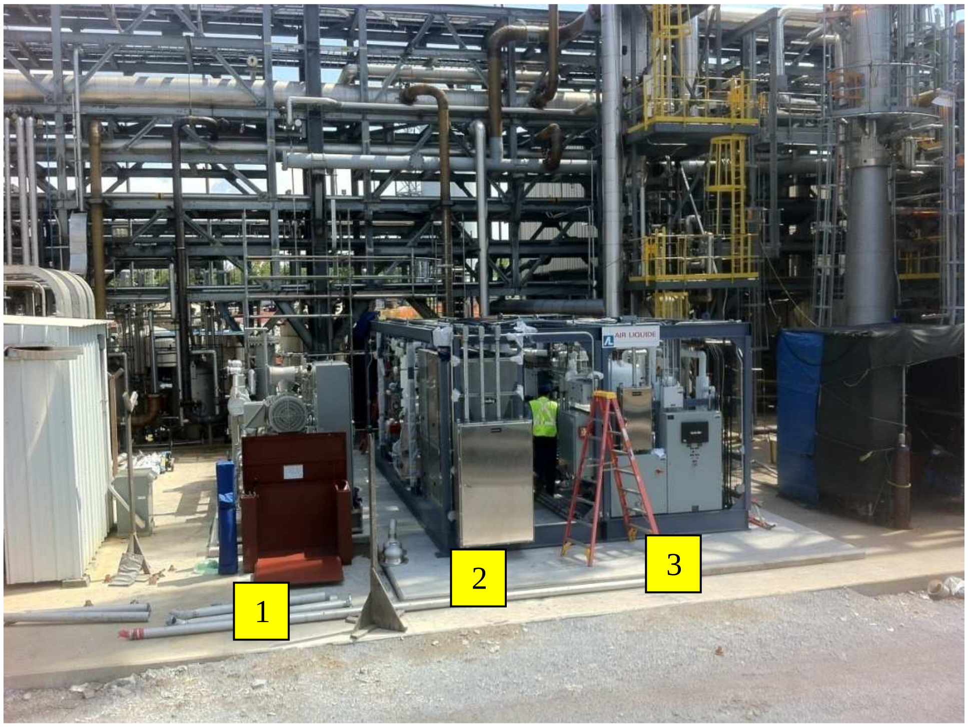


Exhibit 12. Air Liquide Field-Test Unit Installed at the NCCC

In Exhibit 12, Label 1 indicates the compressor skid, Label 2 indicates the pre-treatment skid, and Label 3 indicates the membrane skid.

Air Liquide participated in two post combustion campaigns under DE-FE0013163, PO4 campaign from October to December 2015 and PO5 campaign from May to November 2016. The field test unit (FTU) was operated for approximately 3600 hours during the two campaigns. The equipment was delivered, installed and commissioned at the beginning of PO4 campaign.

Exhibit 13 shows the membrane bundles tested at NCCC with stable long term performance:

Exhibit 13. Bundles tested at 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, Parametric test (CO_2 capture rate, Permeate pressure, Feed temperature, sweep rate)	900 hours
1” PI-1 Bundle	Long term test, parametric test by changing 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 by changing the CO_2 capture rate	1401hours

Various data reconciliation schemes were evaluated with the assistance of the DRTC Applied Mathematics Group. The mass balance error was typically less than 1%.

Analytical method

Analytical campaigns were conducted at the NCCC in the PO-4 and PO-5 test campaigns to measure trace impurities such as mercury, arsenic, selenium, NOx and sulfate 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.[3] 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.[4] 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 remove moisture from wet sample streams before sending them to the analyzer.

Exhibit 14 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 the 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.

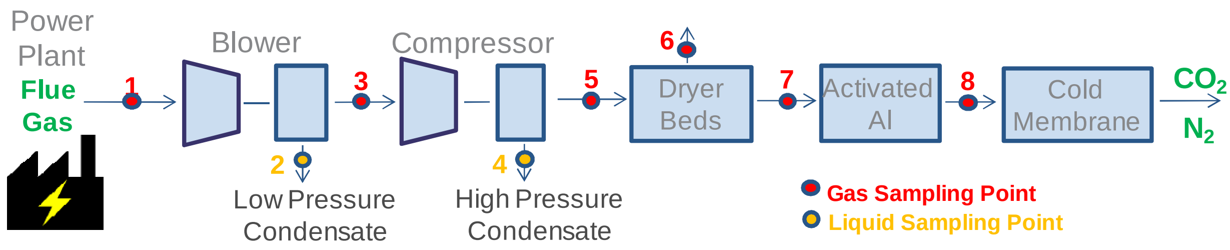


Exhibit 14. Simplified Block Flow Diagram of 0.3 MWe FTU with Analysis Sampling Points

5. RESULTS AND DISCUSSION

5.1. Synthetic Flue Gas Test

5.1.1. PI-1 Bundle Optimization Test Results

In a previous NETL funded, bench scale project (DE-FE0004278) a drop in bundle performance was noticed as the bundle diameter was increased from 1” to 6” to 12”. This section describes the efforts made to optimize the 12” bundle design, which resulted in significant improvement for PI-1 bundles. The optimization was performed by an iterative combination of CFD analysis, bundle modifications, and bundle testing.

A two dimensional, axi-symmetric CFD model of bore-fed bundles was created. A large number of variables were analyzed in both physical testing of bundles at DRTC and simulated testing using CFD. Using CFD, digital experiments were performed on systems where it was impossible to make physical measurements. In physical testing, it was seen that the membrane separation performance droped with increased CO_2 capture rate, indicating bundle non-ideality. Work was concentrated on variables that show bundle non-ideality behavior. Exhibit 15 shows the summary of PI-1 bundle optimization efforts in this project and highlights the key parameters that contributed to improved bundle performance. In simulated testing, the CFD was good at predicting trends, but under predicted the loss of performance. The CFD model remains qualitative rather than quantitative.

Exhibit 15. Summary of PI-1 Bundle optimization efforts

Parameter	CFD Analysis	Experimental Analysis
Uniform packing	Important parameter	Difficult to measure by experiment
Fiber performance variation	Not critical parameter	Difficult to measure by experiment
Fiber OD/ID variation	Not critical parameter	Not measured
Sweep addition	Critical parameter	Validated by experiment
Sweep location	Not critical parameter	Difficult to measure by experiment
Permeate pressure	Critical parameter	Validated by experiment
Permeate opening size variation	Not critical parameter	Inconclusive by experiment
Pressure resistance variation	Not critical parameter	Difficult to measure by experiment

The most important conclusion from this work was that the performance losses were primarily related to non-idealities on the low pressure permeate side. Significant performance improvements were realized when permeate side ideality was addressed.

Sweep Addition

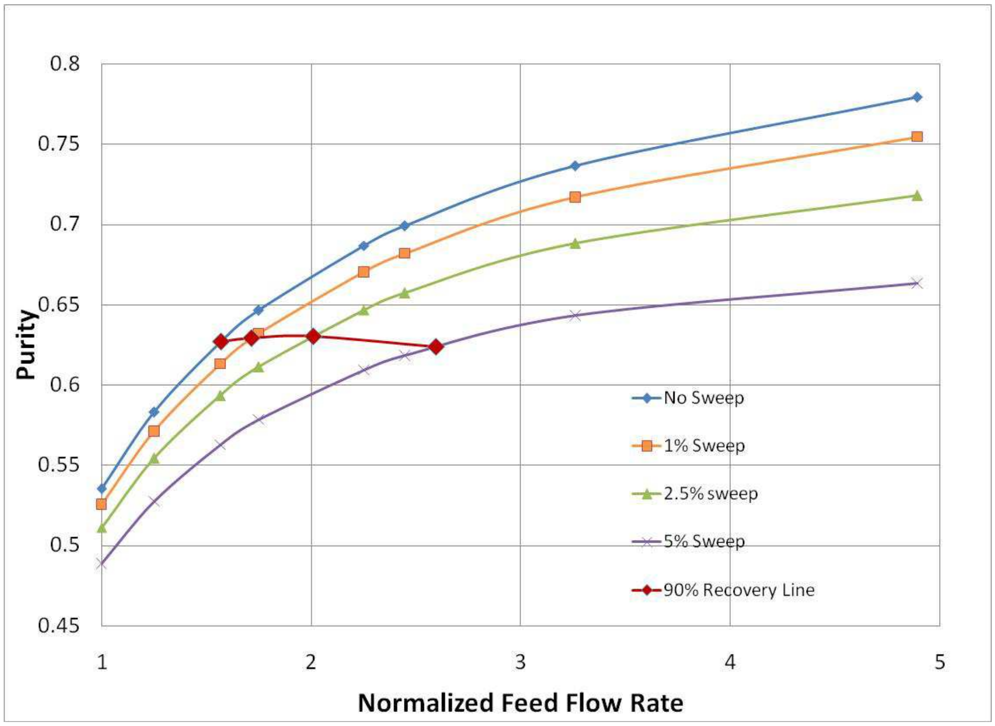


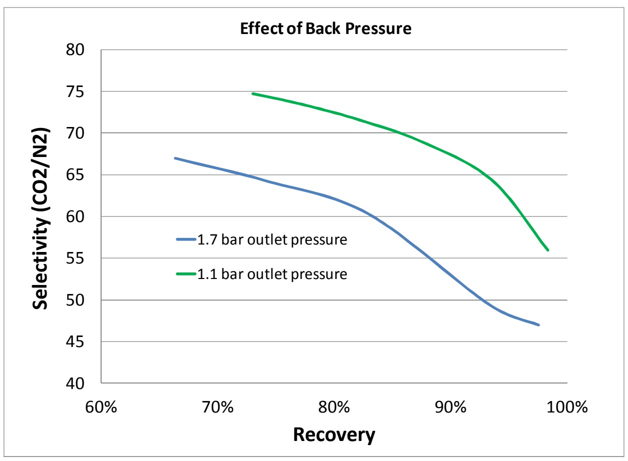
Exhibit 16. CFD simulation plot showing impact of sweep flow for a 12" bundle with 18% CO_2 in N_2 at 216 psi and -45ºC

CFD simulations were conducted to evaluate the benefits of sweep flow and to estimate the optimal sweep flow rate. The sweep stream was generated by returning 1% - 5% of the CO_2 depleted retentate flow back to the bundle shell side. Sweep flow increases the CO_2 partial pressure driving force by introducing a CO_2 depleted stream to dilute the CO_2 concentration on the shell side. The net result was an increase in bundle productivity without any significant decrease in CO_2 permeate purity. To verify this idea, CFD simulations were performed for 1%, 2.5% and 5% of sweep flow cases. Results were plotted with the baseline case without sweep flow as shown in Exhibit 16.

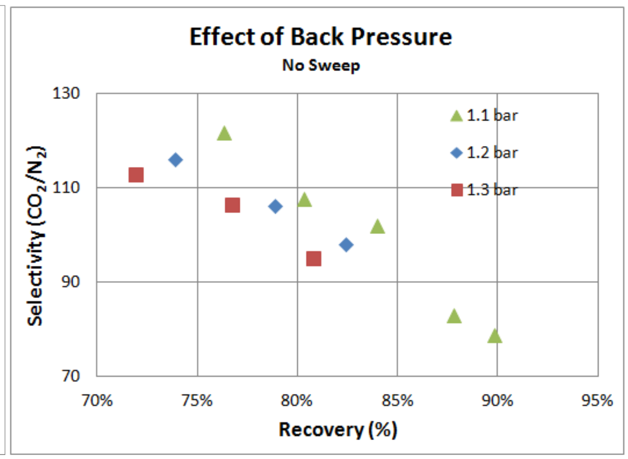
It was clear that introducing sweep flow increased the productivity significantly with only a minimal change in permeate CO_2 purity at constant CO_2 capture rate (recovery) for a 12" bundle with 18% CO_2 in N_2 at 216 psia and -45°C feed temeprature. Based on CFD simulation, at 5% sweep, it is possible to increase the feed flow rate more than 65% relative to the case without sweep at 90% recovery, while maintaining the same CO_2 purity .

Permeate Back Pressure

CFD simulations were performed to assess the impact of permeate back pressure to the bundle performance. A significant amount of the optimization process was a result of iterative progress between CFD and physical tests. One excellent example of the iterative nature of the optimization process was the gradual lowering of the permeate pressure. It was noticed that in the original test campaign, the higher performing 6" bundle had lower permeate back pressure than the 12" bundle. The difference in back pressure was partly by design, as it was envisioned that by raising the back pressure, total flow could be managed and also by the fact that the larger bundle has more flow. Further investigation demonstrated that within the normal ranges of back pressure, lower back pressures generally gave better permeances. CFD work suggested that this was a valid area of concern. Exhibit 17 shows the CFD simulation and experimental validation of improved membrane performance with lower permeate back pressure.



[a]



[b]

Exhibit 17 Effect of Permeate Back Pressure. [a] CFD simulation and [b] Experimental testing is at 200 psig with 18% CO_2 in the feed.

As a result of bundle optimization work, a permeate blower was added to the NCCC FTU and DRTC bench scale skid to allow testing of membrane bundles at varying permeate back pressure. The permeate back pressure turned out to be a critical parameter to improve the bundle CO_2 separation performance at high capture rate.

0.1 MWe Bench Scale Test – 90% CO_2 capture

Several hollow fiber commercial membrane bundles were tested at the 0.1 MWe bench scale skid using a synthetic flue gas (CO_2/N_2) mix to optimize the PI-1 bundles. As mentioned earlier, an iterative process was used to optimize the PI-1 bundle with CFD simulation followed by bundle testing and vice versa. Several attempts were made to optimize the bundle performance by fabricating and testing bundles with different fiber lay down patterns, different post-treatments, lower fiber defects, etc. Due to the limitations of 0.1 MWe bench scale skid, the impact of higher feed flow rate and lower permeate pressure was simulated for various bundles.

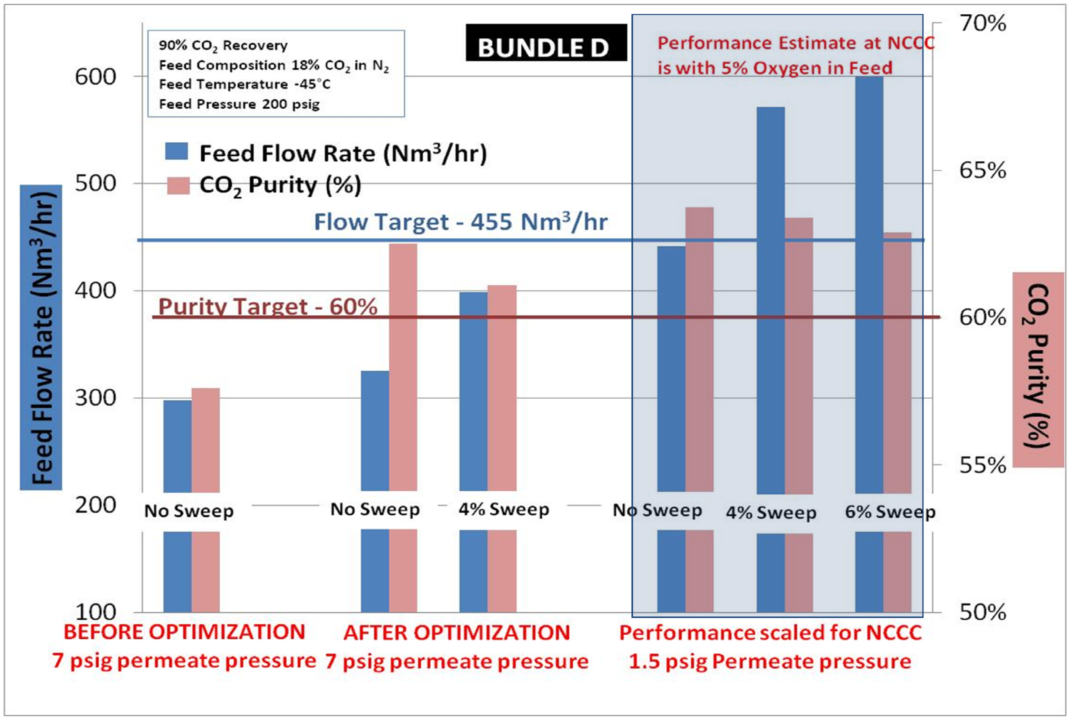


Exhibit 18. 12" PI-1 bundle test at DRTC 0.1 MWe bench scale skid

Exhibit 18 summarizes 90% CO_2 capture data for Bundle D before and after optimization for the experimental data at DRTC and estimated performance at NCCC. Bundle D was tested using simulated flue gas with 18% CO_2 in N_2 at 200 psig feed pressure and -45°C feed temperature for 90% CO_2 capture at DRTC. An extrapolation of the bundle performance at NCCC was made assuming 5% O_2 in the feed gas, similar to the NCCC flue gas condition. Bundle productivity increased after optimization with sweep introduction by >30% compared to the non- optimized bundle without sweep. The decrease in permeate pressure from 7 psig to 1.5 psig, increased bundle productivity from 325 Nm^3/hr to 425 Nm^3/hr without sweep. The bundle productivity is predicted close to the target of 455 Nm^3/hr at NCCC test conditions without sweep and as high as 600 Nm^3/hr with 6% sweep gas, significantly in excess of the target. The predicted data with higher sweep rate was validated at NCCC test.

The non-optimized, bundle without sweep produces 58% CO_2 purity, below the 60% permeate purity target. The optimized bundle without sweep produces 62% CO_2 purity with a feed flow of 325 Nm^3/hr. Simulation predicts a CO_2 purity of around 62-63% at 1.5 psig permeate pressure at NCCC test condition. The predicted data was validated with field testing at NCCC. The permeate purity dropped by 1-3% for sweep cases compared to the cases without sweep, as retentate gas with low CO_2 content was introduced on the permeate end. The CO_2 purity was above the 60% target for all cases except the non-optimized case without sweep, thereby validating that the majority of the non-ideality in 12" bundles was overcome by the addition of sweep and optimizing the bundle design.

Four optimized bundles tested at 0.1 MWe skid qualified for NCCC field testing, meeting the success criteria for bundle performance with the combination of simulation and experiments. The 12" bundle performance was improved significantly beyond the baseline target based on the optimization. The same optimization technique was applied to a 6" PI-1 bundle and the bundle was tested with synthetic flue gas. This optimized, 6" PI-1 bundle demonstrated superior performance relative to the previous baseline performance in DE-FE0004278 project. Exhibit 19 shows significant improvement in normalized CO_2 permeance and CO_2/N_2 selectivity for the optimized 6" and 12" PI-1 bundles compared to the previous baseline performance. The CO_2 permeance was normalized with CO_2 permeance at room temperature. The intrinsic fiber performance indicated in Exhibit 19 was collected from mini-permeator tests performed in the laboratory under very ideal test conditions. There was significant improvement in 12" bundle performance compared to previous baseline, however there was still a gap in performance between 6" and 12" bundle with 6" bundle exhibiting superior performance.

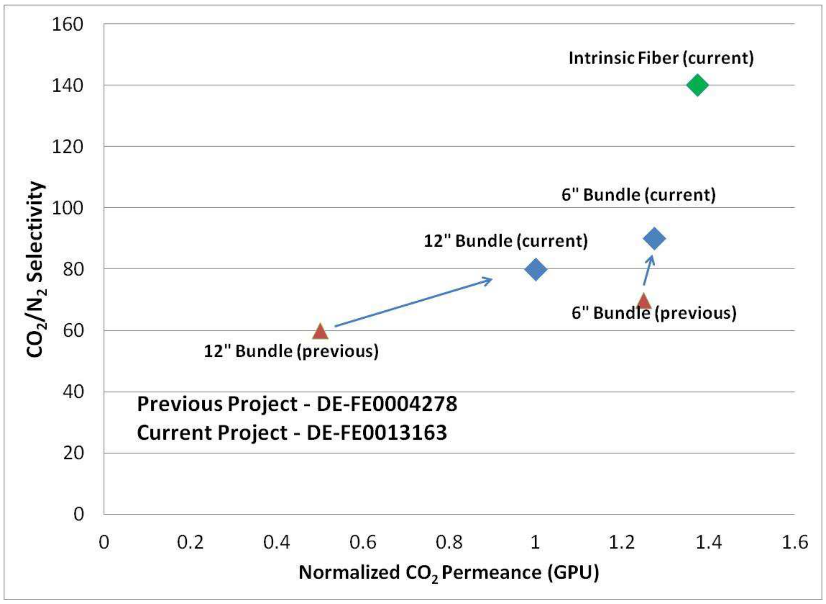


Exhibit 19. Summary of PI-1 Bundle Optimization test results

5.1.2. PI-2 bundle development test results

Next generation high permeance PI-2 membrane was developed from lab scale mini-permeator to 1" full scale bundle with 250X flow and tested at cold temperature. PI-2 membrane development was conducted in three phases as follows:

Mini-permeator development

Fiber spinning procedures were developed at the laboratory scale. Several mini-permeators were fabricated and tested at cold temperature. Mini-permeators development was challenging due to potting issues which limited the pressure resistance of the module. Six PI-2 mini-permeators were fabricated with shell feed configuration using alternative fabrication techniques. Cold temperature testing demonstrated improved mechanical integrity with 100% survival rate on all PI-2 tested mini-permeators as shown in Exhibit 20. The PI-2 mini-permeators were tested at varying feed pressure from 100 psig to 200 psig with 18% CO_2 in N_2 at cold temperature with stable performance for 23 days. The "normalized" CO_2 permeance (PI-2 CO_2 permeance/ with

PI-1 CO_2 permeance at room temperature) was 4-6X , showing superior performance of PI-2 fiber with potential to reduce membrane count significantly.

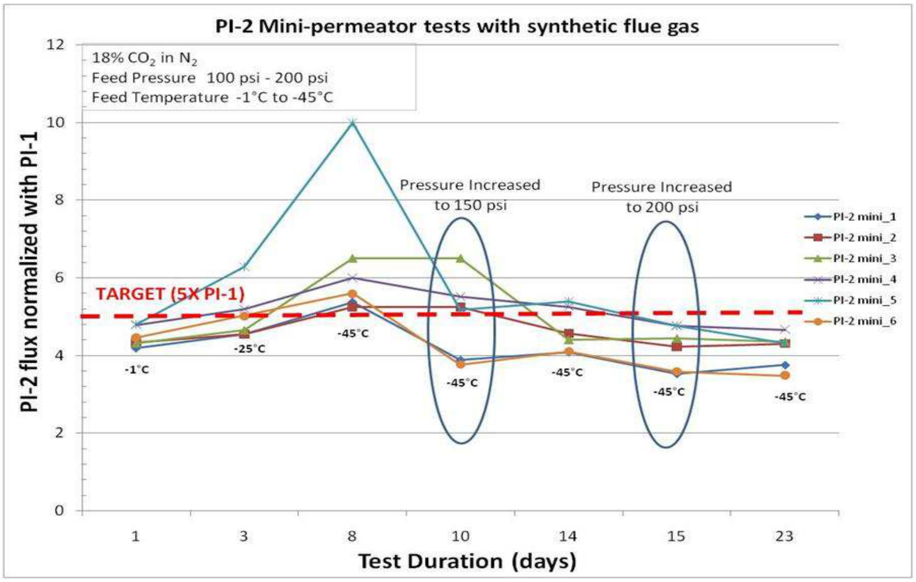


Exhibit 20. PI-2 mini-permeator long term test

<u>1" permeator development</u>

PI-2 fibers were further used to fabricate 1" permeators with 25X flow capacity compared to the mini-permeators. Several permeators, made using MEDAL prototype 1" bundle hardware, were tested at cold temperature for parametric and long term testing. Exhibit 21 shows a plot from one of the 1" permeator tests at cold temperature with synthetic flue gas containing 19% CO_2 in N_2 at 100 psig feed pressure, -45C feed temperature and 70% CO_2 capture rate. The CO_2 permeance normalized with PI-1 permeance was 6-7X and the CO_2 purity was ~67% with no deterioration in performance for >500 hours of testing. Due to the limited fiber mass in a comparatively large shell, these permeators demonstrated inefficient counter-current flow. The fiber performance was reasonably well estimated at lower CO_2 capture rates and long term stability of the fiber and bundle hardware was verified at 70% CO_2 capture. The 1" permeators were qualified with synthetic flue gas and selected for field testing at NCCC in PO-4 campaign.

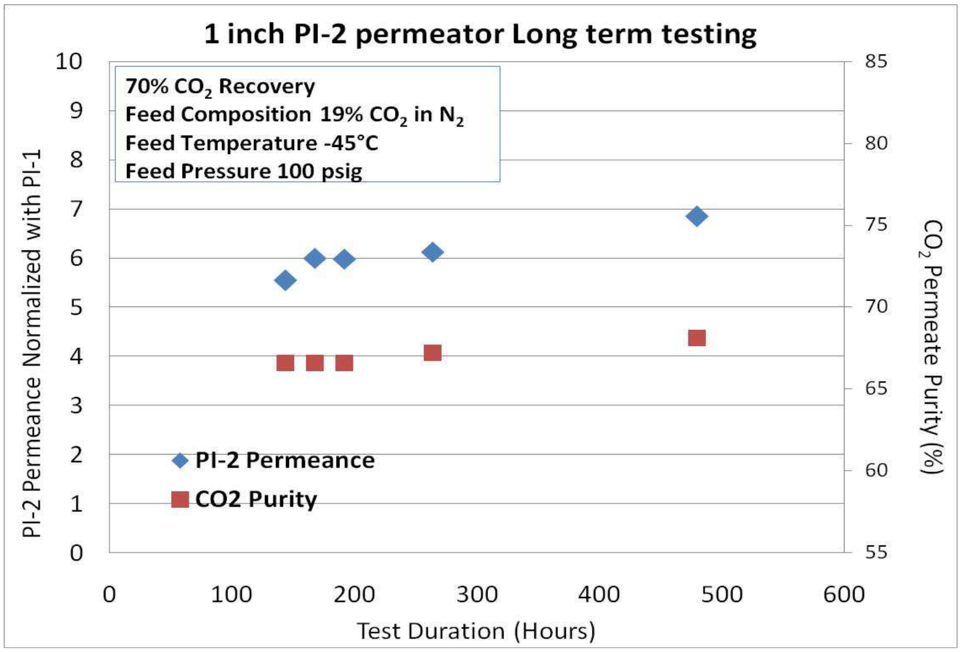


Exhibit 21. 1" PI-2 permeator test at cold temperature

<u>1"prototype bundle development – DSU</u>

The PI-2 permeator was scaled to the full 1" prototype bundle with 250X flow capacity compared to the mini-permeator. The Development Spin Unit (DSU) was used to simultaneously spin multiple fibers and fabricate bundles with large quantities of fiber. Six 1", PI-2 bundles were fabricated using fibers from three DSU batches. Prior to bundle forming, fibers from different DSU batches were tested for membrane separation performance by forming mini permeators. Following minipermeator testing, 1" bundles were formed, and tested with air as a final qualification step for field testing at NCCC.

5.2. Real Flue Gas Test

Air Liquide commercial PI-1 bundles and next generation novel PI-2 membranes were tested with real coal fired flue gas at NCCC in a 0.3 MWe FTU. The bundles were tested in PO-4 and PO-5 campaign for 3600 hours.

5.2.1. 12" PI-bundle test

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

5.2.1.1. 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 22 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 22 also shows the actual performance (indicated by stars) 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 (non-CFD) simulation model used to predict the NCCC performance).

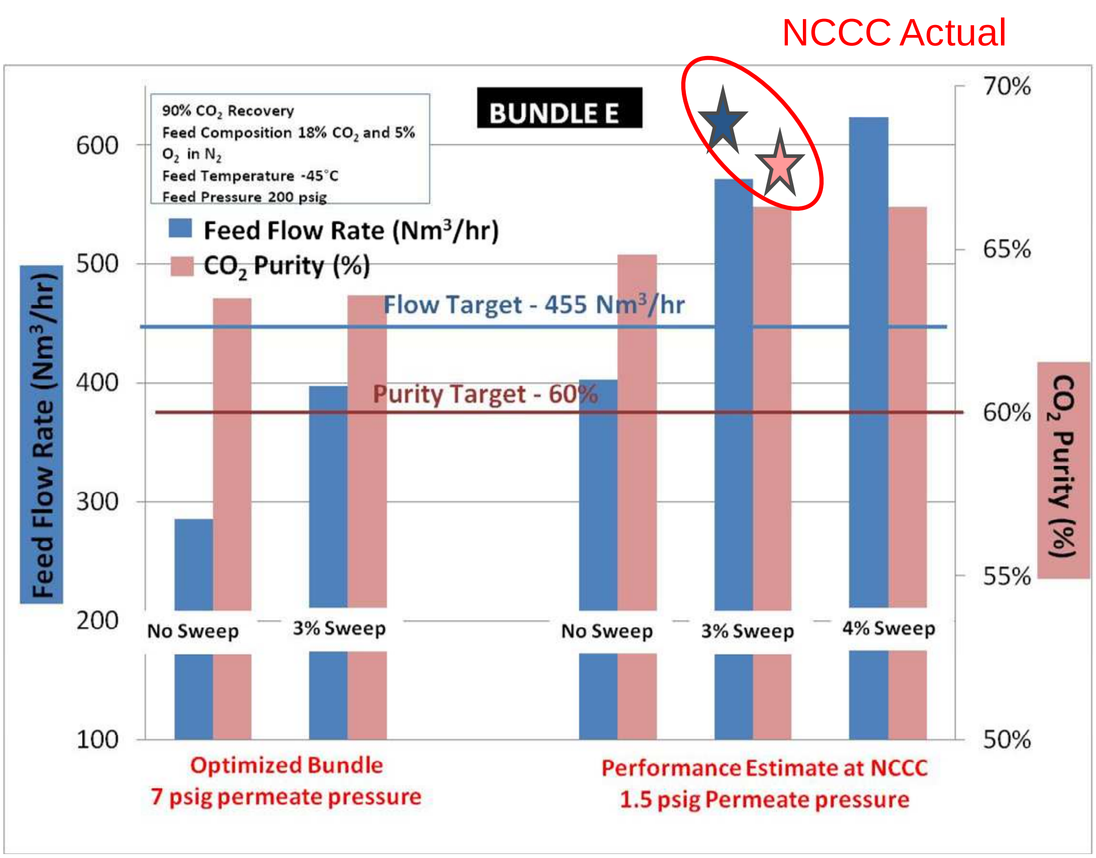


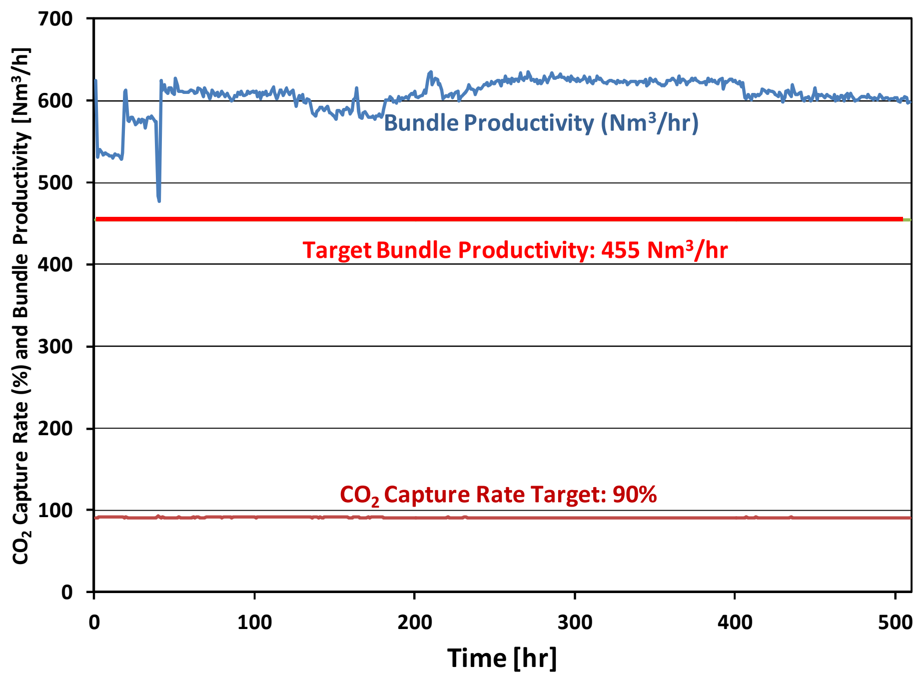
Exhibit 22. Bundle E Productivity and CO_2 Purity for the 12” Membrane Bundle Tested at DRTC (7 psig permeate pressure) and NCCC (1.5 psig permeate pressure estimated and actual).

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.

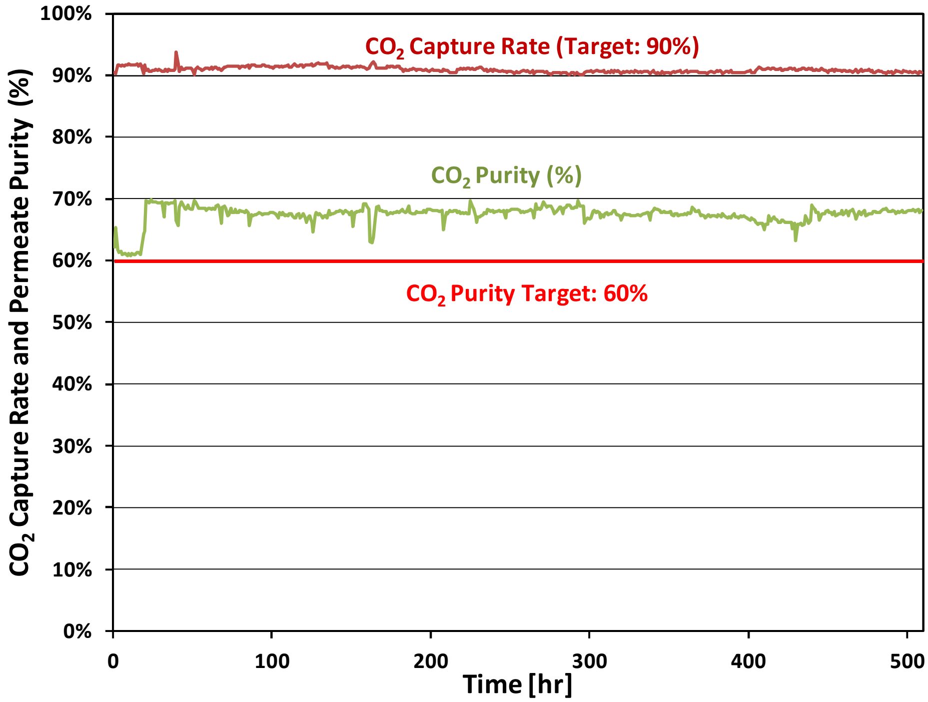
5.2.1.2. 12” PI-1 bundle steady state test

Steady state testing was conducted for 500 hours, as shown in the Exhibit 23, 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 23a and 23b. 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. The bundle productivity was ~610 Nm^3/hr and the purity was ~68% where the productivity target was set at 455 Nm^3/hr and the purity target was set at 60%. No degradation in the membrane performance was seen over the entire run.



(23a). Bundle Productivity Over Time



(23b). CO_2 Capture Rate and Permeate Purity Over Time

Exhibit 23. Steady State Test of Bundle F at NCCC

5.2.1.3. 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 24. Both the bundles had similar performance based on previous synthetic flue gas 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.

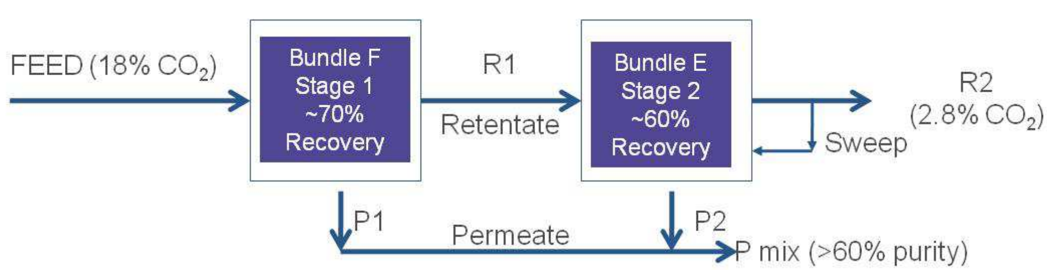


Exhibit 24. Two Bundles in Series Operation at NCCC

Exhibit 25 shows that the single bundle productivity was higher than the two bundles in series (productivity per bundle) at the same operating conditions (higher permeate pressure 7 psig). The single bundle productivity at 7 psig permeate pressure was 450 Nm3/hr versus 600 Nm3/hr at 1.5 psig permeate pressure. Identical test condition was used for comparison. Based on simulation, the two bundles in series were predicted to meet the performance target at lower permeate pressure (1.5 psig permeate pressure). Still, their use in series was inferior to the single bundle performance and was not deemed fit for further study based on the test conditions.

Exhibit 25. Preliminary Comparison of Single-Bundle Versus Two Bundles in Series (18% CO_2, 9% O_2, balance N_2, at -45°C, and 200 psig feed, 7 psig permeate pressure)

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%

5.2.2. 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.

5.2.2.1. 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 capture. Exhibit 26 shows stable bundle productivity over 900 hours of testing at 90% capture. 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, despite having approximately 3.7 times more surface area. This is one of the indicators of more ideal bundle performance with the 6” bundle.

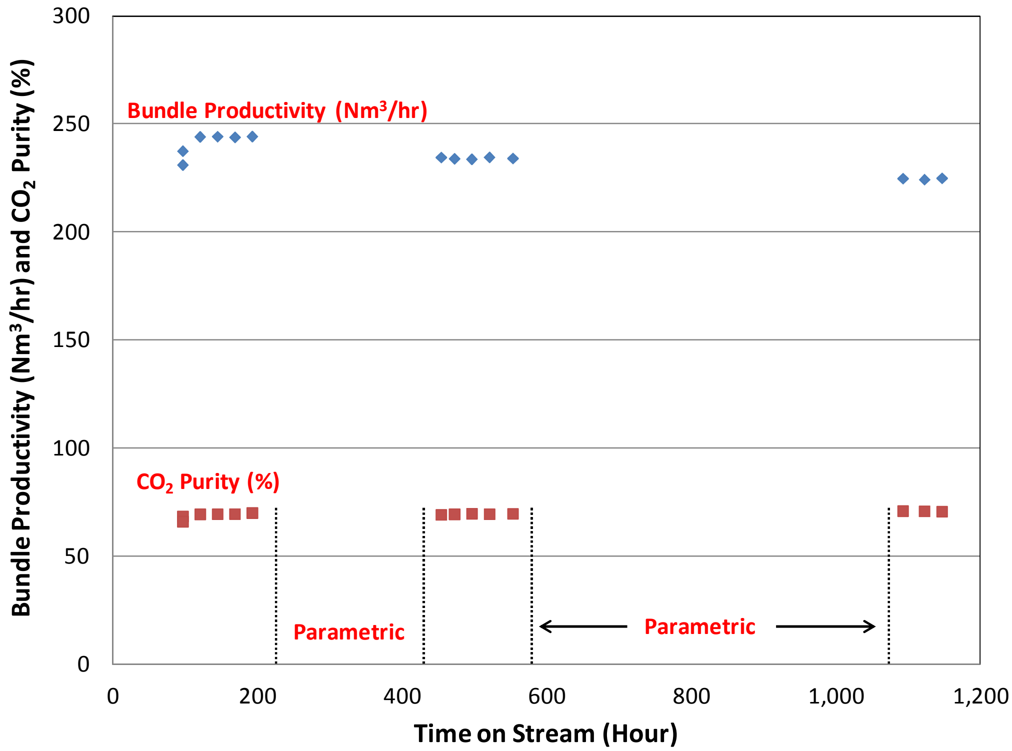


Exhibit 26. 6” PI-1 Bundle G Performance Stability Over Time

5.2.2.2. 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 capture. Exhibit 27 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.

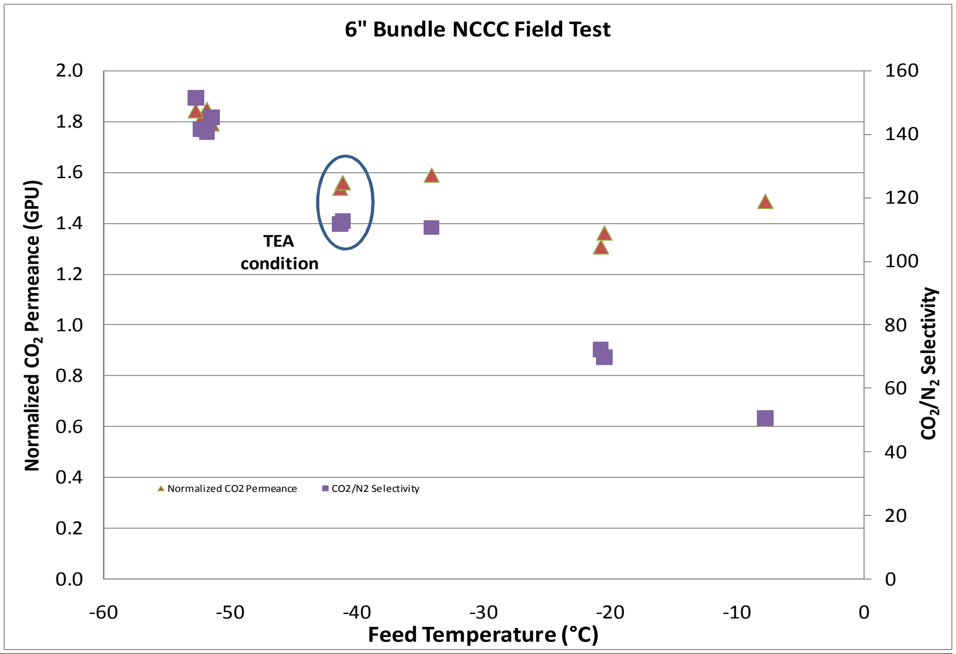


Exhibit 27. 6" PI-1 Bundle Parametric Test

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.

5.2.3. 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 capture 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 28 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.

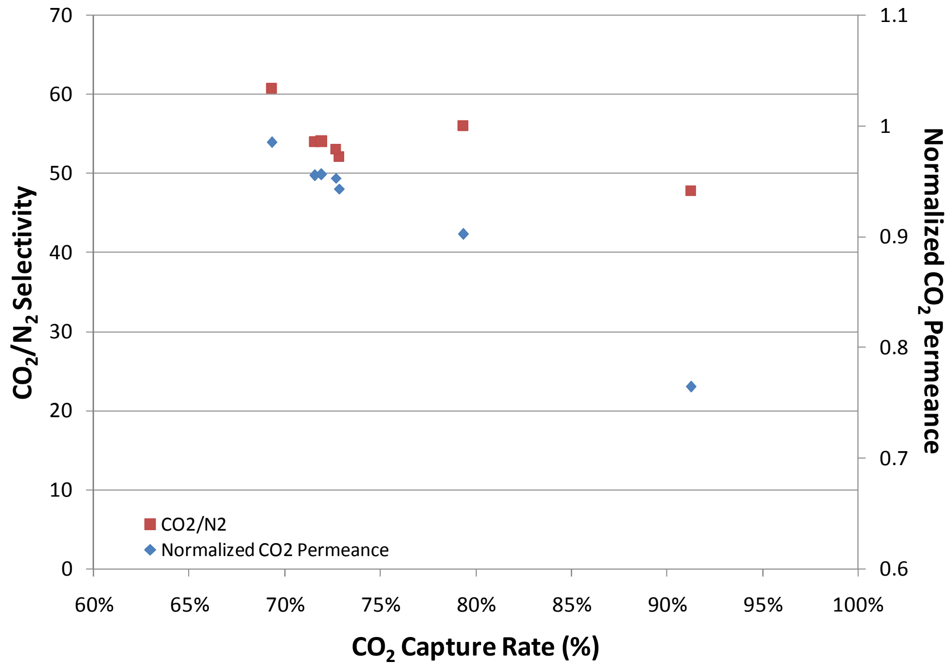


Exhibit 28. 1” PI-1 Bundle Parametric Test

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 29 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.

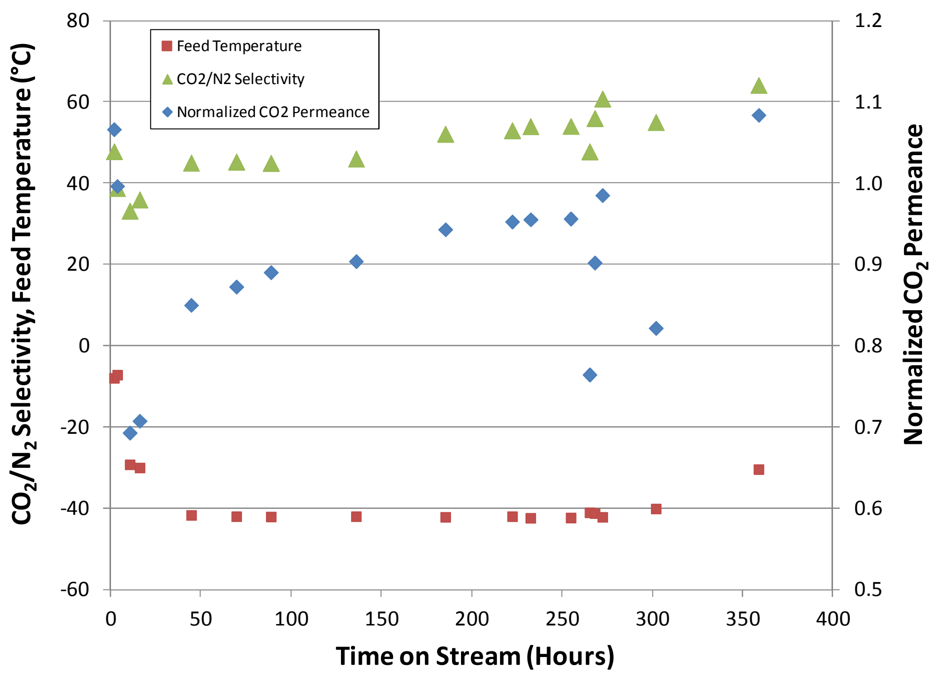


Exhibit 29. 1” PI-1 Bundle Parametric and Long-term Test

5.2.4. 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 relatively low 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 30 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.

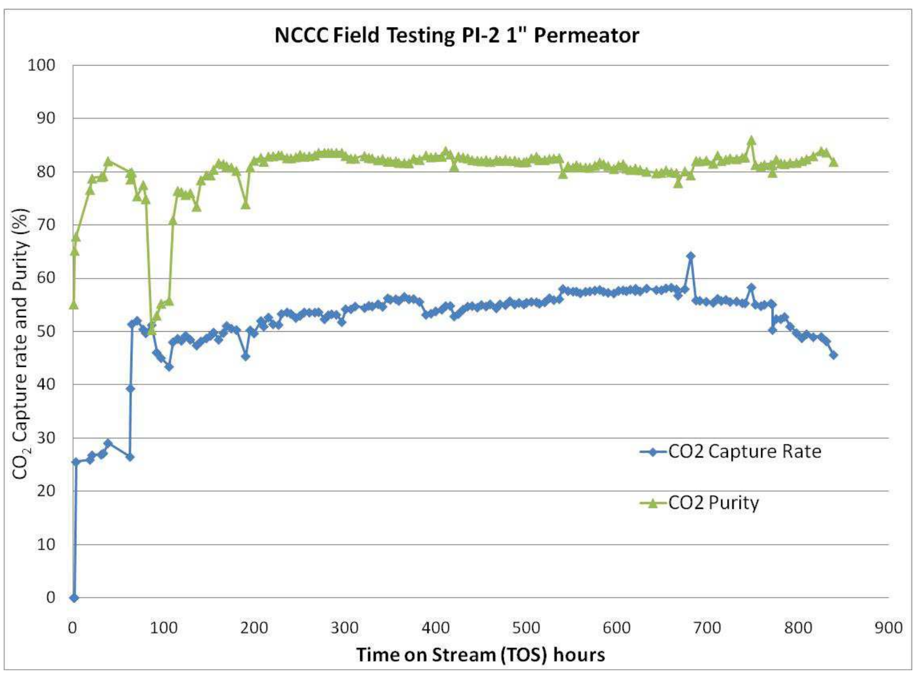


Exhibit 30. 1" PI-2 Permeator Long-term Test

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 31. 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.

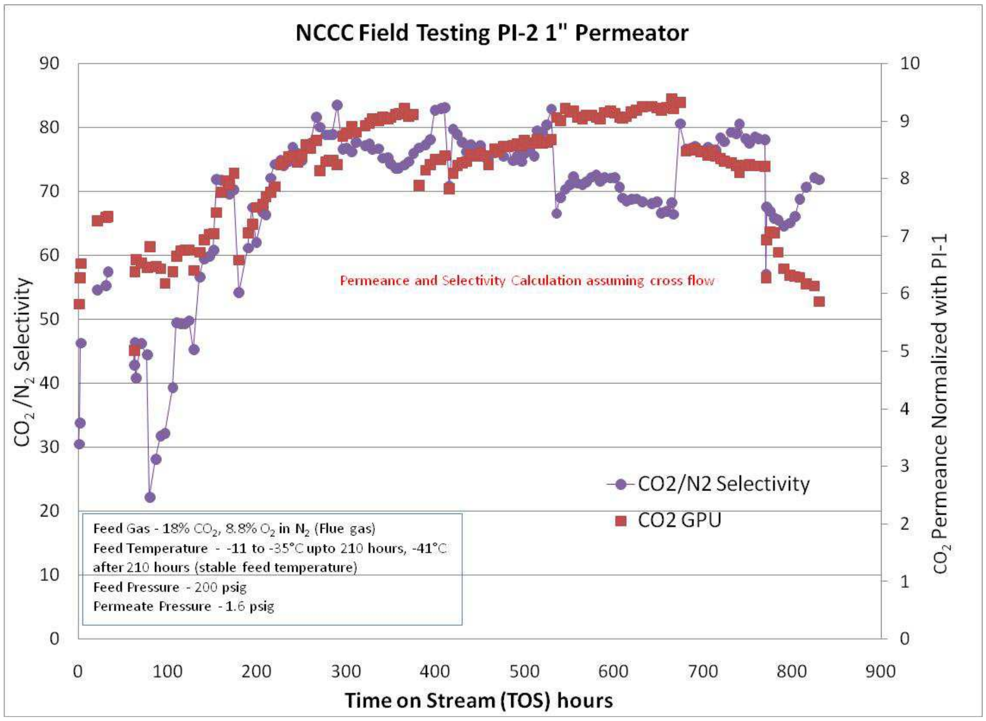


Exhibit 31. CO_2/N_2 Selectivity and Normalized CO_2 Permeance Versus Time on Stream for the 1" PI-2 Permeator

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 will be discussed in Section 5.2.8.

5.2.5. 1" PI-2 bundle testing

By mid-2016, synthesis of the PI-2 fiber had been scaled up such that small (1") prototype 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 32 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).

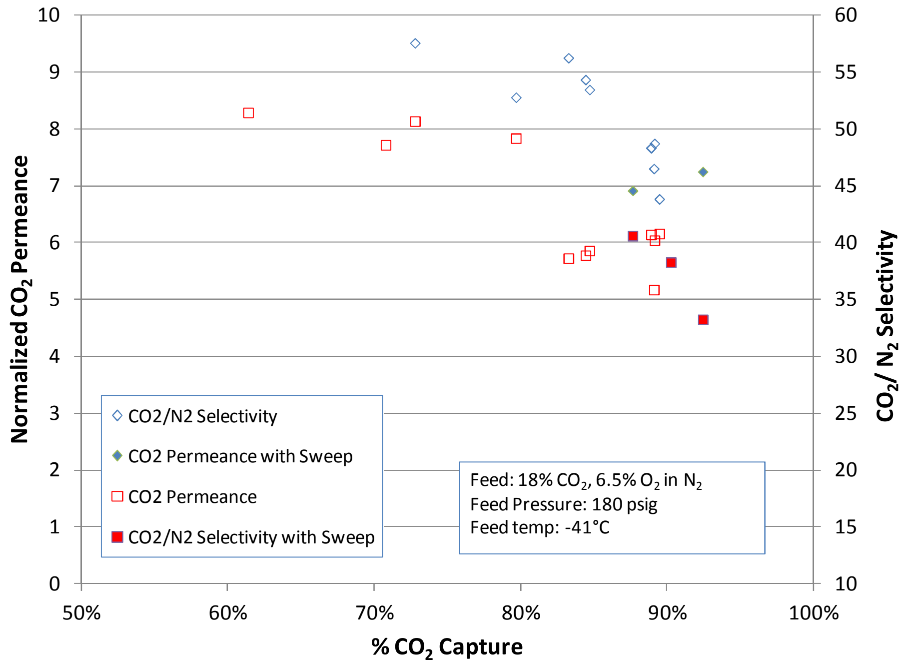


Exhibit 32. PI-2 Bundle (#3-2) Parametric Test

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 5.2.3 demonstrated a drop in membrane performance at higher capture rate in Exhibit 28 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. The CO_2 permeance was normalized with the PI-1 CO_2 permeance at room temperature. As shown in Exhibits 33 and 34, 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.

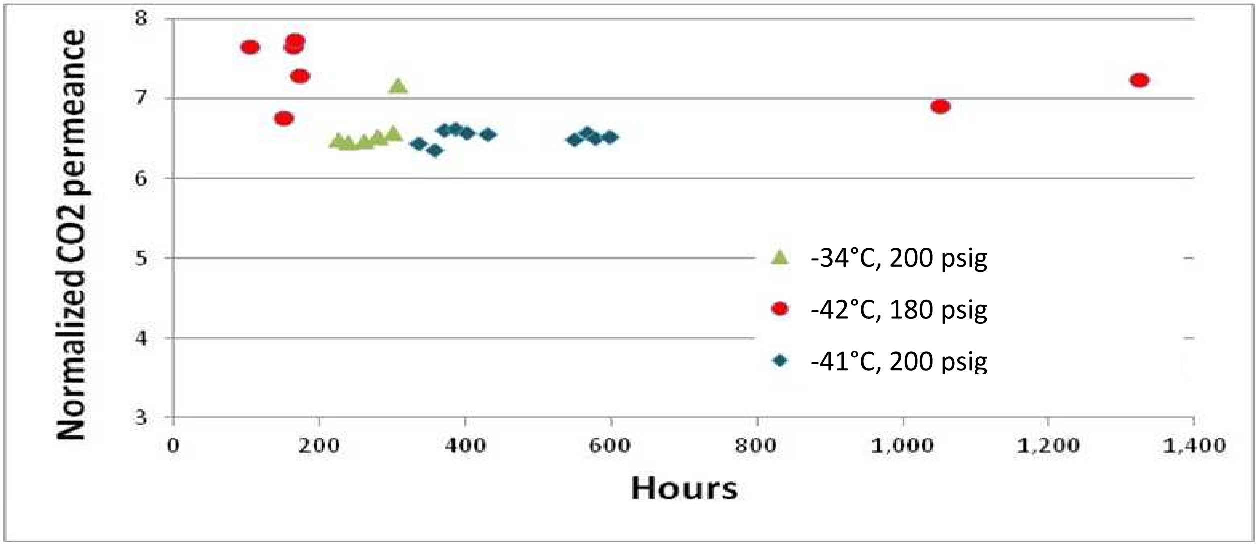


Exhibit 33. Normalized CO_2 Permeance over Time for the PI-2 Bundle

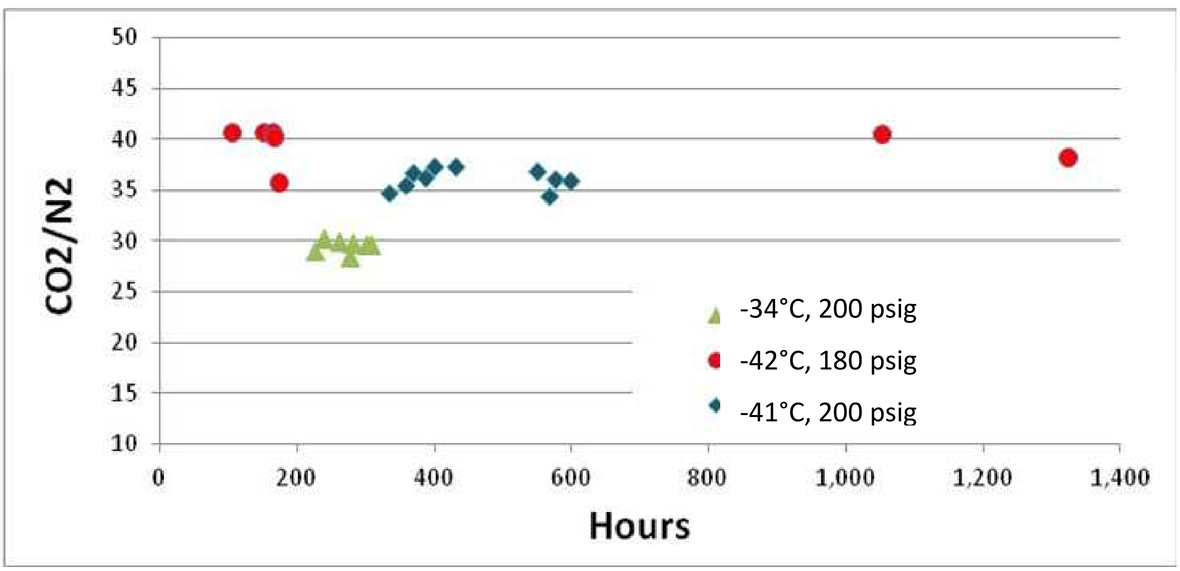


Exhibit 34. CO_2/N_2 Selectivity over Time for the PI-2 Bundle

Exhibit 35 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 23a and 23b.

Exhibit 35. 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.

5.2.6. 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 capture. Exhibits 36 and 37 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 37.

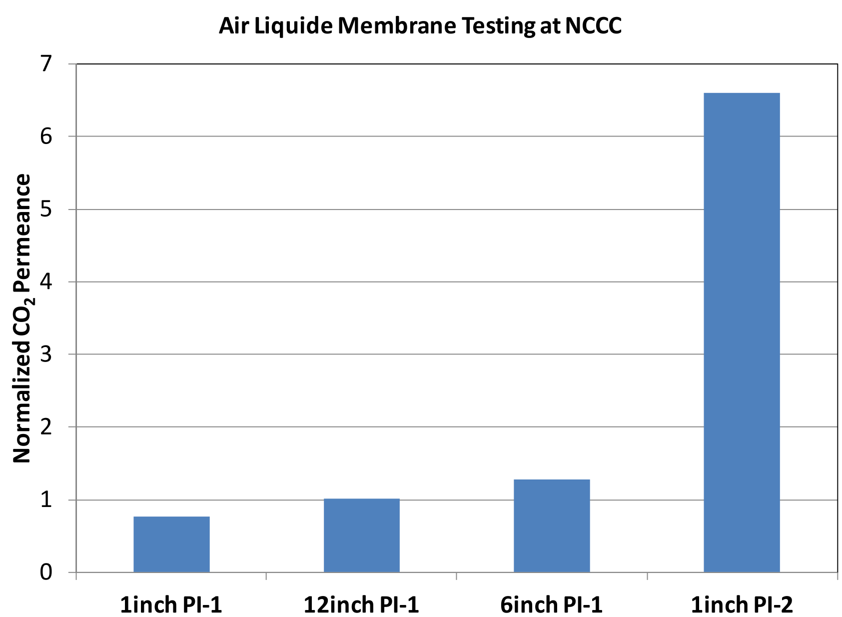


Exhibit 36. Normalized CO_2 Permeance for Membrane Bundles Tested at 90% CO_2 Capture

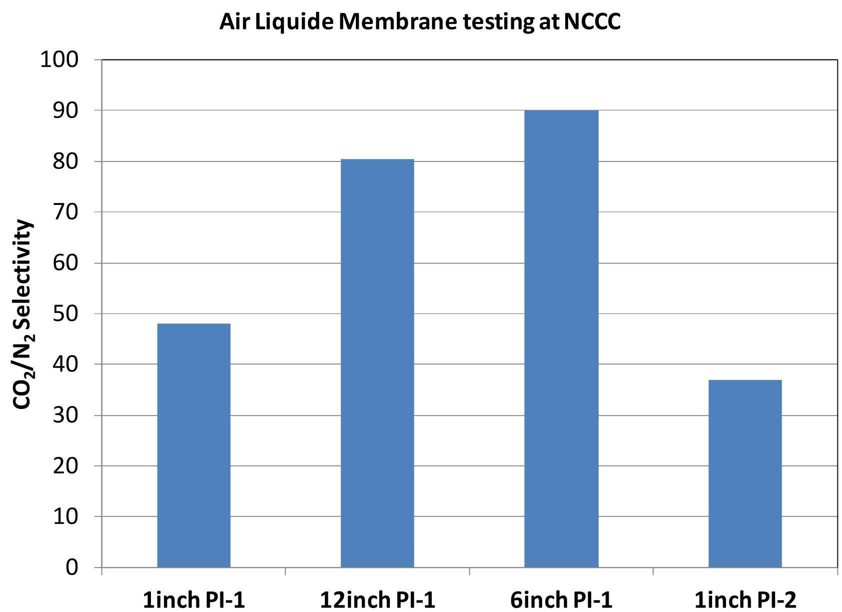


Exhibit 37. CO_2/N_2 Selectivity for Membrane Bundles Tested at 90% CO_2 Capture

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.

5.2.7. Analytical Campaign

Analytical testing was conducted in PO-4 and PO-5 campaigns as discussed in section 4.3. Exhibits 38 and 39 summarize the analytical results from gas and liquid samples, respectively for different sample points as described in Exhibit 14. Exhibit 38 shows the metal impurities, Hg, As, and Se in micrograms per normal cubic meter ($\mu g/Nm^3$), in the gas samples along with NO and NO_2 levels in ppmv. Exhibit 39 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 38. 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 39. 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 38 and 39 for metal impurities represent samples taken at different points in time, one month apart in campaign PO-5. The values reported for NOx also varied widely over the 30 minute measurement duration. Exhibit 40 shows the approximate contaminant distribution based on the analytical results of gas and liquid samples presented in Exhibits 38 and 39. Arsenic was below the detection limit in all of the condensate streams.

Exhibit 40. 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) in PO-5 campaign. These were found to be below the detection limit (<0.40 mg/L) due to 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. NO and NO_2 concentrations were very low at the membrane feed, indicating NOx adsorption in the dryer and activated alumina bed.

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 39 indicating the flue gas contained little or no sulfur species. This was not surprising considering the presence of the upstream FGD and pre-scrubber units.

5.2.8. 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 Air Liquide on-site staff.

Incidents of membrane bundle performance decline

Specific events caused membrane bundles to show a decline in 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 compressor oil breakthrough from the pretreatment system. With the support of NCCC contractors, the elements and adsorbent media were replaced. Exhibit 41 shows the pictures of knock-out vessel and the filter element during the change-out process.

Exhibit 41. 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 due to economy at that scale. At larger scale, an oil free compressor will be used and this issue would not apply.

- **Moisture contamination -** A 12" PI-1 bundle was tested during PO-5 and experienced a 40% loss in CO_2 permeance during the cool down phase. 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. A thorough bundle purge procedure will be in effect in future before cold temperature exposure.

Compressor Issues

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 such as visual appearance, pH measurement, FTIR spectra, IC and ICP-MS analysis. Exhibit 42 shows a visual comparision of the virgin and used oil. The fresh sample had a yellow hue. The used oil had a darker appearance, most likely resulting from oxidation. Minor corrosion was also noted in the coalescing filter element, as shown in Exhibit 42.

Exhibit 42. Compressor Oil Samples and Coallescing Element Corrosion

Based on the oil analysis it was clear that unwanted by-product formation occurred, 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 in the acceptable range and no new compounds were detected. The new oil was judged suitable for the flue gas application and will continue to be used in future campaigns under DE-FE0026422.

Equipment issues

Several equipment related issues were encountered such as a faulty HMI screen, a 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.

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.

- **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. A short term solution was implemented, however future modification of flue gas piping is recommended.

- **Particulate:** The pre-treatment section of the FTU experienced higher pressure drop due to plate and frame heat exchanger fouling as shown in Exhibit 43. 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.

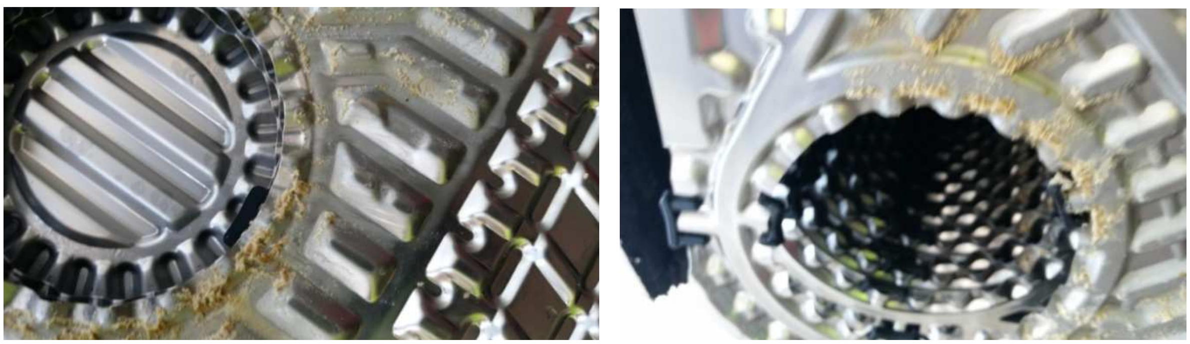


Exhibit 43. Picture of Heat Exchanger Fouling

- **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. Surprisingly, hydrocarbon was also detected at the inlet flue gas from NCCC. 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.

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.

6. Techo-Economi Analysis

Techno-economic analysis (TEA) was conducted for 550 MWe (net) supercritical pulverized coal (PC) power plant integrated with Air Liquide's hybrid cold membrane carbon capture process. A detailed report on this study was submitted in the form of topical report.[10] The cost target by NETL was set at $40/tonne for nth of a kind plant by 2025. The capture cost was calculated with 12" PI-1 bundle, 6" PI-1 bundle and projected 12" PI-2 bundle and compared with Case 11 (no CO_2 capture) and Case 12 (CO_2 capture using amine). Case study was conducted at **90% CO_2 capture** from coal power plant flue gas to produce >99.99 vol. % CO_2 at 2,215 psia pressure. The TEA study was validated by Parsons Government Services (PGS).

The TEA study included four cases utilizing Air Liquide's commercial PI-1 membrane bundle and next generation, higher permeance PI-2 membrane as follows:

- 12" PI-1 membrane bundle – Based on field test data from 90% CO_2 capture with 12" PI-1 bundle at the National Carbon Capture Center (NCCC), 0.3 MWe field test unit
- 6" PI-1 membrane bundle - Based on field test data from 90% CO_2 capture with 6" PI-1 bundle at NCCC
- Projected 12" PI-2 Bundle Case 1 – Based on field test data from 90% CO_2 capture with 1" PI-2 bundle at NCCC
- Projected 12" PI-2 Bundle Case 2 - Based on field performance of 1" PI-2 bundle at 70% CO_2 (ideal performance) at NCCC extrapolated to 90% capture TEA case

The actual field data was used for the 6" and 12" PI-1 bundles at NCCC; however the results for the 12" PI-2 was projected from actual testing with a 1" bundle. The PI-2 bundle performance showed considerable non-ideality due to its lower packing density, shorter feed path and higher permeate pressure. The two projections for PI-2 were based on the actual membrane performance at 90% capture as well as the expected performance using the 70% capture performance data.

Aspen HYSYS was used to model and simulate the cold membrane hybrid process. The process simulations were optimized to reduce the overall capture cost and improve the efficiency of the process. This TEA adds considerably more rigor over our past analysis in 2012 (DE-FE004278). Detailed analysis included motor losses and updated rotating machinery efficiencies as well as line segment pressure drops. Waste heat from the carbon capture process was integrated with the power plant to generate boiler feed water (BFW). A credit was used in the operating expenditure for BFW generation and saving low pressure steam that is normally used to generate BFW. The material and energy balance was reviewed and validated by PGS.

The resulting material and energy balance (M&EB) data was used to generate process data sheets (PDS) for major equipment, which were supplied to the vendors for quotations. Quotes were received for major equipments from reliable US suppliers that account for >75% capital cost. Capital cost was significantly reduced by obtaining quotes from reliable low cost suppliers vetted by Air Liquide. A detailed cost quote was also obtained for the membrane and skid installation. Process simulations were adapted based on the vendor feedback on equipment efficiency and motor losses. Air Liquide references/database of similar equipment configuration was used to scale the cost for the remaining equipments, which totaled about ~25% of the capital cost. Sensitivity analysis was conducted with +/-20% variation on the equipment cost.

The cost estimation methodology used NETL guidelines to compare PC power plant with Air Liquide hybrid cold membrane process TEA cases in comparison to Case 11 (no capture) and Case 12 (capture with amine).[5-9] Carbon capture cost was calculated in 2011$ using NETL guidelines.[5-6] Equipment quotes were received from 2010 to 2016. The cost was converted to 2011$ using Consumer Price Index (CPI) as listed in Equation 1. CPI index for each year was calculated based on an annual average.

Equation 1

$$\text{Cost 2011\$} = \text{Cost QY} * CPI_{2011}/CPI_{QY}$$

Where QY is the Quote Year, CPI_{2011} is the CPI equipment index for 2011, and CPI_{QY} is the CPI equipment index for quote year.

Bare Erected Cost (BEC) was the sum of equipment cost, secondary component cost and direct/indirect labor cost. The secondary component cost was assumed to be 20% on non-membrane major equipments (compressor, turbines) for valve, piping etc. There was no secondary equipment cost on membrane as the detailed cost was obtained on the membrane skid.

Engineering fee and contingencies (process and project) were assumed to be proportional to Case 12. Exhibit 44 lists assumptions used for engineering fee and contingencies. Case 12 is carbon capture using amine process from 550 MWe (net) coal fired power plant which has been thoroughly studied by NETL funded projects. It is assumed that the level of complexity for a plant using cold membrane hybrid process for carbon capture will be same or lower than for the amine plant.

Exhibit 44. Engineering fee and contingency assumptions

Parameter	Case 12	Cold Membrane	NETL QGESS (Ref. [4])
Engineering fee	9.3% of BEC	9.3% of BEC	8-10% of BEC
Process contingency	20% on CO_2 removal	20% on membrane	5-20% on full size module
Project contingency	20% on sum of BEC, engineering fee and process contingency	20% on sum of BEC, engineering fee and process contingency	15-30%

Total Plant Cost is sum of the BEC, Engineering fee, process contingency and project contingency.[5,6] Capital cost scaling methodology was used to scale the power plant cost with carbon capture.[7] Power plant cost for carbon capture using cold membrane process was scaled using scaling exponents.[7] The scaling exponents were logarithmically derived from Case 11 and Case 12 using Equation 2. Exponents were calculated using BEC for Case 12 and Case 11 employing the reference parameter.

Equation 2

$$Exp = \ln(RC_{case12}/RC_{case11})/\ln(RP_{case12}/RP_{case11})$$

Where Exp is the exponent, RC_{case12} is the Reference cost for Case 12, RC_{case11} is the Reference cost for Case 11, RP_{case12} is the Reference parameter for Case 12, and RP_{case11} is the Reference Parameter for Case 11

Equation 3 was used to calculate the scaled BEC for cold membrane cases based on case 11 BEC.

Equation 3

$$SC = RC * (SP/RP)^{Exp}$$

Where SC is the Scaled cost for cold membrane, RC is the Reference cost for Case 11, SP is the scaling parameter, RP is the reference parameter for Case 11, Exp is the Exponent calculated using Equation 4

Quality guidelines for energy system studies (QGESS) cost estimation methodology was employed for calculating Total Overnight Capital (TOC) and Total As Spent Capital (TASC) from BEC.[8] The estimation method for owner's cost was used to calculate preproduction costs, working capital, inventory capital, land, financing cost and other owner's cost. Initial cost of catalyst and chemical included the cost of loading the dryer bed(s) and other pre-treatment chemicals. This cost was assumed similar to amine plant Case 12; however, it is expected that this cost will be lower than the Case 12. Membrane bundles tend to age over time. There was no aging noticed in the previous cold membrane bundle tested in Delaware Research and Technology Center (DRTC) for 6-8 months under DE-FE0004278 project. Additional membrane cost was added on an annual basis to account for membrane aging.

Exhibit 45 shows the cost breakdown of 12" PI-1 bundle TEA case and 12" Projected PI-2 bundle TEA case 2. At 550 MWe net power plant size, economy of scale has been achieved for the rotating machinery. For the PI-1 membrane case, CO_2 removal cost is ~50% compared to rest of the plant. The CO_2 removal cost was minimized to 22% with PI-2 membrane showing significant benefit of using PI-2 membrane bundles.

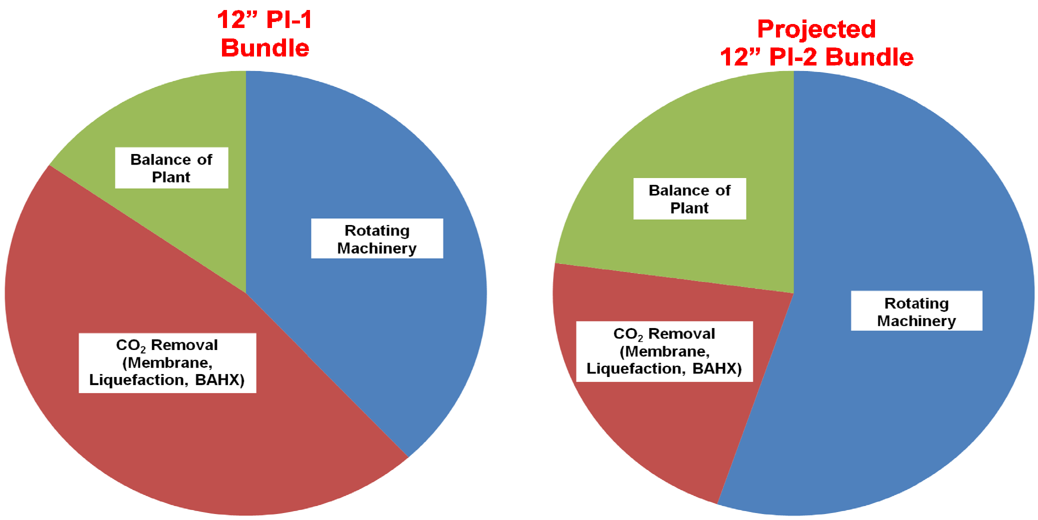


Exhibit 45. Cost Breakdown for PI-1 and PI-2 membrane case

The costing methodology used by National Energy Technology Laboratory (NETL) for estimating future costs of mature commercial nth of a kind (NOAK) plants / technologies from initial first of a kind (FOAK) estimates was used to estimate costs for future plants.[9]

First of a kind estimate (FOAK)

Exhibit 46 shows the total plant cost for FOAK plant for different membrane bundle cases with total overnight cost and total as-spent cost. All membrane cases were lower than Case 12 (amine capture). Carbon capture cost was significantly reduced with PI-2 membrane bundle cases.

Exhibit 46. Cost Summary FOAK plant

	Case 12 (Amine)	**12" Bundle PI-1**	**6" PI-1 Bundle**	**12" Projected PI-2 Bundle Case 1**	**12" Projected PI-2 Bundle Case 2**
Power Plant Cost (k$)	$1,365,905	$1,305,231	$1,300,951	$1,332,516	$1,326,237
Carbon Capture Cost (k$)	$593,496	$356,683	$353,891	$271,151	$254,164
Total Plant Cost (k$)	**$1,959,401**	**$1,661,915**	**$1,654,842**	**$1,603,668**	**$1,580,401**
Total Overnight Cost (TOC)	**$2,414,736**	**$2,043,781**	**$2,035,059**	**$1,974,294**	**$1,945,923**
Total As-Spent Cost (TASC) k$	**$2,752,799**	**$2,329,910**	**$2,319,967**	**$2,250,695**	**$2,218,353**

Nth of a kind estimate (NOAK)

Exhibit 47 shows the cost summary table for four TEA cases for NOAK plant compared to Case 12 (amine capture). Due to higher maturity of major components in the hybrid cold membrane process, the carbon capture cost is not significantly lower compared to the FOAK cost. The total plant cost was lower for all cold membrane cases compared to Case 12. Carbon capture cost was significantly reduced with PI-2 membrane bundle cases.

Exhibit 47. Cost Summary NOAK plant

	Case 12 (Amine)	**12" PI-1 Bundle**	**6" PI-1 Bundle**	**12" Projected PI-2 Bundle Case 1**	**12" Projected PI-2 Bundle Case 2**
Power Plant Cost (k$)	$1,302,062	$1,243,011	$1,238,950	$1,268,881	$1,262,920
Carbon Capture Cost (k$)	$552,971	$335,159	$333,293	$255,731	$239,980
Total Plant Cost (k$)	**$1,855,033**	**$1,578,171**	**$1,572,243**	**$1,524,612**	**$1,502,900**
Total Overnight Cost (TOC)	**$2,277,747**	**$1,943,121**	**$1,935,774**	**$1,879,269**	**$1,852,767**
Total As-Spent Cost (TASC) k$	**$2,596,631**	**$2,215,158**	**$2,206,783**	**$2,142,366**	**$2,112,154**

TEA Summary

Exhibit 48 summarizes the plant performance and carbon capture cost for four different cold membrane cases in comparison to Case 12 (amine). Cold membrane process utilized auxiliary power load to drive rotating machinery resulting in higher gross power output. NCCC field data was used for 12” PI-1 Bundle TEA case, 6” PI-1 Bundle TEA case at 90% capture. 1” PI-2 bundle data from the field was used to project 12” Bundle performance. Auxiliary load of the power plant was highly dependent on the CO_2/N_2 membrane selectivity or CO_2 purity from the membrane. As the CO_2 purity increased the auxiliary load resulting from permeate compressor decreased. PI-2 membrane cases had ~3% higher auxiliary load due to lower selectivity of 1” membrane bundle tested in the field compared to PI-1 cases.

Even though the gross power output for cold membrane cases was higher than the amine case; the coal flow rate was 2-5% lower than the amine case. Amine uses significant amount of steam for regeneration resulting in larger overall power plant size and coal flow rate but lower gross power output. The plant efficiency gain was approximately 1-2% points compared to the amine case.

Cost of Electricity (COE) and Levelized Cost of Electricity (LCOE) was calculated using NETL guidelines.[5-9] Increase in COE/LCOE was 61-64% for cold membrane cases compared to 82% for Case 12 (amine). CO_2 capture cost was calculated using Equation 4.

Equation 4

$$CO_2 \text{ Capture Cost} = (COE_{casex} - COE_{case11})/CO_2 \text{ captured}$$

Where COE_{casex} is the COE for the new case (Case 12 or cold membrane case), COE_{case11} is the COE for Case 11, and CO_2 capture is in tonne/MWh

Sensitivity analysis was conducted with +/-20% on the capture equipment cost to assess the impact on the CO_2 capture cost. First of a kind cost and nth of a kind cost was estimated in 2011$ excluding transport, storage and monitoring (TS&M). Nth of kind cost was ~$1/tonne lower for all the cases due to high maturity of the technology. Lower membrane cost due to scaling or lower process contingencies was not included in NOAK estimate. 12” PI-1 bundle case was estimated at the same CO_2 capture cost as 6” PI-1 case (even though the 6” Bundle was more ideal with higher efficiency) due to high bundle installed cost for 6” bundle. PI-2 case 2 was estimated to be $2-3/tonne lower capture cost than PI-1 case due to reduced membrane cost. The nth of a kind cost estimate for PI-2 case 2 was $38-42/tonne compared to $55/tonne for Case 12 amine capture case meeting the DOE target of $40/tonne by 2025.

NOx was mitigated in the carbon capture process using cold membrane based on NCCC flue gas analysis, making SCR redundant. Sensitivity analysis was conducted to study the impact of SCR elimination on carbon capture cost. A cost credit of $80-$270/kW was assumed for capital cost of SCR (Ref. [9]). SCR elimination could result in a CO_2 cost reduction of up to $5-6/tonne. This option needs to be investigated further in future studies.

Exhibit 48. Carbon capture plant performance and cost

	Case 11	Case 12 (Amine)	12" PI-1 bundle	6 " PI-1 Bundle	12" projected PI-2 bundle Case 1	12" projected PI-2 bundle Case 2
Gross Power Output (MW)	580.4	662.8	762	758	787	781
Net Power Output (MW)	550	550	550	550	550	550
Coal Flow Rate (lb/hr)	409,528	565,820	537,678	535,025	555,142	551,290
Net Plant Efficiency	39.3%	28.4%	29.9%	30.1%	29%	29.2%
Increase in COE/LCOE		82%	64%	63%	63%	61%
FOAK ($/tonne of CO_2) *		56	41-46	41-46	40-44	39-43
NOAK ($/tonne of CO_2) *		55	40-45	40-45	39-43	38-42
NOAK w SCR Elimination #			35-40	34-40	33-39	32-37

** Range of CO_2 capture cost for FOAK and NOAK is presented assuming +/-20% on TPC of CO_2 capture equipment cost excluding TS&M*

 # Range of CO_2 capture cost with SCR elimination is presented assuming $80-270/KW credit at plant gate excluding TS&M

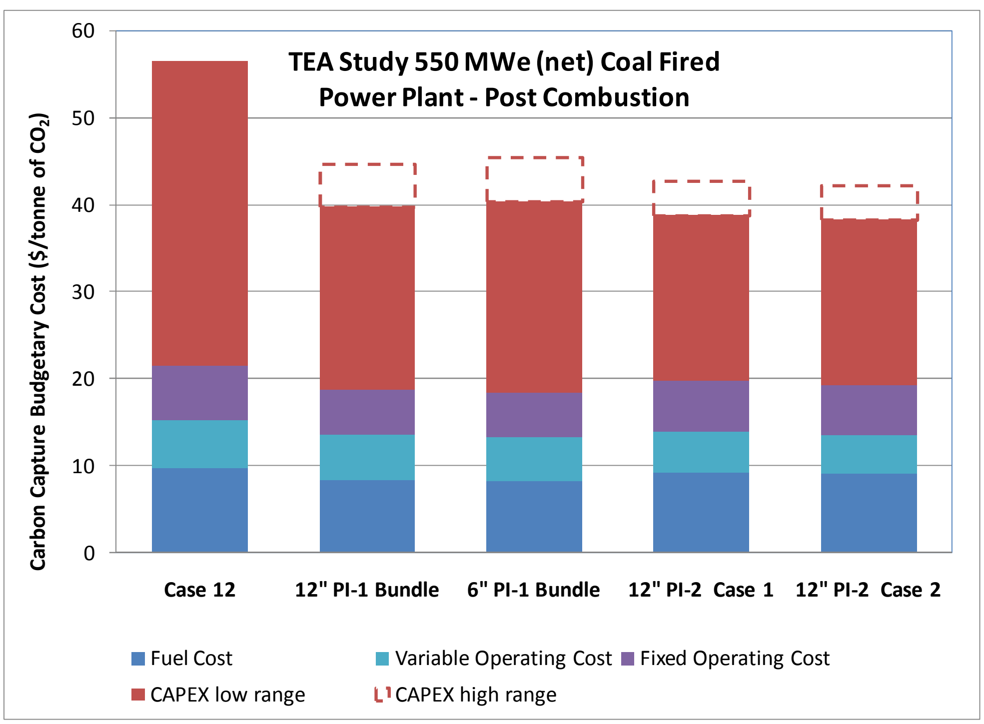


Exhibit 49. Carbon Capture cost breakdown for various cold membrane cases in comparison to Case 12

Exhibit 49 shows the carbon capture cost breakdown in terms of fuel cost, variable operating cost, fixed operating cost and capital cost. Capital cost is shown in the high and low range to show the sensitivity analysis with +/-20% on carbon capture cost. 12" and 6" PI-1 bundle has identical cost breakdown. PI-2 bundle cases has slightly higher fuel cost and operating cost due to larger size power plant but lower capital cost resulting in overall $2-3/tonne saving on the carbon capture cost.

Possibilities to further reduce CO_2 capture cost below the present DOE target will be evaluated in a separate NETL funded project DE-FE0026422 in the following ways:

- PI-2 commercial bundle development and validation of improved membrane performance
- Improvements in the hybrid cold membrane process scheme
- Evaluation of SCR elimination option
- Use of steam instead of electricity to power rotating machinery
- Evaluate possibilities to reduce Nth of a kind estimate

7. EH&S analysis

The Environmental Health and Safety (EH&S) analysis was conducted for a 550 MWe (net) supercritical pulverized coal (PC) power plant integrated with Air Liquide's hybrid cold membrane carbon capture process. A detailed report on this study was submitted in the form of topical report.[11] The emission estimates were based on the process simulations for 12" PI-1 bundle case coupled with an analytical campaign run during skid testing at NCCC. Pollutants from a power plant are released in the form of air emissions, liquid wastes and solid wastes. Air emissions were calculated for SOx, NOx, particulates, Hg and CO_2. The amount of liquid waste water from the process such as from the cooling tower drain and high pressure acidic condensate from the compressor was predicted based on the process simulation and analytical campaign. The amount of solid waste in the form of dust was assessed based on the particulate removal efficiency.

The quantity of waste associated with membrane bundle manufacturing was calculated and was significantly lower compared to the waste generated from the power plant. The waste generated was reported for the initial membrane charge when the plant is installed (including 20% additional bundles for process contingency) and then yearly emissions to account for manufacturing additional bundles needed due to membrane aging.

PC power plant with cold membrane CO_2 capture process

Air emissions are significantly lower for the cold membrane process compared to Case 12 (amine capture) as shown in Exhibit 50. The improvement compared to Case 12, is due to both the reduction in gross power plant size resulting from more efficient CO_2 capture as well as the pre-treatment of flue gas feed to the membrane. The emissions associated with the main streams are summarized below.

Exhibit 50. Emissions from Cold membrane carbon capture process

Contaminants	Case 12 (Amine Capture)	Cold Membrane 12" PI-1 Bundle Case		
Air Emissions (Power Plant with Carbon Capture)				
	kg/GJ ($lb/10^6$ Btu)	**kg/GJ ($lb/10^6$ Btu)**	**Tonne/year (ton/year) 85% CF**	**kg/MWh (lb/MWh)**
SO_2	0.001 (0.002)	0.000 (0.000)	5 (5)	0.001 (0.002)
NO_x	0.030 (0.070)	0.017 (0.040)	1,186 (1307)	0.21 (0.46)
Particulates	0.006 (0.0130)	0.0002 (0.0005)	14 (16)	0.002 (0.005)
Hg	4.91E-7 (1.14E-6)	4.9E-8 (1.1E-7)	3.4E-3 (3.7E-3)	5.9E-7 (1.3E-6)
CO_2	8.8 (20.4)	6.0 (13.984)	413,223 (455,594)	73 (161)
Liquid Waste (Cold Membrane Carbon Capture Process Only)				
LP condensate to Cooling Tower	2.8 - 4.1 m^3/min (726 – 1079 gpm) – pH 6, Hg and Se impurities			
HP condensate(s)	0.26 m^3/min (70 gpm) – pH 0-1, trace level of Hg			
Solid Waste (Cold Membrane Carbon Capture Process Only)				
Dust	268 tonne/year			

- **Air -** Air emissions comprise flue gas after CO_2 capture as well as process streams such as dryer regeneration gas. Overall environmental air emissions are significantly improved with the hybrid cold membrane process with reduced SOx, NOx, particulates, mercury and CO_2 emissions in the treated flue gas compared to Case 12. These impurities are mitigated in the pre-treatment process prior to contacting the membrane. For the SCR + FGD treated flue gas entering the cold membrane CO_2 capture unit:
  - SOx are primarily removed through a caustic wash polishing step.
  - NOx are removed primarily in the high pressure (HP) condensate and dryer. The captured CO_2 will contain the residual NOx.
  - Particulates are eliminated through water condensates and subsequent fine filtration
  - Metals (Hg, Se) are primarily removed in the low pressure (LP) condensate with further Hg reduction in the dryer.
- **Liquid –** Liquid waste is reported from the carbon capture process alone. Liquid wastes from the power plant will not change.
  - Low pressure water condensate from the cold membrane unit is relatively clean with few metal impurities and can be partially recycled to the cooling tower. The necessary blow down water from the cooling tower can be discharged directly or further processed if needed with FGD waste water.
  - Hig pressure condensate downstream of the flue gas compressor knock-out along with a small amount of dryer condensate will be acidic with metal impurities. These streams will need neutralization and possibly further treatment along with FGD waste water. This stream is relatively small compared to the waste generated from the power plant.
- **Solids –** Solid waste is reported from the carbon capture process alone.

- Cold membrane process will include filtration steps to remove dust before the gas is sent to the membrane. Disposal method for dusts collected on the filter will be similar to the bag house dust. The quantity of dust is relatively small compared to the amount of dust from the power plant bag house.
- Dryer bed may need special disposal consideration since contamination by heavy metals is possible. However the dryer bed should last through the life of the plant.
- Obsolete equipment, such as replaced membrane bundles, etc. are considered non-hazardous and can be disposed in a landfill.

Membrane manufacturing

The quantity of waste associated with membrane bundle manufacturing is significantly lower than the waste generated from the power plant. The waste generated is reported for the initial membrane charge when the plant is installed (including 20% additional bundles for process contingency) and then yearly emissions to account for manufacturing additional bundles needed due to membrane aging as shown in Exhibit 51.

Exhibit 51. Emissions from membrane manufacturing process

	Emissions over 3 year (initial Batch)	Yearly Emission for Plant Life (Years 1-30)
Air Emissions (tonne/year)		
VOC	0.16	0.02
HAP	0.01	0.00
Particulate	0.22	0.03
SOx	0.01	0.00
NOx	0.70	0.09
CO_2	2.43	0.30
Liquid Waste (gpm)		
Total Water Discharged with <0.01% solvent	10.05	1.26
Hazardous Waste (gpm)		
water/methanol	0.13	0.016
silicones/octane	0.004	0.001

- **Air –** Air Liquide membrane manufacturing division MEDAL uses a Thermal Oxidizer (TOx) with 99.98% efficiency to treat volatile organic compounds (VOC) and hazardous air pollutants (HAP) before emitting to the atmosphere.
- **Non-hazardous Liquid –** Non-hazardous waste water containing traces of solvent is sent to the city waste water treatment facility.
- **Hazardous liquid waste –** Hazardous liquid waste containing methanol/water mix and silicone/iso-octane mix is generated from the solvent recovery unit which is treated as Resource Conservation and Recovery Act (RCRA) hazardous waste.

- **Solid –** Membrane fibers and bundles not meeting the Quality Control (QC) specification are disposed in a municipal landfill. It is expected that expired bundles can be similarly disposed.

Possibilities to further reduce environmental footprint will be evaluated in a separate NETL funded project DE-FE0026422 using PI-2 bundles. Membrane manufacturing emissions will be reduced by 80% since the PI-2 bundles have 5x higher bundle productivity.

8. Next Phase design

A preliminary design and cost of optimized hybrid cold membrane process for the next phase of technology was conducted. A detailed report on this study was submitted in the form of topical report.[12] Based on an assessment of potential markets and the technology readiness, a 550 tpd CO_2 (25 MWe) plant was determined to be an appropriate size for the next phase. Typically, Air Liquide merchant CO_2 commercial plants for the food and beverage industry are in the size range of 100 - 1,000 tpd. At this size, the scale up of membrane based technology is relatively straight forward due to its modular design. The same commercial membrane bundles will be used as were tested with real flue gas at the National Carbon Capture Center (NCCC). Scale up of the non-membrane based equipment in the hybrid cold membrane process such as the compressor, dryer, turbo-expander, and brazed aluminum heat exchanger is straight forward as these equipment items are widely used commercially by Air Liquide and in the gas industry in general.

The primary focus of this work was on the cold membrane process for CO_2 capture from coal power plants, that being the most promising avenue of carbon capture to reduce greenhouse gas emission world-wide. However, for the next phase design, site-specific and regional CO_2 market conditions may significantly influence the project viability. Therefore, the technology development was proposed in a flexible manner in which carbon capture was considered from a range of possible industrial sources including a coal fired power plant, a natural gas (NG) fired boiler, and a steam-methane reformer (SMR). The equipment quotations were solicited for the natural gas fired case as that required the largest volumetric flow rate to capture 550 tonnes of CO_2. The coal power plant and SMR cases were then evaluated by extrapolation from the NG fired case.

Aspen HYSYS was used to develop process simulations of the cold membrane process, with three different flue gas sources: coal, natural gas, and steam methane reforming. The primary difference between these sources was the feed concentration of CO_2. The requirements for each simulation were the same: 90% CO_2 capture, 99.99% CO_2 purity, and at a CO_2 product pressure of 2,200 psig.

The majority of the variable OPEX was attributed to the power consumption of the rotating machinery such as the feed compressor, permeate compressor, and CO_2 pump. The motor losses were considered to be 8%. The electricity price was assumed to be \$50/MW-h. The waste disposal and utility water costs were assumed to be in the proportion as Case 11 from the NETL baseline study. The fixed OPEX was a combination of labor, membrane replacements, maintenance, waste disposal, and utility water.

A similar costing methodology was employed as that of the NETL baseline used for TEA study. [5-9] The capital cost and operating expense estimates for each case are given in Exhibit 52.

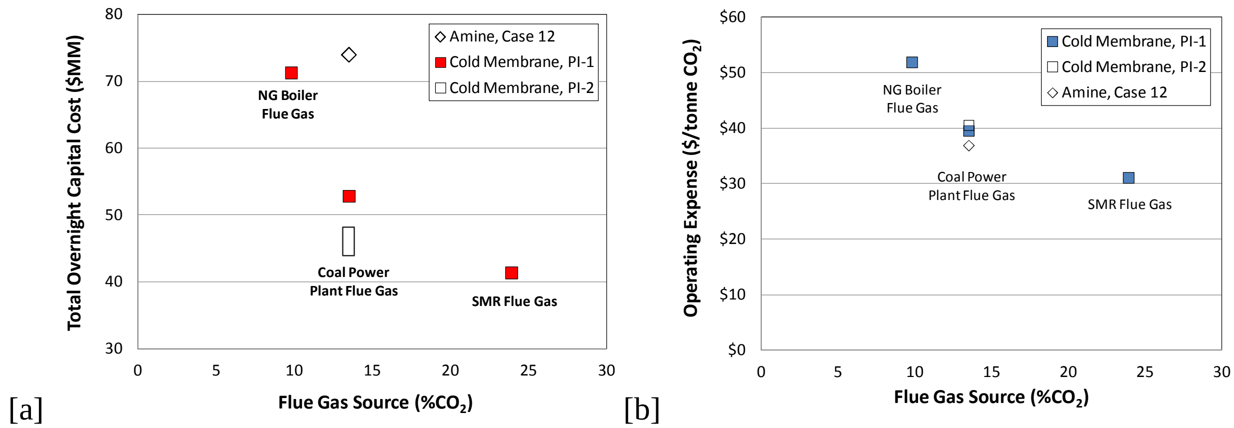


Exhibit 52. Cost details of the cold membrane system sized at 550 tpd, and for different CO_2 containing flue gases [a] Total overnight capital cost [b] Operating expense. Amine capital cost was scaled from ref [4].

The capital cost was the highest for the low CO_2 concentration natural gas boiler source, and the lowest for the high CO_2 concentration steam-methane reformer source since the sizing of most of the equipment was proportional to the flue gas volumetric flow rate. For natural gas flue gas source, a larger total volume of gas was needed to yield the same 550 tpd of CO_2 product. While the major capital cost driver was the rotating equipment, the advanced PI-2 material still resulted in a small cost advantage. The OPEX was also inversely proportional to the CO_2 feed concentration in the flue gas. Overall, the cold membrane technology is expected to be lower cost than a conventional amine system.

The overall Cost of Capture (COC) was estimated by summing the capital and operating contribution. The COC was estimated for two different membrane cases and the conventional amine case as shown in Exhibit 53 for coal fired flue gas. A sensitivity analysis was conducted by using a turnkey factor of 2 and 2.4 to establish the range for the capital portion of the cost based on location and cost variability. This range is typical for construction in the US.

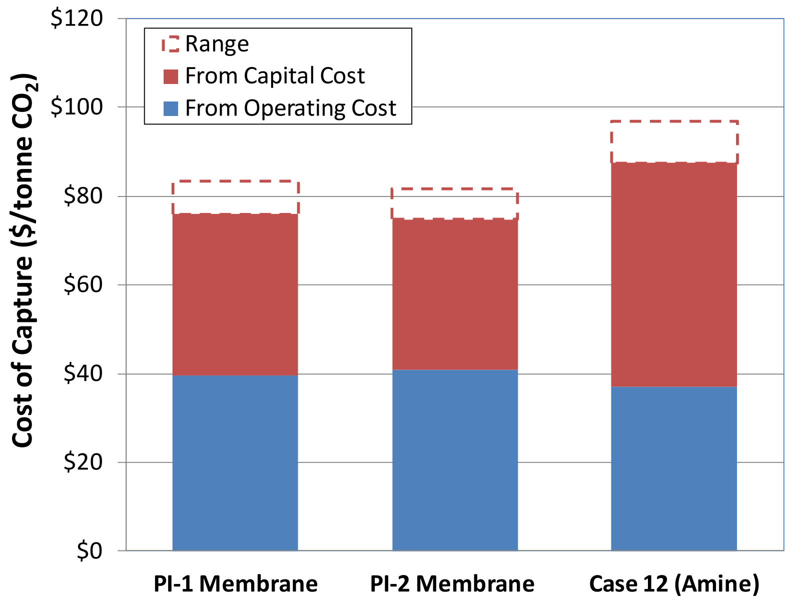


Exhibit 53. Cost of capture for 550 tpd CO_2 from coal fired flue gas using either of two membrane options or the conventional amine process.

The overall cost of capture for the cold membrane process at a 550 tpd scale was estimated to be between $76 and $84/tonne. The cost was slightly less for the novel PI-2 material, and significantly more for the conventional amine system. The contributions of operating and capital costs were almost equal for the cold membrane cases. Case 12 from NETL study was used to scale the cost of amine capture at 550 tpd size. [5-6]

The cold membrane system was approximately $12/tonne lower cost than the amine system, due entirely to a lower capital cost. The physical size of the cold membrane system will be substantially smaller than a similar capacity amine system, resulting in a capital cost advantage.[13] The operating cost of the cold membrane system was slightly higher than the amines since the majority of the energy required was electrical. The primary contributor to the energy requirement of the cold membrane process is compression of flue gas. The amine system had a lower cost of energy primarily due to steam. At a larger scale, the cold membrane process has an advantage of energy integration with the host plant by pre-heating boiler feed water with the heat of compression, lowering the net operating cost significantly as shown in the TEA study. The BFW credit was not accounted in the next phase study due to the size of the plant.

The next step to move this technology forward is to identify a partner site and/or location where flue gas from one of the above sources is readily available and there is a market for the 550 tpd of separated CO_2. Additional funding partners will be identified. Finally, a Front-End Engineering Design (FEED) study will be conducted with consideration for site-specific details.

9. CONCLUSION

In the current project, Air Liquide advanced its post-combustion hybrid cold membrane carbon capture technology from TRL4 to TRL5. Commercial 6” and 12” PI-1 membrane bundles were optimized and next generation novel PI-2 membrane was developed to 1” bundle scale. The membrane bundles were qualified with synthetic flue gas in 0.1 MWe bench scale skid at DRTC and further tested with real coal flue gas at 0.3 MWe FTU at NCCC.

Air Liquide participated in the PO-4 and PO-5 campaigns at NCCC 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 confirm long-term stability of the PI-1 and PI-2 bundles with actual flue gas and evaluate the optimum configuration of bundles.

Key findings from the test were:

- All the bundles exhibited stable performance during long term testing. Specific events, likely associated with hydrocarbon and/or moisture contamination, caused a couple of bundles to lose up to 30% permeance. The bundle experiencing moisture contamination recovered full performance after warm-up; however, the bundle with hydrocarbon contamination could not be recovered.
- The 6” PI-1 bundle exhibited superior membrane separation performance compared to the 12” PI-1 bundle. The 1” PI-1 bundle showed the greatest degree of non-ideality and hence, lowest membrane performance.
- Extensive parametric testing was performed on the 6” PI-1 bundle. Parametric testing showed that the bundle performance can be improved further if operated at -50°C (beyond the baseline performance at -45°C).
- Two bundles in series configuration test with 12” PI-1 bundles did not show superior performance compared to the single bundle configuration based on the test condition.
- PI-2 bundle exhibited 6.5-7.5 times the normalized CO_2 permeance compared to the PI-1 permeance at room temperature. Projected 12” PI-2 bundle productivity was 4-5.5x compared to 12” PI-1 bundle with 61-64% CO_2 permeate purity.
- The analytical campaign confirmed that impurities such as mercury, selenium, and NOx were mitigated to below the analytical measurement detection limit at the membrane feed, due to removal in the pre-treatment, dryer bed and activated alumina bed. Arsenic was below detection limit in all the samples tested. Sulfate levels measured in the condensates were below the blank water sample.

TEA study was conducted following NETL guidelines to calculate the cost of CO_2 capture from 550 MWe net coal power plant with hybrid cold membrane carbon capture.

The predicted CO_2 capture costs were:

- 12” and 6” PI-1 bundle TEA cases resulted in the capture cost of $41-46/tonne for first of a kind (FOAK) estimate and **$40-45/tonne** for nth of a kind (NOAK) estimate, in 2011$ excluding transportation and storage
- PI-2 was projected to result in $2-3/tonne lower capture cost than PI-1 due to reduced membrane cost. The nth of a kind CO_2 capture cost estimate for PI-2 (case 2) was **$38-**

42/tonne, meeting DOE target of $40/tonne by 2025 By comparison, the corresponding estimate for Case 12 amine was $55/tonne excluding transportation at 2011$.

<u>Other TEA findings are outlined below:</u>

- The plant efficiency gain is approximately 1-2% points compared to the amine Case 12.
- Increase in Cost of Electricity (COE)/Levelized Cost of Electricity (LCOE) over Case 11 (no capture) was 61-64% for cold membrane cases compared to 82% for Case 12 (amine).
- Cold membrane cases utilize lower coal flow rate - 5% for PI-1 and 2% for PI-2 cases compared to Case 12 (amine) indicating smaller overall power plant size requirement.
- Auxiliary load of the power plant is highly dependent on the CO_2/N_2 membrane selectivity / CO_2 permeate purity.
- PI-2 membrane cases have ~3% higher auxiliary load due to lower CO_2 permeate purity or membrane selectivity compared to PI-1 cases.
- Nth of kind cost was only ~$1/tonne lower for all the cold membrane cases due to high maturity of the technology components.
- Overall environmental performance is significantly improved with hybrid cold membrane process with reduced mercury, particulates, SOx, NOx emission compared to Case 12. These impurities are mitigated in the pre-treatment process.
- SCR elimination could further result in a CO_2 cost reduction of up to **$5-6/tonne** as NOx and CO_2 can be co-mitigated in the hybrid cold membrane process

The project work showed the potential for significant improvements through initial tests and cost analysis with the novel PI-2 material. The initial PI-2 results showed a step-change in membrane permeance with potential to reduce bundle count by 80%. This enables further cost reduction as shown in the TEA study. In order to capture this value, however, the new material needs to be validated by field testing large bundles representative of commercial production. Lastly, a comprehensive evaluation of novel hybrid processes and costs needs to be completed to ensure optimal use of this improved material performance. Air Liquide is advancing PI-2 membrane to commercial 6” bundle size in DE-FE0026422 in 2015-2018 study funded by NETL.

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12. LIST OF ABBREVIATIONS

AFPC	air-fired pulverized coal plants
AL	Air Liquide
ASU	Air Separation Unit
BAHX	Brazed Aluminum Heat Exchanger
BEC	Bare Erected Cost
BFW	Boiler Feed Water
BP	Budget Period
CAPEX	Capital Expenditure
CFD	Computational Fluid Dynamics
COC	Cost of Capture
COE	Cost of Electricity
CPI	Consumer Price Index
CPU	Compression and Purification Unit
DOE	Department of Energy
DRTC	Delaware Research & Technology Center
E&C	Engineering & Construction
EHS	Environmental Health & Safety
EOR	Enhanced Oil Recovery
FGD	Flue Gas Desulfurization
FOAK	First of a Kind
FTU	Field Test Unit
HAP	Hazardous Air Pollutant
JT	Joule Thomson
LCOE	Levelized Cost of Electricity
µg	microgram (10^{-6} g)
M&EB	Material and Energy Balance
Nm^3	Normal cubic meter
NCCC	National Carbon Capture Center
NETL	National Energy Technology Laboratory
NOAK	Nth of a kind
OPEX	Operating Expenditure
PC	Pulverized Coal
PDS	Process Data Sheets
PI	Polyimide
PGS	Parsons Government Services
PO	Post-combustion (referring to scheduled test windows)
ppm	parts per million (volume)
QC	Quality Control
QGESS	Quality guidelines for energy system studies
QY	Quote Year
R&D	Research and Development
RC	Reference Cost
RCRA	Resource Conservation and Recovery Act
SC	Scaled Cost
SCR	Selective Catalytic Reduction

SMR	Steam Methane Reformer
TASC	Total as-spent cost
TEA	Techno-economic Analysis
TOC	Total Overnight Cost
TPC	Total Plant Cost
TPD	Tonne per day
TRL	Technology Readiness Level
TSA	Thermal Swing Adsorption
TS&M	Transport, storage and monitoring
VOC	Volatile organic compound