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National Carbon Capture Center Test Report: Integrated Membrane Skid Testing at NCCC

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FE0031731: Novel Transformational Membranes and Process for CO_2 Capture from Flue Gas

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Executive Summary

This report summarizes the bench skid testing conducted by The Ohio State University (OSU) under award "DE-FE0031731: Novel Transformational Membranes and Process for CO_2 Capture from Flue Gas" sponsored by the Department of Energy (DOE). The objectives of this project are to develop a cost-effective design and fabrication process for a novel transformational membrane and its membrane modules that capture CO_2 from flue gas. Optimization of the novel transformational membrane, scale-up of the membrane to a prototype size of about 20″ wide in continuous roll-to-roll fabrication, and construction and testing of a bench skid for the integrated membrane process are performed. For the design of this membrane, OSU uses a cost-effective polymer support and coats the support with a thin top layer of the membrane. The simplicity of this membrane design offers a low cost for the membrane element in commercial spiral-wound (SW) configuration. Prototype SW membrane modules (each about 20″ length and 35 m^2 membrane area) are fabricated for testing with simulated flue gas at OSU and with actual flue gas at the National Carbon Capture Center (NCCC), Wilsonville, AL using the skid to capture the CO_2 (at 60–90%) with at least 95% CO_2 purity.

During the field trial at NCCC, two types of SW membrane modules were installed in the integrated bench skid. A SW module with a diameter of 8" and a length of 22" was installed as the primary CO_2 capture stage, which contained 41 membrane leaves with an effective membrane area of ca. 35 m^2. The other SW module contained 14 membrane leaves, resulting in a diameter of 5″, a length of 22″, and a membrane area of ca. 12 m^2. This module further treated the permeate of the first module and enriched it to at least 95% CO_2 purity. The bench skid testing was conducted in the Lab Scale Testing Unit (LSTU) at NCCC from November 1st to December 19th, 2022. During this period, actual natural gas (NG) flue gas and simulated natural gas combined cycle (NGCC) flue gas slipstreams were provided for the skid testing.

First, parametric testing was conducted under the NG flue gas (8.6% CO_2). The skid was operated at three different sets of conditions: (1) 57°C and 0.2 atm permeate vacuum, (2) 67°C and 0.3 atm permeate vacuum, and (3) 77°C and 0.4 atm permeate vacuum, resulting in 99.1%, 95.4%, and 91.0% CO_2 capture degrees, respectively, with dry CO_2 purities all above 95%. Then the steady-state testing was conducted at 77°C and 0.4 atm vacuum. A stable separation performance of 91.0% CO_2 capture with >95% CO_2 purity was achieved. After this, a flue gas shut down was encountered in the packaged NG boiler system. After the NG flue gas returned, the skid showed resilience with the same CO_2 capture and purity results for ca. 390 h under the steady-state conditions. NCCC further provided the simulated NGCC flue gas (4.3% CO_2) by diluting the NG flue gas with air. Additional parametric testing was conducted at (1) 77°C and 0.4 atm permeate vacuum, (2) 67°C and 0.3 atm permeate vacuum, and (3) 50°C and 0.15 atm permeate vacuum, and the skid rendered 90.0%, 95.0%, and 99.0% CO_2 capture degrees, respectively, with dry CO_2 purities all above 95%. Cumulatively, the bench skid was online for >500 h at NCCC with stable CO_2 separation performances. The results achieved were consistent with the testing at OSU by using simulated flue gases, indicating the great potential of the membrane process for CO_2 capture.

1 Project Objectives and NCCC Test Objectives

1.1 Project Objectives

The objectives of this project are to develop a cost-effective design and fabrication process for a novel transformational membrane and its membrane modules that capture CO_2 from flue gas. Optimization of the novel transformational membrane, scale-up of the membrane to a prototype size of about 20″ wide in continuous roll-to-roll fabrication, and construction and testing of a bench skid for the integrated membrane process will be performed. For the design of this membrane, we use a cost-effective polyethersulfone (PES) support and coat a thin top layer of the membrane. The simplicity of this membrane design offers a low cost for the membrane element in commercial spiral-wound (SW) configuration (<$2.00/ft^2). The prototype membrane will be used to fabricate at least 6 pilot-size membrane modules (each about 20″ length and 35 m^2 membrane area) for testing with simulated flue gas at OSU and with actual flue gas at the National Carbon Capture Center (NCCC), Wilsonville, AL using the skid to capture the CO_2 (at 60–90%) with at least 95% CO_2 purity. The prototype membrane modules will be in commercial SW configuration with a minimal pressure drop (<1.5 psi/m).

The work to demonstrate the technology will be performed in two budget periods over a 45-month schedule as follows:

<u>Budget Period 1 (BP1)</u>:

In BP 1, we will optimize the novel transformational membrane aided by advanced computational analysis including density functional theory (DFT), characterize it, test the membrane stability, and design the skid. We will optimize the transformational membrane by taking four approaches, namely (1) investigate carrier structures aided by DFT computations; (2) incorporate nano-fillers; (3) synthesize higher molecular weight polyamine; (4) modify PES support. In addition, we will perform a preliminary techno-economic analysis (TEA).

<u>Budget Period 2 (BP2)</u>:

In BP 2, we will further optimize the membrane, scale it up to the prototype size of about 20 inches wide in continuous roll-to-roll fabrication, fabricate at least 6 prototype membrane modules each with ~20″ length and 35 m^2 membrane area, build the skid, and test it with the modules. Using the skid, we will first conduct the parametric testing using simulated flue gas at OSU and then carry out the parametric testing to achieve >60–90% capture of the CO_2 and the continuous steady-state operation to capture at least 90% of the CO_2 using actual flue gas at NCCC, all with at least 95% CO_2 purity. The modules will be in the commercial spiral-wound configuration for a minimal pressure drop (<1.5 psi/m or 0.103 bar/m). Based on the membrane data obtained, GTI Energy will conduct the final TEA.

In order to achieve the project objectives in BP2, the following tasks are defined:

Task 11.0 – Scale-up Membrane Fabrication
Task 12.0 – Scale-up Membrane Characterization

Task 13.0 – Prototype Membrane Module Fabrication
Task 14.0 – Prototype Membrane Module Testing
Task 15.0 – Skid Testing with Simulated Flue Gas
Task 16.0 – Skid Installation and Commissioning at NCCC
Task 17.0 – Parametric Testing of the Skid at NCCC
Task 18.0 – Continuous Steady Operation of the Skid at NCCC
Task 19.0 – Final Updated Techno-economic Analysis
Task 20.0 – Removal of the Skid from NCCC

1.2 NCCC Test Objectives

The field test conducted at NCCC is based on the testing collaboration agreement between OSU and NCCC and mainly related to Task 16, 17, 18, and 20 of the project. The main objective of the field test is to evaluate the performance of the integrated bench skid with two modules under the actual natural gas (NG) flue gas and diluted NG flue gas produced at NCCC.

2 Technical Background

The average carbon dioxide level in the earth's atmosphere has increased from 280 in the pre-industrial period to 379 ppm in 2005 [1]. A recent study estimates the present concentration at greater than 390 ppm, reaching approximately 400 ppm currently [2]. The increase in CO_2 level is widely accepted as the biggest contributor to increasing global temperatures. Furthermore, the latest report of the Intergovernmental Panel on Climate Change clearly attributes the major cause of CO_2 increase to anthropogenic fossil fuel use [3].

According to the International Energy Agency report on world energy statistics, coal accounted for 25% of the world electricity and 42% of the world CO_2 emissions at about 29 billion metric tons in 2007 [3]. In the absence of any international agreement on greenhouse gas (GHG) reduction, the coal use is projected to increase by more than 55% in 2035 with about 95% of the increase contributed by China and India [3]. The coal-fired electric power sector contributes about 33% of CO_2 emitted by all the fossil fuel sources (coal, petroleum, and natural gas) in the U.S. [3,4]. Thus, it is amply obvious that cost-effective reduction of CO_2 emissions from the coal power plants will be the most important GHG reduction activity in the coming decades.

If the project goals are met, the proposed technology will become available for the cost-effective capture of CO_2 from power plant flue gas. The developed membrane modules and system can be applied in existing and new conventional coal- and natural gas-fired power plants.

Membrane Structure

OSU has developed a highly selective CO_2 capture technology using polymeric facilitated transport membranes (FTMs) on a nanoporous polymer support with a selective amine-containing polymeric cover layer, which operates effectively in flue gas conditions (Figure 1 left). The amine-containing polymer is coated onto a thin-film composite membrane, where CO_2/N_2 separation occurs in the selective amine polymer layer, while the highly gas-permeable nanoporous support provides the necessary mechanical strength for low-cost fabrication and modular separation. Under a transmembrane pressure differential, the selective layer facilitates the dissolution of CO_2 molecules from the feed side through a reaction with the amine carriers, which is accompanied by a weak physisorption as illustrated in Figure 1 (right). The reaction products then diffuse across the membrane and revert to CO_2 molecules via the reverse reaction, eventually releasing to the low-pressure side. However, the permeation of N_2 is slow due to a lack of reactive diffusion. Consequently, the disparate permeation rates lead to CO_2 permeability and CO_2/N_2 selectivity that are usually more than three-time greater than those exhibited by membranes relying on size or condensability discrimination via the solution-diffusion mechanism.

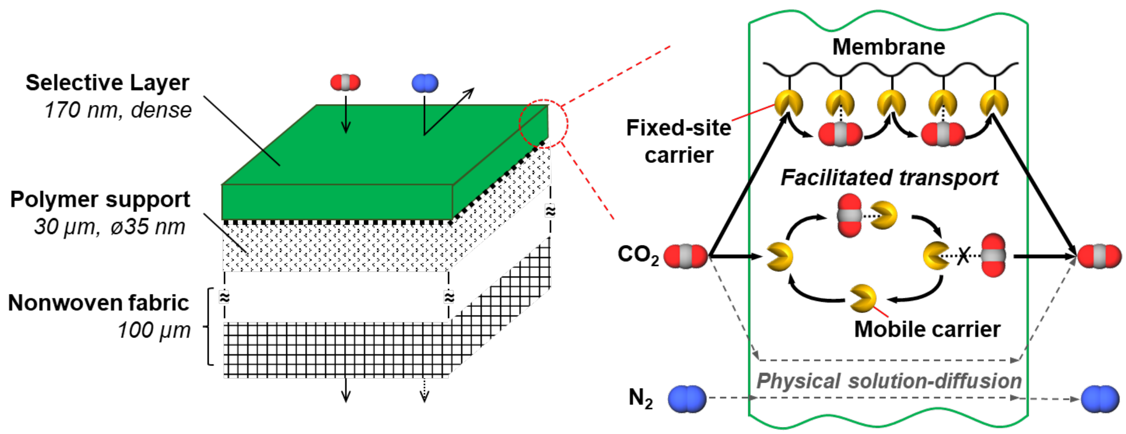

Figure 1. Thin film composite membrane structure and facilitated transport mechanism in membrane.

SW Membrane Element Fabrication

The SW membrane element was prepared according to the following procedure as shown in Figure 2. A carrier layer is taped to the stainless-steel permeate tube, which is used to support all the membrane leaves and provide tension during element rolling. Then, two epoxy glue lines are placed manually using a glue applicator along the sides of the carrier layer. The glue lines are kept 0.25″ away from the long edges of the carrier layer. The third glue line on the carrier layer is placed parallel to the permeate tube, and it is 38″ away from the tube so it is under the first membrane leaf.

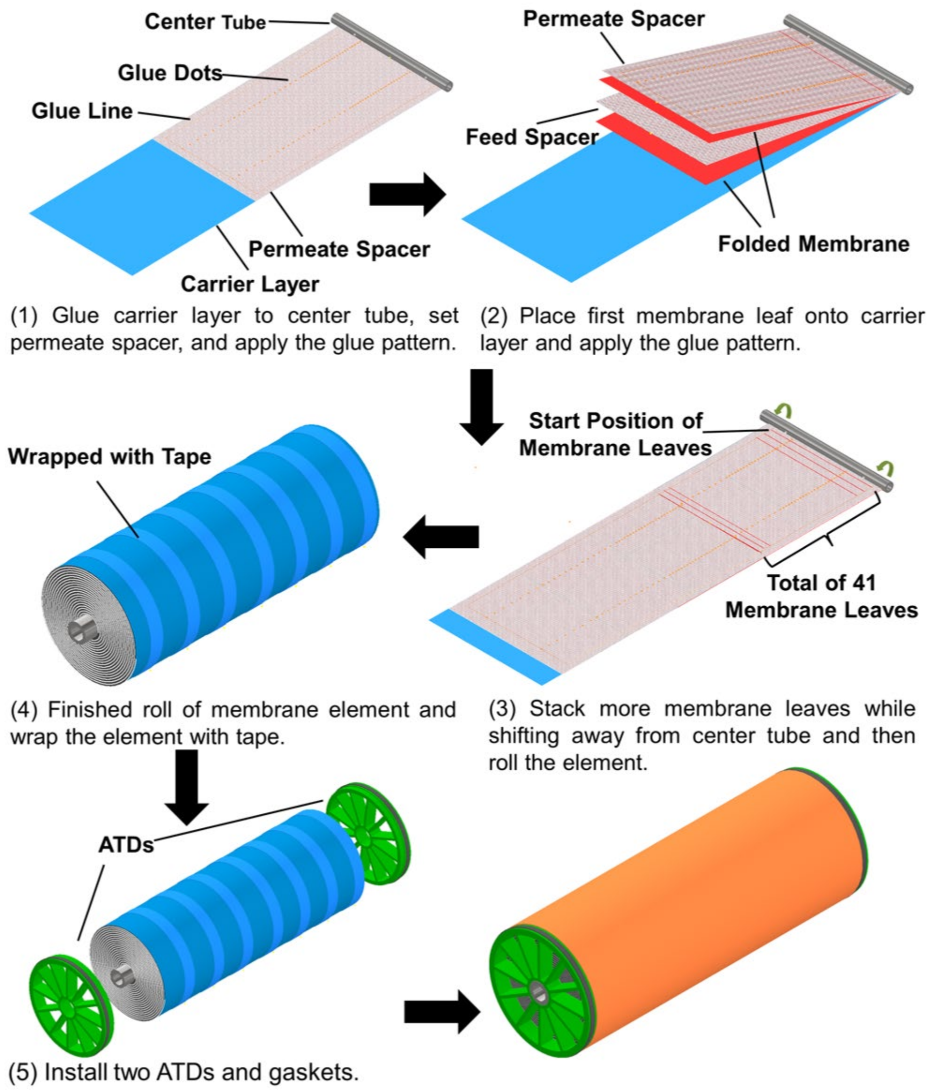

Figure 2. SW element fabrication procedure.

A piece of a scale-up membrane of 20″ × 72″ is folded in half, with the selective layer of the membrane facing inward, and the feed spacer is sandwiched in between. Glue is applied along the inner side of the fold to prevent leakage from the crease, and a permeate is put above the folded membrane. The folded membrane, with the feed and permeate spacers, is treated as one single membrane leaf. The first membrane leaf is placed about 3″ away from the permeate tube, with the folded side of the membrane pointing towards the tube. Next, another layer of three glue lines is applied onto the permeate spacer; the two side glue lines are 0.25″ away from the edges. The third glue line is applied parallel to the membrane leaf's open end and is 0.5″ away from the edge. Next, 40 additional membrane leaves are placed on top of the first leaf, each positioned 0.5″ away from the permeate tube and affixed using the same glue lines and glue dot pattern applied on each leaf, respectively. Finally, the stack of membrane leaves is rolled by using a rolling machine and then the membrane element is wrapped with an outer-wrap tape.

Trimming is then carried out to keep both ends of the rolled membrane leaves flat. Two anti-telescoping devices (ATDs) with 1″ thickness are glued to the permeate tube. Carbon fiber with epoxy glue is applied on the element's outer surface to serve as fiber-reinforced plastic (FRP). The whole element is sat overnight at room temperature for the glue to set. Further curing of the glue is done by placing the element in a conventional oven at 80°C for 24 h.

As shown in Figure 3, the cylindrical housing consists of a main body and two end caps that direct the feed and permeate streams. The fabricated membrane element is fitted tightly into the housing body. Two face-compression O-rings are set in the grooves on each of the end caps to facilitate the sealing. The inner O-ring is pressed against the end surface of the permeate tube to separate the permeate channel from the feed channel. The outer O-ring is positioned in between the flanges of the end cap and the housing body to prevent any leaking of the feed gas into the surroundings. The gaskets on the ATDs are used to stop the bypass of feed gas and hence enhance the CO_2 transport in the element.

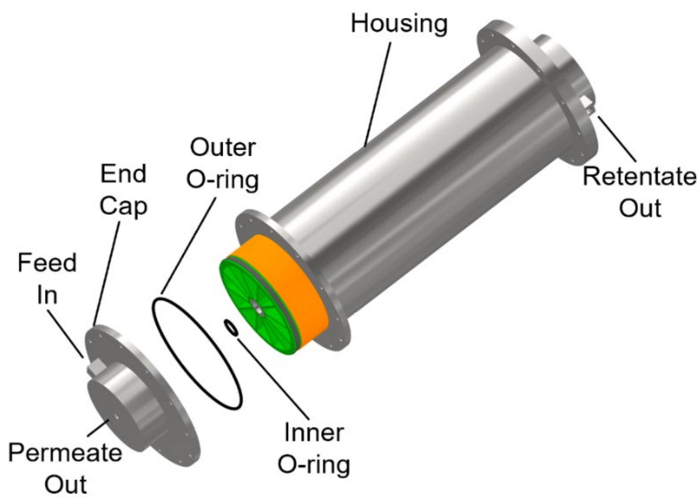

Figure 3. Installation of membrane element into SW module housing.

Two types of spiral-wound membrane elements were installed in the integrated bench skid. A countercurrent element was rolled with a diameter of 8″ and a length of 22″ using 41 membrane leaves of 36″ in length with a width of 20″. The total membrane area was about 35 m^2. This membrane element was installed into the first-stage membrane housing made of stainless steel. Another element for a vacuum permeate operation with a diameter of 5″ in diameter and a length of 22″ using 14 membrane leaves was installed into the second-stage membrane housing. All modules were tested at OSU prior to the field test with simulated flue gas. Figure 4 shows the end and side views of the 8″-diameter SW element fitted tightly into the housing.

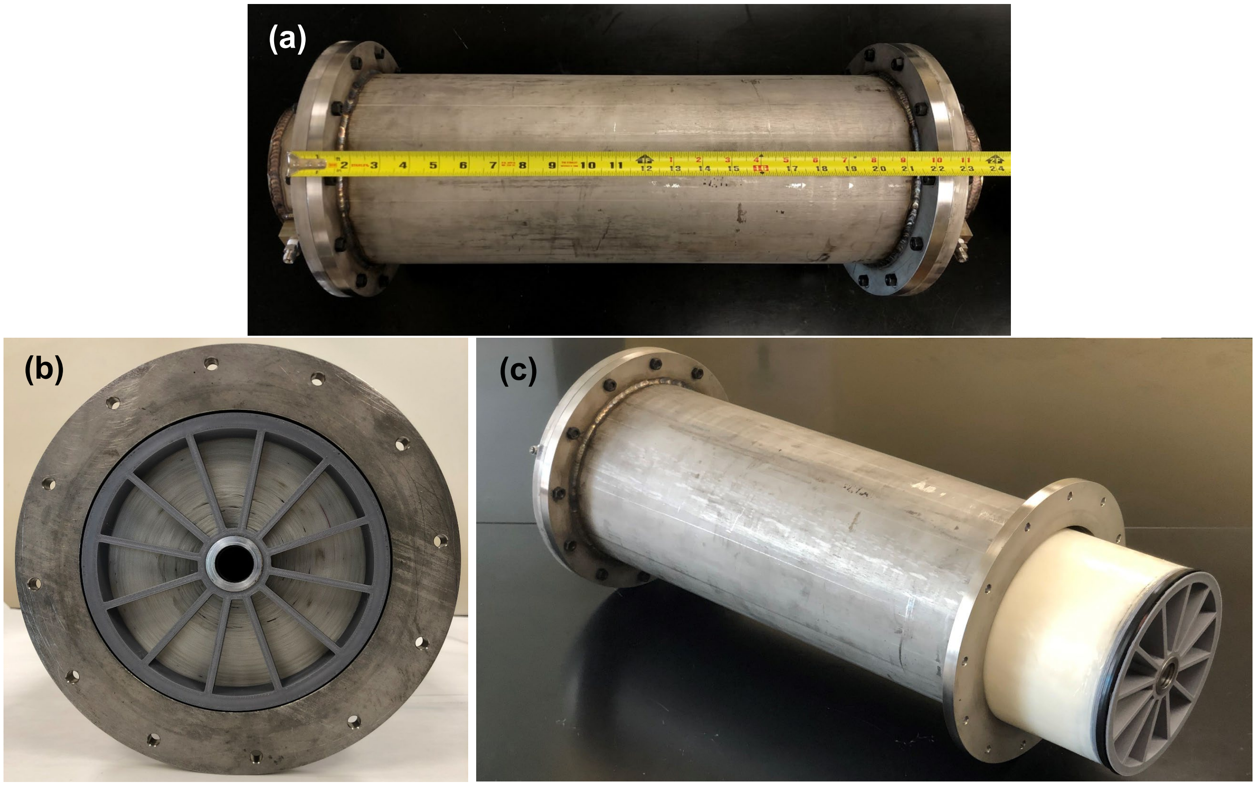

Figure 4. (a) Photo of prototype SW membrane module; (b) end view and (c) side view of the element fitted in the housing.

When the coal flue gas flows through the feed spacers in the membrane module, the CO_2 molecules preferably permeate through the membrane and eventually are collected by the permeate spacers to the central tube (Figure 5 left). For a given membrane area in a SW element, the CO_2 permeation rate largely depends on the CO_2 permeance of the membrane. Under DOE projects DE-FE0007632 and DE-FE0026919, OSU developed the 1st Generation (Gen I) FTM that exhibited a high CO_2 permeance of 1450 GPU (1 GPU = 10^{-6} cm^3(STP) cm^{-2} s^{-1} cmHg^{-1}) with a CO_2/N_2 selectivity >180 at 67°C. Under DE-FE0031731, OSU further developed the Gen II and Gen III FTMs with advanced CO_2 carriers, enhancing the CO_2 permeances to 3500 and 4200 GPU at 77°C, respectively, while maintaining high CO_2/N_2 selectivities of >160. All Gen I, II and III FTMs exceed the Robeson upper bound [5] in terms of CO_2/N_2 separation performance (Figure 5 right).

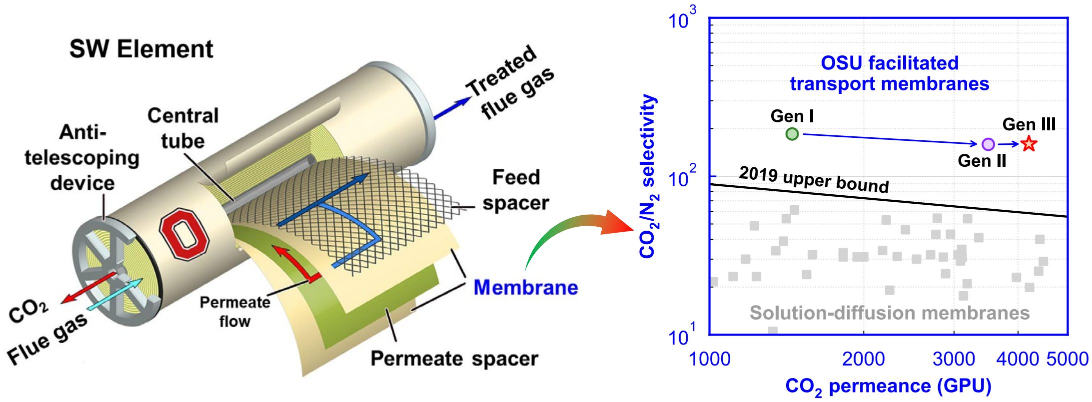

Figure 5. SW membrane element structure (left) and performance of OSU's transformational FTMs vs. the Robeson upper bound (right).

3 Membrane Skid

An integrated bench skid with two SW modules was constructed and installed at NCCC in November 2022. The block flow diagram of the two-stage membrane skid is shown in Figure 6, which was used to measure the transport performance of the SW membrane modules discussed above. The SO_2 and NO_2 in the coal flue gas are polished to 3 ppm each by 20 wt.% NaOH solution (established technology), followed by a filter for particulate removal. For the NG flue gas at NCCC, no polishing was performed. The conditioned flue gas is then compressed to 3.5–4.5 atm and cooled to 57–77°C. This pressurized stream is passed to the first membrane stage as feed. This step separates the feed gas into a CO_2-depleted retentate stream, usually containing ca. ~1% CO_2 and ca. 92% N_2, and a CO_2-enriched permeate stream, usually ~30–37% CO_2 on wet basis. The retentate is expanded by a back pressure regulator, and 0–15% of it is recycled to the permeate side of the first membrane stage as sweep gas. The remaining retentate, which has had 90% of the CO_2 from the flue gas removed, is discharged. The permeate stream is cooled to knock out the excessive water vapor. This stream is then pressurized to 3.5–4.5 atm and passes as feed to the second membrane stage. CO_2 permeates preferentially via the membrane, and >95% CO_2 purity, on dry basis, is achieved in the permeate. The permeate stream goes through an after-cooler and a water knockout, and then is discharged by a vacuum pump. The retentate stream of the second membrane stage is recycled to the feed of the first membrane stage.

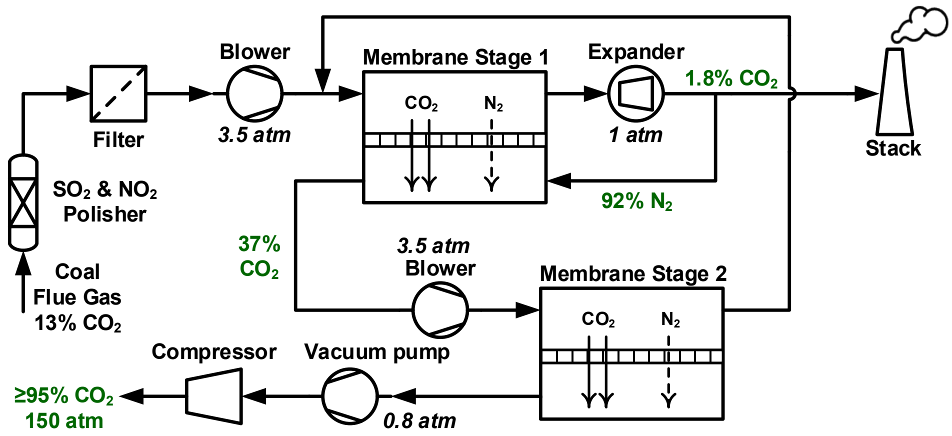

Figure 6. Schematic of the two-stage membrane process.

Figure 7 shows the setup of the integrated bench skid at NCCC. Due to the compact design and thereby the small footprint of the skid, the system was located indoors in the Lab-scale Testing Unit (LSTU) at NCCC. A flue gas slipstream was brought from the natural gas (NG) boiler to the skid as the feed gas. Utility supplies, including demineralize water, electricity, and analytical gases for gas chromatography analysis, were also connected. Necessary equipment grounding was also carried out by the NCCC electricians. An ⌀8″, 35-m^2 SW element was installed into the first-stage membrane housing and a ⌀5″, 12-m^2 SW element was installed into the second-stage membrane housing. Afterwards, a thorough leak check was conducted to ensure (1) the membrane elements were properly installed, (2) the system is gas tight, and (3) the pressure safety valves worked properly. The system was then preheated to 57°C, and the temperature control was closely monitored for 2 h to verify the electric resistance heating setup and the thermal insulation.

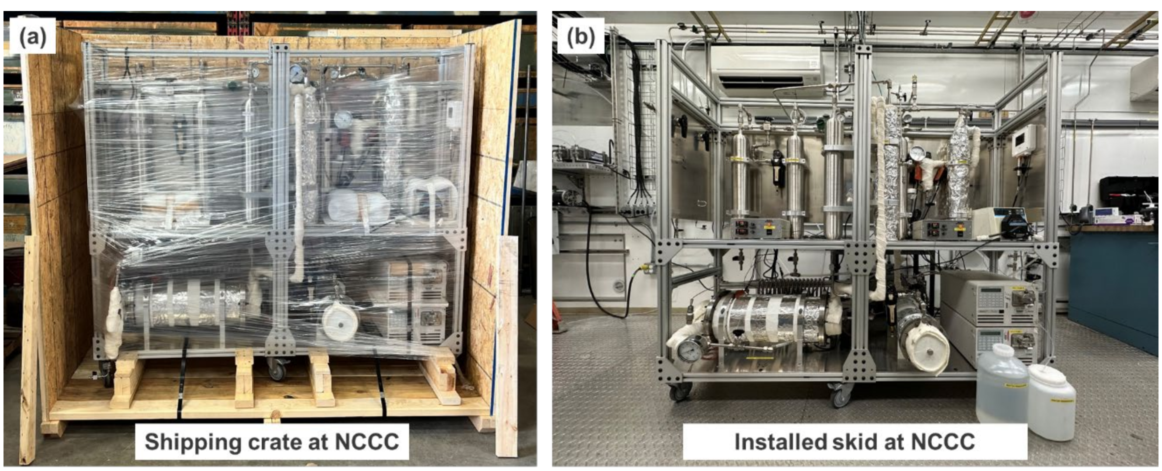

Figure 7. (a) Shipping crate of the bench skid and (b) the installed skid at NCCC.

4 Results and Discussion

4.1 Skid Testing with Simulated Flue Gases at OSU

Prior to the field trial, the integrated bench skid was tested at OSU with a simulated coal flue gas containing 13.0% CO_2, 55.4% N_2, 15.0% O_2, 16.6% H_2O, 3 ppm SO_2, and 3 ppm NO_2 at 77°C. The results are shown in Figure 8. As shown, a CO_2 capture degree of 91.0±0.6% and a CO_2 purity (dry basis) of 95.5±0.3% were achieved. The minor components in the CO_2 product included 4.5% N_2, 9 ppm O_2, 13 ppm SO_2, and 11 ppm NO_2, all on dry basis. The concentrations of these minor components met the CO_2 transportation standard through carbon steel pipeline (i.e., 4–5% N_2, <10 ppm O_2, <100 ppm SO_2, and <100 ppm NO_x) [6]. Subsequently, we conducted the parametric testing and achieved 95% and 99% capture degrees, both with >95% dry CO_2 purity, for 50 h using the simulated coal flue gas. Afterwards, the skid was challenged by a simulated natural gas combined cycle (NGCC) flue gas containing 4.1% CO_2, 64.3% N_2, 15.0% O_2, 16.6% H_2O, and 3 ppm NO_2 at 77°C. Although the CO_2 concentration was significantly lower than the simulated coal flue gas, the skid still demonstrated a stable 90.5% CO_2 capture with 95.6% dry CO_2 purity for 350 h. In the course of the 1200-h testing, the skid separation performance remained stable. The testing with simulated flue gases has demonstrated not only the good stabilities of both the membrane modules and the 2-stage membrane process, but also the capture targets of both a >90% CO_2 capture degree and a >95% CO_2 purity.

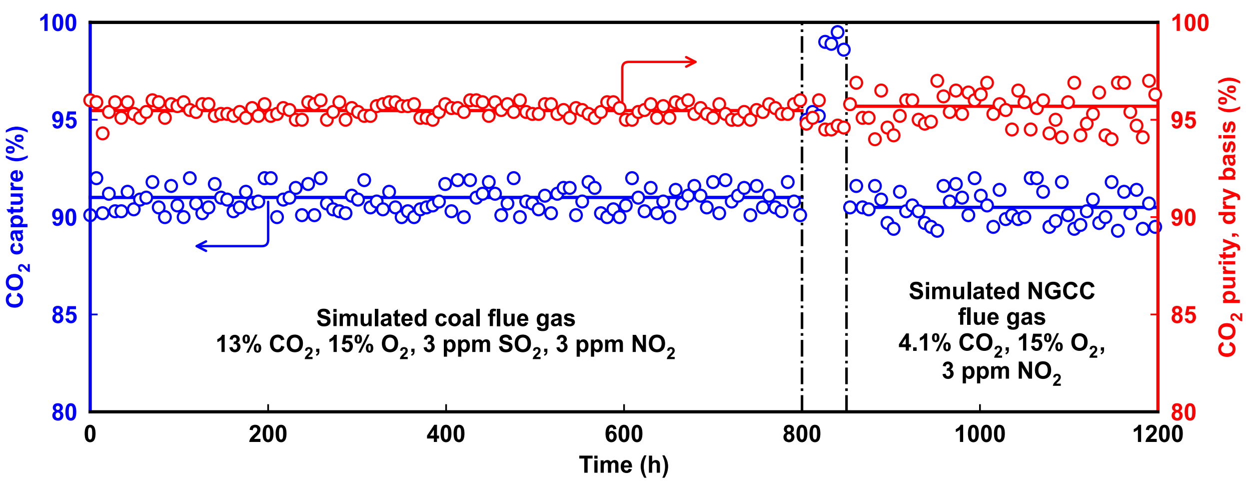

Figure 8. Test results of integrated bench skid with simulated coal and NGCC flue gases at OSU.

4.2 Skid Testing at NCCC

Parametric Testing of the Skid at NCCC

After the skid commissioning was completed at NCCC, parametric testing was conducted under the actual NG flue gas containing 8.6% CO_2, 86.2% N_2, and 5.2% O_2 (on dry basis). Figure 9 summarizes the testing results during the parametric testing. The SW modules were operated at (I) 57°C and 0.2 atm vacuum, (II) 67°C and 0.3 atm vacuum, and (III) 77°C and 0.4 atm vacuum, resulting in 99.1%, 95.4%, and 91.0% CO_2 capture degrees, respectively, with dry CO_2 purities all above 95%. The (III) set of operating conditions was chosen for the steady-state operation.

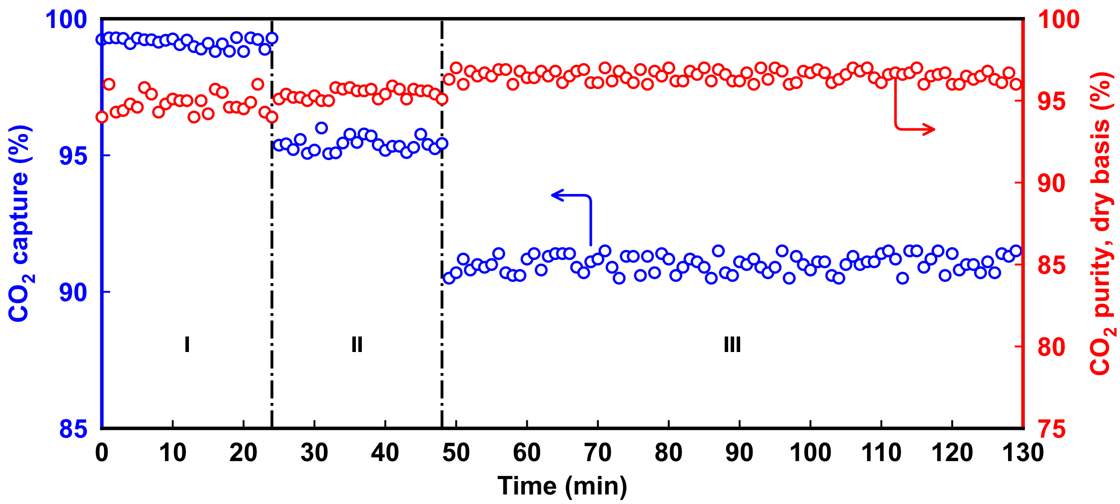

Figure 9. Parametric testing results of integrated bench skid with NG flue gas at NCCC.

Steady-State Operation with NG Flue Gas

After the parametric testing, a flue gas shutdown was encountered. After the NG flue gas returned, the skid was operated at steady state under the (III) set of conditions. As shown in Figure 10, a stable separation performance of 91.0% CO_2 capture with 96.5% dry CO_2 purity was achieved for ca. 390 h. During the steady-state testing, the NG boiler tripped temporarily for a second time, which only led to a short period of low flue gas supply and did not affect the skid performance.

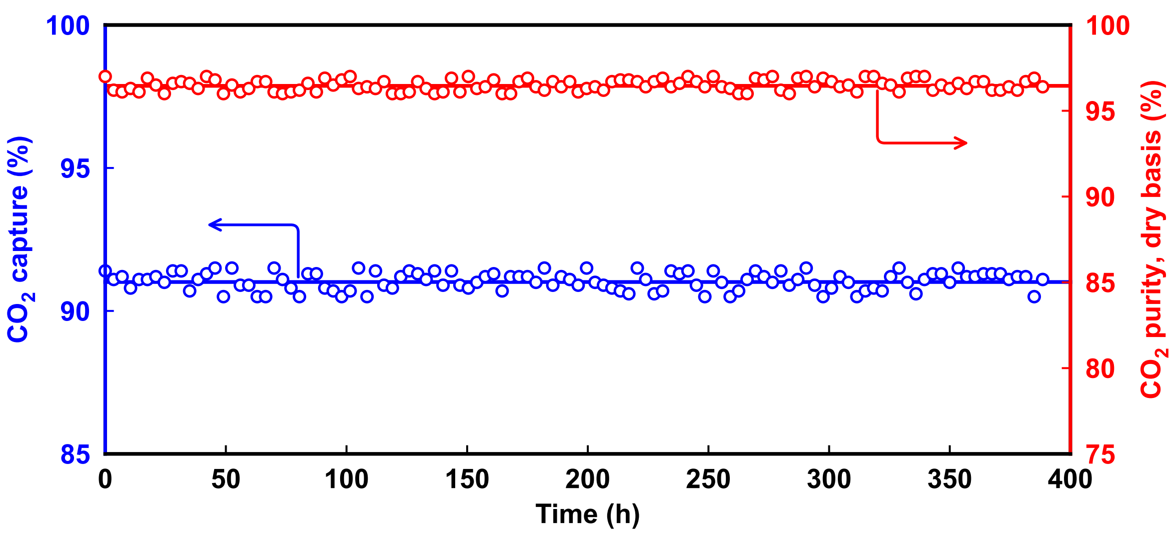

Figure 10. Steady-state testing results of integrated bench skid with NG flue gas at NCCC.

Additional Parametric Testing with Diluted NG Flue Gas

Following the steady-state operation, OSU conducted additional parametric testing when NCCC diluted the NG flue gas by air to simulate the NGCC flue gas with a 4.3% CO_2 concentration. At (IV) 77°C and 0.4 atm vacuum, (V) 67°C and 0.3 atm vacuum, and (VI) 50°C and 0.15 atm vacuum, the skid rendered 90.0%, 95.0%, and 99.0% CO_2 capture degrees, respectively, with dry CO_2 purities all above 95% as shown in Figure 11.

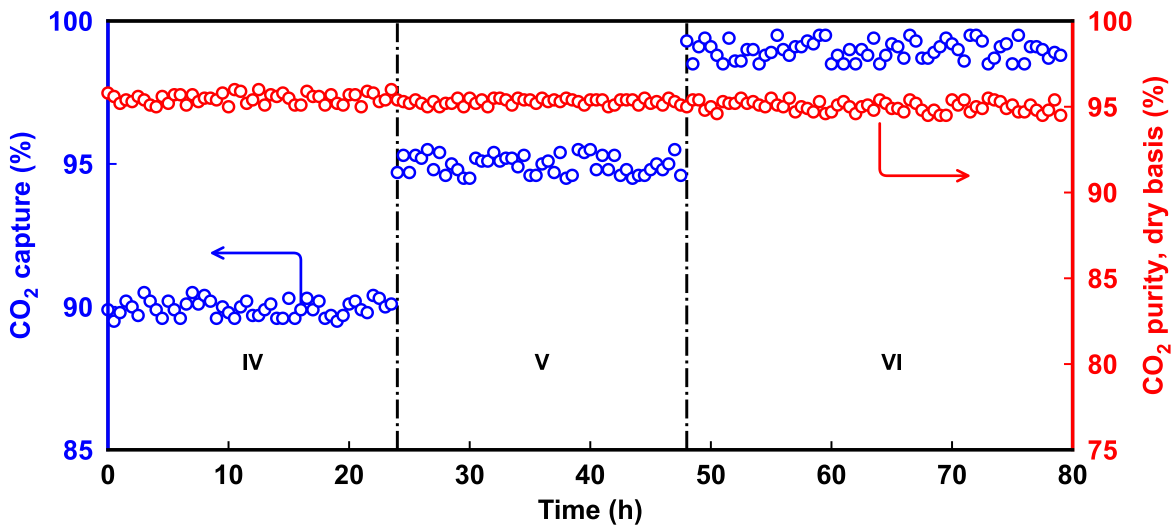

Figure 11. Parametric testing results of integrated bench skid with diluted NG flue gas at NCCC.

5 Conclusions and Future Work

During November 1st to December 19th, 2022, the field trial campaign at NCCC showed that stable FTM module performance for carbon capture from NG flue gas can be achieved. An integrated bench skid with two-stage membrane process was developed for this project and were shown to operate efficiently. Two types of SW membrane elements were installed in the integrated bench skid. A countercurrent element was rolled with a diameter of 8″ and a length of 22″ using 41 membrane leaves of 36″ in length with a width of 20″. The total membrane area was about 35 m^2. This membrane element was installed into the first-stage membrane housing made of stainless steel. Another element for a vacuum permeate operation with a diameter of 5″ in diameter and a length of 22″ using 14 membrane leaves was installed into the second-stage membrane housing, and the membrane area was about 12 m^2. Important for multi-year operations, the modules also demonstrated stable performance over flue gas shutdown and restart of the testing system.

The separation performance of the bench skid tested at NCCC reproduced results that were obtained in the OSU lab in terms of CO_2 capture degrees and CO_2 purities. The steady-state testing under the actual NG flue gas was reached with an average CO_2 capture degree of 91.1% and 96.5% dry CO_2 purity. Parametric testing of the skid was also conducted under the NG flue gas and the diluted NG flue gas, both of which demonstrated 90–99% CO_2 capture degrees with >95% dry

CO_2 purities. The data obtained from this campaign provide a basis for the design and fabrication of full commercial-size SW module with a membrane area of ca. 100 m^2. Lessons learned from the field trial will be applied to the design and construction of engineering- to large pilot-scale membrane skid for 90+% carbon capture.

6 Acknowledgments

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