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National Carbon Capture Center Field Test Report

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FE0007632: Novel Inorganic/Polymer Composite Membranes for CO_2 Capture

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1 Project Objectives and NCCC Field Test Objectives

1.1 Project Objectives

The objective of this project is to develop a cost-effective design and manufacturing process for new membrane modules that capture CO_2 from flue gas in coal-fired power plants. The membrane consists of a thin selective layer containing inorganic, embedded in a polymer structure so that it can be made in a continuous manufacturing process. It is incorporated in membrane modules (e.g., spiral-wound), for bench scale tests at simulated flue gas conditions. Using the modules for post-combustion CO_2 capture is expected to achieve the DOE target of <$40/tonne CO_2 captured for 2025.

Currently, the project is in the Budget Period 3 (BP 3), which includes the fabrication of the scale-up membranes into three prototype membrane modules for continuous testing with simulated or real flue gas. In order to achieve the project objectives in BP3, the following tasks are defined:

Task 17 – Project Management and Planning

Task 18 – Further Improved Membrane Synthesis

Task 19 – Membrane Characterization

Task 20 – Optimized Prototype Membranes Fabrication

Task 21 – Optimal Prototype Membrane Characterization

Task 22 – Prototype Module Fabrication

Task 23 – Membrane Module Testing

Task 24 – Use and Refining of System and Cost Analysis

1.2 NCCC Field Test Objectives

The field test conducted at the National Carbon Capture Center (NCCC) in Wilsonville, AL is based on the testing collaboration agreement between the Ohio State University (OSU) and NCCC and mainly related to Task 22 and Task 23 of the project. The main objective of the field test is to evaluate the performance of the spiral-wound membrane module with the actual flue gas at the NCCC as the feed gas in comparison with that obtained using the simulated flue gas in the OSU lab. Particularly, the effect of the impurities in the actual flue gas such as O_2, SO_2, and NO_x is investigated. Additionally, the preliminary stability of the spiral-wound membrane module can also be explored.

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 [2]. The increase in CO_2 level is widely accepted as the biggest contributor to global warming [1,3]. The report of the Intergovernmental Panel on Climate Change clearly attributes the major cause of CO_2 increase to anthropogenic fossil fuel use [1].

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 [4]. 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 [5]. 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. [6]. 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.

The recent progress of this project reported elsewhere has shown a good potential to achieve the target set by DOE [7,8]. If the project goals are met, the proposed technology will become available for the cost-effective capture of CO_2 from flue gas in coal-fired power plants. The developed membrane modules and system can be applied in existing and new conventional coal-fired power plants.

Spiral-Wound Membrane Element Fabrication

The membrane element was prepared according to the following procedure. Firstly, the 30-inch of the scale-up membrane was folded and the permeate spacer is inserted in between. An epoxy glue was used to seal the membrane leaf at three sides and to prepare the glue lines required to enable the cross-current flow inside the permeate channel. Afterwards, the membrane leaf was glued and taped to the central tube, and the feed spacer was placed on the membrane leaf. Finally, the membrane leaf was rolled by using the rolling machine that we developed at the Ohio State University, and then the membrane element was wrapped with an outer-wrap tape.

Each of the spiral-wound membrane elements was rolled with about 1.8" in diameter (using a 1.5" OD central tube) by 12" in length using a single membrane leaf of 15" in length with a width of 12". The membrane leaf consisted of two pieces of the zeolite/polymer composite membrane (each at 15" in length with a width of 12"), a permeate spacer in between these two pieces of the composite membrane, and a feed spacer. The length of the membrane element was about 14 inches, and the total membrane area was about 300 cm^2.

Spiral-Wound Membrane Module: New Design

Commonly encountered in conventional spiral-wound membrane modules is a major drawback involving the feed gas bypass. The ineffective sealing of the end-cap flanges associated with the conventional spiral-wound membrane module has led to significant “bypass” of the feed gas to the feed outlet (retentate) without even flowing between the wrapped membrane layers. This has resulted in low CO_2 permeance (lower than the flat-sheet membrane performance). In principle, if the issue of the feed gas bypass is resolved, the performance and quality of the spiral-wound membrane element/module fabrication will be much improved.

The quality of the spiral-wound membrane element fabrication was improved by optimizing the glue-line procedure. The new procedure aided in adequate sealing of the non-woven fabric in the membrane leaf and sealing between the membrane leaf and the central tube. The quality of fabrication was successfully improved as the new elements during testing demonstrated essentially no leakage. The image of the fabricated spiral-wound membrane element is shown in Figure 1.

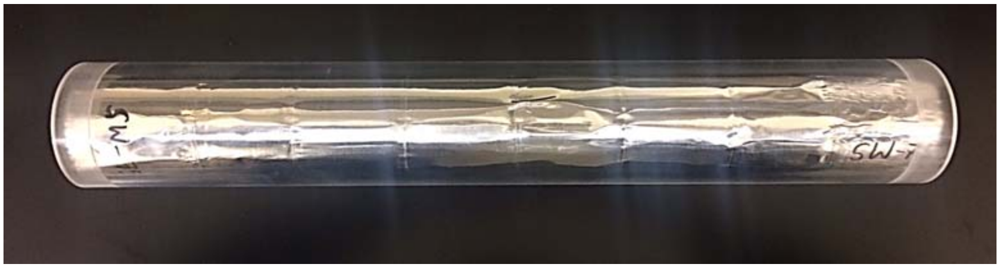

Figure 1. Spiral-wound membrane element fabricated.

The spiral-wound membrane element was eventually loaded in the housing to become the membrane module. Figure 2 shows the fabricated membrane module. The membrane module was used for testing the transport performance. The new design along with the improved glue application procedure successfully helped in enhancing the transport by demonstrating ~ 800 GPU of CO_2 permeance and > 200 CO_2/N_2 selectivity using the thin-film composite amine-containing polymer cover layer on the ZY/PES substrate for the membrane element (Approach 1).

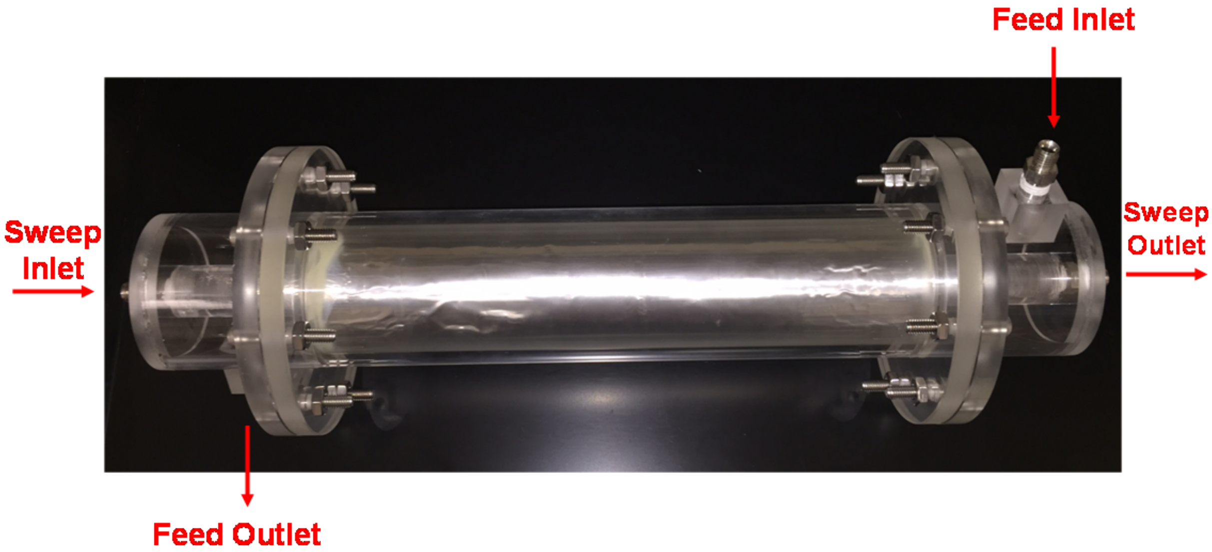

Figure 2. Spiral-wound membrane module consisting of the membrane element inside a housing.

The pressure drops of the feed and sweep gas along the spiral-wound membrane element can be reduced significantly by using a thicker permeate spacer. Significant efforts have been focused on the preparation of membrane elements with a thicker permeate spacer (> 20 mils) and followed by flow rates optimization for the respective permeate spacer thicknesses.

3 Experimental Procedure

3.1 Membrane Module Testing

The gas permeation unit shown schematically in Figure 3 is used to measure the transport performance of the spiral-wound membrane module discussed above. Figure 4 shows the setup of the gas permeation unit inside the Analytical Lab at NCCC. The unit consisted of mass flow controllers, water pumps and humidifiers to simulate the actual gas compositions in the gas mixture. The membrane module for testing was placed inside the oven of the unit as shown in Figure 5. That is, this membrane module was placed as shown in Figure 3 schematically inside the oven of the unit. The feed and sweep gases entered the module in a countercurrent configuration. During the testing, the dry feed gas flow rate used was 1000 cc/min at 1.5 psig, and the dry sweep gas flow rate used for the permeate side was also 1000 cc/min at 1 psig. Both the feed gas and the sweep gas were humidified with water vapor by injecting controlled flow rates of water into them to obtain the controlled concentrations of water vapor in them. At the typical flue gas temperature of 57^{o}C, the saturated water vapor concentration in each of the feed and sweep gas streams is 17%. This temperature was used for the module testing at NCCC.

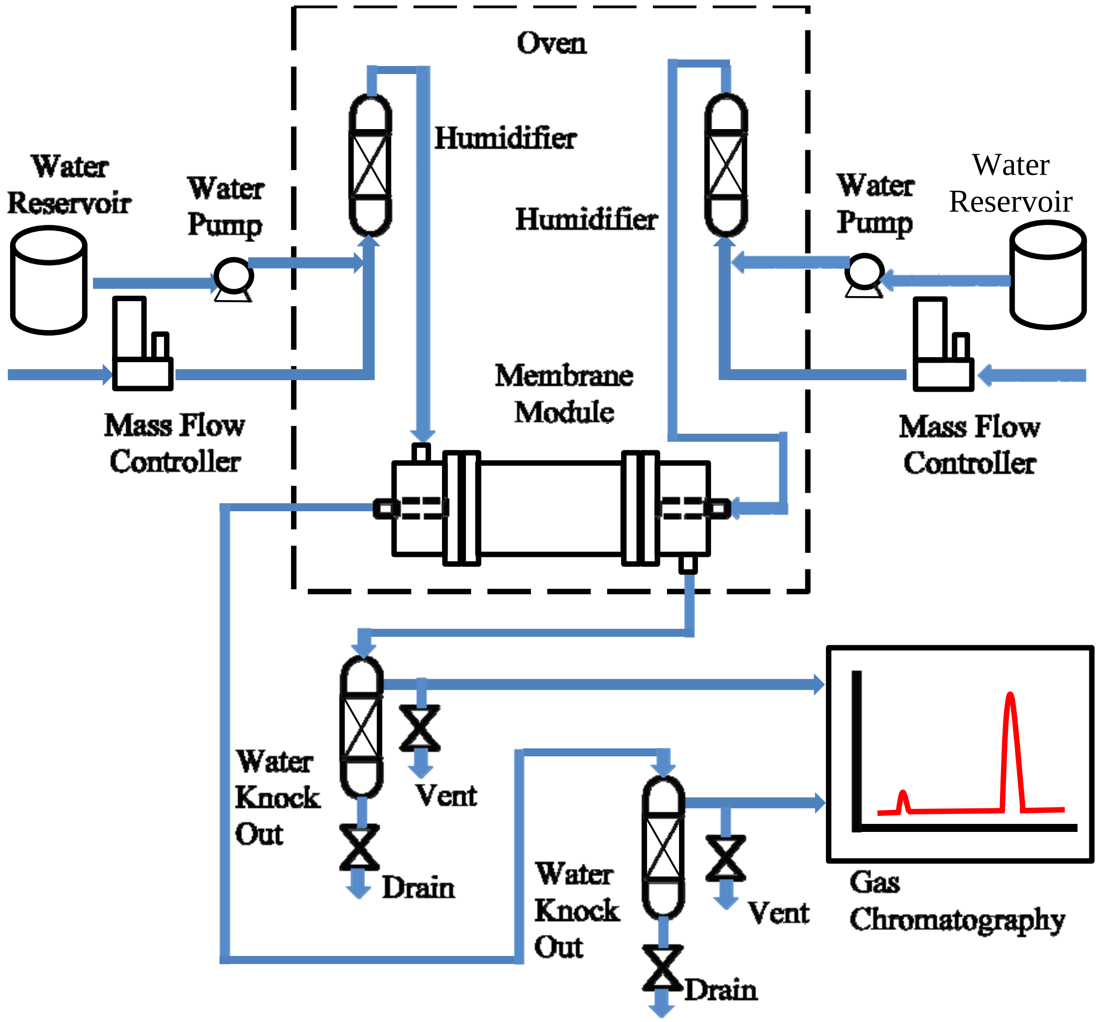

Figure 3. Schematic of the gas permeation unit for gas transport measurements.

Figure 4. The setup of the gas permeation unit at NCCC.

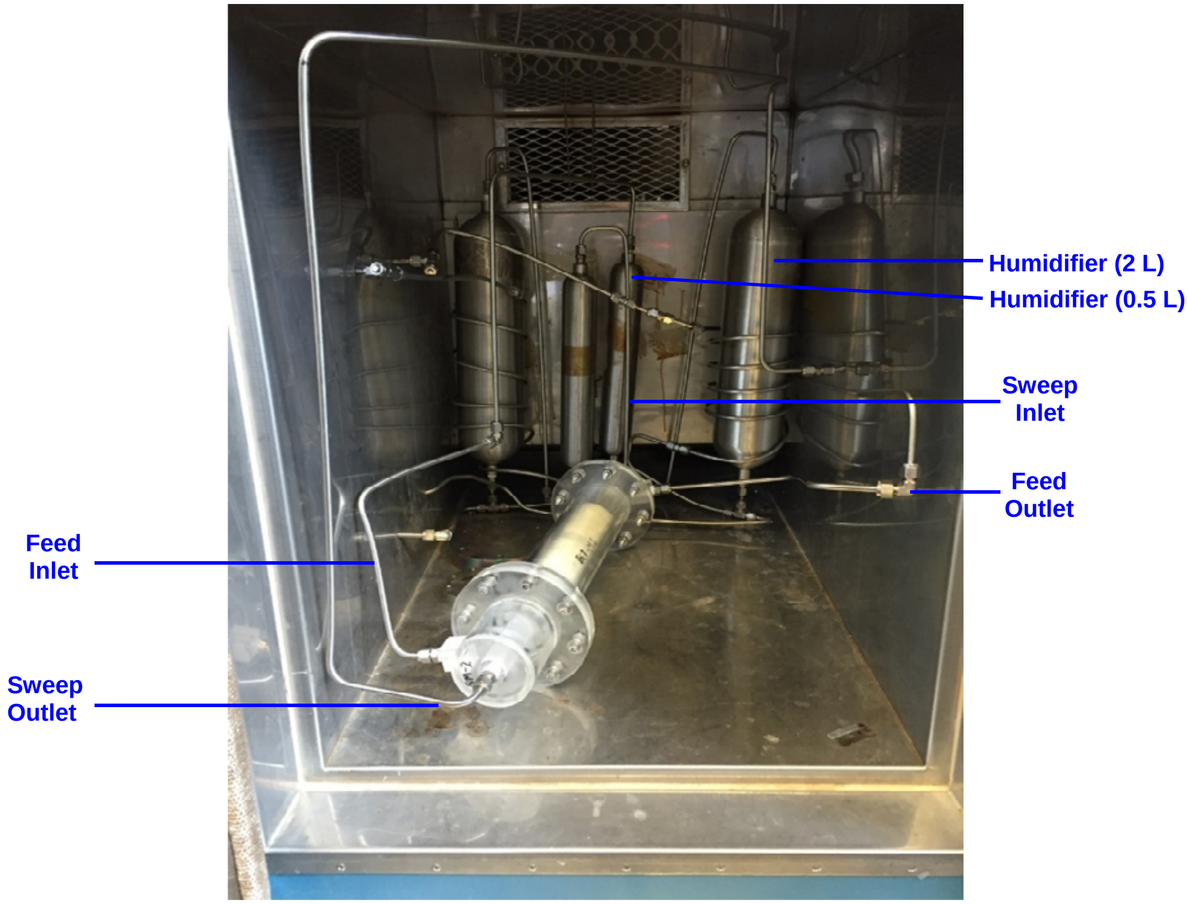

Figure 5. A spiral-wound membrane module placed inside the oven of the gas permeation unit for gas transport measurements.

3.2 Modeling for Spiral-wound Membrane Module

The purpose of this modeling study is to provide a rigorous mathematical model to extract CO_2 permeance and CO_2/N_2 selectivity accurately from the module permeation test data. A set of differential equation is developed for a crossflow module configurations as shown in Figure 6.

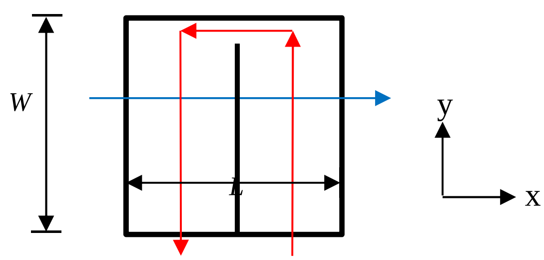

Figure 6. Flow patterns in a crossflow module with a middle glue line, feed and sweep entering from opposite sides. Blue and red arrows denote the feed and sweep flows, respectively.

We assume idealized plug flow inside of the module. Based on mass conservation and membrane permeation properties, we can write the molar balance for each species *i* for the crossflow module as:

$$\frac{\partial n_{fi}}{\partial x} = -2WJ_i = -2WP_i(p_f x_{fi} - p_s x_{si}), \qquad 0 \le x \le L$$

$$\frac{\partial n_{si}}{\partial y} = -LJ_i = -LP_i(p_f x_{fi} - p_s x_{si}), \qquad 0 \le x < \frac{L}{2}$$

$$\frac{\partial n_{si}}{\partial y} = LJ_i = LP_i(p_f x_{fi} - p_s x_{si}), \qquad \frac{L}{2} \le x \le L$$

where n_{fi} and n_{si} are the molar flow rate of species *i* on the feed and sweep sides, respectively; x is the axial direction of module element; y is the longitude direction of the membrane leaf in the material coordinate as shown in Figure 6; P_i is the permeance of species *i*; p_f and p_s are the absolute feed and sweep pressures, respectively; x_{fi} and x_{si} are the molar fractions of species *i* on the feed and sweep sides, respectively; W is the length of membrane leaf; L is the axial length of the module element. The boundary conditions for the countercurrent flow module are:

$$n_{fi}\big|_{x=0} = n_{fi,0}$$

$$n_{si}\big|_{y=0, \frac{L}{2} \le x \le L} = n_{si,0}$$

$$\int_0^{\frac{L}{2}} (n_{si}|_{y=W})dx = \int_{\frac{L}{2}}^{L} (n_{si}|_{y=W})dx$$

where $n_{fi,0}$ and $n_{si,0}$ are the molar flow rates of species *i* at the entrances of the feed and sweep sides, respectively.

Above equations were fed into the partial differential solver of Comsol Multiphysics®. To extract the CO_2 permeance (P_{CO2}) and CO_2/N_2 selectivity ($\alpha = P_{CO2}/P_{N2}$) from the module permeation test data, the molar fractions of CO_2 and N_2 on the retentate and permeate sides, respectively, were determined based on the gas chromatograph analysis results. Then, an optimization node was incorporated in the partial differential solver to calculate the required CO_2 permeance and CO_2/N_2 selectivity that could fulfill the retentate and permeate stream compositions.

4 Results and Discussion

4.1 Membrane Module Test Results at OSU

As a comparison to the NCCC field test results, the spiral wound membrane modules SW-173 and SW-67 were tested at the Ohio State University with a simulated flue gas. The membrane transport performance of the membrane modules are summarized in Table 1. Figures

7 and 8 include the stability test results of the models SW-173 and SW-67, respectively, as a comparison to the spiral-wound modules tested at NCCC.

The membrane module SW-173 stability was tested with the simulated flue gas consisting of 20% CO_2, 7% O_2, 3 ppm SO_2, and balance of N_2 (on dry basis) before humidification. After humidification, as mentioned earlier, the water vapor was at 17% at 57^{o}C. As can be seen from Figure 7, the subject module (SW-173) showed a CO_2 permeance of around 700 GPU throughout the test. The CO_2/N_2 selectivity fluctuated around 210 until the 150th hour of test, then dropped to 160.

The membrane module SW-67 stability was tested with the simulated flue gas consisting of 20% CO_2, 3% O_2, 1 – 3 ppm SO_2, and balance of N_2 (on dry basis) before humidification. After humidification, as mentioned earlier, the water vapor was at 17% at 57^{o}C. As can be seen from Figure 8, the subject module (SW-67) showed a CO_2 permeance of around 590 GPU and a CO_2/N_2 selectivity of about 205 for a total test time of about 200 hours. This result indicated that the module was reasonably stable to 3% O_2 and 1 – 3 ppm SO_2, which were the key impurities in the flue gas.

Table 1. Transport performances of spiral-wound membrane elements at 57^{o}C tested at OSU.

Module No.	Selective layer thickness (nm)	Feed/sweep flow rate (cc/min)	CO_2 permeance (GPU)	CO_2/N_2 selectivity	Feed/sweep pressure drop (psi/m)
SW-173	180	1000/1000	~700	210 → 160	1.48/1.48
SW-67	195	1500/1000	~585	205	1.97/2.30

4.2 Membrane Module Field Test Results at NCCC

OSU membrane module testing at NCCC lasted from May 28th, 2015 to June 22nd, 2015. During this period, three spiral-wound modules were tested, after passing the leak test. The flue gas composition provided by NCCC contained approximately 12% (± 1%) CO_2, 7% (± 1%) O_2, 81% (± 1%) N_2, 0.5 – 5 ppm SO_2, and 1.5 – 4 ppm NO_2 (on dry basis). Among those components, the oxygen concentration was much higher than the typical average of 2.3% in flue gas in coal-fired power plants. Our gas chromatograph (GC) settings, including the GC column, were incapable of separating the oxygen concentration from the nitrogen concentration in the permeate stream samples. However, we were able to solve this problem with the great help from the analytical lab team of NCCC by using an oxygen analyzer to measure the oxygen concentration in the retentate stream. By using this concentration, we were able to determine the permeate oxygen concentration from the mass balance, and further obtain the accurate CO_2/N_2 selectivity of our membrane.

As shown in Table 2, the three modules tested at NCCC showed repeatable results with ~ 800 GPU CO_2 permeance and ~ 200 CO_2/N_2 selectivity. Those results agreed well with the modules tested in our OSU lab. The first module (SW-154) was tested for 96 hours and showed a stable result at 820 GPU and 150 CO_2/N_2 selectivity. This module showed promising 96 hours stability of performance; however, we stopped the test since we believed the other modules could exhibited higher CO_2/N_2 selectivity.

Table 2. Transport performances of spiral-wound membrane modules at 57°C tested at NCCC.

Module No.	Selective layer thickness (nm)	Feed/sweep flow rate (cc/min)	CO_2 permeance (GPU)	CO_2/N_2 selectivity	Feed/sweep pressure drop (psi/m)
SW-154	165	1000/1000	820	150	0.98/1.31
SW-162	145	1000/1000	800	170 → 60	0.98/1.48
SW-161	145	1000/1000	800 → 630	270 → 180	1.31/1.48

The second module (SW-162) was tested for 208 hours, and there was a flue gas shutdown for a period of 60 hours in the middle of the test. The SW-162 showed an initial CO_2 permeance of around 800 GPU and a CO_2/N_2 selectivity of 170 before the flue gas shutdown; however, the selectivity dropped to around 60 after the restart of the test following the flue gas return. Figure 7 shows the stability plot of the membrane module SW-162 and the comparison to the membrane element SW-173 that was tested at OSU. Both the membrane modules showed a reasonably stable CO_2 permeance throughout the test and a drop of CO_2/N_2 selectivity. We believe that the insufficient curing of the glue used and the membrane indentations caused by the rough surface of the feed spacer might have introduced the leakage of the module and resulted in the CO_2/N_2 selectivity drop. The membrane indentations caused by the rough surface of the feed spacer are shown in Figure 9 for the module SW-162. Also shown in this figure were no such indentations for the original membrane before rolling into the spiral-wound module configuration.

The third module (SW-161) was tested for 200 hours, and there was a flue gas shutdown for a period of 48 hours in the middle of the test. The SW-161 with a longer glue curing time showed reasonably stable selectivity of 180 – 270 for 200 hours. Figure 8 shows the stability plot of the membrane module SW-161 and the comparison to the membrane module SW-67 that had a similar longer glue curing and was tested at OSU. Both the membrane modules showed a reasonably stable CO_2/N_2 selectivity throughout the test, with the exception of the drop of CO_2/N_2 selectivity after the restart of the test following the flue gas return (after its shutdown) for the module SW-161 at NCCC. However, this selectivity after the flue gas shutdown was stabilized at about 180, which is still very high. This module showed an initial CO_2 permeance of around 800 GPU; however, the CO_2 permeance dropped to ~ 630 GPU after the restart of the test following the flue gas return. This permeance drop was presumably due to the feed gas bypass caused by the glue failure, which was indicated by the change of epoxy glue color from gray to green-yellowish after 208 hours of test. We will further improve glue curing and minimize membrane indentations. Currently, we have good ideas to make the improvement, and we are conducting the work that has shown promising results.

Table 2 also shows the results of the pressure drops for the feed and sweep sides measured from the three spiral-wound membrane modules tested at NCCC. As shown in this table, all the pressure drops measured were lower than 1.5 psi/m.

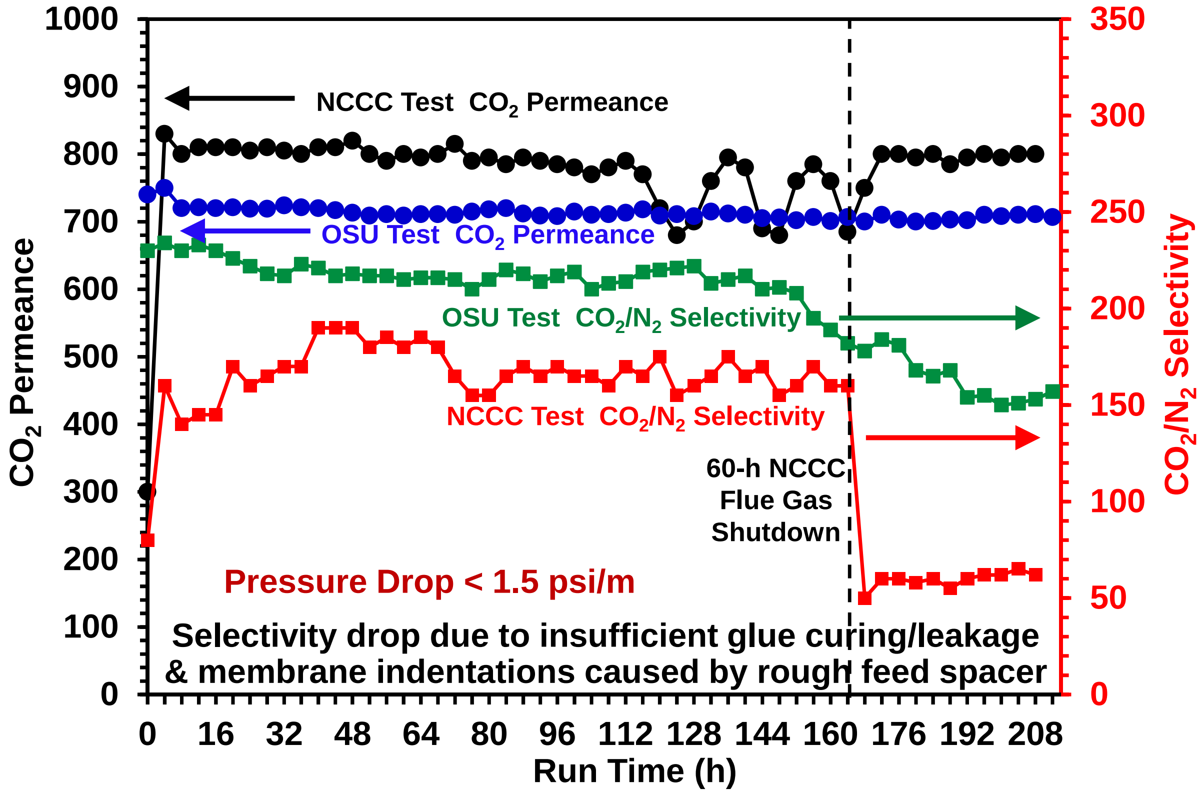

Figure 7. The stability plot of the spiral-wound membrane module SW-162 tested at NCCC for comparison with that of SW-173 tested at OSU.

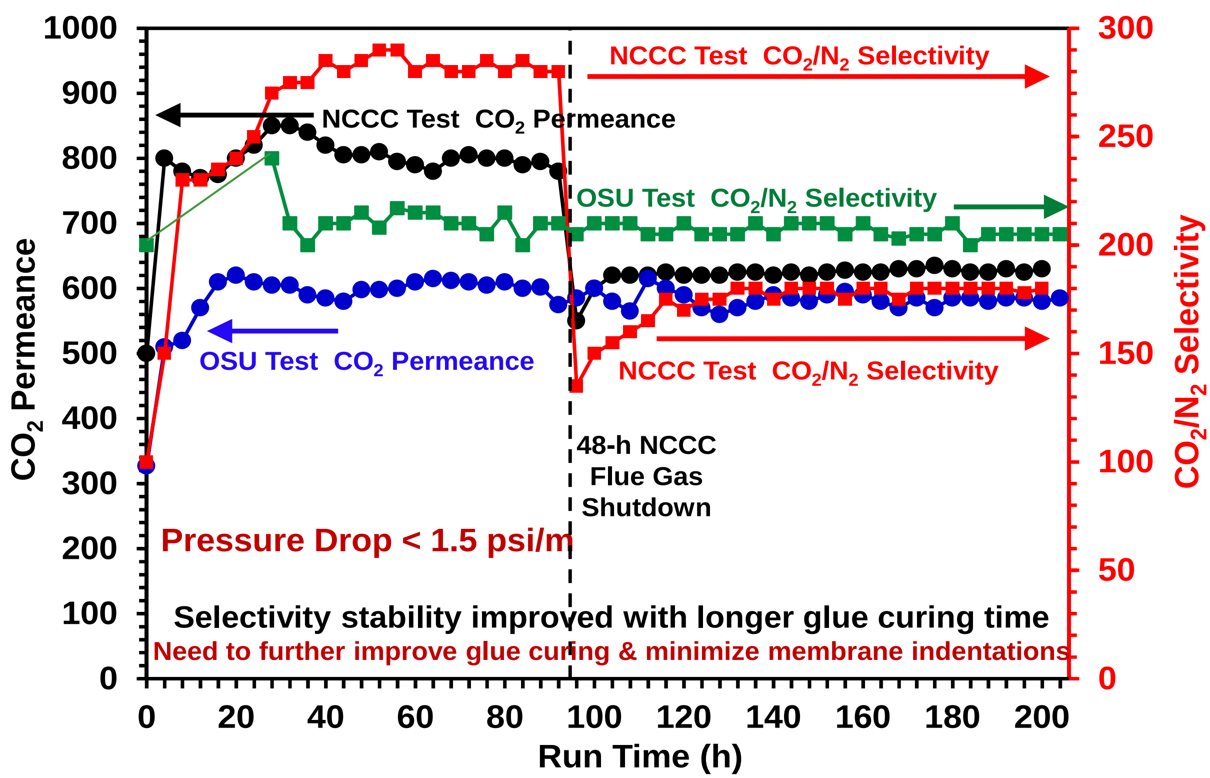

Figure 8. The stability plot of the spiral-wound membrane module SW-161 tested at NCCC for comparison with that of SW-67 tested at OSU.

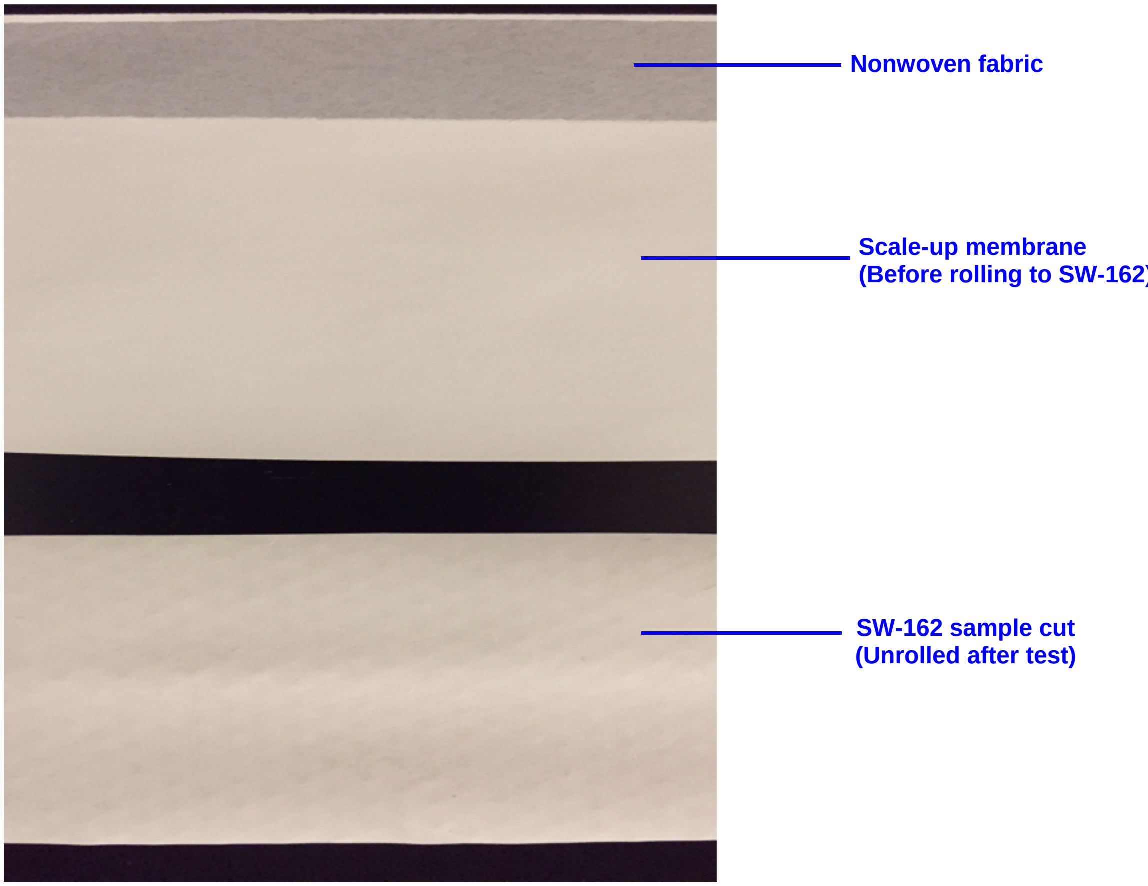

Figure 9. The image of indentations of the feed spacer on the membrane selective layer surface.

5 Conclusions and Future Work

Overall, the membrane module testing at NCCC went smoothly, and the membrane module results achieved the same level of performance as compared to our OSU lab test results with the simulated flue gas. In other words, the results showed that the modules tested at NCCC behaved similarly to those in the OSU lab, indicating the great potential of the membrane modules for CO2 capture from flue gas in coal-fired power plants. The modules showed ~ 800 GPU permeance and ~ 200 selectivity as well as a pressure drop of less than 1.5 psi/m. As mentioned, we will further improve the glue curing and minimize membrane indentations for the improvement of membrane module performance and stability.

6 Acknowledgements

The smooth membrane testing at NCCC would not be possible without the great efforts of NCCC team members, particularly Tony Wu and Bob Lambrecht. We are grateful for their excellent analytical and mechanical supports including the arrangements of lifting our membrane unit into their analytical lab, setting it up, connecting all tubings and electrical parts outside of our membrane module testing unit, installing air flow to our oven for accurate temperature control, providing an oxygen analyzer to measure the oxygen concentration in the retentate stream, and giving us the concentration data log (including CO_2, O_2, SO_2, NO_2, and NO concentration from the flue gas, and O_2 concentration from the retentate stream). NCCC support and cooperation for our membrane module testing were wonderful and professional, and we truly enjoyed working with the NCCC people.

We would also like to acknowledge José D. Figueroa for his great inputs and efforts in coordinating with the National Carbon Capture Center and providing us an opportunity for the field testing of the membrane developed in this project.

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