Field Tests Performed at NCCC

for

Robust and Energy Efficient Dual-Stage Membrane- Based Process for Enhanced CO_2 Recovery

DE-FE0013064

by

Media and Process Technology Inc

October 17, 2017

Executive Summary

A dual stage membrane process (DSMP) was proposed by Media and Process Technology Inc (MPT) for pre-combustion CO_2 capture and sequestration. Our carbon molecular sieve (CMS) membrane is used as a first stage (rougher) to remove the 75 to 85% of the hydrogen from the shifted gasifier off-gas. The residual hydrogen in the CO_2 rich retentate stream is then recovered downstream using the Pd/Pd-alloy membrane following cold gas cleanup (CGCU) and compression just prior to CO_2 sequestration. MPT has conducted two field tests at NCCC in 2016-17 with the focus on (i) evaluating the physical integrity and the flow distribution of our full-scale 2nd generation CMS membrane module for the first stage, (ii) demonstrating the suitability of our Pd membrane/bundle as the 2nd stage, and (iii) further verifying at NCCC the simulation for gas separations via our DSMP for Techno-Economic Analysis (TEA).

In order to provide a reliable simulation for gas separations via our membranes for the TEA analysis, significant effort has been taken under this project to modify the test system to obtain a reliable water content measurement in-situ within 1-2 hours of time frame. The water content estimates thus obtained using our newly-installed water collection units appear to be highly accurate when matched against actual SRI-NCCC collected data reported on daily basis. Improvements to the gas composition analysis, particularly as a result of a reliable in-situ water content determination, have made it possible to close the modeling gap based upon the field test data generated in 2016. The gas separation model thus verified can provide reliable performance simulation required for the TEA analysis. With the in-situ performance results from about 400 hours of test, the CMS membrane/bundle developed and prepared by MPT has been demonstrated to be highly stable, which can consistently deliver high performance in the presence of the wide range of gasifier off-gas contaminants.

In this proposed DSMP scheme, because CGCU is practiced upstream of the Pd/Pd-alloy membrane, the intrinsic deficiencies of the Pd membrane technology, particularly its poor sulfur and other contaminant resistance, can be sidestepped to maximize hydrogen (power) production while achieving the DOE/NETL CO_2 sequestration targets. In one of our previous NCCC field tests, we demonstrated high purity hydrogen (99+%) could be obtained using a single tube MPT PdAg alloy membrane fed with tar and sulfur free gasifier off-gas. In 2017, multiple-element Pd membrane bundles (3 total) prepared by MPT were tested at NCCC. All showed a high degree of loss in hydrogen permeance as expected due to poison by the tar-laden syngas. The N_2 permeances of the Pd membranes after regeneration, however, did not change appreciably throughout this testing of ~150 hours, indicating that no irreversible physical damage or failure of the multiple element Pd/PdAg alloy bundles through exposure to the high temperature and high-pressure syngas stream. The bundling technique developed for the Pd and Pd alloy thin films (~5 μm) supported on our commercial ceramic membrane provides a technically and economically viable avenue to implement the Pd membrane technology in field installations. Further, the Pd membranes poisoned by tar-laden syngas at NCCC were effectively regenerated by the protocol we developed. The regeneration condition, in particular temperature and treatment duration, has been optimized for future implementation in the field.

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1. Introduction

In our proposed dual stage membrane process (DSMP) for pre-combustion CO_2 capture and sequestration, our carbon molecular sieve (CMS) membrane is used as a first stage (rougher) to remove the 75 to 85% of the hydrogen from the shifted gasifier off-gas. The residual hydrogen in the CO_2 rich retentate stream is then recovered downstream using the Pd/Pd-alloy membrane following cold gas cleanup (CGCU) and compression just prior to CO_2 sequestration. The CMS-based membranes were originally developed by several academic groups, including our subcontractor, University of Southern California (USC). Media and Process Technology Inc (MPT) has developed the manufacturing methodology to scale up the lab deposition technique developed by USC to large scale production in the past >10 years. MPT conducted several side stream tests at NCCC during 2008 to 2009 to verify the material stability of the CMS membrane under the proposed operating condition, i.e., hydrogen recovery from the raw syngas without pre-treatment for tar removal at an intermediate temperature (200 to 300°C) with a single tube configuration (see Figure 1). Subsequently, MPT developed the bundling technique which allows the ceramic membrane based gas separation tubular membranes to be technically feasible for commercial scale applications (see Figure 1). Prior to entering this project, MPT has conducted several field tests in 2010 to 2012 at NCCC's coal gasification facility to verify the robust nature of the CMS membrane bundle for hydrogen recovery under a similar operating condition as a single tube. Under the current project, MPT has been continuing in the refinement of the CMS membrane and bundles (2nd generation), and conducted the planned field tests at NCCC in 2016-17 to validate the 2nd generation bundle. Further we have improved the performance prediction of our mathematical model and verified its prediction

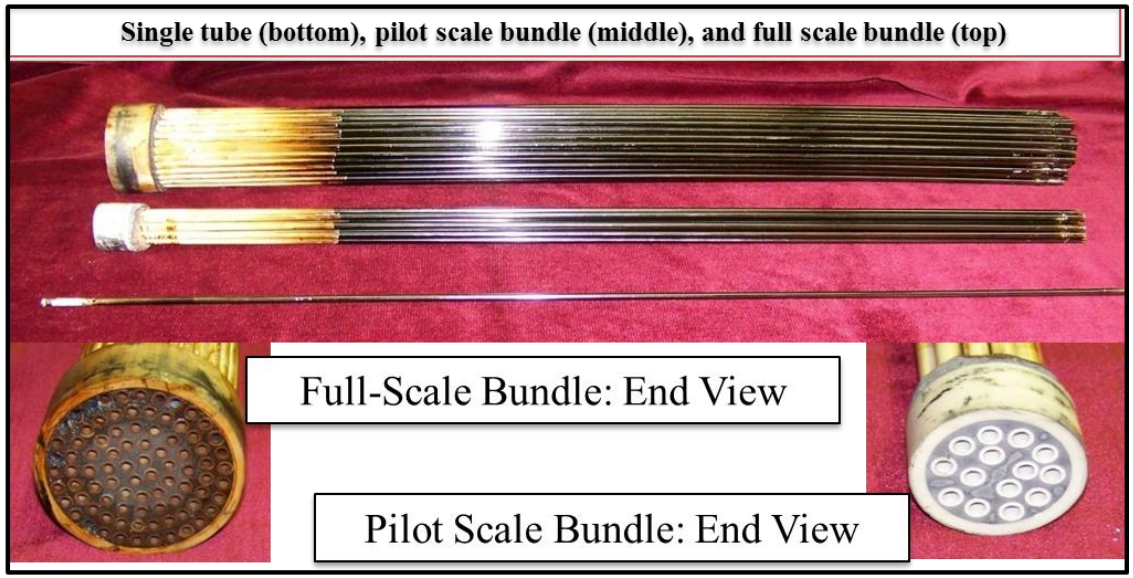

Figure 1. Picture of single tube, and pilot and full-scale bundles of carbon molecular sieve membranes.

with the field data obtained from NCCC. The mathematical model and simulation is now ready to support the TEA analysis of the proposed DSMP by our subcontractor, Technip Stone & Webster (Technip).

Another objective of this current project was to demonstrate hydrogen recovery by our Pd-alloy based membrane bundles as the second stage of our proposed DSMP. In this scheme, because CGCU is practiced upstream of the Pd/Pd-alloy membrane, the intrinsic deficiencies of the Pd membrane technology, particularly its poor sulfur and other contaminant resistance, can be sidestepped while achieving the DOE/NETL CO_2 sequestration targets and maximizing the hydrogen recovery with this Pd membrane. In one of our previous NCCC field tests, we demonstrated high purity hydrogen (99+%) could be obtained using a single tube MPT PdAg membrane fed with tar and sulfur free gasifier off-gas. In that work, the feed gas was permeate generated from our CMS membrane (thus, tar was eliminated) that was further polished in a ZnO bed (for sulfur elimination). In this current project, sweet-shifted syngas was provided to us by the NCCC which contained very low levels of sulfur (<1ppm sulfur), but significant levels of tar-like heavy hydrocarbons. The focus of our NCCC test in this campaign was to (i) evaluate physical integrity of the full-scale Pd and PdAg membrane bundles under actual syngas operating environment, (ii) determine the impact of syngas contaminants and potential poisoning of the Pd membrane in the presence of tar-like species, and (iii) confirm the regenerability of the Pd membrane after poisoning in actual syngas environment. The completion of this part of the testing program at the NCCC is essential to our project objective with respect to the use of our full-scale Pd-alloy membranes as the second stage in our proposed DSMP.

This report summarizes the field test activities conducted at NCCC under this current project, including (i) the field test results with the 2nd generation CMS membranes/bundles developed under this project, (ii) the comparison of the field test data vs the performance prediction from our mathematical model, and (iii) regeneration of the Pd membranes poisoned through its exposure to the tar-containing syngas at NCCC.

2. Preparation of CMS Membrane Bundles for Field Tests

Two different pathways have been developed to assembly the CMS membrane tubes into a bundle. In the past, our earlier style PCG (Potted Ceramic Glass) bundles were used for the field tests. The ceramic membrane substrate (i.e., 40Å) was potted together into a bundle first with a ceramic glass binder as shown in Figure 2; then, the CMS deposition was conducted by bundle. The advantage of this style is its dense packing. However, its maximum operating temperature and pressure are limited by the condition used to pot the tubes into a bundle. For some hydrogen separation applications, for instance, coal gasification gas separation applications, the temperature and the pressure of syngas as received could be much higher than the upper limit the PCG can provide.

Figure 2. Two styles of ceramic tube bundling developed by MPT: Dense Ceramic Tubesheet (DCT) and Potted Ceramic Glass (PCG).

As a result, we developed a second pathway, i.e., dense ceramic tubesheet (DCT), as a second generation product under this project. The DCT style bundle can sustain the much higher pressures (>1,000 psig) and temperatures (>500°C) than the upper limit of the PCG bundle (<350 psig and <300°C). Given expected membrane operating conditions in the implementation of our DSMP for the IGCC system with carbon capture process (specifically >800 psig and >250°C), the DCT type bundle developed during this project is a necessity.

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In this project, the 63-tube DCT bundle was prepared and challenge tested to confirm its suitability for the proposed application. Leak testing of bundles prepared using dense (gas impermeable) tubes to pressures up to ca. 1,000 psig has been conducted and the results are presented in Figure 3. The result from a PCG style bundle is also shown here for comparison. Two important features should be noted based upon the data shown in Figure 3. First, the N_2 leak rate of the DCT style of membrane is approximately two orders of magnitude lower than that for the bundles prepared with the PCG approach. Second, much higher pressures are attainable with the DCT style part. Here the leak permeance data at pressures up to 1,000 psig are considered acceptable. Finally, we have conducted pressure testing of the DCT style of bundles up to 1,300 psig with no tube or tube sheet failure. Overall, the initial development of the DCT style bundle has proven to be highly successful and yields a product design that is clearly suitable for applications in high pressure high temperature environments consistent with the hydrogen separations applications interested to us. Finally, the DCT bundle packed with the CMS membrane was subjected to the long term thermal stability testing at 250°C as shown in Figure 4. The He permeance and its selectivity over nitrogen throughout the 8,000 hours remain relatively constant, indicating the DCT style potting in addition to the CMS membrane is thermally stable at 250°C, which is the CMS membrane operating temperature of the syngas delivered to our system. Nevertheless, the DCT style bundle based upon the challenge test performed in the lab is believed to be able to sustain the temperature >> 250°C.

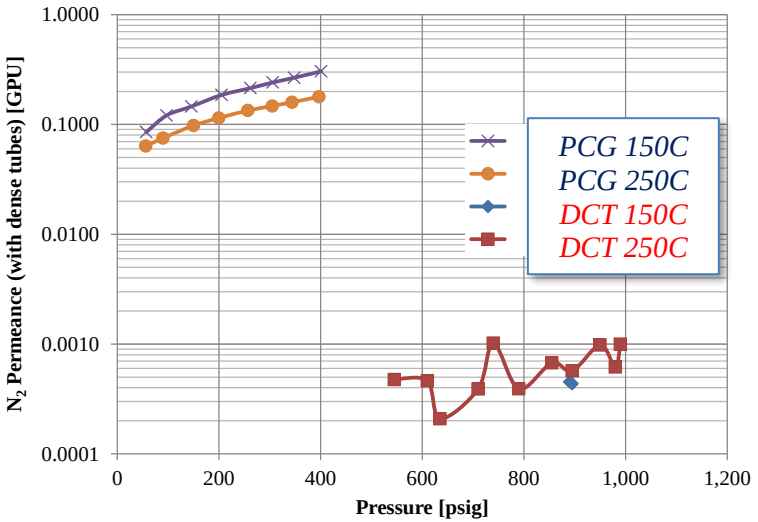


Figure 3. Gas pressure testing of the PCG and DCT style membrane bundles showing the N_2 permeance versus pressure. Note that the tubes used in these bundles were impermeable so that the leak rates observed are through the seals and potting.

The DCT style bundle evaluated comprehensively in our lab in terms of its physical integrity, temperature and pressure stability, and performance and its stability was selected for the field test at NCCC during 2016 to 2017. Both membranes required for our DSMP, i.e., CMS and Pd/Pd-Ag membrane bundles, were prepared with this approach.

3. Improvement of The Field Testing Unit at the NCCC for Water Concentration Measurement

3.1. *Our Past Experience and Limitations*

Our previous testing at the NCCC established that the CMS membrane performance was very stable based upon determination of the He and N_2 pure gas permeances at various intervals during the several hundred hour runs. However, we have had difficulty in reconciling the actual in-situ H_2 and other gas permeances against the simulated values based upon model calculation during these runs. We suspect that the much larger than expected deviations noted at the NCCC are likely due to miscalculation of the in-situ (i.e., wet) gas phase compositions. In particular, the actual water content in syngas, which was significant in the range of 10 to 50%, could lead to miscalculated in-situ gas compositions. We took a significant effort to modify the system in order to obtain a reliable water content measurement as a first step of our field test activities at NCCC under this project.

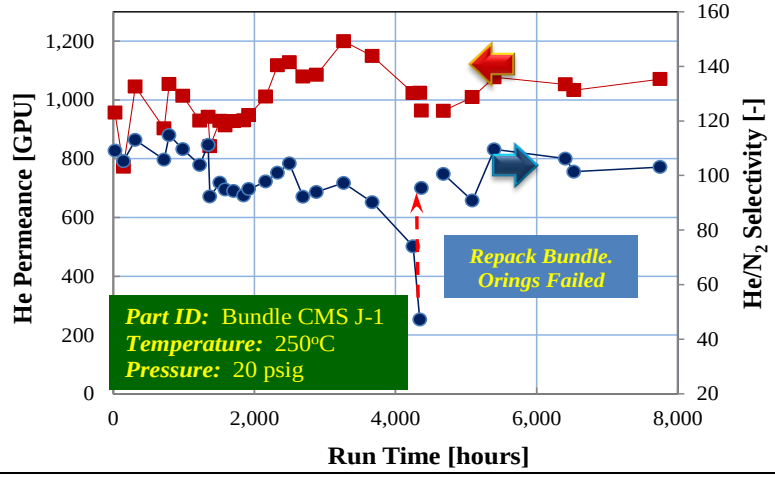


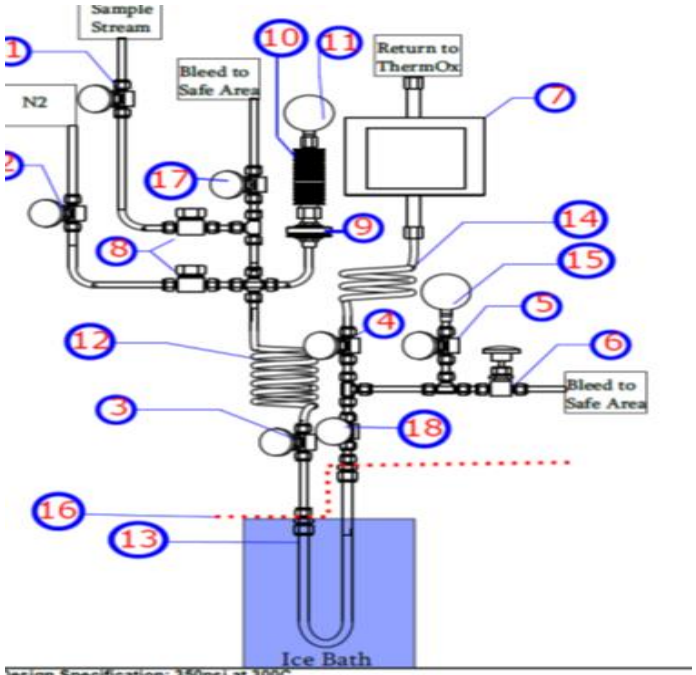
Figure 4. Long term thermal stability of the 86-tube CMS membrane bundle, CMS J-1, at 250°C and 20psig.

3.2. *Description of the In-situ Water Capture Units*

Under this project, the water capture units for the permeate and the reject lines were fabricated and installed at the NCCC. Figure 5 is the engineering drawing for the water capture unit, which was prepared by MPT, reviewed by NCCC and finalized by MPT before fabrication. Figure 6&7 below show the units installed on our membrane testing system at the NCCC. Further description and shakedown testing of the units is discussed below.

The water collection units implemented for hydrogen separation from syngas at the NCCC consists of two small scale slip stream systems; one for the permeate stream and one for the reject stream. They are identical in plumbing and function but operate slightly differently due to the differences in gas stream conditions. The reject stream is operated at syngas or shifted syngas pressures (between 160 and 210psig) while the permeate stream is operated at less than ten psi.

The basic concept used here is that a controlled flow of warm moist syngas after membrane treatment is sent through a cooling coil then into an ice (or similar cold) bath to condense water from the gas stream. After a certain period of time, the collected water is weighed and its concentration in the gas stream is calculated. A typical test run is conduced as follows. Initially, the water collection subsystems are isolated via valving from the main process streams and kept under nitrogen purge to keep ambient air (oxygen) and moisture out of the system as well as serve as a supplementary leak check. Prior to gas stream sampling, the nitrogen purge inlet line is closed, the unit is vented to depressurize the system, and then the purge and vent lines are closed. Once the vent valves and nitrogen supply valves are verified as closed, the gas sampling valves are opened to deliver process gas to the water collection subsystem. The flows on the flow meters are adjusted to the desired rate and then the trap is immersed in ice (or similar cold fluid) to start the collection timer. Adjustments are made as needed to keep the flows as stable as possible. Every five to ten minutes flow readings are recorded so that cumulative gas volume can be calculated at the end of the run. Typical test runs last between 45 minutes and an hour, but can be shortened or lengthened depending on flow rates, system stability, and other issues. At the end of the test run, the valves are closed isolating the process gas from the water collection subsystem and the system is depressurized through the flow meters. Following this, the nitrogen control valves are opened to flush the system with nitrogen to remove any remaining process gas and to push any liquid water in the lines into the condensate trap. The subsystems are left under a



esign Specification: 350psi at 300C

#	Description	Part/Component
1	Sample Stream Control Valve	Swagelok SS-1RS-6-PK
2	Nitrogen Purge Control Valve	Swagelok SS-1RS-6-PK
3	Sample Loop Isolation Valve	Swagelok SS-1RS-6-PK
4	Sample Loop Isolation Valve	Swagelok SS-1RS-6-PK
5	Gauge Isolation Valve	Swagelok SS-1RS-6-PK
6	Sample Loop Bleed Valve	Swagelok SS-1RS-6-PK
7	Sampling Loop Outlet Flow meter	Swagelok VAF-M3
8	Check Valves	Swagelok SS-5C5
9	Gauge Diaphragm	Wika L990.10
10	Gauge Cooling Tower	Wika 1600885
11	Pressure Gauge	Wika 232.30 400psi
12	Cooling Coil	SS316 3/8" OD x 0.035"
13	Sampling Loop U-Bend	SS316 1/2" OD x 0.049"
14	Reheat Coil	SS316 3/8" OD x 0.035"
15	Sampling Loop Pressure Gauge	Wika 232.30 400psi
16	Sampling Loop Disconnect Location	
17	Inlet Stream Bleed Valve	Swagelok SS-1RS-6-PK
18	ThermOx Return Bleed	Swagelok SS-1RS-6-PK
-	Any Tubing Not Indicated	SS316 3/8" OD x 0.035"

Figure 5. Final design drawing of the water capture device to determine water composition in the reject and permeate gas streams at the NCCC.

Figure 6. MPT test unit with the added water capture units

Figure 7. The water capture units installed and the engineering drawing for the unit.

slight nitrogen sweep for five to ten minutes to ensure all flammable gases have been purged out of the system. Once the nitrogen purge is complete, the nitrogen control valve is closed and the system is again depressurized. At this point, the isolation valves are closed and the vent valves are opened to ensure no pressure on the condensate trap. A double block and bleed valve combination is installed between the trap and any source of gas pressure both upstream and downstream of the condenser. The condensate trap is removed from the system, surface water is dried off and the entire trap is weighed, and then the collected sample is drained out of the trap and reweighed. Then, a fresh dry condensate trap is placed back onto the system. Once the vent valves are closed and isolation valves are re-opened, the new trap can be purged and leak checked using the low pressure nitrogen before being used to the next test run.

3.3. *Shakedown Testing and Data Validation*

Testing at the NCCC was conducted with the new water collection units with an 86-tube CMS membrane bundle to verify the system operation and composition analysis. Approximately 250 hours of live gas testing was conducted using this membrane element. Our goal during the shakedown testing was to confirm the operation of the water capture units and validate our data against composition analysis available from the NCCC. In reality, the window available for water composition analysis was very narrow at the NCCC. Although dry gas compositions for our system (permeate and reject) were available throughout the day, water composition analysis of the feed gas from the NCCC was only available once per day, typically by early afternoon (and not available for our permeate and reject). This was a typical problem for the membrane operation since two streams were generated from the membrane, i.e., permeate and reject streams, from the feed. Hence, estimates of the water content for each stream were problematic for us in previous runs outside the analysis window (and even inside the window given variability in the gasifier run conditions). An important requirement to verify our water collection data and composition analysis was accurate and stable readings of gas compositions and the water content in the feed gas stream provided by NCCC. For this purpose, (i) NCCC's lab daily raw syngas water content measurement by SRI (Southern Research Institute) and (ii) the sour shift vessel's steam and syngas feed rates and gas composition analysis data (by GC) were used to estimate moisture contents in the shifted syngas feed to our unit.

Table 1 shows the estimated water contents from a series of runs conducted by NCCC and MPT separately over several days at the NCCC. For the SRI raw gas analysis, % water content is the calculated water content of the raw syngas from the gasifier. This data is generally captured once per day over a several hour period typically some time during later morning/early afternoon. The green shaded data would be the data that MPT obtained with our unit at the time which was closest to the "SRI" collection time on that particular day (or series of days). The data that follows with the same SRI's % water content (i.e., first column of Table 1) is the carryover from this original data collection and does not represent new data for the remaining data sets. The steam spike (2^{nd} column) and syngas (3^{rd} column) are the pounds per hour of added steam and gasifier syngas respectively just prior to the sour gas shift reactor. Note that the syngas stream includes water and the water content is estimated from the SRI raw syngas column. The steam spike is additional water beyond this level that was added (downstream of the SRI analysis point) to improve conversion in the WGS reactor. The calculated % in Inlet and Outlet is the water content in the feed and exhaust from the WGS reactor estimated from these various gas/water inputs.

Table 1. Water composition analysis based upon NCCC (left side) and MPT (right side) data. Only the green shaded data sets are actual water concentration data obtained by the NCCC. The remaining data in the NCCC data set is not physically captured but simply carried down from the actual data sets to fill out the table. All of the data in the MPT data set is actual data from our collection unit.

SRI's	NCCC Data Shifted Syngas #/hr				MPT Water Collection Unit Data				GC Dry Gas
Raw Syngas	#/hr		Calculated Steam		Perm	Reject	Calculated	Water Closure	Mass Closure
% Water	steam spike	syngas	% in Inlet	% in Outlet	%	%	Feed %	[%]	[%]
6.2	50	350	22.3%	15.2%	51.8%	5.1%	11.6%	76.5%	101.8%
6.2	25	300	16.2%	8.5%	39.5%	5.7%	8.8%	103.9%	105.1%
6.2	15	300	12.3%	4.3%	23.5%	3.6%	5.2%	123.3%	102.0%
6.2	15	300	12.3%	4.3%	16.1%	3.6%	4.5%	106.3%	102.0%
8.4	15	770	10.5%	6.6%	36.7%	2.2%	5.1%	77.5%	107.1%
8.4	16	749	10.6%	6.7%	23.2%	5.3%	6.5%	96.4%	101.7%
8.4	14	732	10.4%	6.4%	22.6%	9.1%	9.9%	154.4%	101.6%
8.4	15	740	10.5%	6.5%	28.6%	6.5%	7.9%	120.5%	101.6%
8.4	15	760	10.4%	6.6%	27.3%	6.2%	7.4%	112.1%	101.7%
8.4	15	758	10.5%	6.6%	23.3%	7.0%	7.9%	119.6%	101.2%
8.1	0	750	7.5%	2.5%	19.9%	5.5%	6.6%	267.2%	99.5%
8.1	0	750	7.5%	2.6%	37.2%	13.3%	15.1%	581.8%	108.2%
5.3	0	750	5.0%	1.7%	23.5%	0.2%	1.6%	98.4%	102.3%
5.3	0	750	5.0%	1.7%	13.6%	0.9%	1.5%	91.7%	102.3%
8.0	0	750	7.4%	2.7%	31.1%	0.6%	2.6%	98.5%	103.0%

The feed to MPT's membrane unit is the outlet from the sour gas shift. The water content estimated from the NCCC data capture is in the "% in Outlet" stream. MPT data shows the estimated water content in the permeate and reject streams and the calculated feed water content by mass balance. The water closure is the ratio of the estimated water content based upon the NCCC data (% in Outlet) and MPT data (Calculated Feed %).

One would expect good data closure between the two data sets at times near the SRI (NCCC) collection time (green shaded data sets). The MPT measured data would deviate from closure at times away from the SRI collection time as the actual gasifier water content varied through the run, which was not captured by the SRI measurement. In general, this trend is observed in Table 1. For the green shaded regions where the actual in-situ water collection data by MPT, all but one of the Water Closure %'s is under 4%. This suggests that our "in-situ" water collection system is quite accurate in the determination of the water content in the feed (based upon the measured water contents in the permeate and the reject). Good agreement between the MPT and the SRI (NCCC) data was observed where NCCC data was actually available. Further, outside of the shaded regions the error in the "closure" can be quite high and likely reflects real changes in the gasifier water content. Again, actual water content data is unavailable from the NCCC in these data sets. Thus estimate was made with the data from the "nearby" water content. This highlights the fluctuation nature of the water content generated from the gasifier and the WGS reactor. Real time in-situ water content analysis is recommended for the purpose of verification of the model prediction for a membrane-based separator. Also note that the final column shows the "dry" gas composition estimated from the gasifier feed upstream of the WGS unit and MPT's reject and permeate streams. Unlike the SRI (NCCC) water content, the gasifier dry gas content is monitored continuously throughout the day by NCCC. Agreement between NCCC and MPT data here is generally within 2 to 3% and likely supports our assessment of the accuracy of our water content determinations. Overall, the water content estimates obtained using our in-situ water collection units appear to be highly accurate when matched against actual SRI (NCCC) collected data. Given this, we believe that our estimates of the water co ntent for the balance of the day can be used reliable to reflect the "real-time" gasifier conditions. One measurement per day to estimate gasifier moisture content throughout the day made previously was inadequate for our purpose and likely accounts for much of the difficulty we have had in the past with modeling in-situ gas separation performance. In Section 4, the CMS membrane gas separation data analysis for the field test

Figure 8 MPT laboratory test system for mixed gas testing with water delivery (HPLC pump) and collection (cold traps for both permeate and reject) shown in the top. The bottom photo is the GC sampling system we used for the mixture composition analysis.

performed in 2016 is presented. The results from the water measurements using our collection system is incorporated into the gas separation analysis in this section.

3.4. Effect of Steam on Gas Separations via CMS Membranes

In addition to the water measurement, we have also conducted a series of testing using our standard CMS membranes in lab to verify the performance agreement in mixed gas and pure component data in the presence of steam. Previously our mathematical model was verified satisfactorily in the lab in the absence of steam. Here, the lab test results involving mixture separation in the presence of steam are presented. Under this project, a standard CMS single tube membrane in candle filter configuration was tested at varying water concentrations and feed pressures to determine the impact of water concentration on the in-situ determination of the permanent gas permeances. The lab system for this study is shown in Figure 8 for reference. It is a standard gas system with added components for water delivery (HPLC pump) and water trapping on the permeate and reject streams. The GC system shown is common to this unit and several of the dry gas test units throughout our laboratory. The overall approach used for the lab water delivery and collection system is based upon the same concept/approach used now at the NCCC and has been practiced by us for some time. Water is added at a controlled rate to the dry gas stream via an HPLC pump. It is pre-vaporized in the furnace and then mixed with the dry gas (pure component or gas blend) prior to entering the membrane. On exhaust,

Table 2. He permeance in the presence of water for a range of pressures and water contents compared with pure component results (0% water).

	Feed Pressure [psig]	Water Content [vol%]	He Permeance [$m^3/m^2/hr/bar$]
Day 1	81.0	0	1.86
	79.4	13.6	1.82
	79.2	13.6	1.83
	74.9	9.1	1.81
Day 2	65.0	0	1.87
	65.3	15.2	1.98
Day 3	60.0	0	1.86
	65.1	18.2	1.97
	66.0	19.5	1.99
Day 4	48.8	0	1.96
	62.2	38.2	2.07
	61.8	36.9	2.31
Day #5	40.4	0	2.19
	60.8	23.3	2.14
	60.6	27.2	2.32
Day #6	15.9	0	2.16
	11.3	88.1	2.12

both the reject and permeate water are collected in cold traps. In this testing, water capture was done at ca. -20°C using a $CaCl_2$ saturated ice-water bath. All three gas lines can be routed to the GC for analysis as necessary. Membrane testing was conducted at our standard 250°C. Total feed pressures between ca. 15 and 80 psig were studied with water concentrations varied between ca. 10 and 90% in mixed gas testing. The test runs are generally conducted over a 2 to 4 hour span to permit sufficient elapsed time to collect adequate reject and permeate water in the traps. Again, this methodology is similar to that practiced at the NCCC.

Table 2 shows the membrane performance results comparing the He permeance in pure component and mixed He/water experiments. Over the entire range of test conditions, it does not appear to be any significant reduction in the He permeance obtained from in-situ mixed gas relative to the pure component permeances over a wide range of water concentrations and pressures. These results demonstrate that it is highly unlikely that water significantly retards the "fast" gas permeance during mixed gas runs. Hence, the reduction in fast gas (H_2) permeance we observed in past field testing at the NCCC is most likely due to (i) incorrect estimates of the water content in the feed gas and/or (ii) bypass flow of feed gas around the membrane bundle due to failure of the membrane baffles. The former factor was eliminated with the installation of the in-situ water capture subsystem as discussed in this section. The latter was resolved by the improvement of the internal baffle structure and installation as discussed in the next section. Comparing of the field test results with the performance prediction by the mathematical model would provide the insight on how good our mathematical simulation is and how confidence we could in using the prediction for our Techno-economic Analysis (TEA) as part of the deliverables for this project.

4. Field Test Results with the 2nd Generation CMS Membranes/Bundles at NCCC

4.1. *Background*

MPT conducted several field tests at National Carbon Capture Center (NCCC) of US DOE from 2010 to 2015. We have evaluated the CMS membrane in the configuration of single tubes, pilot scale bundles (2" dia) and the full scale bundle (3"x34"L in candle filter configuration). Throughout these tests, the CMS membrane has demonstrated its robust in the presence of coal derived syngas without pre-treatment for up to 400 hours on-stream continuously. The CMS membrane hydrogen permeance and selectivity remain unchanged through these tests. The results from these previous tests have been documented in a previous publication[1].

Our primary goal during this phase of the NCCC testing was to confirm the membrane performance and performance stability using the in-situ permeate flux and composition data generated during the test. In the past, the membrane performance was verified highly stable using measurements of the pure component helium and nitrogen permeance taken periodically during the NCCC testing. However, we have not been able to successfully predict in-situ membrane performance running on gasifier off-gas using our simulation, even though this has been successfully demonstrated by us in mixed gas testing in laboratory and pilot scale. Hence, up to now we have been uncertain if the membrane performance in-situ at the NCCC has been consistent with pure component performance data. This is an important hurdle to overcome, since our modeling is used to conduct the techno-economic evaluation of the membranes in the proposed IGCC with carbon capture process. With the introduction of the water capture units as described in Sec. 3, we have been able to overcome this gap.

4.2 Field Test

[1] "Field evaluation of carbon molecular sieve membranes for the separation and purification of hydrogen from coal-and biomass-derived syngas" by D. Parsley, etc., in *Journal of Membrane Science*, *450*(2014)81–92.

As for the previous tests, a single full-scale CMS membrane bundle was used for this test. Figure 9 shows an overview of the membrane operating conditions including temperatures, pressures, and flow rates throughout the approximately 410 hours of testing conducted during this campaign at the NCCC. Target operating temperature was ≥220°C. As has been documented by us in the past, severe membrane flux reductions can occur at lower temperatures due to condensation of organic vapors and "tars" on the membrane surface. Importantly, this flux reduction has been demonstrated by us to be easily reversible by increasing the temperature above the 220°C minimum. Operating pressures of 150 to 175 psig were typical with some excursions due to process changes and/or upsets. Figure 10 shows the hydrogen composition of the feed, reject and permeate gas streams throughout the testing period. The N_2 content is also shown to offer some perspective on the large quantity of nitrogen in the feed (air blown gasifier) and hence the suppressed hydrogen recovery potential. In general, the CO content in the membrane feed was typically less than 1% (downstream of the WGS reactors). CO_2 content ranged from ca. 12 to 15%. Since no gas pretreatment was conducted, H_2S content in the membrane feed ranged from ca. 500 to 2,000 ppm depending upon the coal source used as feed to the gasifier. During this current round of NCCC testing there were also two short term tests for a cumulative of about 8 hours conducted at higher H_2 contents to simulate more realistic oxygen blown gasifier concentrations which should be expected to be in the range of 35 to 45%. These spike runs can be seen in at ca. 8, 310, and 375 hours. Higher H_2 content was achieved by injecting cylinder H_2 directly into the exhaust gas of the WGS reactor just prior to the CMS membrane inlet.

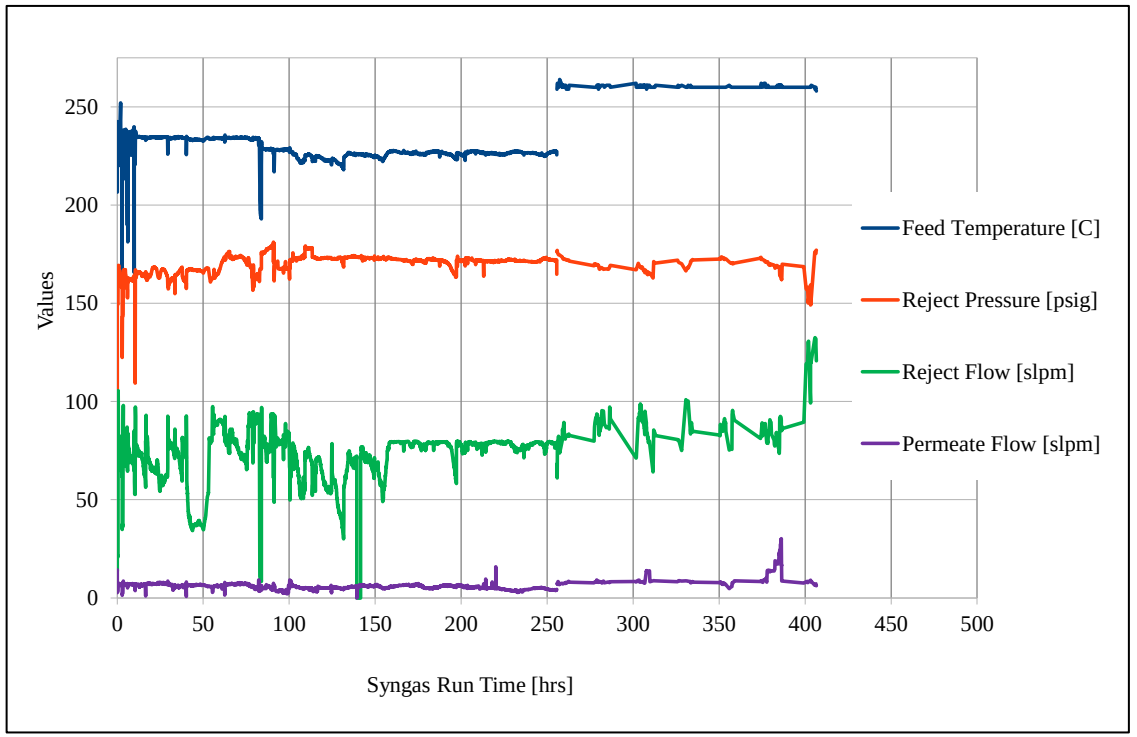


Figure 9. Operating pressure, temperature, and flow rates for membrane during the Field Test at NCCC

Two key parameters are of primary interest in terms of the modeling of the membrane performance, specifically the overall membrane permeate flow, which will establish the membrane area requirements, and permeate composition, which will determine the approach to the target capture levels and purity of the CO_2 and H_2 streams. Figure 11 shows the model predictions of the membrane total permeate flux compared with the actual measurements made at the NCCC for the ca. 410 hour test campaign. Also shown in Figure 11 is the ratio of actual to predicted performance. Under well controlled operating conditions and well characterized mixed gas feed conditions, it is straightforward to observe ratios of the actual to predicted permeate flows in the 90 to 100% range. During the first 220 hours of testing at the NCCC, the model prediction of the mixed gas performance was relatively poor and in the 50 to 70% range. This performance error is also observed in the permeate gas composition analysis which is shown in Figure 12. The predicted H_2 content is consistently well above the actual membrane performance in this initial time window. At the time of the testing, this was a highly surprising and somewhat discouraging result. However, given our past experience with other mixed gas systems, we suspected that there may have been a problem with the bundle feed gas flow distribution. In fact, this is the purpose and power of the modeling, specifically, to show that there is a problem with the functional performance of the membrane during in-situ operation.

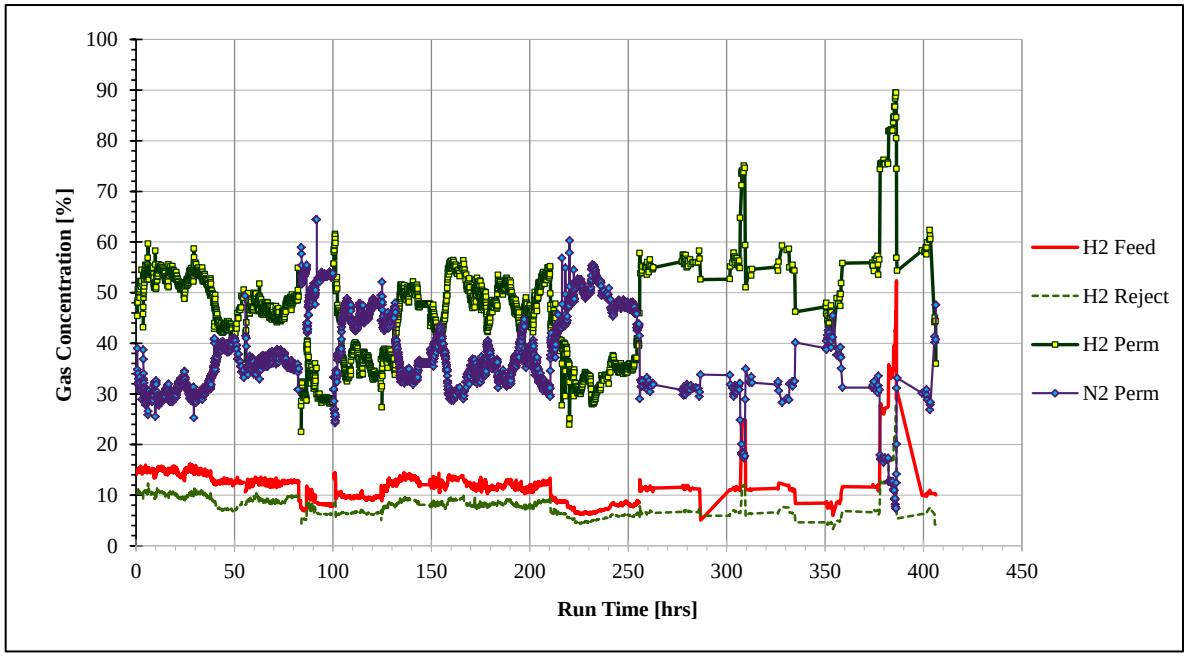


Figure 10. CMS membrane feed, reject and permeate gas composition analysis for the Field Test at NCCC

At the ca. 220 hour mark, the membrane was removed from service and inspected. It was clear based upon the inspection that the Teflon baffles used for feed flow distribution to the CMS tubes had shifted during operation. In fact, based upon the results shown in Figure 10 and Figure 11, it was highly likely that this problem occurred during initial installation of the bundle into the housing at the NCCC, since significant performance deviation was observed from the start of the testing. At the 220 hour mark, the baffles were readjusted and the bundle was reinstalled into the housing. As Figure 11 and Figure 11 show, the bundle performance is clearly superior to that observed in the earlier testing. The actual H_2 permeate content is nearly identical to the predicted values. Similarly, the permeate flow rate is consistent with the model prediction with ratios of actual to predicted performance often exceeding 90%. Interestingly, ratios below the 90% level during this timeframe appeared to generally correlate with lower total feed rates. Although not definitive, this observation suggested that with lower feed velocities and possibly reduced feed gas turbulence at the CMS membrane surface may be the source of this discrepancy. Hence, more aggressive baffles and feed turbulence promoters may be necessary for the DCT-style bundle. This problem was examined more closely in pilot scale testing of a DCT-style bundle at our facility under highly controlled conditions as discussed in Sec. 5.

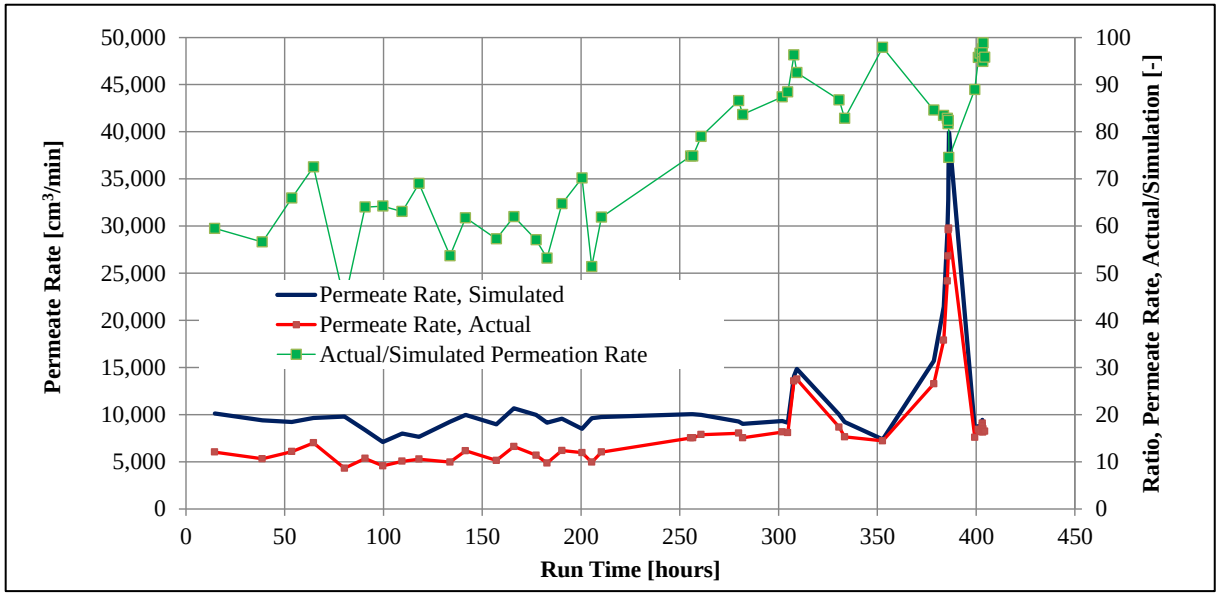


Figure 11. CMS membrane performance modeling at the NCCC showing the permeate rate generated from pure component data, the actual permeate rate. and the ratio of the actual to simulation derived rate.

Overall, we have demonstrated that the CMS membrane performance is highly stable in the presence of gasifier off-gas (no pretreatment; sour shifted), based upon predictions of the in-situ performance using pure component data as inputs to our membrane model. This is the first time we have been able to properly calculate in-situ membrane performance and thereby demonstrate the membrane performance and stability in-situ. In the past, modeling data suggested that the in-situ performance of our CMS membrane bundles at the NCCC was as much as 40 to 50% below predictions based upon pure component gas data. Improvements to the gas composition analysis, particularly with respect to the water content determinations, have made it possible to close this modeling gap. More interestingly, the model can be used now as a diagnostic tool to assess membrane performance on-line and therefore predict and diagnose possible membrane performance problems. As we have demonstrated with ex-situ pure gas testing during previous NCCC testing campaigns, and now with in-situ performance results, the CMS membrane is highly stable and can consistently deliver high performance in the presence of the wide range of gasifier off-gas contaminants.

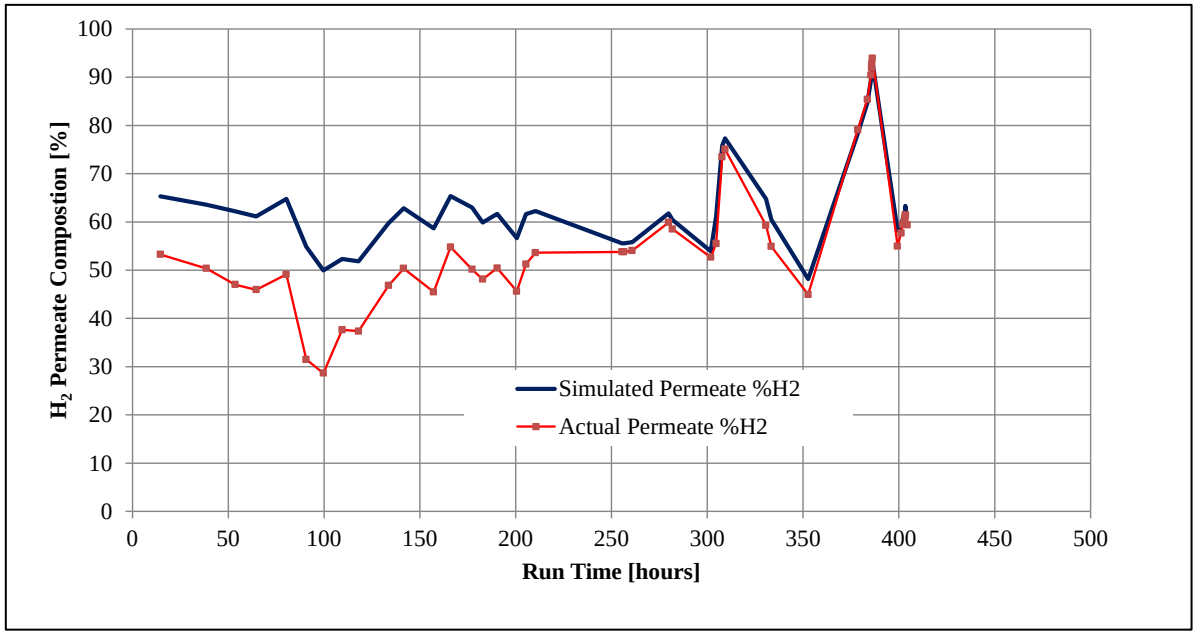


Figure 12. CMS membrane performance modeling at the NCCC showing the predicted and actual H_2 content in the permeate stream throughout the testing.

5. Flow Distribution Study of the DCT Style Bundles/Modules used for Field Tests

Single tube CMS membrane performance in mixed gas testing in the presence and absence of water could be well predicted over a wide range of pressures and feed rates as shown in our previous tests at NCCC as well as our lab. Here we present a series of test results with gas mixtures using our DCT-style membrane bundles with the objective to isolate the source of the poor agreement between the simulation predicted and the actual membrane bundle performance particularly during the first ca. 220 hours of field testing as shown in Figure 10&11. Although the major source of discrepancy between predicted and actual performance at the NCCC was shown to be due to shifting of the membrane baffles (fixed at ca. 220 hours) and hence bypass of feed flow directly to the reject, the in-situ membrane performance at the NCCC was still poorer than predicted at various times even after this fix. More specifically, in single tube testing agreement between the simulation predicted and actual membrane performance is typically in the range of 97 to 100%. Further, we have been able to achieve this level of agreement in our older PCG-style bundles with incorporation of exterior baffles to control feed flow distribution. In mixed gas bundle testing at the NCCC with the DCT-style bundle, even after repairing the bundle baffles, membrane mixed gas predictions were often in the 80 to 90% range and it appeared that high feed flows were necessary to deliver actual performance at 90 to 100% of the predicted values. The compilation of these results (single tube and NCCC bundle testing) suggested that the distribution of feed gas flow in the DCT-style bundle is not ideal and improvements in the baffle approach may be necessary.

In response to this, a series of tests were conducted by us in our pilot testing facility on a DCT-style bundle to confirm the NCCC testing results and ultimately to look at additional solutions to improve bundle performance in mixed gas testing.

In this series of tests, a standard 57 tube DCT-style bundle was used. Testing was conducted at room temperature at pressures between 30 and 60 psig over a wide range of feed flow rates. Two synthetic gas mixtures were used in this testing, specifically some 80/20 and 50/50 vol% He/N_2 blends. Figure 13 shows the ratio of the actual to simulation predicted bundle permeate flow versus total gas feed rate. Pure component permeances are used in the simulation to predict mixed gas performance. Values at 100% indicate exact agreement between the actual and predicted performance. Below 100% indicates the bundle performance is poorer than the predicted values. Test 1 was conducted with only minimal feed side baffles to establish preliminary bundle performance under poor feed flow distribution conditions as control. In this configuration, only two baffles are installed, one at the closed tip end and one at the potted end of the bundle to prevent gross bypass of feed gas around the part. As Figure 13 shows, in this baffle arrangement, agreement between the actual and predicted performance never exceeds about 80% throughout the range of testing.

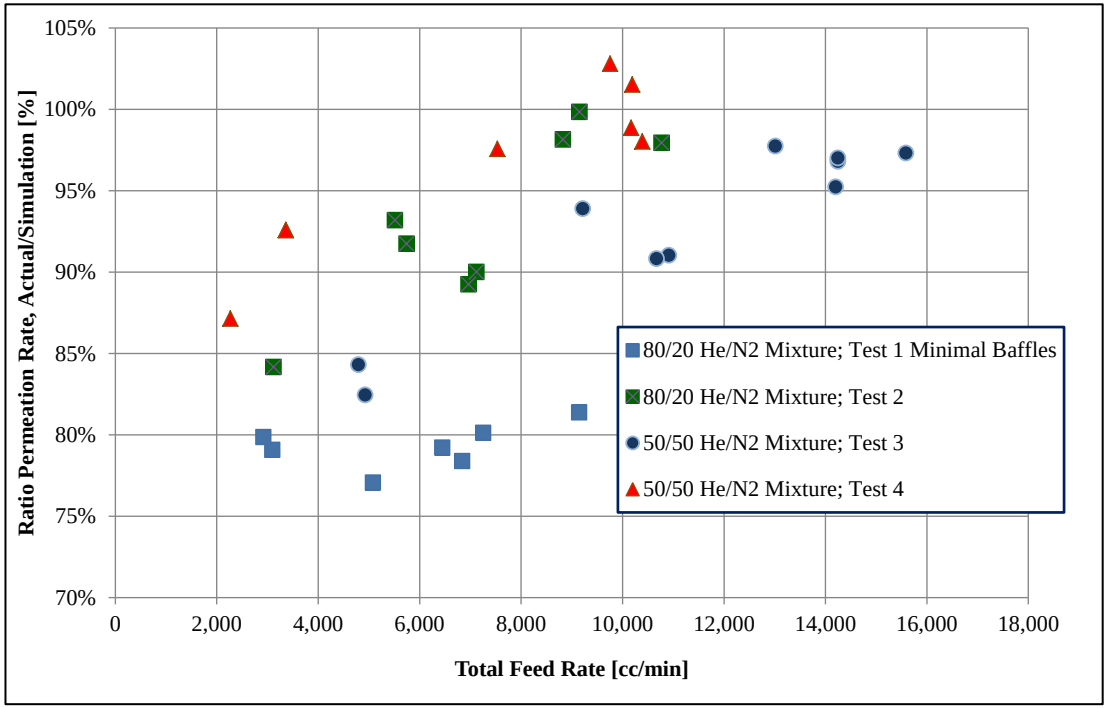


Figure 13. DCT-style bundle performance (ratio of actual to predicted) versus total feed rate for various baffle arrangements.

In Test 2, additional baffles were added along the length of the bundle (a total of four), to further limit feed gas channeling between the housing ID and bundle OD. As can be seen in Figure 13, considerable improvement in the bundle performance is observed, with actual and predicted performance in the 95 to 100% range at the higher feed rates. Test 3 was conducted using the same baffle configuration as in Test 2 but at lower feed gas He concentration. Under these conditions, considerably higher feed gas rates are required to achieve good agreement with the simulation predictions. In Test 4, the baffle arrangement was again modified. The baffle at the "tip end" of the bundle (gas feed entrance) was overhauled to better distribute gas into the center of the bundle. In addition, the exterior of the bundle was completely wrapped with an impermeable film (Saran wrap).

The objective here was to completely retain the feed gas "inside" the bundle and not permit any "annulus" flow between the exterior of the bundle and the housing ID. Both of these modifications were made to improve gas flow to the tubes at the interior of the bundle. In Test 5, the bundle wrap was replaced using Teflon tape to permit higher operating temperatures.

As Figure 13 shows, significant improvement in the mixed gas actual versus simulation predicted performance is observed in Test 4 and Test 5, considerably better than the previous Test 3 data under the same feed gas composition. Still the relatively poor performance persists at low feed gas rates. This suggests that feed gas velocity and hence turbulence at the membrane surface may be inadequate in the DCT-style bundle at these lower feed rates. In the older style PCG bundles, significant feed rate dependent performance was not observed using Test 2/3 style baffling. However, the PCG style bundle is a "close packed" configuration (tubes physically touching along much of the length), so that feed velocities were higher. In comparison, the DCT-style bundle is a "spaced tube" configuration with a tube to tube gap on the order of ca. 2mm. It is likely that this difference accounts for the poorer agreement in actual versus predicted performance of the DCT-bundles. Further modifications of the DCT bundle to include interior flow disrupters are currently being considered.

Overall, however, it is clear that feed flow distribution in the DCT-style bundles, as shown in both NCCC and MPT pilot testing, is a potential problem that requires some additional changes in the bundle engineering. Under the proper configuration, however, it is evident that good agreement between actual mixed gas performance and simulated performance based upon pure component data can be achieved, thereby permitting modeling of the membrane performance as required for cost development. On the other hand, a practical approach is also currently under consideration. Since most full-scale installations requires multiple membrane modules in series connection, the stage cut in each stage is expected to be low, which implies that the ratio could approximate ideal based upon the results shown in Figure 13. The exit and entrance effect of the reject and feed streams respectively would introduce sufficient mixing to deliver a homogeneous fresh feed to the next stage. Thus, we believe that for a full-scale installation, the flow distribution within the housing, though exists, its real impact with respect to the gas separation efficiency is expected to be within the acceptable range.

6. Field Testing of Pd and PdAg Membrane Bundles at the NCCC

6.1. *Characterization of Pd and PdAg Membrane Bundles for Testing at the NCCC*

Two Pd membranes and one PdAg membrane bundles were prepared for this NCCC test. Figure 14 shows the pictures of the PdAg bundle (middle, designated as PdAg-DCT-28) and the Pd bundles (left, Pd-DCT-3 and right, Pd-DCT-7). Each bundle contains (typically) 12 MPT standard 5.7mm OD x 12" L tubes in a candle filter configuration with ceramic-glass potting in a dense ceramic tube sheet (designation DCT). A Pd or PdAg alloy thin film was coated on the outer surface of the tubes as shown in the figure. These bundles were characterized in our pilot plant with H_2, N_2, and CO_2 prior to shipment to the NCCC for field testing. Detailed characterization of these bundles are presented in Figure 15 and Figure 16 for two of the bundles. Table 3 shows the pre-NCCC test data for each of the bundles.

As shown in Figure 15, the hydrogen permeance for the Pd-DCT-7 ranges from ca. 2,900 to 4,100 GPU at 350°C and 20psig feed pressure. The fluctuations observed in the membrane permeances, particularly for H_2, have been attributed to contamination of the membrane during exposure to the atmosphere from storage or in the gas testing system. All of our systems are used for a large array of gas phase testing of various membranes and introduction of minor contaminants has been an issue in general for our Pd-alloy membrane development and testing. As discussed below, membrane "contamination" occurring during storage is easily dealt with via air oxidation (cleaning) with no damage to the membrane

Figure 14. Photographs of the PdAg (center) and Pd (left/right) bundles used in the NCCC testing during 2Q2017. Two of the stainless steel sealing inserts constructed during this quarter to permit testing of these bundles in the NCCC housing are also shown.

performance. Further, no permeance fluctuations are generally observed in ultra-clean systems. The N_2 permeance in general is below 2 GPU so that the resultant ideal selectivity for H_2/N_2 is >1,000. Figure 16 shows the H_2, N_2 and CO_2 permeances for the PdAg-DCT-28 bundle. The H_2, N_2, and CO_2 permeances are about 5200, 2.0, and <1.0 GPU, respectively. Obviously, these bundles exhibit excellent H_2/N_2 and H_2/CO_2 selectivity and hence are ideal as the second stage for our proposed dual stage membrane process. In addition, both bundles demonstrated excellent thermal stability during 150 to 200 hours performance testing, consistent with the >25,000 hours of thermal stability of several typical PdAg membrane prepared by us and detailed in various quarterly reports issued for this project.

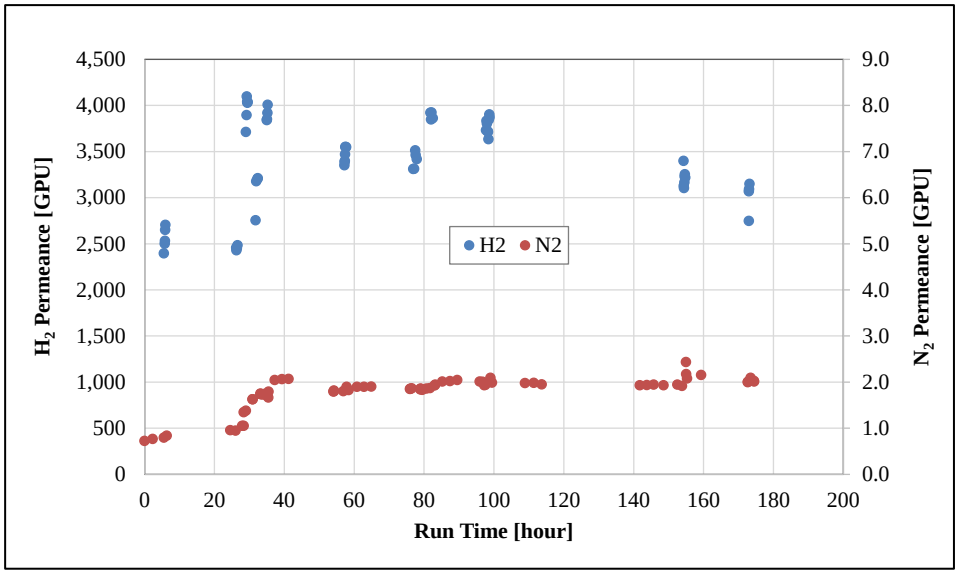


Figure 15. Characterization of the Pd membrane bundle (Pd-DCT-7) at 350°C prior to NCCC field testing.

6.2 NCCC Test Overview and Pre-test Preparations

Our Pd-alloy membrane test campaign at the NCCC began in late March 2017. During the first week of pre-gasifier shakedown testing, we modified our testing system to permit (i) pure hydrogen characterization of the membranes and (ii) air regeneration as necessary for contaminant removal. Gasifier off-gas syngas testing began in the first week of April 2017 (4/3/2017) when "sweet" shifted syngas became available and was completed on 4/30/2017 when the syngas to our unit was shut down. A cumulative of 156 hours of syngas permeation runtime and 176 hours of membrane regeneration was performed. For the balance of the test, the system was down due to the maintenance issues associated with the gasifier, primarily as a result of the significant tar presence during this campaign. Based upon the input from the gasifier operators, it was clear that significant "tar" was present in the "sweet" shifted syngas. Further, due to the previous extensive amount of syngas testing on our field unit (>3,000 hours) with our CMS membranes, contamination of our unit was also likely extensive. Although our field test unit was extensively flushed with N_2 at 300°C prior to Pd and PdAg membrane testing, it was not possible for us to properly air oxidize the unit due to safety concerns on the test pad. It is this air oxidation however that is generally required in the laboratory to fully recover Pd-alloy membrane performance following contamination. Due to the presence of tar of the syngas available to us, we attempted to clean the system and membrane with nitrogen before the test. However, we believe that inert flushing and air oxidation at 300°C is most likely not sufficient. It should be noted that the very time-consuming process of converting from syngas running configuration to air oxidation configuration did cost us time available for running syngas.

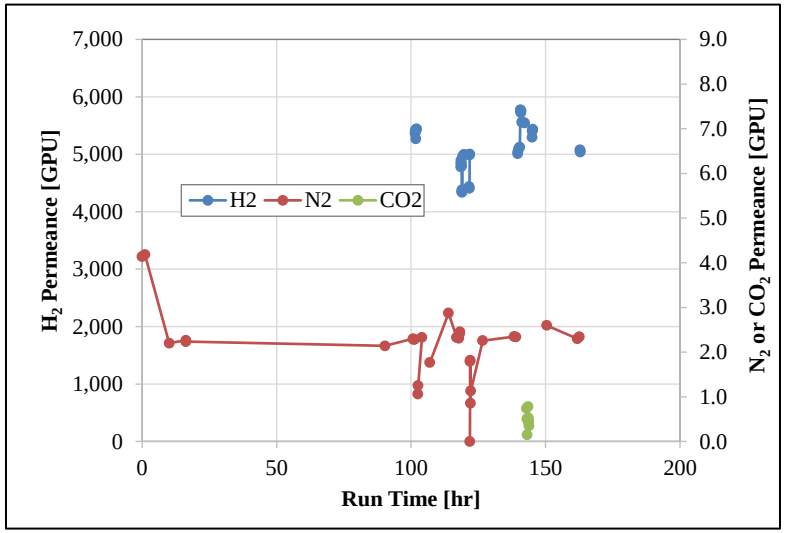


Figure 16. Characterization of the PdAg membrane bundle (PdAg-DCT-28) at 350°C prior to NCCC field testing.

6.3 Operating Condition of NCCC Syngas Runs

Figure 14 shows the picture of the three Pd and PdAg-based membrane bundles (12 tubes each bundle) tested during 2Q2017 at the NCCC. Throughout most of the testing, the feed temperature was maintained at 300°C (upper design limit of our pressure housing) and the reject temperature was measured typically at 250 and 275°C. The hydrogen concentration in our permeate, independent of bundle tested, was typically enriched from ~13% to ~50% for the syngas as received and from ~40% to up to 90% for the syngas spiked with hydrogen. These results contrast with the 99%+ purity that our Pd single tube membranes delivered in our previous test at the NCCC. The poor H_2 recovery performance was directly attributable to the

rapid and significant H_2 permeance losses during live gas testing due to the significant presence of tar in the feed. Based upon both in-situ gas modelling and post-test pure gas measurements, we observed H_2 permeances on the order of 370 to 750 GPU, well below the typical 3,000 to 5,000 GPU of the clean membrane.

6.4 Bundle Testing with Gasifier Syngas at the NCCC

In this current campaign, the first phase of the NCCC testing was conducted with the Pd-DCT-3 bundle (preliminary performance is shown in Table 3).
It was the lowest quality bundle and was commissioned for the purpose of shakedown testing of the system before moving on to PdAg bundle (Figure 15). Figure 18 shows the overall membrane hydrogen separation performance, which is quite poor for a typical palladium based membrane. The pure hydrogen permeances taken intermittently during the test period confirm very low hydrogen permeances in the 300 to 550 GPU range. It should be noted that during hour 5-7 and 42, the feed gas was sent to both the feed and permeate gas analyzers to confirm the accuracy of the measurements and verify that we were not observing a problem with one of the GC's. Around hour 44, this bundle underwent in-situ oxidation which led to the slight increase in permeate H_2 content as shown from hour 44 to ca. 50. After approximately 50 hours, the decision was made to move on to the 2nd Pd bundles, Pd-DCT-7, and started post-mortem testing on Pd-DCT-3 once it was removed from the system.

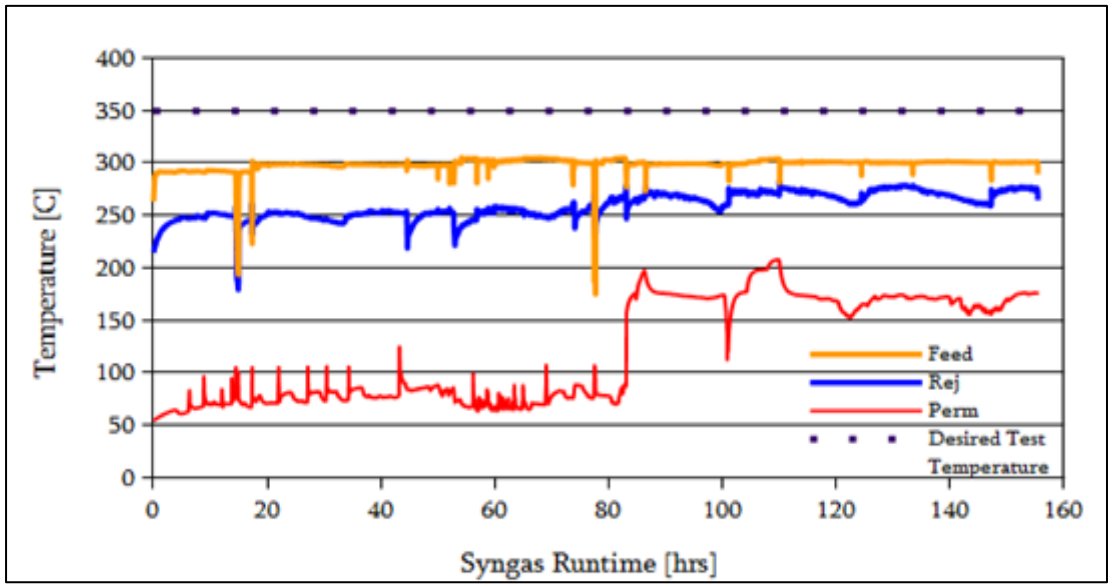


Figure 17. Operating temperatures during live gasifier syngas testing of the MPT Pd-alloy bundles during 2Q2017.

Table 3. Summary of preliminary characterization data for the three bundles tested at the NCCC.

Membrane ID	Permeance [GPU]		
	N_2	H_2	H_2/N_2
Pd-DCT-3	3.8	4,170	1,100
Pd-DCT-7	2.0	3,620	1,810
PdAg-DCT-28	2.5	5,180	2,030

Typical pure component hydrogen permeances measured for the 2nd bundle, Pd-DCT-7, before shipping to NCCC are shown in Table 3. Just after installation at the NCCC, the bundle was in-situ air oxidized relatively shortly before exposure to syngas. The overall gas separation performance of this bundle based upon the feed and permeate gas composition is shown in Figure 19. As with the first bundle at approximately hour 58 (Figure 19) feed gas was sent to both gas analyzers (i.e., not through membrane) as a GC performance check/verification to confirm no problems with the GC's. Despite having a higher gas separation efficiency and recent air oxidation, this bundle performed no better than the first bundle. The in-situ pure component hydrogen permeance even before syngas testing fell to ca. 300 to 500 GPU (from >3,200 GPU), indicating that the system and plumbing had released tar or other contaminants, which then poisoned the membrane. Further, the pure hydrogen permeance taken intermittently during the first portion of the live gas test run ranged from 400-500 GPU range. During this run, the bundle was in-situ oxidized at hours 74, 80, and 85 with only modest improvements in pure hydrogen permeance up to the 500 - 700 GPU range and slight improvement in syngas separation performance as shown in Figure 19. In addition to the hour 85 air oxidation, we attempted to help maintain system temperatures as close to 300°C by adjusting the locations of heating and insulation on the main vessel. While this adjustment impacted local temperatures modestly, as shown in Figure 17 after hour 85, the overall impact on membrane performance was negligible.

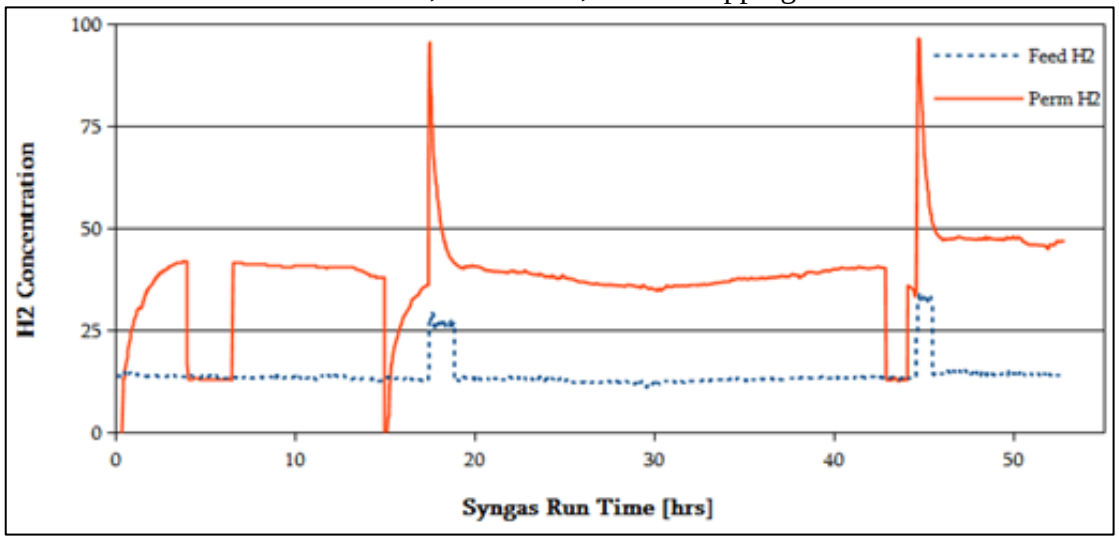


Figure 18. Hydrogen concentration in the feed and permeate gas streams during system shakedown testing of the Pd-DCT-3 Pd bundle.

The third bundle tested at the NCCC was a PdAg alloy bundle (center bundle in Figure 14). We had planned to use the first two Pd bundles as sacrifice parts to line out the system, debug any problems, and get the test procedure in place prior to testing the PdAg bundle. However, based upon our extended testing of the Pd bundles above, our expectations were modest for this new bundle. Further, we were initially unsure how much damage we were doing to the bundles on exposure to NCCC syngas

and were concerned about sacrificing a PdAg bundle to this test. Near the end of the test campaign, we decided to move ahead with the PdAg bundle as we became more confident that the membranes could be regenerated. Preliminary post mortem analysis on the first Pd bundle in our laboratory (see below) suggested that the flux losses were not irreversible and no permanent damage to the membrane would occur due to exposure to the tar-laden gasifier syngas. Prior to testing with live gas with bundle PdAg-DCT-28, we conducted a preliminary in-situ air oxidation at 300°C for ca. 2 hours. However, as expected based upon the problems faced with the previous two bundles, the in-situ hydrogen permeances fell rapidly to ca. 400 to 625 GPU within the first two hours of startup at the NCCC. Further, permeate quality was similarly poor, and we were unable to achieve H_2 enrichment above 55%. In total, we logged under 10 hours of run time on the PdAg-DCT-28 before the gasifier was shut down unexpectedly early. This membrane was returned to our lab for regeneration as discussed in the following sections.

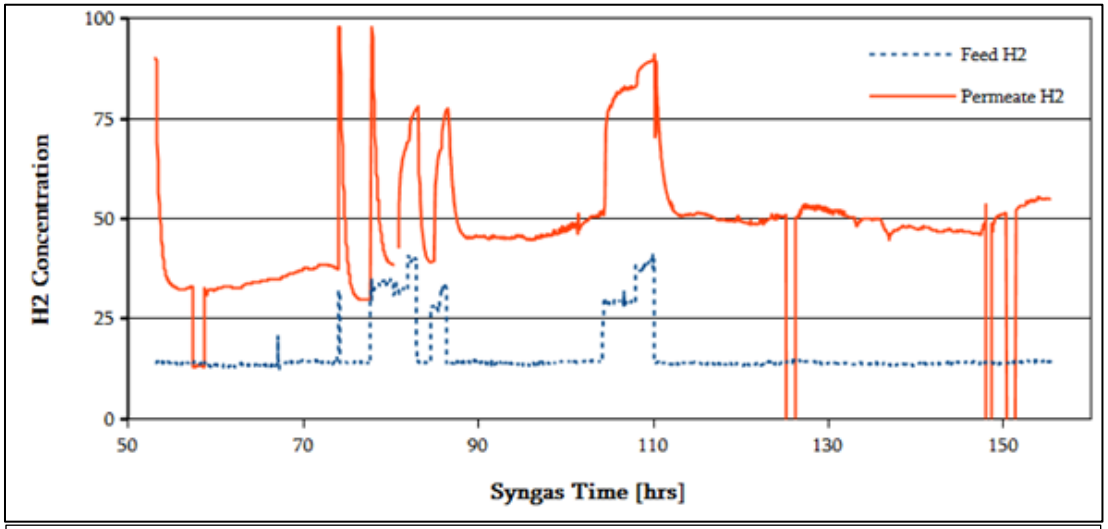


Figure 19. Hydrogen concentration in the feed and permeate gas streams during system shakedown testing of the Pd-DCT-7 Pd bundle.

The three bundles tested during this campaign all showed a high degree of loss in hydrogen permeance as would be expected with tar-laden pyrolysis gas. Though on-site in-situ regeneration was attempted to restore the membrane activity, the presence of tar in the syngas and the residual tar deposited in the system prevented us from obtaining high hydrogen permeances during in-situ testing. However, since the N_2 permeances did not change appreciably during testing, ultimately no long term catastrophic damage to the membranes had occurred. As discussed below, relatively straightforward regeneration at our laboratory facility confirmed this. Hence, although the gas separation performance was negatively impacted by the presence of tar in the NCCC syngas, this was simple surface contamination of the membrane and did not represent a serious irreversible failure of the part. The multiple element bundles we have developed were subject to the high temperature and high pressure syngas gas stream without any irreversible physical damage or failure. Due to the lack of syngas free of tar in this test, our focus had been placed on the effect of tar on membrane performance and the regeneration. This test generated membranes

poisoned by the actual syngas, which are ideal candidates for us to confirm the effectiveness of our Pd-alloy membrane regeneration protocol as discussed in the next section.

7. Regeneration of Pd Membranes Poisoned by Tar-like Materials at NCCC

The three membrane bundles tested at the NCCC were sent back to our laboratory for post mortem analysis and regeneration. Our study here included: (i) characterizing the membranes as received to confirm our observation in the field and (ii) performing regeneration of the used membranes to verify the effectiveness of the regeneration protocol we have developed. Since we were unsure of the extent of membrane poisoning and potentially required multiple tests to develop a regeneration protocol, instead of using full bundles for one-shot deal, we selectively removed several single tubes from each bundle to be statistical significant for our post mortem study here. The results from each tube are discussed in detail as follows:

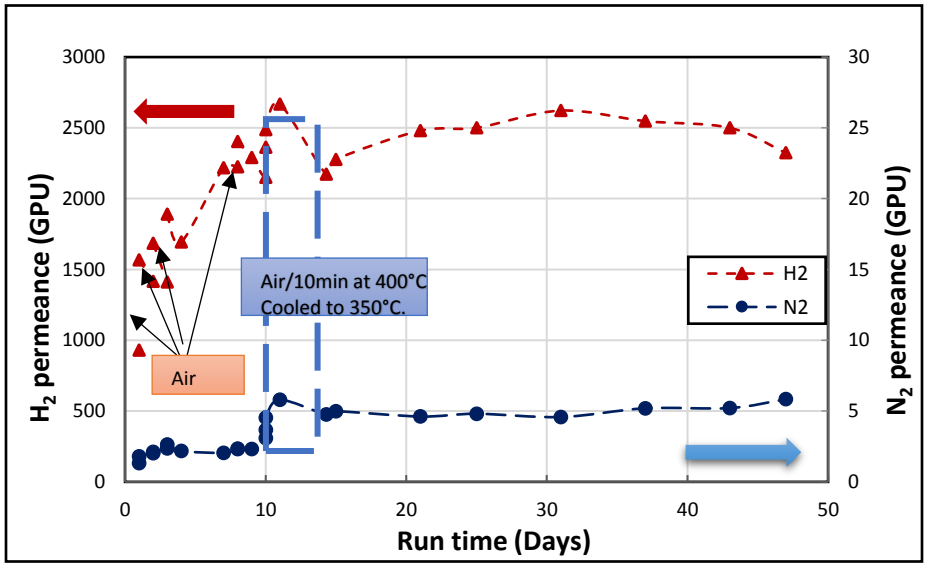


Figure 20. Characterization of the Pd-DCT-3-2 tube as received (post NCCC testing) and during regeneration.

7.1 Bundle Sample #1: Pd-DCT-3

The first bundle tested at the NCCC, Pd-DCT-2, was returned to our laboratory for post mortem analysis and testing. Several individual tubes were removed from the bundle and a variety of tests were conducted. The first tube obtained from Pd-DCT-3, designated as Pd-DCT-3-2, was heated to 350°C to determine its hydrogen permeance as received, which would be representative of the performance at the end of the run at the NCCC. The hydrogen permeance as received was 930 GPU as shown in Figure 20 (at 350°C versus ca. 290 to 300°C at the NCCC), which is much lower than the typical permeance of our Pd membrane, i.e., 2,900 to >4,000 GPU. Obviously, the membrane was significantly poisoned by tar in the field. After regeneration, via four 10 minute air oxidations at 350°C as indicated in Figure 20, its permeance increased to about 2,400 GPU as shown in Figure 20. Following this, a 2nd phase of air regeneration was conducted at 400°C to assess the impact of slightly more aggressive conditions. As can be seen, at 350°C the H_2 permeance of the bundle was only marginally higher, although the N_2 permeance appears to have increased slightly. Following this, a longer-term performance stability test was conducted. Little change in the membrane performance was noted after nearly 40 days. In summary, the first tube obtained from the first

bundle, Pd-DCT-3, poisoned at NCCC was effectively regenerated using our regeneration protocol. Further the regenerated membrane maintained its permeance in the inert atmosphere for more than 40 days.

The initial hydrogen permeance measurement for the second tube designated as Pd-DCT-3-3 was also low at ca. 1,300 GPU as shown in Figure 21, again indicating that significant poisoning occurred during live gas testing at the NCCC. Regeneration with air for this membrane was performed but was not as simple as the previous tube. The initial hydrogen permeance after air oxidation increased rapidly but then decayed unexpectedly after the first three regeneration passes. Interestingly, the H_2 permeance eventually reached ca. 5,500 GPU on continuous purging. The saw-tooth-shaped recovery of the H_2 permeance in this membrane is not well understood (although it has been observed with other Pd-alloy membranes by us over the years). Because of the intermittent and relatively odd performance, we believe that the reduction was most likely due to contaminants of the house N_2 used in this test (available at our facility) during this period. Still, very good H_2 permeance recovery, i.e., from ~1,300 to >4,000 GPU, is observed during this testing.

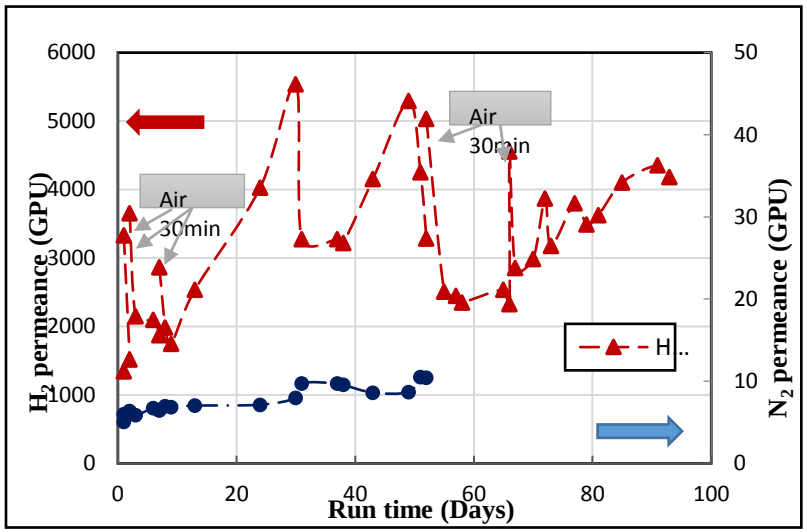


Figure 21. Characterization of the Pd-DCT-3-3 tube as received (post NCCC testing) and during

The initial hydrogen permeance of the 3rd tube designated as Pd-DCT-3-5 was ca. 1,100 GPU, similar to the previous two tubes. As shown in Figure 22, significant H_2 permeance recovery was achieved after air regeneration to >3,000 GPU. The hydrogen permeance remained reasonably stable in the 2,500 to 3,000 GPU range from day 20 to 42. Further, regeneration had no impact on the membrane N_2 permeance demonstrating the stability of this membrane on exposure both the NCCC live gas as well as following air regeneration.

Table 4. Summary of characterization data for the tubes removed from the Pd-DCT-3 bundle following testing at the NCCC.

Membrane ID	Before/After Regeneration	Permeance [GPU]		
		N_2	H_2	H_2/N_2
Pd-DCT-3-2	Post NCCC	1.3	930	715
	Post Regen	5.8	2,300	396
Pd-DCT-3-3	Post NCCC	5.1	1,350	266
	Post Regen	N/A	4,200	N/A
Pd-DCT-3-5	Post NCCC	4.4	1,120	252
	Post Regen	4.4	3,310	750

Table 4 summarizes the membrane permeance as received (i.e., returned from NCCC after test) and after regeneration in the lab. Prior to regeneration, the hydrogen permeances obtained in our lab for Pd-MCC-3-3 & -5 were in the range of ca. 900 to 1,300 GPU, significantly lower than the pre-NCCC permeance of the bundle (see Table 3). Obviously, poisoning of the Pd membranes by the tar present in the syngas at NCCC took place. After regeneration, we were able to restore the hydrogen permeance to 3,300 to 4,200 GPU at 350°C as shown in the table. The recovered hydrogen permeances from Pd-MCC-3-3 and 3-5 are in line with our typical Pd membrane performance; the regeneration protocol we have developed is thus considered to be highly effective.

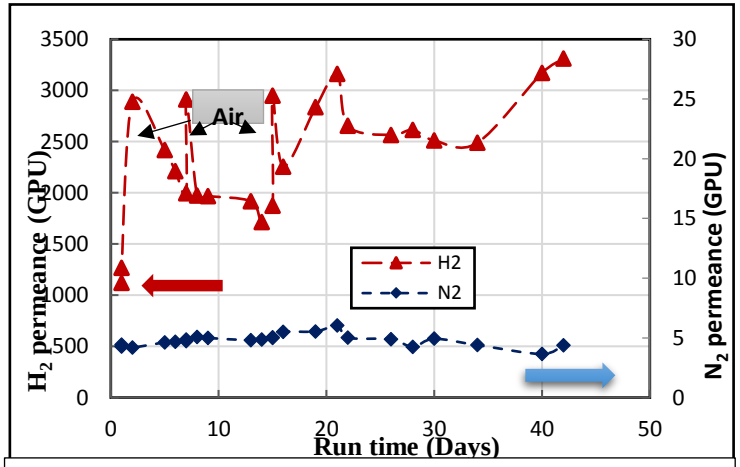
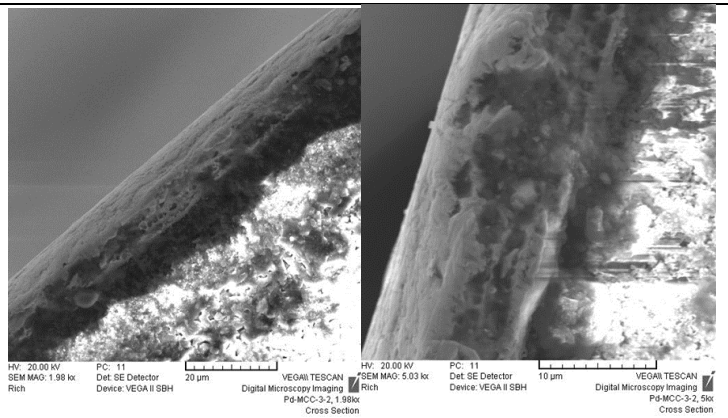


Figure 22. Characterization of the Pd-DCT-3-5 tube as received (post NCCC testing) and during regeneration.

Interestingly, the hydrogen permeance of the Pd-MCC-3-2 after regeneration, i.e., 2,300 GPU, appears to be much lower than our typical permeance for the Pd membrane. For this reason, the

membrane tube was sacrificed so that SEM examination could be conducted. Figure 23 shows the cross section of a portion of this membrane. In general, the layer thickness is ca. 5 to 8 µm although in some regions it exceeds 10 µm. Since the typical Pd layer thickness for our standard membrane is ≤5 µm, the somewhat lower permeance of this tube is in-line with the significantly thicker active layer.



(a) Pd-MCC-3-2, 2kx (b) Pd-MCC-3-2, 5kx

Figure 23. SEM Examination of the Pd-DCT-3-2 for the Membrane Layer Thickness

7.2 Membrane Bundle Sample #2: Pd-MCCC-7

The second bundle tested at the NCCC, Pd-DCT-7, was returned to the lab for similar analysis as the Pd-DCT-3. Again, three membrane tubes, i.e., Pd-MCC-7-1, -2 and -3 were cut from the bundle for characterization. The results are summarized below:

Similar to Pd-DCT-3, the membrane tubes were severely poisoned as indicated by their permeance as-received as shown in Table 5. The performance was restored via air regeneration to yield H_2 permeances in the range of 3,700 to 5,200 GPU at 350°C. These values are again in line with our typical virgin membrane performance. The results from each tube are presented in Figure 24, Figure 25, and Figure 26.

Table 5. Summary of characterization data for the tubes removed from the Pd-DCT-7 bundle following testing at the NCCC.

Membrane ID	H_2 Permeance [GPU]		
	As-received (post NCCC)	Post Regeneration	
	310°C	310°C	350°C
Pd-MCC-7-1	785	4,560	5,260
Pd-MCC-7-2	863	3,450	3,780
Pd-MCC-7-3Dull	1,530	4,130	4,370
Pd-MCC-7-3Bright	870	3,510	N/A

In summary, the two bundles which were poisoned at NCCC through exposure to the tar laden syngas were effectively regenerated using the protocol we have developed. Three single tubes from each bundle were removed from the bundles for the regeneration study. All of them except one were restored effectively to 3,000 to 4,000 GPU range from ≤1,000 GPU. The exception was likely attributed to the low permeance before the poison due to the non-uniform layer thickness of the Pd membrane.

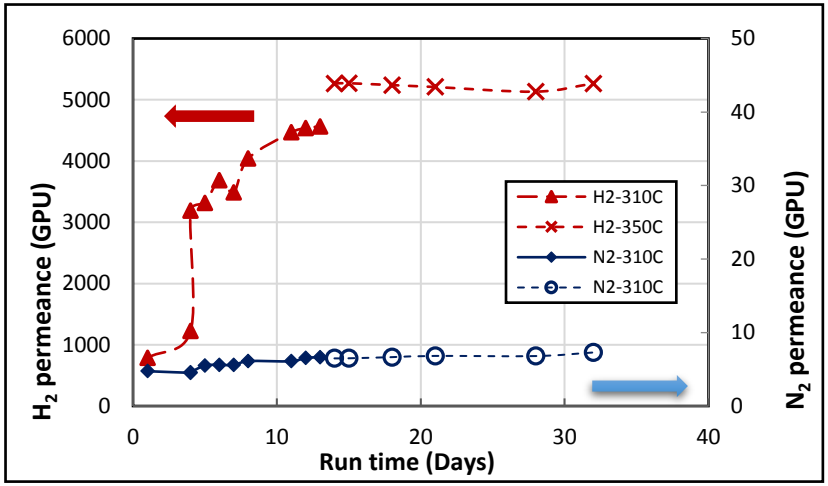


Figure 24. Characterization of the Pd-DCT-7-1 tube as received (post NCCC testing) and during regeneration.

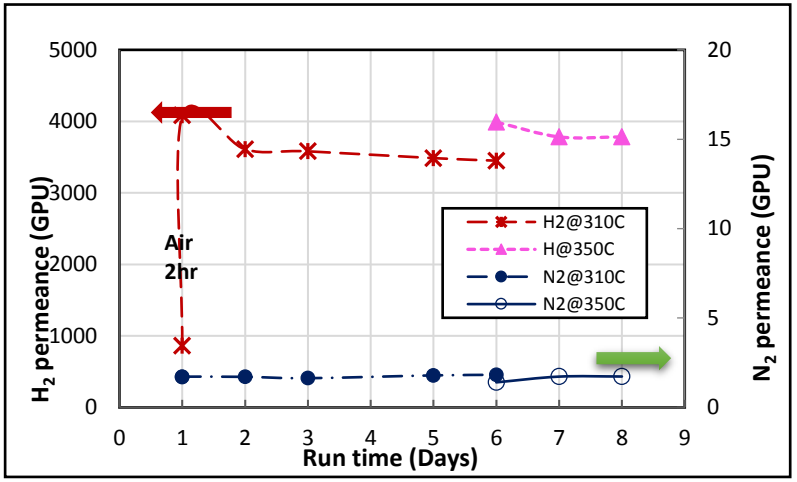


Figure 25. Characterization of the Pd-DCT-7-2 tube as received (post NCCC testing) and during regeneration.

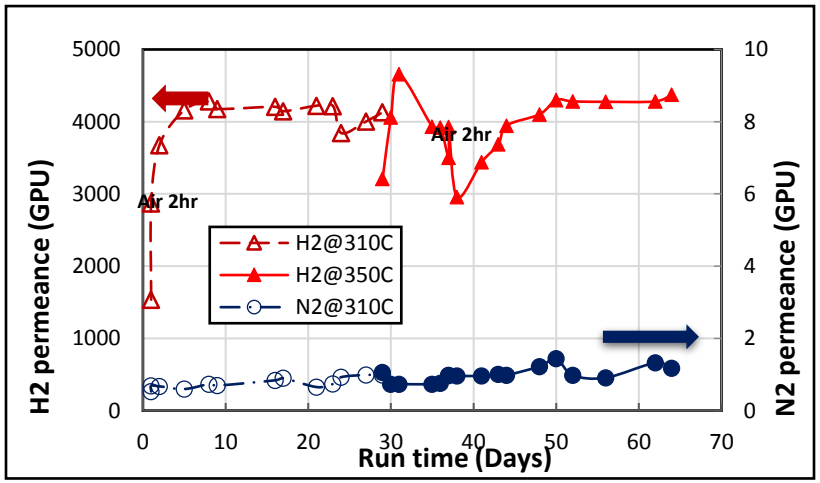


Figure 26. Characterization of the Pd-DCT-7-3 dull tube as received (post NCCC testing) and during regeneration.

8. Optimization of Our Regeneration Protocol using Pd Membranes Poisoned at NCCC

Obviously, the Pd-alloy membrane was susceptible to poisoning in the NCCC off-gas, likely by tar-like or similar organic materials (since air regeneration is very effective). To be a commercially viable Pd-alloy membrane, an effective regeneration protocol must be developed. Air regeneration at 350°C was found to be effective as demonstrated in our lab studies. In this section, this regeneration protocol was verified against the Pd membranes poisoned by syngas produced at NCCC.

8.1 Impact of Regeneration Temperature

The tube, Pd-DCT-3-4, was used to study various air treatment protocols to determine important operating parameters associated with H_2 permeance recovery (while avoiding N_2 permeance increases due to introduction of membrane flaws). In the initial study phase, air treatment of a poisoned membrane for 15 minutes was applied at different temperatures. In this study, air regenerations were conducted consecutively at 290, 310, and 350°C. Figure 27 shows that some permeance recovery can be achieved at the lowest temperatures, although it is clear that the higher temperatures are likely necessary to achieve stable recovery at values consistent with the as-prepared membrane. Further, even at the highest temperature, very little change in the N_2 permeance is observed, consistent with data presented in previous sections.

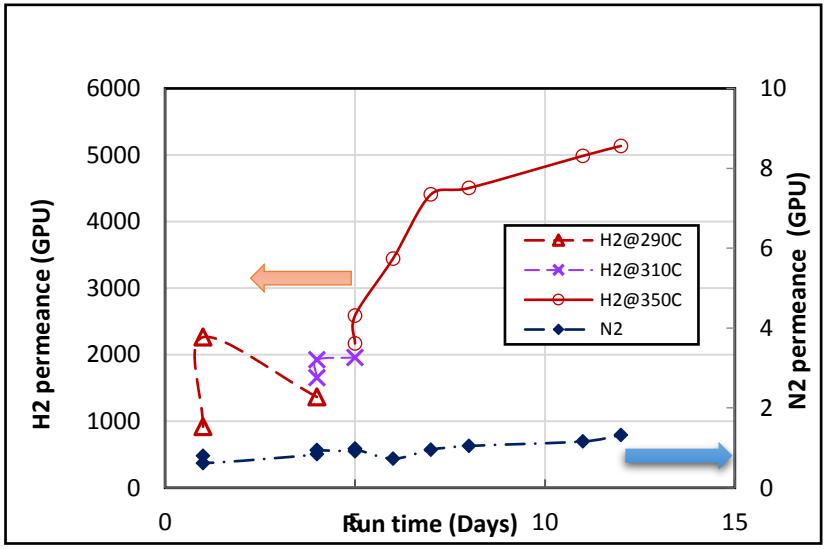


Figure 27. Effect of air regeneration temperature on membrane performance following poisoning at the NCCC (tube is Pd-DCT-3-4)

8.2 Impact of Regeneration Time/Frequency

The effect of regeneration frequency was also studied during the regeneration of several of the membranes discussed above. Figure 28 shows the impact of various regeneration times on the H_2 recovery for several of the tubes cut from bundles exposed to syngas at the NCCC. In general, the first regeneration is typically the most effective one based upon the H_2 permeance recovery with subsequent regenerations clearly showing a diminishing degree of recovery. Beyond the 3rd air cycle, the benefit of thermal regeneration becomes negligible. Single step two hour of air treatment was also applied to the study of the Pd-DCT-7-2, Pd-DCT-7-3Dull and Pd-DCT-7-3Bright

membranes. The results show that a two-hour duration is sufficient to increase hydrogen permeance and may reduce the frequency of air treatment needed. From this study, several 10 to15 minute duration air exposure of the fouled membrane appears to be adequate for full regeneration.

In summary, the Pd membranes poisoned by tar-like materials at NCCC have been effectively regenerated by the protocol we developed. The regeneration condition, in particular temperature and treatment duration, has been optimized for future implementation in the field.

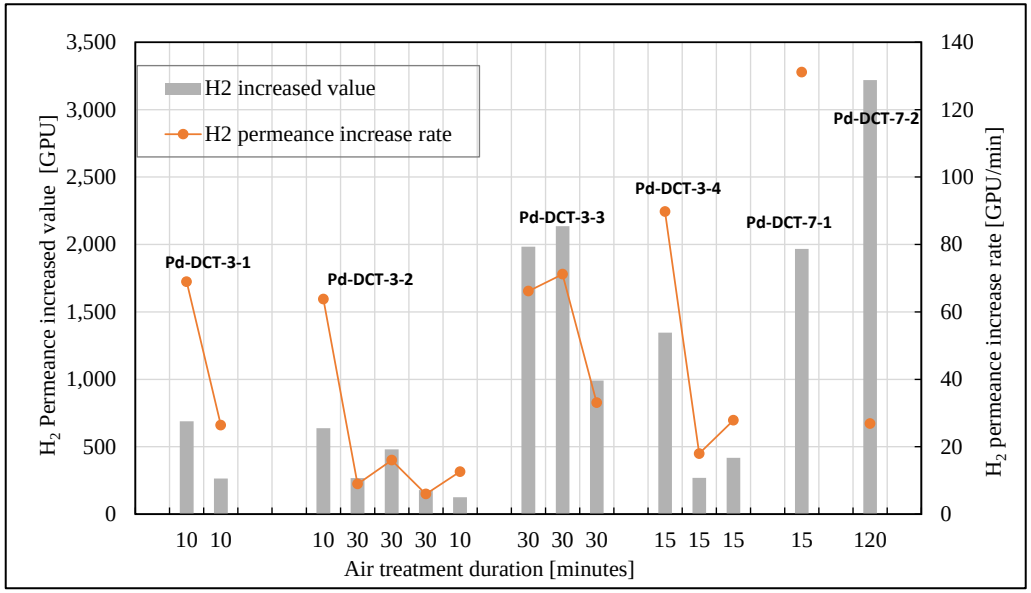


Figure 28. Effect of air regeneration time and/or frequency on H_2 permeance recovery at 350°C.

9. Summary and Conclusions

In this program, a wide array of challenge and performance testing was conducted in live gas testing at the NCCC of our proposed CMS and Pd-alloy membranes. The testing was conducted on multiple-tube membrane bundles consistent with packages that would be used in commercial application of the technologies. Overall, we have demonstrated in this testing that both membrane technologies display excellent separation performance and are highly stable in the proposed application environments. In addition, the field generated performance data after taking into account the water content determined with the installed water capture subsystems is in good agreement with the simulation from our model.

A summary of the results and conclusions from our NCCC live syngas testing of the CMS membrane with the DCT style bundles is given below:

1. *Functional performance stability of our DCT style CMS membrane bundles (second generation) for over 400 hours at NCCC has been demonstrated…* Over 400 hours of testing of the new DCT-style 57 tube CMS membrane bundle was conducted at the NCCC with sour shifted syngas. The membrane performance was shown to be stable throughout the test, similar to the results obtained from the previous tests with single tubes and multiple tube potted ceramic glass (PCG, first generation)-style bundles. The DCT-style bundles can sustain pressures ≥1000 psig at temperatures ≥500°C making them suitable for the entire range of operating conditions contemplated by the IGCC industry. The first generation PCG-style bundle is inadequate for the high temperature and high-pressure regime of the IGCC operation.

2. *In-situ water capture subsystems installed during this project allows us to reliably determine the wet-gas composition necessary for the in-situ live gas membrane separation modeling…* Implementation of two water capture subsystems to determine the reject and the permeate gas composition in-situ respectively was successfully completed. The water capture subsystems were designed, fabricated and then installed in our membrane testing unit at NCCC. The subsystems were successfully tested throughout 400 hours of live gas testing of our CMS bundle. The in-situ real time water content analysis available along with real time dry gas analysis permits highly accurate assessment of the membrane performance, providing reliable wet gas composition analysis necessary for the in-situ live gas membrane modeling.

3. *Model predictions of the in-situ CMS membrane performance at the NCCC were in very good agreement with the actual measured results taking into account the water content determined by our in-situ water capture subsystem….* This is the first time that our models have successfully predicted in-situ membrane performance without the incorporation of any correction factors. The addition of the water capture units to establish feed gas composition and the incorporation of bundle feed flow distribution baffles were found to resolve the problems we previously had with accurately predicting in-

situ membrane performance. The model can now be used to as a diagnostic tool to troubleshoot membrane performance issues during live gas testing. Further, this model predictive capability can thereby reliably support the gas separation performance simulation required in the techno-economic analysis.

4. *The DCT-style CMS membrane bundle has been demonstrated in NCCC live gas testing to be an ideal platform for the first stage of the Dual Stage Membrane Process….* We have demonstrated that the CMS membrane is capable of long-term stable operation in the proposed operating environment as the "roughing" stage in the Dual Stage Membrane Process. Further, the DCT-style bundle concept offers a clear pathway forward for large scale CMS membrane commercial implementation.

A summary of the results and conclusions from our NCCC live syngas testing of the Pd and Pd-Ag bundles is given below.

1. *High quality high performance multiple tube Pd and Pd-Ag bundles based upon our DCT potting configuration can be readily prepared by us.* This configuration, i.e., Pd and Pd-Ag thin film supported on ceramic membrane bundles overcomes the well-known barriers in Pd cost and supply associated with the large-scale development for the Pd and Pd alloy membrane. Three bundles were prepared by us for testing at the NCCC. These bundles displayed high H_2 permeance (3,000 to 5,000 GPU), excellent H_2/N_2 and H_2/CO_2 selectivity (>>1,000) and long-term operational stability (over 25,000 hours of thermal stability testing).

2. *The three DCT configured Pd and Pd-Ag bundles tested at the NCCC displayed excellent mechanical stability.* No leaking of the tubes, potting, seals or other components of the bundles and modules was observed during the NCCC testing for >150 cumulative hours. No irreversible damage was found to occur in any of the bundles. Our ceramic membrane supported Pd alloy based membrane in the DCT configured bundle provides a realistic and economical pathway to fabricate Pd membranes for commercialization.

3. *The Pd and Pd-Ag bundles showed significant fouling in the presence of "sweet shifted" gasifier syngas due to the high tar-like species content.* Although sweet shifted low sulfur syngas was provided to us, no tar was removed from this stream. Hence, significant levels of tar-like species both present in the syngas and released from the system plumbing, fouled the membranes yielding in-situ H_2 permeance 8 to 10-fold below the pure gas values. In our proposed Dual Stage Membrane Process, the Pd-Ag membrane will be downstream of the Cold Gas Cleanup Unit. *No tar species are expected in the actual application*.

4. *The Pd and Pd-Ag bundles fouled at the NCCC were effectively restored to the original H_2 permeance and H_2/N_2 selectivity on air regeneration in a follow-up laboratory study.* The original hydrogen permeances of the membranes were effectively restored in our lab during the post mortem study with the simple regeneration protocol we developed previously. Using the poisoned membranes returned from this field test, we confirmed that a 2-hour air oxidation at 350°C is adequate to fully regenerate the membranes. No irreversible damage was noted in any of the membranes. It should be noted that, in our proposed dual stage process, the Pd-Ag membrane is downstream of the cold gas cleanup unit and CO_2 compressors. At this stage, high purity tar-free gas is available and membrane poisoning is expected to be far less severe or negligible.

5. *Preliminary study of Pd membrane fouling in the laboratory via naphthalene as a simulated tar confirmed that poisoning by these species can be severe.* A Pd membrane exposed to as little as 50ppm of naphthalene at 275°C was immediately poisoned yielding 60 to 70% H_2 permeance reductions. Although a portion of the H_2 permeance could be recovered with inert gas or H_2 purging (naphthalene free), air regeneration was required to fully recover the membrane permeance. Our membranes poisoned by exposure to tars in the NCCC syngas were similarly regenerated by air oxidation.

6. *High purity H_2 can be delivered with Pd-alloy membranes with tar-free syngas making this membrane an ideal choice for the 2nd Stage of our proposed Dual Stage Membrane Process.* In our previous field test with single tubes, we demonstrated the superior hydrogen permeance and selectivity of these membranes which can enrich the hydrogen concentration to 99%+ from syngas containing no/low tar or sulfur. The physical integrity, effectiveness and regenerability of our full-scale Pd membrane/bundle for our proposed dual stage membrane system has been demonstrated in the current tests at NCCC. In summary, the suitability of our full-scale Pd and Pd-Ag membrane bundle and housing has been fully demonstrated through field tests at the NCCC.