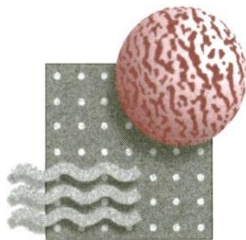
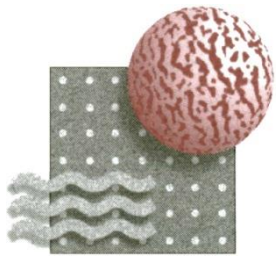


# **Robust & Energy Efficient Dual-Stage Membrane-Based Process for Enhanced Carbon Dioxide Recovery**

**DE-FE0013064**

- **Dr. Paul KT Liu, Media and Process Technology Inc., Pittsburgh, PA**
- **Professor Theo T. Tsotsis, University of Southern California, Los Angeles, CA**
- **Dr. Eric C. Wagner, Technip Stone & Webster Process Technology, Inc., Claremont, CA**





# The Big Picture

## *Pre-Combustion Carbon Capture and Membrane Process*

### 1. US Energy Consumption:

Separation processes are ~43% of energy consumption in petroleum and refinery industries.

### 2. Energy Efficiency:

Membrane process is considered one of the most energy efficient unit operations. Nevertheless, similar to conventional filters, a membrane process requires pressure (or other) energy to overcome the semi-permeable barrier to achieve separations.

### 3. Synergy with Membrane Processes:

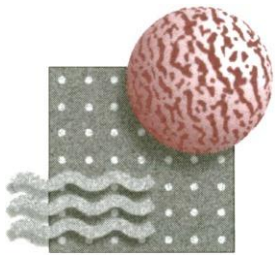
In-situ separations without heating/cooling offers great potential in improving energy efficiency. Further, process intensification can improve reaction efficiency and streamline the process.

## IMPLICATIONS & SIGNIFICANCE

❑ **Pre-Combustion Carbon Capture** through  $H_2$  separations and  $CO_2$  capture via membranes can potentially take the full advantage of the above, i.e., *in-situ separations*, *process intensification*, and *pressure energy* available.

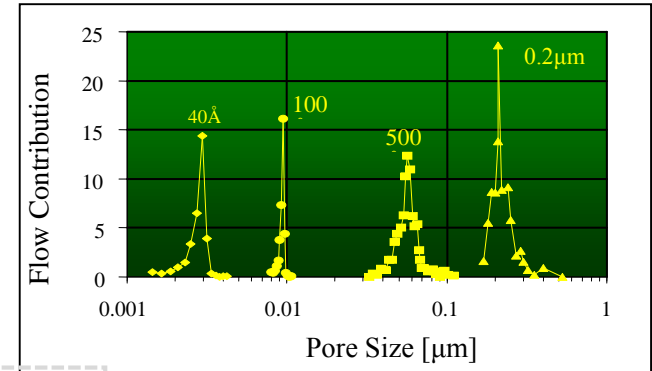
❑ **Inorganic membranes** **material stability** particularly under *harsh environment*, *such as coal gasification*, is an ideal platform for us to pursue this mission – pre-combustion carbon capture.

❑ **As a US-based inorganic membrane manufacturer**, we have made a *major advancement in this mission* with our ceramic membrane products through this project.



# MPT TECHNOLOGY BACKGROUND

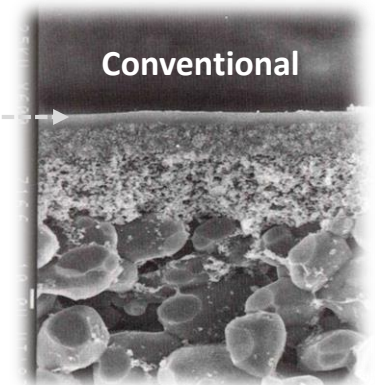
## *Thin Film Deposition on Low Cost Substrate*



40Å to 100Å  
Layer

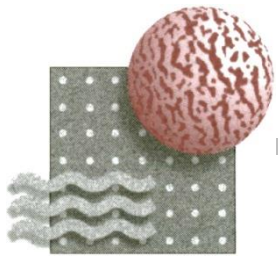
500Å  
Sublayer

0.2µm  
Sublayer



**Our Core  
Expertise/Technology**

#1: Near perfect thin film deposition on less-than desirable but low cost porous tubular substrates



# MPT TECHNOLOGY BACKGROUND

*Multiple Tube Membrane Bundles – versatile, low cost*



Single tubes



Close-packed

*Example: conventional micro- and ultrafiltration*



Spaced

*Example: porous heat exchangers & catalytic membrane reactors*



Candle Filter

*Example: high pressure intermediate temperature gas separations*



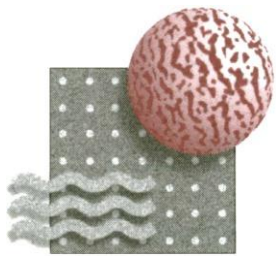
Codeline Style Bundle

*Example: Centerline permeate take-off for direct drop-in to commercial Codeline Vessels*

**Our Core Expertise/Technology**

**#2: Packaging individual membrane tubes into commercially viable modules for field use.**

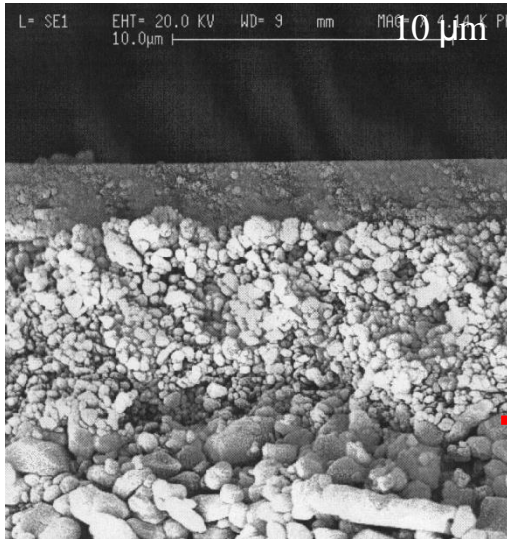




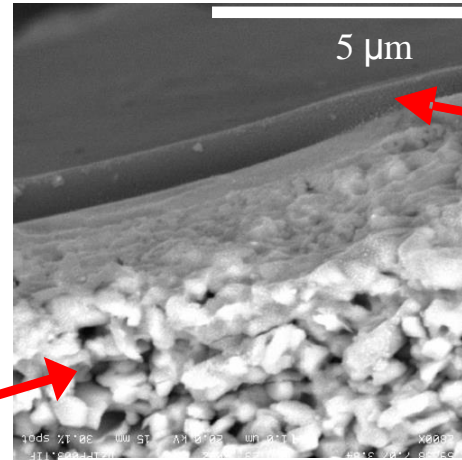
# MPT Advanced Inorganic Membranes

*Specific thin film deposition for advanced separations*

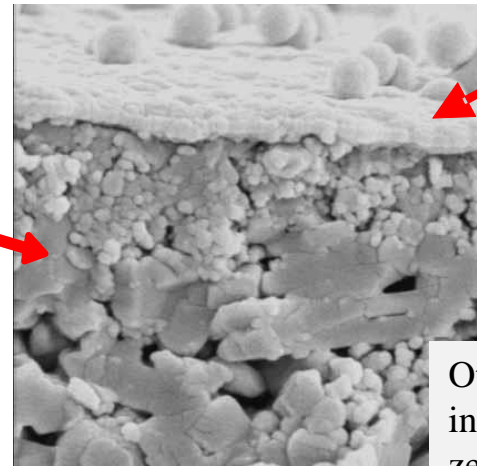
## Ceramic Substrate



Ceramic  
Substrate



Carbon  
molecular  
sieve  
(porous,  
sulfur  
resistance)



Palladium  
(dense,  
excellent  
selectivity)

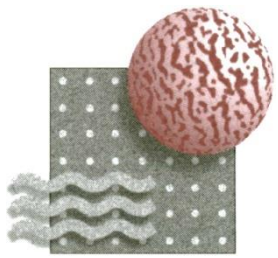
Others,  
including  
zeolites, fluorinated  
hydrocarbons, etc.

### ❑ Unique Features of Supported Membranes

Low cost, flexible, and convenient

### ❑ Technical Challenges of Supported Membranes

Layer adhesion and defect control



# MPT Technical Approach for IGCC/CCS

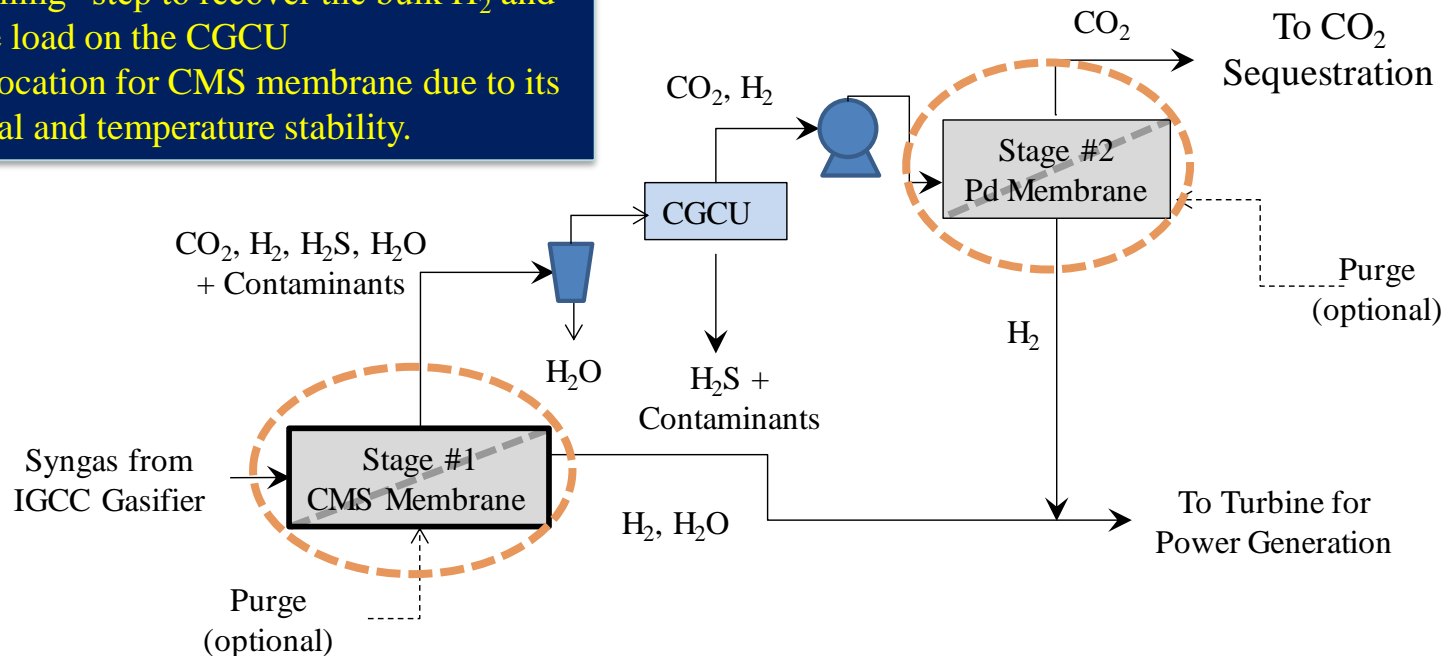
## *Dual Stage Membrane Process Scheme and Key Components*

### CMS Membranes (coupled with WGS reactor)

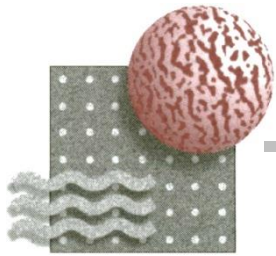
1. Deliver enhanced CO conversion with reduced water consumption versus conventional WGS.
2. “Roughing” step to recover the bulk H<sub>2</sub> and reduce load on the CGCU
3. Ideal location for CMS membrane due to its material and temperature stability.

### Pd-Alloy Membrane

1. High selectivity yields excellent residual H<sub>2</sub> recovery.
2. Ideal to achieve the CO<sub>2</sub> capture and purity targets.



- ❑ Our unique two-stage process avoids the capital and compression costs associated with the conventional two stage operation.
- ❑ The strengths of CMS and Pd membranes are fully utilized while their weaknesses are compensated for by the synergy that is being created by this novel two-stage process.

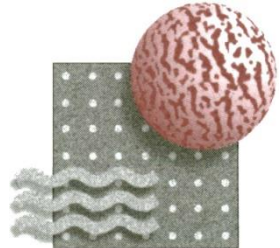


# MPT Dual Stage Membrane Process

## *Presentation Outline – Section 1*

| SECTIONS       | SUB-SECTIONS                                       | SPECIFIC TOPICS  |
|----------------|--|--|
| 1. Membranes   | a. Carbon Molecular Sieve (CMS) Membranes          | Permeance & Selectivity                                  |
|                |  | Thermal & Material Stability                             |
|                | b. Palladium(Pd) Alloy Membranes                   | Permeance & Selectivity                                  |
|                |  | Material (Thermal + H <sub>2</sub> ) Stability           |
|                | c. Bundles & Housing                               | Bundle Engineering & Configuration                       |
| 2. Process     | a. Integrated Membrane Reactor or in Series        | Process Configuration                                    |
|                | b. Modeling and Process Simulation                 | Mathematical Modeling                                    |
|                |  | WGS Reaction Kinetic Study                               |
| 3. Field Tests | a. Previous Tests with 1st Gen CMS Bundle          | Performance and Stability                                |
|                | b. Current test with 2nd Gen CMS Bundle            | Long Term Material Stability                             |
|                | c. Verification of Model Prediction                | Field Obtained Data vs Prediction                        |
|                | d. Pd Membranes & Bundles                          | Performanc and Stability                                 |
|                | e. Pd Membrane Poisoned by Tar                     | Regeneration & Activity Restroation                      |
| 4. TEA/EHS     | a. Proposed Process Scheme                         | Block Flow Diagram                                       |
|                | b. Techno-economic Analysis (TEA)                  | Costs of Power & Carbon Capture                          |
|                | c. TEA Sensitivity Analysis                        | Impact of Membrane Selectivity & Configuration           |
|                | d. Environmental, Health and Safety Analysis (EHS) | Evaluation on Key Separation and Manufacturing Processes |

- ❑ Conclusions and Background infor on MPT Commercial Activities for Hydrogen Recovery
- ❑ (1) project milestones; (2) project success criteria; (3) Peer Review milestones; and (4) updated State-Point Data tables.



# CMS Membrane Functional Performance

## Typical Performance and Performance Targets

### CMS Single Tube Characterization

| CMS Membrane Characteristic                         | Preliminary Target to Achieve DOE Goals <sup>1</sup> | Laboratory Single Tubes Performance |
|---|--|-------------------------------------|
| Permeance, H <sub>2</sub> [GPU]<br>@ 250°C, 20 psig | 550  | 420 to 1,100                        |
| Selectivity, H <sub>2</sub> /X                      |  |                                     |
| H <sub>2</sub> /N <sub>2</sub>                      | 70   | 80 to >180                          |
| H <sub>2</sub> /CO                                  | 70   | 70 to >130                          |
| H <sub>2</sub> /CO <sub>2</sub>                     | 35   | >65                                 |
| H <sub>2</sub> /H <sub>2</sub> S                    | N/A <sup>2</sup>                                     | >100 to 150 <sup>2</sup>            |
| H <sub>2</sub> /H <sub>2</sub> O                    | 1.5  | 1.5 to 3                            |

#### Notes:

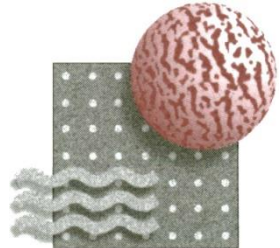
1. Target performance is that required to achieve 90% CO<sub>2</sub> capture at 95% purity with 95% fuel utilization (H<sub>2</sub> + CO to the turbine).
2. At this selectivity, approximately 200 ppm H<sub>2</sub>S in the fuel to turbine.

### CMS 86-Tube Bundle Characterization

| CMS Bundle ID | He Permeance [GPU] | He/N <sub>2</sub> Selectivity [-] |
|---------------|--------------------|-----------------------------------|
| 86-6          | 731                | 100                               |
| 86-7          | 1,020              | 187                               |
| 86-8          | 658                | 91                                |
| 86-9          | 950                | 102                               |
| 86-10         | 365                | 200                               |
| 86-11         | 584                | 142                               |
| 86-12         | 548                | 77                                |
| 86-13         | 840                | 126                               |
| 86-14         | 1,020              | 117                               |
| 86-J1         | 973                | 120                               |
| 86-MB1        | 421                | 122                               |
| 86-MB2        | 665                | 87                                |
| 86-MB3        | 438                | 85                                |



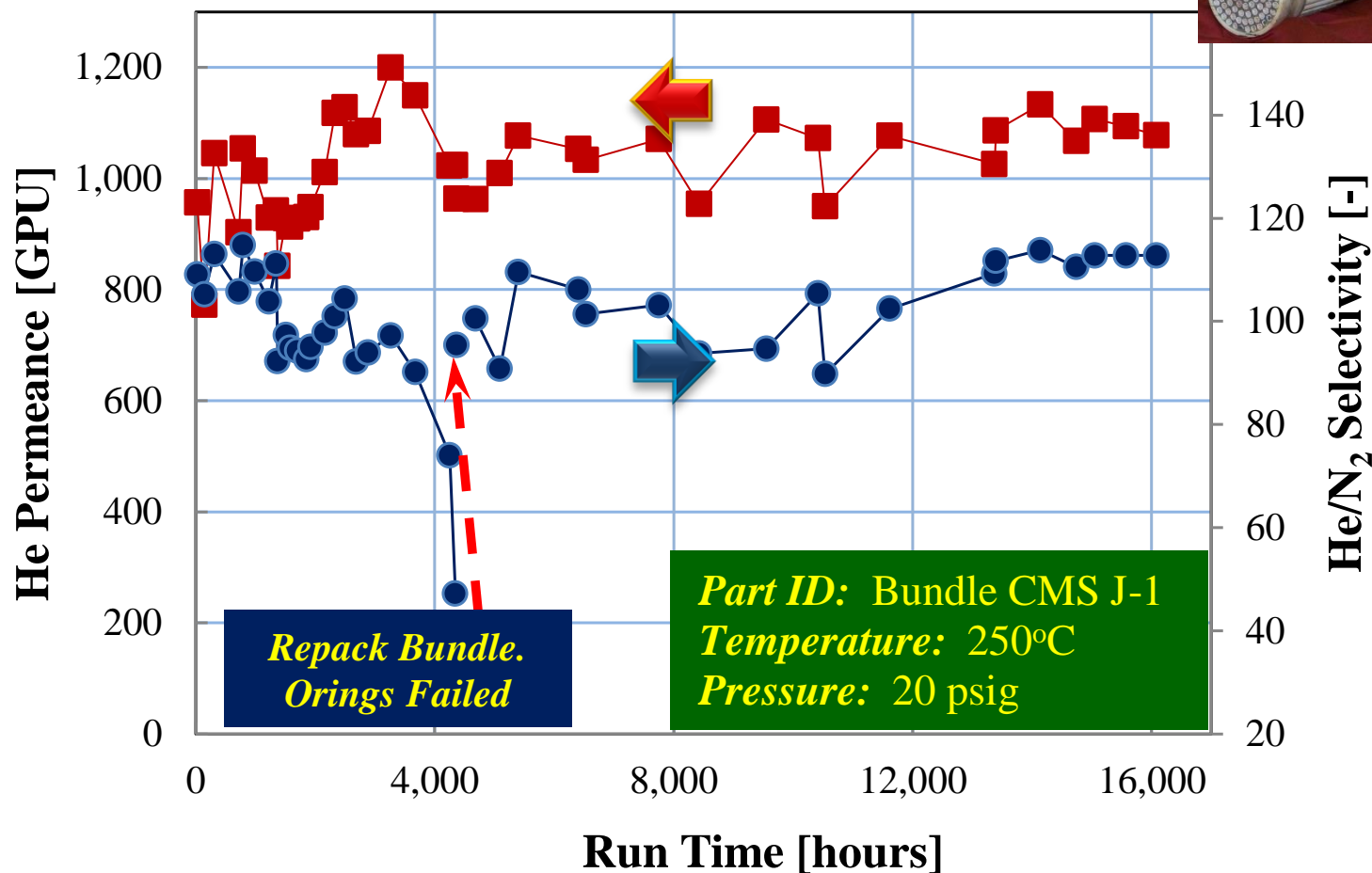


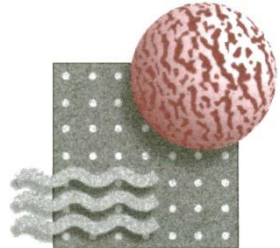


# CMS Membrane Long Term Stability

*Key Technical Hurdles Focused on Long Term Stability (CMS Membrane)*

*CMS 86 -Tube Bundle Long Term Stability (>16,000 hrs)*

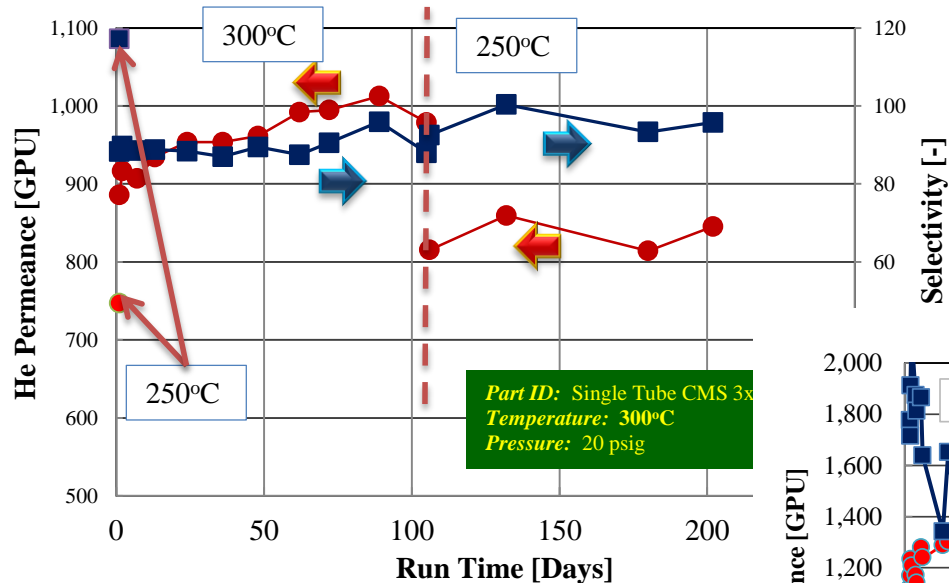




# CMS Membrane Thermal Stability

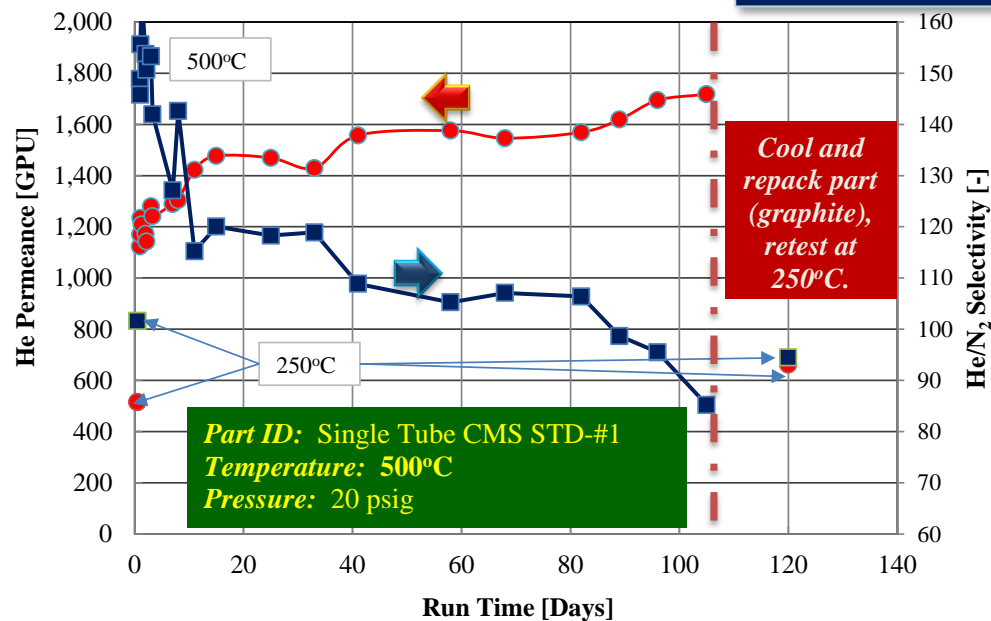
*Key Technical Hurdles Focused on Long Term Stability (CMS Membrane)*

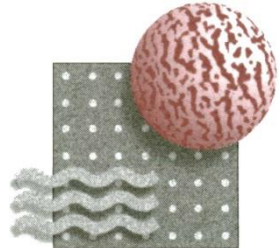
**300°C**



*High Temperature Excursions above the 250°C Design Temperature*

**500°C**





# CMS Membrane Material Stability

*Contaminant Stability: CMS Membrane Actual Refinery Gas (higher hydrocarbons,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ )*

**Chevron Pilot Testing Facility**

Membrane CMS Tube

Operating Conditions

$T \sim 240^\circ\text{C}$

$P \sim 300 \text{ psig}$

Pretreatment  
None.

Composition

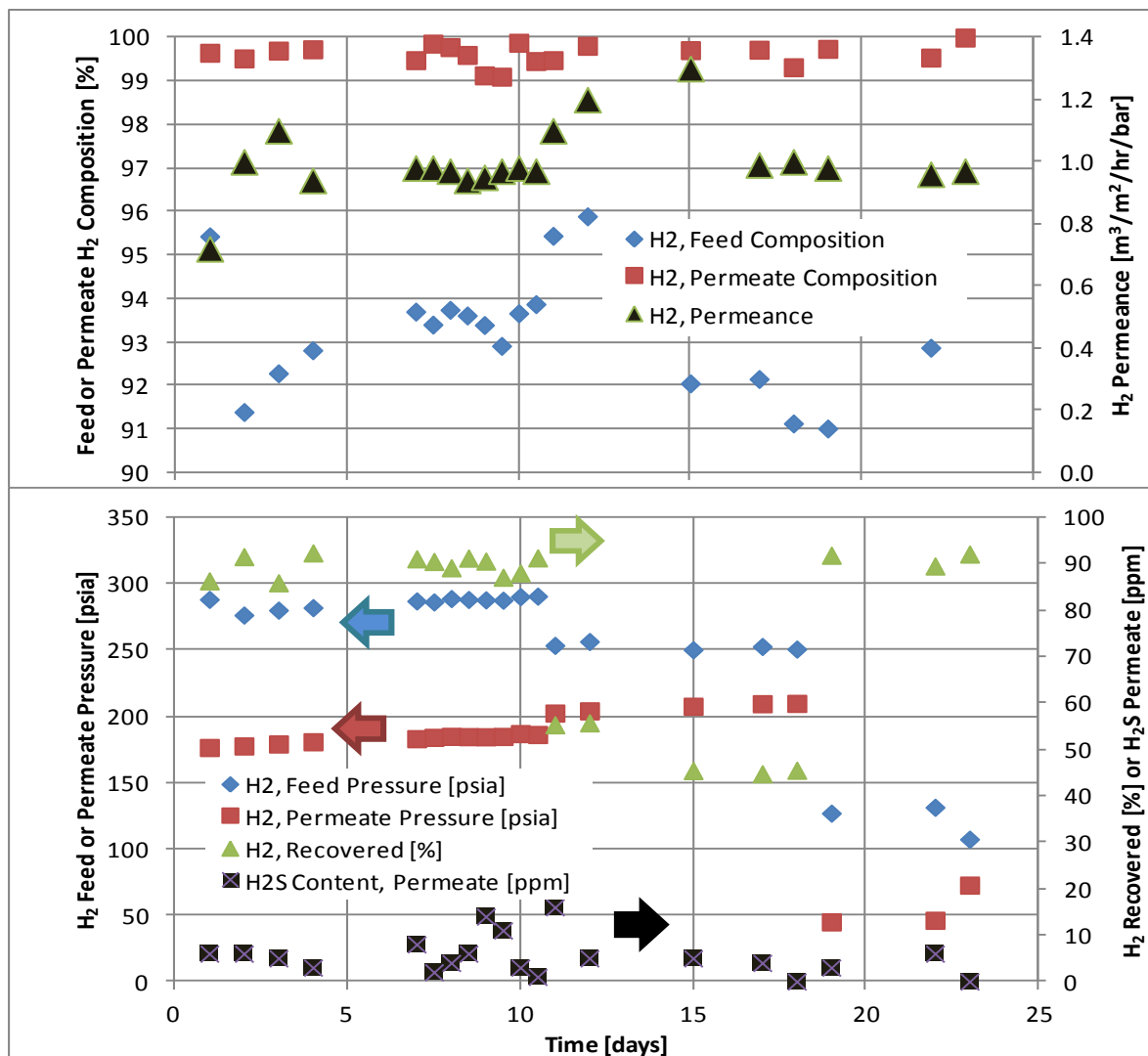
$\text{H}_2 \sim 90 \text{ to } 95\%$

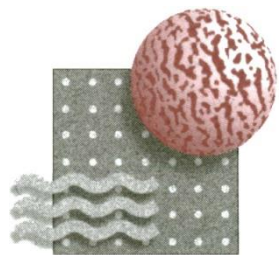
Hydrocarbon balance.

Trace Contaminants

$\text{NH}_3 \sim 1,000 \text{ ppm}$

$\text{H}_2\text{S} \sim 15,000 \text{ ppm}$





# Pd-Alloy Membrane Functional Performance

## *Typical Performance and Performance Targets from Economic Analysis*

### *Pd-Alloy Single Tube Characterization Overview*

| Pd-Alloy Membrane Characteristic                    | Preliminary Target to Achieve DOE Goals <sup>1</sup> | Laboratory Single Tubes Performance |
|---|--|-------------------------------------|
| Permeance, H <sub>2</sub> [GPU]<br>@ 350°C, 20 psig | 3,470  | 1,750 to >5,500                     |
| Selectivity, H <sub>2</sub> /X                      |  |                                     |
| H <sub>2</sub> /N <sub>2</sub>                      | 300  | 300 to >3,000                       |
| H <sub>2</sub> /CO                                  | 300  | 300 to >3,000                       |
| H <sub>2</sub> /CO <sub>2</sub>                     | 300  | 300 to >3,000                       |
| H <sub>2</sub> /H <sub>2</sub> S                    | N/A <sup>2</sup>                                     | NA <sup>2</sup>                     |
| H <sub>2</sub> /H <sub>2</sub> O                    | 300  | 300 to >3,000                       |

#### Notes:

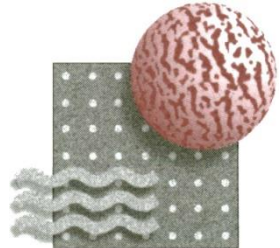
1. Target performance is that required to achieve 90% CO<sub>2</sub> capture at 95% purity with 95% fuel utilization (H<sub>2</sub> + CO to the turbine).
2. Feed gas to the Pd-alloy membrane has been pretreated to remove residual sulfur species in the CGCU.

### *Pd/PdAg 12-Tube Bundle Characterization*

| Bundle ID   | H <sub>2</sub> Permeance [GPU] | H <sub>2</sub> /N <sub>2</sub> |
|-------------|--------------------------------|--------------------------------|
| Pd-DCT-3    | 4,170                          | 1,100                          |
| Pd-DCT-7    | 3,620                          | 1,810                          |
| Pd-DCT-12   | 3,100                          | 1,160                          |
| PdAg-DCT-27 | 4,750                          | 2,260                          |
| PdAg-DCT-28 | 5,180                          | 2,030                          |



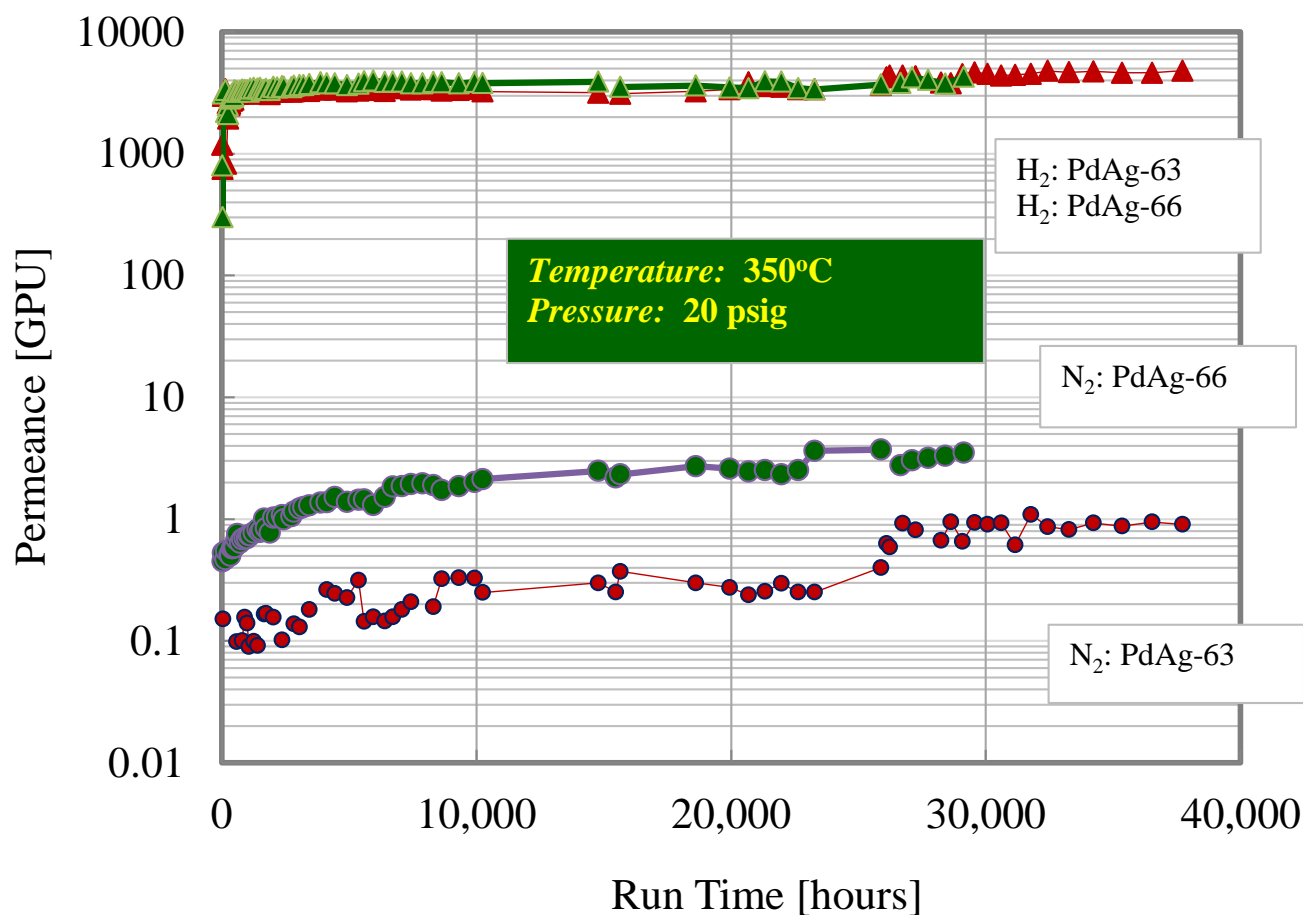


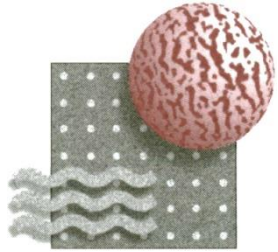


# Pd-alloy Membrane Long Term Stability

## *Key Technical Hurdles Focused on Long Term Stability (Pd-alloy)*

*Pd-Alloy Pd-Ag (80/20) Long Term Stability (>35,000 hours)*



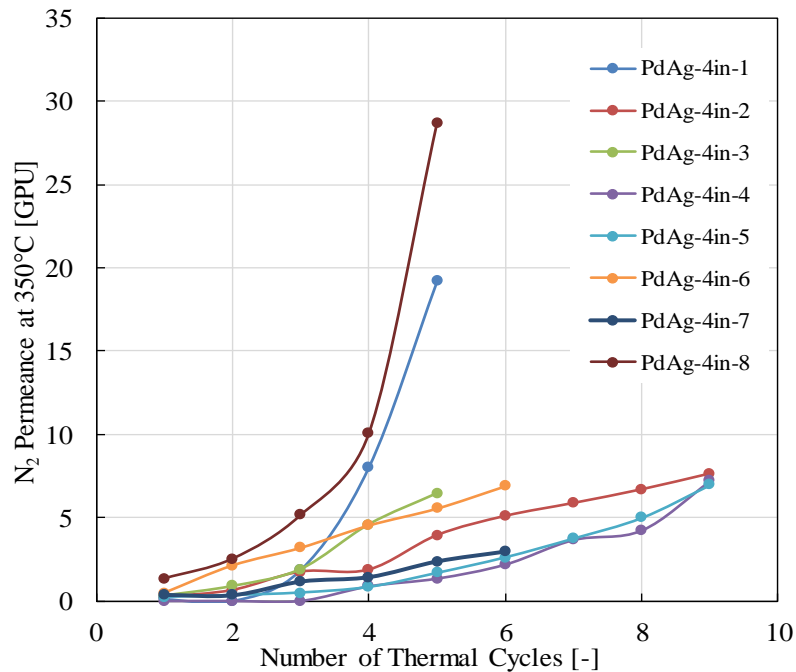


# Pd-alloy Membrane Stability

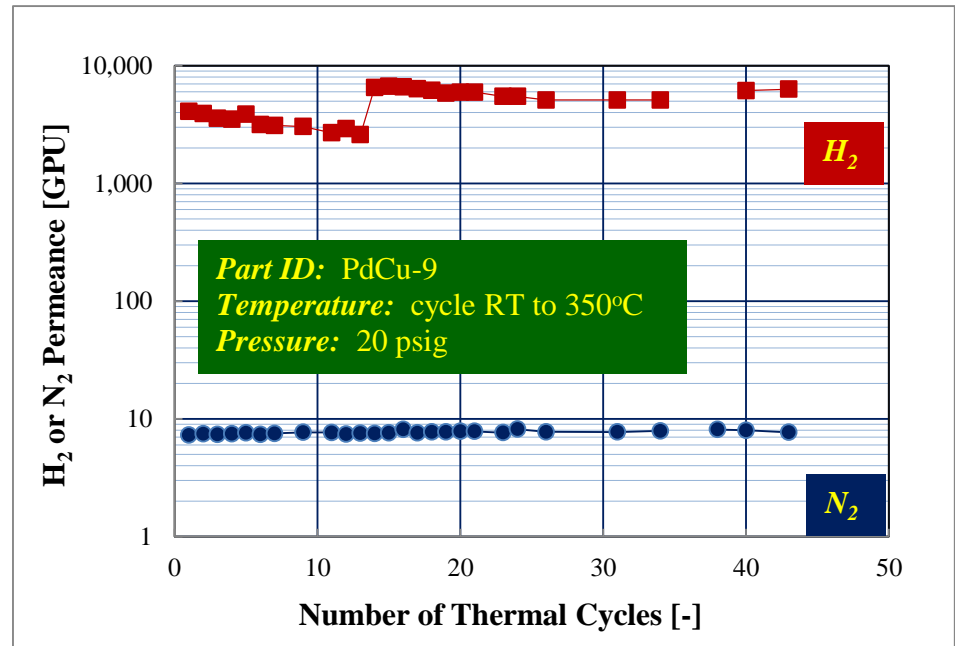
*Key Technical Hurdle: Thermal Cycle Stability in  $H_2$  (Pd-alloy)*

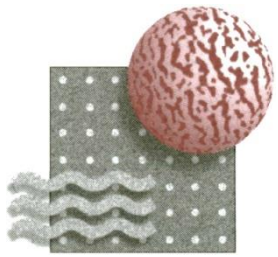
*Thermal Cycling in  $H_2$ : RT to 350°C*

*Pd-Ag (75/25)*



*Pd-Cu (60/40)*





# Multiple Tube Bundle Potting Development

## High Pressure/Temperature Stability

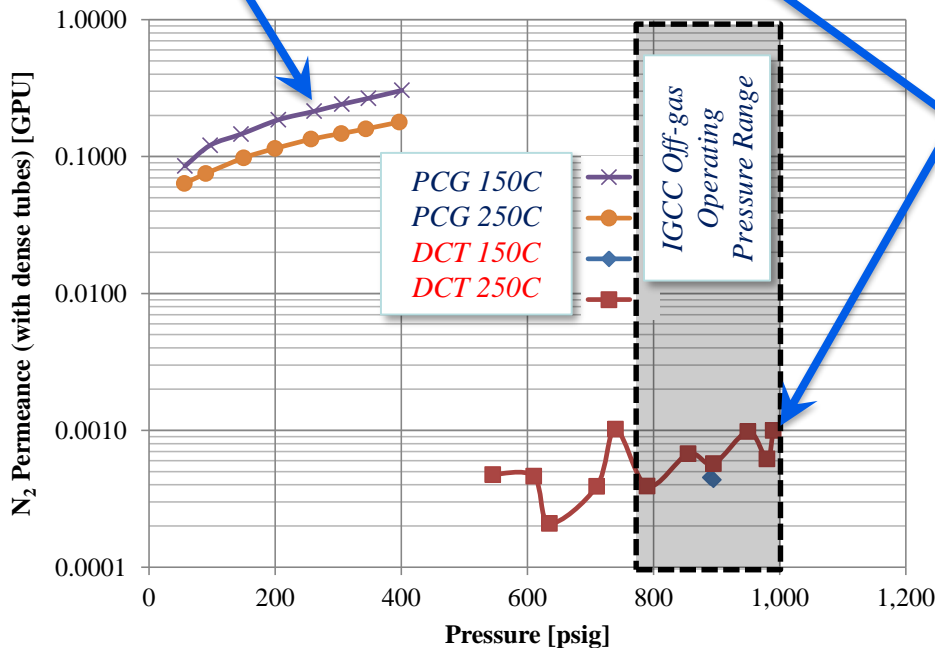
### Potted Ceramic/Glass (PCG)



### Dense Ceramic Tube Sheet (DCT - CMS)



### Dense Ceramic Tube Sheet (DCT-Pd Alloy)



### Why PCG v. DCT?

*Performance, PCG v. DCT*

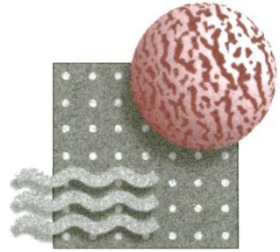
**Temperature [°C]: <300 v. >500**

**Pressure [psig]: <400 v. >1,100**

*IGCC Operating Conditions*

**Temperature [°C]: 250 to 350**

**Pressure [psig]: >700 to 2,000**



# M&P Hydrogen Selective Membrane Modules

## *Multiple Membrane Bundle Modules*

Membrane Bundle

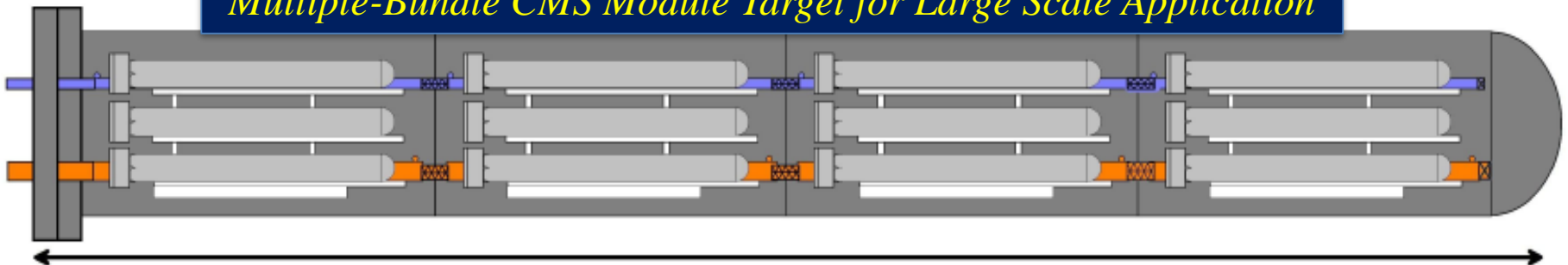


Membrane Bundle Enclosure



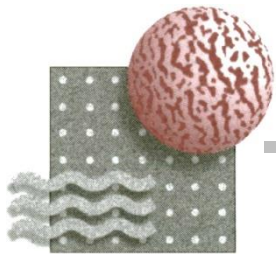
Multiple Bundle Module

## *Multiple-Bundle CMS Module Target for Large Scale Application*



Total Pressure Jacket Length 200" of 24" Pipe, 4 sections of 7 Bundles connected with flexlines.

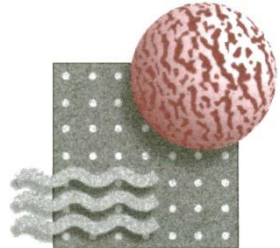




# MPT Dual Stage Membrane Process

## *Presentation Outline – Section 2*

| SECTIONS       | SUB-SECTIONS                                       | SPECIFIC TOPICS  |
|----------------|--|--|
| 1. Membranes   | a. Carbon Molecular Sieve (CMS) Membranes          | Permeance & Selectivity                                  |
|                |  | Thermal & Material Stability                             |
|                | b. Palladium(Pd) Alloy Membranes                   | Permeance & Selectivity                                  |
|                |  | Material (Thermal + H <sub>2</sub> ) Stability           |
|                | c. Bundles & Housing                               | Bundle Engineering & Configuration                       |
| 2. Process     | a. Integrated Membrane Reactor or in Series        | Process Configuration                                    |
|                | b. Modeling and Process Simulation                 | Mathematical Modeling                                    |
|                |  | WGS Reaction Kinetic Study                               |
| 3. Field Tests | a. Previous Tests with 1st Gen CMS Bundle          | Performance and Stability                                |
|                | b. Current test with 2nd Gen CMS Bundle            | Long Term Material Stability                             |
|                | c. Verification of Model Prediction                | Field Obtained Data vs Prediction                        |
|                | d. Pd Membranes & Bundles                          | Performanc and Stability                                 |
|                | e. Pd Membrane Poisoned by Tar                     | Regeneration & Activity Restroation                      |
| 4. TEA/EHS     | a. Proposed Process Scheme                         | Block Flow Diagram                                       |
|                | b. Techno-economic Analysis (TEA)                  | Costs of Power & Carbon Capture                          |
|                | c. TEA Sensitivity Analysis                        | Impact of Membrane Selectivity & Configuration           |
|                | d. Environmental, Health and Safety Analysis (EHS) | Evaluation on Key Separation and Manufacturing Processes |

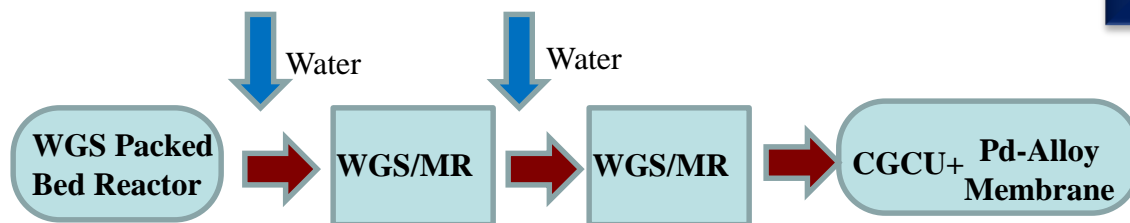


# Process Simulation Results

## *Membrane + Reactor in series vs Integral Membrane Reactor*

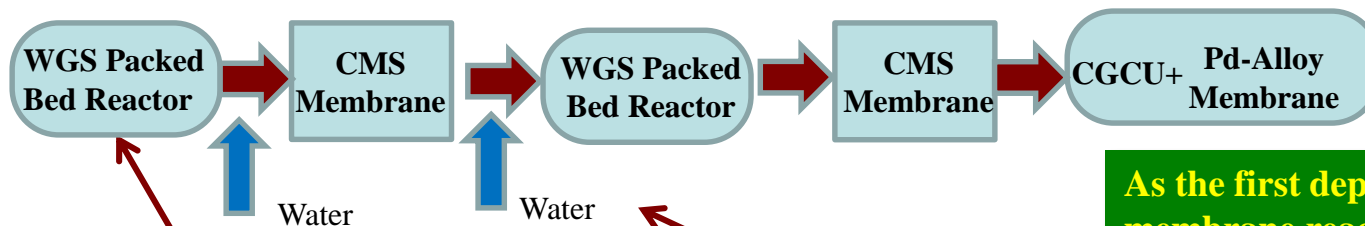
### SCHEME 1

WGS/MR x n + Pd-Alloy Membrane



### SCHEME 2

(PBR + CMS Membrane) x n + Pd-Alloy Membrane



### MR v. PBR-MS

Area [m<sup>2</sup>]: 14,600 v. 16,500 (+12%)

CO<sub>2</sub> Recovery [%]: >90% (NC)

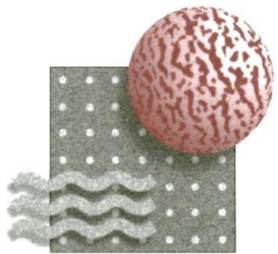
CO<sub>2</sub> Purity [%]: 93.5 to 94.5% (NC)

Based upon the operating condition of our proposed dual stage process, approximately 12% membrane surface area savings could be achieved with the integral membrane reactor according to our simulation.

As the first deployment of such a membrane reactor process, we chose the series process scheme, which was also recommended by the industrial review panel.

1. WGS PBR to pre-shift the syngas. Lose too much CO and H<sub>2</sub>O to permeate in MR

2. Water injection for cooling due to reaction exotherm.



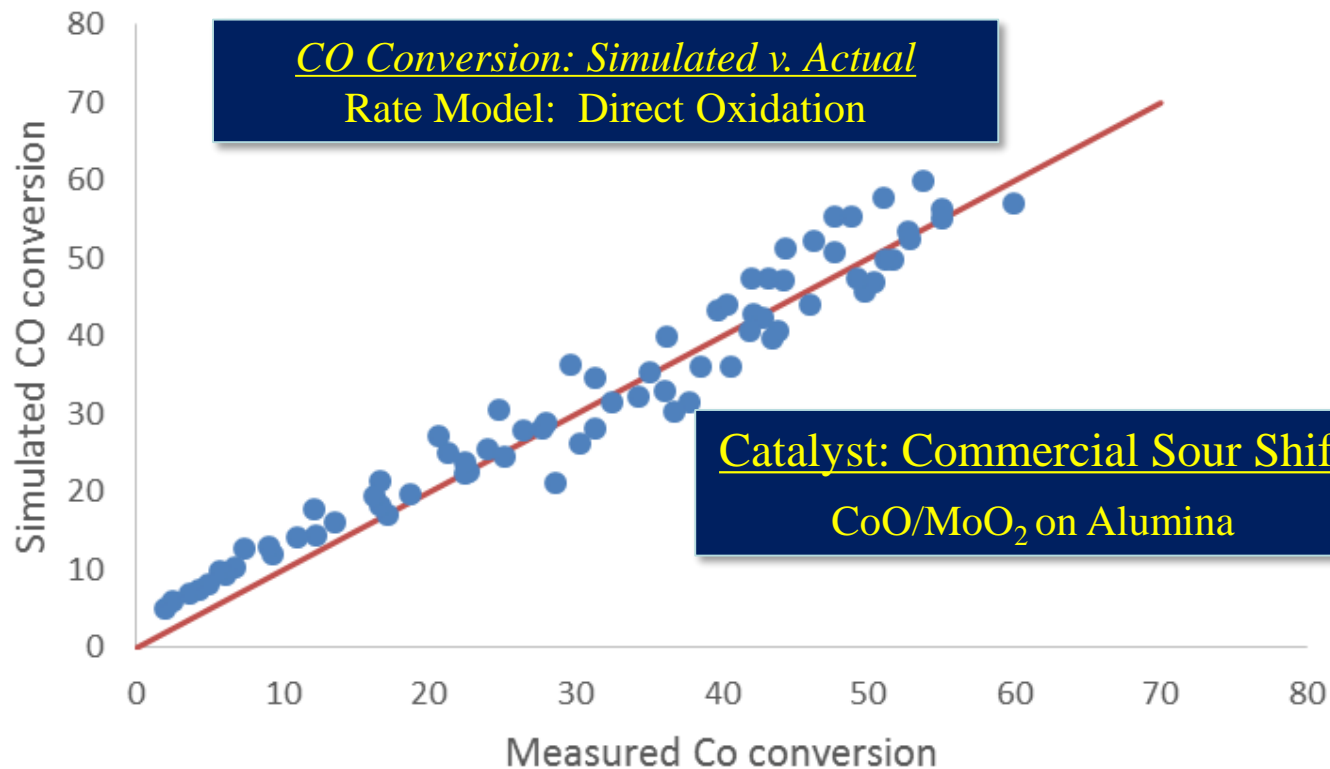
# WGS-Membrane Reactor Model Development

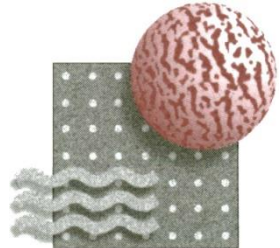
## *WGS Reaction Kinetics at Elevated Pressure*

### Reaction Model Development

**Operating Conditions:** 220 to 300°C; up to 200psig

**Rate Models:** Formate Intermediate; Associative; Direct Oxidation





# Membrane Performance Model Development

## *Single Tube Mixed Gas Performance and Model Predictions*

### *Membrane Model Development*

CMS Membrane, 300°C, 200psig

| Gas [-]          | Feed Composition [vol%] | Mixed-gas Permeance [GPU] | Pure Gas Permeances [GPU] |
|------------------|-------------------------|---------------------------|---------------------------|
| H <sub>2</sub>   | 28.2                    | 452                       | 464                       |
| CO               | 10.2                    | 10.2                      | 10.2                      |
| CH <sub>4</sub>  | 8.2                     | 6.9                       | 8.0                       |
| CO <sub>2</sub>  | 22.0                    | 16.8                      | 17.5                      |
| H <sub>2</sub> S | 0.48                    | 8.0                       | 8.0                       |
| H <sub>2</sub> O | 30.9                    | 343                       | 372                       |

### *Typical Results for Single Tubes*

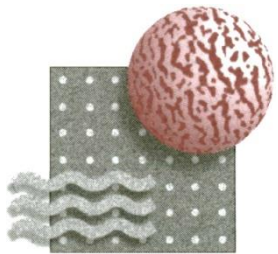
1. Very good agreement with pure component data with single tubes.
2. Consistently see this in our laboratory with both CMS and Pd membranes.
3. Deviations observed at times but not common, not well understood.

### *MPT Single Tube CMS Membrane*

Candle Filter Configuration







# WGS-Membrane Reactor Model

## *Combined Reaction and Membrane Models: Membrane Reactor*

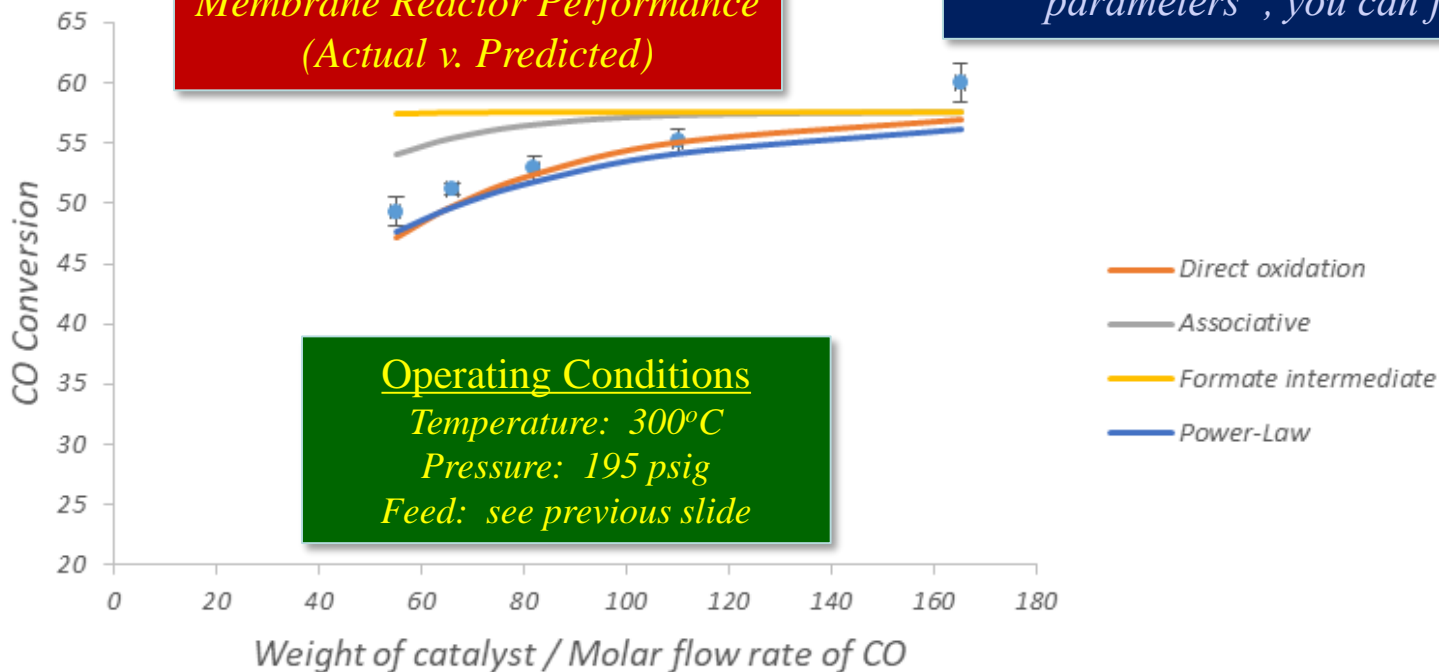
### *Membrane Reactor Module (Single Tube)*

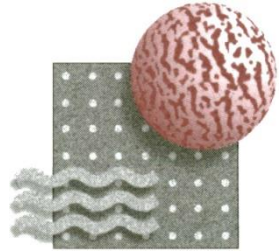


### Predicted versus Actual Results

- ✓ *Very good agreement between model predictions and actual MR performance.*
- ✓ *DO mechanism superior model as expected from earlier kinetics study.*
- ✓ *Power law...if you add enough adjustable "parameters", you can fit any data set.*

### *Membrane Reactor Performance (Actual v. Predicted)*

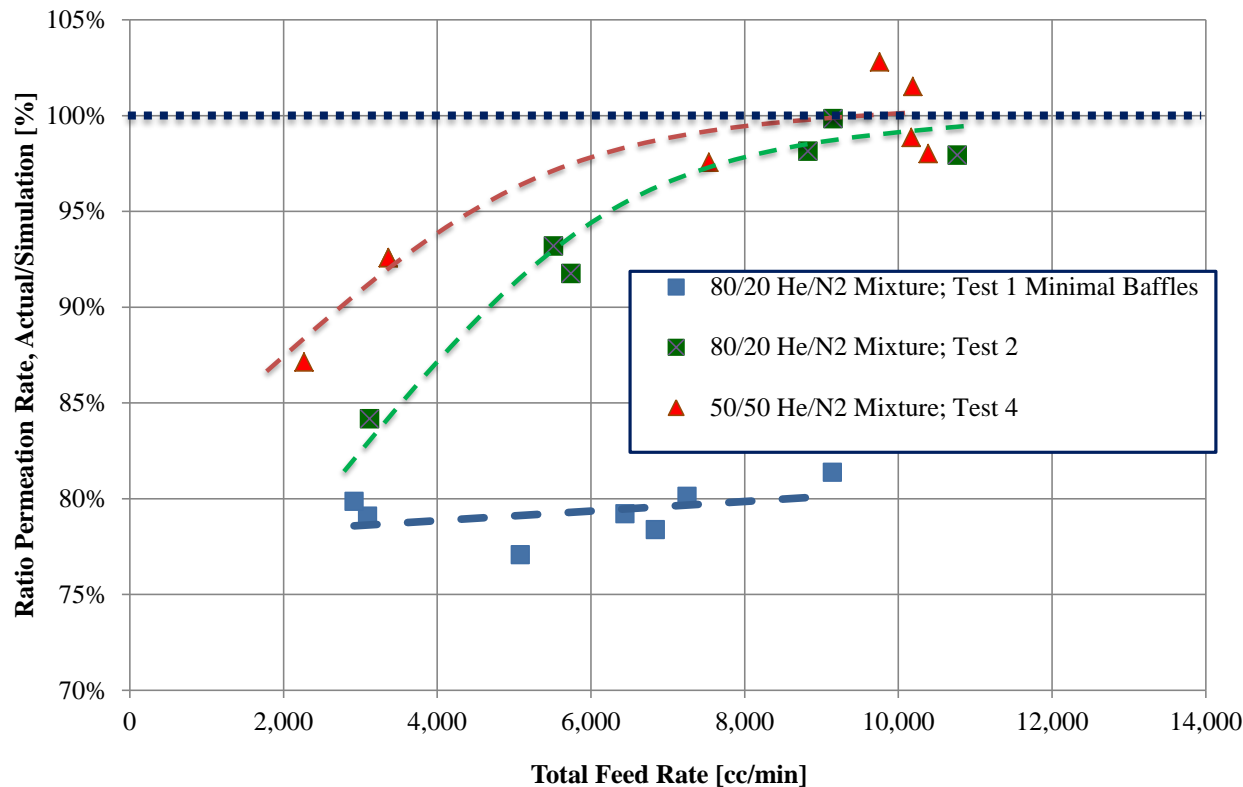
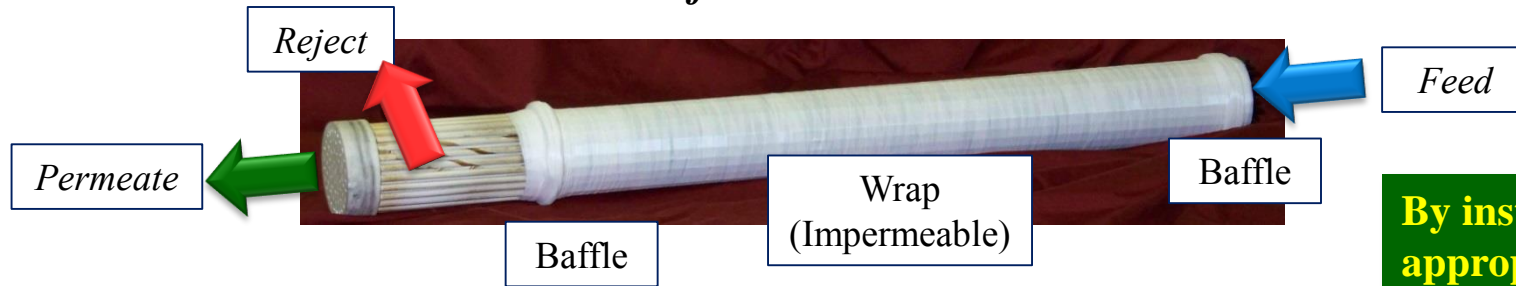




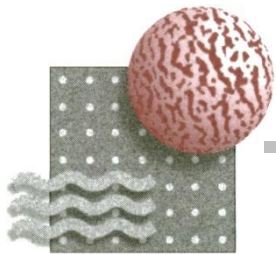
# Verification of Membrane Performance Modeling

## *Effect of Total Gas Feed Rate on Membrane Performance with Baffles*

### *Ratio of Actual to Predicted Permeate Rates*



**By installing appropriate internal baffles, our mathematical model successfully predicted the gas separation performance for a multiple tube bundle at a lower stage cut, which is the most efficient operation model for a large scale operation.**



# MPT Dual Stage Membrane Process

## *Presentation Outline - Section 3*

| SECTIONS       | SUB-SECTIONS                                       | SPECIFIC TOPICS  |
|----------------|--|--|
| 1. Membranes   | a. Carbon Molecular Sieve (CMS) Membranes          | Permeance & Selectivity                                  |
|                |  | Thermal & Material Stability                             |
|                | b. Palladium(Pd) Alloy Membranes                   | Permeance & Selectivity                                  |
|                |  | Material (Thermal + H <sub>2</sub> ) Stability           |
|                | c. Bundles & Housing                               | Bundle Engineering & Configuration                       |
| 2. Process     | a. Integrated Membrane Reactor or in Series        | Process Configuration                                    |
|                | b. Modeling and Process Simulation                 | Mathematical Modeling                                    |
|                |  | WGS Reaction Kinetic Study                               |
| 3. Field Tests | a. Previous Tests with 1st Gen CMS Bundle          | Performance and Stability                                |
|                | b. Current test with 2nd Gen CMS Bundle            | Long Term Material Stability                             |
|                | c. Verification of Model Prediction                | Field Obtained Data vs Prediction                        |
|                | d. Pd Membranes & Bundles                          | Performanc and Stability                                 |
|                | e. Pd Membrane Poisoned by Tar                     | Regeneration & Activity Restroation                      |
| 4. TEA/EHS     | a. Proposed Process Scheme                         | Block Flow Diagram                                       |
|                | b. Techno-economic Analysis (TEA)                  | Costs of Power & Carbon Capture                          |
|                | c. TEA Sensitivity Analysis                        | Impact of Membrane Selectivity & Configuration           |
|                | d. Environmental, Health and Safety Analysis (EHS) | Evaluation on Key Separation and Manufacturing Processes |

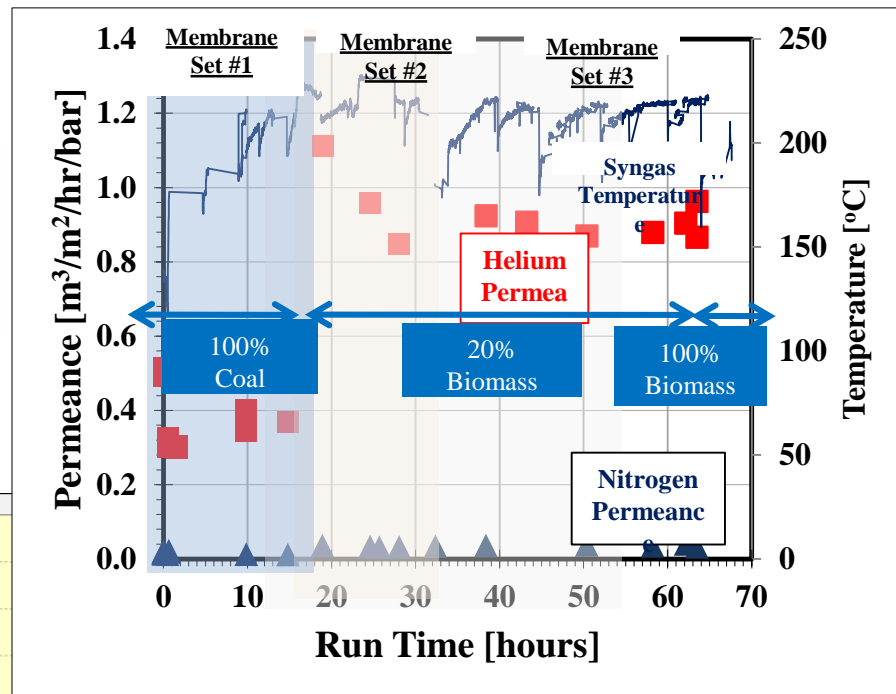
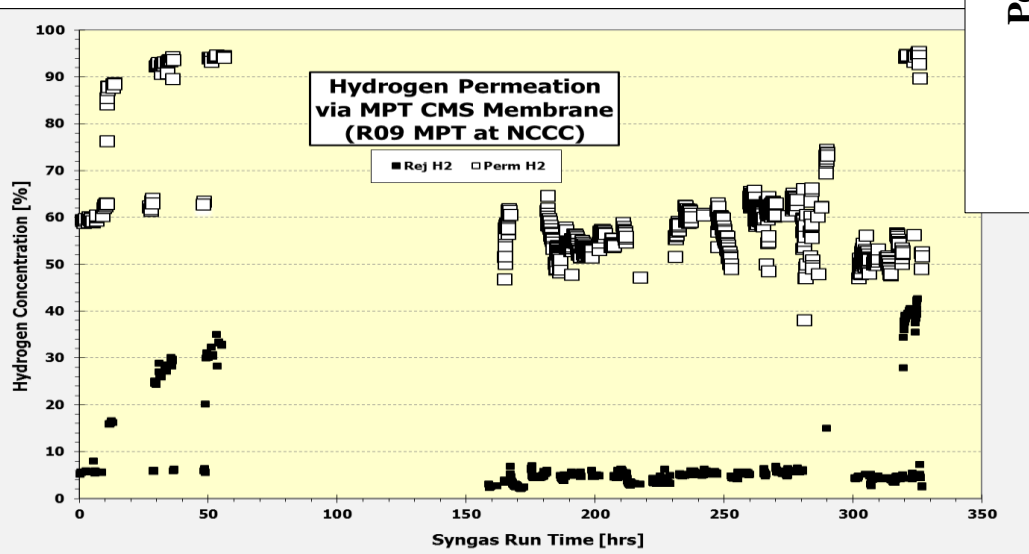
# Our Previous Accomplishments in Field Tests at NCCC -1

## NCCC Testing: CMS Membranes Highly Stable in Coal Gasifier Syngas

### Membrane Material Stability

**CMS membrane shows high resistance to tar-like contaminants and sulfur at  $\geq 250^{\circ}\text{C}$ .**

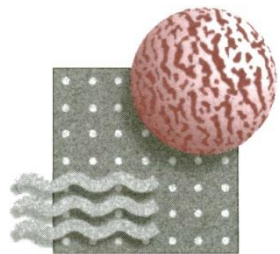
*250°C and 250 psi Syngas with No Pretreatment*



### Membrane Performance Stability

**CMS membrane is stable with no pretreatment beyond particulate removal for a variety of gasifier feedstocks.**





# Our Previous Accomplishments in Field Tests at NCCC -2

## NCCC Testing: CMS Bundles Highly Stable in Coal Gasifier Syngas

### Testing Parameters

Membrane  
86-tube CMS

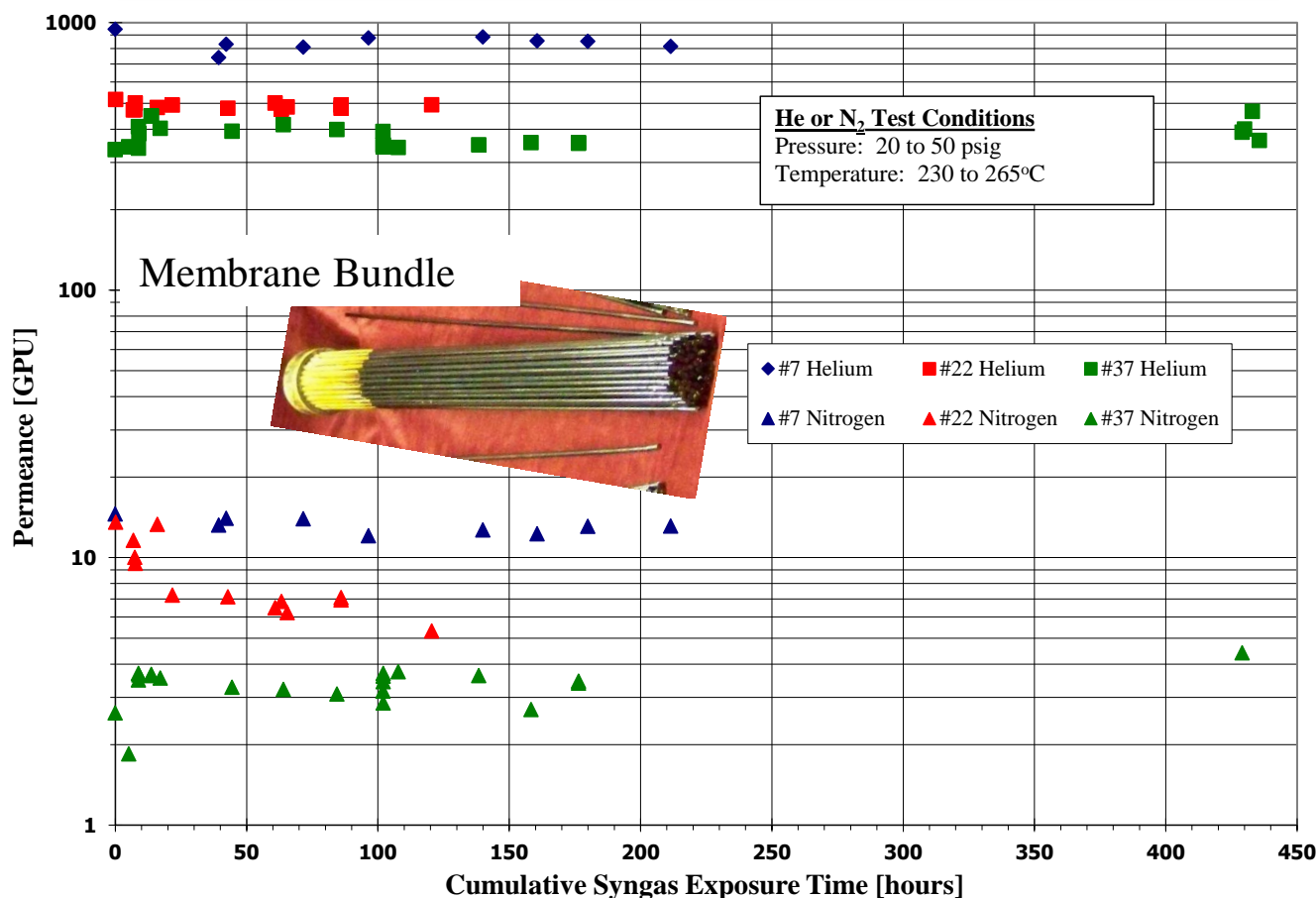
Operating Conditions  
 $T \sim 250$  to  $300^\circ\text{C}$   
 $P \sim 150$  to  $300$  psig

Pretreatment  
Particulate trap only,  
no other gas cleanup.

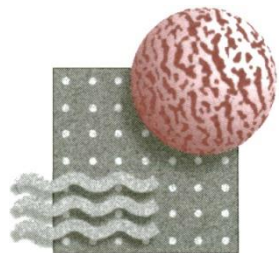
Composition  
 $\text{H}_2 \sim 10$  to  $30\%$   
 $\text{CO} \sim 10\%$   
 $\text{CO}_2 \sim 10\%$   
 $\text{N}_2, \text{H}_2\text{O} \sim \text{Balance}$

Trace Contaminants  
 $\text{NH}_3 \sim 1,000\text{ppm}$   
Sulfur Species  $\sim 1,000\text{ppm}$   
 $\text{HCl}$ ,  $\text{HCN}$ ,  
Naphthalenes/Tars, etc.

### NCCC Slip Stream Testing: No gasifier off-gas pretreatment

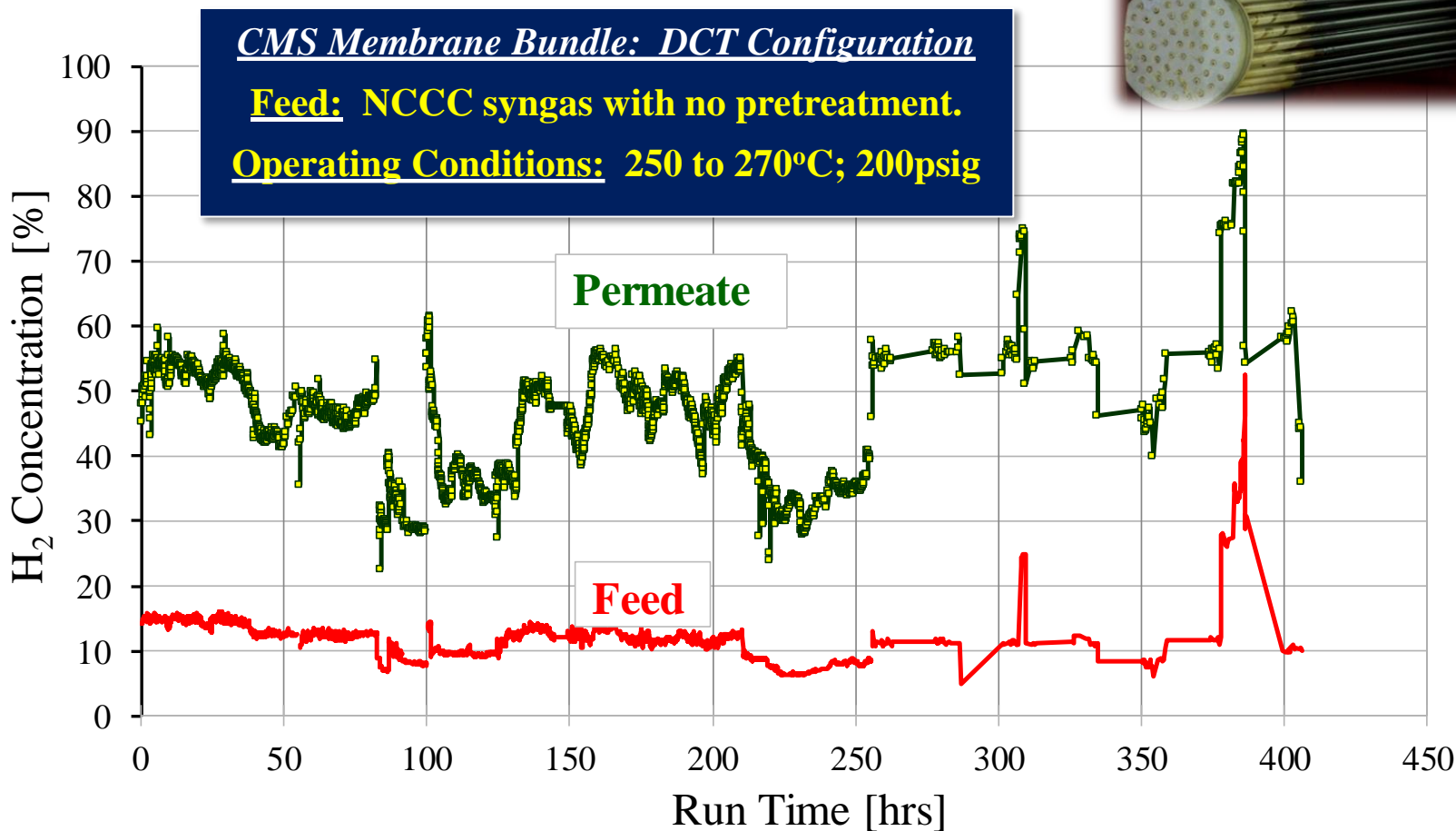


*Performance stability of multiple tube CMS membrane bundles during  $\text{H}_2$  recovery from NCCC slip stream testing. He and  $\text{N}_2$  Permeances measured periodically during >400 hr test.*

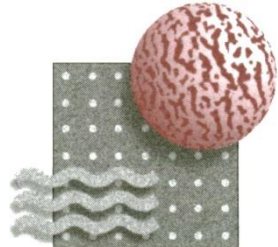


# NCCC Testing: Dual Stage Membrane Process

## *Physical Integrity Test of CMS 57-Tube DCT Style Bundle*



Through the >400 hrs testing at NCCC, the permeate composition is kept at relatively stable, indicating the physical integrity of the CMS membrane in the DCT style bundle.



# NCCC Testing: Predicting Membrane Performance

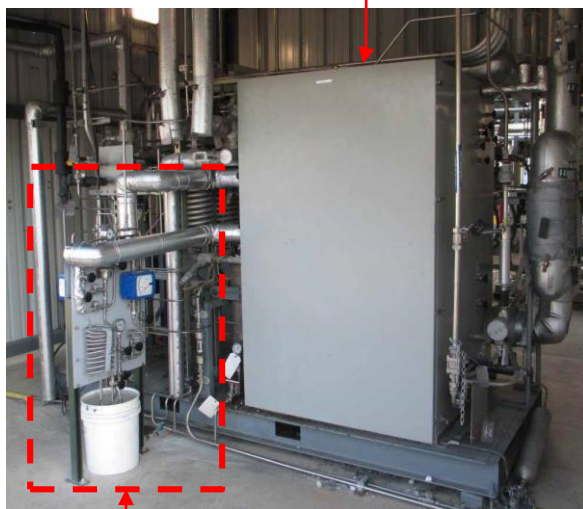
## NCCC Testing: Improve Prediction of Membrane Performance

*In-situ real time water composition analysis required*

*Added water capture units prior to recent NCCC testing round.*

**Membrane**

**Test  
Cabinet**



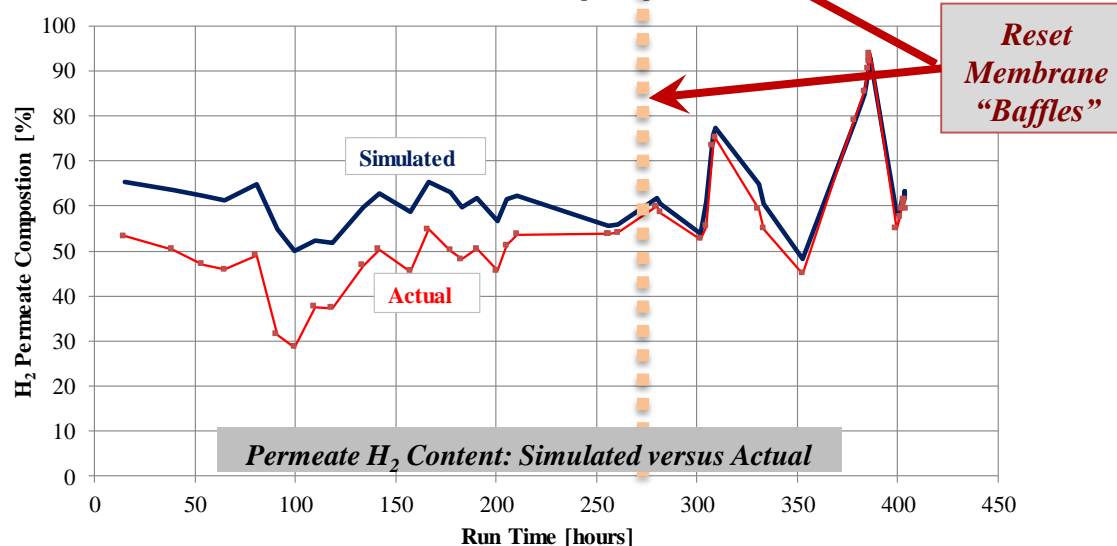
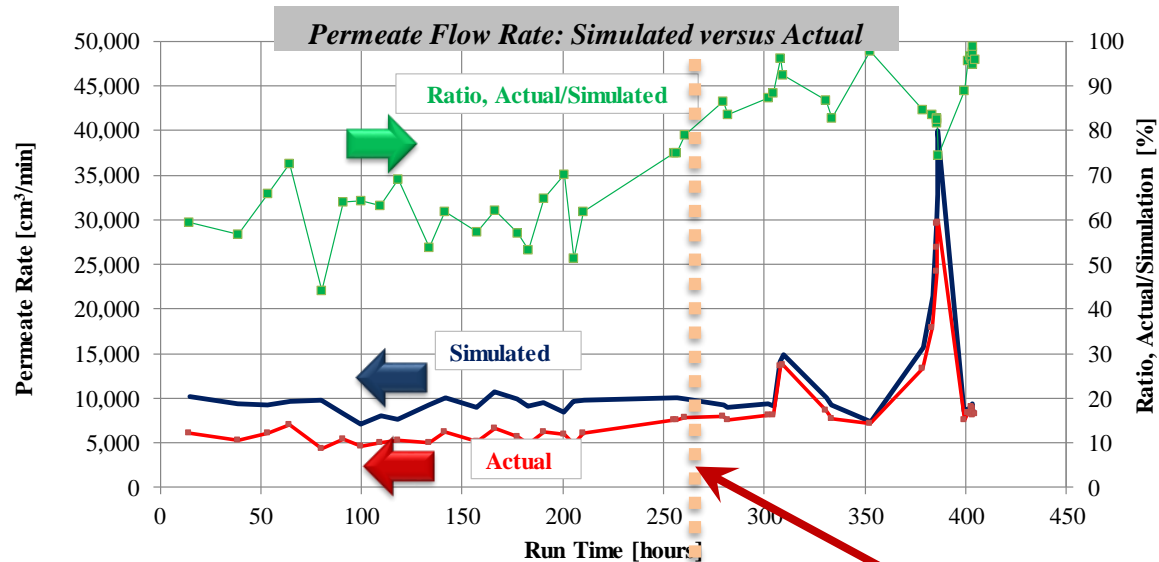
**Water Capture  
Units**

|       | NCCC<br>Determined<br>Raw Syngas<br>Water<br>% | NCCC Shifted<br>Syngas Water<br>Content |         | MPT Water Collection Units |             |                                   |                                     | NCCC GC<br>Dry Gas<br>Mass<br>Closure<br>[%] |
|-------|--|---|---------|----------------------------|-------------|-----------------------------------|-------------------------------------|--|
|       |  | WGS In                                  | WGS Out | %<br>Perm                  | %<br>Reject | MPT<br>Calculated<br>WGS Out<br>% | NCCC/MPT<br>Water<br>Closure<br>[%] |  |
|       |  | 22.3%                                   | 15.2%   | 51.8%                      | 5.1%        | 11.6%                             | 136.7%                              | 101.8%                                       |
| Day 1 | 6.2  | 16.2%                                   | 8.5%    | 39.5%                      | 5.7%        | 8.8%                              | 103.9%                              | 105.1%                                       |
|       |  | 12.3%                                   | 4.3%    | 23.5%                      | 3.6%        | 5.2%                              | 123.3%                              | 102.0%                                       |
|       |  | 12.3%                                   | 4.3%    | 16.1%                      | 3.6%        | 4.5%                              | 106.3%                              | 102.0%                                       |
|       |  | 10.5%                                   | 6.6%    | 36.7%                      | 2.2%        | 5.1%                              | 77.5%                               | 107.1%                                       |
| Day 2 | 8.4  | 10.6%                                   | 6.7%    | 23.2%                      | 5.3%        | 6.5%                              | 96.4%                               | 101.7%                                       |
|       |  | 10.4%                                   | 6.4%    | 22.6%                      | 9.1%        | 9.9%                              | 154.4%                              | 101.6%                                       |
|       |  | 10.5%                                   | 6.5%    | 28.6%                      | 6.5%        | 7.9%                              | 120.5%                              | 101.6%                                       |
|       |  | 10.4%                                   | 6.6%    | 27.3%                      | 6.2%        | 7.4%                              | 112.1%                              | 101.7%                                       |
|       |  | 10.5%                                   | 6.6%    | 23.3%                      | 7.0%        | 7.9%                              | 119.6%                              | 101.2%                                       |
| Day 3 | 8.1  | 7.5%                                    | 2.5%    | 19.9%                      | 5.5%        | 6.6%                              | 267.2%                              | 99.5%  |
|       |  | 7.5%                                    | 2.6%    | 37.2%                      | 13.3%       | 15.1%                             | 581.8%                              | 108.2%                                       |
| Day 4 | 5.3  | 5.0%                                    | 1.7%    | 23.5%                      | 0.2%        | 1.6%                              | 98.4%                               | 102.3%                                       |
|       |  | 5.0%                                    | 1.7%    | 13.6%                      | 0.9%        | 1.5%                              | 91.7%                               | 102.3%                                       |
| Day 5 | 8.0  | 7.4%                                    | 2.7%    | 31.1%                      | 0.6%        | 2.6%                              | 98.5%                               | 103.0%                                       |

1. Good agreement with NCCC “once per day” water content determinations.
2. Substantial water content variability outside this “once per day” window.
3. We now can determine accurate real time water composition in the membrane feed.

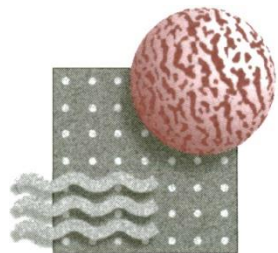
# CMS Membrane Performance Model Verification at NCCC

## NCCC Testing: DCT-Style 57-tube CMS Membrane Bundle



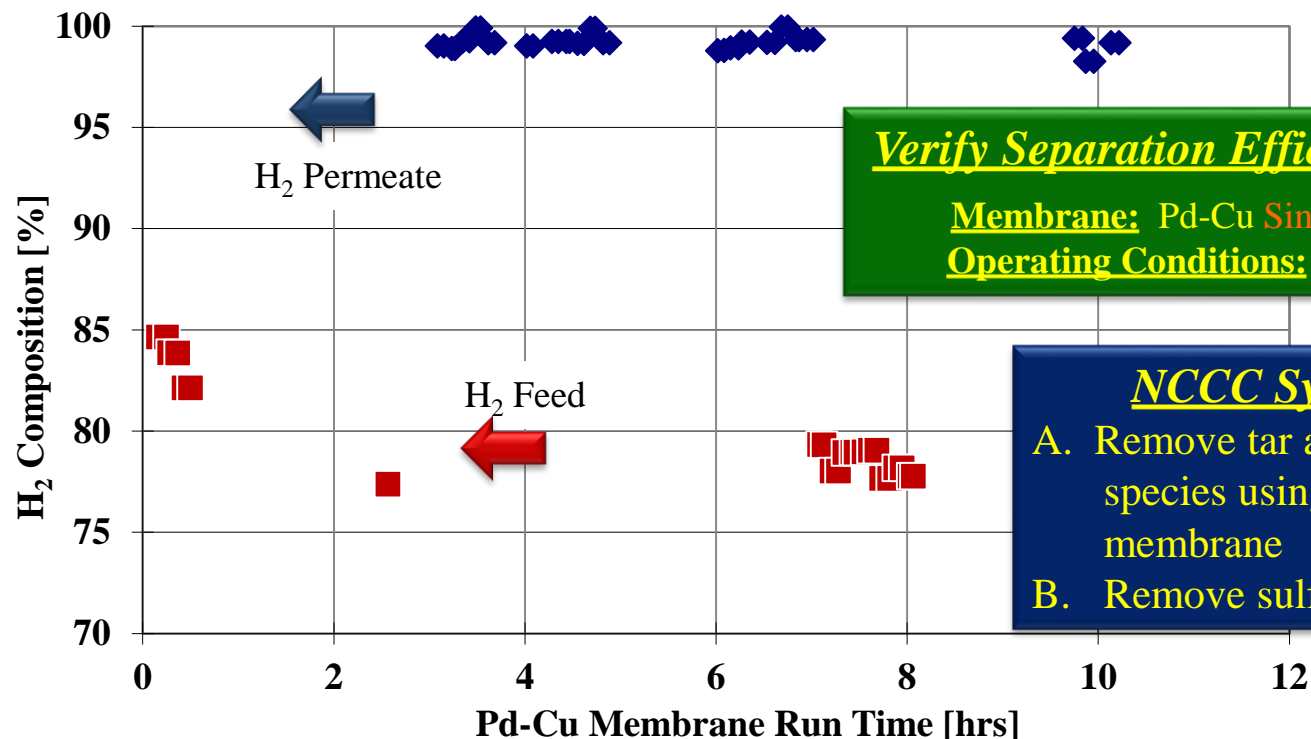
### Actual v. Simulated Results

NCCC bundle test results indicate that the mathematical model prediction is consistent with the permeate composition obtained from NCCC with proper feed flow baffles and accurate gas phase (water) composition analysis.



# Pd Alloy Membrane Challenge Testing at NCCC

## *Asymmetric Pd-alloy Membrane for Residual $H_2$ Recovery (Single Tube)*



**Verify Separation Efficiency at the NCCC**

**Membrane:** Pd-Cu Single Tube, 24" length

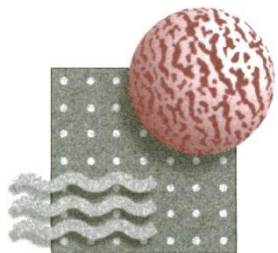
**Operating Conditions:** 250°C, 25 to 45psig

### **NCCC Syngas Pretreatment**

- A. Remove tar and high molecular weight species using permeate from a CMS membrane
- B. Remove sulfur via ZnO bed

**Our Pd alloy membrane has demonstrated its ability to deliver high purity hydrogen from a “clean” syngas stream, indicating its stability for recovery of residual hydrogen in our two stage membrane process.**





# MPT Pd and Pd Alloy Challenge Testing at NCCC

## *Pd and Pd-alloy Bundles for Residual $H_2$ Recovery*

### *Preliminary Membrane Performance*

#### *DCT-Style 12-tube Pd and Pd-Ag Membrane Bundles*



Bundle integrity test is critical to the technical viability of an asymmetric membrane, such as Pd thin film supported on ceramic substrate.

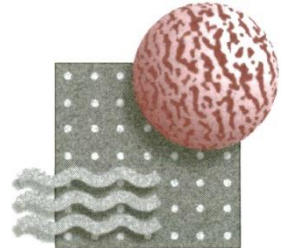
#### **Preliminary Characterization Data**

| Membrane ID | Permeance [GPU] |       | $H_2/N_2$ |
|-------------|-----------------|-------|-----------|
|             | $N_2$           | $H_2$ |           |
| 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     |

Pd-DCT-3

Pd-DCT-7

PdAg-DCT-28



# Pd Alloy Membrane Challenge Testing at NCCC

## NCCC Testing: In-situ Membrane Bundle Performance

### Testing Parameters

#### Membrane

12-tube Pd and Pd/Ag

#### Operating Conditions

$T \sim 250$  to  $300^\circ\text{C}$

$P \sim 180$  psig

#### Pretreatment

Sulfur removed

Sweet Shifted

#### Feed Composition

$\text{H}_2 \sim 13\%$  (spikes to  $\sim 30\%$ )

$\text{CO} \sim 1\%$

$\text{CO}_2 \sim 15\%$

$\text{N}_2, \text{H}_2\text{O} \sim \text{Balance}$

#### Trace Contaminants

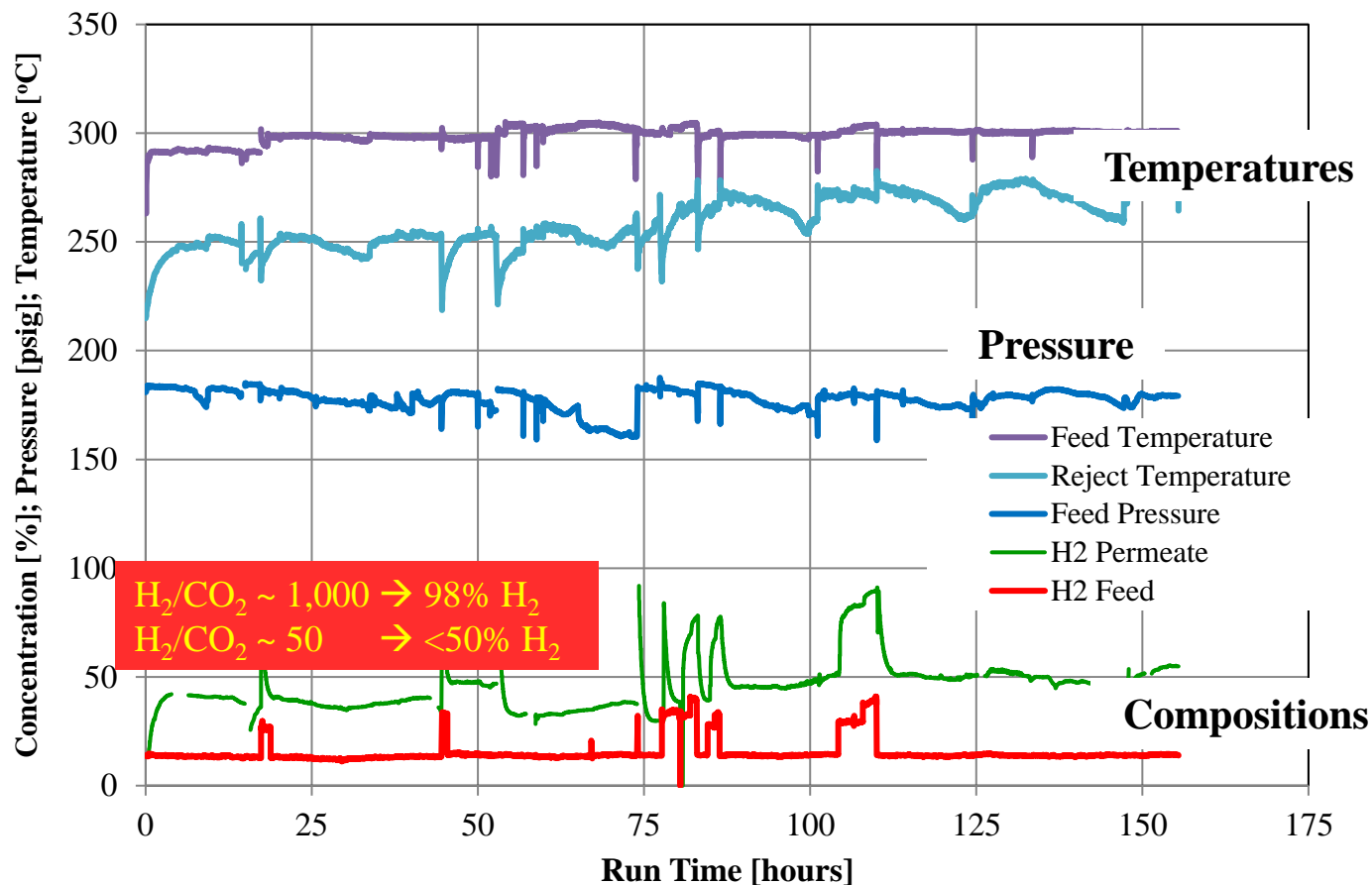
Sulfur Species  $\sim 0$  ppm

$\text{NH}_3 \sim 1,000$  ppm

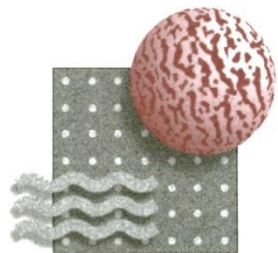
HCl, HCN,

Naphthalenes/Tars, etc.

### Slip Stream Testing with Sweet Shifted Gasifier Off-gas



**The Pd and Pd alloy membrane bundles maintain their physical integrity through >150 hrs of cumulative testing at the NCCC.**

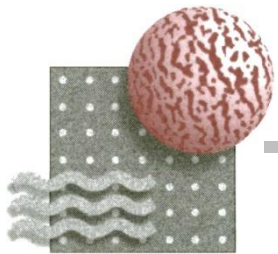


# Poison of Pd Membranes with Tar-containing Syngas

## *Summary of In-situ (NCCC) and Ex-situ Performance and Regeneration*

| Membrane ID  | Permeance [GPU] |                | H <sub>2</sub> /N <sub>2</sub> |
|--|-----------------|----------------|--------------------------------|
|  | N <sub>2</sub>  | H <sub>2</sub> |                                |
| Pd-DCT-7 (pre-NCCC)                                | 2.0             | 3,620          | 1,810                          |
| Pd-DCT-7 (in-situ NCCC)                            |                 | <300           | <50                            |
| Pd-DCT-7 (pure gas, periodic during NCCC test)     | <2.0            | 400 to 500     | <250                           |
| Pd-DCT-7-2 (lab, <u>single tube</u> , post-NCCC)   | 2.5             | 860            | 340                            |
| Pd-DCT-7-2 (lab, <u>single tube</u> , regenerated) | 2.7             | 3,850          | 1,425                          |

1. Performance decay is due to H<sub>2</sub> permeance reduction.
2. No membrane damage.
3. Fouling is reversible with regeneration.



# MPT Dual Stage Membrane Process

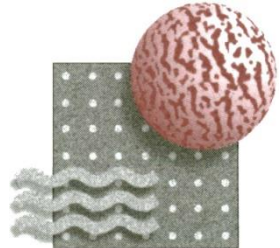
## *Presentation Outline – Section 4*

| SECTIONS       | SUB-SECTIONS                                       | SPECIFIC TOPICS  |
|----------------|--|--|
| 1. Membranes   | a. Carbon Molecular Sieve (CMS) Membranes          | Permeance & Selectivity                                  |
|                |  | Thermal & Material Stability                             |
|                | b. Palladium(Pd) Alloy Membranes                   | Permeance & Selectivity                                  |
|                |  | Material (Thermal + H <sub>2</sub> ) Stability           |
|                | c. Bundles & Housing                               | Bundle Engineering & Configuration                       |
| 2. Process     | a. Integrated Membrane Reactor or in Series        | Process Configuration                                    |
|                | b. Modeling and Process Simulation                 | Mathematical Modeling                                    |
|                |  | WGS Reaction Kinetic Study                               |
| 3. Field Tests | a. Previous Tests with 1st Gen CMS Bundle          | Performance and Stability                                |
|                | b. Current test with 2nd Gen CMS Bundle            | Long Term Material Stability                             |
|                | c. Verification of Model Prediction                | Field Obtained Data vs Prediction                        |
|                | d. Pd Membranes & Bundles                          | Performanc and Stability                                 |
|                | e. Pd Membrane Poisoned by Tar                     | Regeneration & Activity Restroation                      |
| 4. TEA/EHS     | a. Proposed Process Scheme                         | Block Flow Diagram                                       |
|                | b. Techno-economic Analysis (TEA)                  | Costs of Power & Carbon Capture                          |
|                | c. TEA Sensitivity Analysis                        | Impact of Membrane Selectivity & Configuration           |
|                | d. Environmental, Health and Safety Analysis (EHS) | Evaluation on Key Separation and Manufacturing Processes |

[illegible]

### *Pd-alloy Membrane (Residual $H_2$ Recovery)*



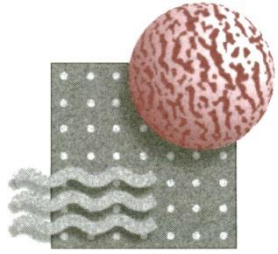


# Techno-economic Analysis (TEA)

## *Process Performance and Economics*

| Parameter                                   | Baseline Case B5B* | MPT B5M-HP | Target | MPT vs B5B |
|---|--------------------|------------|--------|------------|
| Carbon Capture                              | 90.0%              | 90.3%      | 90%    |            |
| CO <sub>2</sub> Purity                      | 99.48%             | 94.5%      | 95%    |            |
| H <sub>2</sub> in Fuel                      | 99.98%             | 98.7%      | NA     |            |
| Net Power Production, MW                    | 543                | 559        | N/A    | +3.0%      |
| Cost of CO <sub>2</sub> Captured [\$/tonne] | 63.1               | 58.2       | N/A    | -8.0%      |
| Cost of CO <sub>2</sub> Avoided [\$/tonne]  | 91.6               | 82.0       | N/A    | -10.6%     |
|   |                    |            |        |            |
| COE no T&S [\$/MWh]                         | 135.4              | 130.1      | N/A    | -3.9%      |
| Total as-spent Cost [\$/kW]                 | 4,782              | 4,621      | N/A    | -3.4%      |

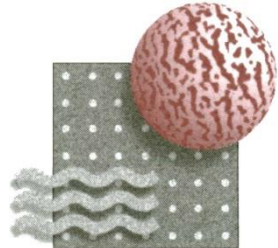
\* *Cost and Performance Baseline for Fossil Energy Plants. Volume 1b. Revision 2b, July 2015. DOE/NETL02015/1727. GEE IGCC with 2-stage Selexol*



# Techno-economic Analysis: Sensitivity

## *Basic Approach and Concepts*

| Objective   | Problem   | Impact                       |
|---|---|------------------------------|
| Carbon Loss <10%  | CMS permeates CO and CO <sub>2</sub>  | Miss Sequestration Target    |
| Minimize Parasitic Loss:<br><b>H<sub>2</sub> Fuel Compression</b> | H <sub>2</sub> needs compressed<br>(460psig) to the CT                        | Increased<br>COE; Plant Size |
| Minimize Parasitic Loss:<br><b>Steam Lost to Permeate</b>         | CMS permeates water<br><br>Need makeup steam to WGS<br>= Power loss at the ST | Increased<br>COE; Plant Size |

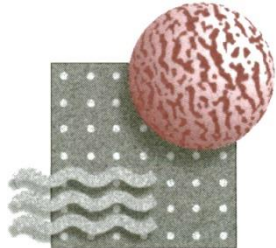


# Techno-economic Analysis (TEA) Sensitivity

## *Sensitivity Considerations – 2011 Base Dollar*

|  |   | <b>Net<br/>Power<br/>Output</b> | <b>Net<br/>Increase<br/>v. B5B</b> | <b>Total<br/>COE<br/>no T&amp;S</b> | <b>COE<br/>Increase<br/>v. B5A</b> | <b>Cost CO<sub>2</sub><br/>Capture<br/>v. B5A</b> | <b>Cost CO<sub>2</sub><br/>Capture<br/>v. 12A</b> |
|--|---|---------------------------------|------------------------------------|-------------------------------------|------------------------------------|---|---|
| <b>Case</b>  | <b>Comments</b>   | <b>[MWe]</b>                    | <b>[MWe]</b>                       | <b>[\$/MWhr]</b>                    | <b>[\$/MWhr]</b>                   | <b>[\$/tonne]</b>                                 | <b>[\$/tonne]</b>                                 |
| <b><i>MPT Base Cases</i></b>                                   |   |                                 |                                    |                                     |                                    |   |   |
| MPT #2: B5M  | 2015 Base Case  | 554                             | 11                                 | 134                                 | 31.4                               | 38.2  | 62.9  |
| <b><i>MPT Sensitivity Cases (Demonstrated Performance)</i></b> |   |                                 |                                    |                                     |                                    |   |   |
| MPT #2: B5M-HP   | 2017 Optimized Permeate Pressur                           | 559                             | 16                                 | 130.1                               | 27.5                               | 33.5  | 58.2  |
| MPT #3: B5M-HP.Sensitivity #1                                  | Raise H <sub>2</sub> /CO <sub>2</sub> ; Optimize Pressure | 560                             | 17                                 | 129.9                               | 27.3                               | 33.2  | 57.9  |
| <b><i>MPT Sensitivity Cases (Technical Challenge)</i></b>      |   |                                 |                                    |                                     |                                    |   |   |
| MPT #4: B5M-HP.Sensitivity #2                                  | Raise H <sub>2</sub> /H <sub>2</sub> O                    | 569                             | 26                                 | 127.8                               | 25.2                               | 30.7  | 55.4  |
| MPT #5: B5M-HP.Sensitivity #3                                  | N <sub>2</sub> Sweep CMS                                  | 569                             | 26                                 | 127.8                               | 25.2                               | 30.7  | 55.4  |
| MPT #6: B5M-HP.Sensitivity #4                                  | N <sub>2</sub> Sweep Pd                                   | 572                             | 29                                 | 127.1                               | 24.5                               | 29.9  | 54.6  |
| MPT #7: B5M - Maximum Potential                                | No H <sub>2</sub> Compr; No steam loss                    | 585                             | 42                                 | 122.3                               | 19.7                               | 24.0  | 48.7  |
| <b><i>IGCC Base Cases</i></b>                                  |   |                                 |                                    |                                     |                                    |   |   |
| IGCC Base Case (B5A)   |   | 622                             | NA                                 | 102.6                               | Base                               | Base  | NA  |
| IGCC Base Case with CCS (B5B)                                  | 2-Stage Selexol   | 543                             | Base                               | 135.4                               | 32.8                               | 38.9  | 63.0  |
| <b><i>Conventional Base Cases</i></b>                          |   |                                 |                                    |                                     |                                    |   |   |
| Pulverized Coal, SC, Base (12A)                                |   | 622                             | NA                                 | 82.3                                |                                    |   | NA  |
| Pulverized Coal, SC w/CCS (12B)                                | 2-Stage Selexol   | 550                             | NA                                 | 133.2                               |                                    |   | 58.2  |

According to our sensitivity analysis, approx. 15% cost reduction in CO<sub>2</sub> capture (in comparison with the base case of IGCC with CCS) can be achieved with our existing technology and the proposed process. With the introduction of the “purge-able” module, up to 39% reduction in CO<sub>2</sub> capture cost can potentially be achieved.



# Environmental, Health and Safety (EH&S) Analysis

## Our Approach





### Our Approach

- Assess all major risks from product fabrication to final decommissioning/end of life.
- Identify Severity of a potential hazard for each major steps involved in our proposed process was evaluated with respect to **Environment & Health, Flammability, or Instability** exposures.
- Predict Probability of the potential hazard occurrence.

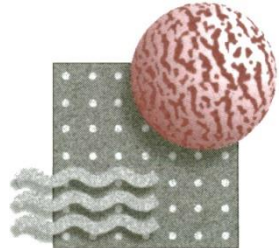
$$\text{Risk} = f(\text{Likelihood}, \text{Severity})$$

|          |   |                         |                     |                       |          |
|----------|---|-------------------------|---------------------|-----------------------|----------|
| SEVERITY | 4 | 4                       | 8                   | 12                    | 16       |
|          | 3 | 3                       | 6                   | 9                     | 12       |
|          | 2 | 2                       | 4                   | 6                     | 8        |
|          | 1 | 1                       | 2                   | 3                     | 4        |
|          | 0 | 0                       | 0                   | Review<br>Instability |          |
|          |   | 1                       | 2                   | 3                     | 4        |
|          |   | Extremely<br>Improbable | Extremely<br>Remote | Remote                | Probable |
|          |   | PROBABILITY             |                     |                       |          |

### Risk Category

|   |                     |
|---|---------------------|
|  | "Minor" Risk        |
|  | "Major" Risk        |
|  | "Hazardous" Risk    |
|  | "Catastrophic" Risk |

| Risk ID             | Risk Description                   | Severity             |   | Likelihood | Safety Matrix* | Risk Mitigation Strategy/Comments   |
|---------------------|------------------------------------|----------------------|---|------------|----------------|---|
| Membrane Production |                                    |                      |   |            |                |   |
| 5A.102a.04          | Methanol handling, and evaporation | Environment & Health | 1 | 4          | 4              | No extraordinary use. Common industrial chemical; standard handling and drying practice consistent with eg: paint finishing. Work under well-ventilated environment or with exhaust is recommended. |
|                     |                                    | Flamability          | 4 | 4          | 16             | No extraordinary use. Common industrial chemical; standard handling and drying practice consistent with eg: paint finishing. Work under well-ventilated environment or with exhaust is recommended. |
|                     |                                    | Instability          | 0 | 1          | 0              |   |



# Environmental, Health and Safety (EHS) Analysis

## *Key EH&S Risks Identified in Our Proposed Dual Stage Process*

### **Catastrophic Category**

- CMS membrane subsystem: use of solvent methanol in the preparation of the carbon precursor.
- Pd membrane subsystem: use of hydrogen for membrane annealing.

*Since methanol and hydrogen use are common in the industrial material preparation, their risk mitigation approaches are well established and readily available.*

### **Hazardous Category**

- CMS membrane subsystem: 5 areas
- Pd membrane subsystem: 3 areas

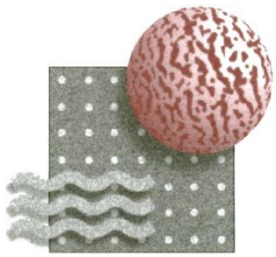
*Primarily associated with the exposure to vapor emitted during the membrane material preparation.*

*Industrial standard practice in ventilation, exhaust collection and discharge is considered adequate.*

### **Major Category (membrane process specific)**

- The stability of the membrane seal through the long-term exposure.
  - ✓ *Our mitigation approach includes installation of the monitoring device during operation and implementation of regular maintenance. Thus, early detection can be identified and corrective actions can be taken timely.*
  - ✓ *Though “major” risk is assigned to the membrane seal according to our analysis, its impact to the operation is considered to be minor due to the “gradual” versus “sudden” failure mode.*

**Conclusion: Thus, there is no reason to believe that a production process meeting the EH&S satisfaction cannot be established to commercialize the proposed technology and process.**

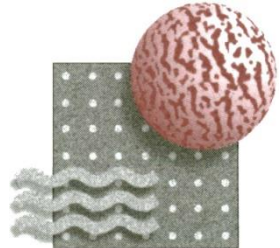


# MPT Dual Stage Process for IGCC with CCS

## *Conclusions*

- **Meet the CCS Targets.** Synergy of the proposed Dual Stage Membrane (CMS and Pd-alloy) process meets or exceeds the performance targets required to deliver the DOE CCS goals.
- **Long Term Membrane Stability.** The CMS (250°C) and Pd-alloy (350°C) membrane tubes and bundles (full ceramic) have been demonstrated to be stable in thousands of hours of thermal stability testing.
- **CMS Membrane Highly Stable in Gasifier Off-gas at the NCCC.** The CMS membrane bundle has been shown to be stable in various tests for hundreds of hours of exposure to synthetic and actual coal gasifier syngas with only particulate pretreatment.
- **Pd/Pd-alloy Membrane Undamaged at NCCC.** The Pd/Pd-alloy membrane is not damaged at the NCCC in sulfur free off-gas. Fouling occurs on exposure to “tar” like species which will not be present in the proposed process downstream of the Cold Gas Cleanup Unit.
- **Extreme pressures.** >1,000psig can be achieved with our DCT-style bundles making them suitable for the proposed IGCC with CO<sub>2</sub> capture environment.
- **Power Production Increased.** Base Case net power production for the process is 553MWe, 1.8% above the NETL base case. Optimization can boost this by +6 to +18 MWe (+2.9 to 5.2%). Base Case total capital cost for the process is \$32MM (3%) below the NETL base case.
- **CO<sub>2</sub> Capture Cost.** About 15% reduction in comparison with the base case of IGCC/CCS. Sensitivity analysis indicates that ~39% reduction can potentially be achieved with the introduction of a purge-able membrane module



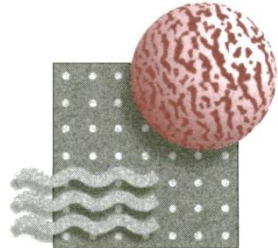


# Project Overview

## *Summary of Progress on Project Milestones and Success Criteria*

| ID | Milestone Description and Success Criteria   | Comment    |
|----|--|------------|
| A  | Generation of performance database. (Show >90% CO conversion and >70% H <sub>2</sub> recovery at target operating conditions). | Completed. |
| B  | Verification of the mathematical model. (Demonstrate model deviation from actual performance <20%).                            | Completed. |
| C  | Operation under extreme pressure.  | Completed. |
| D  | Conceptual design of the CMS/MR. (Complete conceptual design of the WGS/MR).   | Completed. |
| E  | Field test on real syngas. (Conduct >720 hours of actual syngas testing).  | Completed. |
| F  | Design and Engineering Analysis. (Complete the process design for >90% capture and 95% purity).                                | Completed. |
| G  | Economic and Environmental Analysis. (Complete the TEA and EHS)  | Completed. |

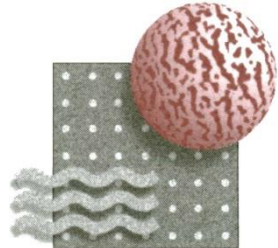
| ID  | Milestone Description  | Comment    |
|-----|--|------------|
| RC1 | Add partner with power plant expertise.  | Completed. |
| RC2 | Down-select WGS and membrane configuration.                                    | Completed. |
| RC3 | Down-select from N <sub>2</sub> purge option based upon technical feasibility. | Completed. |
| RC4 | Down-select Pd-Cu or Pd-Ag for bundle NCCC testing.                            | Completed. |
| RC5 | Consider Pd material potential supply problems.                                | Completed. |



# Point State Details

## *Summary of CMS Membrane Point State - 2017*

|  | Units             | Value  |
|--|-------------------|--|
| <b>Materials Properties (CMSM)</b>           |                   |  |
| Materials of Fabrication for Selective Layer | —                 | Carbon Molecular Sieve (CMS)   |
| Materials of Fabrication for Support Layer   | —                 | Alumina  |
| Nominal Thickness of Selective Layer         | μm                | 2 to 3   |
| Membrane Geometry                            | —                 | Tubular  |
| Max Trans-Membrane Pressure                  | Bar (psig)        | <u>Tubes:</u> >75 (1,100)<br><u>DCT Tube Sheet:</u> >75 (1,100)  |
| Hours Tested Without Significant Degradation | —                 | <u>Single Tube</u><br>Thousands of hours in various challenge conditions (steam, H <sub>2</sub> S, vapors, etc).<br><br><u>Multiple Tube (50 to 85) Bundles</u><br>>16,000 hours in thermal stability testing<br>>1,000 hours in untreated coal gasifier off-gas |
| Manufacturing Cost for Membrane Material     | \$/m <sup>2</sup> | <750   |
| <b>Membrane Performance (CMSM)</b>           |                   |  |
| Temperature                                  | °C                | 250 to 300   |
| H <sub>2</sub> Pressure Normalized Flux      | GPU or equivalent | H <sub>2</sub> : 550 to 900  |
| H <sub>2</sub> /H <sub>2</sub> O Selectivity | —                 | 2 to 4   |
| H <sub>2</sub> /CO <sub>2</sub> Selectivity  | —                 | >50  |
| H <sub>2</sub> /H <sub>2</sub> S Selectivity | ppm               | >100   |
| Type of Measurement                          | —                 | Mixed gas  |



# Point State Details

## *Summary of Pd Alloy Membrane Point State - 2017*

|  | Units                             | Value   |
|--|-----------------------------------|---|
| <b>Materials Properties (Pd membrane)</b>        |                                   |   |
| Materials of Fabrication for Selective Layer     | —                                 | Pd-Ag Alloy   |
| Materials of Fabrication for Support Layer       | —                                 | Alumina   |
| Nominal Thickness of Selective Layer             | μm                                | 2 to 5  |
| Membrane Geometry                                | —                                 | Tubular   |
| Max Trans-Membrane Pressure                      | Bar (psig)                        | <u>Tubes:</u> >75 (1,100)<br><u>DCT Tube Sheet:</u> >75 (1,100)   |
| Hours Tested Without Significant Degradation     | —                                 | <u>Single Tube</u><br>>35,000 hours in thermal stability challenge test.<br><br><u>Multiple Tube (12) Bundles</u><br>150 hours in pre-treated coal gasifier off-gas |
| Manufacturing Cost for Membrane Material         | \$/m <sup>2</sup>                 | <1,200  |
| <b>Membrane Performance (Pd-alloy membranes)</b> |                                   |   |
| Temperature                                      | °C                                | 250 to 400  |
| H <sub>2</sub> Pressure Normalized Flux          | GPU or equivalent<br>(at 20 psig) | 2,000 to >5,500   |
| H <sub>2</sub> /H <sub>2</sub> O Selectivity     | —                                 | 1,000 to >5,000   |
| H <sub>2</sub> /CO <sub>2</sub> Selectivity      | —                                 | 1,000 to >5,000   |
| H <sub>2</sub> /H <sub>2</sub> S Selectivity     | ppm                               | NA  |
| Type of Measurement                              | —                                 | Mixed Gas   |