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

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**Dr. Richard J. Ciora, Jr, Media and Process Technology Inc.**

- **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, TechnipFMC plc., Morovia, CA**

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# M&P Dual Stage Membrane Process

## *Project Overview*

### *Overall Theme:*

- ***Use inorganic membrane technology advantages to achieve CCS goals.***
- ***Move inorganic membrane technology from lab scale novelty to commercial reality.***

### *Overall Project Objectives:*

1. ***Demonstrate the carbon molecular sieve membrane as a bulk $H_2$ separator and to improve the efficiency of the WGS reactor***
2. ***Demonstrate the Pd-alloy membrane for residual $H_2$ recovery from "captured" high pressure $CO_2$***
3. ***Perform bench scale testing (equivalent to a syngas throughput for 0.01MWe power generator) of the innovative pre-combustion process scheme for power generation with $CO_2$ capture and sequestration (CCS).***
4. ***Key process components will be tested under simulated and real gasifier syngas conditions for their potential to effectively separate $H_2$ and $CO_2$.***
5. ***Collected data will be utilized to assess the potential of the concept for achieving the DOE Carbon Capture Program goal.***

# M&P Dual Stage Membrane Process

## *Project Overview*

***Funding:*** ***Overall project budget: $2.5MM including $500,000 (20%) cost share***

***Overall Project Performance Dates:*** ***October 1, 2013 - September 30, 2016***

***Project Participants:***

- ***Media and Process Technology…Membrane manufacturer/supplier and technology developer***
- ***University of Southern California…Membrane reactor testing, membrane model development***
- ***Technip FMC…Engineering and system design, analysis and economics***

# APPROACH

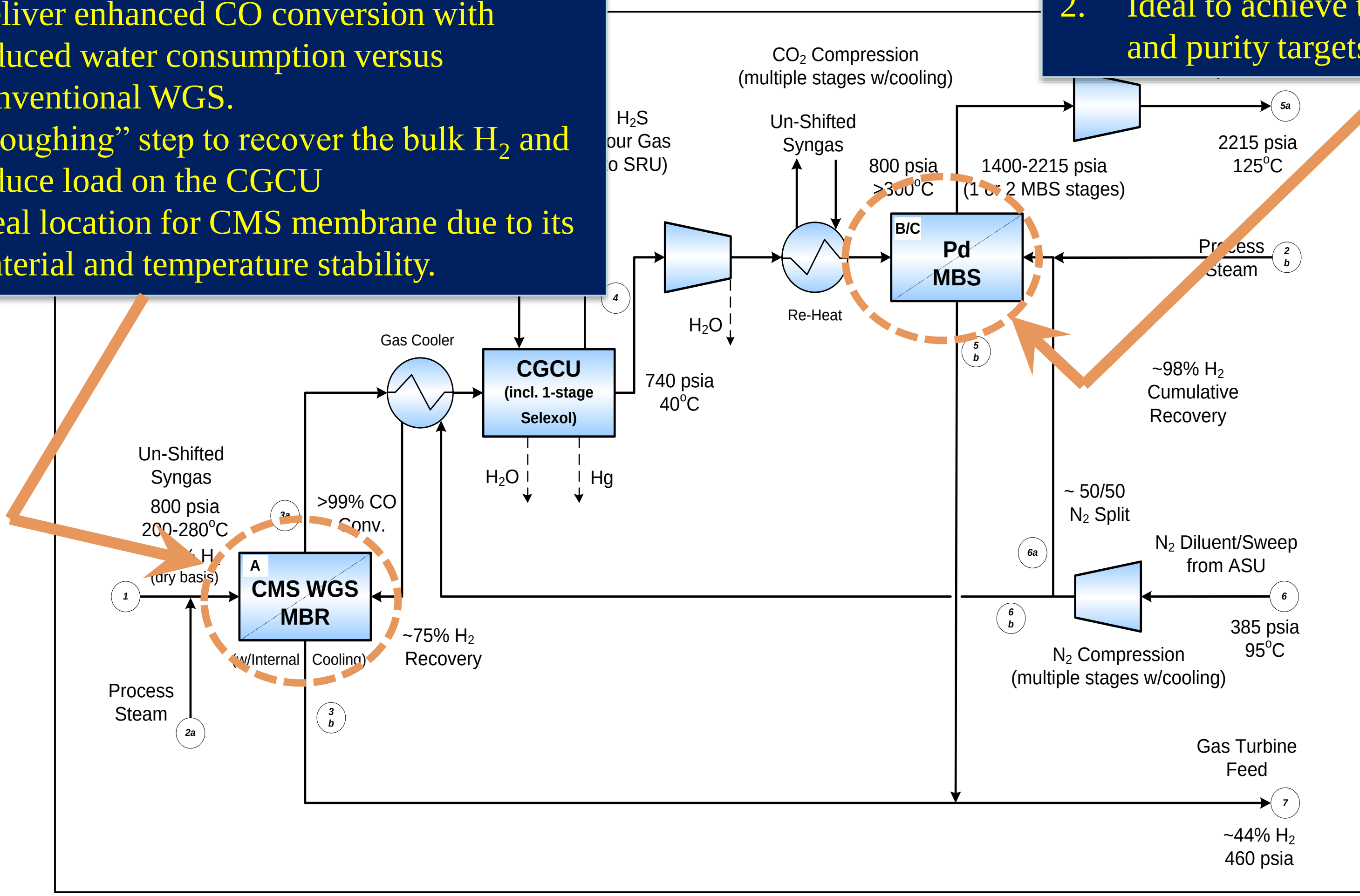
## *Dual Stage Membrane Process Scheme and Key Components*

**Pd-Alloy Membrane**

1. High selectivity yields excellent residual $H_2$ recovery.
2. Ideal to achieve the $CO_2$ capture and purity targets.

**CMS Membrane (coupled with WGS reactor)**

1. Deliver enhanced CO conversion with reduced water consumption versus conventional WGS.
2. "Roughing" step to recover the bulk $H_2$ and reduce load on the CGCU
3. Ideal location for CMS membrane due to its material and temperature stability.



# TECHNOLOGY BACKGROUND

***Multiple Tube Membrane Bundles – versatile, low cost***


*Example: conventional micro- and ultrafiltration*

Single tubes


*Ex: porous heat exchangers & catalytic membrane reactors*


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

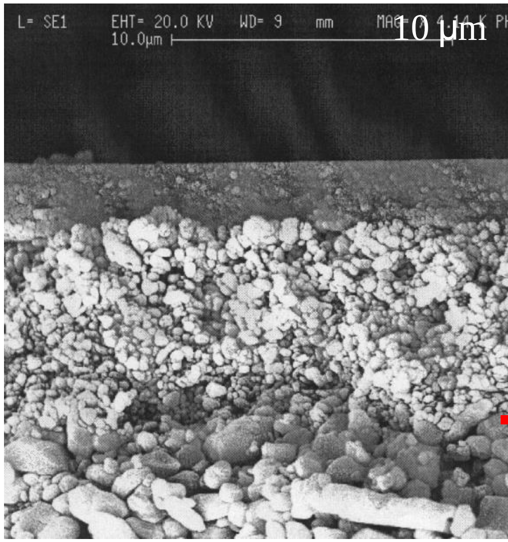
**Our Core Expertise/Technology**

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

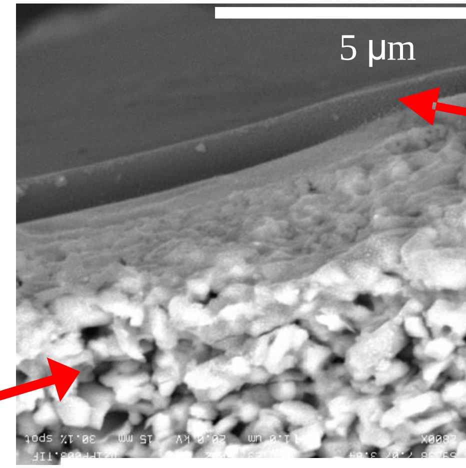
# TECHNOLOGY BACKGROUND

***Specific thin film deposition for advanced separations***

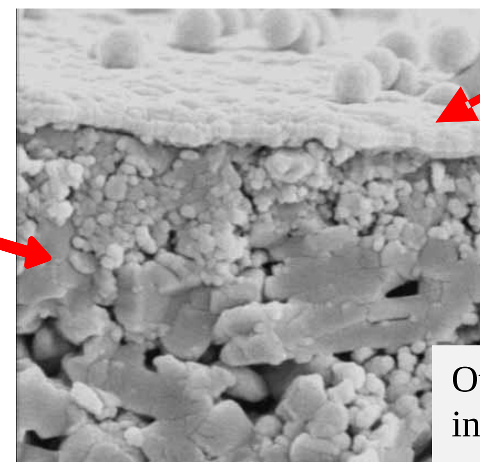
**Ceramic Substrate**




Ceramic
Substrate




Carbon molecular sieve (porous, sulfur resistance)



Palladium (dense, excellent selectivity)

Others, including zeolites, flourinated hydrocarbons, etc.

**Important Features of MPT Inorganic Membranes**

- Low cost commercial ceramic support
- High packing density, tube bundle
- Module/housing for high temperature and pressure use

**Our Core Expertise/Technology**

#2: Thin film deposition a on less-than desirable but low cost porous tubular substrates

# TECHNOLOGY BACKGROUND

***Membrane Bundles for Separations at High Temperature and Pressure***

## ***Multiple Tube Bundle Styles***

## ***Common Features***

Glass Transition Zone

Dense alumina "tips"
for Candlefilter

### ***Dense Ceramic Tube Sheet (DCT-style)***

***Performance: >500$^{o}$C; >1,000 psig***

***Packing: 57-tube current and 71-prototypes, spaced pack***

CMS Membrane

Pd-alloy Membrane

### ***Potted Ceramic Glass (PCG-style)***

***Performance: ~300$^{o}$C; <450 psig***

***Packing: 86-tube, close pack***

CMS Membrane

# TECHNOLOGY/PROCESS ADVANTAGES

## *Dual Stage Membrane Process: Advantages over SOTA*

**Our Innovation**

- ***CMS membrane to enhance CO conversion efficiency with concomitant bulk $H_2$ recovery*** to improve power generation efficiency.

- ***Pd-alloy membrane for residual $H_2$ recovery*** during the post compression of $CO_2$ for CCS to achieve the $CO_2$ capture goals and fuel efficiency requirements.

**Unique Advantages**

- ***No syngas pretreatment required***. CMS membrane is stable in all of the gas contaminants associated with coal derived syngas.

- ***Improved CO conversion efficiency and bulk $H_2$ separation***. Separation of hydrogen as well as enhanced CO conversion from the raw syngas occurs at elevated temperatures at reduced steam requirement for the WGS reaction.

- ***Reduced Gas Load to CGCU:*** The proposed use of the CMS membrane with the WGS reactor results in substantial hydrogen and steam recovery, resulting in reduced stream size for the CGCU.

- ***CCS Post Compression Power Reduction***: $CO_2$-enriched gas is delivered to the CGCU at relatively high pressure reducing total compression load.

- ***Enhanced residual $H_2$ recovery from the CCS stream to achieve the $CO_2$ recovery goals***. The Pd-alloy membrane is ideally suited to remove residual $H_2$ from the CCS stream to deliver the $CO_2$ purity and capture targets.

# CHALLENGES

## *Dual Stage Membrane Process: Advantages over SOTA (cont.)*

**Our Solutions to the Well-known Deficiencies of a Membrane Process**

- ***Bulk Separation Limitation***… Membranes are generally intended for bulk separation, usually not very efficient for fine separations. Our use of very high selectivity Pd-alloy membranes to supplement CMSM overcomes this deficiency to achieve the program goals.

- ***High Cost of Pd Membranes***… Pd-based membranes are expensive and the worldwide supply is constrained considering commercially available technology. Our ceramic substrate and bundle designs permit thin films to overcome both of these problems.

- ***Pd Membrane Stability***…The Pd-based membranes in this application is exposed to a $H_2/CO_2$ stream after CGCU. Thus, chemical stability of the membrane is not an issue.

# Progress to Date on Key Technical Challenges

## *BP1 and BP2 Accomplishments*

**<u>BP1 Tasks Completed to Overcome Key Technical Challenges</u>**

- CMS/Pd membrane operation meeting targets for $CO_2$ sequestration and cost.
- Long term and other membrane performance stability
- Full-scale WGS-MR and membrane separator designs for mega-scale applications
- Updated membrane and membrane reactor modeling

**<u>BP2 Tasks Underway/Completed to Overcome Key Technical Challenges</u>**

- ✓ *Performance stability in actual gas testing (NCCC) with multiple tube bundles.*
- ✓ *Model verification in actual gas testing with multiple tube bundles.*
- ✓ *Long term membrane performance stability.*
- ✓ *Process design and techno-economic evaluation.*
- ✓ *Environmental, health and safety assessment.*

# Progress and Current Status of Project

**Media and Process Technology Inc. (M&P)**
**1155 William Pitt Way**
**Pittsburgh, PA  15238 - 1678**

# PROGRESS: CMS Membranes

## *Typical Performance and Performance Targets*

### *CMS Single Tube Characterization*

| CMS Membrane Characteristic | Preliminary Target to Achieve DOE Goals[1] | Laboratory Single Tubes Performance |
|---|---|---|
| Permeance, $H_2$ [GPU] @ **250°C, 20 psig** | 550 | 420 to 1,100 |
| Selectivity, $H_2/X$ | | |
| $H_2/N_2$ | 70 | 80 to >180 |
| $H_2/CO$ | 70 | 70 to >130 |
| $H_2/CO_2$ | 35 | 35 to >65 |
| $H_2/H_2S$ | N/A[2] | 100 to 150[2] |
| $H_2/H_2O$ | 1.5 | 1.5 to 3 |

Notes:

1. Target performance is that required to achieve 90% $CO_2$ capture at 95% purity with 95% fuel utilization ($H_2$ + CO to the turbine).
2. At this selectivity, approximately 200 ppm $H_2S$ in the fuel to turbine.

### *CMS 86-Tube Bundle Characterization*

| CMS Bundle ID | He Permeance [GPU] | $He/N_2$ 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 |

# PROGRESS: Pd-Alloy Membranes

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

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

| Pd-Alloy Membrane Characteristic | Preliminary Target to Achieve DOE Goals[1] | Laboratory Single Tubes Performance |
|---|---|---|
| Permeance, $H_2$ [GPU] @ **350ºC, 20 psig** | 3,470 | 1,750 to >5,500 |
| Selectivity, $H_2/X$ | | |
| $H_2/N_2$ | 300 | 300 to >3,000 |
| $H_2/CO$ | 300 | 300 to >3,000 |
| $H_2/CO_2$ | 300 | 300 to >3,000 |
| $H_2/H_2S$ | N/A[2] | NA[2] |
| $H_2/H_2O$ | 300 | 300 to >3,000 |

Notes:

1. Target performance is that required to achieve 90% $CO_2$ capture at 95% purity with 95% fuel utilization ($H_2$ + CO to the turbine).
2. Feed gas to the Pd-alloy membrane has been pretreated to remove residual sulfur species in the CGCU.

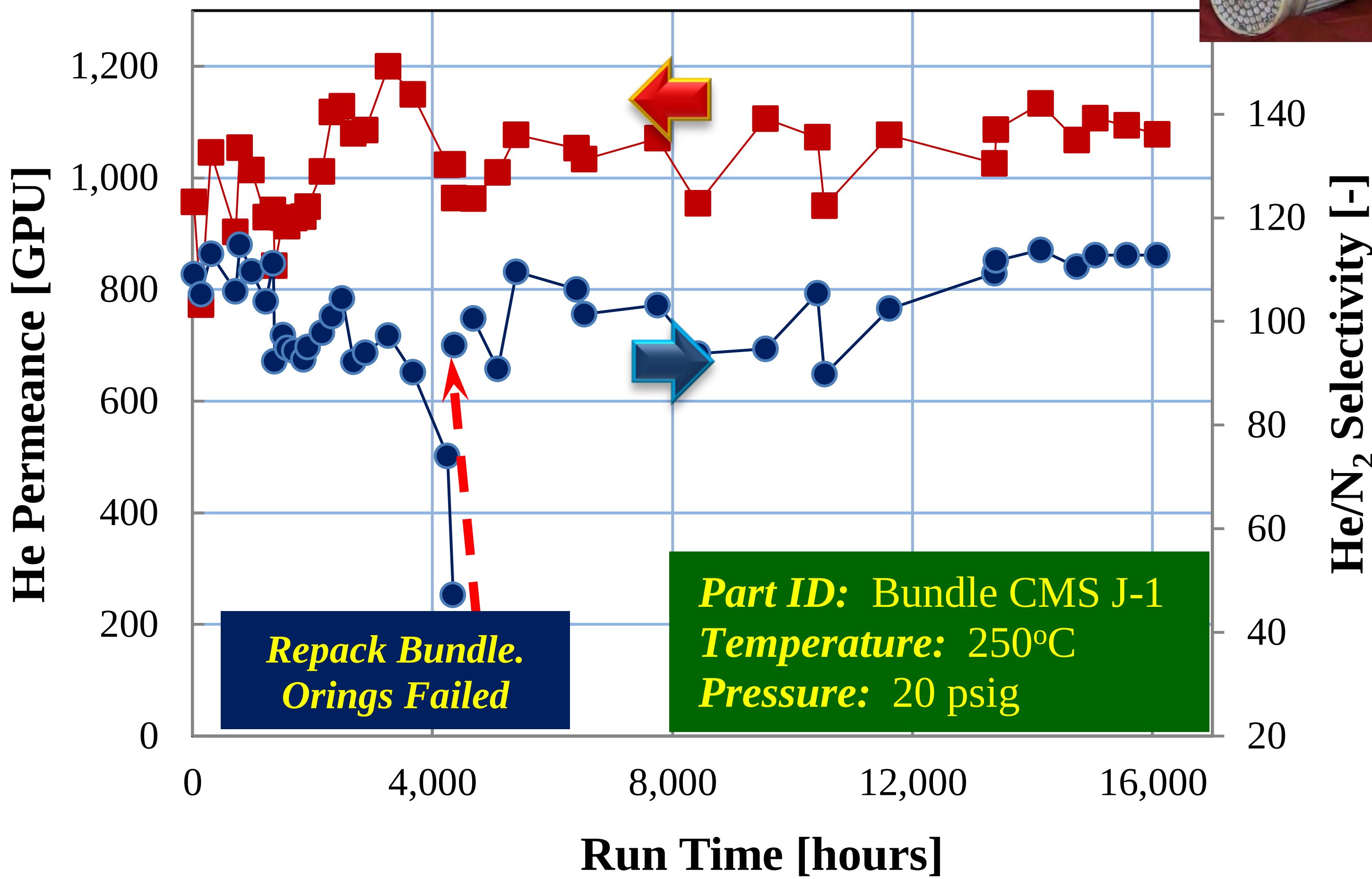
### *Pd/PdAg 12-Tube Bundle Characterization*

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

# PROGRESS: CMS Membrane Stability

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

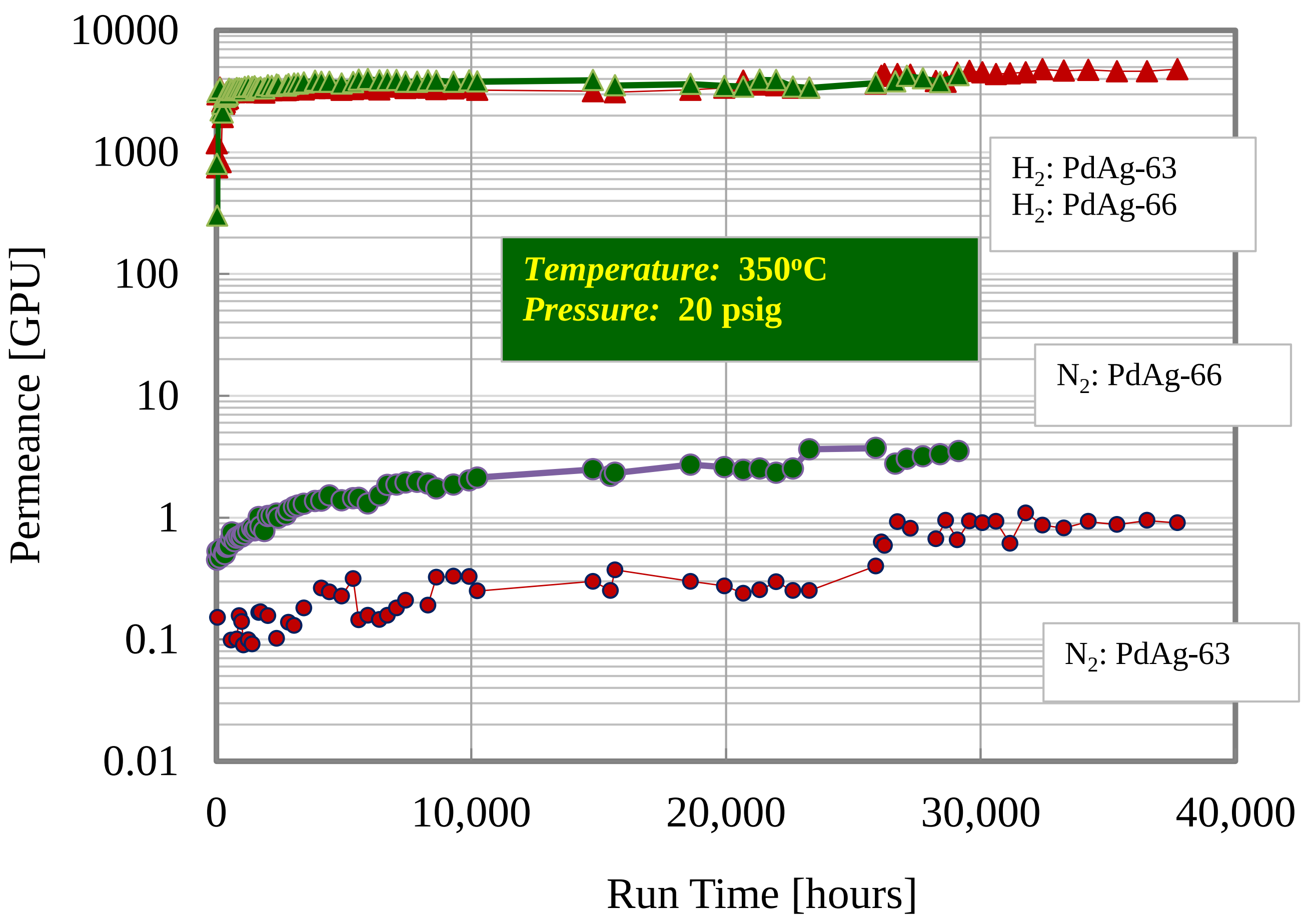
*CMS 86 -Tube Bundle Long Term Stability (>16,000 hrs)*



# PROGRESS: Pd Membrane Stability

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

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



# PROGRESS: CMS Membrane Bundle Stability

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

***Testing Parameters***

*Membrane*
*86-tube CMS*

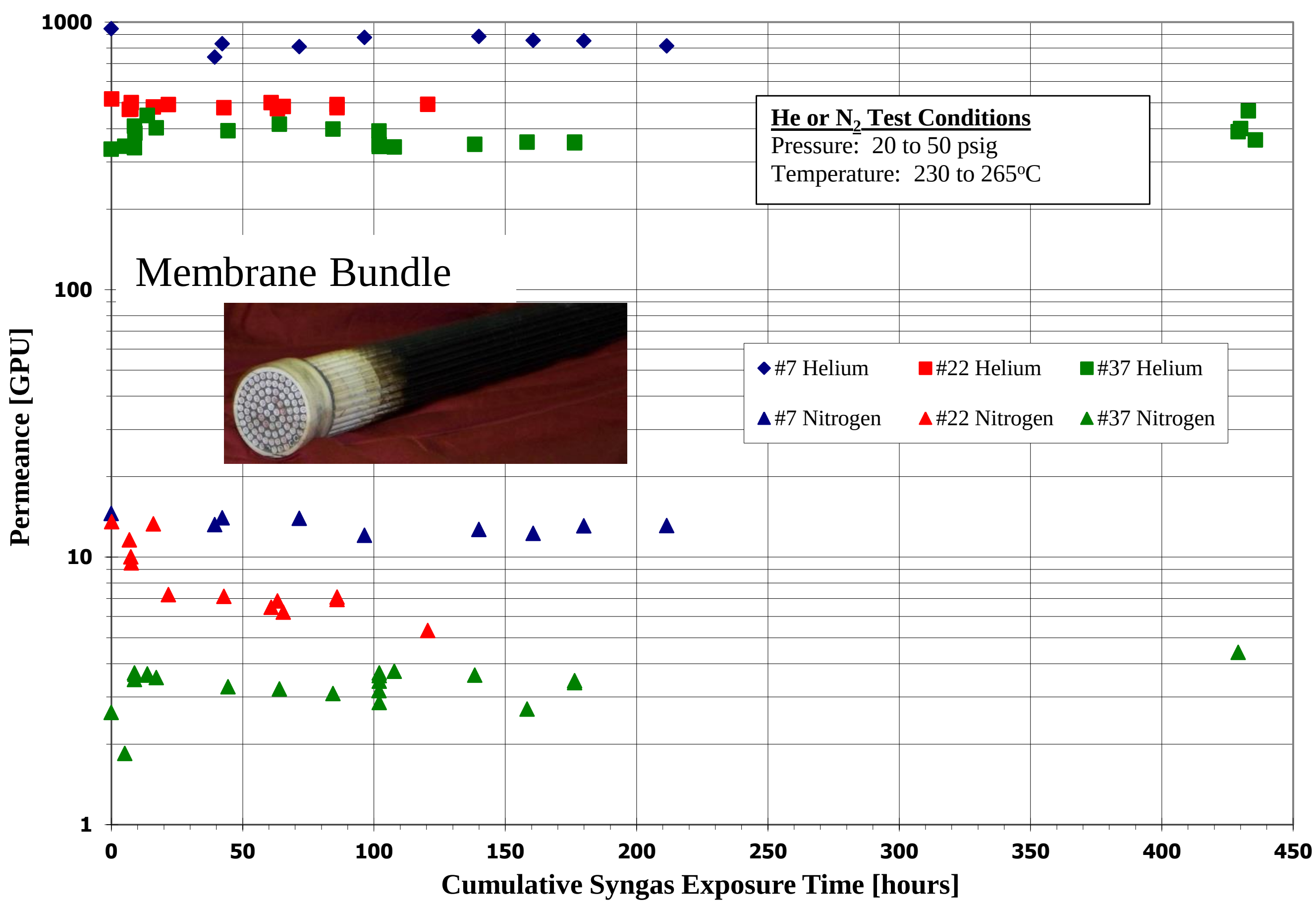
*Operating Conditions*
*T~ 250 to 300°C*
*P~ 150 to 300 psig*

*Pretreatment*
Particulate trap only,
no other gas cleanup.

*Composition*
$H_2$ ~ 10 to 30%
CO ~ 10%
$CO_2$ ~10%
$N_2$,$H_2O$ ~Balance

*Trace Contaminants*
*$NH_3$ ~ 1,000ppm*
*Sulfur Species ~ 1,000ppm*
*HCl, HCN, Naphthalenes/Tars, etc.*

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



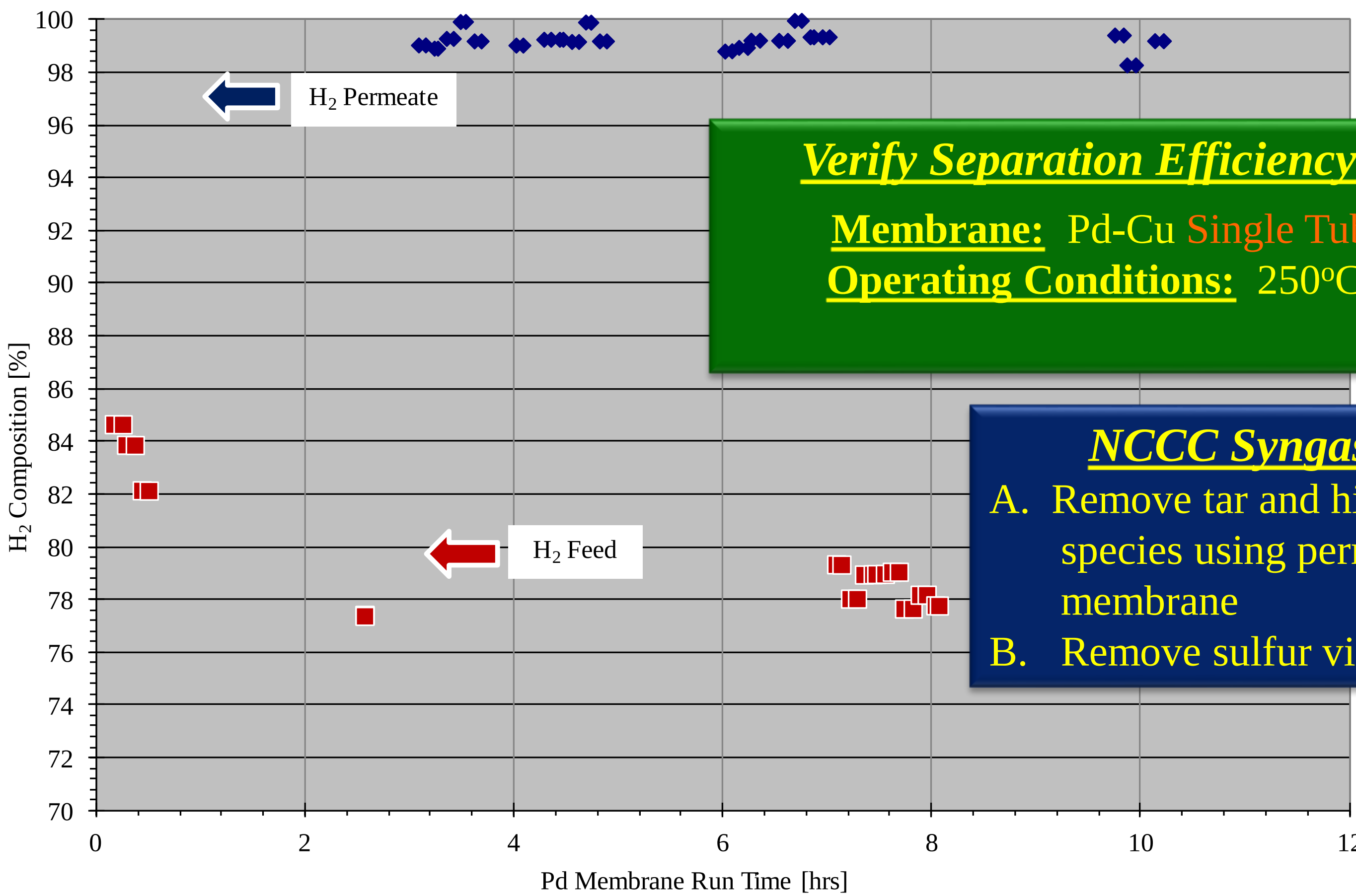

*Performance stability of multiple tube CMS membrane bundles during $H_2$ recovery from NCCC slip stream testing. He and $N_2$ Permeances measured periodically during >400 hr test.*

# PROGRESS: Membrane NCCC Challenge Testing

## *Pd-alloy Membrane for Residual $H_2$ Recovery*

***"2nd Stage" of the Dual Stage Membrane Process***

***Clean** $CO_2$ **Stream before Sequestration (minimal contaminants)***




***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

# PROGRESS: Membrane NCCC Challenge Testing

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

## ***Preliminary Membrane Performance***

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

Pd-DCT-3

PdAg-DCT-28

Pd-DCT-7

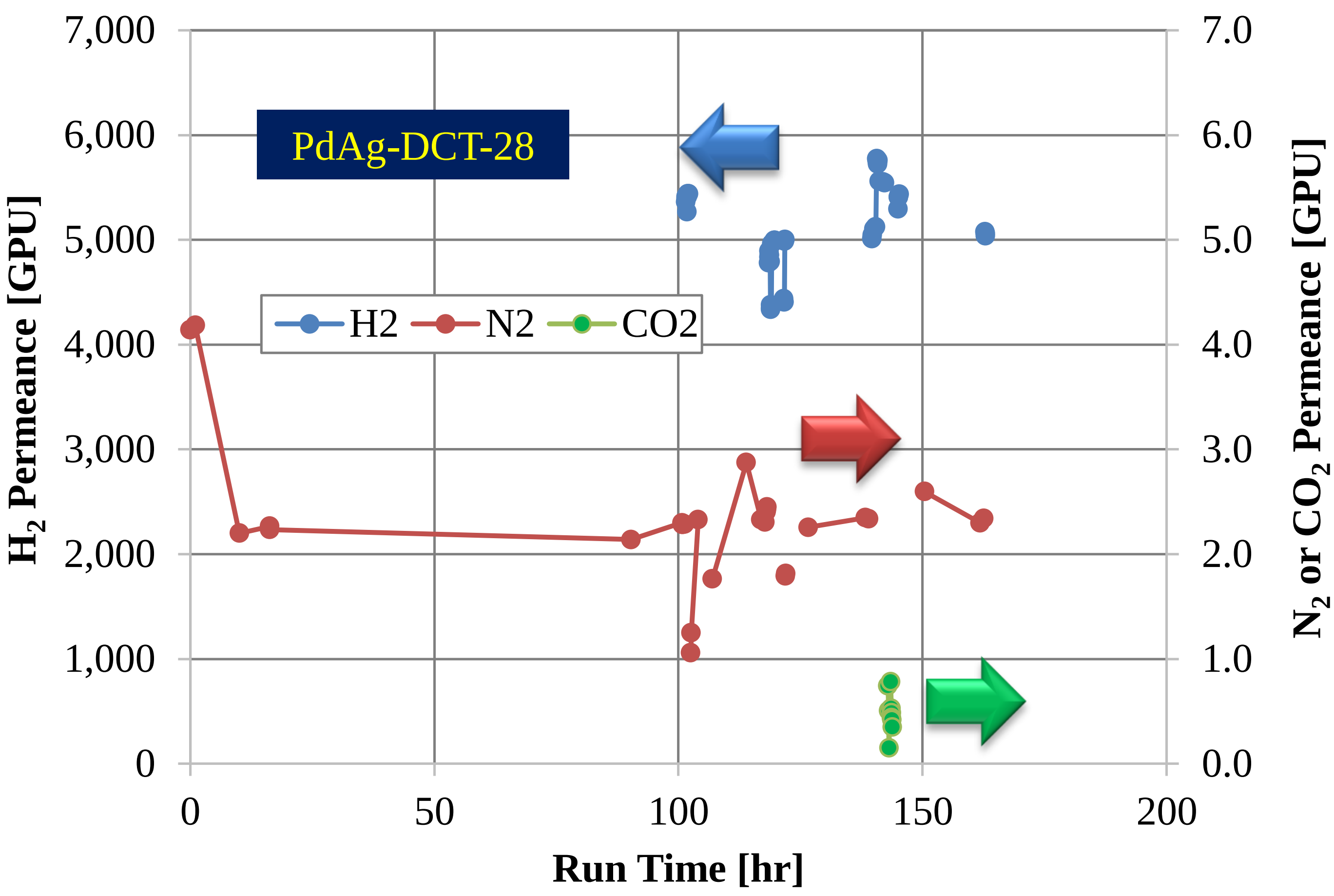
| Preliminary Characterization Data | | | |
|---|---|---|---|
| **Membrane ID** | Permeance [GPU] | | $H_2/N_2$ |
| | $N_2$ | $H_2$ | |
| **Pd-DCT-3** | 3.8 | 4,170 | 1,100 |
| **Pd-DCT-7** | 2.0 | 3,620 | 1,810 |
| **PdAg-DCT-28** | 2.5 | 5,180 | 2,030 |

# PROGRESS: Membrane NCCC Challenge Testing

***Multiple Tube Pd-alloy Bundles for Residual $H_2$ Recovery***

## ***<u>Preliminary Bundle Performance (pre-NCCC)</u>***

***Intermediate term stability testing at 350°C***



# PROGRESS: Membrane NCCC Challenge Testing

## *NCCC Testing: In-situ Membrane Bundle Performance*

***Testing Parameters***

*Membrane*
*12-tube Pd and Pd/Ag*

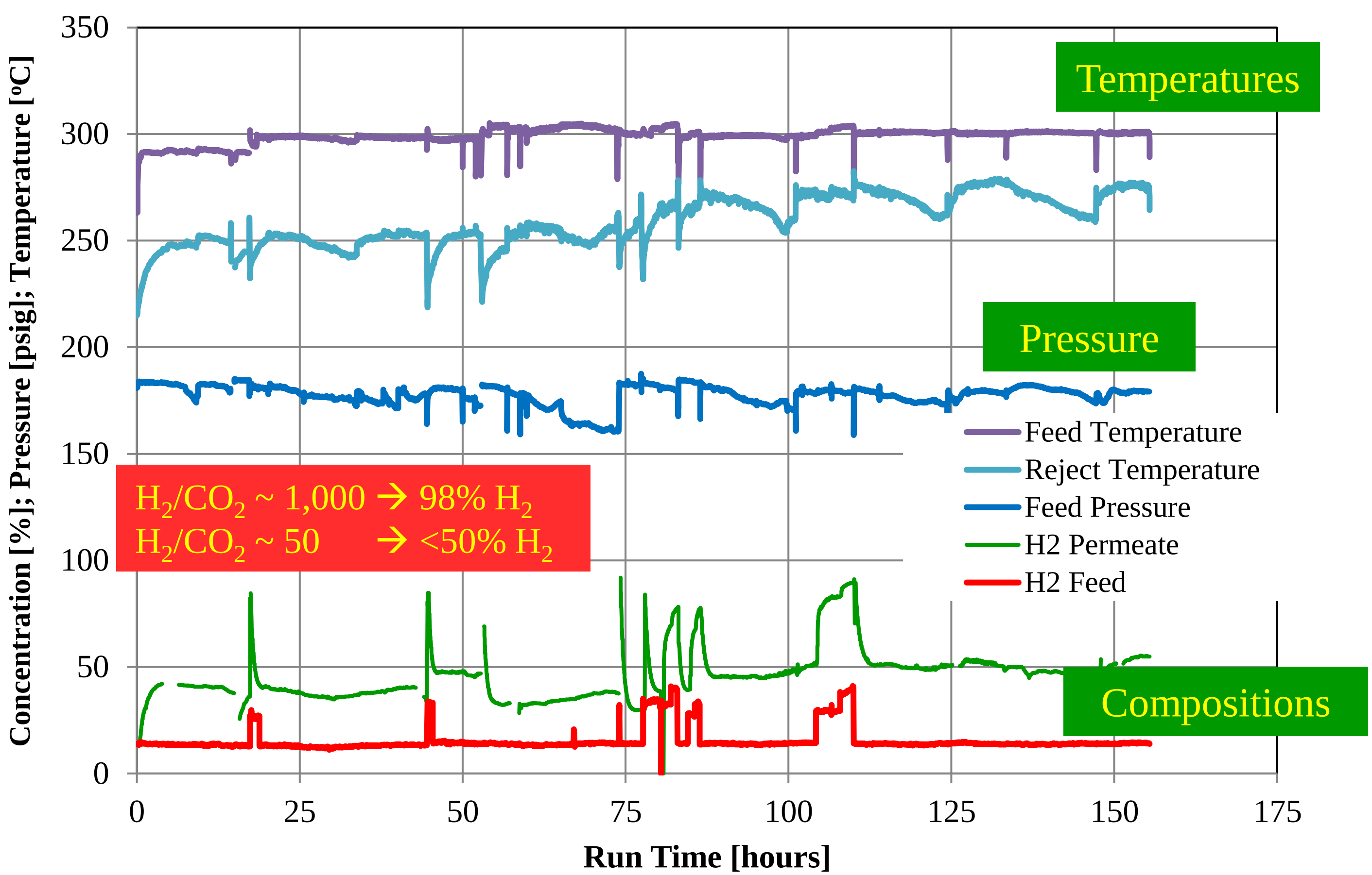
*Operating Conditions*
*T~ 250 to 300ºC*
*P~ 180 psig*

*Pretreatment*
**Sulfur removed**
**Sweet Shifted**

*Feed Composition*
$H_2$ ~13% (spikes to ~30%)
CO ~ 1%
$CO_2$ ~15%
$N_2$,$H_2O$ ~Balance

*Trace Contaminants*
*Sulfur Species ~ 0ppm*
*$NH_3$ ~ 1,000ppm*
*HCl, HCN,*
*Naphthalenes/Tars, etc.*

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



# PROGRESS: Membrane NCCC Challenge Testing

## *Multiple Tube Pd-alloy Bundles for Residual $H_2$ Recovery*

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

| Membrane ID | Permeance [GPU] | | $H_2/N_2$ |
|---|---|---|---|
| | $H_2$ | $N_2$ | |
| **Pd-DCT-7 (pre-NCCC)** | **3,620** | **2.0** | **1,810** |
| **Pd-DCT-7 (in-situ NCCC)** | <*300* | | <50 |
| **Pd-DCT-7 (pure gas, periodic during NCCC test)** | 400 to 500 | <2.0 | <250 |
| **Pd-DCT-7-2 (lab, single tube, post-NCCC)** | 860 | 2.5 | 340 |
| **Pd-DCT-7-2 (lab, single tube, regenerated)** | 3,850 | 2.7 | 1,425 |

**Summary**

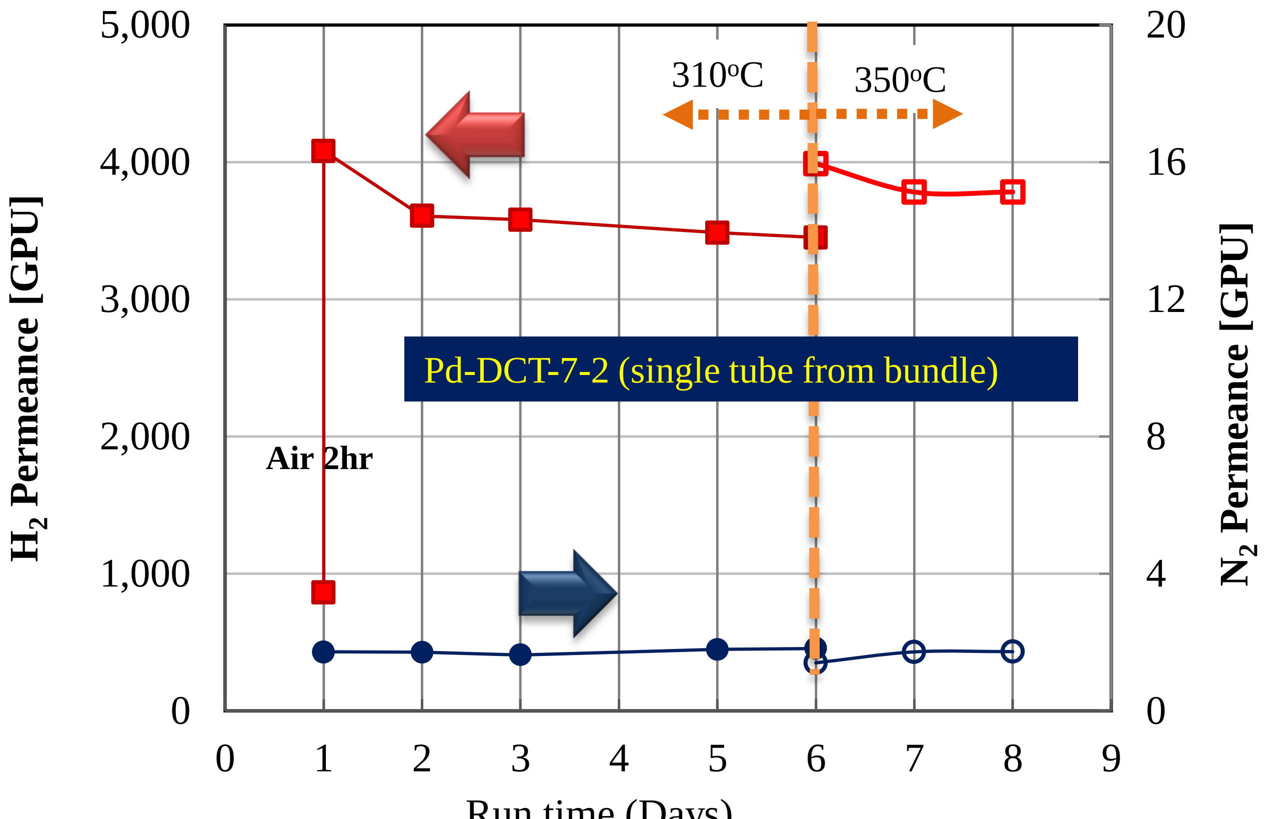
1. Performance decay is due to $H_2$ permeance reduction.
2. Fouling is reversible with regeneration.
3. No membrane damage.

# PROGRESS: Membrane NCCC Challenge Testing

## ***Membrane Regeneration with No Damage Post NCCC***

***Removed and regenerated single tubes from NCCC tested bundles***

***Regeneration via air calcination***




# PROGRESS: NCCC Challenge Testing

***Source of In-situ Performance Degradation: Tar-like Species?***

***CMS Membrane Experience: Fouling below about 250°C with untreated NCCC off-gas***

**Typical CMS Membrane Operating Temperatures ~270°C → No membrane fouling**

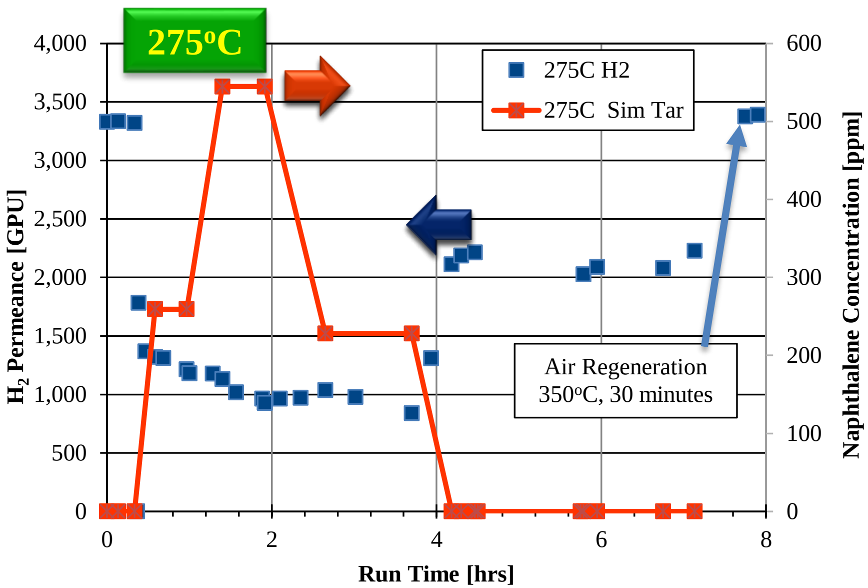
***Temperatures ≤250°C***
***Tar or other residue buildup evident***

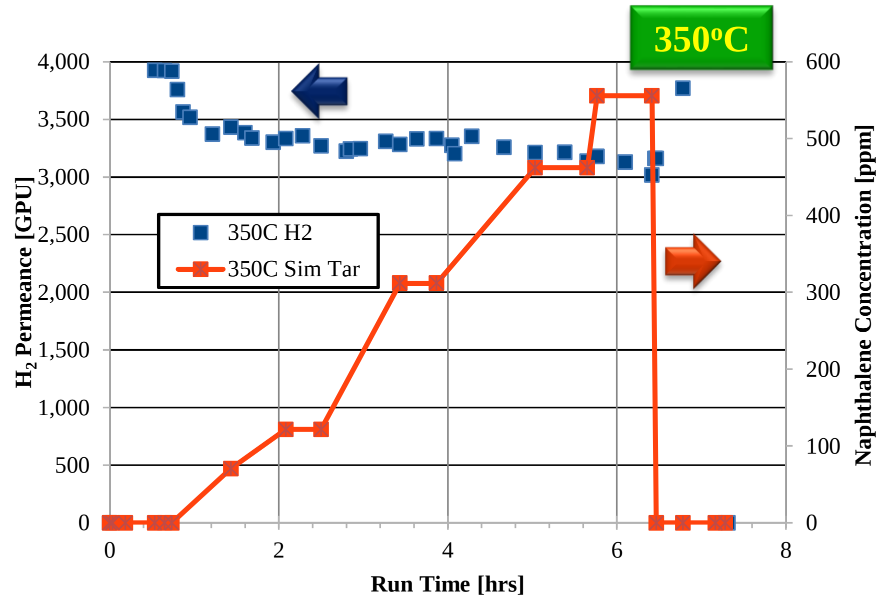
***Temperatures >250°C***
***No evidence of tar or other residue buildup***

# PROGRESS: NCCC Challenge Testing

## *Source of NCCC In-situ Performance Degradation: Tar-like Species?*

### *$H_2$ Permeance in the Presence of Naphthalene as a "Tar" Simulant*




## ***Results***

1. Fouling occurs rapidly at very low "tar" concentrations
2. Fouling is independent of "tar" concentration
3. Fouling is highly dependent upon operating temperature.
4. At 350°C, membrane permeance recovers with removal of "tar".
5. At 275°C, membrane regeneration is required.

# PROGRESS: NCCC Challenge Testing

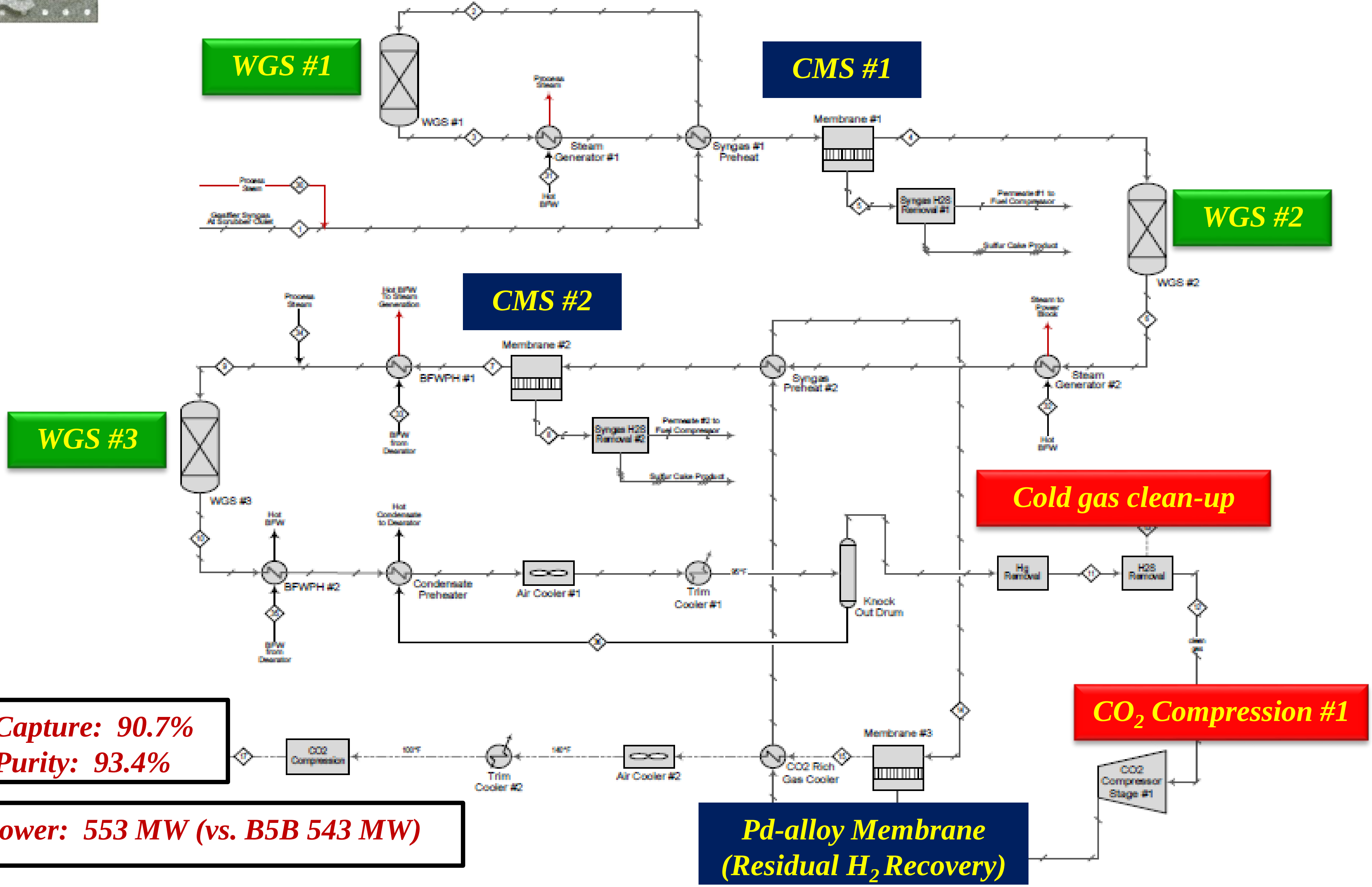
## *Recap of Pd and Pd-alloy Membrane Testing at the NCCC*

***Features of Pd/Pd-alloy Membranes***

1. Stable performance… Pd/Pd-alloy membrane performance is stable in sulfur-free and "tar"-free gas.
2. Robust… >155 hours of NCCC testing experience shows Pd and Pd-alloy membranes to be very robust in no sulfur environment; no permanent membrane damage due to tar exposure.
3. Fouling will occur in the presence of tar-like species… However, our process has the Pd-alloy downstream of the Cold Gas Cleanup. No tar or other contaminants expected.
4. Regenerable… Pd/Pd-alloy membranes can be regenerated with no damage to the membrane if exposed to "tar"-like species.

# PROGRESS: Techno-economic Analysis

## *Process Flow Diagram*




***$CO_2$ Capture: 90.7%***
***$CO_2$ Purity: 93.4%***

***Net Power: 553 MW (vs. B5B 543 MW)***

# PROGRESS: Techno-economic Analysis

***Preliminary Process Performance and Economics***

| Parameter | Case B5B* | Case MPT | Target | MPT vs B5B |
|---|---|---|---|---|
| Carbon Capture | 90.0% | 90.7% | 90% | |
| $CO_2$ Purity | 99.48% | 93.4% | 95% | |
| $H_2$ in Fuel | 99.98% | 98.7% | NA | |
| Net Power Production, MW | 543 | 553 | N/A | +1.8% |
| Cost of $CO_2$ Captured [$/tonne] | 63.1 | 62.0 | N/A | -1.7% |
| Cost of $CO_2$ Avoided [$/tonne] | 91.6 | 87.8 | N/A | -4.1% |
| | | | | |
| COE no T&S [$/MWh] | 135.4 | 134.0 | N/A | -1.1% |
| Total as-spent Cost [$/kW] | 4,782 | 4,639 | N/A | -3.0% |

* *Cost and Performance Baseline for Fossil Energy Plants. Volume 1b. Revision 2b, July 2015. DOE/NETL02015/1727*

# PROGRESS: Techno-economic Analysis

## *Preliminary Sensitivity Analysis – Basic Concepts*

| Objective | Problem | Impact |
|---|---|---|
| Carbon Loss <10% | CMS permeates CO and $CO_2$ | Miss Sequestration Target |
| Minimize Parasitic Loss:<br>$H_2$ Fuel Compression | $H_2$ needs compressed (460psig) to the CT | Increased COE; Plant Size |
| Minimize Parasitic Loss:<br>Steam Lost to Permeate | CMS permeates water<br><br>Need makeup steam to WGS = Power loss at the ST | Increased COE; Plant Size |

# PROGRESS: Techno-economic Analysis

***Preliminary Sensitivity Analysis - Summary***

| Variable | Impact | Limits |
|---|---|---|
| Optimize CMS Permeate Pressure | +5 MWe | No membrane technology limits.<br>$H_2$ recovery limited by carbon losses. |
| Increase CMS $H_2/CO_2$ (from 30 to 50) | +6 MWe | No membrane technology limits.<br>Steam loss increase with $H_2$ recovery in CMS membranes. |
| Increase CMS $H_2/H_2O$ (from 3 to 6) | +15 MWe | Modest membrane technology limit.<br>Slight improvement in CMS membrane selectivity required. |
| Permeate Sweep CMS#1<br>or<br>Permeate Sweep Pd-alloy | +15MWe<br><br>+18 MWe | Dual ended bundle required |

# PLANS for Remaining Technical Issues

## ***Final Remaining Tasks***

- ***Complete Sensitivity Analyses on the Process Design and Economics (also, Introduction of RTI warm gas cleanup for $H_2S$ removal)***
- ***Finalize TEA Based Upon Sensitivity Analysis***
- ***Complete the Environmental, Health, and Safety Evaluation***

# Summary and Conclusions

## ***Project Successes***

- 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 $CO_2$ 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%).
- Capital Cost Reduced. Base Case total capital cost for the process is $32MM (3%) below the NETL base case.

END