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

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U.S. Department of Energy
National Energy Technology Laboratory
Strategic Center for Coal's
FY15 Carbon Capture Peer Review
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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 and development***
- ***Technip Stone and Webster Process Technology Inc…Engineering and system design, analysis and economics***

APPROACH

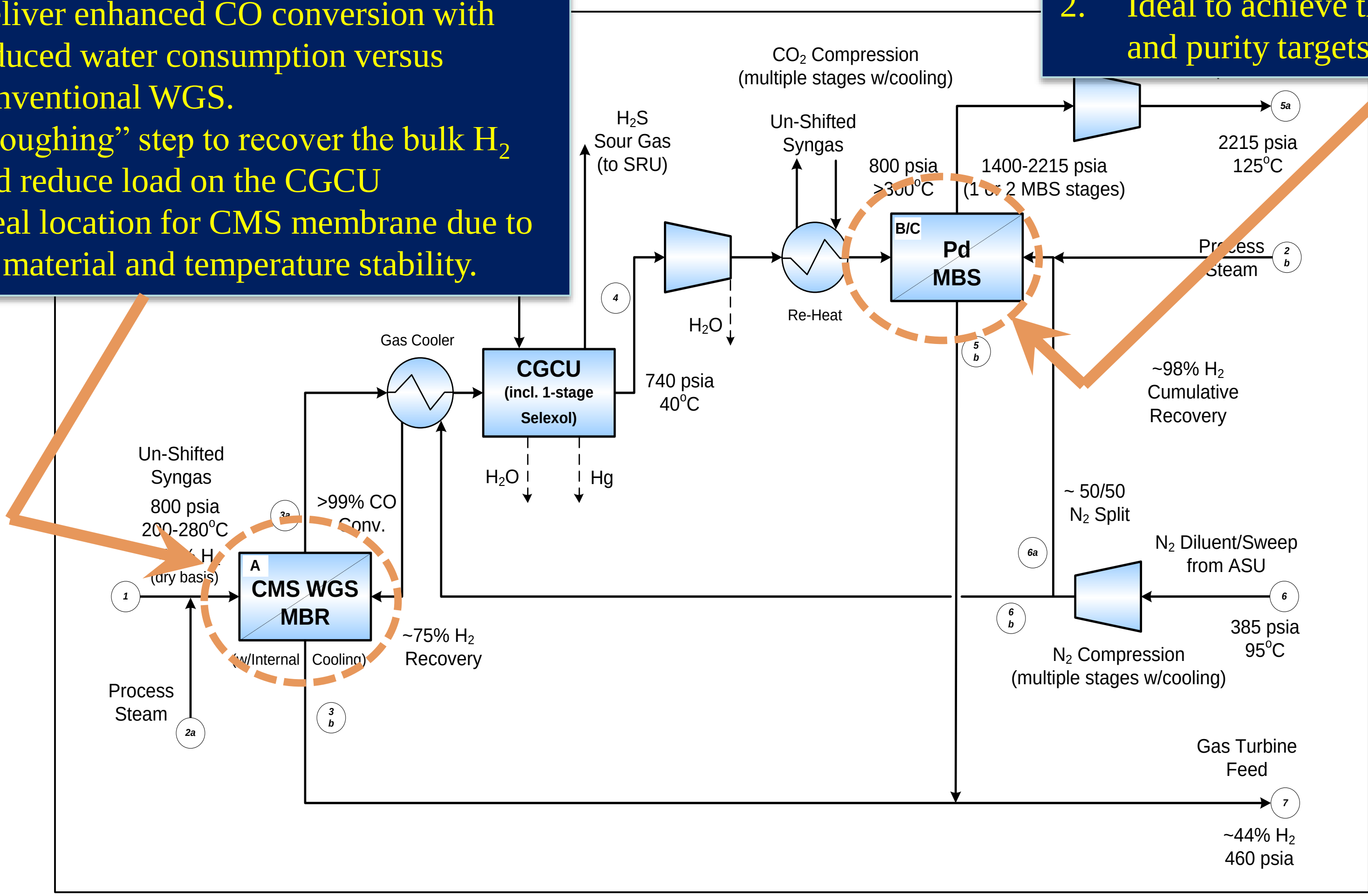
Proposed Process Scheme and Key Components

CMS Membrane as Membrane 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.

Pd-Alloy Membrane

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



BACKGROUND

Multiple Tube Membrane Bundles – versatile, low cost

Single tubes

Example: conventional micro- and ultrafiltration

Ex: porous heat exchangers & catalytic membrane reactors

Ex: high pressure intermediate temperature gas separations

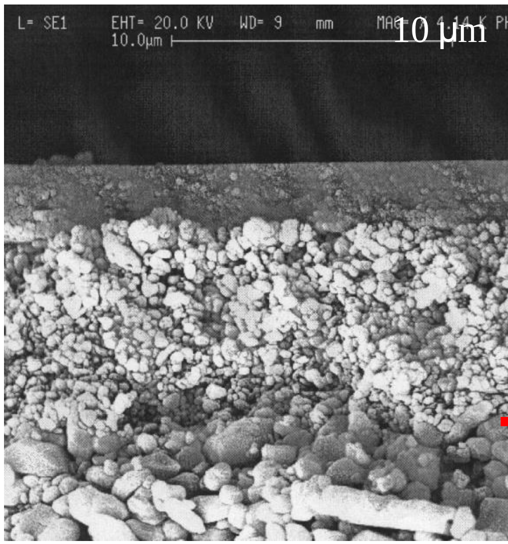
Our Core Expertise/Technology

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

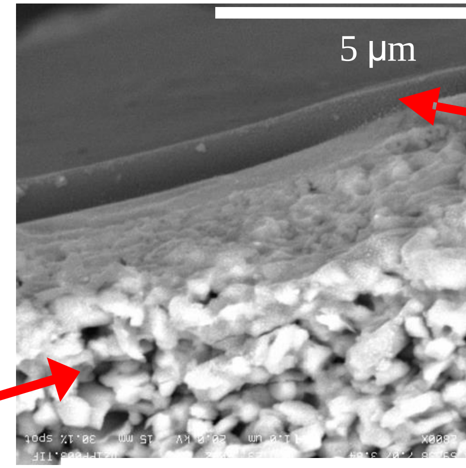
BACKGROUND

Specific thin film deposition for advanced separations

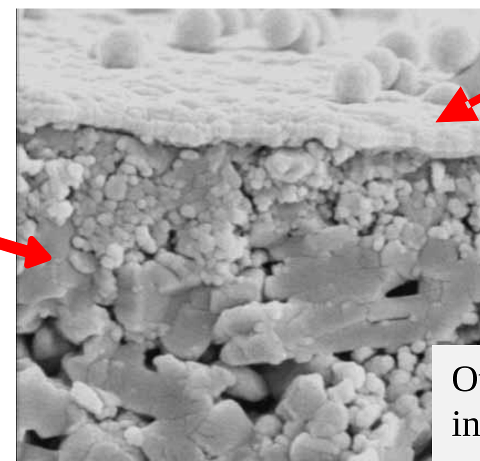
Ceramic Substrate



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

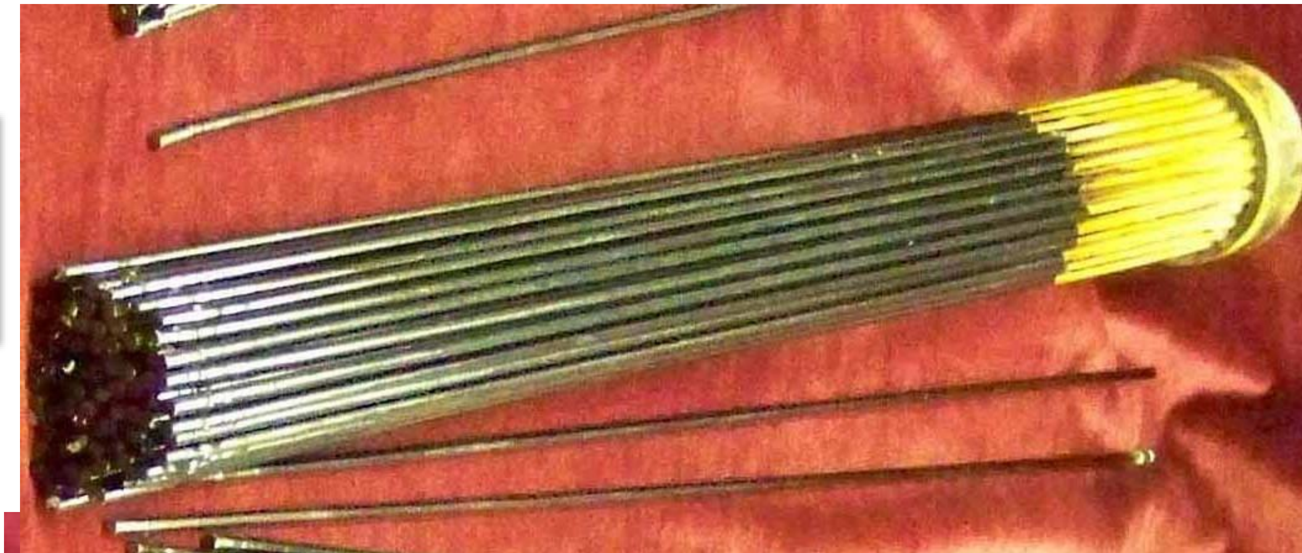
Our Core Expertise/Technology

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

BACKGROUND

Multiple Tube Bundles for Large Scale Applications

CMS Multiple Tube Bundle with Ceramic-Glass Potting



Pd-Alloy Multiple Tube Bundle with Full Ceramic Tube Sheet

ADVANTAGES

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 CCUS 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

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.

Our Original (Proposal) Economic and Environmental Benefit Analysis

Case Descriptions	Production Electricity	HHV Efficiency	Required Selling Price Electricity	Required Selling Price Electricity	CO_2 Capture	CO2 Capture Cost
	MWh/Ton	%	mills/kWh	% Increase	%	$/tonne
1a: Baseline for IGCC w/o CCS - 1-Stage Selexol ™	2.66	39.0	76.3	-	0	-
2a: IGCC w/ CCS - 2-Stage Selexol ™	2.23	32.6	105.5	38	90	42.46
3a: IGCC w/ CCS - CMS & Pd Membranes & 1-Stage Selexol ™	2.31	33.8	97.4	28	98	27.67

Progress to Date on Key Technical Challenges

BP1 Accomplishments

BP1 Tasks Completed to Overcome Key Technical Challenges

- CMS/Pd membrane operation meeting targets for CO_2 sequestration and cost. *(Milestone A, BP1)*
- Long term and other membrane performance stability (Milestone A, BP1)
- Full-scale WGS-MR and membrane separator designs for mega-scale applications *(Milestone D, BP1)*
- Updated membrane and membrane reactor modelling *(Milestone B, BP1)*

Item No.	Original Process Analysis	Performance Delivered Based Upon our BP1 Accomplishments	Program Goals	Critical Membrane Performance Requirements
1	CO Conversion (WGS-MR): 99%	97%	NA	$H_2/CO_{,min}$ CMS = 70
2	CO_2 Capture: 98%	90%	90%	$H_2/CO_{2,min}$ CMS = 35 $H_2/CO_{2,min}$ Pd = 300
3	CO_2 Purity: 95% (3% fuel; balance inert)	95% (3% fuel, balance inerts)	95%	$H_2/CO_{2,min}$ CMS = 35 $H_2/CO_{2,min}$ Pd = 300
4	Fuel Efficiency: H_2+CO to turbine: 98%	95 to 96%	NA	$H_2/CO_{,min}$ CMS = 70
5	H_2S to Turbine: ~40 ppm	~200ppm at H_2/H_2S = 140	NA	H_2/H_2S, CMS > 400
6	Reduction in Syngas to CGCU: 50%	~60% reduction	NA	H_2/CO_2 CMS = 35

Project Technical Approach

Overview of Project Technical Approach - Workplan

Budget Period 1	Budget Period 2

Task 1. Project Management and Planning

Task 2. Establish Performance Database: Focus here is to complete the membrane performance database under more severe operating conditions in the presence of simulated WGS contaminants at long times. Also reactivate the bench top WGS-MR system for Task 3 activities.

Task 3. CMS WGS-MR experimental verification and modeling under extreme conditions: Focus here is lab scale testing of the CMS WGS-MR at gasifier conditions and includes model development/verification.

Task 4. Preparation of CMS and Pd for bench testing at NCCC: Focus here is design and fabrication of the pilot scale (86-tube bundles) for process evaluation at the NCCC.

Task 5. Preparation of Pd Module for 2nd Stage H_2 Recovery for bench scale test at NCCC: Focus here is design and fabrication of the pilot scale Pd module.

Task 6. NCCC Field Testing: Focus here is testing at the NCCC of the two stage process for demonstration and operational stability.

Task 7. Process Design and Engineering: Focus here is comprehensive process development and economic evaluation.

Task 8. Conduct Economic and Environmental Analysis: Focus here is assessment of the environmental impact.

Progress and Current Status of Project

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PROGRESS: CMS Membranes

Typical Performance and Performance Targets

CMS Single Tube Characterization

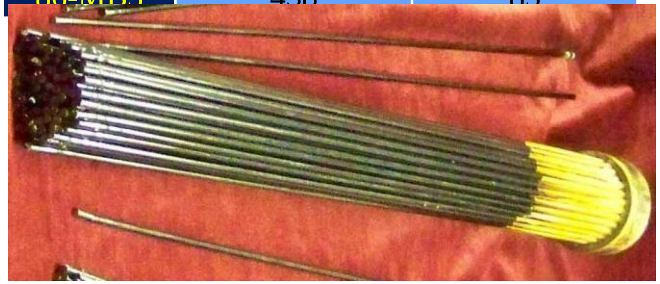
CMS Membrane Characteristic	Preliminary Target to Achieve DOE Goals[1]	Laboratory Single Tubes Performance
Permeance, H_2 [GPU] @ 250°C, 20 psig	550	420 to 1,100
Selectivity, H_2/X		
H_2/N_2	70	80 to 110
H_2/CO	70	80 to 110
H_2/CO_2	35	35 to 50
H_2/H_2S	N/A[2]	100 to 150[2]
H_2/H_2O	1.5	1.5 to 3

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

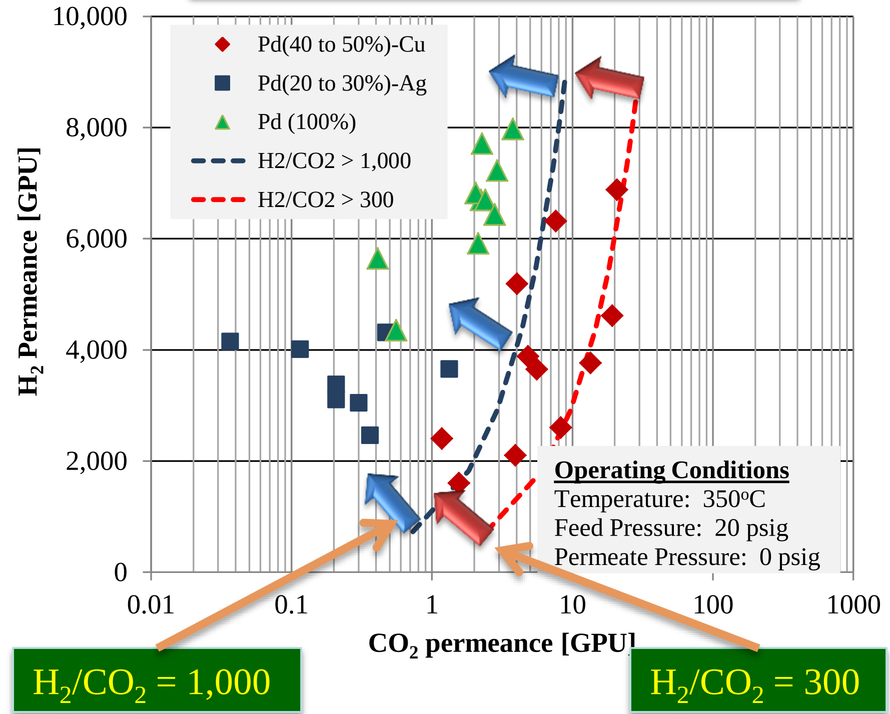
Typical Performance and Performance Targets from Economic Analysis

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] @ 250°C, 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.

Detailed Pd-Alloy Performance Data



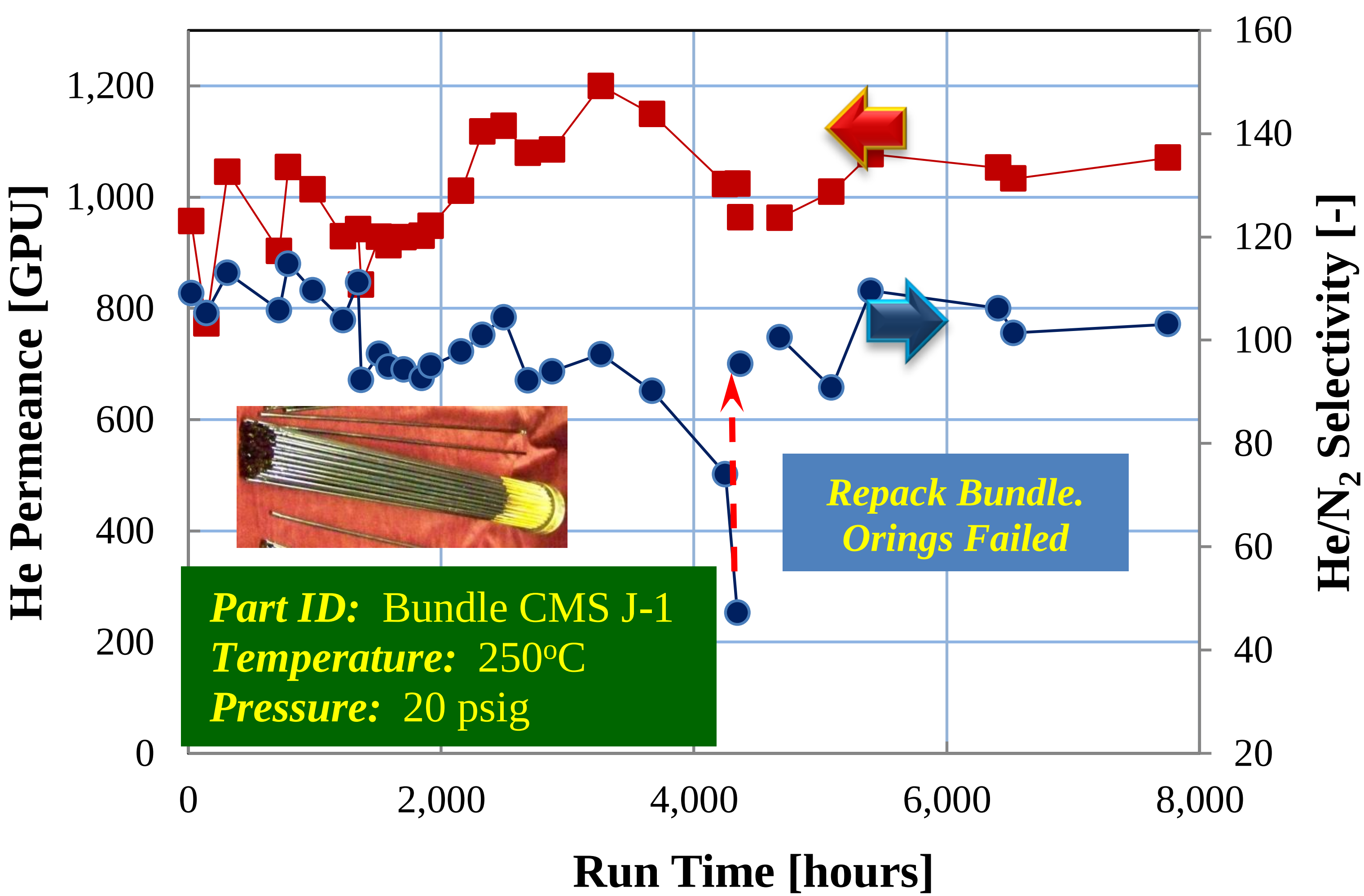
Pd-Alloy Comments

1. *Pd-Cu offers thermal cycling stability and low temperature operational capability (>200°C).*
2. *Pd-Ag offers higher flux and selectivity but higher minimum operating temperature (>300°C)*

PROGRESS: CMS Membrane Stability

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

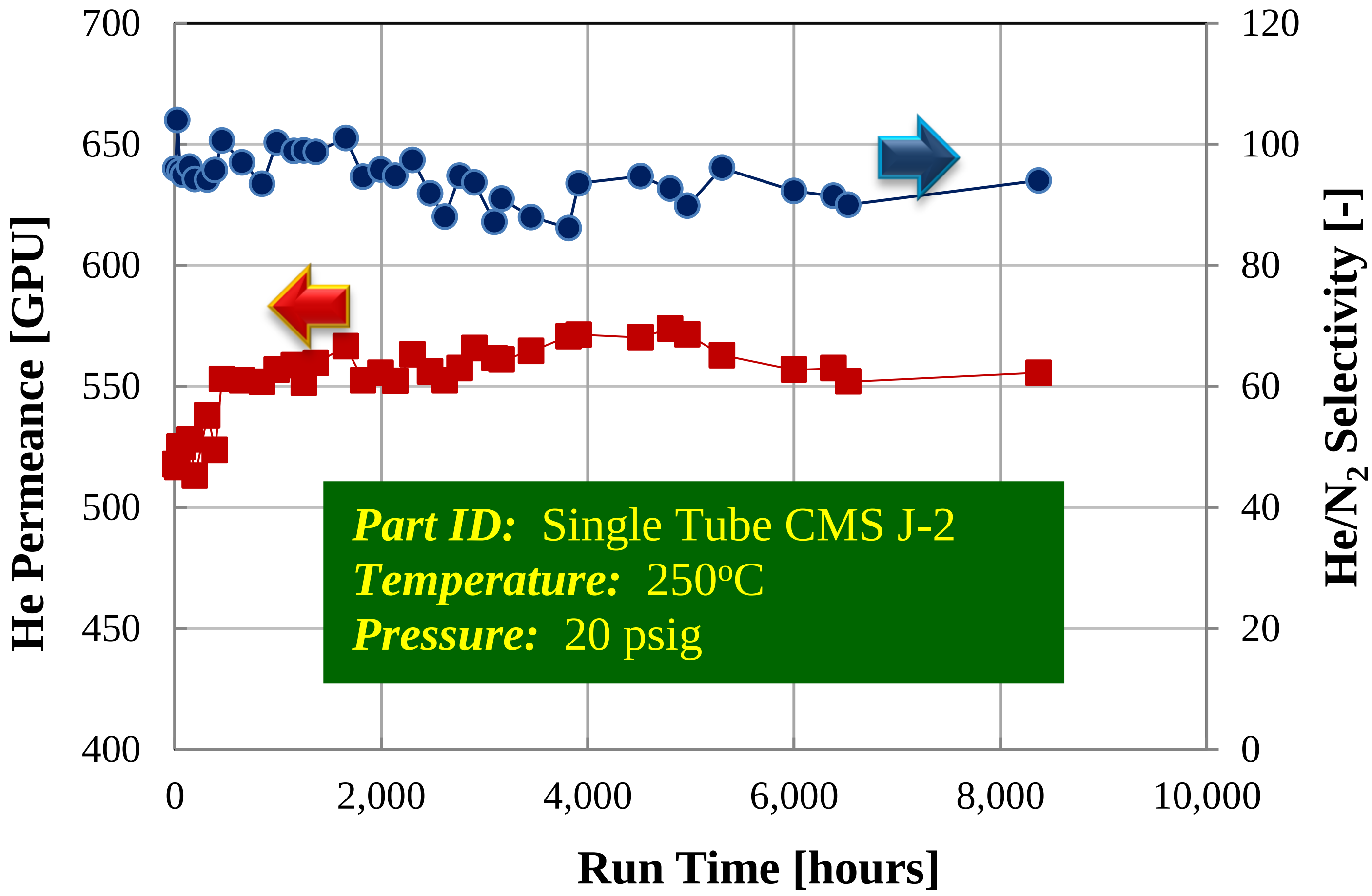
CMS 86-Tube Bundle Long Term Stability (8,000 hrs)



PROGRESS: CMS Membrane Stability

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

CMS Single Tube Long Term Stability (8,000 hrs)

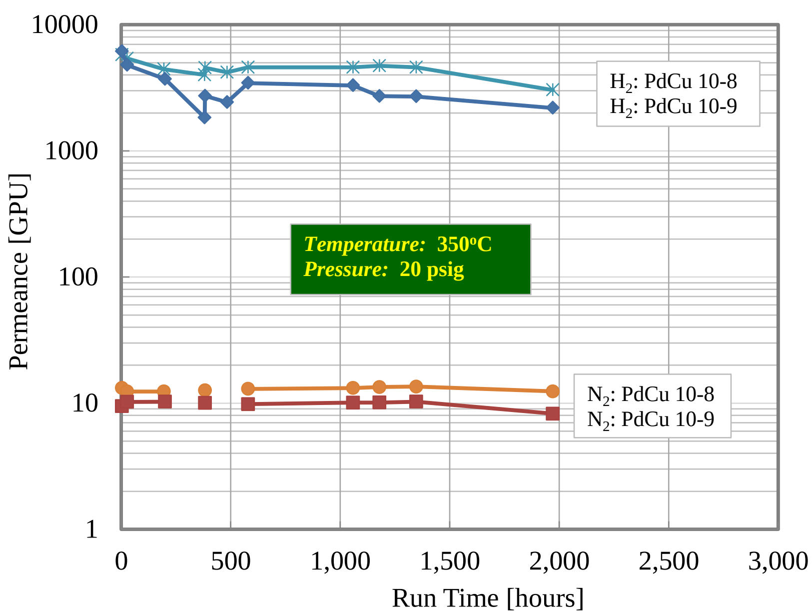


Part ID: Single Tube CMS J-2
Temperature: 250°C
Pressure: 20 psig

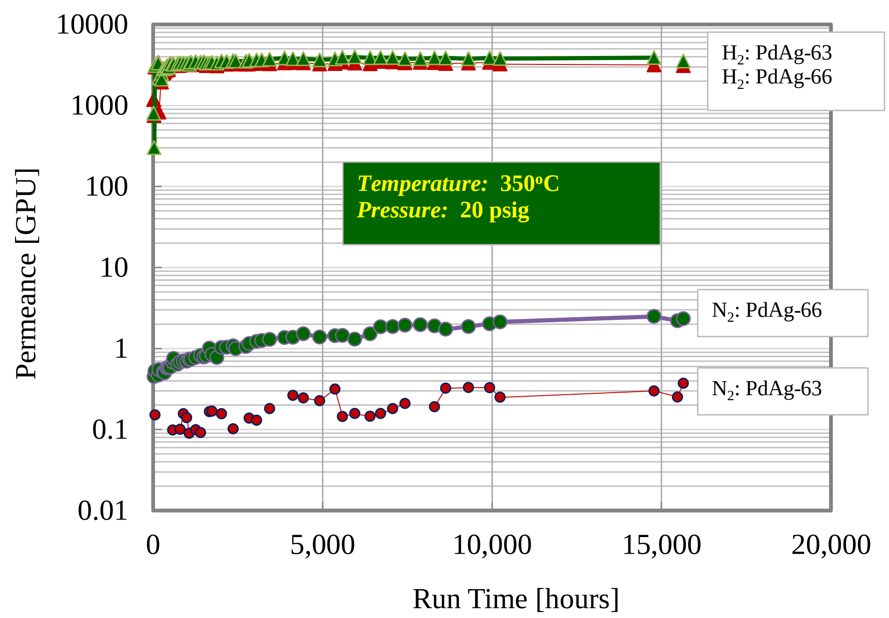
PROGRESS: Pd Membrane Stability

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

Pd-Alloy Pd-Cu (60/40)
Long Term Stability

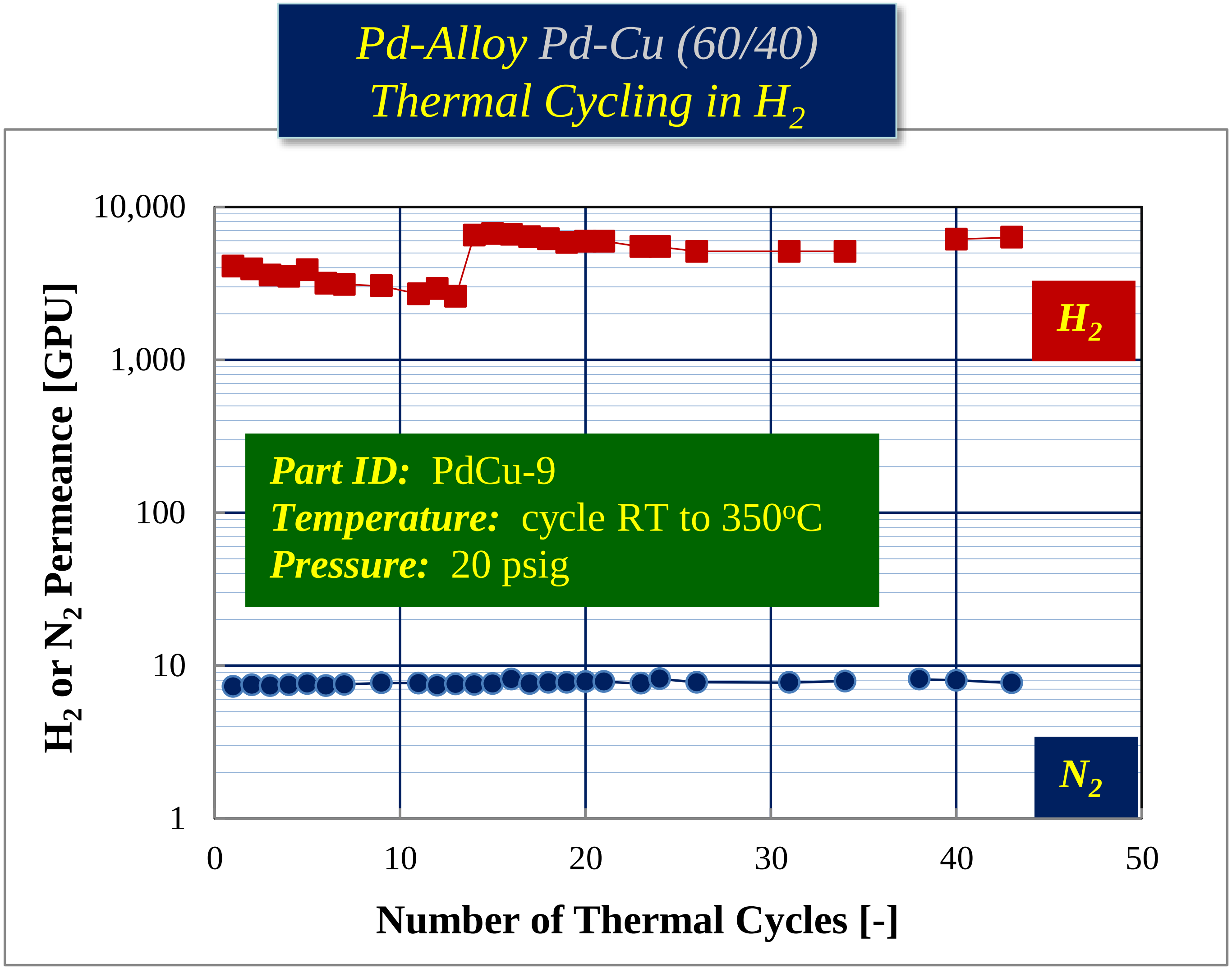


Pd-Alloy Pd-Ag (80/20)
Long Term Stability



PROGRESS: Pd Membrane Stability

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



PROGRESS: CMS Membrane Stability

NCCC Testing: CMS Membranes Highly Stable in Coal Gasifier Syngas

Testing Parameters

Membrane
86-tube CMS

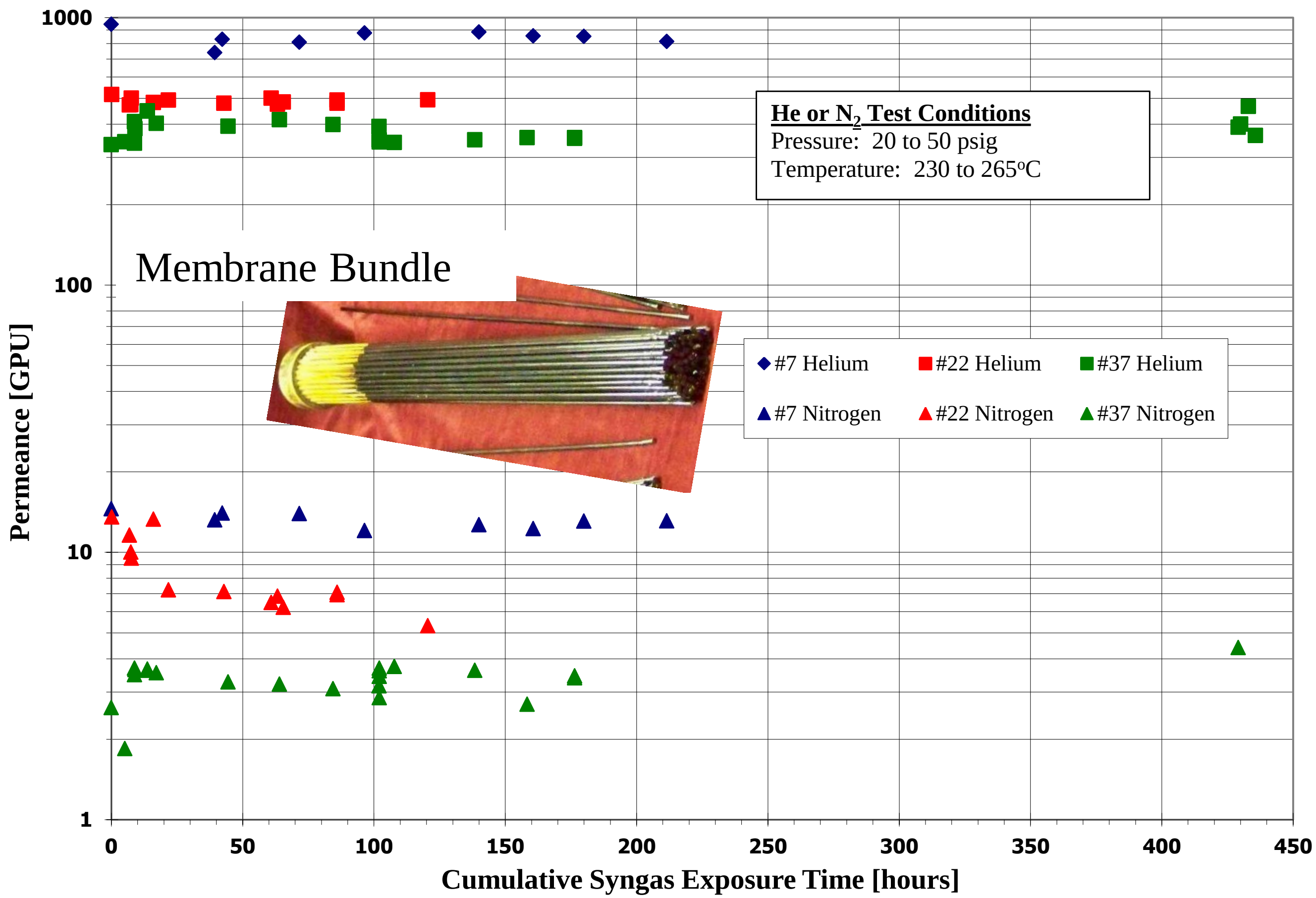
Operating Conditions
T~ 250 to 300ºC
P~ 200 to 300 psig

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: CMS Membrane Stability

CMS Performance Stability: Tar-like Species in Gasifier Off-gas

Operating Temperatures Above 250^{o}C Required to Prevent Condensation of Tar-like Contaminants

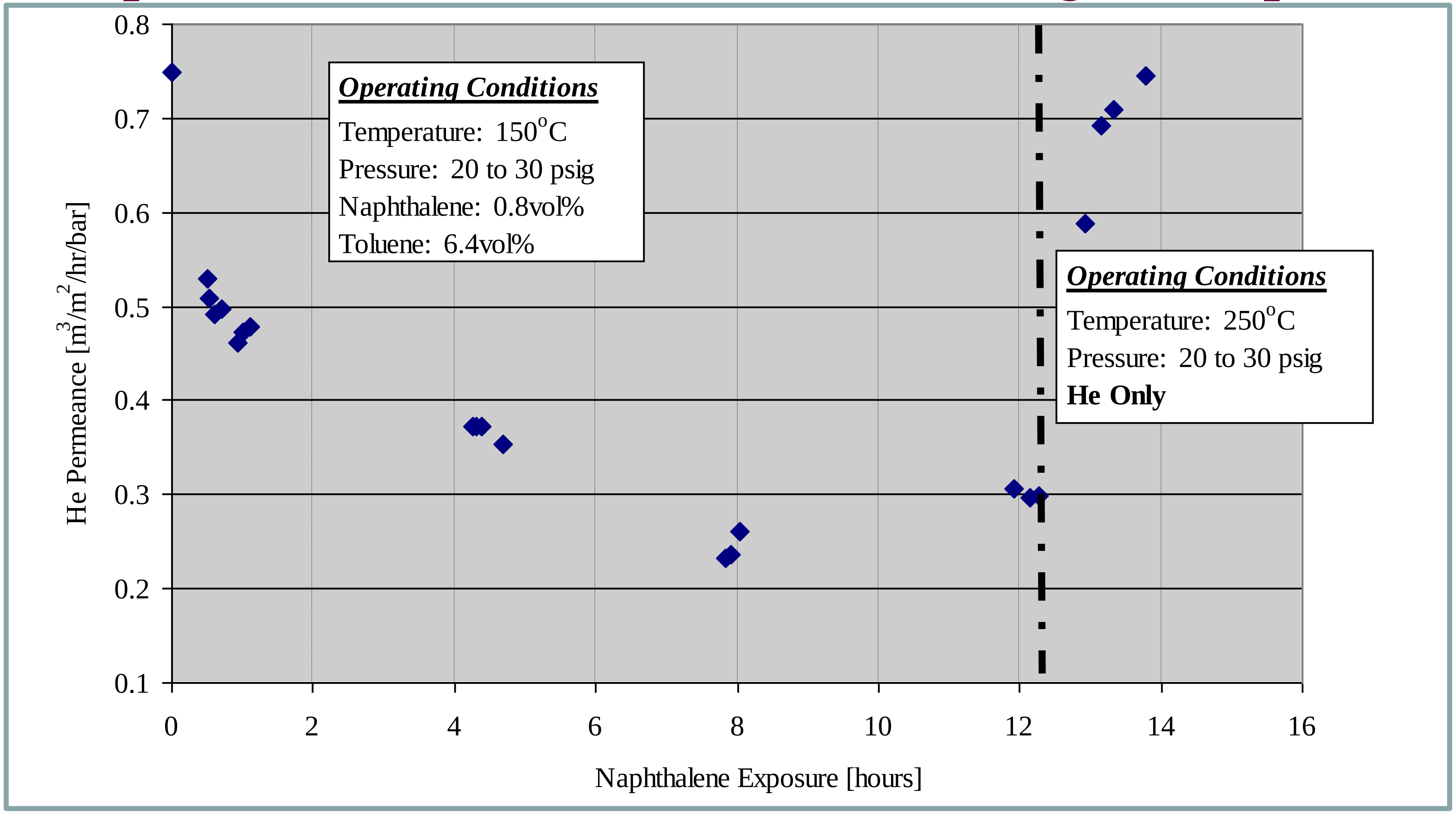
Temperatures ≤230^{o}C
Tar or other residue buildup evident

Temperatures >250^{o}C
No evidence of tar or other residue buildup

PROGRESS: CMS Membrane Stability

Effect of Temperature in the Presence of Model Tar Compounds

Naphthalene/toluene as model tar and organic vapors

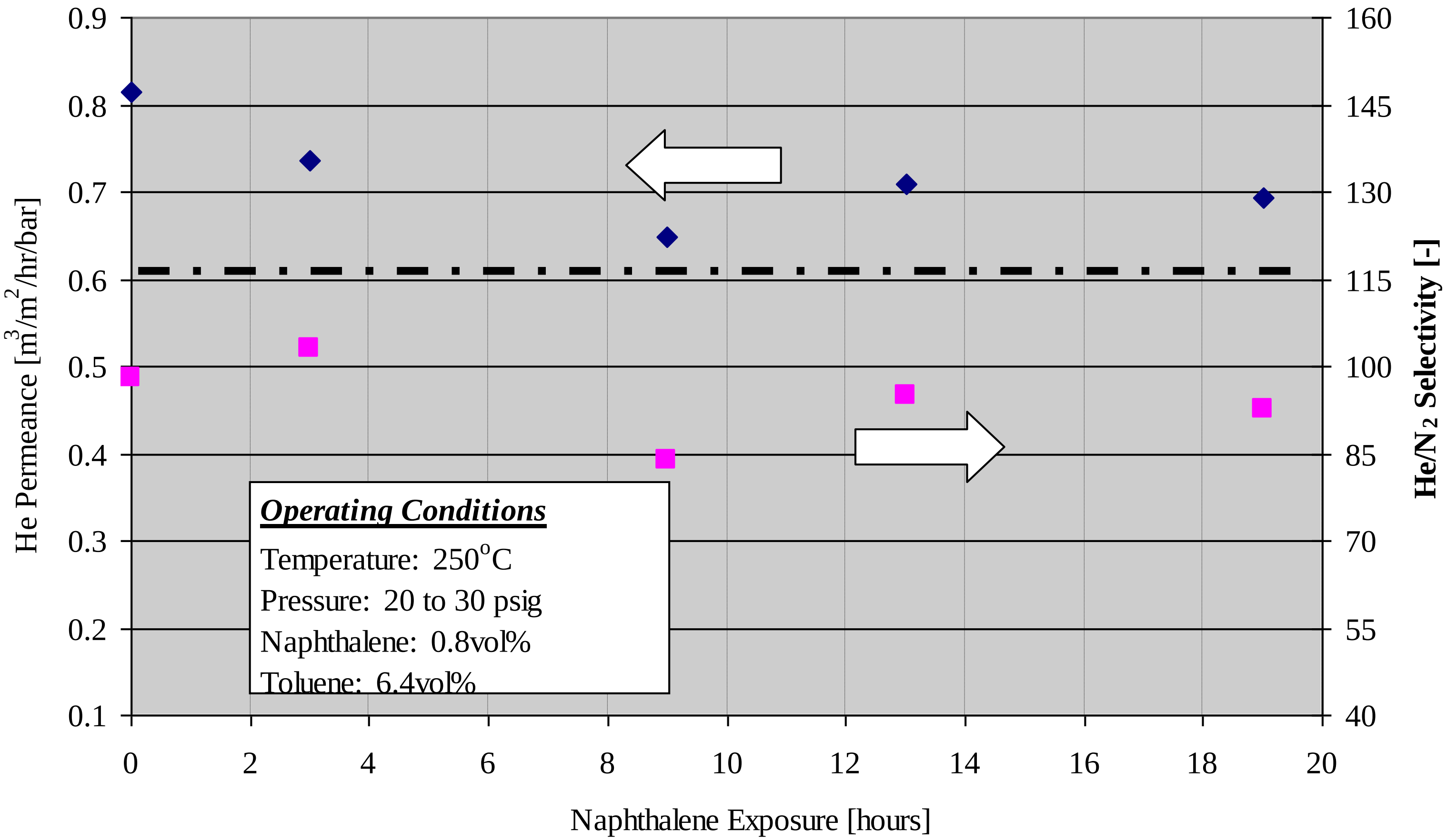


- ❑ **Membrane fouling occurs at low temperature.**
- ❑ **Membrane regeneration can be achieved rapidly at high temperature.**

PROGRESS: CMS Membrane Stability

CMS Membrane Stability in the Presence of Model Tar Compound

Membrane performance is stable at high operating temperatures (250°C) in the presence of naphthalene/toluene as model tar and organic vapors compounds.



PROGRESS: High Pressure Stability

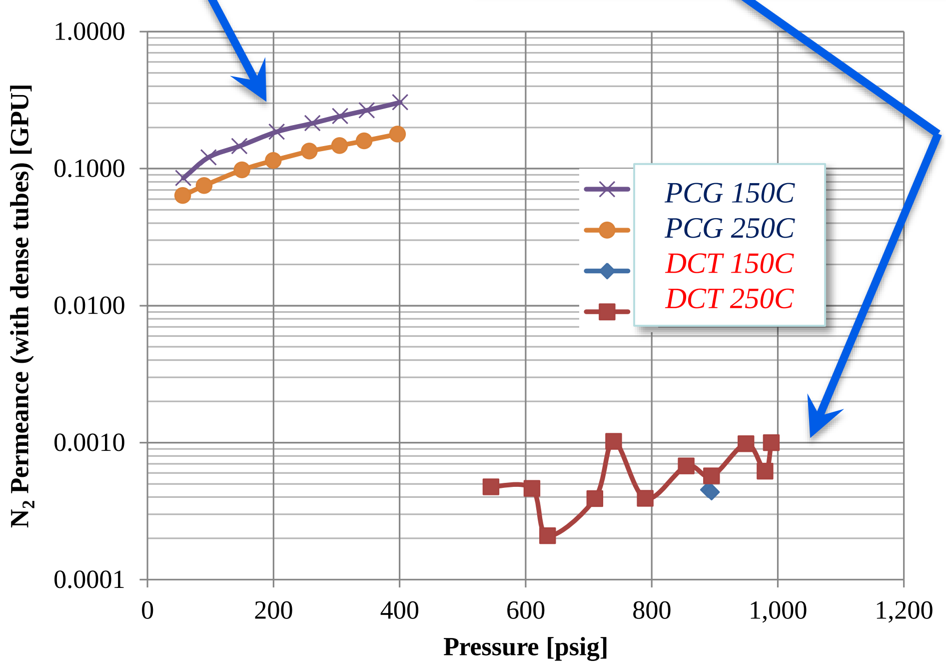
Multiple Tube Bundle Potting Design: Pressure Stability

Ceramic/Glass Potting vs. Ceramic Tube Sheet

"Dense" Membrane Tube Leak Rate at Potting

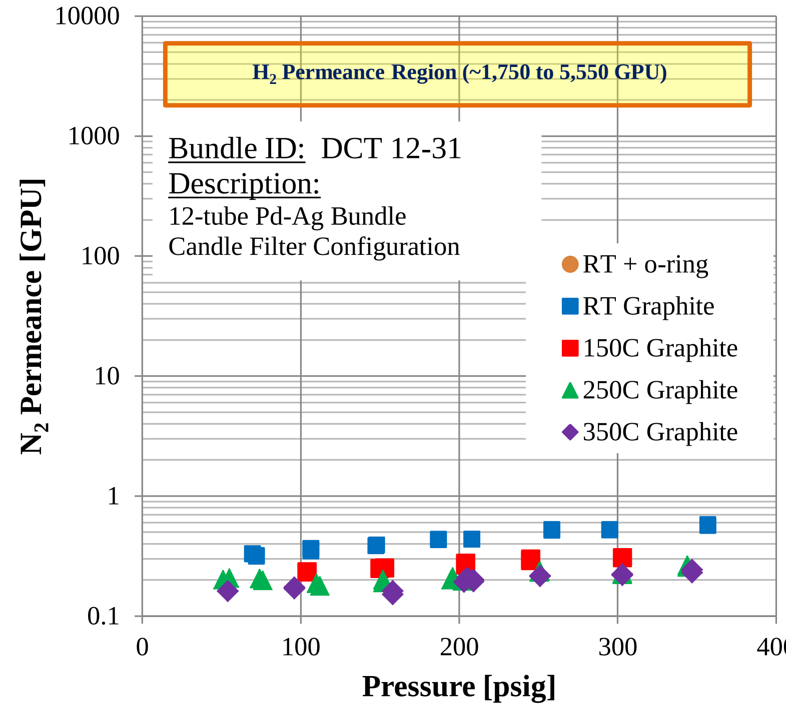
Potted Ceramic/Glass (PCG)

Dense Ceramic Tube Sheet (DCT)



Pd Bundle w/ Dense Ceramic Tube Sheet

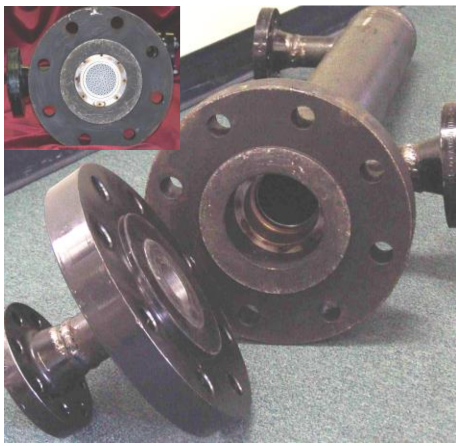
N_2 Permeance vs. T and P



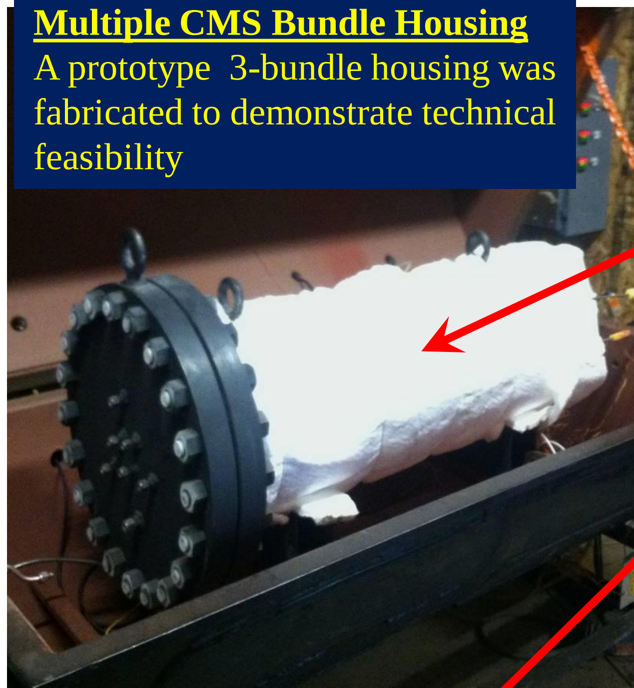
Preparation for Field Test

Full Scale Module Design Concepts

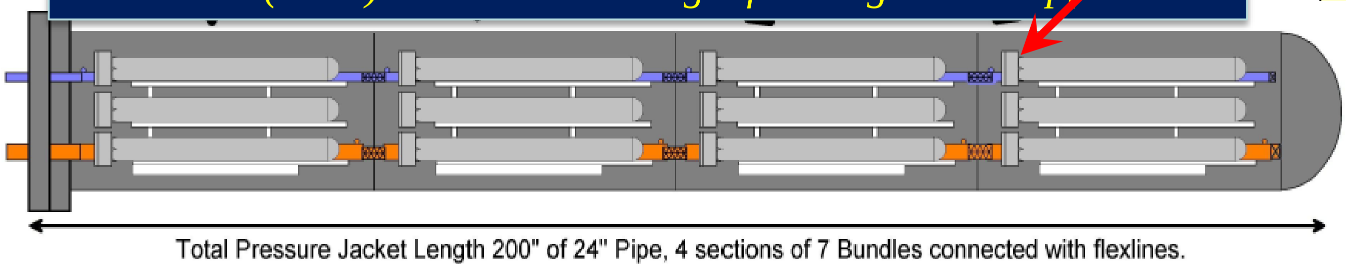
Single CMS Bundle Housing
Used in NCCC testing.



Multiple CMS Bundle Housing
A prototype 3-bundle housing was fabricated to demonstrate technical feasibility



28-Bundle ($56m^2$) CMS Module Target for Large Scale Application



- **According to our estimate, ~16,000 m^2 CMS membrane requirement for 500 MW via IGCC with CCS.**
- **MPT has designed and constructed a 3-bundle module uniquely suitable for high temperature and pressure.**
- **About 350 of the 56 m^2 modules are needed for 500 MW application.**
- **Our design offers a viable avenue to overcome the barrier of the number of module requirement for mega applications, such as power generation.**

Our design could reduce the CMSM sale price to ≤ $750/m^2.

PROGRESS: Simulation Results

Process Simulation

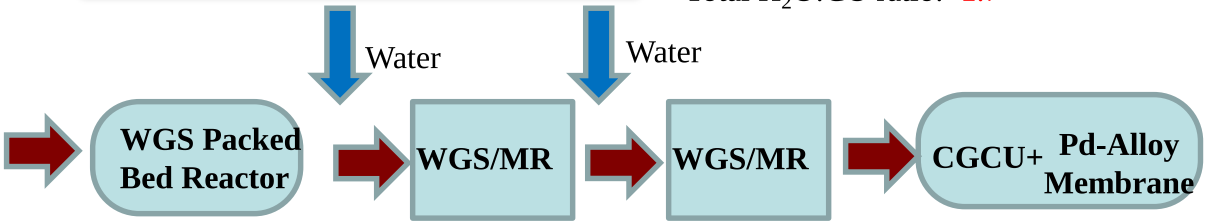
GE Energy Gasifier
Radiant Cooled + Water Quench

Component	Composition [mol%]
N_2	0.55
H_2	26.9
CO	28.2
CO_2	10.8
H_2O	31.9
CH_4	0.1
Ar	0.7
H_2S	0.57
COS [ppm]	~100
P [psig]	800
T [°C]	55

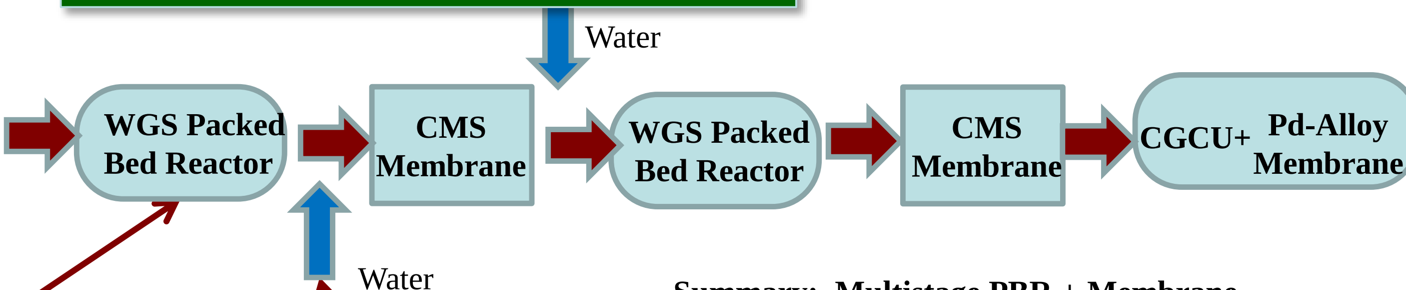
Source: "Cost and Performance Baseline for Fossil Energy Plants, Vol. 1", DOE/NETL-2010/1397

Summary: Multistage WGS/MR
CMS Membrane Area: 14,300m^2
Pd-Alloy Membrane Area: 1,800m^2
CO_2 Sequestered: 91.2%
CO_2 Purity: 95.5% (2.7% fuel; balance inert)
H_2 + CO to Fuel: 95.7
Total H_2O:CO ratio: 1.7

SCHEME 1
WGS/MR x N + Pd-Alloy Membrane



SCHEME 2
(PBR + CMS Membrane) x N + Pd-Alloy Membrane



1. WGS PBR to pre-shift the syngas. Lose too much CO and H_2O to permeate in MR

2. Water injection for cooling due to reaction exotherm.

Summary: Multistage PBR + Membrane
CMS Membrane Area: 16,500m^2
Pd-Alloy Membrane Area: 1,800m^2
CO_2 Sequestered: 90%
CO_2 Purity: 95% (3% fuel; balance inert)
H_2 + CO to Fuel: 95.7%
Total H_2O:CO ratio: 1.7

PLANS for Remaining Technical Issues

- ***Near Term (next 6 months):***

➢ ***WGS-MR Kinetics, Stability, and Modeling at High Pressure***

➢ ***Sensitivity analysis on the H_2 permeance and selectivities and impact on overall DOE targets***

➢ ***Optimize the CMS membrane performance based upon the sensitivity analysis.***

- ***Intermediate Term (next 12 months):***

➢ ***Continue Bench Scale Field Testing at the NCCC***

➢ ***High pressure (up to 800 psig) mixed gas H_2/CO_2 performance testing with Pd-alloy membranes***

➢ ***Engineering design and analysis of the overall process scheme***

➢ ***Economic and pollution prevention/CO_2 capture analysis***

Summary and Conclusions

Key Findings to Date

- Database updates show that the capabilities of our CMS and Pd-alloy membranes meet or exceed the performance targets required to deliver the DOE CCS goals.
- The CMS (250^oC) and Pd-alloy (350^oC) membrane tubes and bundles (full ceramic) have been demonstrated to be stable in thousands of hours of thermal stability testing.
- The CMS membrane 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.
- Extreme pressures to >1,000psig can be achieved with our ceramic tube sheet based bundles.
- Simulations show that relatively low H_2O:CO ratios can be used (<2:1) and still meet the DOE CCS targets.
- Multiple packed beds + membrane separators in series can approach true membrane reactor operation. There may be operational advantages and hardware simplifications to this mode.

PROGRESS: CMS Membrane Stability

CMS Performance Stability: H_2S Removal during NCCC Testing

Testing Parameters

Membrane
86-tube CMS

Operating Conditions
T~ 250 to 300°C
P~ 200 to 300 psig

Pretreatment
Particulate trap, no other gas cleanup.

Composition
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NCCC Slip Stream Testing: H_2S Feed and Permeate Composition