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

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U.S. Department of Energy
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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 Stone and Webster Process Technology Inc…Engineering and system design, analysis and economics***

APPROACH

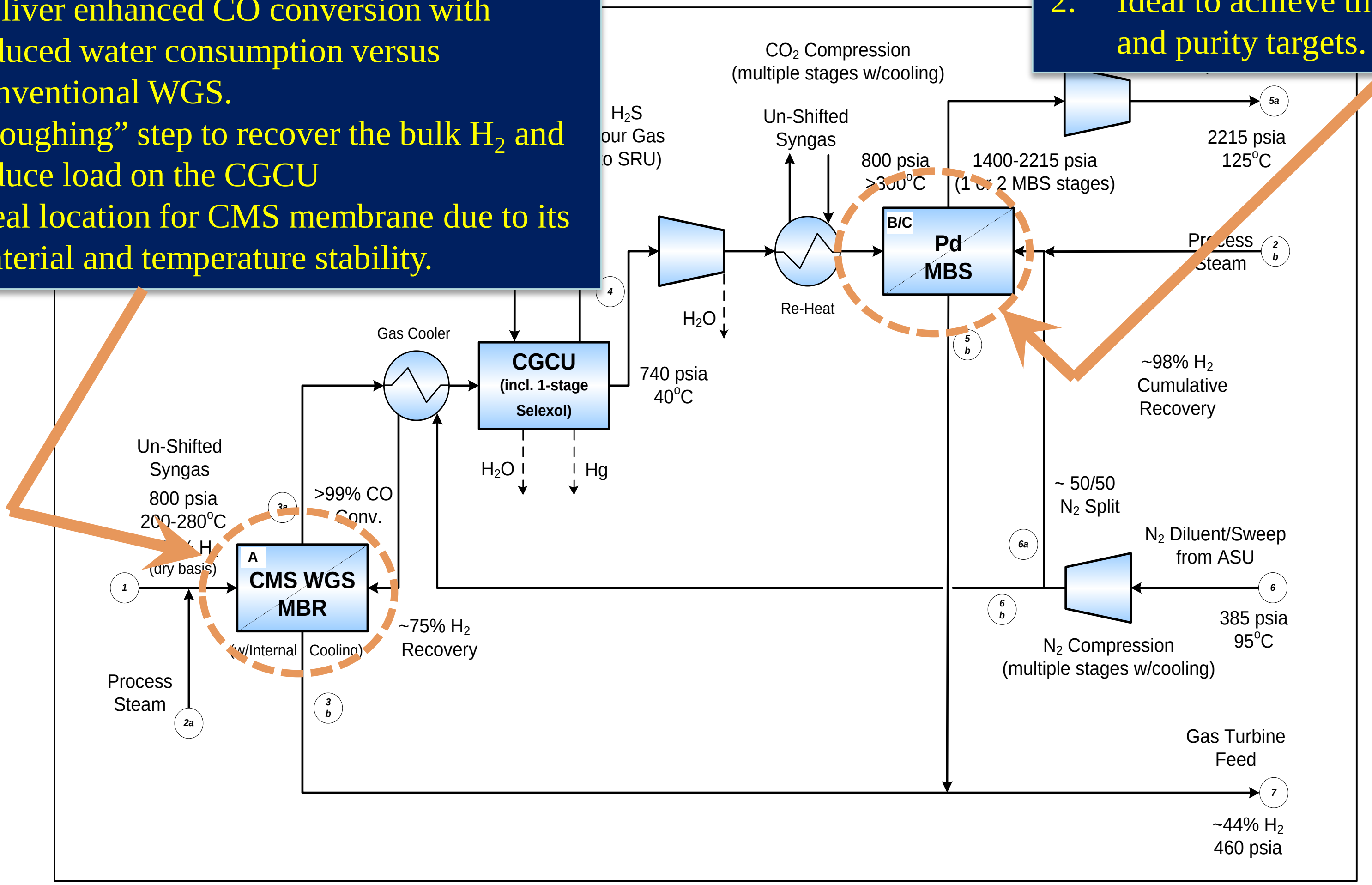
Proposed Process Scheme and Key Components

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

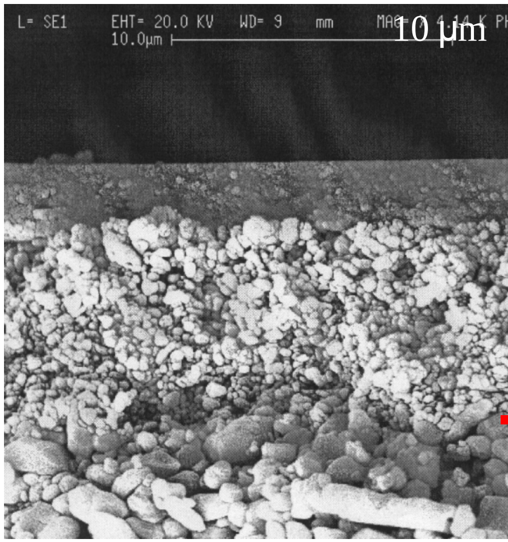
Our Core Expertise/Technology

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

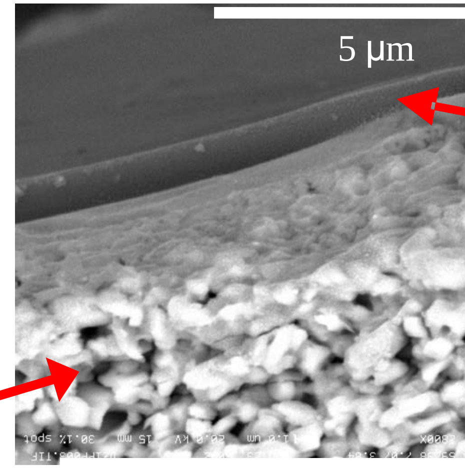
TECHNOLOGY BACKGROUND

Specific thin film deposition for advanced separations

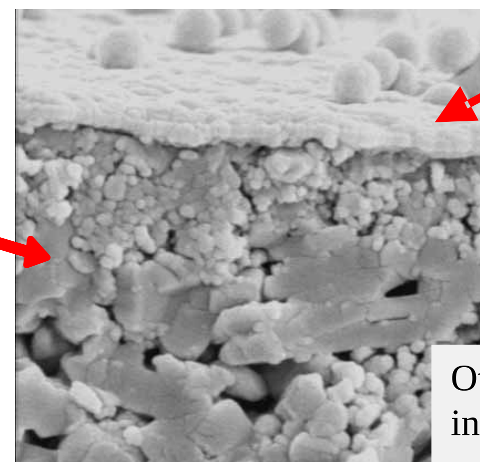
Ceramic Substrate



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

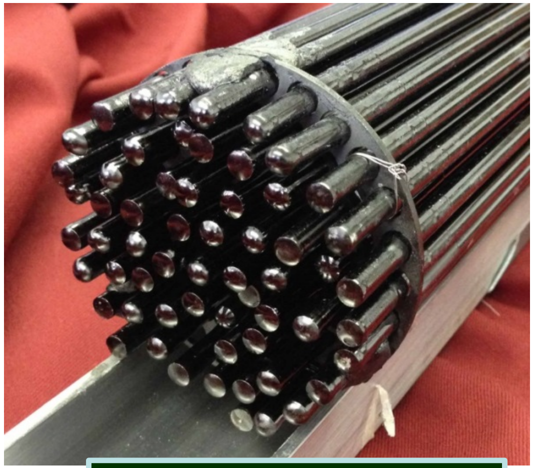
TECHNOLOGY BACKGROUND

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°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°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 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

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

BP1 Tasks Completed to Overcome Key Technical Challenges

- 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

BP2 Tasks Underway/Completed to Overcome Key Technical Challenges

- *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.*

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 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 Environmental Health and Safety 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

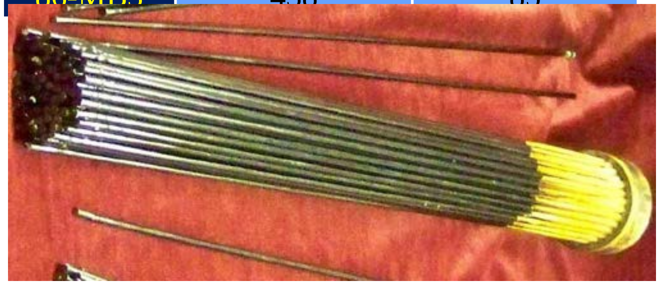
CMS Membrane Characteristic	Preliminary Target to Achieve DOE Goals[1]	Laboratory Single Tubes Performance
Permeance, H_2 [GPU] @ **250°C, 20 psig**	550	420 to 1,100
Selectivity, H_2/X		
H_2/N_2	70	80 to >180
H_2/CO	70	70 to >130
H_2/CO_2	35	35 to >65
H_2/H_2S	N/A[2]	100 to 150[2]
H_2/H_2O	1.5	1.5 to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

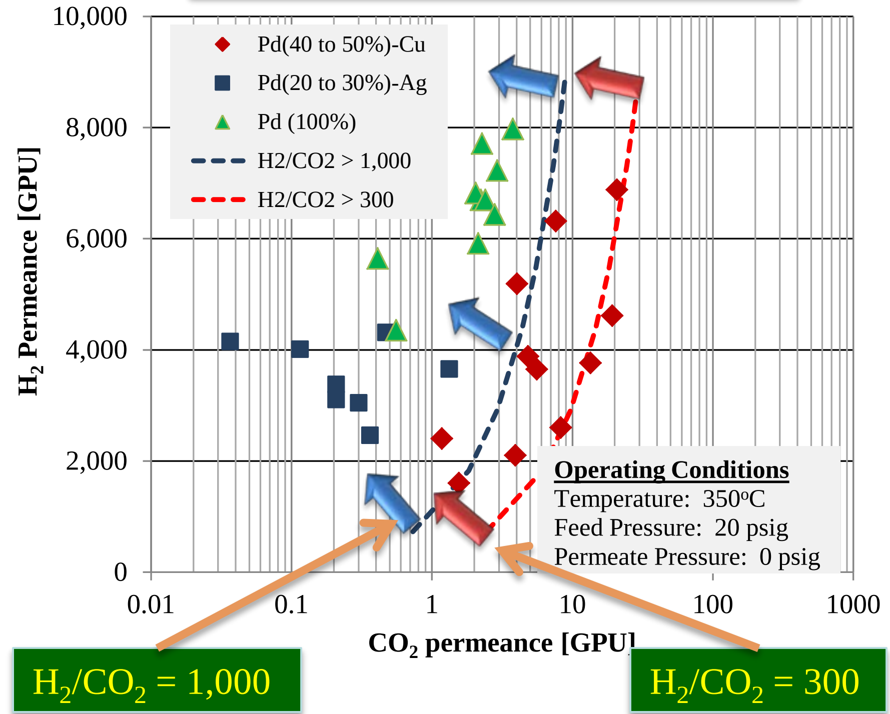
Pd-Alloy Single Tube Characterization Overview

Pd-Alloy Membrane Characteristic	Preliminary Target to Achieve DOE Goals[1]	Laboratory Single Tubes Performance
Permeance, H_2 [GPU] @ **350°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



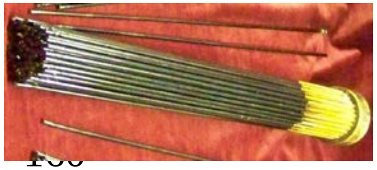
Pd-Alloy Comments

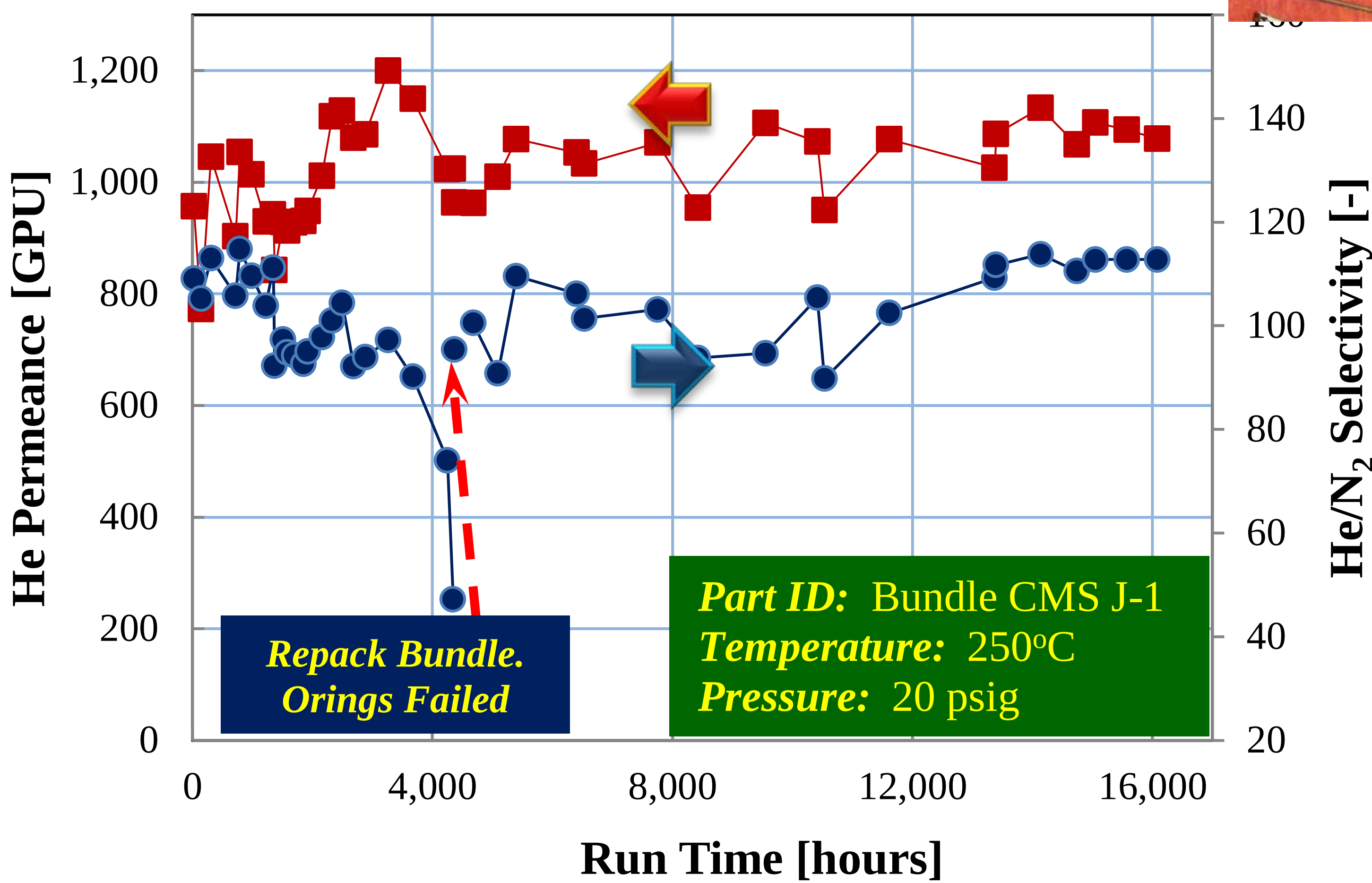
1. *Pd-Cu offers thermal cycling stability and low temperature operational capability (>200°C).*
2. *Pd-Ag offers higher flux and selectivity but higher minimum operating temperature (>300°C)*

PROGRESS: CMS Membrane Stability

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

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

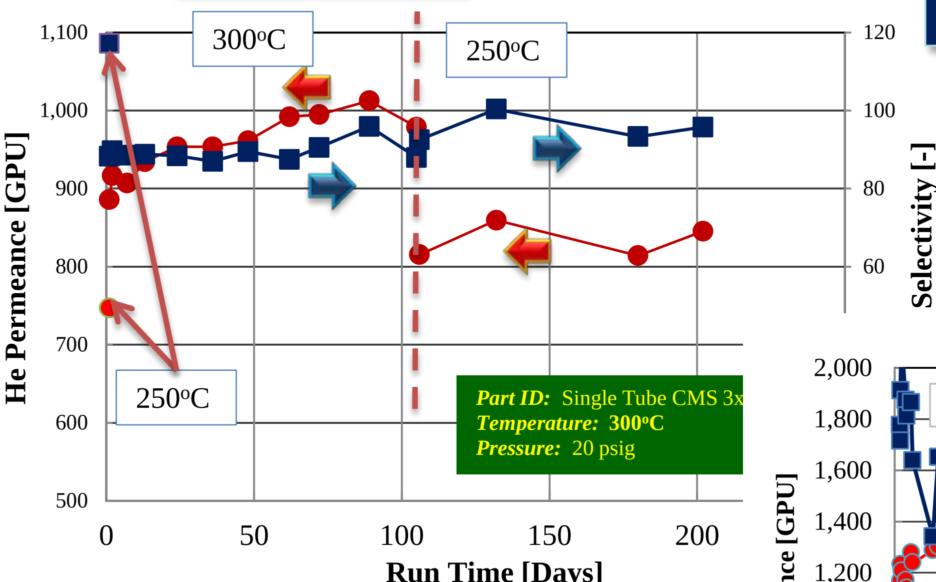




PROGRESS: CMS Membrane Stability

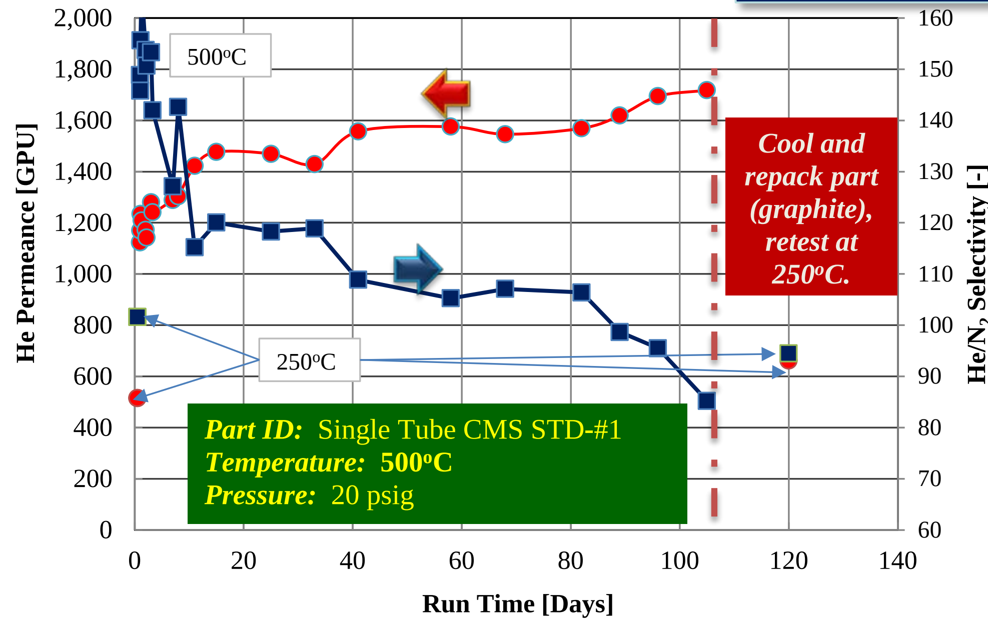
Key Technical Hurdles Focused on Long Term Stability (CMS Membrane)

300°C



High Temperature Excursions above the 250°C Design Temperature

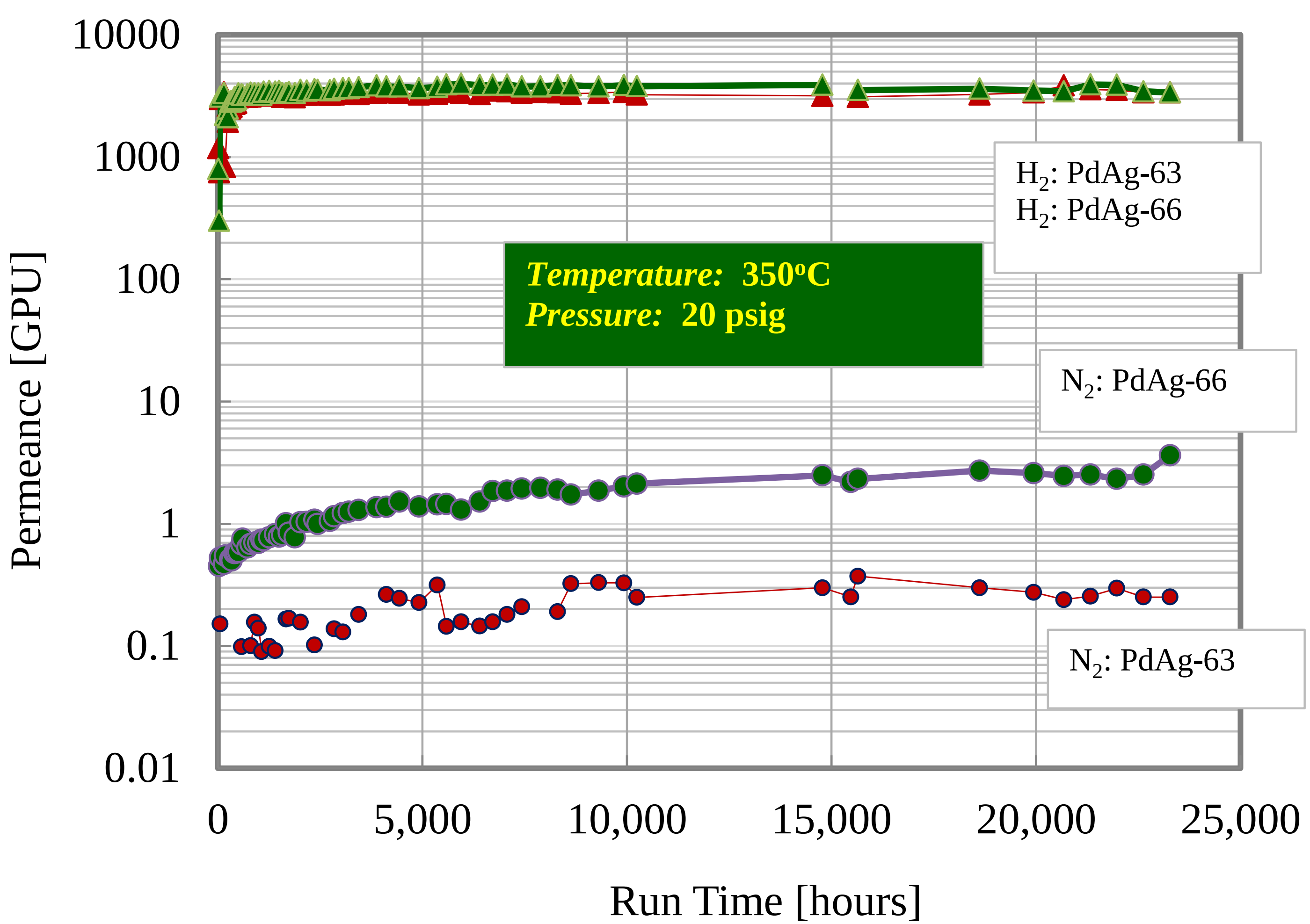
500°C



PROGRESS: Pd Membrane Stability

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

Pd-Alloy Pd-Ag (80/20) Long Term Stability (~24,000 hours)



PROGRESS: CMS Membrane Bundle Stability

NCCC Testing: CMS Membranes Highly Stable in Coal Gasifier Syngas

Testing Parameters

Membrane
86-tube CMS

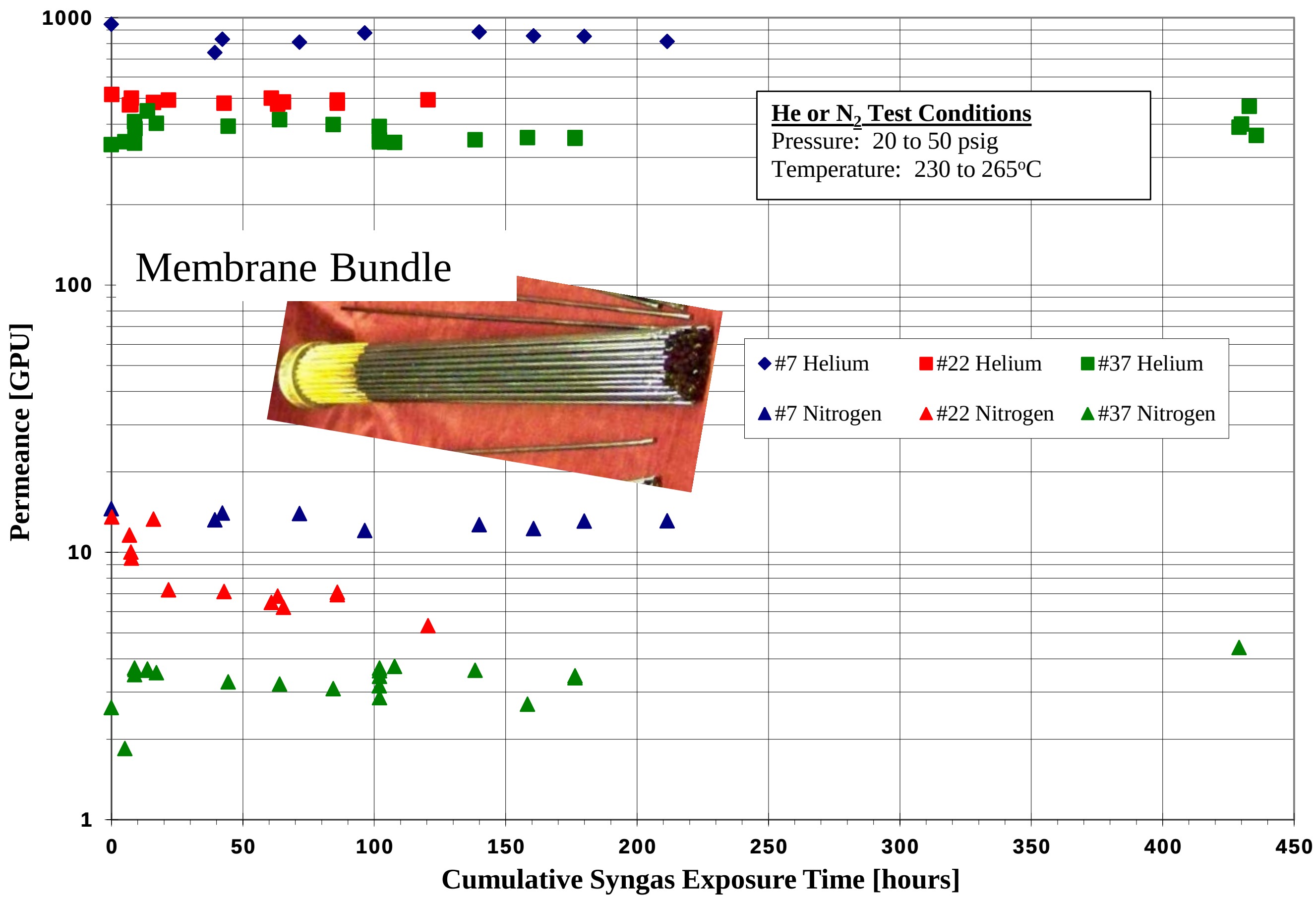
Operating Conditions
T~ 250 to 300°C
P~ 150 to 300 psig

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 Performance Modeling

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.

Results

1. Good agreement with NCCC "once per day" water content determinations using our new reject and permeate water capture units.

2. Substantial water content variability outside this "once per day" window.

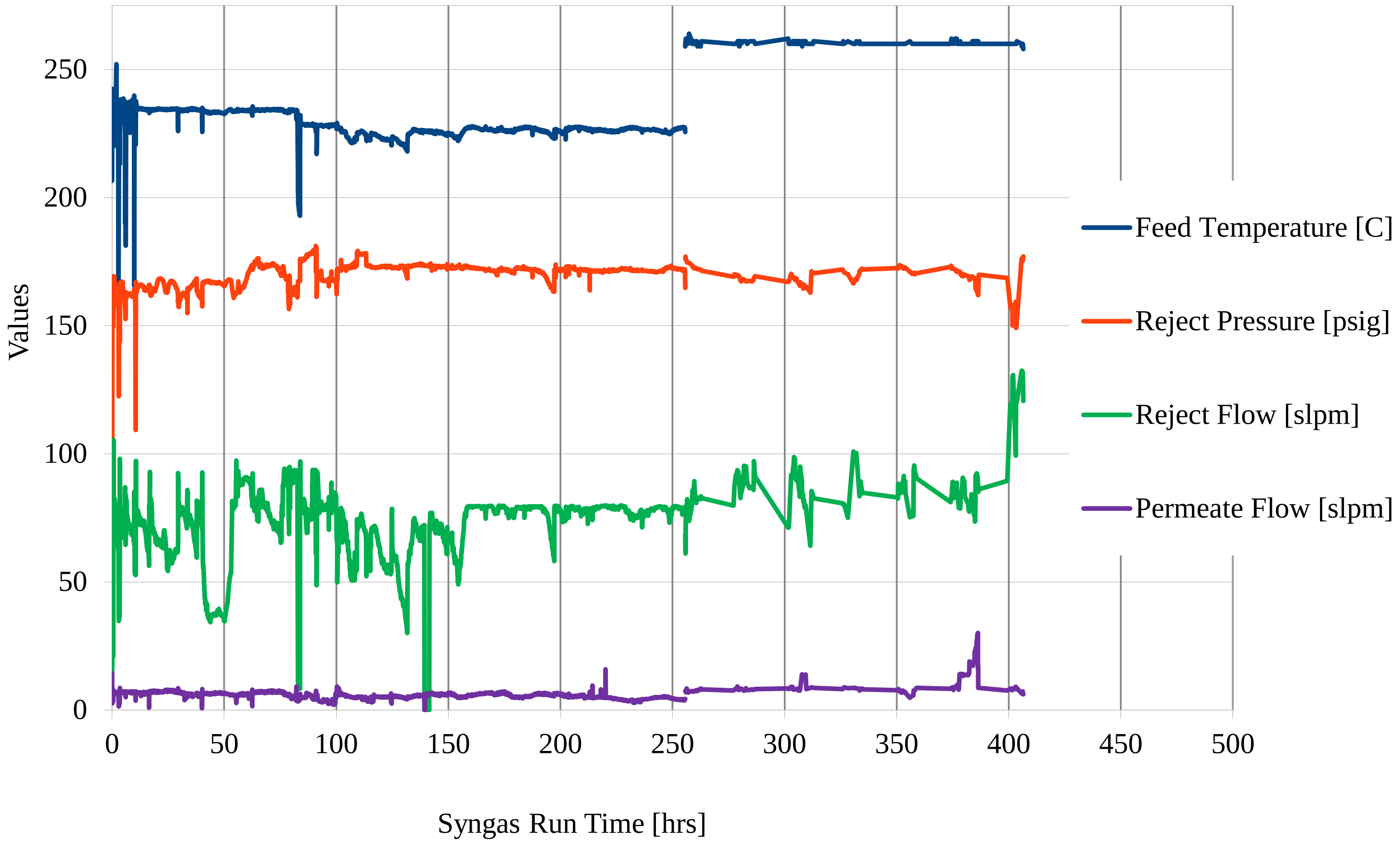
3. We now can determine accurate real time water composition in the membrane feed.

	NCCC Determined Raw Syngas Water	NCCC Shifted Syngas Water Content		MPT Water Collection Units			NCCC/MPT Water Closure	NCCC GC Dry Gas Mass Closure
				%	%	MPT Calculated %		
Time	%	WGS In	WGS Out	Perm	Reject	WGS Out	[%]	[%]
		22.3%	15.2%	51.8%	5.1%	11.[illegible]%	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%

PROGRESS: Membrane Performance Modeling

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

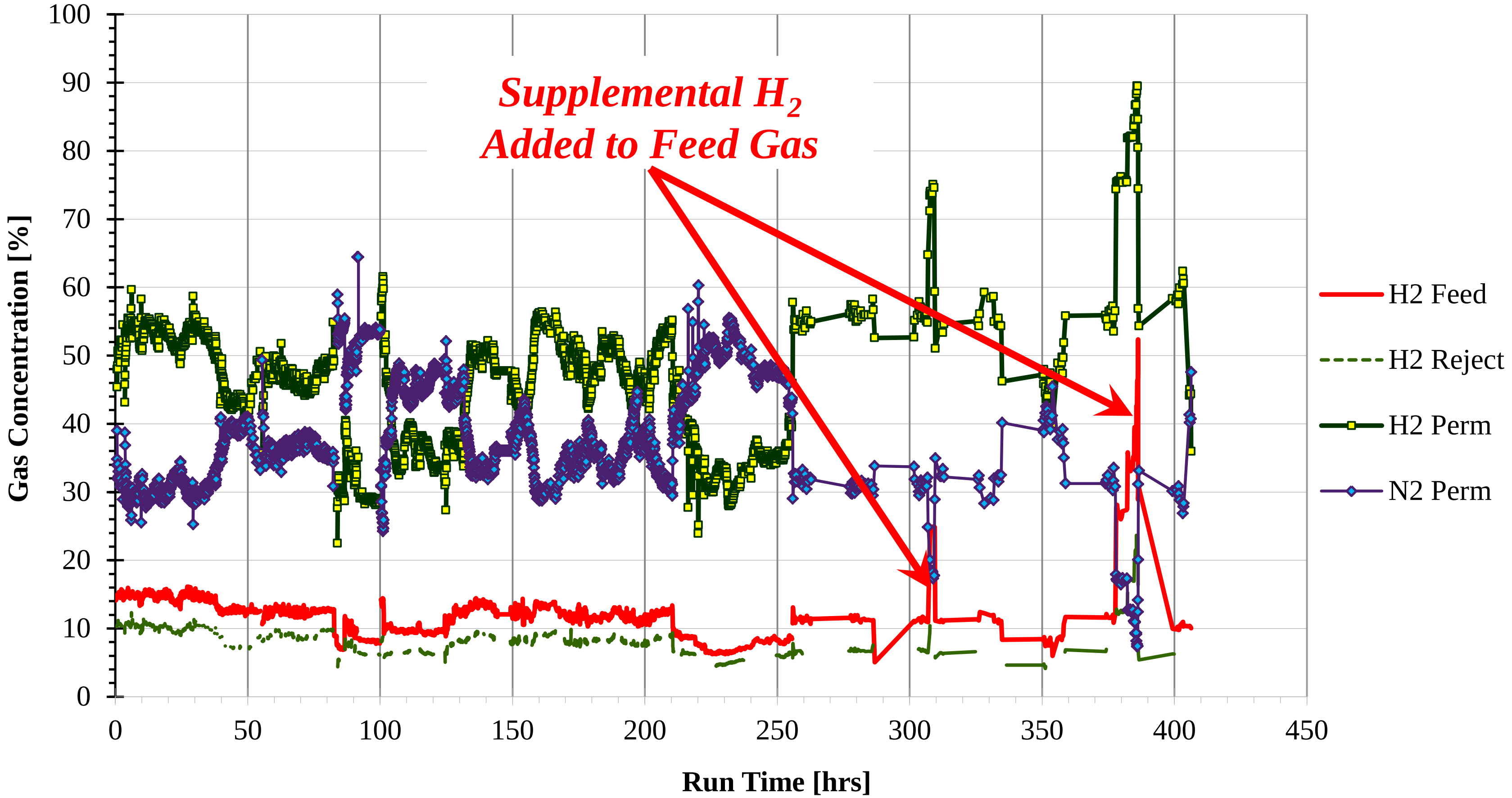
Operating Conditions and Flow Rates



PROGRESS: Membrane Performance Modeling

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

Feed, Permeate and Reject H_2 Composition

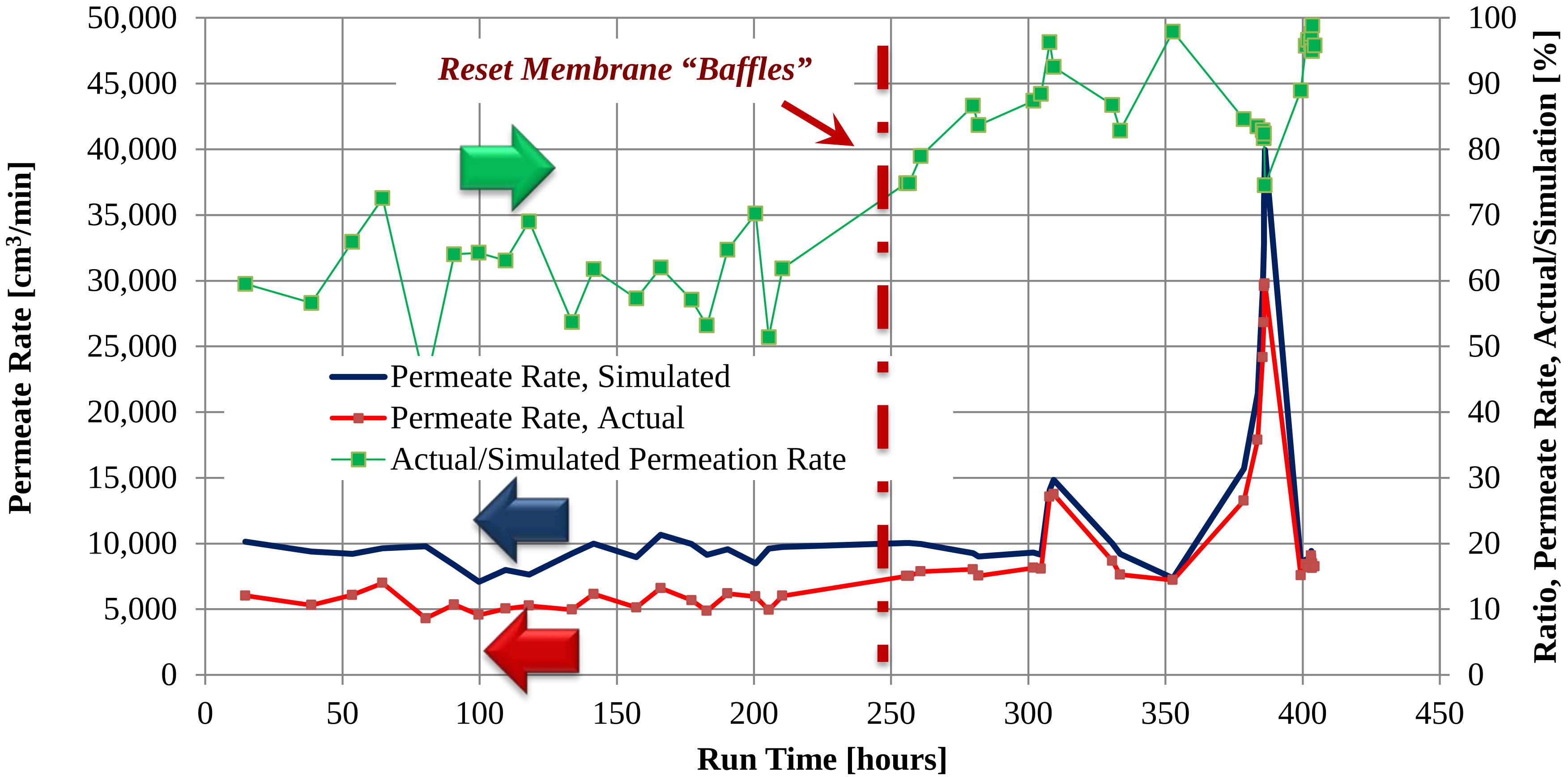


PROGRESS: Membrane Performance Modeling

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

Verification of the Mathematical Model in Actual Gas Testing at the NCCC

Permeate Flow Rate: Predicted versus Actual

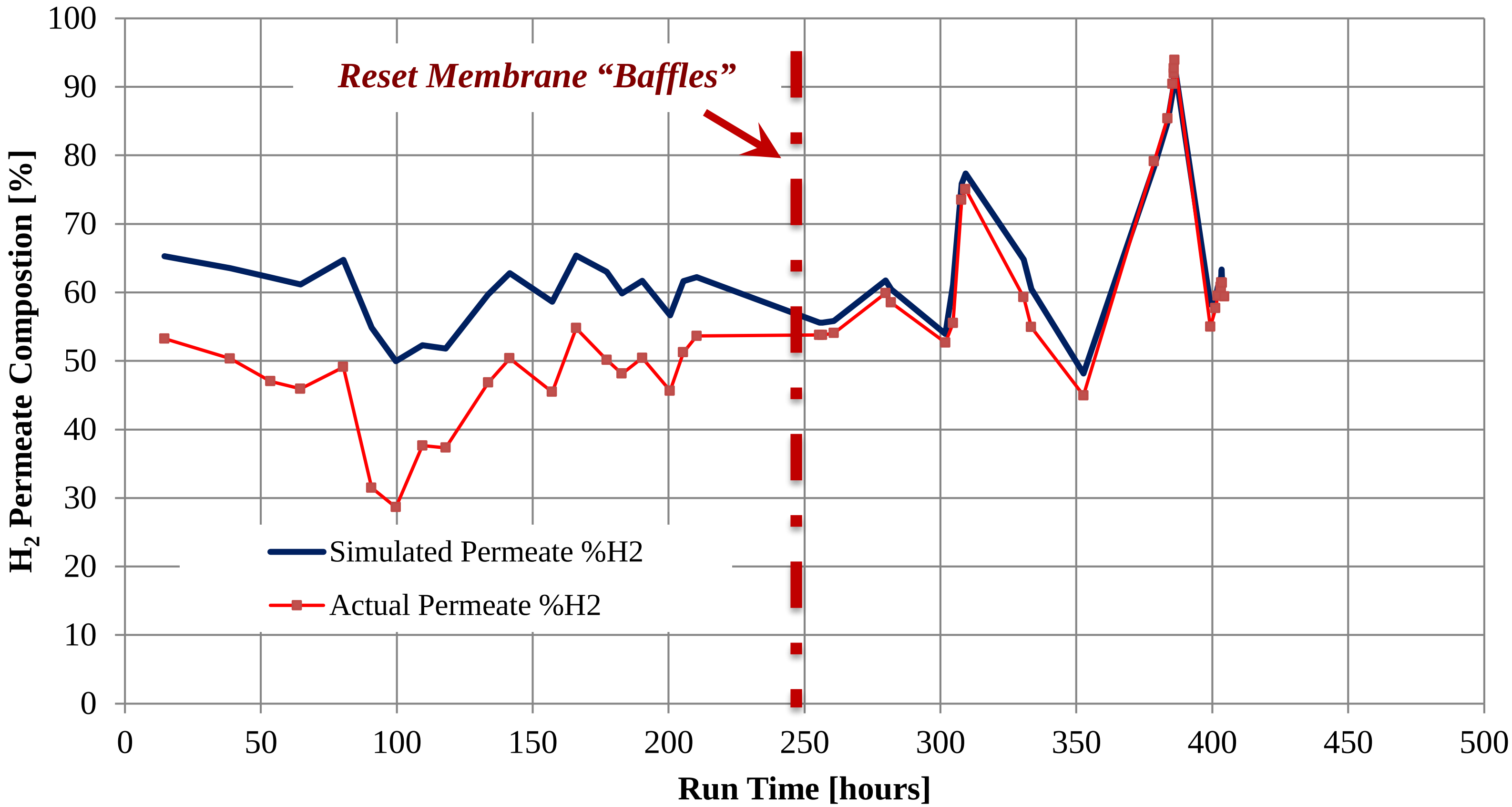


PROGRESS: Membrane Performance Modeling

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

Verification of the Mathematical Model in Actual Gas Testing at the NCCC

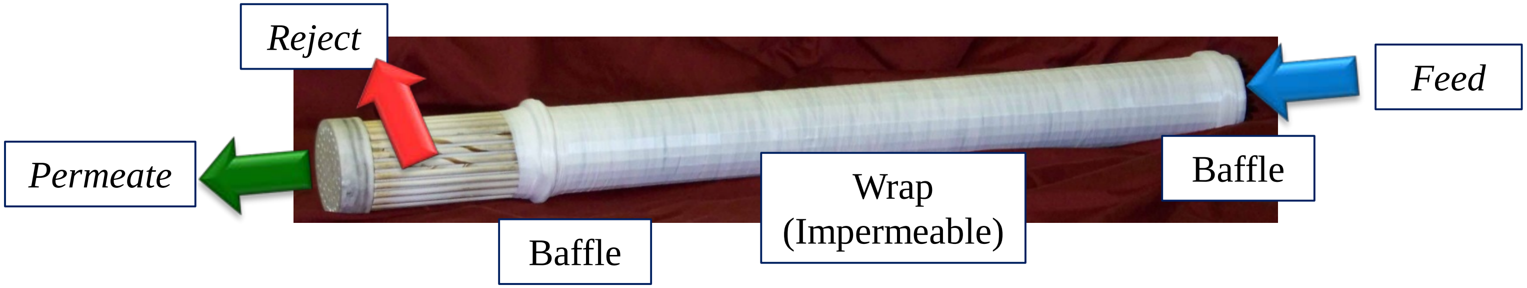
Permeate H_2 Content: Predicted versus Actual

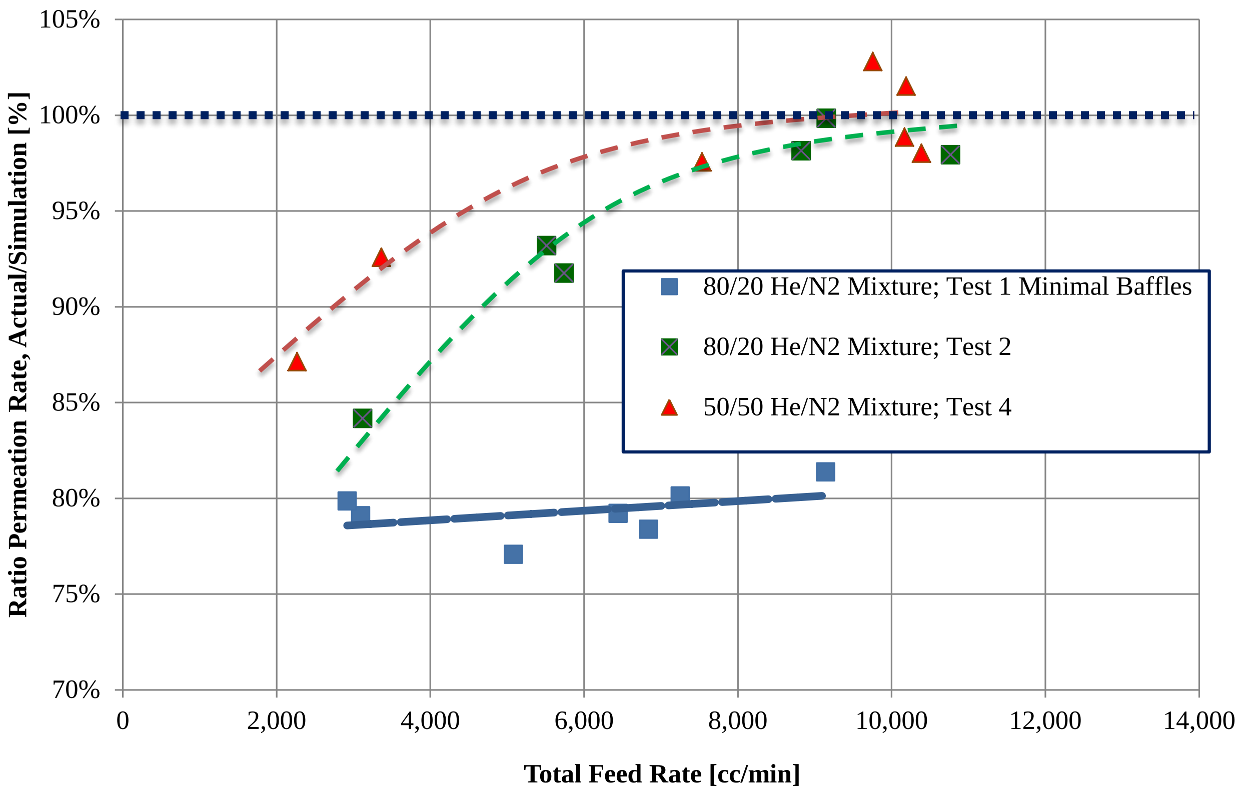


PROGRESS: Membrane Performance Modeling

Effect of Total Gas Feed Rate on Membrane Performance with Baffles

Ratio of Actual to Predicted Permeate Rates

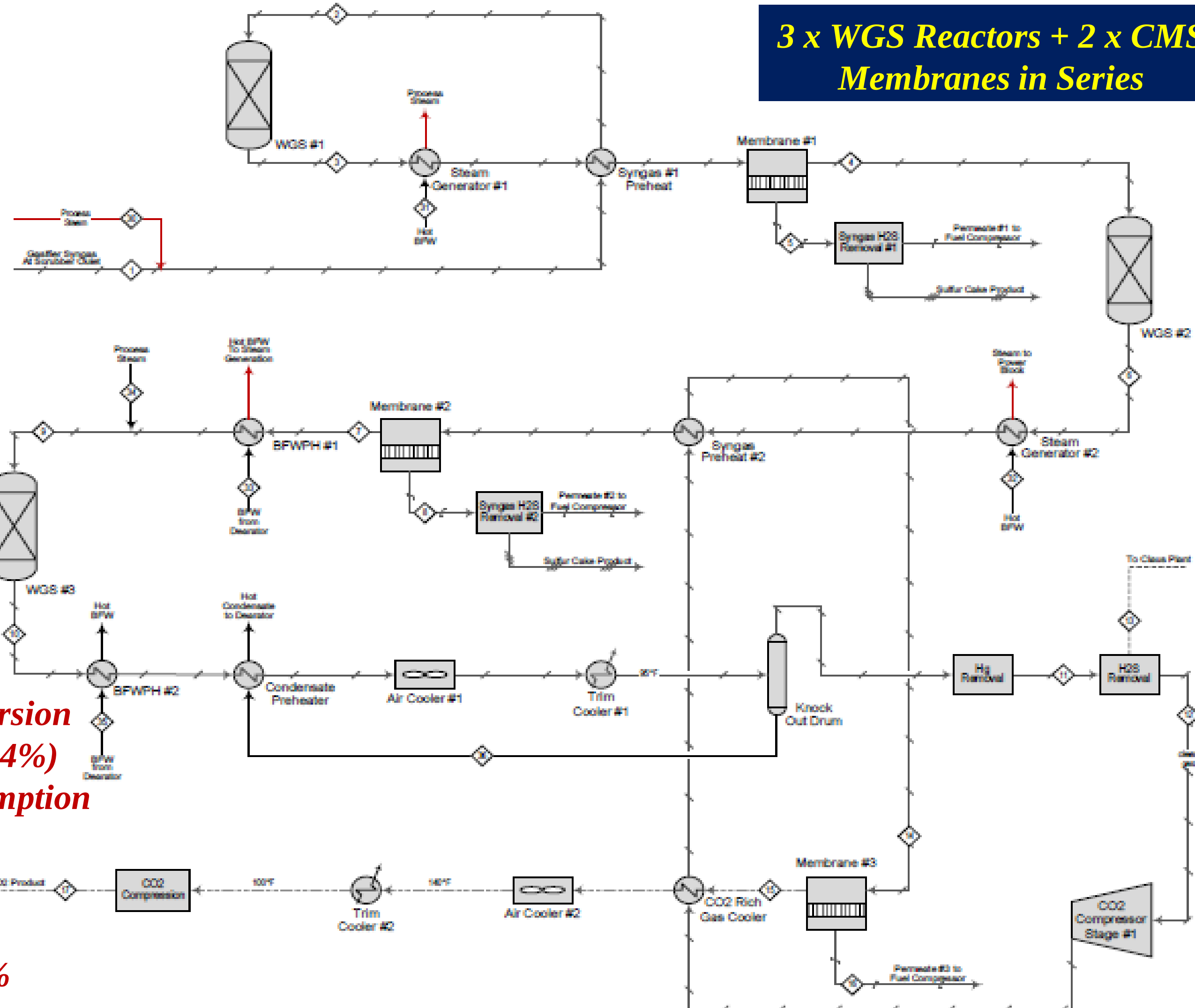




PROGRESS: Techno-economic Analysis

Process Flow Diagram

3 x WGS Reactors + 2 x CMS Membranes in Series



Enhanced CO Conversion
98.1% (v. B5B at 97.4%)
With less steam consumption

CO_2 Capture: 90.7%
CO_2 Purity: 93.4%

Pd-alloy Membrane for Residual H_2 Recovery

PROGRESS: Techno-economic Analysis

Process Performance and Economics

Parameter	Case B5B*	Case MPT	Target	MPT vs B5B
Carbon Capture	90.0%	90.72%	90%	
CO_2 Purity	99.48%	93.4%	95%	
H_2 in Fuel	99.98%	98.72%	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*

PLANS for Remaining Technical Issues

Final Remaining Technical Issues

- ***Complete Bench Scale Field Testing at the NCCC with DCT-style bundle with updated flow distribution/baffles and model verification***
- ***Conduct Bench Scale Field Testing at the NCCC with Pd-alloy bundle***
- ***Conduct high pressure mixed gas H_2/CO_2 performance testing with Pd-alloy membrane***
- ***Conduct Sensitivity Analyses on the Process Design and Economics (Impact of CO_2, H_2S, and other slow gas selectivity; Impact of WGS Operating Temperature; Introduction of RTI warm gas cleanup for H_2S removal)***
- ***Complete the Environmental, Health, and Safety Evaluation***

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^{o}C) and Pd-alloy (350^{o}C) 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 DCT-style bundles making them suitable for the proposed IGCC with CO_2 capture environment.
- Modeling has been successfully used to predict membrane performance at the NCCC.
- The proposed membrane based IGCC with carbon capture process achieves the 90% CO_2 capture target at 93.7% purity, just under the 95% purity target. Sensitivity analysis is underway on the H_2/CO_2 selectivity to establish the minimum target.
- Net power production for the proposed process is 553MW, 1.8% above the NETL base case.
- Total capital cost for the proposed process is $32MM (3%) below the NETL base case.

END