

# Advanced Palladium Membrane Scale-up for Hydrogen Separation

DE-FE0004967

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United Technologies Research Center

13 May 2011

Project ID #PD011

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# Overview (Relevance)

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## ■ Timeline

- Project start: 1 Oct 2010
- Project end: 31 Dec 2011
- Percent complete: 47%

## ■ Budget

- Total project funding
  - DOE share: \$1,492k
  - Contractor share: \$373k
- Funding received in FY10: \$0
- Funding for FY11: \$1,492k

## ■ Barriers

- K. Durability
- L. Impurities

## ■ Partners

- Power+Energy, Inc.
  - Membrane fabrication
- Energy & Environmental Research Center at the University of North Dakota
  - Membrane testing at Coal Gasifier

# Project Objectives (Relevance & Progress)

Primary goal: to construct, test, & demonstrate a Pd-Cu separator capable of producing 2 lb/day H<sub>2</sub> operating downstream of a coal gasifier

- (1) Construct, test, and demonstrate a Pd-Cu metallic tubular membrane micro-channel separator capable of producing 2 lb/day of H<sub>2</sub> at ≥95% recovery when operating downstream of an actual coal gasifier (**Q3**);
- (2) Quantify the impact of simulated gas composition and temperature on separator performance (**in progress**);
- (3) Compare the performance and durability of a surface modified, higher H<sub>2</sub> flux Pd-Cu membrane with the baseline Pd-Cu tubular membrane (**in progress**);
- (4) Evaluate various materials of construction for the separator structural parts to ensure durability under harsh gasifier conditions (**in progress**);
- (5) Perform an engineering analysis using National Energy Technology Laboratory (NETL) guidelines of the separator design based on gasifier test performance for the co-production of electric power and clean fuels (**Q4**); and
- (6) Select a gasification facility partner for Phase III.

# Project Overview: Milestones (Approach & Progress)

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**Title:** First delivery of lab-scale separator by P+E (Task 1.2).

**Planned Date:** 01/03/2011

**Actual Date:** 12/23/2010

**Verification Method:** Memo to FPM describing milestone achievement.

**Title:** First delivery of pilot scale (2lb/day H<sub>2</sub>) separator by P+E (Task 1.2).

**Planned Date:** 04/01/2011

**Verification Method:** Memo to FPM describing milestone achievement.

**Title:** Pilot-scale gasifier test completed (Task 1.4).

**Planned Date:** 09/01/2011

**Verification Method:** Test results described in quarterly progress report.

**Title:** Submit renewal application to DOE for authorization to proceed to Phases II and III (Task 1.1).

**Planned Date:** 09/30/2011

**Verification Method:** Submission of renewal application.

**Title:** Process simulation/Engineering analysis completed

**Planned Date:** 12/30/2011

**Verification Method:** Documentation in final report

# Technical Approach

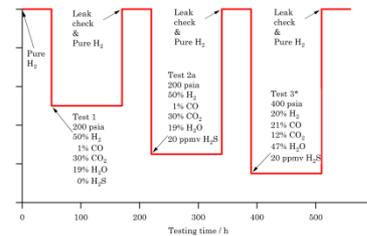
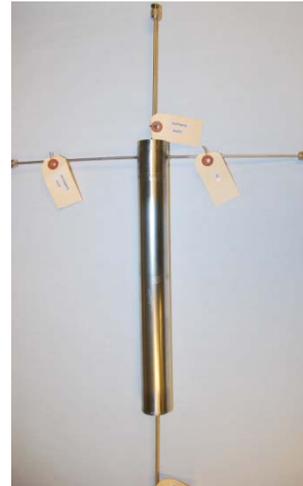
Quantify gas composition impact on durability and performance of 2 lb/day H<sub>2</sub> dense metallic PdCu separators operating downstream of a coal gasifier



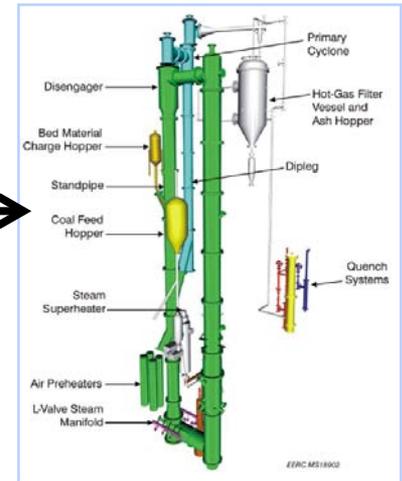
Construct laboratory-scale (<2 lb/day H<sub>2</sub>) separators



Quantify impact of gas species on performance & Materials testing and characterization



Construct pilot-scale (2 lb/day H<sub>2</sub>) Separators & DOE test protocol durability tests



Performance testing on coal gasifier syngas



# Commercial Readiness (Approach)

Leverage commercial experience in H<sub>2</sub> purifiers for coal-derived syngas



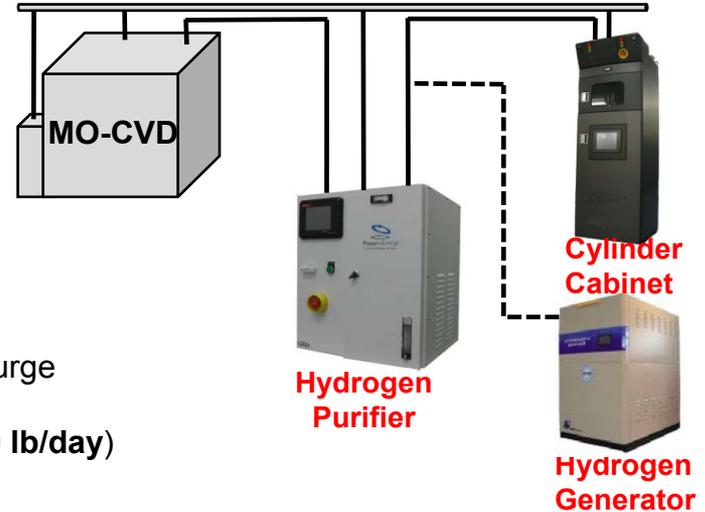
PE2100 Series  
Instrument / Lab  
Purifiers



PE9000S Purifiers



PE9000S Systems with Z-Purge  
Cabinets  
(up to 320 Nm<sup>3</sup>/h H<sub>2</sub> ≈ 1500 lb/day)



- P+E established 1993, Philadelphia, PA, USA
- Commercial Supplier of H<sub>2</sub> Purifiers for Semiconductors, Labs, Instruments
- Global customer base; more than 850 H<sub>2</sub> purifiers/separators shipped
- Membrane configuration is highly scalable
- P+E has developed and operates an automated manufacturing process
- Manufacturing processes are already established and demonstrated in commercial products.



## H<sub>2</sub> Separator Module Assembly (HSMA)

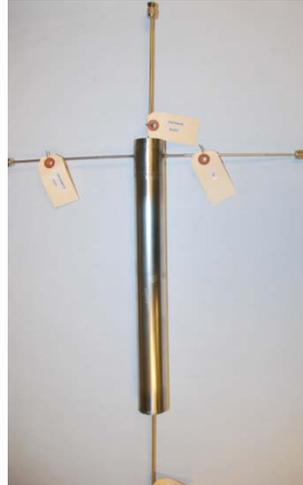
- Large area systems shipped to commercial customers and to Navy
- P+E has developed membrane technology partially funded by Navy
- **Equivalent to 100 lb/day H<sub>2</sub> for coal-derived syngas**

# Separator Scalability (Approach & Future Work)

Modify demonstrated commercial designs to achieve scale-up for Phase II/III



**Laboratory-scale  
( $<2$  lb/day  $H_2$ )  
Separators  
[Phase I]**



**Pilot-scale  
(2 lb/day  $H_2$ )  
Separators  
[Phase I-III]**

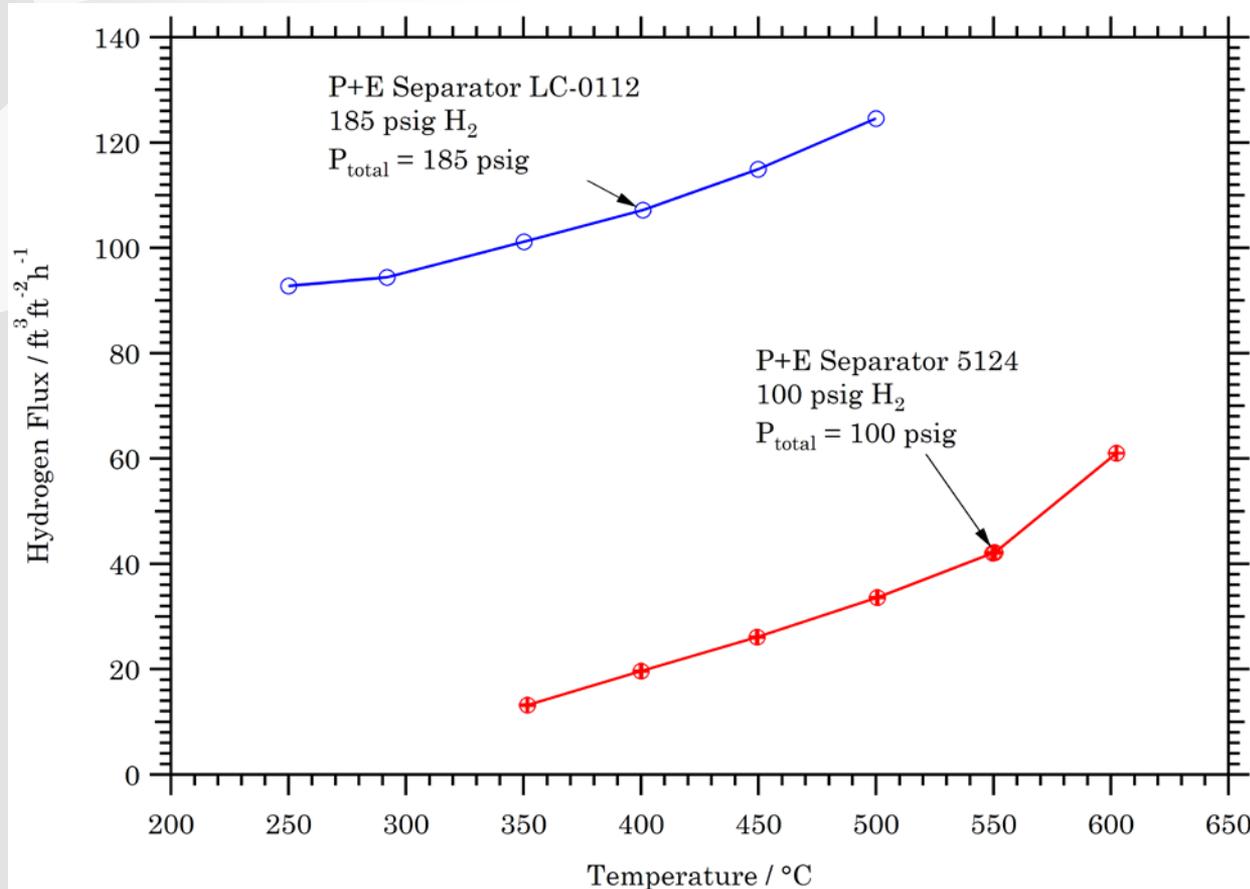


**Demonstration-scale  
(100 lb/day  $H_2$ )  
Separators  
[Phase II/III]**

- Phase I: Laboratory-scale for simulated gas tests; Pilot-scale separators for lab testing and small-scale gasifier tests
- Phase II/III: Pilot-scale separators for lab testing; Demonstration-scale for large-scale gasifier tests
- Add modules to achieve desired scale (up to 4 tpd  $H_2$ ) in enclosures with instrumentation

# Enhanced FCC PdCu Membranes (Approach)

Path to increase H<sub>2</sub> permeability and flux with proprietary surface modification



- Retain sulfur resistance of standard PdCu, but with enhanced H<sub>2</sub> flux
- If surface modification is not successful, will get same performance as PdCu
- Permeability is 5-6 times higher than standard PdCu

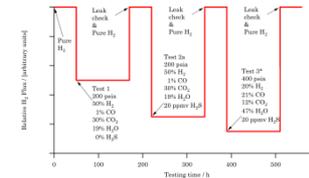
# Materials of Construction Coupon Testing (Approach)

DOE Test 2A to downselect best materials for separator construction

- H<sub>2</sub>S & CO<sub>2</sub> with water attacks stainless steel alloys
  - Corrosion
  - Carbon metal dusting
- Corrosion resistant alloys needed for long-term durability
- 8 alloys selected for evaluation
- Down select materials based on:
  - DOE Test 2A condition durability results
  - Availability of alloys
  - Fabrication criteria for P+E

	C-276	SS-309	SS-310	SS-316	HR-120	C-22	OC-10	OC-11
<b>Component</b>	<b>Wt. %</b>	<b>Wt. %</b>	<b>Wt. %</b>	<b>Wt. %</b>	<b>Wt. %</b>	<b>Wt. %</b>	<b>Wt. %</b>	<b>Wt. %</b>
Ni	57	12-15	19-22	10-14	37	56	12	25
Fe	5	60.5	56.75	65.75	33	3	Bal.	Bal.
Cr	16	22-24	19-21	16-18	25	22	14	15
Mo	16	0	0	2-3	2.5max	13	0	0
Co	2.5 max	0	0	0	3	2.5 max	0	0
Mn	1 max	2 max	2 max	2 max	0.7	0.5 max	7	0
W	4	0	0	0	2.5 max	3	0	0
Si	0.08 max	0.75 max	1.5 max	0.75 max	0.6	0.08 max	0	0
C	0.01 max	0.2 max	0.25 max	0.08 max	0.05	0.010 max	0	0
<b>Others</b>	P: 0.03 max, S: 0.015 max	P: 0.045 max, S: 0.03 max	P: 0.045 max, S: 0.03 max	P: 0.045 max, S: 0.03 max, N: 0.1 max	Nb: 0.7 max, Al: 0.1, B: 0.004, N: 0.20	V: 0.35 max	Al: 3, Nb: 1	Al: 4, Nb: 2.5+ Hf, Y

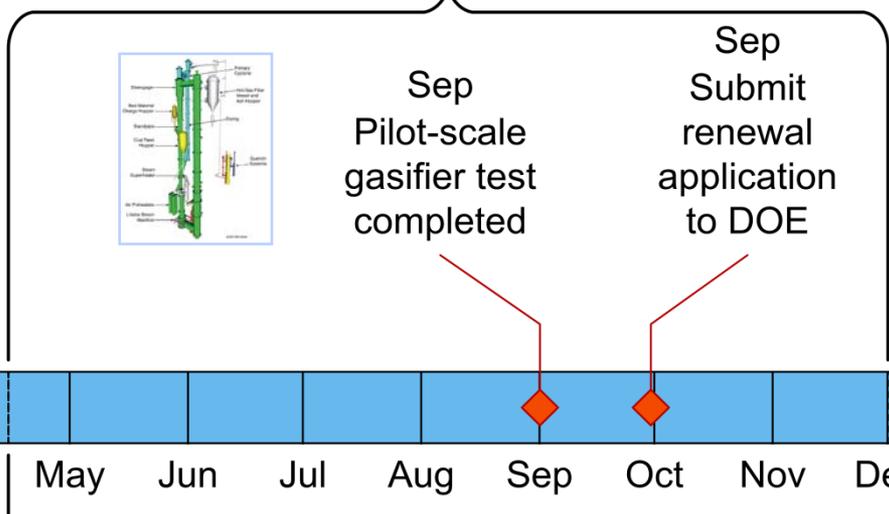
# Testing Plan for Phase I (Approach & Future Work)



Dec  
Complete test stand modifications & Construct laboratory-scale separators

Apr  
Delivery of first 2 lb/day H<sub>2</sub> separator

Apr - Dec  
Pilot-scale separator testing



Oct-10

Nov Dec Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

Dec-11

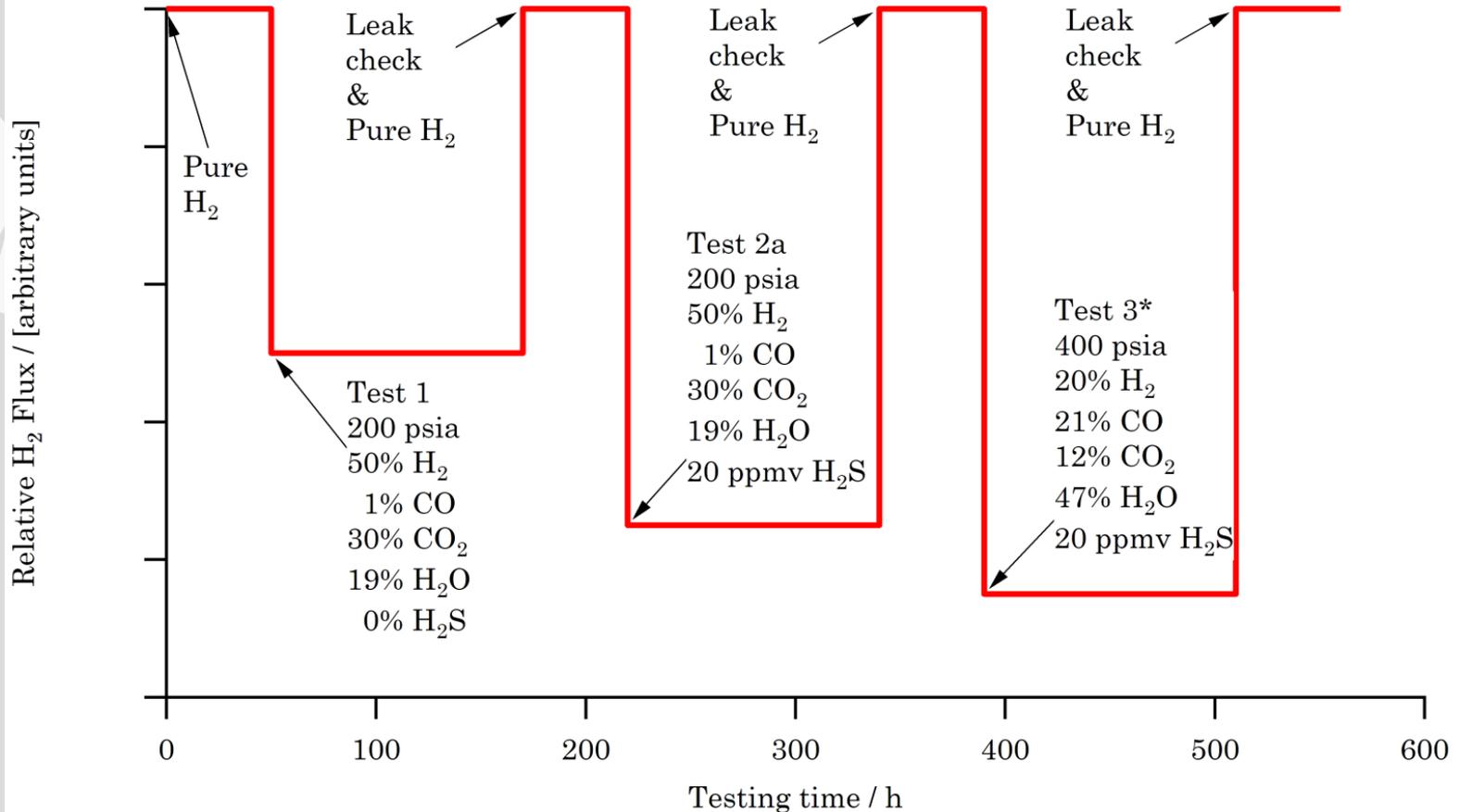
Dec - Apr  
Sub-scale separator testing



$$Q_{eff} = \frac{Q_{H_2}}{1 + K_{CO} P_{CO} + K_{CO_2} P_{CO_2} + K_{H_2O} P_{H_2O} + K_{N_2} P_{N_2} + K_{H_2S} P_{H_2S}}$$

Dec - Dec  
Alloy coupon testing

# DOE Protocol Durability Tests for Phase I (Approach)



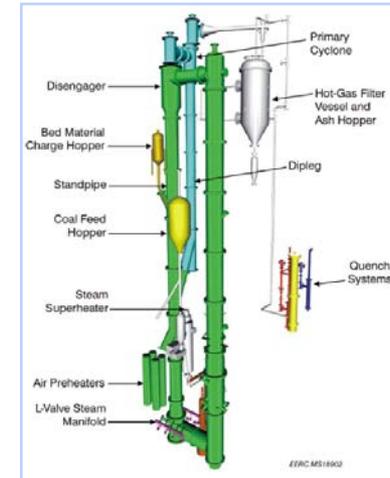
- Four tests before end of Phase I
- Examine temperature (2) and materials of construction (2 alloys)
- Perform thermal cycling tests at end of durability test
- Perform detailed breakdown and characterization of separators

# Test at EERC Gasifier (Approach & Future Work)

Evaluate performance on coal-derived syngas and compare to laboratory data

Expected test parameters at EERC's coal gasifiers and expected syngas composition before water-gas shift during Phases I and II.

Syngas component (Mole %)	Phase I		Phase II
	EFG	FBG	TRDU
H <sub>2</sub>	20-30	25-40	25-40
CO	20-30	15-25	15-25
CH <sub>4</sub>	0-0.5	1-5	0.5-4
C <sub>2</sub> H <sub>6</sub>	0	0.5-1	<0.5
C <sub>2</sub> H <sub>4</sub>	0	0.5-1	<0.5
C <sub>3</sub> H <sub>8</sub>	0	0-0.5	<0.5
CO <sub>2</sub>	25-35	25-35	20-40
N <sub>2</sub>	5-15	5-15	5-15
Sulfur compounds [ppm] (cleaned vs. raw)	0.01- 3000	0.01- 3000	0.01- 3000
Syngas Pressure [psia]	200-450	200-450	200-450
Coal [lbs/h]	6-10	6-10	300-500
O <sub>2</sub> /coal ratio	0.5-1.0	0.3-0.8	0.3-0.8
H <sub>2</sub> O/coal ratio	0.1-0.5	0.3-0.8	0.2-0.8
LHV [Btu/scf]	150-250	150-250	150-250
Flow rate [scfh]	90-240	120-300	9000-15000



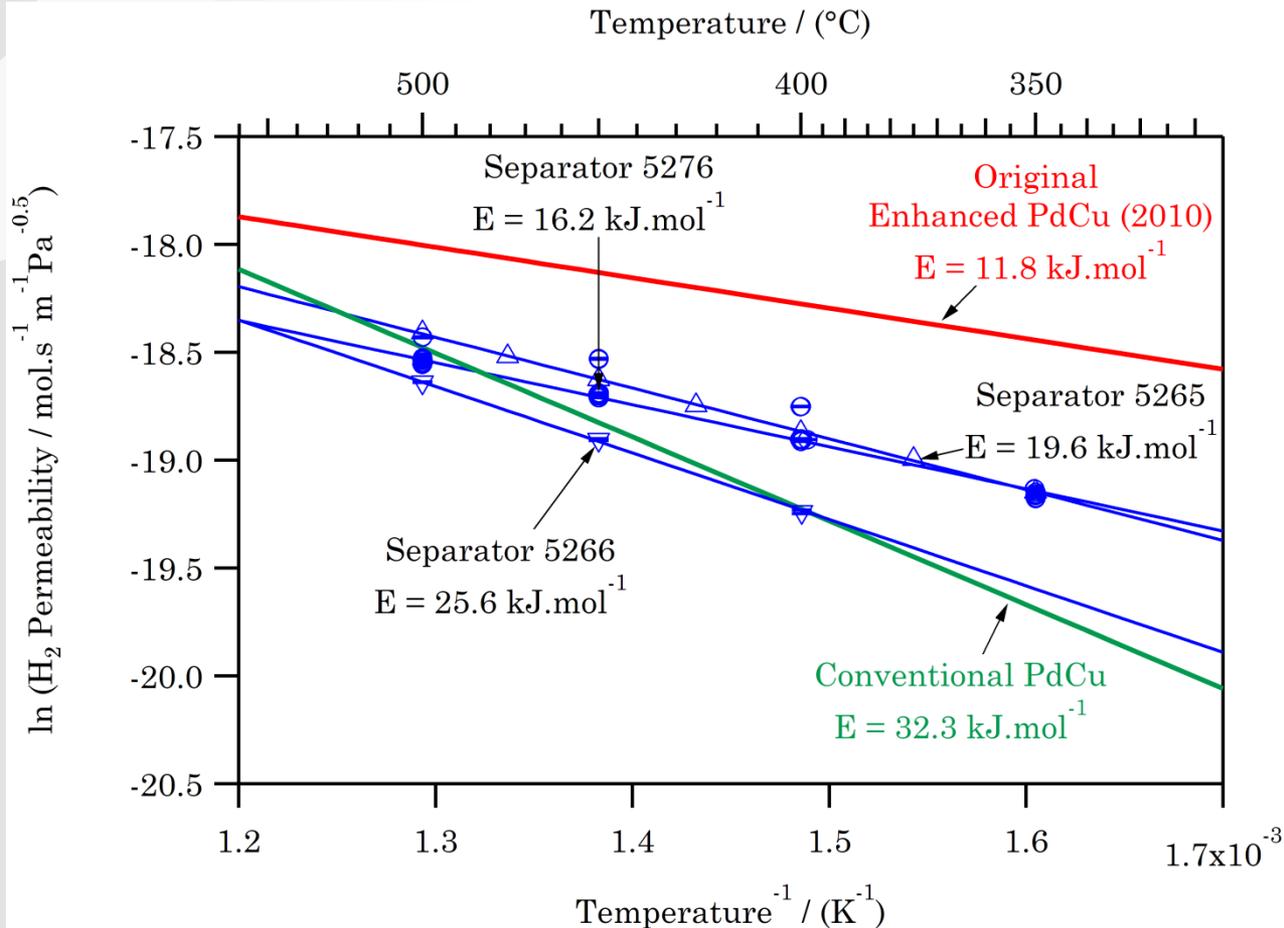
Performance testing on coal gasifier syngas



- One-week demonstration test during Phase I with 2 lb/day H<sub>2</sub> separator
- Use EERC's small, bench-scale gasifiers capable of producing up to 10 lb/day H<sub>2</sub>

# H<sub>2</sub> Permeability versus Temperature (Technical)

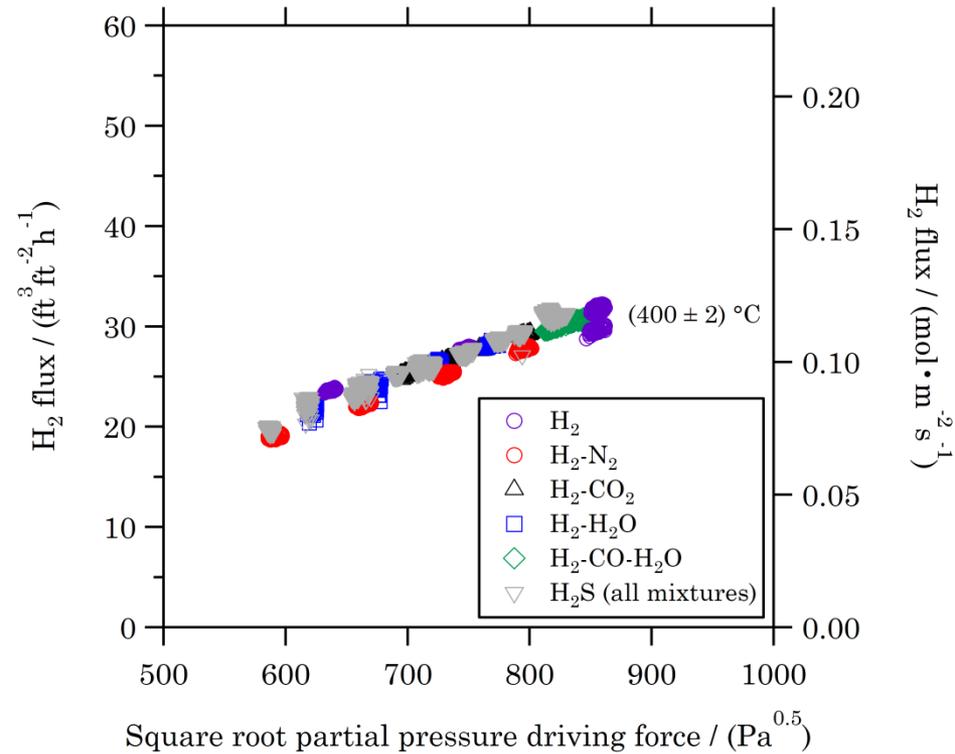
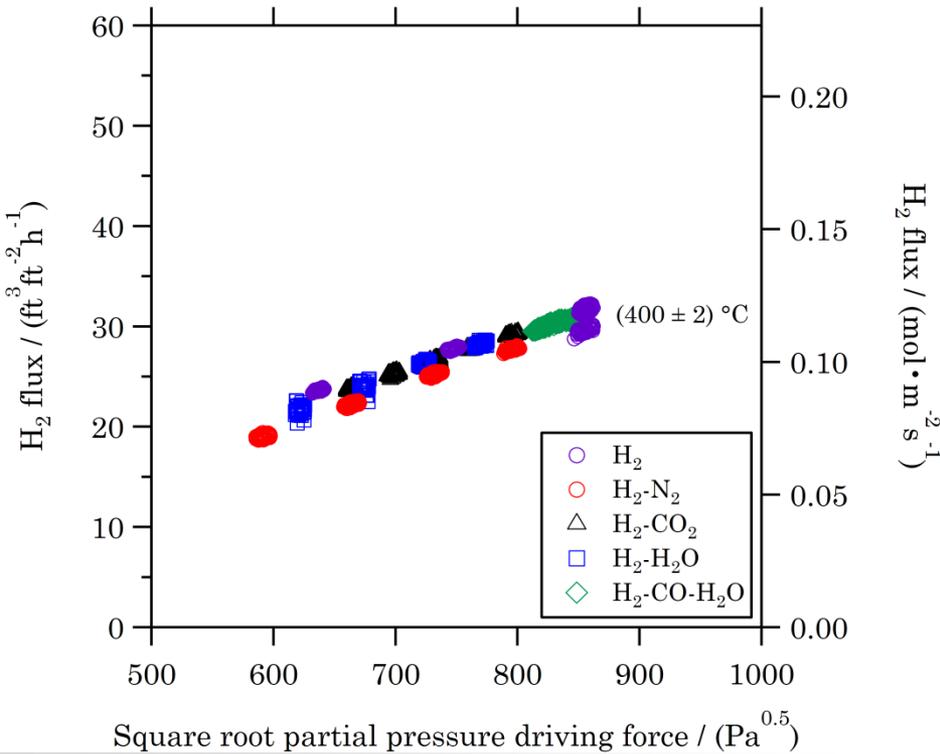
Initial enhanced PdCu membranes are improved over conventional PdCu;  
Coating application will be improved for next separators



- Permeability of new separators less than original one tested in 2010
- Membrane processing under improvement for next separators

# Impact of Gas Contaminants on H<sub>2</sub> Flux (Technical)

H<sub>2</sub>S and CO have negligible impact on H<sub>2</sub> flux at temperatures  $\geq 400$  °C

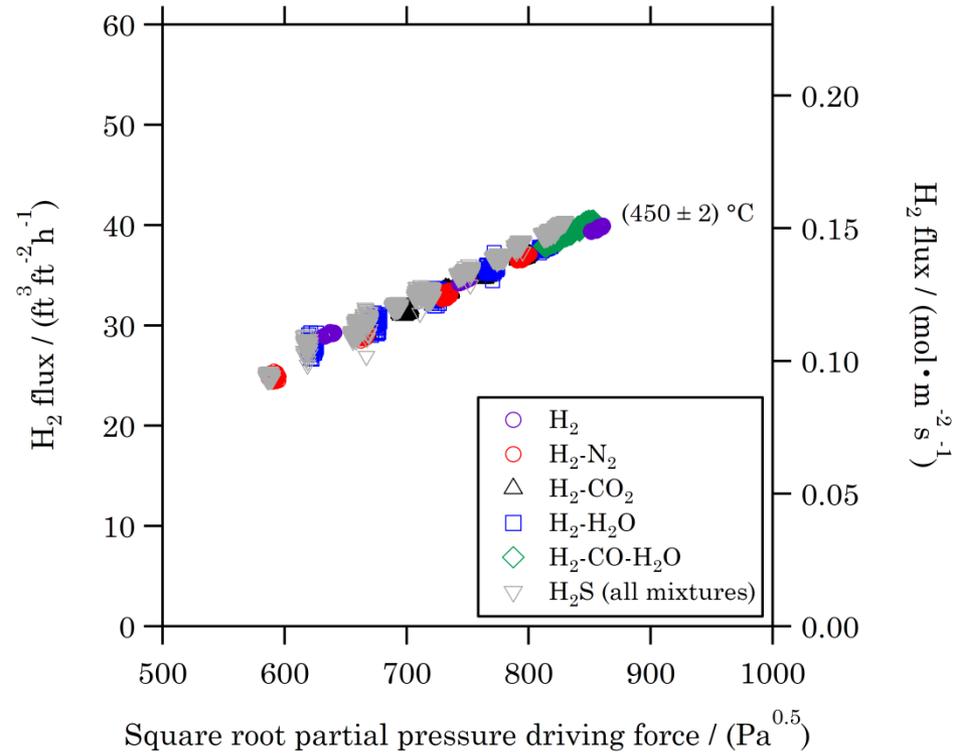
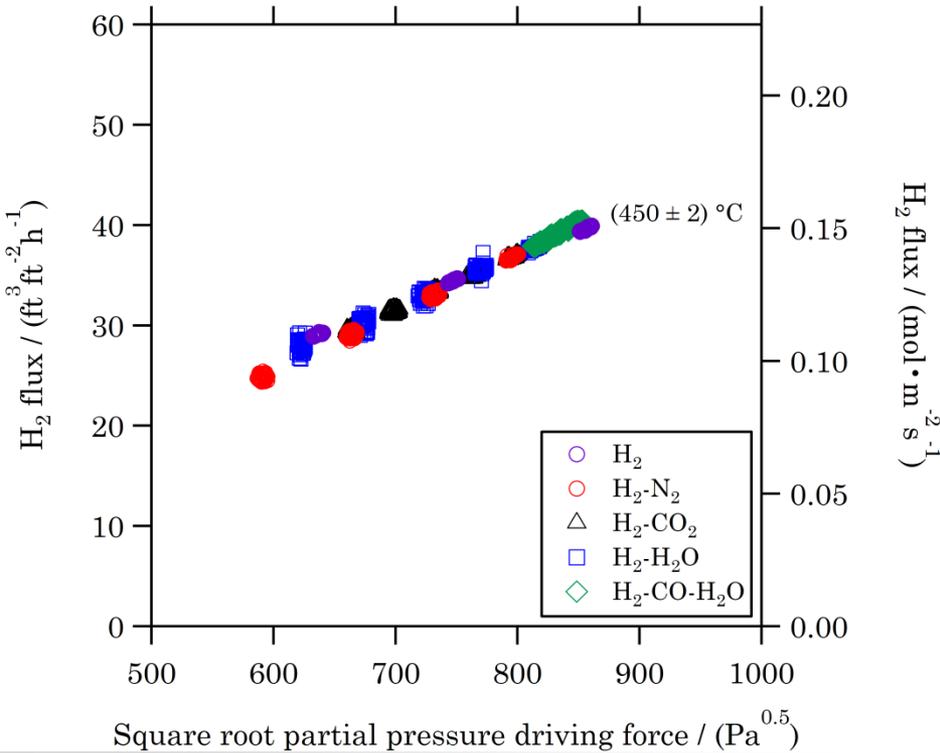


- Total pressure = 14.7 psig to 185.2 psig
- Temperature = 400 °C to 500 °C
- H<sub>2</sub> = 60% to 100%
- N<sub>2</sub> = 10% to 40%

- CO<sub>2</sub> = 10% to 30%
- H<sub>2</sub>O = 7% to 36%
- CO = 0.5% to 2.1% (with 0.9% to 4.5% H<sub>2</sub>O to prevent coking)
- H<sub>2</sub>S = 5 ppmv to 39 ppmv

# Impact of Gas Contaminants on H<sub>2</sub> Flux (Technical)

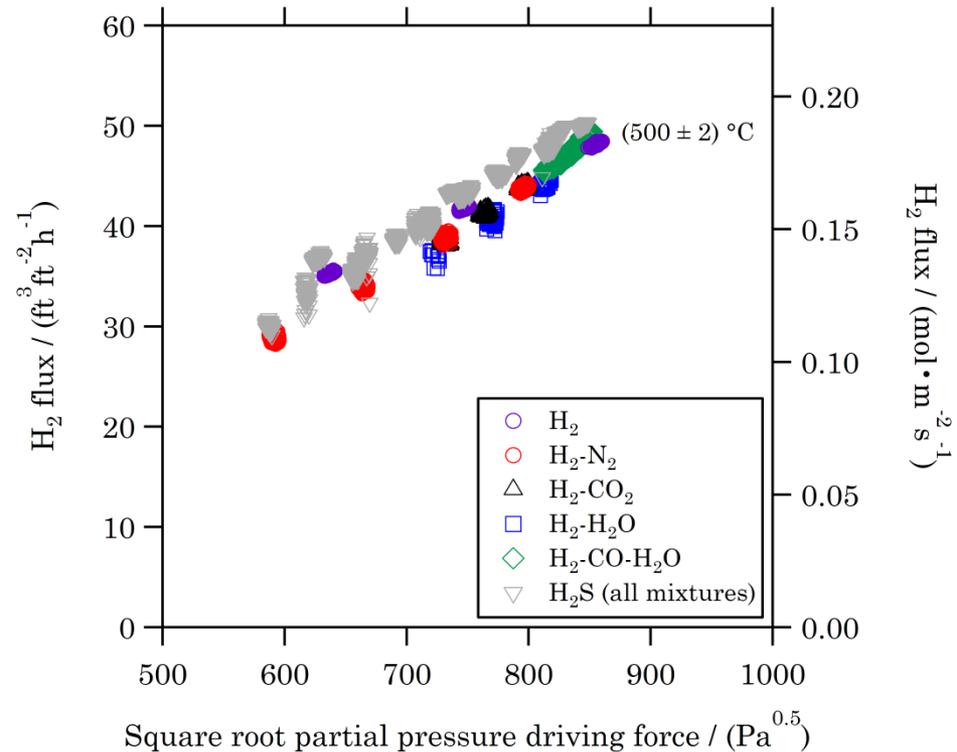
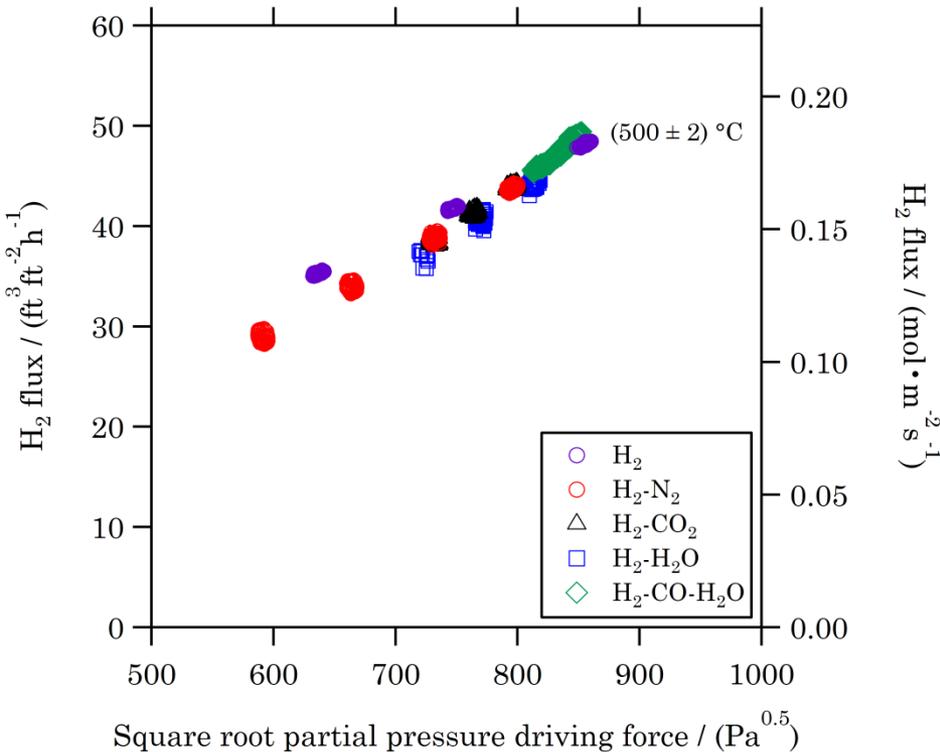
H<sub>2</sub>S and CO have negligible impact on H<sub>2</sub> flux at 450 °C



- Results similar to 400 °C data
- Performance at temperatures ≥400 °C driven by H<sub>2</sub> partial pressure

# Impact of Gas Contaminants on H<sub>2</sub> Flux (Technical)

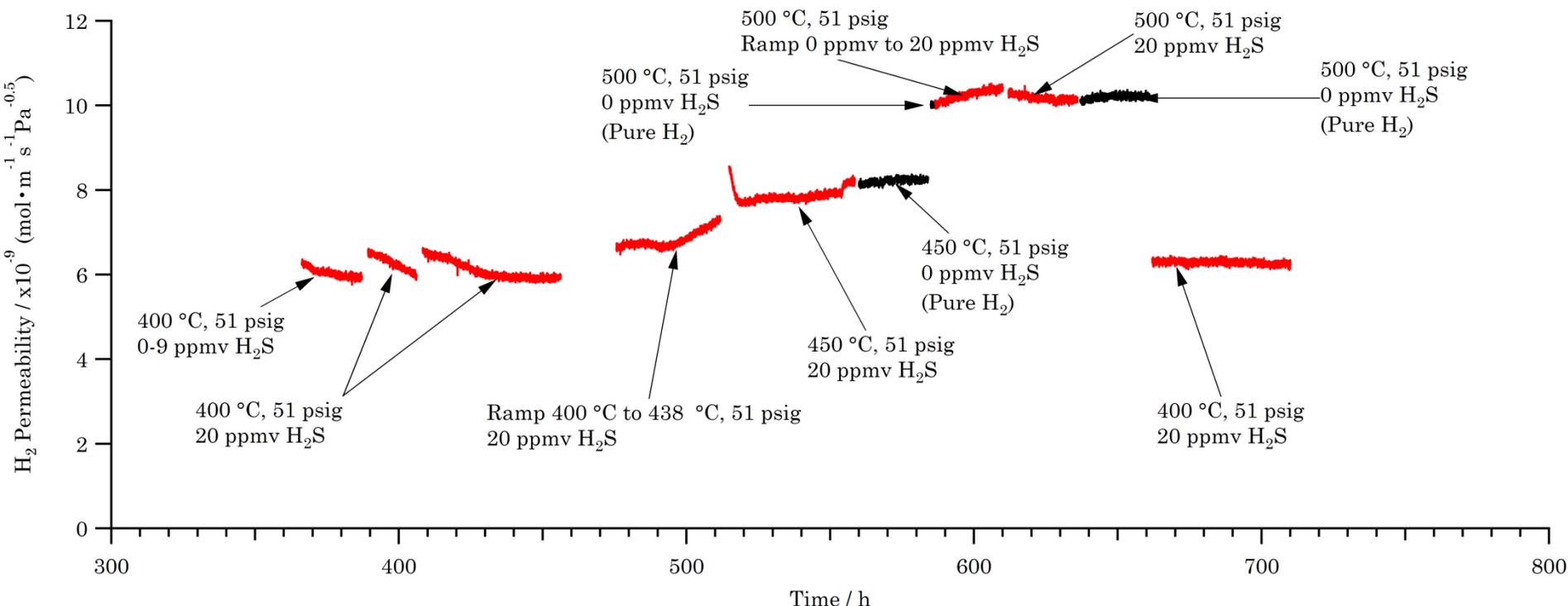
H<sub>2</sub>S and CO have negligible impact on H<sub>2</sub> flux at 500 °C



- Results similar to 400 °C & 450 °C data
- More data variance present in some 500 °C data
- Performance at temperatures ≥400 °C driven by H<sub>2</sub> partial pressure

# H<sub>2</sub>S Durability Experiments (Technical)

Separators need to be tested for a minimum of 100 hours to saturate non-Pd membrane components (e.g., steel manifolding)

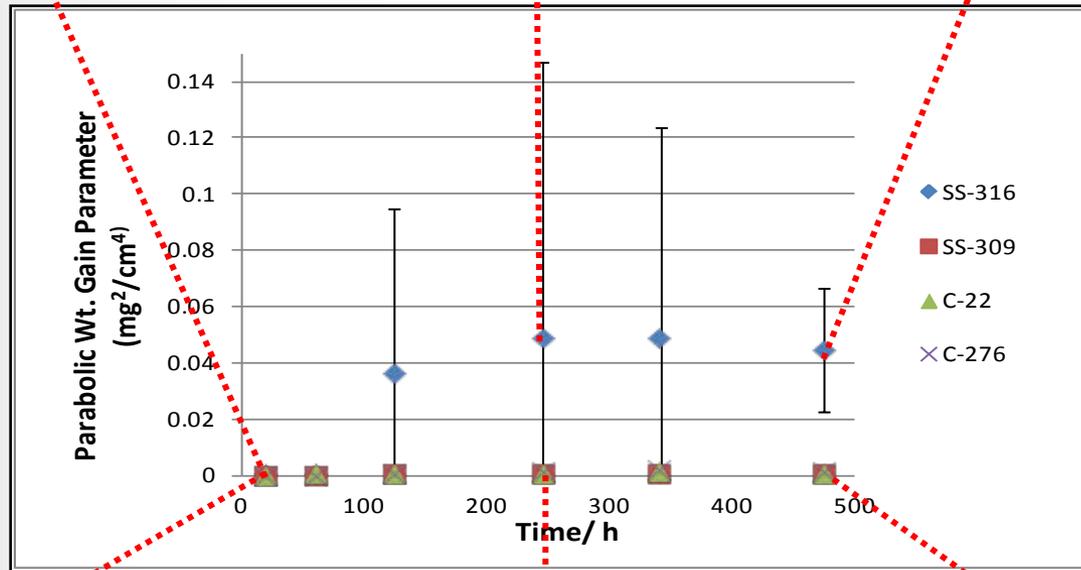
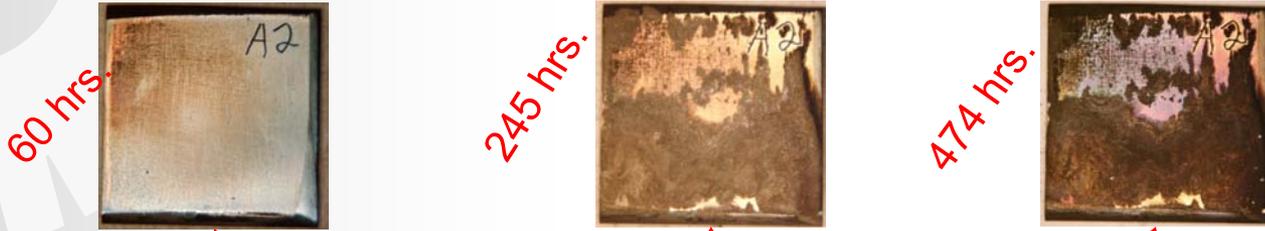


- Dräger tube measurements for H<sub>2</sub>S verified feed concentration
- Additional evidence that sulfur has a negligible impact on H<sub>2</sub> flux at temperatures ≥400 °C with 20 ppmv H<sub>2</sub>S
- Separator tested for a total time of 1031 hours (618 hours with H<sub>2</sub>S)

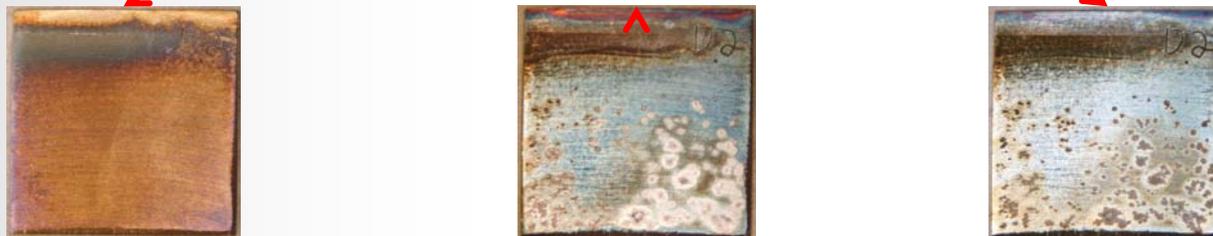
# Materials of Construction Coupon Testing (Technical)

SS-309, C-22 and C-276 show orders of magnitude improved performance over SS-316 in preliminary testing

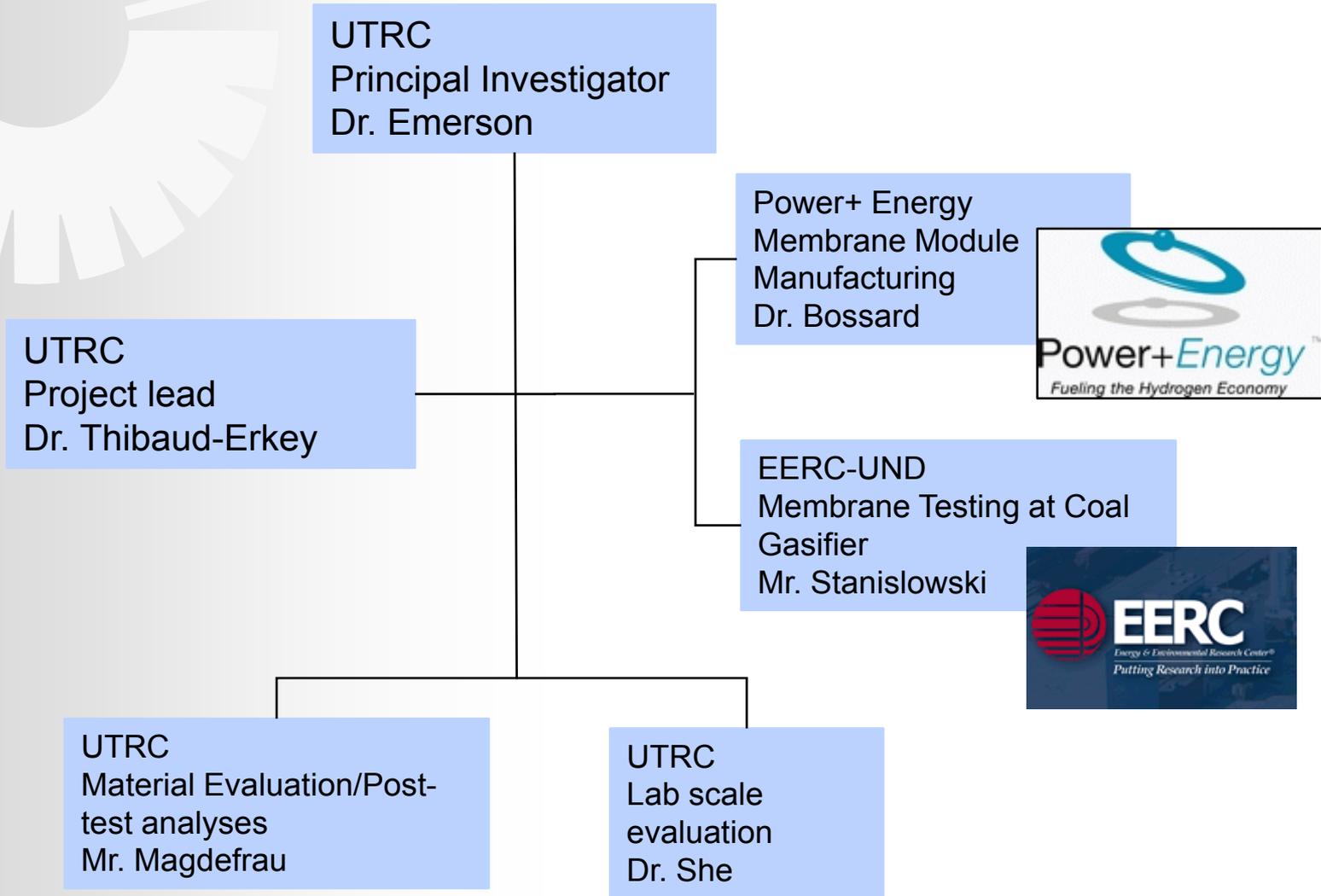
**SS-316**



**C-276**



# Collaborations



# Project Summary

Performance Criteria	Units	DOE 2015 Target	Current Status
H <sub>2</sub> Flux	ft <sup>3</sup> h <sup>-1</sup> ft <sup>-2</sup>	300	125 (500 °C, enhanced PdCu) (200 psia feed, 185.3 psid)
Temperature	°C	250–500	250–600
Sulfur tolerance	ppmv	>100	800 h at 100 ppmv S 618 h at 5–39 ppmv S 4 h at 487 ppmv S
Cost	\$/ft <sup>2</sup>	<100	400–500 (without recycle & leasing strategy)
ΔP operating capability	psi	800–1000	200
CO tolerance	–	Yes	13.3% CO at 90 psia >9% CO at 204.7 psia
H <sub>2</sub> purity	%	99.99	99.9999
Stability/Durability	Years	5	1031 h

- Demonstrated negligible impact of gas species for T ≥400 °C & P ≤ 200 psia
- Working on improving enhanced PdCu membrane flux
- Identified potential materials of construction superior to SS-316

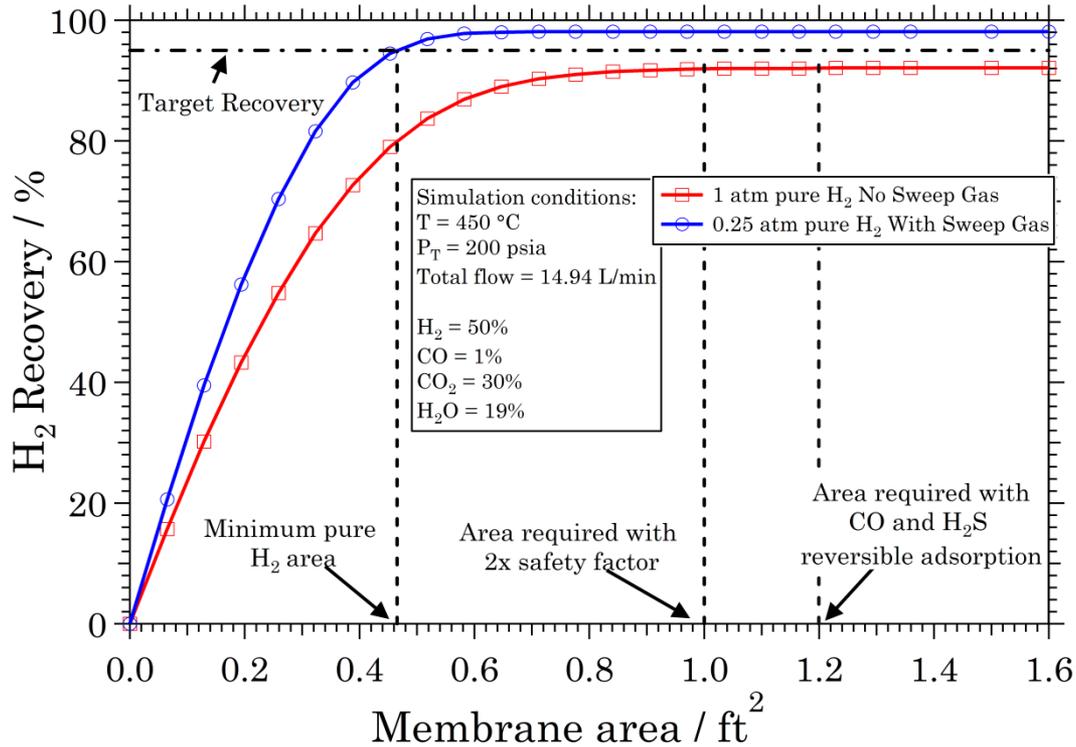


# Technical Back-Up Slides

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# Methodology for Membrane Sizing (Approach)

Reduce performance risk by appropriately sizing initial 2 lb/day H<sub>2</sub> separators based on current PdCu alloy



- Sweep gas necessary to achieve >95% H<sub>2</sub> recovery
- Increased minimum area needed for pure H<sub>2</sub> by a factor of 2
- Further increase to adjust for the impact of Test 2a/2b on previous membrane performance

# Laboratory-scale Screening Tests (Approach)

Quantify separator permeability & effects of major gas species to enable proper sizing of separators

$$J = \underbrace{\frac{Q_{\text{eff}}}{l}}_{\text{Permeance}} \left( P_1^{0.5} - P_2^{0.5} \right)$$

Flux Permeability Hydrogen driving force

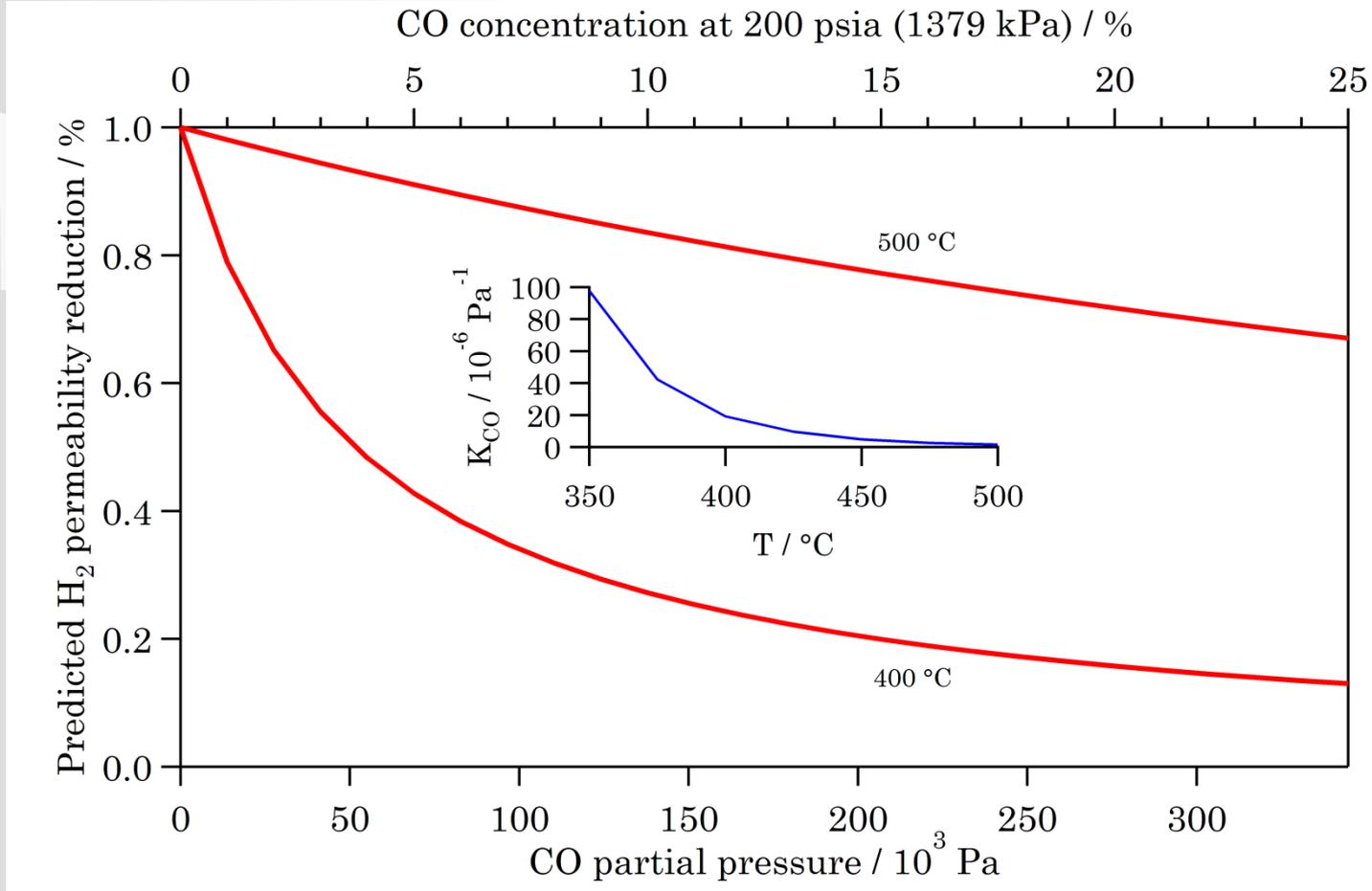
$$Q_{\text{eff}} = \frac{Q_{H_2}}{1 + K_{CO} P_{CO} + K_{CO_2} P_{CO_2} + K_{H_2O} P_{H_2O} + K_{N_2} P_{N_2} + K_{H_2S} P_{H_2S}}$$

## Experimental Objectives

- Obtain separators' permeability as a function of temperature with pure H<sub>2</sub>
- Quantify the effect of different non-poison gas species on H<sub>2</sub> permeability
- Determine adsorption coefficients (K<sub>i</sub>) for each significant gas species
- Operate at low hydrogen recovery (differential conditions) to improve determination of adsorption coefficients

# Impact of CO on Separator Performance (Technical)

CO estimated to have strong impact at 400 °C based on 2010 preliminary data



- Original expectation was for 1% CO to reduce the H<sub>2</sub> flux by ≈20% at 400 °C
- Thorough testing in 2011 shows negligible impact at temperatures ≥400 °C

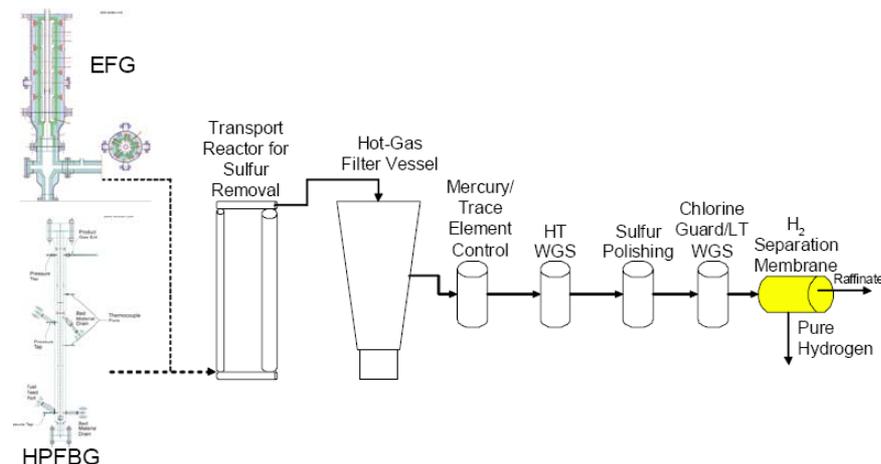
# Syngas Contaminant Mitigation (Approach)

Two strategies to mitigate syngas contaminant effects in Phase I



**Laboratory-scale  
( $<2$  lb/day  $H_2$ ) separators**

- PdCu sulfur tolerance previously demonstrated
  - Atomistic modeling
  - Laboratory testing
- Conservatively size separators
- Materials of construction selection
- Contaminant laboratory testing prior to gasifier tests



**EERC gasifier with clean up train**

- Warm gas clean up at EERC gasifier
  - Bulk sulfur removal
  - Particulate filtration
  - Mercury, Arsenic sorption
  - Water gas shift for syngas composition adjustment
- Simulate gasifier plant clean up
- Adjust gas composition to test membrane separator