# Advanced Palladium Membrane Scale-up for Hydrogen Separation

DE-FE0004967

S. Emerson, Z. Dardas, R. Hebert, G. Janowsky, N. Magdefrau, Y. She, C. Thibaud-Erkey, & J. Wittenzellner

United Technologies Research Center

13 May 2011

Project ID #PD011



United Technologies Research Center

DOE Hydrogen Program

# Overview (Relevance)

- 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 $H_2$ 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 $H_2$ 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 $H_2$ 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)

**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 $H_2$) 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

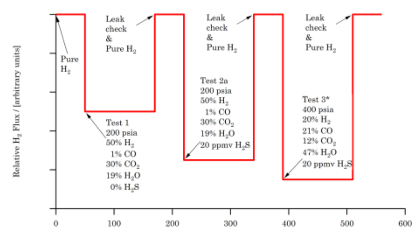
# Technical Approach

Quantify gas composition impact on durability and performance of 2 lb/day $H_2$ dense metallic PdCu separators operating downstream of a coal gasifier

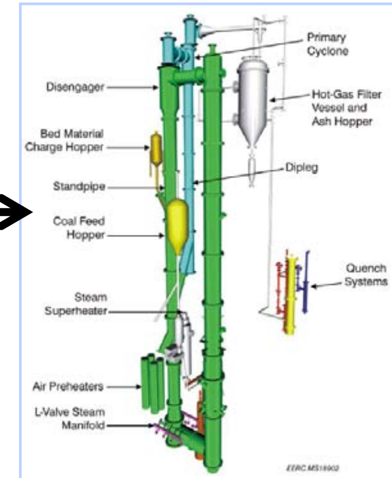
Construct laboratory-scale (<2 lb/day $H_2$) separators

Power+Energy — Fueling the Hydrogen Economy

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




Construct pilot-scale (2 lb/day $H_2$) Separators & DOE test protocol durability tests




Performance testing on coal gasifier syngas

EERC Energy & Environmental Research Center

# Commercial Readiness (Approach)

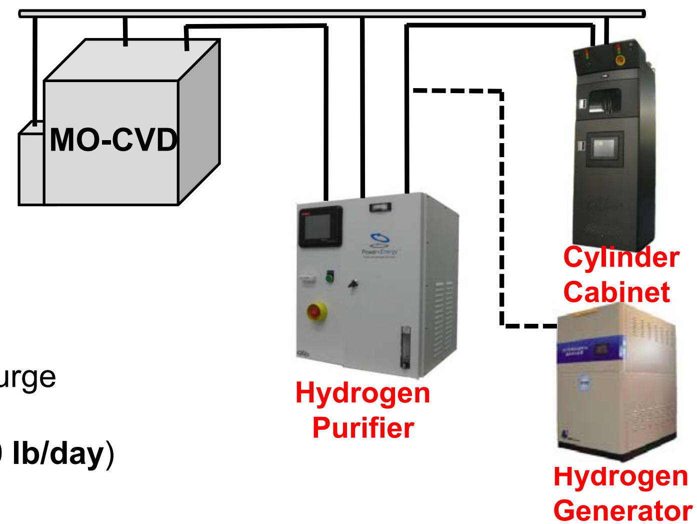
## Leverage commercial experience in $H_2$ purifiers for coal-derived syngas

PE2100 Series Instrument / Lab Purifiers

Power+Energy
Fueling the Hydrogen Economy


PE9000S Purifiers


PE9000S Systems with Z-Purge Cabinets
(**up to 320 Nm³/h $H_2$ ≈ 1500 lb/day**)




- P+E established 1993, Philadelphia, PA, USA
- Commercial Supplier of $H_2$ Purifiers for Semiconductors, Labs, Instruments
- Global customer base; more than 850 $H_2$ 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.


**$H_2$ 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 $H_2$ for coal-derived syngas**

United Technologies Research Center

# 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]**

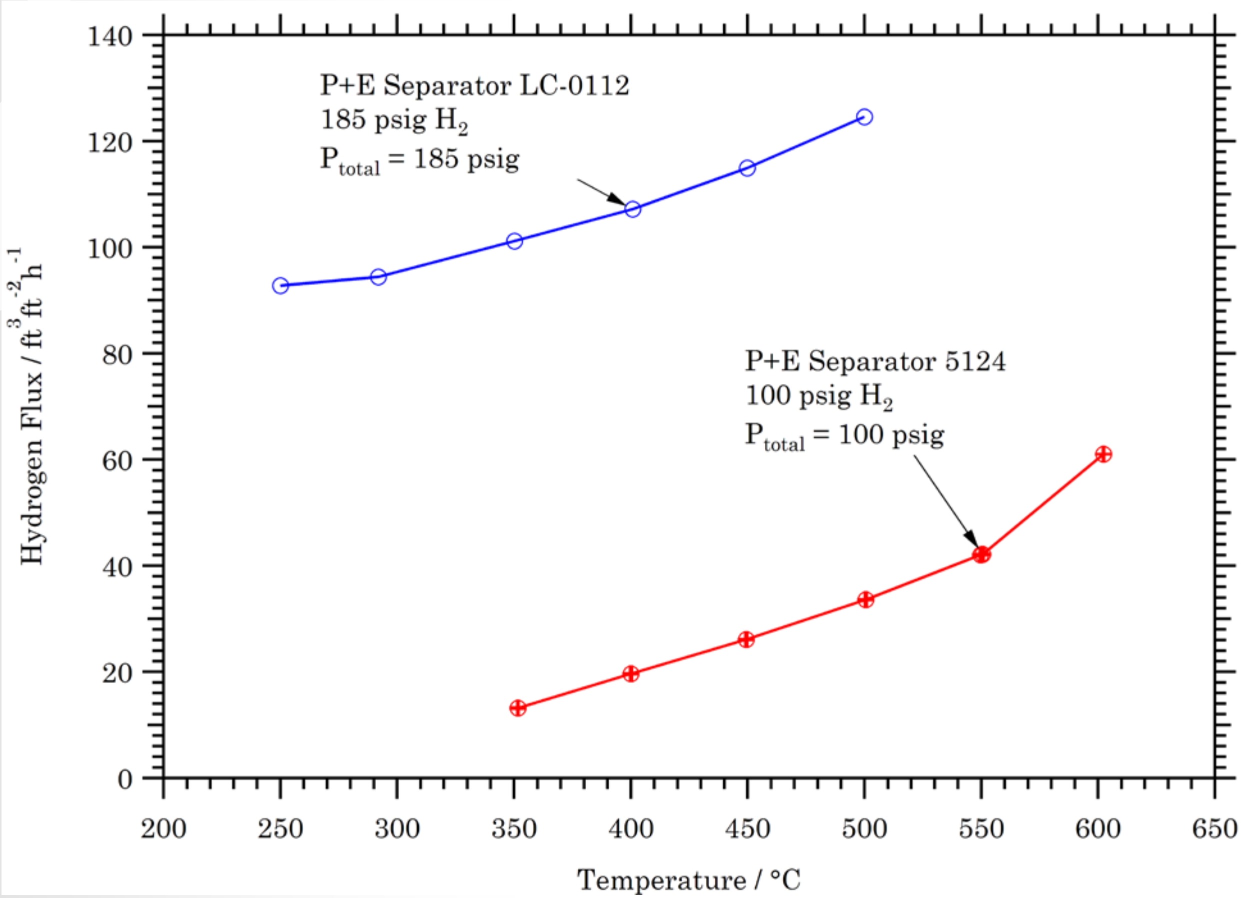
**Pilot-scale (2 lb/day $H_2$) Separators [Phase I-III]**


**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 $H_2$ permeability and flux with proprietary surface modification




- Retain sulfur resistance of standard PdCu, but with enhanced $H_2$ flux
- If surface modification is not successful, will get same performance as PdCu
- Permeability is 5-6 times higher than standard PdCu

United Technologies Research Center

# Materials of Construction Coupon Testing (Approach)

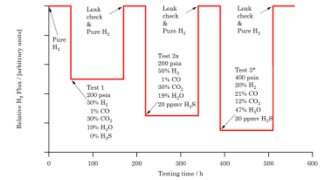
## DOE Test 2A to downselect best materials for separator construction

- $H_2S$ & $CO_2$ 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 |
|---|---|---|---|---|---|---|---|---|
| Component | Wt.% | Wt.% | Wt. % | Wt.% | Wt.% | Wt.% | Wt. % | Wt. % |
| 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 | 2.5max | 3 | 0 | 0 |
| Si | 0.08 max | 0.75 max | 1.5max | 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 |
| Others | 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 |

United Technologies Research Center

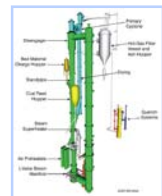
# Testing Plan for Phase I (Approach & Future Work)




Dec
Complete test stand modifications & Construct laboratory-scale separators

Apr
Delivery of first 2 lb/day $H_2$ separator

Apr - Dec
Pilot-scale separator testing



Sep
Pilot-scale gasifier test completed

Sep
Submit renewal application to DOE

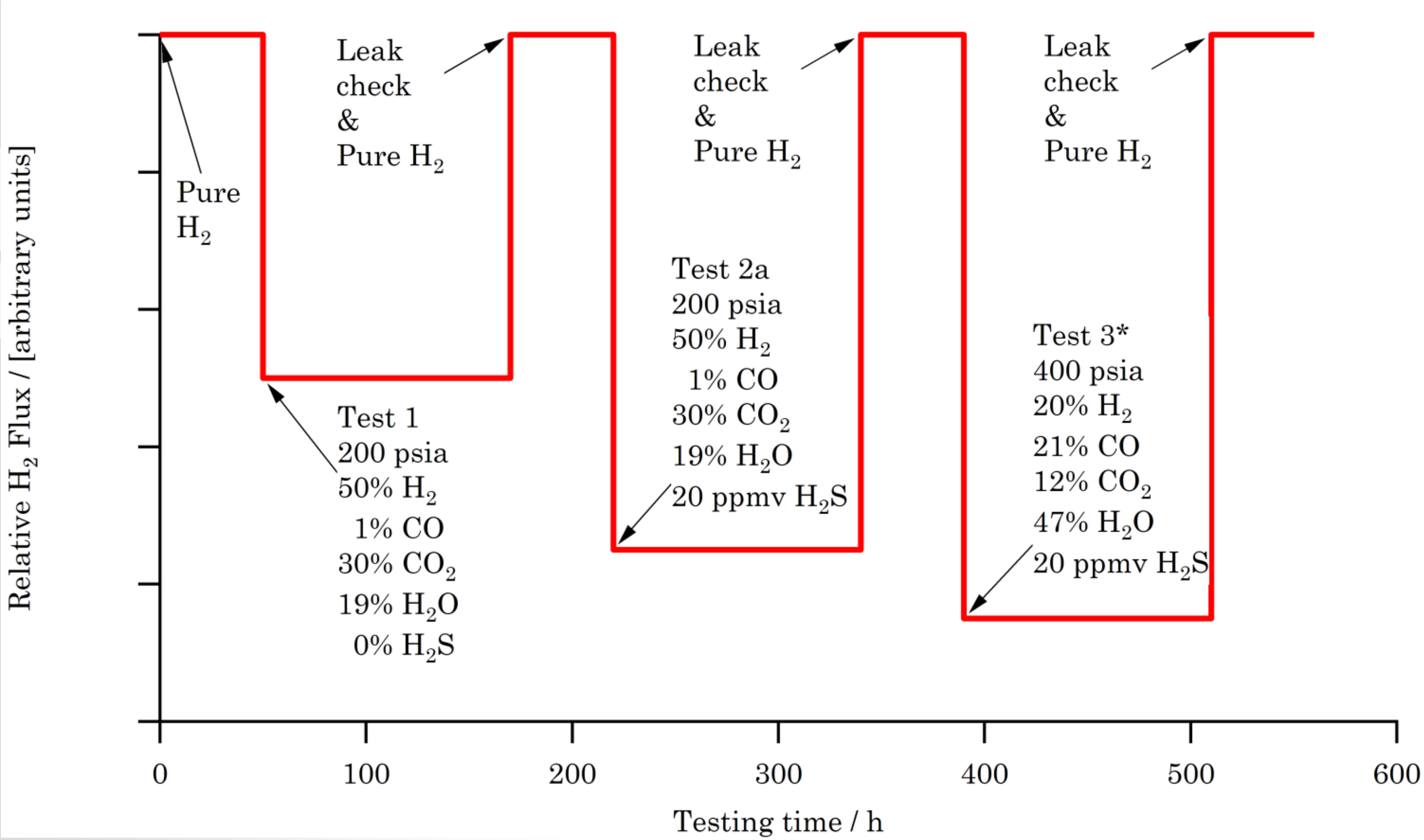
Oct-10 | Nov | Dec | Jan | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec | Dec-11

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)



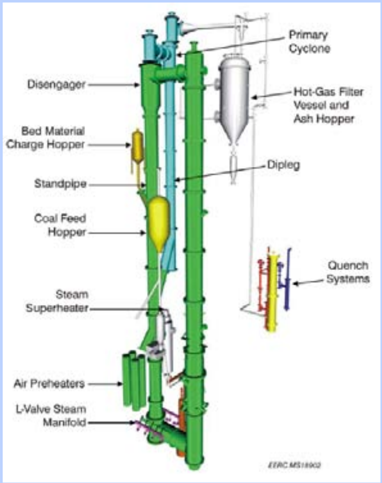

- Four tests before end of Phase I
- Examine temperature (2) and materials of construction (2 alloys)
- Perform thermal cycling tests at end of durability test
- Perform detailed breakdown and characterization of separators

# 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.

| | Phase I | | Phase II |
|---|---|---|---|
| Syngas component (Mole %) | EFG | FBG | TRDU |
| $H_2$ | 20-30 | 25-40 | 25-40 |
| CO | 20-30 | 15-25 | 15-25 |
| $CH_4$ | 0-0.5 | 1-5 | 0.5-4 |
| $C_2H_6$ | 0 | 0.5-1 | <0.5 |
| $C_2H_4$ | 0 | 0.5-1 | <0.5 |
| $C_3H_8$ | 0 | 0-0.5 | <0.5 |
| $CO_2$ | 25-35 | 25-35 | 20-40 |
| $N_2$ | 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 |
| $O_2$/coal ratio | 0.5-1.0 | 0.3-0.8 | 0.3-0.8 |
| $H_2O$/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 |



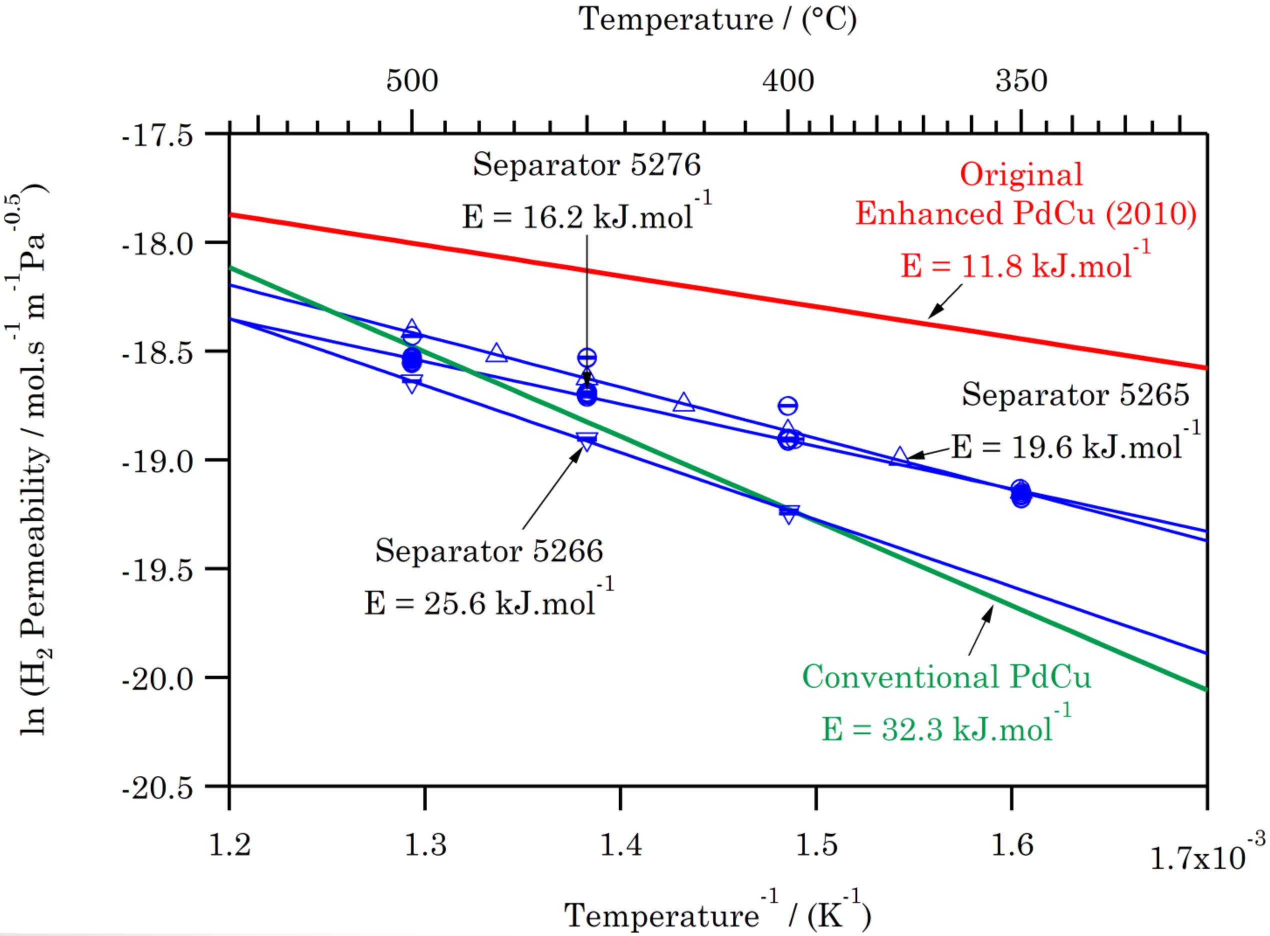

Performance testing on coal gasifier syngas

EERC Energy & Environmental Research Center

- One-week demonstration test during Phase I with 2 lb/day $H_2$ separator
- Use EERC's small, bench-scale gasifiers capable of producing up to 10 lb/day $H_2$

# $H_2$ Permeability versus Temperature (Technical)

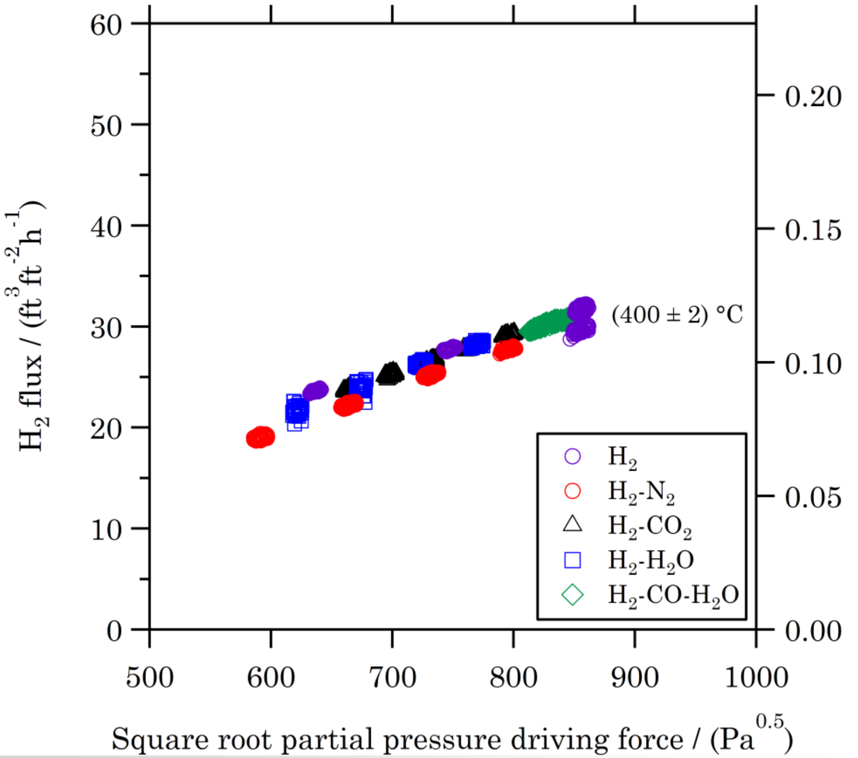
## Initial enhanced PdCu membranes are improved over conventional PdCu; Coating application will be improved for next separators

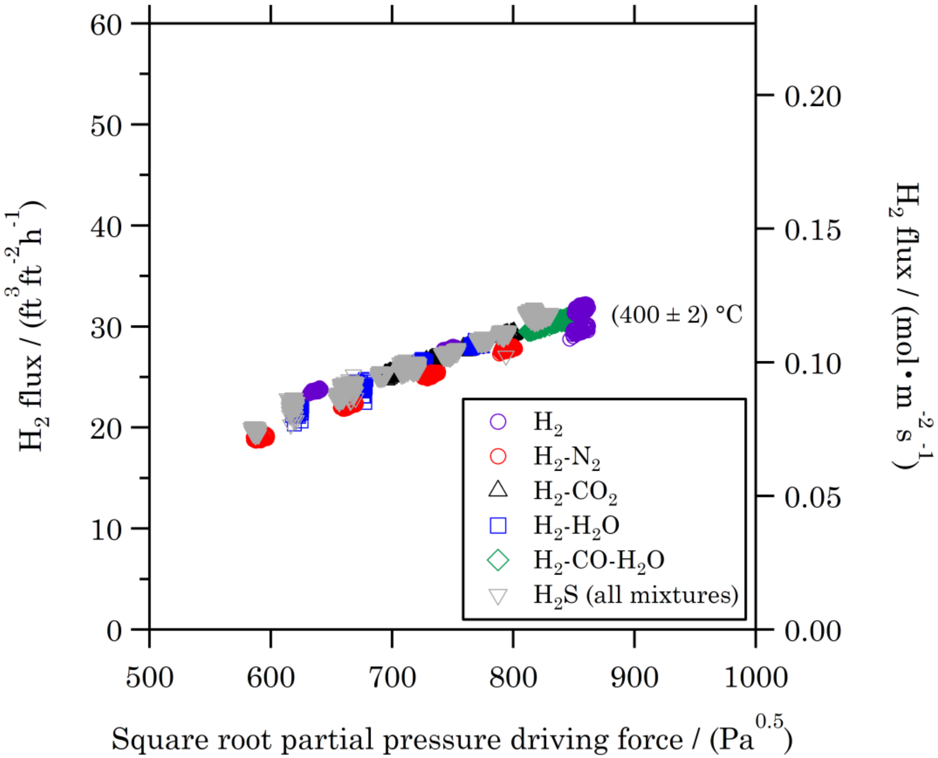



- Permeability of new separators less than original one tested in 2010
- Membrane processing under improvement for next separators

# Impact of Gas Contaminants on $H_2$ Flux (Technical)

## $H_2S$ and CO have negligible impact on $H_2$ flux at temperatures ≥400 °C



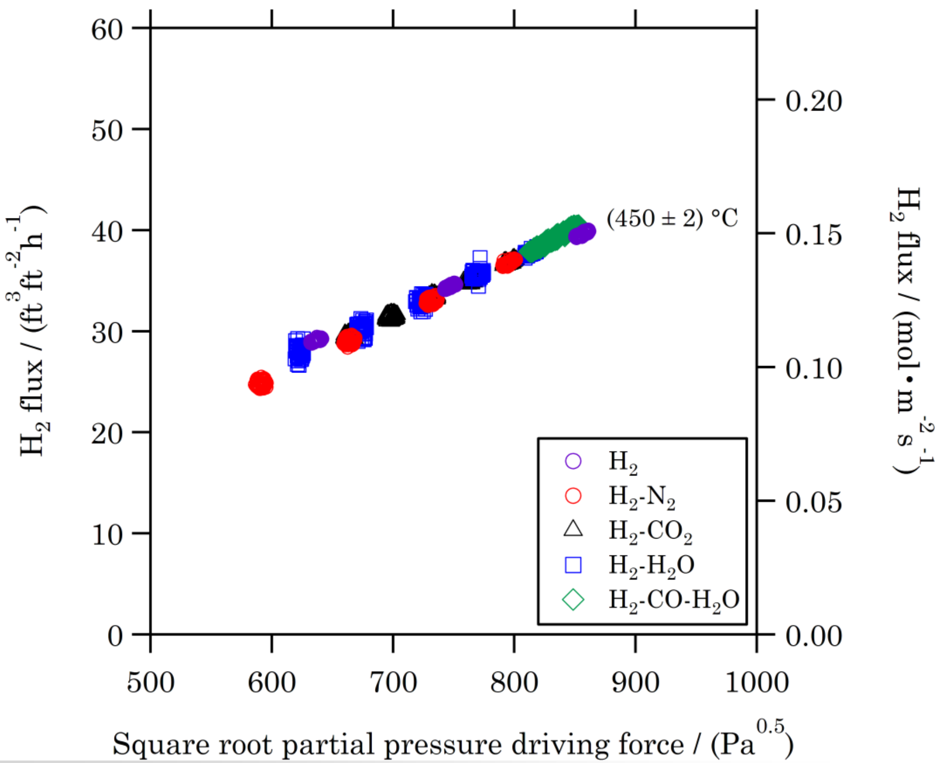



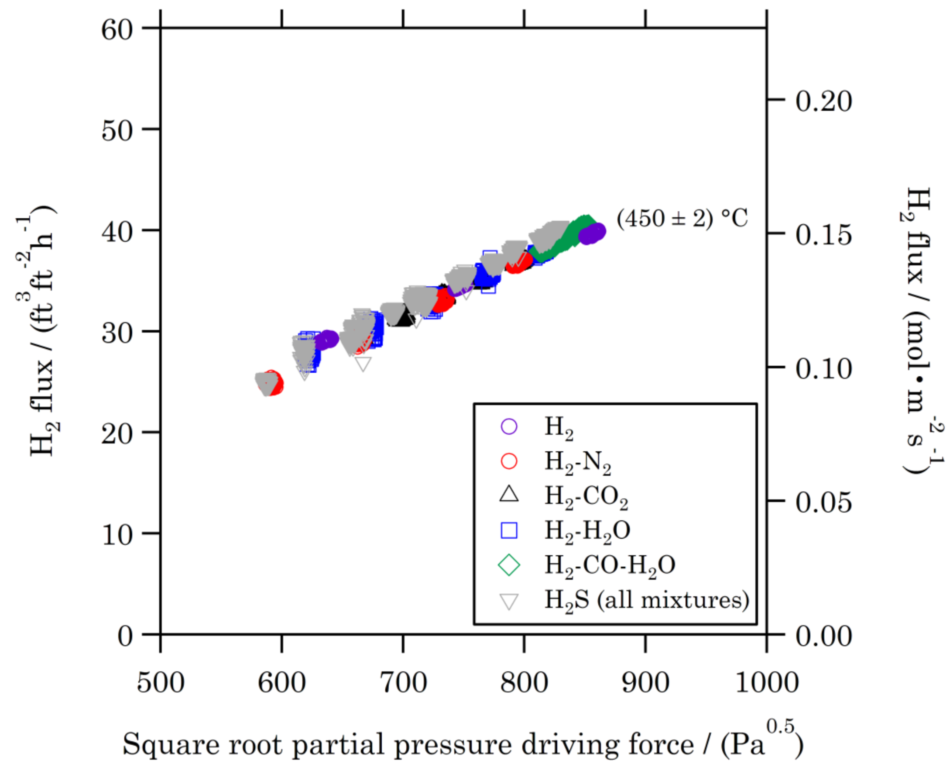

- Total pressure =14.7 psig to 185.2 psig
- Temperature = 400 °C to 500 °C
- $H_2$ = 60% to 100%
- $N_2$ = 10% to 40%
- $CO_2$ = 10% to 30%
- $H_2O$ = 7% to 36%
- CO = 0.5% to 2.1% (with 0.9% to 4.5% $H_2O$ to prevent coking)
- $H_2S$ = 5 ppmv to 39 ppmv

United Technologies Research Center

# Impact of Gas Contaminants on $H_2$ Flux (Technical)

## $H_2S$ and CO have negligible impact on $H_2$ flux at 450 °C



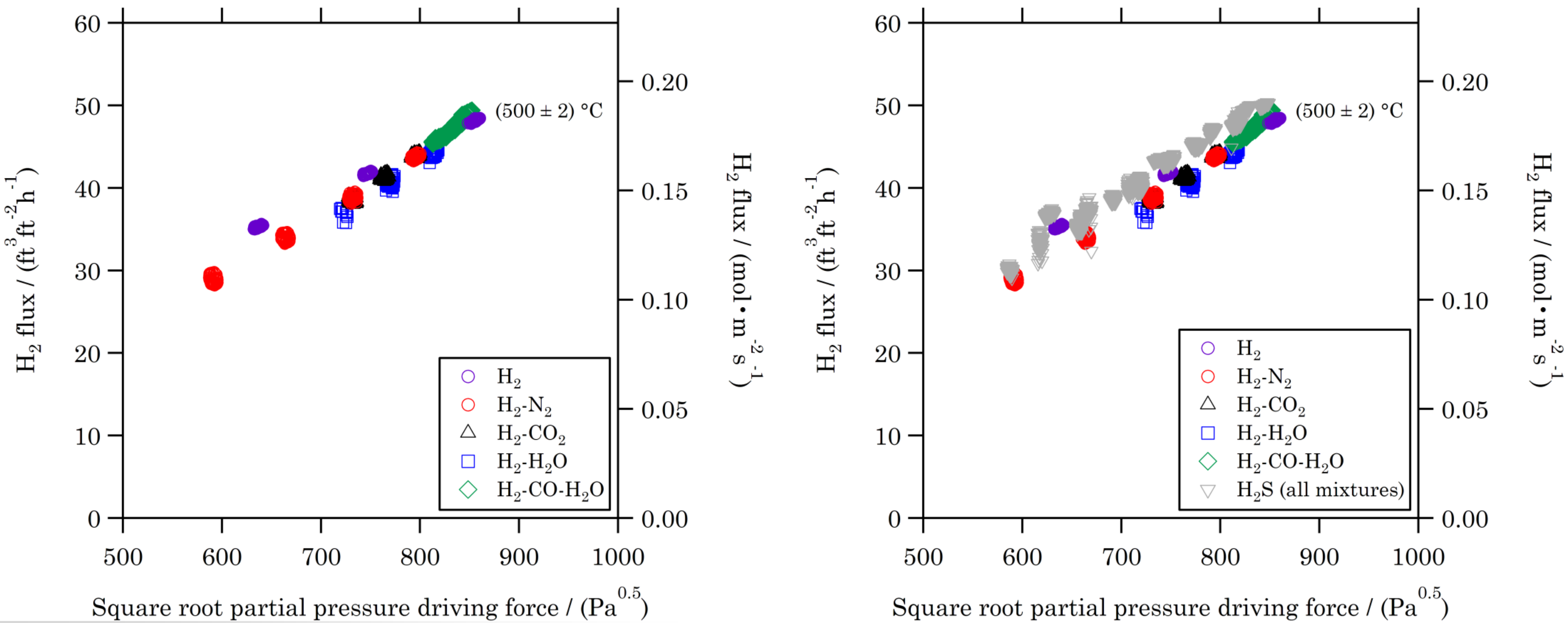




- Results similar to 400 °C data
- Performance at temperatures ≥400 °C driven by $H_2$ partial pressure

United Technologies Research Center

# Impact of Gas Contaminants on $H_2$ Flux (Technical)

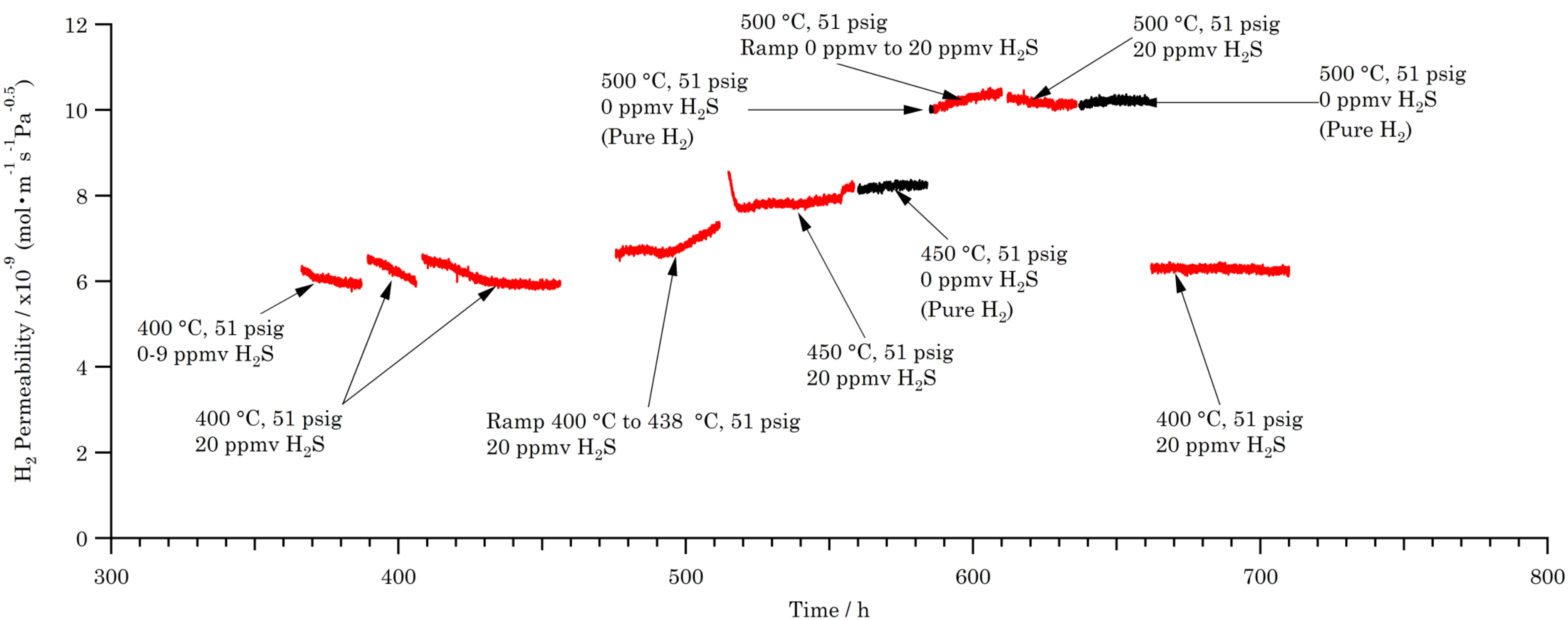
$H_2S$ and CO have negligible impact on $H_2$ flux at 500 °C




- Results similar to 400 °C & 450 °C data
- More data variance present in some 500 °C data
- Performance at temperatures ≥400 °C driven by $H_2$ partial pressure

# $H_2S$ Durability Experiments (Technical)

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



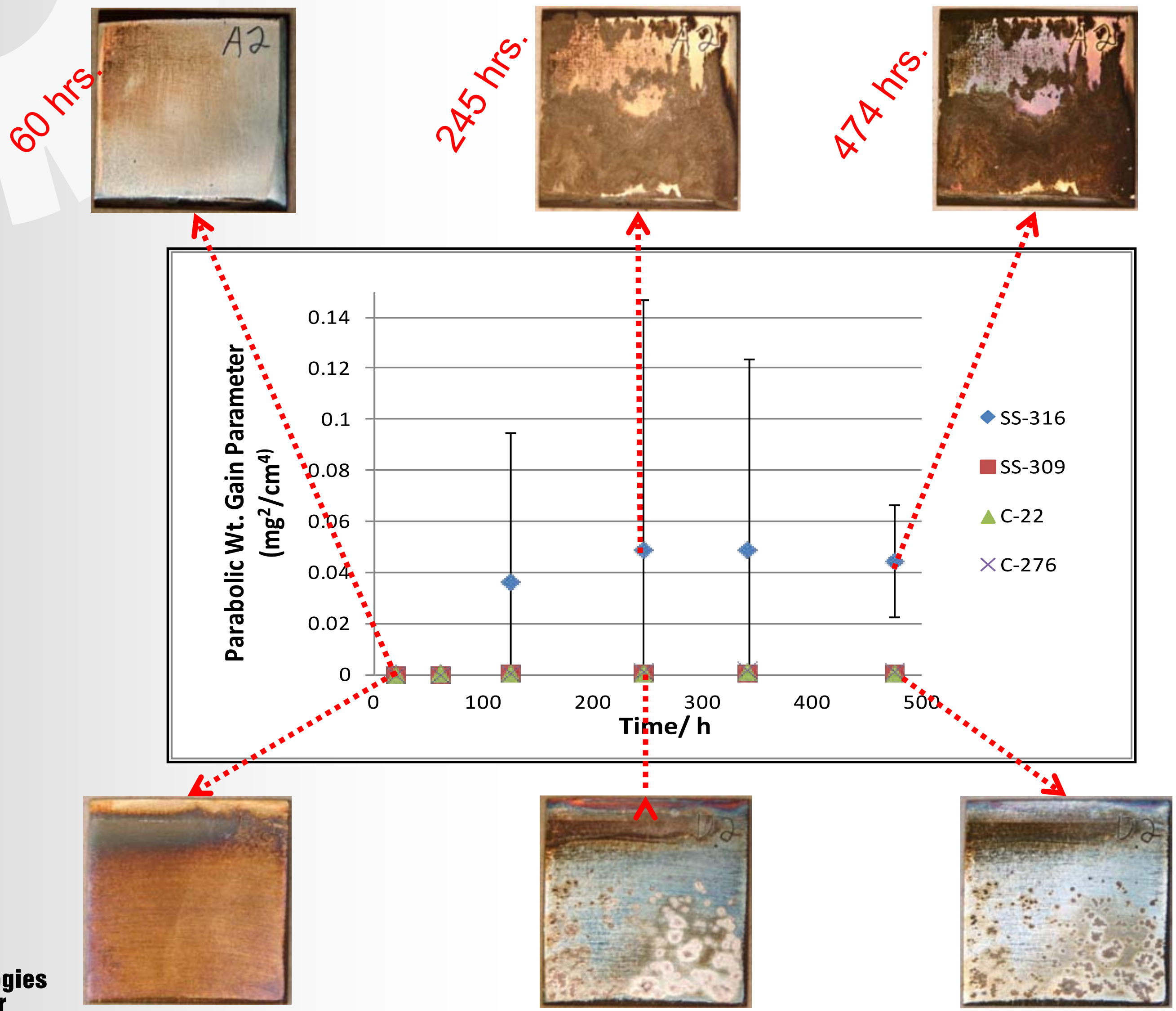

- Dräger tube measurements for $H_2S$ verified feed concentration
- Additional evidence that sulfur has a negligible impact on $H_2$ flux at temperatures ≥400 °C with 20 ppmv $H_2S$
- Separator tested for a total time of 1031 hours (618 hours with $H_2S$)

United Technologies Research Center

# 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

UTRC
Principal Investigator
Dr. Emerson

UTRC
Project lead
Dr. Thibaud-Erkey

Power+ Energy
Membrane Module Manufacturing
Dr. Bossard

Power+Energy
Fueling the Hydrogen Economy

EERC-UND
Membrane Testing at Coal Gasifier
Mr. Stanislowski

EERC
Energy & Environmental Research Center
Putting Research into Practice

UTRC
Material Evaluation/Post-test analyses
Mr. Magdefrau

UTRC
Lab scale evaluation
Dr. She

# Project Summary

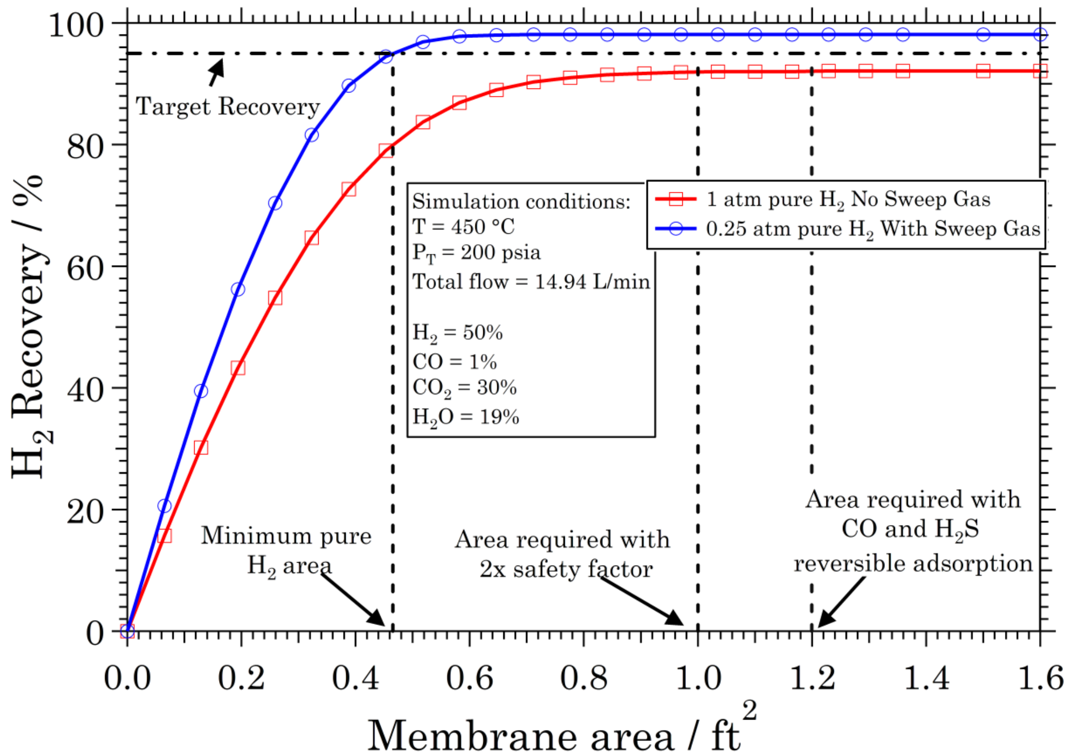
| Performance Criteria | Units | DOE 2015 Target | Current Status |
|---|---|---|---|
| $H_2$ Flux | $ft^3h^{-1}ft^{-2}$ | 300 | 125<br>(500 °C, enhanced PdCu)<br>(200 psia feed, 185.3 psid) |
| Temperature | °C | 250–500 | 250–600 |
| Sulfur tolerance | ppmv | >100 | 800 h at 100 ppmv S<br>618 h at 5–39 ppmv S<br>4 h at 487 ppmv S |
| Cost | $/ft^2$ | <100 | 400–500<br>(without recycle & leasing strategy) |
| ΔP operating capability | psi | 800–1000 | 200 |
| CO tolerance | – | Yes | 13.3% CO at 90 psia<br>>9% CO at 204.7 psia |
| $H_2$ 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

# Methodology for Membrane Sizing (Approach)

Reduce performance risk by appropriately sizing initial 2 lb/day $H_2$ separators based on current PdCu alloy




- Sweep gas necessary to achieve >95% $H_2$ recovery
- Increased minimum area needed for pure $H_2$ 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

$$J = \frac{Q_{\mathrm{eff}}}{l}\left(P_1^{0.5} - P_2^{0.5}\right)$$

Flux: $J$; Permeability: $Q_{\mathrm{eff}}$; Permeance: $\frac{Q_{\mathrm{eff}}}{l}$; Hydrogen driving force: $\left(P_1^{0.5} - P_2^{0.5}\right)$

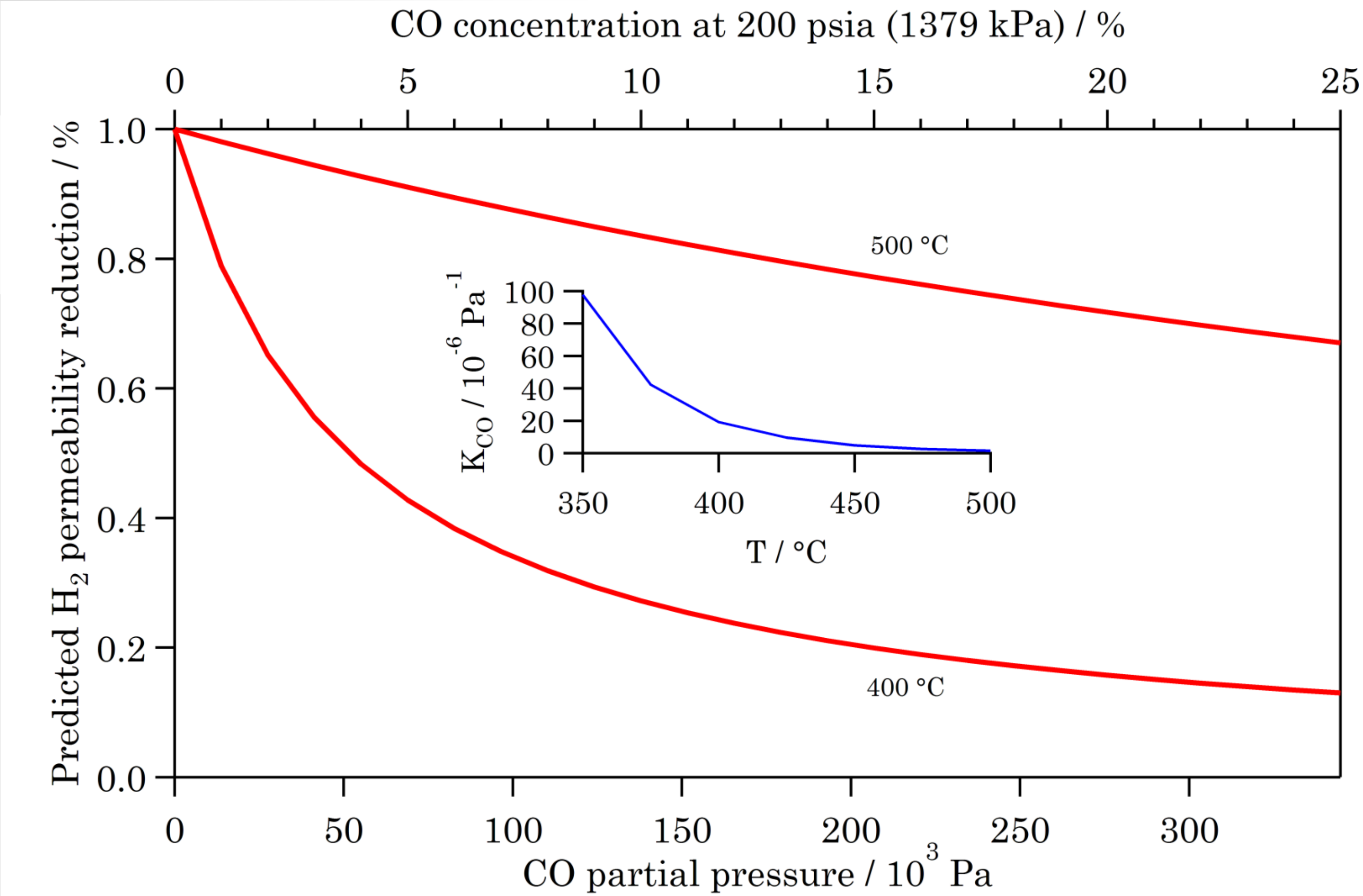
$$Q_{eff} = \frac{Q_{H_2}}{1 + K_{CO}P_{CO} + K_{CO_2}P_{CO_2} + K_{H_2O}P_{H_2O} + K_{N_2}P_{N_2} + K_{H_2S}P_{H_2S}}$$

**Experimental Objectives**

- Obtain separators' permeability as a function of temperature with pure $H_2$
- Quantify the effect of different non-poison gas species on $H_2$ permeability
- Determine adsorption coefficients ($K_i$) 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



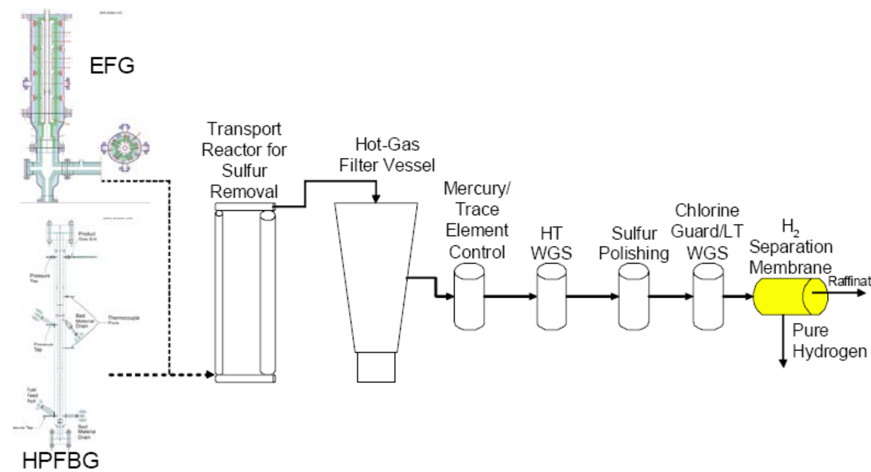

- Original expectation was for 1% CO to reduce the $H_2$ flux by ≈20% at 400 °C
- Thorough testing in 2011 shows negligible impact at temperatures ≥400 °C

# 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