

# Experimental Demonstration of Advanced Palladium Membrane Separators for Central High-Purity Hydrogen Production

(DE-FC26-07NT43055)

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United Technologies Research Center

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Project ID #PD41

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# Overview & Objectives

## ■ Timeline

- 6/15/07 to 6/14/09
- 42% complete

## ■ Budget

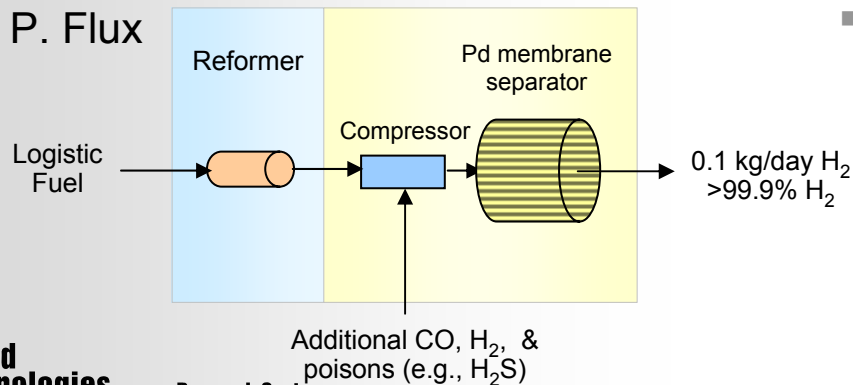
- \$1497k (\$1198k from DOE)

## ■ Partners

- Power+Energy
  - Membrane separator fabrication
- Metal Hydride Technologies
  - H<sub>2</sub> solubility measurements

## ■ Barriers

- K. Durability
- L. Impurities
- N. Hydrogen Selectivity
- P. Flux



## ■ Objectives

- **Confirm the high stability and resistance of a PdCu trimetallic alloy** to carbon and carbide formation and, in addition, resistance to sulfur, halides, and ammonia
- **Develop a sulfur, halide, and ammonia resistant alloy membrane** with a projected hydrogen permeance of  $25 \text{ m}^3\text{m}^{-2}\text{atm}^{-0.5}\text{h}^{-1}$  at 400 °C and capable of operating at pressures of 12.1 MPa (~120 atm, 1750 psia)
- **Construct and experimentally validate the performance of 0.1 kg/day H<sub>2</sub> PdCu trimetallic alloy membrane separators** at feed pressures of 2 MPa (290 psia) in the presence of H<sub>2</sub>S, NH<sub>3</sub>, and HCl

# DE-FC26-07NT43055 Project Status Scorecard

## P+E & UTRC alloy separators can meet or exceed DOE targets

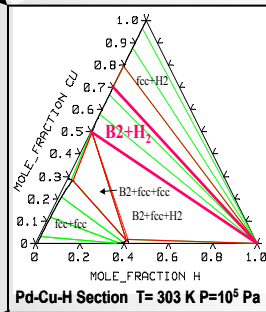
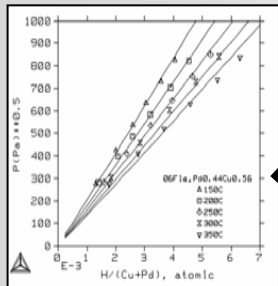
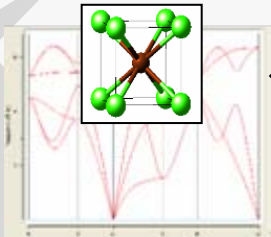
| Metric                               | 2010 DOE Target                                          | Current Project Status                                                                                                                                                                                                                | Notes                                                                                                                                                                                                                                                                                 |
|--------------------------------------|----------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Flux rate</b>                     | 200–250 ft <sup>3</sup> ft <sup>-2</sup> h <sup>-1</sup> | <b>525 ft<sup>3</sup>ft<sup>-2</sup>h<sup>-1</sup> ( UTRC alloy prediction)</b><br><b>120 ft<sup>3</sup>ft<sup>-2</sup>h<sup>-1</sup> (P+E alloy, 400 °C)</b><br><b>252 ft<sup>3</sup>ft<sup>-2</sup>h<sup>-1</sup> (P+E, 530 °C)</b> | <ul style="list-style-type: none"> <li>Alloy modeling predicts permeabilities much greater than PdCu (fcc) alloys</li> <li>P+E alloy can exceed DOE target at temperatures ≈&gt;480°C</li> </ul>                                                                                      |
| <b>Impurity tolerance</b>            | 20 ppmv Sulfur<br>CO/Coke tolerant                       | <b>5 ppmv H<sub>2</sub>S (P+E alloy)</b><br><b>11 ppmv NH<sub>3</sub> (P+E alloy)</b><br>CO/Coke tolerant                                                                                                                             | <ul style="list-style-type: none"> <li>P+E alloy tested subscale up to 200 hours at UTRC with no degradation</li> <li>P+E demonstrated 800 h operation with 100 ppmv H<sub>2</sub>S</li> <li>Plan to test with &gt;40 ppmv H<sub>2</sub>S, HCl; and 10 ppmv NH<sub>3</sub></li> </ul> |
| <b>Hydrogen purity</b>               | 99.5%                                                    | <b>99.9999%</b>                                                                                                                                                                                                                       | <ul style="list-style-type: none"> <li>P+E manufacturing design and manufacturing ensures no leaks</li> <li>CO &lt; 1 ppm, S &lt; 15 ppbv desired for fuel cell applications</li> </ul>                                                                                               |
| <b>ΔP and T operating capability</b> | Up to 400 psi ΔP<br>300–600 °C                           | <b>290 psid</b><br><b>350 °C – 475 °C (UTRC alloy)</b><br><b>350 °C – 600 °C (P+E alloy)</b>                                                                                                                                          | <ul style="list-style-type: none"> <li>Facilities &amp; current separator design limited to 20 atm testing</li> </ul>                                                                                                                                                                 |
| <b>Cost</b>                          | 100–1000 \$/ft <sup>2</sup>                              | <b>137–600 \$/ft<sup>2</sup> initial estimate</b>                                                                                                                                                                                     | <ul style="list-style-type: none"> <li>Based on initial estimate of \$5/scfh H<sub>2</sub></li> </ul>                                                                                                                                                                                 |
| <b>Durability</b>                    | 3 years                                                  | <b>200 h (P+E alloy at UTRC)</b>                                                                                                                                                                                                      | <ul style="list-style-type: none"> <li>P+E proven more than 2 years operation</li> <li>Planned demonstration up to 2000 h</li> </ul>                                                                                                                                                  |

# Milestone Schedule (DE-FC26-07NT43055)

Project is on track to meet milestones

| Task # | Project Milestone                                                                                                                         | Task Completion Date |                | Percent Complete |
|--------|-------------------------------------------------------------------------------------------------------------------------------------------|----------------------|----------------|------------------|
|        |                                                                                                                                           | Planned Start        | Planned End    |                  |
| 1      | Complete initial technical and economic modeling.                                                                                         | June 15, 2007        | Dec. 31, 2007  | 100%             |
| 2      | Complete advanced membrane property simulations by atomistic and thermodynamic modeling calculations.                                     | June 15, 2007        | Dec. 31, 2007  | 100%             |
| 3      | Complete the design and construction of membrane separators using sulfur resistant palladium alloy and membrane separators using Pd-CuTM. | June 15, 2007        | May 30, 2008   | 83%              |
| 4      | Complete hydrogen solubility tests using various alloys for six-to-twelve separators, and predict hydrogen permeability performance.      | Mar. 15, 2008        | June 30, 2008  | 0%               |
| 5.2    | Complete testing of "best of class" separators.                                                                                           | Mar. 15, 2008        | Sep. 30, 2008  | 0%               |
| 5.3    | Complete evaluation of advanced PdCuTM separator units.                                                                                   | June 15, 2008        | April 30, 2009 | 0%               |
| 6      | Complete the revised technical and economic modeling.                                                                                     | Dec. 1, 2008         | June 1, 2009   | 0%               |

# Technical Approach



**Virtual modeling of phase behavior & properties**

**Construction of “best commercial” & virtually developed alloy separators**

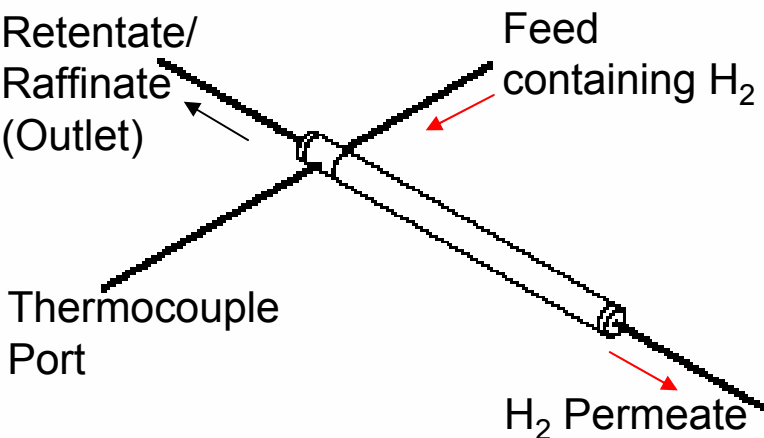


**Low pressure laboratory screening: quantify performance**



**High pressure screening: quantify durability & poison resistance**

# Power+Energy Membrane Separators



- Robust, scalable commercial design
- Design minimizes external mass transfer resistances
- Tubular design allows for membrane growth & leak free sealing
- Ten (10) separators delivered by P+E
  - Five (5) with P+E PdCu alloy
  - Five (5) with UTRC alloy
- Two (2) additional separators to be delivered mid-year



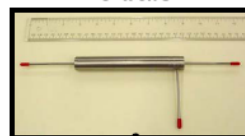
High Capacity 1300 slpm  
Modular H<sub>2</sub> Purifier System



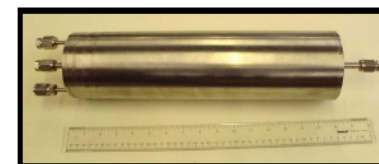
100 Watt  
5" x 0.5"



500 Watt  
6" x 0.75"



50 kWatt  
16" x 4"



# Laboratory Screening Rig ( $\leq 6$ atm)



- Steam generator for  $\text{H}_2\text{O}$  addition to gas mixture
- Operation from 1–6 atm (absolute)
- Furnace capable of temperatures 300–650 °C
- Capable of simulating different gas compositions ( $\text{CO}$ ,  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{N}_2$ ) from cylinders and house  $\text{H}_2$
- Addition of poisons from gas cylinders or water supply
- Computer automated testing plans

# Laboratory Screening Tests

Quantify separator permeability & effects of major gas species

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

Flux

Permeability

Effective Permeability Neglecting External Mass Transfer Resistance

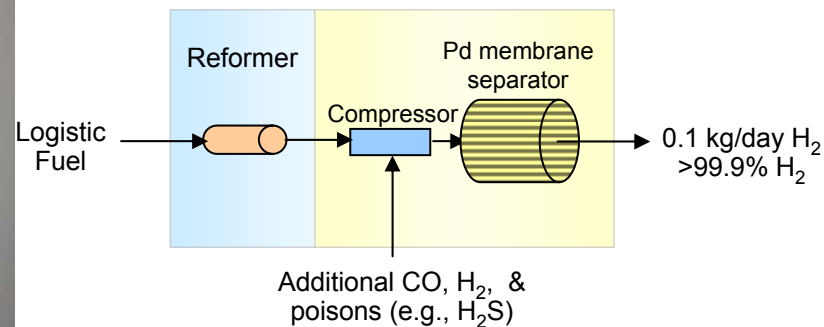
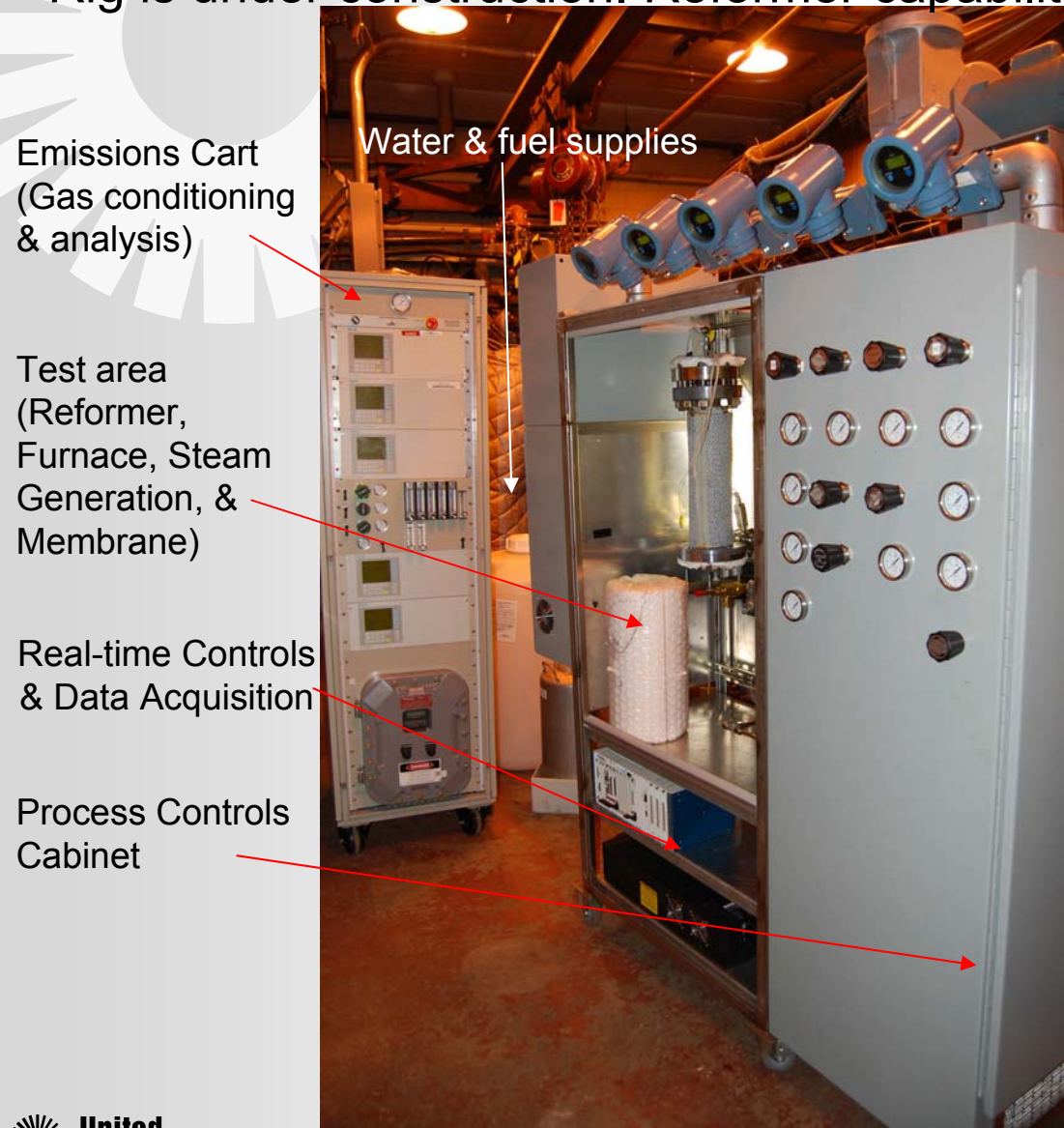
$$Q_{\text{eff}} = \frac{aQ_0}{1 + \sum K_i p_i}$$
$$= \frac{aQ_{H_2}}{1 + K_{CO}p_{CO} + K_{CO_2}p_{CO_2} + K_{H_2O}p_{H_2O} + K_{N_2}p_{N_2}}$$

## Experimental Objectives

- Obtain separators' permeability as a function of temperature with pure H<sub>2</sub> (Q<sub>H2</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

# Pressurized Reformate Testing Rig (>10 atm)

Rig is under construction. Reformer capability enabled; fully operational May.



**Test Configuration**

# High Pressure Tests on Real Reformate

Quantify separator durability & effects of poisons

Effective Permeability Neglecting External Mass Transfer Resistance

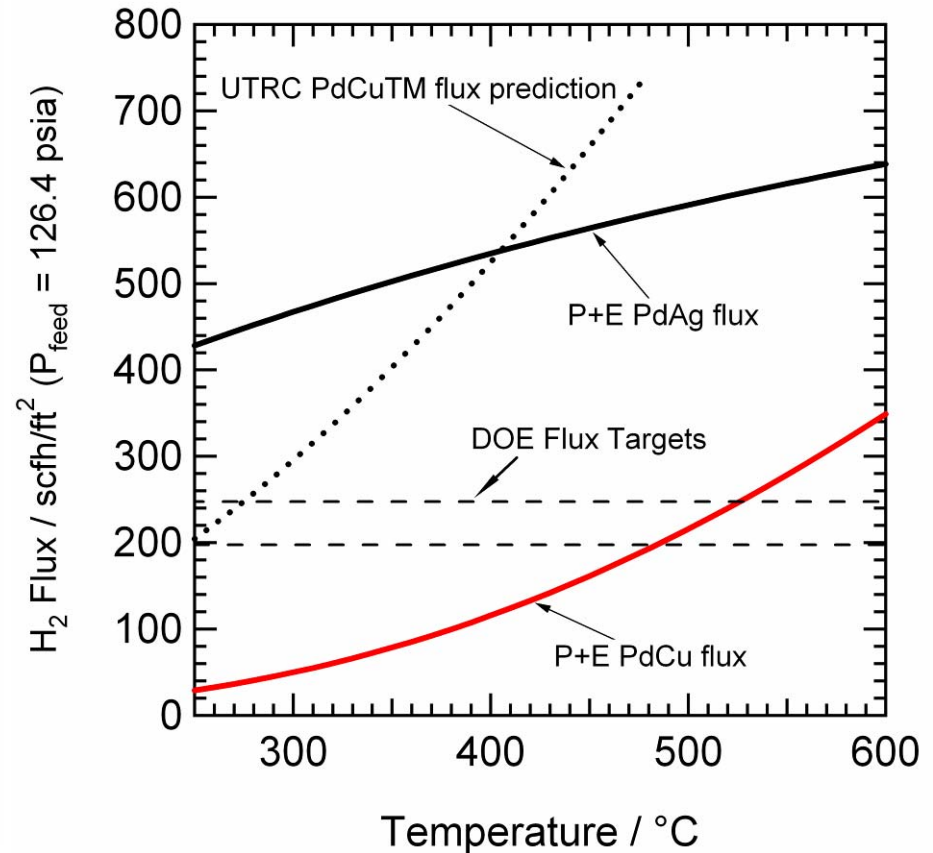
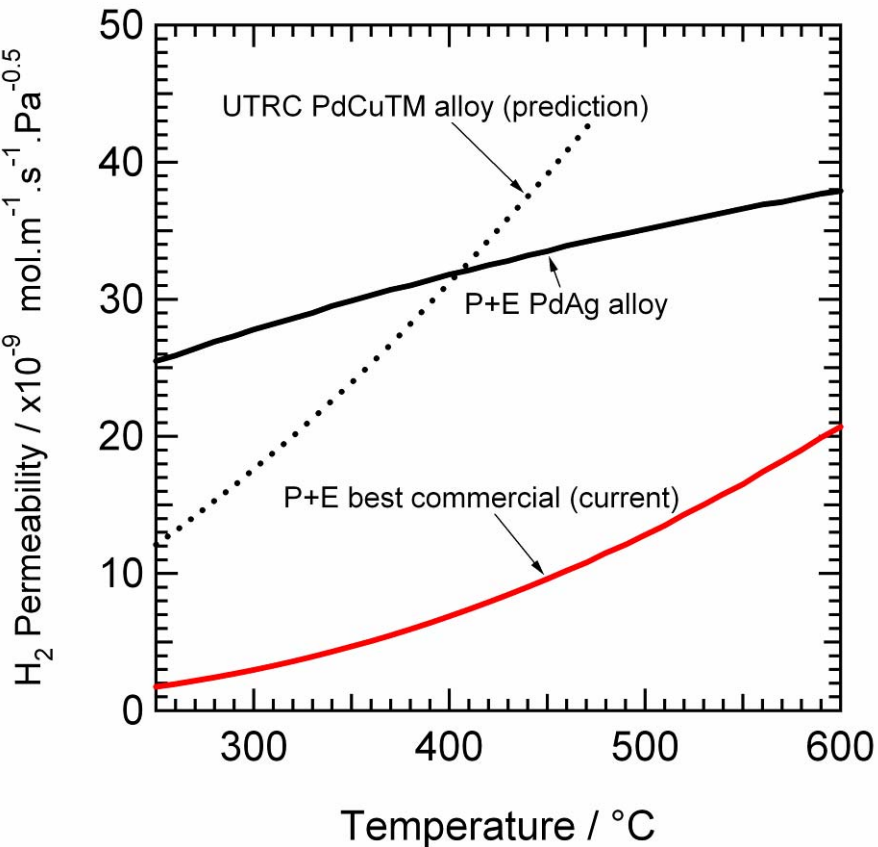
$$Q_{\text{eff}} = \frac{aQ_{H_2}}{1 + \underbrace{K_{CO}p_{CO} + K_{CO_2}p_{CO_2} + K_{H_2O}p_{H_2O} + K_{N_2}p_{N_2}}_{\text{Values from laboratory experiments}} + \underbrace{K_{H_2S}p_{H_2S} + K_{HCl}p_{HCl} + K_{NH_3}p_{NH_3}}_{\text{Quantify during reformat higher pressure tests}}}$$

## Experimental Objectives

- Quantify effect of three poisons on separators'  $H_2$  permeability
- Operate separators off of “real” gas generated from diesel reformer
- Evaluate 500-h durability of separators
- Downselect best separator alloy for longer durability testing (2000 h)

# Hydrogen Flux/Permeability for Different Alloys

Commercial P+E alloy separator can satisfy DOE's membrane requirements



- Modeling projections for UTRC PdCu ternary alloy satisfy DOE flux targets at all operating temperatures
- P+E commercial PdCu alloy meets DOE targets above 480 °C

# Preliminary Effect of Major Gas Species on PdCu Separators

Gas species compete reversibly with  $H_2$ ; CO adsorption most dominant

Preliminary fcc permeability results

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

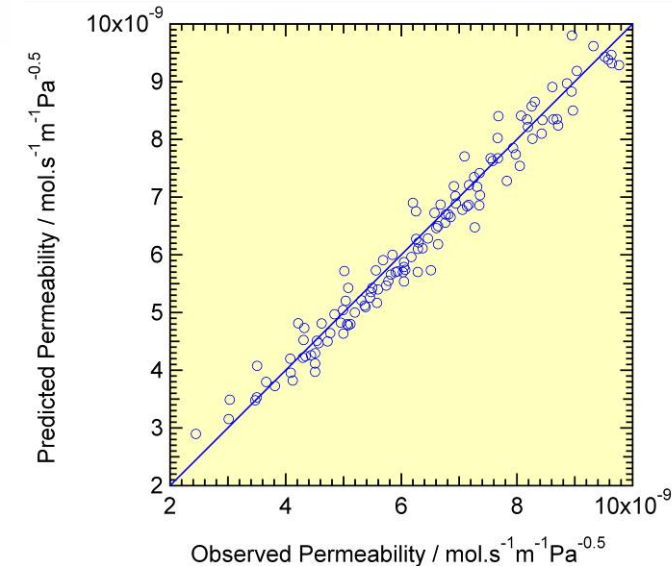
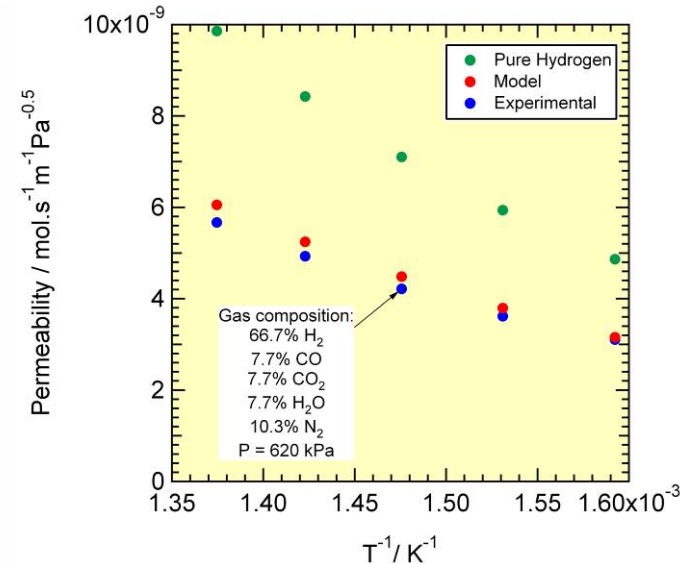
$$Q_{H_2} = \exp\left(-18.795 + 4.8187\left(1 - \frac{673.15 \text{ K}}{T}\right)\right) = 8.5 \times 10^{-7} \exp\left(\frac{-26968}{RT}\right)$$

$$K_{CO} = \exp\left((-11.831 \pm 0.115) + \ln\frac{T}{673.15 \text{ K}}\right) = 1.08 \times 10^{-8} T$$

$$K_{CO_2} = \exp\left((-13.134 \pm 0.223) + \ln\frac{T}{673.15 \text{ K}}\right) = 2.94 \times 10^{-9} T$$

$$K_{N_2} = \exp\left((-13.551 \pm 0.111) + \ln\frac{T}{673.15 \text{ K}}\right) = 1.94 \times 10^{-9} T$$

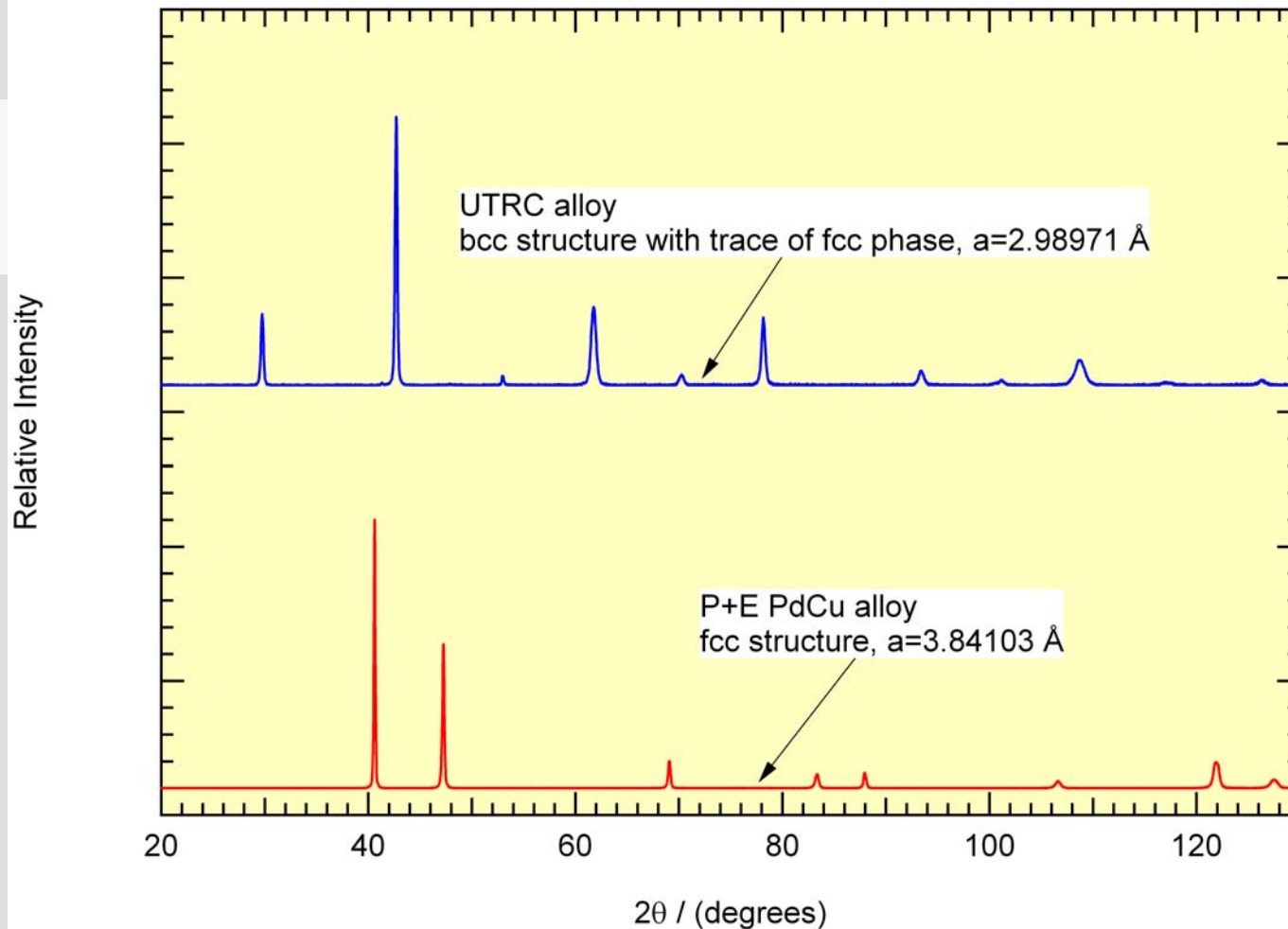
$$K_{H_2O} = \exp\left((-13.6 \pm 0.156) + \ln\frac{T}{673.15 \text{ K}}\right) = 1.84 \times 10^{-9} T$$



- Single separator preliminary results based on 123 experiments
  - T = 353 °C – 455 °C; P = 203 kPa – 620 kPa (29.4 – 89.9 psia)
  - Pure H<sub>2</sub> tests
  - Mixtures H<sub>2</sub>–N<sub>2</sub>, H<sub>2</sub>–CO–H<sub>2</sub>O, H<sub>2</sub>–CO<sub>2</sub>–H<sub>2</sub>O, H<sub>2</sub>–H<sub>2</sub>O
- Weak temperature dependence on adsorption over experimental range (≈100 °C)
  - Heats of adsorption statistically insignificant
  - Linear temperature dependency describes data
- Model agreement within 5.2% on validation mixture composition
  - 66.7% H<sub>2</sub>, 7.7% CO, 7.7% CO<sub>2</sub>, 7.7% H<sub>2</sub>O, 10.3% N<sub>2</sub>

# X-ray Diffraction Patterns of Alloy Tubes

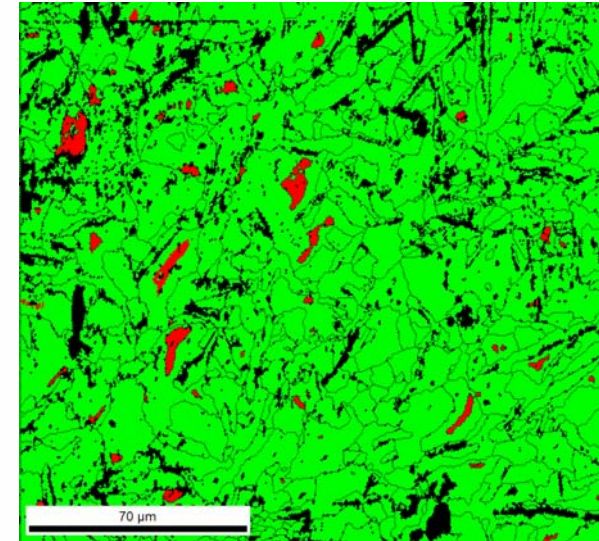
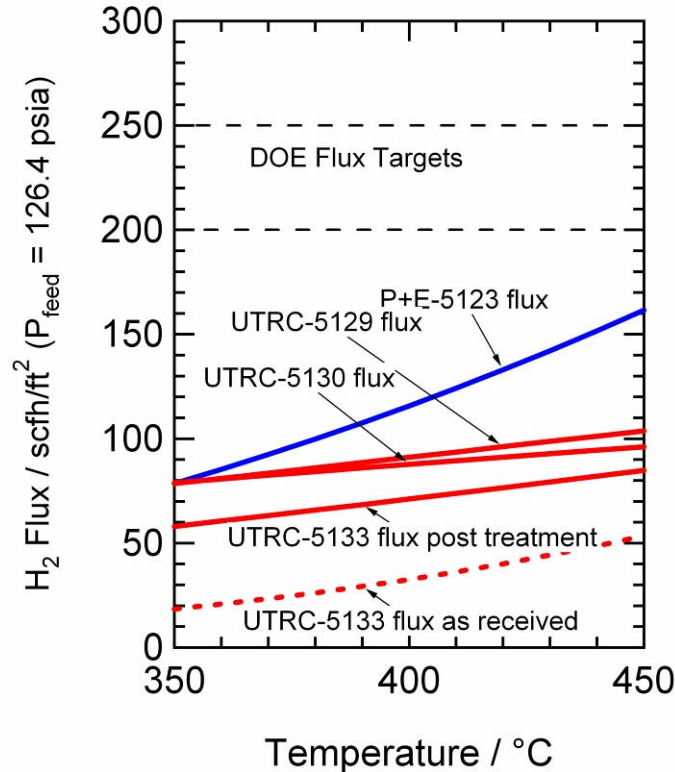
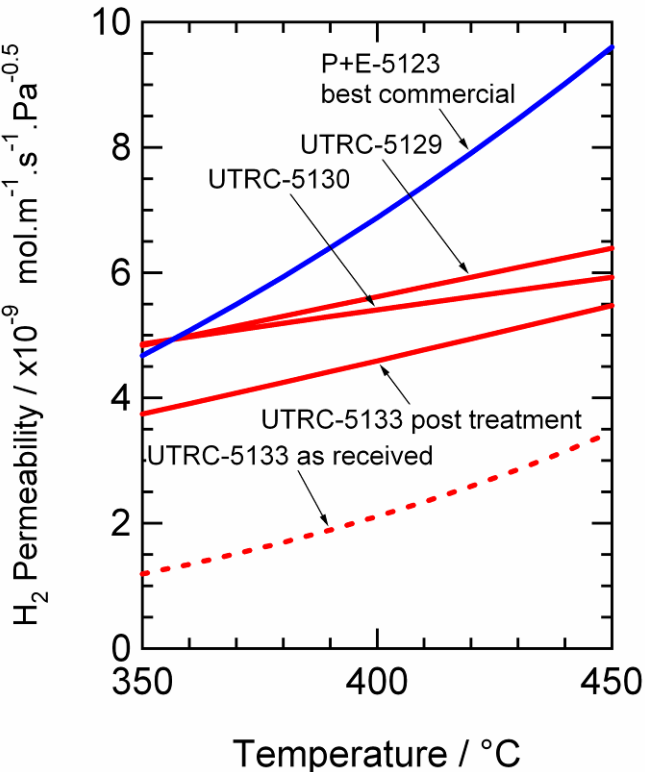
## Partial confirmation of modeling predictions on UTRC alloy



- Lattice parameters are within 1.7% of atomistic modeling predictions
- PdCu bcc phase formed in UTRC alloy as predicted

# Permeability of UTRC Alloy Separators Less Than Expected

Characterization indicates presence of binary alloy on surface



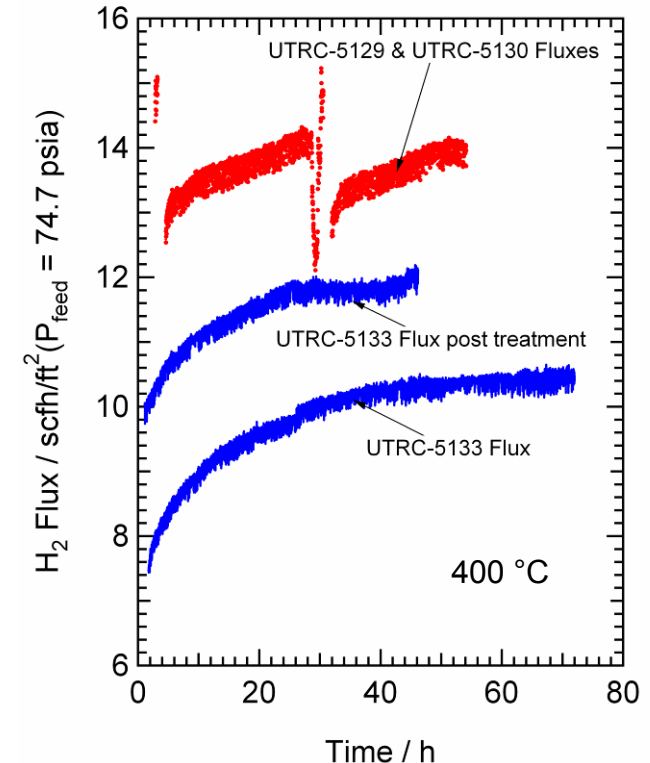
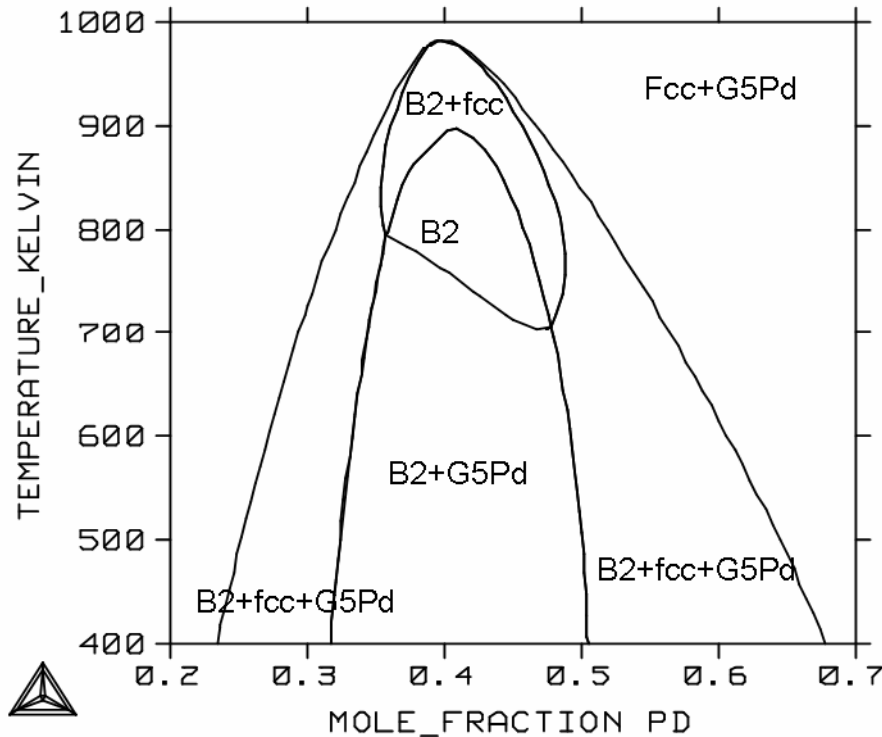
**EBSD phase map**

Green = PdG5; Red = PdCu

- Electron Backscatter Diffraction (EBSD) on individual tube indicates presence of binary Pd alloy covering surface of membrane
- Surface alloy layer 500 Å – 700 Å thick by microprobe analysis
- Heat treatments to desegregate/homogenize can improve membrane

# Removal of Low Permeability Binary by Thermal Treatment

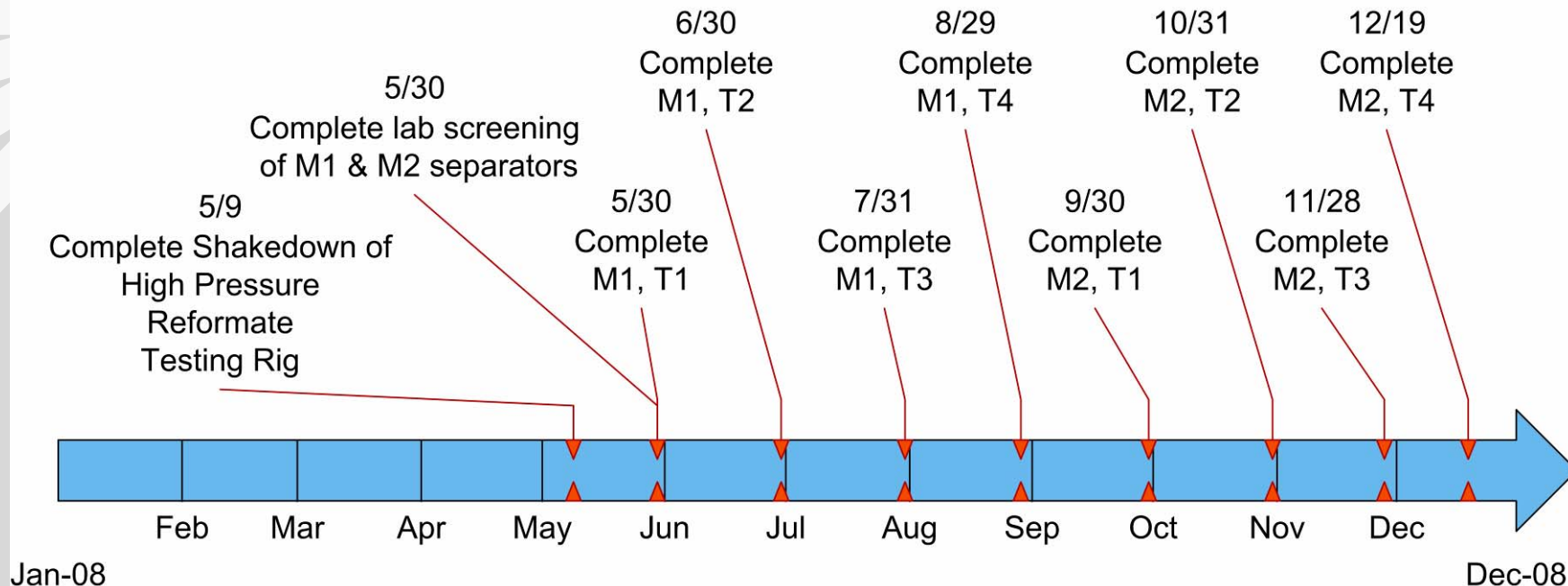
Homogenization/Desegregation work in progress



- UTRC alloy contains 47 at% Pd, targeting B2 phase
- Surface binary alloy between Pd & G5 element exists at low and high temperatures
- Binary could be formed during initial melt or during separator construction
- Heat treatments & quenching improves performance
- Etching may be necessary to remove surface resistance

# Future Work

## Focus on P+E alloy testing & UTRC alloy improvements



- Each reformate test will nominally be 500 h
- Nomenclature
  - M1 = P+E alloy; M2 = UTRC alloy
  - T1: Reformate with baseline sulfur in fuel
  - T2: Reformate plus H<sub>2</sub>S (<100 ppm H<sub>2</sub>S)
  - T3: Reformate plus NH<sub>3</sub> (<15 ppm NH<sub>3</sub>)
  - T4: Reformate plus HCl (<100 ppm HCl)
- Follow-on tests (end 2008 to mid 2009)
  - Test with a reduced steam to carbon ratio for 500 h
  - 2000 h durability demonstration with poisons

# Project Summary

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- Constructed ten (10) commercially manufactured separators for evaluation
- Evaluated performance of first fcc PdCu separator
  - Quantified effect of CO, CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O on H<sub>2</sub> permeability
  - Commercial unit can meet DOE flux targets for T>480 °C
- Produced five (5) separators with UTRC ternary composition
  - Phase segregation occurred on outer surface of membrane
  - Work in progress to improve current separator performance
- Opportunity to improve on UTRC alloy separator performance
  - Construction of two additional separators
- Higher pressure experiments using poison-doped reformat to be conducted this year
  - Quantify effect of H<sub>2</sub>S, HCl, and NH<sub>3</sub> on H<sub>2</sub> permeability

# Acknowledgments

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- United Technologies Research Center
  - Testing: John Costello, Tom Hale, Robert Hebert, Gayle Marigliani, Jeffrey Walker, & Ying She
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  - Characterization: Jeff Covington, Bruce Laube, & C. Barila
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- Metal Hydride Technologies
  - Ted Flanagan
- U.S. Department of Energy
  - Arun Bose & Daniel Cicero