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

(DE-FC26-07NT43055)

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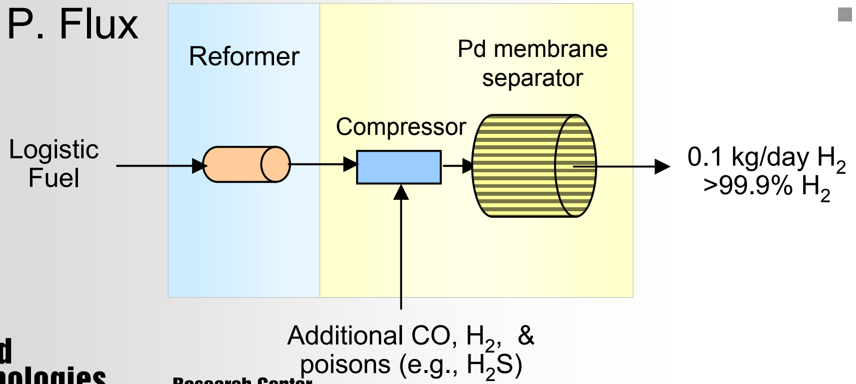
Project ID #PD41

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_2 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 $m^3m^{-2}atm^{-0.5}h^{-1}$ 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_2 PdCu trimetallic alloy membrane separators** at feed pressures of 2 MPa (290 psia) in the presence of H_2S, NH_3, and HCl

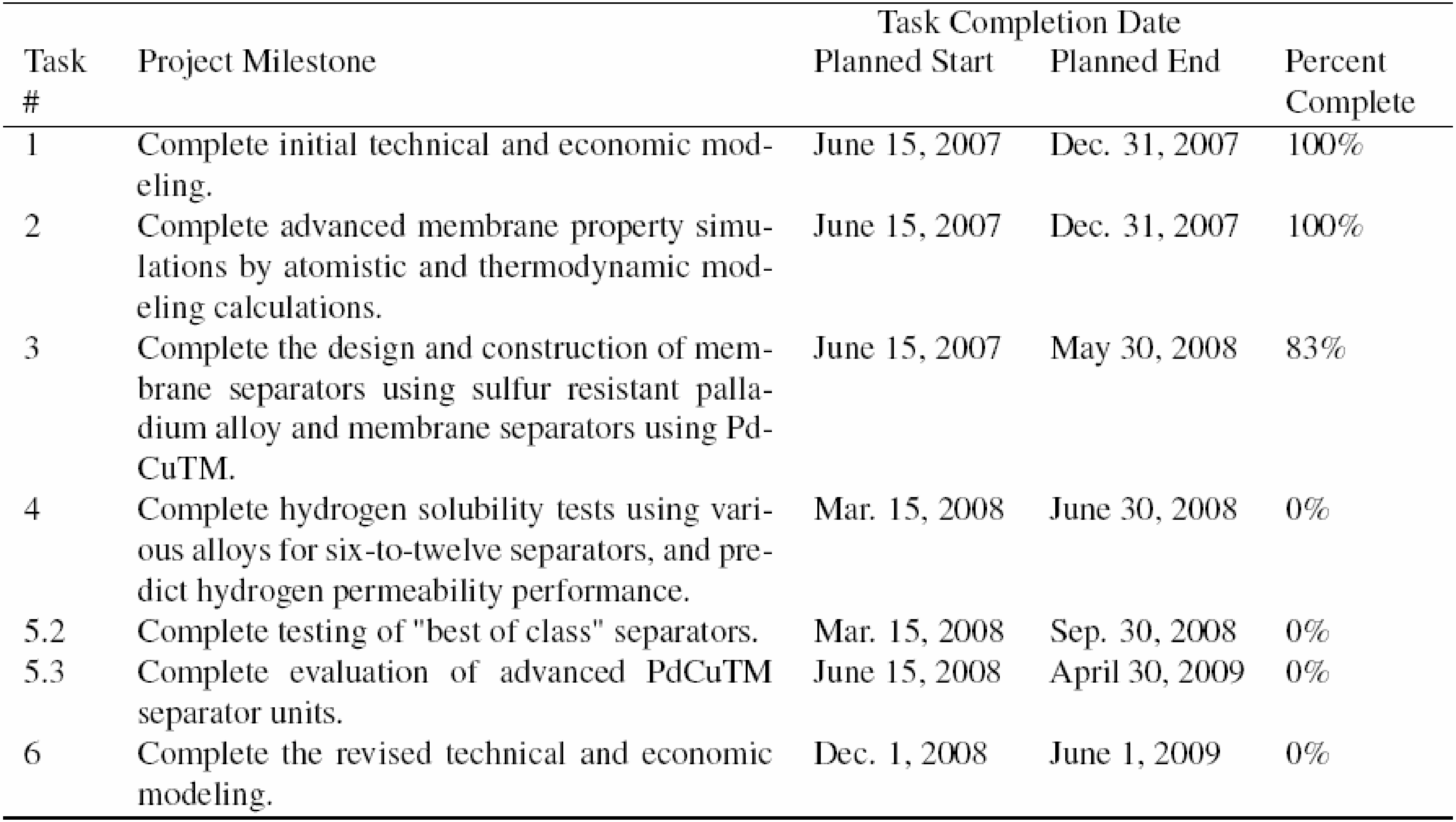
DE-FC26-07NT43055 Project Status Scorecard

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

Metric	**2010 DOE Target**	**Current Project Status**	**Notes**
Flux rate	200–250 $ft^3ft^{-2}h^{-1}$	**525 $ft^3ft^{-2}h^{-1}$ (UTRC alloy prediction)** **120 $ft^3ft^{-2}h^{-1}$ (P+E alloy, 400 °C)** **252 $ft^3ft^{-2}h^{-1}$ (P+E, 530 °C)**	- Alloy modeling predicts permeabilities much greater than PdCu (fcc) alloys - P+E alloy can exceed DOE target at temperatures ≈>480°C
Impurity tolerance	20 ppmv Sulfur CO/Coke tolerant	**5 ppmv H_2S (P+E alloy)** **11 ppmv NH_3 (P+E alloy)** CO/Coke tolerant	- P+E alloy tested subscale up to 200 hours at UTRC with no degradation - P+E demonstrated 800 h operation with 100 ppmv H_2S - Plan to test with >40 ppmv H_2S, HCl; and 10 ppmv NH_3
Hydrogen purity	99.5%	**99.9999%**	- P+E manufacturing design and manufacturing ensures no leaks - CO < 1 ppm, S < 15 ppbv desired for fuel cell applications
ΔP and T operating capability	Up to 400 psi ΔP 300–600 °C	**290 psid** **350 °C – 475 °C** (UTRC alloy) **350 °C – 600 °C** (P+E alloy)	- Facilities & current separator design limited to 20 atm testing
Cost	100–1000 $/ft²	137–600 $/ft² initial estimate	- Based on initial estimate of \$5/scfh H_2
Durability	3 years	200 h (P+E alloy at UTRC)	- P+E proven more than 2 years operation - Planned demonstration up to 2000 h

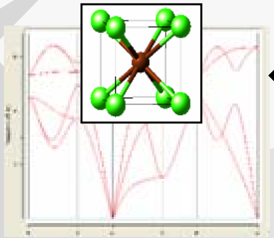
Milestone Schedule (DE-FC26-07NT43055)

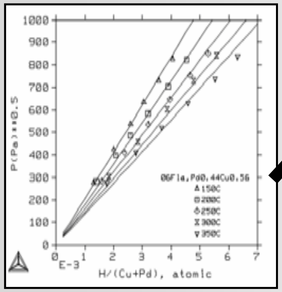
Project is on track to meet milestones

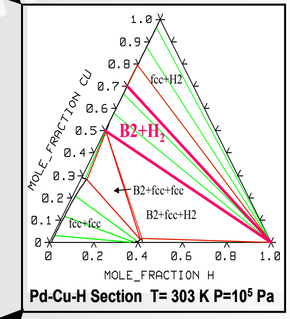


Task #	Project Milestone	Task Completion Date Planned Start	 Planned End	Percent Complete
1	Complete initial technical and economic modeling.	June 15, 2007	Dec. 31, 2007	100%
2	Complete advanced membrane property simulations by atomistic and thermodynamic modeling calculations.	June 15, 2007	Dec. 31, 2007	100%
3	Complete the design and construction of membrane separators using sulfur resistant palladium alloy and membrane separators using PdCuTM.	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







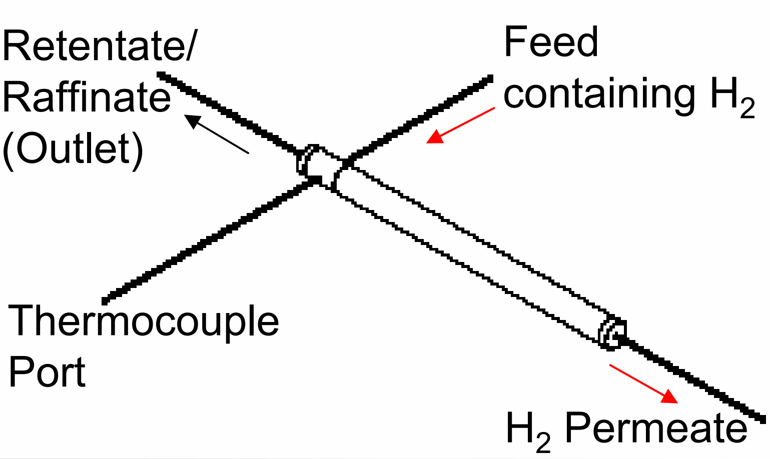
Virtual modeling of phase behavior & properties

Construction of “best commercial” & virtually developed alloy separators

Low pressure laboratory screening: quantify performance

High pressure screening: quantify durability & poison resistance

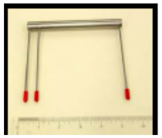
Power+Energy Membrane Separators



- 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

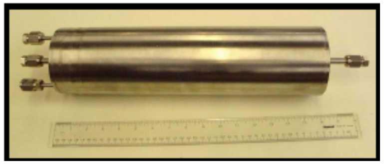
High Capacity 1300 slpm Modular H_2 Purifier System

100 Watt
5" x 0.5"

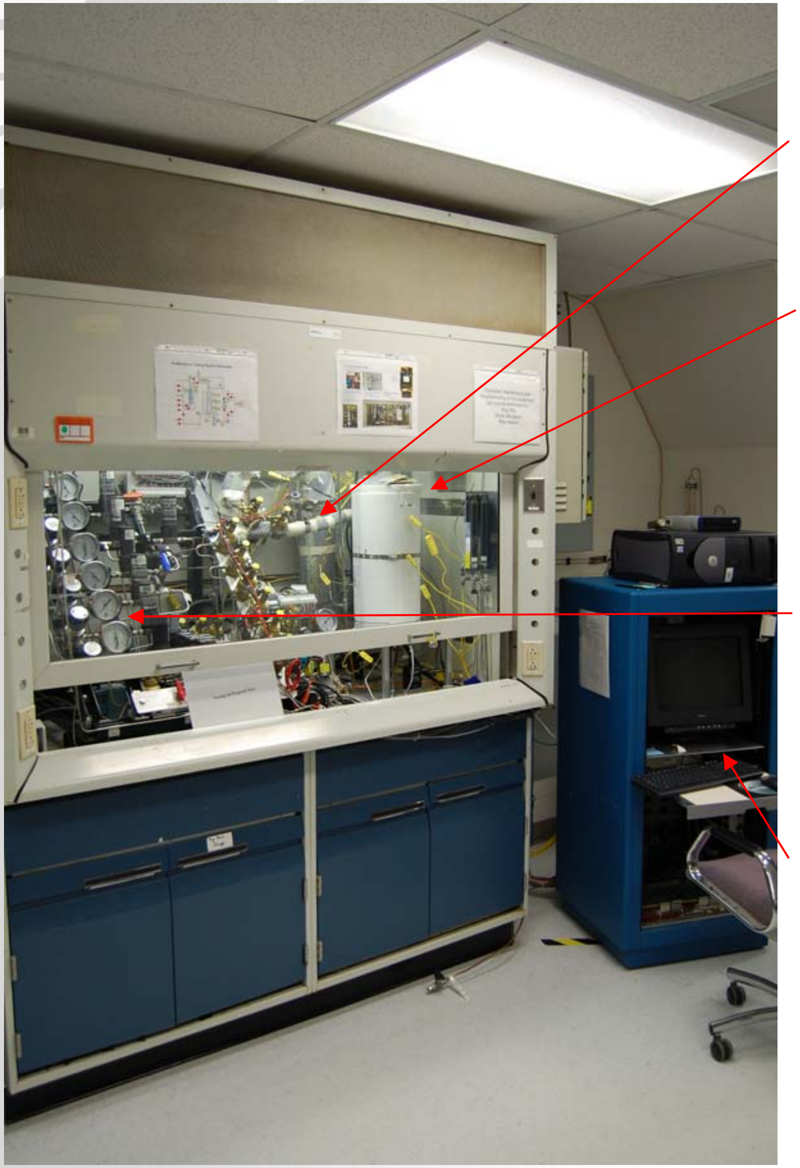


500 Watt
6" x 0.75"

50 kWatt
16"x 4"



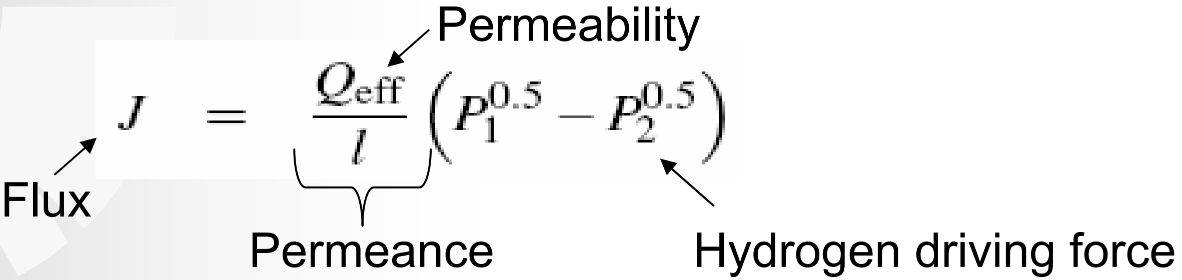
Laboratory Screening Rig (≤6 atm)



- Steam generator for H_2O addition to gas mixture
- Operation from 1–6 atm (absolute)
- Furnace capable of temperatures 300–650 °C
- Capable of simulating different gas compositions (CO, H_2, CO_2, N_2) from cylinders and house 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



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

Effective Permeability Neglecting External Mass Transfer Resistance

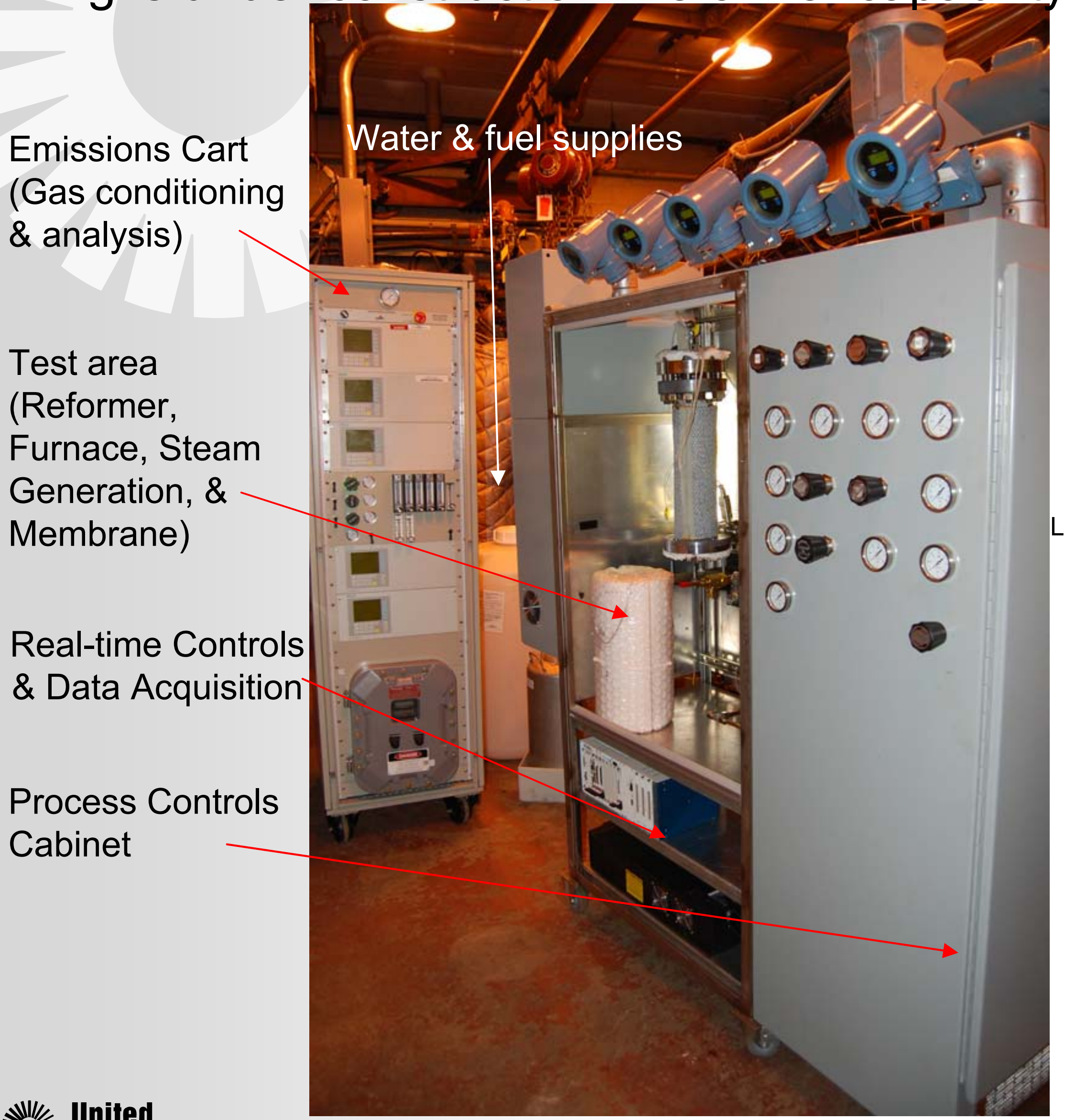
$$\begin{aligned} Q_{\mathrm{eff}} &= \frac{aQ_0}{1 + \sum K_i p_i} \\ &= \frac{aQ_{H_2}}{1 + K_{CO}p_{CO} + K_{CO_2}p_{CO_2} + K_{H_2O}p_{H_2O} + K_{N_2}p_{N_2}} \end{aligned}$$

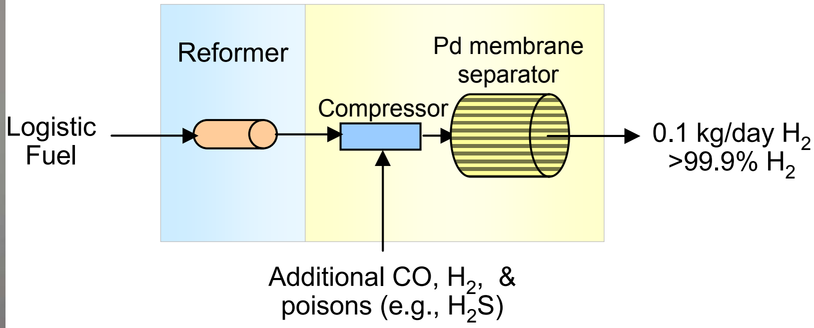
Experimental Objectives

- Obtain separators' permeability as a function of temperature with pure H_2 (Q_{H2})
- Quantify the effect of different non-poison gas species on H_2 permeability
- Determine adsorption coefficients (K_i) 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

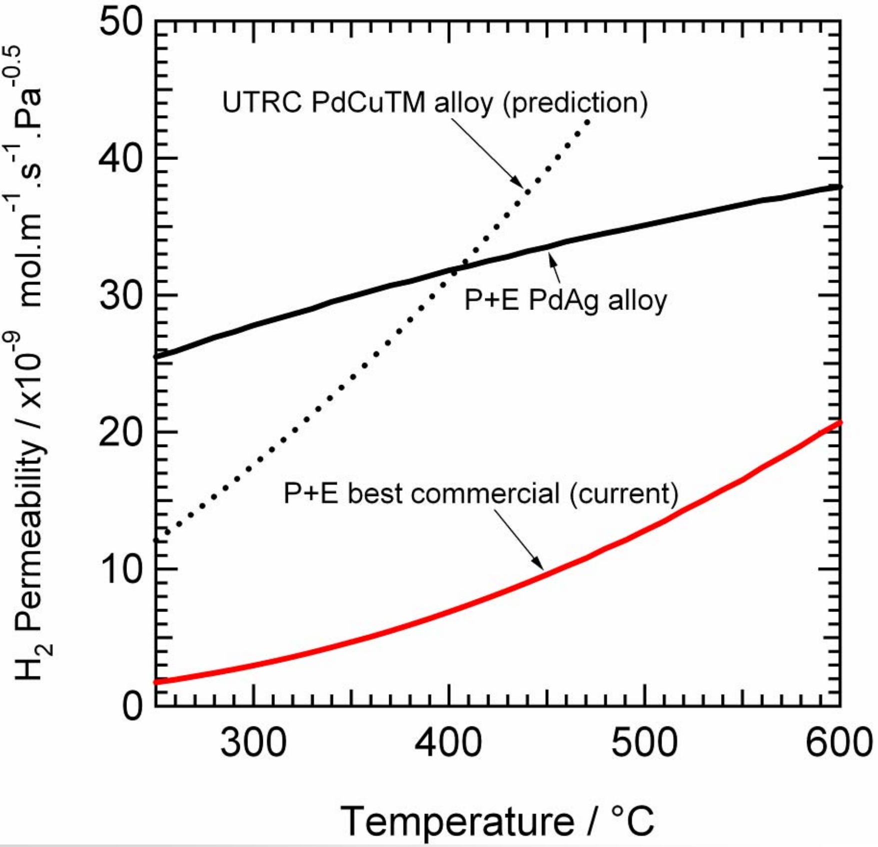
$$Q_{\mathrm{eff}} = \frac{aQ_{H_2}}{1 + \underbrace{K_{CO}p_{CO} + K_{CO_2}p_{CO_2} + K_{H_2O}p_{H_2O} + K_{N_2}p_{N_2}}_{\text{Values from laboratory experiments}} + \underbrace{K_{H_2S}p_{H_2S} + K_{HCl}p_{HCl} + K_{NH_3}p_{NH_3}}_{\text{Quantify during reformate higher pressure tests}}}$$

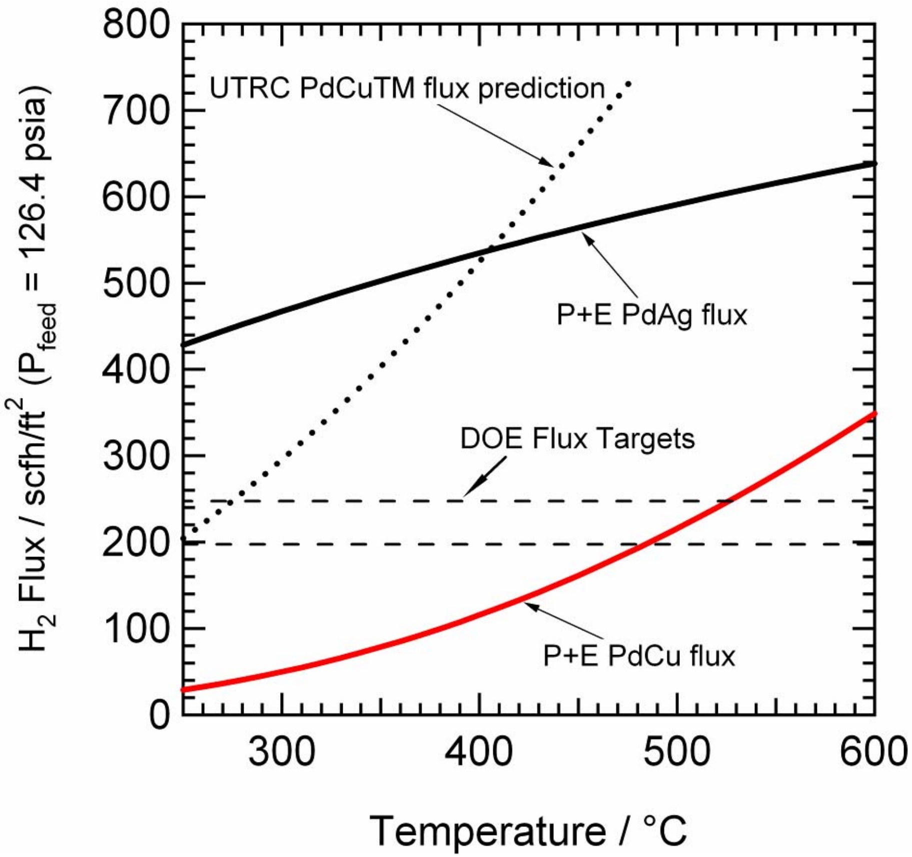
Experimental Objectives

- 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

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

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

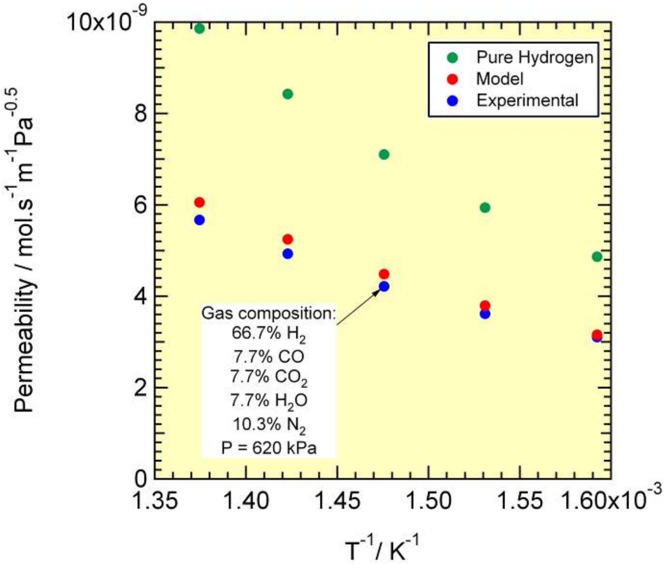
$$K_{CO} = exp\left((-11.831 \pm 0.115) + ln\frac{T}{673.15\ \mathrm{K}}\right) = 1.08 \times 10^{-8} T$$

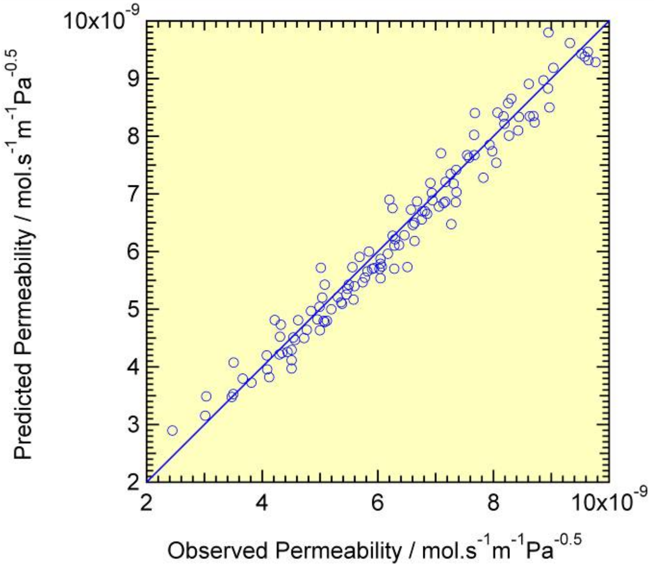
$$K_{CO_2} = exp\left((-13.134 \pm 0.223) + ln\frac{T}{673.15\ \mathrm{K}}\right) = 2.94 \times 10^{-9} T$$

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

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

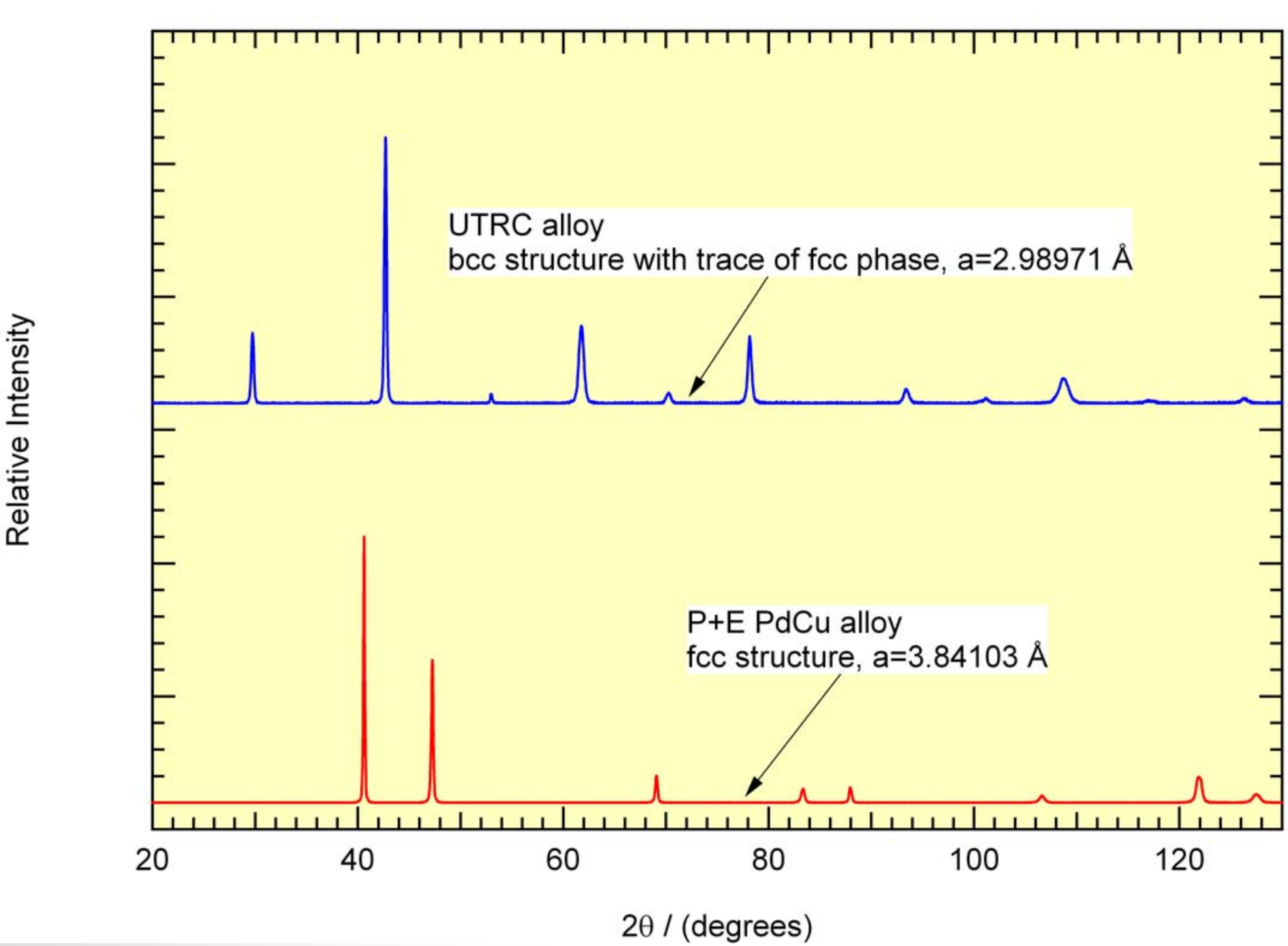
- Single separator preliminary results based on 123 experiments
  - T= 353 °C – 455 °C; P = 203 kPa – 620 kPa (29.4 – 89.9 psia)
  - Pure H_2 tests
  - Mixtures H_2–N_2, H_2–CO–H_2O, H_2–CO_2–H_2O, H_2–H_2O
- Weak temperature dependence on adsorption over experimental range (≈100 °C)
  - Heats of adsorption statistically insignificant
  - Linear temperature dependency describes data
- Model agreement within 5.2% on validation mixture composition
  - 66.7% H_2, 7.7% CO, 7.7% CO_2, 7.7%H_2O, 10.3% N_2





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

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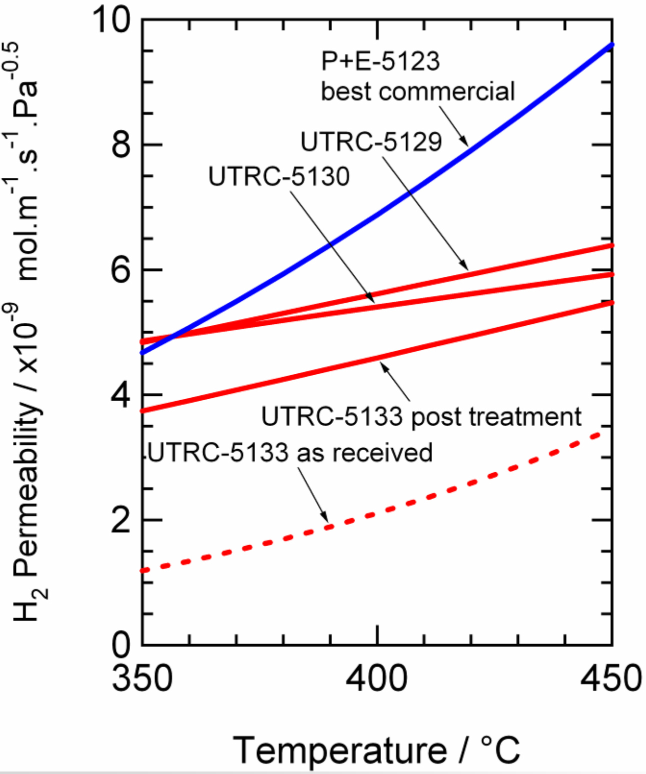
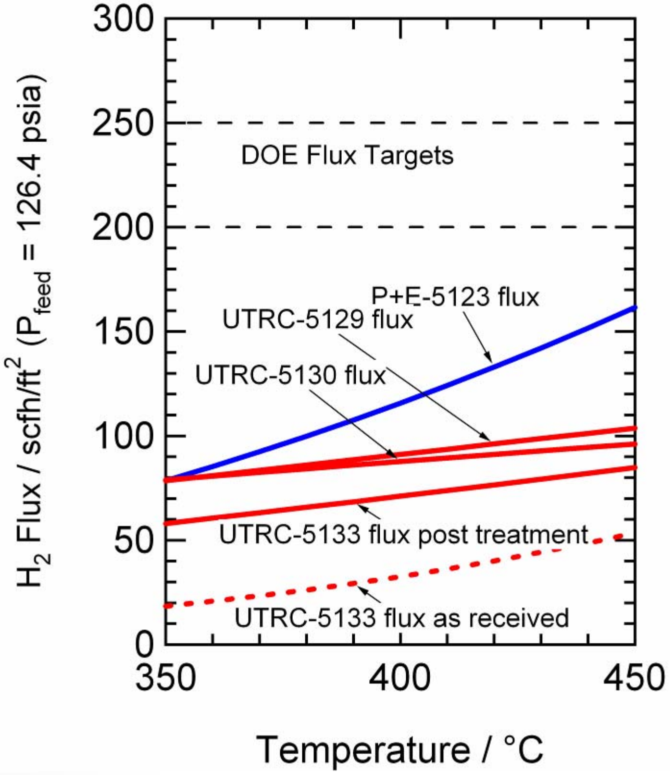
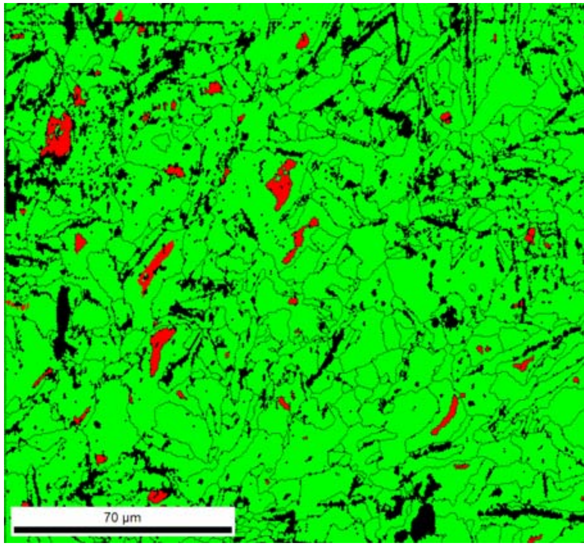
Permeability of UTRC Alloy Separators Less Than Expected

Characterization indicates presence of binary alloy on surface







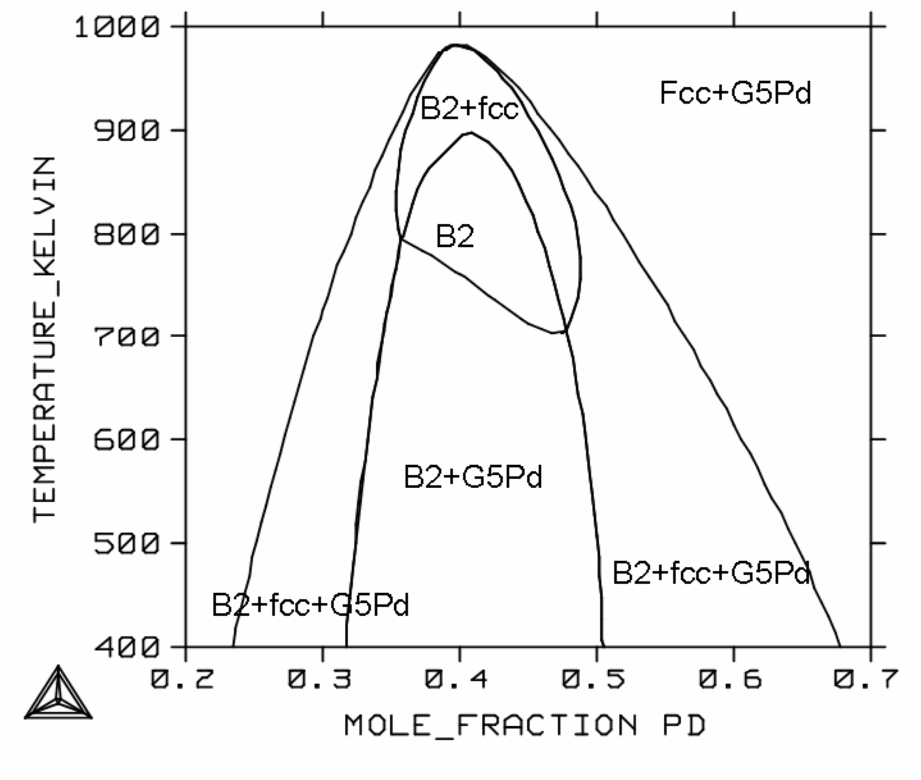
EBSD phase map

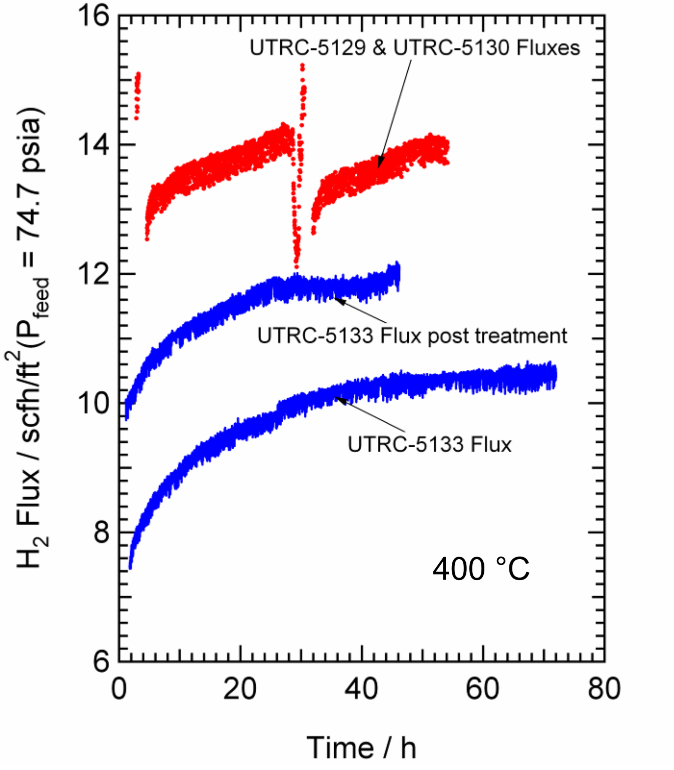
Green = PdG5; Red = PdCu

- 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

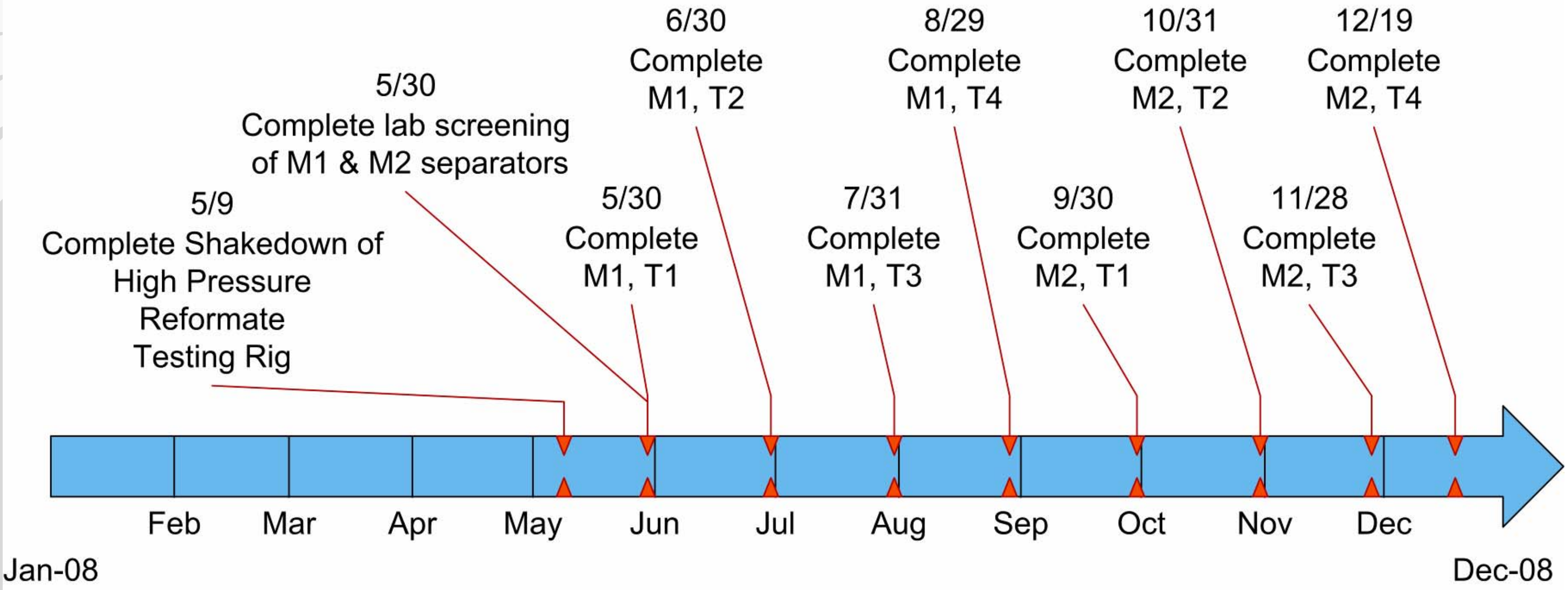




- UTRC alloy contains 47 at% Pd, targeting B2 phase
- Surface binary alloy between Pd & G5 element exists at low and high temperatures
- Binary could be formed during initial melt or during separator construction
- Heat treatments & quenching improves performance
- Etching may be necessary to remove 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_2S (<100 ppm H_2S)
    - T3: Reformate plus NH_3 (<15 ppm NH_3)
    - 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

- Constructed ten (10) commercially manufactured separators for evaluation

- Evaluated performance of first fcc PdCu separator
  - Quantified effect of CO, CO_2, N_2, and H_2O on H_2 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 reformate to be conducted this year
  - Quantify effect of H_2S, HCl, and NH_3 on H_2 permeability

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  - Testing: John Costello, Tom Hale, Robert Hebert, Gayle Marigliani, Jeffrey Walker, & Ying She
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