High-Performance, Durable, Palladium-Alloy Membrane for Hydrogen Separation and Purification

Project ID# PDP11

Presented by Pall Corporation

PURIWG Meeting

7 Nov. 2007

1 Minute Overview on Innovation

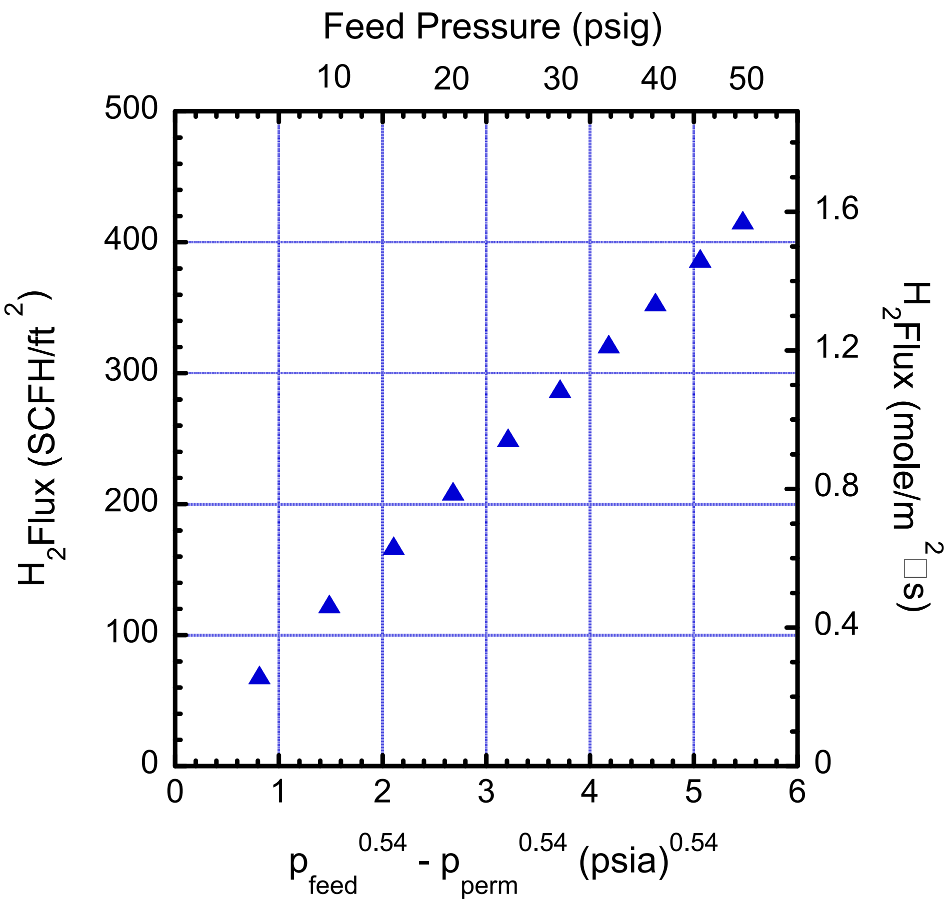
- Commercialization of Pd alloy membranes would provide a new tool for design of energy efficient systems through process integration and intensification

- Innovative accomplishments to date:
  - Correlated the interaction between the macro porous substrate and functional gas separation layer
  - Defined the surface and bulk properties of the porous tubular substrate needed to enable the formation of a thin, defect free Pd alloy membrane
  - Produced a functional Pd alloy membrane less than 3μ thick

- Future innovation:
  - Optimize composition of the composite structure (membrane + substrate) for use in the application of interest
  - Design cost efficient manufacturing processes for fabrication of all components and sub-components of a commercial membrane separation device

Innovation – Functional Pd Alloy Membrane

- Pall ZrO_2/ss AccuSep® substrate
- ~2.5 μm thick
- Pressure exponent or n-value = 0.54
- Pure H_2 flux exceeds 2010 DOE target value
- Permeability ~ pure Pd
- $\alpha(H_2/N_2) \geq 400$
- Permeate flow rate at ΔP H_2 of 50 psi = 5 liters/minute at RTP



Pd/Au Alloy (Sample #89) tested at 400 °C

2 Minute Review of Key Performance Metrics

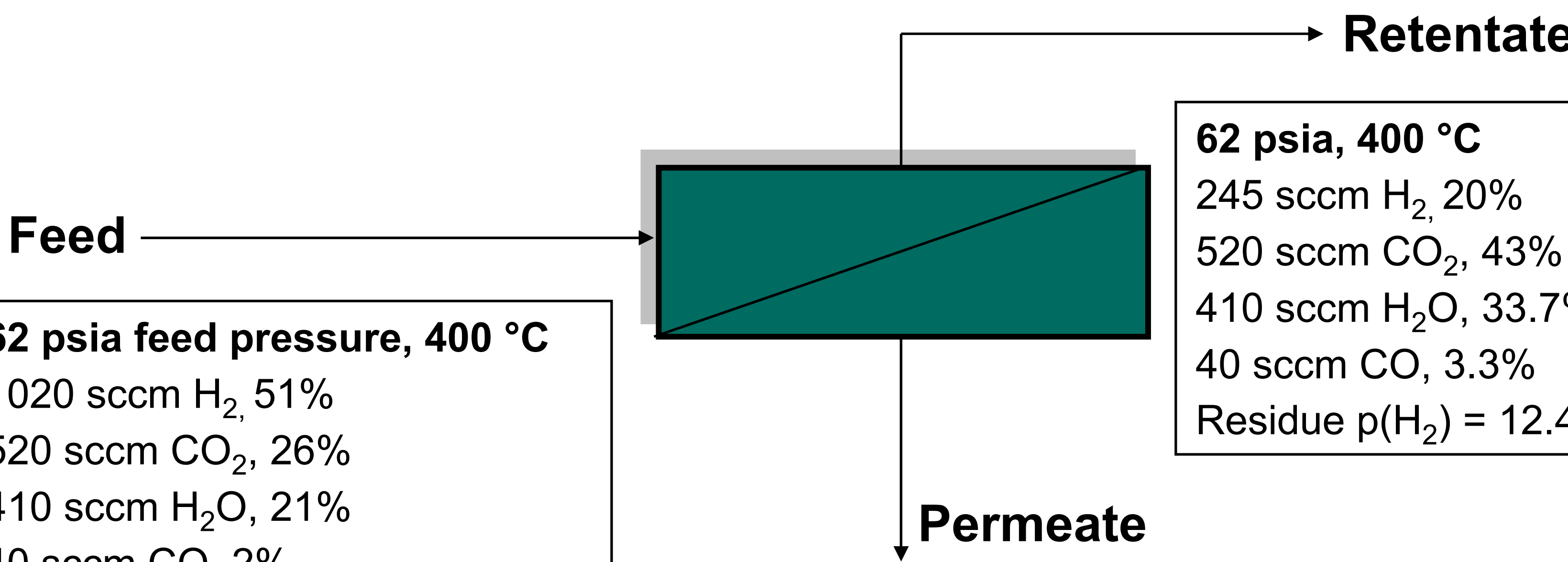
- DOE Multi-Year RD&D plan established targets for gas separations with metallic membranes
  - Phase one of the three phase project has focused on meeting the RD&D targets (PURIWG metrics)
- Operating capability (differential pressure) is depended on mechanical properties of the tubular substrate
  - Testing at ORNL to confirm tube strength at operating temperature
- Flux testing with model gas pair (H_2/N_2) used to optimize film thickness and "separation factor"
  - Flux rate is a function of film thickness
  - H_2 quality is a function of separation factor
  - H_2 recovery is a function of separation factor

Key Performance Metrics & Results

Performance Criteria	Units	Progress toward DOE goals	
		2010 Target	**Verified test data**
Module Cost	$/ft2	1,000	**1,500**
Hydrogen Quality	% of total (dry) gas	>99.99	**99.999**
H2 Flux Rate (Pure gas)	$scfh/ft^2$	250	**280***
H2 Flux Rate w/ $85H_2/7.5CO_2/7.5CH_4$ Feed stream	% of total gas	250	**250****
H_2 Recovery w/ $85H_2/7.5CO_2/7.5CH_4$ Feed stream	% of total gas	>80	**78****
Operating capability	psi	400	**400**
Durability	hrs	26,280	**1,600*****

*Flux at 20psid ΔP H_2 partial pressure and 15 psig permeate side pressure, 400ºC with pure gas.
**Flux and recovery at 30psid ΔP H_2 partial pressure and 15 psig permeate side pressure, 400°C with $85H_2/7.5CO_2/7.5CH_4$ at 3000 SCCM total flow.
*** Durability test stopped at this time with good membrane performance

Key Performance Metrics – H_2 Recovery



62 psia feed pressure, 400 °C
1020 sccm H_2, 51%
520 sccm CO_2, 26%
410 sccm H_2O, 21%
40 sccm CO, 2%
Feed gas $p(H_2)$ = 31.6 psia

62 psia, 400 °C
245 sccm H_2, 20%
520 sccm CO_2, 43%
410 sccm H_2O, 33.7%
40 sccm CO, 3.3%
Residue $p(H_2)$ = 12.4 psia

12 psia, 400 °C
775 sccm H_2, 99.95%
450 ppm CO_2, 0.045%
75 ppm CO, 0.0075%

775/1020 x 100% = 76 % H_2 recovery

$Dp(H_2)$ log-mean = (31.6-12)-(12.4-12)/ln(19.6/0.4) = 4.9 psi

$Pd_{90}Au_{10}$ Composite Membrane (#105) in simulated WGS Mixture Test

H2A Inputs

- Economics are based on several factors
  - Module cost (substrate, membrane, hardware and pressure vessel) not membrane cost is the relevant capital cost metric
  - Membrane separation opens up new process design options
- Process integration will impact overall economics
  - Conditions used for testing (PURIWG metrics) are a baseline for data reporting but do not match actual operating conditions
  - Operational feed stream composition, temperature, pressure will impact membrane durability and H2 flux rate
  - Membranes are not "plug and play" need process integration to optimize economic benefit
- Process intensification will impact economics
  - Capital cost can be reduced by combining unit operations
  - Operating cost based on mass and energy balance including balance of plant operations need to be factored in

H2A Inputs

- Membrane performance can be maximized using PURIWG metrics
- Membrane and module cost can be minimized by use of advanced manufacturing techniques
- Relevant economics ($/Kg of H_2) is highly dependent on process integration and process intensification

H2A Inputs – Modeling Plan

- Carry out an H2A analysis with our membrane as a direct substitute for the PSA in a 1500kg/day, 500 unit/year case
- Recommend that DOE modifies the current H2A model to include a membrane reactor process design
- Conduct sensitivity analyses with the membrane reactor H2A model including changes to the process (e.g., sweep gas, etc.) and membrane cost and performance
- Determine the minimum membrane cost, maximum performance achieved and the optimum process design and compare the results to the PSA approach and to the DOE goals

Merit Review Comments - Durability

Reviewer Comments

- Need to establish reliability and durability after repeated cycling
- No discussion of a duty cycle for durability testing
- Measurements were not made using reformer gas streams
- Reformate should include trace species which may poison the membrane
- No tests yet on sulfur tolerance
- Longer term stability and performance

Response

- Parts are being ordered for test stand s at Pall and CSM
- Pall will carry out relatively short term (~2 week) tests with a nominal mixed gas composition (51% H_2, 21 %H_2O 26% CO_2, 2% CO) at temperatures up to 550°C at steady state and under cyclic conditions for up to 10 cycles
- CSM will carry out long-term tests (up to 6 months in duration with a few thermal cycles) and will extrapolate the data obtained for long range performance projections.
- Trace impurities such as sulfur will be tested

Merit Review Comments – Economic Analysis

Reviewer Comments

- It is unclear what the estimate is for the cost of H2 at 300 psi
- An economic analysis, even preliminary, would have been helpful to provide a first-cut at the potential costs
- It is unclear what the estimate is for the cost of hydrogen at 300 psi.
- Economic analysis needed.
- Risk assessment is recommended to achieve market goals.

Response

- A preliminary analysis was conducted but not reported since the input was designed for an actual small advanced SMR distributed H_2 system (40kg/day) and not the DOE recommended size of 1500kg/day
- A plan was developed with DOE to consider modifying the H2A model to reflect a membrane reactor system where we would just be required to provide the membrane performance and membrane module cost data and the cost of H_2 could be determined from a modified H2A model

Merit Review Comments – Differential Pressure

Reviewer Comments

- Unclear how the system is viable with only 20-40 psi transmembrane pressure
- Unclear how high recovery is possible if only <40 psid delta P
- Operating pressures are a little high for SMR materials
- Hope for additional work to reduce the operating pressure down to 100-300 psi range

Response

- The SMR product gas pressure considered was 115 psia. This determined the feed hydrogen partial pressure of ~57 psia
- The maximum H_2 recovery from a membrane process can be calculated via material balance by determining at what recovery the retentate H_2 partial pressure is equal to the permeate pressure which is pure H_2. Therefore, the H_2 recovery is a function of the feed gas H_2 composition, total feed pressure, and the permeate pressure
- Our Pd alloy composite membranes have been operated with feed pressures as high as 135 psia, and DP as high as 50 psi at 400 °C. The fluxes are so large, even a small membrane had a permeate flow rate of 5 liters/minute when DP H_2 = 50 psi so we usually limit the driving force for safety considerations
- In several experiments with different membranes, we have observed H_2 recoveries above 70% for gas mixtures, including a water-gas shift composition with 2% carbon monoxide. The average DP H_2 in one case was only 5 psi, recovery was 76%

Merit Review Comments – Cost & Performance

Reviewer Comments

- Addresses barriers but unclear how costs and performance will be improved
- It is hoped that capital cost will be reduced. It looks to be $2,000/kg H_2
- Project proposes to used conventional manufacturing but has limited capabilities
- Lacks communication with a supplier for the stainless steel support tubes
- No innovation on architecture

Response

- Continuing work to further reduce diffusion barrier thickness to increase flux and to reduce cost of housing and seals
- Pall Corporation is the substrate supplier and has extensive membrane and module manufacturing capabilities
- Shell and tube design has been optimized, innovation has been made on tubular substrate manufacturing process

Questions ?