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


Photo courtesy of Pall Corporation

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Project #PD9

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Objectives

- Project objective is the development, demonstration and economic analysis of a Pd-alloy membrane that enables the production of 99.99% pure H_2 from reformed natural gas at a cost of $2-3/gge by 2010

- Objective for the past year was to identify and control the variables that influence the performance, economics and manufacturability of a suitable Pd-alloy membrane

Overview

Timeline

- July, 2005 start date
- September, 2009 end date for Phase II
- 65% complete

Barriers

- Operational durability
- Compatibility to impurities
- Manufacturing cost

Budget

- $4 Million Project Total
  - $2.4M DOE share
  - $1.6M Contractor share
- $1.52 Million DOE cumulative obligations as of April 2008

Partners

- Colorado School of Mines
- ORNL – High Temperature Materials Lab

DOE HFI Membrane Performance Targets*

Performance Criteria	2006Status	2010 Target	2015 Target
Flux SCFH/ft^2 @20 psi ΔP H_2 partial pressure & 15 psig permeate side pressure	>200	250	300
Membrane Cost, \$/ft^2 (including all module costs)	\$1,500	\$1,000	<\$500
ΔP Operating Capability, system pressure, psi	200	400	400 - 600
Hydrogen Recovery (% of total gas)	60	>80	>90
Hydrogen Permeate Quality	99.98%	99.99%	>99.99%
Stability/Durability	<1 year	2 years	>5 years

* 2007 Technical Plan. Technical Targets: Dense Metallic Membranes for Hydrogen Separation and Purification
www1.eere.energy.gov/hydrogenandfuelcells/mypp

Milestones

Milestones	Progress Notes	Comments	% Comp
Demonstrate progress toward H_2 quality goal	Achieved 99.999% on a mixed gas test.	The potential of Pd-alloy membranes to achieve very high levels of H_2 purity has been confirmed.	70%
Demonstrate progress on 2010 H_2 recovery goal	Achieved 78% on a mixed gas test.	Need to increase H_2 recovery to >80%. Can be achieved by optimizing process conditions. Modeling indicates a recovery of over 80% is possible for a reformate stream containing 50% H_2 at 200 psia or higher, with a permeate pressure of 30 psia.	55%
Demonstrate achievement of ΔP goal	Ongoing high temperature strength analysis at HTML	Empirical data at high temperature being collected to support room temperature data and modeling for operating pressure rating	15%

Milestones

Milestones	Progress Notes	Comments	% Comp
Membrane module cost analysis to meet 2010 goal	Determined 2010 goal of $\$1000/ft^2$ module is achievable	- Reduced thickness of Pd alloy layer reduces content of precious metals - Reduced membrane cost by increasing yield during scale-up of substrate manufacturing process	30%
Report on progress to achieve H_2 flux goal	Achieved 250 $scfh/ft^2$ on a mixed gas test	- Feasibility established across several samples - Variables that affect repeatability have been identified and will be addressed as part of manufacturing process design	55%

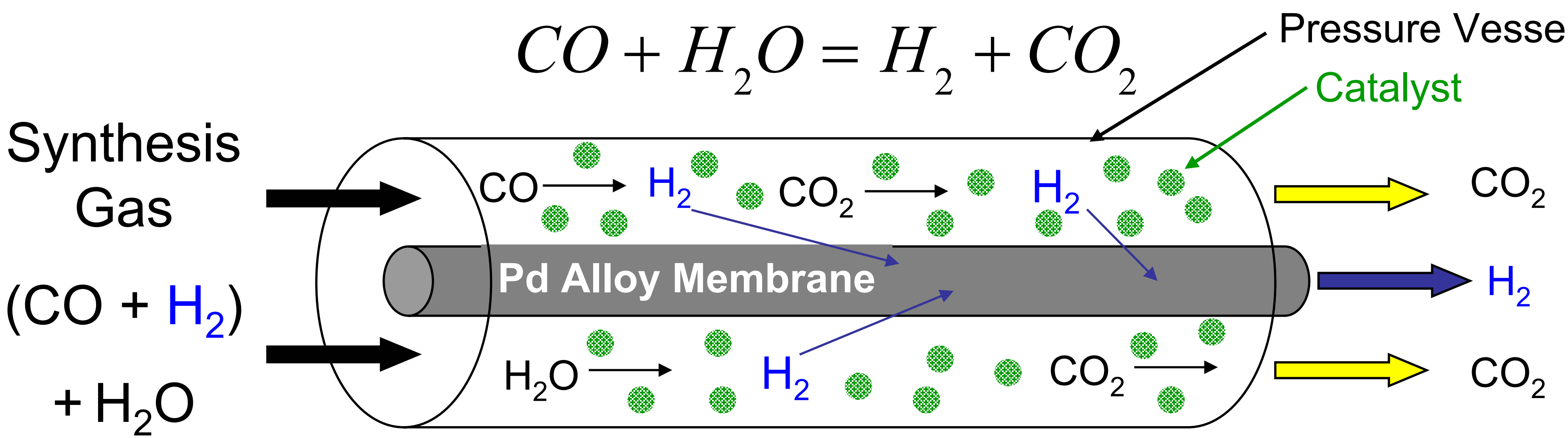
Milestones

Milestones	Progress Notes	Comments	% Comp
Predictive modeling report on progress toward durability goal	Critical operating parameters for field operation identified	Real world operating conditions will vary from lab test conditions. Identified critical start-up, shut-down conditions needed to maintain membrane integrity	25%
Report on system economic/energy model compared to 2010 goal	Membrane surface area calculations done H2A model.	- H2A membrane area calculation validated against Pall in house model - Interacted with Directed Technologies to provide feedback on latest version of H2A that includes integrated membrane reactor modeling	35%

Approach

- **Provide a new tool for process engineers to use for advanced system designs by development of a commercially viable Pd alloy membrane**
  - Pd alloy membrane has been shown to have both high flux rate and high separation factor for H_2 from reformate
  - Commercial scale-up of high quality porous metal substrate enables the development of a technically and economically viable composite membrane
- **Increase the overall energy efficiency of a H_2 reforming system through use of membrane technology for process intensification**
  - Membranes with high operating temperatures can be heat integrated to reduce thermal loss within the system
  - Membranes with high separation factor can reduce energy consumption from compression
  - Membrane reactors can reduce the number / cost of pressure vessels, reduce catalyst volumes, reduce overall capital and operating cost

Water-Gas Shift Membrane Reactor



UNIT OPERATION:

- **The water gas shift catalyst converts CO to CO_2 releasing useful H_2**
- **H_2 is separated from the other components of the gas stream by the membrane**

BENFITS:

- **Process equilibrium is shifted, resulting in more efficient conversion**
- **Process occurs within a single pressure vessel**
- **High temperature operation allows for thermal integration not possible with other separation techniques (PSA & amine absorption)**

Approach – Project Scope

- **Design a composite membrane based on robust, tubular, porous metal media as a substrate**
  - Surface modify the substrate by addition of a uniform, fine pore size diffusion barrier layer
  - Adapt the deposition methods to produce a thin, uniform, functional gas separation layer
- **Optimize the alloy composition to provide maximum stable H_2 flux over time in the mixed gas stream of interest**
  - Analyze membrane physical properties though a range of testing to ensure long term durability under operating conditions
  - Use DOE membrane performance targets as feasibility benchmarks
- **Demonstrate membrane performance under operating conditions in a typical reformed natural gas stream**
- **Use H2A analysis to show economic viability**

Technical Accomplishments

Diffusion Barrier Substrate

- Porous metal media substrate tubes made from 310SC alloy Stainless Steel and rated for use at 550ºC and 20 bar developed and adopted as the standard building block
- Process for producing smooth weld transition from porous media to nonporous fitting now a standardized manufacturing operation
- Manufacturing scale-up of the ZrO_2 diffusion barrier substrate is underway
  - Surface roughness can be controlled within a narrow range
  - Pore size distribution is uniform
  - Cost reduced by increase in yield

High quality substrate is the key to enabling formation of a functional gas separation membrane

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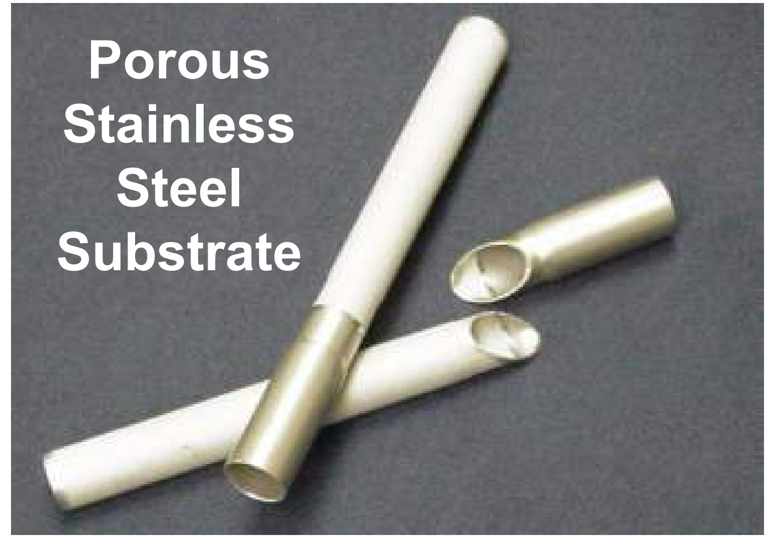
Technical Accomplishments

Membrane Formation

- Modified deposition methods to repeatedly produce thin Pd alloy membranes (2 microns or less) with high separation factors (greater than 20,000)
- Produced various Pd-Au alloy tubular composite membranes within the range of 5-20% Au
- Analyzed the compositional structure of Pd-Au alloy membranes
  - ORNL-HTML used high temperature XRD to analyze the lattice structure of the Pd-Au alloy as a function of time and temperature
  - Results provided insight into the dynamics of the alloying process
- Carried out tensile strength and strain at failure for Pd-alloy foils over the composition range of 0-38 mass % Au to determine high pressure operating capability for the functional membrane layer

Formation of a Pd Alloy Membrane



1
2
3
4

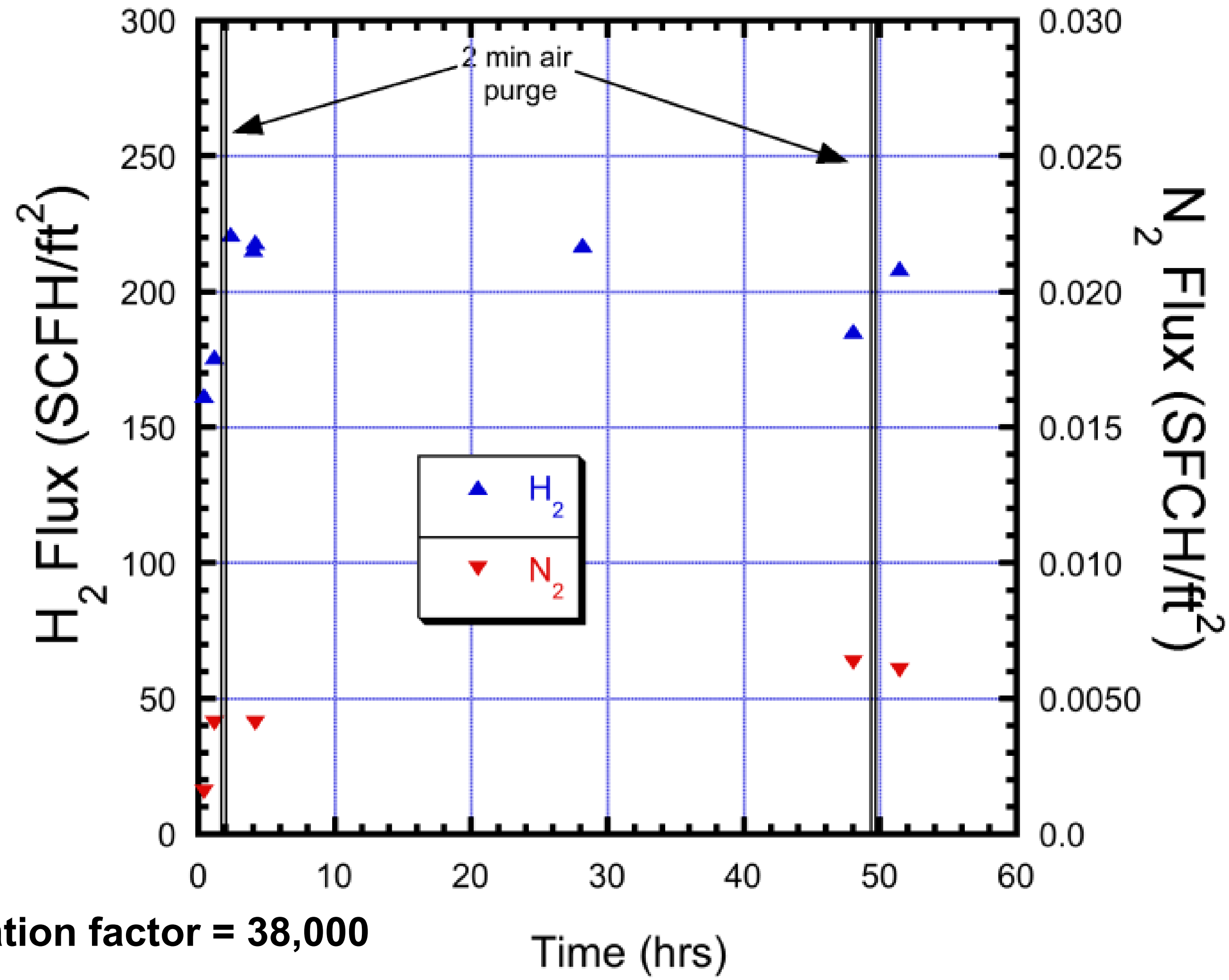
1) Modified diffusion barrier substrate, coated with porous ZrO_2, 0.08 µm pore size
2) Pd activated
3) Pd plated
4) Au plated

Technical Accomplishments

Membrane Testing

- Pure gas testing used as a screening tool to expedite optimization of the membrane formation process
  - Developed methods needed to form thin, high separation factor membranes
- Pd and Pd alloy membranes tested in mix gas streams to determine negative effect of the other gas components
  - Identified conditions where steam to carbon ratio prevents coking
  - Identified conservative start-up and shut-down conditions that maintain membrane integrity
- Initiated H_2S compatibility testing in April 2008
- Designed and initiated fabrication of two mixed gas test stands
  - Both stands to be completed in June 2008
  - One stand for alloy development and characterization
  - One for long term durability testing

Hydrogen and Nitrogen Flux for Membrane, CSM-Pall-134, at 20 psi Transmembrane Pressure and 400 °C.

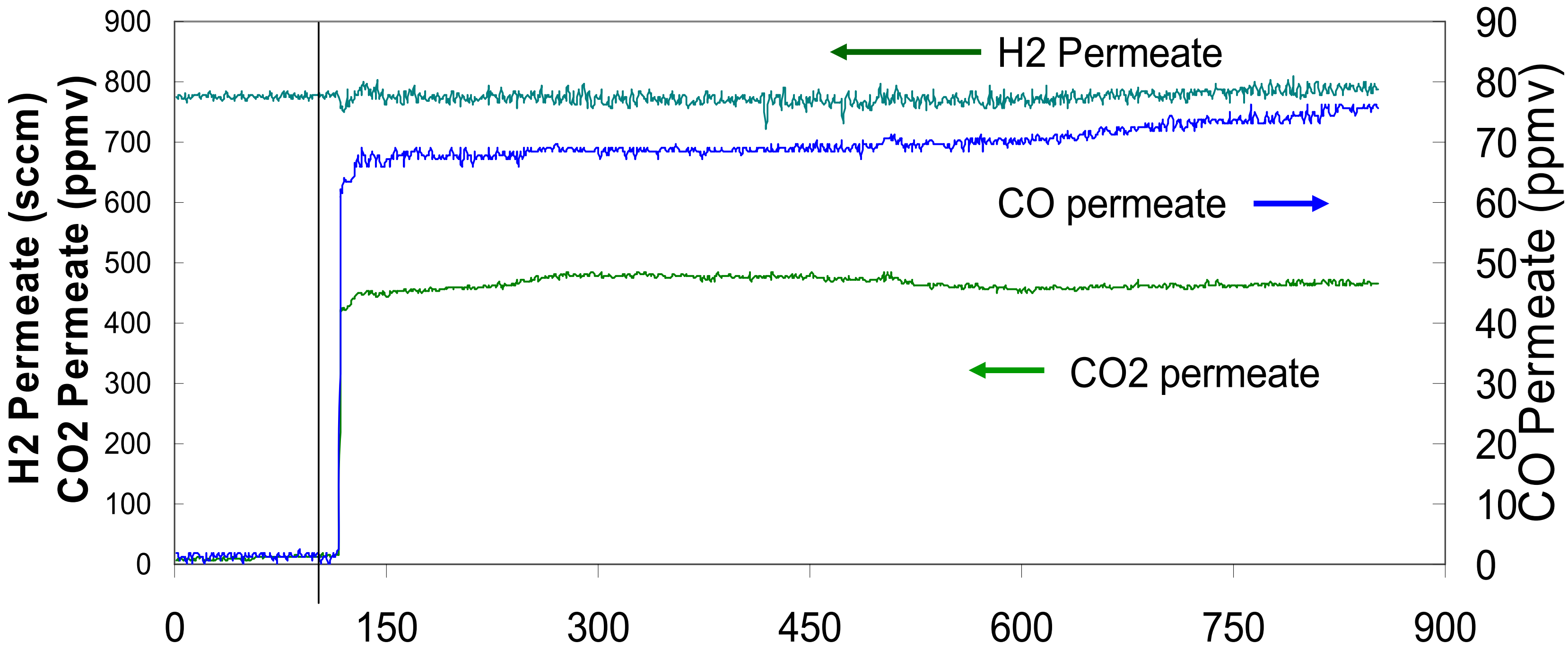


H_2/N_2 Separation factor = 38,000

Film thickness = 2.5 micron

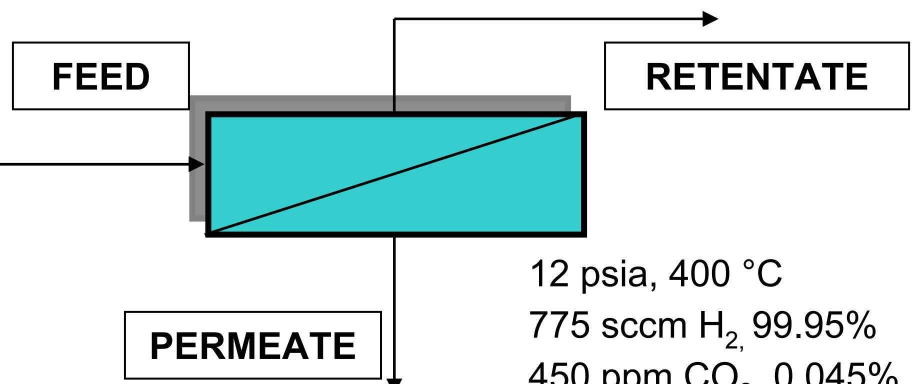
Pd_{95} Au_5

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



Test Conditions: 400 c & 50 psid

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%

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

Technical Accomplishments

Cost

- Produce 310SC Stainless Steel Substrate on commercial scale
  - Alloy change increases the operating temperature and pressure without increasing cost
  - High volume production increases yield and minimizes labor content, resulting in reduced cost

- Modified Diffusion Barrier Substrate (ZrO_2 membrane) Scale-up
  - Improved quality enables thinner membrane formation
  - Controlled process increased yield and reduced cost per tube
  - Increase from 4” to 12” length tubes reduced costs per unit area

- Reduced Pd alloy membrane thickness
  - Increases H_2 flux and reduces the amount of membrane area needed
  - Reduces the material cost of Pd and Au per unit area of membrane

Technical Accomplishments

Cost

- Module and Process Design
  - Developed analytical method to ensure process flow conditions maximize use of membrane area
  - Preliminary evaluation of module design, fabrication techniques and materials for a stand alone membrane separator device show that $1,000 per ft^2 of area cost to end user is achievable

- Provided feedback to Directed Technologies on Modified H2A model
  - H2A model now accounts for use of a combined membrane reactor
  - Membrane area calculations match Pall model
  - Preliminary results show the cost of the separation device (PSA or membrane) is a small percent (<5%) of capital cost of the reforming system, so membrane module cost is not the dominating factor
  - Membrane separation enables design of a more efficient reforming system, reducing operating cost and lowering the cost per Kg of H_2, so membrane performance and process integration are key

Future Work

Membrane composition

- High temperature XRD in cross-sectional mode to determine alloy composition and structure.
  - Analyze additional Pd-Au alloy compositions
  - Study multiple deposition techniques
  - Correlate XRD data with performance and durability in mixed gas streams.
- Durability tests in mixed gas streams to determine membrane system operating cost
  - Complete the test stands
  - Initiate long term testing in syngas mixtures
- Design module to minimize cost and maximize efficiency
  - Select alloy with the best cost/performance data after mixed gas testing
- Carry out techno-economic modeling for a “combined” membrane reactor with modified H2A model
- Conduct sensitivity analyses using H2A model to optimize benefit from process integration

Summary

- Progress demonstrated towards the membrane targets that will enable achievement of the overall program goals of 99.99% pure H_2 from reformed natural gas at a cost of $2-3/gge by 2010
- Commercial production of 310SC St. Stl. tubular substrate is progress towards achieving the operating pressure, durability and cost targets
- Scale up of ZrO_2 diffusion barrier substrate is progress towards the quality, flux and cost targets
- Deposition methods, alloy composition and analytical testing is progress towards the flux, quality and durability targets
- In-house and H2A modeling work is progress towards the H_2 recovery and overall system economic targets
- Test stands currently being fabricated will re-establish capabilities previously provided by end user partner for syngas testing
- Determined $1,000 per ft^2 cost to end user is achievable

2007 & 2008 Progress Against Targets

Performance Criteria	2010 Target	2015 Target	Accomplished FY07	Accomplished FY08
Flux SCFH/ft² @20 psi ΔP H_2 partial pressure & 15 psig permeate side pressure	250	300	270	220*
Membrane Cost, \$/ft² (including all module costs)	\$1,000	<\$500	\$1,500	\$1,000
ΔP Operating Capability, system pressure, psi	400	400 - 600	TBD	TBD
Hydrogen Recovery (% of total gas)	>80	>90	78**	TBD
Hydrogen Permeate Quality	99.99%	>99.99%	99.999%***	99.999%***
Stability/Durability	2 years	>5 years	TBD	TBD

*** FY07 flux based on best sample, FY08 flux consistently achieved across many samples**

**** Measured on a 95%H_2/2.5%CO_2/2.5%CH_4 mixed gas stream. Measurements to be made with other impurities starting in June 2008 when new test stands are operational**

***** Projected purity based on H_2/N_2 ideal selectivity**