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


Photo courtesy of Pall Corporation

Jim Acquaviva
Pall Corporation

May 19, 2009

Project PD 07

Project ID: pd_07_acquaviva

Overview

Timeline

- July, 2005 start date
- June 30, 2010 end date
- 80% 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 March 2009

Partners

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

Relevance- Objectives

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

The objectives from June 08-May 09 were to:

- ✓ Fabricate a series of membranes covering a specific range of alloy composition and functional layer thickness
- ✓ Optimize the membrane formation process
- ✓ Test the membranes in pure gas streams prior to WGS testing
- ✓ Complete the equipment needed for extended WGS testing
- ✓ Obtain initial WGS test results
- ✓ Initiate the techno-economic modeling as soon as the combined membrane reactor model is available from DTI

Relevance - Impact on Barriers

- **Operational Durability**
  - Addressed through:
    - Alloy and composite membrane structure
    - Process conditions
    - Operational procedures
- **Compatibility to Impurities**
  - Alloy selection based on application specific requirements
  - Confirm compatibility through long term testing at actual conditions
- **Manufacturing Cost**
  - Cost estimate based on sale price to end user for membrane in a module
  - Manufacturing scale-up increases yield and reduces cost

DOE HFI Membrane Performance Targets*

Performance Criteria	2006 Status	2010 Target	2015 Target
Flux SCFH/ft^2 @20 psi ΔP H_2 partial pressure, 400ºC (Pure H_2 gas)	>200	250	300
Membrane Cost, \$/ft^2 (including all module costs)	1500	1000	<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**

Approach - Overall Technical Approach

- **Develop a commercially viable Pd alloy membrane to enable the design of economical processes for hydrogen production**
  - Pd alloy membrane has been shown to have both high flux rate and high separation factor for separating H_2 from ethanol/NG reformate gas
  - Commercial scale-up of high quality porous metal substrate along with alloy development, deposition methods and module design pursued
- **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 system complexity, size and operating cost
  - Membrane reactors can reduce the cost of pressure vessels, reduce catalyst volumes and overall capital and operating cost

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Approach – Progress FY08/09

- **Membrane Development**
  - Consistently produced substrate and initiated manufacturing scale up
  - Improved deposition methods and post treatment during fabrication of Pd-alloy membrane inventory
  - Analyzed alloy composition and microstructure
  - Evaluated alloy composition, process conditions and operational procedures as variables affecting membrane performance
- **Economic Evaluation**
  - Updated costs based on scaled up membrane manufacturing
  - Design and cost evaluation of modules
  - Estimated H_2 production cost using combined membrane reactor model though interaction with DTI

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Milestones – Technical Accomplishments

Milestones	Progress Notes	Comments	% Comp
Demonstrate progress toward H_2 quality goal	Achieved ≥99.9% in a 80hr WGS mixed gas test w/ max value 99.98%	- The potential of Pd-alloy membranes to achieve very high levels of H_2 purity has been confirmed	80%
Demonstrate progress on 2010 H_2 recovery goal	Achieved 78% in a WGS mixed gas test	- Likely to achieve 80% or greater by optimizing process conditions. Modeling indicates this is a reasonable target for economic viability	70%
Demonstrate achievement of ΔP goal	Test program in process at HTML for thin foil and substrate. Specialized pressure collapse test equipment currently being modified	- Empirical data at high temperature measured for foil strength. Substrate tube data to be collected at temperature to verify calculated operating pressure rating	65%

Milestones – Technical Accomplishments

Milestones	Progress Notes	Comments	% Comp
Membrane module cost analysis to meet 2010 goal	Achieved 2010 goal of $1000/ft^2$ module. Design in progress	- Increased yield and reduced production cost through scale up of substrate manufacturing process - Reliable deposition of the functional layer below 5 micron reduces cost of precious metal	60%
Report on progress to achieve H_2 flux goal	Achieved 245 scfh/ft^2 on a WGS mixed gas test w/ differential pressure = 170 psi, T = 400 °C	- Established feasibility and repeatability across a range of samples - H2 flux used as a metric for control of deposition process along with separation factor - Process flux will vary significantly based on operational conditions	70%

Milestones – Technical Accomplishments

Milestones	Progress Notes	Comments	% Comp
Predictive modeling report on progress toward durability goal	Testing for over 100 hours conducted and reported	- Extended testing to be done with recently completed test stands - Multiple thermal cycle testing to be done for predictive modeling	50%
Report on system economic/energy model compared to 2010 goal	Input provided to Directed Technologies used for initial analysis	- Continue to interact with Directed Technologies to provide feedback on latest version of H2A that includes integrated membrane reactor	20%

Approach – Key Milestones and Decision Points

- **Phase 2 Milestone: Use projected cost estimate for membrane modules (area & $/ft2) and DTI's H2A based analysis to establish economic viability for integrated membrane reactor in a NG and/or Ethanol reformer system**
  - **Go/no go decision November 2009**

- **Scope of Phase 3: Confirm stable performance (H_2 flux, purity and recovery) of Pd-alloy membrane under typical post WGS operating conditions**

Technical Accomplishments & Progress
Summary of Previous Accomplishments

- **Develop substrate process:** Porous metal media substrate tubes made from 310SC alloy stainless steel and rated for use at 550ºC and 20 bar that can be made in longer lengths and ZrO_2 diffusion barrier fabrication process is scaled up to 12-inch lengths
- **Improve membrane deposition process:** Modified deposition methods to repeatedly produce thin Pd alloy membranes (≤2 microns) with high separation factors (greater than 20,000)
- **Fabricate test samples:** Produced various Pd-Au alloy tubular membranes 5-30% Au and thickness 1.0-3.5 microns
- **Design membrane for high ΔP:** 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
- **Performed preliminary testing in mixed gas streams:** A limited amount of testing was carried out in mixed gas test streams to determine effect of other gas components
- **Estimated cost:** 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
- **Initiated techno-economic analysis:** Directed Technologies' used Pall provided information in a modified H2A economic model. Initial results showed the cost of the separation device (PSA or membrane) is a small percent (<10%) of capital cost of the reforming system, so membrane module cost is not the dominating factor. Membrane separation enables 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

Technical Accomplishments & Progress
Summary of Accomplishments for June 08 - May 09

- Developed new membrane synthesis process (air oxidation and layering sequences) to improve membrane performance
- Established an inventory of membranes with various Pd-Au composition (0-30% Au) and thickness (1.0-3.5 microns)
- Analyzed the effect of alloy composition, process conditions and operational procedures on membrane performance
- Fabricated two WGS test stands, one for sensitivity analysis, the second for long-term durability analysis
- Conducted preliminary H2 production cost analysis using DTI's H2A based model and Pall provided costs

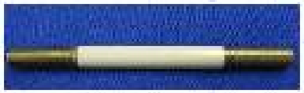
Significant progress towards establishing viability

2008 AICHE Poster

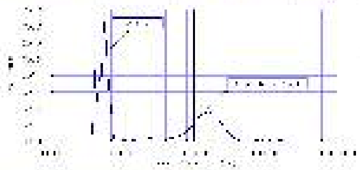
Gas Separation Membrane

Substrate Development

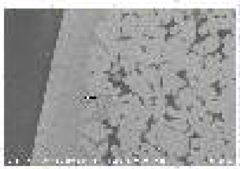
"It is all about substrate!!!! - Prof. Douglas Way"



- Ceramic Coated Porous Stainless Steel Substrates
- Available in 316L and 310 SS with welded fitting



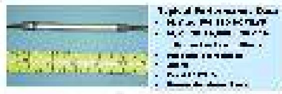
- Uniform pore size distribution
- Average Pore Size = 70 nm
- First Bubble/Largest Pore > 30 psig
- Air Permeance = 1.9x10⁻³ scc cm⁻² s⁻¹ cmHg⁻¹



- Excellent adhesion between Stainless Steel and ceramic layer.

- Excellent adhesion to zirconia layer, uniform thickness, surface contour following of Pd-alloy metal film

Hydrogen Separation Membrane



- Syn-gas automated Testing Capability

Palladium-Alloy membranes

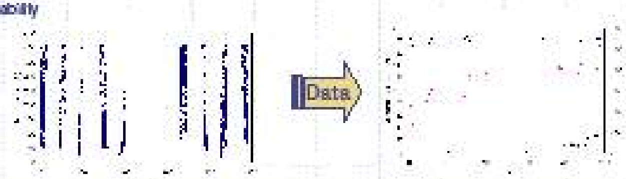
- Composite and alloy development in collaboration with CSM.
- Extensive fabrication and testing.
- Robust: Thermal stability and start-up/shut-down cycling test.
- Module design and innovation to improve performance.
- 15cm² modules available for field testing.

- Engineering design optimization for enhanced performance. Data at 400 C; 75 psig feed pressure; 70/30=H_2/Ar, Atmospheric permeate

Each cycle represents a thermal cycle

Environment	Air → Air → Argon → H_2 → Air
Pressure (psig)	0 → 20 → 20 → 20 → 0
Temperature (C)	25 → 400 → 400 → 400 → 25

Temperature ramp-up/down in 1 hour



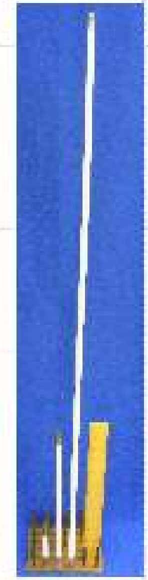
Polybenzimidazole Membrane

	Pure Gas H_2 Permeance [GPU] 250°C	Ideal H_2/CO_2
Membrane 1	189	22.6
Membrane 2	166	23.9

- Recent Data – Optimized composite design

- High temperature polymeric membrane development in collaboration with Los Alamos National Laboratory
- Long term stability at temperatures exceeding 250 C.
- Exceptional stability in H_2S and CO environment.
- Innovative composite design for 25 fold performance improvement.

Progressing towards Industrial Scale



- Large scale manufacturing capability.
- Unique weld design developed and commercialized.
- Porous stainless steel and ceramic coated stainless substrates suitable for high temperature and pressure gas and vapor separation applications.

- Contact

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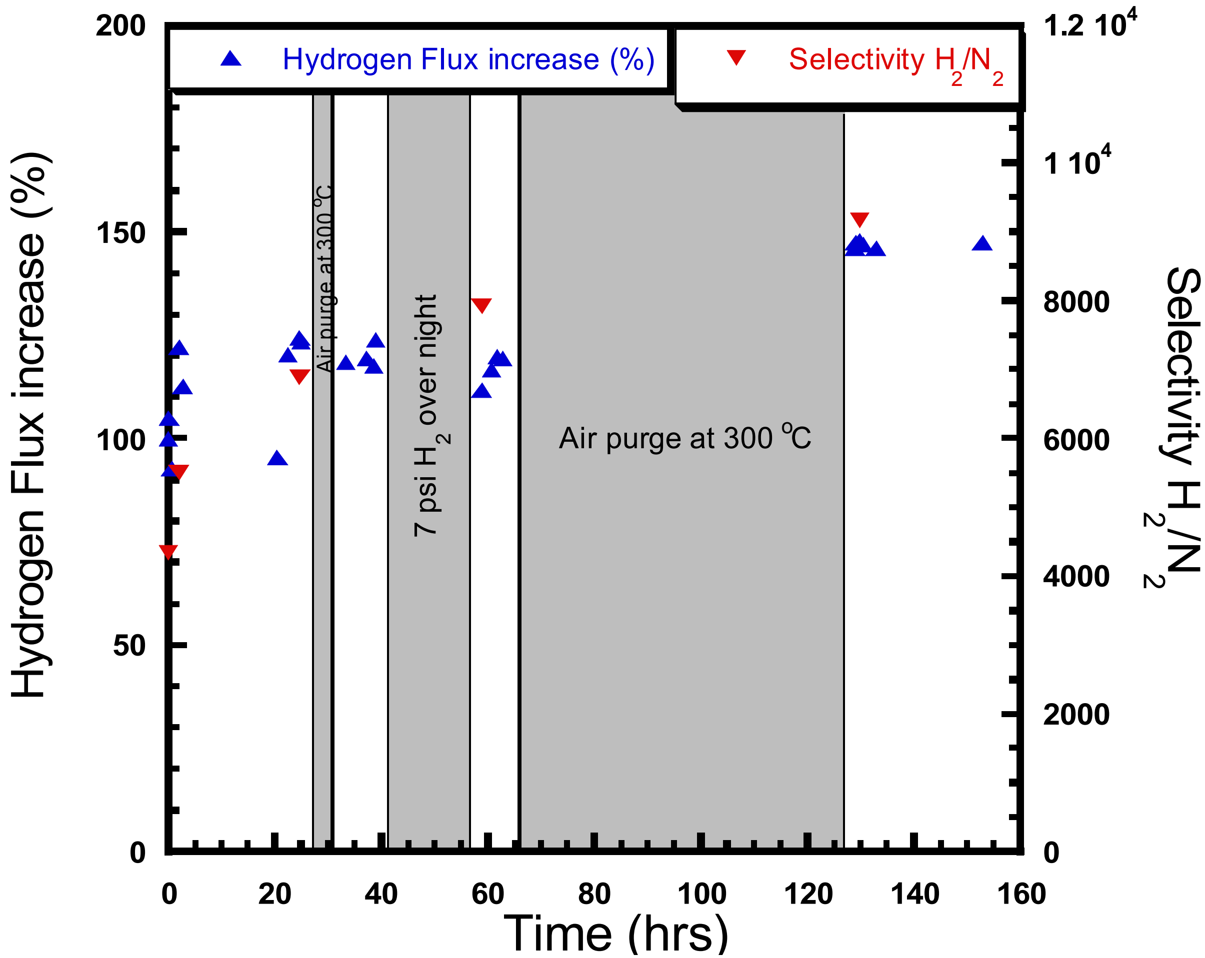
Technical Accomplishments & Progress

CSM235 1.9 micron $Pd_{92}Au_8$ increase in Hydrogen Flux and pure gas selectivity at 400 °C with successive air purges at 300 °C



- CSM developed membrane and process
- Deposition method and alloy composition varied
- Air purge cycle added to the test
- Showed surface effects were reversible with the right alloy and process conditions

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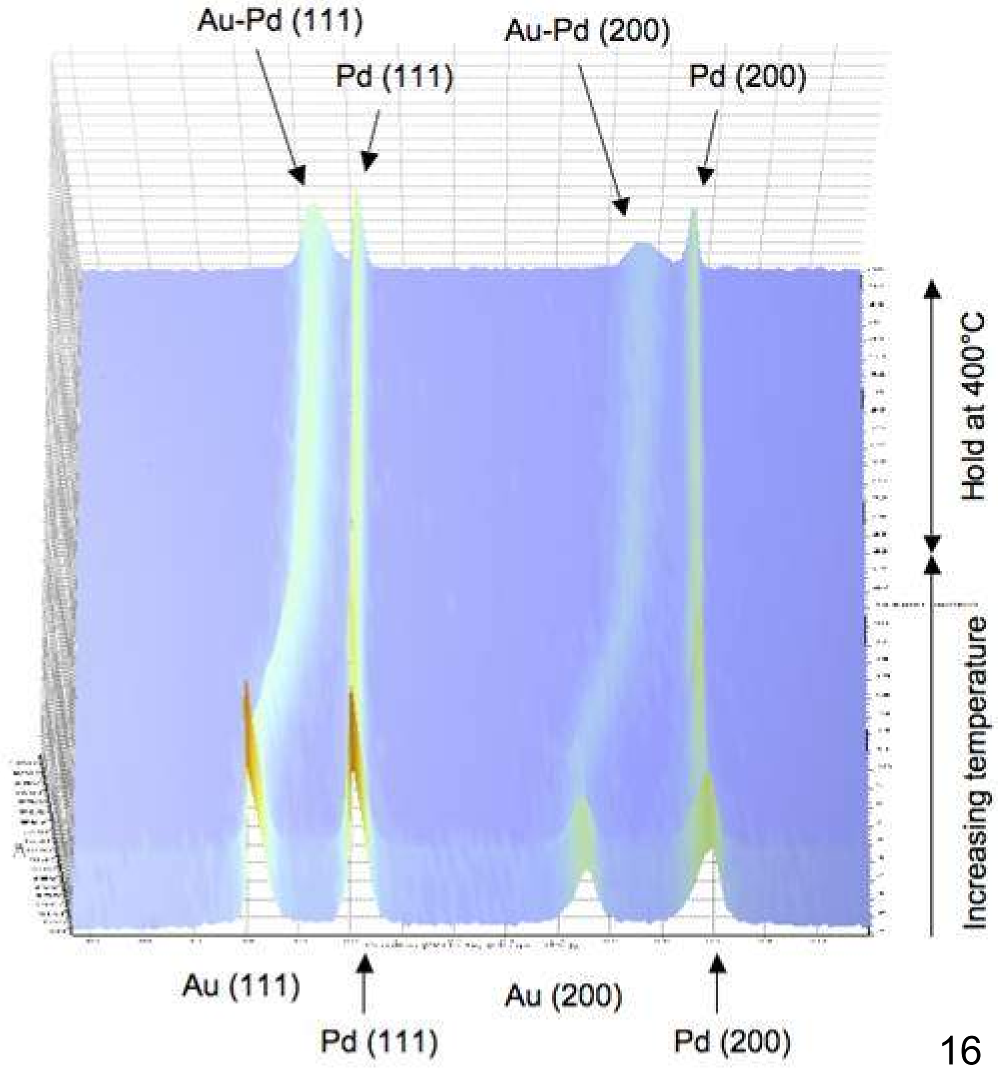
Technical Accomplishments – ORNL/HTML Progress

In Situ, High Temperature XRD

- Test has proved useful for membrane characterization at operational temperature
- Alloying is not complete but appears to be stable
- Further analysis to be conducted

Discussion

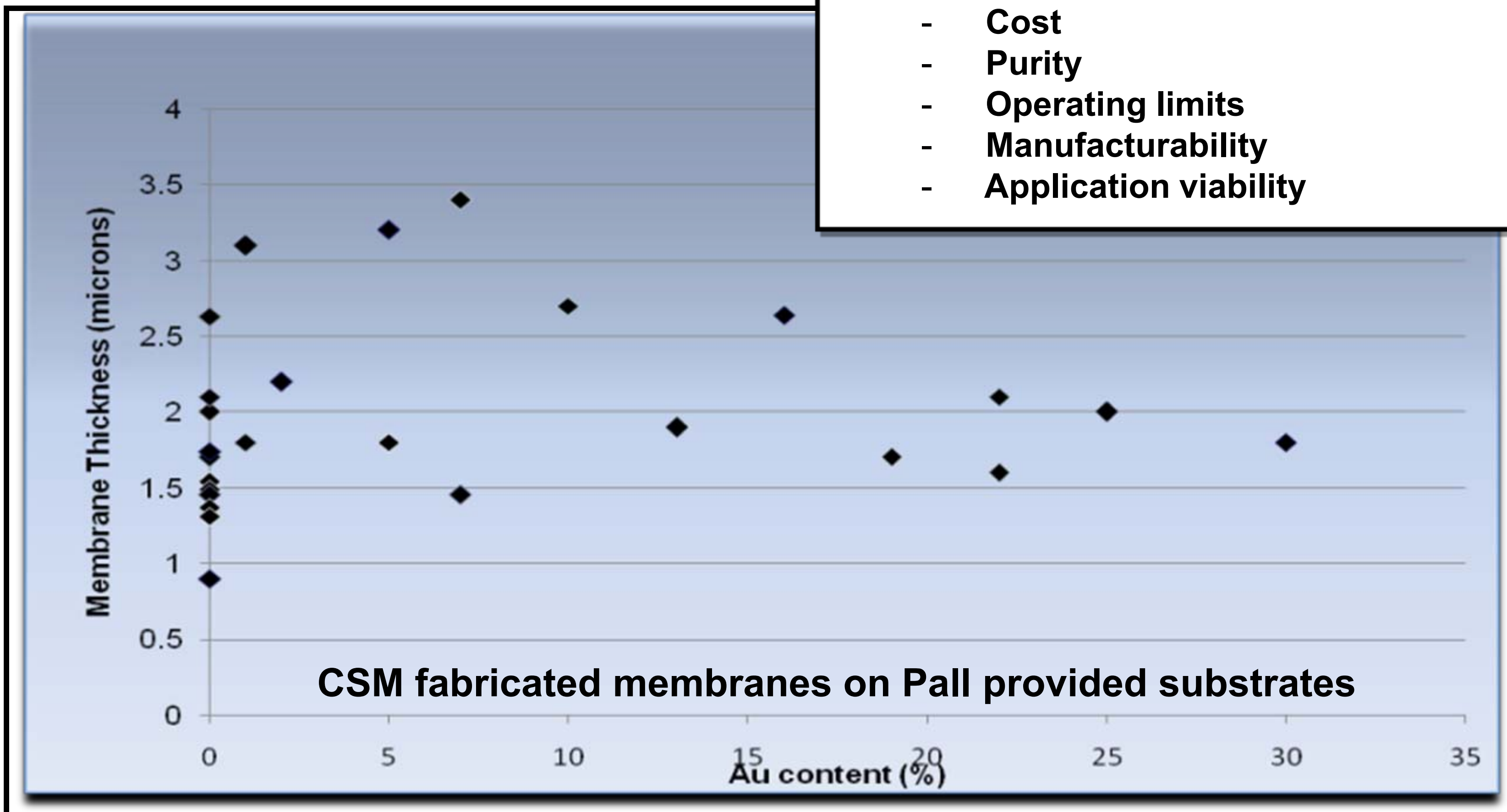
The front most scans show two distinct pairs of diffraction peaks corresponding to the Pd and Au starting layers. As the temperature is increased, the Au peaks shift to higher diffraction angle, corresponding to a smaller lattice spacing, which may be interpreted as alloying of the Au with smaller Pd atoms. Two features stand out from this data set. First, that there are no equivalent shifts of the Pd peaks, meaning that there remains an unalloyed Pd layer under the Au-Pd alloy. Second, the peak shift stops at some temperature well below 400°C, meaning that the **Au-Pd alloy is stable and in equilibrium with the underlying Pd layer.** This demonstrates that the process yields a Pd membrane protected by a thin Au-Pd alloy layer of uniform composition. These results are yet to be quantified, and will be supplemented by an electron microprobe analysis through the thickness of the foil.



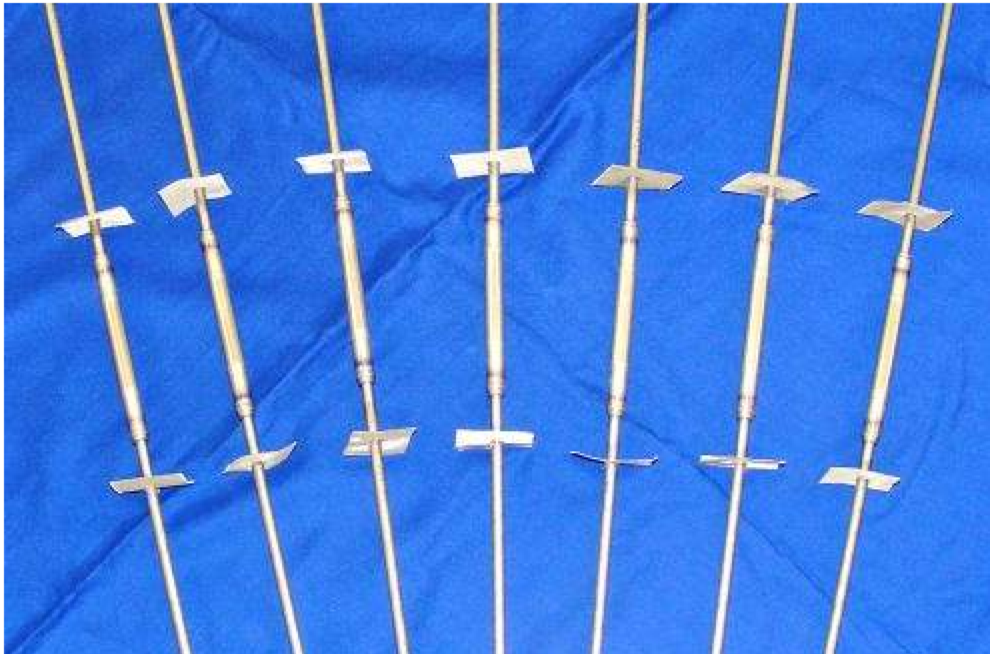
Technical Accomplishments & Progress
Inventory of Membranes for WGS Performance Testing

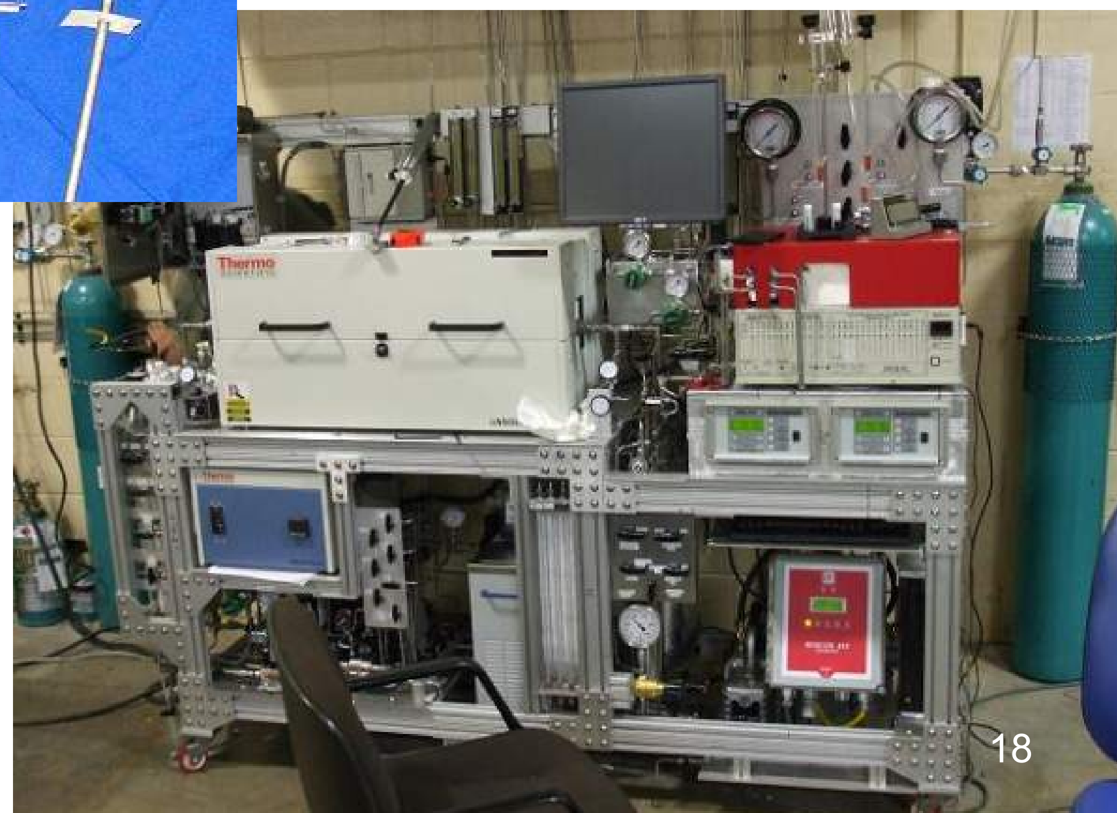
Pd alloy membranes with Au content ranging from 0-30% and thickness from 1.0-3.5 microns
Alloy composition can affect:

- Stable operational flux rate
- Cost
- Purity
- Operating limits
- Manufacturability
- Application viability



Technical Accomplishments Membrane Fabrication and Testing





Selection of tubes of varying Pd-Au alloys ready for testing on the automated water gas shift test stand

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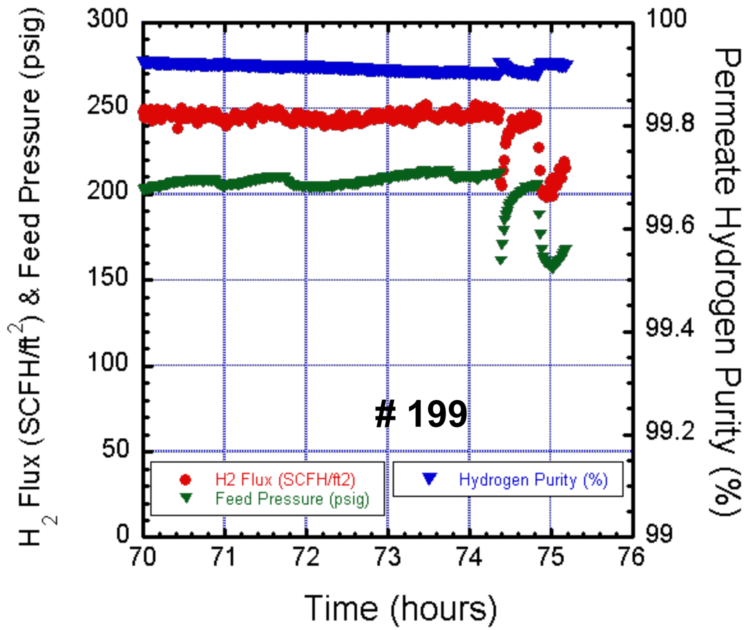
Technical Accomplishments & Progress
High Pressure WGS Test

CSM Membrane Sample #	201	199
Permeance		
Pure Gas (SCFH/ft^2·atm$^{0.5}$)	303	331
Mixed Gas (SCFH/ft^2·atm$^{0.5}$)	219	149
Flux - Mixed Gas (SCFH/ft^2)	245	216
H_2 Recovery (%)	67	60
Purity (%)	99.5	99.96
Test time (hrs)	120	75



- Feed gas: 50% H2, 1% CO, 30% CO2, 19% H2O
- T = 400°C, dP= 180 psid
- Feed pressure = 12.6 bar (182 psia)
- Permeate pressure = 0.8 bar (12 psia)
- Testing done at TDA Research Inc, Wheat Ridge, CO

Reduced flux likely due to concentration polarization

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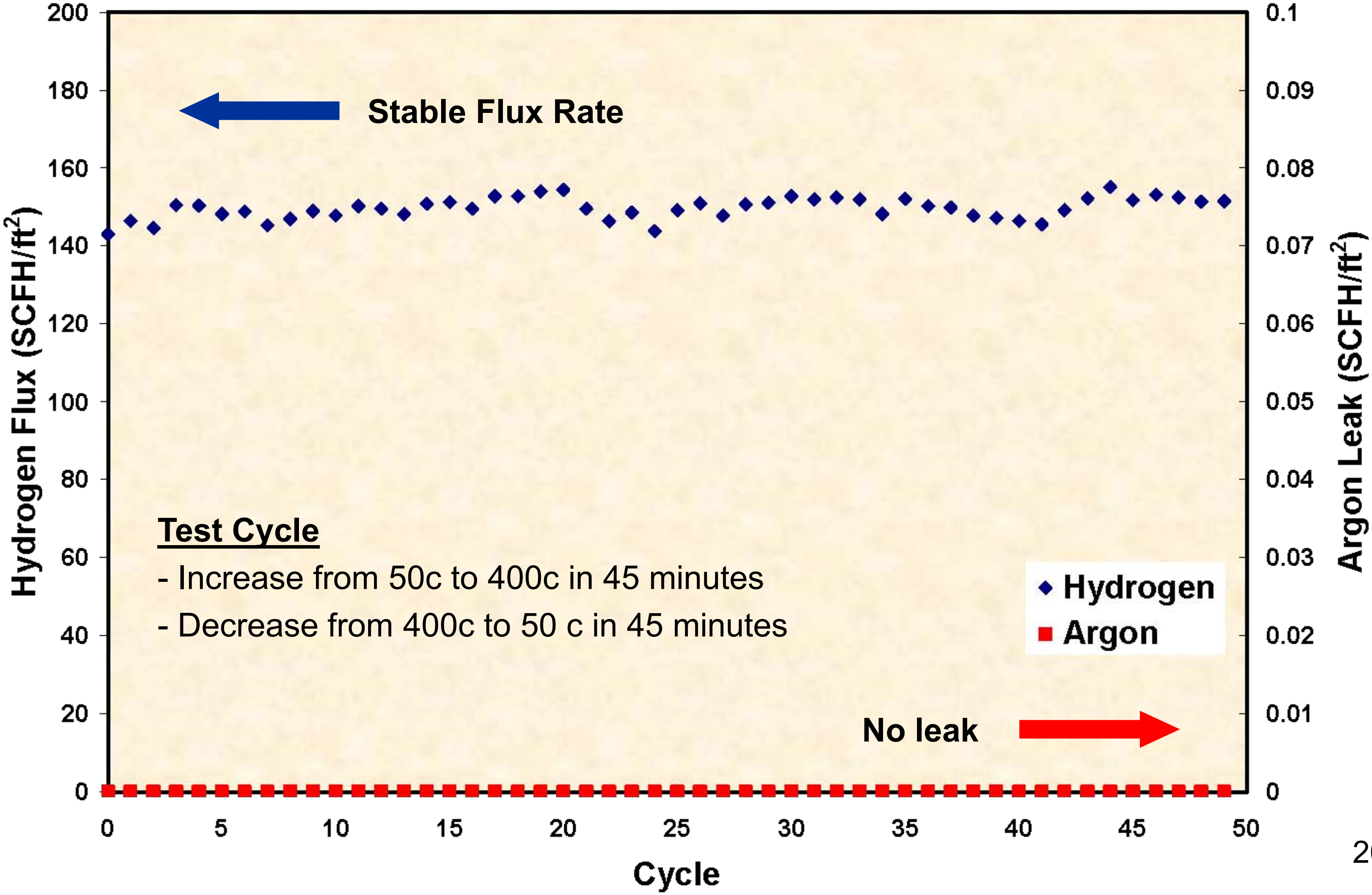
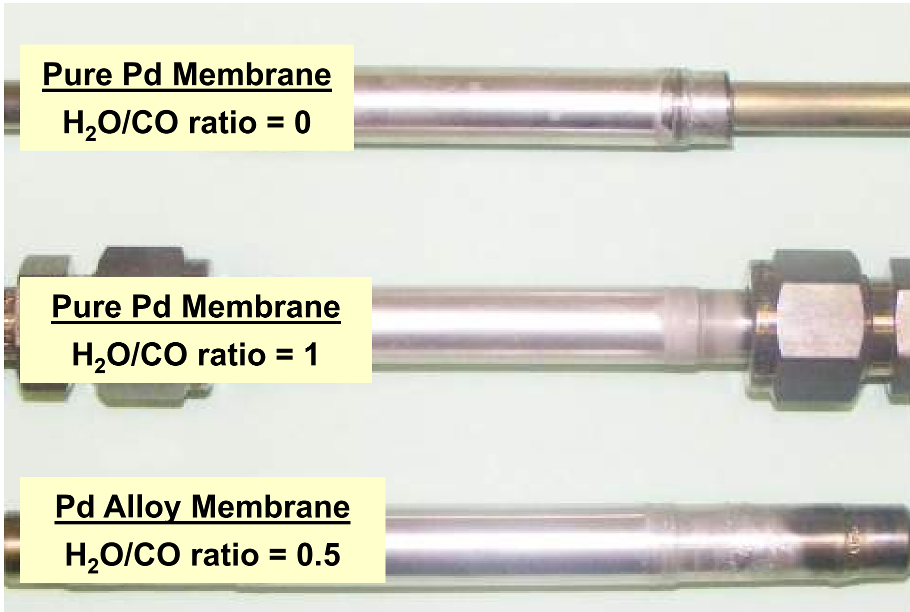
Technical Accomplishment – Thermal Cycle Durability



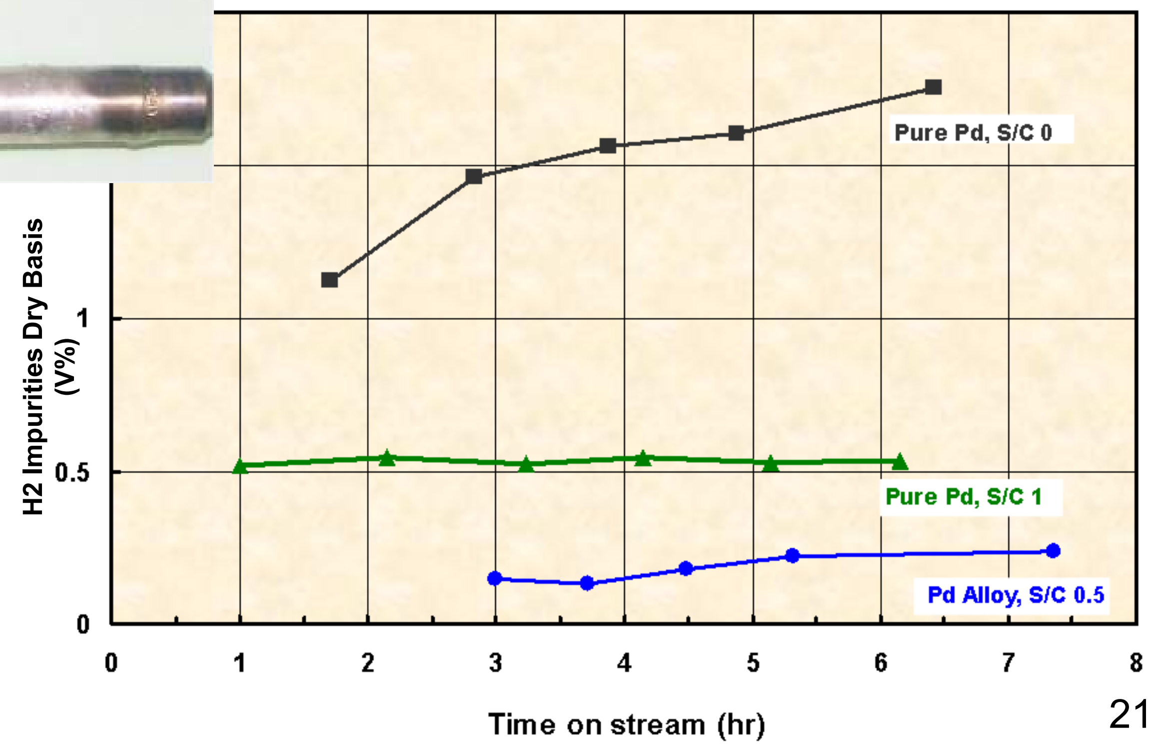
Technical Accomplishment – Operational Conditions



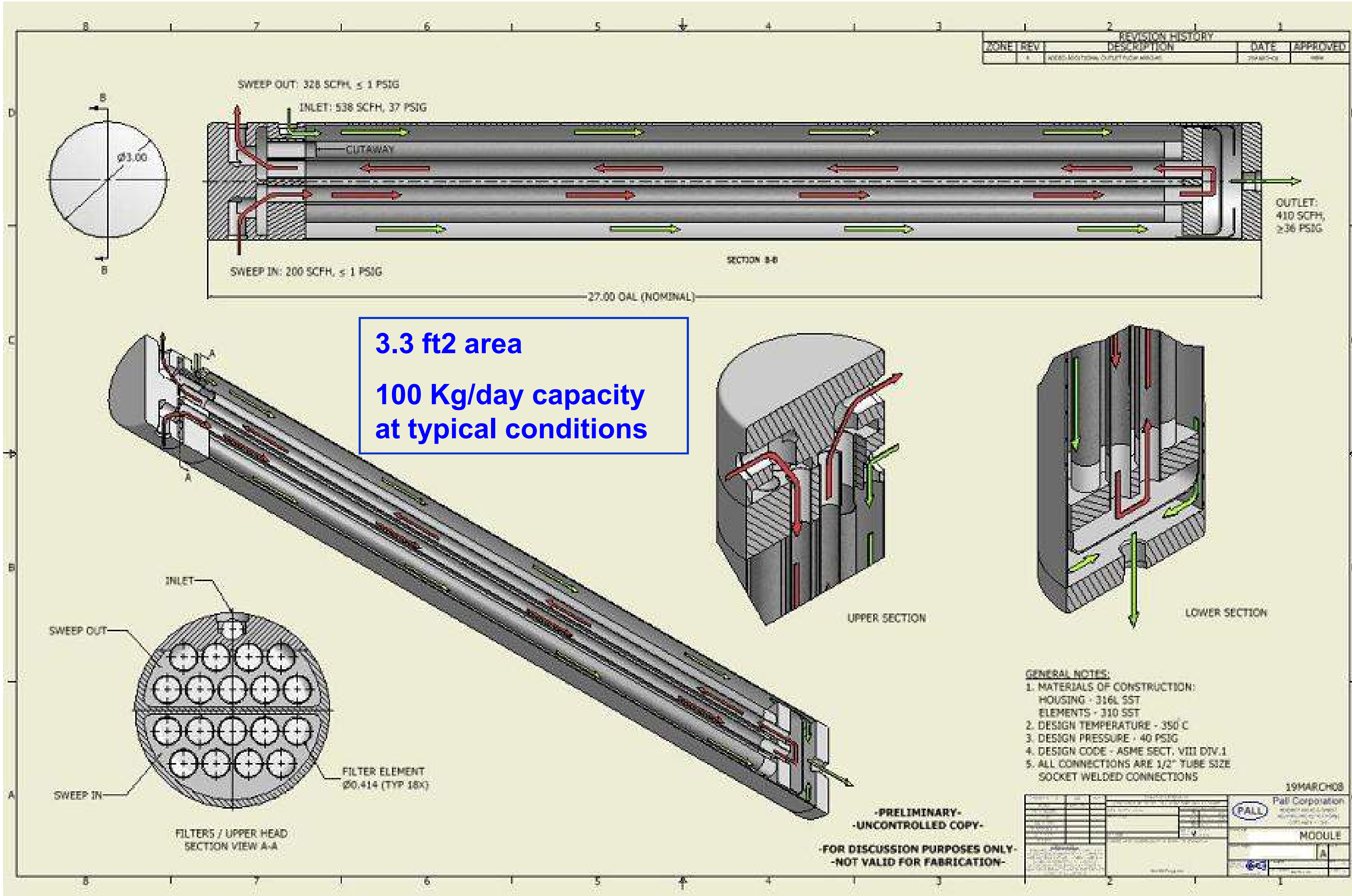
- S/C ratio of 1 is a minimum to prevent carbon formation
- Pd alloy allows for stable operation even in low steam conditions
- **Need to match alloy to process conditions for optimized performance**

Conditions for membrane testing:

Feed H_2 70%
CO 15%
H_2O/CO changed
CO_2 balance
Pressure 80 PSIG
Temperature 400°C
H_2 Recovery 65-70%



Technical Accomplishment - Module Design/Cost Estimate



3.3 ft2 area

100 Kg/day capacity at typical conditions

Technical Accomplishments & Progress
Techno-Economic Modeling Background

- Membrane cost analysis done by Pall Corp. as part of manufacturing scale-up evaluation and includes economies of scale estimates for volume production
- Membrane “cost” is based on sales price to end user of a membrane in a pressure vessel (ie: membrane module)
- Directed Technologies Inc. has developed a H_2 production model for cost analysis of medium temperature ethanol integrated reformer/WGS/membrane separator system coupled with H2A forecourt model
- H_2 production cost in “gallon of gas equivalent” (GGE) is determined for given process, operating conditions and capital costs
- Preliminary sensitivity analysis was conducted by DTI for determining the influence of membrane permeance and overall H_2 recovery on the cost of H_2 for 1500 kg/d H_2 production rate

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Technical Accomplishments & Progress

Techno-Economic Modeling Preliminary Results

H_2 Compressed to 300 psig	H_2 Recovery	Cost of H_2 – ($/kg)		
Membrane H_2 flux (400 C, 20 psid)		150 scfh/ft²	200 scfh/ft²	250 scfh/ft²
	70 %	$3.19	$3.18	$3.18
	80 %	$3.08	$3.07	$3.06
	90 %	$3.01	$3.00	$2.98

Integrated ethanol reformer/WGS/ membrane separator

H_2 production rate: 1500 kg/day

- Membrane flux rate (area/cost) has minor impact on cost of H_2
  - Cost of membranes <10% of total capital cost
- Increasing hydrogen recovery decreased cost of H_2 in this range
- Ethanol efficiency – 68.87% at 90% H_2 recovery,
  - 63.36% at 70% H_2 recovery
- Increasing ethanol efficiency to 79.4% was shown to reduce the cost of hydrogen to $2.67/kg by DTI in last year's AMR presentation

Preliminary results approach DOE target of $2-$3 per GGE

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Collaborations

- **Colorado School of Mines:** Sub-contractor focused on the material science. Responsibility includes selection of Pd-alloy compositions, fabrication of membranes and testing for compatibility. Extensive collaboration for compositional/process development, analytical testing and WGS testing will continue.

- **ORNL-HTML:** Sub-contractor focused on the evaluation of material properties using unique test equipment and techniques. Includes mechanical properties and alloy structure at operating temperature.

- **Directed Technologies Inc.** Independent contractor to the DOE. Used module costs and membrane performance estimates provided by project team to estimate H2 production cost. Uses computer model for both stand alone membrane separator and combined membrane/water gas shift reactor configurations. Plan to collaborate more interactively to analyze process variations that could reduce cost for both NG and Ethanol reforming.

Future Work

- Increase test time to establish membrane durability
  - Focus on post WGS test conditions for applicable reforming process
  - Use physical analysis and accelerated aging techniques to predict membrane life
- Improve membrane formation process
  - Increase separation factor / H_2 purity
  - Reduce cost
- Evaluate the effect of process variables and operating procedures on membrane performance
- Develop knowledge base to be used for selecting optimum alloy composition, process conditions and/or operating procedures
  - Match to system requirements for applications of interest
- Refine the techno-economic analysis to include optimized membrane and reforming process

Establish overall economic viability for H_2 production via membrane based reforming

Summary
Technical Accomplishments Achieved This Year

- Improved **membrane deposition** & conditioning
- Produced **membrane inventory** of various alloy compositions and thickness
- Obtained initial **performance and durability data** on high pressure WGS test
- Began development of **knowledge base** for matching alloy composition, process conditions and operating procedures
- Fabricated two **WGS test stands**, one for sensitivity analysis, the second for long-term durability analysis.
- Established baseline **economic analysis** showing feasibility of achieving DOE target

FY08 & FY09 Progress Against Targets

Performance Criteria	2010 Target	2015 Target	Accomplished FY08	Accomplished FY09
Flux SCFH/ft^2 @20 psi ΔP H_2 partial pressure, 400ºC (Pure H2 gas)	250	300	220	250
Membrane Cost, \$/ft^2 (including all module costs)	$1,000	<$500	$1,000	$1,000
ΔP Operating Capability, system pressure, psi	400	400 - 600	TBD	>170
Hydrogen Recovery (% of total gas)	>80	>90	TBD	>60
Hydrogen Permeate Quality	99.99%	>99.99%	99.999%	>99.99%*
Stability/Durability	2 years	>5 years	TBD	TBD

* Permeate quality in excess of 99.99% consistently achieved