

# DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program

## **High-Performance Palladium Based Membrane for Hydrogen Separation and Purification**

### **Final Project Report**

Pall Corporation  
Colorado School of Mines  
Oak Ridge National Laboratory

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## *FINAL TECHNICAL REPORT*

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## 1. EXECUTIVE SUMMARY

Expanded use of hydrogen as an energy carrier for America could help address concerns about energy security, global climate change, and air quality. Hydrogen can be derived from a variety of domestically available primary sources, including fossil fuels, renewables, and nuclear power. Another key benefit is that the by-products of conversion are generally benign for human health and the environment<sup>1</sup>.

Hydrogen and fuel cells have the potential for use in a broad range of applications, across virtually all sectors—commercial, industrial, residential, portable, and transportation. Hydrogen can be used as an energy carrier for a diverse range of end-use applications, including stationary power, backup power, specialty vehicles, transportation, and portable power. However, hydrogen also poses the most significant technical challenges, including the high cost of production and delivery, and the need for improved performance and lower cost in hydrogen storage systems. While the most significant long-term benefits will come from the use of hydrogen produced from renewable or low-carbon resources, the technologies exist today for hydrogen to be produced from natural gas cost-competitively with gasoline. The mission of the DOE's Fuel Cell Technologies' Hydrogen Fuels R&D effort is to research, develop, and validate technologies for producing, storing, and delivering hydrogen in an efficient, clean, safe, reliable, and affordable manner. A key program technical milestone for hydrogen technology readiness is to produce hydrogen from diverse, domestic resources at \$2.00-\$3.00 per gallon of gasoline equivalent (gge) delivered, untaxed.

Low-cost, high-temperature hydrogen separation membranes represent a key enabling technology for small-scale distributed hydrogen production units. Availability of such membranes with high selectivity and high permeability for hydrogen will allow their integration with hydrocarbon reforming and water gas shift (WGS) reactions, potentially reducing the cost of hydrogen produced. In this project Pall Corporation and team members Colorado School of Mines (CSM) and Oak Ridge National Laboratory – High Temperature Material Lab (ORNL-HTML) established the technical and economic viability of the use of a palladium (Pd) alloy composite membrane in a distributed H<sub>2</sub> production system. Results from this research added technology and product design information that offers the potential to significantly advance the commercial viability of hydrogen production.

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<sup>1</sup> [http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/national\\_h2\\_roadmap.pdf](http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/national_h2_roadmap.pdf)



This project focused on development of thin Pd-alloy film composite membranes deposited on porous inorganic supports. When compared to other high temperature inorganic membranes, these Pd-alloy membranes offer lower temperature operation and greater permeability than dense ceramic membranes, and near complete hydrogen selectivity than that provided by micro-porous inorganic membranes. Pd-metal-based dense membranes are known for their excellent hydrogen selectivity and permeability characteristics for decades; however, utilization of these membranes has so far been limited to small scale niche markets for hydrogen purification primarily due to the relatively high cost of Pd-alloy tubes compared to pressure swing adsorption (PSA) units. To utilize Pd-based membranes in bulk hydrogen production, it is necessary to reduce the cost of these membranes. This project was therefore aimed at development of thin-film Pd-alloy membranes deposited on Pall Corporation's DOE-based Pall AccuSep<sup>®</sup> porous metal tube substrates to form a composite hydrogen separation membrane for these applications. Porous metal substrates provide the structural strength to the composite membranes allowing utilization of thin Pd-alloy film for hydrogen separation. Pall's composite membrane development addressed the typical limitations of composite structures by developing robust membranes capable of withstanding thermal and mechanical stresses resulting from high temperature (400°C), high pressure (400 psi steam methane reformer, 1000 psi coal) operations and thermal cycling involved in conventional hydrogen production. In addition, the Pd-alloy membrane composition was optimized to be able to offer the most stability in the typical synthesis gas environments produced by reforming of natural gas and bio-derived liquid fuels (BILF) validating the technical effectiveness and economic feasibility of the technology demonstrated. The technology and system design information developed on the project is also of benefit to the public in its potential to offer a low-cost supply of hydrogen to fuel cells, one of the factors limiting their widespread application.

Achievements include optimization of the composition, microstructure and process for manufacturing of a porous metal tubular substrate and on development of a diffusion barrier coating on the substrate to support the Pd-alloy H<sub>2</sub> separation membrane. The Pd-alloy membrane composition and thickness were optimized and a process was developed to fabricate the composite membrane in 12-inch lengths. The membranes were analyzed by high temperature x-ray diffraction and an analysis of the results predicted the alloy to be stable at 400°C. Processes for fabrication of tubes and welding techniques were developed. A multi-tube module was designed to minimize concentration polarization and multi-tube modules were assembled. Tests were conducted on performance and durability and a techno-economic analysis was completed.

## 2. GOAL

The overall project goal is to verify that Pd-Alloy membrane coated on Pall Corporation's DOE-based Pall AccuSep<sup>®</sup> porous metal tube substrates, meet or exceed the DOE target goals under typical commercial operating conditions. i.e., 20 psi hydrogen partial pressure differential with a minimum permeate side total pressure of 15 psig, preferably >50 psi and 400°C.

## 3. OBJECTIVE

The objective of the project is to develop, demonstrate and conduct an economic analysis on a Pd-alloy membrane that enables the production of 99.99% pure H<sub>2</sub> from reformed natural gas as well as reformed bio-derived liquid fuels (BILF) such as ethanol at a cost of \$2-3/gge by 2015.

## 4. TASKS AND TECHNICAL TARGETS

Our project is focused on optimizing the overall composition of the Pd alloy, intermediate layers and tubular support, as well as the manufacturing methods required to produce a very thin, high-flux membrane for H<sub>2</sub> separation and purification on a robust, porous, inorganic substrate.

## PROJECT TASKS

An overview of the project tasks is listed in Table I.

**Table I – Project Tasks**

Task 1.	Optimize the Pd-alloy membrane on Pall AccuSep® porous metal substrates to assure stable performance with respect to product hydrogen flux and purity in water-gas-shift (WGS) reaction environments.
Task 2.	Fabricate tubes and modules by developing processes to coat porous metal AccuSep® tubular substrates with a diffusion barrier, a Pd-alloy membrane, a commercial process to weld non-porous fittings to the porous tubes, a technique to minimize concentration polarization in modules and assembling multi-tube modules having up to 12 tubes of 12-inch length.
Task 3.	Test performance and durability of the modules in synthesis gas environments to determine the effect of high pressure, time, steam and CO, H <sub>2</sub> S and thermal cycling. Maximize H <sub>2</sub> recovery. Test the membranes in more severe feed gas conditions than typically encountered in order to accelerate the decline in performance of the membranes
Task 4.	Characterize and analyze membranes using high temperature x-ray diffraction measurements at ORNL-HTML to develop a preliminary concept of the mechanism of Pd-Au alloy formation.
Task 5.	Compare projected system performance to goals with respect to H <sub>2</sub> flux rate and H <sub>2</sub> purity for up to 120 hours at an operating feed side pressure of >200 psig, demonstrate up to 500 hours durability testing in syngas water gas shift (WGS) reaction environments. Confirm performance in short term tests with multi-tube modules and measure H <sub>2</sub> flux in low concentration H <sub>2</sub> S exposure.
Task 6.	System techno-economic analysis using a preliminary techno-economic modeling analysis with Directed Technologies Inc. (DTI) for an integrated Pd-alloy membrane reformer/separator system at 1,500 kg/day distributed hydrogen production based on ethanol reforming.

## PERFORMANCE TARGETS

Performance targets are as defined in the DOE's 2011 Interim Update HFCIT Multiyear RD&D plan for hydrogen production using dense metallic membranes. These targets are shown in Table II.

**Table II**

**DOE Technical Targets: Dense Metallic Membranes for Hydrogen Separation and Purification<sup>a</sup>**

<b>Performance Criteria</b>	<b>Units</b>	<b>2006 Status</b>	<b>2010 Target</b>	<b>2015 Target</b>
Flux Rate <sup>b</sup>	SCFH/ft <sup>2</sup>	>200	250	300
Module Cost (including membrane material) <sup>c</sup>	\$/ft <sup>2</sup> of membrane	1,500	1,000	<500
Durability <sup>d</sup>	hr	<8,760	26,280	>43,800
Operating Capability <sup>e</sup>	psi	200	400	400-600
Hydrogen Recovery	%	60	>80	>90
Hydrogen Quality <sup>f</sup>	% of total (dry) gas	99.98	99.99	>99.99

<sup>a</sup> Based on membrane water-gas shift reactor with syngas.

<sup>b</sup> Flux at 20 psi hydrogen partial pressure differential with a minimum permeate side total pressure of 15 psig, preferably >50 psi and 400°C.

<sup>c</sup> Although the cost of Pd does not present a significant cost barrier due to the small amount used, the equipment and labor associated with depositing the material (Pd), welding the Pd support, rolling foils or drawing tubes account for the majority of membrane module costs. The \$1,500 cost status is based on emerging membrane manufacturing techniques achieved by our partners and is approximately \$500 below commercially available units used in the microelectronics industry.

<sup>d</sup> Intervals between membrane replacements.

<sup>e</sup> Delta P operating capability is application dependent. There are many applications that may only require 400 psi or less. For coal gasification 1000 psi is the target.

<sup>f</sup> It is understood that the resultant hydrogen quality must meet the hydrogen quality requirements as described in Appendix C. These membranes are under development to achieve that quality. Membranes must also be tolerant to impurities. This will be application specific. Common impurities include sulfur and carbon monoxide.

**PROJECT MILESTONE SUMMARY.**

1. Test Pd-Au alloy membranes to determine parametric performance in WGS reaction environments for 100 hrs
2. Test a Pd-Au alloy membrane in WGS for 500 hrs. to determine performance
3. Test the Pd-Au alloy series in WGS for 100 hours to determine performance.
4. Determine performance trends as a function of Au level and membrane thickness
5. Based on average performance data calculate the surface area to produce 1500 kg/day H<sub>2</sub>
6. Design a membrane module based on this surface area to produce 1500 kg/day H<sub>2</sub>

7. Estimate the cost of this membrane module in high volume production
8. Submit the surface area and production cost to DTI for cost of H<sub>2</sub> production analysis
9. Design and fabricate a 4-inch long single tube membrane module
10. Test the module at 400°C and feed side and permeate side pressure of 70 and 50 psi, respectively.
11. Test the housing at 400°C and 400 psi

## 5. APPROACH

A primary objective of the Hydrogen, Fuel Cells and Infrastructure Technology (HFCIT)<sup>2</sup> Multi-year RD&D plan is to produce and deliver H<sub>2</sub> that is economically competitive for applications in transportation and stationary PEM fuel cell based power generation. Therefore, when commercially-deployed the Pd-alloy membrane-based process must enable the distributed production of hydrogen from natural gas or biomass-derived renewable liquids (BIL) such as ethanol in the range of \$2.00-\$3.00/gge (delivered, untaxed, 2005 dollars) by the year 2015. The goal of our project is maximizing the performance and minimizing the cost of the Pd-alloy based membranes to meet the performance targets shown in Table I.

Our project focused on optimizing the overall composition of the Pd alloy, intermediate layers and tubular support, as well as the manufacturing methods required to produce a very thin, high-flux membrane for H<sub>2</sub> separation and purification on a robust, porous, inorganic substrate. The substrate used is Pall's AccuSep<sup>®</sup> inorganic porous metal media which is readily scalable to high volume production as it is manufactured in long lengths. Robust high-area modules can be made by welding multiple tubes into a pressure vessel, eliminating low temperature seal materials. The experimental project work through three phases progressed through logical steps and involved selection of Pd-alloy system; selection of porous support materials; optimization of the substrate tube properties with ceramic diffusion barrier coating; optimization of alloy composition and film thickness to assure maximum durability; evaluation of membrane performance in pure gases, binary mixed gases, and simulated synthesis gas environments; demonstration of the membrane performance to meet milestones targets set for the Phase II program; development of approaches to minimize concentration polarization in designing multi-tube modules; and finally demonstration of the membrane performance to meet milestones set for the Phase III program. Technical and economic analysis of the membrane-based hydrogen production was conducted in collaboration with Directed Technologies Inc. using the H2A

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<sup>2</sup> Currently the Fuel Cell Technologies Program

model in the Phase II program and in collaboration with an end user (a large oil company involved in on-site hydrogen production) in the Phase III program.

## 6. ACCOMPLISHMENTS

### 6.1 ACCOMPLISHMENTS ON ACHIEVING OBJECTIVE AND TASKS

#### Task 1. Optimize the Pd-alloy membrane on Pall AccuSep® porous metal substrates

The objective of this task was to develop the optimal Pd-alloy membrane to assure stable performance with respect to product hydrogen flux and purity in water-gas-shift (WGS) reaction environments. This task included development of substrate and Pd-alloy membrane.

Substrate development:

- A 310SC porous stainless steel substrate was developed and scaled up as an upgrade to the original 316 stainless steel tube.
- The substrate tube manufacturing capability was scaled up to 1 meter in length.

Diffusion barrier layer development.

- A ceramic zirconia coating on the porous metal tubes was developed as a diffusion barrier (DB) to facilitate deposition of Pd-alloy membrane.
- The DB was optimized to yield a low profile weld and a controlled surface finish with a narrow pore size distribution.
- Sintering temperature of the diffusion barrier was optimized to increase the surface roughness and improve the bonding of Pd-alloy film to DB preventing membrane delamination.
- Commercial scale capability for the DB is now available for producing lengths up to 12 inches.

Pd-alloy Membrane development.

- Pd and Pd/Cu alloy membranes were initially formed on various AccuSep® substrates with the DB intermediate layer. Pd/Cu membranes were tested for their stability over pure Pd membranes.
- A second Pd alloy system, Pd/Au, however, appeared to be more stable in mixed gas streams of interest and was pursued in this project.
- Pd/Au alloy membrane composition and thickness have been optimized for durability.

- The membrane fabrication process has been scaled up to produce 12-inch long Pd-alloy membrane tubes.
- Determined optimal Pd-alloy membrane composition as Pd<sub>90</sub>Au<sub>10</sub> to assure stable performance with respect to product hydrogen flux and purity in WGS reaction environments.

## Task 2. Fabricate tubes and modules

### Development of welding technique

- Developed a commercial process for welding non-porous fittings to porous tubes.
- These welding techniques for the porous tubes to the transition fitting and then to the module tube sheet are now well established to allow fabrication of multi-tube modules.

### Fabrication of multi-tube modules

- Techniques were developed for minimizing concentration polarization in modules.
- Multi-tube modules were fabricated with up to 12 tubes of 12-inch length for testing in syngas environment and to verify performance observed with single tubes.

## Task 3. Test performance and durability

- Two identical water gas shift (WGS) test stands were set up, one at Pall and one at CSM and tests were conducted in synthesis gas environments to determine the effect of high pressure operation; long term operation; steam and CO as major constituents; H<sub>2</sub>S as trace constituent; thermal cycling; and maximization of H<sub>2</sub> recovery.
- Membranes were subjected to more severe feed gas conditions than typically encountered in order to accelerate the decline in performance of the membranes so that a greater number of membranes can be screened in a shorter period of time for optimization.
- Confirmed that concentration polarization effects were minimized while maintaining high hydrogen recoveries for a 12 tube, 12-inch long, multi-tube module.

## Task 4. Characterize and analyze membranes

- High temperature x-ray diffraction measurements at ORNL-HTML resulted in a preliminary concept of the mechanism of Pd-Au alloy formation.

#### Task 5. Compare projected system performance to goals

- Observed high mixed gas hydrogen flux rate (145 SCFH/ft<sup>2</sup>) and high hydrogen purity (<99.95%) for up to 120 hours at an operating feed side pressure of >200 psig.
- Met Phase III performance goal demonstrating up to 500 hours of durability testing on Pd-alloy membranes in syngas/WGS reaction environments with >75% hydrogen recovery and >75 SCFH/ft<sup>2</sup> overall hydrogen flux rate for the membrane.
- Demonstrated membrane performance stability with thermal cycling (50° – 400°C).
- Confirmed the membrane performance in short term tests with multi-tube modules.
- Observed a reversible H<sub>2</sub> flux decline with H<sub>2</sub>S exposure during testing with low concentration H<sub>2</sub>S exposure.

#### Task 6. System techno-economic analysis

- Preliminary techno-economic modeling analysis with DTI indicates that a H<sub>2</sub> cost of <\$3.10/kg is achievable with an integrated Pd-alloy membrane reformer/separator system for 1,500 kg/day distributed hydrogen production based on ethanol reforming.
- Hydrogen recovery was found to have much stronger influence on cost of hydrogen production compared to the membrane flux rate and module cost.
- Cost of hydrogen production with CO<sub>2</sub> capture was determined by an end user for a large scale (36,000 kg/hr) hydrogen production system at about \$2/kg. The capital cost of a Pd-membrane based hydrogen production process was found to be about 8% less than a PSA-based hydrogen production process.



## 6.2 ACCOMPLISHMENTS ON ACHIEVING TECHNICAL TARGETS

The accomplishments were compared with the Technical Targets as summarized in Table II and are discussed in greater detail below.

**Table III. Summary of Accomplishments vs. Technical Targets**

	2010 Target	2015 Target	Pall Status 2011
Flux (SCFH/ft <sup>2</sup> @20 psi $\Delta P$ H <sub>2</sub> partial pressure & 15 psig permeate side pressure)	250	300	270*
Membrane Cost (\$/ft <sup>2</sup> including all module costs)	\$1,000	<\$500	<\$2,000****
$\Delta P$ Operating Capability, system pressure (psi)	400	400 - 600	>600
Hydrogen Recovery (% of total gas)	>80	>90	>80**
Hydrogen Permeate Quality (%)	99.99%	>99.99%	99.999%***
Stability/Durability (years)	2	>5	TBD

\*Maximum observed. Averaged over more than 20 samples ~ 190 SCFH/ft<sup>2</sup>

\*\* Measured on a 50%H<sub>2</sub>/21%H<sub>2</sub>O/up to 3.5% CO/balance CO<sub>2</sub> mixed gas stream.

\*\*\* Projected purity based on H<sub>2</sub>/N<sub>2</sub> ideal selectivity.

\*\*\*\* Module cost includes membrane tubes and insert reducing polarization concentration to lower overall hydrogen production cost

### FLUX TARGET.

The 2010 flux target of 250 SCFH/ft<sup>2</sup> was exceeded on individual samples with thinner membranes. However, the economic analysis clearly indicated that the hydrogen flux rate exhibited a minor influence on the cost of hydrogen production. It was therefore deemed much more desirable to use a thicker membrane with a slightly lower hydrogen flux rate as a trade-off for hydrogen product purity and long term durability. The average value on several samples of the selected alloy (Pd<sub>90</sub>Au<sub>10</sub>) was ~190 SCFH/ft<sup>2</sup>. It was determined in the techno-economic analysis that flux is not as critical as H<sub>2</sub> recovery

and using this value was adequate to yield the required economic performance. These results are shown in Task 6 Section 6.3.

#### MEMBRANE COST TARGET

The new module design that lowers the overall effect of concentration polarization increased the cost above the target of \$1,000/ft<sup>2</sup>. The module design allowed for higher hydrogen recovery therefore lowering the overall cost of hydrogen production. The module cost including tubular Pd-alloy membranes and concentration polarization reduction inserts is estimated to be \$2,000/ft<sup>2</sup> with possible reductions when large scale production begins. The H<sub>2</sub> production cost as a function of membrane cost is presented in the DTI techno-economic analysis section of this report (Task 6.2). At a module cost of \$2,000/ft<sup>2</sup> (membrane cost of \$1,500/ft<sup>2</sup>), a H<sub>2</sub> production cost of ~\$3.06 gge is projected at a 90% H<sub>2</sub> recovery and 150 SCFH/ft<sup>2</sup> flux.

#### ΔP OPERATING CAPABILITY TARGET

The 2010 target goal of 400 psi was exceeded and the module was designed for 600 psi at 400°C. In the actual high-pressure collapse test, the membrane was found to survive 3,000 psi feed side pressure at room temperature.

#### HYDROGEN RECOVERY TARGET

The experimentally observed recovery in several individual experiments is determined by chosen operating conditions and is not necessarily a limit of the membrane performance. Greater than 80% hydrogen recovery was achieved at selected operating conditions. For the Phase III milestone a hydrogen recovery value of 75% was selected and was demonstrated during testing using the WGS compositions.

#### HYDROGEN PERMEATE QUALITY TARGET

A purity of 99.999% was achieved using pure H<sub>2</sub> and Ar gas streams. This purity is based on H<sub>2</sub>/N<sub>2</sub> ideal selectivity. A maximum flux of 270 (SCFH/ft<sup>2</sup> @ 20 psi ΔP H<sub>2</sub> partial pressure & 15 psig permeate side pressure) was achieved. The average flux was ~190 SCFH/ft<sup>2</sup> over 20 samples.

#### STABILITY/DURABILITY TARGET

A durability of 500 hours was achieved in a WGS stream on the Pd<sub>90</sub>Au<sub>10</sub> alloy membrane. The test was intentionally ended at 500 hours to conclude the project.

## 7. PROJECT ACTIVITIES

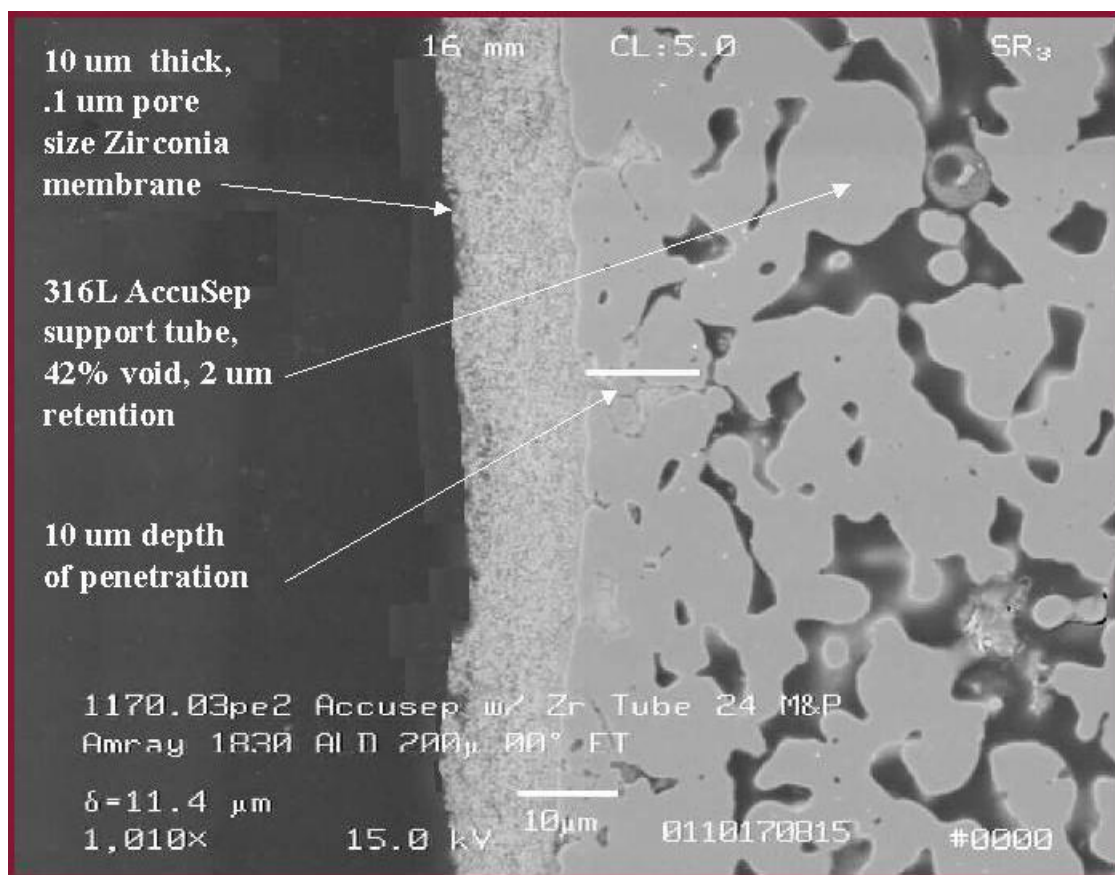
### TASK 1. OPTIMIZE THE FORMATION OF THE PD ALLOY MEMBRANE TO ACHIEVE THE TARGET GOALS.

#### 1.1 DEVELOP SUBSTRATE

The original AccuSep® porous stainless steel technology was acquired from Oak Ridge National Laboratory prior to the start of this contract. Pall Corporation has established a manufacturing facility to produce these porous stainless steel tubes in a classified environment at Oak Ridge. A 310SC porous stainless steel substrate was developed and scaled up as an upgrade to the original 316 stainless steel tube. The 310SC stainless is a higher strength high temperature alloy as compared to 316L. The 310SC substrate allows for continuous operation at 400°C and 400 psi, which is outside the safe operating conditions of the 316 stainless steel. The substrate tube manufacturing capability was scaled up from 4-inch lengths to up to 1-meter in length. Scale up to the longer lengths included requirements for development of the diffusion barrier and module. These requirements include a narrow pore size distribution, surface finish, and surface chemistry.

#### 1.2 DEVELOP DIFFUSION BARRIER COATING

A zirconium oxide diffusion barrier was developed to limit the interdiffusion of elements in the stainless steel substrate into the palladium membrane. A cross section of the microstructure of the zirconium oxide diffusion barrier and the stainless steel substrate is shown in Figure 1.



**Figure 1.** Cross section of the microstructure of the zirconium oxide diffusion barrier layer and the porous stainless steel substrate.

Zirconium oxide was chosen because it has a coefficient of thermal expansion similar to the 310SC stainless steel. The diffusion barrier coating also allows for a thinner membrane to be applied to the substrate by creating a smaller pore structure that is easily bridged by the palladium membrane. Optimization consisted of developing a coating that stopped interdiffusion of the substrate and membrane, allowed a thin dense palladium membrane to be applied, and was stable during the DOE target goal thermal and pressure cycles. Four inch substrates were developed for initial trials, twelve inch substrates were produce after the initial development was proven. The process for applying the coating should be easily scaled to 1 meter lengths in the future.

### 1.3 DEVELOP ELECTROLESS PLATING MEMBRANE SYNTHESIS PROCESS

The electroless plating process is a cost-effective, scalable process for depositing thin, uniform membrane layers.

#### 1.3.1 PROCESS

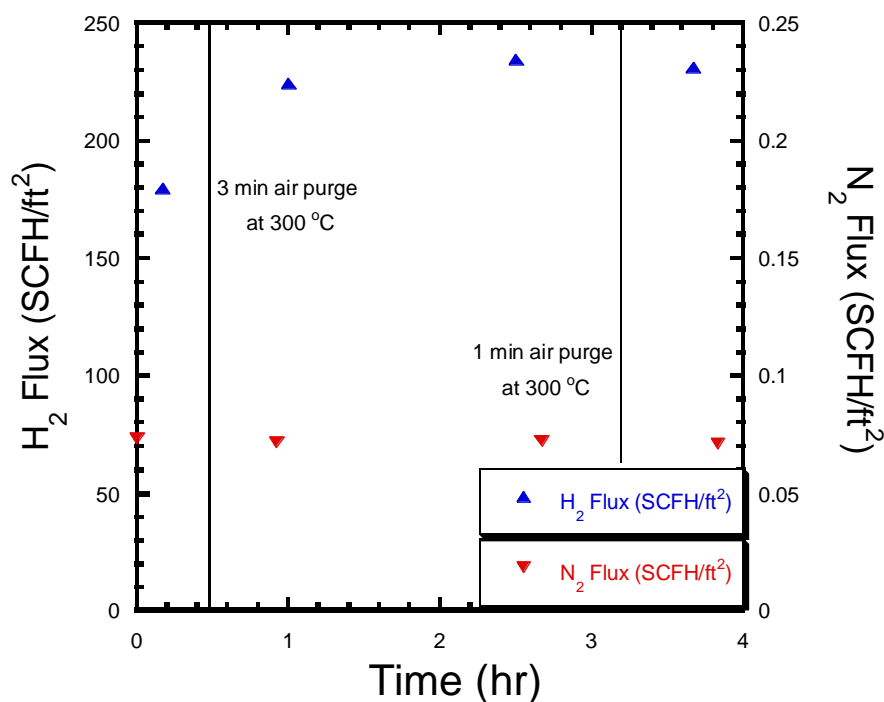
Accusep® supports were evaluated by nitrogen dry gas flow at 20 psig in addition to performing a pore distribution profile (wet/dry flow). Supports were then air brushed with activating solution and fired at 350°C in air for 5 hours. This process was repeated for a total of two activations. The supports were then placed in reducing solution for 30 minutes before they were plated with 100 mL flowing Pd plating solution at 50-55°C for 20 minutes followed by overnight Pd repair (described below) and overnight gold plating at 55°C. Following each plating step, the membrane was dried, weighed and measured for nitrogen leak flow. Membrane thickness was determined by weight gain. With each plating cycle, adding 1-1.5 micron membrane thickness the plating process was repeated until the desired membrane thickness, alloy composition and leak rate were achieved. Compositions of plating solutions used are given in Table IV.

**Table IV. Plating solution compositions**

Solution	Component	Quantity	Concentration
Activating	Palladium(II)Acetate	33 g/L	147 mM
	Chloroform HPLC grade		
Reducing	Deionized water	650mL/L	5.1 M
	28-30 wt% NH <sub>4</sub> OH	340mL/L	10 mM
	Hydrazine (1M)	10 mL/L	
Pd Plating	Deionized water	599 mL/L	130.8 mM
	37 wt% HCl	11 mL/L	5.85 M
	28-30 wt% NH <sub>4</sub> OH	390 mL/L	30.7 mM
	PdCl <sub>2</sub> 99% pure	5.45 g/L	10 mM
	Hydrazine (1M)	10 mL/L	
Gold Plating	AuCl <sub>3</sub>	1 g/L	3.3 mM
	NaOH	10 g/L	250 mM

### 1.3.2 PROCESS IMPROVEMENT TO INCREASE FLUX

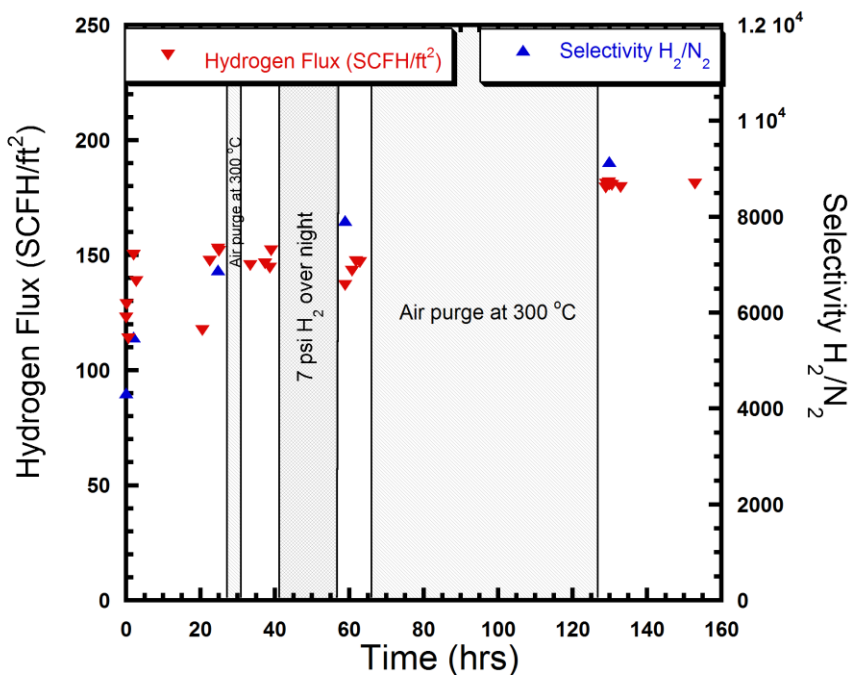
Air oxidation of the membrane during (or after) the annealing process has been observed to increase the hydrogen flux. Repetitive oxidation does not increase the flux ad infinitum, but reaches a maximum level dependent on the composition and processing conditions. As an example, the flux vs. time performance for membrane #245 (1.6 micron, pure Pd) oxidized at 300°C is shown in Figure 1. The air oxidations are performed at 300°C while the flux measurements are performed at 400°C. Note that the first oxidation step increases the hydrogen flux without increasing the nitrogen leak flux. The second air oxidation step does not change either flux rate.



**Figure 2.** The pure gas hydrogen and nitrogen flux vs. time is given for membrane #245 a 1.6 micron pure Pd membrane oxidized at 300°C.

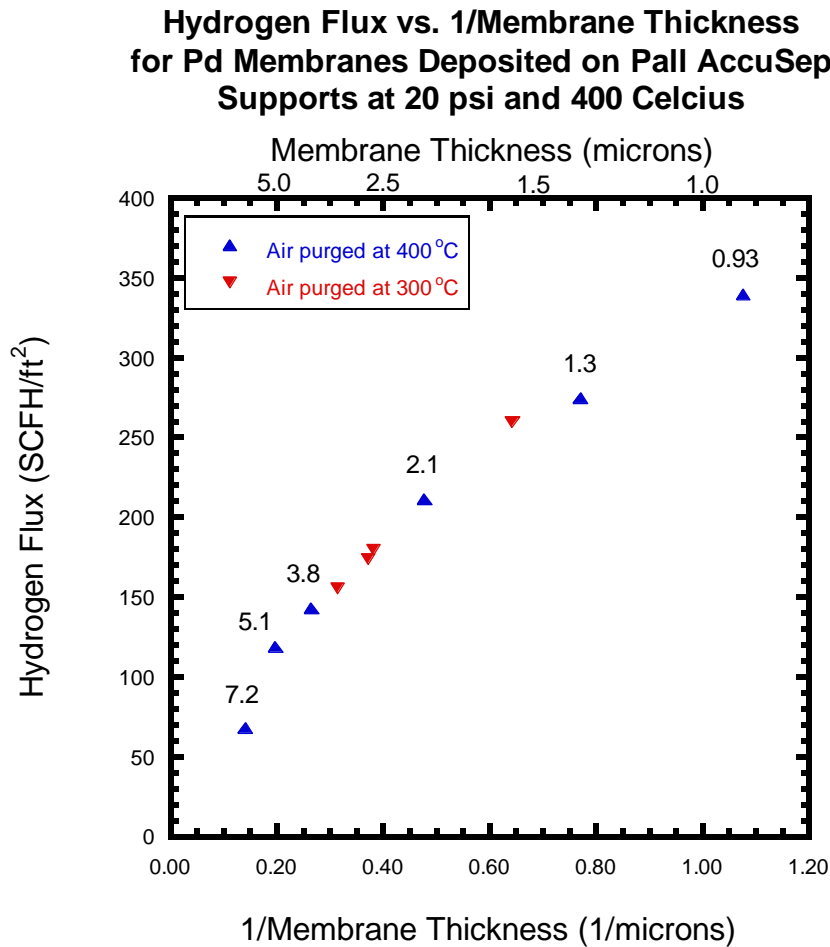
An increase in both hydrogen flux and selectivity in pure gas tests on membrane #235 oxidized at 300°C is shown in Figure 3. Since oxidative treatment at 300 °C has no effect on nitrogen leak rate, both hydrogen flux and selectivity increase under these oxidizing conditions.

**CSM235 1.9 micron Pd<sub>92</sub>Au<sub>8</sub>**  
**increase in Hydrogen Flux and pure gas selectivity**  
**at 400 °C with successive air purges at 300 °C**



**Figure 3.** The pure gas hydrogen flux and selectivity of membrane #235 upon consecutive air purges at 300°C. Note that both hydrogen flux and pure gas selectivity increase with air oxidation.

Air oxidation was also studied at 400°C. Membranes oxidized at both 300°C and 400°C have the expected flux with regard to the membrane thickness as shown in Figure 4. When air oxidation is performed at 400°C the nitrogen leak rate also increases to give a small decrease in selectivity[1]. This increase in nitrogen leak rate is believed to come from rearrangement of the palladium (or alloy) membrane leading to pinhole formation.



**Figure 4.** Hydrogen flux vs. inverse membrane thickness for membranes oxidized at 300°C and 400°C.



The increase in nitrogen leak rate observed at 400°C is not observed for membranes oxidized at 300°C., resulting in generally higher selectivities (Table V) for 300°C oxidative treatment. Changing the air oxidation temperature from 400°C to 300°C resulted in minimal to no increase in nitrogen leak rate with an increase in hydrogen flux (235 SCFH/ft<sup>2</sup>), leading to an increase in pure gas selectivity[2]. Oxidation at 300°C was adopted as our standard process. Researchers at SINTEF have observed very similar flux increases of very thin Pd-Ag alloy membranes after oxidation at 300°C[2].

**Table V. Membrane oxidation study**

CSM#	Oxidation Temperature (°C)	Thickness (μm)	H <sub>2</sub> Flux at 20 psi ΔP, 400 °C (SCFH/ft <sup>2</sup> )	H <sub>2</sub> /N <sub>2</sub> Ideal Selectivity
77	400	7.2	68	3,210
69	400	5.1	119	1,240
76	400	3.8	143	802
80	400	2.1	212	6,170
93R*	400	1.3	275	1,740
93	400	0.93	340	560
245	300	1.56	260	3,600
245R*	300	2.63	180	50,000
227	300	2.7	174	7,500
228	300	3.2	156	3,000

\*Membranes #93 and #245 were re-plated with additional Pd after permeation testing to produce membranes #93R and #245R, respectively.

#### ASSESSMENT OF IMPACT ON PROJECT RESULTS.

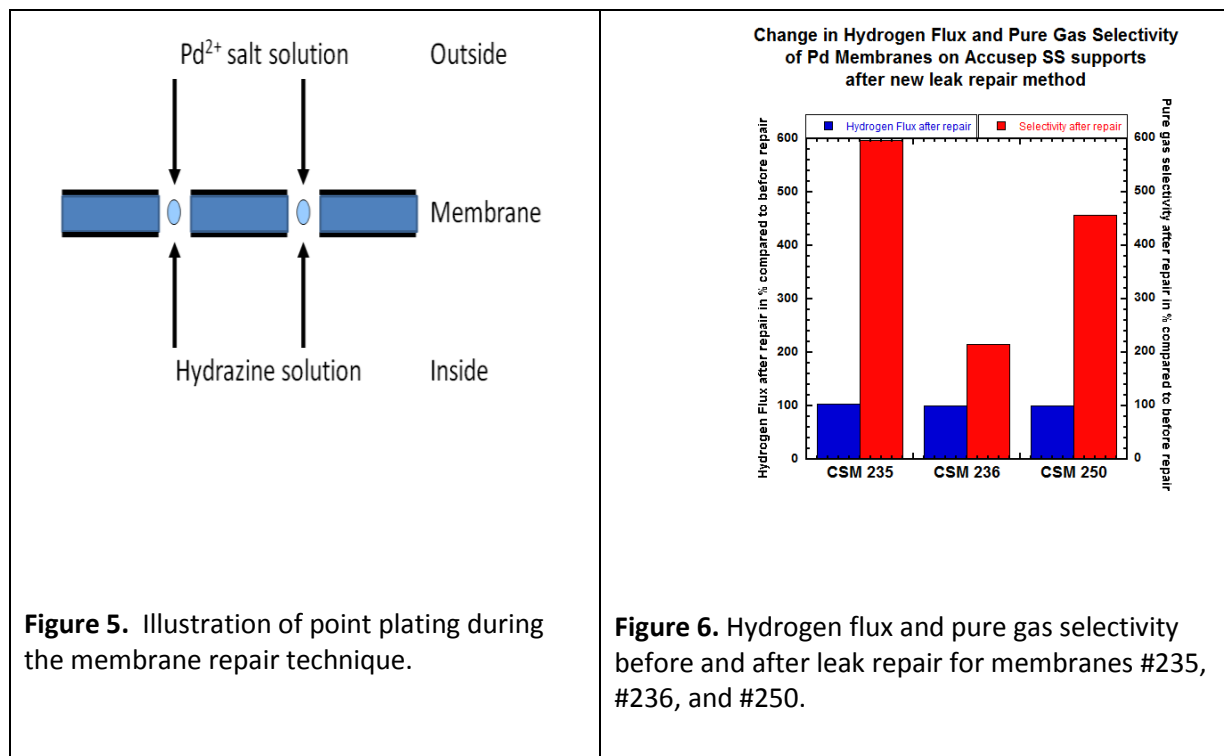
Higher flux and selectivities were observed with the oxidation process and oxidation at 300°C was adopted as our standard process.

#### 1.3.3 PROCESS IMPROVEMENT TO DECREASE LEAKAGE

During synthesis membranes are evaluated after each plating cycle by reverse pressurizing the membrane and submerging in water to observe location of leaks. Small holes were observed in several

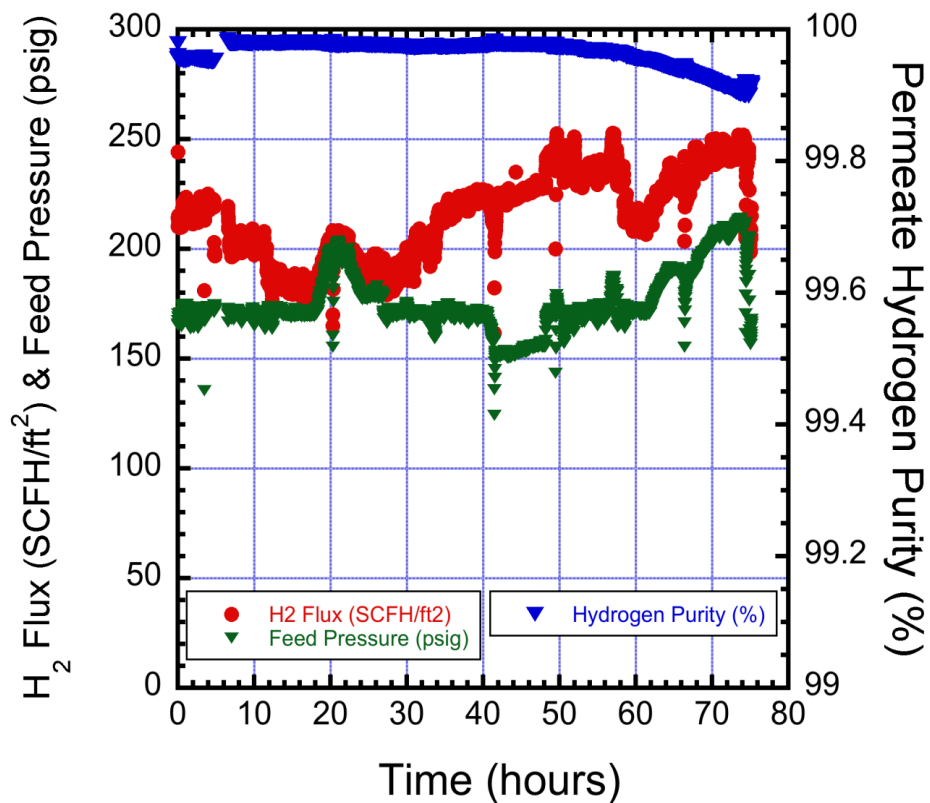
membranes giving rise to leakage. While repetitive plating will eventually cover all these holes, this approach leads to thicker membranes. To achieve thinner leak free membranes a repair method was developed using a plating solution on the outside of the membrane and reducing solution in the lumen of the support leading to point plating in the holes (as illustrated in Figure 5) decreasing the leak without adding thickness to the membrane. The hydrazine reducing agent, located in the lumen of the support, can only contact the Pd salt solution in the pin holes, leading to selective point plating.

Figure 6 shows the hydrogen flux and pure gas selectivity for three membranes after single repair. Evidence for the repair process adding no thickness to the overall membrane is both that the dry weight of the membrane stays constant and the pure gas hydrogen flux is the same before and after repair. The pure gas selectivity increase in each instance suggests selective plating in the holes.



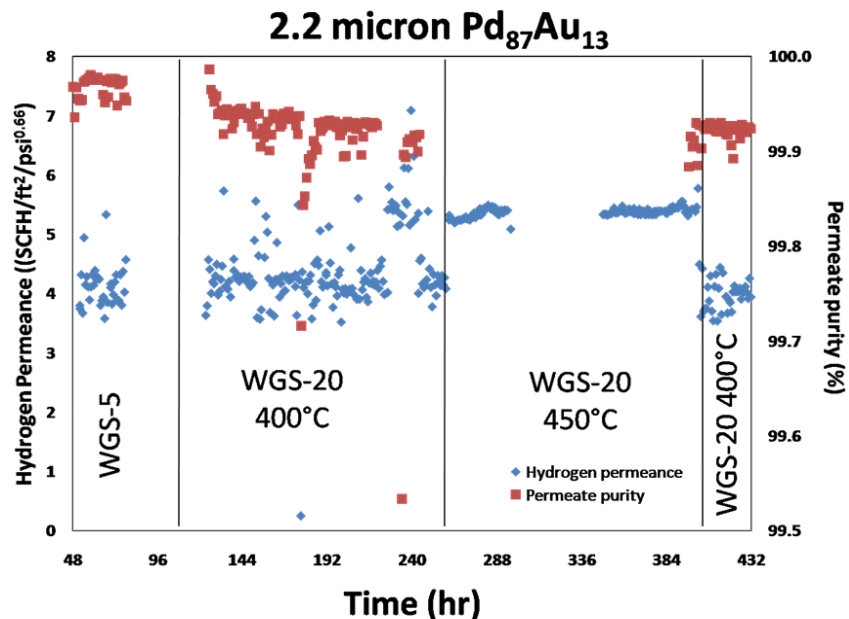
Membranes that had interstitial repair plating after each palladium plating showed higher lifetime, measured as stable permeate purity, than membranes with a single or no repair. Mixed gas hydrogen permeation was performed on membrane #199 (2.4 micron, 4% Au) with one repair plating performed as the last plating step. The test was conducted at 400°C with a feed stream composition of 50% H<sub>2</sub>, 30%

CO<sub>2</sub>, 1% CO and 19% steam at 170 psig feed pressure and 0 psig permeate pressure. As shown in Figure 7, after 50 hours on stream, the hydrogen purity of the single repair membrane starts to decrease.



**Figure 7.** Mixed gas H<sub>2</sub> permeation test of membrane #199 with one repair cycle.

When the interstitial repair process was implemented, the time before permeate purity decline was observed to increase to over 200 hours as seen for membrane #357 in Figure 8.



**Figure 8.** Test of membrane #357 in high CO feed stream environment and elevated temperature show no decrease in membrane H<sub>2</sub> flux or H<sub>2</sub> permeate purity.

#### ASSESSMENT OF IMPACT ON PROJECT RESULTS.

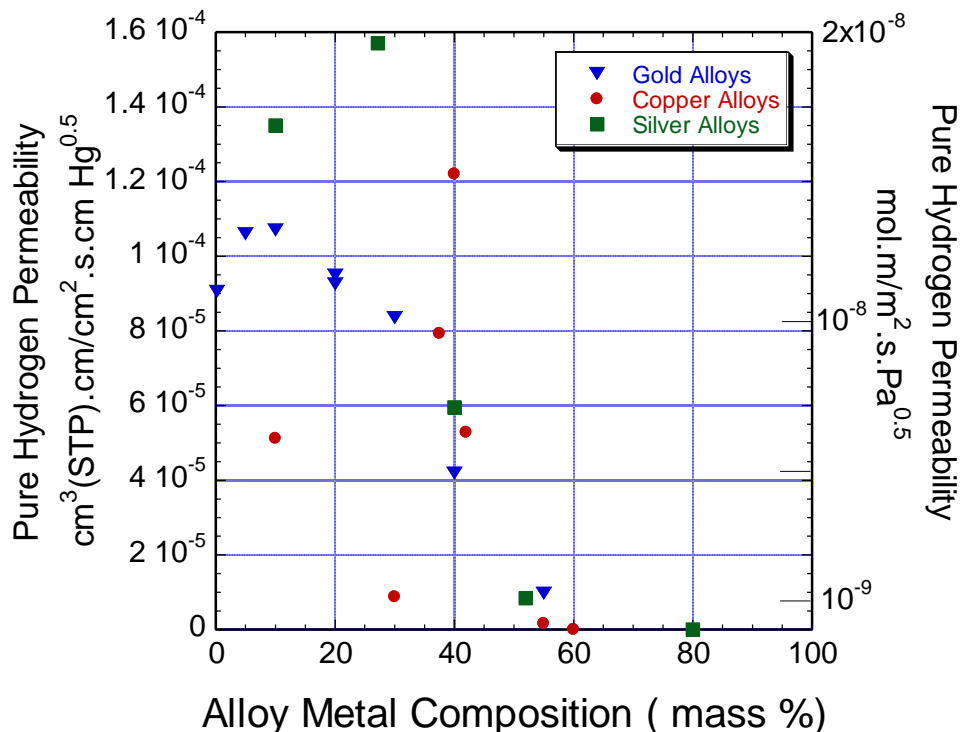
The repair technique improved the performance without significantly increasing the thickness of membranes synthesized with the electroless process.

#### 1.4 DEVELOP A PD-ALLOY MEMBRANE THAT WILL ACHIEVE THE PERFORMANCE TARGETS

Several Pd-alloys were considered for the membrane to achieve the performance targets. It was initially hypothesized that a Pd-Cu alloy offers the potential to meet the performance goals.

Figure 9 shows the influence of alloy composition on the pure hydrogen permeability of palladium alloy foils at 350°C[3]. Note that the maximum permeability for the Pd-Cu binary alloy occurs only at the 40 mass % Cu composition, where the crystal structure of the material is body centered cubic (BCC). At Cu compositions other than 40%, the material has a face centered cubic (FCC) lattice. In previous work, we were able to produce BCC phase Pd-Cu alloys with close to the optimal composition[4, 5] using electroless plating. However, it is quite difficult to control the electroless deposition to consistently obtain the 40% Cu composition in the alloy film. Although the FCC PdCu alloys are much easier to fabricate, they have low permeability.

However, the  $H_2$  permeability for the Pd-Au alloy in Figure 9, shows that the maximum permeability occurs at approximately 10% Au, and the permeability is the same as pure Pd or higher for all compositions below 20% Au. The McKinley patents also suggest that the chemical resistance of the Pd-Au alloy system is superior to both pure Pd and Pd-Cu[3, 6, 7] .



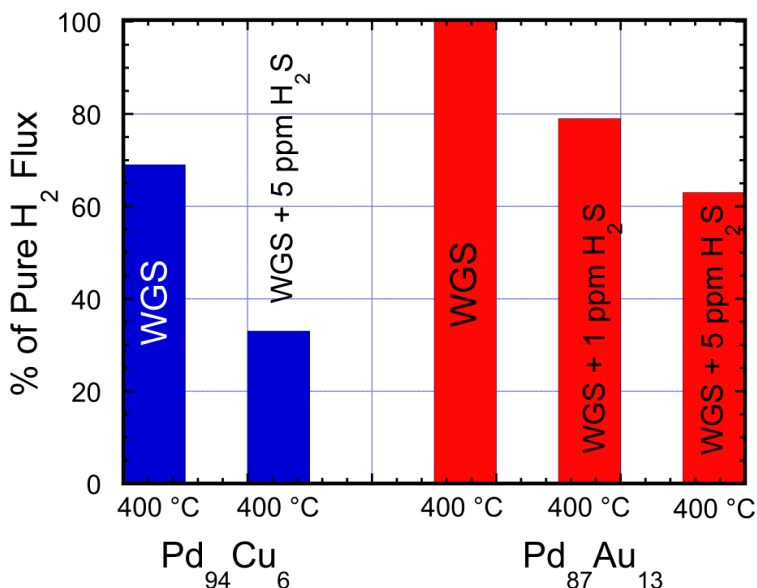
**Figure 9.** The influence of alloy metal composition on the pure hydrogen permeabilities of Pd alloy foils at 350°C.

In a parallel research project at CSM<sup>3</sup>, the permeation performance of Pd-Cu (GTC-30) and Pd-Au (GTC-75) composite membranes fabricated by electroless plating [7] on porous ceramic substrates were measured in gas mixtures representative of a water-gas shift (WGS) product mixture<sup>4</sup>. At 400°C with a feed pressure of 60 psig, the feed composition was 51%  $H_2$ , 26%  $CO_2$ , 2 % $CO$ , 21 %  $H_2O$ . As shown in Figure 10, for the Pd-Au membrane, the flux in WGS was the same as in pure gas at constant driving force. However, for the Pd-Cu membrane, there was ~ 30% reduction in the flux compared to the pure gas value keeping the hydrogen partial pressure driving force constant.

<sup>3</sup> DE-FG26-03NT41792, "Palladium/Copper Alloy Composite Membranes for High Temperature Hydrogen Separation"

<sup>4</sup> Prof. Way was invited by SSIRO (Commonwealth Scientific and Industrial Research Organization) Australia to give these lectures. CSIRO paid for Prof. Way's travel expenses and no project funds were spent on this international travel.

When 1 ppmv H<sub>2</sub>S was added to the water gas shift mixture, there was a 21% reduction in the permeate flow or hydrogen flux of the Pd-Au membrane. The 21% decrease is considerably less than the 38% drop in H<sub>2</sub> flux previously observed for a Pd<sub>94</sub>Cu<sub>6</sub> alloy composite membrane tested at 350°C with the same 1 ppmv H<sub>2</sub>S feed composition [7] (not shown below). The inhibition, or reduction in hydrogen flux due to H<sub>2</sub>S, was 37% in the Pd<sub>87</sub>Au<sub>13</sub> sample and by 68% in the Pd<sub>94</sub>Cu<sub>6</sub> sample when the H<sub>2</sub>S feed composition was increased to 5 ppmv.



**Figure 10.** Comparison of the performance of PdCu and PdAu composite membranes (porous alumina support) in water-gas shift mixtures with and without H<sub>2</sub>S. Feed pressure was 60 psig and gas composition was 51% H<sub>2</sub>, 26% CO<sub>2</sub>, 2 %CO, 21% H<sub>2</sub>O

The pure H<sub>2</sub> flux for the Pd<sub>87</sub>Au<sub>13</sub> membrane (GTC-75) was about 33% higher than that of the Pd<sub>94</sub>Cu<sub>6</sub> (GTC-30) membrane after correcting for the small difference in thickness [7].

From Figure 7, this is reasonable given the higher H<sub>2</sub> permeability of the Pd-Au alloy compared to Pd-Cu. A Cu composition of 6% (FCC phase) was used for this test since researchers at the DOE NETL reported that the sulfur resistance of the FCC PdCu alloys was the highest observed in this system[8]. Additional details regarding the permeation experiments with H<sub>2</sub>S can be found in the Appendix.

#### DEPARTURE FROM PLANNED METHODOLOGY

Based on the combination of factors including ease of fabrication, high flux, and improved resistance to carbon species and  $H_2S$  it was concluded that the Pd-Au alloy system offers the potential to be a better membrane system than Pd-Cu and was selected for the balance of the program.

#### ASSESSMENT OF IMPACT ON PROJECT RESULTS.

The decision to change the development effort from the Pd-Cu alloy system to the Pd-Au alloy system was a good decision in that the Pd-Au system did achieve the objectives of the contract and had a positive impact on the project results.

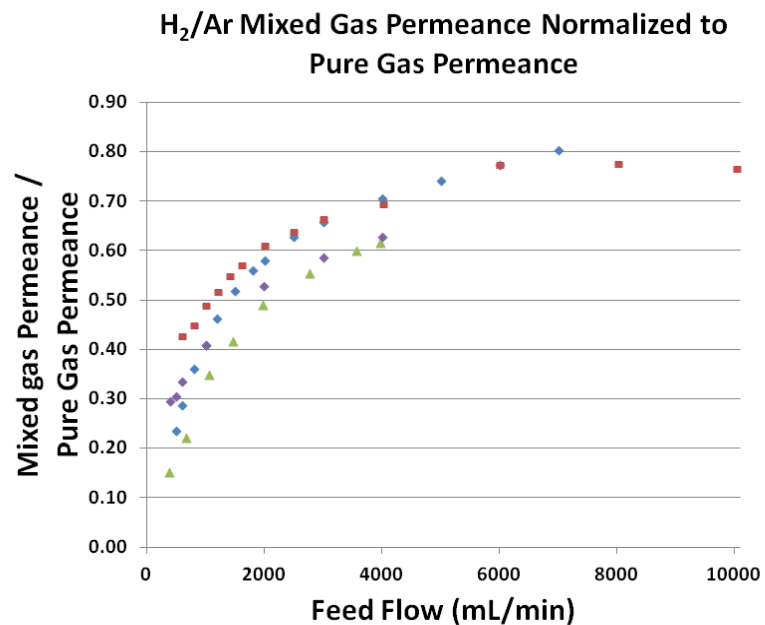
### TASK 2. FABRICATE TUBES AND MODULES

#### 2.1 MINIMIZE CONCENTRATION POLARIZATION EFFECT

Palladium membranes are known for their ability to allow hydrogen to permeate through them while being mostly impermeable towards other gases. Given a feed of hydrogen mixed with other gases, the permeate should be mostly hydrogen. However, even though the membrane is impermeable to the other gases, the other gases can still interfere with the permeance of hydrogen through the membrane, primarily by preventing the hydrogen from diffusing to the surface of the membrane from the bulk gas. This effect is known as concentration polarization – as hydrogen is removed from the surface region into the membrane and the other species do not, the concentration of the other species is higher on the surface region of the membrane than it is in the bulk. This results in a boundary layer that depresses the flux of hydrogen through the membrane. The effects of concentration polarization are especially pronounced on the retentate side of palladium membranes in mixed gas where, because hydrogen has been removed by the membrane from the bulk, the bulk gas is hydrogen poor.

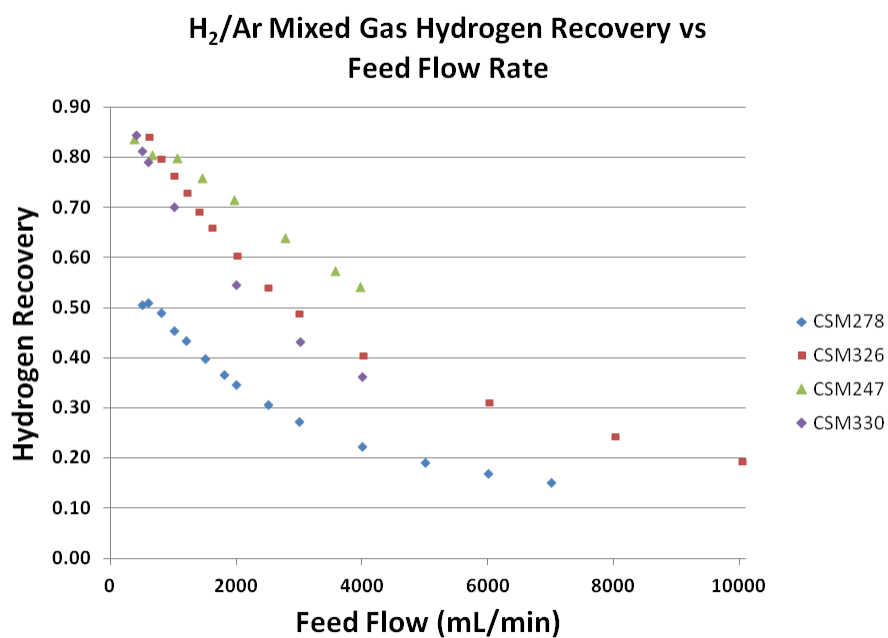
Hydrogen permeation tests were performed on membranes deposited on a 2-inch long active area Accusep® support in a non-optimized housing. During mixed gas testing a concentration boundary layer developed on the membrane surface. Increasing feed flow rate decreased the thickness of the boundary layer resulting in an increase of the hydrogen flux but also a decrease in the hydrogen recovery. The results for normalized permeance (Figure 11) and hydrogen recovery (Figure 12) are plotted vs. feed flow rate for four membranes tested in 50/50  $H_2$ /Ar feed stream. As can be seen ~80% of pure gas permeance can be achieved at high flow rates, but the hydrogen recovery at these feed flows are reduced to 15-30% of the low feed rate value. An improved module design to reduce the dead

volume and increase the velocity of the feed gases was developed as described in the following section to reduce this boundary layer formation effect.



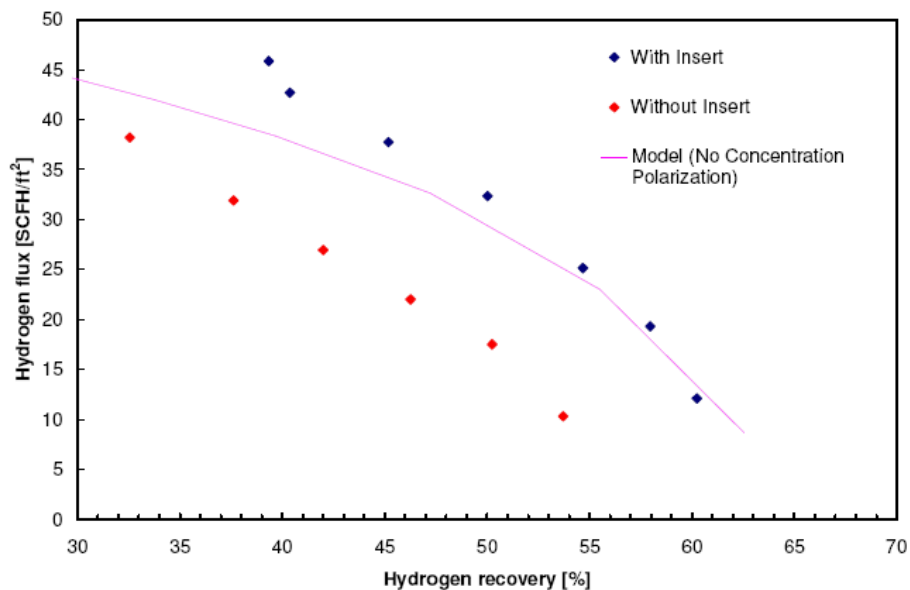
**Figure 11.** Normalized H<sub>2</sub> permeance vs. feed flow rate for four Pd-Au alloy membranes in non-optimized test housing.



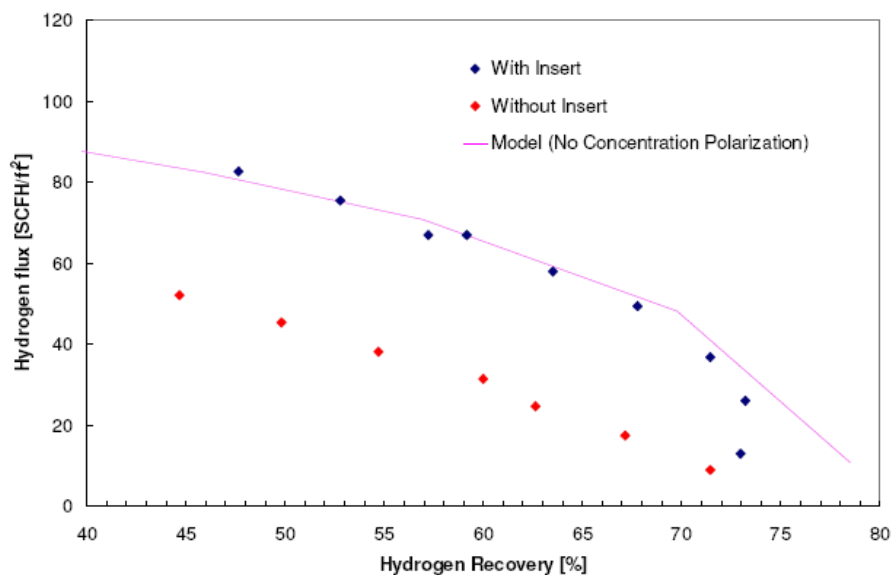


**Figure 12.** H<sub>2</sub> recovery vs. feed flow rate for four Pd-Au alloy membranes in non-optimized test housing.

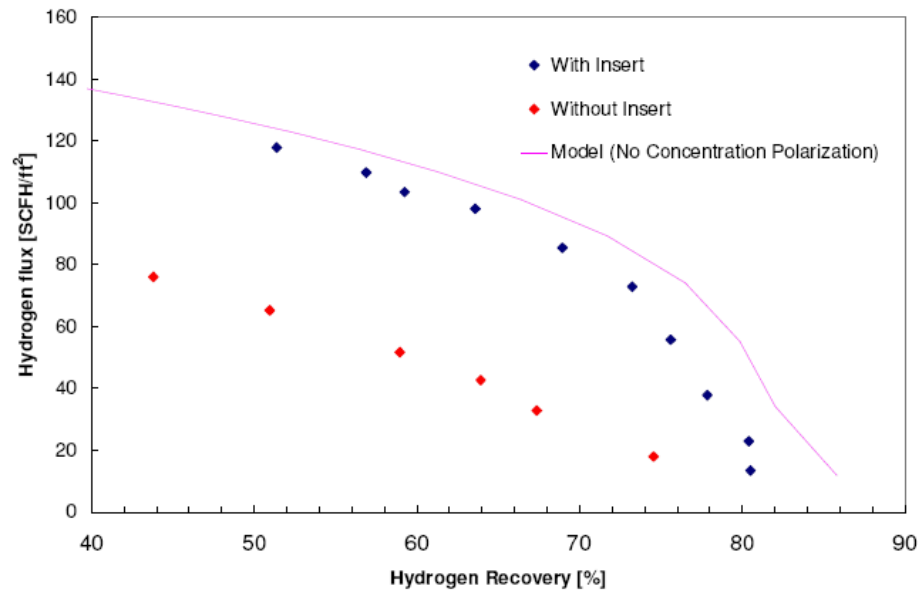
Process and equipment design changes were used to lower the effect of concentration polarization, denoted below as “with insert”. These design elements which are confidential were developed to reduce the effect of concentration polarization. Tests to confirm the effectiveness of the insert are shown in Figures 13-18.



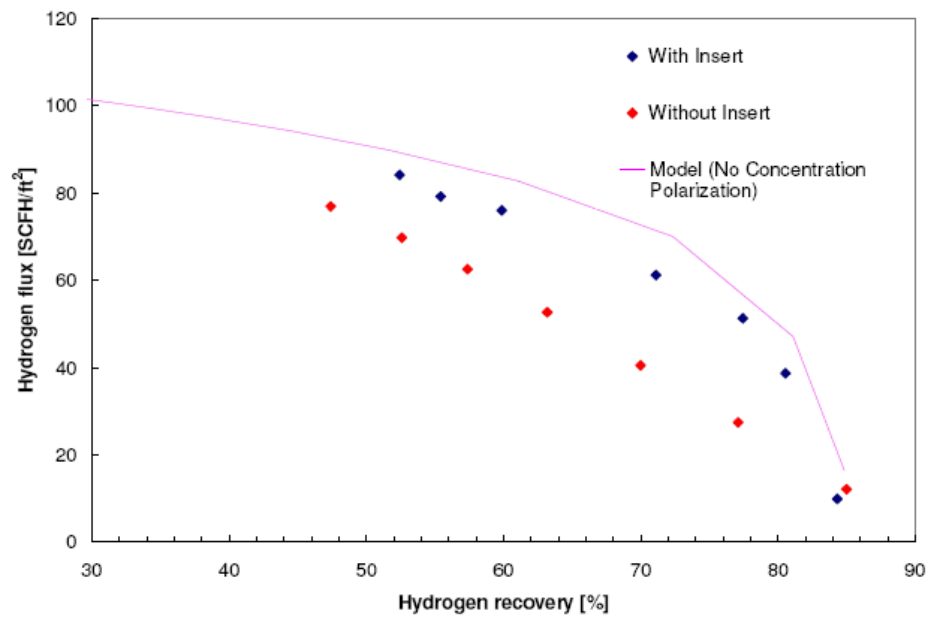
**Figure 13.** H<sub>2</sub> flux vs. recovery for 50:50 H<sub>2</sub>:Ar feed (retentate pressure = 35psig).



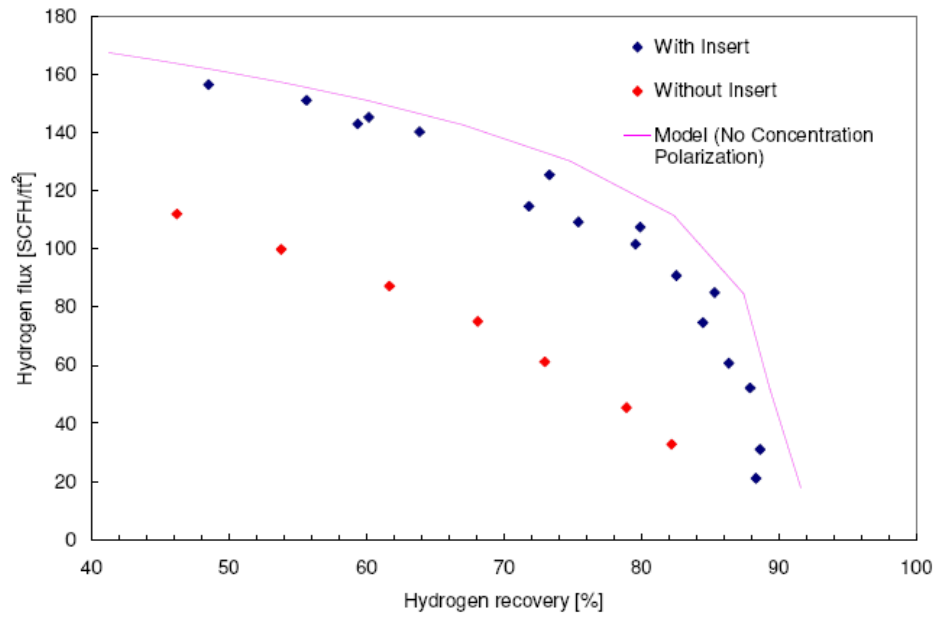
**Figure 14.** H<sub>2</sub> flux vs. recovery for 50:50 H<sub>2</sub>:Ar feed (retentate pressure = 55psig)



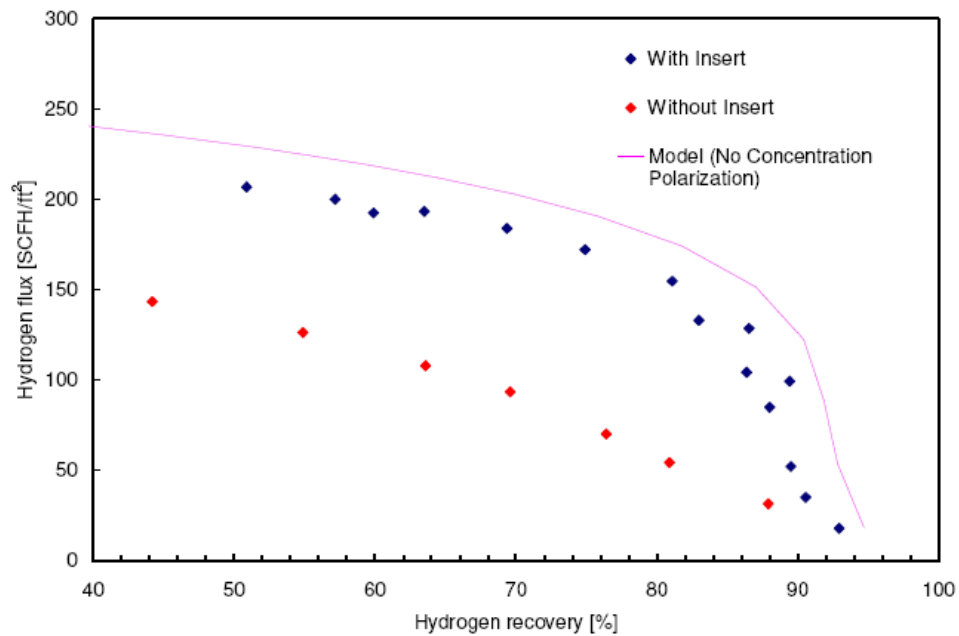
**Figure 15.** H<sub>2</sub> flux vs. recovery for 50:50 H<sub>2</sub>:Ar feed (retentate pressure = 75psig).



**Figure 16.** H<sub>2</sub> flux vs. recovery for 70:30 H<sub>2</sub>:Ar feed (retentate pressure = 35psig).



**Figure 17.** H<sub>2</sub> flux vs. recovery for 70:30 H<sub>2</sub>:Ar feed (retentate pressure = 55psig).



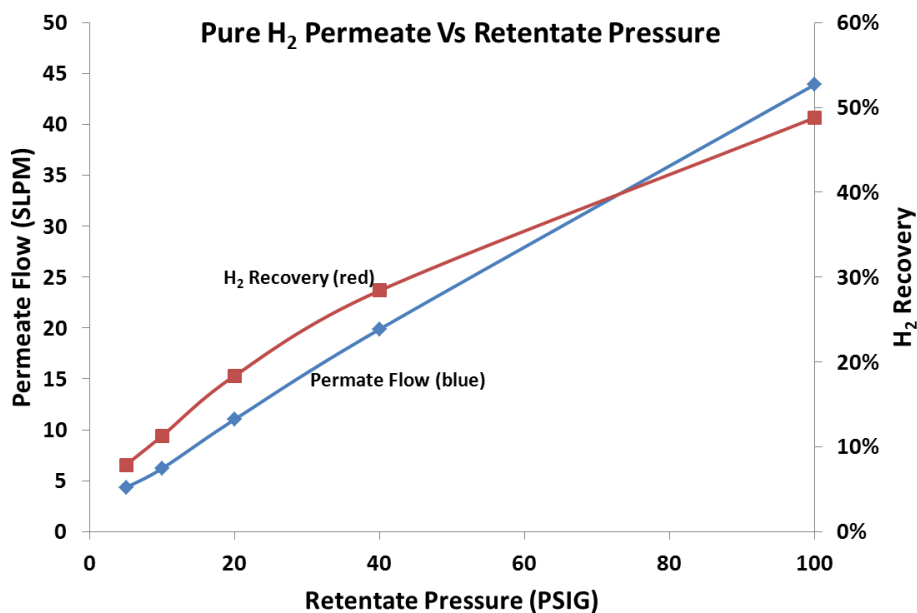
**Figure 18.** H<sub>2</sub> flux vs. recovery for 70:30 H<sub>2</sub>:Ar feed (retentate pressure = 75psig).

It is concluded as shown in the Figures 13-18 that at a given recovery, the hydrogen flux through the membrane is significantly higher with the insert. This confirms that the new design has effectively

overcome the effect of concentration polarization. When the  $H_2$  recovery reaches a is high enough, the design is less effective.

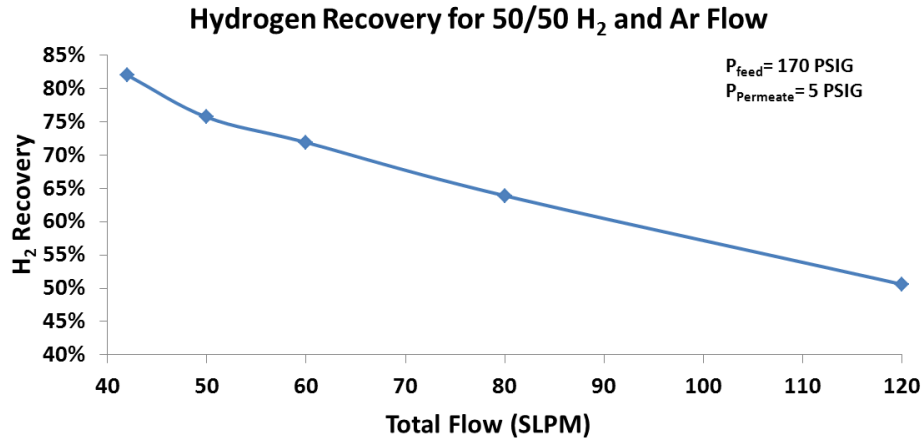
## 2.2 MULTI-TUBE MODULE DEVELOPMENT

A multi-tube module was built using techniques developed for the single tube testing. The multi-tube module was tested to verify the module design had limited concentration polarization. This testing was conducted by TDA Research in Wheat Ridge, Colorado. A baseline test consisted of using pure hydrogen to determine flux, followed by a mixture of 50/50 Ar/ $H_2$  and lastly a mixed gas. The testing produced a hydrogen flux that was less than anticipated; consequently an air purge of the module was performed to determine if this would facilitate an increase in hydrogen flux to the anticipated levels. The initial pure hydrogen test data is shown in Figure 19.



**Figure 19.** Permeate flow vs. retentate pressure in pure  $H_2$

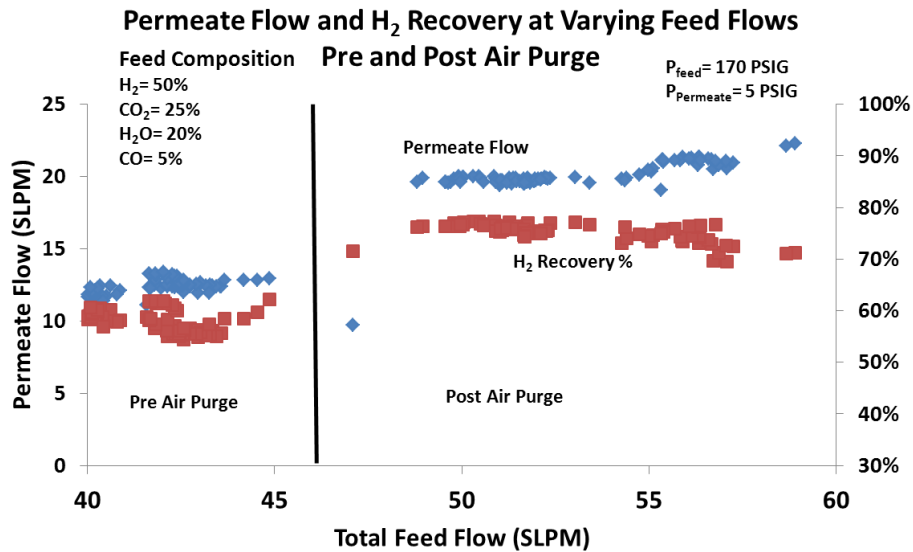
The mixed 50/50 Ar/ $H_2$  testing was performed to determine if the module design would limit concentration polarization with the absence of possible poisoning gases such as carbon monoxide or steam. The results are given below in Figure 20.



**Figure 20.** H<sub>2</sub> recovery vs. flow in a 50/50 H<sub>2</sub>/Ar mixture

The final testing was performed using the following WGS composition. The volume percent is noted for each gas component as follows: H<sub>2</sub> (50%), CO<sub>2</sub> (25%), H<sub>2</sub>O (20%) and CO (5%).

After the initial mixed gas testing was performed, an air purge was completed to try to increase the hydrogen permeate. The results are given in Figure 21.



**Figure 21.** Permeate flow vs. total feed flow in a WGS composition

From the above results it has been shown that the module design has lowered the effect of concentration polarization. When the data from the multi-tube module is compared with the results from the single tube it can be seen that concentration polarization has been lowered. The project goals have been reached of 75 SCFH/ft<sup>2</sup> with a recovery of <75%.

### 2.3 WELDING TECHNIQUE FOR END ADAPTER FITTINGS AND TUBE SHEET

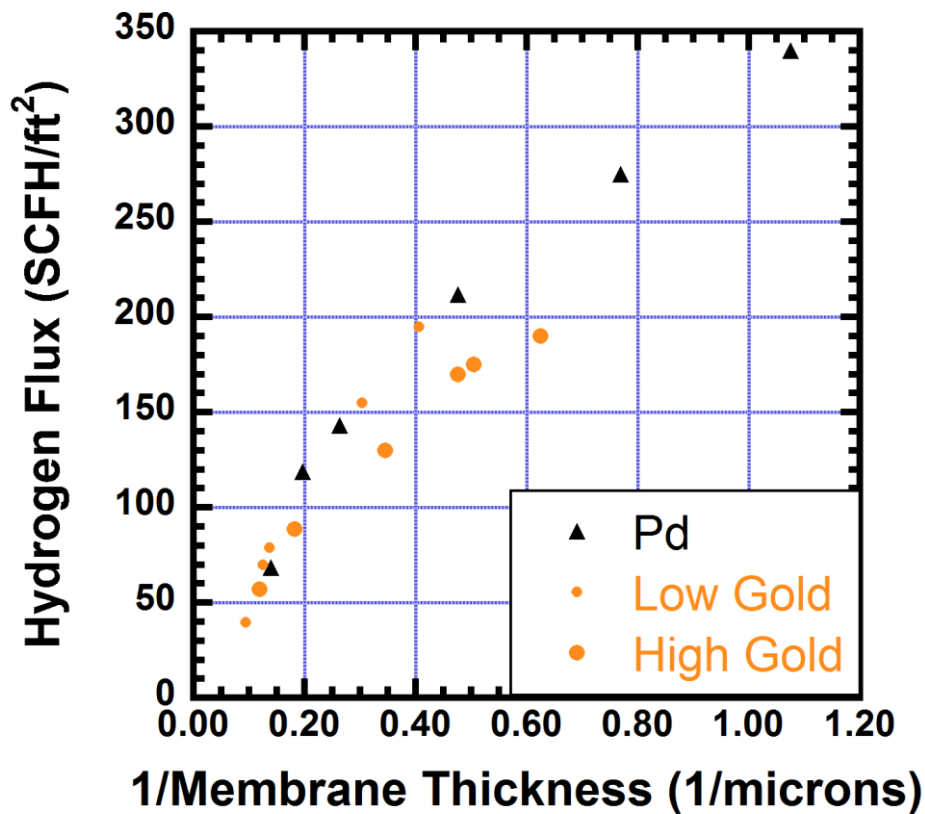
A major advantage of using stainless steel substrates is the ability to attach solid fittings to the membranes that can be welded into a tube sheet. Previous work using ceramic substrates used graphite seals to connect the membrane with the housing. This technique can lead to leaks after cycling, while welded junctions will last indefinitely. A significant amount of development work was carried out to develop a welding process to seal the porous/dense metal tube interface as leakage was a problem in the membrane covering this area. Through the techniques developed, a process was developed that enabled a strong, tight seal that was scalable for manufacturing.

## TASK 3. TEST PERFORMANCE AND DURABILITY

### 3.1 TEST PERFORMANCE IN PURE GAS STREAMS

#### 3.1.1 DEVELOP A PERFORMANCE BASELINE

As seen in Figure 4, the hydrogen flux of pure palladium membranes correlates well with 1/membrane thickness in a predictable manner. If diffusion of atomic hydrogen is rate limiting, then the flux should be linearly related to the reciprocal of membrane thickness. This is seen in Figure 4 and Figure 22 for membranes with a thickness greater than 3.8 microns. For thinner membranes, the flux becomes a weaker function of reciprocal thickness. This is attributed to the pressure drop in the substrate limiting the flux[9]. For membranes with gold content of 0-14 wt% (low gold), flux follows the same correlation. Alloy membranes with gold content from 20-25 wt% (high gold) show a similar correlation, but with lower hydrogen flux values than we measured for pure Pd membranes. All of these membranes have been air oxidized to achieve maximum hydrogen flux. Figure 22 shows the hydrogen fluxes of palladium and palladium-gold alloy membranes as a function of inverse membrane thickness.



**Figure 22.** H<sub>2</sub> flux vs inverse membrane thickness for pure Pd (triangles), low gold 4-14 wt% (small circles) and high gold 20-25 wt% (large circles).

### 3.1.2 DETERMINE THE EFFECT OF THERMAL CYCLING

Operation of palladium membranes and palladium alloy membranes with hydrogen below the critical temperature of the hydride phase transition can lead to membrane swelling, rupturing and failure. This is due to large differences between the lattice constants of the  $\alpha$  and  $\beta$  hydride phases. A simple solution to avoiding membrane failure due to hydride phase transitioning is to work above the critical temperature of the phase transition. However, constant operation at high temperatures is not always feasible and the palladium membrane may need to be periodically cooled to lower temperatures.

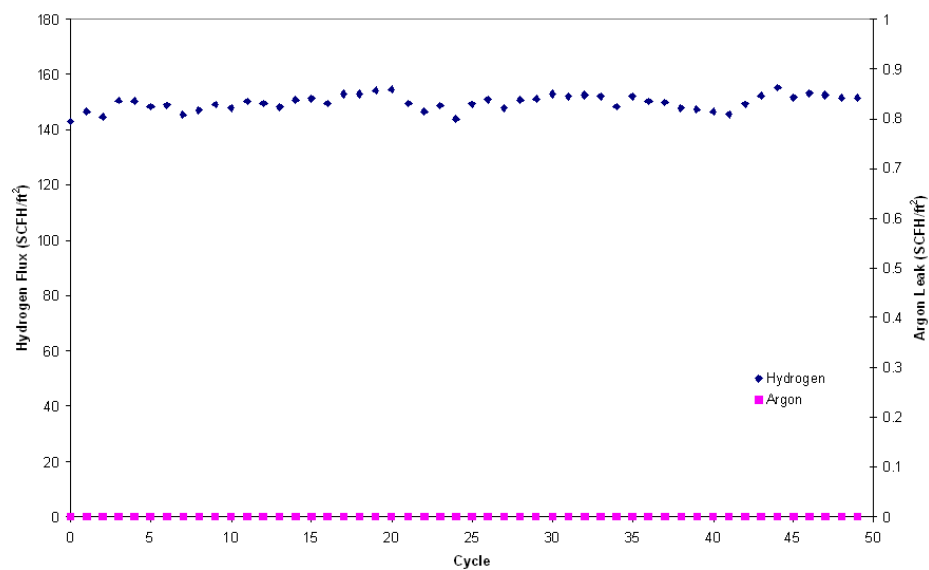
It is recommended to completely purge a palladium membrane system of hydrogen before descending below the critical temperature to prevent hydrogen embrittlement. This can be accomplished by flowing an inert gas (helium, nitrogen, argon) through the feed and sweep ports for a period of time,



typically on the order of two hours. Smaller testing facilities (especially portable ones) may not have the luxury of an inert gas to feed. In these cases, it may be possible to minimize damage from hydrogen embrittlement by simply opening the module ports to ambient air prior to shutting down the furnace. By doing so, the hydrogen that is in the module and saturated into the membrane can diffuse out before the membrane begins undergoing hydride phase transitioning.

The stability of palladium gold membranes was tested by repeatedly and rapidly thermally cycling the membranes. Cooling from 400°C to 50°C was done in 45-60 minutes and ramping from 50°C to 400°C was done in 45 minutes. For both cooling and ramping, the module was left with its ports open to the atmosphere. Hydrogen was not purged from the module prior to cooling. The condition of the membrane was measured by recording the pure gas flux of argon and hydrogen at 20 psig. Specifically, the objective was to ensure that the performance of the Pd-Au membranes would be stable if the membrane was cooled quickly to room temperature without prior purging of hydrogen from the system.

Several membranes were tested using the above procedure for thermal durability. Each of the membranes exhibited similar results. One membrane with no detectable leak rate prior to cycling also had no detectable leak after 50 cycles as shown in Figure 23 illustrating the potential to avoid embrittlement in this alloy system.

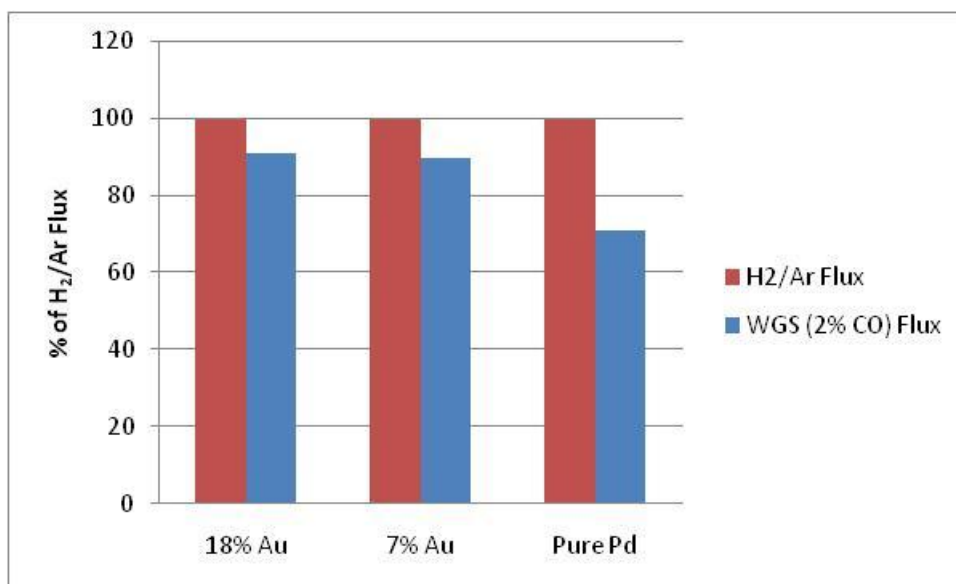


**Figure 23.** Effect of thermal cycling on flux on a Pd-Au alloy membrane

## 3.2 TEST PERFORMANCE IN WATER GAS SHIFT STREAMS

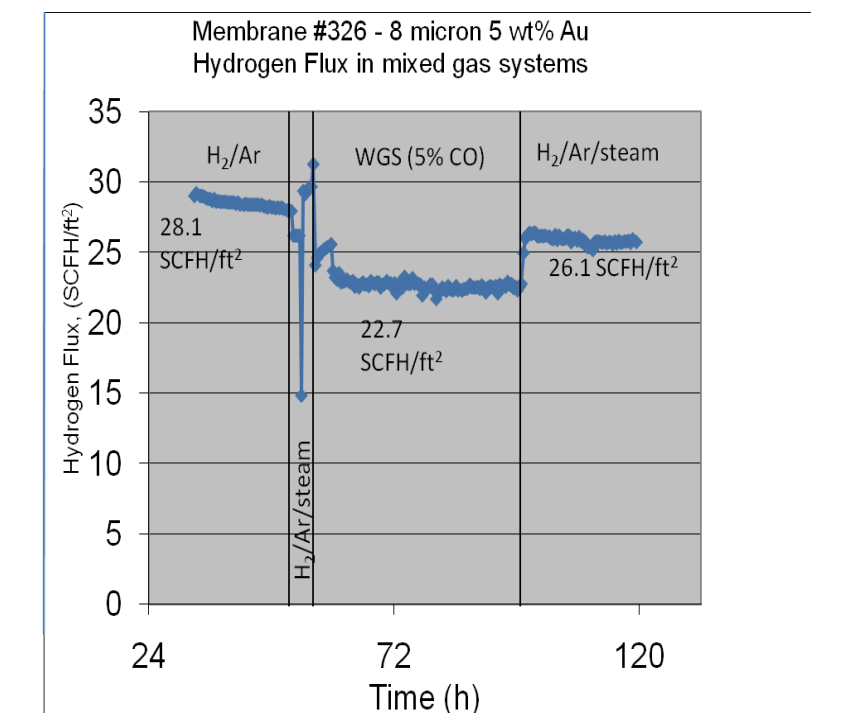
### 3.2.1 EFFECT OF WGS ON FLUX

Upon exposure to a standard WGS stream the flux was observed to decrease. The decrease was most significant on the pure Pd membrane compared to Pd-Au alloy membranes. The decrease was similar in the alloys containing 7 and 18% Au as shown in Figure 24.



**Figure 24.** Effect of WGS on the flux of Pd and Pd-Au alloy membrane #259 (5.2 micron, 18%Au), #258 (5.4 micron, 7%Au), and #270 (5.3 micron, 0%Au).

Mixed gas test results on membrane #326 are shown in Figure 25. The data illustrate the effects of steam and WGS mixtures in the feed stream on membrane hydrogen flux. All compositions were run at the same pressures, temperature and feed flows. In H<sub>2</sub>/Ar, the flux was ~28 SCFH/ft<sup>2</sup>. When steam was added (H<sub>2</sub>/Ar/steam 50/30/20), the first few flux data points are ~26 SCFH/ft<sup>2</sup> before some erratic measurements were observed. When CO<sub>2</sub> and CO are added to replace the Ar in WGS-5, the flux is reduced to 22.7 SCFH/ft<sup>2</sup>. The flux increased back to 26.1 SCFH/ft<sup>2</sup> when the composition was shifted back to the H<sub>2</sub>/Ar feed stream. The observed decreases in hydrogen flux were 7% from the addition of steam to the feed and 19.2% from the WGS-5 stream in the feed.

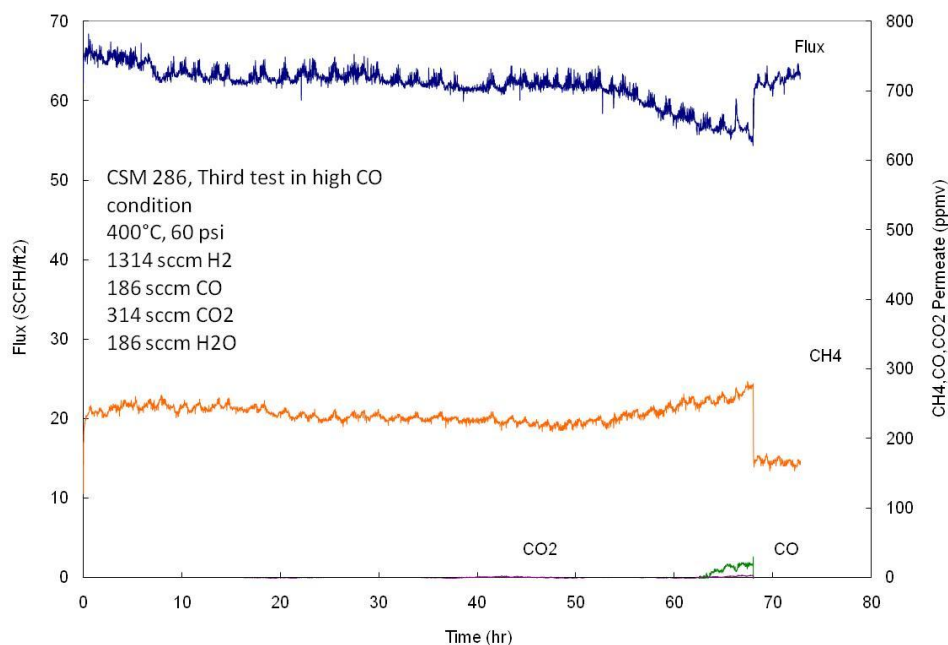


**Figure 25.** H<sub>2</sub> flux vs. time for membrane #326 in varying feed stream compositions.

### 3.2.2 STEAM/CO RATIO

The flux data from mixture permeation testing of membrane #286 at a CO to steam ratio of 1:1 is shown in Figure 26<sup>5</sup>. The membrane was tested for three 70 hour time periods and it was temperature cycled to room temperature in between the three mixture tests. The last 70 hour testing period is shown in Figure 21 below. The hydrogen flux and permeate purity showed good stability over the whole test. It is recommended that the steam/CO ratio in the feed gas mixture should be maintained >1.

<sup>5</sup> Test conducted by TDA Research



**Figure 26.** Membrane #286 was tested in methanol reformat feed streams with two shutdowns to determine durability and shutdown procedures. Each test sequence had a 70 hour duration. Permeation data is shown for the third 70 hr test (after the second shutdown).

### 3.2.3 ACCELERATED DURABILITY TEST AND SELECTION OF OPTIMAL Pd-AU ALLOY

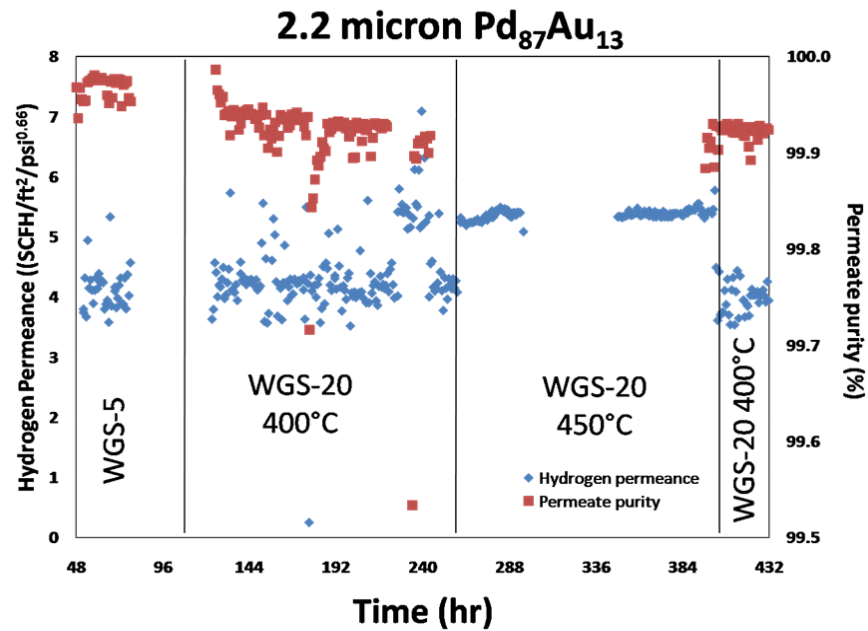
Initially it was assumed that the membrane performance would decline after a few days of testing in a standard WGS stream enabling several tests to be carried out in a reasonable period to determine the optimal alloy composition and thickness. However, the Pd-Au alloy membranes all performed well and no degradation was observed in several days of operation.

To evaluate lifetime stability of the different membrane alloys an accelerated durability test was devised to evaluate the best alloy to use for the 500 hr lifetime test. A thin membrane (#357, 2.2 micron, 13% Au) was selected to develop this accelerated life test. The criteria for the accelerated life test conditions was to observe a significant decline in the permeate purity or hydrogen permeance in less than 100 hours. Three test conditions shown in Table VI were selected as possible accelerated test protocols.

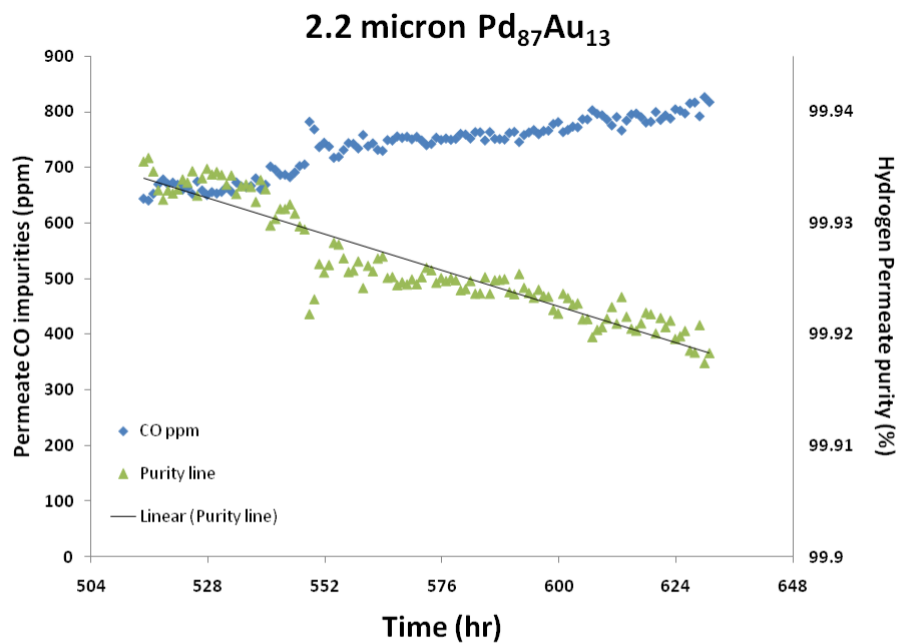
**Table VI Accelerated failure test conditions**

	Temp. (°C)	H <sub>2</sub>	CO <sub>2</sub>	CO	H <sub>2</sub> O	Ar
WGS-20	400	50	10	20	20	
WGS-20	450	50	10	20	20	
WGS-20D	400	50		20		30

As shown in Figure 27, permeation testing of membrane #357 in high CO feed streams at 400°C or at 450°C does not lead to a decrease in either permeate purity nor hydrogen permeance. It is not until the WGS-20D composition is used that the desired performance decline is achieved (Figure 28). The hypothesized failure mechanism in a WGS feed stream is carbon deposition on the membrane surface with subsequent diffusion of carbon into the membrane. Palladium carbide has a larger lattice constant than the Pd-Au alloy and this may result in the formation of cracks in the membrane[10]. When both CO<sub>2</sub> and H<sub>2</sub>O are in the feed stream, they may react with surface carbon to suppress membrane formation of palladium carbide. In the WGS-20D feed stream, both CO<sub>2</sub> and H<sub>2</sub>O were replaced with Ar to accelerate the hypothesized reaction to form of carbon on the membrane surface and subsequent diffusion of carbon into the membrane. Two sets of three membranes of approximate 4 micron thickness and varying alloy composition were tested in the aggressive WGS-20D stream to evaluate which alloy performed best. The data in Table VII show that the 9% and 11% Au compositions were the most durable alloys in this test as they exhibited the lowest rate of purity decline. A nominal composition of Pd<sub>90</sub>Au<sub>10</sub> was selected as the optimum composition for the long term durability test.



**Figure 27.** Test of membrane #357 in high CO feed stream environment and elevated temperature



**Figure 28.** Accelerated life test on membrane #357. The feed stream used is WGS-20D (50% H<sub>2</sub>, 30% Ar and 20% CO).

**Table VII Permeate purity decline in WGS-20D feed conditions**

<b>Thickness (micron)</b>	<b>Au content (wt%)</b>	<b>Purity Decline (ppm/day)</b>
3.0	0	42
4.1	0	74
4.0	9	0
3.9	11	6
3.6	20	356
3.6	24	652

Assessment of their impact on the projet results

The accelerated life test resulted in the conclusion that the 10% Au alloy composition was optimal.

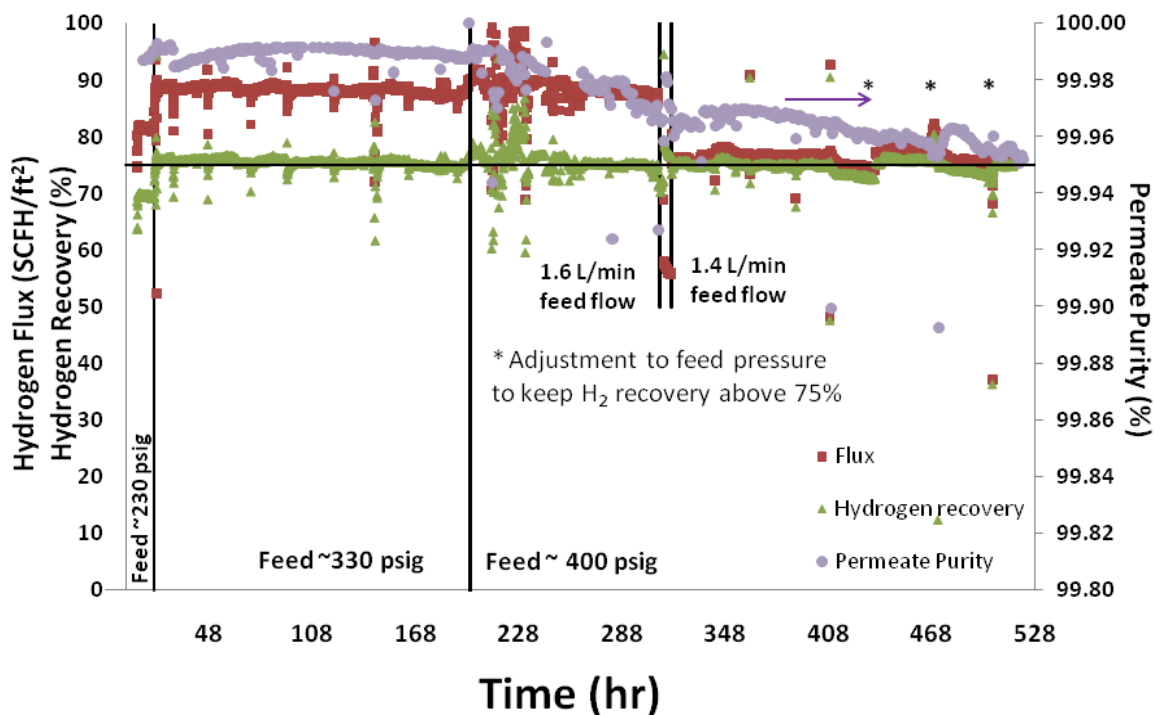
**3.2.4 DURABILITY TEST - 500 HOURS**

A successful 500 hour test was completed on membrane #434 (4 micron, 10% Au) for over 500 hour under the standard WGS-5 conditions while meeting the predetermined performance targets (>75 SCFH/ft<sup>2</sup> Hydrogen flux, >75% hydrogen recovery and >99.95% purity). The conditions for the 500 hour test are shown in Table VIII. The hydrogen flux, hydrogen recovery, and permeate hydrogen purity as a function of time for this test are shown in Figure 29.

**Table VIII Conditions for the 500 hour durability test**

<b>Temperature</b>	450°C
<b>Feed pressure</b>	300-420 psig
<b>Permeate pressure</b>	0-0.5 psig
<b>Feed flow rate</b>	1.4-1.6 L/min
<b>Feed composition WGS-5</b>	50% H <sub>2</sub> , 20% H <sub>2</sub> O, 25% CO <sub>2</sub> , 5% CO





**Figure 29.** H<sub>2</sub> flux, H<sub>2</sub> recovery and permeate purity for 500 hr test performed at the CSM test stand with the concentration polarization reducing insert.

The test was conducted using the concentration polarization reducing insert on a 4 micron thick, Pd<sub>90</sub>Au<sub>10</sub> membrane deposited on a 2-inch long active area Accusep® support. The periodic irregularities seen approximately every 24 hours were caused by the refill of the syringe pump and the drop in pressure associated with emptying the retentate side condenser. For the first 200 hours, the membrane performance exhibited no decline in hydrogen flux or permeate purity. At ~200 hours, the retentate side condenser was not emptied at the appropriate time and the back pressure regulator filled with water causing an unintentional increase in pressure. This pressure increase led to the shutoff of hydrogen, steam and carbon monoxide leaving the membrane under pure carbon dioxide feed stream for several hours. The unintended change in feed stream composition damaged the membrane and an increase in feed pressure was necessary to meet the test performance targets. After another ~100 hours the recovery had decreased to below 75%, prompting a change in feed flow to maintain the hydrogen flux and hydrogen recovery above the test targets. After 400 hours, adjustments were made as indicated by (\*) to the feed pressure to maintain performance that met the test target milestones.

#### TASK 4. CHARACTERIZE AND ANALYZE MEMBRANES

ORNL/HTML carried out a series of tests to determine the nature and kinetics of Pd-Au alloy formation. The membranes were tested using the in-situ high-temperature x-ray diffraction system at ORNL. Precursor Pd foils with Au coatings of different thicknesses were analyzed.

An x-ray analysis revealed 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. This may be interpreted as alloying of the Au with smaller Pd atoms. Two features stand out from this data set. First, 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. It is recommended that these results be quantified with additional testing supplemented by an electron probe analysis through the thickness of the foil. A greater detailed analysis was published by CSM as cited in Section 10 reference 3.

#### TASK 5. COMPARE PROJECTED SYSTEM PERFORMANCE TO GOALS

Table IX summarizes the 500 hour test results and confirms that the Phase III milestone targets were achieved in this long term durability test in a typical WGS stream.

**Table IX Comparison of the results from the CSM 500 hour durability test to the targets**

	Target	500 hr test results
Hydrogen Flux	>75 SCFH/ft <sup>2</sup>	75 SCFH/ft <sup>2</sup>
Hydrogen Recovery	>75 %	75 %
Permeate Purity	>99.95 %	99.95 %

## TASK 6. CONDUCT A TECHNO-ECONOMIC ANALYSIS TO DETERMINE IF THE MEMBRANE MEETS THE GOAL

### 6.1 ECONOMIC ANALYSIS OF HYDROGEN PRODUCTION

To meet the objectives of the FCT Hydrogen Production Multi-year RD&D plan, the cost of distributed production of hydrogen from natural gas or biomass-derived renewable liquids (BIL) such as ethanol needs to be less than \$3.00/gge (delivered, untaxed, 2005 dollars) by the year 2015. A typical scale of distributed hydrogen production is considered to be at 1,500 kg/day as would be needed for a hydrogen fueling station supporting 300 hydrogen powered vehicles/day. The cost of membrane-based hydrogen production at the scale of 1,500 kg/day was therefore determined in collaboration with Directed Technologies, Inc. (DTI) during the Phase II of this project. During the Phase III of this project, cost of hydrogen production was determined in collaboration with an end user (a large oil company) for a large scale hydrogen production process for refineries with CO<sub>2</sub> capture as being of most interest for a near-term application of a membrane-based hydrogen production process.

### 6.2 COST OF MEMBRANES AND MODULES

The estimated cost of the module including the Pd-alloy tubular membrane elements and concentration polarization reduction inserts is \$2,000/ft<sup>2</sup> with possible reduction when large scale production begins. The cost of the module is higher than initially envisioned since the design which lowers the effect of concentration polarization also increases the cost. However, without lowering the effect of concentration polarization, the overall cost of hydrogen production is even higher. The module design that was developed for this program was done so to balance the costs of the Pd-alloy element and module to allow for the lowest cost hydrogen production.

### 6.3 COST OF PD-MEMBRANE BASED DISTRIBUTED HYDROGEN PRODUCTION (1,500 KG/DAY)

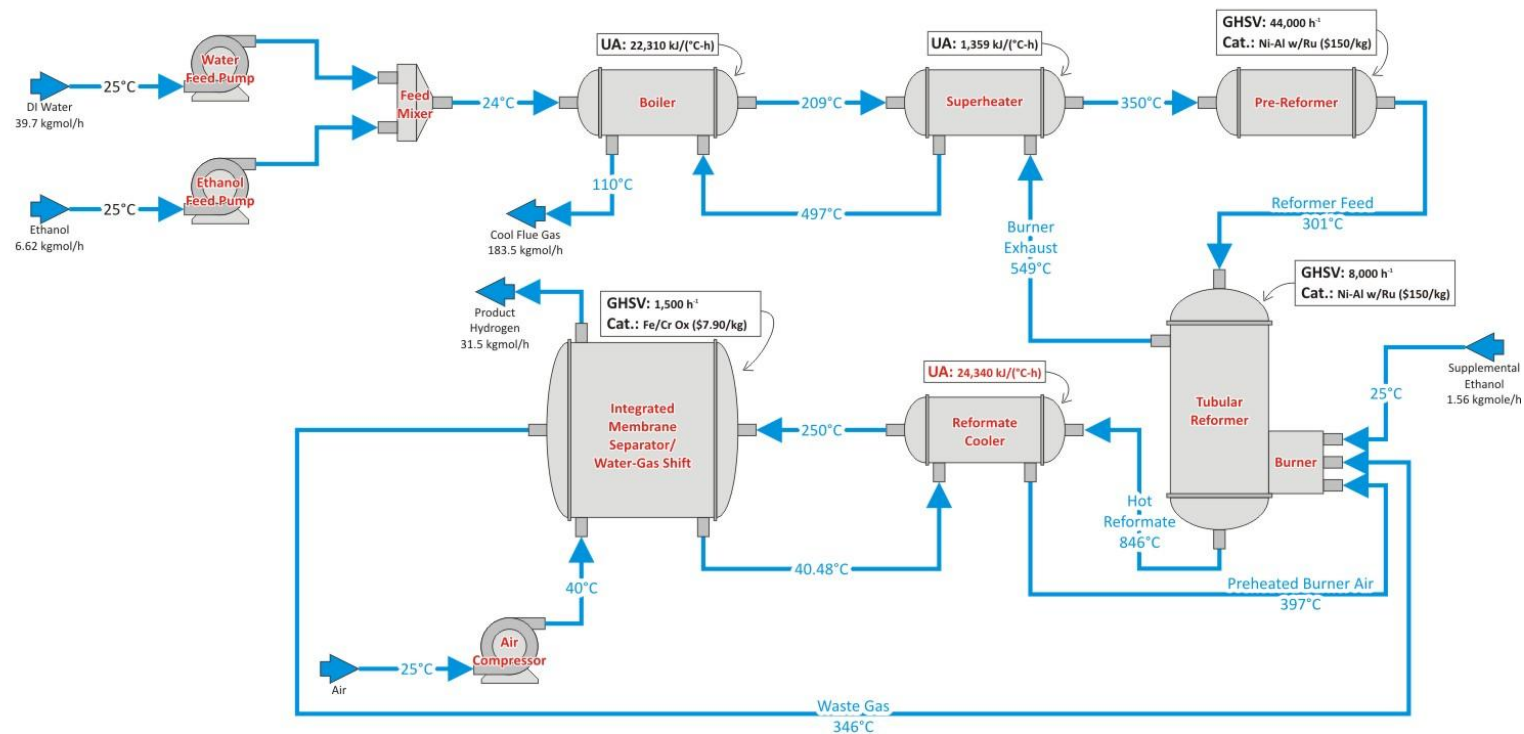
In a conventional hydrogen production process a hydrocarbon fuel such as natural gas or ethanol is first reformed with steam followed by a water gas shift (WGS) reactor and a hydrogen purification unit. The current commercial process for hydrogen purification is based on Pressure Swing Adsorption (PSA). A Pd-alloy based membrane, such as developed in this project, can be used just for a hydrogen purification replacing the conventional unit. However, since this membrane operates at elevated temperatures of more than 400°C, this membrane may also be integrated with the WGS reaction process or even with the reforming process. Such integration of reaction and separation steps is expected to provide greater

hydrogen yield because of forward shift in the equilibrium-limited WGS and reforming reactions resulting from the product hydrogen separation and is also expected to lower the overall capital cost by reduction in equipment because of the combination of steps in a single vessel.

A fully integrated ethanol reformer/WGS reactor/hydrogen separator unit was therefore considered by DTI in their analysis of hydrogen production costs at 1,500 kg/day scale derived from ethanol (BILI) fuel. The integrated membrane reformer/WGS reactor/hydrogen separator process based on medium temperature (500°C) ethanol reforming is shown schematically in Figure 30 with the pertinent values of various stream flow rates. The process is assumed to use non-precious metal catalysts at 20 bar (300 psig) pressure and a steam to ethanol ratio of 8:1 (same as steam to carbon ratio of 4:1 typically used in steam methane reforming.) Such integration is expected to provide the least cost of hydrogen for Pd-membrane-based hydrogen production processes. The cost of membrane separator/reactor is determined by the total membrane area that needs to be provided for certain process conditions and cost of fabricating membranes and membrane modules per unit area. For given process conditions of feed composition, steam to carbon ratio, temperature, and pressure, the required membrane area depends on the hydrogen permeation rate of the membrane used as well as the targeted hydrogen recovery from the overall process. The rate of hydrogen permeation through a membrane in turn depends on the hydrogen permeability of the Pd-alloy composition and the thickness of the Pd-alloy membrane. The cost of the membrane and modules per unit area primarily depends on the membrane thickness and the fabrication process used for the membranes and modules. The alloy composition also has a minor effect on the membrane cost per unit area.

**Capacity:** 1500 kg/day  
**Ethanol Efficiency:** 75.5%  
**Overall Efficiency:** 75.0%  
**Elec. Load:** 0.322 kW<sub>e</sub>/kg H<sub>2</sub>  
**Pressure:** ~22 bar  
**H<sub>2</sub> Recovery:** 31.5 kgmol/h  
**Capital Cost:** \$859,457

## System 12: Tubular High-Temperature Ethanol System with Integrated Membrane Separator/Water-Gas Shift



**Figure 30.** Integrated reformer/WGS/membrane separator process (DTI presentation at 2008 DOE Annual Merit Review Meeting)

A sensitivity analysis was therefore conducted to determine the influence of hydrogen flux rate, target hydrogen recovery, and cost of membrane and module fabrication per unit area. The range of respective parameters used were: a) membrane hydrogen flux rate of 150 SCFH/ft<sup>2</sup>, 200 SCFH/ft<sup>2</sup>, and 250 SCFH/ft<sup>2</sup> at reference conditions of 20 psig feed pressure, 0 psig permeate pressure and 400°C membrane temperature; b) overall hydrogen recovery of 70%, 80%, and 90% of the maximum possible hydrogen yield per unit mole of feed (ethanol), and c) the cost of membrane tube fabrication of \$1000/ft<sup>2</sup>, \$1250/ft<sup>2</sup>, and \$1500/ft<sup>2</sup>. The membrane area required for the combination of hydrogen recovery and permeability cases is shown in Table X

**Table X Estimated membrane area for assumed H<sub>2</sub> flux rate and recovery**

	Estimated membrane surface area (ft <sup>2</sup> )		
H <sub>2</sub> flux rate	150SCFH/ft <sup>2</sup>	200SCFH/ft <sup>2</sup>	250SCFH/ft <sup>2</sup>
70% recovery	61.8	46.3	37
80% recovery	67.2	50.6	40.9
90% recovery	96.7	72.2	57.5

The results of the sensitivity analysis for determining the influence of membrane flux, hydrogen recovery and the cost of membranes on the cost of H<sub>2</sub> for 1500 kg/day H<sub>2</sub> production capacity are shown in Tables XI-XIII.

**Table XI Cost of H<sub>2</sub> production (\$/gge) as a function of membrane cost, flux and H<sub>2</sub> recovery at 150 SCFH/ft<sup>2</sup> H<sub>2</sub> flux**

Flux	150 SCFH/ft <sup>2</sup>		
Membrane cost	\$1000/ft <sup>2</sup>	\$1250/ft <sup>2</sup>	\$1500/ft <sup>2</sup>
70% recovery	\$3.21	\$3.22	\$3.23
80% recovery	\$3.10	\$3.11	\$3.12
90% recovery	\$3.04	\$3.06	\$3.06

**Table XII Cost of H<sub>2</sub> production (\$/gge) as a function of membrane cost, flux and H<sub>2</sub> recovery at 200 SCFH/ft<sup>2</sup> H<sub>2</sub> flux**

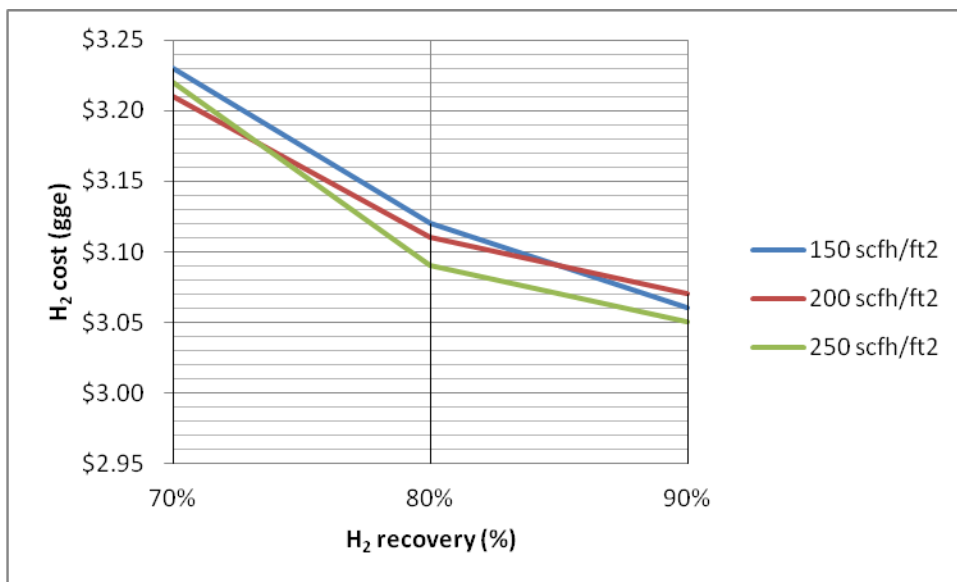
Flux	200 SCFH/ft <sup>2</sup>		
Membrane cost	\$1000/ft <sup>2</sup>	\$1250/ft <sup>2</sup>	\$1500/ft <sup>2</sup>
70% recovery	\$3.19	\$3.20	\$3.21
80% recovery	\$3.09	\$3.10	\$3.11
90% recovery	\$3.03	\$3.05	\$3.07

**Table XIII Cost of H<sub>2</sub> production (\$/gge) as a function of membrane cost, flux and H<sub>2</sub> recovery at 250 SCFH/ft<sup>2</sup> H<sub>2</sub> flux**

Flux	250 SCFH/ft <sup>2</sup>		
Membrane cost	\$1000/ft <sup>2</sup>	\$1250/ft <sup>2</sup>	\$1500/ft <sup>2</sup>
70% recovery	\$3.20	\$3.21	\$3.22
80% recovery	\$3.07	\$3.08	\$3.09
90% recovery	\$3.01	\$3.03	\$3.05

The sensitivity analysis showed that:

- Membrane flux rate has a minor impact on cost of  $H_2$  production compared to  $H_2$  recovery as shown in Figure 31.



**Figure 31.** Sensitivity of  $H_2$  recovery and  $H_2$  flux on  $H_2$  production cost for a membrane cost of \$1500/ft<sup>2</sup>

- Cost of membrane tubes is <10% of total capital cost
- Increasing the  $H_2$  recovery decreased the cost of  $H_2$  regardless of membrane cost
- Estimated membrane area requirement for 1,500 kg/day hydrogen capacity for an integrated ethanol reformer membrane reactor-based process is:
  - 97 ft<sup>2</sup> for 90% hydrogen recovery (150 SCFH/ft<sup>2</sup>  $H_2$  flux at 20 psid and 400°C reference conditions)
  - 67 ft<sup>2</sup> for 80% hydrogen recovery (150 SCFH/ft<sup>2</sup>  $H_2$  flux at 20 psid and 400°C reference conditions)
- Estimated total membrane cost for 1,500 kg/d  $H_2$  production is:
  - < \$ 194,000 for 90% hydrogen recovery
  - < \$ 134,000 for 80% hydrogen recovery



- Ethanol efficiency of the hydrogen production process depends on hydrogen recovery
  - 68.87% at 90% H<sub>2</sub> recovery,
  - 63.36% at 70% H<sub>2</sub> recovery
- Increasing ethanol efficiency to 79.4% (achievable by lower steam to ethanol ratio of 6:1) was shown to reduce the cost of hydrogen (2008 DTI presentation at DOE Annual Merit Review)

## 8. CONCLUSIONS

Based on a test data and a techno-economic analysis, a H<sub>2</sub> production cost of about \$3 gge is currently achievable with an integrated Pd-alloy membrane ethanol reformer/WGS reactor/H<sub>2</sub> separator system.

A further lowering of the cost may be achievable with additional cost reductions during large scale production.

As an example, at a membrane cost of \$1500/ft<sup>2</sup>, a H<sub>2</sub> production cost of \$3.06 gge is projected at a 90% H<sub>2</sub> recovery and 150 SCFH/ft<sup>2</sup> flux.

Variation of the cost of the membrane tubes from \$1000/ft<sup>2</sup> to \$1500/ft<sup>2</sup> and inclusion of approximately \$500/ft<sup>2</sup> housing cost resulted in only a ~1 percent difference in the projected production cost of H<sub>2</sub>.

The capital cost of the membrane unit is a small fraction of the capital cost of the overall reforming system and, therefore, has a very minor influence on the cost of hydrogen produced.

The results of the analysis de-emphasized the focus on membrane flux rate in this membrane development project. Hydrogen recovery, on the other hand, determines the yield of hydrogen per unit amount of feed stock (ethanol) and, therefore, strongly influences the operating costs of hydrogen production. This analysis indicated that separation factor rather than the hydrogen flux rate is a stronger determinant of the hydrogen production cost.

Slightly thicker membranes with a tradeoff for greater selectivity and durability over membrane flux may be preferable. Greater membrane selectivity and assuring membrane durability of 5 years, as assumed in this analysis, was deemed to have a stronger influence on reducing cost of hydrogen production.

## 9. IDENTIFY PRODUCTS DEVELOPED UNDER THE AWARD AND TECHNOLOGY

### TRANSFER ACTIVITIES

The Pd<sub>90</sub>/Au<sub>10</sub> alloy composition was adopted as a membrane to be used in a Pall hydrogen separation product.

The module design minimizing concentration polarization effects was scaled up into a production design module.

## 10. PUBLICATIONS, CONFERENCE PAPERS AND OTHER PUBLIC RELEASES OF RESULTS

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2. Gade, S. K. Coulter, K. E. and J. D. Way, "Effects of fabrication technique upon material properties and permeation characteristics of palladium-gold alloy membranes for hydrogen separations, *Gold Bulletin*, **43**(4), 287-297(2010).
3. Gade, S. K., Payzant, E. A., Park, H. J., Thoen, P. M. and J. D. Way, "The effects of fabrication and annealing on the structure and hydrogen permeation of Pd–Au binary alloy membranes," *J. Membrane Science*, 340(1-2), 227–233 (2009).
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5. Way, J. D., "Palladium and Palladium Alloy Membranes for Hydrogen Separation and Production: History, Fabrication Strategies, and Current Performance," Proceedings of the 10th International Conference on Inorganic Membranes (ICIM 10), Tokyo, Japan, August 18-22, 2008.
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7. Keeling, M. K., Davidson, A. P., Gade, S. K., Thoen, P. M. and J. D. Way, "Fabrication and characterization of Pd-Ru alloy composite membranes by electroless co-deposition," Proceedings of the 10th International Conference on Inorganic Membranes (ICIM 10), Tokyo, Japan, August 18-22, 2008.
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9. Keeling, M. K., Davidson, A. P., Gade, S. K., Thoen, P. M. and J. D. Way, "Fabrication and characterization of Pd-Ru alloy composite membranes by electroless co-deposition," 10th International Conference on Inorganic Membranes (ICIM 10), Tokyo, Japan, August 18-22, 2008.
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11. Damle, A.S. and J. Acquaviva, "Steam Methane Reforming in a Membrane Reactor for Hydrogen Production," Presented at the AIChE Annual Meeting, Philadelphia, PA, November 2008.
12. Way, J. D., "Pd Alloy Membranes for Hydrogen Production," Invited Lecture, NanoMem Course (European Union), Lillestrom, Norway, March 14, 2009.
13. Way, J. D., "High Temperature, Inorganic Membranes for Hydrogen Production," Invited plenary talk to the University of Colorado Student Annual Research Symposium, University of Colorado, Boulder, October 5, 2009.
14. Way, J. D., "High Temperature, Inorganic Membranes for Hydrogen Production with CO<sub>2</sub> Capture," Colorado Clean Energy Solutions Series Meeting, Colorado School of Mines, Golden, CO, October 1, 2009
15. Way, J. D., "Palladium alloy composite membranes for hydrogen production," Presentation made to the Dept. of Energy Conversion and Materials, SINTEF, Oslo, Norway, March 13, 2009.
16. Way, J. D., "High Temperature, Inorganic Membranes for Hydrogen Production," Invited plenary talk to the University of Colorado Student Annual Research Symposium, University of Colorado, Boulder, October 5, 2009.

17. Way, J. D., "High Temperature, Inorganic Membranes for Hydrogen Production with CO<sub>2</sub> Capture," Colorado Clean Energy Solutions Series Meeting, Colorado School of Mines, Golden, CO, October 1, 2009.
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20. Ø. Hatlevik, M. K. Keeling, K. Rekcis, J. D. Way, " High carbon monoxide test conditions for accelerated qualitative evaluation of palladium gold alloy membranes for use in CO<sub>2</sub> capture from water-gas-shift mixtures ," presented at the North American Membrane Society annual meeting, Las Vegas, NV, June 2011.
21. A. Damle, "Commercialization of Pd Membrane for H<sub>2</sub> Production," presented at the Fuel Cell Seminar, San Antonio, TX, October, 2010.
22. J. D. Way, "High Temperature, Inorganic Membranes for Hydrogen Production with CO<sub>2</sub> Capture," presented at the School of Chemical Engineering, University of Queensland, Brisbane, Queensland, Australia, March 22, 2011.
23. J. D. Way, "High Temperature, Inorganic Membranes for Hydrogen Production with CO<sub>2</sub> Capture," presented at Monash University/CSIRO, Clayton, Victoria, Australia, March 3, 2011.
24. J. D. Way, "High Temperature Membranes for Hydrogen Production," presented at CSIRO, Newcastle, New South Wales, Australia, March 1, 2011

## 11. INVENTIONS/PATENT APPLICATIONS, LICENSING ARRANGEMENTS

Fabrication of Composite PdRu Alloy Membranes by Electroless Co-plating, US Provisional Patent Application, July 2008.

"Multilayer Composite Sulfur Resistant Membranes and Methods for Making and Repairing the Same," U. S. Patent Application 13/183,579, 2011.

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### 13. APPENDIX - DURABILITY IN APPLICATIONS CONTAINING H<sub>2</sub>S

It was suggested by DOE that if additional test data could be obtained on durability testing of the selected membrane in H<sub>2</sub>S, that it would be beneficial to report on this information to provide an indication of its potential in more demanding applications such as coal-fired applications. The information is provided in this appendix.

#### **1 and 5 ppm H<sub>2</sub>S exposure at 400°C on porous ceramic supports**

The performance of Pd-Cu and Pd-Au composite membranes on porous alumina supports in water-gas shift mixtures with and without H<sub>2</sub>S are summarized in Table A-I and the properties are shown in Figure A-1. For all mixture tests discussed in this Appendix, the feed pressure was 60 psig and the gas composition was 51% H<sub>2</sub>, 26% CO<sub>2</sub>, 2 %CO, 21 % H<sub>2</sub>O. Testing of the ceramic and AccuSep® supported membranes in gas mixtures with and without H<sub>2</sub>S was conducted at TDA Research in Wheat Ridge, CO. As shown in Figure A1, the PdAu alloy membrane performed much better than the PdCu membrane. The flux inhibition from the WGS feed mixture was also superior for the PdAu membrane. The lack of flux inhibition for the PdAu membrane in WGS feed mixture may be due to the lower total feed pressure which would reduce the concentration polarization effect discussed above. In addition, the flux decrease after exposure to the WGS feed mixture containing 5 ppm H<sub>2</sub>S was much better for the PdAu membrane compared to the PdCu membrane. The superiority of the PdAu alloy in feed mixtures containing H<sub>2</sub>S is consistent with the McKinley patents from the 1960s<sup>6</sup>. Near surface alloy membrane compositions were measured by EDAX spectroscopy.

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<sup>6</sup> McKinley, D.L., Metal alloy for hydrogen separation and purification, U. S. Patent 3,350,845, 1967.

**Table A-I. Summary of Membranes Fabricated and Tested**

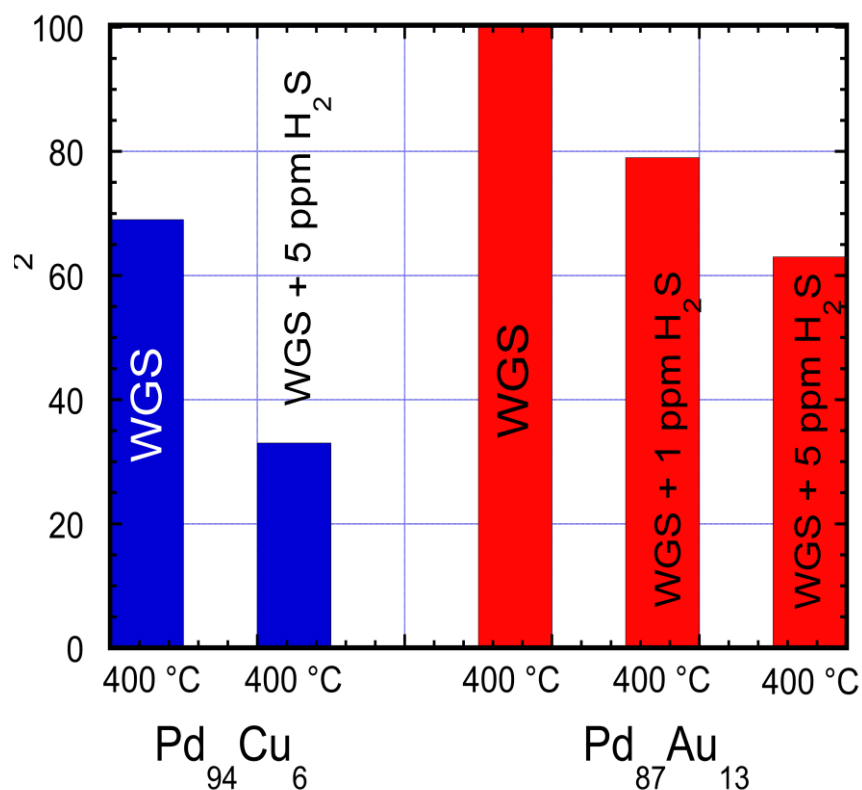
Sample #	Substrate	Thickness (μm)	Composition (mass %)	H <sub>2</sub> Flux at 20 psig, 400°C (mol/m <sup>2</sup> .s)	N <sub>2</sub> Flux at 20 psig, 25°C (mol/m <sup>2</sup> .s)	Ideal H <sub>2</sub> /N <sub>2</sub> Selectivity 400°C
GTC-30	0.2 μm Al <sub>2</sub> O <sub>3</sub>	6	Pd <sub>94</sub> Cu <sub>6</sub>	0.12	2.9 x 10 <sup>-4</sup>	414
GTC-75	0.2 μm Al <sub>2</sub> O <sub>3</sub>	7.1	Pd <sub>87</sub> Au <sub>13</sub>	0.128	3.2 x 10 <sup>-5</sup>	3940
CSM-105	Pall AccuSep®	2.8 <sup>†</sup>	Pd <sub>95</sub> Au <sub>5</sub>	0.562	2.0 x 10 <sup>-5</sup>	28,500
CSM-121	Pall AccuSep®	2.2 <sup>†</sup>	Pd	0.73*	-	-

\*Estimated from correlation of pure hydrogen flux versus reciprocal thickness<sup>7</sup>

<sup>†</sup>Estimated from mass gain after plating

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<sup>7</sup> Hatlevik, Ø., S.K. Gade, M.K. Keeling, P.M. Thoen, A.P. Davidson, and J.D. Way, *Palladium and palladium alloy membranes for hydrogen separation and production: History, fabrication strategies, and current performance*. Separation and Purification Technology, 2010. **73**: p. 59-64.



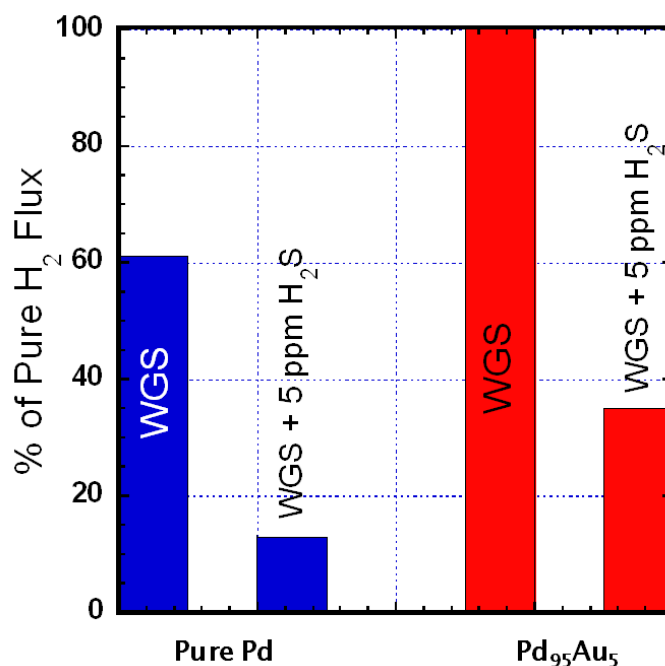
**Figure A-1.** Comparison of the performance of Pd-Cu (GTC-30) and Pd-Au (GTC-75) composite membranes on porous alumina supports in water-gas shift mixtures with and without H<sub>2</sub>S.

#### 1 and 5 ppm H<sub>2</sub>S exposure at 400°C on porous metal supports

Similar mixed gas results were observed for PdAu membranes on AccuSep® substrates as seen in Figure A-2. Membrane #105 was additionally tested with respect to the hydrogen flux in WGS and WGS + H<sub>2</sub>S mixtures at a lower temperature of 400°C. These data are compared to a pure Pd membrane #121 in Figure A2. There was no change in the hydrogen flux in the WGS environment for the 5% Au alloy while the pure palladium membrane experienced a 40% decrease. This observation is consistent with the data in Figure A1 also. The lack of inhibition in the WGS feed mixture is most likely due to the lower feed pressure (60 psig) compared to the other mixed gas data presented in this report. The lower feed pressure would minimize the effects of concentration polarization. When 5 ppm H<sub>2</sub>S is added to the feed stream the decrease for the Pd-Au alloy was 62% while the pure Pd lost ~85% of the hydrogen flux. Although there are limited data, Figures A1 and A2 suggest that the flux inhibition from H<sub>2</sub>S will



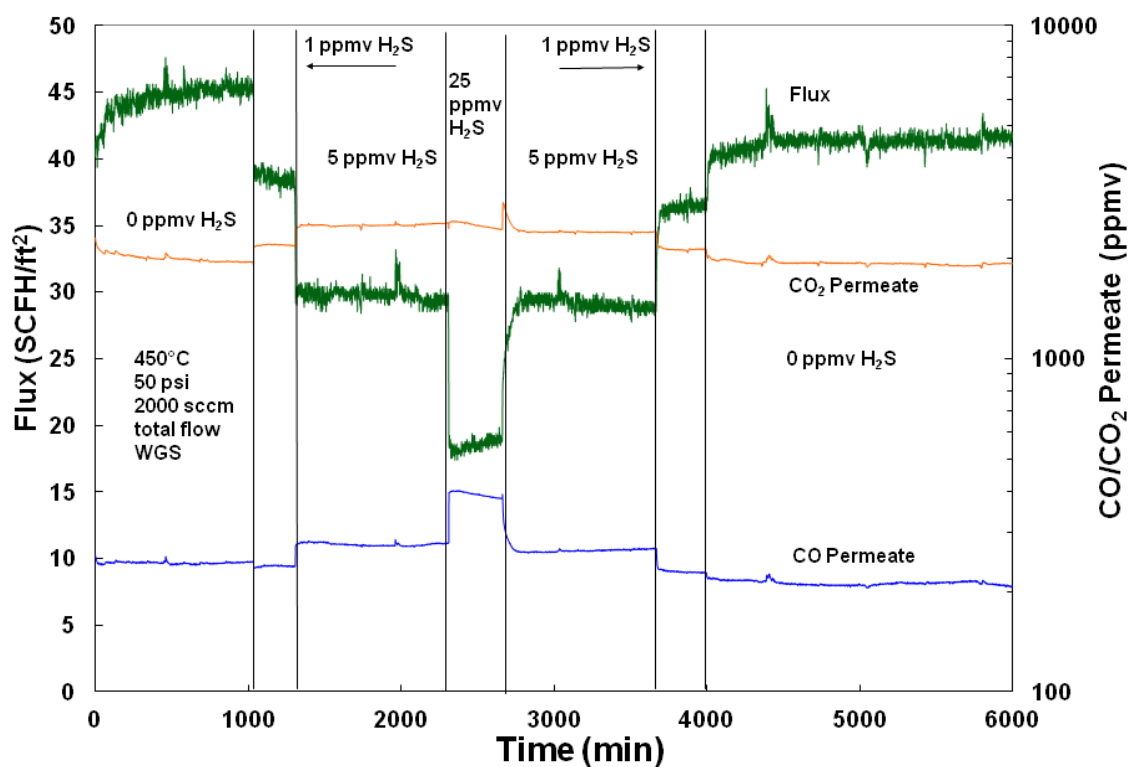
decrease at higher temperatures. The difference in the tests, shown in Figures A1 and A2, of the effect of  $H_2S$  are dependent on multiple factors such as pressures, feed flow and temperature among others.



**Figure A-2.** Effect of gold alloy on the  $H_2$  flux in WGS and WGS +  $H_2S$  feed mixtures as compared to pure  $H_2$  flux at 400°C. The pure Pd membrane is #121 while the Pd-Au membrane is #105.

### 1, 5 and 25 ppm $H_2S$ exposure at 450°C on porous metal supports

The effect of  $H_2S$  in WGS feed mixtures on the hydrogen permeation was investigated with a  $Pd_{95}Au_5$  alloy membrane #105 at 450°C as shown in Figure A-3. The reduction of the hydrogen flux for membrane #105 at 450 °C was much less than at 400 °C. A reversible flux depression was observed with increasing  $H_2S$  content in the feed. A possible mechanism is that  $H_2S$  is chemisorbed on the membrane surface without any penetration into the bulk of the membrane since both permeate purity and hydrogen flux return to their initial values after  $H_2S$  is removed from the stream. The hydrogen flux decreased only ~33% when the feed mixture contained 5 ppm  $H_2S$ . The temporary decrease in permeate purity is thus believed to be caused by the decrease in hydrogen flux rather than an increase in flux of impurities.



**Figure A-3.** Permeation test of palladium alloy membrane #105 in a WGS environment containing H<sub>2</sub>S at 450°C.

It is concluded that the Pd-Au alloy membrane system has the potential for application in streams containing H<sub>2</sub>S. Additional studies are required to understand the interaction of S with the alloy to determine its full potential in more demanding applications.