Pall Corporation

Centre for Applied Materials Science

High Throughput Design of Ternary Pd Alloys for Optimum Sulfur / Carbon Resistance in Hydrogen Separation & Carbon Capture Membrane Systems

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NETL CO_2 Capture Technology Meeting
Pittsburgh / July 9 – 12, 2012

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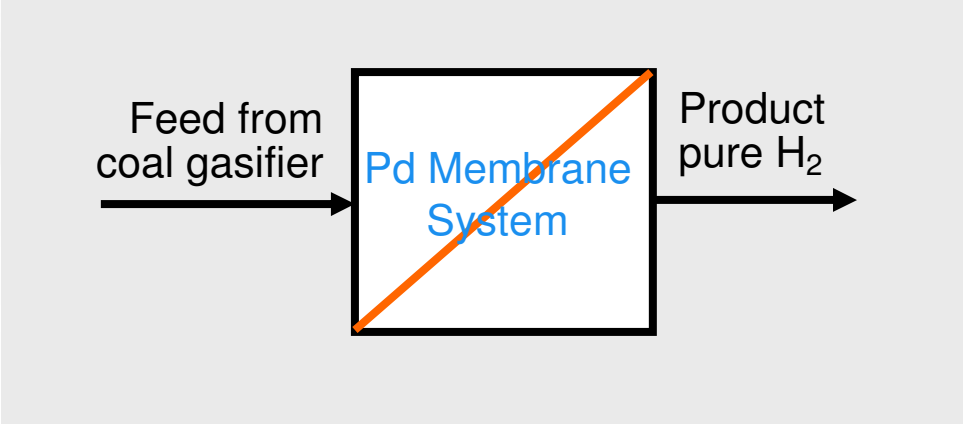
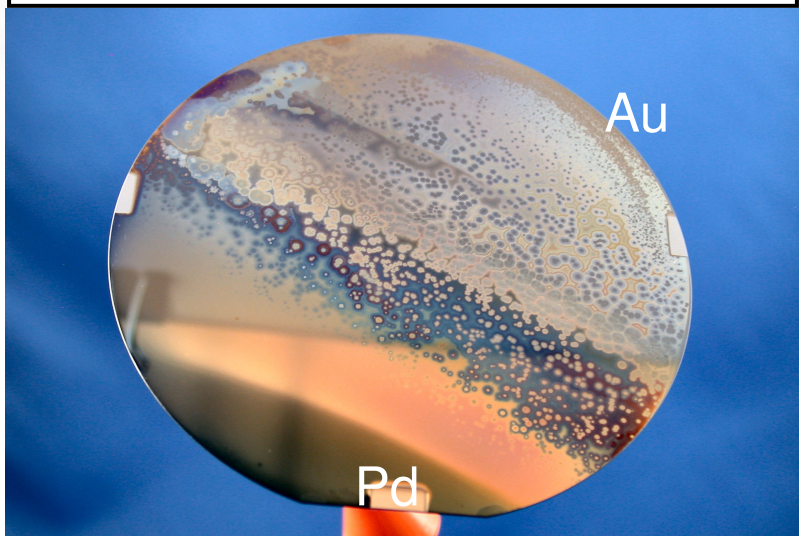
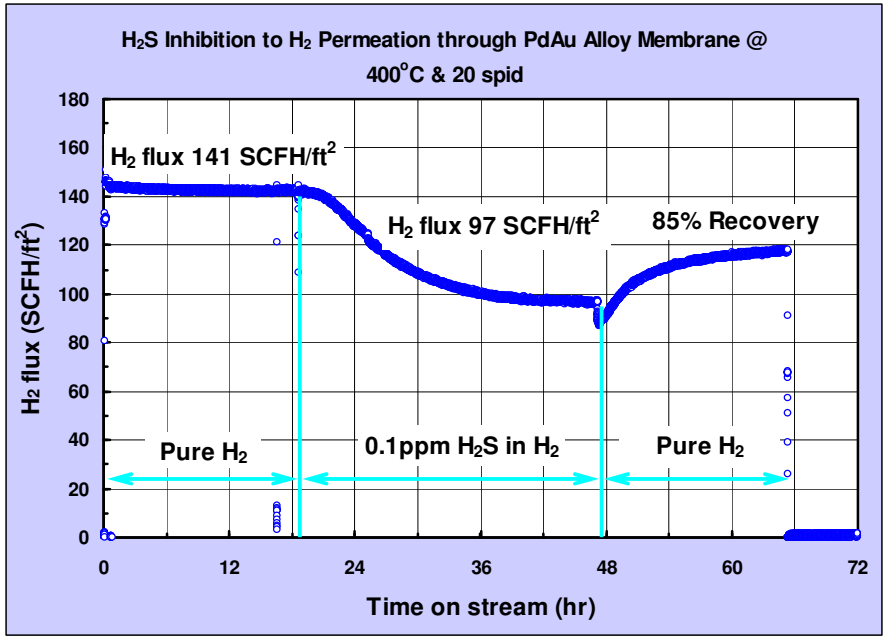
Project Background: Problem and Approach



Coal Gas Corrosion Test of PdAu Alloy Film

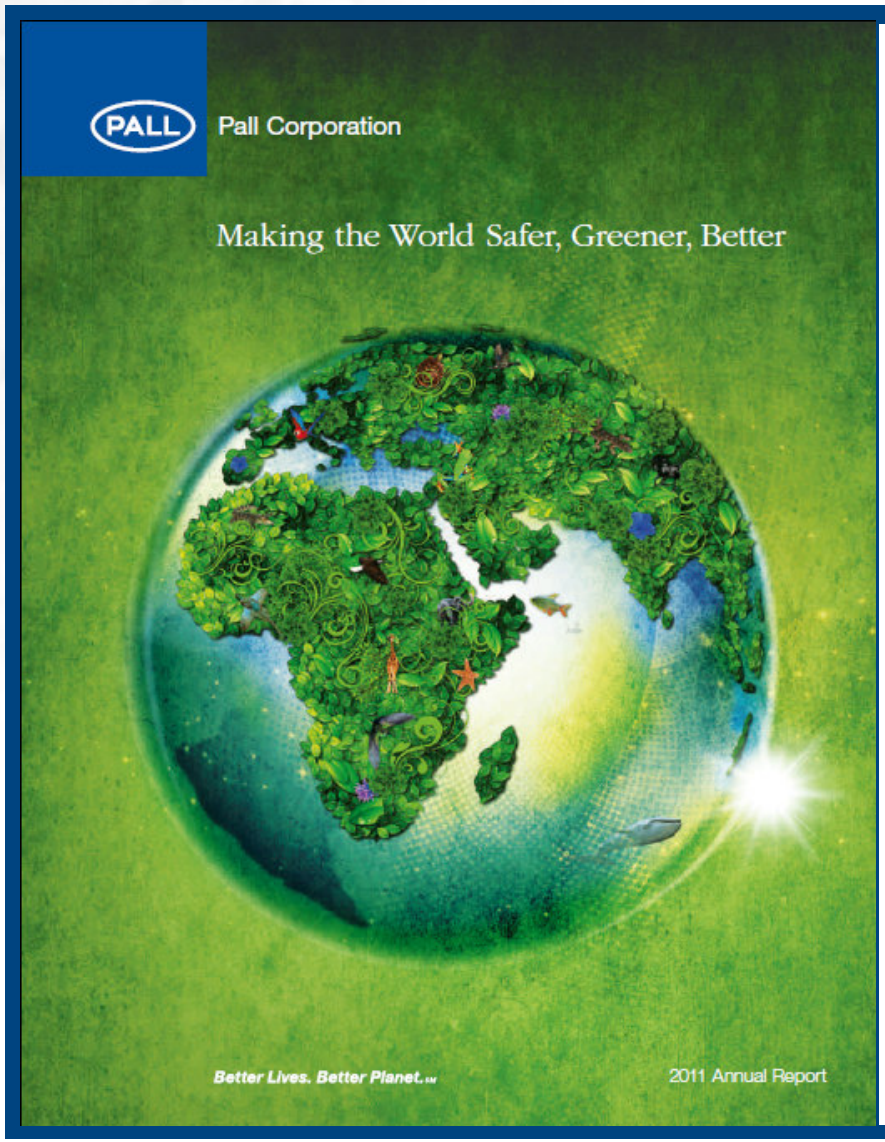




Outline

- Project overview
- Palladium membrane technology background
- Project progress as of 06/30/2012
- Future plans

Profile of Pall Corporation



Pall Corporation is a global leader in the high-tech filtration, separation and purification industry. We've become a $2.7 billion company with nearly 11,000 employees around the world by helping customers solve complex fluid management challenges. (www.pall.com/profile)

Project Overview

Project Objectives

- Develop an economic, high temperature and pressure, hydrogen separation membrane system for CO_2 capture that resists moderate levels of contaminants, typical in gasified coal.
- Create an advanced palladium alloy for optimum hydrogen separation performance using combinatorial material methods for high-throughput screening, testing, and characterization.
- Demonstrate durability by long term testing of a pilot membrane module at a commercial coal gasification facility.
- Understand long term effects of the coal gasifier environment on the metallurgy of the membrane components.

Project Overview

Participants

- Pall Corporation (project management, membrane fabrication and its scale-up technology, prototype membrane and module test)
- Cornell University (Combinatorial sample fabrication)
- Georgia Institute of Technology (Surface characterization of alloys)
- Oak Ridge National Laboratory (in-situ XRD of alloy phases)
- Southern Company (Long-term membrane module test)

Funding

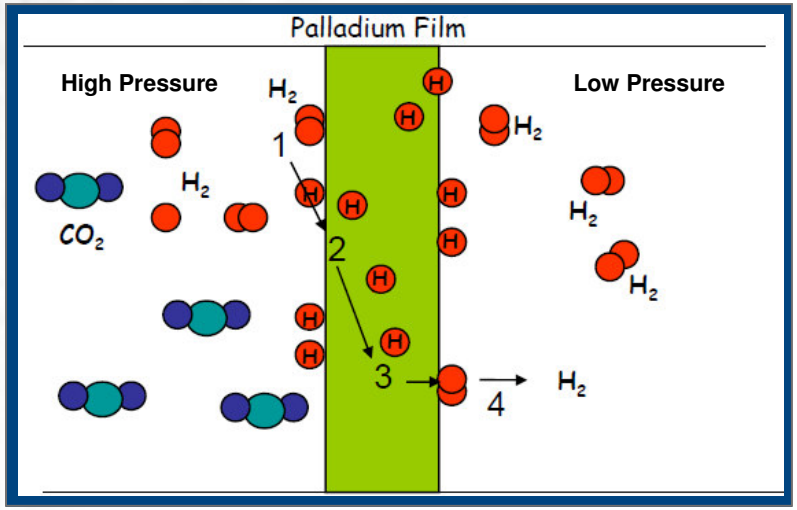
- $1,517,000 Total
- $1,207,000 U.S. Department of Energy
- $310,000 Cost Share

Performance Period

- Oct 1, 2009 to Sept 31, 2012 as proposed (three-year project)

How Palladium Membrane Works

Hydrogen Transport Through Palladium Film



- H_2 dissociation on metal
- H dissolves into metal
- H diffuses through metal
- Recombination to form H_2

Hydrogen Selectivity

- Infinite for defect-free palladium film

Hydrogen Flux Equation

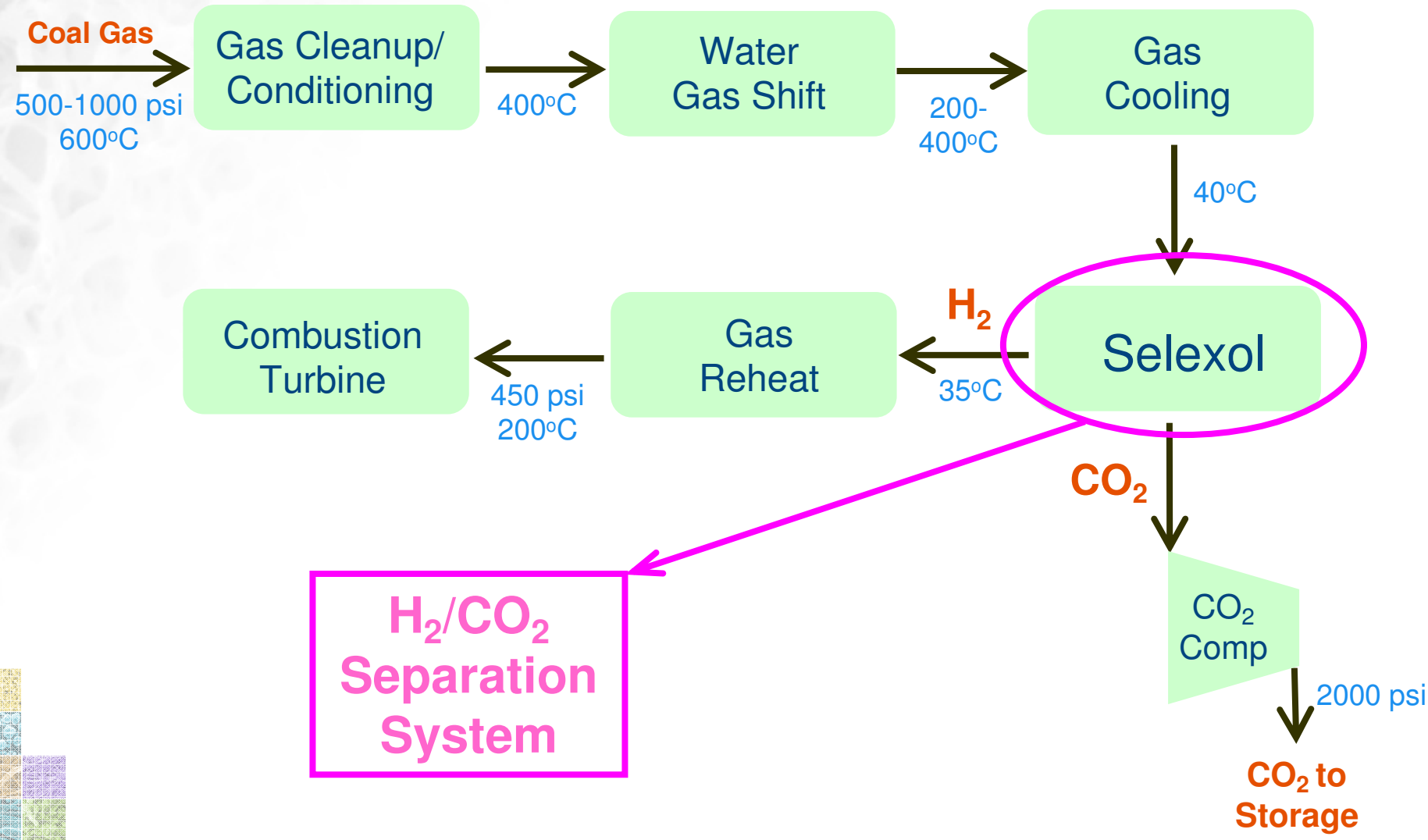
- **Q: H_2 permeability of palladium**
- **L: Thickness of palladium film**
- **$P_{H2,\ feed}$: H_2 partial pressure in feed**
- **$P_{H2,\ permeate}$: H_2 pressure in permeate**

$$J_{H_2} = \frac{Q}{L}\left(P_{H_2,feed}^{0.5} - P_{H_{2,permeate}}^{0.5}\right)$$

Design & Operating Considerations

- High hydrogen permeable metal alloy
- Free membrane fouling materials
- Thin membrane
- High membrane area
- High pressure
- High temperature

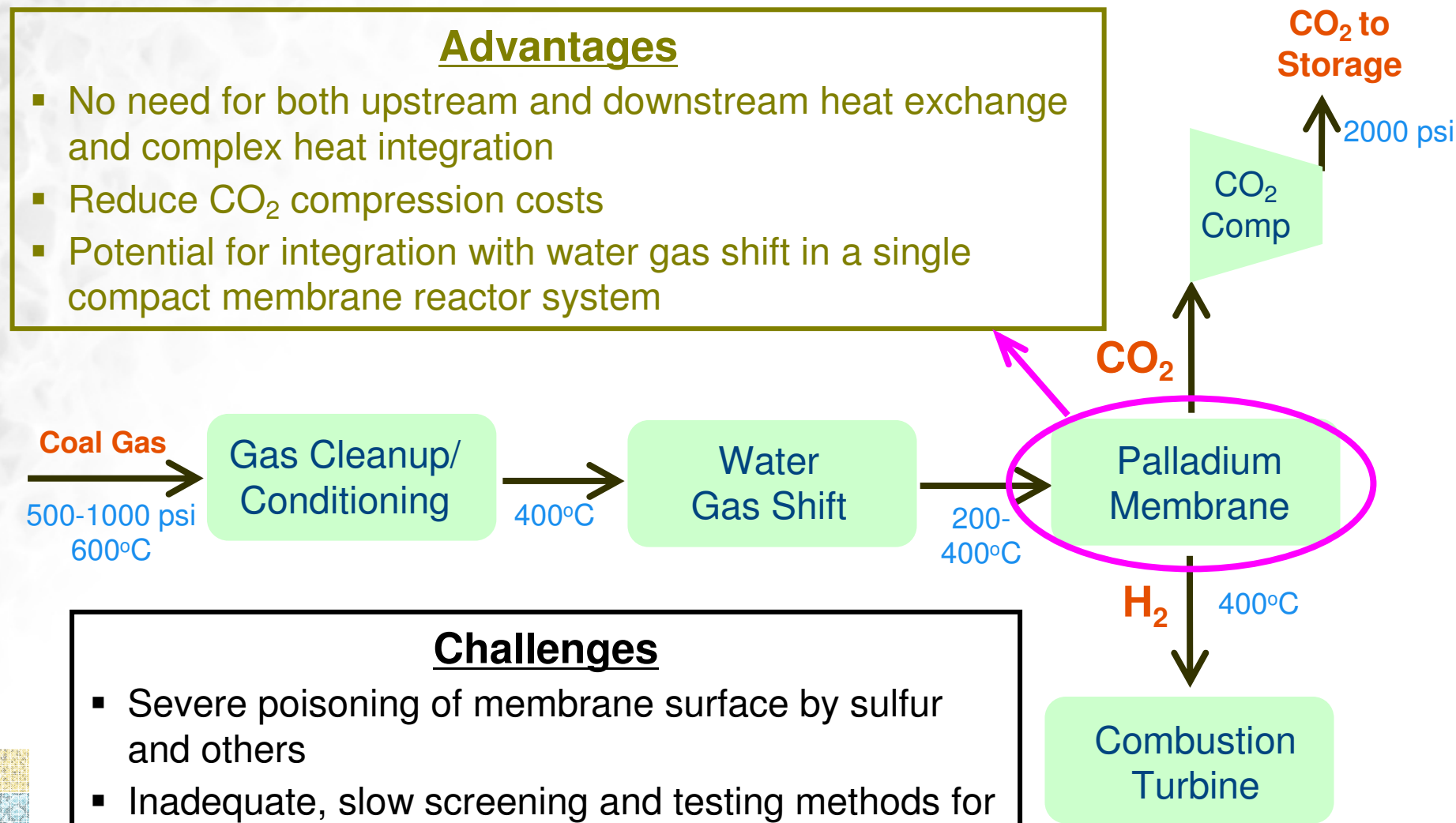
IGCC Power Plant with Pre-Combustion CO_2 Scrubbing



Palladium Membranes in IGCC Power Plants

Advantages

- No need for both upstream and downstream heat exchange and complex heat integration
- Reduce CO_2 compression costs
- Potential for integration with water gas shift in a single compact membrane reactor system



Challenges

- Severe poisoning of membrane surface by sulfur and others
- Inadequate, slow screening and testing methods for identification of new alloys

Project Schedule & Milestones

		2009		2010				2011				2012			
Task#	Project Milestone Description	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1	Project management and planning														
2	Literature and patent search														
	Milestone 1 Report demonstrating understanding of previous work														
3	Design and modeling of binary and ternary Pd alloys														
	Milestone 2 Report on use of combinatorial method														
4	Construct and test 15 cm^2 active membrane area prototypes						9 months no-cost extension								
	Milestone 3 Report on testing of small scale membranes														
5	Scale up active membrane area from 15 to 75 cm^2														
	Milestone 4 Report on testing of scaled-up membranes														
6	Construct and test a working membrane module														
	Milestone 5 Report on long-term performance of membranes														
7	Provide complete analysis of relevant data sufficient of permit economic evaluatoin of the process														
	Milestone 6 Report on advancement necessary to commercialize membrane process														

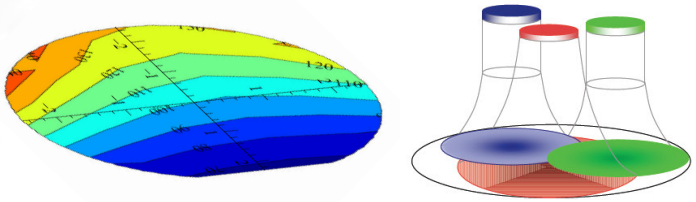
Progress and Current Status

Task	Timeline	Completion
Task 4 Construct and test 15 cm^2 active surface area prototypes of novel Pd alloy membranes for use as high temperature, high pressure gas separation membranes under coal gasifier conditions ▪ Optimize process for making zirconia substrates suitable for each candidate Pd alloy ▪ Fabricate best candidate palladium alloys into thin film membrane prototypes with 15-cm^2 active surface area over optimized zirconia substrate ▪ Test hydrogen separation performance of each best candidate alloy under coal gas conditions with trace amounts of impurities, including sulfur, for extended period	Oct 2010 to Sept 2011 (nine months of no cost extension due to limit to thin film deposition facility from subcontractor)	30%

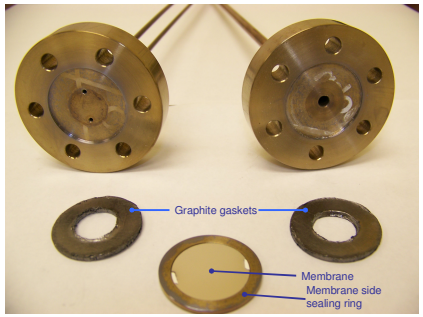
Combinatorial Pd Alloy Development Workflow

Freestanding Alloy Membrane Fabrication

Combinatorial Discovery

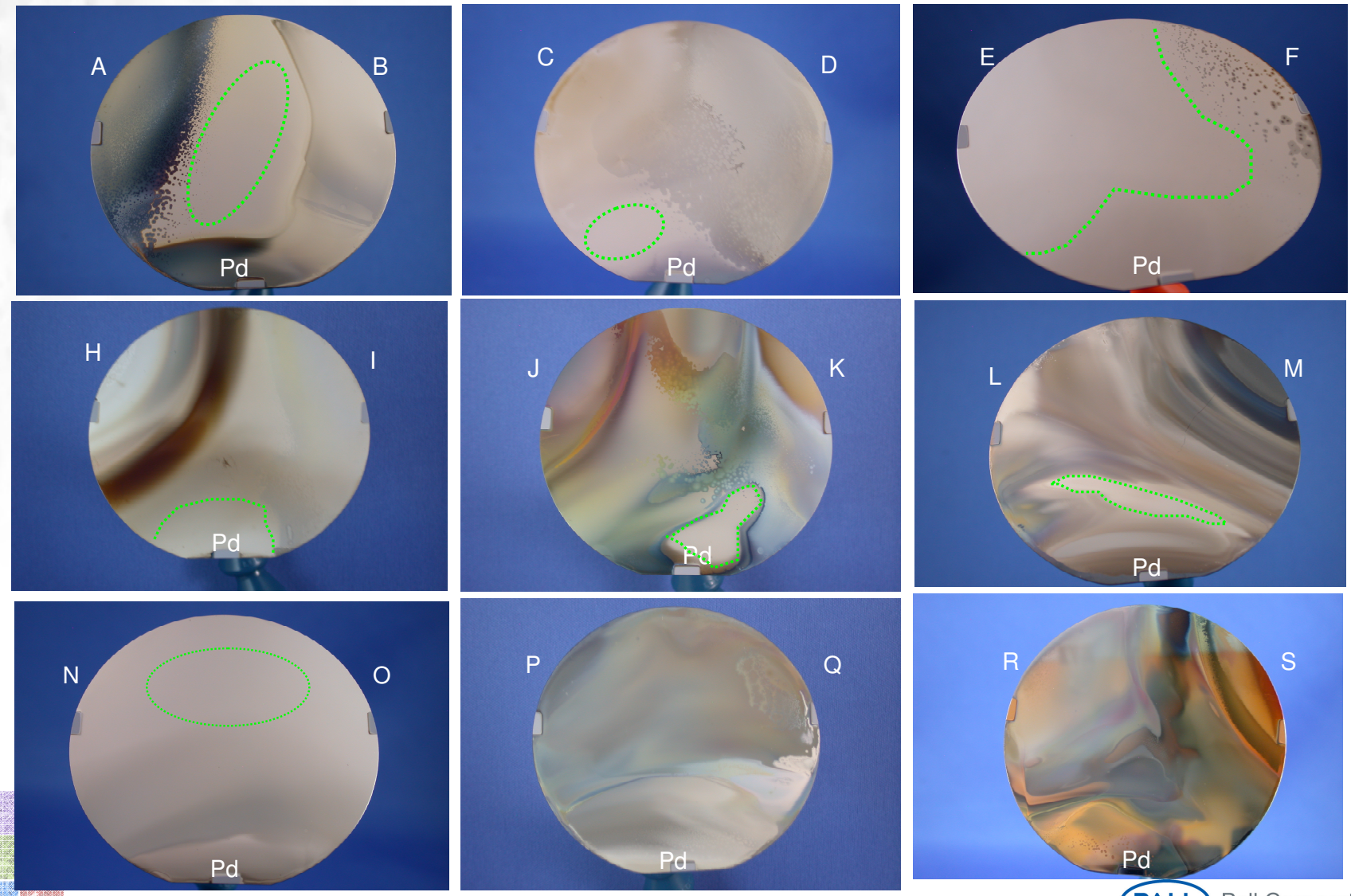


Gas Permeation Performance Testing



Combinatorial Discoveries (Task #3)

No Corrosion Spots on Seven Ternary Composition Spreads

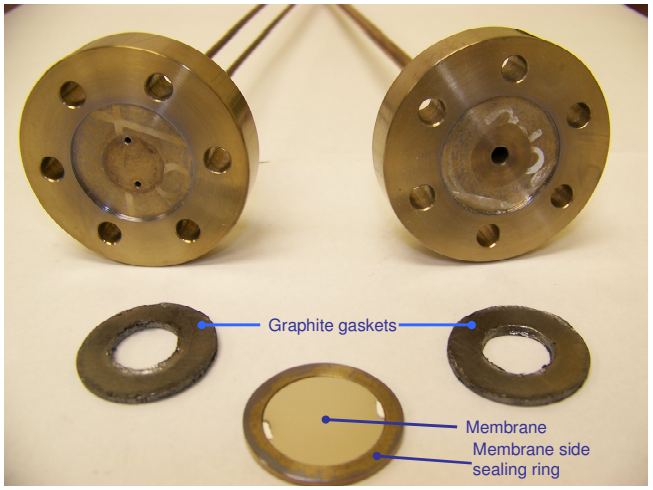


Pd Alloy Screening Test Protocol

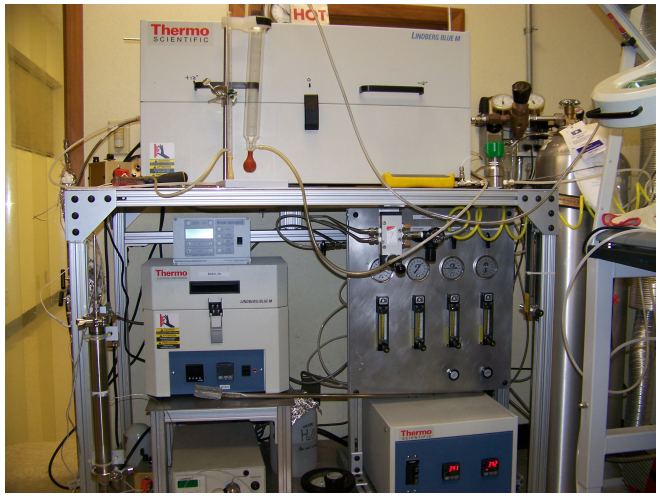
- Sulfur challenge test @ 400°C & 20 psid with a gas mixture of H_2S and H_2.
- Coal gas test @ 400°C & 200 psig (*coal gas composition H_2=17.6%, CO_2=17.9%, H_2O=2.6%, CO=2.6%, N_2=59.3%, H_2S up to 170 ppm)

***The composition of coal gas is provided by U.S. DOE / NCCC (site for future field test).**

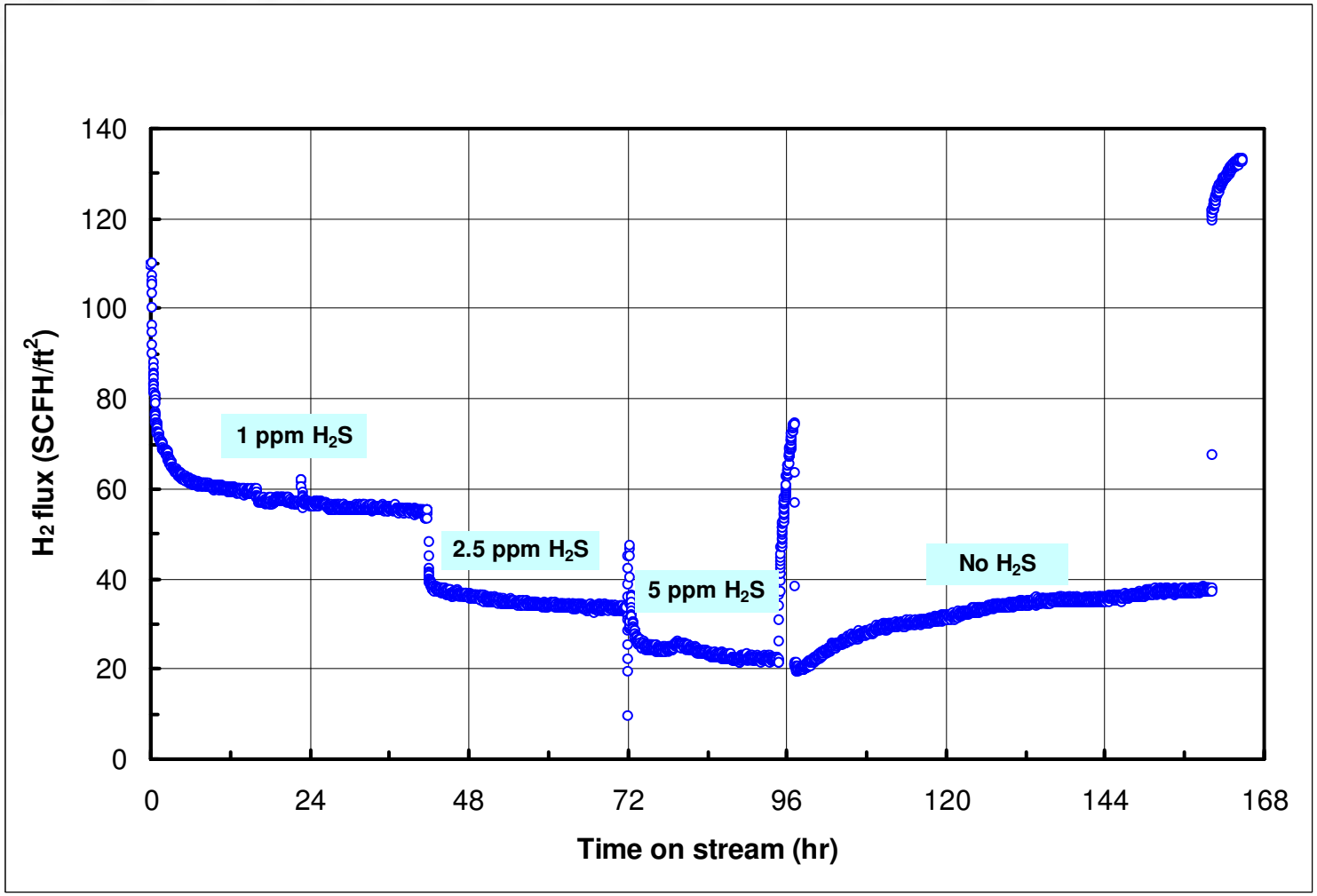
Gas Permeation Cell



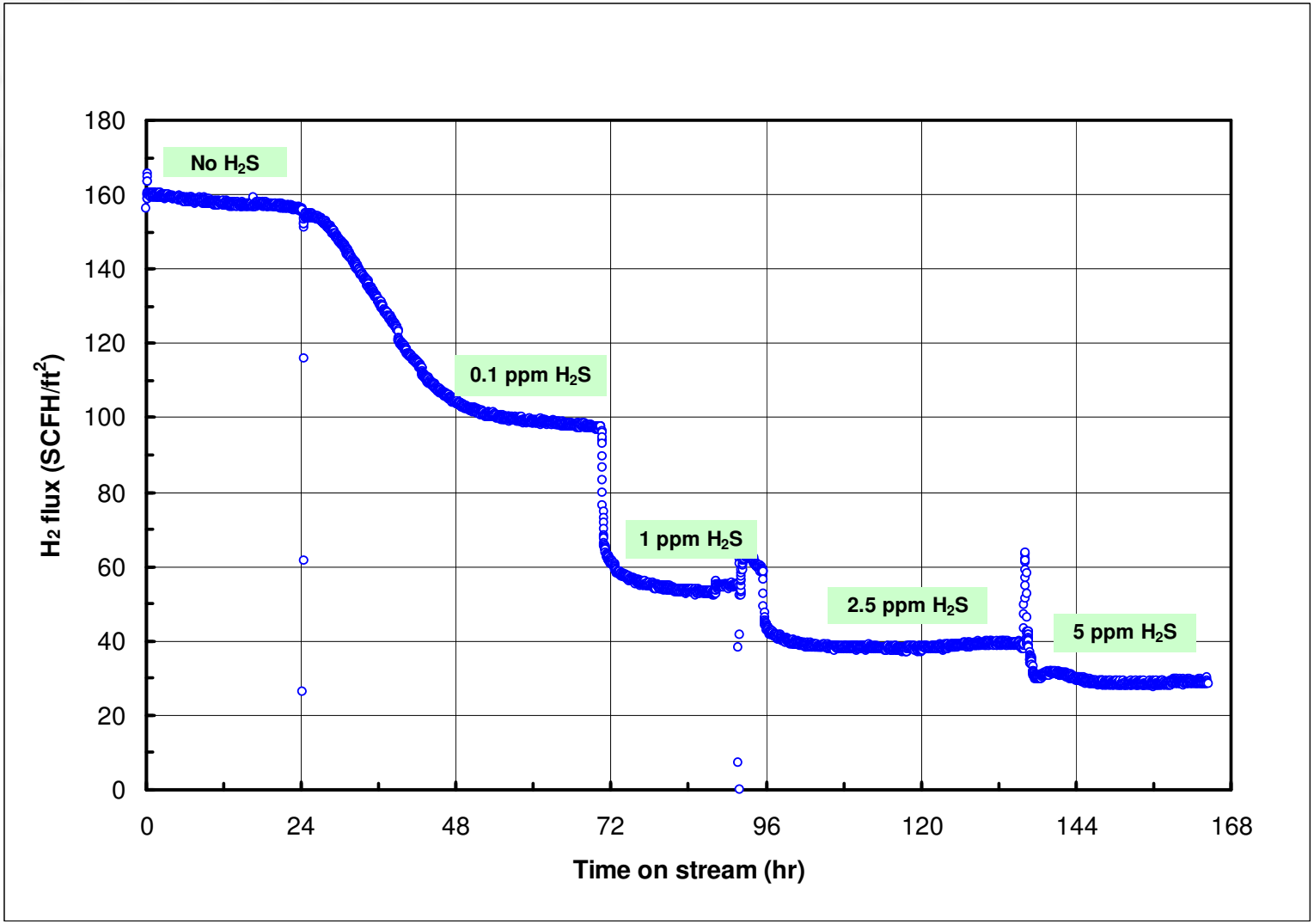
Gas Permeation Test Stand



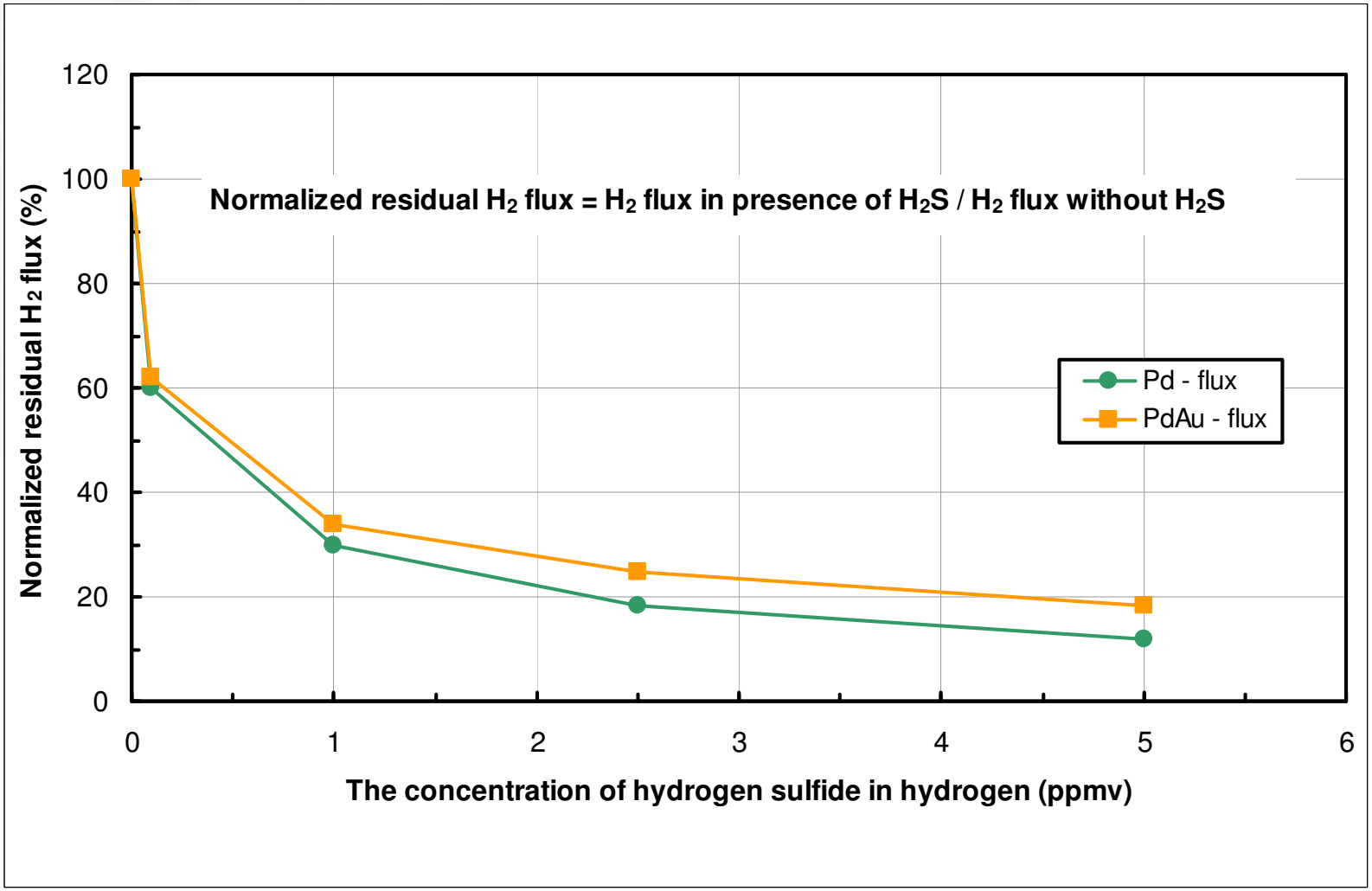
Sulfur Challenge Test on Pd Membrane



Sulfur Challenge Test on PdAu Alloy Membrane



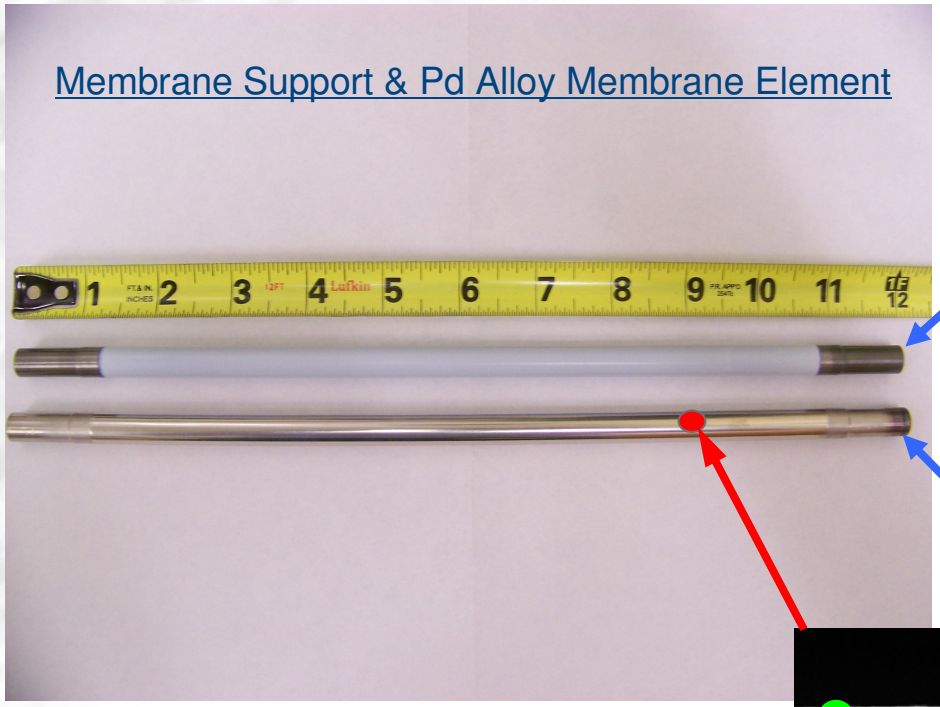
Comparison of Sulfur Inhibition: Pd versus PdAu Alloy



Plans to Complete Project

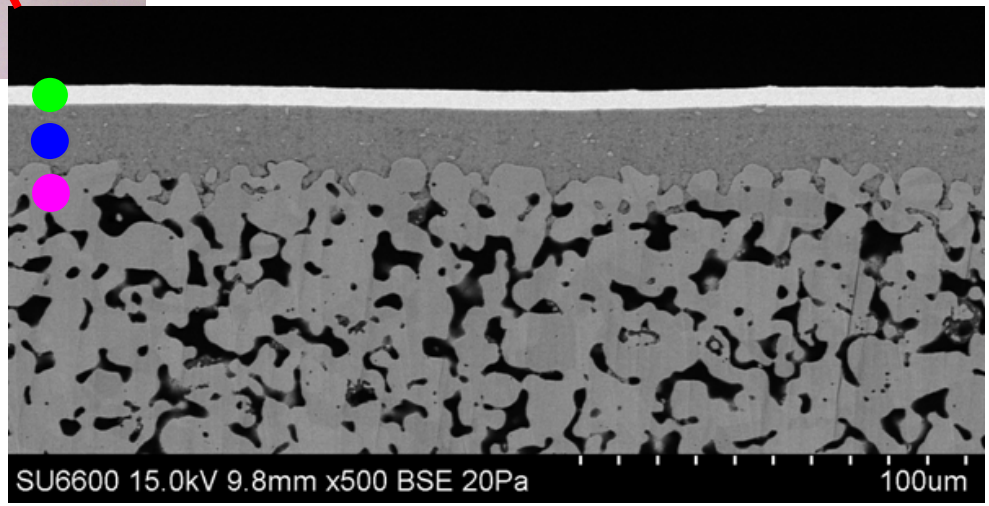
- Make flat sheet samples of alloy candidates selected from task #3 and test them in disc form to screen the best alloys based on sulfur tolerance level
- Select the best alloys and directly make full scale (active surface area 75 cm^2) membrane element of novel palladium alloy prototypes
- Conduct 100-500 hour test on these 75 cm^2 samples in simulated coal gas with trace amounts of impurities including sulfur.
- Construct a working membrane module capable of extended service as a hydrogen separation system
- Conduct 500 hour relevant field test with real gasifier feed at U.S. DOE / NCCC
- Detailed process and economic modeling using field membrane performance data

Pall's Capability in Palladium Membranes



Membrane support

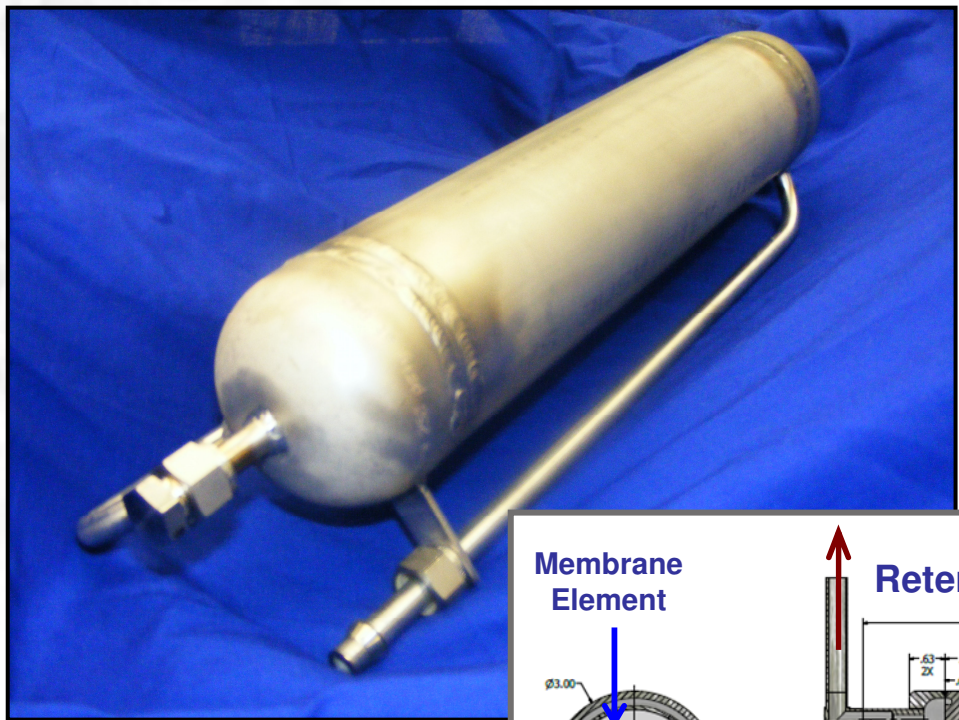
Pd alloy membrane

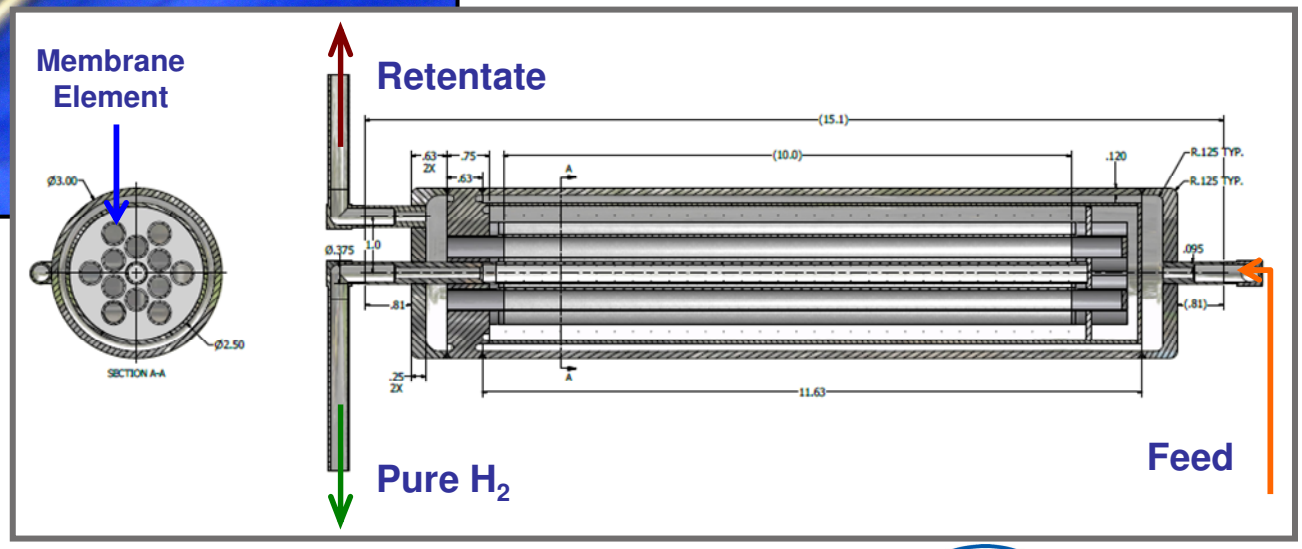


- Pd alloy top layer
- Ceramic intermediate layer
- Porous stainless steel substrate

Pall's Capability in Palladium Membranes

5kw Palladium Alloy Membrane Module





Summary

- Discovered seven coal gas corrosion resistant ternary palladium alloy systems as candidates for sulfur tolerance level screening test
- Free-standing thin film deposition technique with uniform composition for ternary palladium alloy is being developed
- Capability for manufacturing and marketing of portable fuel cell size palladium alloy membrane module is fully established at Pall Corporation.
- Pall's capability above provides infrastructure for this project to complete and meantime success of this project will expand Pall's capability into other markets.

Acknowledgements

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  - Patricia Rawls
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