Pall Corporation

Combinatorial Design of Pd Ternary Alloys for Sulfur/Carbon Tolerant Hydrogen Separation

(Pre-Combustion Capture)

2010 NETL CO2 Capture Technology Meeting
Sheraton Station Square Pittsburgh, PA

Dan Henkel
Pall, Technical Director
September 16, 2010

Agenda

Introduction to Pall Corporation (www.pall.com)

Project Overview

Technology Fundamentals

Progress and Current Status

Plans for Development and Commercialization

Pall Corporation

- Annual sales of +US $ 2.2 Billion
- 78 Locations in 34 Countries
- Approximately 10,000 Employees
- Traded on the NYSE (PLL)

Market Segments

Pall Life Sciences
- Medical
- Biopharm

Pall Industrial
- Aerospace & Transportation
- Food & Beverage
- Fuels & Chemicals
- Industrial Manufacturing
- Materials
- Microelectronics
- Power Generation
- Water

Offices and Plants

Argentina
Australia
Austria
Belgium
Brazil
Canada
China
France
Germany
Hong Kong
India
Indonesia
Ireland
Italy
Japan
Korea
Malaysia
Mexico
Netherlands
New Zealand
Norway
Poland
Puerto Rico
Russia
Singapore
South Africa
Spain
Sweden
Switzerland
Taiwan
Thailand
United Arab Emirates
United Kingdom
United States
Venezuela

Project Overview

Funding:

- $1,517,000 total
- $1,207,000 (NETL)
- $310,000 (Pall)

Performance:

- Oct 1, 2009 to Sept 31, 2012

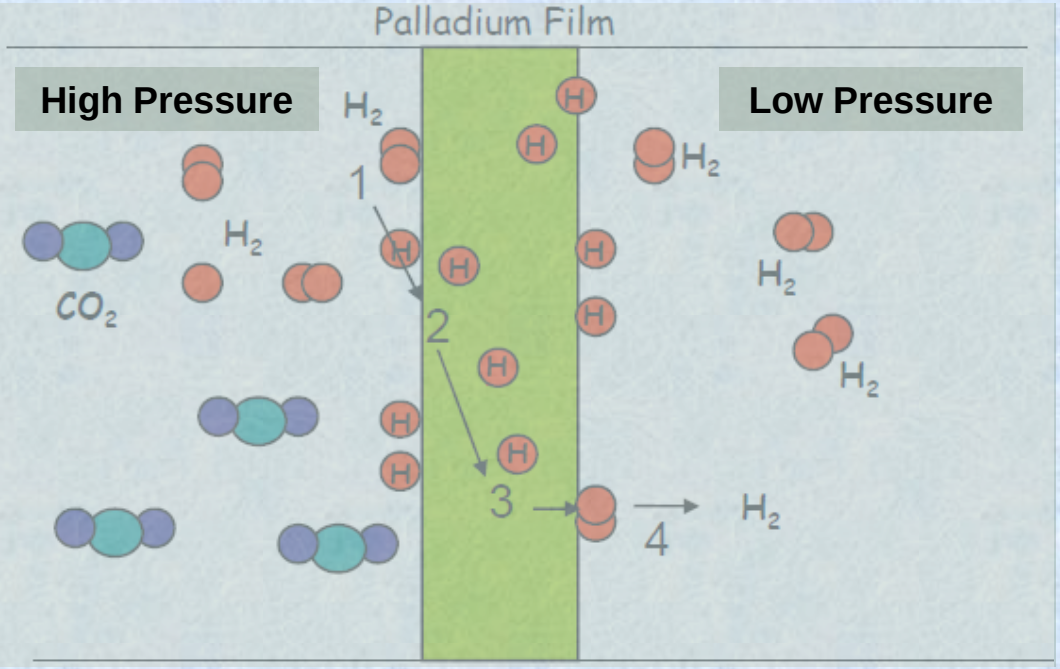
Participants:

- Pall Corporation
- Cornell University
- Georgia Institute of Technology
- Oak Ridge National Laboratory
- Southern Company

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.

Pd Membranes for H_2 Separation



H_2 Permeation Mechanism

1. H_2 dissociation on metal
2. H dissolves into metal
3. H diffuses through metal
4. Recombination to form H_2

Hydrogen Permeation Rate

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

Q - Hydrogen permeability of Pd alloy

L - thickness of Pd membrane

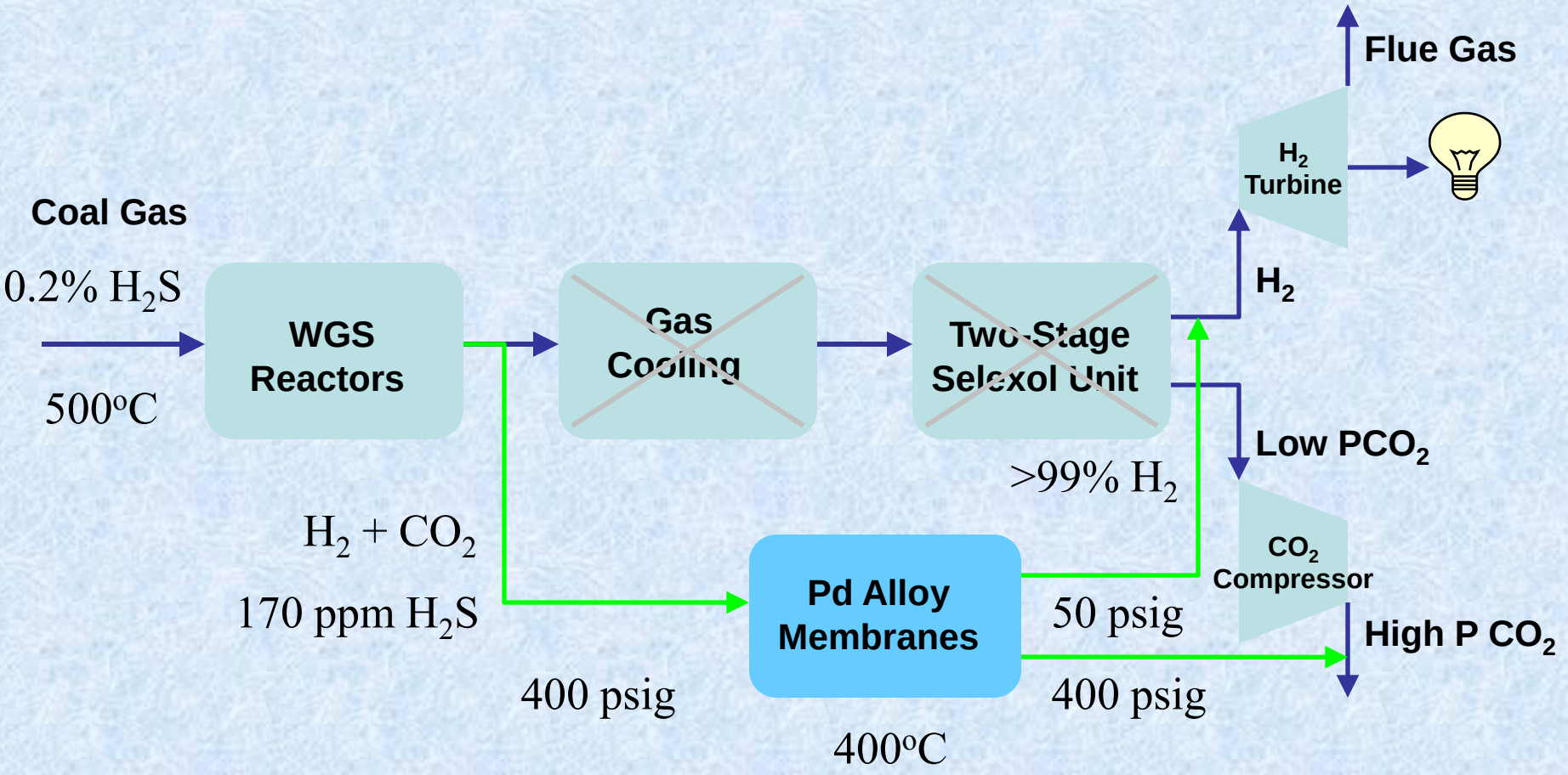
$P_{H2,\,feed}$ – hydrogen partial pressure in feed

$P_{H2,\,permeate}$ – hydrogen pressure in permeate

H_2/CO_2 selectivity

$$\alpha_{H_2/CO_2} = \frac{Q_{H_2}}{Q_{CO_2}}$$

The Technology – In Operation

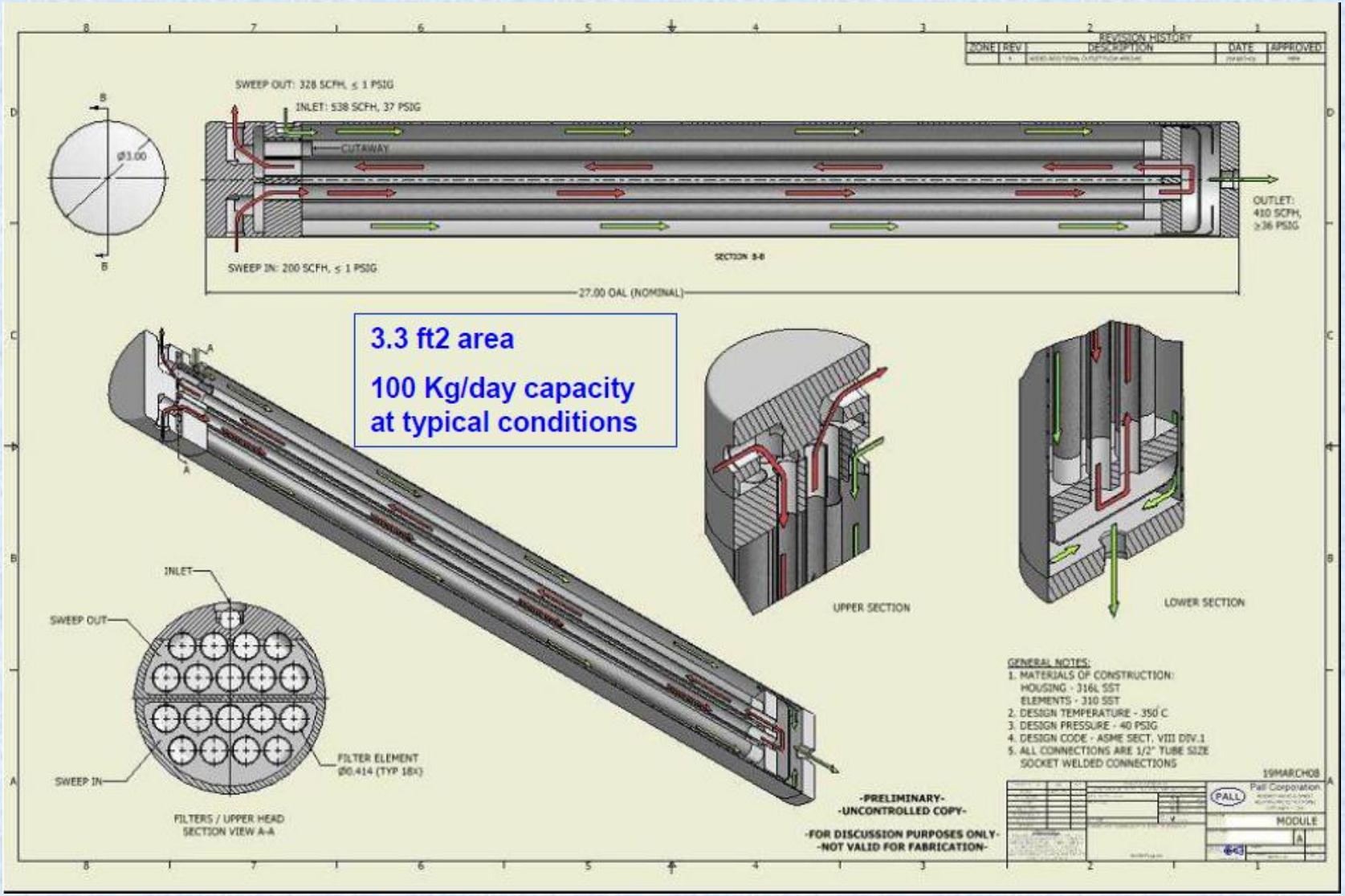


Technology Description – Membrane Element

Pall's palladium alloy membrane system will include:

- Porous 310 stainless steel support tube; solid end fittings
- Nanoporous yttria-stabilized zirconia (YSZ) substrate
- Directly welded to tube sheet without need for sealing
- Uniform thermal expansion of housing and module.

Technology Description – Membrane Module



Advantages and Challenges

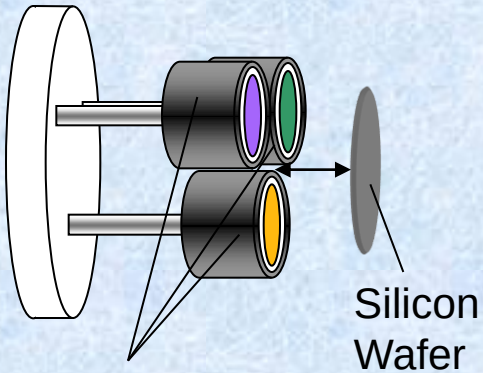
- Any alloy composition can be fabricated
- CO_2 is produced at a higher pressure
- The hydrogen product is high purity
- Hydrogen is produced at higher temperature
- Lower parasitic loading (no compressor, etc.)

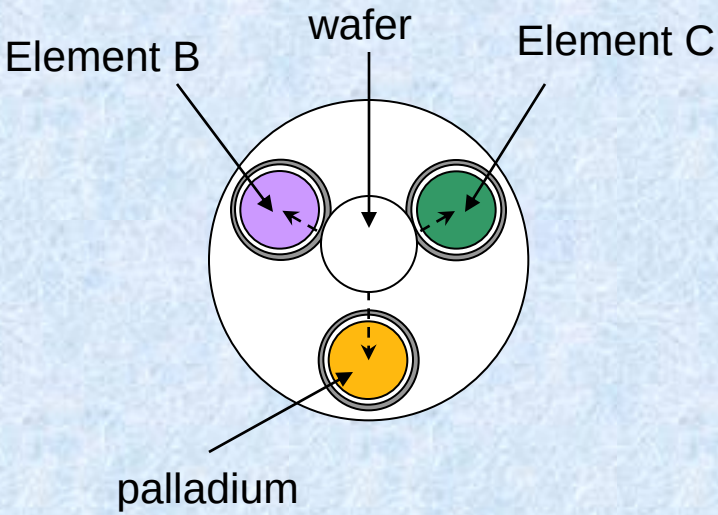
- Lack of ternary phase diagrams
- Membranes must remain defect-free for years
- Long term microstructural changes are unknown.
- Long term hydrogen flux, separation data are unknown

Project Milestones and Timeline

		2009		2010				2011				2012			
		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														
3	Design and modeling of binary and ternary Pd alloys														
	Milestone 2 Report on use of combinatorial method														
4	Construct and test 15 cm2 active surface area prototypes														
	Milestone 3 Report on testing of small scale membranes														
5	Scale up active surface area from 15 cm2 to 75 cm2														
	Milestone 4 Report on testing of scaled up membranes														
6	Construct and test a working membrane module														
	Milestone 6 Report on long-term performance														
7	Provide complete analysis of relevant data sufficient to permit economic evaluation of the process														
	Milestone 7 Report on advancement necessary to commercialize														

Combinatorial Materials Design

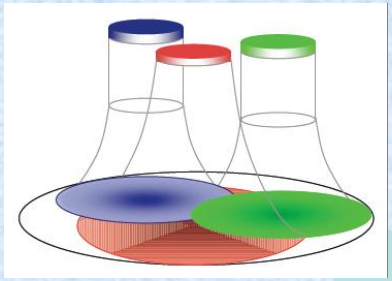




A continuous spread of ternary alloys are synthesized at once into a single thin film

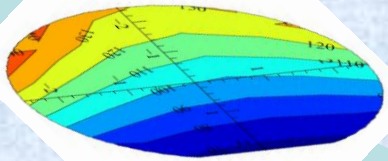
Quick, high throughput

Combinatorial Alloy Development Workflow

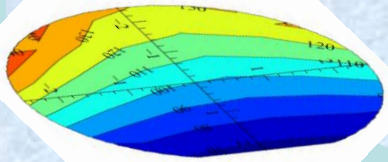


Compositional Spreads

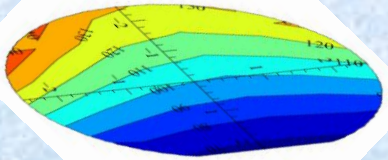
Exposure to Coal Gas



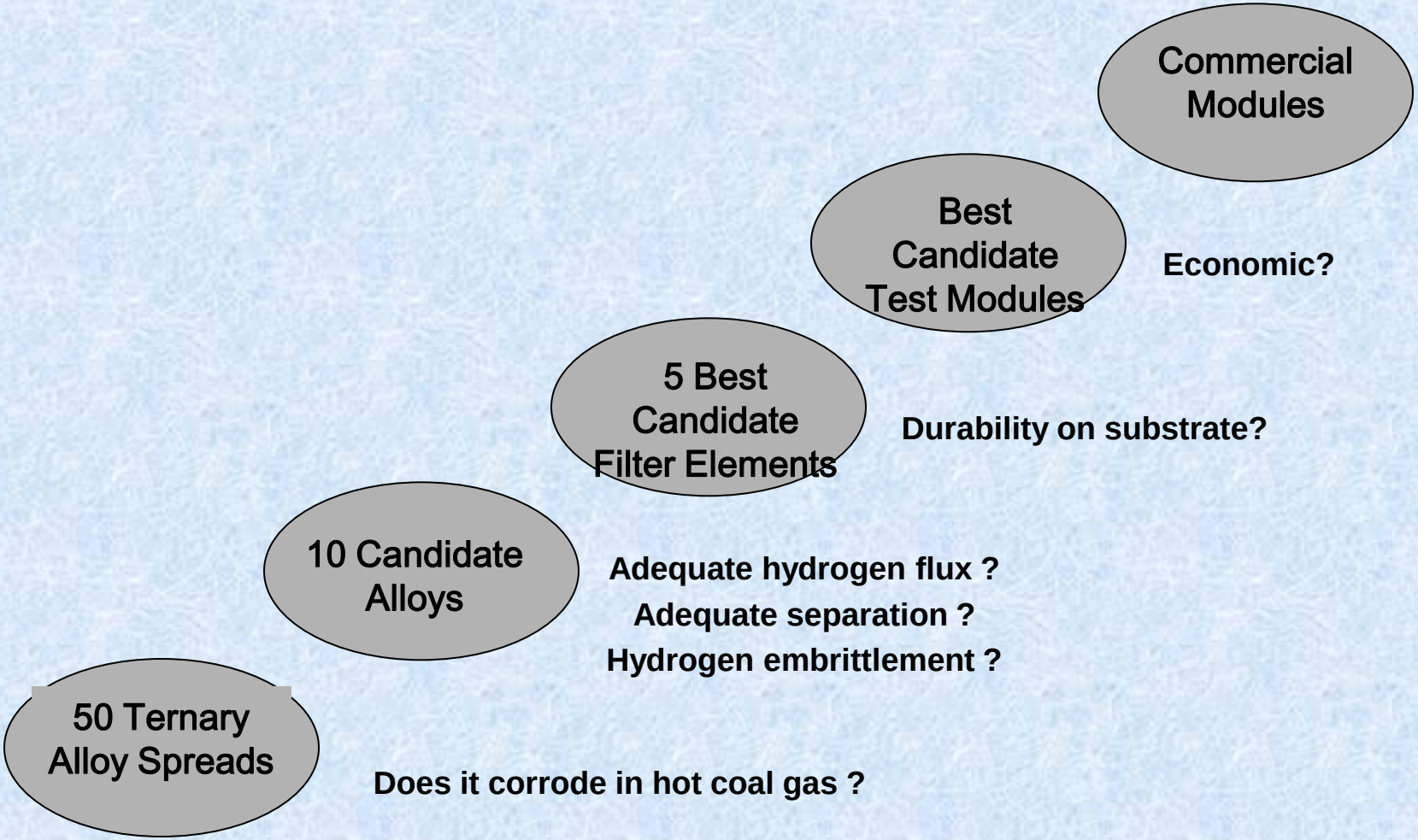
Visual High-Throughput Screening



Raman Mapping “Sweet” Spots



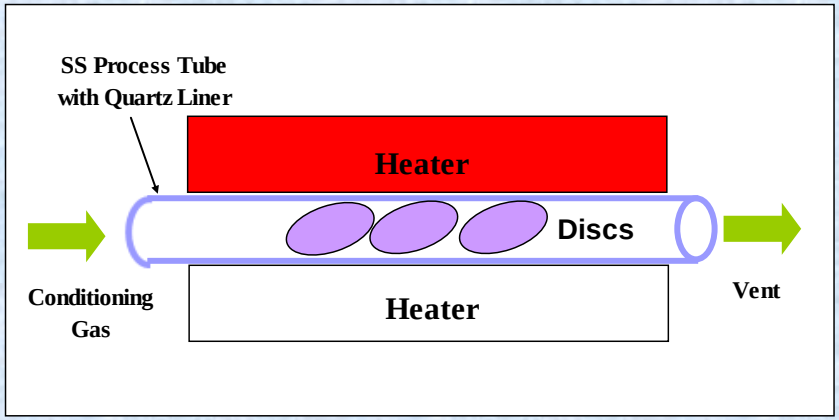
Technology Development Path



Progress and Status

Task 2.0	**Literature and patent search of previous work on metallic hydrogen separation membranes.** ▪ Long-term effects of syngas constituents on metallic membrane surfaces ▪ Combinatorial materials development ▪ Substrate quality and its characterization ▪ Chemical modeling	**Dec 1, 2009 to Feb 28, 2010**	**100%**
Task 3.0	**Design and modeling of binary and ternary palladium alloys for use as high temperature, high pressure gas separation membranes under coal gasifier conditions.** ▪ Baseline testing of Pd-Au membranes in coal gas ▪ Combinatorial fabrication of ternary alloys to identify those resistant to coal gas ▪ Model hydrogen permeation of candidate Pd alloys	**Dec 1, 2009 to Sept 30, 2010**	**In progress**

Testing Ternary Alloys in Coal Gas

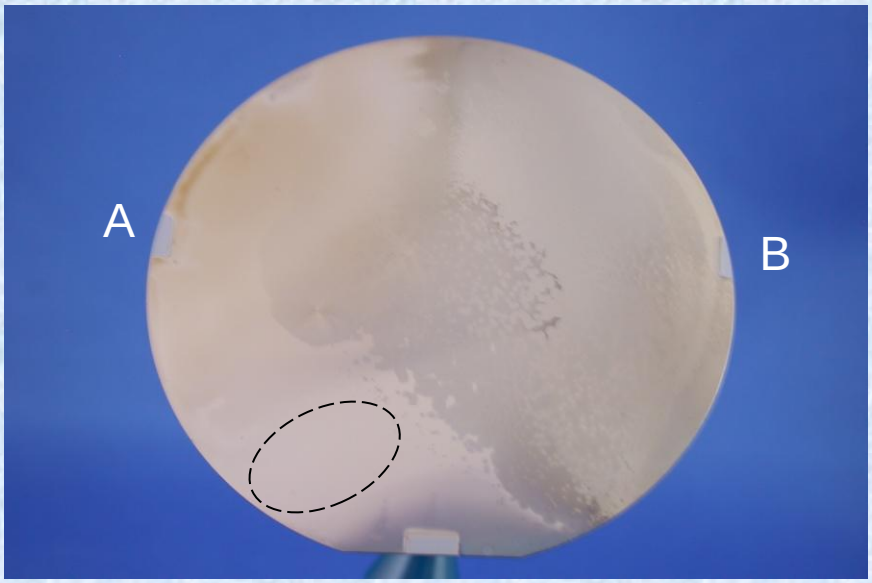


- A setup was built to expose compositional spreads to typical coal gas conditions
- 350°C for 24 hr, 1 atm
- 17.6* H, 17.9* CO_2, 2.6* H_2O, 2.6* CO, 59.3* N, 170 ppm (bottle gas w/ injected steam)
- Visually examine if any spots across composition spread film still appear metallic and shiny.

*Volume Percent

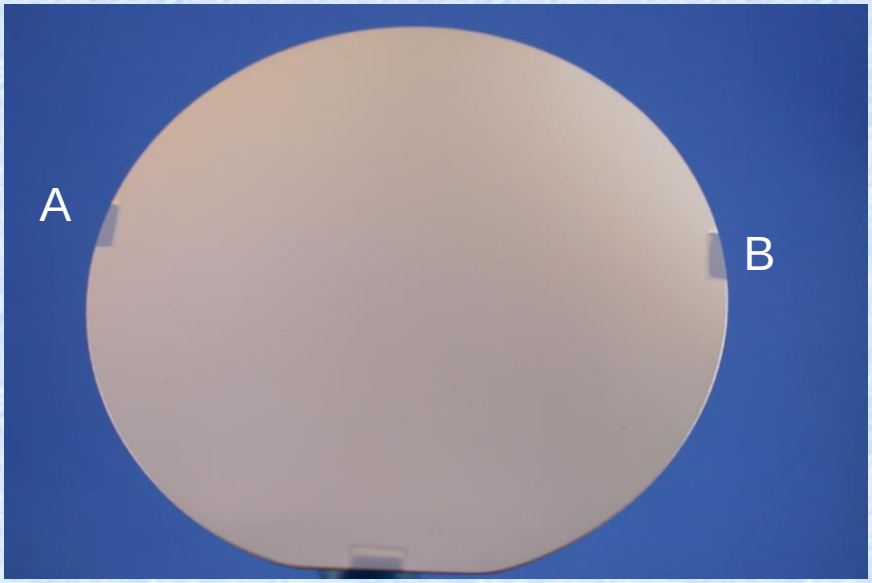
Visual Screening Example 1

Spread Pd-A-B Coal Gas Exposure



Pd

Spread Pd-A-B No Exposure

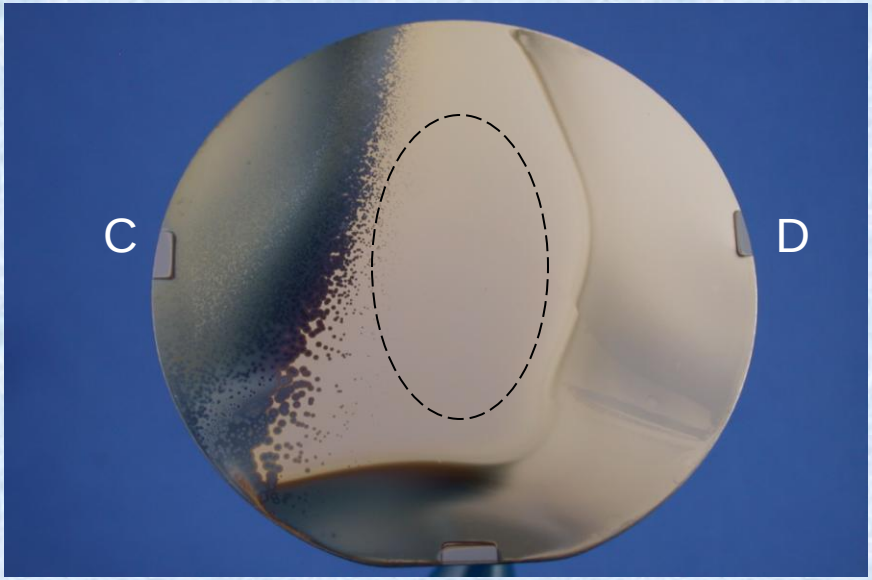


Pd

Small range of unaffected surface
Demonstrated hydrogen permeability

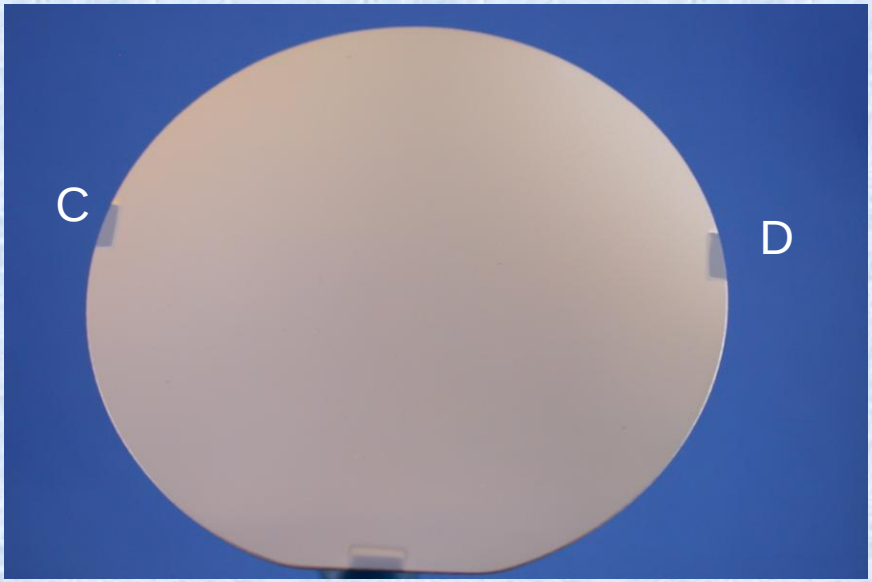
Visual Screening Example 2

Spread Pd-C-D Coal Gas Exposure



Pd

Spread Pd-C-D No Exposure

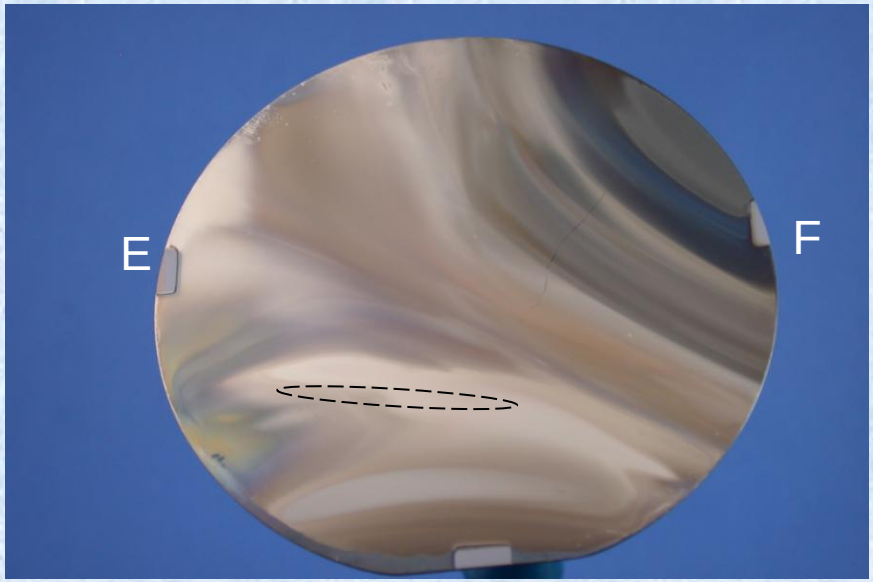


Pd

Balanced range of C and D
Low to high level of Pd

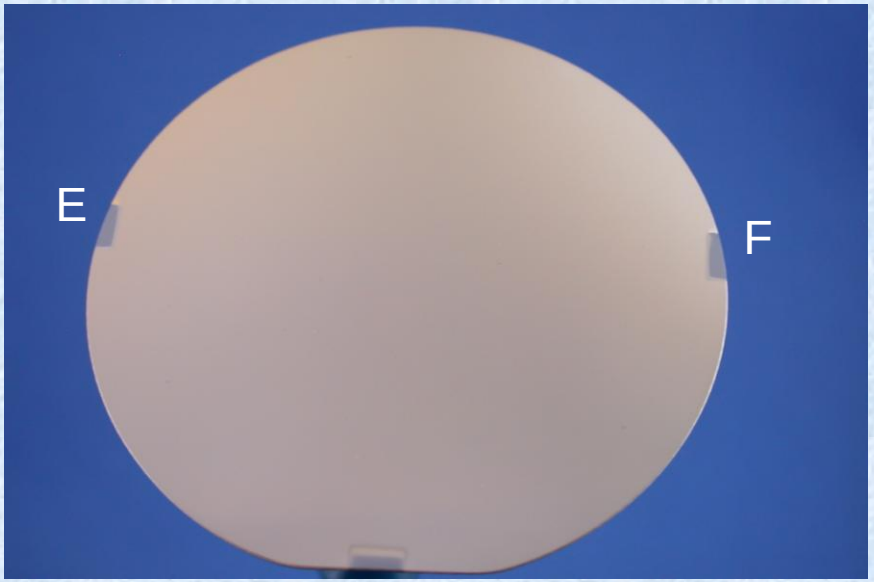
Visual Screening Example 3

Spread Pd-E-F **Coal Gas Exposure**



Pd

Spread Pd-E-F **No Exposure**

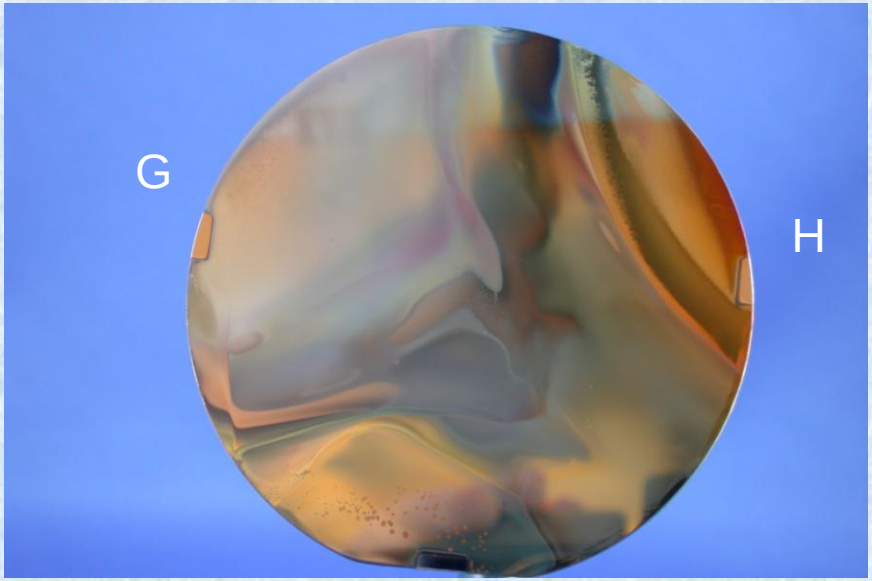


Pd

Narrow compositional range
High Pd level

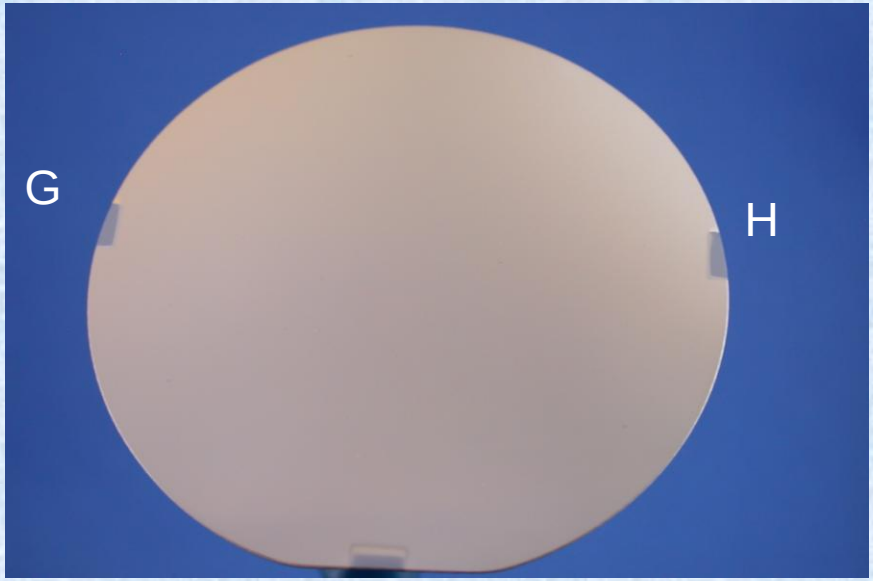
Visual Screening Example 4

Spread Pd-G-H Coal Gas Exposure



Pd

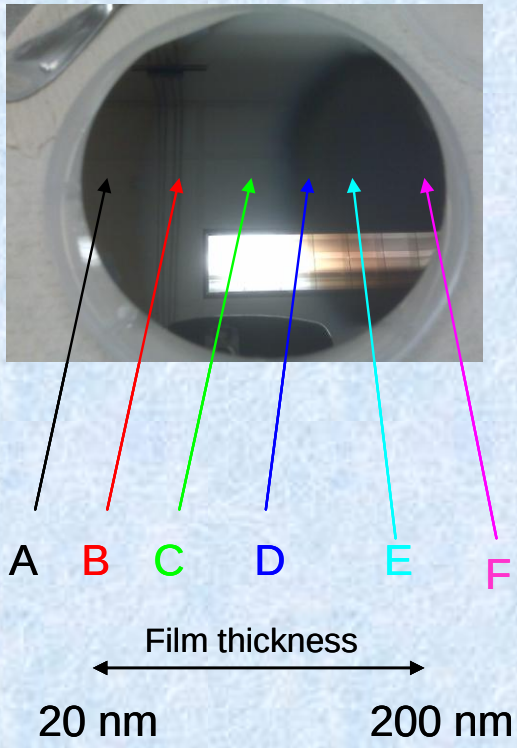
Spread Pd-G-H No Exposure

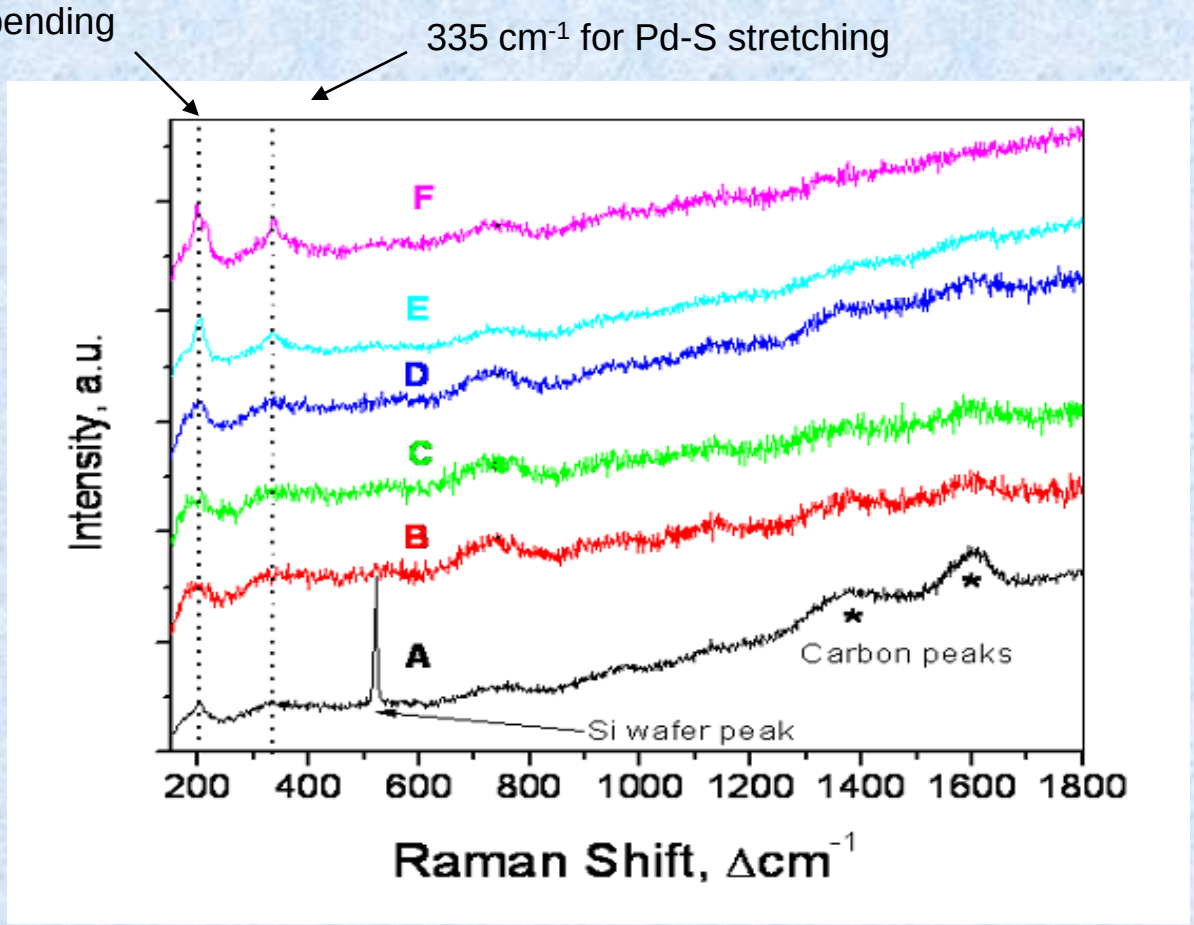


Pd

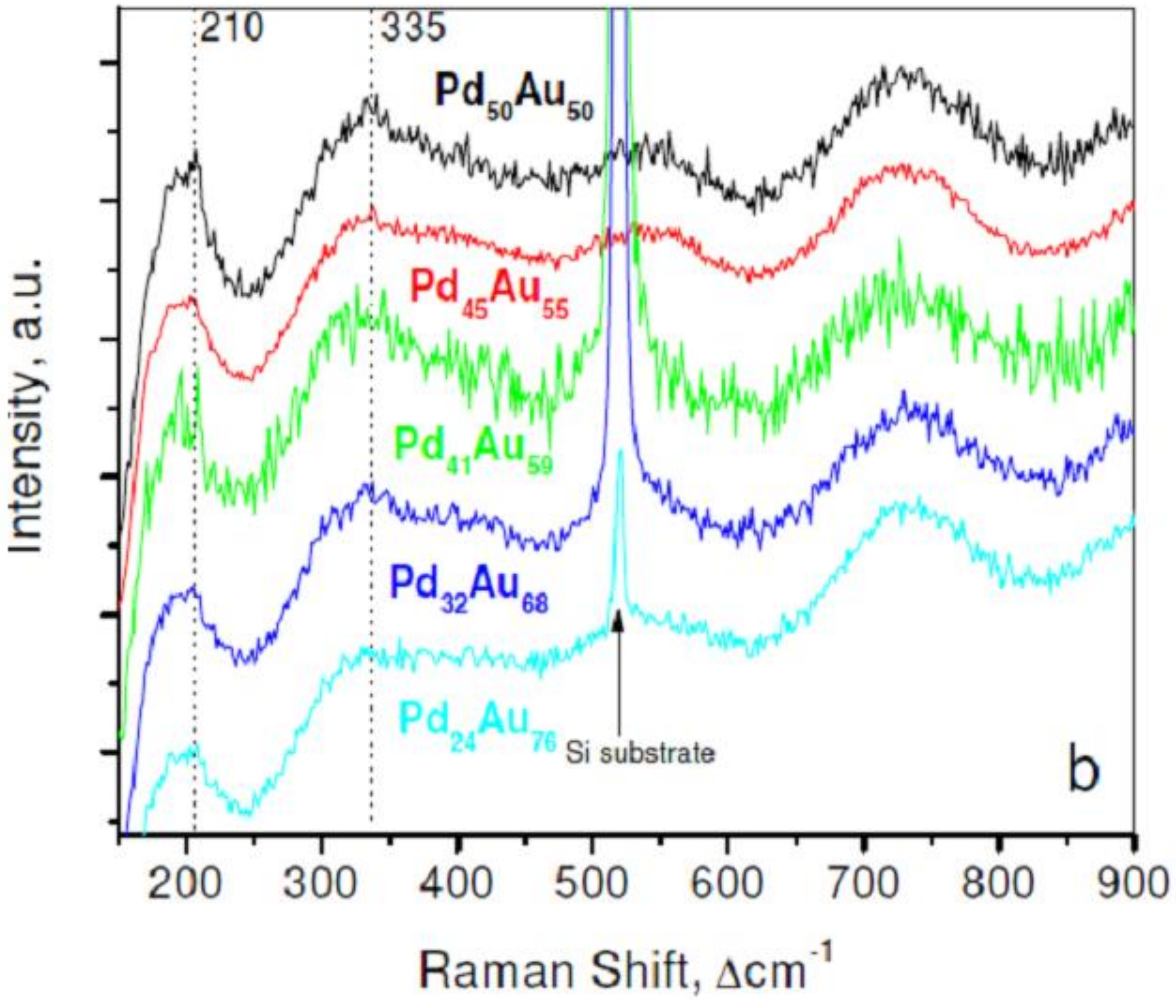
Entire surface affected by coal gas
No shiny area visible

Raman Signal – A Function of Thickness

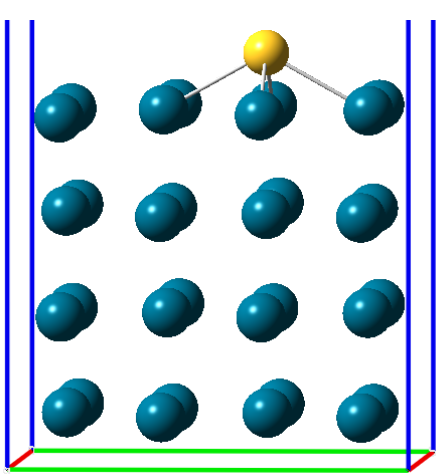
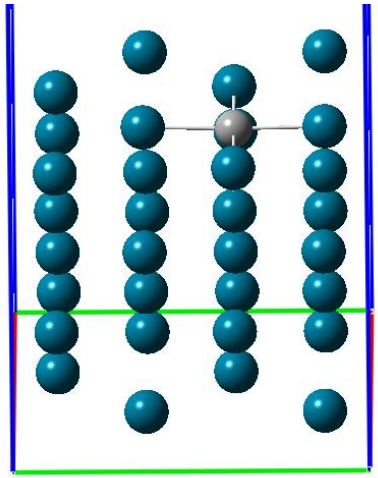
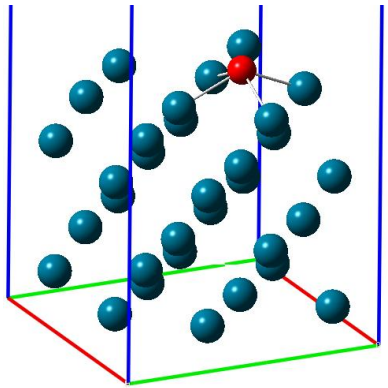
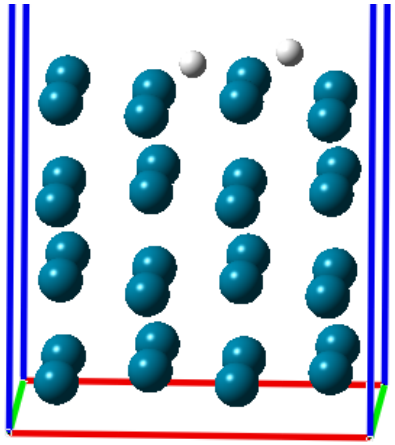




…and a Function of Composition



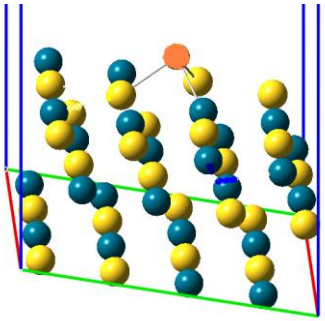
Modeling of Pd Binding Energies

S-Pd on Pd(100)	C-Pd on Pd(100)	O-Pd on Pd(100)	H-Pd on Pd(100)
			
BE -130 kcal/mole	BE -184 kcal/mole	BE -105 kcal/mole	BE -19 kcal/mole

The projector-augmented wave (PAW) method using the Perdew-Wang (PW91) GGA functional by the VASP code was performed for the structure optimization, frequency, and PES calculations. The nudged elastic band (NEB) method was applied to the located transition states.

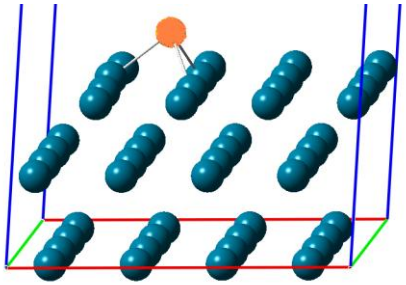
Modeling of Pd Alloy Binding Energies

S on $Pd_{50}Au_{50}(111)$



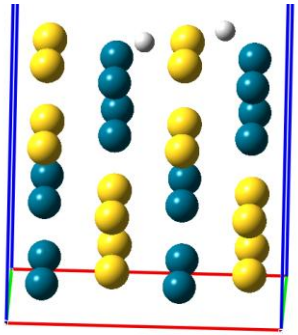
BE -117 kcal/mole

S on Pd(111)



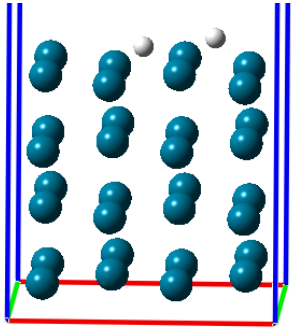
BE -133 kcal/mole

H on $Pd_{50}Au_{50}(100)$



BE -16 kcal/mole

H on Pd(100)



BE -19 kcal/mole

Second Year Plans

Task 3.0 Design and modeling of binary and ternary alloys

- Continue using combinatorial spreads to identify alloys resistant to coal gas
- Continue modeling alloys that optimize the membrane's corrosion resistance and hydrogen flux

Task 4.0 Construct and test 15 cm^2 active surface area prototypes

- Optimize process for porous YSZ-coated stainless substrates for Pd alloy coatings.
- Fabricate best candidate palladium alloys into membrane prototypes with 15-cm^2 active surface area over optimized ceramic-coated substrate tubes.
- Test hydrogen separation performance and longevity of best alloys in coal gas

Task 5.0 Scale up active surface area from 15 cm^2 to 75 cm^2

- Develop or modify membrane fabrication to increase surface area by a factor of five
- Build test stand and membrane module for use in coal gasification conditions.
- Test hydrogen separation performance and longevity of best alloy in a 75-cm^2 membrane module under coal gas conditions in 100-500 hours campaigns.