Pall Corporation

Designing and Validating Ternary Pd Alloys for Optimum Sulfur/Carbon Resistance in Hydrogen Separation and Carbon Capture Membrane Systems Using High-Throughput Combinatorial Methods

November 12, 2009

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Rick kleiner

This presentation does not contain any proprietary or confidential information

Participating Organizations

- Pall Corporation
  - ✓ Pall Cortland Research and Development (PRDC)
- Cornell University
  - ✓ Cornell Center for Materials Research (CCMR)
- Georgia Institute of Technology
  - ✓ Dept. of Materials Science and Engineering
- Oak Ridge National Laboratory
  - ✓ High Temperature Materials Lab (HTML)
- Southern Company Services, Inc.
  - ✓ National Carbon Capture Center (NCCC)

Project Objectives

- **Develop an economic, high temperature and pressure, hydrogen separation membrane system for CO_2 capture** while resisting 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 under 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 by comparing controlled diffusion studies with in-service membranes.

Background

- Current membrane research uses individual specimen prep methods and slow evaluation, common in the pharmaceutical industry twenty years ago.

- Pharma now uses a combinatorial methods to study millions of chemical reactions in parallel; the results have revolutionized that industry.

- Pall sees an opportunity to do rapid, combinatorial development of palladium alloys. Our proprietary thin film process accommodates rapid compositional change.

Scientific Challenges Being Addressed

- An economic hydrogen membrane must provide high flux, good separation, resistance to carbon/sulfur poisoning, and durability.
- The substrate is critical to membrane development.

  Pall has a unique porous, metallic, tubular design with a ceramic coating as a diffusion barrier. The surface is optimized with an unmatched balance of surface topography, porosity, and chemistry.
- Palladium membrane research has been slow and redundant.

  Pd-Ag, Pd-Cu, and Pd-Au alloys appear over and over again in the literature with little improvement in performance. Some work has been done in ternary and quaternary alloys.
- A systematic effort to examine a full range of ternary alloys has not been attempted.

Scope of Project

- Combinatorial screening of a large number of ternary Pd-alloys.
- Test and rank ternary Pd alloys by hydrogen flux and selectivity while optimizing tolerance to sulfur and carbon.
- Unique S/C characterization before and after contaminant exposures
- Synthesis of thin, defect-free, Pd-alloy membranes of selected compositions on porous tubular substrates
- Testing in syngas environment will be done by Pall.
- Structural evaluations before and after contaminant exposures
- Multi-membrane module will be pilot tested in an existing coal gasification facility.
- Final objective is a pilot scale H_2/CO_2 separation membrane system with a product plan for commercialization of the technology.

Relevance to the Objectives

- Pall is proposing their proprietary process to create ultrathin, economical, palladium alloy membranes in virtually any alloy system.
- Pall has the advantage of quickly advancing the state-of-the-art by applying combinatorial methods to continuous alloy spreads.
- Novel characterization methods can rapidly scan through the alloys after syngas exposure to identify the most resistant compositions.
- Pall has experienced R&D and mfg. teams ready to scale up existing membrane capabilities and test a range of advanced alloys in a commercial coal gasification facility.

Technical Approach

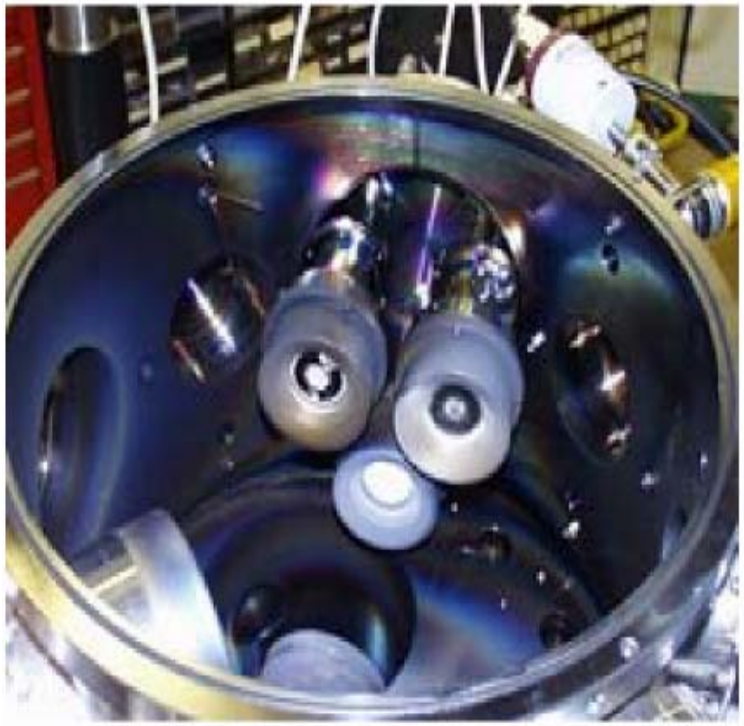
- Literature search of all pertinent hydrogen separation membrane alloys and processes
- Baseline testing of traditional Pd-Au alloy membranes in syngas mixtures
- Combinatorial alloy spreads on thin film support disks to identify potential alloys Measure and model permeabilities and diffusion rates of best candidate alloys
- Characterize sulfur and carbon resistance of best candidate alloys
- Fabricate best alloys into 15 cm^2 tubular membranes and test.
- Fabricate best alloys into 75 cm^2 tubular membranes and test.
- Fabricate best alloy into module that uses 75 cm^2 tubular membranes and test in commercial coal gas in 500 hr campaigns.
- Complete economic analysis of scale up and system integration.

Combinatorial Co-Sputtering

- Two or three spatially-separated elements in a vacuum chamber create thin film palladium alloy spreads.
- The ratio of each element varies with position on the substrate, creating a vast number of compositions on a single supporting disk.
- Three sputter guns are positioned on an equilateral triangle, each loaded with a different element target. The chamber holds a 3-in substrate 1.5-in from the guns, centered on the gun triangle. The concentration is greatest at points closest to the gun and lowest at points farther away.

Technology Description

Combinatorial Co-Sputtering



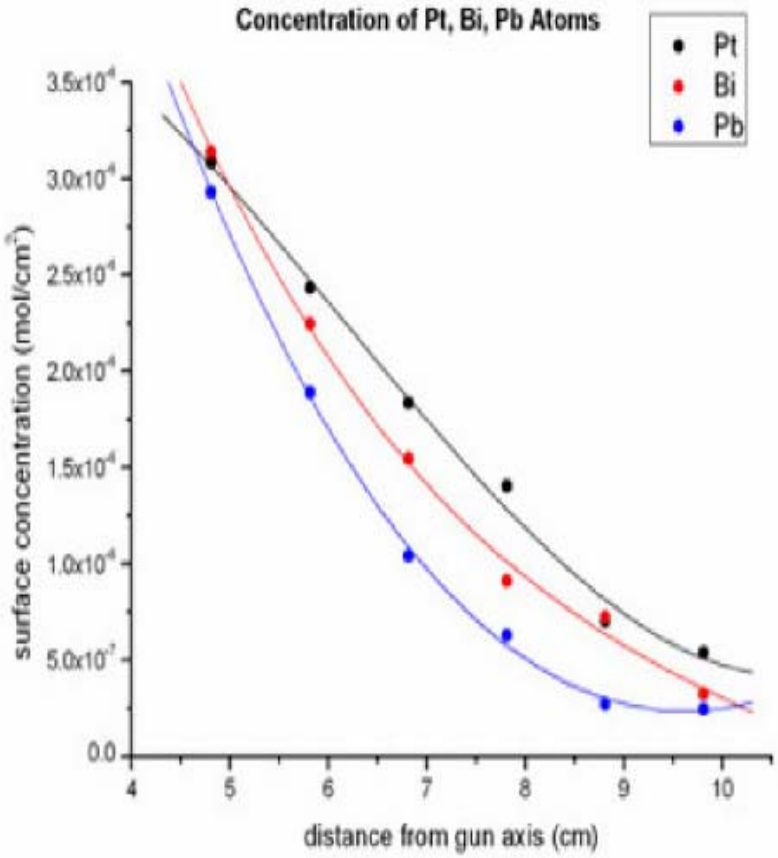
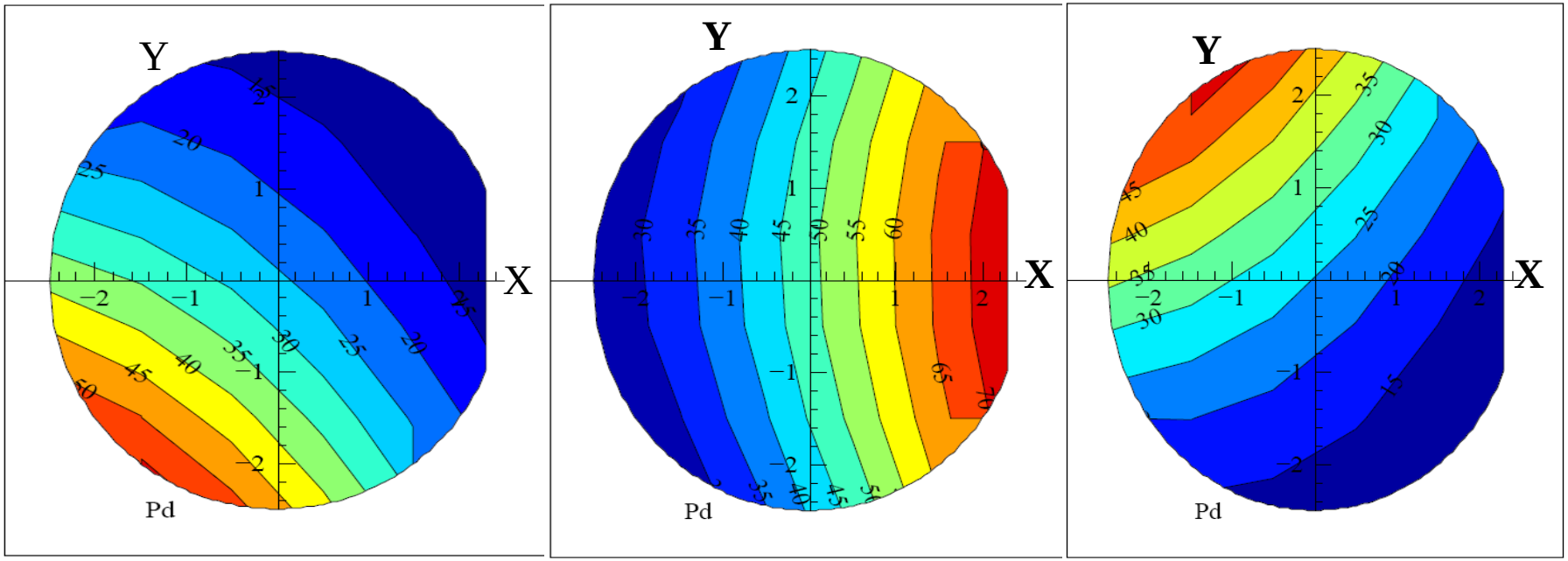


Figure 1. Image of co-sputtering chamber and graph of atom concentration as a function of distance from the gun axis for Pt, Bi, and Pb targets. Courtesy: R. B. van Dover

Technology Description

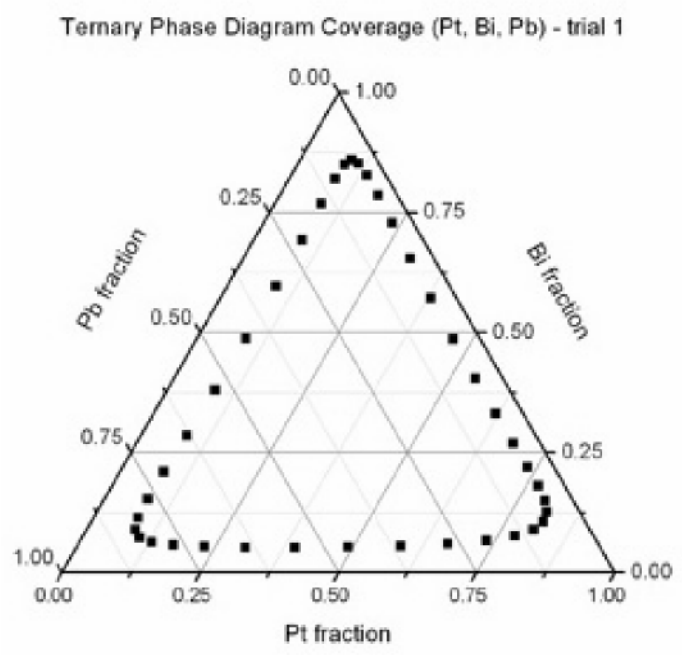
Co-Sputtering Compositional Spread

Pd (%) X (%) Y (%)



Combinatorial Co-Sputtering

All the compositions inside the points shown on the ternary phase diagram can be synthesized on a single Pt-Bi-Pb thin film composition spread.



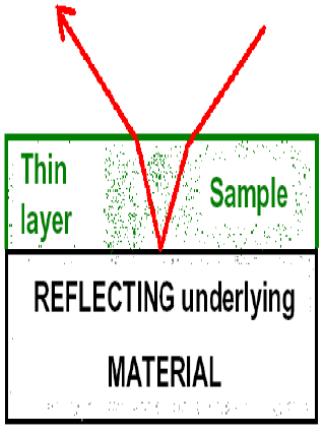
Background: Sulfur Resistance

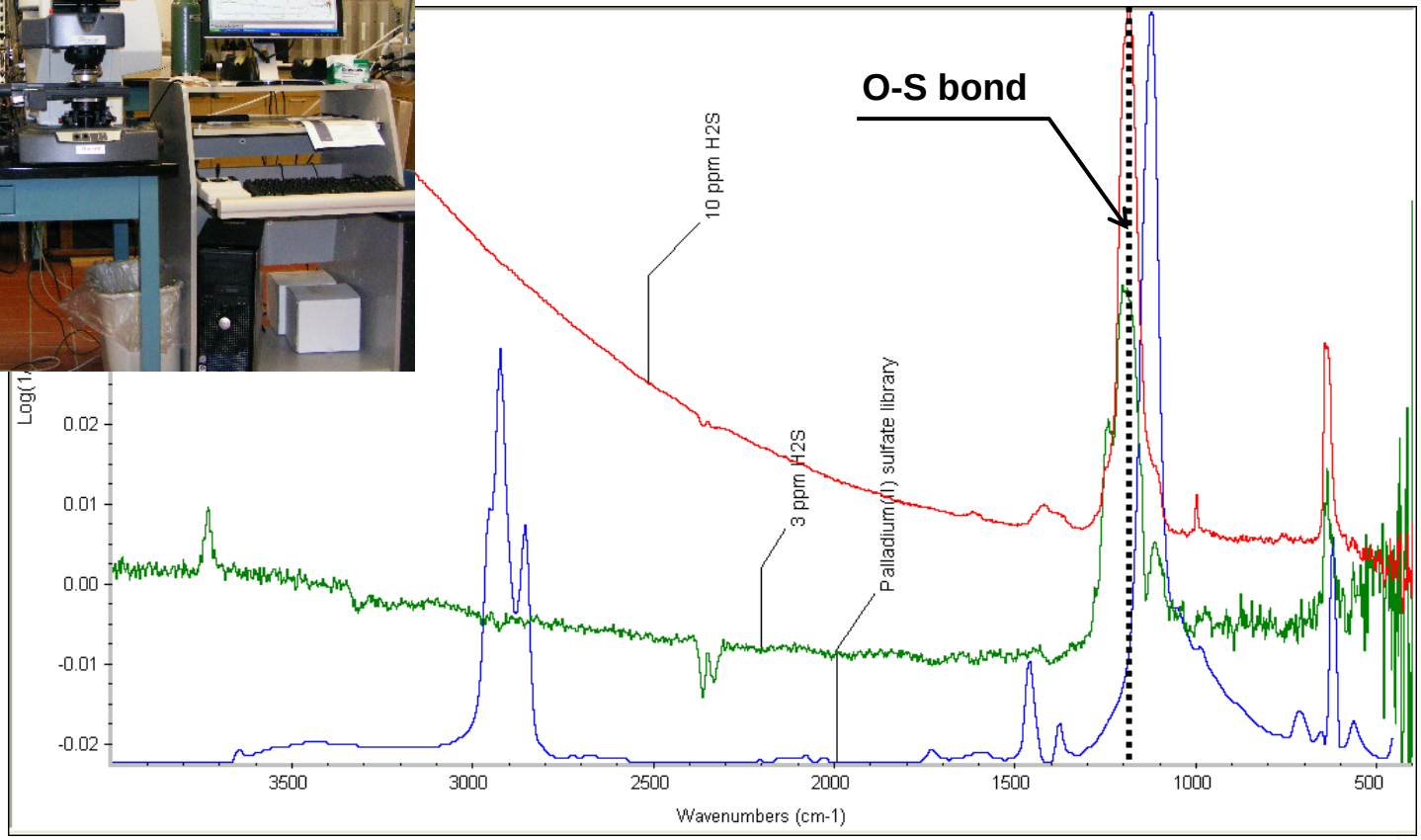
- Pure Metals: Palladium
  - ✓ Sulfur severely inhibits hydrogen permeation.

- Binary Alloys: Pd-Cu, Pd-Au, Pd-Pt
  - ✓ Sulfur tolerance of Pd-Cu & Pd-Au not yet been demonstrated.
  - ✓ Pd-Pt has shows significant promise for sulfur tolerance.

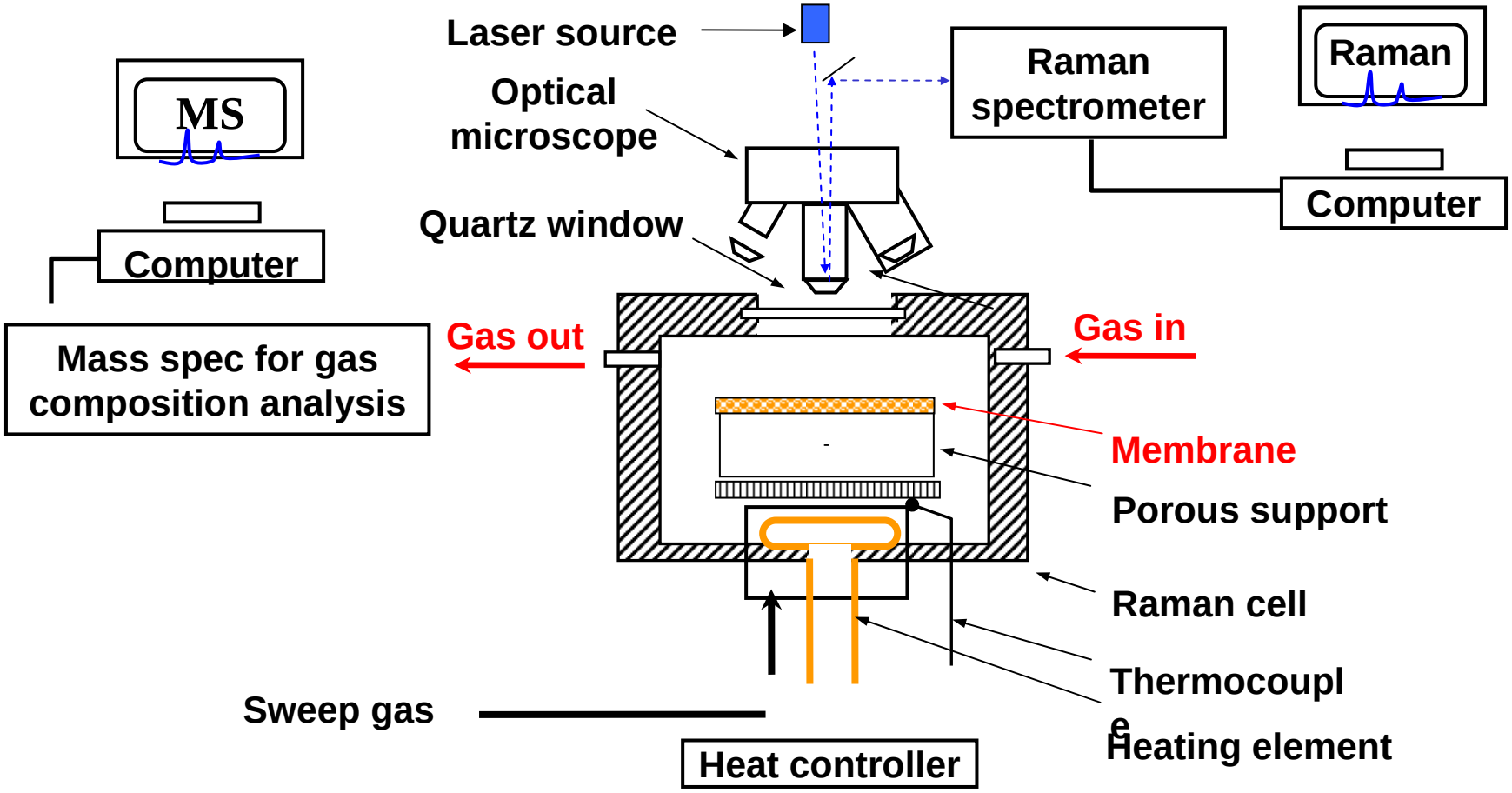
- Ternary Alloys: Pd-Cu-TM and Pd-Au-X
  - ✓ Under development for better sulfur resistance and H_2 flux

FT-IR for Sulfur Mapping of Combinatorial Spreads



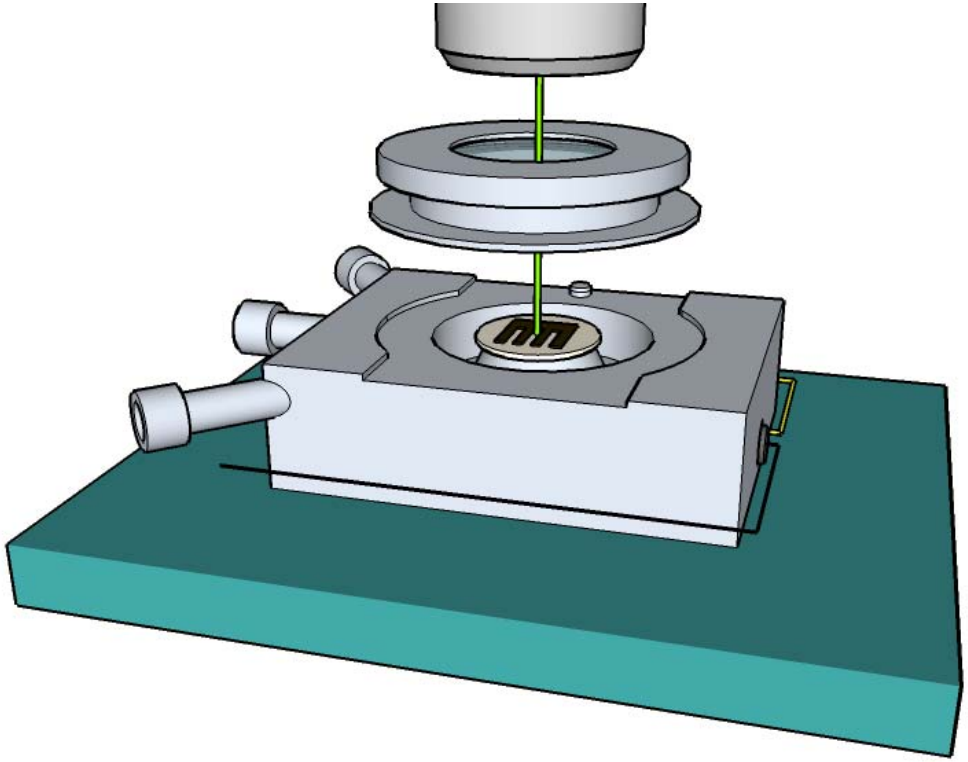


In-situ Raman Spectroscopy



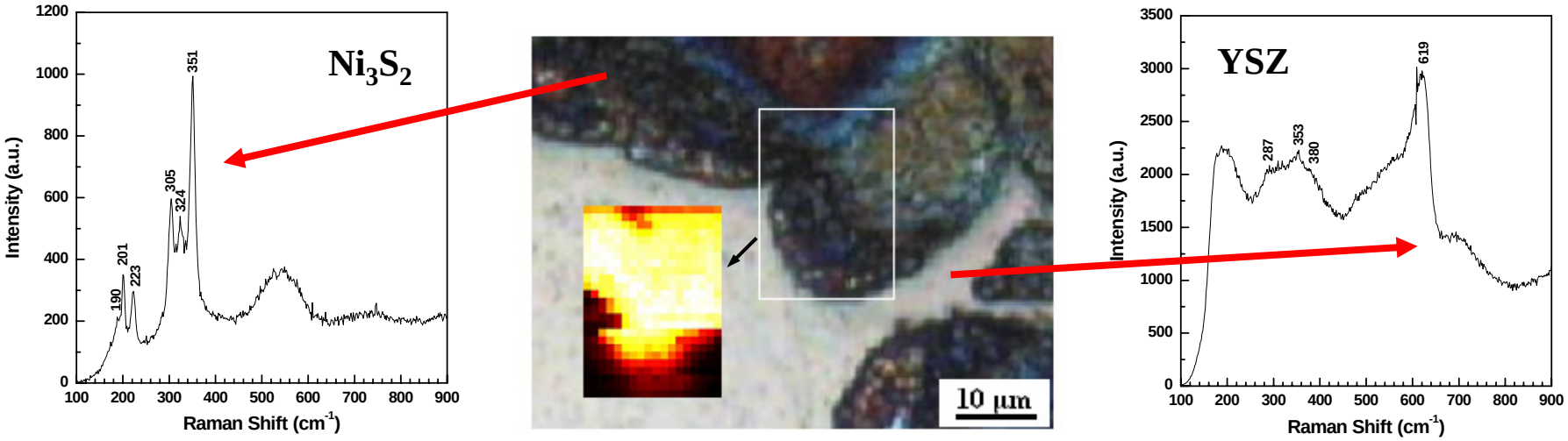
Schematic of *in-situ* Raman coupled with mass spectrometry (MS) for gas composition under service conditions for hydrogen separation. Courtesy: M. Liu

In-situ Raman Resolution



X-Y-Z motorized stage moves in 0.02mm increments
Spectra can be collected from 1 mm diameter spot
Courtesy: M. Liu

Sulfur Mapping with In-situ Raman

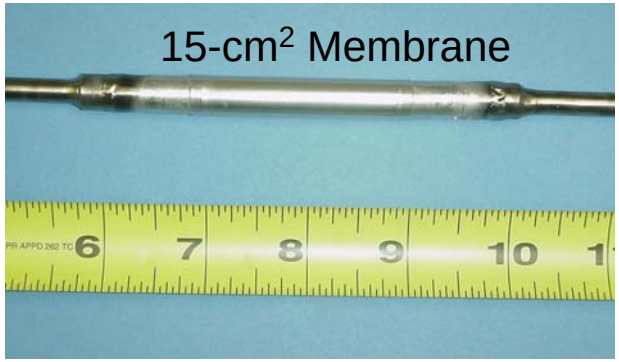


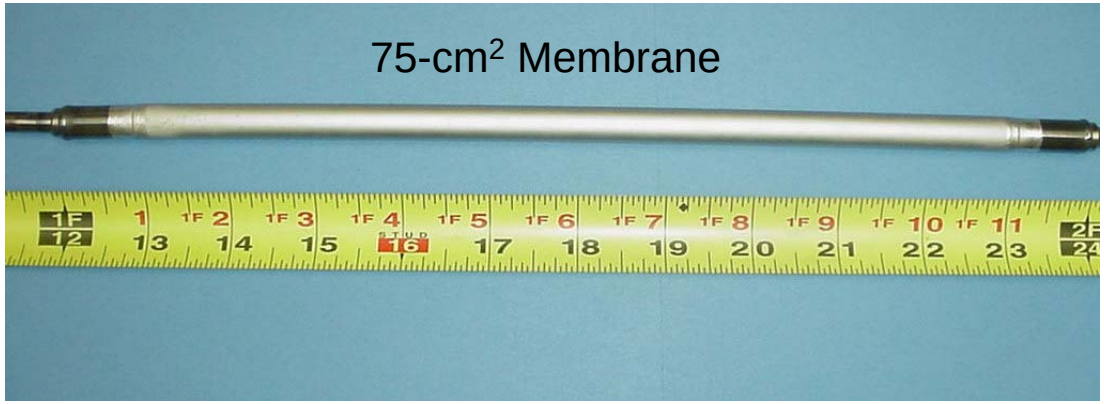
Raman map of Ni_3S_2 on Ni/YSZ composite after exposing to fuels containing 50 ppm H_2S for 18 h followed by heat treatment in 4% H_2 (balance Ar) for 2 h at 600ºC. Note: sulfur species confined to nickel region

Z. Cheng et al., ***J. Phy. Chem. C***, **111**, 17997, 2007

Technology Description

- Pall's Pd alloy membrane system will include:
- Porous 310 stainless steel support tube
- Nanoporous yttria-stabilized zirconia (YSZ) coated substrate
- All welded design with no polymer seals for higher temperatures
- Uniform thermal expansion with the housing and module components
- Directly weldable to a tube sheet without need for intricate sealing





Technical Approach
Year 1

- A working database of binary and ternary palladium alloy characteristics will be created from an extensive literature search and from a series of compositional spreads
- Hi temp, mixed gas testing of the thin films on support disks.
- Alloys that show the greatest potential for both hydrogen separation and corrosion resistance will be the first cut for membranes.
- Membrane performance will be measured by separation factor and permeability, then compared with the baseline Pd-Au alloy, as well as other data in the literature.

Technical Approach
Year 2

- Forming thin film membranes on the outside diameter of inorganic porous tubes with 15-cm^2 of active surface area.
- As with the combinatorial disks, the 15-cm^2 active area tubes will be exposed to conditions representative of a coal gasifier environment: high temperature and high pressure in the presence of contaminating species.
- Emphasis on identification and characterization of membrane defects, surface analysis of the regions affected by the contaminants, and assessment of the surface quality of the ceramic substrate.

Technical Approach
Year 3

- Using the best candidate alloys, the 15-cm^2 membranes will be scaled up by a factor of five to 75-cm^2
- After a series of performance tests and membrane characterization, A pilot module of 75-cm^2 tubes, made with the best performing alloy, will be assembled.
- The pilot module will be subjected to 500 hr service tests at a commercial coal gasification facility.

Technical Targets

- Levels of H_2S and CO will be regulated in the coal gas slip stream to monitor the effect of each contaminant on the hydrogen separation performance of the membrane modules.
- A successful membrane would be tolerant of up to 20 ppm H_2S.
- Hydrogen flux of 200 $ft^3/hr/ft^2$ at 400^oC and a trans-membrane pressure of 400 psi.
- The membrane cost must be in the range of \$100/ft^2.
- Permeate hydrogen purity should be at a level of 99.5%.
- The membrane must be resistant to coking with relatively low steam-to-carbon ratio.
- The system should be stable for a minimum of 3 years in service.

Participant's Roles

- Pall Corporation as the applicant is the prime contractor.
- Southern Company, Cornell University, Georgia Tech and Oak Ridge National Laboratory are subcontractors to Pall Corporation.
- Our team philosophy is to continue the working relationship that has been instituted among all of the team members and utilize the contract award to further enhance and expand our relationship to meet the contract goals and to commercialize the product.
- All of the team members have a mutual interest in not only meeting the goals but also to realize a new product that will have major impact in the emerging hydrogen market.

Project Structure

Pall Corporation
Overall program responsibility & management
Fabricate membranes & substrates
Scale-up technology
Test prototype membranes and modules

Georgia Institute of Technology
Surface characterization of alloy systems after high temperature exposure to coal gas

Cornell University
Combinatorial approach for screening ternary phase space to optimize Pd-alloy system for maximum sulfur and carbon tolerance

Oak Ridge National Laboratory
High temperature in situ mechanical testing
XRD of alloy phase transitions

Southern Company
Long term membrane module testing at National Carbon Capture Facility in high temperature/high pressure slip stream from coal gasifier

Pall's Role

- Pall Corporation, as the prime on the contract, will have the overall responsibility for the performance on the contract.
- With input from all of the subcontractors, Pall will make the final decisions with regard to the task definition, level of effort and timing and will convey this information in writing to the subcontractors.
- Pall's technical roles will include providing dense palladium-base alloy membranes and interfacial coatings on Pall AccuSep® substrates.
- Pall will work with Georgia Tech to optimize the support layer and palladium-alloy membrane, modifying the layer as needed to produce the best overall membrane cost and performance.
- Pall will also fabricate single-tube "mini-modules" for lab testing and a multi-tube module for pilot-scale testing at Southern Company.
- Pall will evaluate key technical issues related to scale-up of the project from a single membrane process with an active surface area of 15 cm^2 to a multiple unit module consisting of 75 cm^2 membranes.

Selected Pall Facilities

- Pall Research and Development Cortland (PRDC) Cortland, NY
- Pall Inorganic Membranes and Nanostructures – Cortland, NY
- Pall Scientific Laboratory Services (SLS) - Cortland Chemistry Lab
- Pall Advanced Separation Systems (PASS) – Cortland, NY
- Pall Industrial Membranes (PIM) - Oak Ridge, TN
- Pall Technical Center (PTC) – Port Washington, NY

Cornell's Roles and Resources

- Dr. Bruce Van Dover's experience with combinatorial materials design at Cornell makes him a logical colleague in the first two years.
- Cornell Center for Materials Research (CCMR) advances, explores and exploits the science and engineering of advanced materials. The unifying theme of their research is the study of materials purposefully structured at the nanoscale.
- One hundred faculty members from twelve departments are active in CCMR.
- Eight CCMR facilities comprise an integrated system for materials synthesis and preparation, analysis, testing and characterization, together with advanced research computing capability.
- Cornell High Energy Synchrotron Source (CHESS) will be used for compositional mapping of the palladium alloy spreads.

Georgia Tech's Roles & Resources

- Dr. Meilin Liu expertise at Georgia Tech in surface analysis will be used in the second and third years to characterize sulfur and carbon interactions on the Pd membrane surfaces.
- Scanning Raman spectroscopy to map the formation of sulfur and carbon species on specific Pd compositions with a spatial resolution of <1-micron.
- Once the regions of S/C are localized, their compositions will be measured with microprobe and Rutherford back-scattering (RBS).
- GT will observe the surface texture and grain size using scanning electron microscopy (SEM)
- X-ray diffraction in a general area diffraction detection system (GADDS) to reveal the crystal structure.
- Georgia Tech will also study hydrogen diffusion and model hydrogen fluxes of Pd alloys as functions of alloy composition, phase, temperature and pressure.

ORNL-HTML's Roles and Resources

- Oak Ridge National Laboratory (ORNL) High Temperature Materials Laboratory (HTML) will analyze the membrane stability and *in situ* structural changes that may affect durability.

- ORNL has the essential facilities such as: high temp tensile testing, thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), and specialized facilities for in-situ X-ray and neutron diffraction investigations.

- In particular, facilities exist to perform X-ray diffraction studies at high temperatures, in a variety of gas environments, and to obtain spatially-resolved spectra on a sub-micron scale.

Southern Company's Roles and Resources

- Southern Company's new National Carbon Capture Center (NCCC) in Wilsonville, AL is one of the nation's leading energy technology facilities for coal gasification studies.

- NCCC is a proving ground for many new advanced power systems. The facility is large enough to give industry real-life data, yet small enough to be cost-effective and adaptable to a variety of industry needs. A key feature is its ability to test new systems at an integrated, semi-commercial scale.

- Mostly in the third year, Southern Company will pilot test our H_2/CO_2 separation membrane module, provide conceptual commercial plant designs and cost estimates.

Project Management and Planning

- Task 1.1 Develop and maintain a comprehensive Project Management Plan that clearly identifies the organizational structure, roles and responsibilities of the project team members, technical scope, budget, schedule baselines, key milestones and decision points, cost and schedule control, and project risk management.
- Task 1.2 Monitor progress on the Project Management Plan with respect to technical progress on each task, achievement of milestones and deliverables, Gantt chart schedule progress and financial comparisons to the budget.
- Task 1.3 Provide reports according to the “Federal Assistance Reporting Checklist”.

Task 2.0

Literature/patent search of previous work on metallic hydrogen separation membranes

- Task 2.1 Search: long term effects of syngas constituents on metallic membrane surfaces
- Task 2.2 Search: combinatorial materials development
- Task 2.3 Search: gas separation membrane substrate quality and its characterization
- Task 2.4 Search chemical modeling of hydrogen separation and diffusion through membranes

- **Milestone 1:** Summary report demonstrating thorough understanding of previous work on hydrogen separation with palladium membranes and their resistance to carbon and sulfur.

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

- Task 3.1 Baseline testing of conventional Pd-Au membranes at high temperature and high pressure to determine the effects of syngas atmosphere and trace levels of impurities.
- Task 3.2 Advanced palladium alloy development using combinatorial techniques to identify potential binary and ternary alloys resistant to coal-based gas environment.
  - ✓ Task 3.2.1 Fabrication of thin film palladium alloys having near-continuous gradient of composition from pure elements to binary and ternary blends.
  - ✓ Task 3.2.2 Exposing thin film palladium alloys to coal gas conditions with trace amounts of impurities, including sulfur, for 500-hr periods
  - ✓ Task 3.2.3 Characterization of thin film palladium alloy surfaces to identify the effects of exposure to coal gas conditions with trace amounts of impurities

Task 3.0 (Cont.)

- Task 3.3 Assess surface quality of porous yttria-stabilized zirconia as substrate for palladium gas separation membranes
- Task 3.4 Model hydrogen permeabilities and diffusion rates of candidate palladium alloys using a modified version of the Georgia Tech code including both surface chemistry and bulk properties
  - ✓ Task 3.4.1 Validate modeling results with tests of conventional Pd-Au membranes under various coal gas conditions (pressure, composition, and temperature).
  - ✓ Task 3.4.2 Modify modeling as necessary for use with best candidate palladium alloys to rank chemical stability under various high temperature, high pressure conditions.

- **Milestone 2:** Summary report on use of combinatorial methods to identify and characterize performance of palladium alloys in coal gas conditions and demonstrate high throughput screening of ternary Pd alloys.

Task 4.0

Construct and test 15 cm^2 active surface area prototypes of novel palladium alloy membranes for use as high temperature, high pressure gas separation membranes under coal gasifier conditions

- Task 4.1 Optimize process for making zirconia substrates suitable for each candidate Pd alloy
- Task 4.2 Fabricate best candidate palladium alloys into thin film membrane prototypes with 15-cm^2 active surface area over optimized zirconia substrate.
- Task 4.3 Test hydrogen separation performance of each best candidate alloy under coal gas conditions with trace amounts of impurities, including sulfur, for extended periods.

- **Milestone 3:** Summary report on fabrication and laboratory testing of small-scale ternary Pd alloy membranes on Pall tubular substrates

Task 5.0

Scale up active surface area of novel palladium alloy prototypes from 15-cm^2 to 75-cm^2 for use as high temperature, high pressure gas separation membranes under coal gasifier conditions.

- Task 5.1 Develop or modify membrane fabrication to increase surface area by a factor of five per prototype sample.
- Task 5.2 Build test stand for scaled-up prototypes in simulated coal gasification conditions.
- Task 5.3 Test hydrogen separation performance of each alloy in a 75-cm^2 membrane under coal gas conditions with trace amounts of impurities, including sulfur, in 100-500 hour campaigns.

- **Milestone 4:** Summary report on fabrication and laboratory testing of scaled-up ternary Pd alloy membranes on Pall's tubular substrates

Task 6.0

Construct a working membrane module capable of extended service as a hydrogen separation system in high temperature and pressure, under coal gasifier conditions.

- Task 6.1 Design a module composed of best candidate palladium alloy with consideration of maximum pressures on feed and permeate sides, scale up, geometry, and manufacturability.
- Task 6.2 Fabricate membranes with 75-cm^2 surface area per unit and assemble into the module for testing in a commercial coal gasification system.
- Task 6.3 Model the module performance with input parameters, i.e. membrane element performance parameters (permeance & selectivity), tube-in-shell module geometry, feedstock composition and flow rates, operating temperatures and partial pressures.
- Task 6.4 Test hydrogen separation performance of the module in a 400°C, 100 psi slip stream at NCCC in Wilsonville, AL in 500 hour commercial coal gasification campaigns.

- **<u>Milestone 5</u>: Summary report on design, fabrication, and long term performance testing of Pd membrane module in a coal gasification facility.**

Task 7.0

Provide complete analysis of relevant data sufficient to permit economic evaluation of the process, its scale-up to a commercial system, and conceptual integration with appropriate power plant components.

- **Milestone 6:** Project report on advancement in the science and technology necessary to overcome the challenges of commercializing Pd alloy hydrogen separation in coal gasification plants.

Project Management Plan

- Executive summary
- Risk management
- Milestone log
- Funding and cost profile
- Project timeline
- Success criteria at decision points

Risk Management

- H_2 separation performance may not achieve target performance by membrane design alone.
  - ✓ Supplements such as additional gas reforming capabilities may be required either upstream or downstream of the membrane module.
- Scale-up of the Pd-alloy surface area from 15 cm^2 to 75 cm^2.
  - ✓ Pall's membrane fabrication process has been designed for 75 cm^2 on AccuSep® tubular substrates, the actual scale-up has not been attempted.
- Membrane durability during thermal cycling and its effect on stability of the Pd alloy/AccuSep elements.
  - ✓ Focus will be placed on optimum adhesion in Task 3. The stability of the ceramic coated AccuSep® support has been demonstrated but not the long term stability with a Pd-alloy membrane in place.
- Economic viability has not been established
  - ✓ An economic analysis will be conducted to determine the cost of hydrogen production and potential benefits including cost of carbon capture.
  - ✓ The extensive experience of the team members on their respective tasks and utilization of the Stage Gate Process will mitigate these risks.

Milestone Log

- **Milestone 1: Literature report.** Provide a summary report demonstrating thorough understanding of previous work on hydrogen separation with palladium membranes and their resistance to carbon and sulfur. December 31, 2009.
- **Milestone 2: Design and modeling report.** Provide a summary report on use of combinatorial methods to identify and characterize performance of palladium alloys in coal gas conditions and demonstrate high throughput screening of ternary Pd alloys. June 30, 2010.
- **Milestone 3: Small-scale membrane report.** Provide a summary report on fabrication and laboratory testing of small-scale ternary Pd alloy membranes on Pall tubular substrates. September 30, 2011.
- **Milestone 4: Large-scale membrane report.** Provide a summary report on fabrication and laboratory testing of scaled-up ternary Pd alloy membranes on Pall's tubular substrates. March 30, 2012.
- **Milestone 5: Module testing report.** Provide a summary report on design, fabrication, and long term performance testing of Pd membrane module in a coal gasification facility. September 30, 2012.
- **Milestone 6: Technology advancement report.** Provide a project report on advancement in the science and technology necessary to overcome the challenges of commercializing Pd alloy hydrogen separation in coal gasification plants. September 30, 2012.

Pall Corporation

Funding and Cost Profile

		Year 1 Budget	Year 2 Budget	Year 3 Budget	Total Budget
Pall	Non Federal	100	105	105	310
	Federal	155	231	396	782
	Total	255	336	501	1092
Cornell	Non Federal	0	0	0	0
	Federal	100	50	0	150
	Total	100	50	0	150
Georgia Tech	Non Federal	0	0	0	0
	Federal	100	75	0	175
	Total	100	75	0	175
ORNL	Non Federal	0	0	0	0
	Federal	0	50	50	100
	Total	0	50	50	100

Pall Corporation

Project Timeline

		2009		2010				2011				2012			
		Q 3	Q 4	Q 1	Q 2	Q 3	Q 4	Q 1	Q 2	Q 3	Q 4	Q 1	Q 2	Q 3	Q 4
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														

Success Criteria at Decision Points

- Task 1 Maintain on-time management of project plan and progress on each task with respect to achievement of milestones and deliverables, Gantt chart scheduling, and financial comparisons to the budget.
- Task 2 Thorough understanding of previous work on hydrogen separation with palladium membranes and their resistance to carbon and sulfur.
- Task 3 Successful use of combinatorial alloy design and performance characterization for high throughput screening of ternary palladium alloys.
- Task 4 Successful fabrication and lab testing of small-scale ternary Pd alloy membranes on Pall's tubular substrate
- Task 5 Successful fabrication and lab testing of scaled-up ternary Pd alloy membranes on Pall's tubular substrate
- Task 6 Successful design, fabrication, and long term performance testing of Pd membrane module in a coal gasification facility.
- Task 7 Successful advancement in the science and technology necessary to overcome the challenges of commercializing Pd alloy hydrogen separation in coal gasification plants.

Summary

- Objective is hydrogen and CO_2 separation in high temp coal gas
  - ✓ Combinatorial methods for rapid screening of ternary Pd alloy systems
  - ✓ Novel scanning spectroscopy for understanding sulfur/carbon effects
  - ✓ Proprietary Pall membrane fabrication
  - ✓ Long term durability testing of best candidate Pd membrane system

- Pall manages project, fabricates and scales up membranes
- Cornell provides thin film spreads of ternary Pd alloys
- Georgia Tech characterizes sulfur attack and models H diffusion
- ORNL measures high temp structural properties of membranes
- Southern Company tests membranes in coal gas slip stream

QUESTIONS?