Fifth Annual Conference on Carbon Capture & Sequestration

Steps Toward Deployment

Capture - Membranes

Novel Polymeric-Metallic Composite Membranes for CO_2 Separations at Elevated Temperatures

K.A. Berchtold, J.S. Young, K.W. Dudeck, J. Acquaviva, F. Onorato, S.D. Hopkins, A.R. Greenberg, S. Brahmandam , E.S. Peterson, J.R. Klaehn

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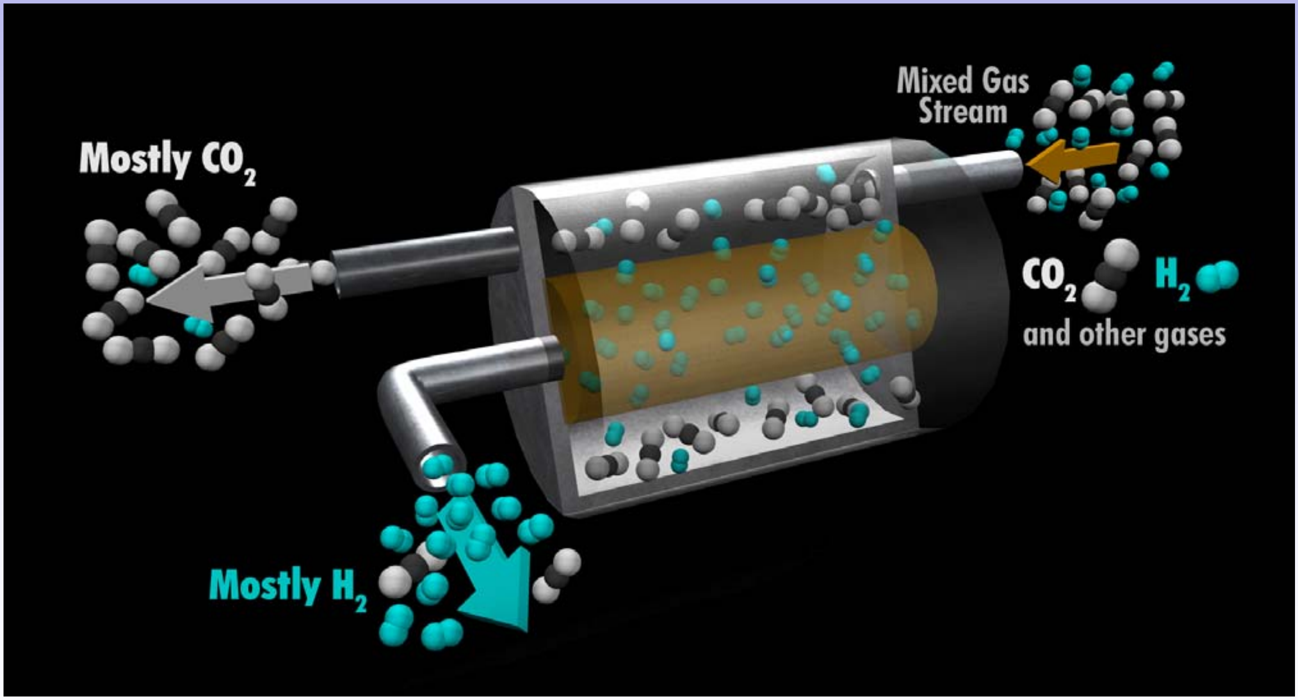
Project Team

- **Los Alamos National Laboratory**
  - Kathryn Berchtold, Jennifer Young, and Kevin Dudeck
- **Pall Corporation**
  - Jim Acquaviva, Scott Hopkins, Frank Onorato, Bill Palmer, and Sean Meenan
- **University of Colorado**
  - Alan Greenberg and Sudhir Brahmandam
- **Idaho National Laboratory**
  - Eric Peterson and John Klaehn
- **National Energy Technology Laboratory**
  - Jared Ciferno and John Marano

Project Manager: José D. Figueroa

Specific Objective

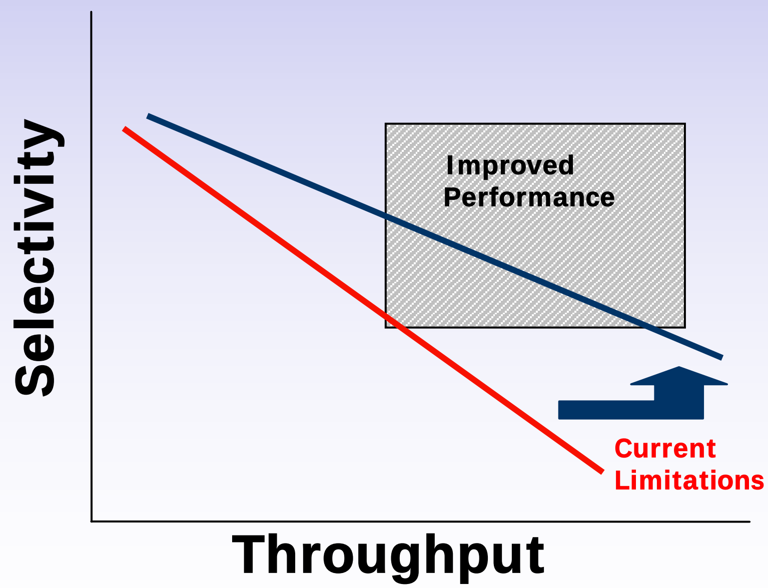
Produce a high temperature membrane and module for *pre-combustion capture* capable of operation at temperatures significantly higher than 150 °C and industrially relevant conditions.



- **Temperature Stability**
- **Chemical Stability**
- **Mechanical Stability**
- **Industrially Attractive Separation Characteristics**

High T_g Polymeric Membranes

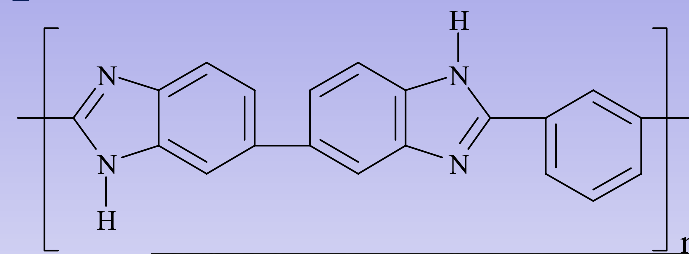
- **Commercially available polymer membranes are limited to 150 °C operating temperature**
  - Economic advantages of membrane separations are strongly tied to process/separation temperature
- **Tradeoff between selectivity and productivity has proven difficult to overcome**
  - Key Sequestration Program Goals
    - >90% CO_2 Capture
    - <10% increase in COE
- **Chemical & mechanical stability and durability are often elusive**



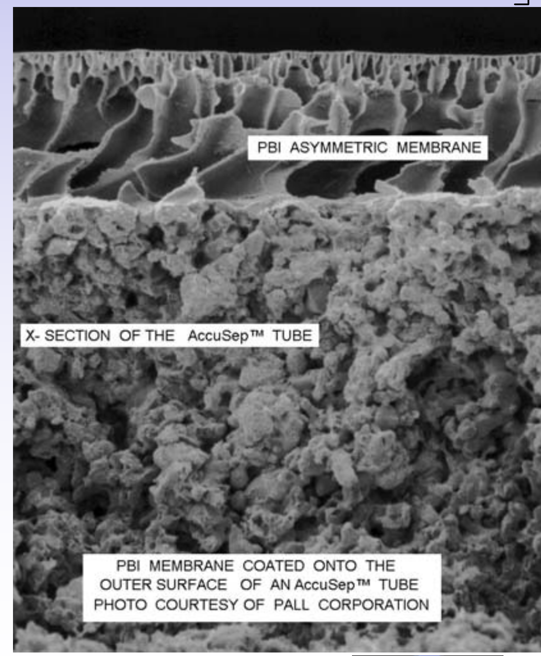
Project Overview

Efforts Focused on Pre-Combustion Capture

- Higher Driving Force (Pressure/Concentration)
- Focused on Development of High T_g Polybenzimidazole (PBI)-based Polymeric-Metallic Composite Membranes
  - Thermally stable ($T_g \sim 450$ °C): Facilitates process integration
  - Chemically resistant: Sulfur tolerant at operation temperatures
  - Processable



- Integrate Polymer with Specially Designed Porous Metal Substrates
  - Support and interfacial layer optimized for realization of defect free thin film deposition
- CO_2 Remains at Pressure
  - Compression Costs to Pipeline Pressures Minimized
- Systems Integration Efforts to Optimize % CO_2 Capture and Minimize Cost

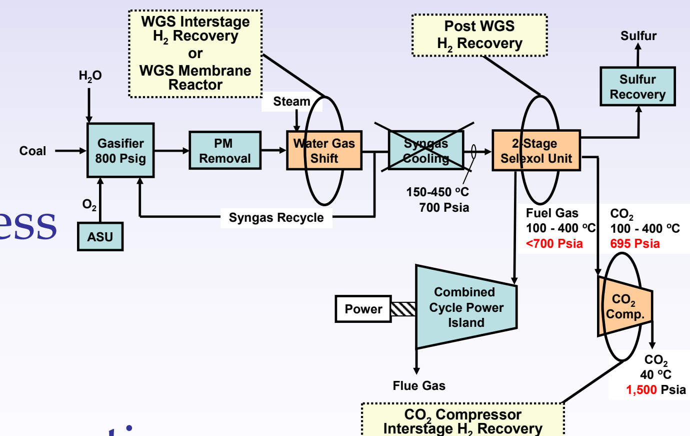


Development Pathways

I. ⇕ II. → **Technically and Economically Viable Carbon-Capture Technology** → **Technology Commercialization**

I. Extending the Current polybenzimidazole (PBI)-based polymeric-metallic composite membrane to its limits

- Membrane Productivity Optimization
- Module Design
- In-Lab Testing/Demonstration
- Out-of-Lab Testing/Demonstration
- Strategic Selection of Future Partnerships/ Collaborations to Facilitate Continued Progress
- Systems Integration / Economic Analysis
  - Optimize %CO_2 Capture and Minimize Cost
- Commercialization Plan Development and Execution



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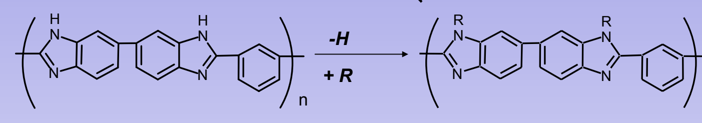
Development Pathways

I. ⇕ II. → **Technically and Economically Viable Carbon-Capture Technology** → **Technology Commercialization**

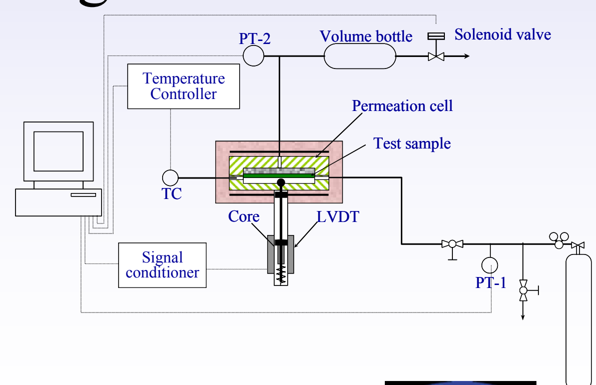
II. Rational Design, Synthesis, & Development of New (*and Improved*) Selective Barrier Materials



- Predominantly PBI-based Compounds
  - Enhanced Gas Separation Properties (H_2/CO_2 Selectivity, H_2 Flux)
  - Maintain or Improve Upon Chemical, Thermal, Mechanical Stability and Polymer Processability

I.b/II.b Develop an Improved Understanding of Long-Term Membrane Performance

- Comprehensive Data Establishing Relationship between Mechanical & Transport Behavior
- Data Provide Basis for Prediction & Optimization of Long-Term Performance



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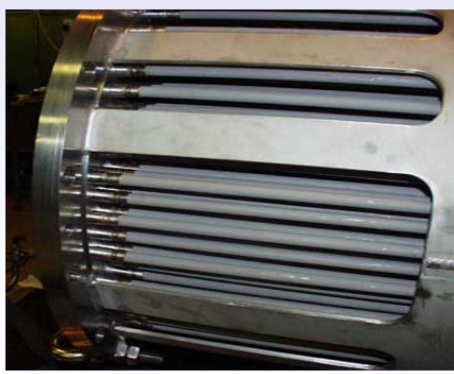
Scale-Up and Optimization

Scale-up and optimization are ongoing

Uncoated

~0.5 cm²

Coated



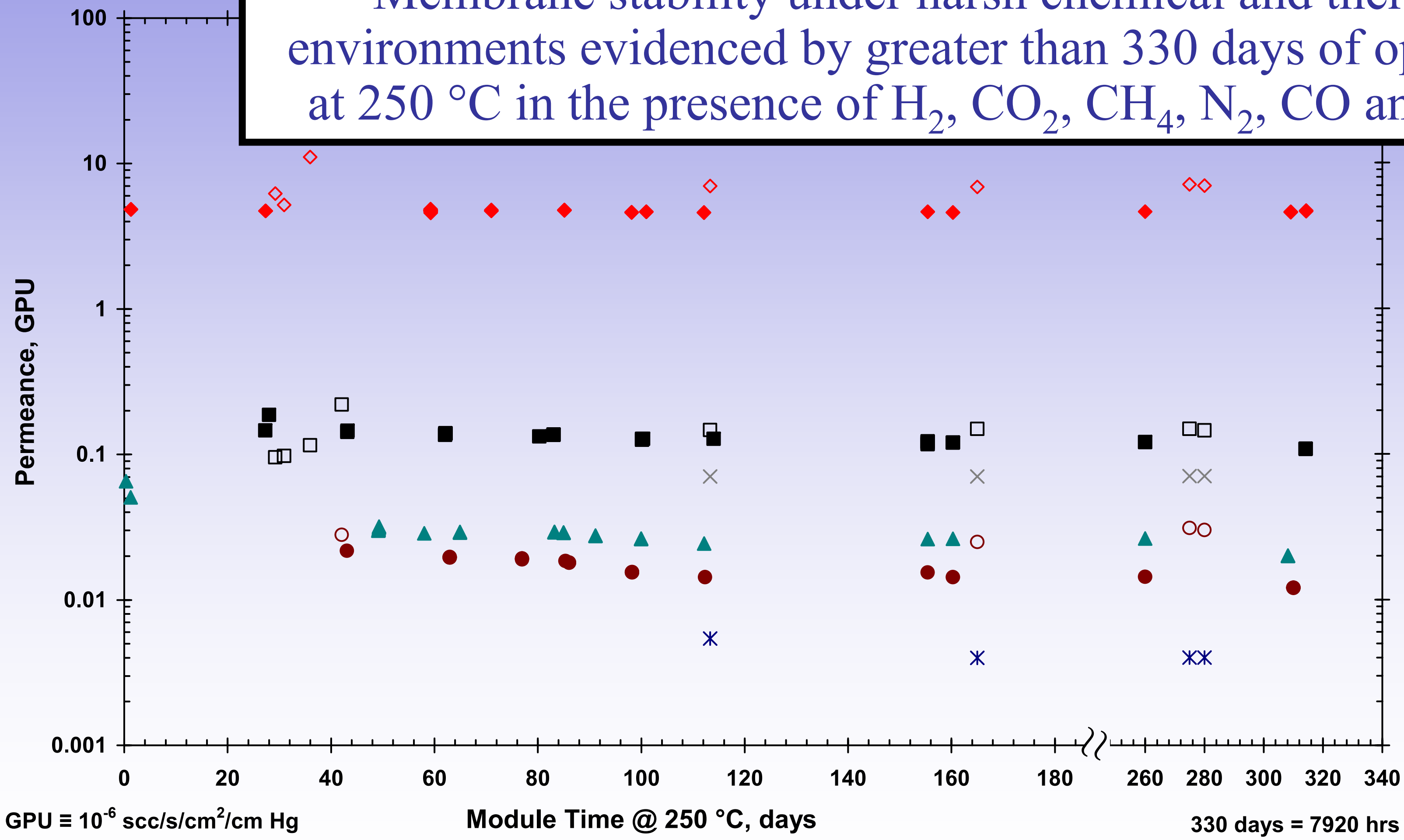
- Scale-up
  - Membrane area scale-up has been significant ($0.5\ cm^2 \rightarrow 67\ cm^2$)
  - Scalability of permselectivity characteristics demonstrated
- Minimization of Defect Free Film Apparent Thickness
  - Membrane thickness continues to be optimized
    ($100+\ \mu m \rightarrow 70\ \mu m \rightarrow 15\ \mu m \rightarrow < 7\ \mu m \rightarrow < 3\ \mu m$)
  - Selective layer thickness reductions result in concomitant permeance increase
- Testing under industrially relevant conditions
  - H_2, CO_2, CH_4, N_2, CO, H_2O and H_2S containing streams
  - Single gas & mixed gas testing

Durability

Single Gas Experiments: H_2, CO_2, CH_4, N_2

Mixed Gas Experiments: H_2, CO, CH_4, N_2, CO, H_2S

Membrane stability under harsh chemical and thermal environments evidenced by greater than 330 days of operation at 250 °C in the presence of H_2, CO_2, CH_4, N_2, CO and H_2S.



H_2S is at detection limit of our analytical equipment.
Thus, Permeance is between the reported value and zero.

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NG Fuel Processor – Slip Stream Testing

- **Natural Gas Fuel Processor at the Gas Technology Institute (GTI)**
  - **Fuel Processor: Tubular Fixed Bed Reactor**
    - Reformer: Ni-based reforming catalyst, 750 °C, 36 – 130 psig
    - WGS: Cu/Zn water-gas-shift catalyst, 250 °C
  - **Membrane Feed = Steam Saturated, Shifted Reformate**
    - Single Stage Membrane Operation
    - Operating Temperature: 250 – 400 °C
    - Operating Pressure: 36 – 130 psig
    - Varied Stage-Cut
    - 13 days of operation with reformate feed

Module Baselining

- Validation of Laboratory Test Data and Module Integrity
  - Correlation with LANL High Temperature Membrane Test Facility Evaluation
    - Cylinder Fed: 60/40 H_2/CO_2, 250 °C
    - GTI: Mixed Gas Testing Capability ONLY

	Temperature, °C	Trans-Membrane Pressure, psi	H_2/CO_2 Selectivity
LANL	235	35.5	43.0
GTI	255	37.9	40.3

Selectivities determined via mixed gas testing using dry gases are comparable between the two facilities.

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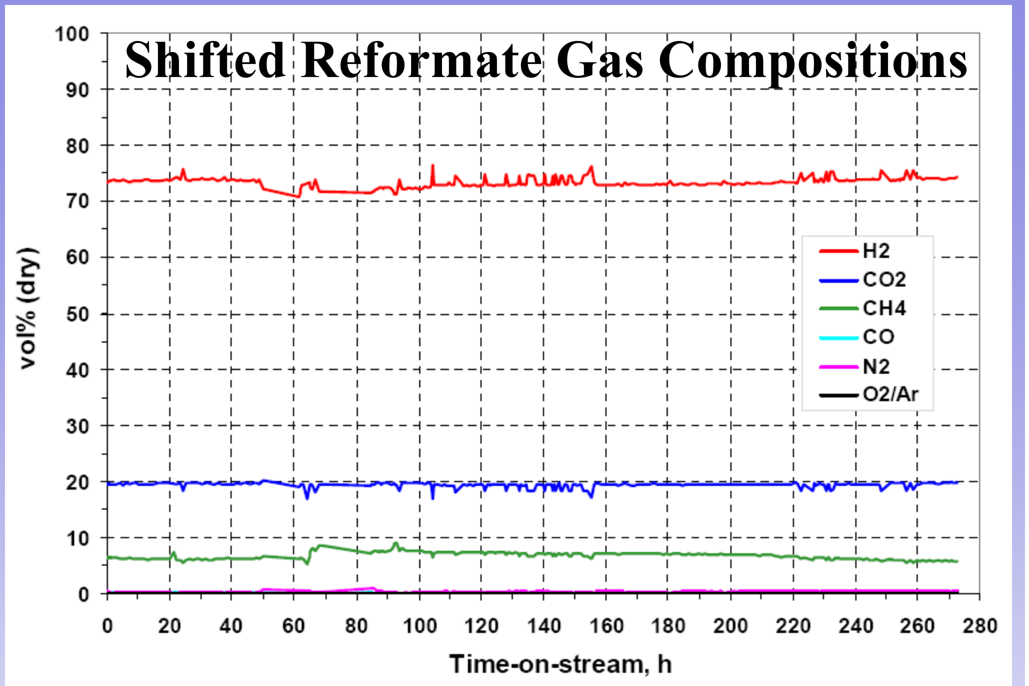
Hydrated Feed Effect

- Shifted Reformate/ Membrane Feed is Steam Saturated
  - Correlation with "Dry" Gas Evaluations



	Temperature, °C	Trans-Membrane Pressure, psi	H_2/CO_2 Selectivity
LANL – "Dry"	235	35.5	43.0
GTI – "Dry"	255	37.9	40.3
GTI – "Wet"	258	35.6	41.4

Effect of water/steam on membrane selectivity is not statistically significant

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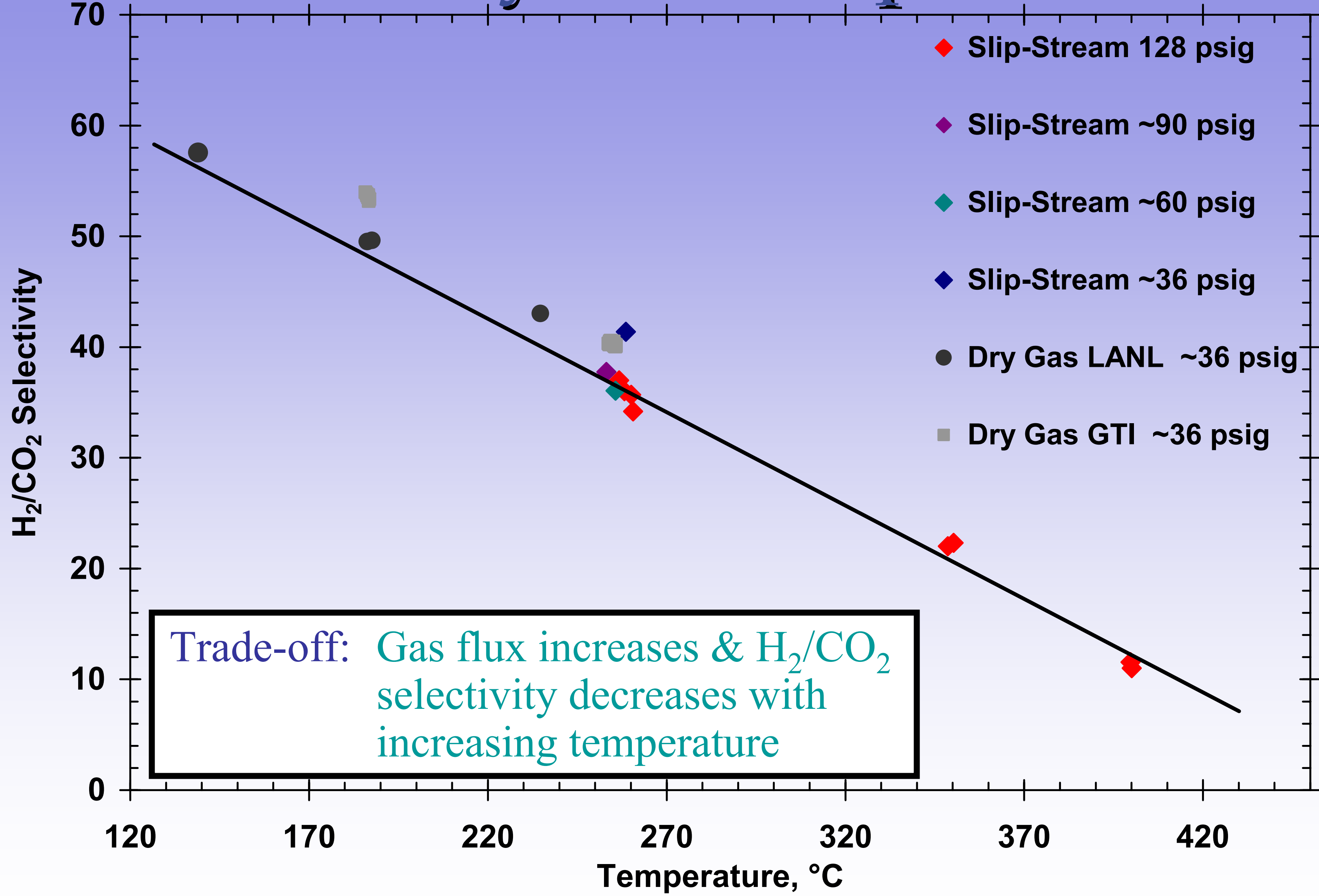
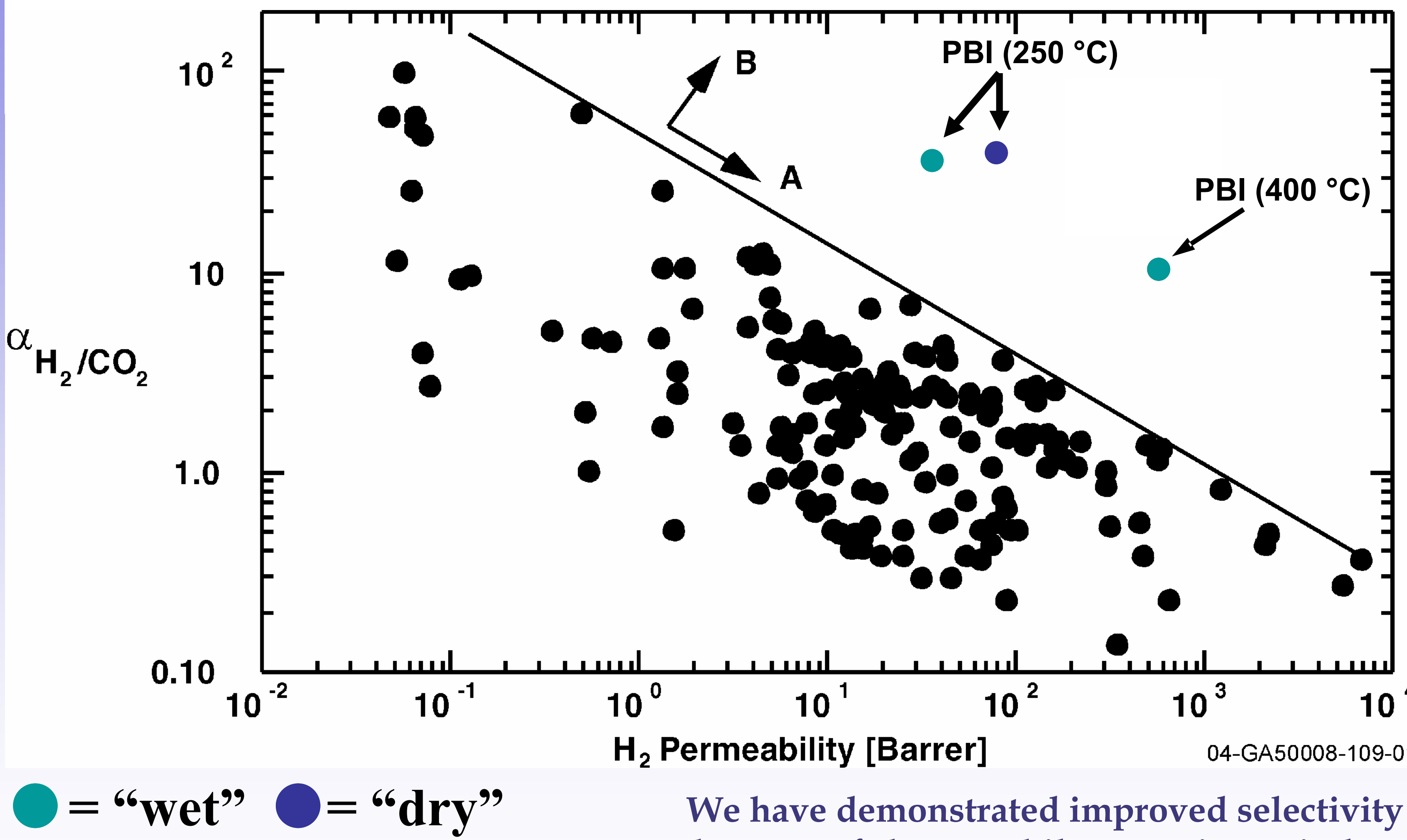
Selectivity vs. Temperature



Trade-off: Gas flux increases & H_2/CO_2 selectivity decreases with increasing temperature

Selectivity vs. Permeability: H_2/CO_2



We have demonstrated improved selectivity over the state-of-the-art while operating at industrially attractive conditions

1 barrer = 10^{-10} cm^3-cm/s-cm^2-cmHg

From J. Membr. Sci. 62, L.M. Robeson, Correlation of Separation Factor Versus Permeability for Polymeric Membranes, 1991.

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Project Highlights

- Highest demonstrated operating temperature (400 °C) of a polymer-based membrane with permeabilities and selectivities of interest
- Coating of tubular metal supports for implementation in a module
  - Planar to tubular substrate transition is a critical step forward on commercialization pathway
  - Intermediate layer fabrication and polymer deposition optimization efforts led to a >>500% increase in productivity in FY 05-06
- Successful testing of the polymeric-metallic composite membrane in dry gas environments containing H_2, CO_2, CH_4, N_2, CO, and H_2S from 25 to 400 °C.
- Demonstration of the membrane's thermal stability via 330+ days in operation at 250 °C.
- Successful testing of the polymeric-metallic composite membrane on fully hydrated natural gas reformate up to 400 °C.
  - Results indicate NO PERFORMANCE DEGRADATION in the presence of the fully steam saturated shifted reformate
- This work has demonstrated promise for future commercialization

RD&D and Strategic Selection of Future Partnerships to Facilitate Continued Progress Towards Meeting the Program Targets of >90% Capture and < 10% Increase in COE

- Slip Stream/Pilot Scale Testing
  - **Phase 1: NG Fuel Processor (Successfully Conducted FY06)**
    - **Separation of a steam saturated reformate post WGSR (conducted at GTI, DesPlaines, IL)**
    - **Results indicate NO PERFORMANCE DEGRADATION in the presence of the fully steam saturated shifted reformate**
    - **Testing up to 400 °C and 130 psig**
  - Phase II Pilot Testing
    - Gasifier/Simulated Gasifier Slip-Stream Testing
- Productivity Optimization
  - Selective layer thickness optimization
  - System integration
  - Materials design → Step change in performance
  - Multi-tube module design & development
- Systems and Economic Analysis
  - Collaboration with NETL (FY 05-06)
  - Pall Corporation in-house evaluations
- Commercialization Plan Development
  - Module and Separations Package Design
    - A&E firm
    - Discussion ongoing with NETL and others re: CFD

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Project Manager: José D. Figueroa

Collaborators on the High T_g Polymer for Carbon Capture Project

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Pall Corporation

NETL

INL