

FABRICATION AND SCALE-UP OF POLYBENZIMIDAZOLE (PBI) MEMBRANE BASED SYSTEM FOR PRECOMBUSTION BASED CAPTURE OF CARBON DIOXIDE

2010 NETL CO₂ Capture Technology Conference

September 16, 2010, Pittsburgh, PA

Project Overview

- **Overall objective**

- Produce a high temperature membrane and module for pre-combustion capture capable of operation at temperatures significantly higher than 200°C and industrially relevant conditions.

- **Period of Performance:**

- 2-22-2007 through 1-30-2011

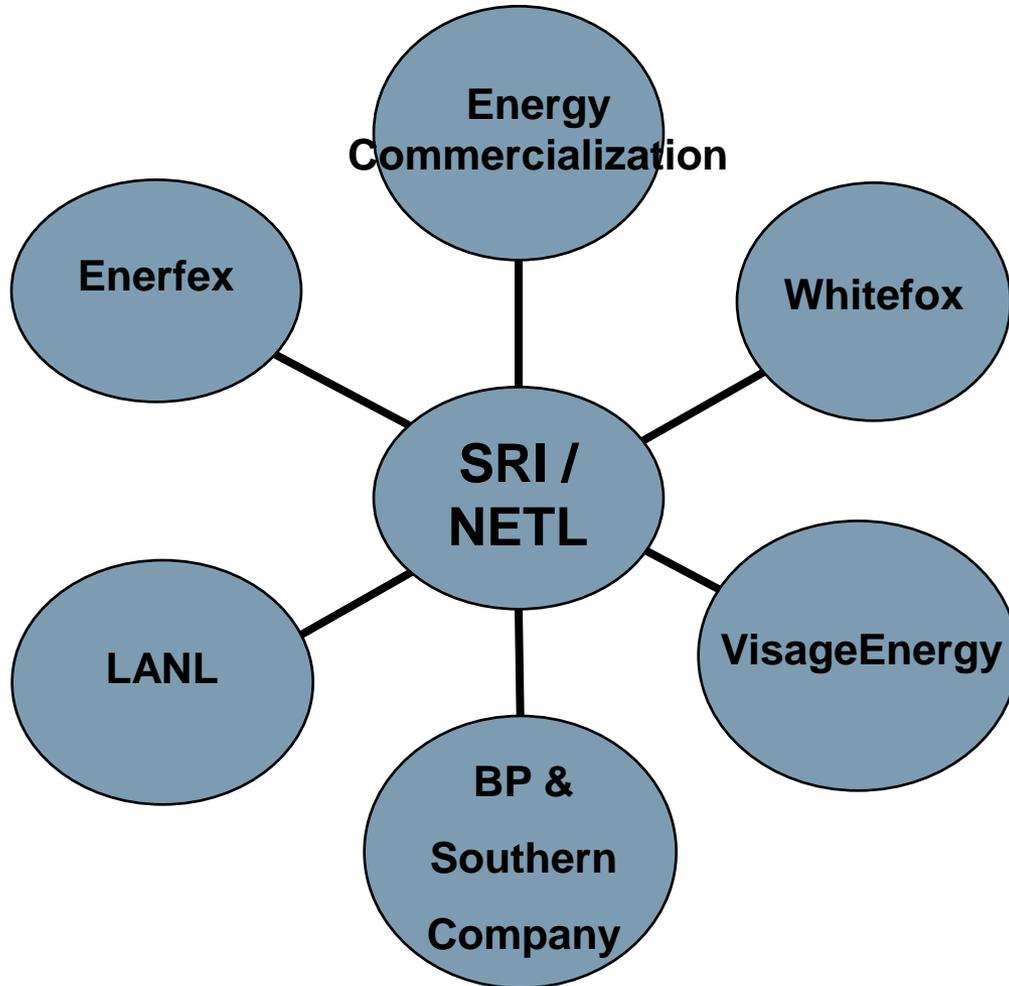
- **Funding:**

- U.S.: Department of Energy: \$3.9 million

- Cost share: \$1.2 million

- Total: \$5.1 million

Project Team



LANL:

Technology Developer /Testing

SRI:

System Integration / Testing

BP & Southern:

End Users of Technology

Whitefox:

Commercial PBI Membrane
Manufacturer

Enerfex:

Commercial Membrane System
Design Firm

Visage Energy:

Commercialization Analysis

Energy Commercialization

Commercialization Analysis

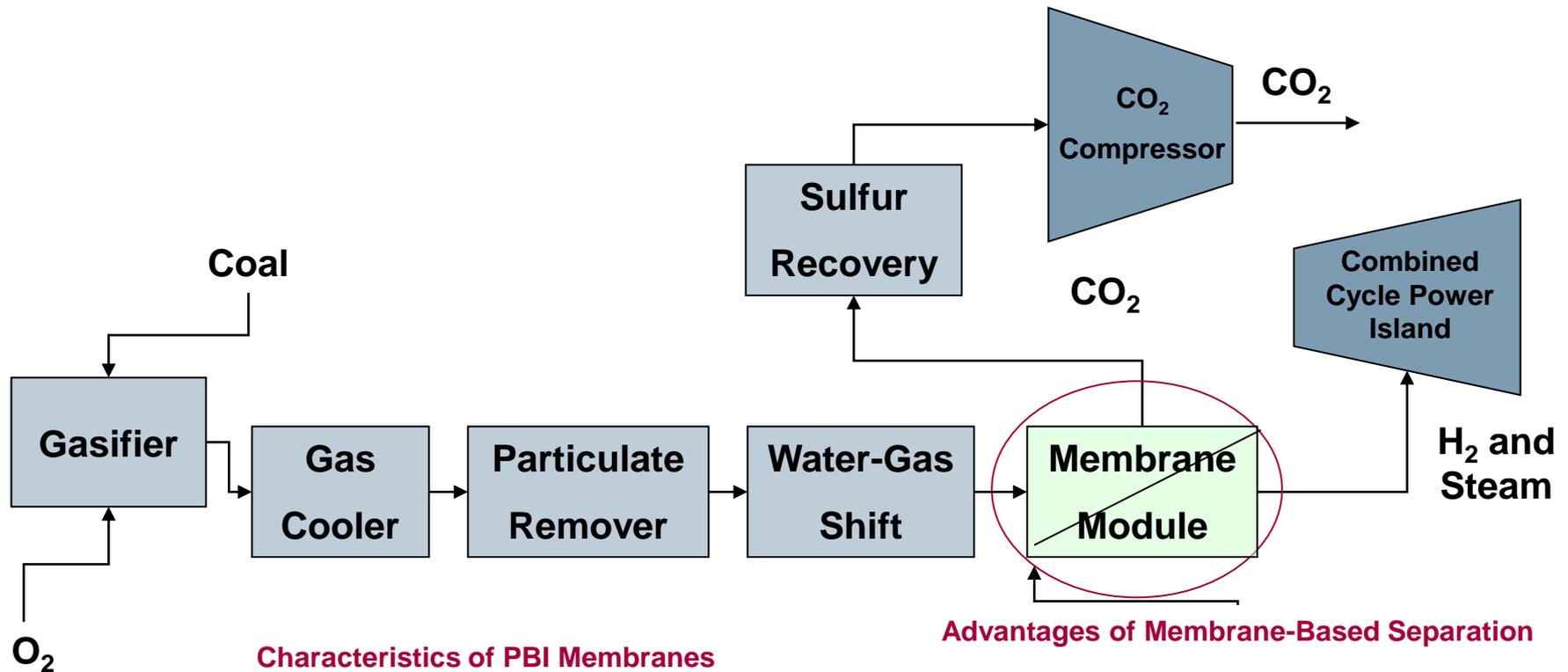
NETL:

Funding and technology oversight

Project Objective Details

- Design, construct, and test a pre-combustion-based CO₂ capture system (50 kW_{th}) skid using PBI membranes as the separating element:
 - Operate at temperatures above 200°C and pressures up to 700 psi.
 - Test the skid at an end-user facility in Phase II.
- Develop membrane elements using industrially relevant practices.
- Evaluate the performance of the membrane elements for CO₂ separation.
- Assemble the membrane modules with commercially available connectors and control systems into a skid. Test the skid with a simulated gas stream.
- Evaluate the COE of the membrane-based CO₂ capture for its ability to meet DOE goals.
- Evaluate financial and commercialization issues
- Develop a plan for technology transfer.

Why the High Temperature Membrane Separation of CO₂?



Characteristics of PBI Membranes

- PBI has attractive combination of throughput and degree of separation
- Thermally stable up to 450°C and sulfur tolerant.
- Tested for ~ 1 year at 250°C by LANL

Advantages of Membrane-Based Separation

- No need to cool syngas
- Reduced CO₂ compression costs
- Emission free, i.e. no solvents
- Decreased capital costs
- Low maintenance

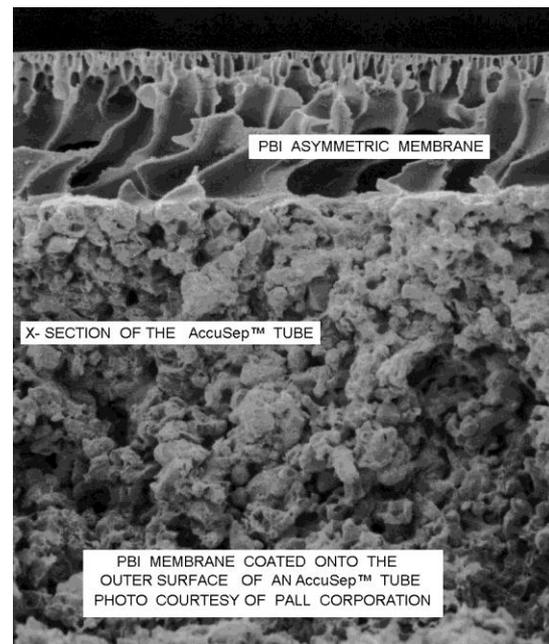
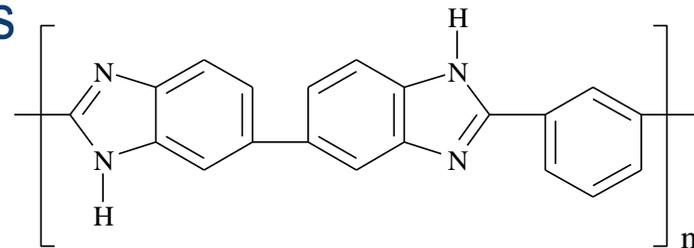
Project Tasks

- Completed Tasks:
 - Establish specifications and testing protocol
 - Design review on substrates and selection
 - Develop of strategic plan and technology transfer
 - Commercialization plan recommendation
 - Compilation of commercialization issues and requirements
- On-going tasks:
 - Membrane substrate development and selective layer coating – Optimization and quality control
 - Permselectivity characterization in simulated coal derived syngas environments
 - Subcomponent design and evaluation (Housing and fiber)
 - Integrate membrane module with commercially available skids, control systems, and connectors
 - Long term testing of a complete prototype skid mounted membrane system
- Management & reporting

***PBI Fiber Development
Characterization and Permeation Testing***

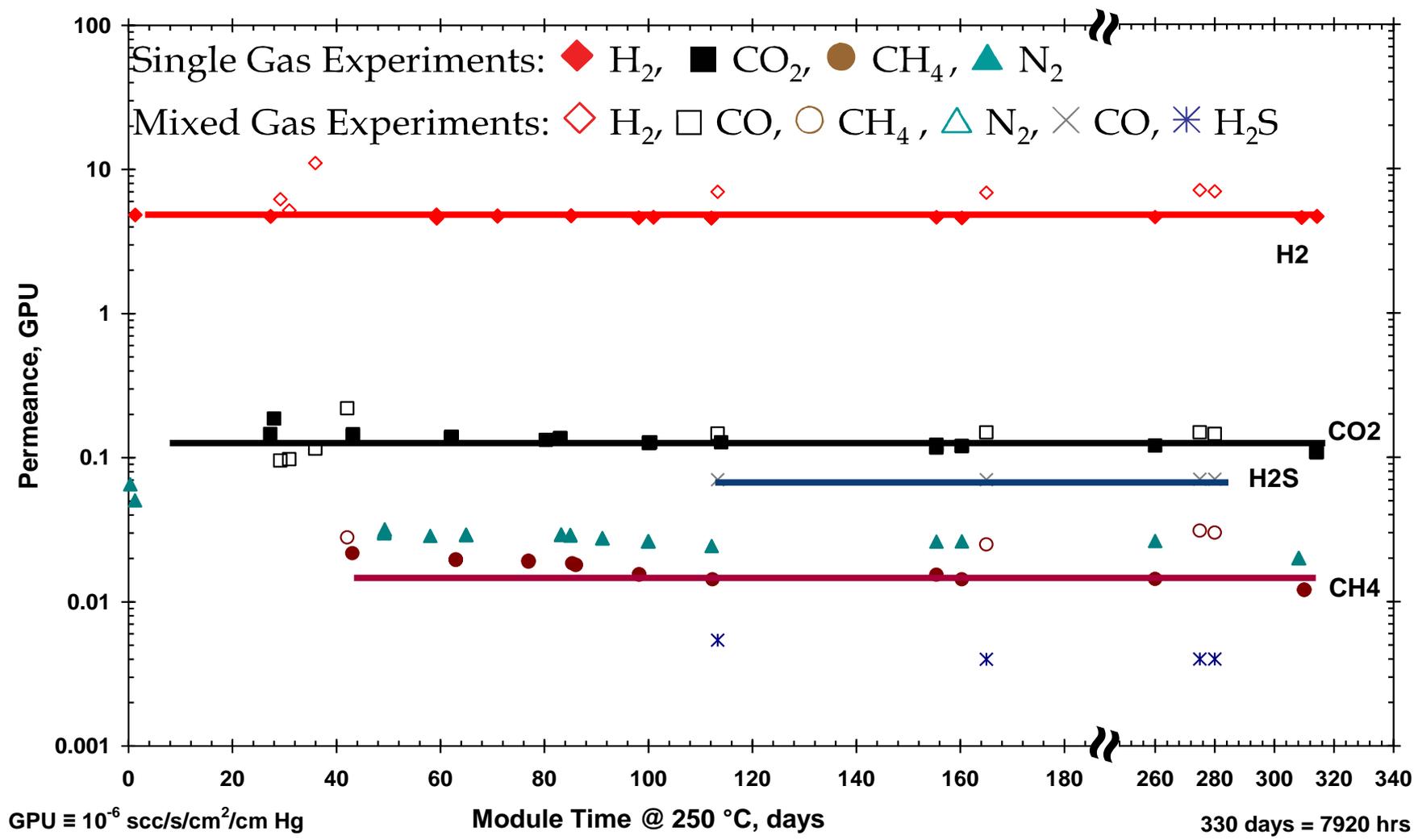
Previous PBI Efforts at LANL

- 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 ($T_g \sim 450^\circ\text{C}$): Facilitates process integration
 - Chemically resistant: Sulfur tolerant at operation temperatures
 - 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



PBI Membrane Durability (PBI on metal substrate)

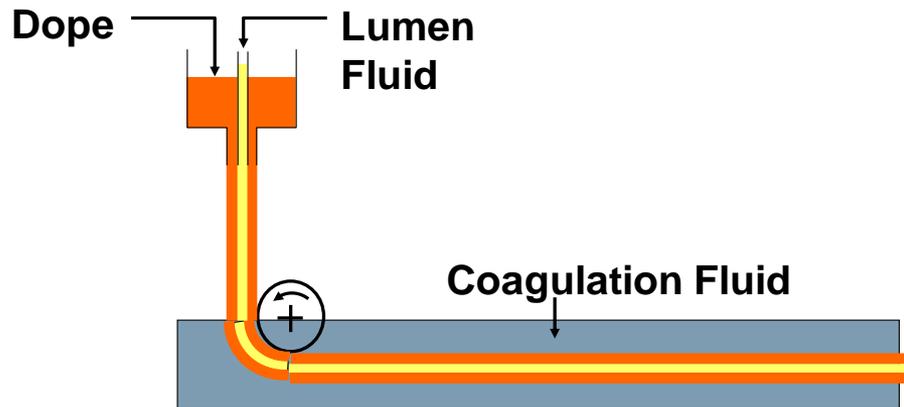
Membrane stability at 250°C for 330 days in the presence of H₂, CO₂, CH₄, N₂, CO and H₂S.



PBI Hollow Fiber Test Results

- PBI hollow fibers were fabricated by Whitefox Technologies
- A dense layer ($\sim 1 \mu\text{m}$) on porous PBI substrate
 - PBI substrate cost is lower than metallic substrates
- Membrane characterization at SRI and LANL
 - Morphology characterization using SEM
 - X-ray tomography to detect macro-defects
 - Permeation testing at ambient and elevated temperature
 - Permeability was measured using pure gases and mixed gases.

Production Scale Fiber Spinning Line at Whitefox Technologies



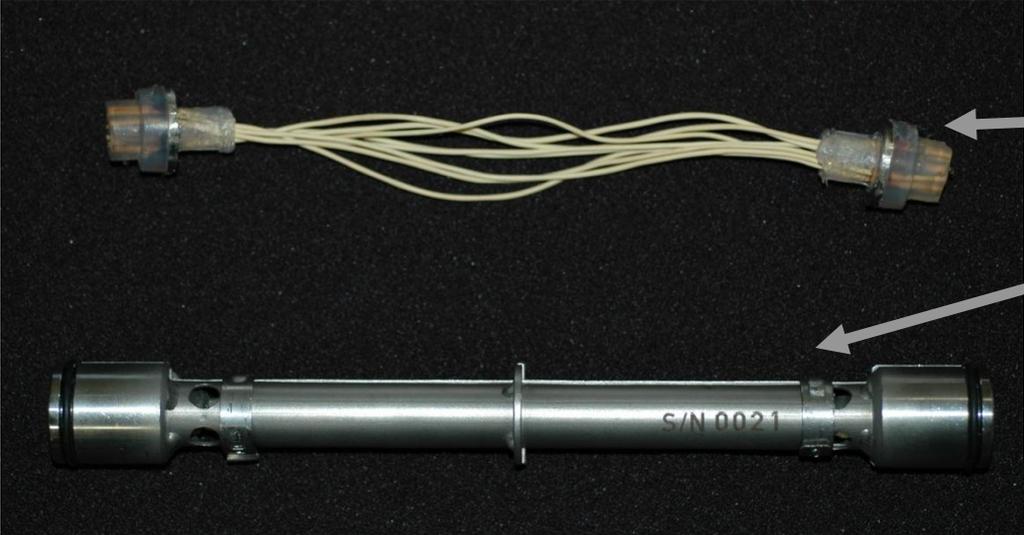
Components of the Membrane Module

**Bundle of PBI-Based
Asymmetric Hollow
Fibers**

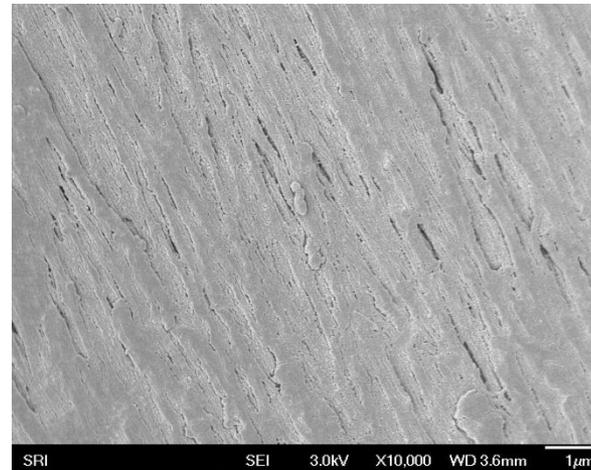
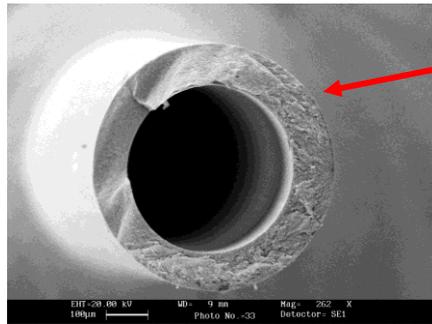
Fiber Potting

**Membrane
Cartridge
Module**

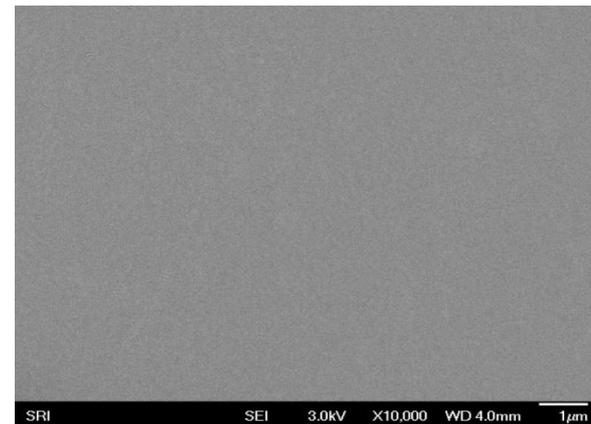
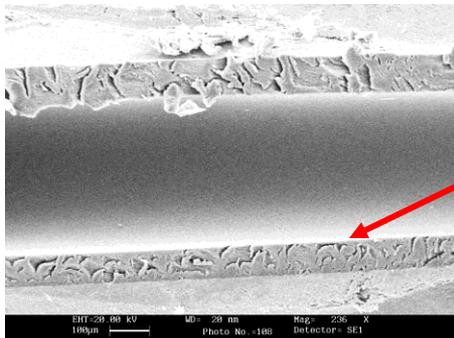
**Module
Housing**



Fiber Morphology (0.6 mm OD x 0.4 mm ID)



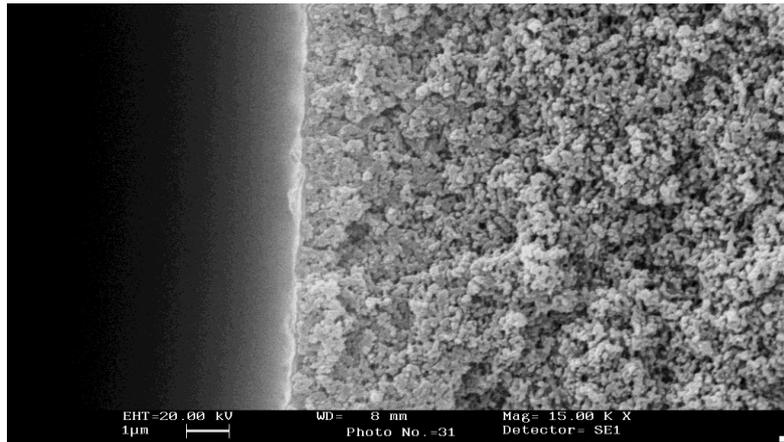
Shell



Lumen

Fiber Morphology (Cross-Section)

Cross section – Lumen side



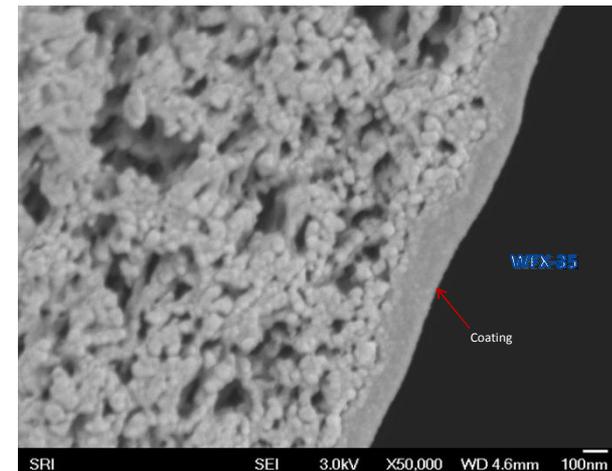
Bulk Morphology



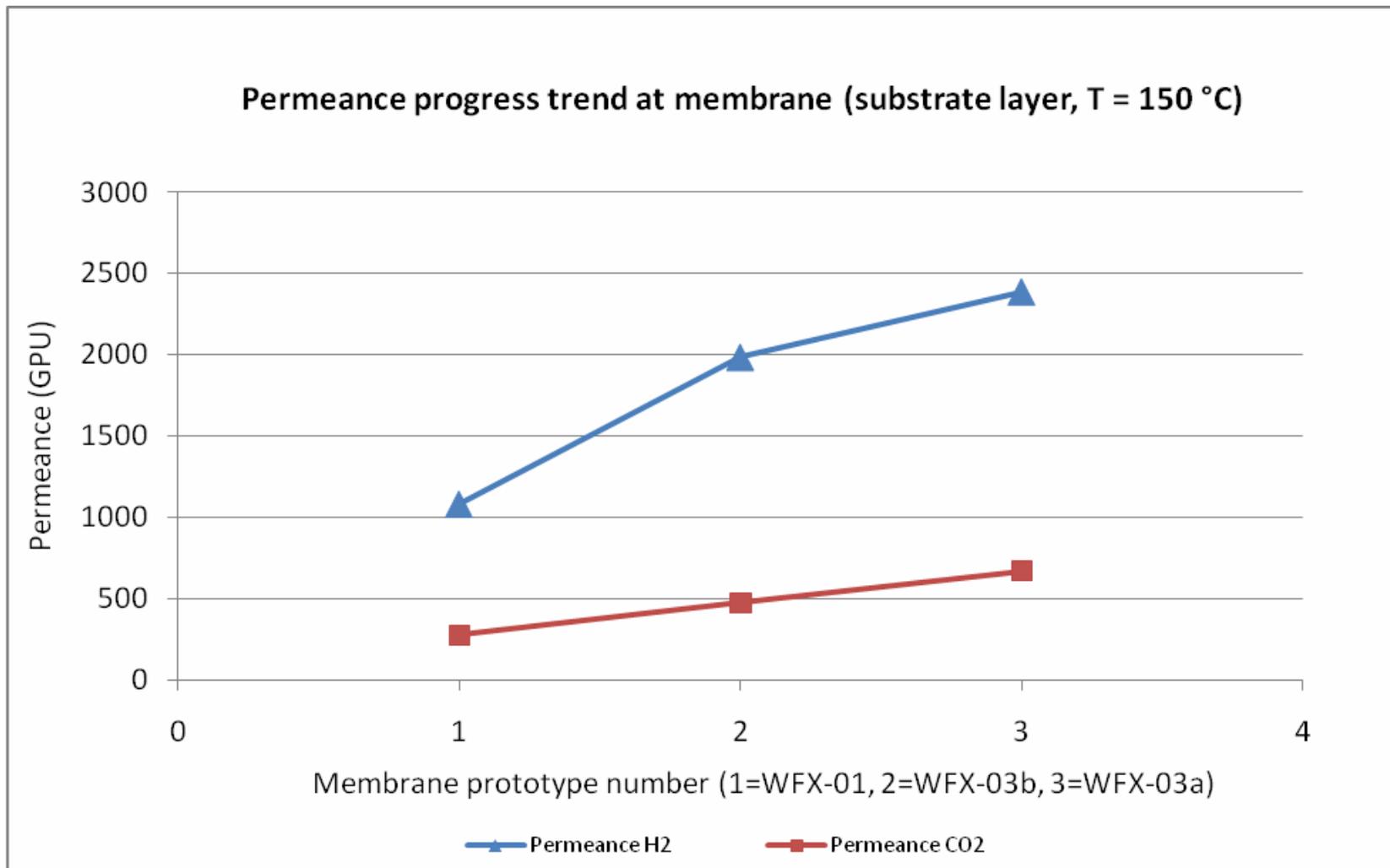
Uncoated Lumen Side



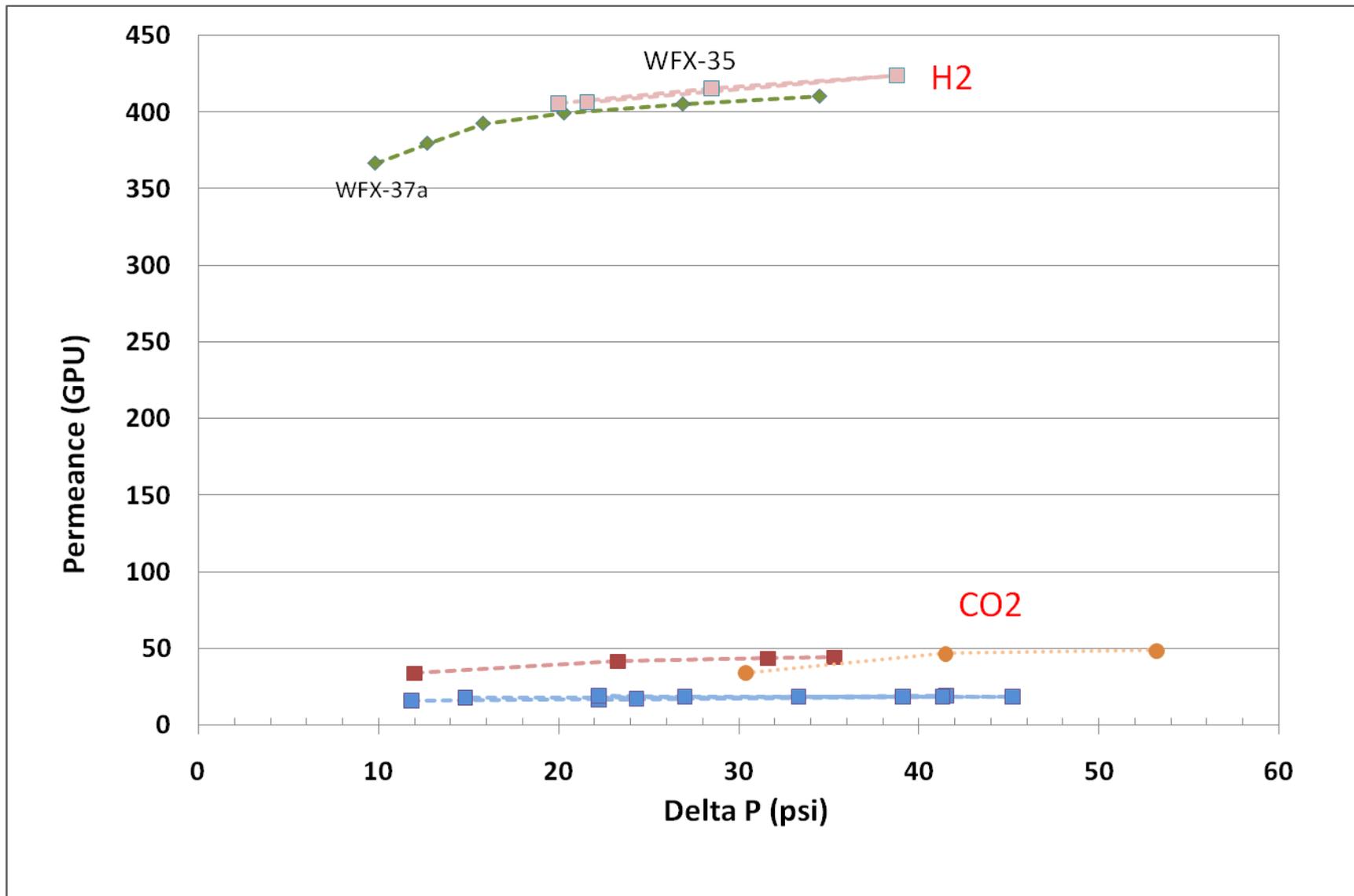
Coating on Lumen Side



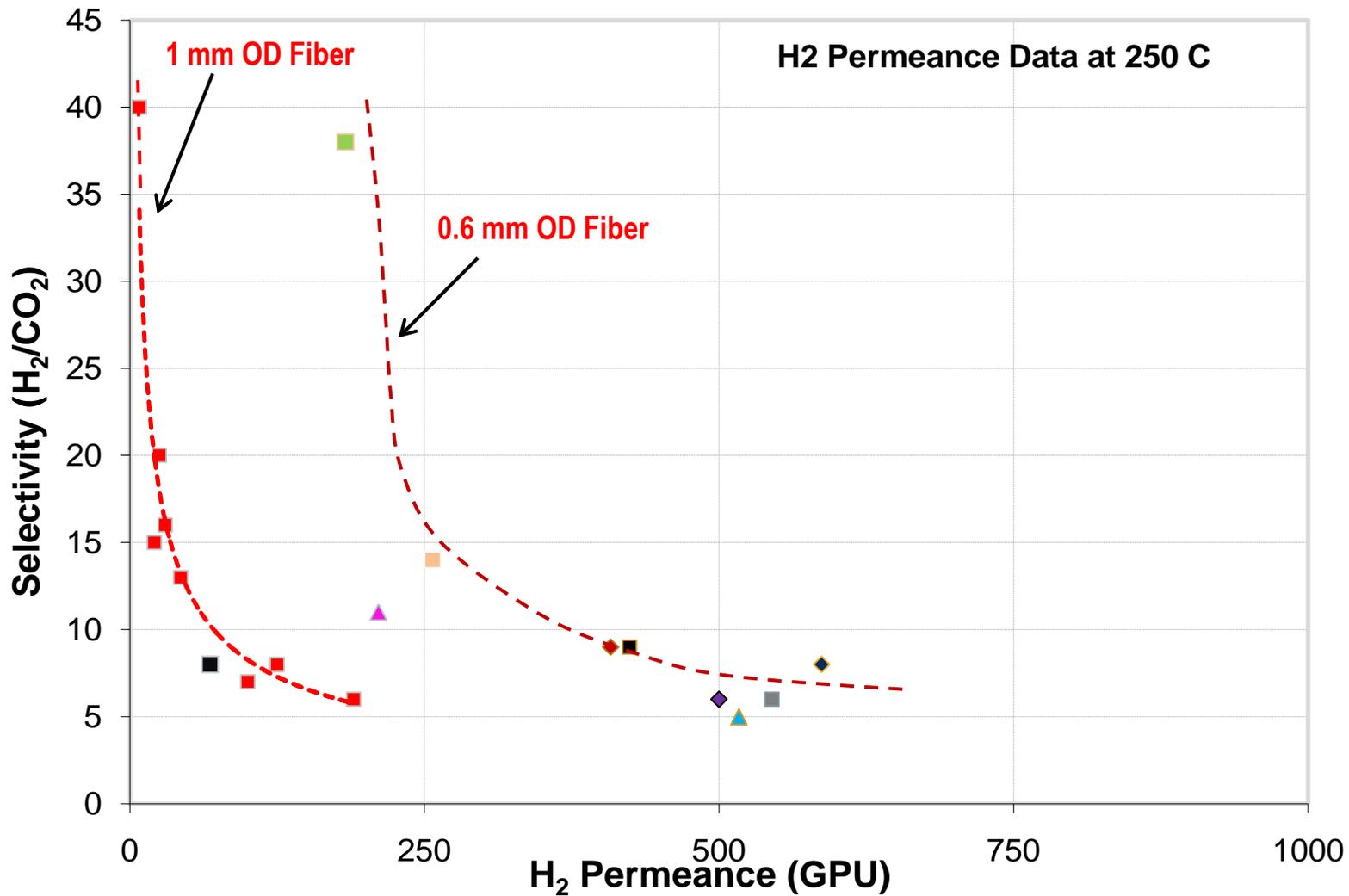
PBI Porous Substrate Development



The measured permeance for H₂, and CO₂ as a function of pressure difference at 250°C



H₂/CO₂ Selectivity vs H₂ Permeance



Membrane Module Simulation
Aspen Process Simulation
GT-Pro Simulation
Estimation of cost of electricity for CO₂ Capture

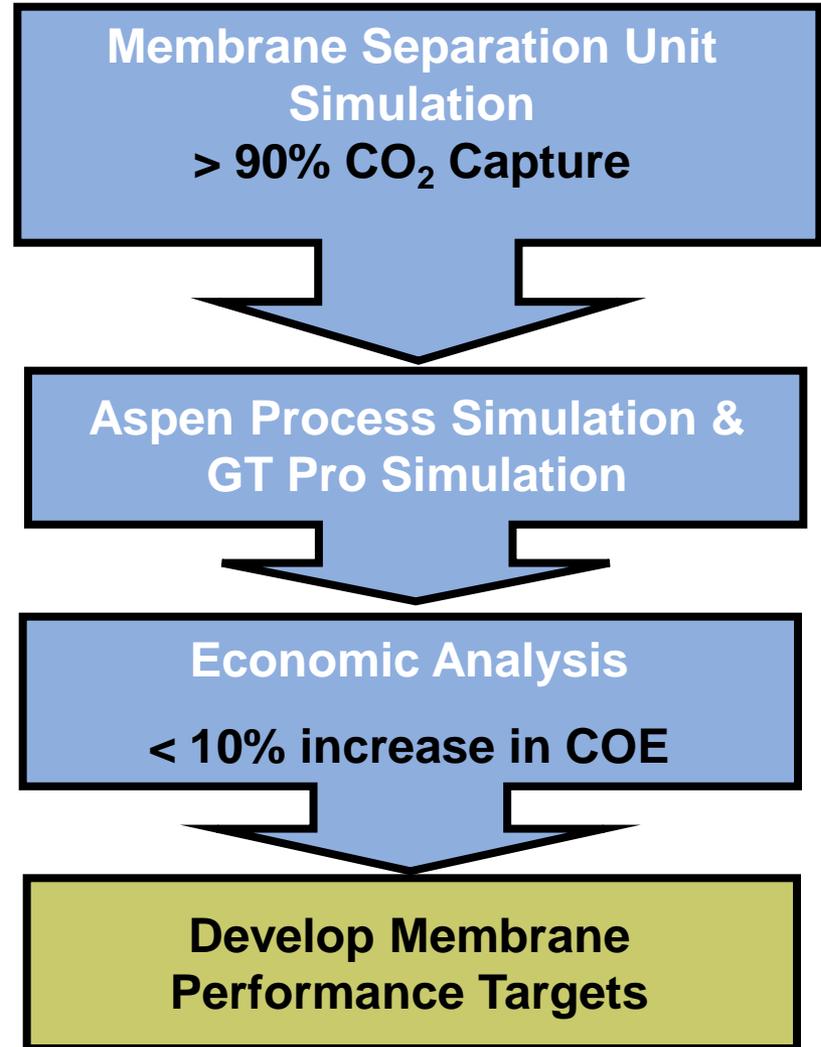
Role of Membrane and Process Simulation

Benchmarked against simulations used by membrane manufacturers & field operational data

Benchmarked against NETL simulations

Metric of success in meeting program goals

Impacts Membrane and Process Development Strategy



Range of Parameters Being Examined with Membrane Separation Unit Simulation (Enerfex)

- Separation layer thickness range: 0.1 to 1 μm
- Feed gas parameters (after WGS reactors)
 - Temperature: 170° to 250°C
 - Pressure: 750 psia
 - Feed Flux: 19.5 to 22.5 scf / ft² / hr
 - Gas composition (v/v):
 - H₂: 43.0%, CO₂: 31.1%, H₂O: 23.3%, H₂S: 0.5%, CO: 0.9%, N₂+Ar: 1.1%
- Retentate:
 - Temperature: 170° to 250°C
 - Pressure: ~ 735 psia
- Permeate:
 - Temperature: 170° to 250°C
 - Pressure range: 250 psia to 450 psia
 - N₂ sweep gas fraction: 40%

Addressing Thickness of Selective Layer

Separation Layer Thickness (Microns)	0.5	0.1
Temperature (°C)	250	250
Permeate Pressure (psia)	250	250
Hydrogen Recovery (%)	91	91
Membrane Area (m ² /MWe)	117	23
Number of Elements / MWe	1.9	0.4

CO₂ Recovery: 90%; Feed pressure: 777 psia

Process Simulation and Estimation of COE*

- Developed an Aspen model to simulate IGCC process with and without CO₂ capture
- Base case assumptions are similar to *Cost and Performance Baseline for Fossil Energy Plants, DOE/NETL 2007 / 1281*
- Feed gas characteristics from Aspen model downstream of water gas shift reactor were the input to the membrane simulation model
- Results from membrane simulation model were used to define process conditions downstream of membrane separator
- GT-Pro program simulated the performance of gas and steam turbines
- The results from the simulation was used to estimate COE using the NETL spreadsheet.

* Cost of electricity

Top Four Scenarios Being Evaluated With Process Modeling

Base Case:

Scenario 1: Base case IGCC plant with no CO₂ capture

IGCC plant equipped with CO₂ capture

Scenario 2: Selexol units are used to separate CO₂ from H₂. Additional Selexol units used for H₂ S removal.

Scenario 3: PBI membrane used to separate CO₂ from H₂. Selexol units used for H₂ S removal.

Scenario 4: PBI membrane used to separate CO₂ from H₂. H₂ S remains with the CO₂

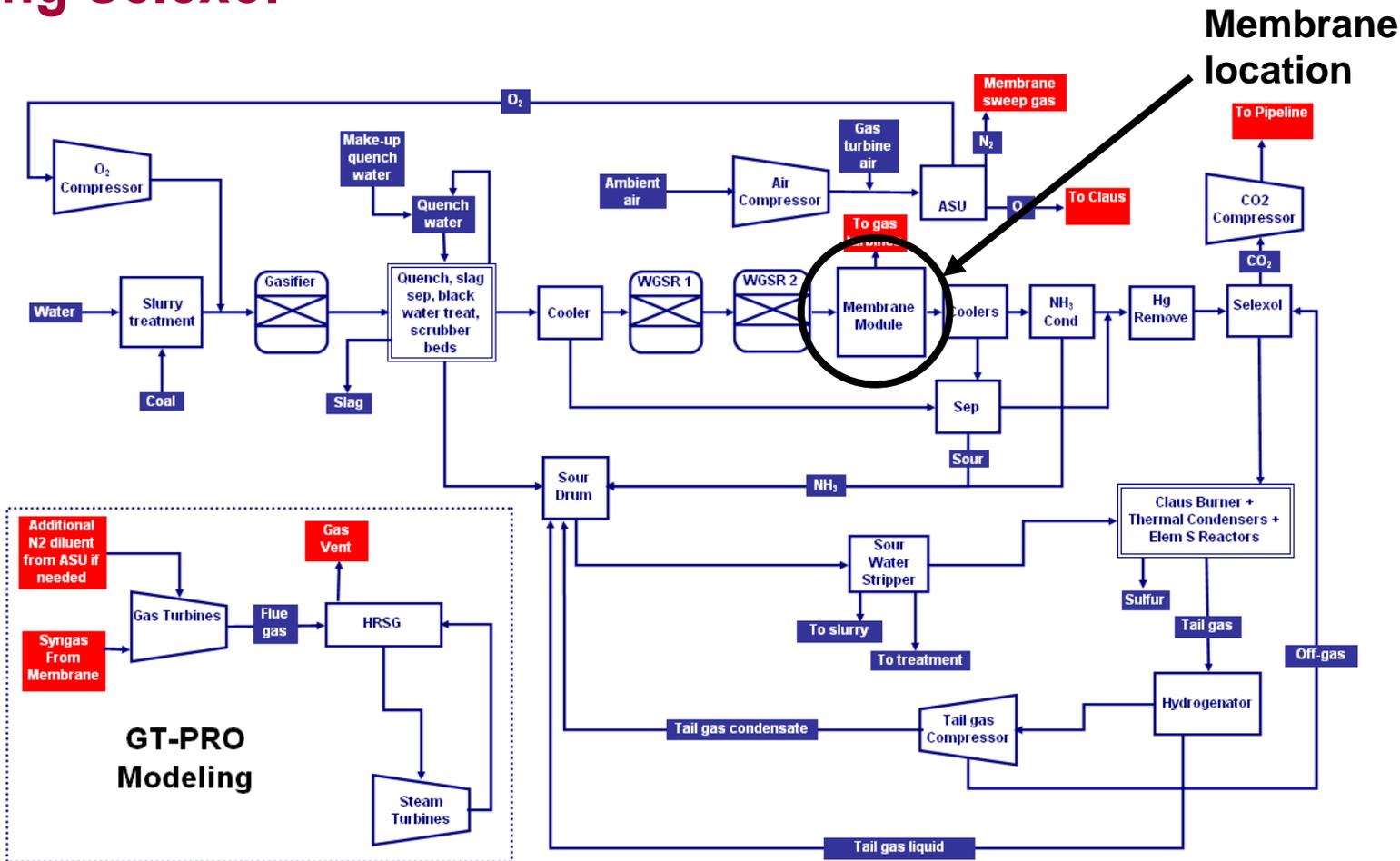
Good Correlation Between Project's Process Simulation and NETL's Process Simulation

CO₂ capture: 3.3 Million tonnes/yr.

	Units	NETL Cases		Project Cases	
		No Capture	Capture w/Selexol	No Capture	Capture w/Selexol
Power Production @ 100% Capacity	GWh/yr	5,609	4,868	5,455	4,788
Power Plant Capacity	Cents/kWh	4.53	5.97	4.50	5.92
Power Plant Fuel	Cents/kWh	1.94	2.28	1.90	2.27
Variable Plant O&M	Cents/kWh	0.75	0.94	0.78	0.94
Fixed Plant O&M	Cents/kWh	0.58	0.72	0.60	0.74
Power Plant Total	Cents/kWh	7.80	9.91	7.78	9.87
CO2 transport, storage & Monitoring	Cents/kWh	0.00	0.39	0.00	0.39
Cost of Electricity (COE)	Cents/kWh	7.80	10.30	7.78	10.25
Increase in COE (over no capture)		n/a	32.0%	n/a	31.5%

Plant operating life: 30 years; Capacity Factor: 80%; Capital charge factor: 17.5%

Scenario 3: Capture with PBI Membrane / H₂S Removal Using Selexol



Preliminary Economic Analysis: PBI Approaches the DOE Goals

CO₂ capture: 3.3 Million tonnes/yr.

	Units	Project Cases			
		No Capture	CO ₂ and H ₂ S Capture w/Selexol	CO ₂ Capture w/PBI & H ₂ S w/Selexol	CO ₂ Capture w/PBI no H ₂ S removal
Power Production @100% Capacity	GWh/yr	5,455	4,461	4,943	5,035
Power Plant Capacity	cents / kWh	4.50	6.19	5.49	5.02
Power Plant Fuel	cents / kWh	1.90	2.47	2.31	2.26
Variable Plant O&M	cents / kWh	0.78	1.00	0.92	0.91
Fixed Plant O&M	cents / kWh	0.60	0.79	0.71	0.70
Power Plant Total	cents / kWh	7.78	10.45	9.43	8.89
Cost of Electricity* (COE)	cents / kWh	7.78	10.45	9.43	8.89
Increase in COE (over no capture)	%	n/a	34%	21%	14%

* Separation and Capture Only

Plant operating life: 30 years; Capacity Factor: 80%; Capital charge factor: 17.5%

Capture with Selexol uses slightly different parameters than NETL cases.

Sensitivity Analysis Results

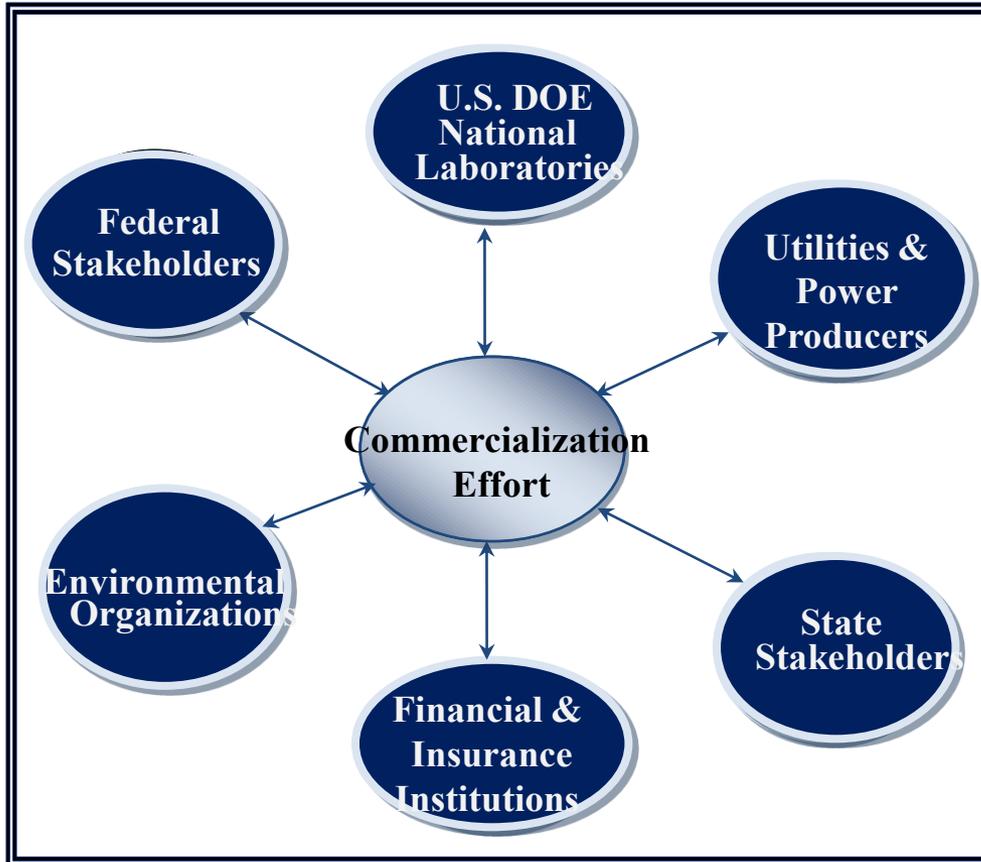
- The COE for CO₂ capture may approach the DOE goals under optimized membrane characteristics.
- The membrane cost is not a major factor in the increase in COE.
- H₂S removal by a method other than Selexol is needed for retaining the advantages of the high temperature membrane separation.
- Gas turbine fuel inlet pressure must be close to that of permeate pressure. Recompression of H₂ fuel adds a significant cost.

Commercialization Effort

Commercialization Effort Objective

- Infuse business perspective and acumen into technology development processes
- Expose business community to technology and highlight its functional and cost benefits over state-of-the-art
- Incorporate feedback from potential customers, financial and insurance communities.
- **Key Benefits:**
 - Reduction of technology commercialization timeline
 - Mitigation of key technical and business risks

Engaging Key CCS Stakeholders



MACRO LEVEL (Market)

- Decrease time to deployment by EARLY dialogue with ecosystem
- “Internet” of developers, deployers and regulators need to leverage Federal, State, & Private efforts

MICRO LEVEL (Project)

- Common language enables dialogue between all members of the network
- Real-time inclusion of customer needs into the technology development process

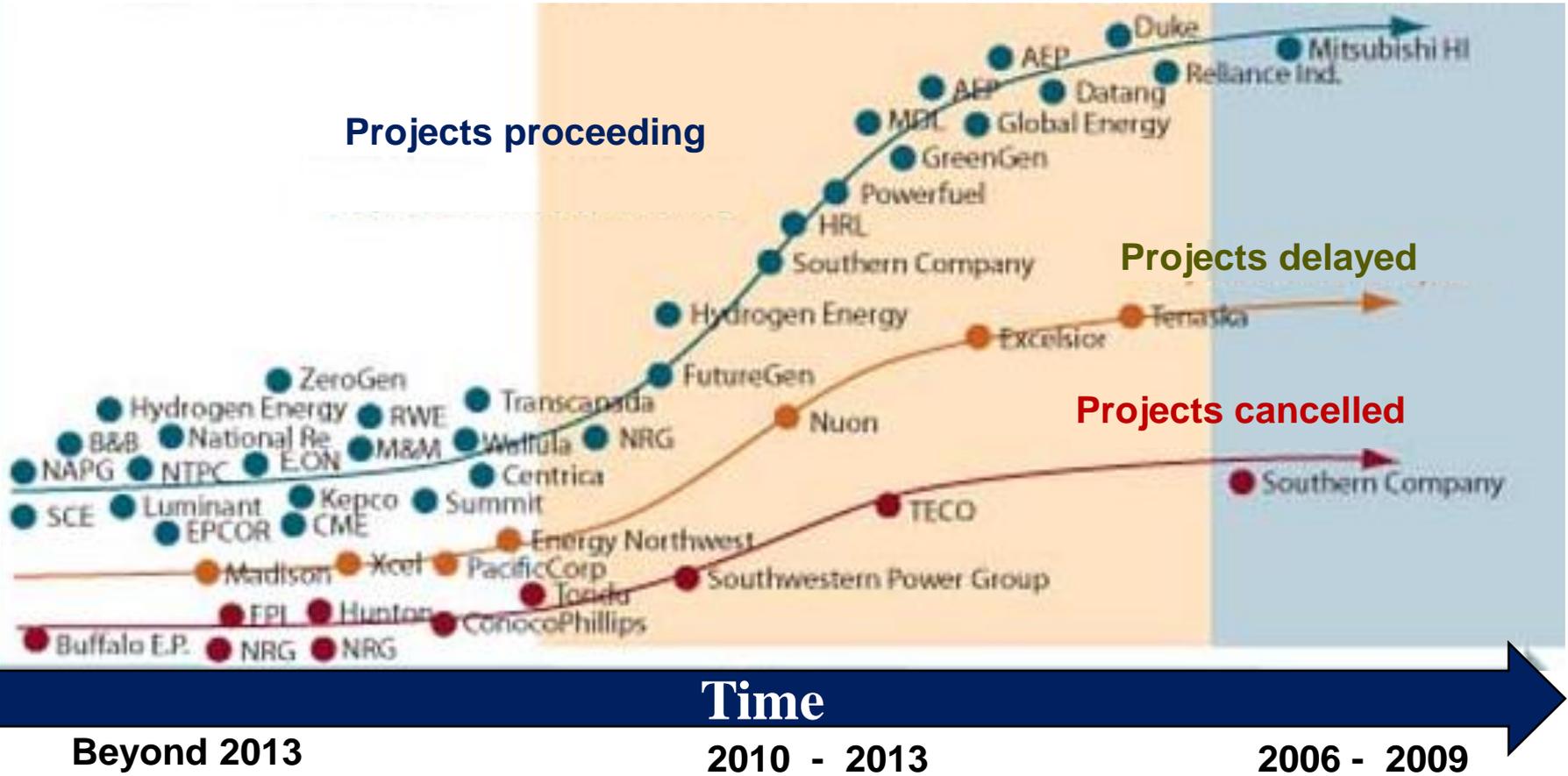
Status of global IGCC project pipeline

Progress toward commercial operation

Announced

Under development

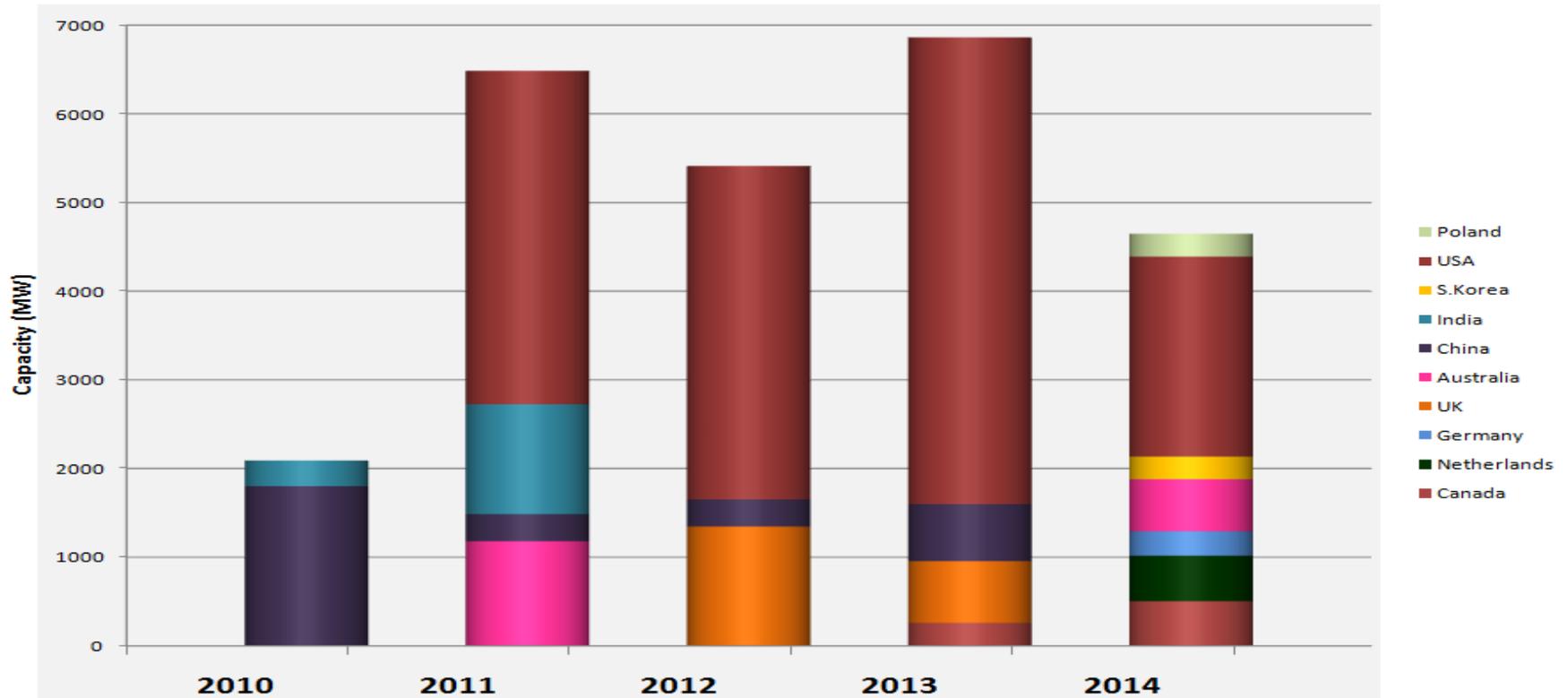
Pilot Scale



50+ projects remain in development (combined capacity=25,000MW)

Source: Emerging Energy Research

Global IGCC project pipeline



U.S. is largest market sector with notable increases projected in Canada, Australia & China

Source: Emerging Energy Research

Strategic Development Report Conclusions

- Upstream factors such as gasifier type and characteristics of fuel source may cause variation in the performance of capture systems
- Non-technical factors such as regulatory changes and public opinion could impact timelines for pilot, demonstration, and deployment of new capture systems
- Commercialization of PBI capture systems will impact supply chains such as the global supply of PBI hollow fibers, and PBI polymer
- Mitigating these risks was important in order to rapidly transition PBI capture systems from pilot to demonstration to deployment

Summary

- PBI hollow fiber membranes have been fabricated:
 - A dense layer of PBI on a porous PBI substrate
 - Physical morphology of the membranes were characterized both at SRI and LANL
- Permeability characteristics were experimentally measured :
 - H_2/CO_2 selectivity >40 has been achieved at a H_2 permeability of 200 GPU at 250 C
- Whitefox Technologies Continue to improve on
 - Hollow fiber membrane quality control issues
- Enerfex has completed the skid specifications and drawings
- Visage Energy, Inc., Energy Commercialization, Inc. and SRI have completed the strategic Development Plan Report and submitted to NETL.

Future Work

- Membrane module assembly.
 - Quality fibers are being fabricated at Whitefox technologies
 - Membrane module will be assembled into a high pressure housing and incorporated in a skid.
- Evaluation of the complete system
 - The system will undergo at least 100 h of continuous testing under mixed gas conditions.
- In the next phase:
 - The skid will be transported to a gasifier site for field testing.

Team Members

- SRI International:
 - Dr. Gopala Krishnan – Associate Director (MRL) and PI
 - Dr. Angel Sanjurjo – Materials Research Laboratory Director and Project Supervisor
 - Dr. Indira Jayaweera, Dr. Jordi Perez, and Dr. Marc Hornbostel
- Los Alamos National Laboratory:
 - Dr. Kathryn Berchtold
- Whitefox Technologies:
 - Mr. Stephan Blum and Dr. Jorge Wong
- Enerfex Inc.:
 - Mr. Richard Callahan
- Visage Energy, Inc.
 - Will Johnson and Daryl-Lynn Johnson
- Energy Commercialization, Inc.
 - Dr. Kevin O'Brien
- Southern Company, Inc.
 - Tony Wu
- DOE-NETL
 - Mr. Robie Lewis and Mr. Jose Figueroa