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Session: Pre-Combustion Capture Projects

Development of Pre-Combustion CO_2 Capture Process Using High-Temperature PBI Hollow-Fiber Membranes

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SRI International

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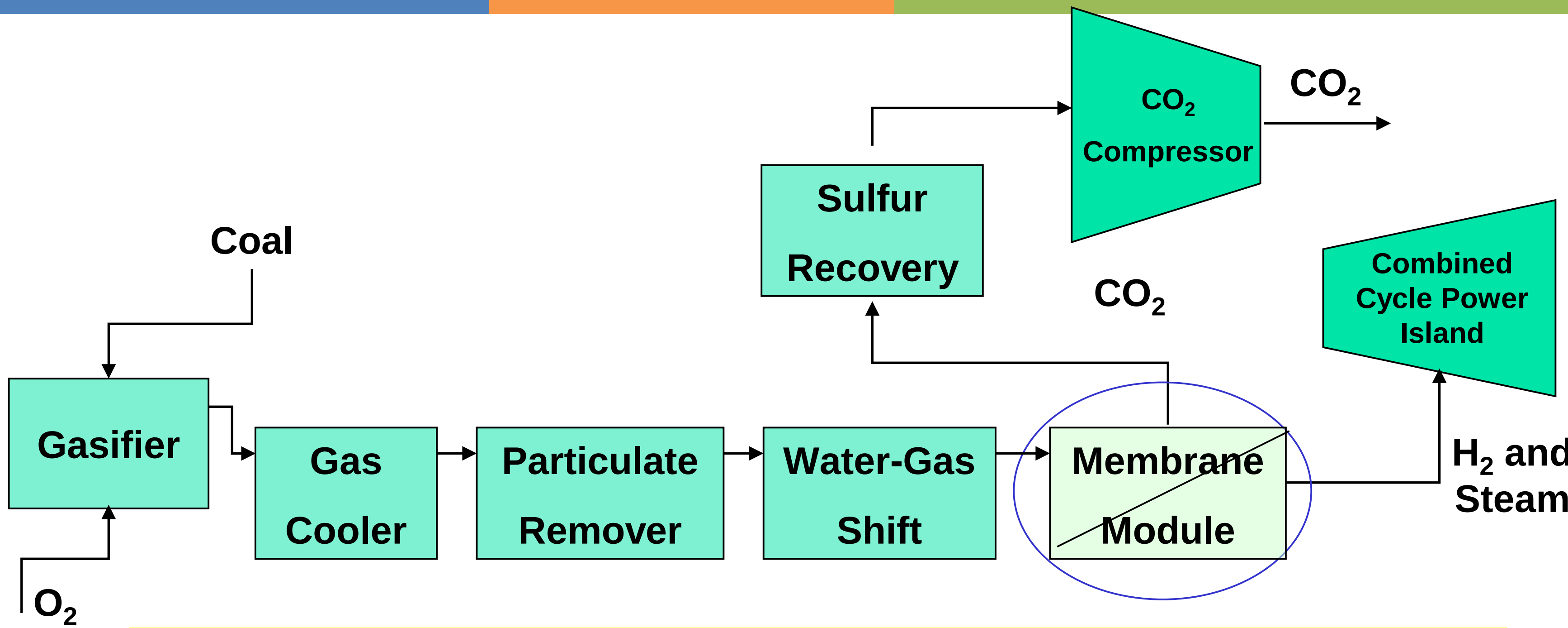
Project Overview and Technology Background

Why the High-Temperature Membrane Separation of CO_2?



Note: PBI hollow fiber membrane (HFM) is a H_2O and H_2 transporting membrane

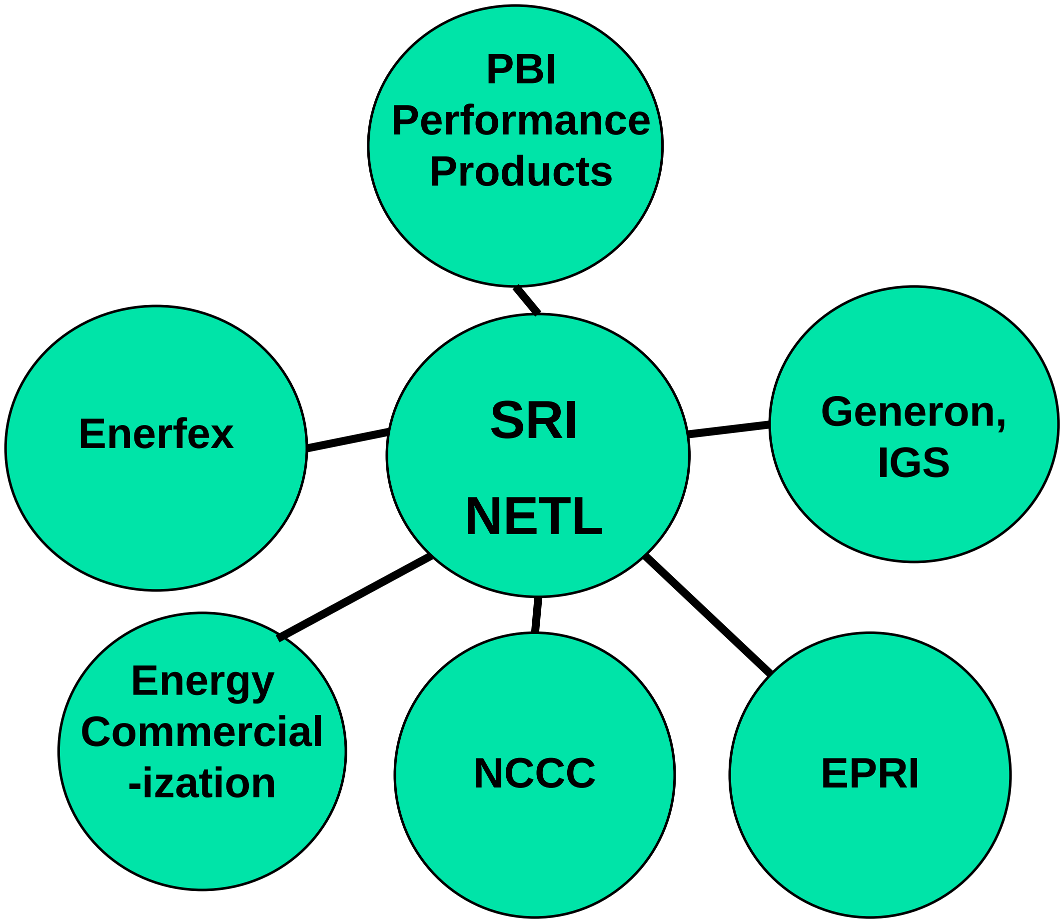
Characteristics of PBI Membranes

- PBI has attractive combination of throughput and degree of separation
- Thermally stable up to ~ 300°C and sulfur tolerant
- Tested for 1000 hr at 225°C by SRI

Advantages of Membrane-Based Separation

- No need to cool syngas
- Reduced CO_2 compression costs
- Emission free, i.e., no solvents
- Decreased capital costs
- Low maintenance

Project Team



SRI

PBI Membrane Fabrication Research

Membrane Testing

PBI Performance Products, Inc.

PBI Manufacturer

Generon

Membrane Fabrication Scale-up

Module Fabrication

Enerfex

Membrane System Modeling

Energy Commercialization

Commercialization Analysis

NCCC

Gasifier Facility Test Site

EPRI

Electric Power Industry Perspective

NETL

Funding and technology oversight

Project Overview

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- **Cooperative agreement grant with U.S. DOE-NETL**
- **Period of Performance**:
  - Budget Period 1: 4-30-2014 through 10-31-2015
  - Budget Period 2: 11-01-2015 through 01-31-2017
- Project Startup Meeting: 06-9-2014
- **Funding**:
  - U.S.: Department of Energy: $2.25 million
  - Cost share: $0.56 million
  - Total: $2.81 million
- **NETL Project Manager**:
  - Ms. Elaine Everitt

Objectives

Program Objective:

To develop polybenzimidazole (PBI) membrane-based H_2/CO_2 separation technology for Integrated Gasification Combined Cycle (IGCC) power plants that shows significant progress towards meeting the overall DOE Carbon Capture Program performance goal of 90% CO_2 capture rate at a cost of $40/tonne of CO_2 captured by 2025.

Project Objectives:

Obtain sufficient *bench-scale data* for high-temperature PBI polymer membrane separation of pre-combustion syngas to H_2-rich and CO_2-rich components. Utilize the data to evaluate the technical and economic viability of PBI-based membrane separation system to achieve NETL's Capture Program Performance Goals.

Approach

Task #	BP	Task	Status	Comments
1	1 & 2	Project management	On-Going	On-track
2	1	• Advanced development of asymmetric hollow fiber spinning • Spinning defect-minimized fibers at km lengths • Assembling of multi-fiber modules 1-in, 2-in, 4-in modules • Installation of sub-scale fiber module test unit in laboratory • Conduct laboratory tests to generate parametric performance test database • Modeling of membrane performance • Technology transfer to initiate industrial scale fiber spinning • Design modification of the 50-kW$_{th}$ skid design to house commercial membrane modules	On-Going	On-track
3	2	Modification of the 50-kW$_{th}$ test unit and installation at NCCC for the field tests		
4	2	Test the skid in a field setting using 50-lb/hr syngas stream from the gasifier at the NCCC and measure membrane performance		
5 & 6	2	• Process technoeconomic analysis (TEA) for ~550 MWe Plant; • Environmental health and safety (EH&S) analysis		
7	2	Decommission the system		

Critical Challenge:
Adapting spinning procedures used for fabricating standard polymeric hollow-fiber membranes to this high-temperature polymer

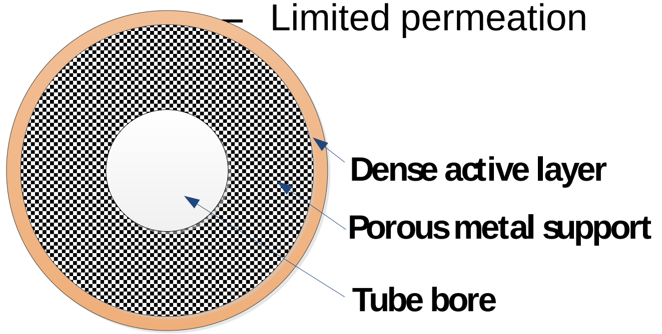
Membrane Architecture

Required membrane architecture for gas separation

- Thin dense layer for gas separation
- Porous support for structural strength to stand high pressures

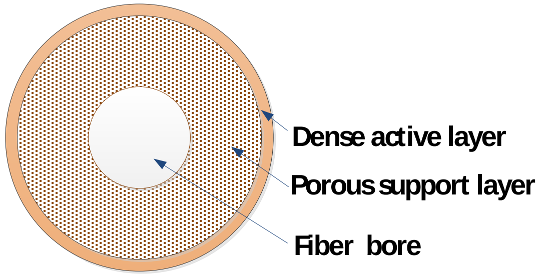
Composite membrane

- Membrane dense layer and porous layer are two different materials (e.g., polymer on porous metal)
  - **Benefits**
    - Ideal for proof of concept
  - **Limitations**
    - High cost of materials
    - Large footprint
    - Limited permeation



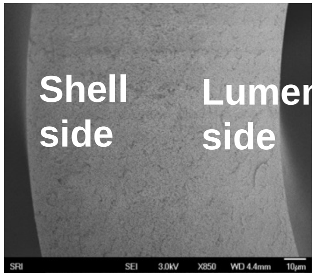
Asymmetric integral structure

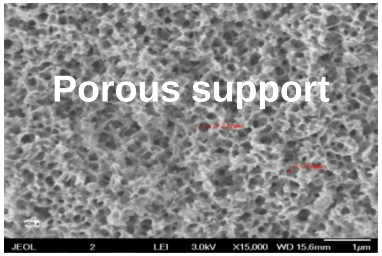
- Fiber is made of one material
  - **Benefits**
    - Low cost
    - Small footprint
    - Easy system scale up
  - **Challenges**
    - Longer fiber-development time

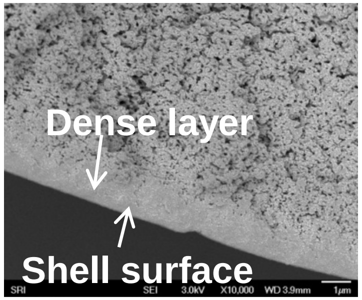


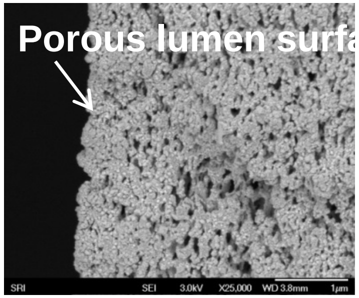
Fibers Developed Under Previous DOE Program

- Development of PBI polymer membrane to replace the original concept that used the PBI-coated porous stainless steel tubes.
- Development of new PBI formulation, installation of a spinning line, and defect free fiber spinning with ~1 µm dense layer (process patent pending).



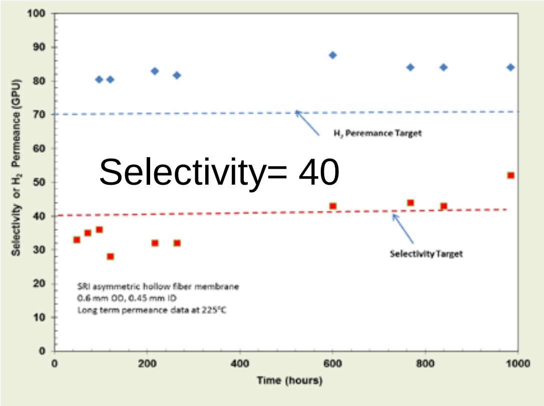




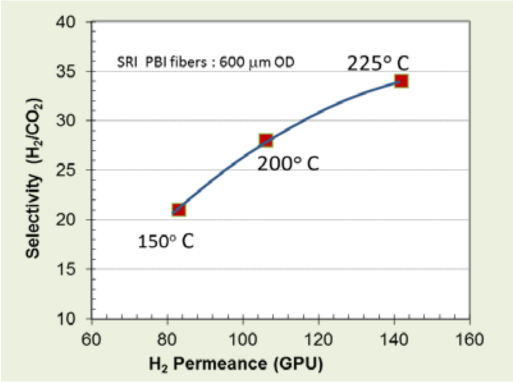


- Membrane stability over 1000 hr was demonstrated.

- H_2/CO_2 selectivities and their permenance data established for 1-µm dense layer.



Measured H_2/CO_2 selectivity and H_2 permeance at 225°C for over 1000 hr.



High-temperature/high-pressure PBI membrane performance for H_2 separation from syngas

A significant achievement in fiber development was made under DE-FC26-07NE43090

Progress and Current Status

Fiber Spinning

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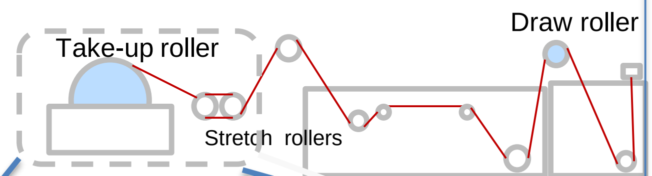
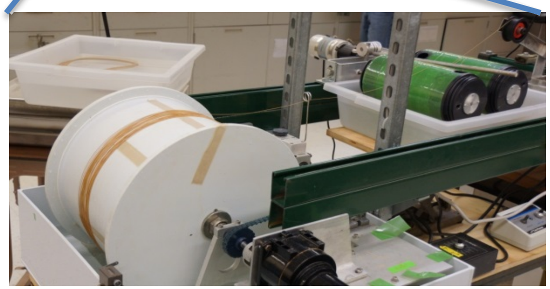
Installation of the second spinning line ~ 1 km/day capacity





Original Spinning System

Second Spinning System

SRI-formulated dope made from commercial PBI (available from PBI Performance Products, Inc.)

1 kg

yields

1 km

Main Focus: Quality Control

Fiber Spinning

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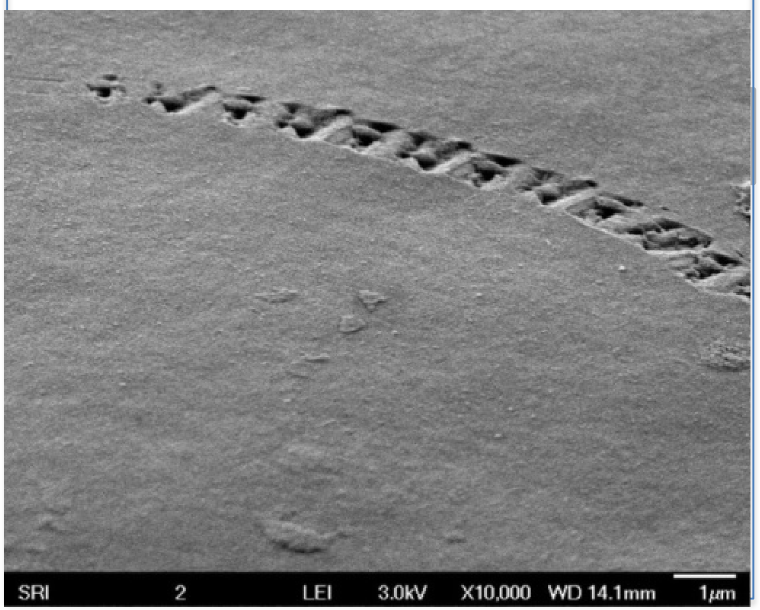
Installation of the second spinning line ~ 1 km/day capacity

Scratch on the fiber surface showing the dense layer and the open porous support structure underneath



Second Spinning System

SRI-formulated dope made from commercial PBI (available from PBI Performance Products, Inc.)

1 kg

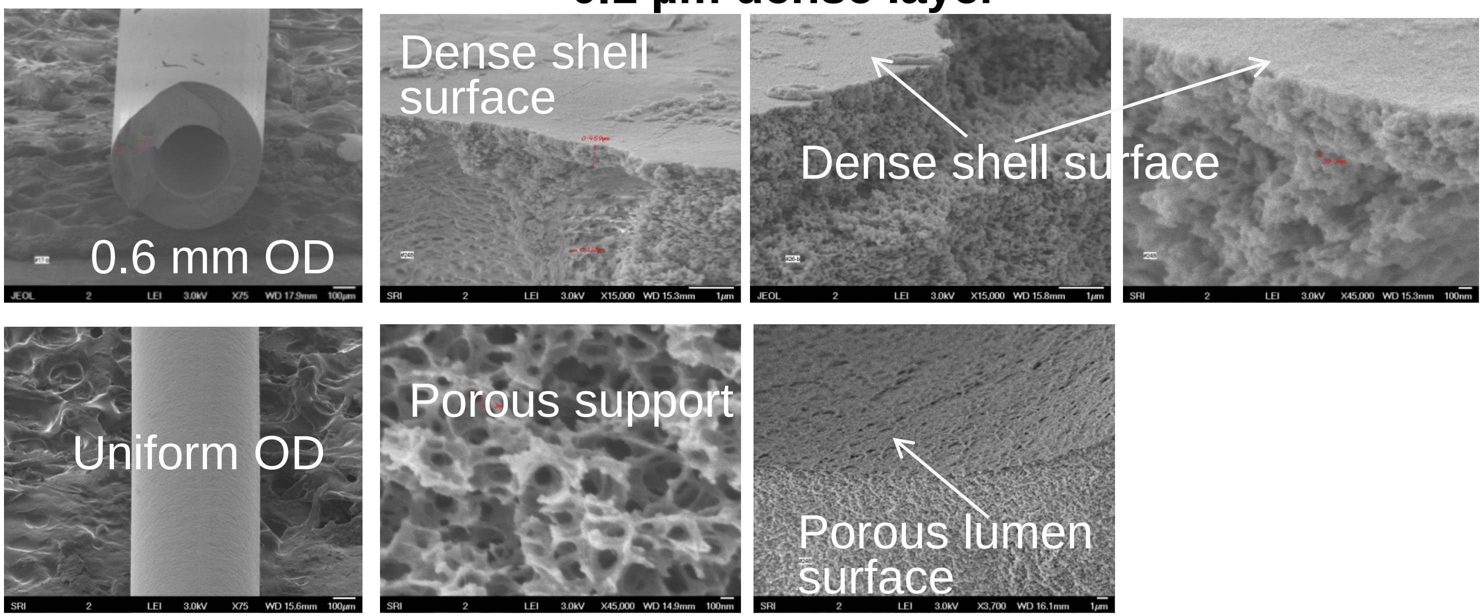
yields

1 km

Main Focus: Quality Control

High-Magnification Pictures of New Fiber Cross Sections

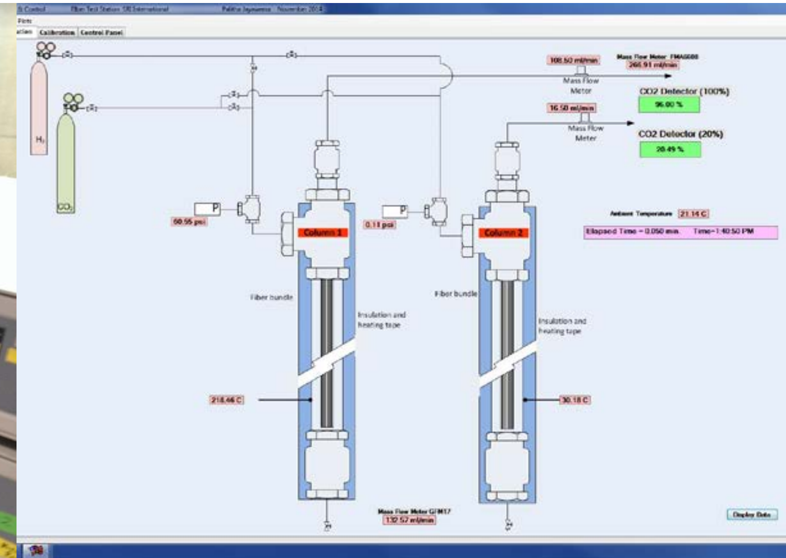
~ 0.1 µm dense layer



- ➢ We have developed protocols for spinning < 0.3 µm micron dense layer hollow fiber membranes with membrane OD 450 to 650 µm. Pictures shown are for ~ 0.1 µm fibers with ~ 600 µm OD.
- ➢ Fabrication of hollow-fiber membrane with a very thin dense layer (< 0.3 µm) in kilometer lengths with very good reproducibility
- ➢ Testing of over 30 1-in fiber bundles for fiber spinning optimization
- ➢ Spinning (>30 km) and shipping of ~ 10 km of fiber to Generon to fabricating a 2-in module for initial testing of the prototype skid

Fiber Performance Testing

Prototype test unit setup at SRI site
~ 1 kW$_{th}$ capacity (~ 0.16 m^2 fiber surface area)



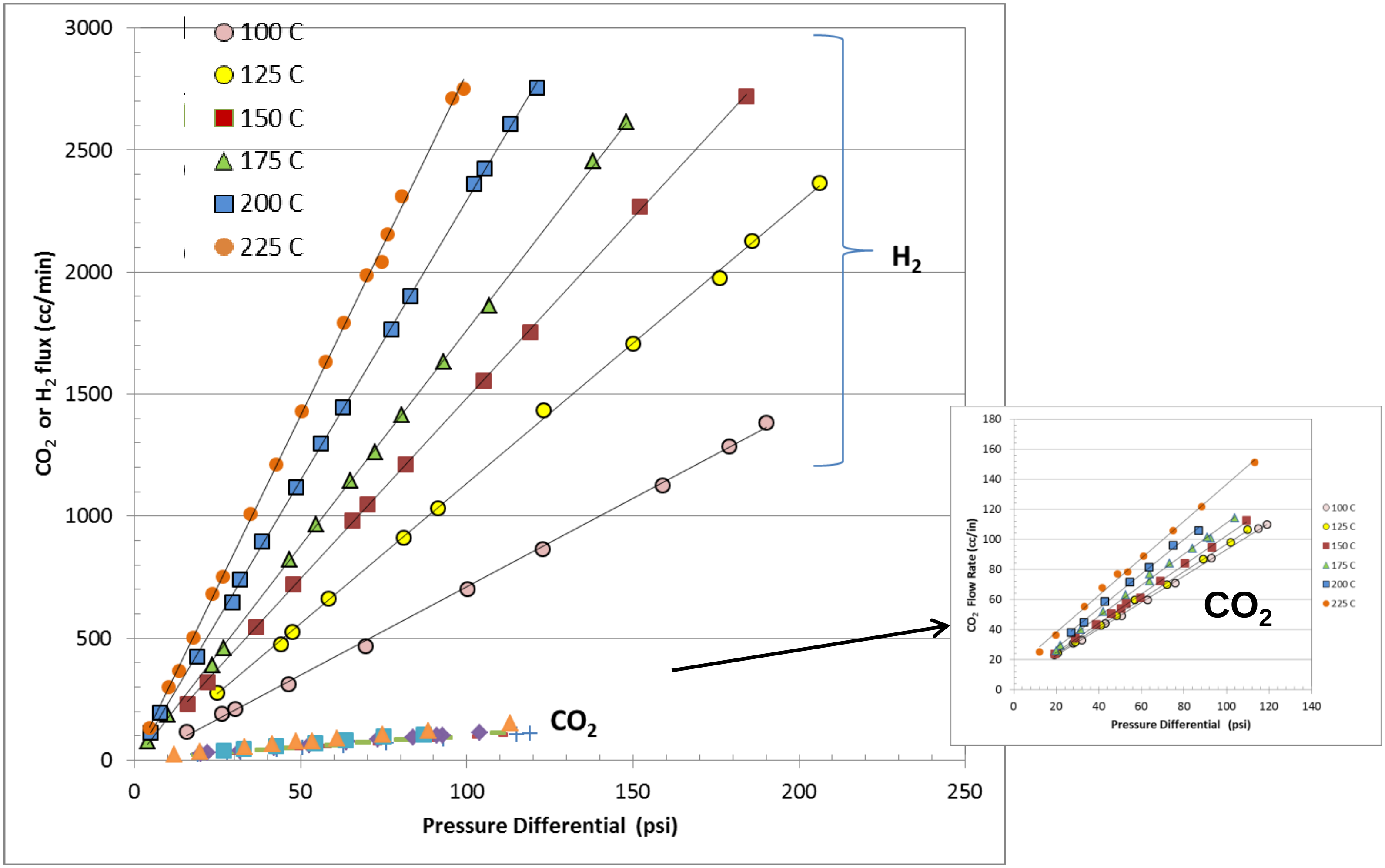
Data acquisition

Feed gas

Potted fiber bundles with 14-in length, 100 fibers, and high packing density

- Single gases tested: CO_2, H_2,CO and N_2
- Gas mixtures tested: CO_2/H_2, $CO_2/H_2/N_2$, $CO_2/H_2/CO$ and $CO_2/H_2/CO/N_2$
- Parameters varied: T, ΔP, composition, stage cut

Gas Permeation Results from Single Gas Testing: Effect of Temperature and Pressure



Measured permeance of H_2 and CO_2 through a <0.3 µm dense layer fiber bundle as a function of temperature and differential pressure.

Single-Gas Testing: Effect of Temperature and Pressure

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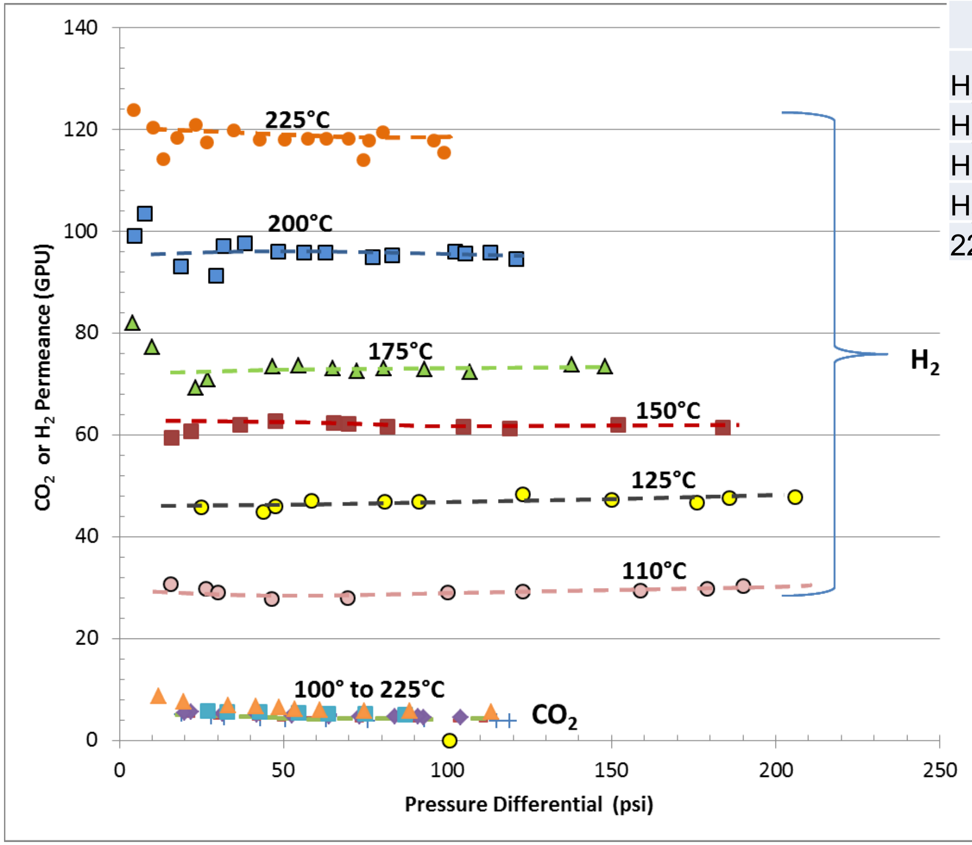
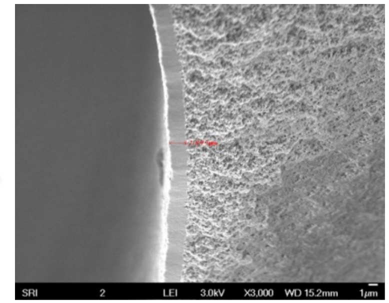


	Selectivity
H_2/CO_2	40
H_2/N_2	98
H2/CO	103
H_2/H_2S	>200*
225 C and 200 psi ΔP	

* Previous work

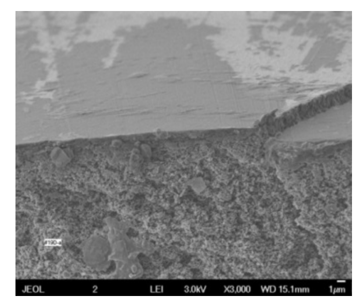


Dense layer ~ 2 μm

H_2/CO_2 selectivity = ~ 40
H_2 permeance = 70 GPU
E_{H2} = 25 kJ/mol

Measured permeance of H_2 and CO_2 through a < 0.3 μm dense layer fiber bundle as a function of temperature and differential pressure. Permeate side at 1 bar

1 GPU =10^{-6} cm^3 s^{-1} cm^{-2} Hg cm^{-1}



Dense layer ≤ 0.3 μm

H_2/CO_2 selectivity = 22 ±2
H_2 permeance = 120 GPU
E_{H2} = 16.1 kJ/mol

Performance monitored over a three-month period with the HFM exposed to -pressure swing at 1 to 15 atm; and temperature swing at 20 ° to 225 ° C.

Mixed-Gas Testing : Effect of CO_2 concentration

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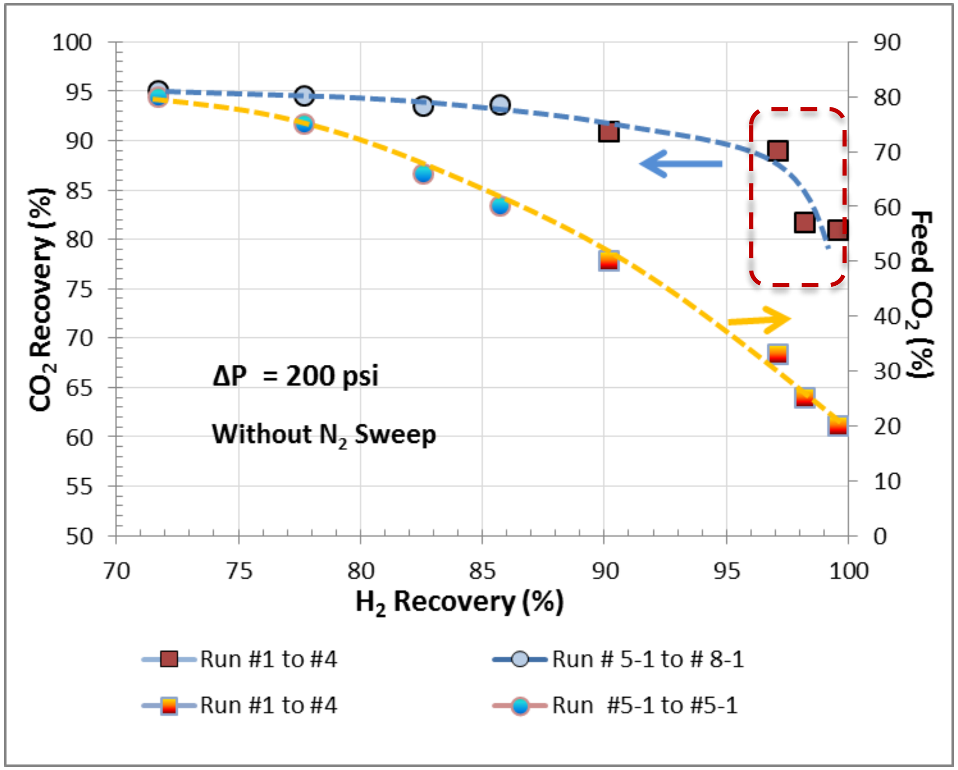
H_2 and CO_2



H_2 recovery and CO_2 capture at varying CO_2/H_2 compositions at 225˚C and at a ΔP of 200 psi (H_2/CO_2 selectivity = ~40)

Observation: >95% H_2 recovery is possible without a cascade

Mixed-Gas Testing: Effect of Selectivity

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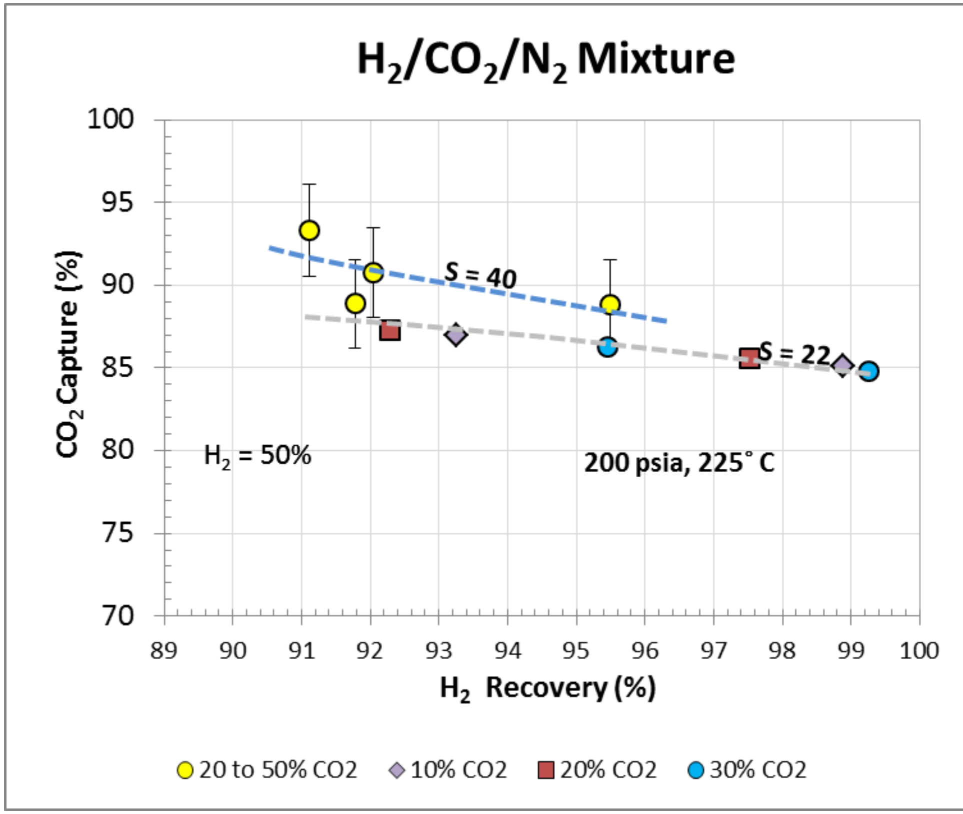
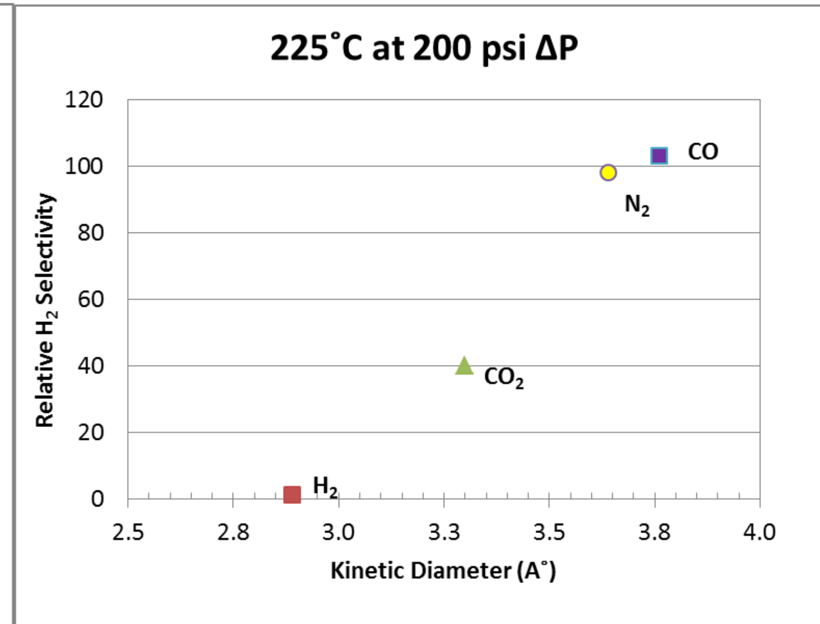




Relationship between H_2 separation factor and the kinetic diameter of the component gases.

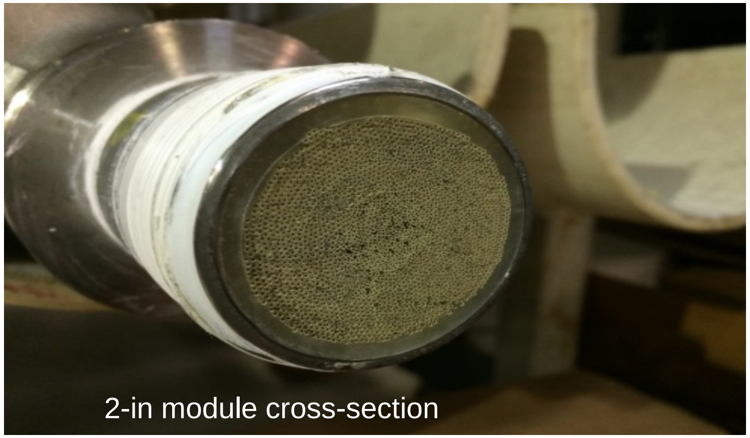
H_2 recovery and CO_2 capture at 225˚C and at a ΔP value of 200 psi (stage cut > 0.5)

Observation:
It is challenging to capture >90% CO_2 at high H_2 recoveries (>95%) with a single element

Fabrication of Large Modules: 2-in Module


Protoype 2-in module


SRI spun fibers (~ 5 km shown)



Actual 2-in module

- **A protocol was developed for potting PBI HFM without dry spots**
- **The method was tested using SRI fibers (1 m^2)**
- **SRI plan to evaluate the performance with H_2O/N_2 mixtures**

Key Findings and Accomplishments

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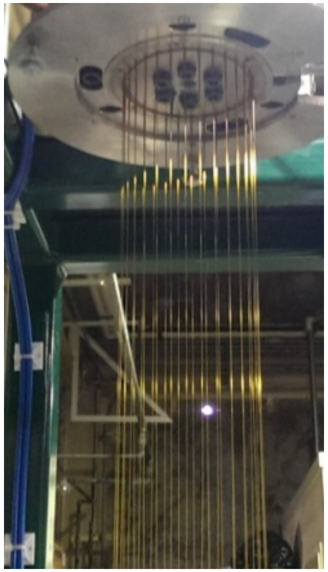
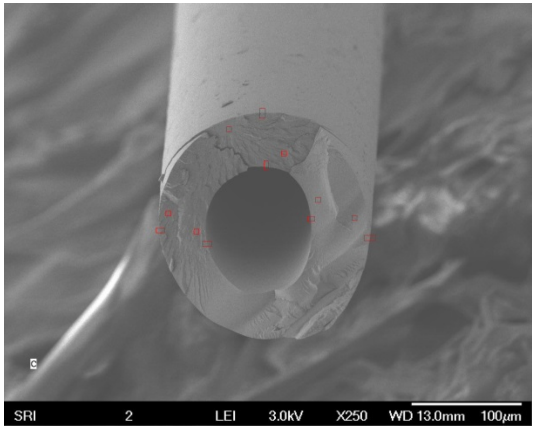
Accomplishments in fiber spinning at SRI have revealed:

- Ways to produce defect-free fibers
- Best use of analytical techniques to determine the trace levels of solvent left in the fibers
- New coagulant for industrial setting



Accomplishments in fiber spinning at Generon:

- Fabricated 150-200 micron OD, 75-100 micron ID, and macro-void free fibers
  - Currently improving the fiber porosity



Accomplishments in fiber module fabrication at Generon:

- Fabricated a 2-in module using SRI fibers
- Completed 4-in module design

Accomplishments in fiber spinning at PBI Performance:

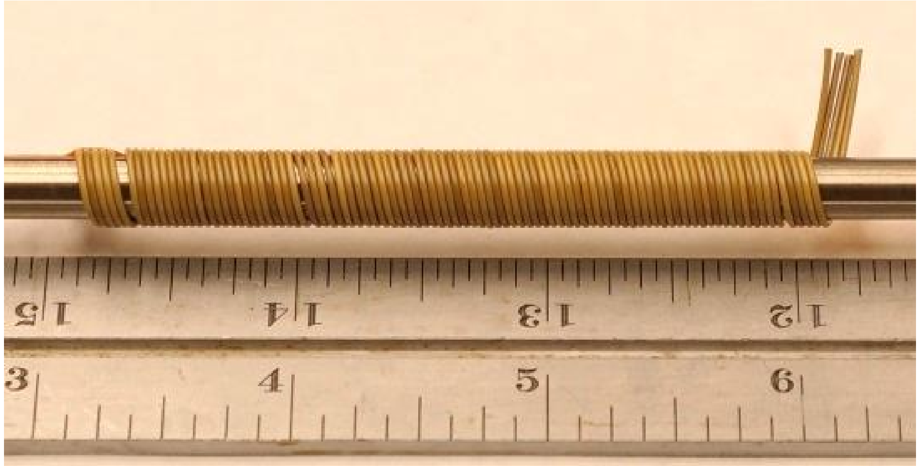
- Produced new formulations for SRI specification in support of Generon and SRI fiber spinning

Lesson learned: Implementation of the spinning technology in an industrial setting requires considerable time.

Key Findings and Accomplishments (Continued)

- PBI HFMs can be produced at km lengths with minimum defects.
- Upper limit for H_2/CO_2 selectivity is ~ 40.
- Practical H_2/CO_2 selectivity for laboratory-scale spun fibers is 20-25 with shell-side dense layer
- Membrane test systems reach steady-state operation very rapidly (within few minutes)
- 50 kW_{th} skid design completed and fabrication contracted
  - Fabrication will be completed in BP2

SRI PBI HFM: ¼-in Mandrel Test



Transition from smaller-module to larger-module testing

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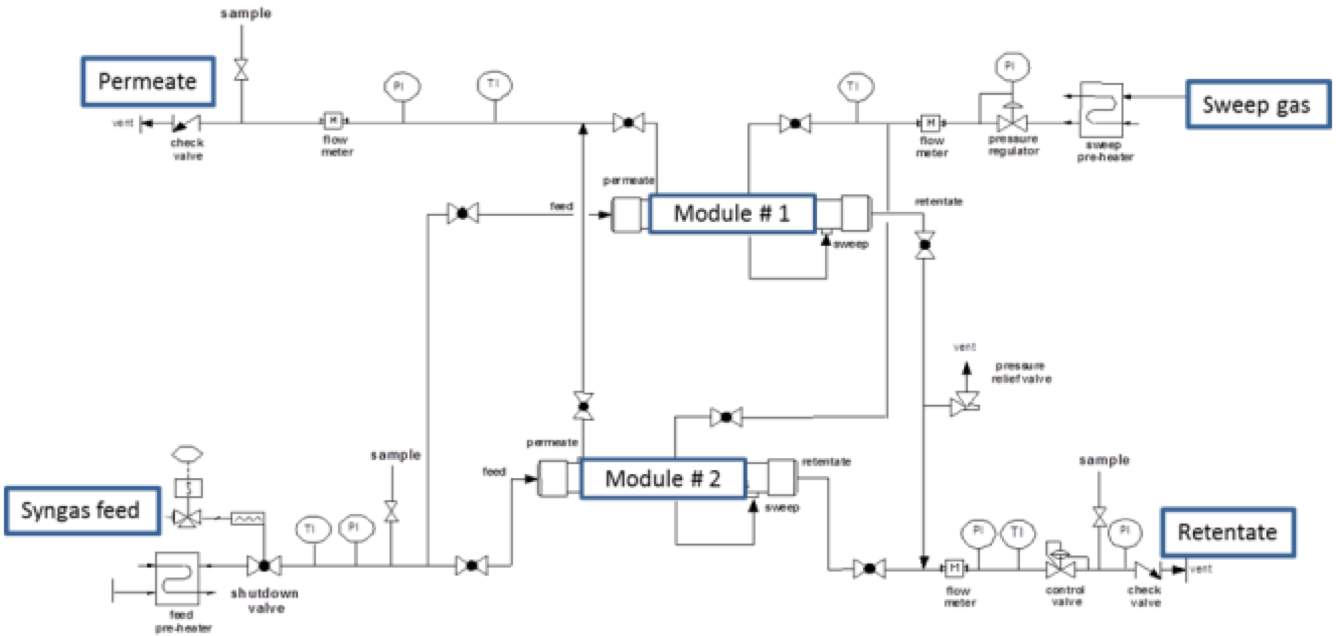
BP1 / BP2

Module Size	Budget Period	Fiber Supplier/ Module Supplier##	Test Site
2-in x 12-in	BP1 and BP2	SRI/Generon	SRI
4-in x 20-in#	BP2	SRI/Generon	NCCC (50 MWth)
6-in x 40-in	BP2	Generon/Generon	NCCC (50 MWth)
#: Module design in BP1, Skid design and fabrication in BP1, Skid update in BP2			
PBI Dope Supplier: PBI Performance Products			

Future Work

Test unit (50 kW$_{th}$) installation and commissioning at NCCC

- Process safety review and Hazard/Operability (HazOp) Study
- Installation of the test unit at NCCC
- Short term and longer duration testing (225 °C, ~ 200 psi)



Membrane Performance Simulation for Field Testing

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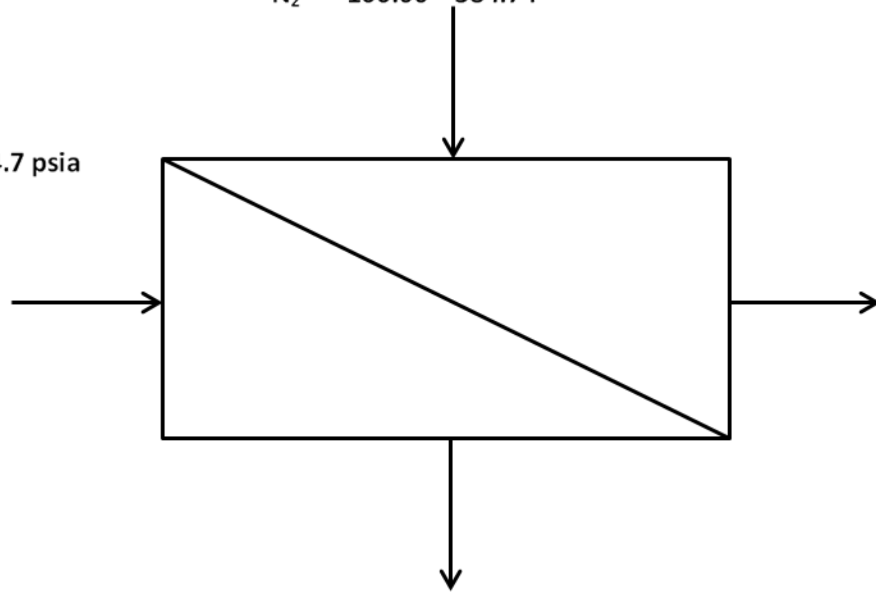
N2 sweep (N2SWP) at 15.1 psia

	%	slpm
N_2	100.00	384.74

Feed (WGSGAS) at 214.7 psia

	%	slpm
CO_2	7.33	44.69
CO	0.87	5.30
CH_4	0.49	2.99
N_2	35.62	217.19
H_2	55.48	338.28
H_2O	0.21	1.28
	100.00	609.73



Permeate (H2FL) at 15.0 psia

	%	slpm
CO_2	0.69	4.96
CO	0.03	0.19
CH_4	0.01	0.05
N_2	0.37	2.63
H_2	44.95	321.73
H_2O	0.17	1.23
N2 SWP	53.78	384.74
	100.00	715.53

Retentate (CO2CAP) at 210.9 psia

	%	slpm
CO_2	14.25	39.73
CO	1.83	5.12
CH_4	1.05	2.93
N_2	76.92	214.56
H_2	5.93	16.55
H_2O	0.02	0.05
	100.00	278.94

Membrane parameters

- H_2 Permeance = 120 GPU
- H_2/CO_2 Selectivity = 25
- Dense layer thickness = 0.3
- Membrane area = 14.6 m^2

89% CO_2 Capture

95% H_2 Recovery

Future Work (continued)

Benchmarked against NETL simulations

Aspen Process Simulation & GT Pro Simulation

Metric of success in meeting program goals

Economic Analysis

< 20% increase in COE

Develop Membrane Performance Targets

New data from current study

Updated COE

Process design and engineering study:

- Determine how the high temperature hollow-fiber PBI membrane process concept would be incorporated into a nominal 550-MWe gasification-based power plant with CCUS.
- Use an IGCC process based on a GE-oxygen-blown gasifier and selexol-based CO_2 removal as the base case.
- Perform the work in collaboration with EPRI

The preliminary estimations show that the CO_2 capture cost for combined process would be ~ \$39 /tonne of CO_2 captured compared to \$52/tonne of CO_2 captured for IGCC with the baseline technology, Selexol.

Acknowledgements

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