Composite Hollow Fiber Membranes for Post Combustion CO_2 Capture

DOE Award: DE-FE0007514

2013 NETL CO_2 Capture Technology Meeting

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Project Team

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GE Global Research

- First U.S. industrial lab
- One of the most diverse industrial labs (over 2000 technologists)
- Founding principle - improve businesses through technology

AMSTC
Ann Arbor, MI

Global Research HQ
Niskayuna, NY

Global Research - Europe
Munich, Germany

China Technology Center
Shanghai, China

Global Software Center
San Ramon, CA

Brazil Technology Center
Rio De Janeiro, Brazil

John F. Welch Technology Center
Bangalore, India

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Project & Team Overview

Project Funding

	Budget Period 1		Budget Period 2	
	10/01/2011–03/31/2013		04/01/2013-09/30/2014	Total
	Total Planned ($)	Total Spent ($) 06/23/2013	Total Planned ($)	($)
GE Global Research	1,097,536	1,243,549	585,394	1,682,930
Western Research Institute	80,777	90,276	42,942	123,719
Georgia Tech	215,922	168,929	186,552	402,474
Idaho National Laboratory	475,000	426,000	264,000	739,000
Total	1,869,235	1,928,754	1,078,888	2,948,123

- 3-year, $3M program, 20 % cost share from GE
- BP-1 date revised by 1Q with no cost extension
- BP-1 tasks & spend rate on-target (<± 5 % deviation)
- Project expected to finish on-budget, on-schedule, delivering on all tasks

Project Summary

- 3-year, $ 3M program, 20 % cost share from GE
- Budget period 1: October 2011 – March 2013 (no-cost extension - June 2013)
- Budget period 2: July 2013 – September 2014

Project Objective: Develop bench-scale thin film coated composite hollow fiber membrane materials and processes for CO_2/N_2 separation in coal flue-gas at 60 °C with at least 90% CO_2 capture with less than 35% increase in levelized cost of electricity

GE Global Research

- Hollow fiber fabrication & characterization
- Module design
- Technical & economic feasibility analysis

Idaho National Laboratory

- Polymer development
- Polymer property optimization
- Coating solution development

Georgia Institute of Technology

- Fiber coating process development
- Effect of fly ash on membranes
- Modeling of key membrane properties

Western Research Institute

- Membrane performance validation in coal flue-gas

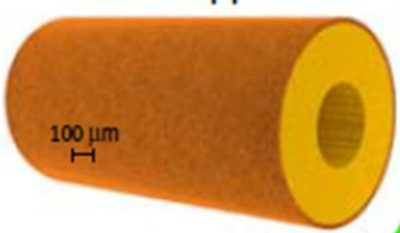
Project Overview

Develop thin film polymer composite hollow fiber membranes & processes for economical post-combustion CO_2 capture

Idaho National Laboratory

High Performance Polymer Coating Solution

High Porosity Hollow Fiber Support

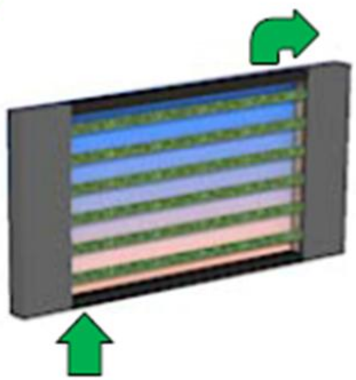


GE Global Research

Georgia Tech Georgia Institute of Technology

GE Global Research

Defect-Free Composite Hollow-Fiber Coating Processes



Georgia Tech Georgia Institute of Technology

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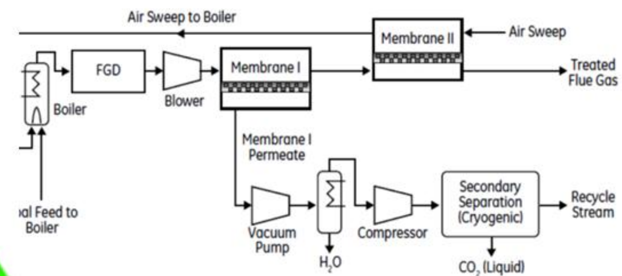
Process and Economic Analysis

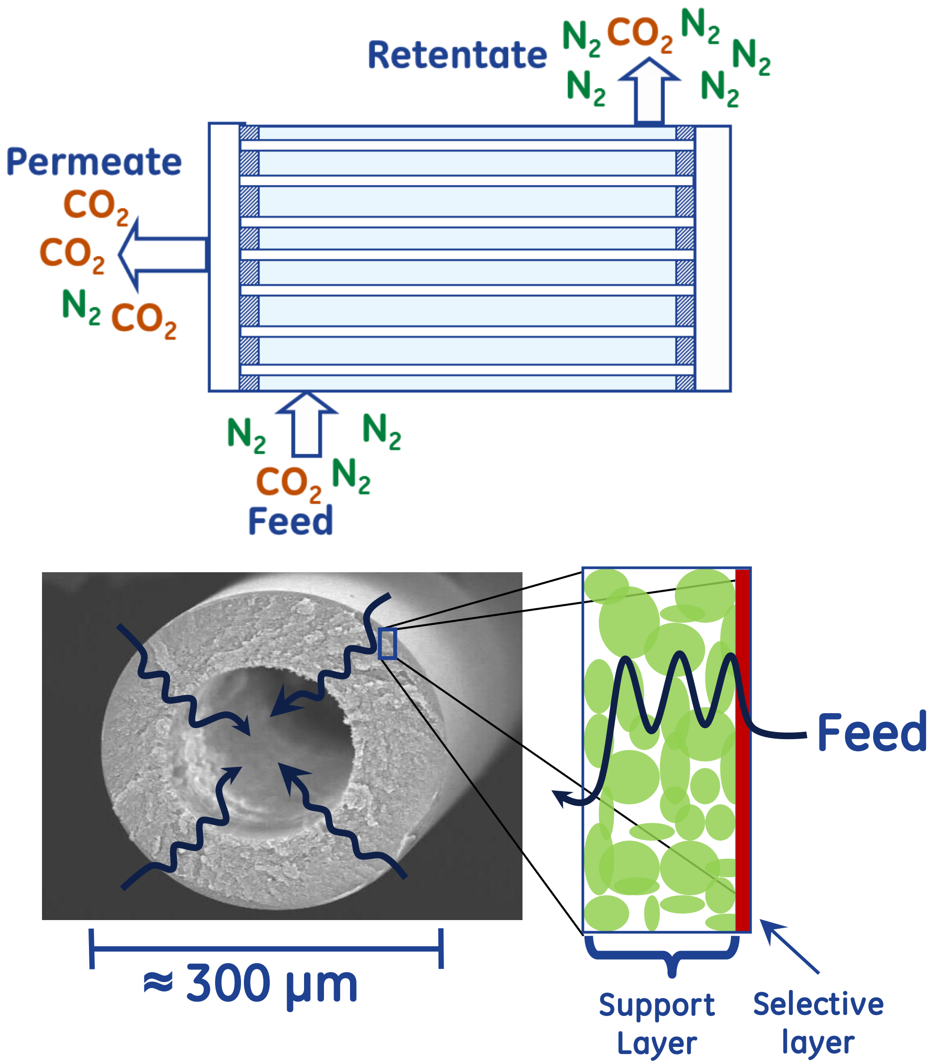


Membrane Testing in Flue Gas

Western Research Institute

Technology Overview

Gas Separations Membrane Fundamentals



Schematic representation of post-combustion CO_2 capture using hollow fiber membranes

Permeance (Productivity)

$$P_{CO2} = D_{CO2} * S_{CO2} = \frac{(\text{Flux})_{CO2} \cdot \ell}{\Delta p_{CO2}}$$

$$\frac{P_{CO2}}{\ell} [=] 1\,\text{GPU} = 10^{6} \frac{\text{cm}^3(\text{STP})}{\text{cm}^2.\text{s.cmHg}}$$

Selectivity (Purity)

$$\alpha_{CO2\text{-}N2} = \frac{P_{CO2}}{P_{N2}}$$

Solution–Diffusion Process

Gases dissolve in and then diffuse through a membrane

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CO_2 Capture Membranes Technology

Key Challenges

Post-Combustion Carbon Capture Technology

- Increase in cost of electricity (COE)
- Low membrane driving force
  - Low CO_2 concentration
  - Low feed gas pressure
- Large feed flow rates
  - Large capture system
- Membrane stability
  - Water vapor
  - SO_2, NO_x
  - Fly-ash

Potential Solution

Hybrid Membrane + Cryogenic Process

- Reduce membrane CAPEX
  - ↓ Membrane module cost
  - ↑ Permeance
- Reduce cryogenic CAPEX
  - ↑ Membrane selectivity
- Increase driving force
  - ↑ CO_2 concentration
  - ↑ Pressure ratio
- Scalable system
  - Composite Hollow fiber membranes
- Robust membrane material
  - Polyphosphazene polymers
  - HF module cleaning methods

Progress & Current Status

Project Activity Schedule

Major Tasks		GE	INL	GT	WRI
Task 1	Project Management	●			
Task 2	Optimize Polyphosphazene Polymer and Coating Solution				
2.1	Produce coating solutions in appropriate solvents		●		
2.2	Adjust Phosphazene cross-linking		●		
2.3	Optimize Phosphazene stabilization		●		
2.4	Refine Phosphazene solution properties		●		
2.5	Optimize Phosphazene performance and coating properties		●		
2.6	Document final results and path forward		●		
Task 3	Fabricate Hollow Fiber Support Layer				
3.1	Produce high porosity hollow fiber supports	●		●	
3.2	Refine hollow fiber spinning process and support material	●			
3.3	Optimize hollow fiber spinning process	●			
3.4	Document final results and path forward	●			
Task 4	Fabricate Composite Coated Hollow Membranes				
4.1	Demonstrate defect-free individual coated hollow fiber	●			
4.2	Adapt fiber coating for "continuous dip coating" process	●			
4.3	Refine continuous fiber dip coating process	●			
4.4	Adapt "in-situ" fiber module coating process			●	
4.5	Refine "in-situ" fiber module coating process			●	
4.6	Reduce coating defects in multi-fiber modules	●		●	
4.7	Create defect-free coated fiber in multi-fiber modules	●		●	
4.8	Conduct preliminary studies on key membrane properties			●	
4.9	Conduct focused studies on key membrane properties			●	
4.10	Refine and develop membrane models			●	
4.11	Document final results and path forward	●		●	
Task 5	Test Membranes at Bench-Scale in Coal Flue Gas				
5.1	Enhance bench-scale testing facilities	●			●
5.2	Coal flue gas performance test to benchmark flat membranes				●
5.3	Coal flue gas performance test composite hollow fiber membrane modules				●
5.4	Coal flue gas performance test optimized composite hollow fiber membrane modules				●
Task 6	Conduct Process Evaluation and Module Design				
6.1	Conduct preliminary technical and economic feasibility study	●			
6.2	Conduct final technical and economic feasibility analysis and EH&S assessment	●			
6.3	Analyze tradeoffs for module designs and flow configuration	●			

Task Owner: GE, INL, GT, WRI — Year 1 (Q1–Q4), Year 2 (Q5–Q8), Year 3 (Q9–Q12)

Legend: ◆ Milestone ▽ Deliverable ◇ Decision Point

Tasks, sub-tasks & ownership inter-linked !!

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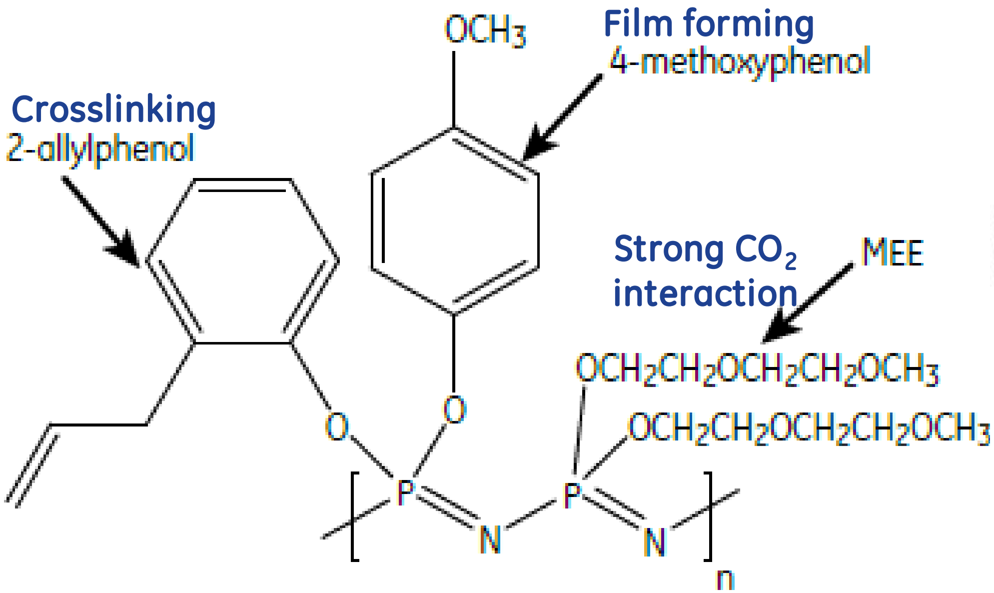
Project Key Objectives

- **Task 1** – Bring together processes, materials & information generated in the project to move the technology towards deployment
- **Task 2** – Synthesize polymer, optimize separation performance & develop easily processable coating solutions
- **Task 3** – Produce highly porous, robust hollow fiber supports
- **Task 4** - Develop processes to apply ultra-thin layer coatings on hollow fiber supports & elucidate fundamental polymer properties
- **Task 5** - Exposure & performance test materials & membranes under coal flue-gas
- **Task 6** - Explore system technical & economic feasibility; conduct module design & fabrication

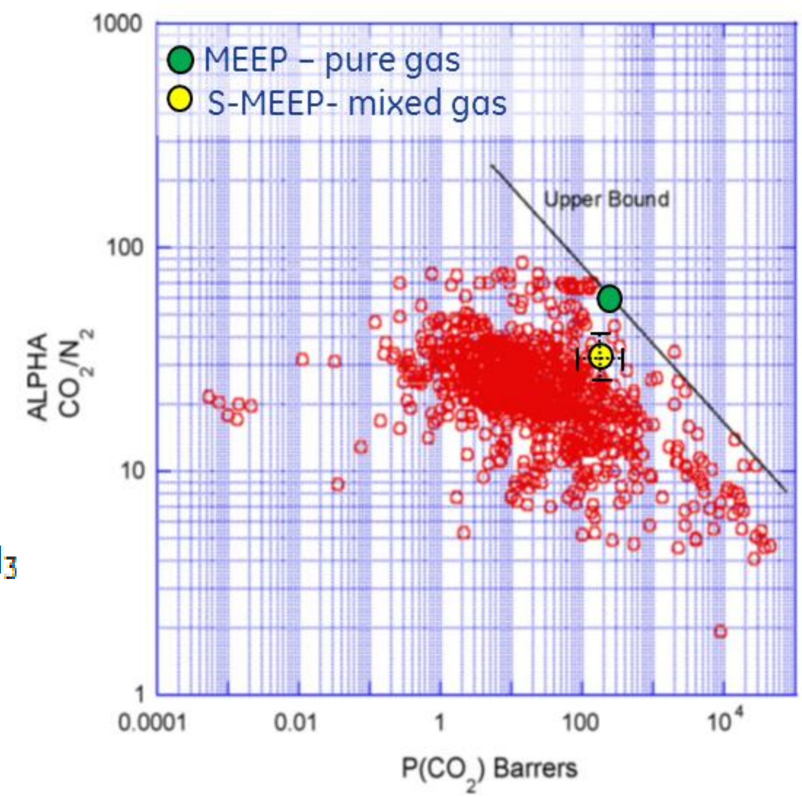
Project BP-1 Report Card

BP-1 Deliverable	BP-1 Status	
CO_2 selective polymer material with P_{CO2} = 200 Barrer, $S_{CO2/N2} \geq 30$	Polyphosphazene materials synthesized with P_{CO2} = 100-300 Barrer, $S_{CO2/N2}$ = 20-40	
Fabricate high porosity hollow fiber supports	Hollow fiber supports fabricated with $P/\ell_{CO2} \approx$ 1,000-20,000 GPU, surface pore size ≈ 20-200 nm	
Develop processes to fabricate defect-free composite hollow fiber membranes	Batch, dip coating (lab-scale); roll-to-roll coating (bench-scale) processes developed. Defect-free 10” membrane modules fabricated.	
Demonstrate stable performance under realistic flue-gas conditions	Hollow fiber membrane module tested under realistic flue-gas mixture. $S_{CO2/N2}$ = 25-30. P/ℓ_{CO2} < 50 GPU. Membrane ageing observed.	
Preliminary techno-economic analysis study	Membrane systems model developed using Aspen Plus® & Aspen Custom Modeler®	

Polyphosphazene Materials



General structure of stabilized (methoxyethoxy) ethanol phosphazene (MEEP)



Permeability-selectivity plot for CO_2/N_2 gas pair*+

- Low T_g polymers with good CO_2 separation & permeability
- Polymer properties tuned for hollow fiber coatability

* L. M. Robeson, The Upper Bound Revisited. J. Membr. Sci. 2008, 320, 390
+C.J. Orme, M.K. Harrup, T.A. Luther, R.P. Lash, K.S. Houston, D.H. Weinkauf, F.F. Stewart, Characterization of gas transport in selected rubbery amorphous polyphosphazene membranes, J. Membr. Sci. 186 (2001) 249

Polyphosphazene Materials

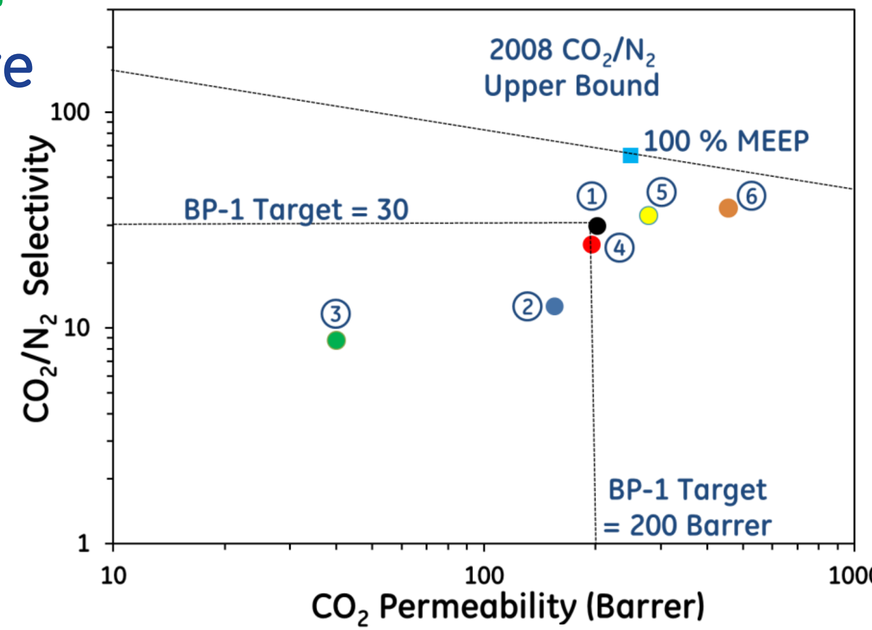
Compatibility
- Solubility in solvents benign to hollow fiber supports

Properties
- Improve physical handling
- High MW to reduce support infiltration

Performance
- Achieve target permeability & selectivity
- Long term stability

X-linking Mech.
- Maintain dimensional integrity

- Desired polymer characteristics are inter-dependent
- Polymers developed to meet BP-1 targets
- Characterization using NMR, DSC, TGA, permeation testing



Permeability-selectivity plot for CO_2/N_2 at 30 °C (Pure gas-Flat sheet))

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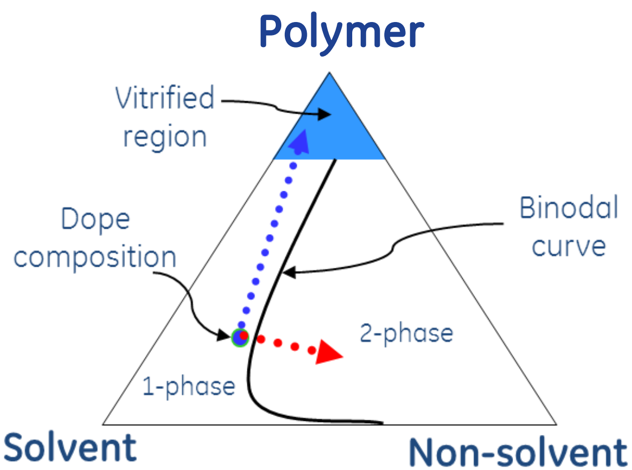
Hollow Fiber Support Layer

Spin Dope Development → Fiber Spinning → Fiber Processing

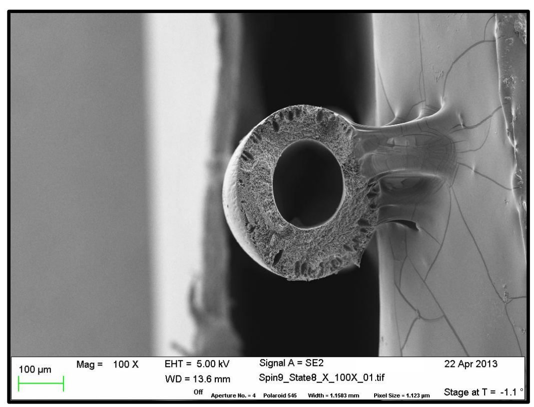


Three phase diagram

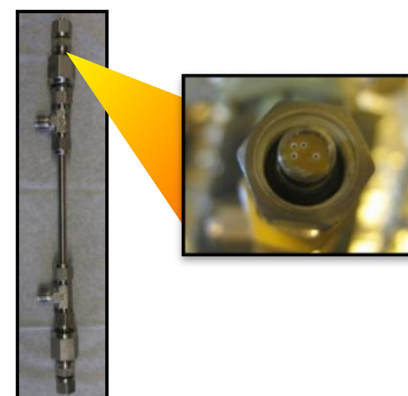
Hollow fiber extrusion process

Fiber solvent exchange process

Spin dope development

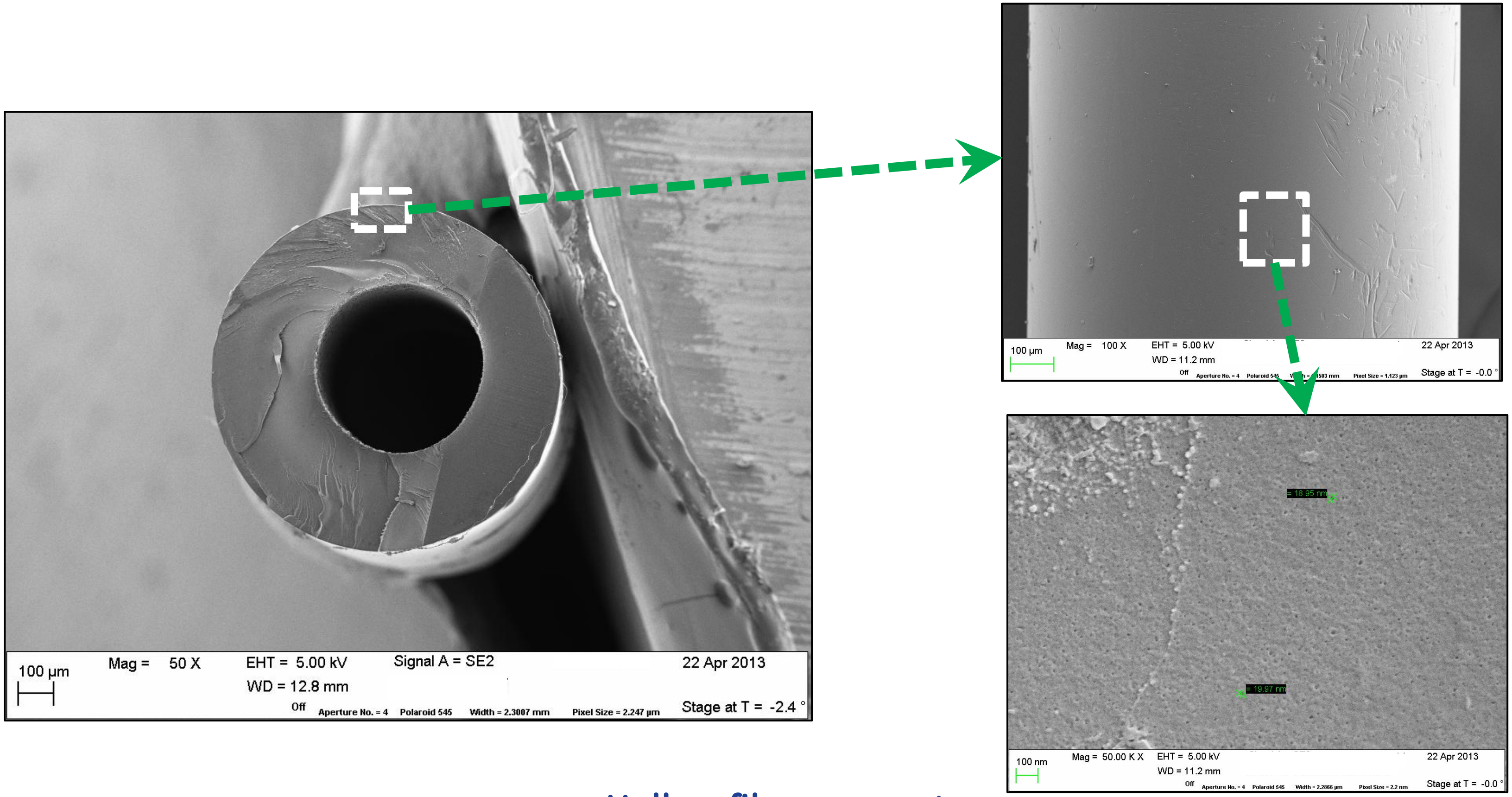


Hollow fiber supports



Hollow fiber module

Hollow Fiber Support Layer



Hollow fiber supports

- Porous, low cost, hollow fiber supports fabricated & spinning parameters optimized
- CO_2 permeance =1,000-20,000 GPU; surface pore size = 20-200 nm

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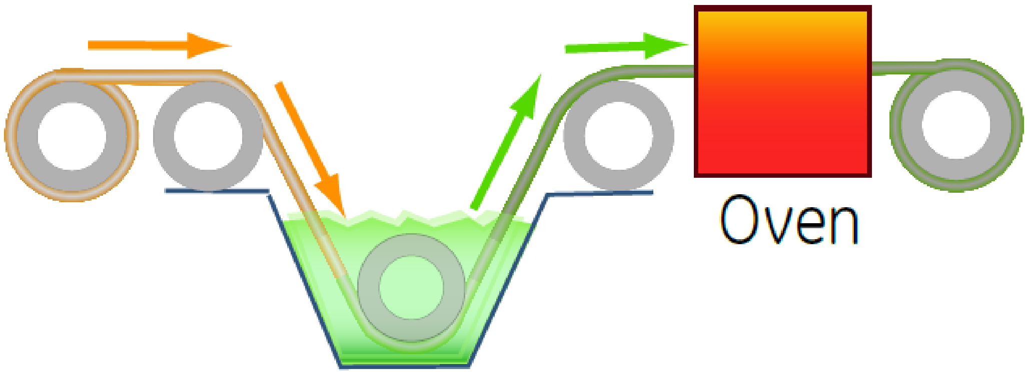
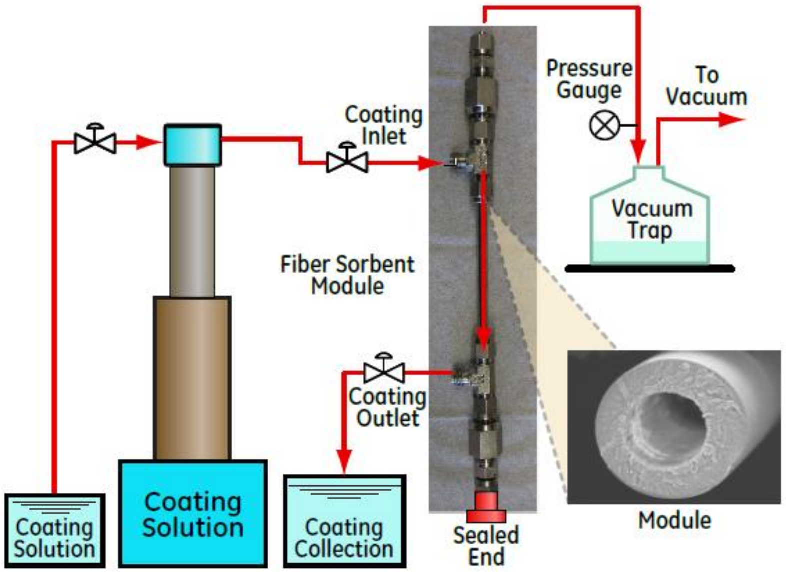
Composite Hollow Fiber Fabrication



Continuous 'roll-to-roll' coating process



Batch 'repair' coating process

- Key factors affecting HF support coatability
  - Reduced surface pore size
  - Substrate pore uniformity
  - Reduced physical handling
- Defect-free membrane modules fabricated & studied for long term performance testing

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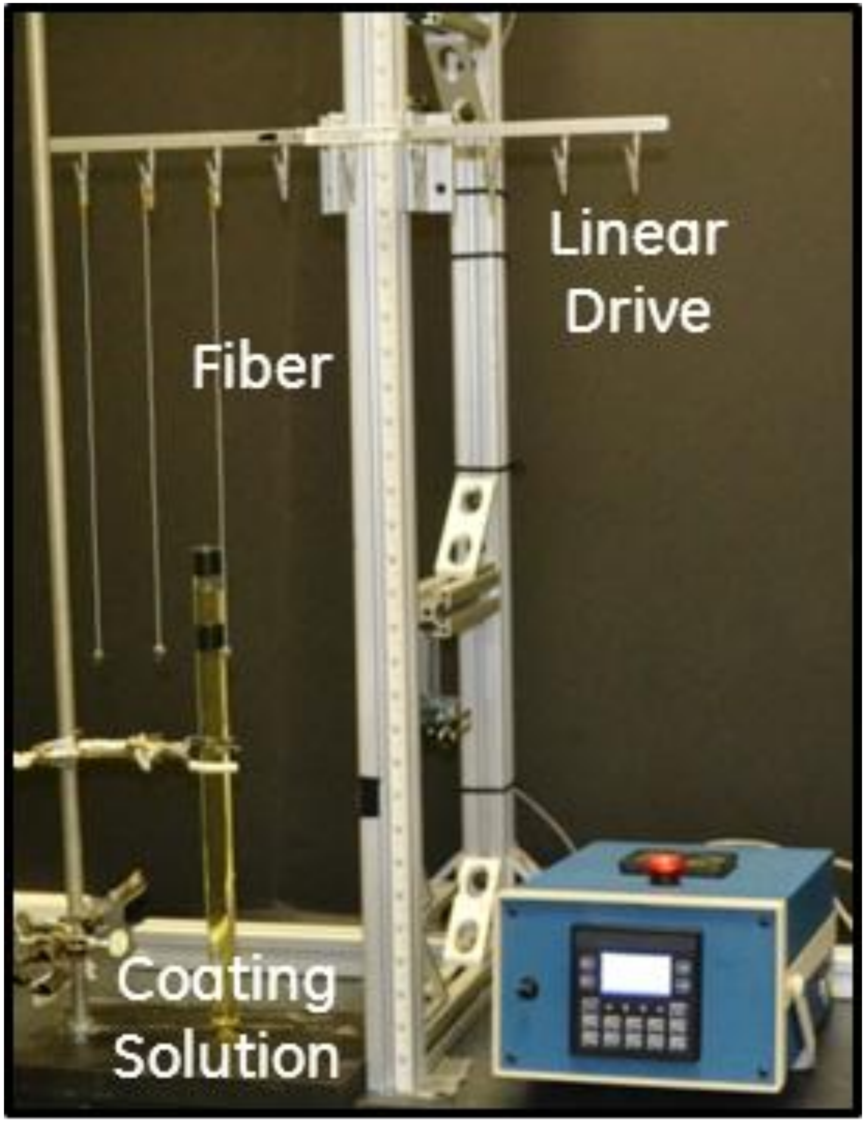
Linear Dip Coating Process



Linear dip coater

Batch Coating Process

Batch coater

Coating solutions

HF modules

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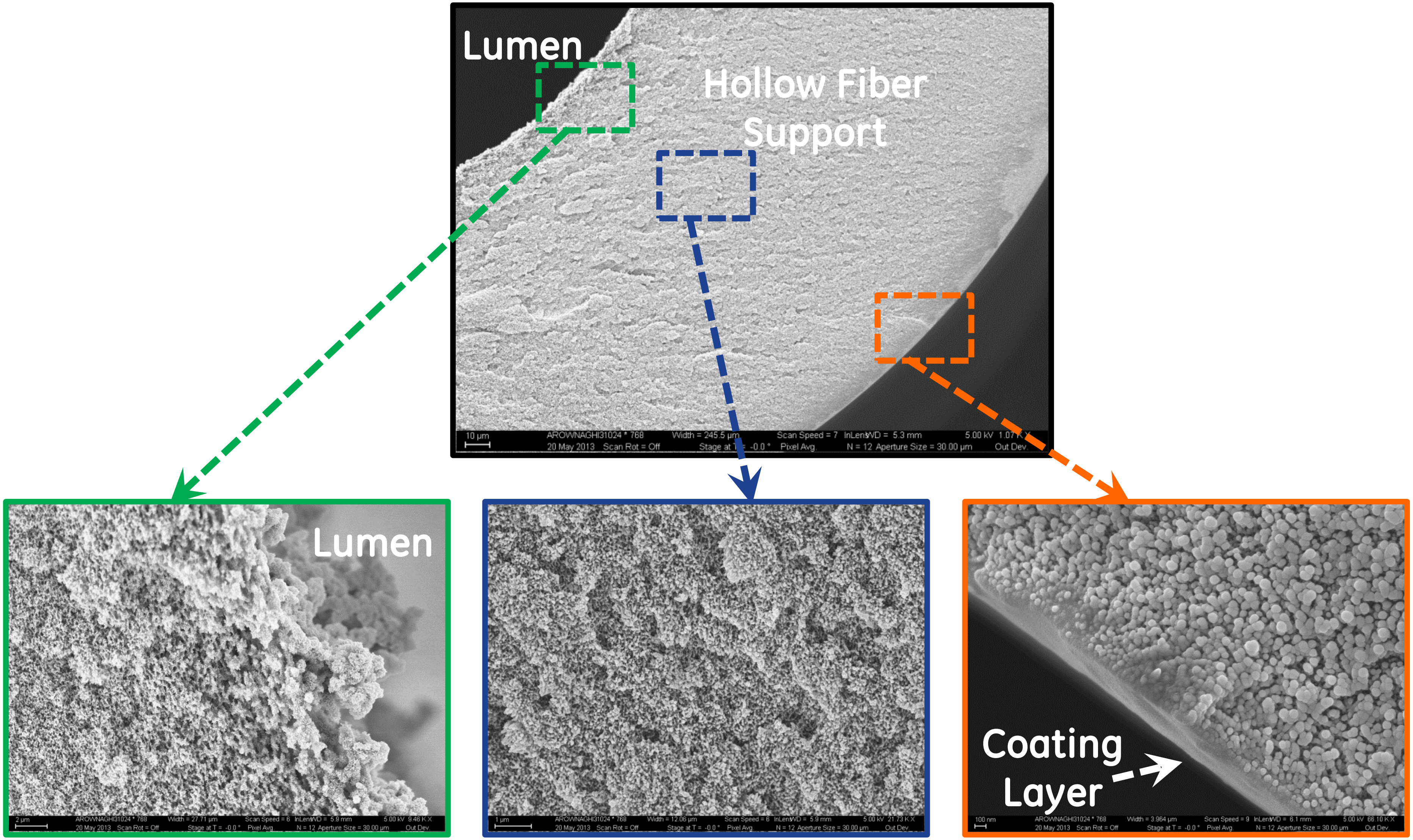
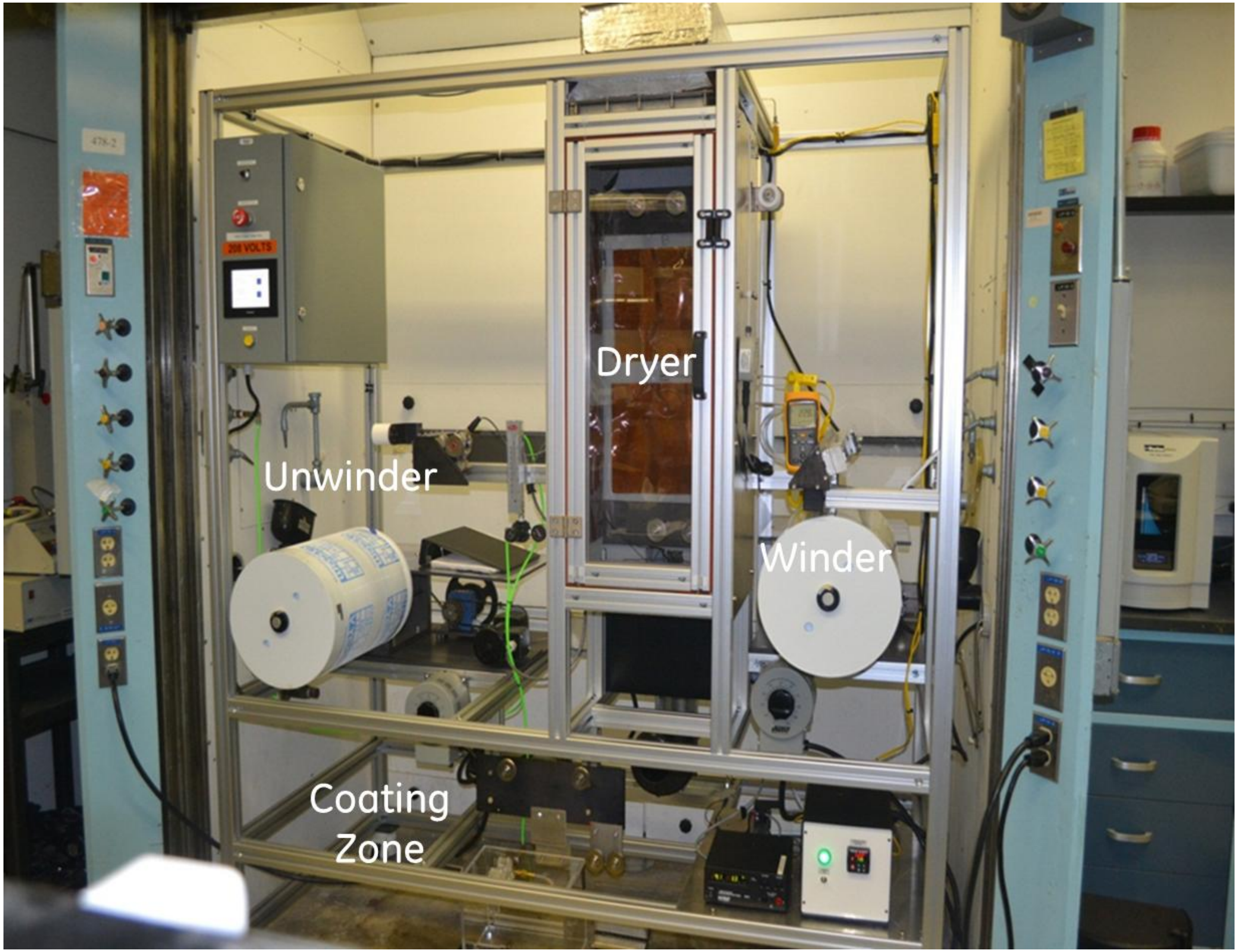
Composite Hollow Fiber Morphology



Composite hollow fiber membrane

Continuous 'Roll-to-Roll' Coating Process



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Membranes Testing

WRI flue gas membrane testing rig (flat sheet & HF modules)

- HF membrane mini-modules (10" length) performance tested for >100 hours under realistic flue gas mixture: $N_2/CO_2/O_2/NO/SO_2$ - 80/15/5/80 ppm/50 ppm (vol. %) saturated with water vapor

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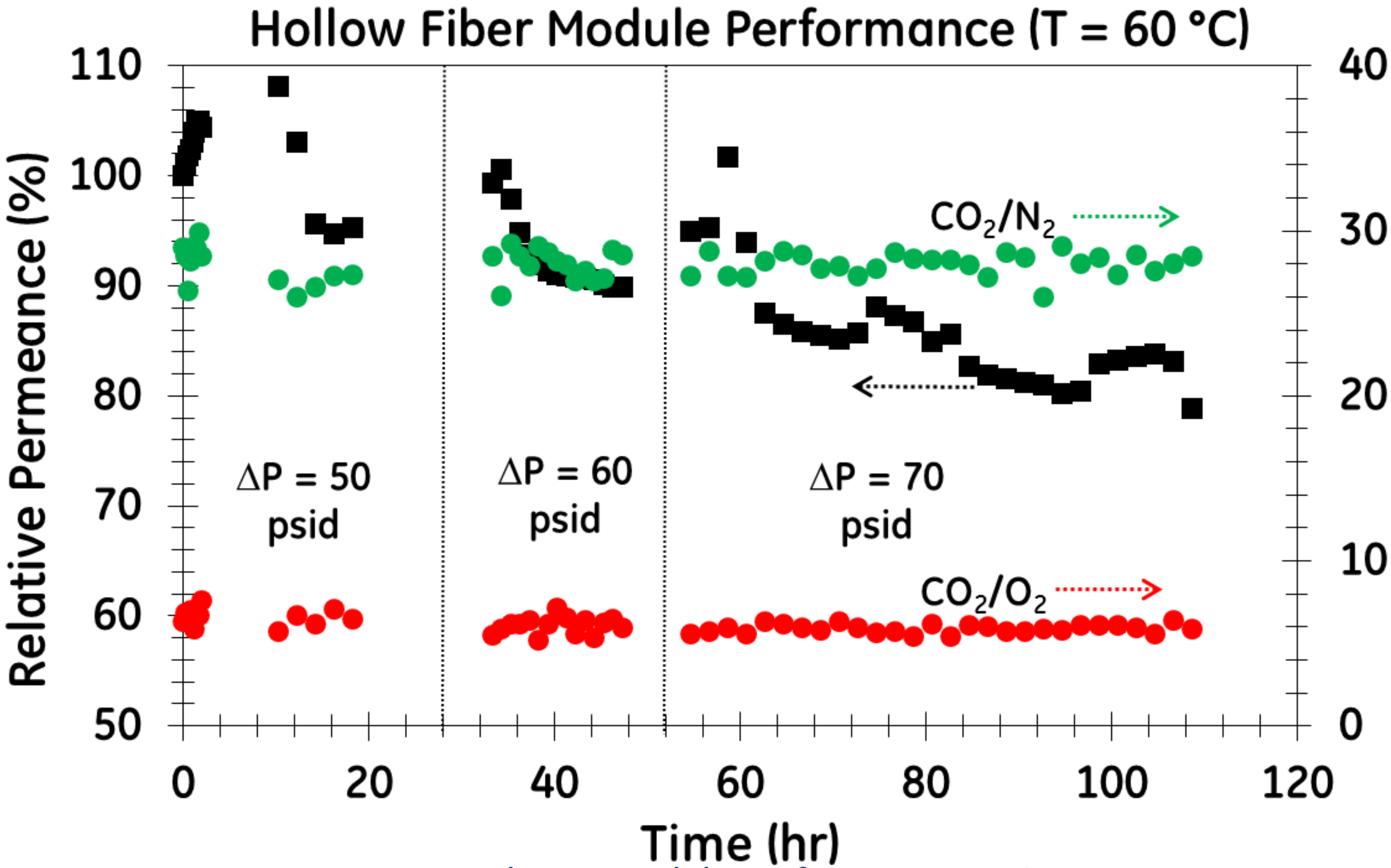
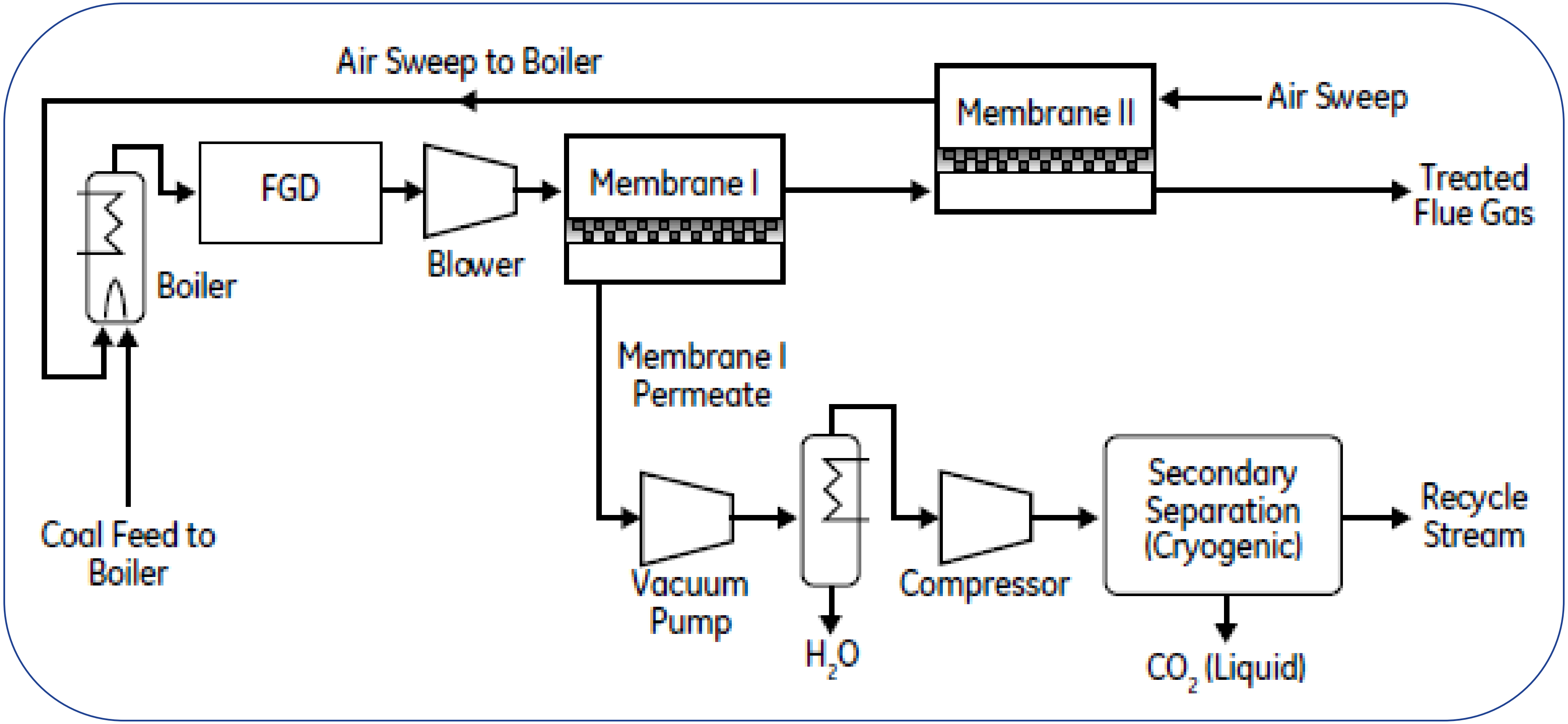
HF Membranes Testing



HF membrane module performance testing

- Hollow fiber membrane module selectivity found to be stable, however; reduction in permeance observed

Membrane Systems Considerations



Schematic representation of the membrane process*

- Various membrane process designs considered
- Two stage membrane process shortlisted for further discussion

*Adapted from Merkel, Tim C., et al. "Power plant post-combustion carbon dioxide capture: An opportunity for membranes." Journal of Membrane Science 359.1 (2010): 126-139.

Membrane Systems Considerations

Parameter	Values
Membrane-I/Membrane-II	Vacuum/air sweep
Flue gas composition	DOE baseline case 11* $CO_2/N_2/H_2O/O_2$(vol.%) 13.53/68.08/15.17/2.40
Flue gas flow rate	540 m^3/s
Flue gas pressure	1.2-3 Bar
Flue gas temperature	45 °C
Membrane Selectivity (CO_2/N_2)	30-80
Membrane Permeance	100-2500 GPU

Summary of economic model assumptions

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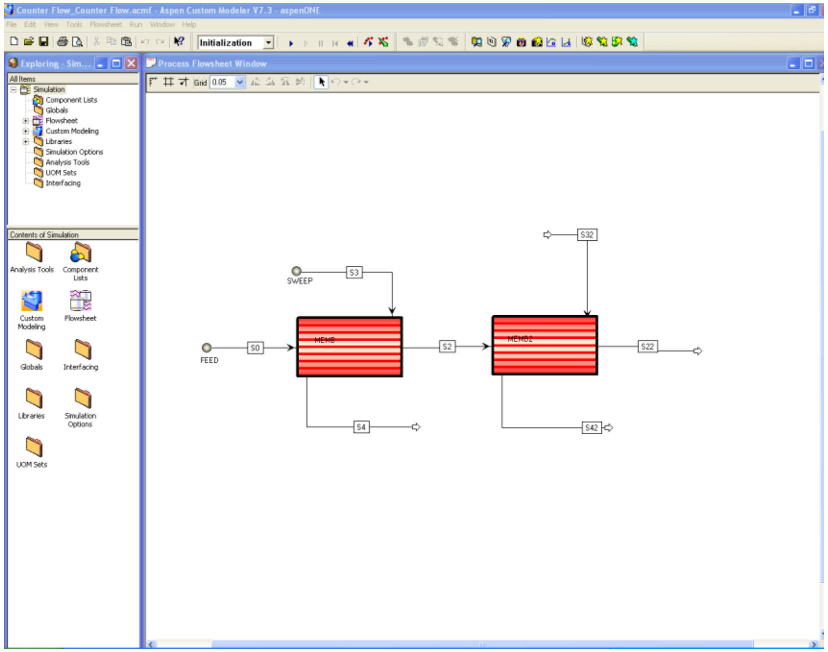
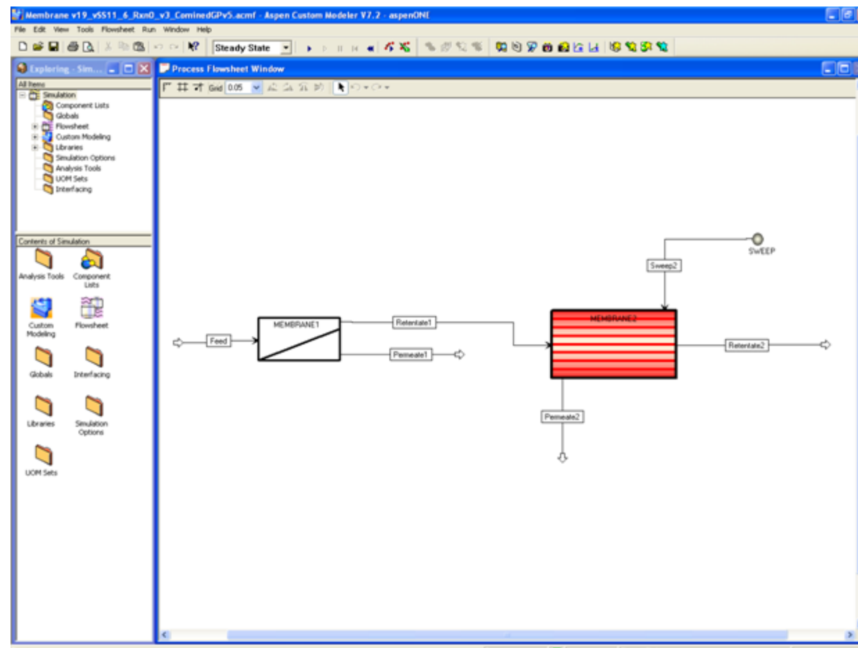
*Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity, Revision 2, November 2010.,DOE/NETL-2010/1397

Membranes Systems Model



Aspen custom model® of counter-current/counter-current membranes



Aspen custom model® of cross-current/counter-current membranes

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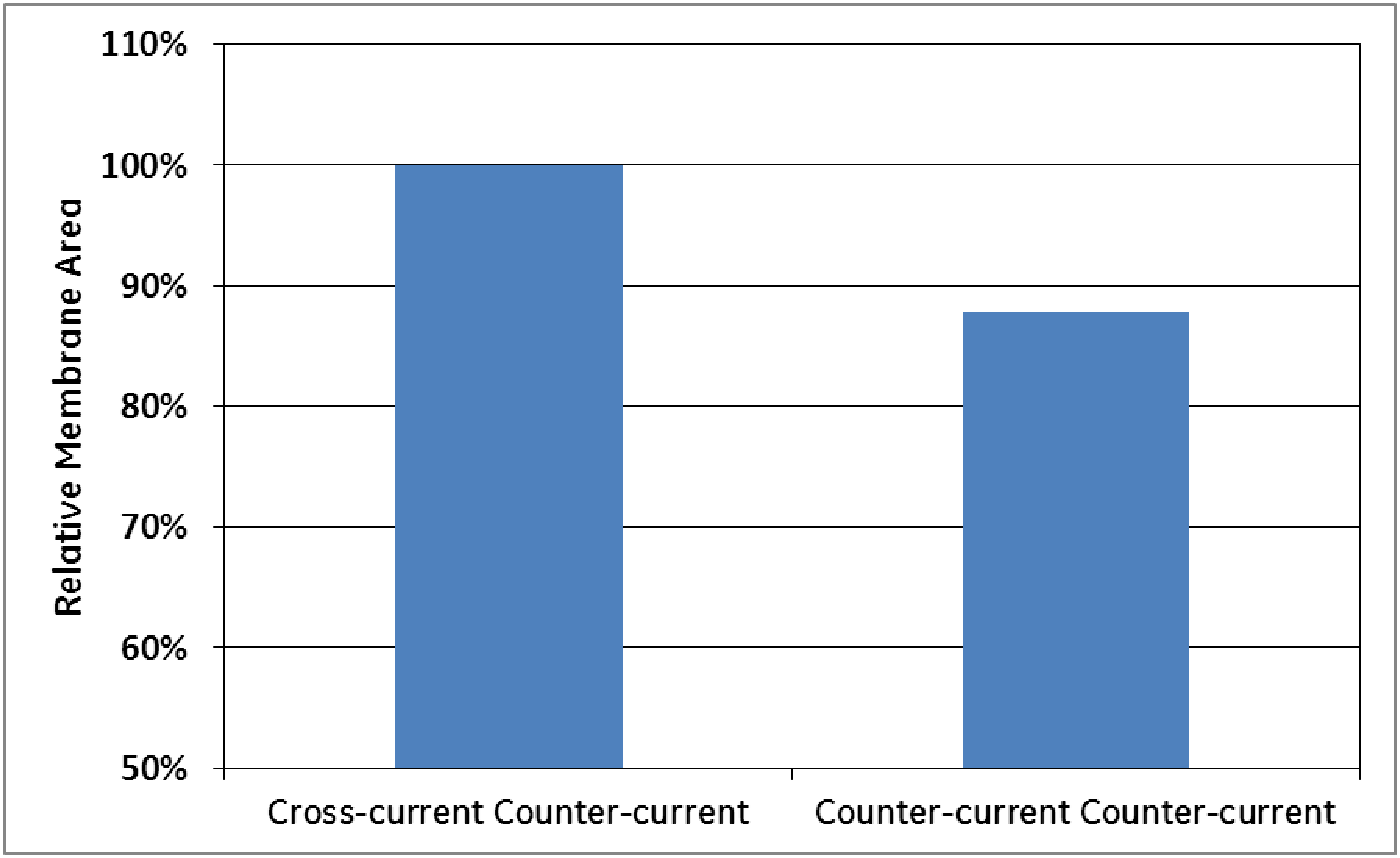
Membranes Model Analysis



Comparison of membrane configurations

- Counter-current/counter-current configuration preferable

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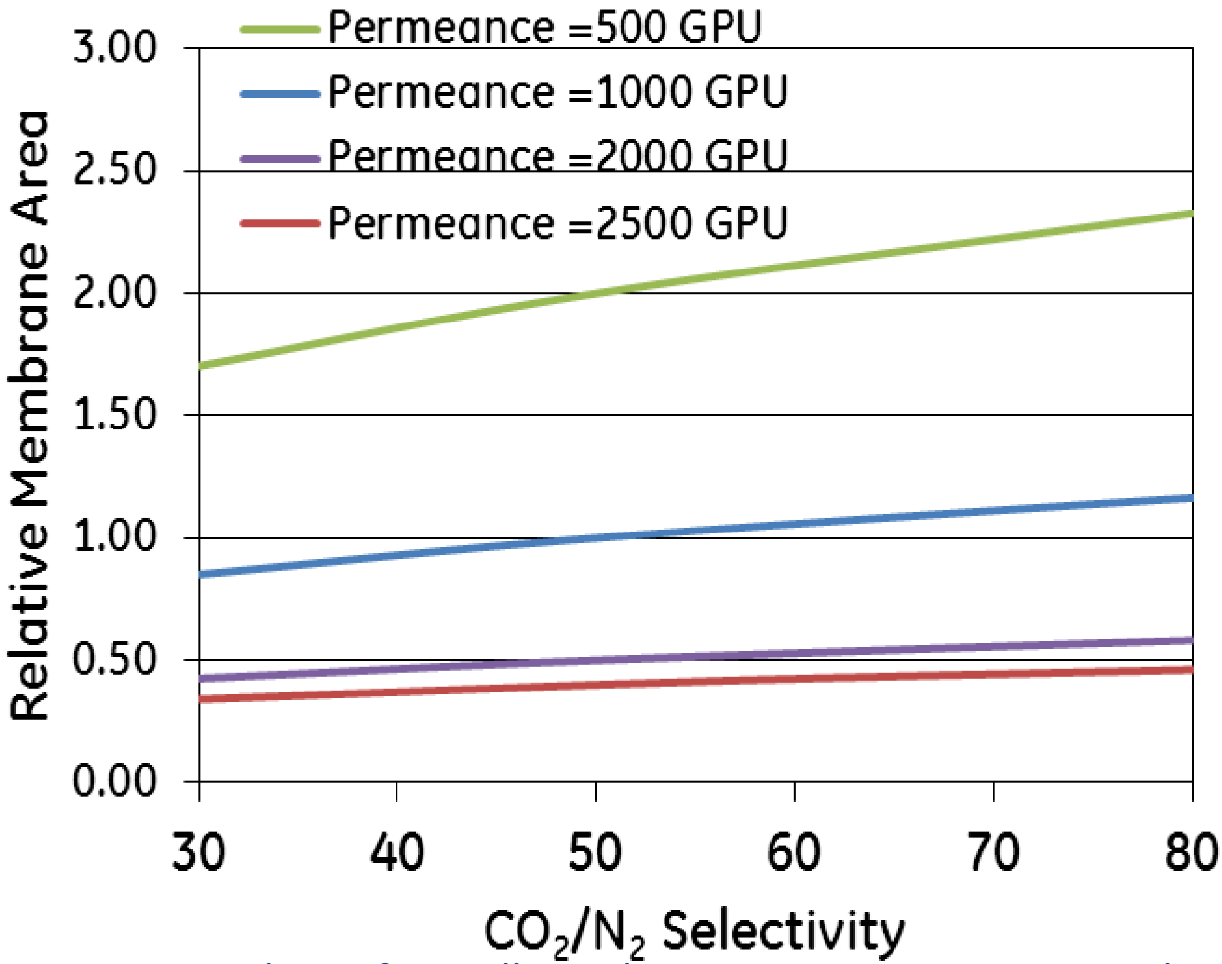
*Assumptions – Membrane-I pressure ratio = 10, Selectivity$_{CO2/N2}$= 50, Permeance$_{CO_2}$ = 1000 GPU

Membranes Model Analysis

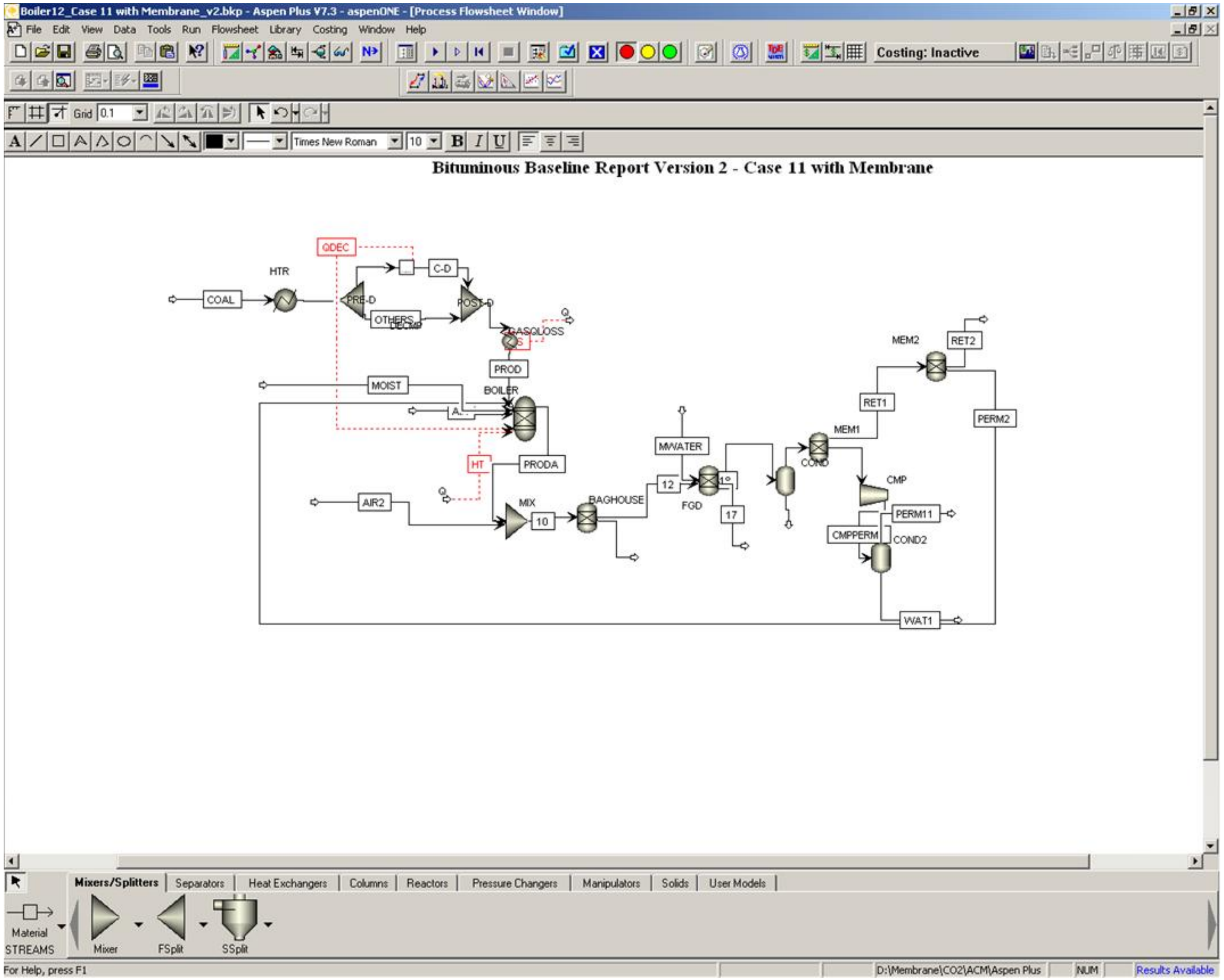


Sensitivity analysis of overall membrane area to permeance & selectivity*

- Overall membrane area highly dependent on permeance and mildly on selectivity in the selected range

*Assumptions – Counter/counter-current membranes, membrane-I pressure ratio = 10

Overall Membranes System Analysis



Aspen Plus® systems model of PC-boiler integrated with CO_2 capture membranes model

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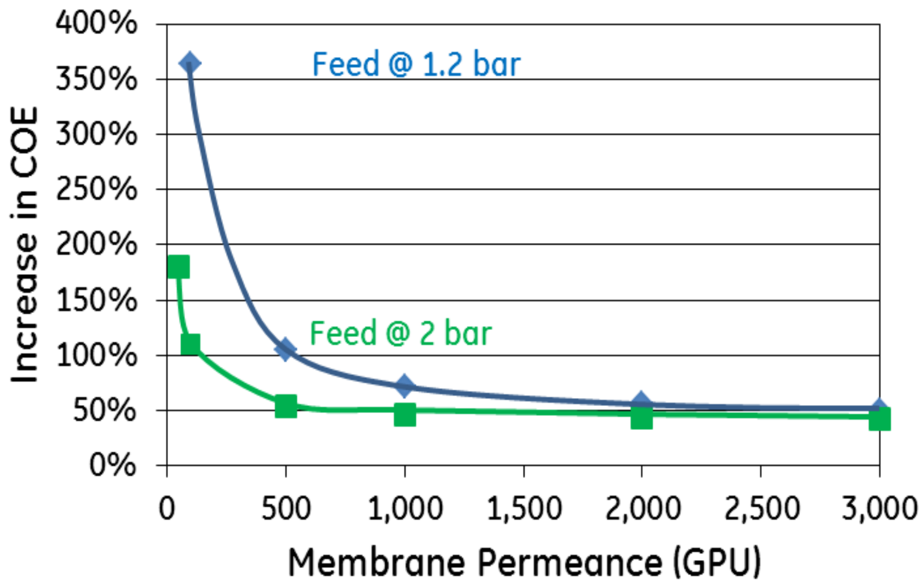
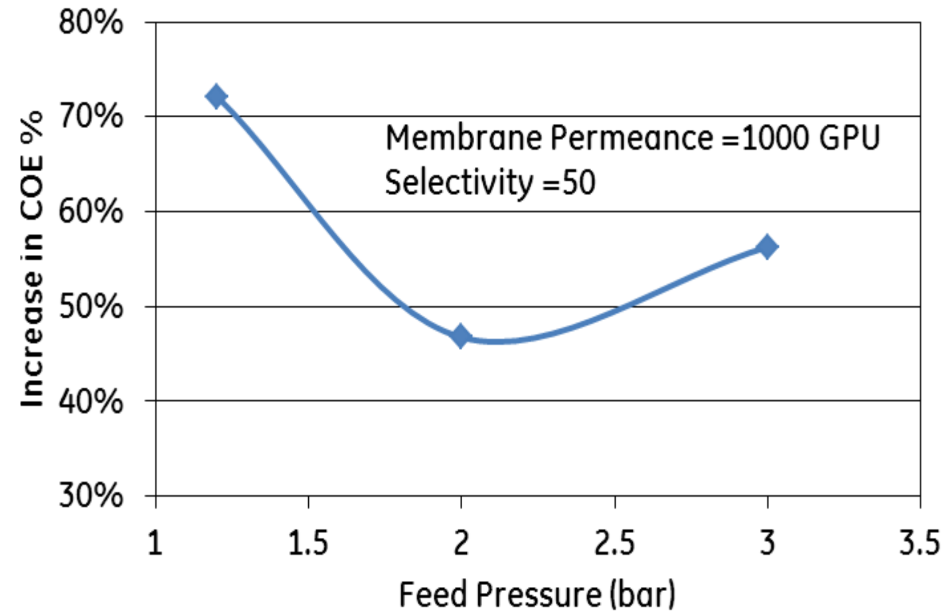
Membrane Process COE Analysis



Sensitivity analysis of increase in COE with membrane permeance



Sensitivity analysis of increase in COE with membrane feed pressure

Increase in COE

- Decreases with increase in membrane permeance in the lower range, plateaus at higher permeance range
- Minimum at ~2 bar feed pressure

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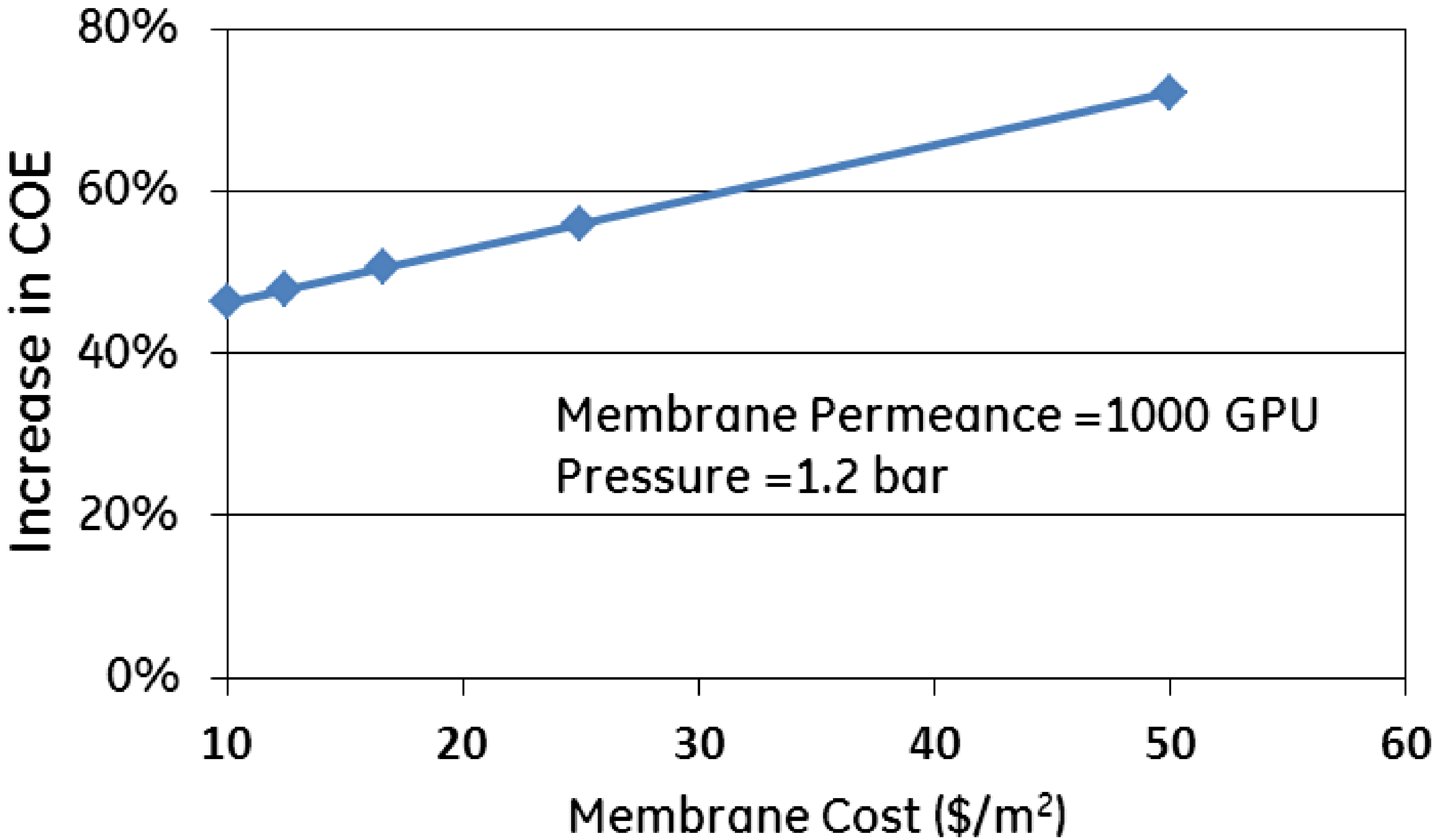
*Assumptions – Counter/counter-current membranes, Membrane-I pressure ratio = 10, Selectivity $_{CO2/N2}$ = 50

Membrane Process COE Analysis



Sensitivity analysis of increase in COE with membrane module cost ($/m²)

Increase in COE

- Decreases with decrease in membrane module cost

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*Assumptions - Counter/counter-current membranes, selectivity$_{CO2/N2}$ = 50, Membrane-I pressure ratio = 5

Risks & Mitigation Plan

Description of Risk	Probability	Impact	Risk Management
Technical Risks			
Flue gas acidic components (SO_x, NO_x)	Low	Low	Hollow fiber membrane performance found to be stable in flue gas testing
Temperature excursions	Low	Low	Processing and operating temperatures (up to 60 °C) will not degrade polymer layers
Insufficient mechanical durability	Moderate	Moderate to High	Hollow fiber membrane modules successfully tested up to Δp = 70 psid
Fouling potential from fly-ash/particulates	Moderate	Moderate to High	Polyphosphazene materials have good surface properties. Fouling analysis system to test membrane performance
Permeability and selectivity at 60 °C lower than anticipated	Moderate	Moderate to High	Optimize synthesis strategy and cross-linker content
Hollow fiber permeance lower than anticipated	Moderate	Moderate to High	Optimize coating protocol, modify support surface pores
Resource Risks			
Polyphosphazene materials scalability & availability affects project	Moderate	High	Polymer synthesis process scaled-up (2X). Prevent pre-mature cross-linking by adjusting pendant group loadings

Budget Period-2 Plans
&
Technology Development Path

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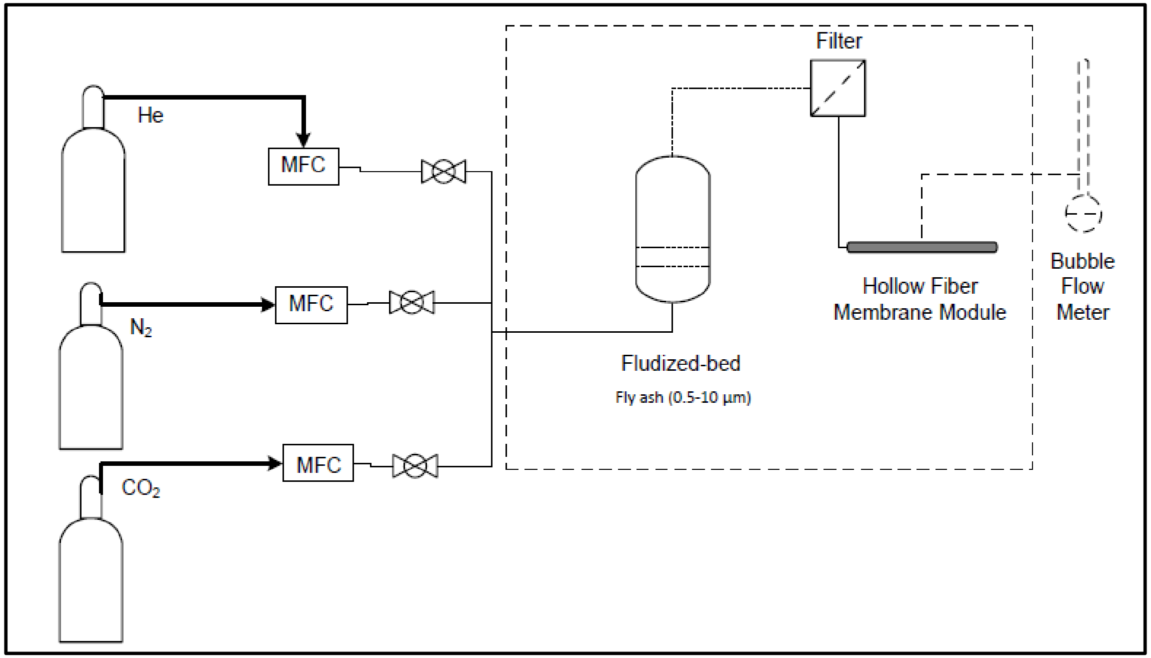
Project Activity Schedule: BP-2

Major Tasks	Task Owner				Year 1				Year 2				Year 3			
	GE	INL	GT	WRI	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 2 Optimize Polyphosphazene Polymer and Coating Solution					■	■	■	■	■	■	■	■	■	■	■	■
2.4 Refine Phosphazene solution properties		●									▬	◆				
2.5 Optimize Phosphazene performance and coating properties		●											▬	◆		
Task 4 Fabricate Composite Coated Hollow Membranes							■	■	■	■	■	■	■	■	■	■
4.6 Reduce coating defects in multi-fiber modules	●		●								▬	◆				
4.7 Create defect-free coated fiber in multi-fiber modules	●		●										▬	◆		
4.8 Conduct preliminary studies on key membrane properties			●						▬	◆						
4.9 Conduct focused studies on key membrane properties			●								▬	◆				
4.10 Refine and develop membrane models			●										▬	◆		
Task 5 Test Membranes at Bench-Scale in Coal Flue Gas					■	■	■	■	■	■	■	■	■	■		
5.4 Coal flue gas performance test optimized composite hollow fiber membrane modules				●									▬	◆		
Task 6 Conduct Process Evaluation and Module Design					■	■	■	■	■	■	■	■	■	■	■	■
6.2 Conduct final technical and economic feasibility analysis and EH&S assessment	●														▬	◆

- Optimize polyphosphazene performance & improve coating solution properties
- Optimize coating protocols for continuous & batch coating processes
- Study HF membrane ageing & fouling
- Conduct final process economics & fabricate 1m HF module

HF Membrane Ageing & Fouling Studies



HF Membrane ageing & fouling analysis setup

- Test setup designed & constructed
- Performance studies on HF modules under →long term saturated simulated flue gas (CO_2/N_2) exposure
- Performance studies on HF modules under →model/real fly ash particle exposure

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Anticipated Technology Roadmap

Project Outcomes:
- Improvement in separation efficiency
- Bench-scale demonstration of HF membrane module
- Energy savings in separation system

Identify Demo. Partner & Application → Prototype Design & Fabrication → Performance Demo. In Full-Scale Plant

2015 | 2016-17 | 2018-20

GE Global Research → GE Business/Licensing

- The team expects to deliver a promising membrane material, HF module & process configuration for membrane CO_2 capture
- Regulatory challenge exists to implement post-combustion CO_2 capture for coal fired power plant
- Emerging opportunities for CO_2 capture in EOR, NG processing, greenhouses, beverage applications

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Conclusions & Work-in-Progress

- ✓ Preliminary techno-economic analysis conducted to determine membrane performance targets
- ✓ Composite hollow fiber membranes developed & performance validated
- Optimize membrane performance & improve coating solution properties
- Optimize coating protocols for continuous & batch processes
- Scale-up membrane module & study HF membrane long-term performance

Thank You