Composite Hollow Fiber Membranes for Post Combustion CO_2 Capture

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Acknowledgment

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Disclaimer

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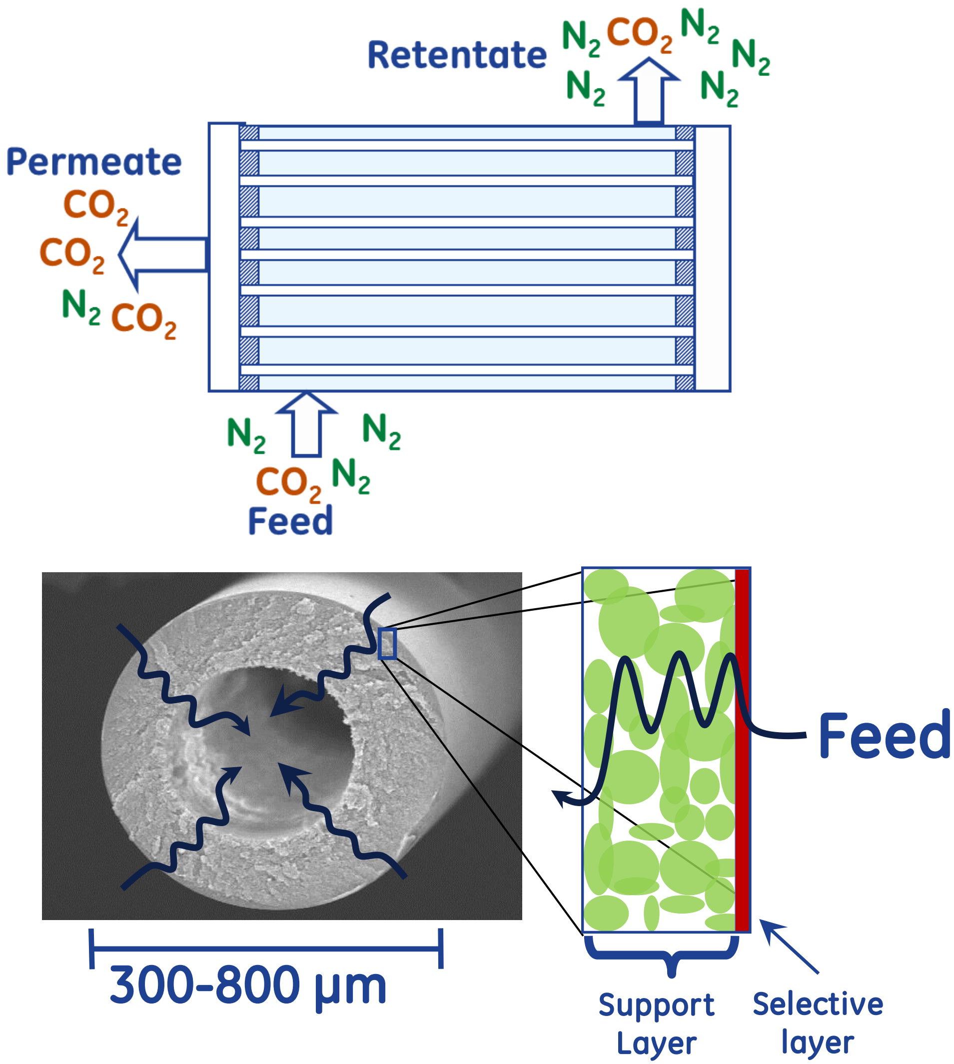
Technology Overview

Gas Separations Membrane Fundamentals



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

Permeance (Productivity)

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

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

Selectivity (Purity)

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

Solution–Diffusion Process

Gases dissolve in and then diffuse through a membrane

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 materials
  - Polyphosphazene polymers
  - HF module cleaning methods

Project and Team Overview

Project Funding

	Budget Period 1		Budget Period 2		Overall Project
	10/01/2011–06/30/2013		07/01/2013-12/31/2014		
	Total Planned ($)	Total Spent ($)	Total Planned ($)	Total Spent ($) 07/14/2014	Total Planned ($)
GE Global Research	1,097,536	1,296,620	585,394	313,891	1,682,930
Western Research Institute	80,777	92,085	42,942	2,467	123,719
Georgia Tech	215,922	171,375	186,552	137,370	402,474
Idaho National Laboratory	475,000	491,933	264,000	217,125	739,000
Total	1,869,235	2,052,013	1,078,888	670,853	2,948,123

- 3-year, $3 Million project, 20% cost share from GE
- BP-1 date revised by 1Q with no cost extension
- Project spend rate on-target
- Project expected to finish on-budget, delivering on key tasks

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Project Summary

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

GE Global Research

- Hollow fiber fabrication & coating
- Module design
- Technical and 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

Western Research Institute

- Membrane performance validation in coal flue-gas

Membrane scale-up | Polymer synthesis | Fundamental studies | Performance validation

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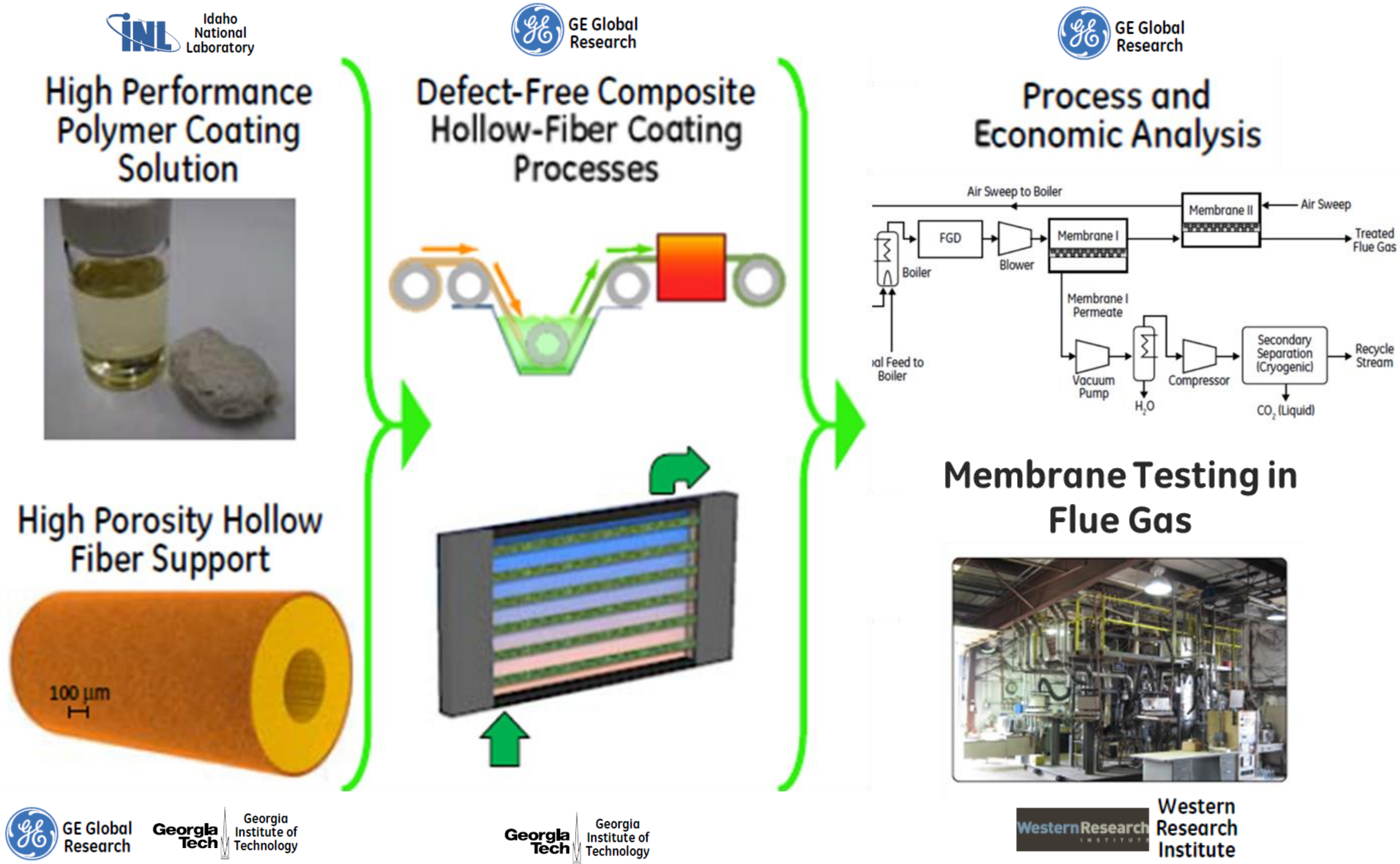
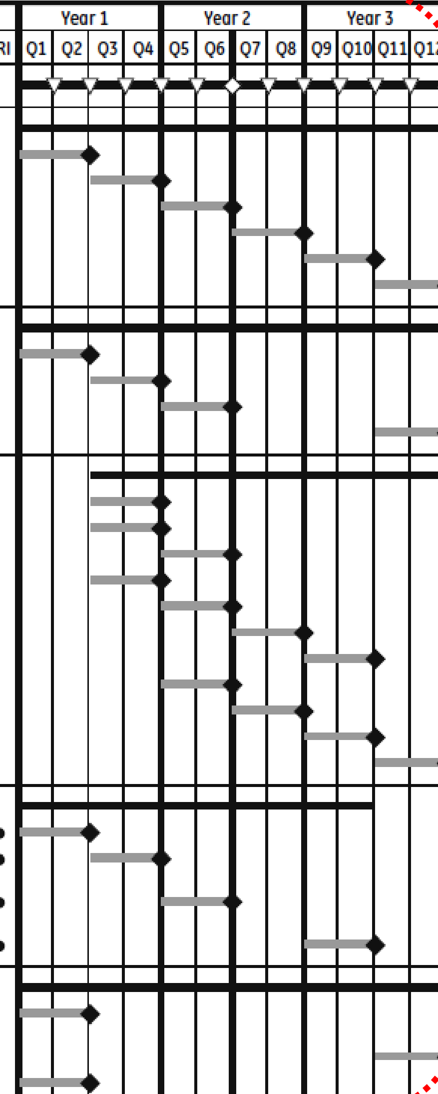
Project Overview

Develop thin film polymer composite hollow fiber membranes and processes for economical post-combustion CO_2 capture from coal flue-gas



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	●			



Legend: ◆ Milestone ▽ Deliverable ◇ Decision Point

Tasks, sub-tasks and ownership interlinked

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Progress and Current Status

Project BP-1 Status (2012-2013)

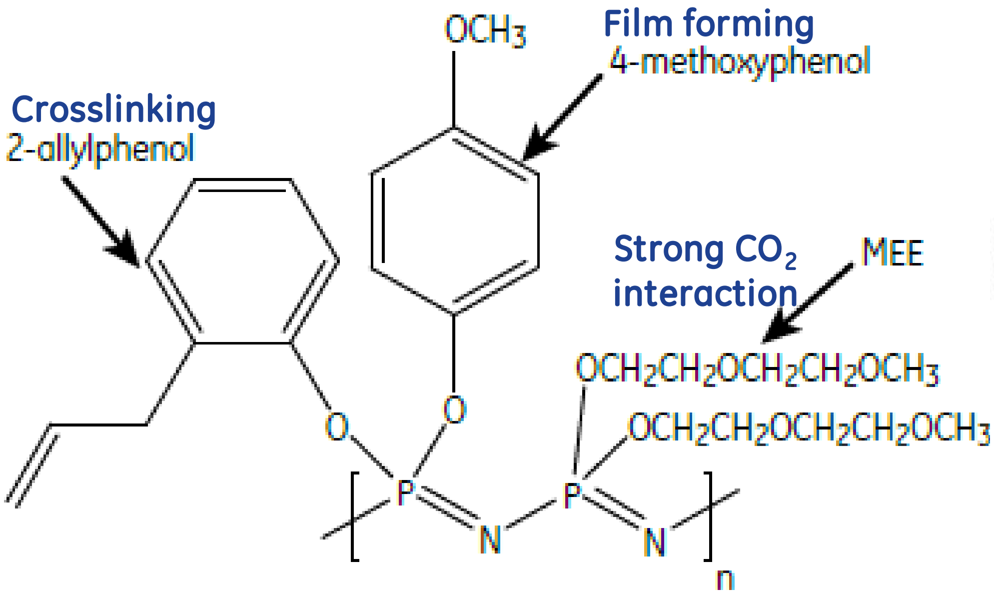
BP-1 Deliverable	BP-1 Status	
CO_2 selective polymer material with P_{CO2} = 200 Barrer, $S_{CO2/N2} \geq 30$	Polyphosphazene materials synthesized with P_{CO2} = 100-500 Barrer, $S_{CO2/N2}$ = 20-40	
Fabricate high porosity hollow fiber (HF) supports	1 m strands of HF support fabricated with P/ℓ_{CO2} > 20,000 GPU, surface pores ≈ 20-50 nm	
Develop processes to fabricate defect-free composite HF 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	Composite HF membrane module tested under realistic flue-gas mixture. $S_{CO2/N2}$ = 25-30, stability > 100 h, P/ℓ_{CO2} < 50 GPU.	
Preliminary techno-economic analysis study	Membrane systems model developed using Aspen Plus® and Aspen Custom Modeler®	

Project BP-2 Status (2013-2014)

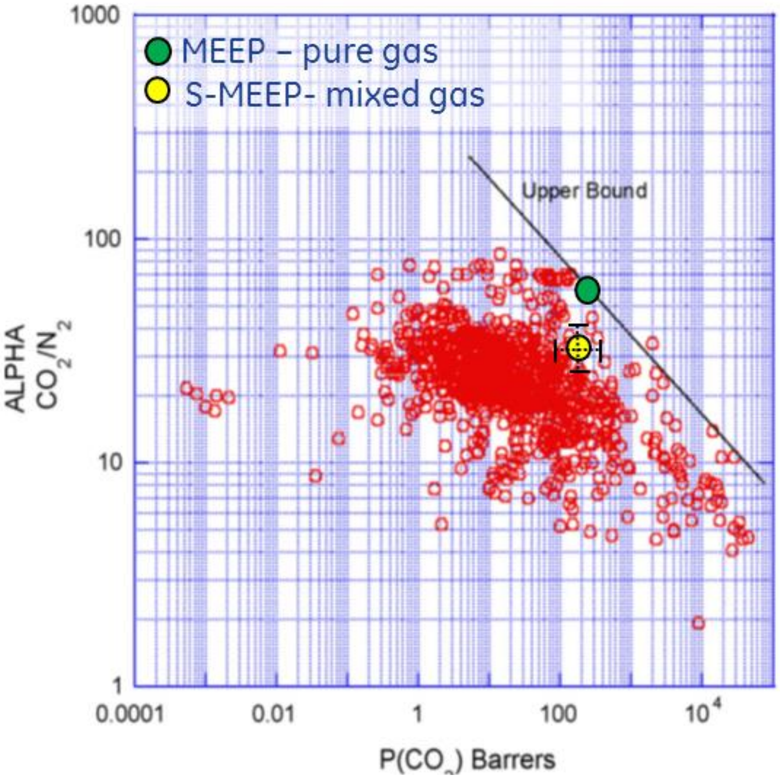
BP-2 Deliverable	BP-2 Status	
Scale-up polymer synthesis process	Polyphosphazene materials synthesized at > 100 g scale with P_{CO2} = 100-500 Barrer, $S_{CO2/N2}$ = 20-40	
Scale-up HF support fabrication	50 m continuous spools of HF support fabricated with surface pore size ≈ 20-50 nm, P/ℓ_{CO2} < 1,000 GPU	
Scale-up composite HF membrane fabrication	Defect-free 10” membrane modules with $S_{CO2/N2} \geq 30$ and P/ℓ_{CO2} up to 1000 GPU fabricated. Composite HF membrane scale-up in progress	
Demonstrate stable performance under realistic flue-gas conditions	Membrane mini-modules with initial $S_{CO2/N2} \geq 30$ and P/ℓ_{CO2} > 1000 GPU → not stable >100 h testing Membrane mini-modules with $S_{CO2/N2} \geq 30$ and 100 h stability → low P/ℓ_{CO2} < 50 GPU	

Membrane permeance-selectivity and stability key to scale-up

Polyphosphazene Materials



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



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

Polyphosphazene polymers provide excellent CO_2 separation, permeability and tunability for coating

* 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 Coating Development

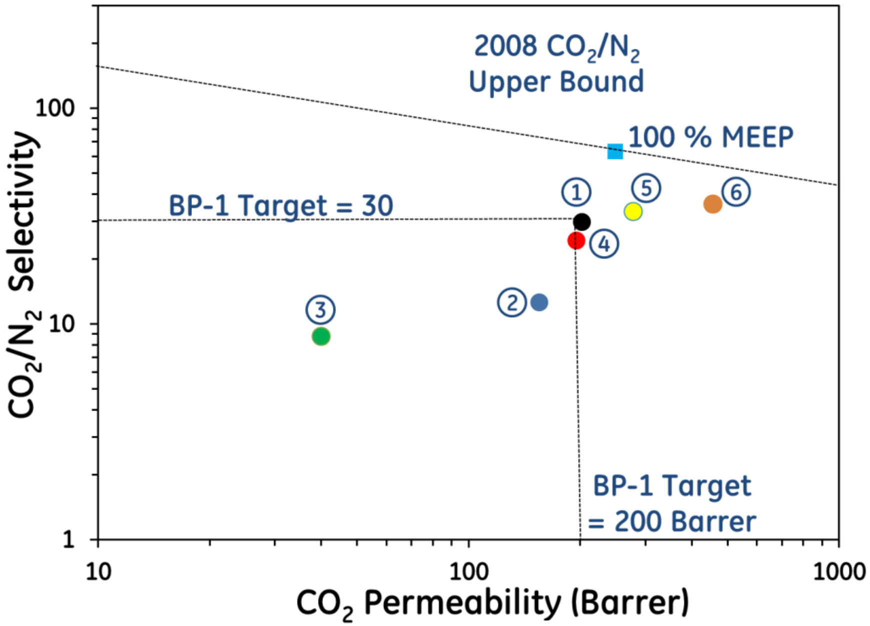
Compatibility
- Solubility in solvents benign to HF supports

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

Performance
- Achieve target permeability and selectivity
- Long term stability

Cross-linking Mechanism
- Maintain dimensional integrity

- Desired polymer characteristics are inter-dependent
- Polymers developed to meet project 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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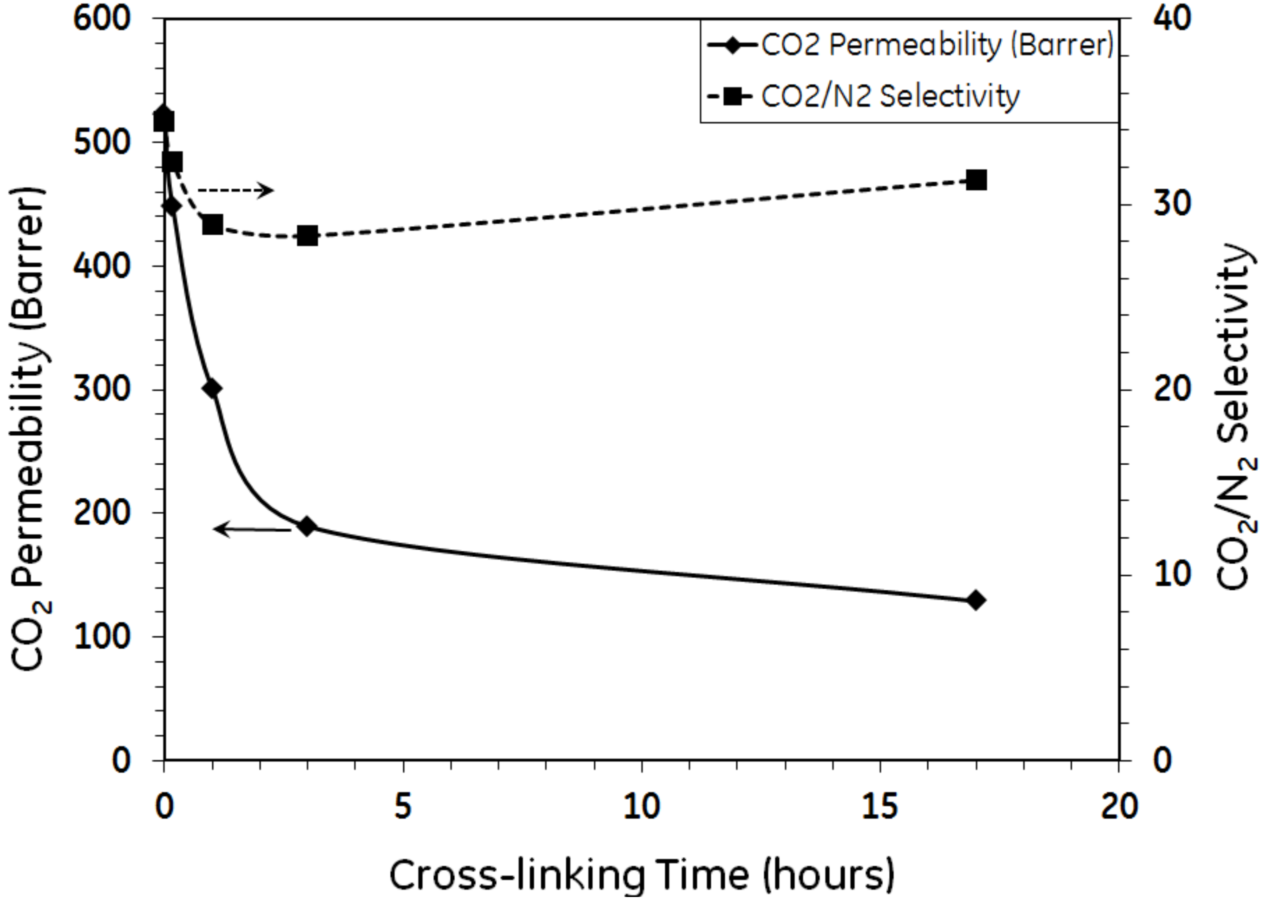
Polyphosphazene Cross-Linking



Effect of cross-linking time on polyphosphazene flat sheet permeability and selectivity

- Polyphosphazene permeability sensitive to thermal cross-linking time
- Optimum cross-linking desired for dimensional stability on HF supports

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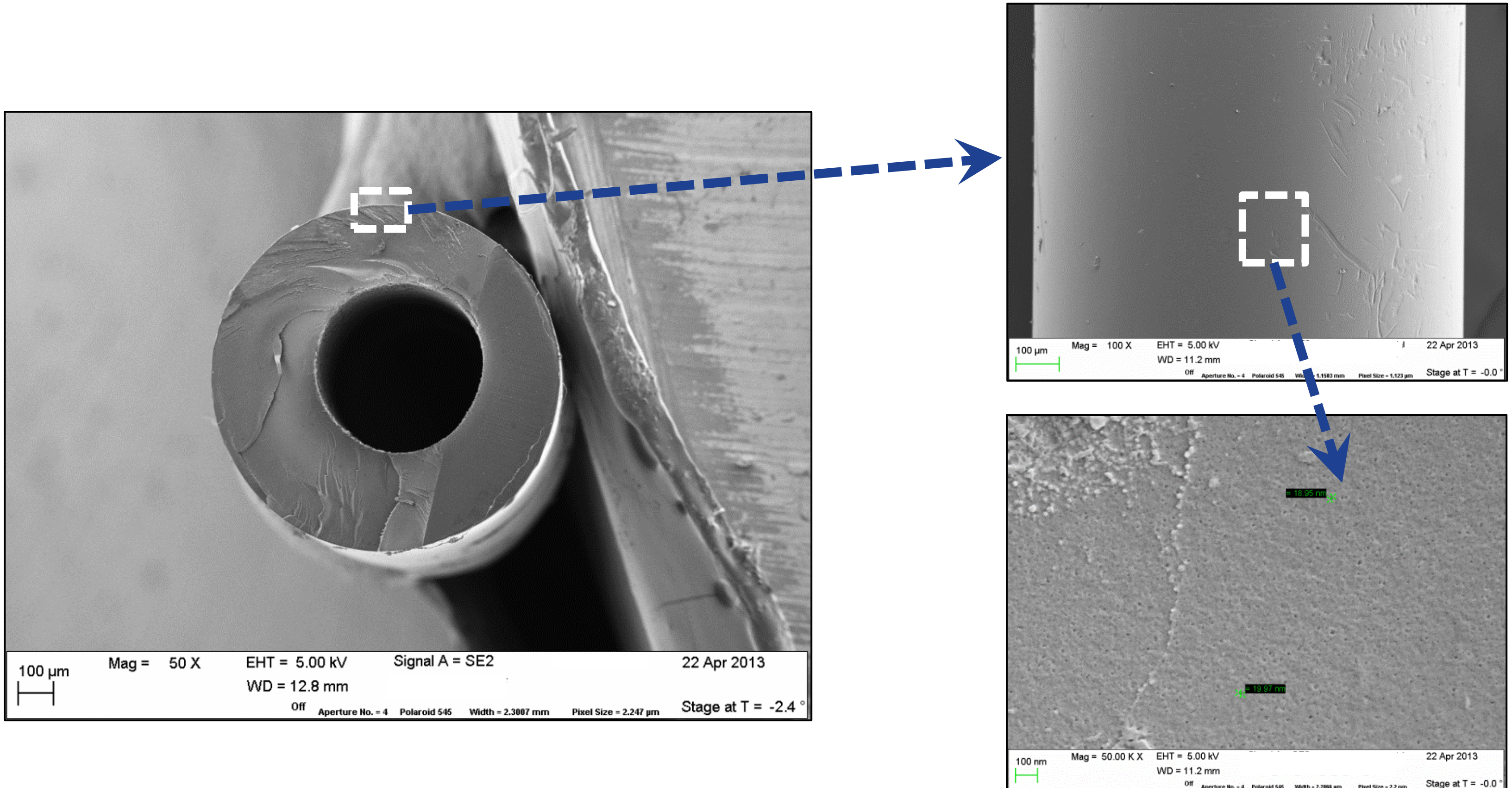
Hollow Fiber Support Layer



Hollow fiber supports

1 m strands of HF support with controlled surface pore size (≈ 20-50 nm), high permeance (P/ℓ_{CO2} > 20,000 GPU) fabricated and spinning parameters developed

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Hollow Fiber Support Scale-up

HF support spool fabrication

HF support spool solvent exchange

HF support spool drying

- 30-50 m continuous spools of HF support fabricated successfully
  - Surface pore size ≈ 20-50 nm achieved
  - P/ℓ_{CO_2} < 1,000 GPU; further improvement desired

Effective solvent exchange and high pore density key to improving permeance

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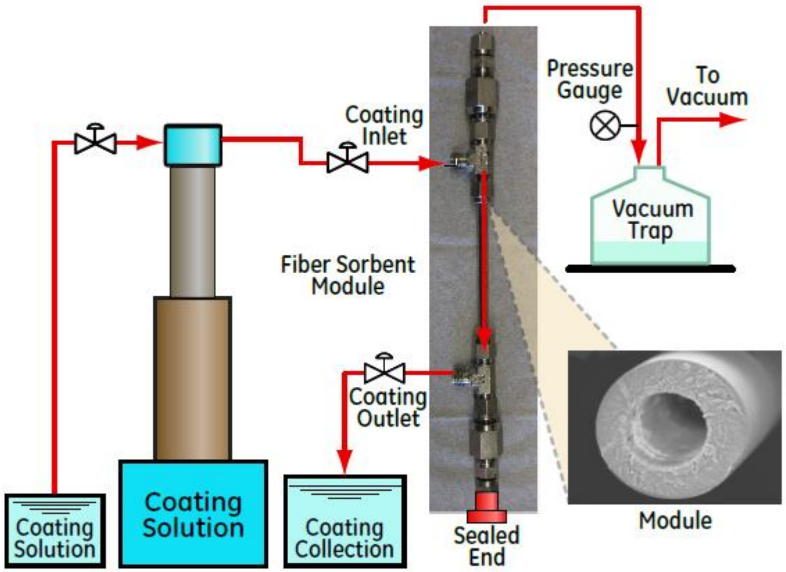
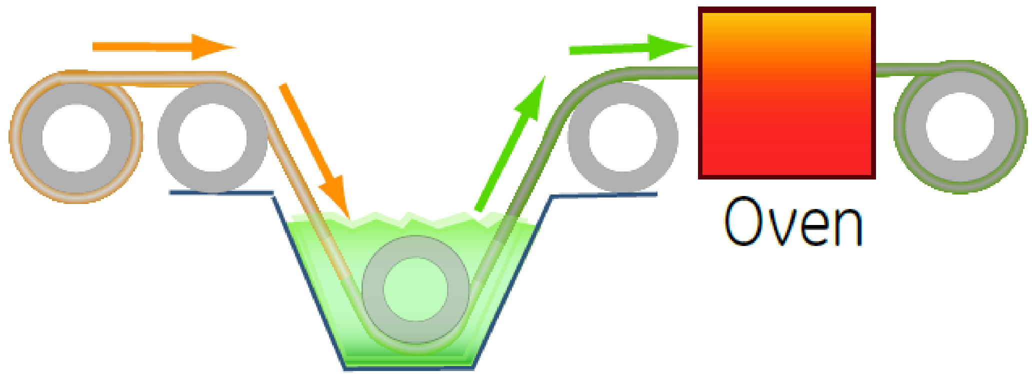
Composite Hollow Fiber Fabrication



Batch 'repair' coating process



Continuous 'roll-to-roll' coating process

- Key factors affecting HF support coatability
  - Reduced surface pore size
  - Substrate pore uniformity
  - Reduced physical handling

Membranes Testing

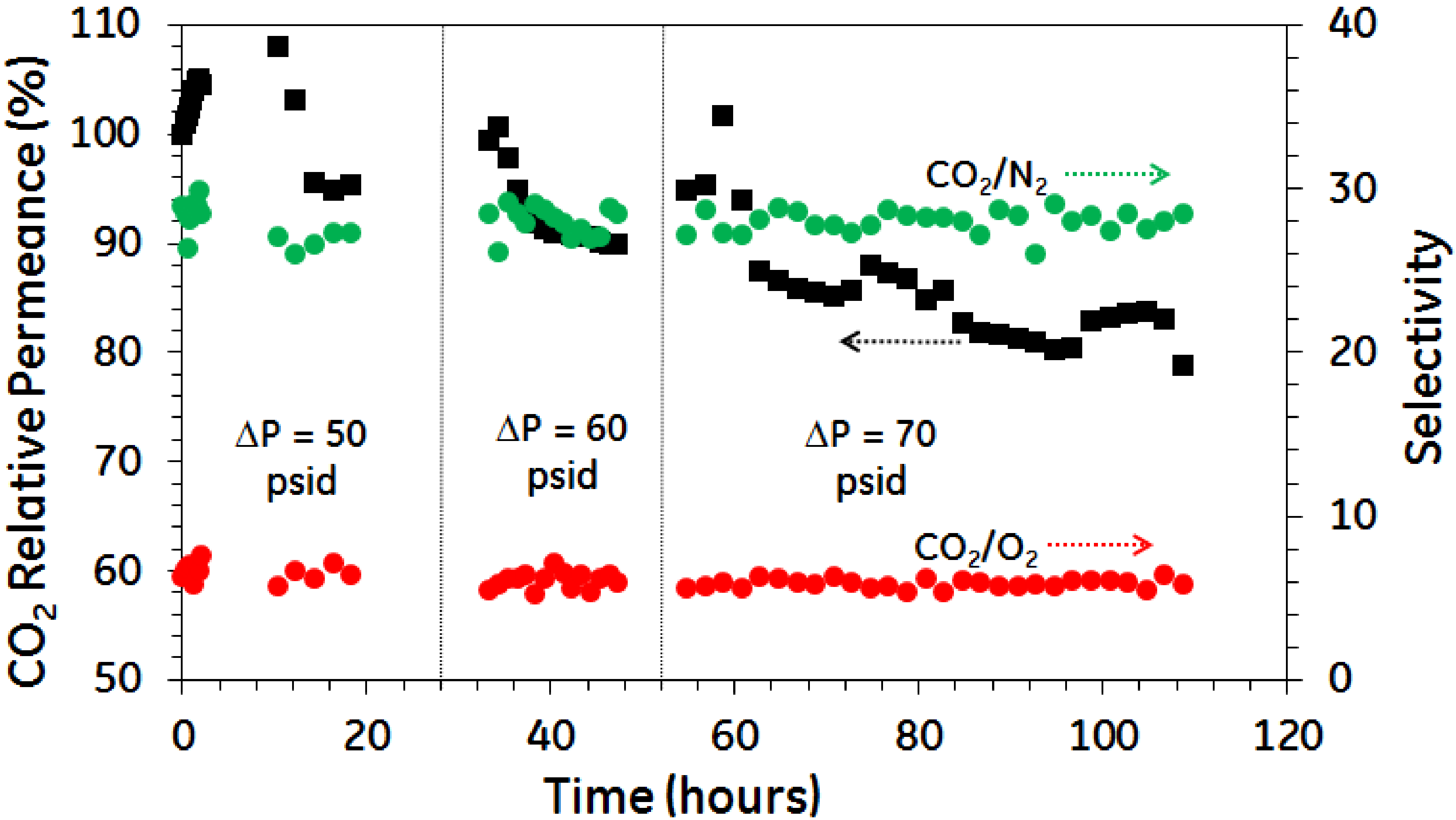
INL test rig

GE test rig

WRI test rig

- Composite HF membrane mini-modules (10″ length) and flat-sheet membranes performance tested
- INL and GE test rigs - $N_2/CO_2/O_2$ - 80/15/5 (vol. %) saturated with water vapor
- WRI test rig - $N_2/CO_2/O_2/NO/SO_2$ - 80/15/5/80 ppm/50 ppm (vol. %) saturated with water vapor

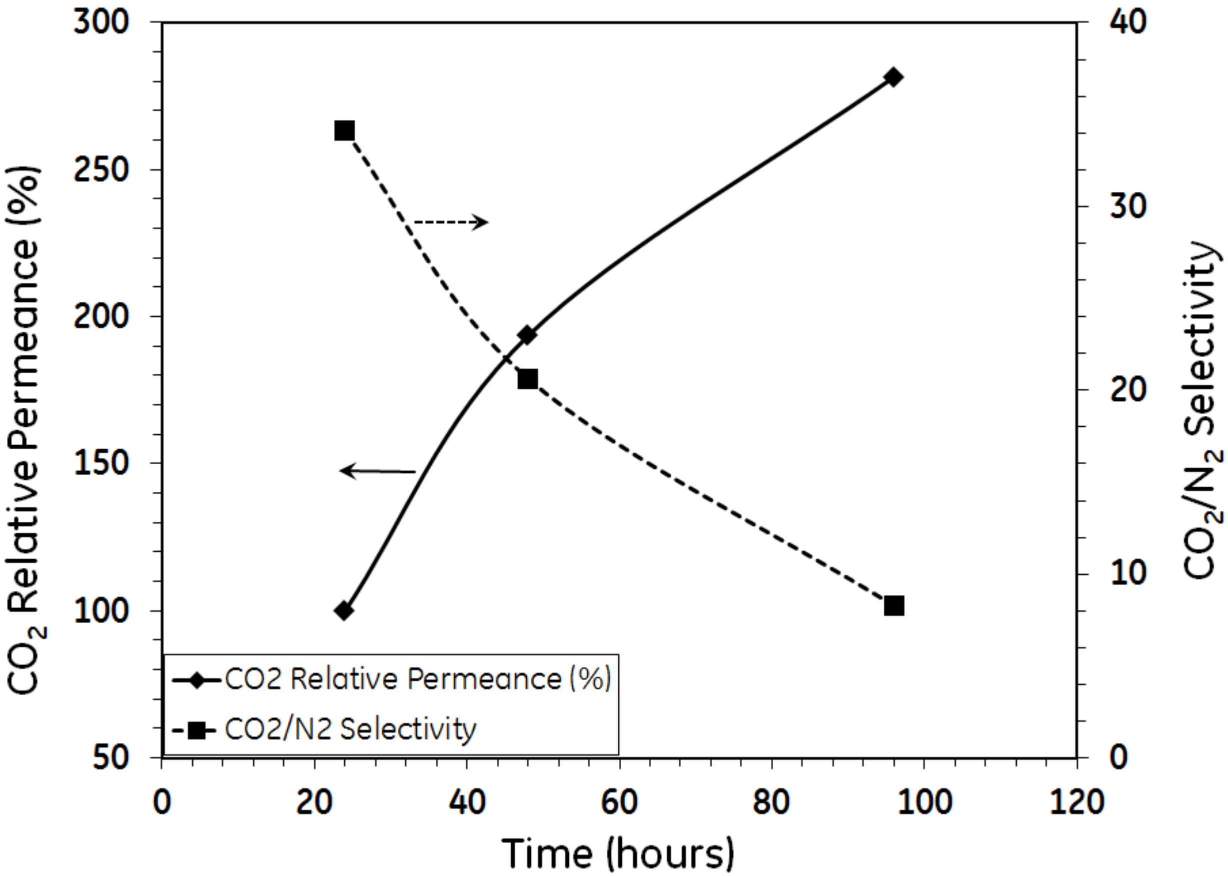
Composite HF Membrane Module Testing



HF membrane module performance testing at WRI under realistic flue gas conditions

Composite HF membrane modules with high cross-linking showed $S_{CO2/N2} \geq 30$ and >100 h stability, but with low $P/\ell_{CO2} < 50$ GPU

Composite HF Membrane Module Testing



HF membrane module performance testing under simulated flue gas conditions

Composite HF membrane modules with lower cross-linking showed initial $S_{CO2/N2} \geq 30$, P/ℓ_{CO2} > 1000 GPU, but poor stability >100 h testing

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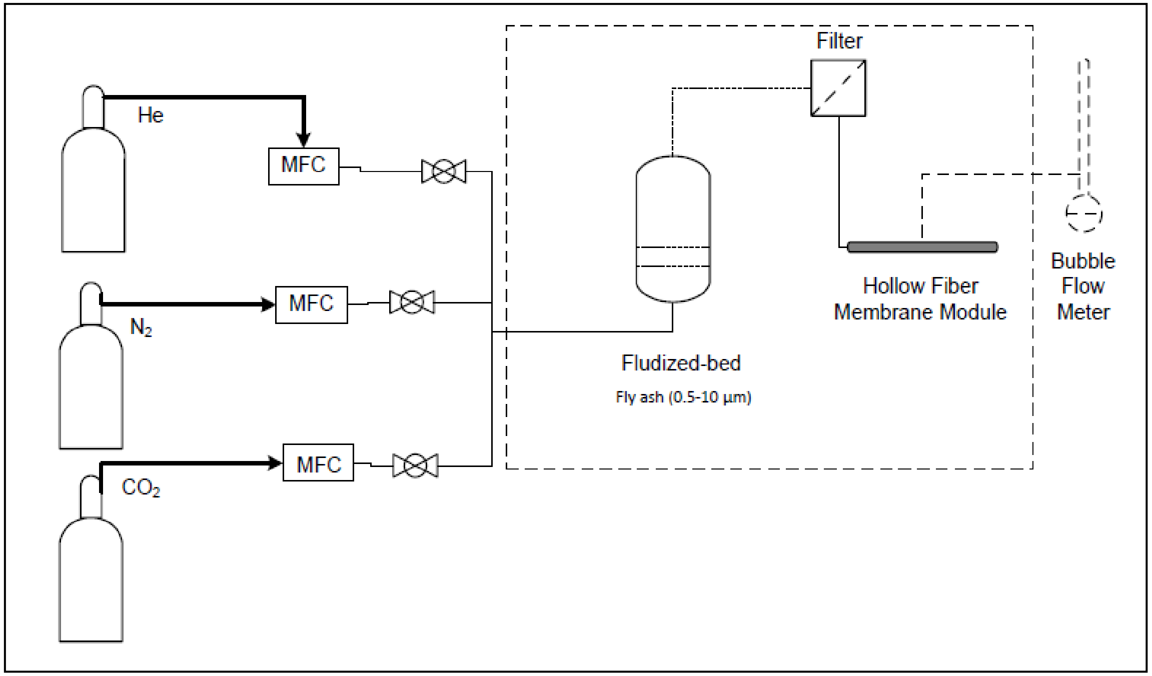
Membrane Fouling Studies



HF Membrane fouling analysis setup

- Composite HF membranes exposed to Bituminous coal fly ash loaded test gas (CO_2/N_2) at 35 psig at 35 °C
- Membrane performance found stable over > 100 h testing
- Membrane surface cleaning procedures under development

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Technology Development Path

Anticipated Technology Roadmap

- The team expects to deliver a promising membrane material, hollow fiber module and process configuration for membrane based CO_2 capture from coal flue gas
- Emerging opportunities for CO_2 capture in enhanced oil recovery (EOR), natural gas processing, greenhouses, beverage applications
- Further R&D required to improve stability of high selectivity and permeance composite hollow fiber membranes
- Effective scale-up of the composite hollow fiber membranes will be a part of any assertions to commercialization pathway

Thank You