Composite Hollow Fiber Membranes for Post Combustion CO_2 Capture

DOE Award: DE-FE0007514

GE Global Research (Lead)
Idaho National Lab (Sub)
Georgia Tech (Sub)
Western Research Institute (Sub)

Project Kick-off Meeting
DOE-NETL, Pittsburgh
January 13th, 2012

GE imagination at work

Acknowledgment

"The material described in the presentation is based upon work supported by the Department of Energy National energy Technology Laboratory (DOE-NETL) under award number DE-FE0007514."

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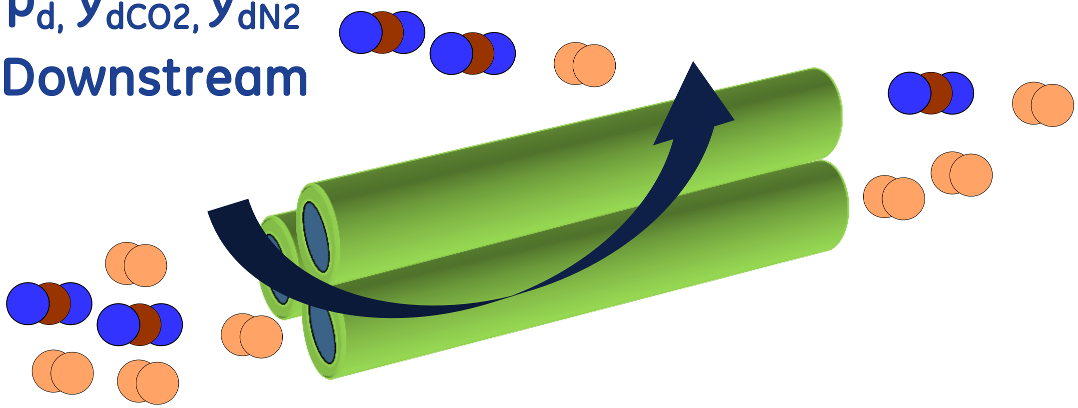
Outline

- Membrane fundamentals
- Project & team overview
- Technology overview
- Project objective & methodology
- Future testing & technology development

Membrane Fundamentals

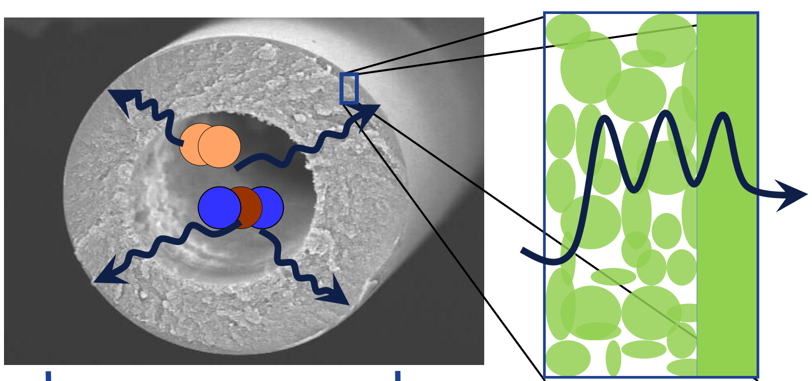
Membrane Fundamentals

p_d, y_{dCO2}, y_{dN2} Downstream



p_u, y_{uCO2}, y_{uN2} Upstream

CO_2 N_2 $p_u >> p_d$



Permeability/Permeance

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

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

Selectivity

$$\alpha_{CO2\text{-}N2} = \frac{y_{dCO2} / y_{dN2}}{y_{uCO2} / y_{uN2}} = \frac{P_{CO2}}{P_{N2}}$$

Solution–Diffusion Process

Gases dissolve in and then diffuse through a membrane

Project & Team Overview

Project Summary

3-Year, $3M Program to Develop Thin-Film Polymer Composite Hollow-Fiber Membranes for CO_2 Capture from Coal-Fired Power Plant Flue Gas

Program Team

GE Global Research

Engineered Hollow Fiber Support Fabrication; Optimization of "Continuous Dip Coating" Method; Module Design, Technical & Economic Feasibility Analysis

Idaho National Laboratory

Polymer Property Optimization; Coating Solution Refinement

Georgia Institute of Technology

Characterization & Modeling of Key Membrane Properties; Engineered Hollow Fiber Support Fabrication; Optimization of "In-Situ" Coating Process

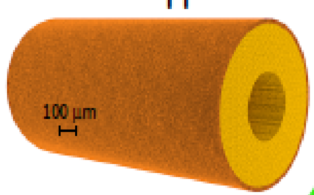
Western Research Institute

Membrane Performance Validation in Coal Flue-Gas

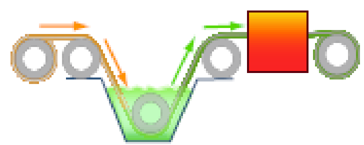
Program Objectives: Bench-scale evaluation of breakthrough ultra-thin film coated composite hollow fiber membranes and processes for CO_2 / N_2 separation from coal flue-gas at 60°C. Process to capture at least 90% of CO_2 with less than 35% increase in cost of electricity.

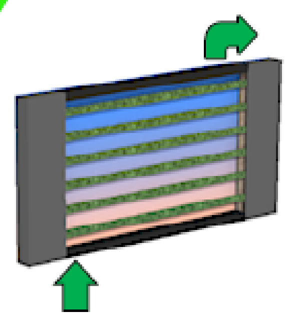
High Performance Polymer Coating Solution

High Porosity Hollow Fiber Support

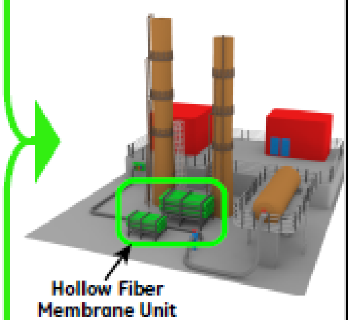


Defect-Free Composite Hollow-Fiber Coating Processes





Process and Economic Analysis



Program Deliverables

- Novel membranes with performance in coal-flue gas proven at bench-scale
- Economical manufacturability of hollow fiber supports
- Ultra-thin, defect-free hollow fiber coating process
- Technical and economic feasibility analysis

Project Funding

	Budget Period 1		Budget Period 2		
	10/01/2011–03/31/2013		04/01/2013–09/30/2014		Total
	DOE Share ($)	GE Cost Share ($)	DOE Share ($)	GE Cost Share ($)	($)
GE Global Research	817,225	280,311	435,884	149,510	1,682,930
Western Research Institute	60,147	20,630	31,975	10,967	123,719
Georgia Tech	160,776	55,146	138,907	47,645	402,474
Idaho National Laboratory	475,000	0	264,000	0	739,000
Total	1,513,148	356,087	870,766	208,122	**2,948,123**

- 3-year, $ 3M program, 20 % cost share from GE
- Budget period 1 (BP1) funds released by DOE*
- GaTech, WRI BP1 funds released by GE*
- INL BP1 funds released by DOE*

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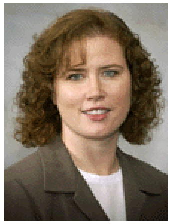
* As presented on January 13th, 2012

Management Team

GE

Dr. Joseph Suriano
Technology Leader,
Engineered Materials Chemistry & Physics



Ms. Johanna Wellington
Advanced Technology Leader,
Sustainable Energy

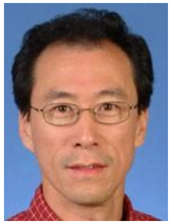
Dr. Paul Glaser
Manager, Fuels Lab

Dr. David Moore
Manager, Membrane & Separation
Technology Lab

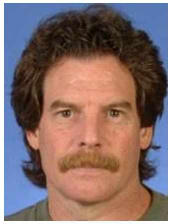
Technical Team

Dr. Dhaval Bhandari
Fiber Fabrication (PI)

Dr. Balajee Ananthasayanam
Module Design



Dr. Hongyi Zhou
Coating Development



Mr. Paul Howson
Fiber Fabrication

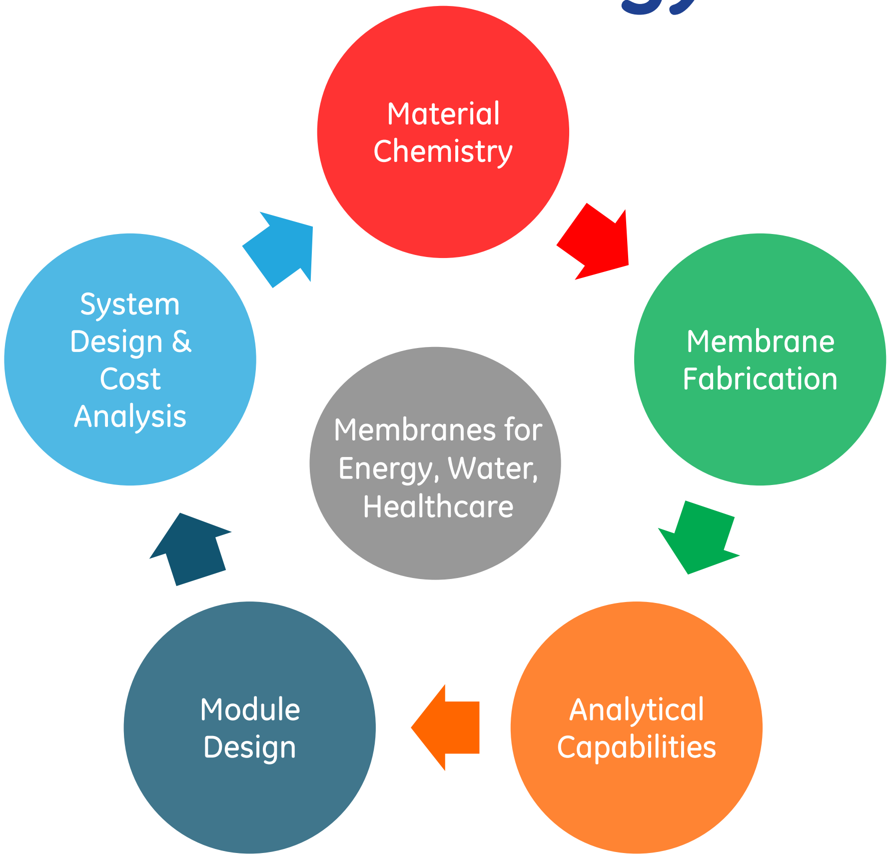
Dr. Patrick McCloskey
Polymer Chemistry

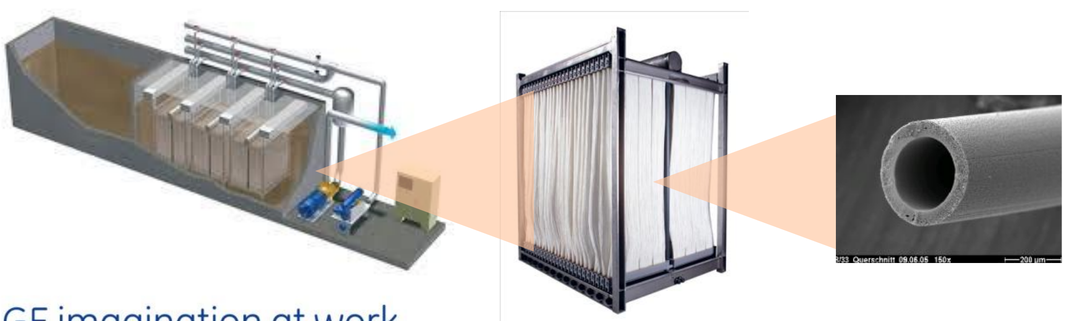
Mr. Paul Wilson
Fiber Coating Line

Dr. Surinder Singh
System Modeling

Mr. Jeff Manke
Membrane Testing

Membrane Technology at GE





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INL Team & Capabilities

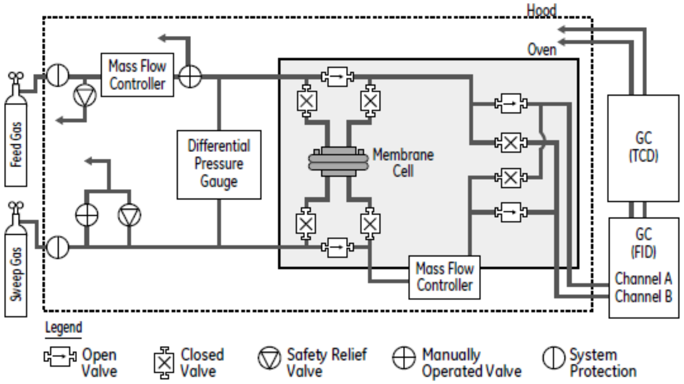
- Phosphazene polymer chemistry
- Instruments for structure analysis
  - Multinuclear NMR – solution & solid state
  - DSC, TGA, TMA & DMA
  - FT-IR, UV-Vis & Raman
  - SEM, ESCA
  - XRD
- Gas permeation analysis
  - Mixed Gas: (multiple gases) up to 400 °C
  - Pure Gas: (single gas) up to 70 °C

Dr. Eric S. Peterson
Business Development Manager

Dr. Frederick F. Stewart (PI)
Polymer Chemistry

Mr. Christopher Orme
Membrane Formation & Characterization

Dr. John R. Klaehn
Polymer Chemistry



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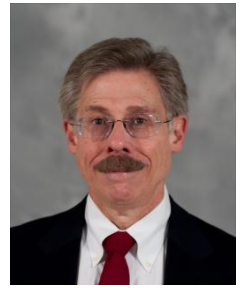
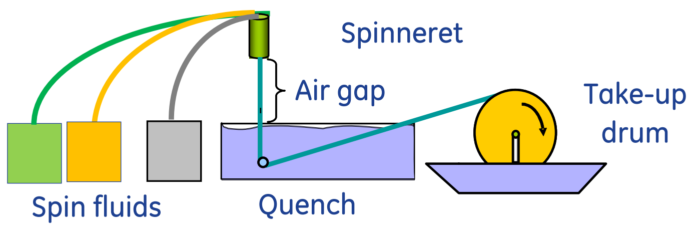
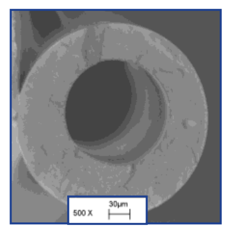
GaTech Team & Capabilities

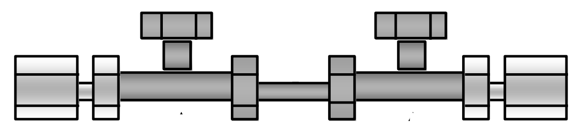


Dr. Bill Koros (PI)
Professor at Georgia Tech

- Dense film gas permeation and sorption testing
- Hollow fiber and module fabrication facilities







Swagelok mini-module

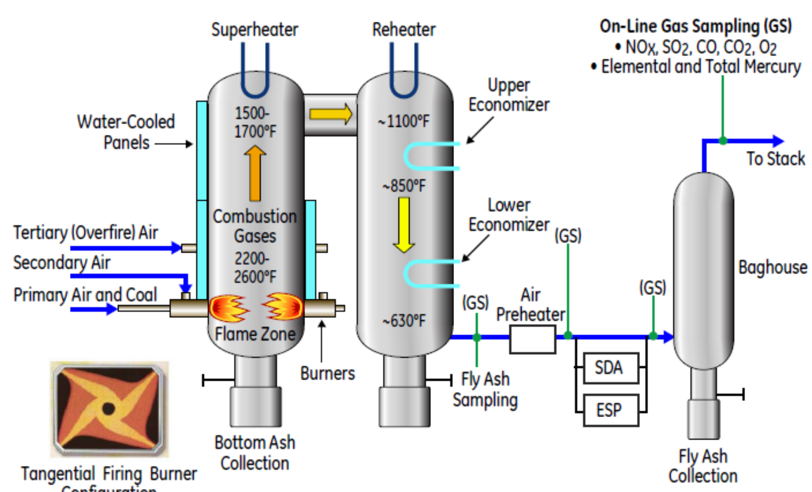
- Hollow fiber permeation testing
- Polymer characterization (NMR, IR, GPC, DSC, TGA, SEM, etc.)

WRI Team & Capabilities

WRI partners with industry and government agencies to develop and demonstrate technology for the clean, efficient, and environmentally acceptable production of energy from fossil and renewable resources

Dr. Vijay Sethi
Sr. Vice President, Energy
Production & Generation (EP&G)

- Coal/Biomass Processing
- Gasification
- Catalyst Development
- Liquid Fuels Synthesis
- Hydrogen production
- Advanced Reactors
- Emissions Control



Technology Overview

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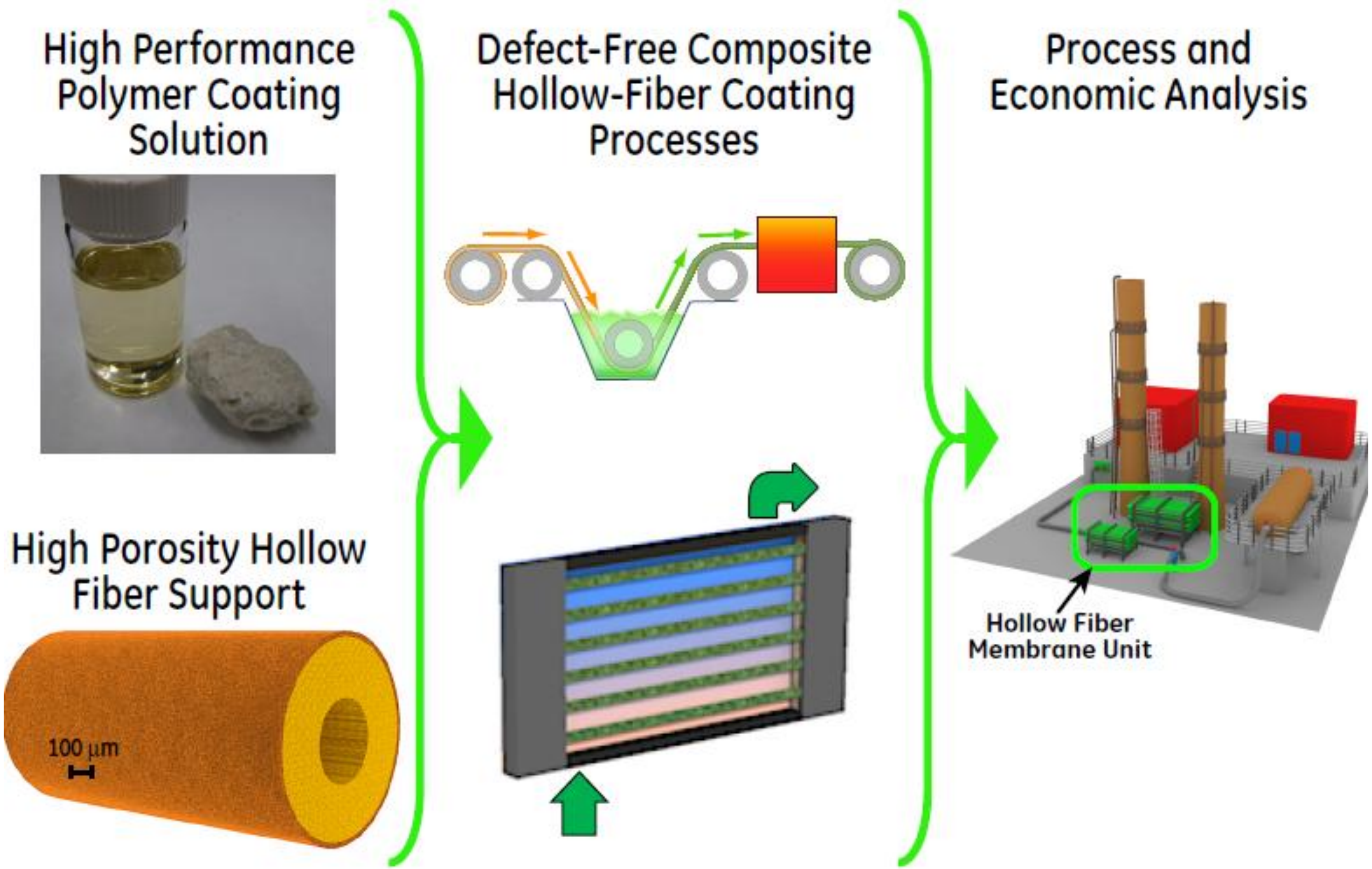
Technology Overview

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



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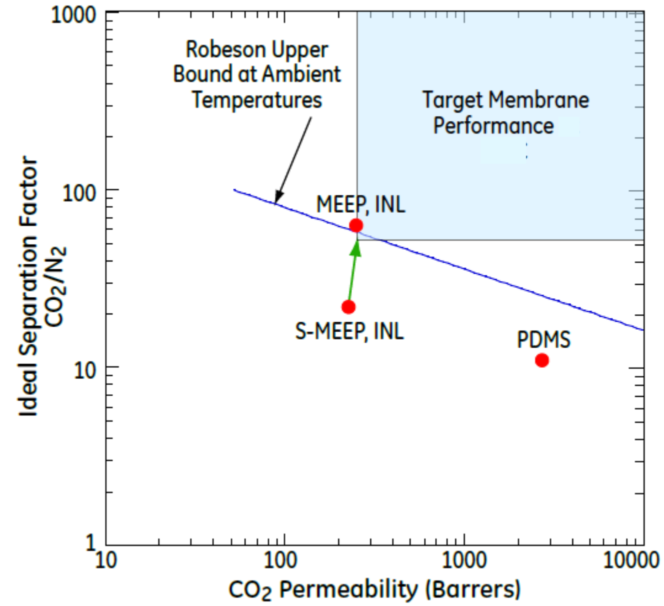
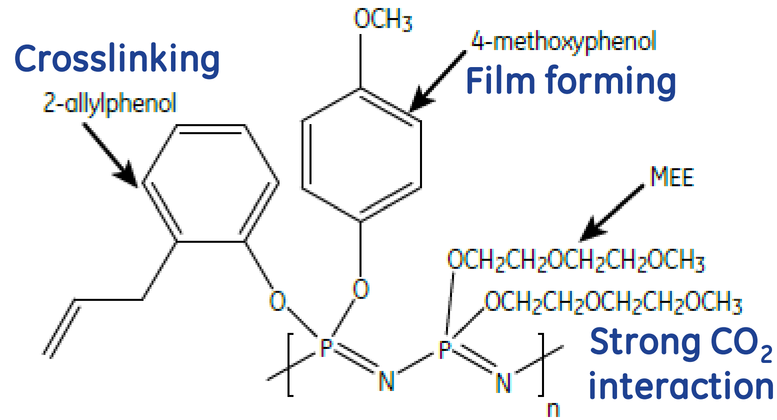
Phosphazene Polymer & Coating Solutions

- Low Tg polymers with excellent CO_2 separation & permeability
- Stabilization desired for hollow fiber application -
  - Dimensional stabilization against polymer flow (4-methoxyphenol)
  - Surface property optimization to reduce fly ash adhesion (2-allylphenol)
  - Maintain gas transport & polymer properties (MEE)



Permeability-selectivity plot for CO_2/N_2 gas pair at ambient temperature



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

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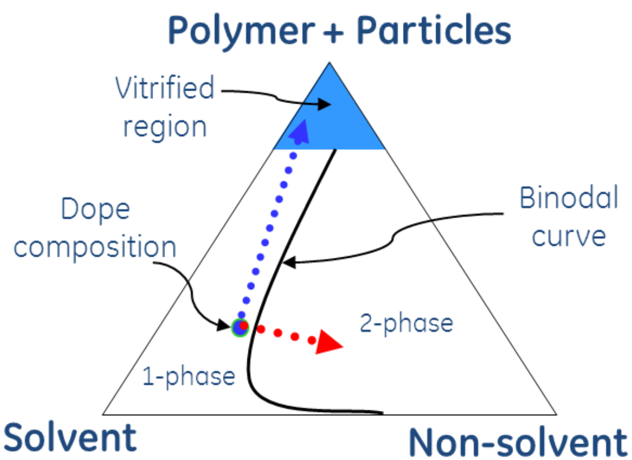
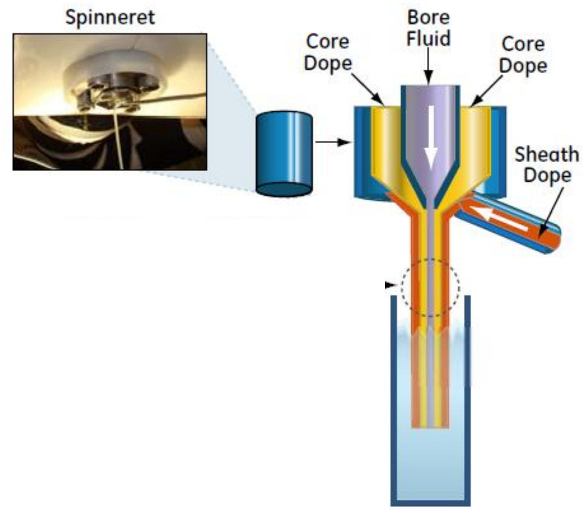
*C.J. Orme, M.K. Harrup, T.A. Luther, R.P. Lash, K.S. Houston, D.H. Weinkauf, F.F. Stewart, Characterization of gas transport in selected rubbery amorphous polyphosphazene membranes, J. Membr. Sci. 186 (2001) 249.

Engineered Hollow Fiber Support Layer

Spin Dope Development → Fiber Spinning → Module Formation

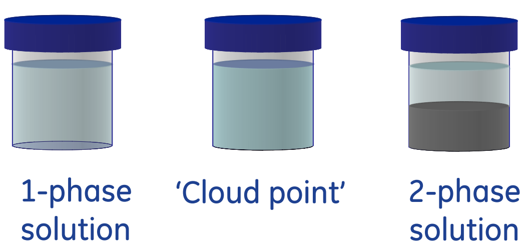


Three Phase Diagram



Dual-layer fiber co-extrusion process

Fiber solvent exchange process



Cloud Point Experiments

Controlled porosity hollow fiber supports

Hollow fiber module

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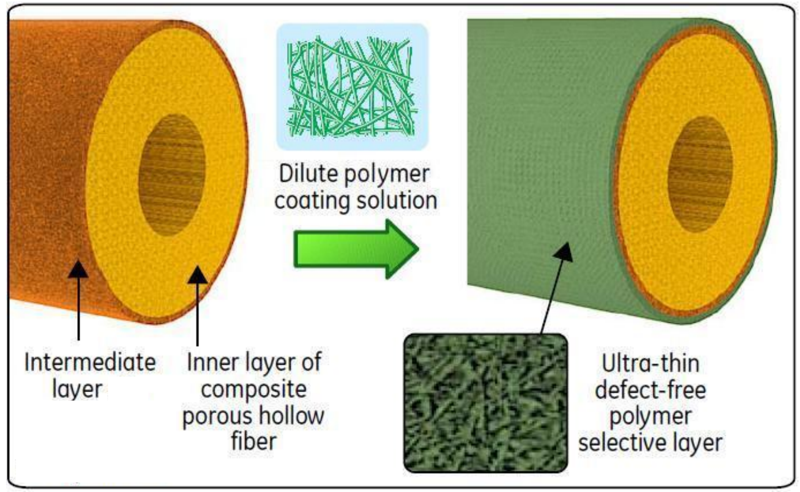
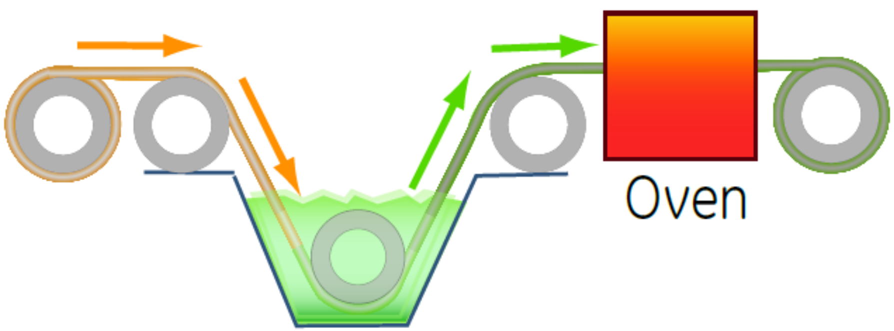
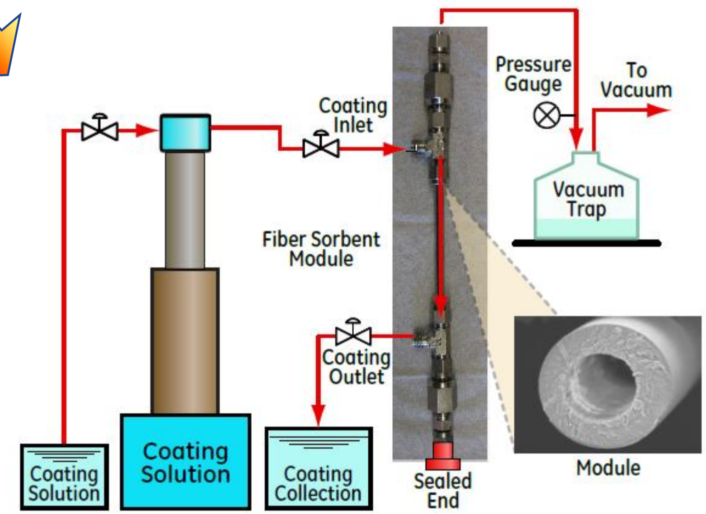
Composite Hollow Fiber Fabrication



Schematic representation of hollow fiber coating process



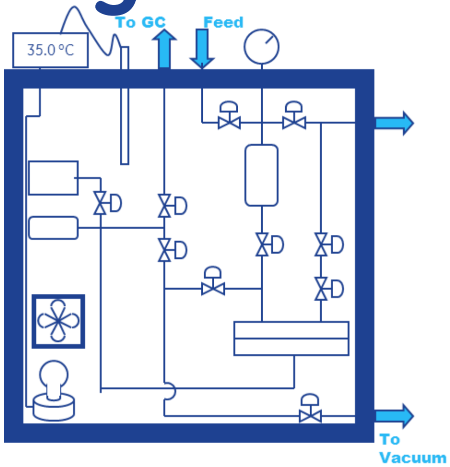


Continuous Coating Process (GE)
Under development

Batch Coating Process (GaTech)
Existing equipment to be modified

Membranes Testing

INL Test Rig



GaTech Test Rig

GE Test Rig

- State of the art membrane testing facilities
- Simulated & coal flue gas testing
- Vacuum, inert sweep systems
- Flat sheet, hollow fiber membranes testing

WRI Test Rig

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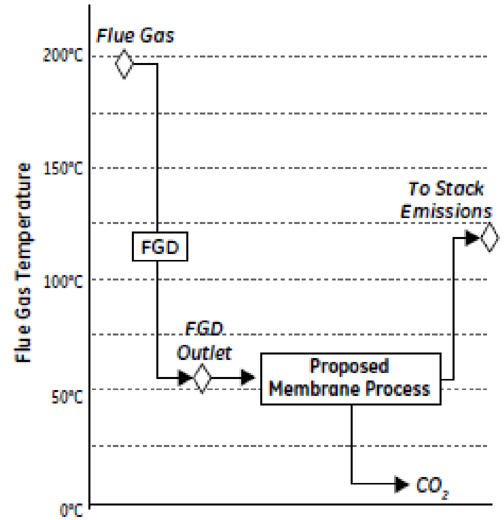
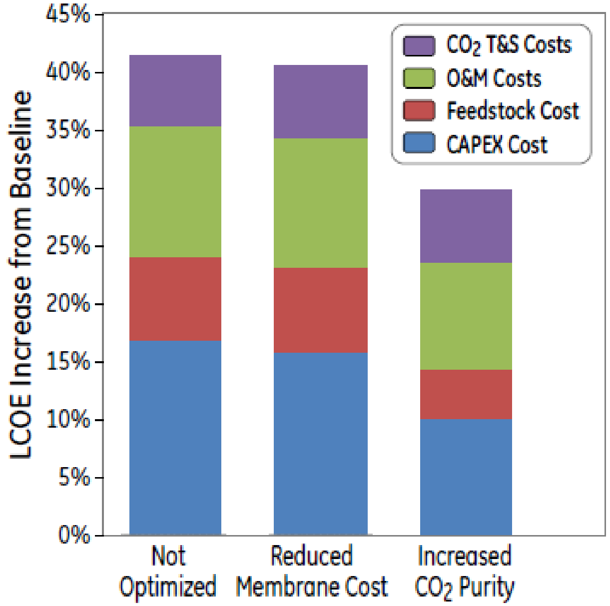
System Design & Economic Analysis



Temperature diagram showing proposed membrane process

- Base membrane case - $ 50/m² & 70 % CO_2 purity
- *Reduced* membrane cost & *increased* CO_2 permeate purity → lower LCOE increase
- *Easier* membrane cleanability to provide longer life



Levelized COE comparison for the membrane process

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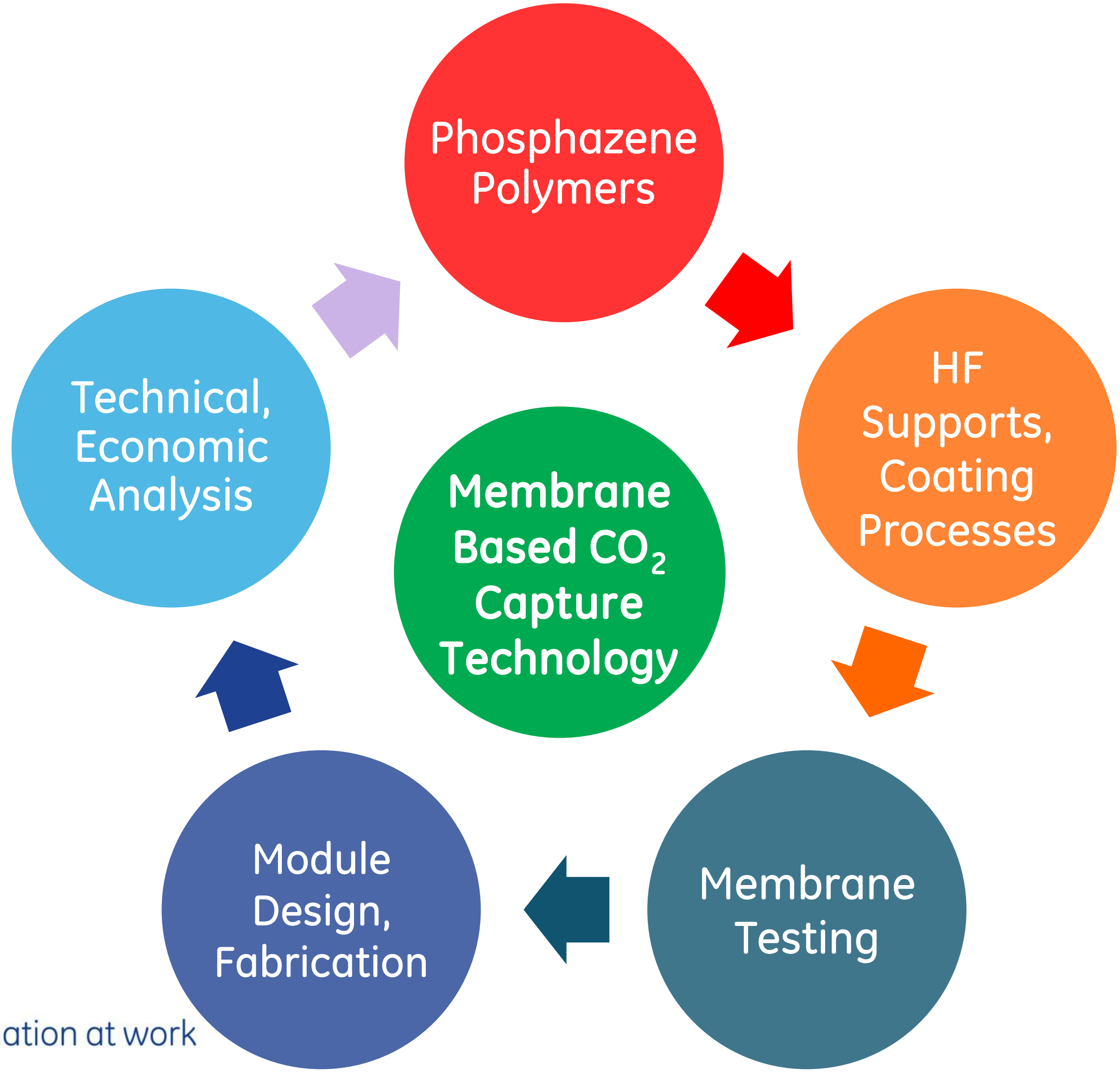
Module Design & Fabrication

- GE to leverage knowledge & capability from previous membrane programs
- Membrane module will be designed & fabricated to optimize -
  - Flow arrangement
  - Module seals
  - Pressure drop

Composite Hollow Fiber Membranes



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Project Objective & Methodology

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Project Objectives

Budget Period 1

- Refine phosphazene polymer, coating properties - **INL, GE**
- Produce, optimize engineered hollow fiber supports - **GE, GaTech**
- Develop, refine fiber coating processes - **GE, GaTech**
- Preliminary systems analysis, module design - **GE**
- Membrane coal flue-gas testing, refine targets - **WRI**

Budget Period 2

- Optimize phosphazene polymer, coating properties - **INL, GE**
- Optimize ‘continuous’ and/or ‘batch’ coating processes - **GE, GaTech**
- Develop membrane fouling & cleanability properties - **GaTech**
- Final systems analysis, module design - **GE**
- Membrane coal flue-gas testing, achieve targets - **WRI**

Go/No-Go Decision at End of BP1

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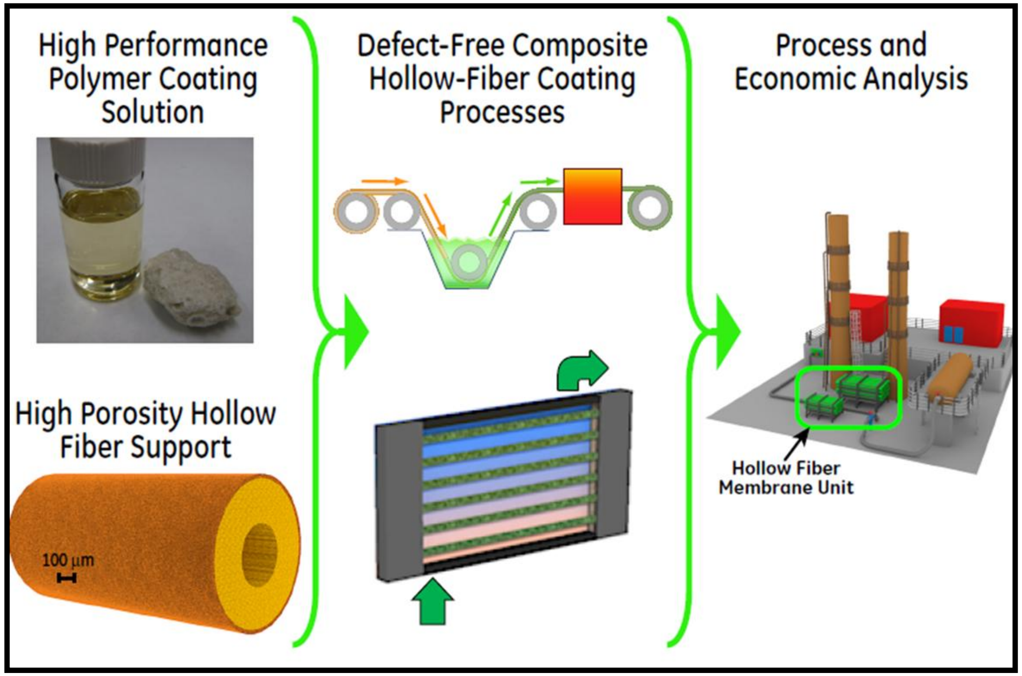
Success Criteria at Decision Points

Decision Point	Date	Success Criteria
Go/no-go decision at end of Budget Period 1	3/31/2013	Composite hollow fiber membrane module with >10 fibers with: • Skin layer thickness < 0.5 μm • CO_2 permeability > 200 Barrer • CO_2/N_2 selectivity > 30
Project completion	9/30/2014	Composite hollow fiber membrane module with >100 fibers with: • Skin layer thickness ≤ 0.25 μm • CO_2 permeability ≥ 200 Barrer • CO_2/N_2 selectivity ≥ 40 • Membrane process capable of >90% CO_2 capture with <35% increase in COE

Project Task Structure



- **Task 1** – Project Management
- **Task 2** – Optimize Polyphosphazene Polymer and Coating Solution
- **Task 3** – Fabricate Hollow Fiber Support Layer
- **Task 4** - Fabricate Composite Coated Hollow Membranes
- **Task 5** - Test Membranes at Bench-Scale in Coal Flue Gas
- **Task 6** - Conduct Process Evaluation and Module Design

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 & ownership inter-linked !!

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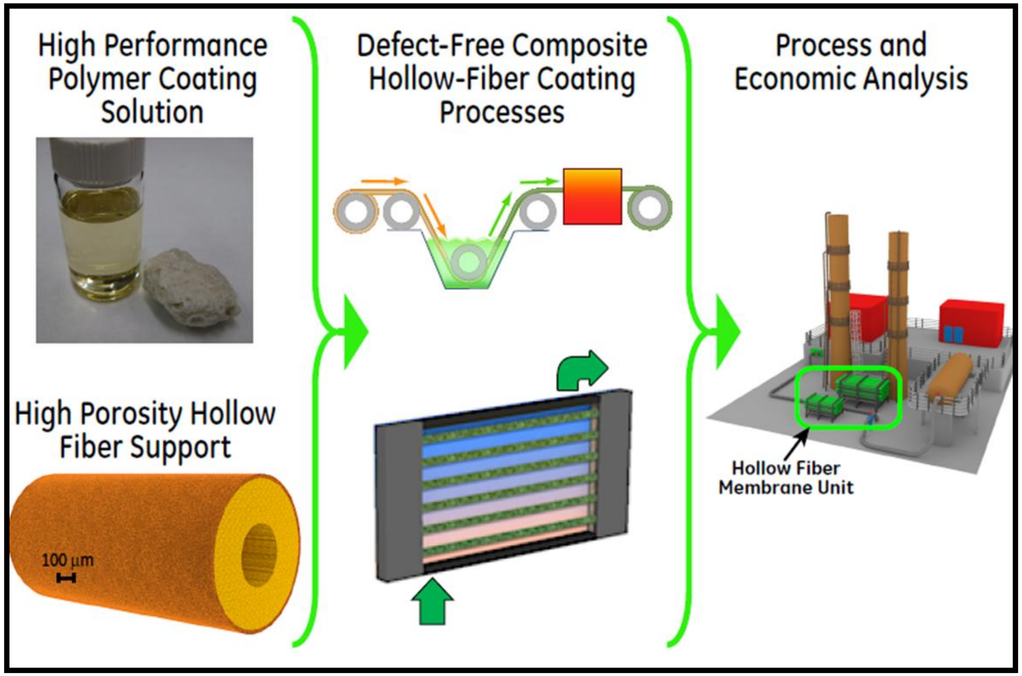
Project Task Structure



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Task 1 – Project Management

Goal: Bring together processes, materials & information generated in the project to move the technology towards deployment

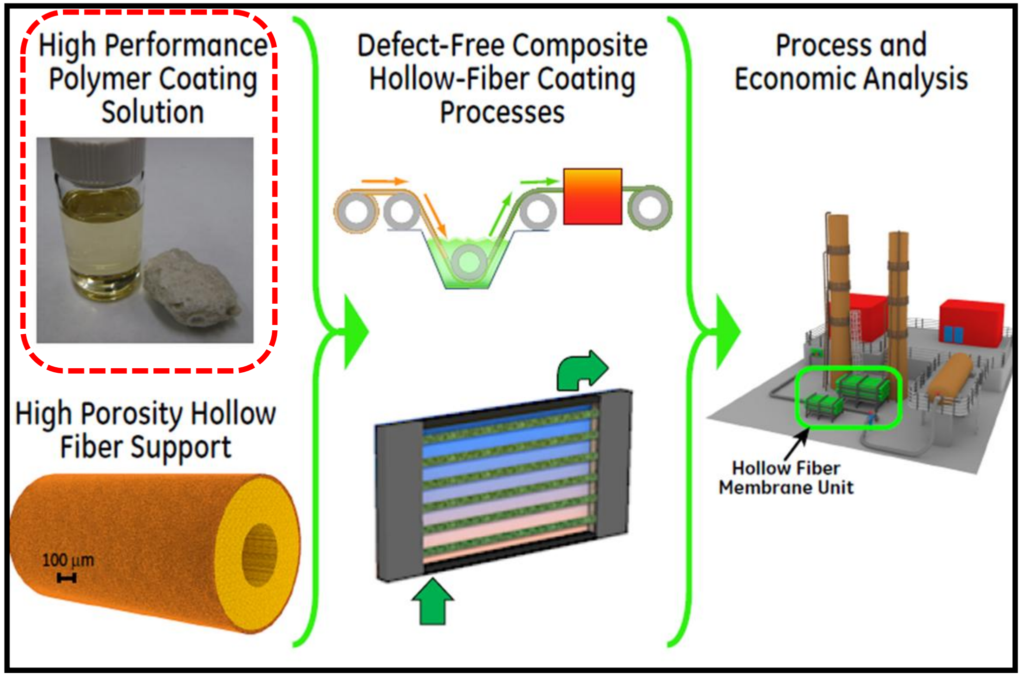
- Deliver quarterly, annual reports to DOE
- Conduct project reviews & briefings to DOE
- Coordinate monthly teleconferences to share technical findings
- Monitor technical & financial progress

Current Progress*

- All relevant documents submitted to the DOE
- 4-party NDA executed
- Individual kick-off meetings conducted

* As presented on January 13th, 2012

Project Task Structure



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Task 2 – Optimize Polymer & Coatings

Goal: Synthesize Phosphazene polymer, optimize separation performance & develop easily processable coating solutions

Task 2.1 - Produce coatings in appropriate solvents (Q1-2)

Milestone - Stabilized polymer material & coating solution compatible with hollow fiber supports

Task 2.2 - Adjust Phosphazene cross-linking (Q3-4)

Milestone – Modified polymer material & coating solution

Task 2.3 - Optimize Phosphazene stabilization (Q5-6)

Milestone - Polymer material & coating solution that meets BP-1 performance targets

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Task 2–Optimize Polymer & Coatings (Cont.)

Task 2.4 - Refine Phosphazene solution properties (Q7-8)

Milestone - Phosphazene polymer with validated performance

Task 2.5 - Optimize Phosphazene performance & coating properties (Q9-10)

Milestone - Optimized polymer & coating solution that meets membrane performance targets

Current Progress*

- Initial INL funds available under CR ($31K)
- Provides INL with travel funds & initial supply purchases

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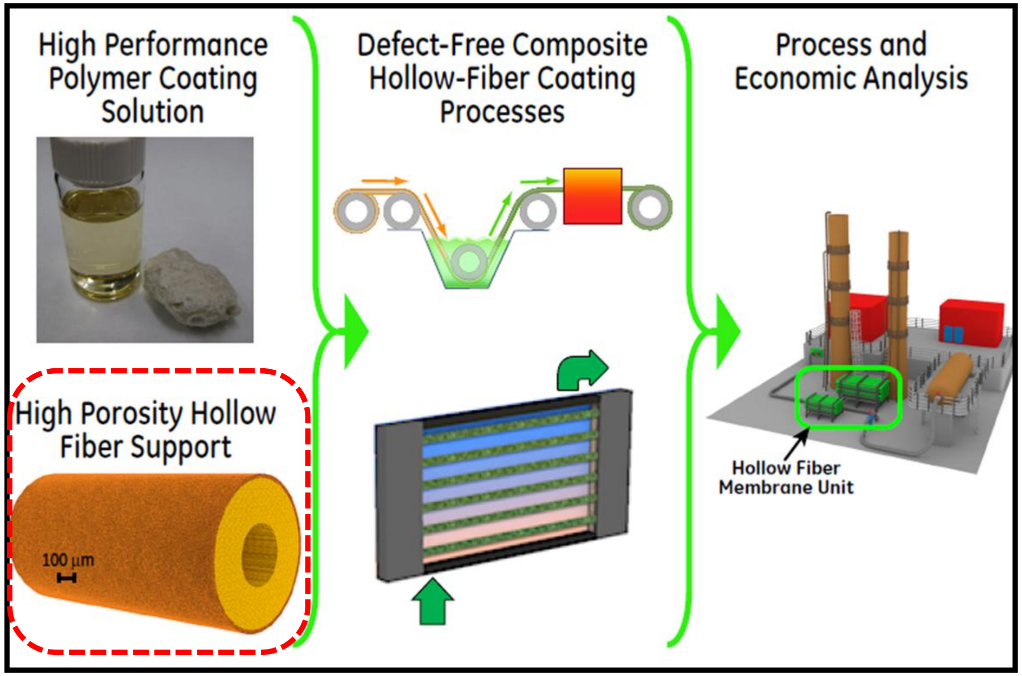
* As presented on January 13th, 2012

Project Task Structure



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Task 3 – Fabricate HF Support Layer

Goal: Produce highly porous, robust hollow fiber supports with controlled surface porosity from commercially available materials

Task 3.1 - Produce high porosity hollow fiber supports (Q1-2)

Milestone – Identified process window for hollow fiber support fabrication

Task 3.2 - Refine hollow fiber spinning process and support material (Q3-4)

Milestone - Transfer functions for key support layer properties vs. formulation and process parameters

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Task 3 – Fabricate HF Support Layer (Cont.)

Task 3.3 - Optimize hollow fiber spinning process (Q5-6)

Milestone - Hollow fiber support fabrication process that yields target composite membrane performance with coal flue gas

Current Progress*

- Support, Intermediate & selective layer materials acquired
- Membrane casting experiments initiated w/GaTech

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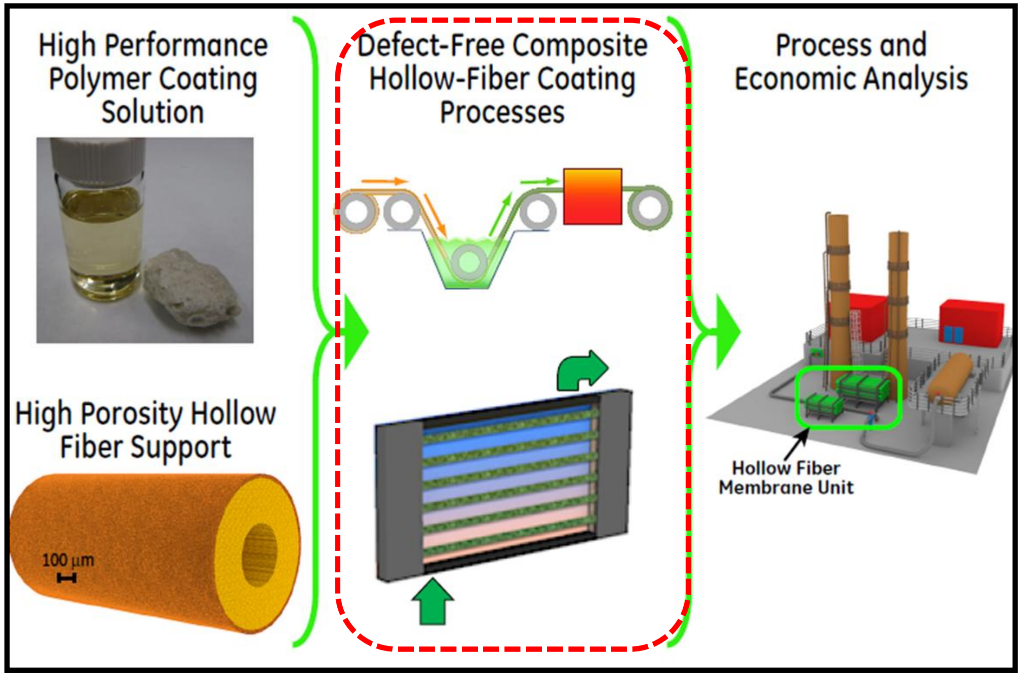
* As presented on January 13th, 2012

Project Task Structure



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Task 4 – Fabricate Coated HF Membranes

Goal: Develop processes to apply ultra-thin layer coatings on hollow fiber supports & elucidate fundamental polymer properties

Task 4.1 - Demonstrate defect-free individual coated HF (Q3-4)

Milestone – Fabrication of defect-free dip-coated hollow fiber

Tasks 4.2-4.3 - Develop & refine continuous coating process (Q3-6)

Tasks 4.4-4.5 - Adapt & refine in-situ coating process (Q3-6)

Milestones – Demonstration of continuous dip & in-situ coating processes (Q3-4)

Reproducible protocol and processes for coated hollow fiber fabrication (Q5-6)

Task 4–Fabricate Coated HF Membranes (Cont.)

Tasks 4.6-4.7 - Reduce coating defects & create defect-free multi fiber modules (Q7-10)

Milestones – Multi HF module performance results (Q7-8)
Defect-free multi HF module performance (Q9-10)

Tasks 4.8-4.10 - Study key membrane properties & develop membrane models (Q5-10)

Milestones – Membrane fouling set-up commissioned (Q5-6)
Fouling studies using model fly-ash (Q7-8)

Aging studies using clean - dry CO_2 (Q5-6), saturated CO_2 (Q7-8), saturated CO_2/N_2 streams (Q9-10)

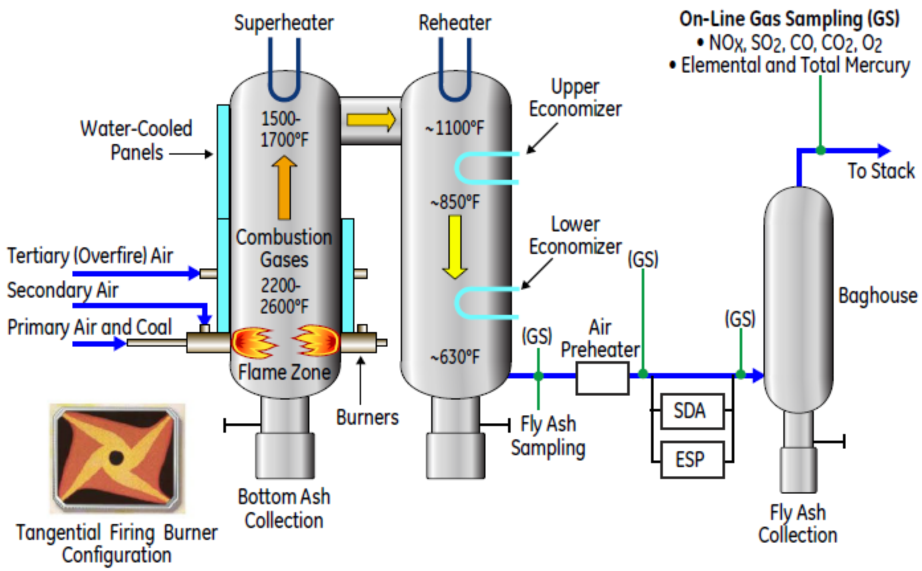
Current Progress*

- GE to leverage existing continuous coating line designs
- GaTech to retrofit existing in-situ coating setup

GE imagination at work

* As presented on January 13th, 2012

Project Task Structure



- **Task 1** – Project Management
- **Task 2** – Optimize Polyphosphazene Polymer and Coating Solution
- **Task 3** – Fabricate Hollow Fiber Support Layer
- **Task 4** - Fabricate Composite Coated Hollow Membranes
- **Task 5** - Test Membranes at Bench-Scale in Coal Flue Gas
- **Task 6** - Conduct Process Evaluation and Module Design

GE imagination at work

Task 5 – Membrane Coal Flue-Gas Testing

Goal: Exposure & performance test materials & membranes under coal flue-gas

Task 5.1 – Enhance bench-scale testing facilities (Q1-2)

Task 5.2 – Exposure & Performance test flat membranes (Q3-4)

Task 5.3 - Performance test hollow fiber membranes (Q5-6)

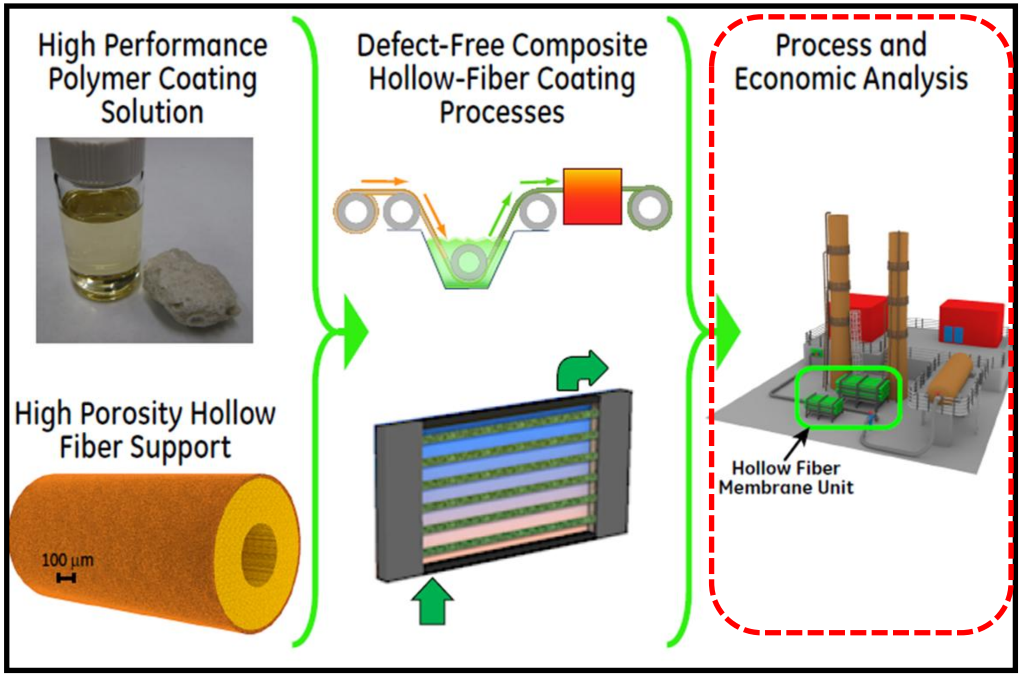
Task 5.4 - Coal flue gas performance test optimized hollow fiber membranes (Q9-10)

Current Progress*

- Project partners upgrading gas testing rig capabilities

* As presented on January 13th, 2012

Project Task Structure



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GE imagination at work

Task 6–Process Evaluation & Module Design

Goal: Explore system technical & economic feasibility; conduct module design & fabrication

Task 6.1 - Preliminary technical & economic feasibility (Q1-6)

Milestone – Go/No-Go decision, feasibility report

Task 6.2 - Final technical & economic feasibility (Q7-12)

Milestone – Final report, Scale-up strategy

Task 6.3 - Membrane module design & fabrication (Q1-12)

Milestone – Module design (Q1-6), module fabrication (Q7-12)

Current Progress*

- GE to leverage existing membrane system & module designs

GE imagination at work

* As presented on January 13th, 2012

Risks & Mitigation Plan

Description of Risk	Probability	Impact	Risk Management
Technical Risks			
Flue gas acidic components (SO_x, NO_x)	Low	Low	Polymer inherently tolerant towards acid gases
Temperature excursions	Low	Low	Processing and operating temperatures will not degrade polymer layers
Insufficient mechanical durability	Moderate	Moderate to High	Optimize cross-linking of selective membrane layer and processing conditions
Fouling potential from fly-ash/particulates	Moderate	Moderate to High	Create non-adhesive surface properties, resist fouling
Permeability and selectivity at 60 °C lower than anticipated	Moderate	Moderate to High	Optimize the stabilizer and cross-linker content
Casting solvent formulation stability	Moderate	Moderate	Optimize casting solvent formulation to give uniform, defect-free polymer film coverage on hollow fibers
Resource Risks			
Materials–availability affects project	Low	High	INL has sufficient manufacturing capacity for initial membrane production for BP1. Vendors identified for larger-scale production

Future Testing
&
Technology Development

Equipment Design & Commissioning Plans

- Hollow fiber winder setup (GE → internal funds)
- Hollow fiber continuous coating line (GE → internal funds)
- New dense film & hollow fiber permeation systems & retrofits (GaTech, INL, WRI, GE → DOE & internal funds)
- Particulate fouling testing facility (GaTech → DOE funds)
- Other unanticipated equipment needs

Thank You