turning knowledge into practice

Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting

CO_2 Capture Membrane Process for Power Plant Flue Gas

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Arkema Inc., King of Prussia, PA

John Jensvold
Generon IGS, Inc., Pittsburg, CA

March 24 – 26, 2009 • Sheraton Station Square • Pittsburgh, Pennsylvania

RTI International

Center for Energy Technology (CET)

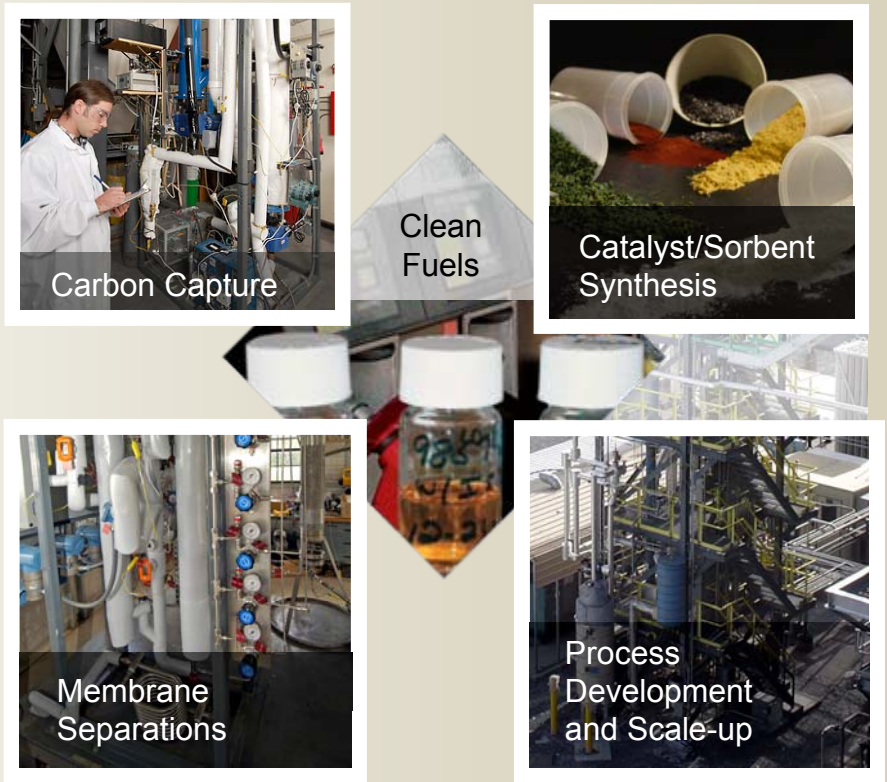
RTI International

- Established in 1958
- One of the world's leading research institutes
- >2,800 staff; >$700M revenue (2008)
- *Mission:* To improve the human condition by turning knowledge into practice

CET Capabilities

- Advanced Gasification
  - Warm gas desulfurization
  - Multicontaminant removal
  - Substitute natural gas production
- Carbon Capture
  - Post- and Pre-combustion CO_2 capture
  - Chemical Looping Combustion
  - Advanced Membranes
- Clean Fuels
  - Syngas to fuels and chemicals
  - Biofuels
- Hydrogen Production and Purification

CET Application Areas



Project Overview

- DOE/NETL Cooperative Agreement # DE-NT0005313
  - DOE Project Manager: José Figueroa
  - RTI Project Manager: Lora Toy
- Period of Performance
  - October 1, 2008 – September 30, 2010

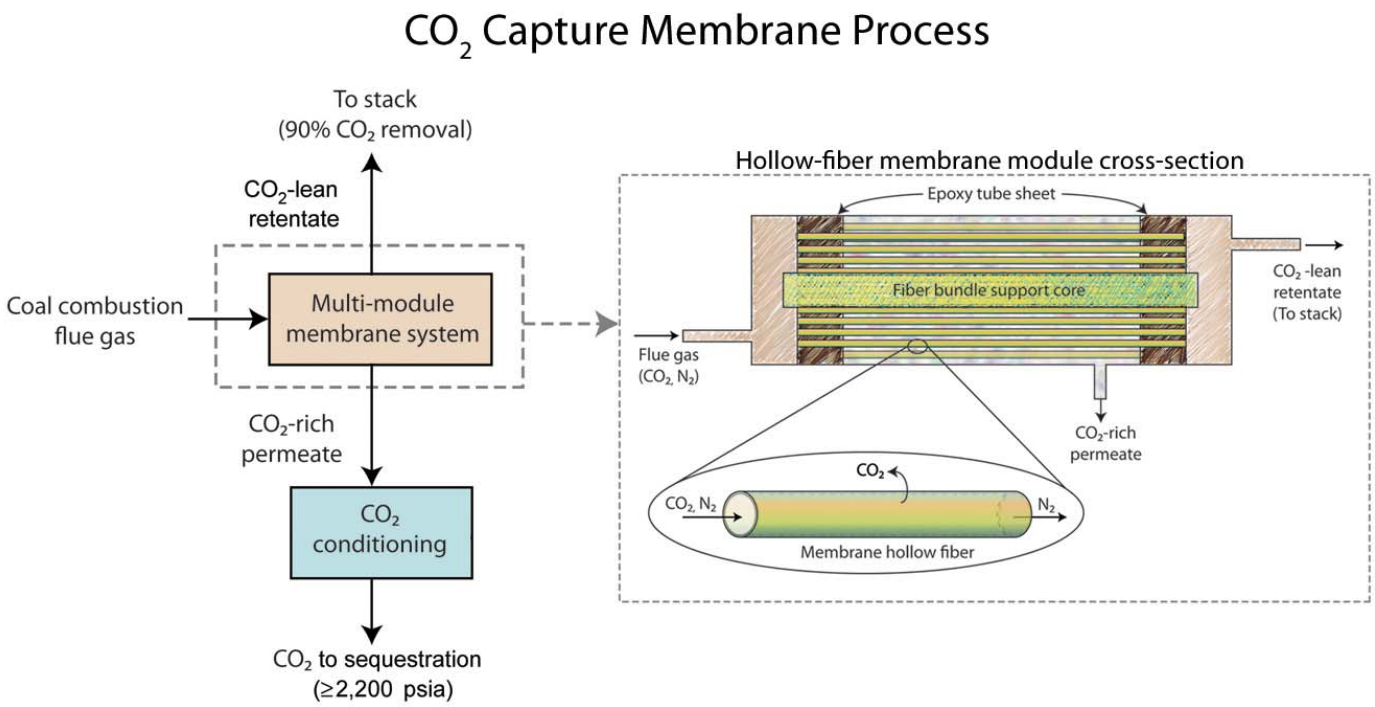
Project Phase	Period of Performance	DOE Share	Cost-Share	Total
Budget Period I	10/08 → 09/09	$974,298	$243,575	$1,217,873
Budget Period II	10/09 → 09/10	$970,523	$242,631	$1,213,154
Totals	10/08 → 09/10	$1,944,821	$486,206	**$2,431,027**

- Project Team
  - RTI (Prime – Technology developer, membrane evaluation, management)
  - Arkema Inc. (Polymer synthesis and development)
  - Generon IGS, Inc. (Membrane module development and fabrication)
  - ARCADIS, Inc. (Test skid operation)
  - U.S. EPA (Test facility provider)

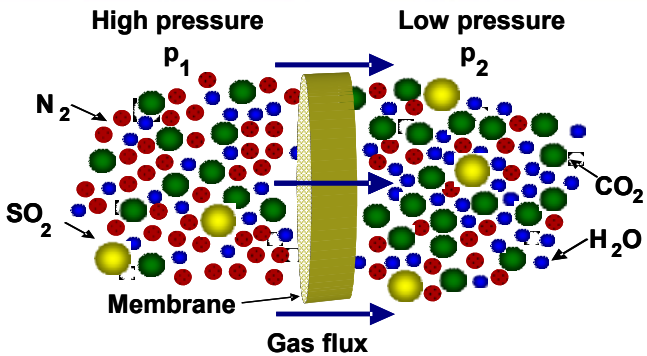
CO_2 Capture Membrane Process for Power Plant Flue Gas (CCM) Project

Overall Project Objective

Develop an advanced polymeric membrane-based process that can be cost-effectively and reliably retrofitted into existing pulverized coal (PC)-fired power plants to capture ≥90% CO_2 from plant's flue gas at 50-60 °C with <35% increase in Cost of Electricity.



Membrane Approach



Solution-diffusion mechanism

(i) Sorption on high-pressure side
(ii) Diffusion down partial pressure gradient
(iii) Desorption on low-pressure side

$$P = S \times D$$

Permeability **Solubility** **Diffusivity**

$$\alpha_{CO_2/N_2} = \frac{P_{CO_2}}{P_{N_2}} = \left(\frac{S_{CO_2}}{S_{N_2}}\right)\left(\frac{D_{CO_2}}{D_{N_2}}\right)$$

Selectivity **Solubility selectivity** **Mobility selectivity**

Advantages

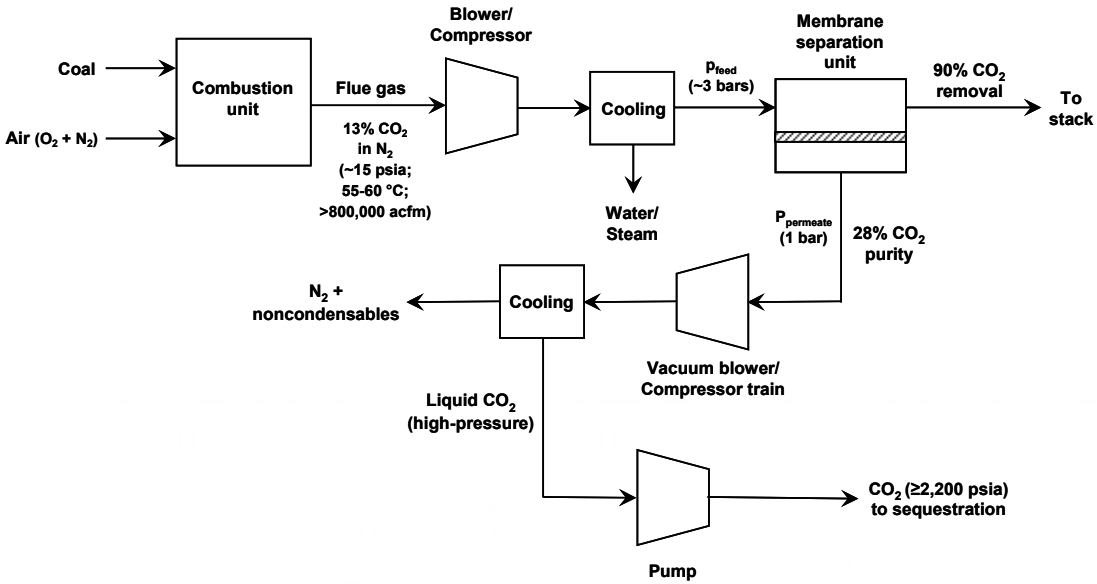
- Passive separation
  - Inherently energy-efficient
  - No heating needed to recover CO_2 (unlike adsorption and absorption processes)
- Simple to operate and maintain
  - No moving parts
- Compact
- Modular
  - Easy scalability
  - Easy to retrofit into existing process infrastructures
- No secondary hazardous waste stream

Challenges of CO_2 Capture Application with Membrane Process

- Low CO_2 concentration (~13-15%) in flue gas
- Low flue-gas pressure (~15 psia)
- Large flue gas volumes
- Presence of flue-gas moisture and contaminants (SO_x, NO_x, etc.)
- High cost and parasitic energy penalty for
  - Flue-gas compression or vacuum
  - Compression of separated CO_2 from low pressure to sequestration pipeline pressure (~2,200 psia)

Example Single-Stage Membrane Process

(~500-MW plant; ~800,000 acfm flue gas;
CO_2 permeance ~ 100 GPU; CO_2/N_2 selectivity ~ 35)



For 90% CO_2 removal in single-stage process, membrane area ~ 23×10^6 m^2 (very large!) is required.

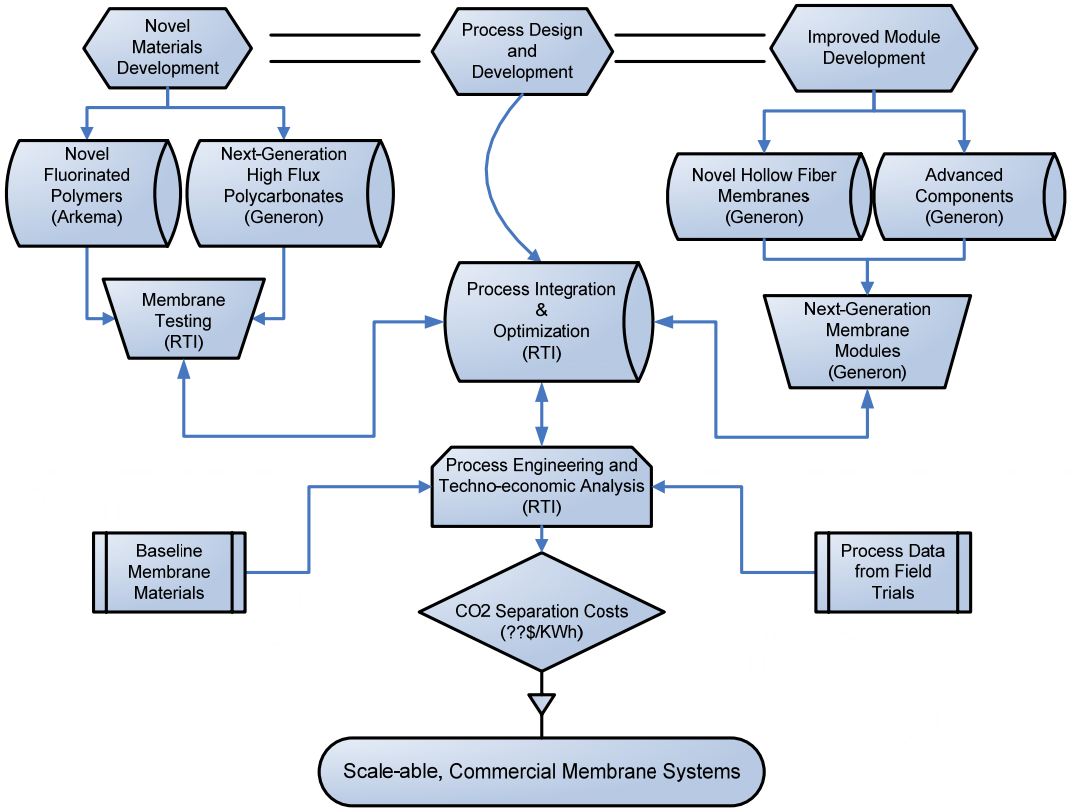
1 GPU = 1×10^{-6} $cm^3(STP)/(cm^2 \cdot s \cdot cmHg)$

Project Approach

Three Parallel Efforts

- Membrane materials development
  - Novel fluorinated polymers
  - Next-generation, high-flux polycarbonate
  - Flux / Selectivity
  - Chemical resistance
- Membrane module design and development
  - Hollow fiber dimensions
  - Module gas flow distribution
  - Module sealing
  - Module fabrication
- Process design and development
  - Process variables
  - Process design options
  - Process integration
  - Technoeconomic analysis

Roadmap of Technical Approach



Specific Objectives and Task Structure

Specific Objectives

- Develop two or three new chemistries/structures of fluorinated polymer membrane materials that have
  - high CO_2 permeance [300-3,000 GPU targeted]
  - high CO_2/N_2 selectivity [30-50 selectivity targeted]
  - excellent chemical stability to moisture, SO_2, and NO_x
- Identify and develop power- and cost-effective CO_2 capture membrane process design/integration strategies with refined membrane CO_2 permeance and selectivity targets.
- Develop and fabricate improved membrane hollow fibers and membrane module designs designed to handle large flue-gas flow rates and high CO_2 permeate flows
- Demonstrate CO_2 capture membrane performance/reliability in field test with real coal-fired process flue gas.

1 GPU = 1×10^{-6} $cm^3(STP)/(cm^2 \cdot s \cdot cmHg)$

Project Tasks

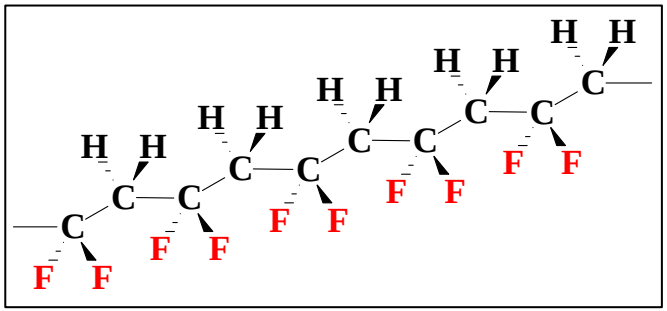
- ***Task 1***. Synthesize Novel Polymers / Prepare Membrane Films
- ***Task 2***. Characterize Permeation Properties of Membrane Films
- ***Task 3***. Produce and Characterize Membrane Hollow Fibers
- ***Task 4***. Make and Characterize Prototype Hollow-Fiber Membrane Modules
- ***Task 5***. Demonstrate Membrane Modules in Field Test
- ***Task 6***. Perform Process Design / Technical and Economic Analysis
- ***Task 7***. Manage Project / Prepare Reports

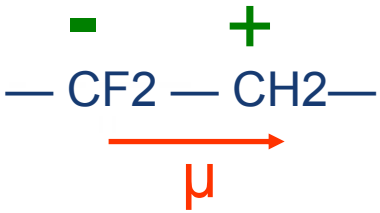
Membrane Materials Development

Arkema

- Polyvinylidene Fluoride (PVDF)-based polymers
  - High resistance to acids and oxidants
  - Specific affinity for CO_2 and
    - High CO_2 solubility due to high polar nature of VDF repeat unit
  - Excellent physical and mechanical properties
  - High thermal stability (T_d ~ 340 °C)
  - Durability and longevity
- PVDF homopolymer
  - Semicrystalline (Degree of crystallinity up to 65%)
  - Crystalline phase reduces gas transport.
  - CO_2 permeance ~ 5 GPU* (for 0.1-micron thickness)
  - CO_2/N_2 selectivity ~ 23* [strongly dependent on CO_2 partial pressure (concentration)]

PVDF repeat unit: $-[CH_2\text{-}CF_2]_n-$





High dipole moment ⟶ Highly polar

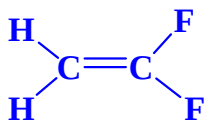
* From El-Hibri and Paul, *J. Appl. Polym. Sci.*, Vol. 31, 2533 (1986).
1 GPU = 1×10^{-6} $cm^3(STP)/(cm^2 \cdot s \cdot cmHg)$

Membrane Materials Development

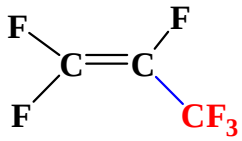
Arkema

Approach #1

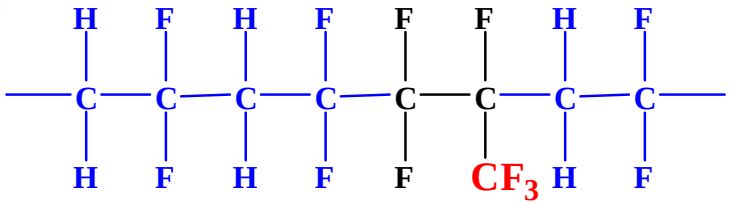
- Copolymerize bulky hexafluoropropylene (HFP) monomer into VDF backbone.
  - Bulky $-CF_3$ disrupts crystallization, reducing crystallinity (down to <2%)
  - Should increase gas transport in membrane



VDF



HFP



VDF-*co*-HFP

Approach #2

- If crystallinity reduction not sufficient, then copolymerize new non-fluorinated monomers (e.g., vinyl esters, acrylic esters, etc.) with VDF to improve CO_2 transport.

Approach #3

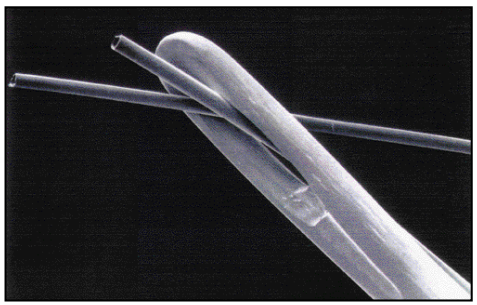
- Design composites (co-continuous phases) of low crystallinity and chemically modified PVDF with other compatible but not miscible polymers (i.e., PEO) to further enhance CO_2 transport without compromising chemical resistance of PVDF.

Next-Generation, High-Flux Polycarbonate (PC) Membrane

Generon

	Relative CO_2 flux	CO_2/N_2 selectivity
Generon Standard PC Membrane	1	20-30
Generon High-Flux PC Membrane	4.0-4.5	30-35

1 GPU = 1×10^{-6} $cm^3(STP)/(cm^2 \cdot s \cdot cmHg)$



Individual Generon® hollow membrane fibers are about the size of a human hair.

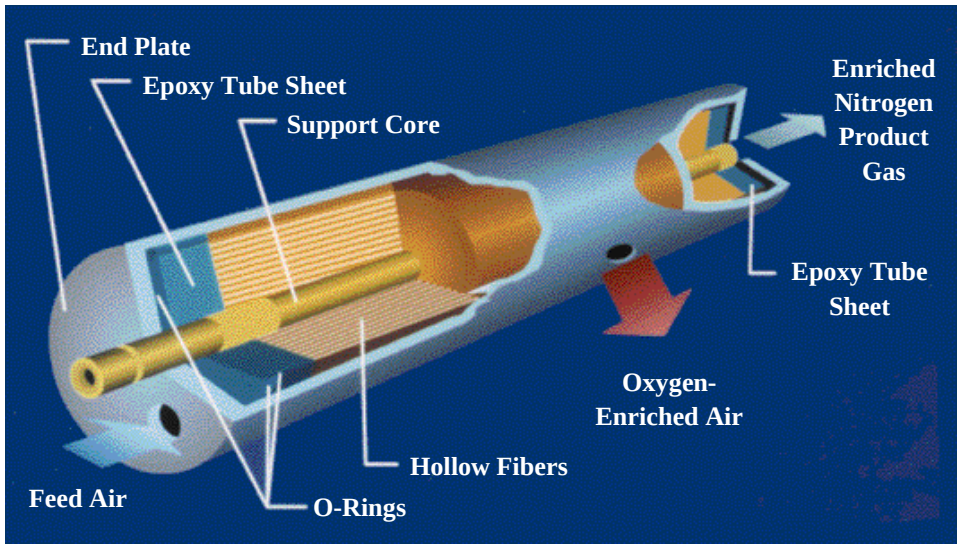
Thousands of miles of hollow fiber membranes make up each Generon® membrane module.

Standard Generon® module sizes range from 100 to 10,000 ft^2 (10 to 1,000 m^2).

Membrane Module Design/Development

- Two widely used module types for industrial gas separation membranes
  - Hollow fiber
  - Spiral wound
- Hollow-fiber module type selected
  - Lower module cost per membrane area
  - Substantially higher membrane packing density
  - Pressure drop ca be an issue with CO_2 capture application.
  - Partner Generon specializes in hollow-fiber membranes and modules.
- Development areas to maximize performance
  - Hollow fiber dimensions
  - Gas flow distribution
  - Development of epoxy tubesheet
  - Module engineering design

Generon membrane module for air separation



Module Fabrication

Generon Facilities

Dedicated Research Spin Lines for Hollow-Fiber Development (2,000 ft^2)

Module Manufacturing

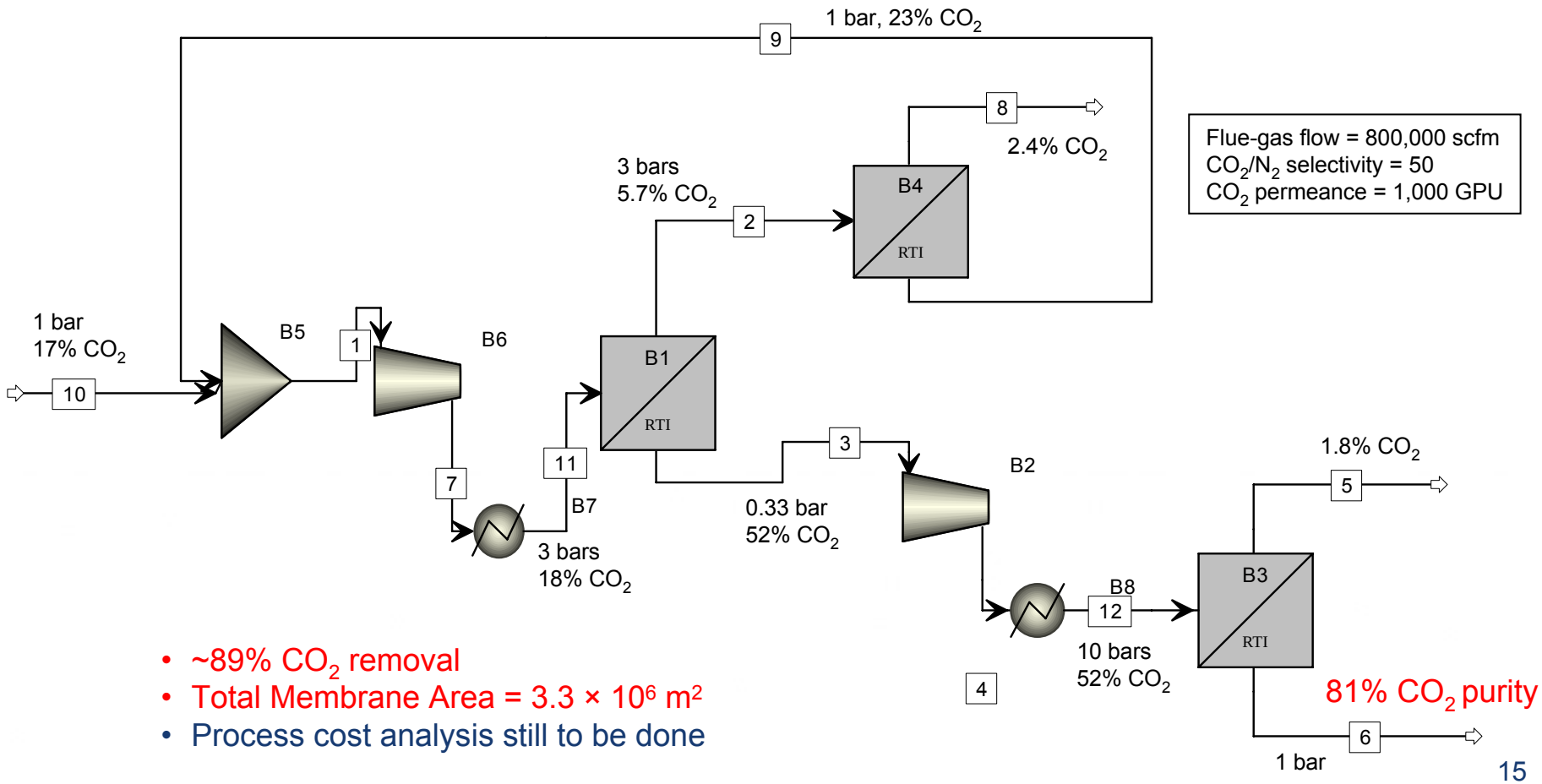
Bundle Making / Potting / Machining

Process Design/Integration Parameters To Be Considered

- Both membrane area and cost vastly affected by membrane properties, process parameters, and process scheme.
  - Compression/Vacuum
  - Multi-step design
  - Multi-stage design
- Optimization dependent on membrane area requirement and operating cost
- Need to look at multi-step and multi-stage process design
- Maximize power management
  (i.e., minimize parasitic energy losses)

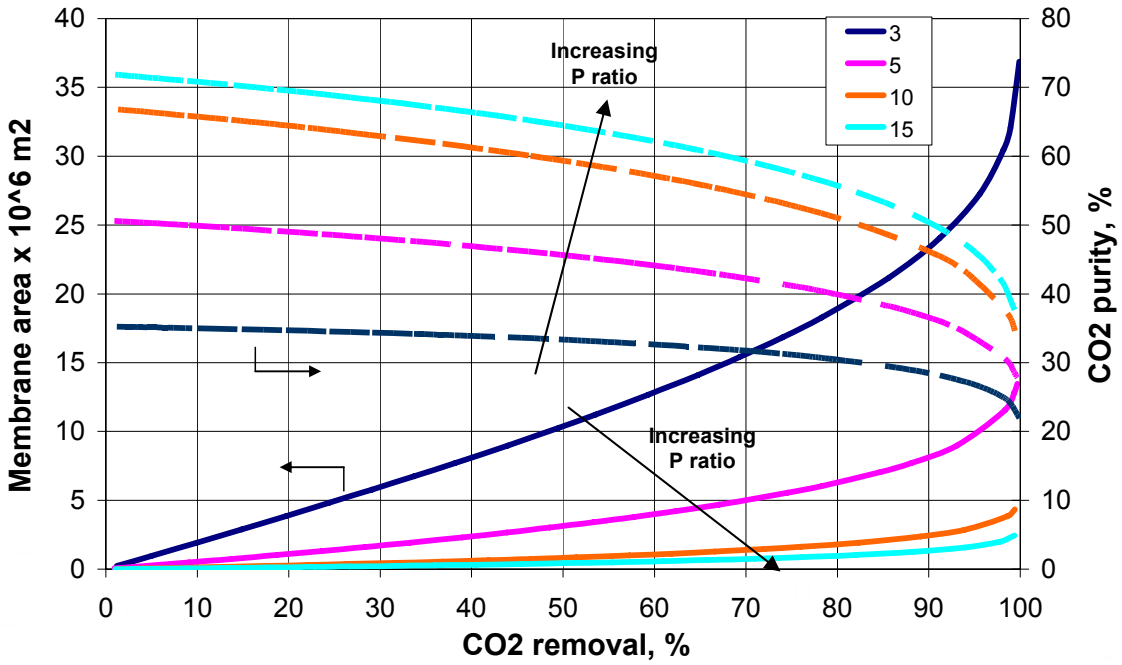
System process design is conducted using an RTI membrane simulation tool that is integrated into AspenPlus process simulation software and its libraries.

Example Multistage Membrane Process Scheme: Preliminary Simulation Results



- ~89% CO_2 removal
- Total Membrane Area = 3.3×10^6 m^2
- Process cost analysis still to be done

Single-Stage Membrane Process Simulation: Effect of Pressure Ratio [Constant permeate pressure 15 psia]

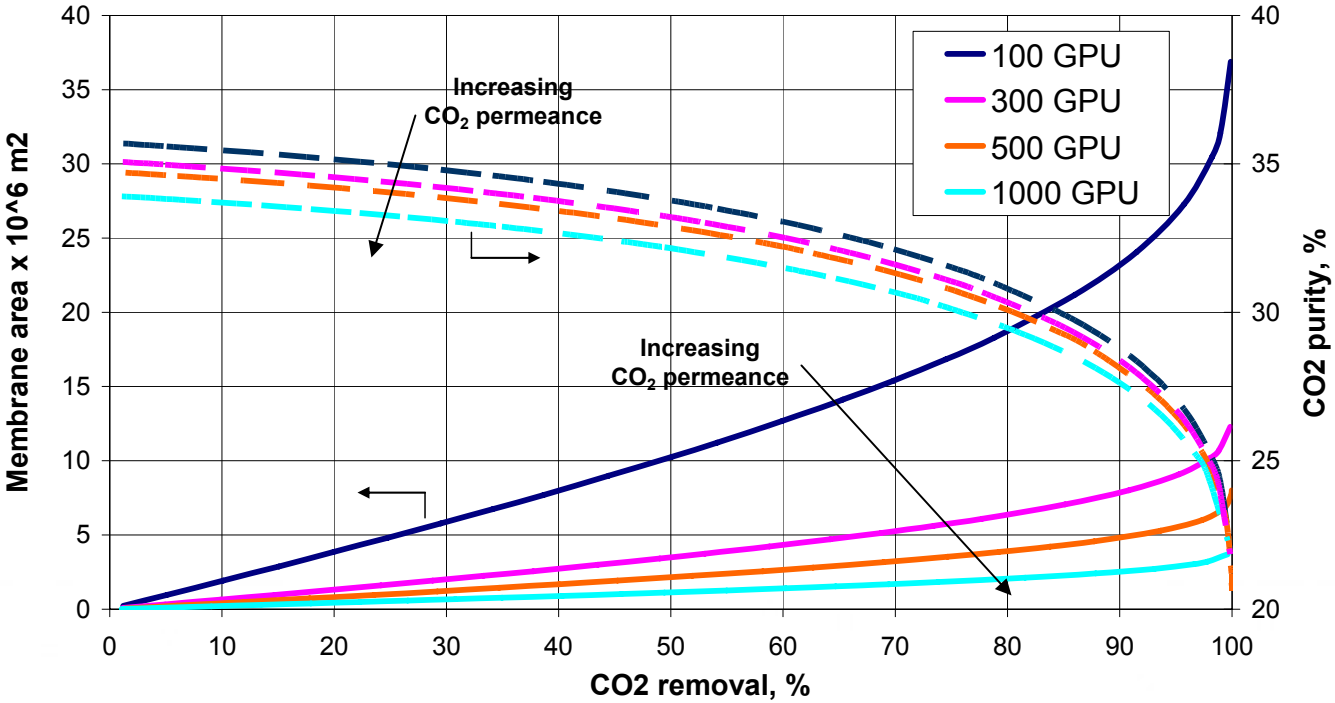


Flue gas FR = 800,000 scfm
CO2 mole fraction = 0.13
CO2 Perm = 100 GPU
N2 Perm = 2.86 GPU
Permeate pressure = 15 psia

Single Stage
Shell Side Feed

- Increasing P ratio decreases membrane area for a given CO_2 removal.
- Increasing P ratio significantly increases permeate-side CO_2 purity.
- Effect of increasing pressure ratio is significant at lower pressure ratios (3-5) compared to that at higher ratios (10-15).

Single-Stage Membrane Process Simulation: Effect of CO_2 Permeance [Constant selectivity]

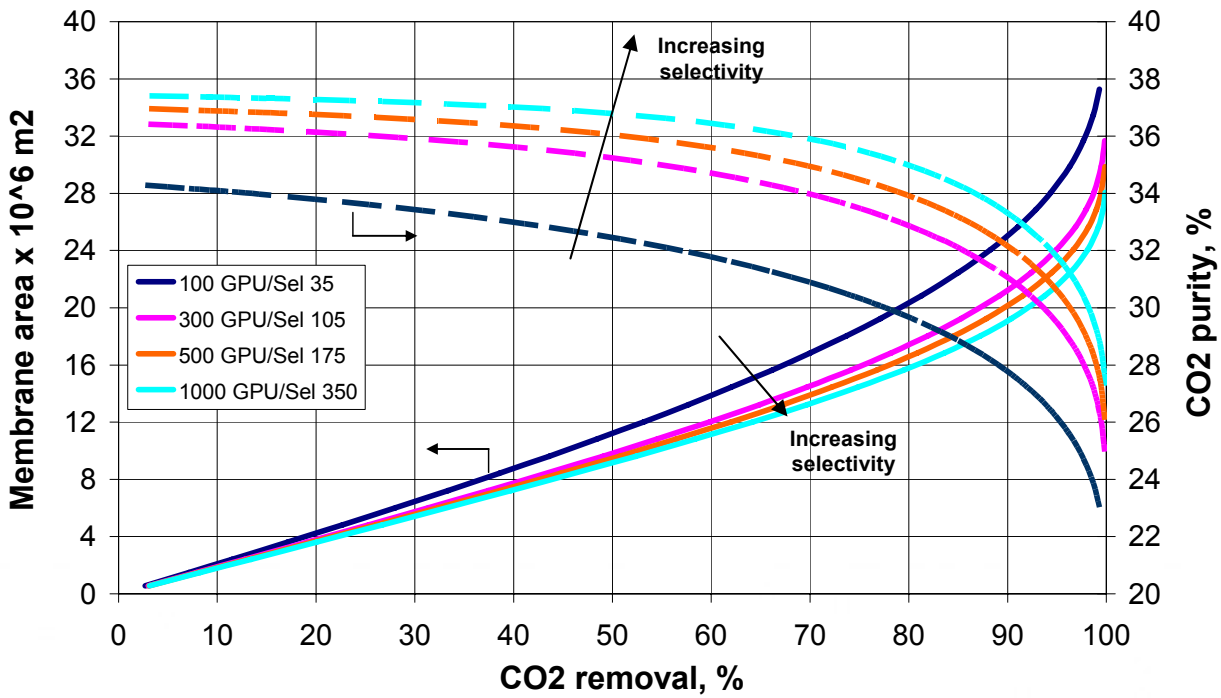


Flue gas FR = 800,000 scfm
CO2 mole fraction = 0.13
CO2/N2 selectivity = 35
Fp = 45 psia, Pp = 15 psia

Single Stage
Shell Side Feed

- Increasing CO_2 permeance decreases the required membrane area proportionally.
  (For 90% CO_2 removal and w/ 10 times increase in CO_2 permeance, membrane area decreases ~10-fold from 24×10^6 to 2.5×10^6 m^2.)
- CO_2 purity decreases marginally with increasing CO_2 permeance.
  (For 90% removal and 10 times increase in CO_2 permeance, CO_2 purity decreases from 28.5 to 27.5%.)

Single-Stage Membrane Process Simulation: Effect of CO_2/N_2 Selectivity [Changing CO_2 Permeance]



Flue gas FR = 800,000 scfm
CO2 mol frac in feed = 0.13
N2 perm = 2.86 GPU
Fp = 45 psia, Pp = 15 psia

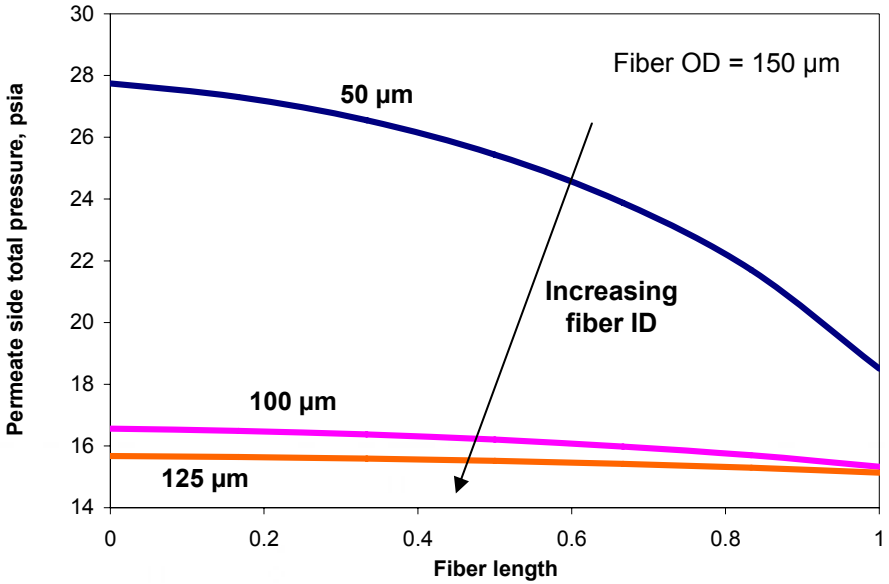
Single Stage
Shell Side Feed

- Increasing selectivity 10 times reduces membrane area only from 25×10^6 to 19×10^6 m^2 for 90% CO_2 removal.
- Increasing selectivity enriches the permeate CO_2 purity, for example, by 5% with 10 times increase in selectivity for 90% CO_2 removal.

Process Design Analysis

- Analyze and compare various candidate process schemes
  - Power consumption
  - Membrane area requirement
- Estimate targets for membrane properties
  - CO_2 flux (permeance)
  - CO_2 selectivity
  - Fiber dimensions
- Analyze pressure drop issues associated with high flue-gas flows and high CO_2 permeate flows

Bore-permeate-side pressure profiles: Effect of fiber ID

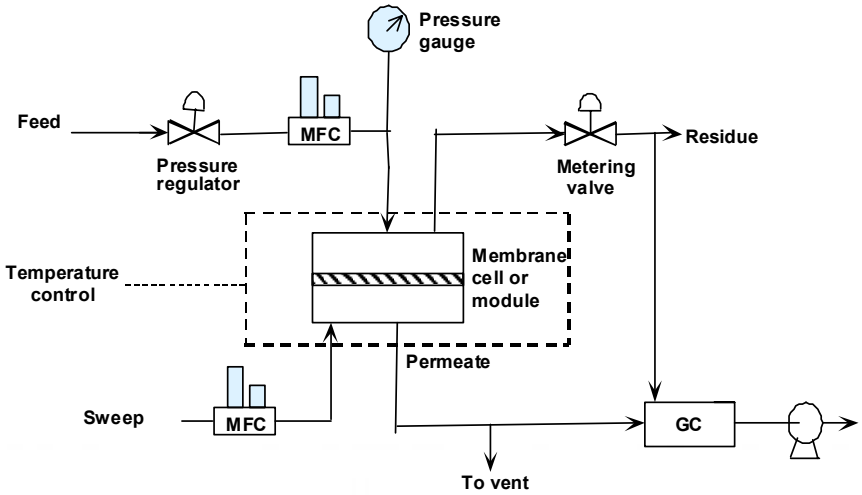


Flue gas FR = 800,000 scfm
CO2 mol frac in feed = 0.13

Single Stage; Shell Side Feed
Feed P = 45 psia; Permeate P = Atmospheric
90% CO_2 removal

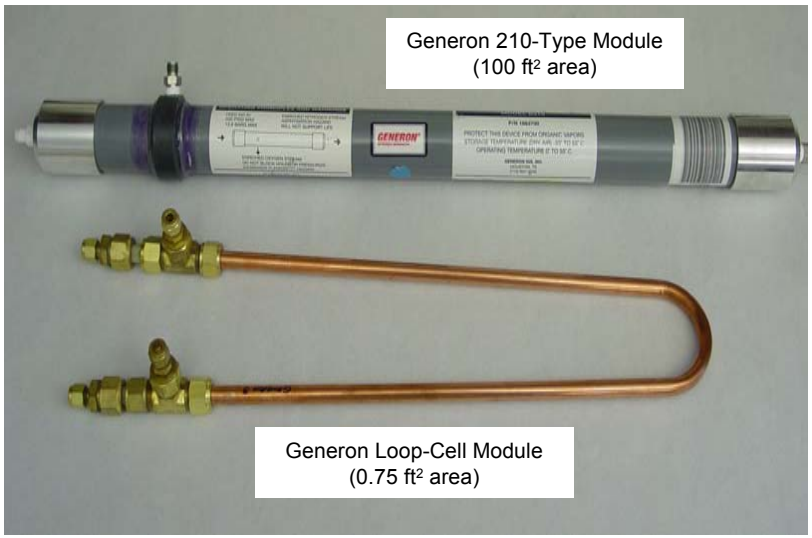
Membrane Permeation Testing

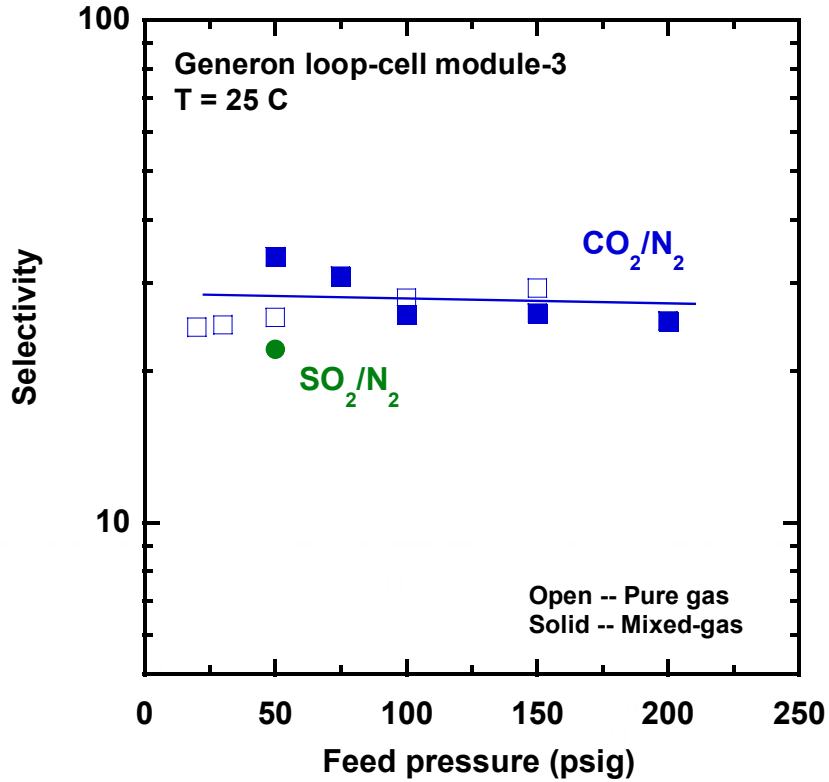
- Membranes
  - Generon polycarbonate-based hollow fiber membrane modules (current- and next-generation)
  - Arkema novel PVDF-based membrane materials
- Gases
  - Pure gases (O_2, N_2, CO_2, SO_2)
  - CO_2/N_2 gas mixtures with and without moisture, SO_2, and NO_x
- Feed pressure range: 10-200 psig
- Temperature range: 25-60 °C



RTI membrane permeation apparatus

Generon Loop-Cell Module: Pure- vs. Mixed-Gas Selectivities





Feed composition: 290 ppm SO_2, 15% CO_2, Balance N_2
Membrane Area = 0.75 ft^2 = 700 cm^2

Field-Test of CO_2 Capture Membrane Modules

- Extended testing to investigate membrane module separation performance and structural stability
  - Slipstream of real coal-fired process flue gas from EPA's combustion facility (Research Triangle Park, NC) will be used.
  - 300-hour field test will be completed.
  - Membrane module skid previously used for a field test will be modified.
  - Test skid will be based on optimized process design.

Previous membrane test skid built
(Skid footprint ~ 4 ft. × 6 ft.)

Anticipated Challenges

- Low CO_2 permeability
  - Co-continuous block copolymer microstructures
- Low CO_2/N_2 selectivity
  - Incorporate CO_2 affinity chemical functionalities (polyethers, polyacrylamide, etc.)
- Susceptible to contaminants
  - Increase degree of fluorination
- Formation of defect-free hollow fibers
  - Multiple fiber formation options will be considered
- Sealing of hollow fibers in module shell
  - New epoxy tubesheet formulations will be developed
- Pressure drop issues
  - Spin fibers of larger dimensions
- Flow distribution issues
  - Fiber weaving process will be optimized
  - Modify module housing design (gas port locations, baffles)

Project Timeline

Task No.	Task Description	Project Duration — Start: 10/1/2008 End: 9/30/2010								Planned Start Date	Planned End Date	Actual Start Date
		Budget Period 1 (10/1/2008 - 9/30/2009)				Budget Period 2 (10/1/2009 - 9/30/2010)						
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4			
1	Synthesize Novel Polymers / Prepare Membrane Films (*Arkema*)									12/1/2008	3/31/2010	1/1/2009
2	Characterize Permeation Properties of Membrane Films (*RTI*)									2/1/2009	5/30/2010	2/7/2009
3	Produce and Characterize Membrane Hollow Fibers (*Generon*)									1/1/2009	6/30/2010	11/1/2008
4	Make and Characterize Prototype Hollow-Fiber Membrane Modules (*Generon*)									1/1/2009	6/30/2010	
5	Demonstrate Membrane Module(s) in Field Test (*RTI/Arcadis*)									8/1/2009	6/30/2010	
6	Perform Process Design / Technical and Economic Analysis (*RTI*)									11/1/2008	9/30/2010	10/20/2008
6.1	Evaluate Membrane System Process Design Options									11/1/2008	11/1/2009	10/20/2008
6.2	Prepare Integrated System Process Desigh/Technical and Ecnomic									7/1/2009	9/30/2010	
7	Reporting and Project Management									10/1/2008	9/30/2010	10/1/2008

Path Forward

- Synthesize novel polymers and membrane films
- Produce membrane hollow fibers
- Fabricate lab-scale, hollow-fiber membrane modules
- Characterize permeation properties of membrane films and lab modules
  - Pure-gas testing
  - Simulated flue-gas testing
- Perform process design and technoeconomic analysis
- Make and characterize prototype (field-test) hollow-fiber membrane modules
- Design and construct membrane test skid for field testing
- Test prototype membrane modules with slipstream of real coal-fired process flue gas for extended time (e.g., 300 h) at EPA's Multipollutant Control Research Facility (MPCRF)

Thank you

Questions?