CO_2 Capture Membrane Process for Power Plant Flue Gas

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Pittsburgh, PA

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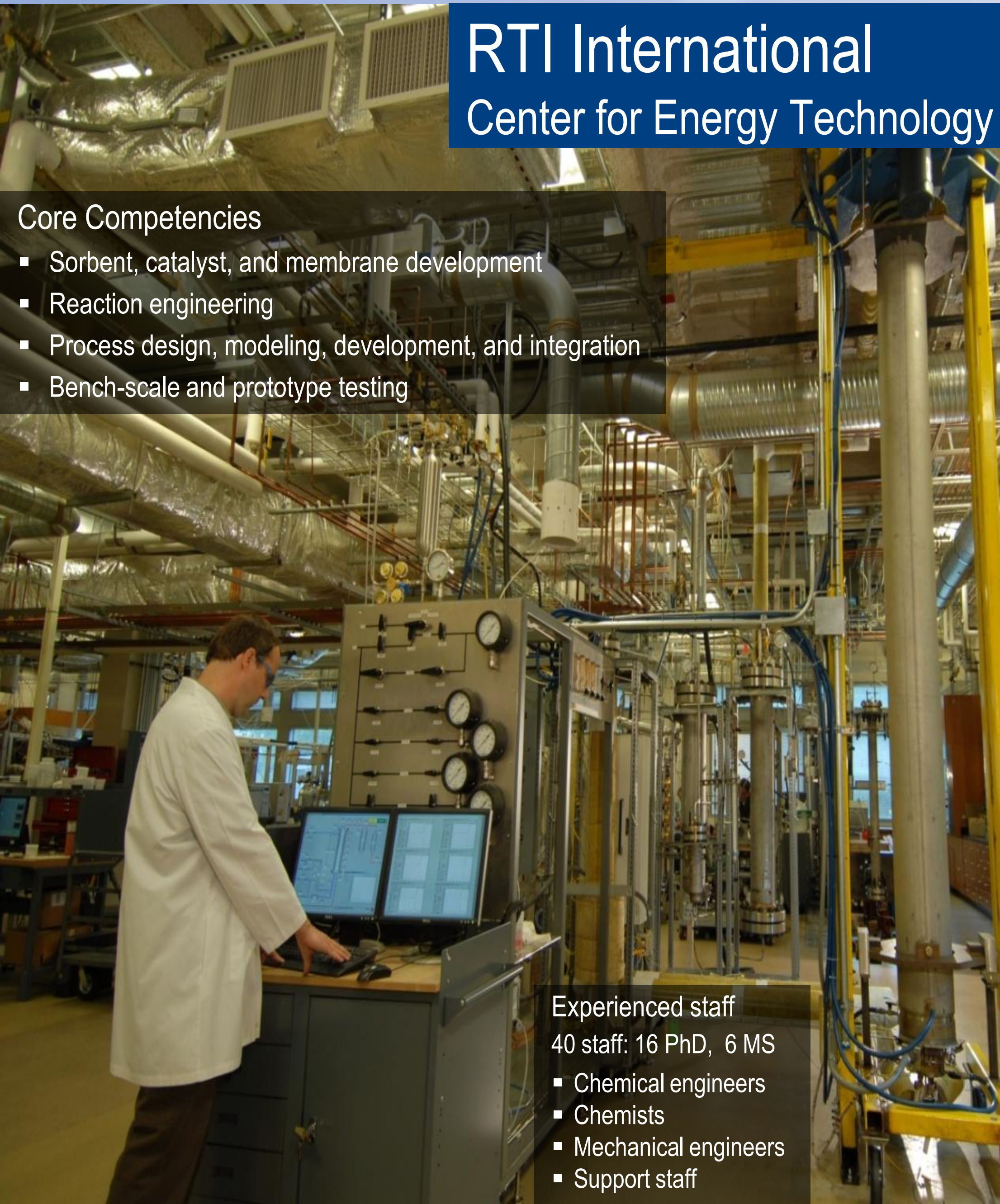
RTI International

Center for Energy Technology (CET)



Core Competencies

- Sorbent, catalyst, and membrane development
- Reaction engineering
- Process design, modeling, development, and integration
- Bench-scale and prototype testing

Experienced staff

40 staff: 16 PhD, 6 MS

- Chemical engineers
- Chemists
- Mechanical engineers
- Support staff

RTI International

- Established in 1958
- One of the world's leading research institutes
- >2,800 staff; >$717MM revenue (2009)
- *Mission*: To improve the human condition by turning knowledge into practice

CET Program Areas

- Advanced Gasification
  - Warm syngas cleanup/conditioning
  - Substitute natural gas (SNG) production
  - Hydrogen production (Iron-steam process)
- Clean Fuels
  - Syngas to fuels and chemicals
  - Hydrocarbon desulfurization
- CO_2 Capture and Reuse
  - Pre- and post-combustion CO_2 capture
  - Membrane separation
  - CO_2 reuse
- Biomass Conversion and Biofuels
  - Biomass gasification; Syngas cleanup/conditioning
  - Biomass pyrolysis

Project Overview

DOE/NETL Cooperative Agreement #DE-NT0005313

- DOE Project Manager: José Figueroa
- RTI Project Manager: Lora Toy

Period of Performance

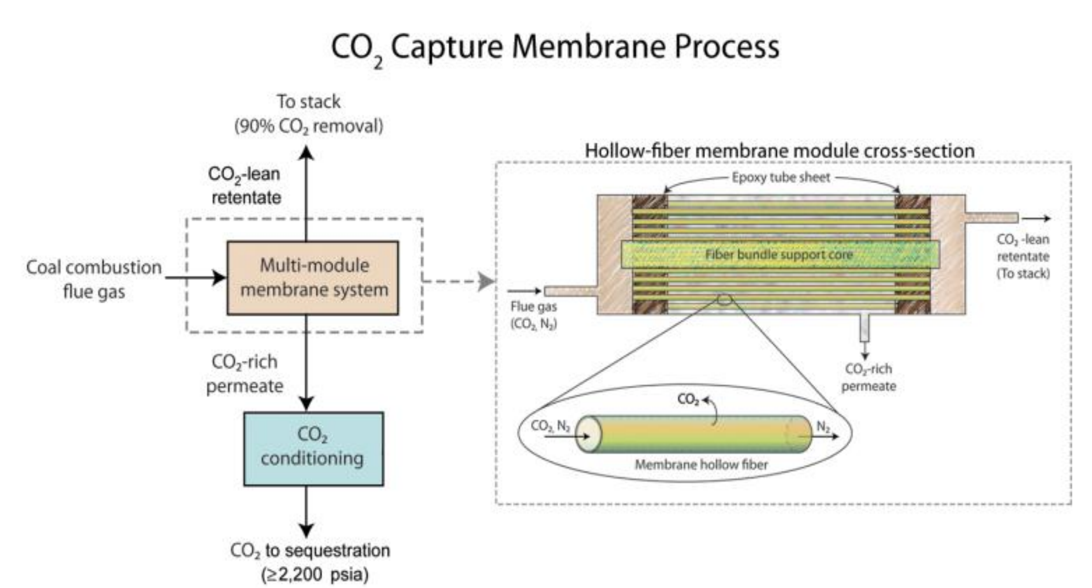
October 1, 2008 – March 31, 2011

Funding

- DOE Share: $1,944,821
- Cost Share: $486,206
- **Total Funding: $2,431,027**

Project Team

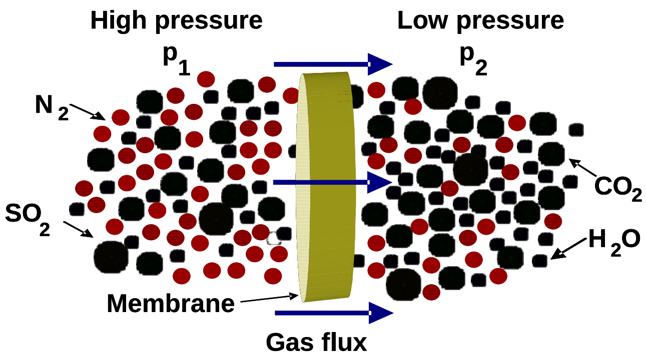
- RTI
- Arkema Inc.
- Generon IGS, Inc.
- U.S. EPA / ARCADIS
- University of North Carolina at Chapel Hill [UNC-CH] Cogeneration Facility



Overall Project Objective

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

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 (P) **Solubility** (S) **Diffusivity** (D)

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

Selectivity (α_{CO_2/N_2}) **Solubility selectivity** (S_{CO_2}/S_{N_2}) **Mobility selectivity** (D_{CO_2}/D_{N_2})

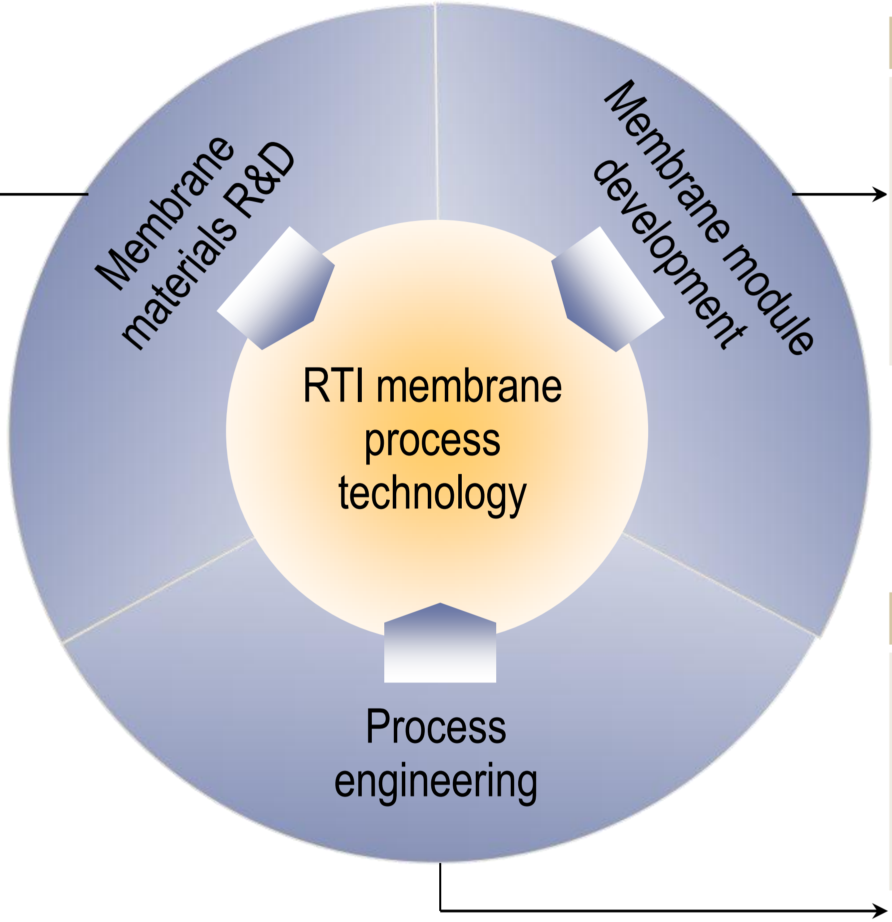
Advantages

- 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

RTI's CO_2 Capture Membrane Process Development

Membrane Materials

- CO_2 permeability (i.e., permeance or flux)
- CO_2/N_2 selectivity
- Contaminant resistance
- Processability into membrane structures



Membrane Modules

- Membrane fiber/module manufacturability
- Membrane sealing in module shell
- Pressure drop effects
- Gas flow distribution

Process engineering

- Process design and development
- Process integration
- Techno-economic evaluation (capture costs; ICOE)

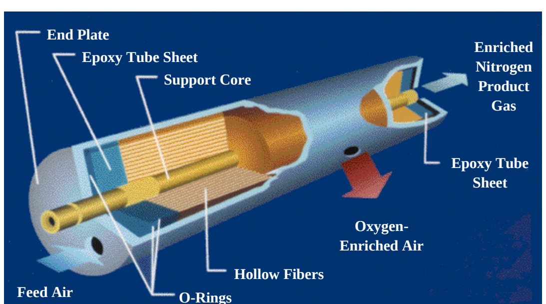
Hollow-Fiber Membrane Modules for High-Volume Applications

Common Membrane Module Designs Used for Gas Separations

Characteristic	Spiral-wound	Hollow-fiber
Packing density (ft^2/ft^3)	300-1,000	3,000-5,000
Cost ($\$/ft^2$)	1-5	0.2-1
Area of std. module (ft^2)	200-640	3,000-7,000

Ref. Baker, R. W., "Membrane Technology and Applications", 2nd ed., John Wiley and Sons: West Sussex, England, 2004, pp. 89-160.

- Hollow-fiber module type selected
  - Lower module cost per membrane area
  - Much higher membrane packing density
  - More suitable and cost-effective for high-volume applications (e.g., air separation)



Generon membrane module

Example Membrane Module Cost Comparison
(550-MWe coal plant; 90% capture; 95% CO_2 purity; $\alpha_{CO2/N2}$ = 35; 1.3 × 10^6 acfm)

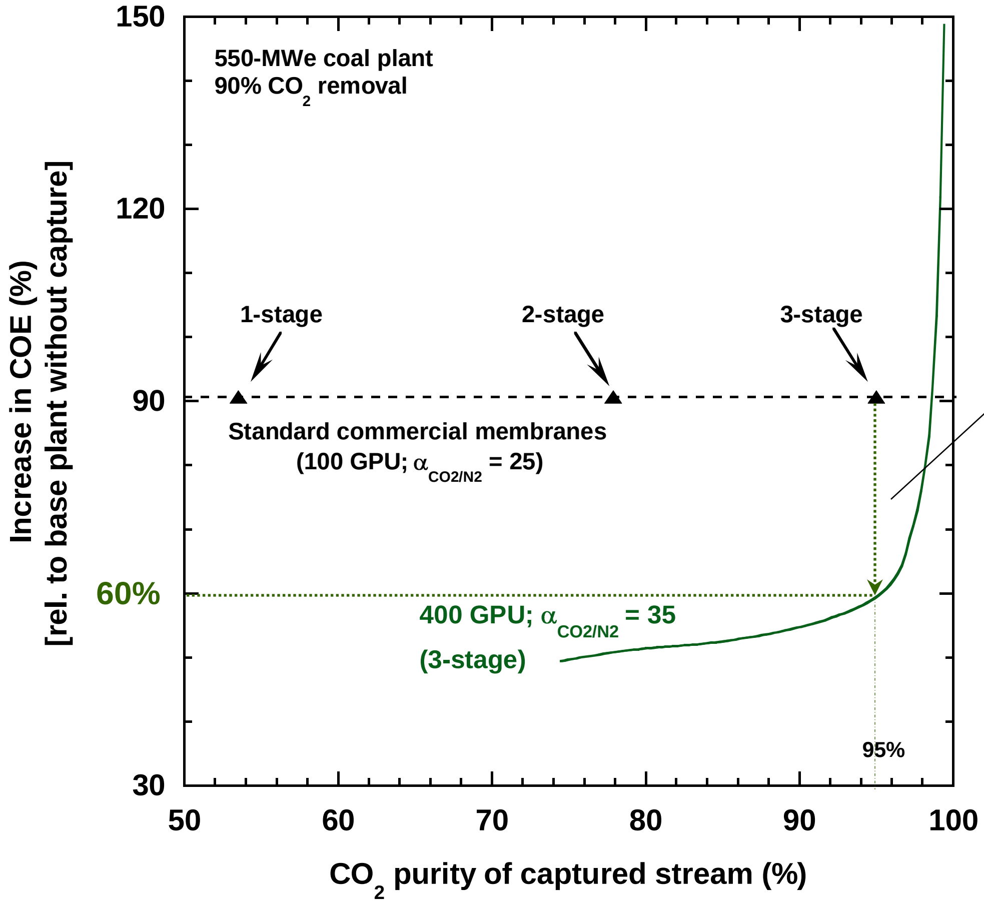
	Spiral-wound	Hollow-fiber
Membrane area	2.6 10^7 ft^2 (400 GPU) 1 10^7 ft^2 (1,000 GPU)	2.6 10^7 ft^2 (400 GPU)
Area per module[a]	1,163 ft^2	2,200 ft^2
No. of modules	22,356 (400 GPU) 8,599 (1,000 GPU)	11,819 (400 GPU)
Module cost (installed)[b]	$4.65/$ft^2$	$1.05/$ft^2$
Total module cost	$121MM (400 GPU) $46.5 MM (1,000 GPU)	$27.3MM (400 GPU)

[a] Assumed standard module size of 8 in. × 40 in. for spiral-wound and 6 in. × 36 in. for hollow-fiber.

[b] Cost for spiral-wound from Merkel et al. [J. Membr. Sci., 359, 126-139 (2010)] and for hollow-fiber from project partner Generon.

For the same membrane permeance and selectivity, the hollow-fiber design is much more cost-effective than spiral-wound.

Progress To Date



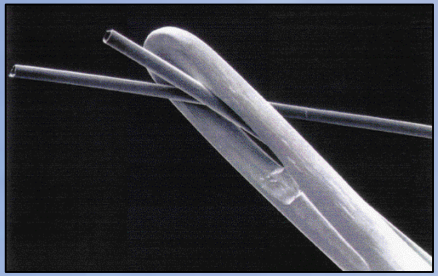
Key Enabling Developments

- Promising 3-stage membrane process design
- Generon high-flux polycarbonate (PC)
  - Formation/Production of membrane hollow fibers
  - Construction of membrane modules from membrane hollow fibers [From lab to larger prototypes (6 in. 36 in.)]

Basis of ICOE calculations: "*Cost and Performance Baseline for Fossil Energy Plants*", Vol. 1: Bituminous Coal and Natural Gas to Electricity Final Report, DOE/NETL-2007/1281, August 2007.

Generon Polycarbonate (PC) Membrane Platform

Next-Generation, High-Flux PC vs. Standard PC



Individual Generon hollow membrane fibers

Generon lab-scale hollow-fiber membrane modules

- Membrane hollow fibers from high-flux PC were successfully formed.
  - Mechanically durable up to at least 10,000 pressure cycles at 135 psig minimum pressure
- New high-flux PC fibers spun have
  - CO_2 permeance **4 times faster** than that of standard PC fibers
  - CO_2/N_2 selectivity similar to that of standard PC fibers

Hollow-fiber module	Gas permeance (GPU)				Gas selectivity		
	N_2	O_2	CO_2	SO_2	O_2/N_2	CO_2/N_2	SO_2/N_2
Standard PC	4.0	26	**100**	130	6.5	25	32
High-flux PC*	19	100	**410**	575	5.3	22	30

* Intrinsic CO_2/N_2 selectivity obtained on high-flux PC films was 35-37.
1 GPU = 1 × 10^{-6} cm^3(STP)/(cm^2·s·cmHg)

- Fibers with 25% larger dimensions were also successfully spun as an option for mitigation of pressure drops (50% lower).
- Production of larger prototype modules (6 in. × 36 in.) with properties similar to the smaller lab-scale modules was completed recently.

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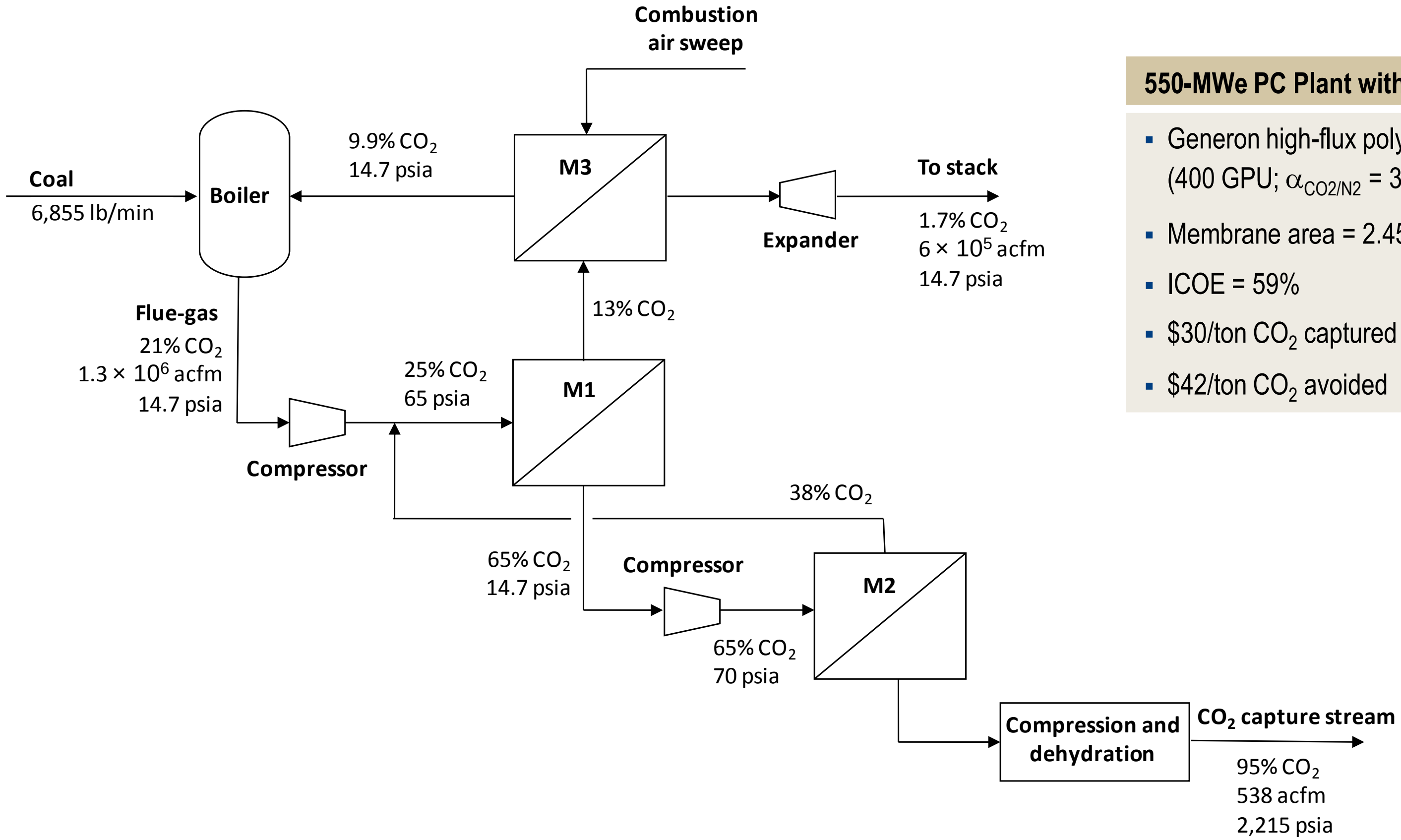
RTI 3-Stage Membrane Process Design



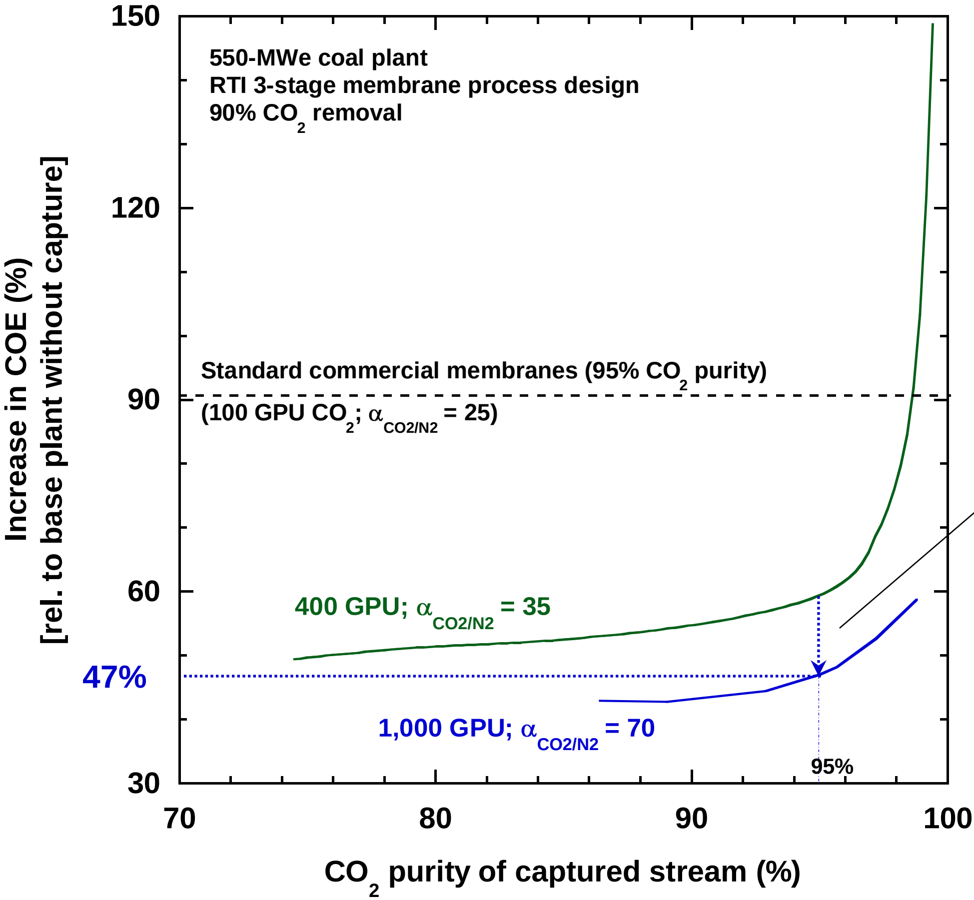
550-MWe PC Plant with 90% CO_2 Capture

- Generon high-flux polycarbonate membrane (400 GPU; $\alpha_{CO2/N2}$ = 35)
- Membrane area = 2.45 10^6 m^2
- ICOE = 59%
- \$30/ton CO_2 captured
- \$42/ton CO_2 avoided

Pipeline CO_2 purity target

- Minimum 95% CO_2 used (Kinder Morgan CO_2 Company, L.P. specifications)
- For very high CO_2 purity (99.5%), additional post-polishing step would be needed for more cost-effective removal of residual impurities (N_2, O_2).

Toward Further Reduction in COE: R&D Efforts in Progress



Efforts in Progress

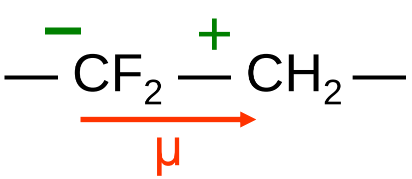
- Development/Synthesis of novel Arkema fluorinated copolymers
  - Poly(vinylidene fluoride) [PVDF] as base platform for next-generation membrane material
  - More robust materials for potentially longer-life membranes
  - Copolymerization technique to tailor polymer microstructure and, in turn, gas separation properties
    - Comonomer A increased CO_2 permeation in base polymer by 17-18 times with no adverse impact on CO_2/N_2 selectivity.
    - Comonomer B increased CO_2 permeation in base polymer by 6-10 times, accompanied by 2.5-3 times higher CO_2/N_2 selectivity.

PVDF-Based Membrane Material Platform

Arkema

Polyvinylidene fluoride (PVDF)-based polymers

- High oxidation resistance
  - Used in O_2/H_2 fuel cell membrane compositions
- High chemical resistance to acids
  - Withstands nitric acid exposure with no dimensional changes and weight loss
- Ease of processing (solution or melt)
  - Used for water purification as porous hollow fibers
- Specific affinity for CO_2
  - High CO_2 solubility due to high polar nature of VDF repeat unit

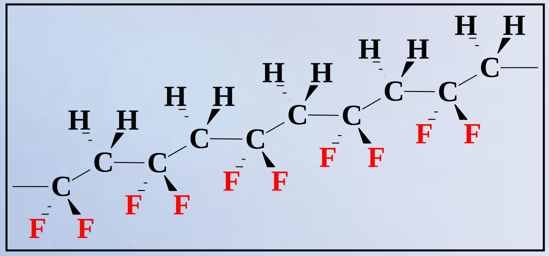


High dipole moment ⟶ Highly polar

PVDF homopolymer

- Highly crystalline (up to 50-65%), reducing gas transport
- Low CO_2 permeance ~ 5 GPU* (for 0.1-µm thickness)
- Moderate CO_2/N_2 selectivity ~ 23*

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



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

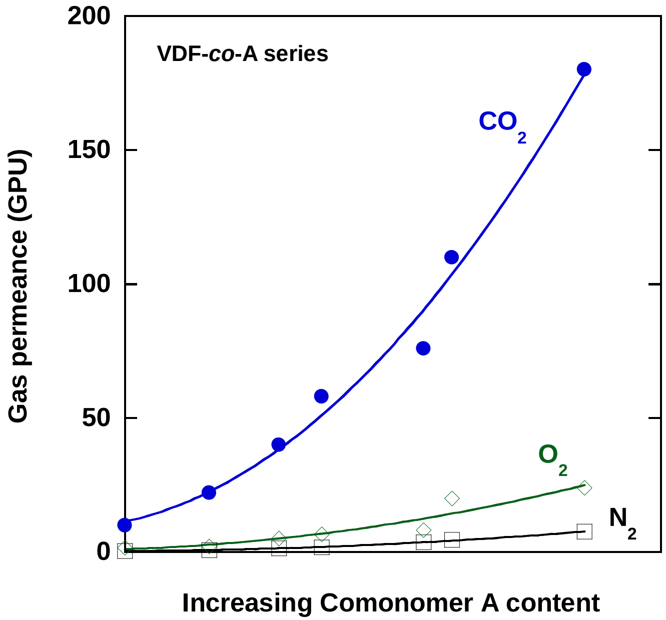
Copolymerization Approach

Arkema

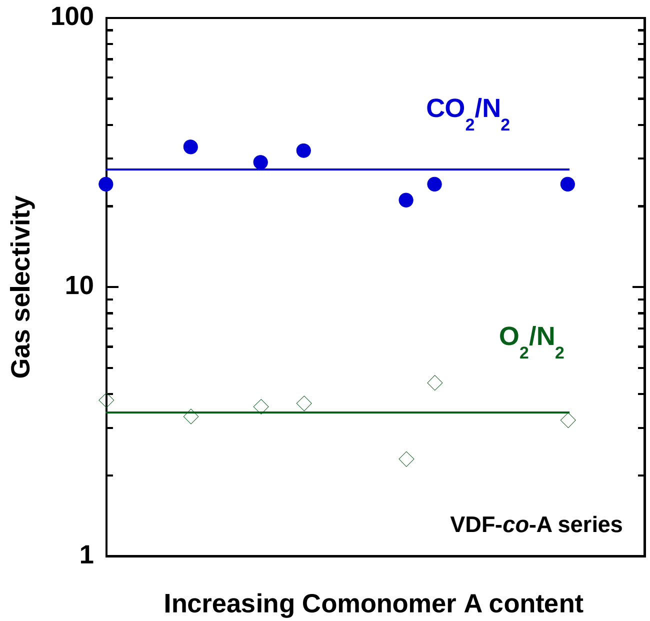
- PVDF backbone can be chemically modified.
  - To increase permeability by lowering crystallinity
  - To have higher CO_2 selectivity by changing backbone dipole moments
- Copolymerize fluoro-comonomers with bulky pendant groups into VDF backbone
  - Bulky comonomer disrupts polymer-chain organization, reducing crystallinity (down to <2%)
  - Intrinsic gas permeability of PVDF increases
  - Bulky perfluorinated Comonomer A successfully synthesized into VDF backbone
- Incorporate comonomers having greater dipole moments
  - Enhances polymer affinity for CO_2 to raise intrinsic CO_2/N_2 selectivity
  - VDF copolymers with very polar, bulky Comonomer B successfully made
    - Dipole of Comonomer B >> Dipole of Comonomer A

VDF-Based Copolymers: CO_2 Permeance Improvement

Gas permeance



Gas/N_2 selectivity



T = 35 °C; 1 GPU = 1 × 10^{-6} cm^3(STP)/(cm^2·s·cmHg)

Addition of bulky Comonomer A into the VDF backbone resulted in

- *18-fold increase in CO_2 permeance*
- *No adverse impact on CO_2/N_2 selectivity*

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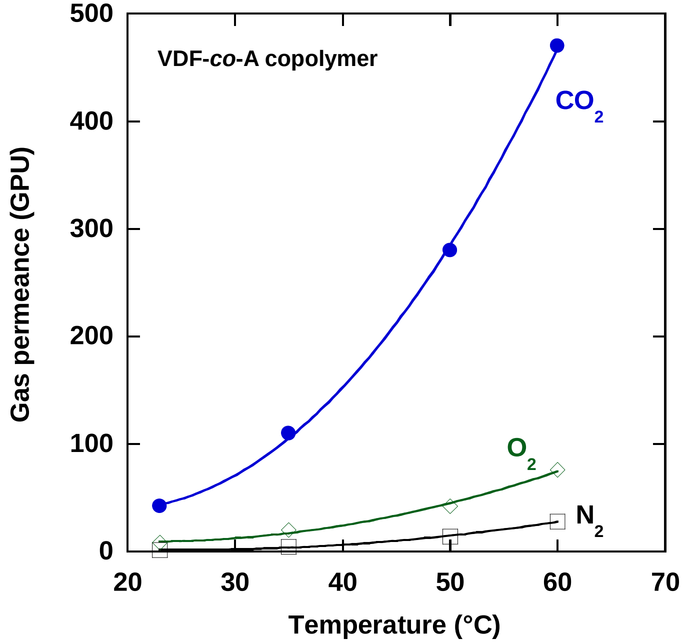
VDF-Based Copolymers: Effect of Temperature and More Polar Bulky Comonomer

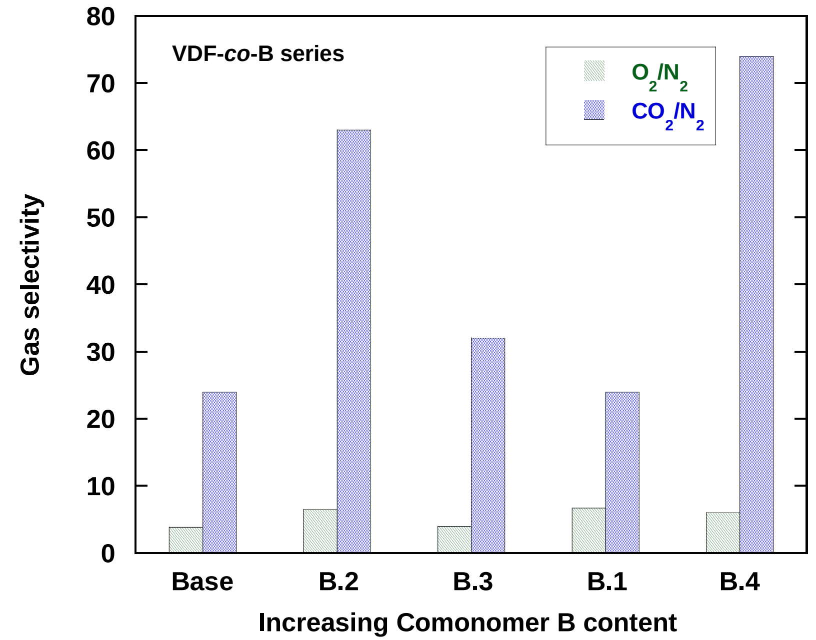
Permeance vs. temperature



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

- Substantial 10-fold increase in CO_2 permeance (>450 GPU) over only a small 35 C temperature interval

More polar comonomer on selectivity



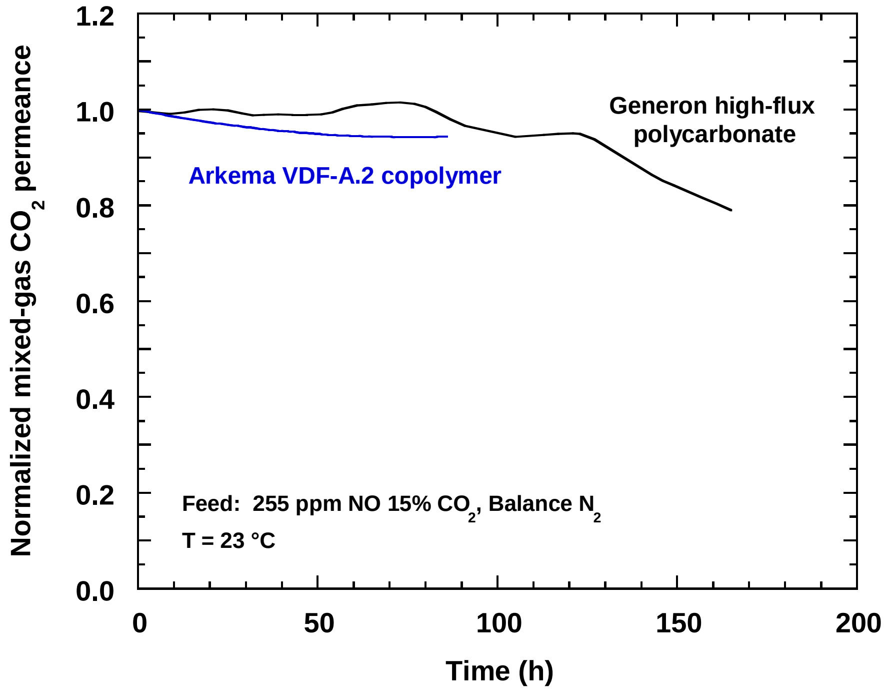
- 2.5-3 times higher CO_2/N_2 selectivity (>70), accompanied by 6-fold increase in CO_2 permeance

VDF-based copolymer properties can be tuned/optimized through process conditions (e.g., temperature) and proper comonomer selection and addition into chain backbone.

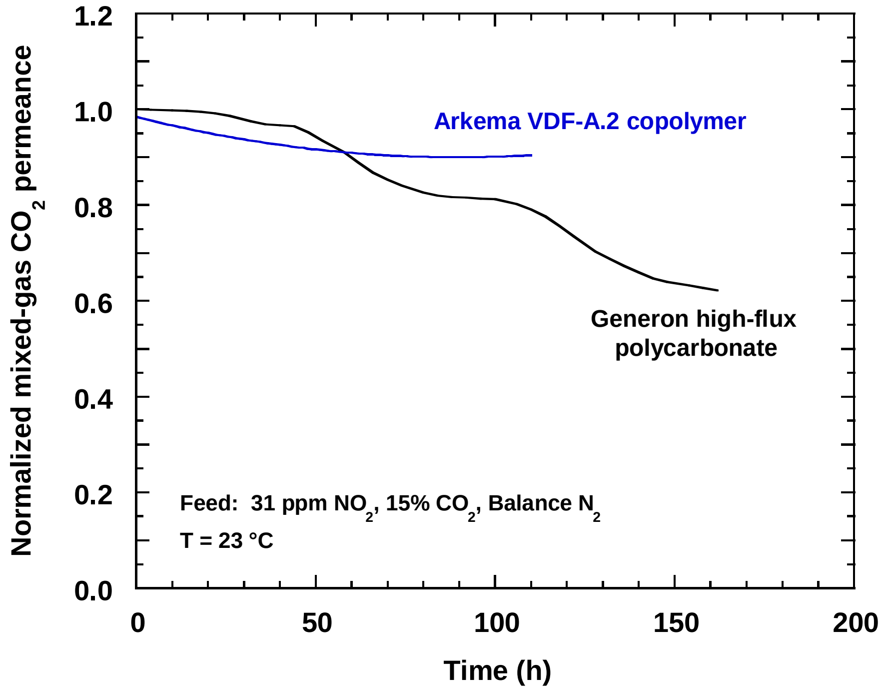
Effect of NO and NO_2 on CO_2 Permeance

Generon High-Flux PC vs. Arkema VDF-Based Copolymer

255 ppm NO in CO_2/N_2 feed



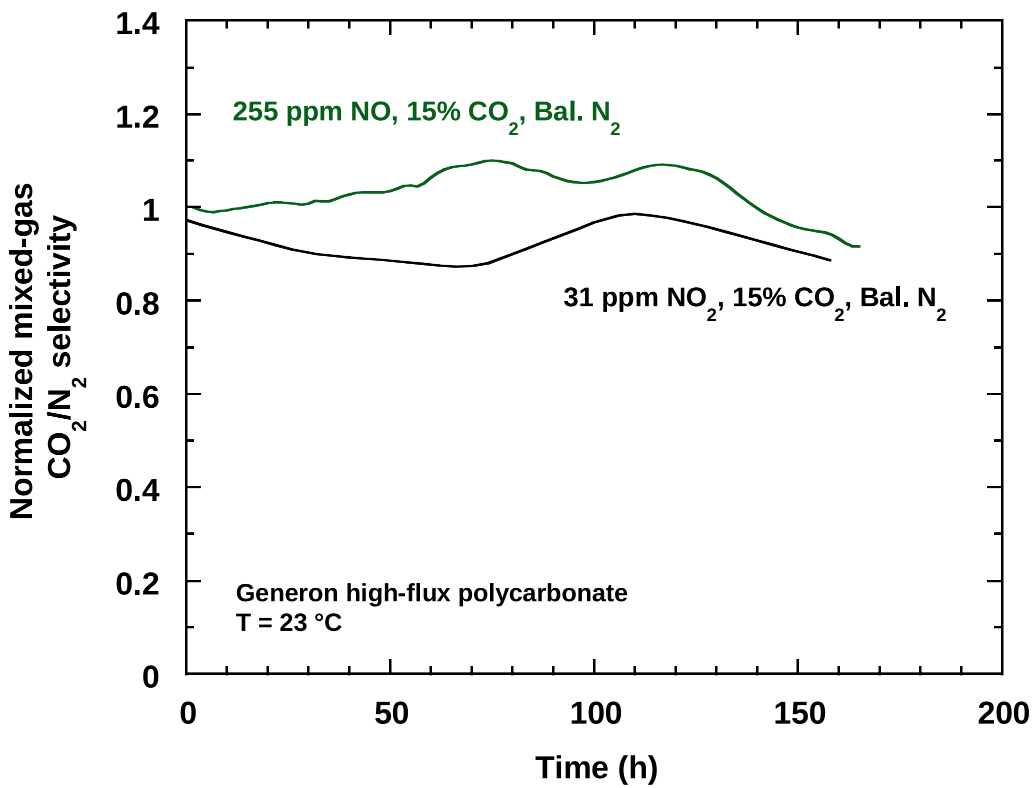
31 ppm NO_2 in CO_2/N_2 feed



VDF-based copolymers are less sensitive to NO_x than high-flux PC.

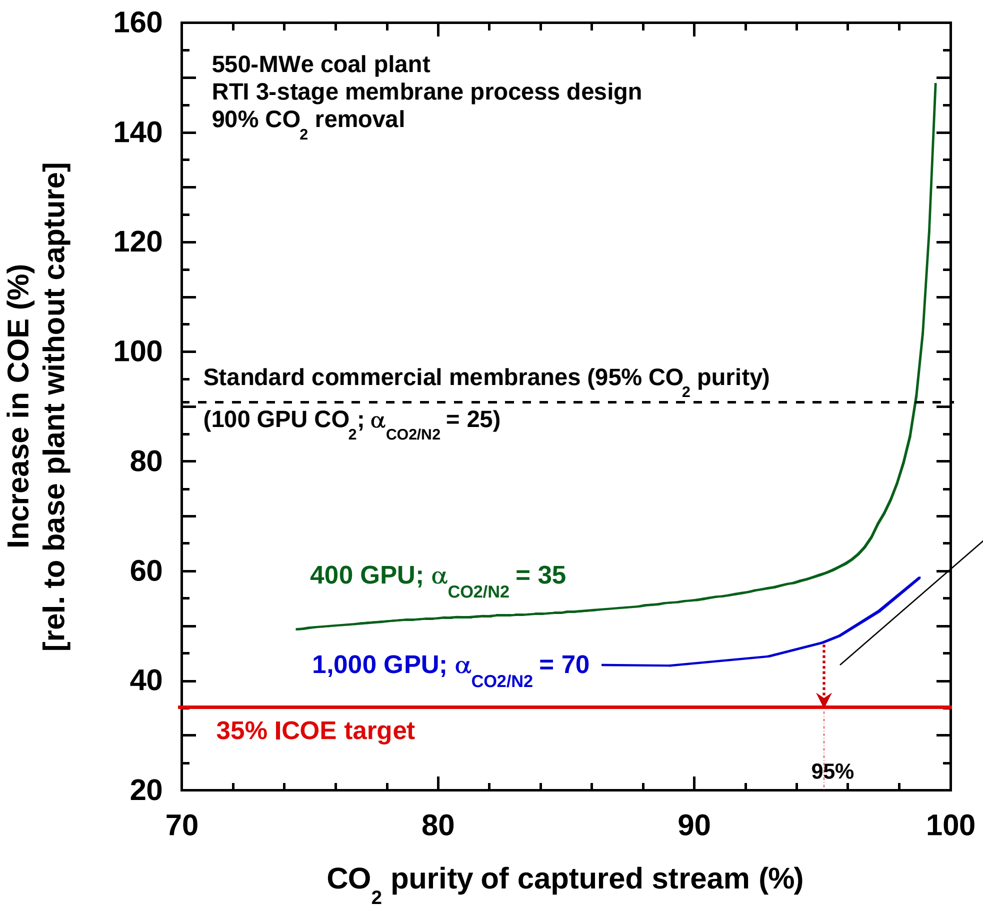
Effect of NO and NO_2 on CO_2/N_2 Selectivity

Generon High-Flux PC



No selectivity loss occurs in high-flux PC in presence of NO_x.

Path Forward To DOE Target for ICOE



Future R&D Directions

- Membrane materials development
- Continued focus on improved chemical durability
- Optimization of hollow-fiber membrane module engineering design
- Alternative ways to create transmembrane driving force for separation

Summary

- Development and synthesis of Arkema VDF-based copolymers with improved CO_2 permeance and improved CO_2/N_2 selectivity
  - 17-18 times higher CO_2 and permeability than base polymer; No adverse impact on base CO_2/N_2 selectivity (VDF-*co*-A)
  - 2.5-3 times higher CO_2/N_2 selectivity and 6 times higher CO_2 permeability than base polymer (VDF-*co*-B)
  - No detrimental interaction effect of SO_2 and NO_x on Arkema copolymers
- Development and scale-up of Generon high-flux polycarbonate (PC) membrane fibers with up to 4 times higher CO_2 flux than that of Generon standard PC fiber
- Successful formation of high-flux PC fibers into good lab-scale modules and larger prototype field modules
- Identification of promising 3-stage CO_2 capture membrane process design to achieve 90% CO_2 capture and 95% CO_2 purity

Next Steps

Genereon® module sizes
(100-10,000 ft^2 or 10-1,000 m^2)

RTI syngas membrane test skid

- Focus on increasing CO_2 permeance and selectivity of Arkema novel copolymers
  - Blend of VDF-*co*-B w/ PVDF as minor phase
  - Terpolymer of VDF-*co*-A-*co*-B synthesized with high concentrations of these comonomers
- Downselect promising Arkema copolymer candidates to evaluate for hollow-fiber fabrication
- Design and construction of field-test membrane skid
- Field test (1,000 h cumulative) of prototype high-flux PC membrane modules with real coal flue gas (robustness; performance stability; process design validation; etc.)
- Techno-economic analysis of "best" integrated/retrofitted CO_2 capture membrane process package in pulverized coal plant

Field Test of Capture Membrane Process: Site and Plans In Progress

UNC-Chapel Hill
Coal-Fired Power Plant (32 MW_e)

UNC-CH[a] Cogeneration Power Plant (Chapel Hill, NC)	
Combustor operation	~32-MW_e;1,000 tpd CO_2 produced; <u>Continuous 24/7 operation</u>
Test duration	≥1,000 h
Skid design	3-stage membrane process; (M1, M2, and M3 stages); Target of 1-tpd CO_2 captured
Membrane modules	1 Type 6150[b] module for M1 + 1 Type 4150[b] module for M3 + 2 Type 210[b] modules for M2
Field-test objectives	(i) Demonstrate field performance of RTI's 3-stage membrane process design for 90% CO_2 removal. (ii) Investigate membrane module stability (structural and performance) to real coal flue-gas. (iii) Study membrane durability/stability to real flue gas in extended field testing.

[a] UNC-CH = The University of North Carolina at Chapel Hill; [b] Membrane module area ~ 2,200 ft^2 (Type 6150); 1,100 ft^2 (Type 4150); 100 ft^2 (Type 210)

Acknowledgements

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