

CO₂ Capture Membrane Process for Power Plant Flue Gas

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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
- CO₂ Capture and Reuse
 - Pre- and post-combustion CO₂ capture
 - Membrane separation
 - CO₂ 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

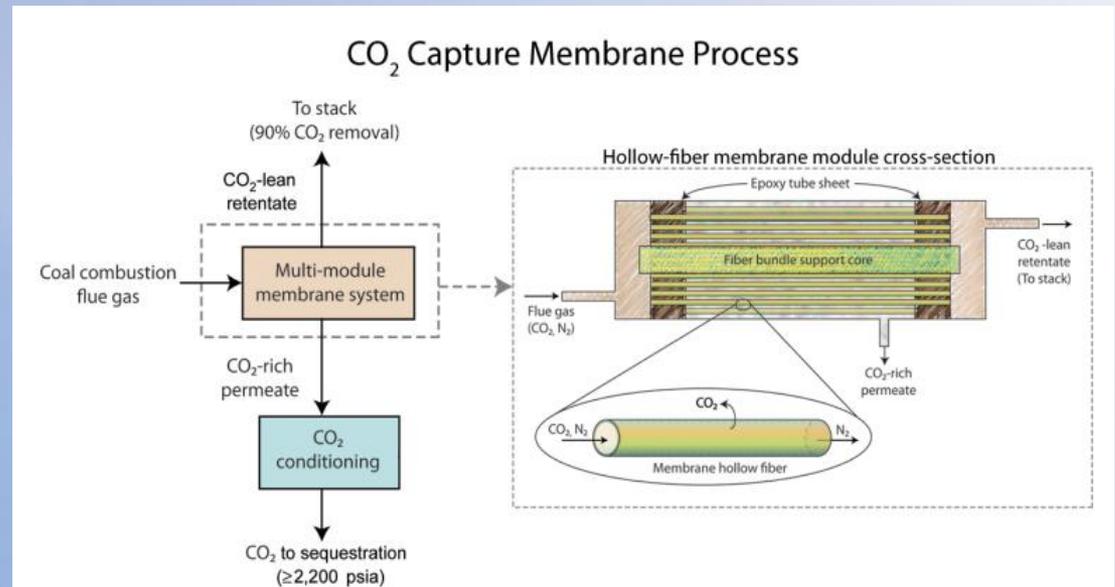
- DOE Share: \$1,944,821
- Cost Share: \$486,206
- **Total Funding: \$2,431,027**

Project Team

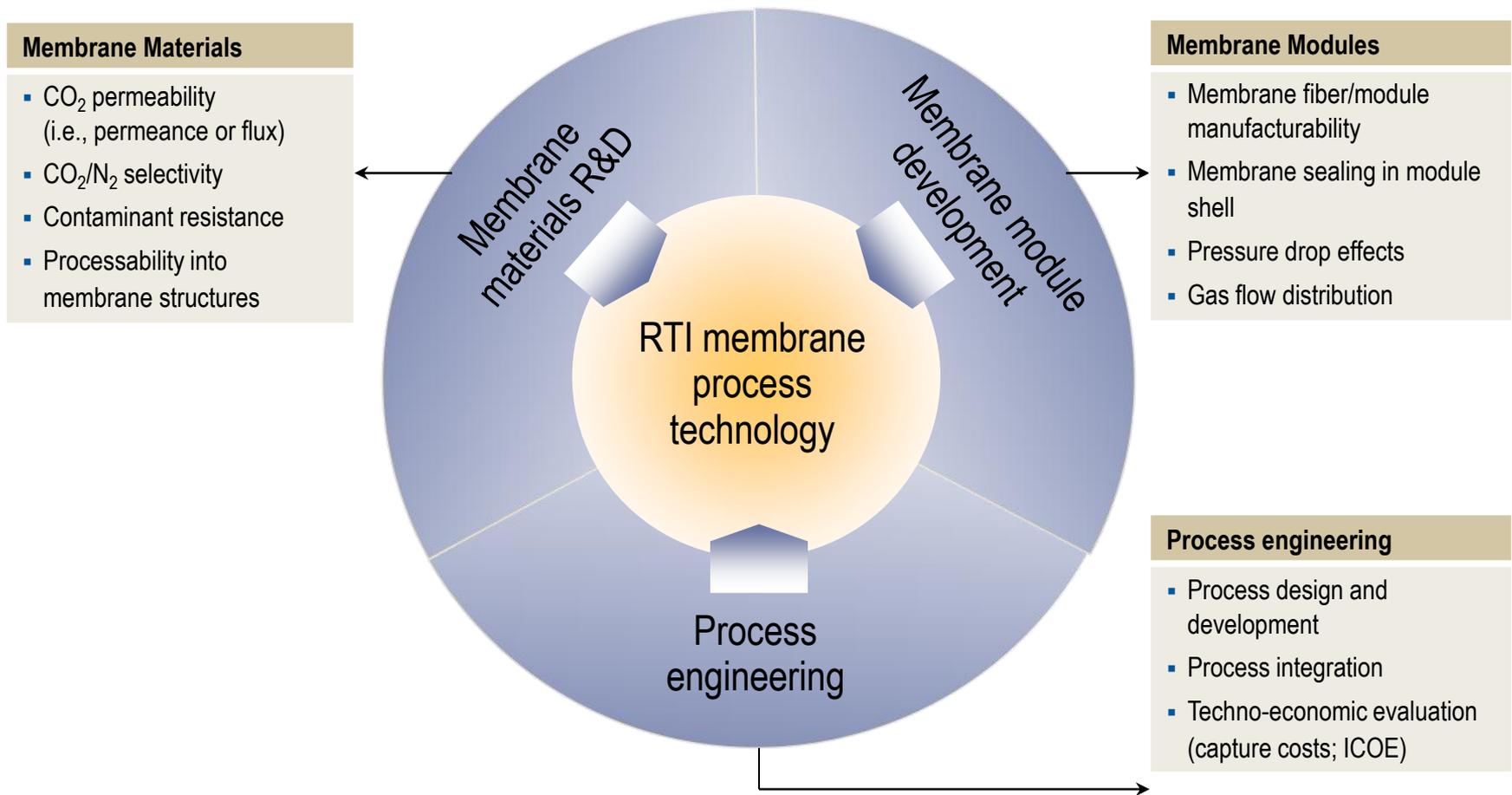
- RTI
- Arkema Inc.
- Generon IGS, Inc.
- U.S. EPA / ARCADIS
- University of North Carolina at Chapel Hill [UNC-CH] Cogeneration Facility

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 $\geq 90\%$ CO₂ from plant's flue gas at 50-60 °C with $\leq 35\%$ Increase in Cost of Electricity (ICOE)



RTI's CO₂ Capture Membrane Process Development



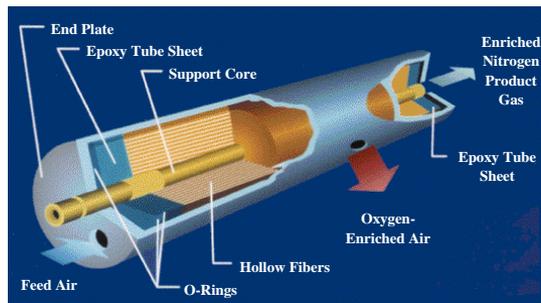
Hollow-Fiber Membrane Modules for High-Volume Applications

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% CO₂ purity; $\alpha_{\text{CO}_2/\text{N}_2} = 35$; 1.3×10^6 acfm)

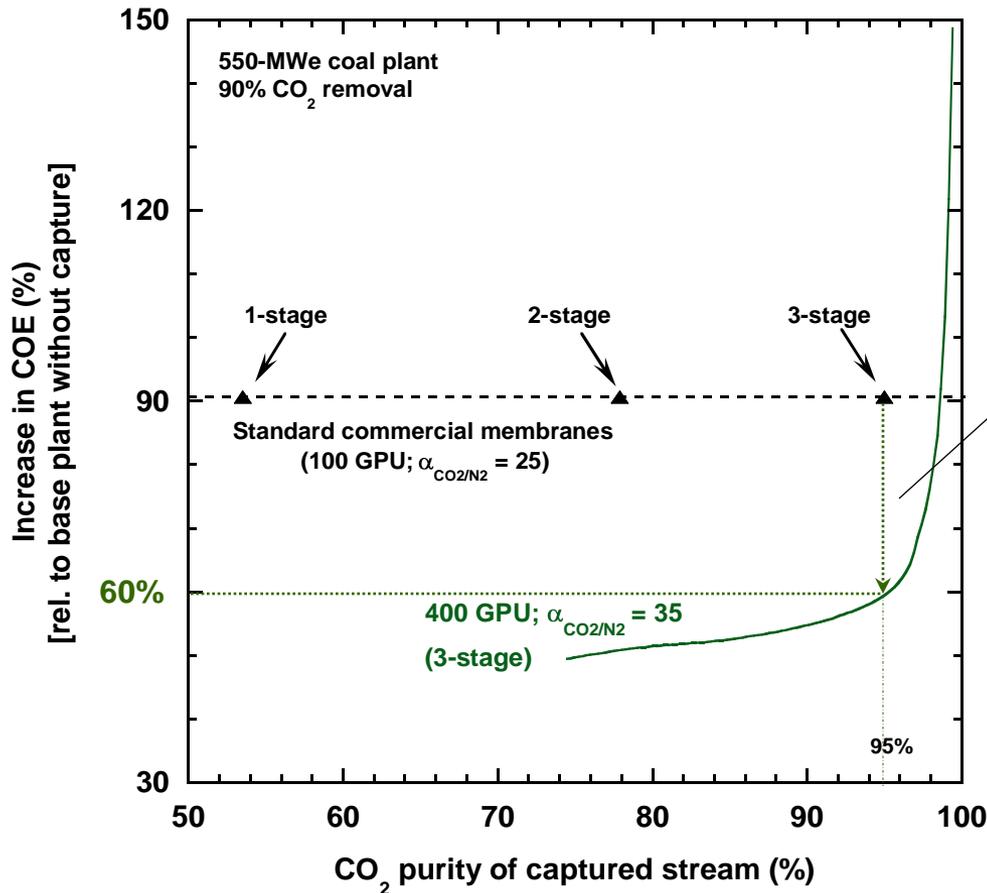
	Spiral-wound	Hollow-fiber
Membrane area	2.6 10^7 ft ² (400 GPU) 1 10^7 ft ² (1,000 GPU)	2.6 10^7 ft ² (400 GPU)
Area per module ^a	1,163 ft ²	2,200 ft ²
No. of modules	22,356 (400 GPU) 8,599 (1,000 GPU)	11,819 (400 GPU)
Module cost (installed) ^b	\$4.65/ft ²	\$1.05/ft ²
Total module cost	\$121MM (400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

^a Assumed standard module size of 8 in. \times 40 in. for spiral-wound and 6 in. \times 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



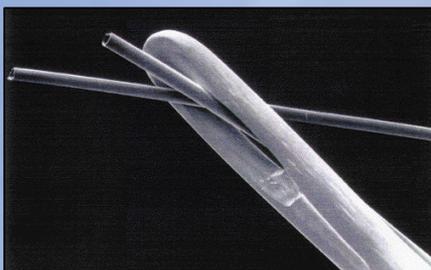
Key Enabling Developments

- 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

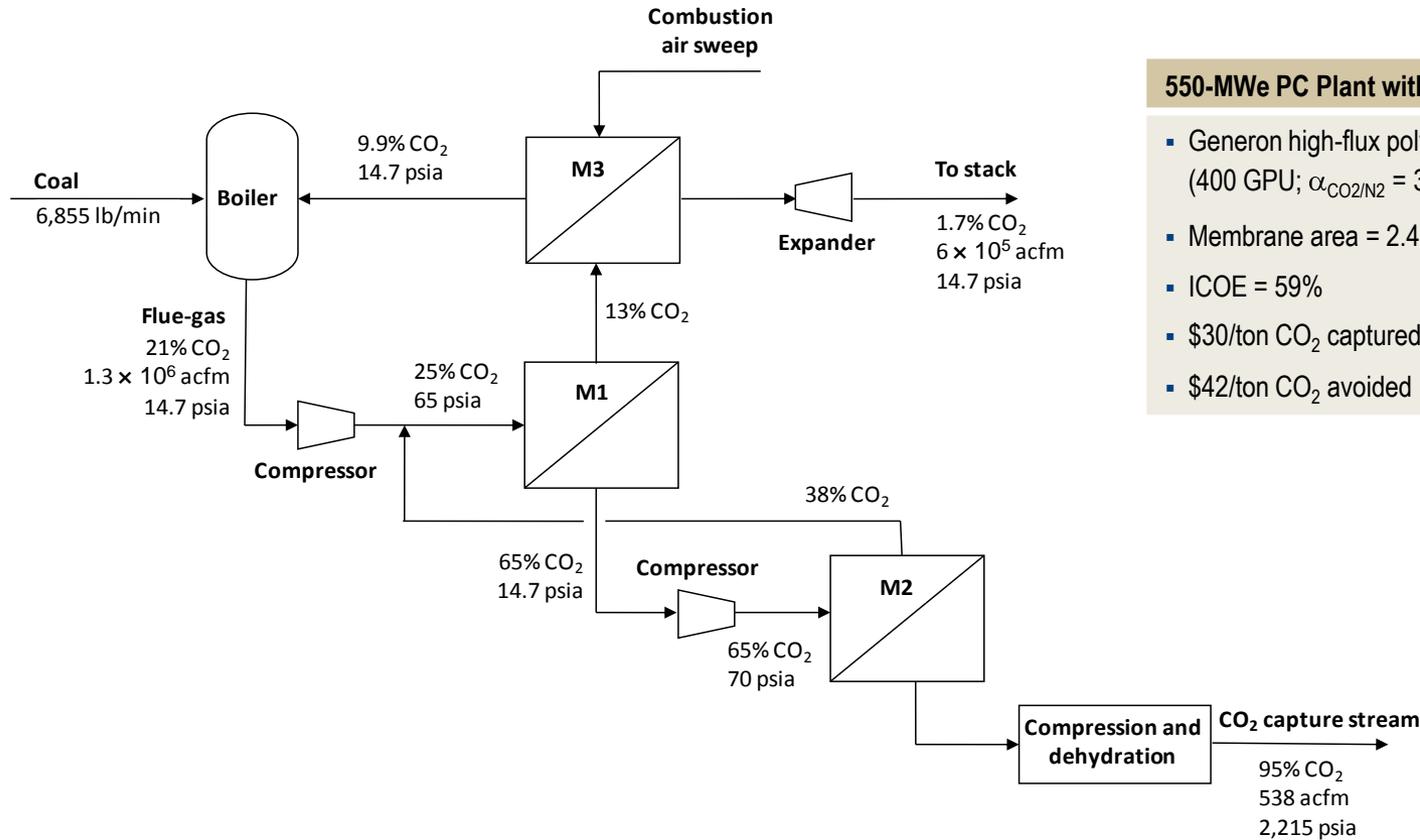
- Membrane hollow fibers from high-flux PC were successfully formed.
 - Mechanically durable up to at least 10,000 pressure cycles at 135 psig minimum pressure
- New high-flux PC fibers spun have
 - CO₂ permeance **4 times faster** than that of standard PC fibers
 - CO₂/N₂ selectivity similar to that 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 CO₂/N₂ selectivity obtained on high-flux PC films was 35-37.
 1 GPU = 1 × 10⁻⁶ cm³(STP)/(cm²·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.

RTI 3-Stage Membrane Process Design



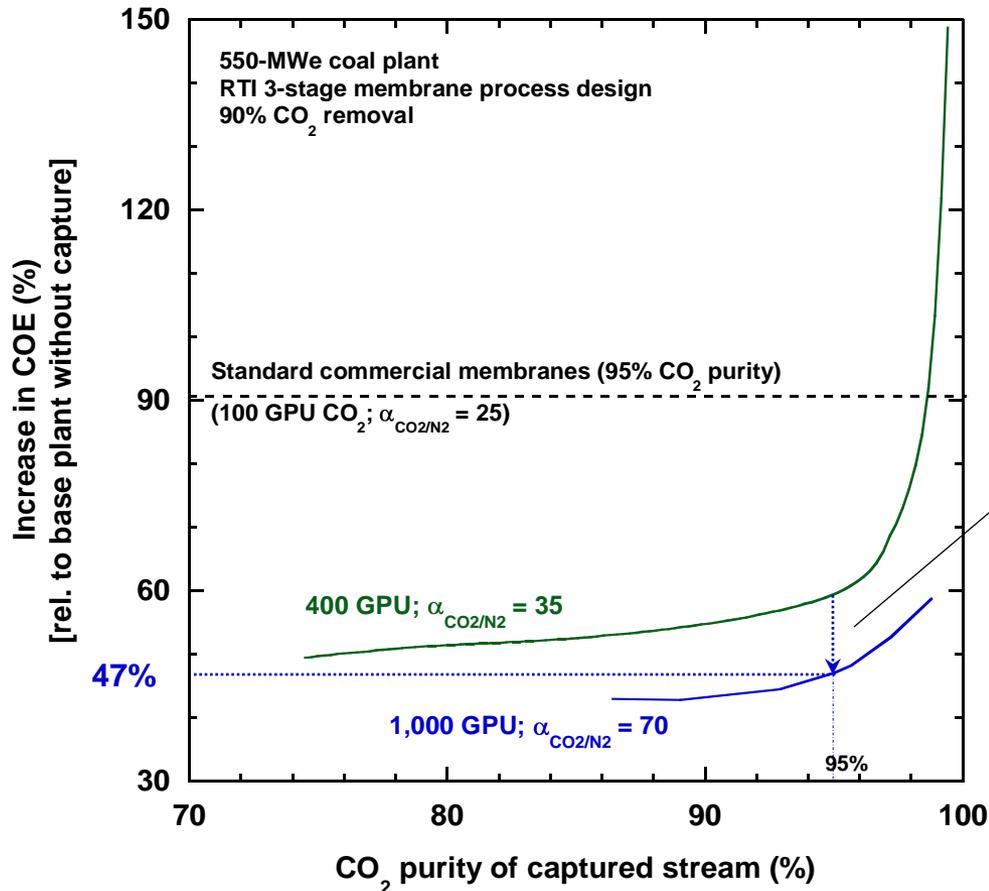
550-MWe PC Plant with 90% CO₂ Capture

- Generon high-flux polycarbonate membrane (400 GPU; $\alpha_{\text{CO}_2/\text{N}_2} = 35$)
- Membrane area = 2.45 × 10⁶ m²
- ICOE = 59%
- \$30/ton CO₂ captured
- \$42/ton CO₂ avoided

Pipeline CO₂ purity target

- Minimum 95% CO₂ used (Kinder Morgan CO₂ Company, L.P. specifications)
- For very high CO₂ purity (99.5%), additional post-polishing step would be needed for more cost-effective removal of residual impurities (N₂, O₂).

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



Efforts in Progress

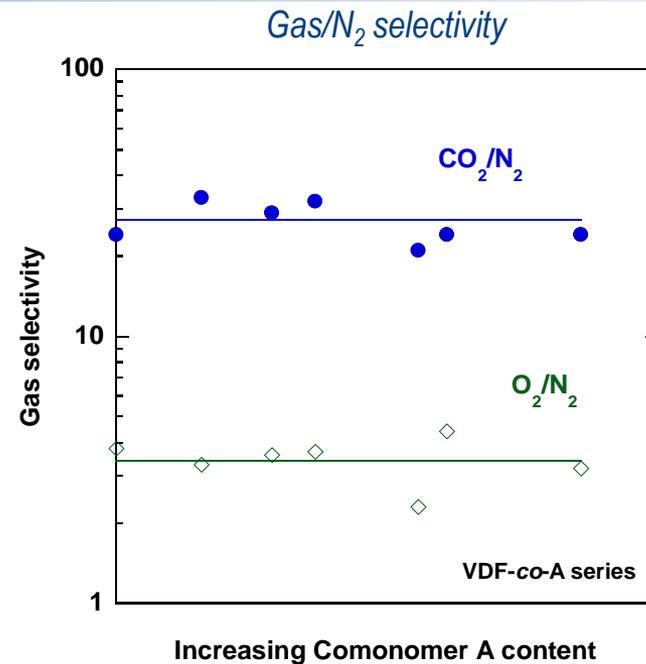
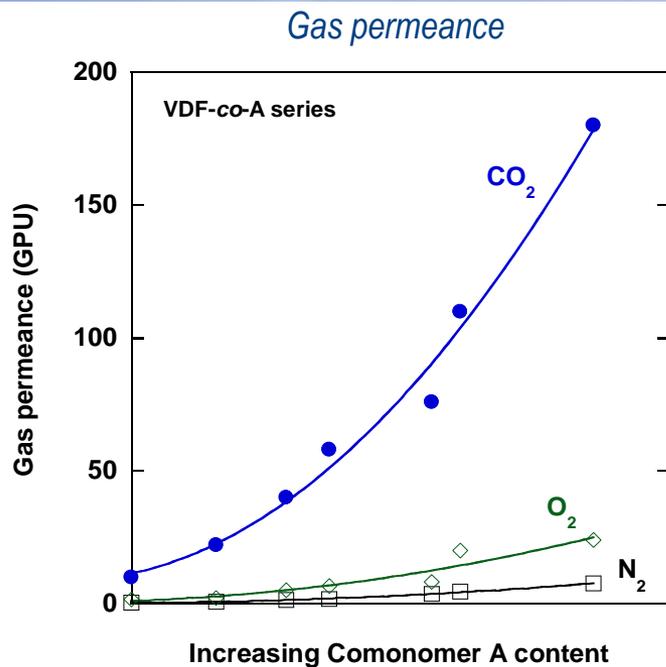
- Development/Synthesis of novel Arkema fluorinated copolymers
 - Poly(vinylidene fluoride) [PVDF] as base platform for next-generation membrane material
 - More robust materials for potentially longer-life membranes
 - Copolymerization technique to tailor polymer microstructure and, in turn, gas separation properties
 - Comonomer A increased CO₂ permeation in base polymer by 17-18 times with no adverse impact on CO₂/N₂ selectivity.
 - Comonomer B increased CO₂ permeation in base polymer by 6-10 times, accompanied by 2.5-3 times higher CO₂/N₂ selectivity.

Copolymerization Approach

Arkema

- PVDF backbone can be chemically modified.
 - To increase permeability by lowering crystallinity
 - To have higher CO₂ 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 CO₂ to raise intrinsic CO₂/N₂ selectivity
 - VDF copolymers with very polar, bulky Comonomer B successfully made
 - Dipole of Comonomer B >> Dipole of Comonomer A

VDF-Based Copolymers: CO₂ Permeance Improvement

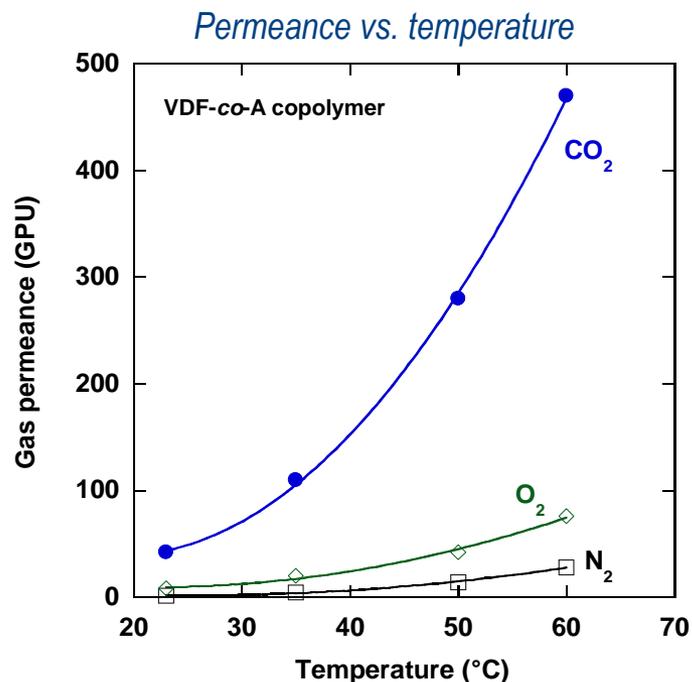


T = 35 °C; 1 GPU = 1×10^{-6} cm³(STP)/(cm²·s·cmHg)

Addition of bulky Comonomer A into the VDF backbone resulted in

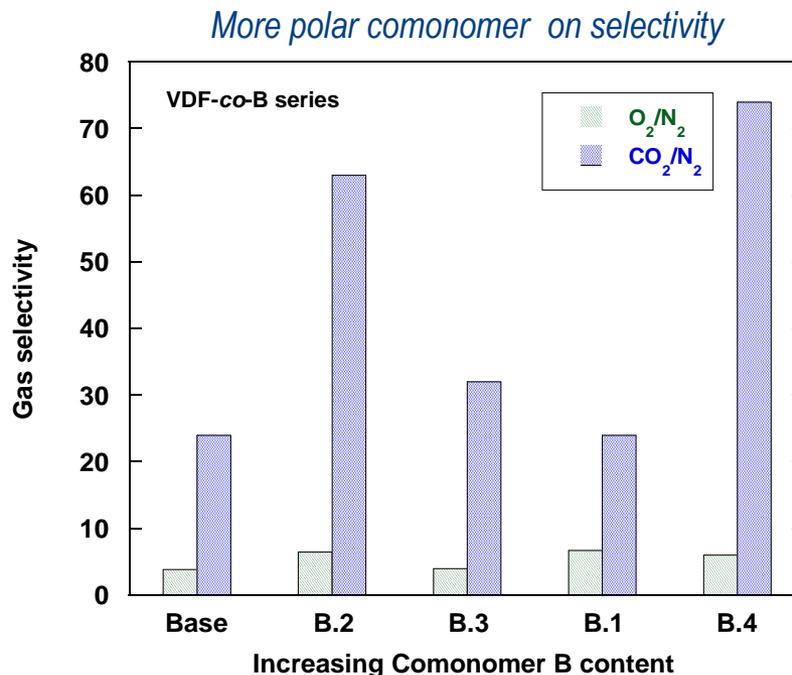
- *18-fold increase in CO₂ permeance*
- *No adverse impact on CO₂/N₂ selectivity*

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



1 GPU = 1×10^{-6} cm³(STP)/(cm²·s·cmHg)

- Substantial 10-fold increase in CO₂ permeance (>450 GPU) over only a small 35 °C temperature interval

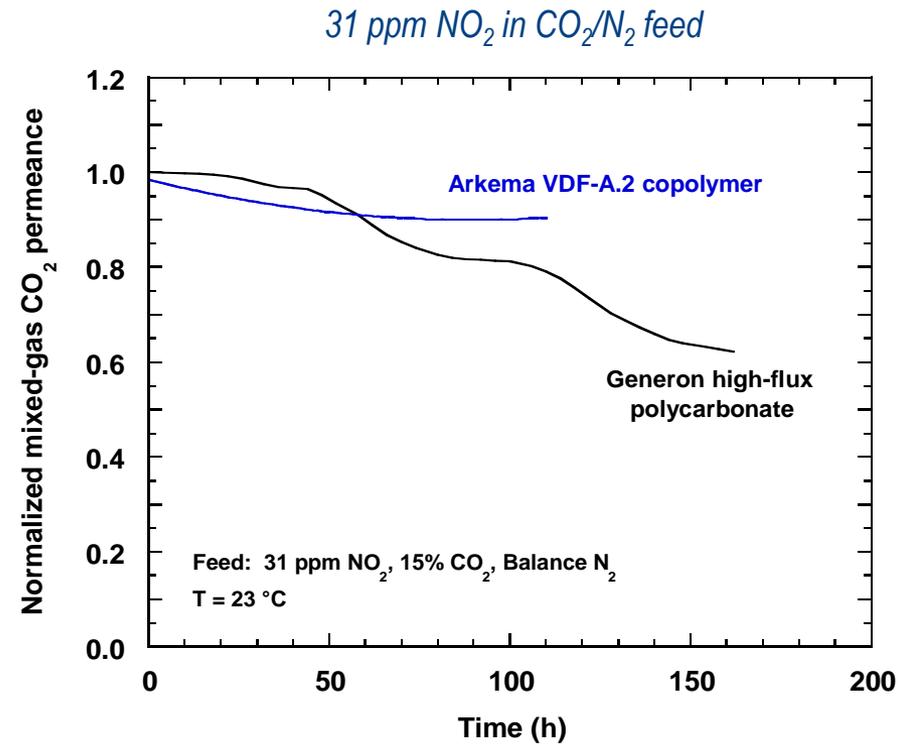
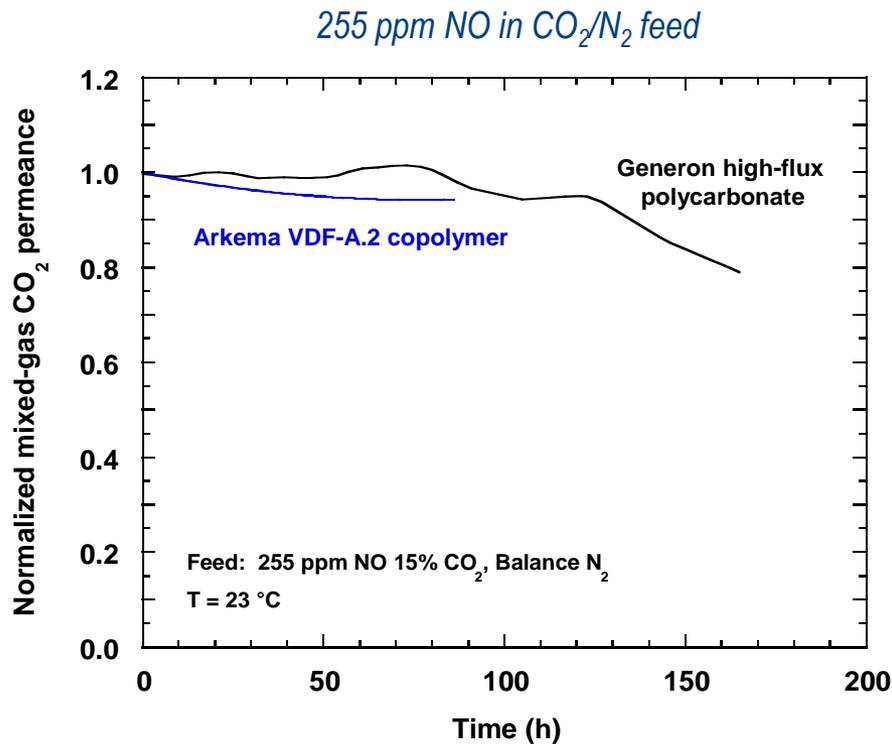


- 2.5-3 times higher CO₂/N₂ selectivity (>70), accompanied by 6-fold increase in CO₂ permeance

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 NO₂ on CO₂ Permeance

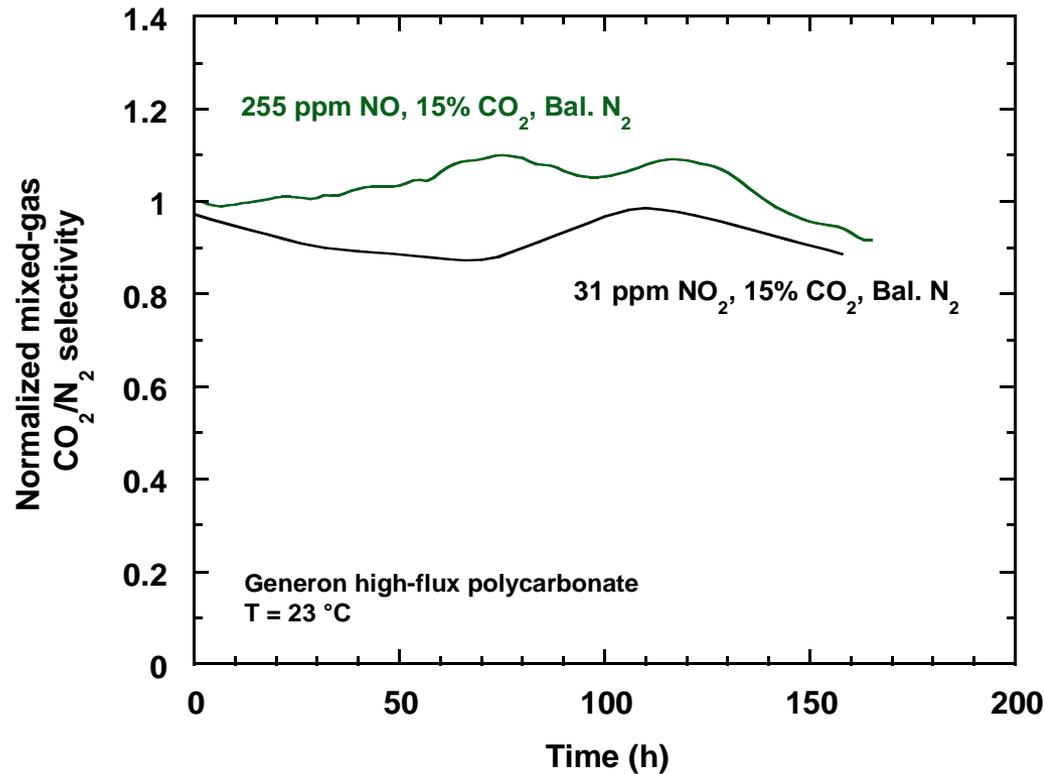
Generon High-Flux PC vs. Arkema VDF-Based Copolymer



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

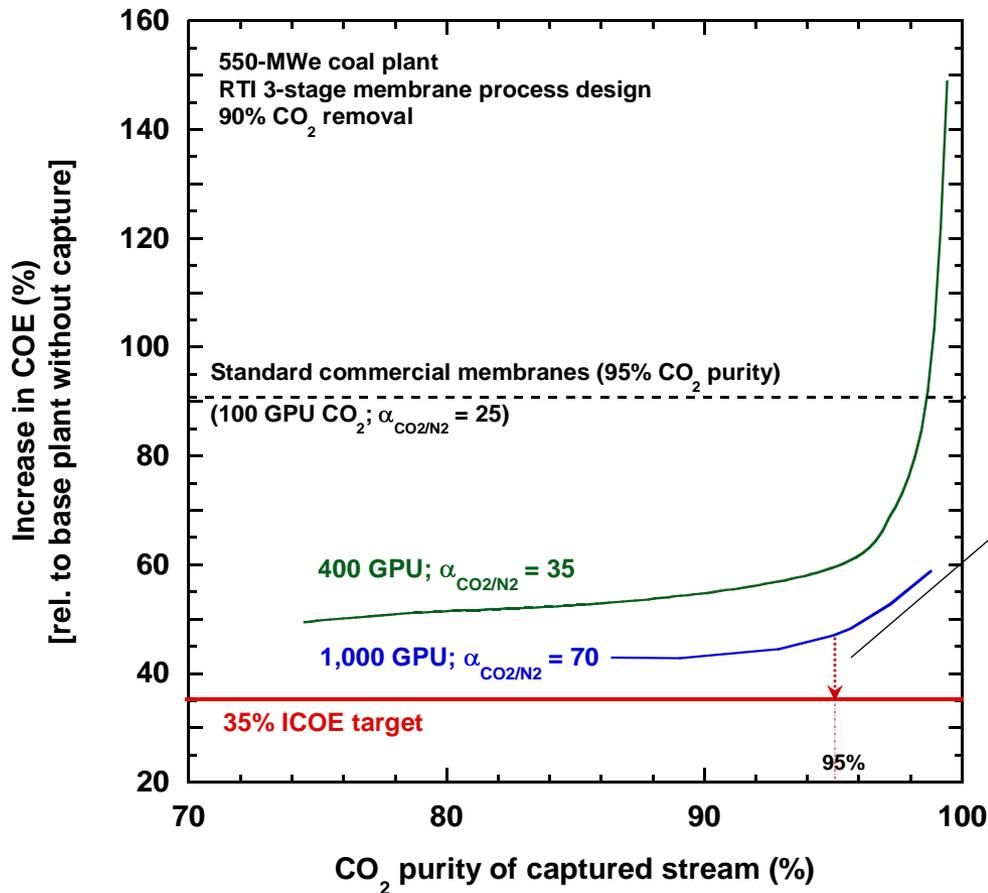
Effect of NO and NO₂ on CO₂/N₂ Selectivity

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 CO₂ permeance and improved CO₂/N₂ selectivity
 - 17-18 times higher CO₂ and permeability than base polymer; No adverse impact on base CO₂/N₂ selectivity (VDF-co-A)
 - 2.5-3 times higher CO₂/N₂ selectivity and 6 times higher CO₂ permeability than base polymer (VDF-co-B)
 - No detrimental interaction effect of SO₂ and NO_x on Arkema copolymers
- Development and scale-up of Generon high-flux polycarbonate (PC) membrane fibers with up to 4 times higher CO₂ 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 CO₂ capture membrane process design to achieve 90% CO₂ capture and 95% CO₂ purity

Next Steps



Generon® module sizes
(100-10,000 ft² or 10-1,000 m²)



RTI syngas membrane test skid

- Focus on increasing CO₂ 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 CO₂ 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 ft² (Type 6150); 1,100 ft² (Type 4150); 100 ft² (Type 210)

Acknowledgements

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