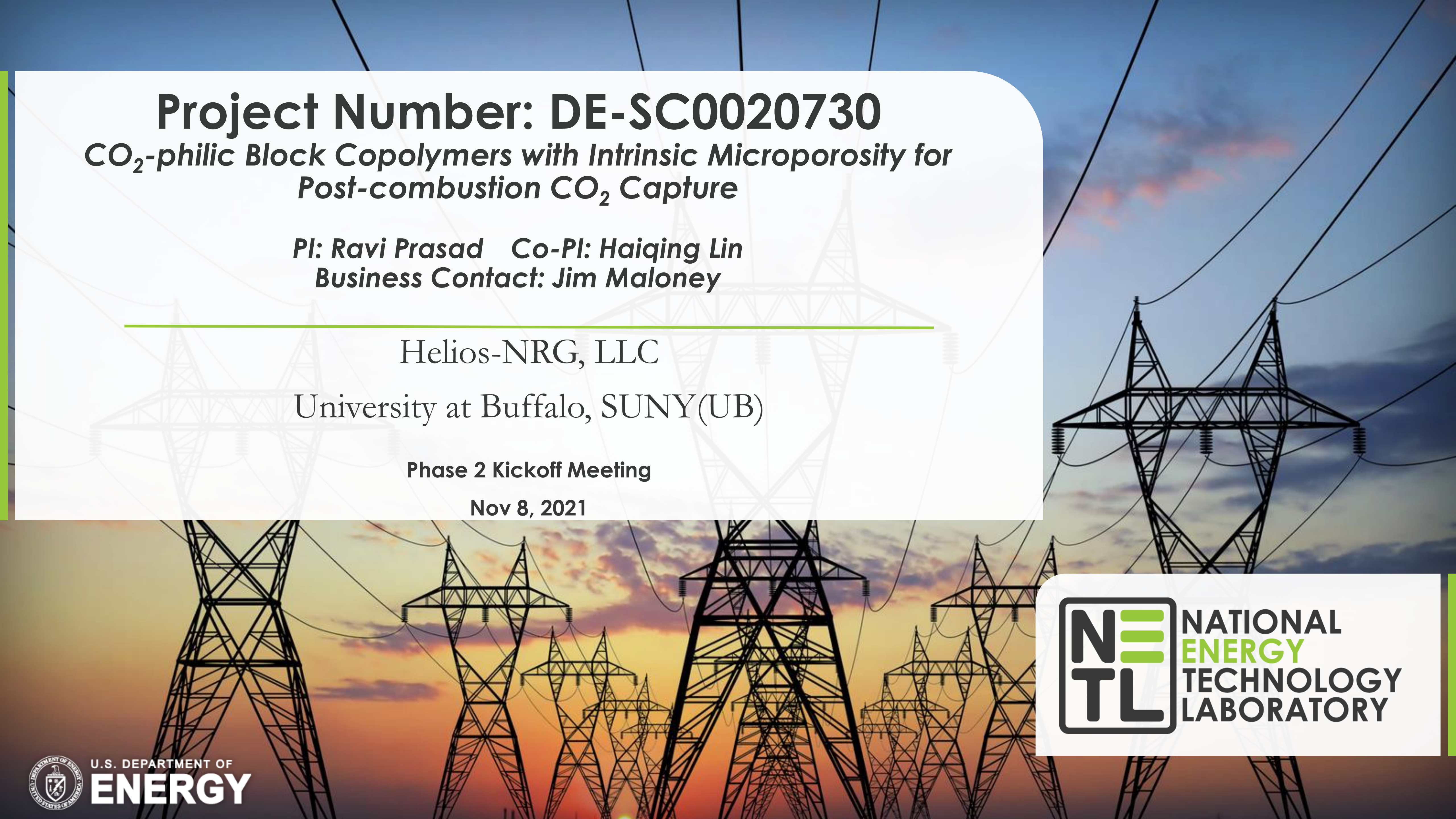

# Project Number: DE-SC0020730

## *$CO_2$-philic Block Copolymers with Intrinsic Microporosity for Post-combustion $CO_2$ Capture*

*PI: Ravi Prasad Co-PI: Haiqing Lin*
*Business Contact: Jim Maloney*

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Helios-NRG, LLC

University at Buffalo, SUNY(UB)

**Phase 2 Kickoff Meeting**

**Nov 8, 2021**

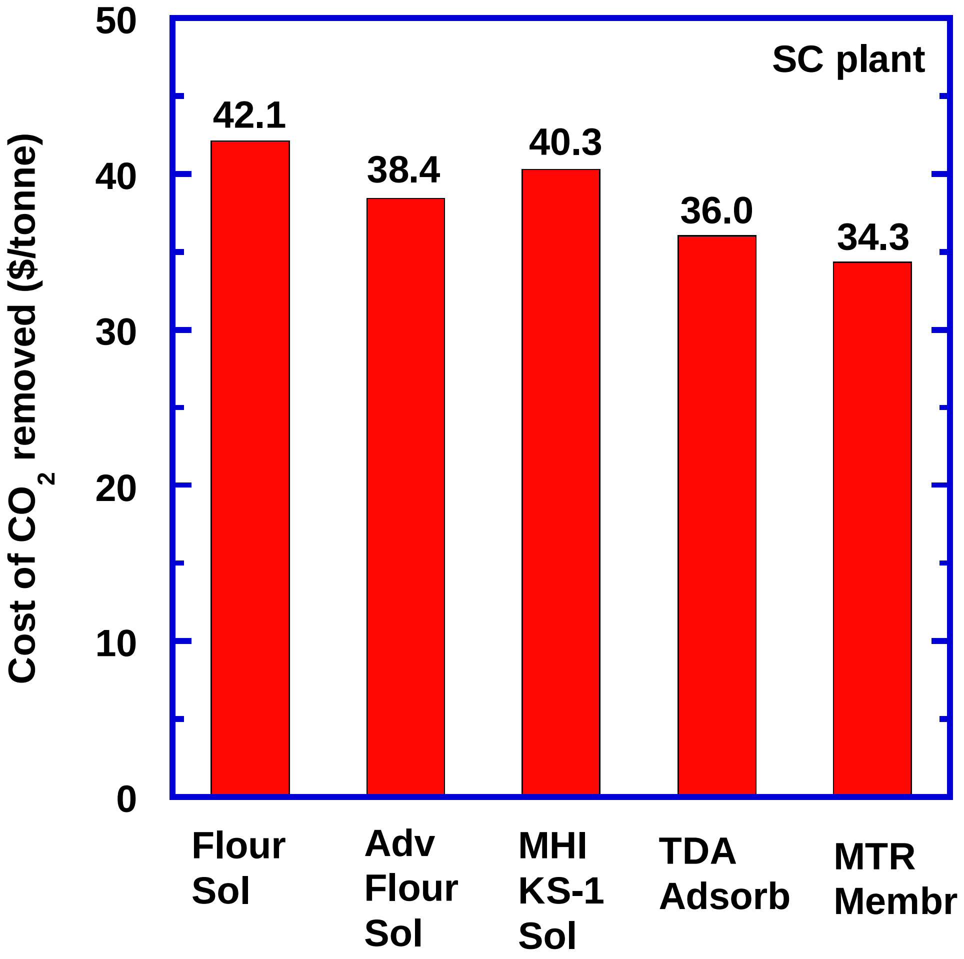
NATIONAL ENERGY TECHNOLOGY LABORATORY

U.S. DEPARTMENT OF ENERGY

# General Project Information

- **Title:** ***$CO_2$-philic Block Copolymers with Intrinsic Microporosity for Post-combustion $CO_2$ Capture***
- **Project Type: SBIR/STTR Phase 2**
  - Lead Organization: Helios-NRG, LLC
  - PI: Ravi Prasad, PhD, PE Co-PI: Dr Haiqing Lin (UB)
  - Federal Project Manager: Dr. Sai Gollakota
  - Partners:
    - University at Buffalo, SUNY (UB)
    - Membrane Technology & Research (MTR)
    - TechOpp Consulting (Comm Advisor)
    - National Carbon Capture Center (NCCC)
- **Project Award Number: DE-SC0020730**
  - Total Project Value: $1,649,928
- **Project Period: Aug 23, 2021 – Aug 22, 2023**

# The high cost of Post-combustion $CO_2$ removal



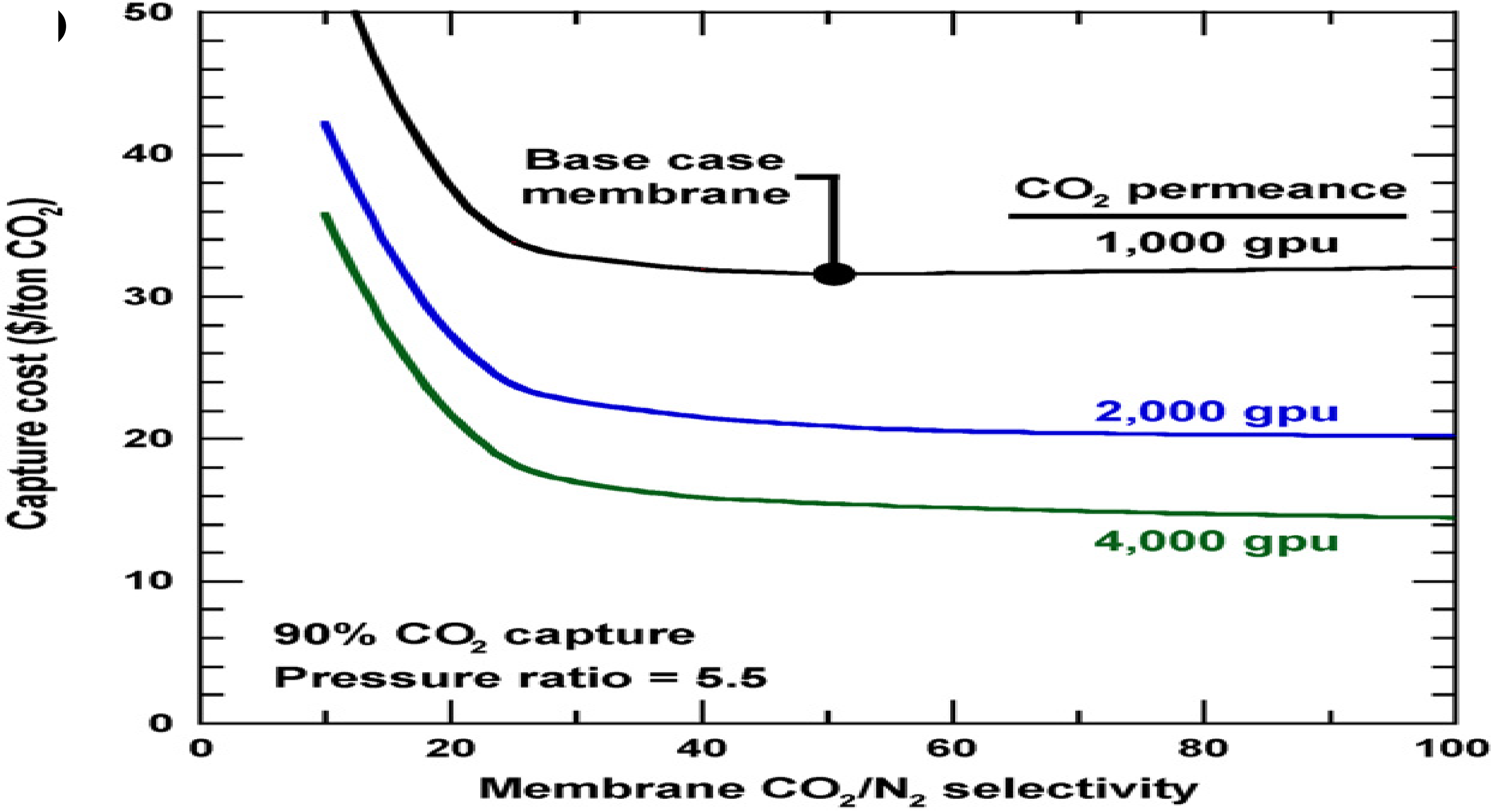
•90% $CO_2$ capture
•95% Purity

**Membranes**:
$CO_2$: 3,500 GPU
$\alpha CO_2/N_2$: 35

*Current and future technologies for power generation with post-combustion carbon capture, DOE/NETL-2012/1557,* 2012.

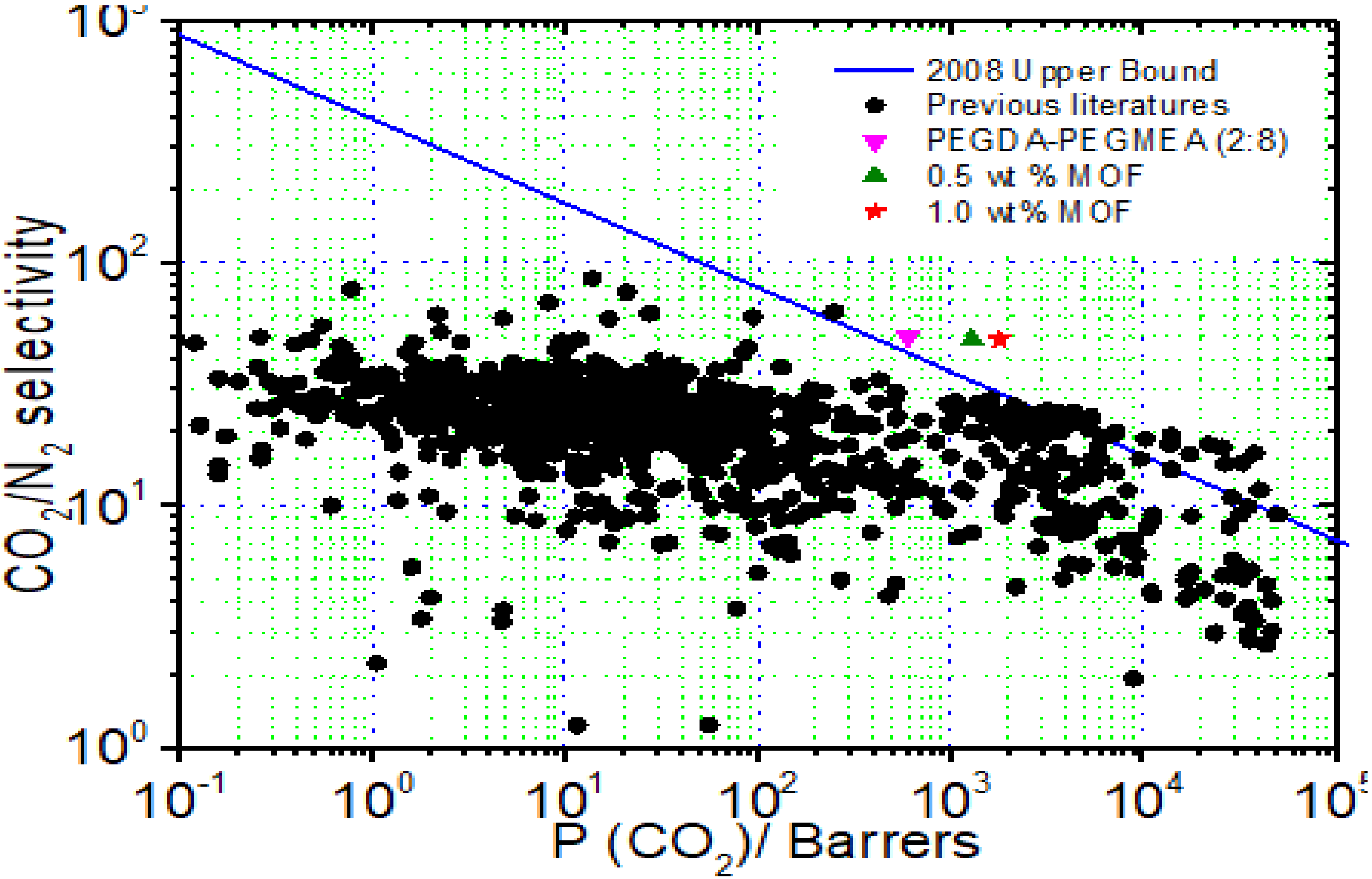
- **$CO_2$ capture from power plants is currently too expensive**
- **Challenges:**
  - Gas is at near ambient pressure
  - Only ~12% $CO_2$ for coal plants
  - Gas has contaminants
  - Product must be relatively pure
- **Many technologies possible - but all have issues**
- **Membrane specific challenges**
  - Low feed pressurization (few psi)
  - Permeate vacuum/sweep gas needed
  - Very low driving force => extremely high $CO_2$ permeance needed
  - Need high selectivity for high purity
  - The two properties are inversely related

# Impact of Membrane Properties on Capture Cost



Merkel, et al., *Pilot testing of a membrane system for post-combustion $CO_2$ capture (DE-FE0005795), Membrane Technology and Research, Inc., final report to DOE NETL, 2015.*

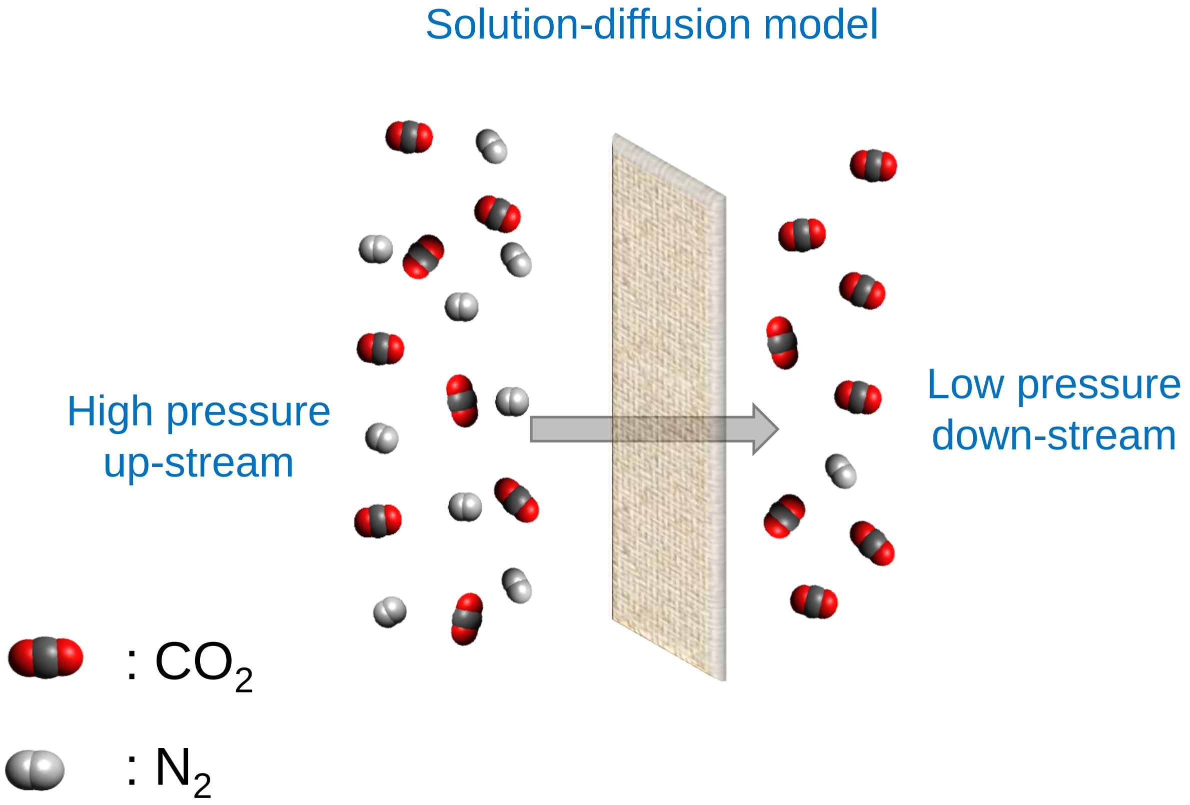
# Tradeoff between Permeability & Selectivity



- SOA commercial membrane:
  $CO_2$ permeance = 2,000 GPU and $\alpha_{CO2/N2}$ = 50
- Our Goal:
  $CO_2$ permeance = 4,500 GPU and $\alpha_{CO2/N2}$ = 40

# Technology Background & Phase1 Progress

# Gas transport through polymers



(1) Sorption on upstream side
(2) Diffusion down partial pressure gradient
(3) Desorption on downstream side

Wijmans and Baker, *J. Membr. Sci.* **107**, 1 (1995)

**Productivity** - **Permeability**

$$P_A = S_A \times D_A$$

**Purity** - **Gas selectivity**

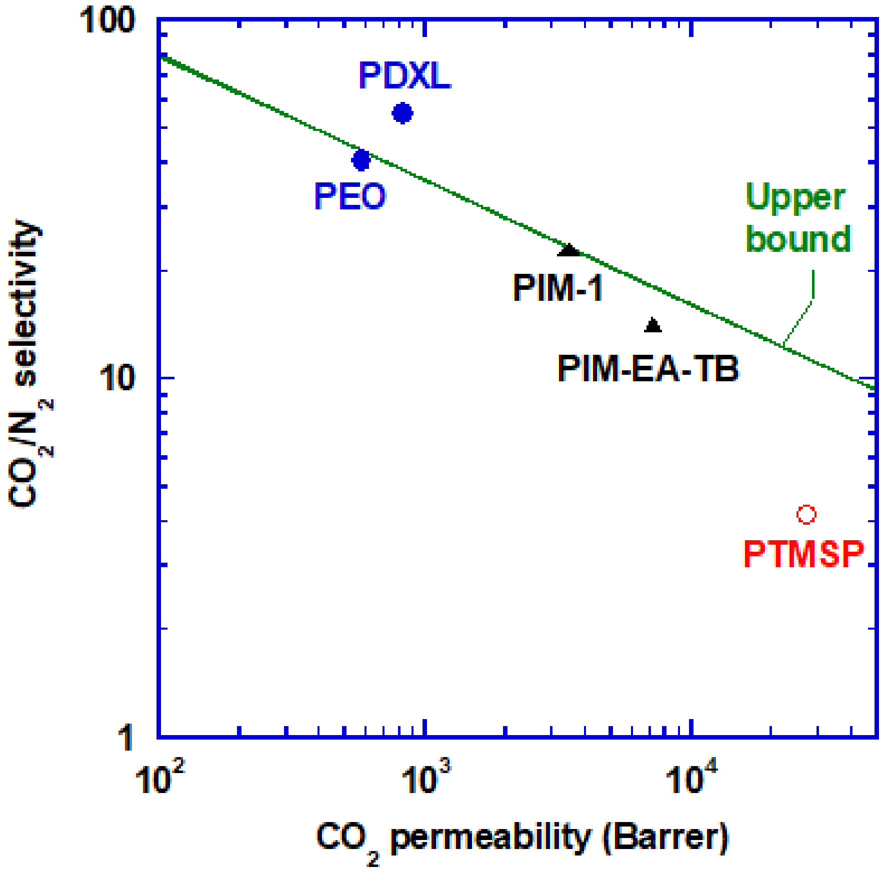
solubility selectivity

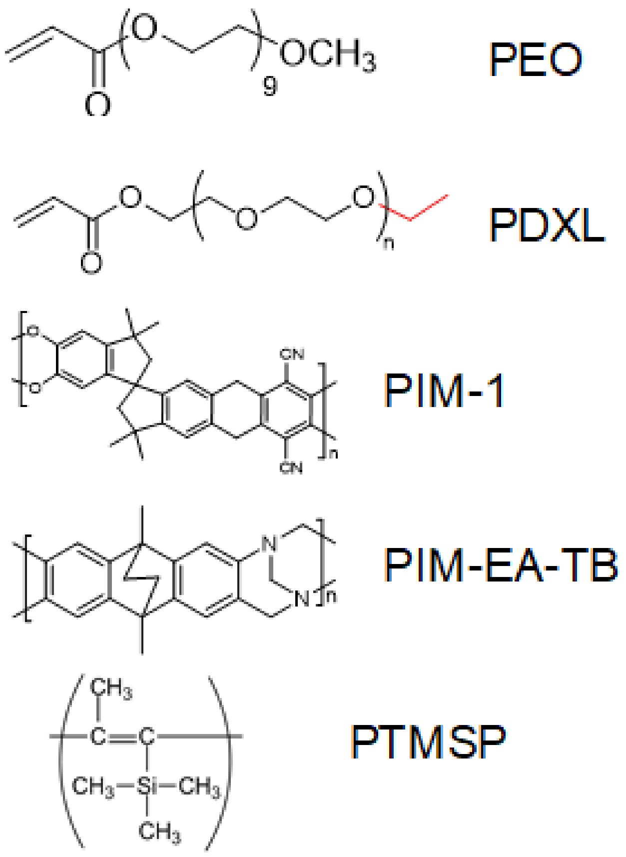
$$a_{H_2/CO_2} = \frac{P_{H_2}}{P_{CO_2}} = \left(\frac{S_{H_2}}{S_{CO_2}}\right) \times \left(\frac{D_{H_2}}{D_{CO_2}}\right)$$

diffusivity selectivity

| Penetrant | **Condensability**<br>*Critical Temperature (K)* | **Size**<br>*Kinetic Diameter (Ă)* | **Size**<br>*Critical volume ($cm^3$/mole)* |
|---|---|---|---|
| $N_2$ | 126 | 3.64 | 89.8 |
| $CO_2$ | 304 | 3.3 | 93.9 |

# Engineering Advanced Polymers



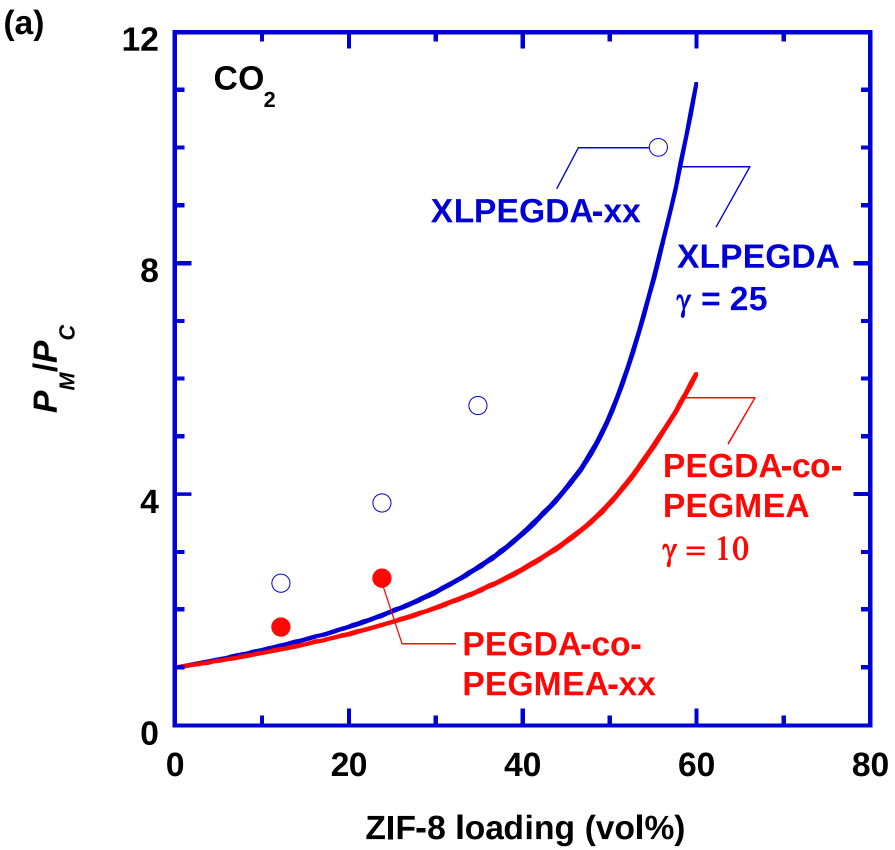


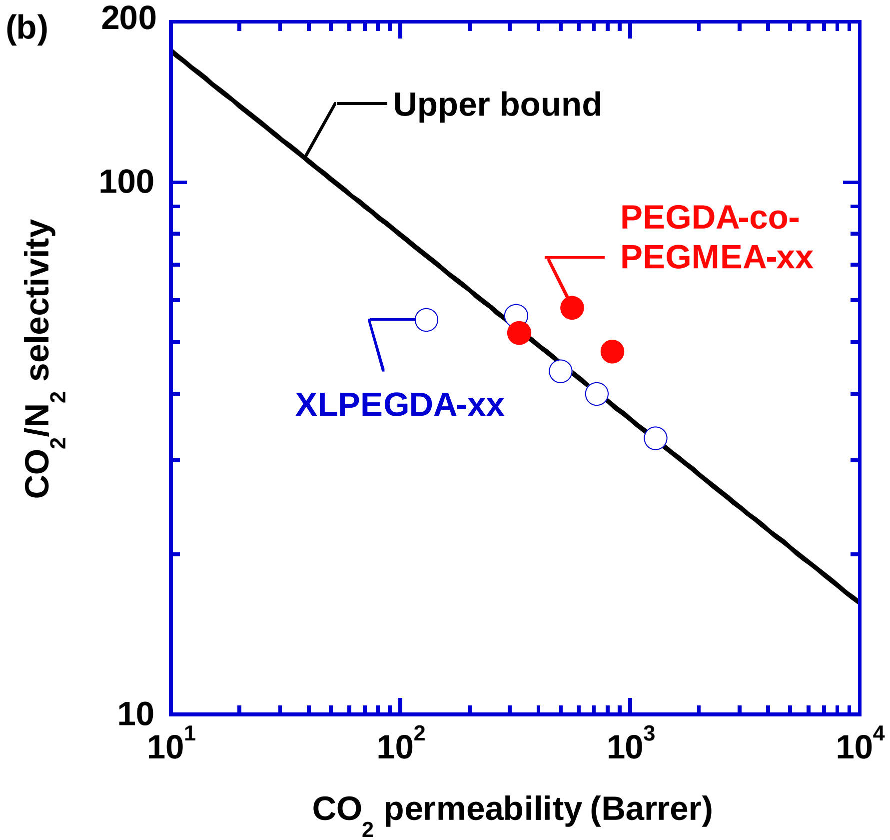
Solubility dominant polymers

Diffusivity dominant polymers

Liu, Hou, Park, and Lin, *Chem. Eur. J.* 2016, 22 (45)15980.
Du, Park, Robertson, Dal-Cin, Visser, Scoles, and Guiver, *Nat. Mater.* 2011, 10, 372.
Park, Jung, Lee, Hill, Pas, Mudie, Wagner, Freeman, and Cookson, *Science* 2007, 318, 254.
Guiver and Lee, *Science* 2013, 339, 284-285

# Prior work in advanced polymers

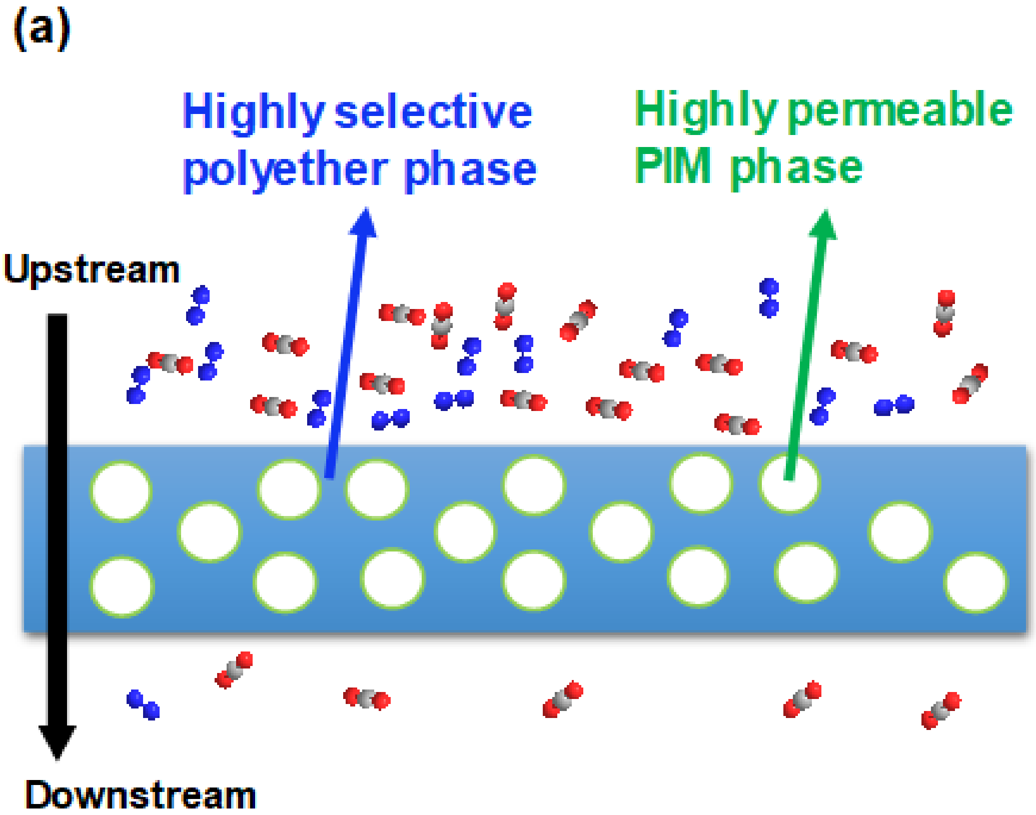


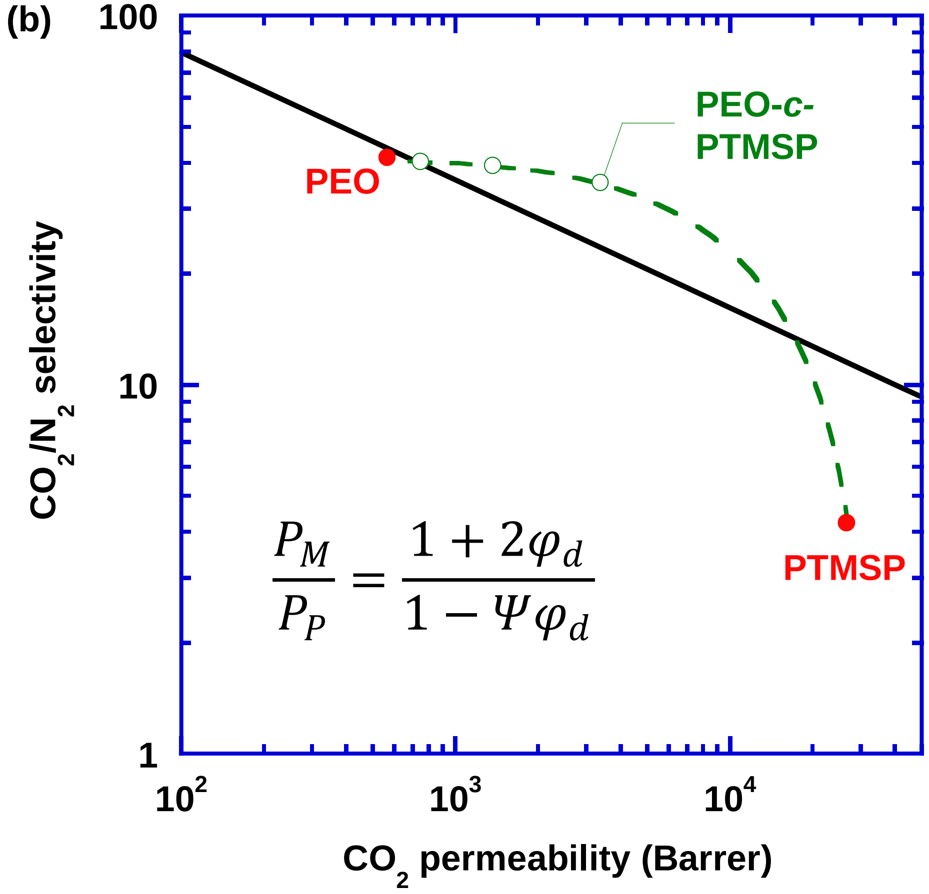


Hu, Lin, et al., Highly permeable mixed matrix materials comprising crosslinked poly(ethylene oxide) and ZIF-8 nanoparticles for CO$_2$ capture. *Sep. Purif. Technol.* 2017, 205 (31), 58-65.

# Strategy for a step change membrane

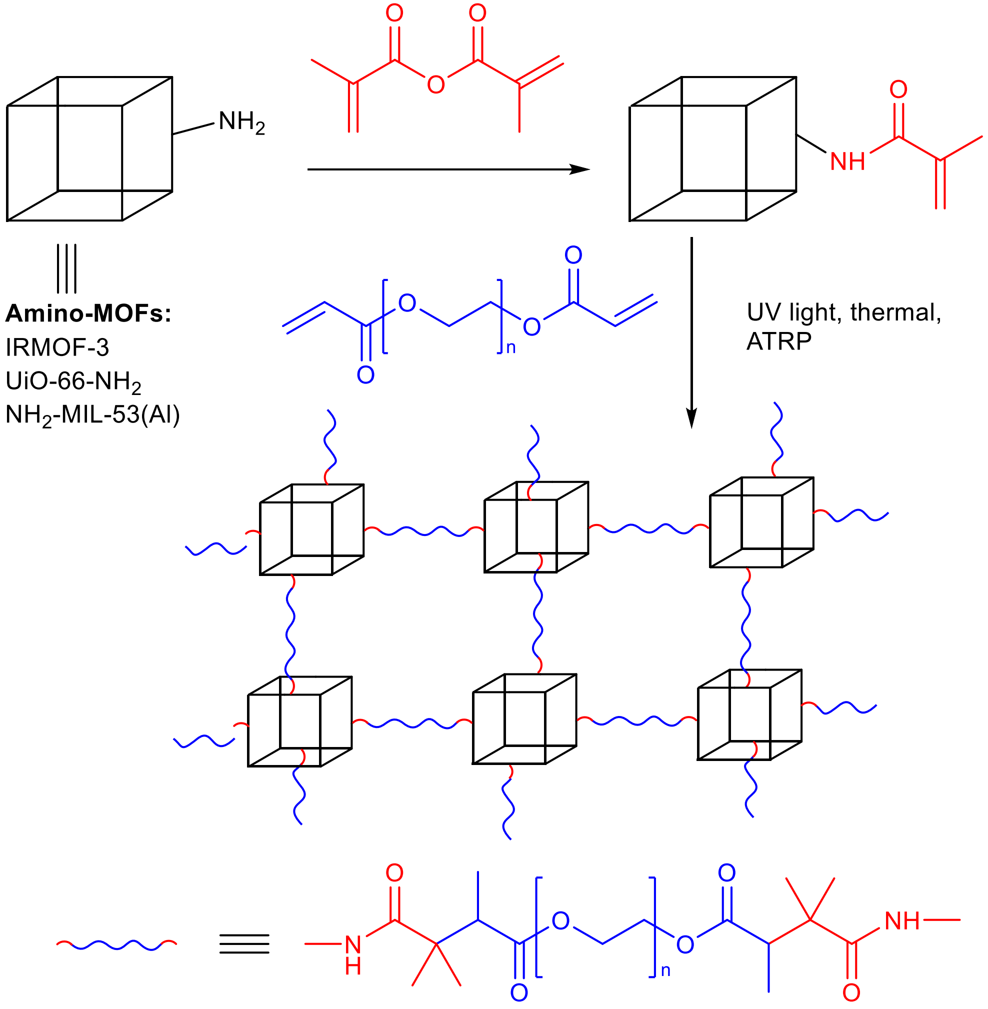
Block copolymers poly(ethylene oxide) with Intrinsic Microporosity (BCPIMs)



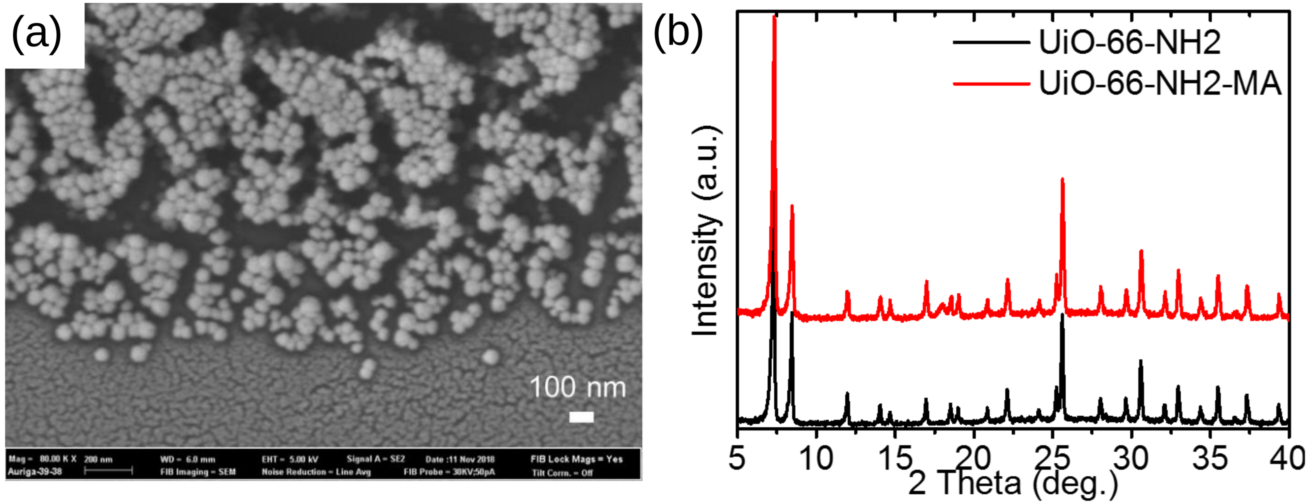


$$\frac{P_M}{P_P} = \frac{1 + 2\varphi_d}{1 - \Psi\varphi_d}$$

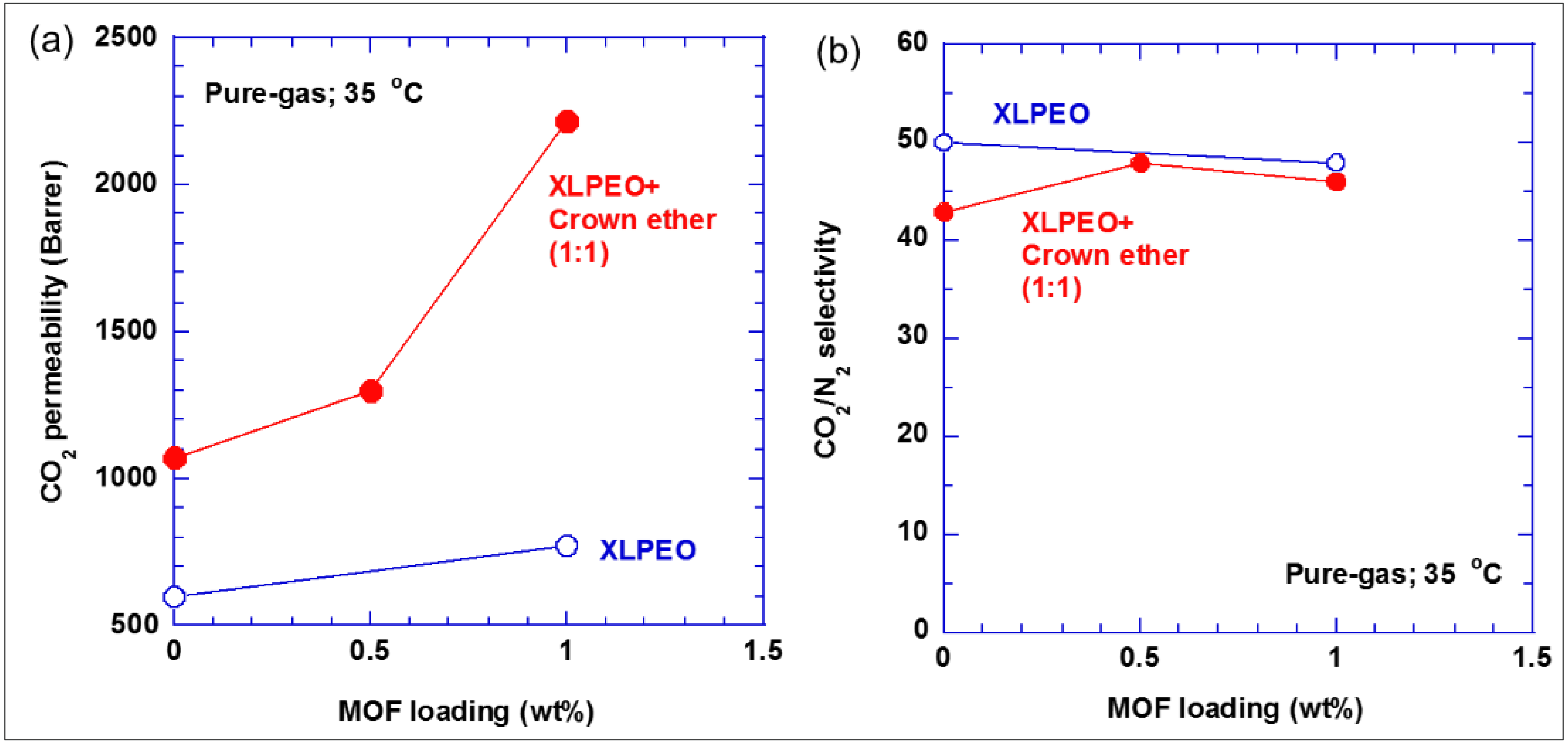
# BCPIMs: UiO-66-NH$_2$



## Synthesis of UiO-66



# Low loading of MOFs increases permeability

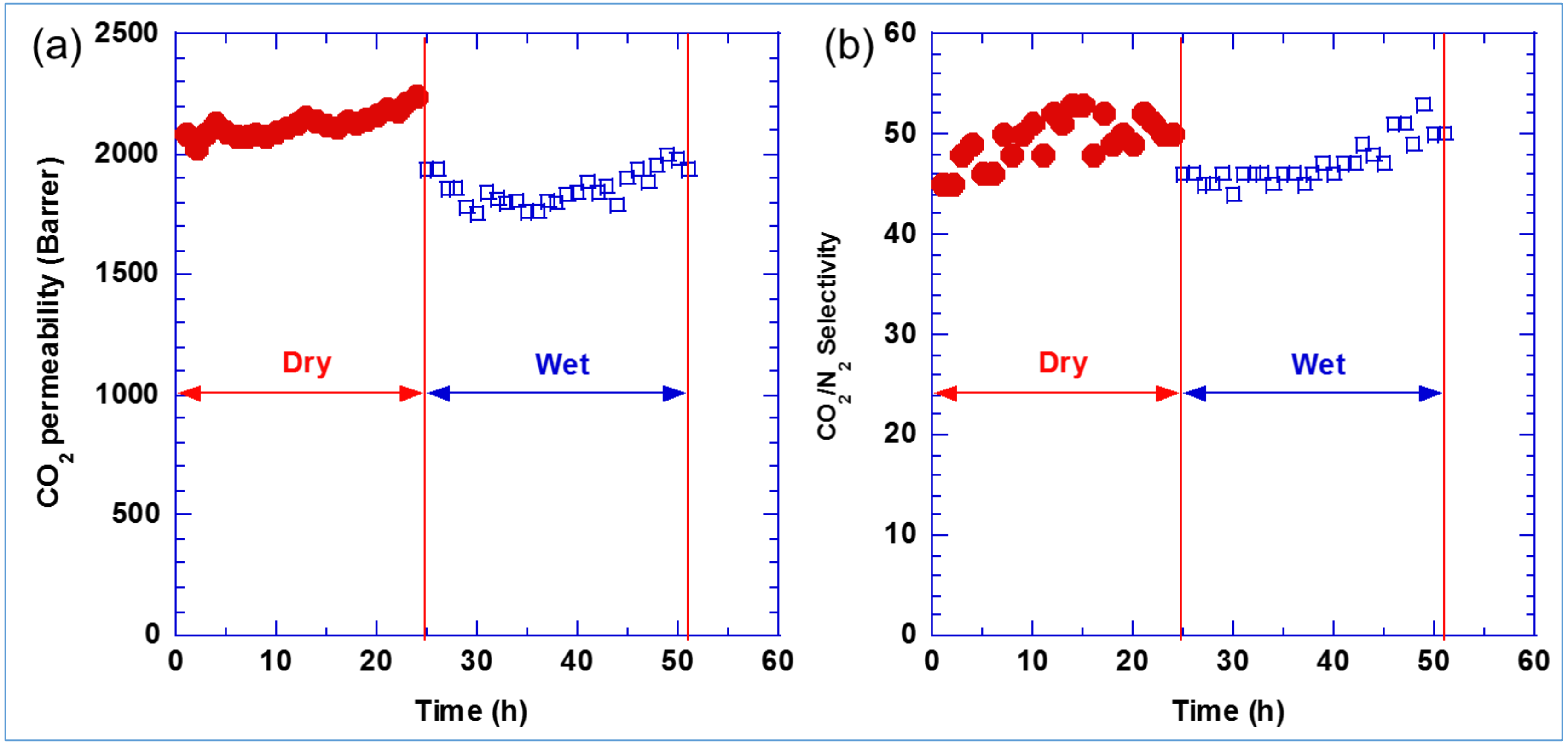


# XLPEO-CE50-MOF1: pure- and mixed-gas tests

| T ($^oC$) | Pure- or Mixed-gas | Feed pressure (psig) | Permeability (Barrer) | | $CO_2/N_2$ Selectivity |
|---|---|---|---|---|---|
| | | | $CO_2$ | $N_2$ | |
| 35 | Pure | 30 | 2200 | 48 | 46 |
| 35 | Mixed | 150 | 2200 | 44 | 50 |
| 50 | Mixed | 150 | 2900 | 100 | 29 |
| 60 | Mixed | 150 | 3000 | 100 | 30 |

The mixed gas contains 20% $CO_2$ and 80% $N_2$ at 150 psig

# XLPEO-CE50-MOF1 with simulated flue gas



The dry gas mixture contains 20% $CO_2$ and 80% $N_2$,
Wet gas contains 0.3 mol% water vapor 35 ℃ in addition.

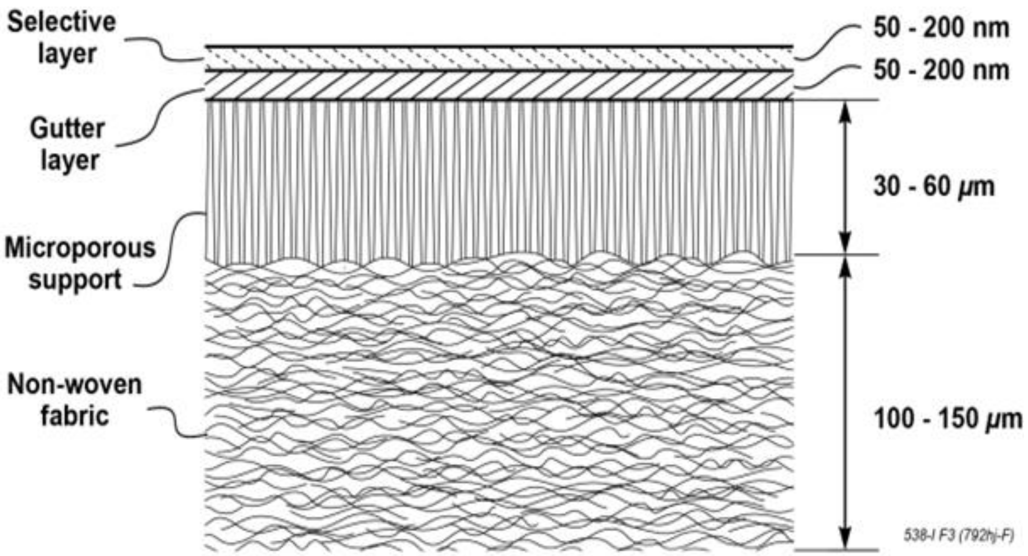
# XLPEO-CE50-MOF1 with simulated flue gas

| Samples | $SO_x/NO_x$ exposure | Permeability (Barrer) | | $CO_2/N_2$ Selectivity |
|---|---|---|---|---|
| | | $CO_2$ | $N_2$ | |
| 1 | No exposure | 2218 | 48 | 46 |
| | After exposure | 2393 | 52 | 46 |
| 2 | No exposure | 1800 | 36 | 50 |
| | After exposure | 1870 | 38 | 49 |

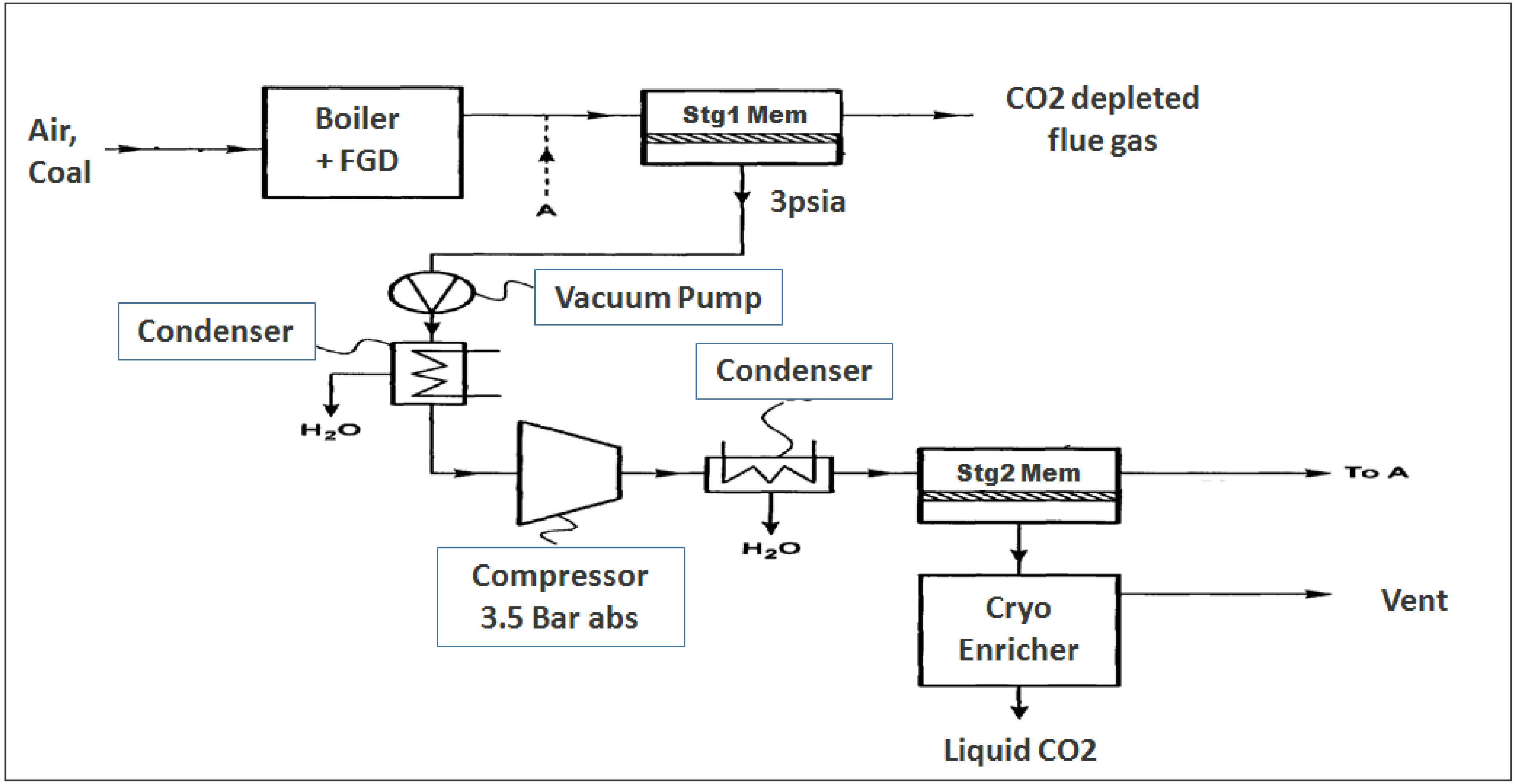
35$^o$C and 30 psig with and without exposure to
75 ppm $SO_x$ and 75 ppm $NO_x$ in $N_2$ for 100 hours.

# Preliminary data on TFC membranes

| Samples | Selective Layer | Permeance (GPU) | | $CO_2/N_2$ Selectivity |
|---|---|---|---|---|
| | | $CO_2$ | $N_2$ | |
| 1 | None | 5400 | 500 | 11 |
| 2 | PEO | 2500 | 85 | 30 |
| 3 | | 1100 | 29 | 38 |
| 4 | | 1070 | 36 | 30 |
| 5 | | 630 | 15 | 43 |
| 6 | 98% PEO<br>+ 2% MOF | 1140 | 45 | 25 |

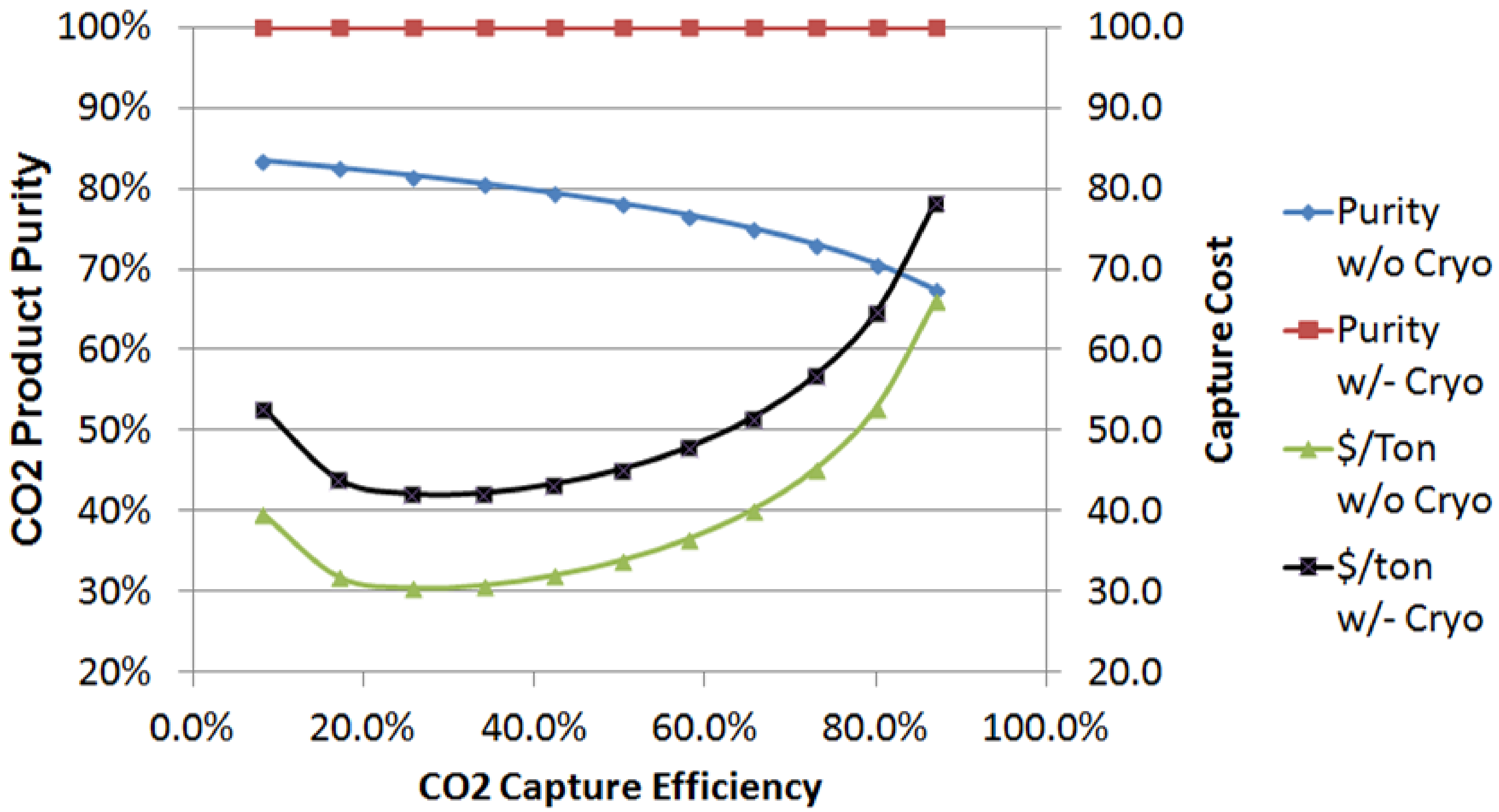


# 2-Stage Process for CO2 Capture

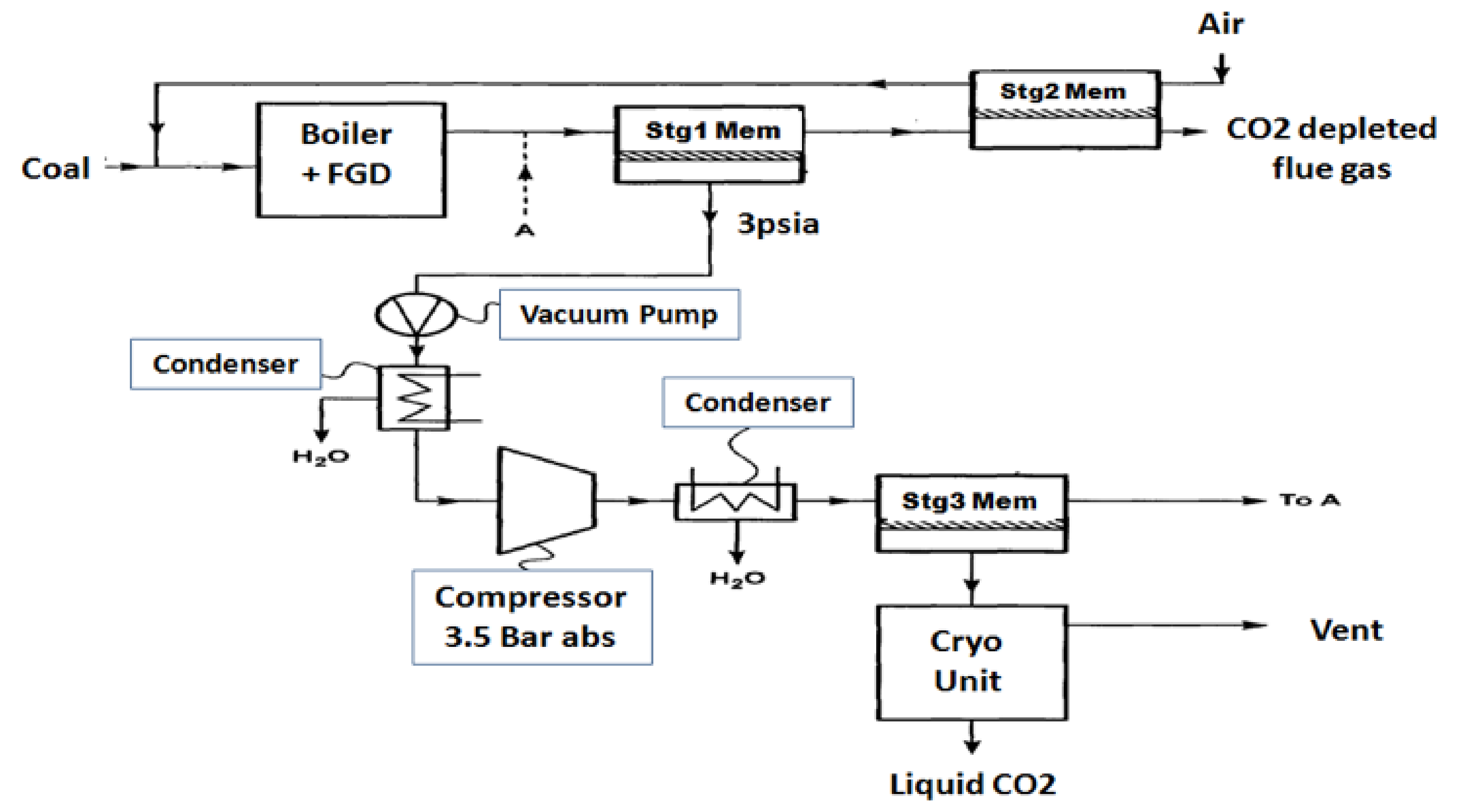


- *No air sweep; no boiler modification - but lower capture efficiency*
- *~50% Capture will reduce CO2 emission from coal plant to level of NG power plant*

# 2-Stage Process - Impact of Capture Efficiency



# 3-Stage Process for CO2 Capture



# TEA for 3-Stage Process

Basis: 550 MW SC PC Power plant

| **Metric** | **Mem 1 - Low End** | | **Mem 2 - High End** | |
|---|---|---|---|---|
| | **W/o Cryo** | **W/- Cryo** | **W/o Cryo** | **W/- Cryo** |
| **Overall Capture Efficiency** | 91.5% | 91.5% | 91.5% | 91.5% |
| **Prod CO2 Concentration** | 85.5% | 100.0% | 87.0% | 100.0% |
| **CO2 Capture Cost ($/ton)** | **21.2** | **29.5** | **20.1** | **28.5** |

# Accomplishments of Phase1

- Advanced materials with $CO_2$ permeability of 2,000 Barrer and $CO_2/N_2$ selectivity of 40 synthesized
- Material stability in the presence of acid gases demonstrated
- Proof of concept thin-film composite (TFC) membranes fabricated
- Substrate coatability and improved gutter layer identified as key improvements to target in Phase2
- TEA work confirmed potential of the advanced membranes to achieve project objective of \$30/ton $CO_2$

# Phase 2 Project Plans

# Phase 2 Project Objectives

1. Develop TFC membrane with $CO_2$ permeance = 4,500 GPU & $CO_2/N_2$ selectivity = 40 at 35-60°C
2. Scale-up TFC membrane fabrication
3. Validate resistance to flue gas contaminants in long-term test
4. Fabricate small modules and validate performance in process tests
5. Define the best process and refine TEA

# Project Tasks - Year1

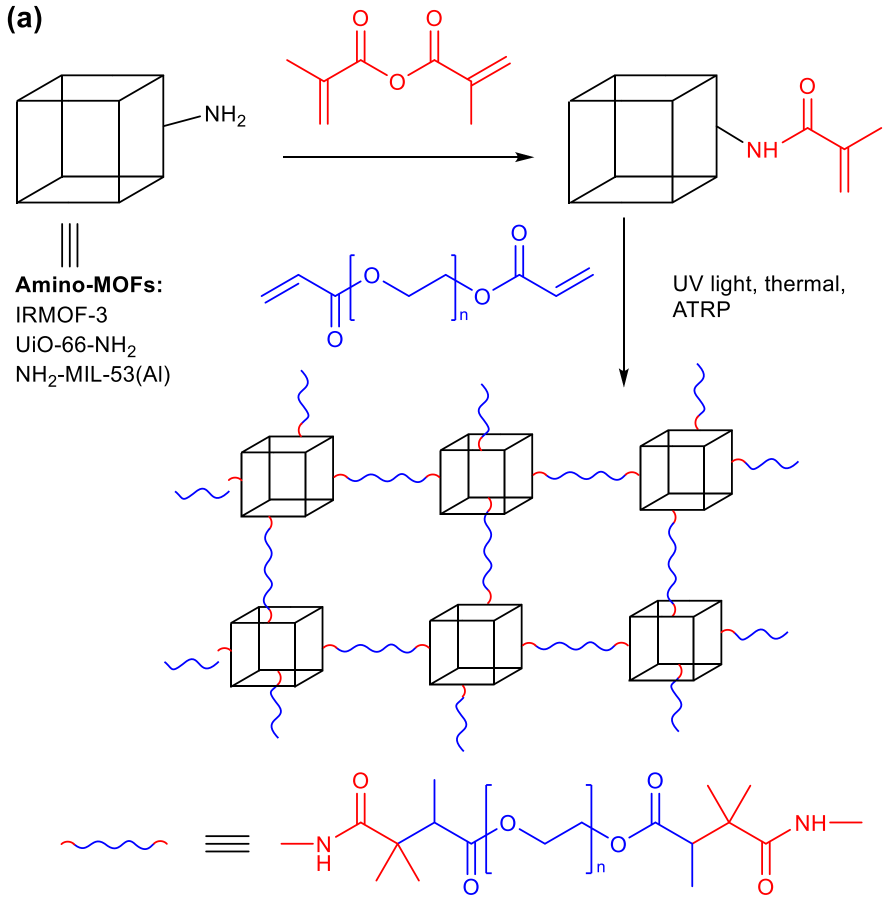
- Task 1 - Project management
- Task 2 - Prepare and optimize TFC membranes
- Task 3 - Conduct parametric tests of TFC membranes
- Task 4 - Assess contaminant stability
- Task 5 - Scale up the fabrication of TFC membranes

# Project Tasks - Year 2

- Task 6 - Project management
- Task 7 - Test membrane coupons at NCCC
- Task 8 - Fabricate bench-scale modules
- Task 9 - Conduct process tests with modules
- Task 10 - Process Development and TEA

# Task 2: Prepare and optimize TFC membranes

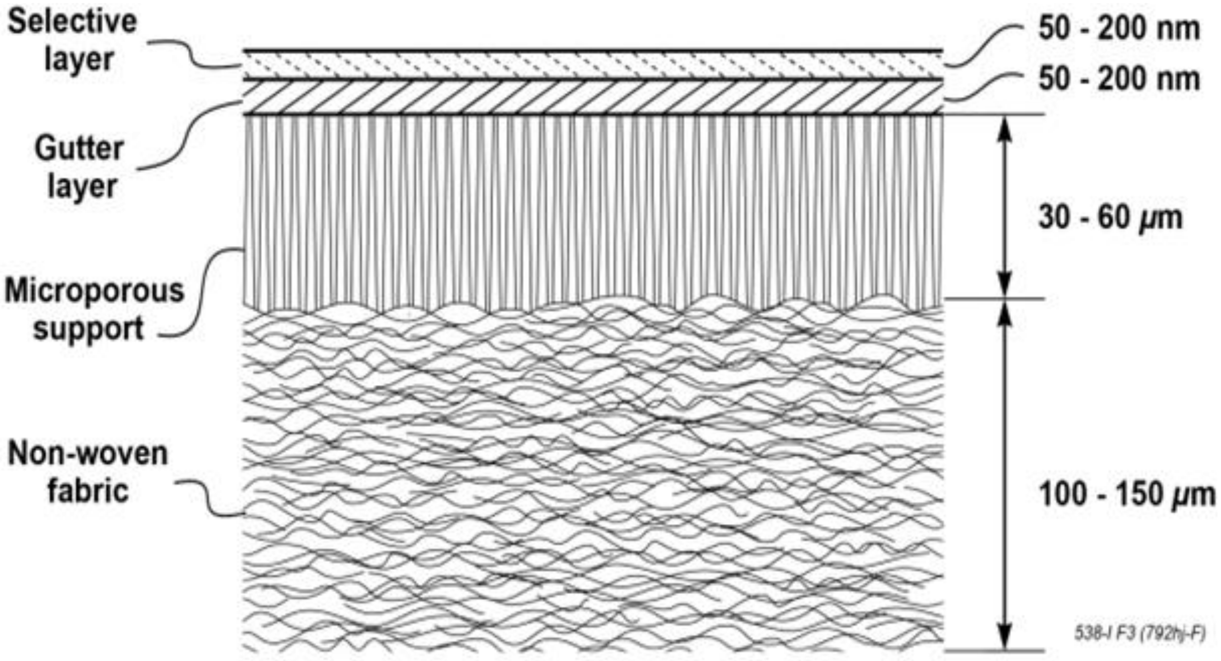
## *Task 2.1 Select materials & scale-up synthesis*



- **Synthesize high molecular weight PEO**
- **Scale up the PEO synthesis to 50 g/batch**
- **Rapid synthesis of UiO66-$NH_2$ in a reproducible way**
- **Scale up the synthesis to 1-5 g/batch**

# Task 2: Prepare and optimize TFC membranes

## *Task 2.2 Optimize gutter layer*

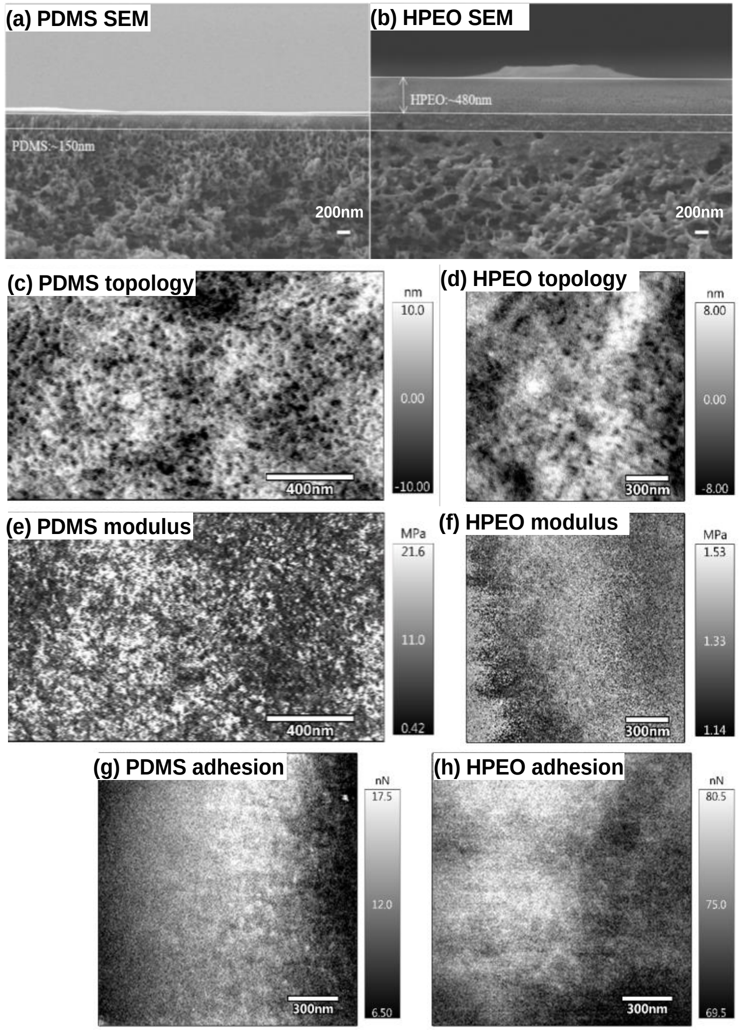


- **Select gutter layer material**
- **Deploy gutter layer on support**
- **Surface modification to improve the compatibility with the coating solution**
- **Plasma treatment (with $O_2$ or $NH_3$)**

# Task 2: Prepare and optimize TFC membranes

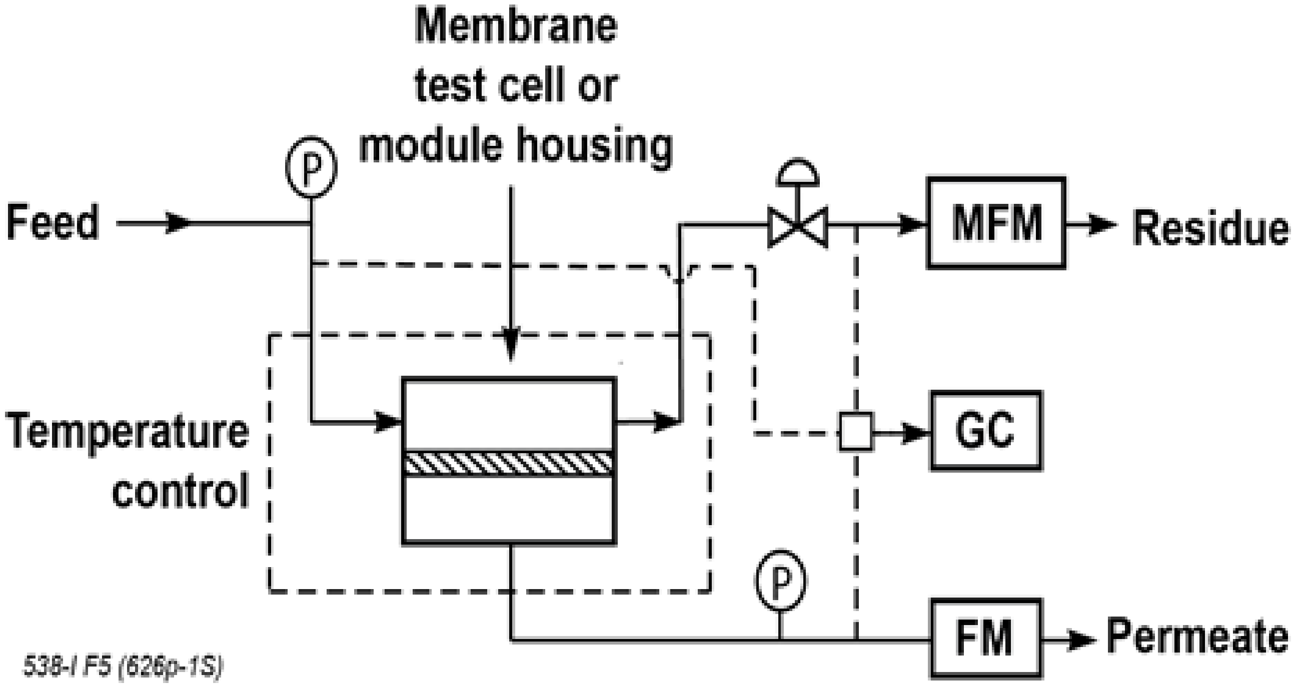
## *Task 2.3 Optimize coating thickness & defect reduction*

- Optimize coating thickness by varying the polymer content in the solutions
- Develop a facile way to measure the film thickness of both layers
- Develop a facile way to determine surface smoothness of gutter layer
- Defect Reduction:
  - Optimize parameters to fabricate defect-free membranes
  - Use defect elimination techniques if needed



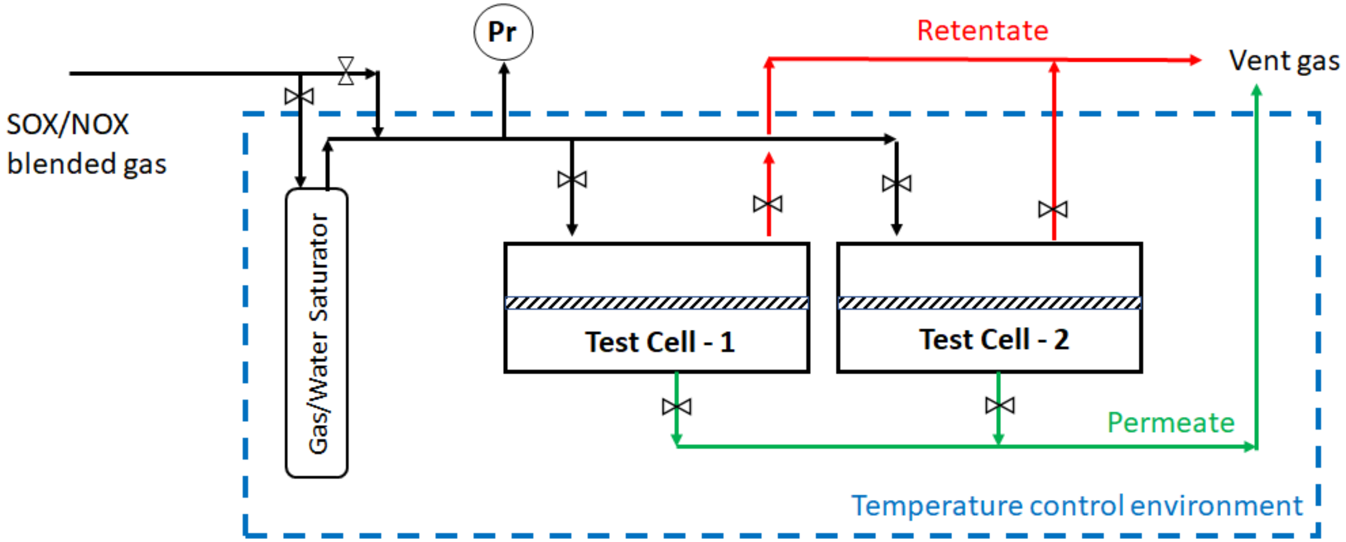
# Task 3: Conduct parametric tests of TFC membranes

- *Determine pure-gas $CO_2/N_2$ separation properties*
- *Determine mixed-gas $CO_2/N_2$ separation properties*
- *2-5 Bar; 35-70C*
- *Use Ar/He purge if needed*

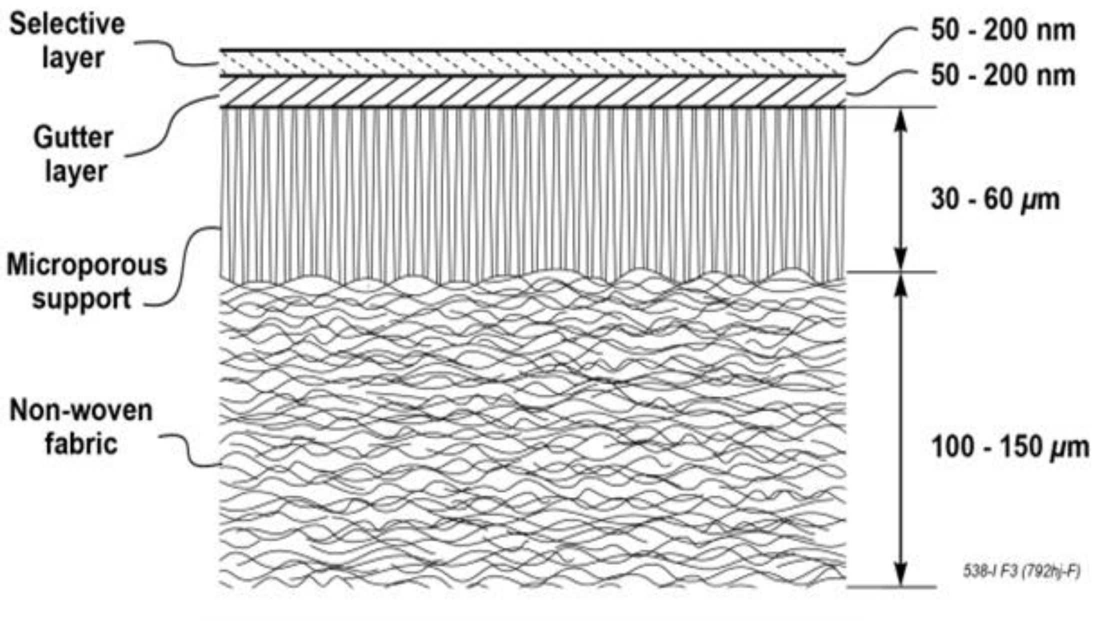


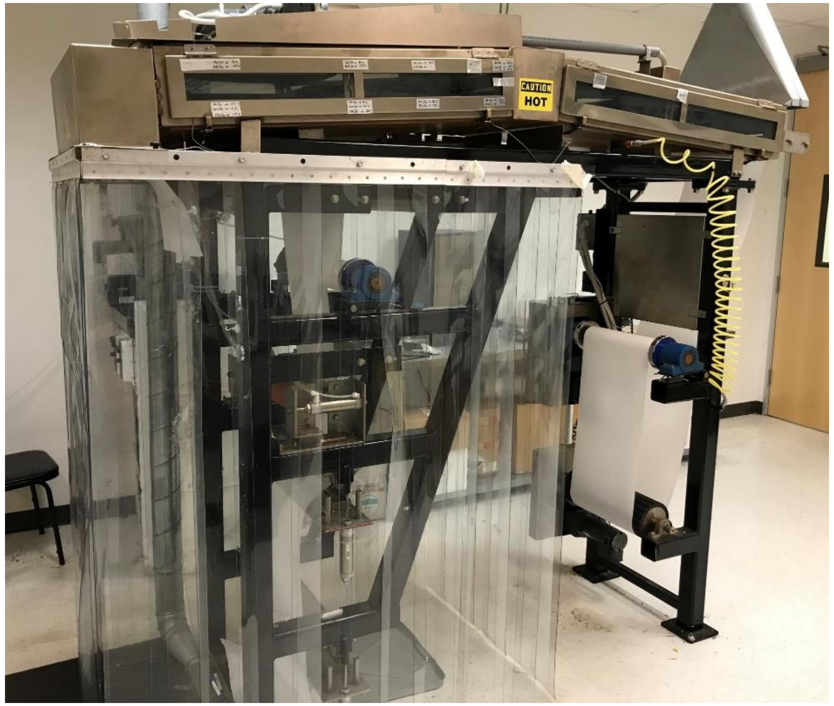
# Task 4: Assess contaminant stability of TFC membranes

- ***Coupon tests on simulated flue gas (H2O, SOX, NOX)***
- ***Measure degradation using standardized tests following "flue gas" exposure***
- ***Address contaminant induced degradation***
  - *Membrane modification*
  - *Process modification*



# Task 5 - Scale up the fabrication of TFC membrane





- ***Thin film composite (TFC) membrane scale up activities; Extensive experience in tuning fabrication parameters to optimize membrane performance***
- ***Research-scale (12-inch width) and commercial (1-m width) roll-to-roll coating equipment available***
- ***Pure gas performance used as QC test to determine membrane quality and reproducibility***

# Task 7 – Test membrane coupons at NCCC

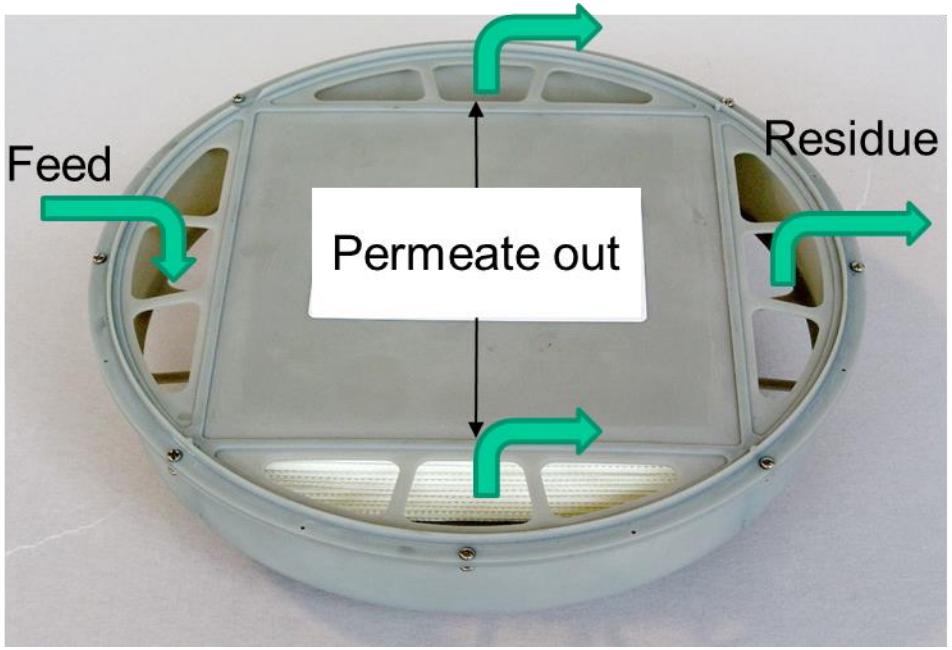
- **Modify existing test skid for operation at NCCC**

- **Test TFC membrane coupons at NCCC on real flue gas**
  - **Long term test**
  - **Performance measured daily**
  - **Post analysis of membranes**

# Task 8 – Fabricate bench-scale modules

- Post-combustion $CO_2$ capture is a low pressure process that requires membrane modules with low pressure drop
- MTR has designed, built, and tested planar modules that offer much lower pressure drop than other module forms
- For lab testing, the new membrane will be made into small prototype modules (1 $m^2$)
- Standard module integrity/QC tests will be performed at MTR before shipping to Helios for parametric testing

**1/6th Scale Housing with Membrane**



# Task 9 – Conduct process tests with modules

- Map module performance over a range of operating conditions
- Understand impact of water vapor and $CO_2$ concentration on separation
  - Study impact of stage cut on performance
  - Check for non-linear property change
- Stage specific process tests
- Post-mortem of module following test

# Task 10 - Process Dev and Economics

- **Design process cycles for $CO_2$ separation from coal-fired flue gas using the novel membranes**
  - Impact of $CO_2$ level on properties
  - Modify based on the measured membrane properties and capture efficiency
- **Map tradeoff between $CO_2$ purity, recovery, specific power, area**
  - Estimate $CO_2$ capture cost as a function of membrane properties & operating conditions
  - Identify best process for $CO_2$ separation at different purities/recovery
- **Understand optimum recovery at which $CO_2$ capture cost is minimized**
- **Refine TEA**

## Acknowledgement

This material is based upon work supported by the Department of Energy under Award Number DE-SC0020730

## Disclaimer