Novel Inorganic/Polymer Composite Membranes for CO_2 Capture

DE-FE0007632

PI: Winston Ho, Professor
Department of Chemical & Biomolecular Engineering
Department of Materials Science and Engineering

Co-PI: Prabir Dutta, Professor
Department of Chemistry
The Ohio State University

Steve Schmit, Chief Technology Officer
Gradient Technology

2015 NETL CO_2 Capture Technology Meeting
Pittsburgh, PA, June 23 – 26, 2015

Project Objective

- **Develop a cost-effective design and manufacturing process for new membrane modules that capture CO_2 from flue gas**

  - **BP1**
    - **Bench scale membrane synthesis, characterization, downselection, and gas separation performance**
    - **Preliminary techno-economic analysis**

  - **BP2**
    - **Bench scale membrane synthesis, characterization and gas separation performance to continue**
    - **Continuous membrane fabrication**
    - **Membrane module testing in lab (CO_2, N_2, MOISTURE)**
    - **Update techno-economic analysis**

  - **BP3**
    - **3 prototype modules for testing with simulated and real flue gas**
    - **Update techno-economic analysis**
    - **EH&S evaluation report being developed**

Project Organization and Roles

Ohio State University
- Technical lead
- Concept development and execution
- Novel membrane synthesis/characterization
- Membrane scale-up/continuous fabrication
- Process demonstration
- Cost calculations

Winston Ho and Prabir Dutta

DOE NETL

Project Manager

José Figueroa

Gradient Technology
- System, cost analysis
- EH&S analysis

Steve Schmit

TriSep Corporation
- Consult on continuous membrane fabrication

Peter Knappe

AEP
- Consult on plant integration, demonstration and EH&S

Dan Duellman

Funding and Performance Dates

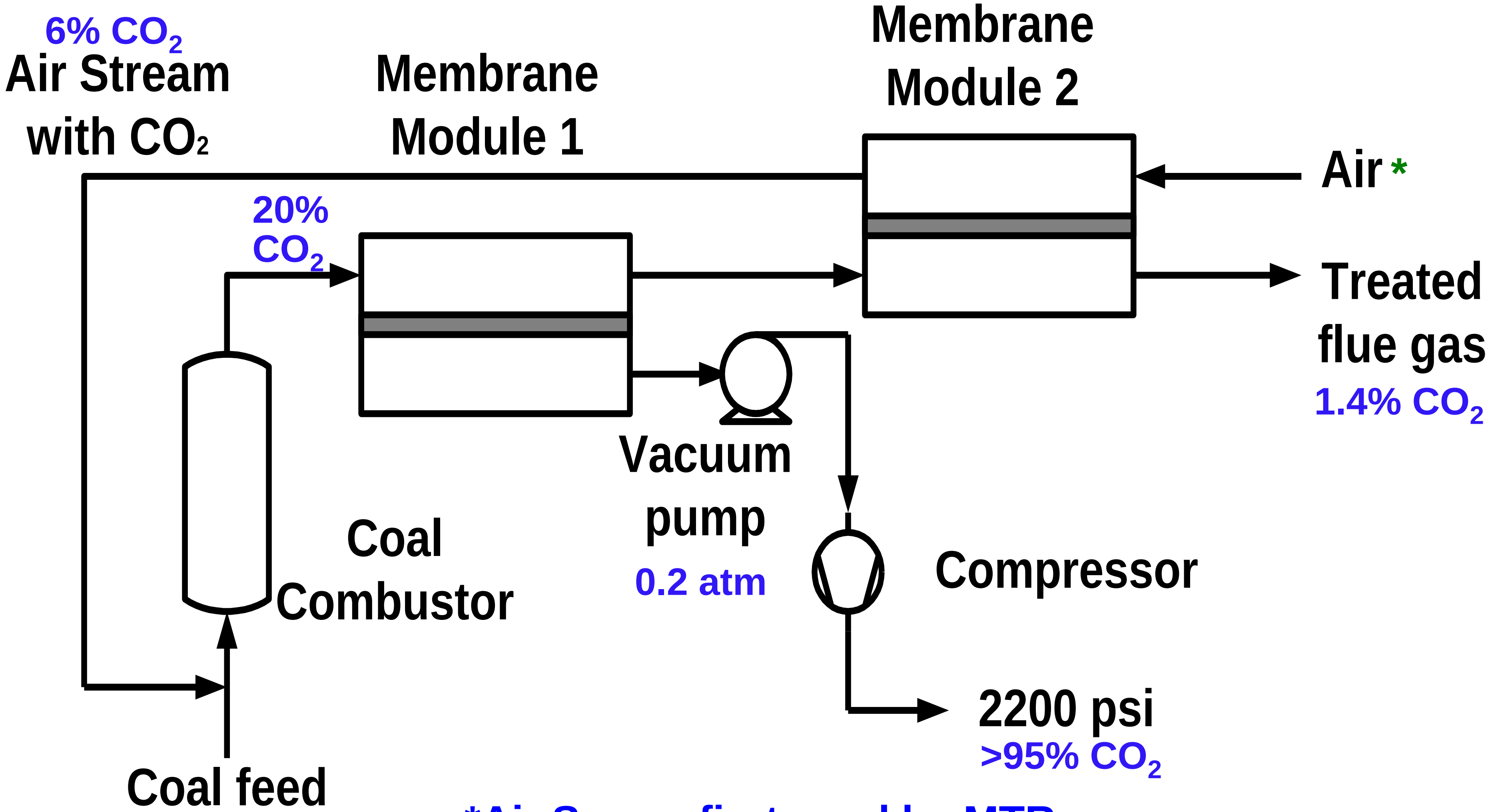
- **Total Budget: 10/01/2011 – 08/31/2015**
  DOE: $3,000K; OSU: $679K; ODOD: $500K

  - **BP1: 10/01/2011 – 05/31/2013**
    DOE: $899K; OSU: $351K

  - **BP2: 06/01/2013 – 08/31/2014**
    DOE: $958K; OSU: $131K; ODOD: $277K

  - **BP3: 09/01/2014 – 08/31/2015**
    DOE: $1,144K; OSU: $197K; ODOD: $223K

Process Proposed for CO_2 Capture from Flue Gas in Coal-Fired Power Plants

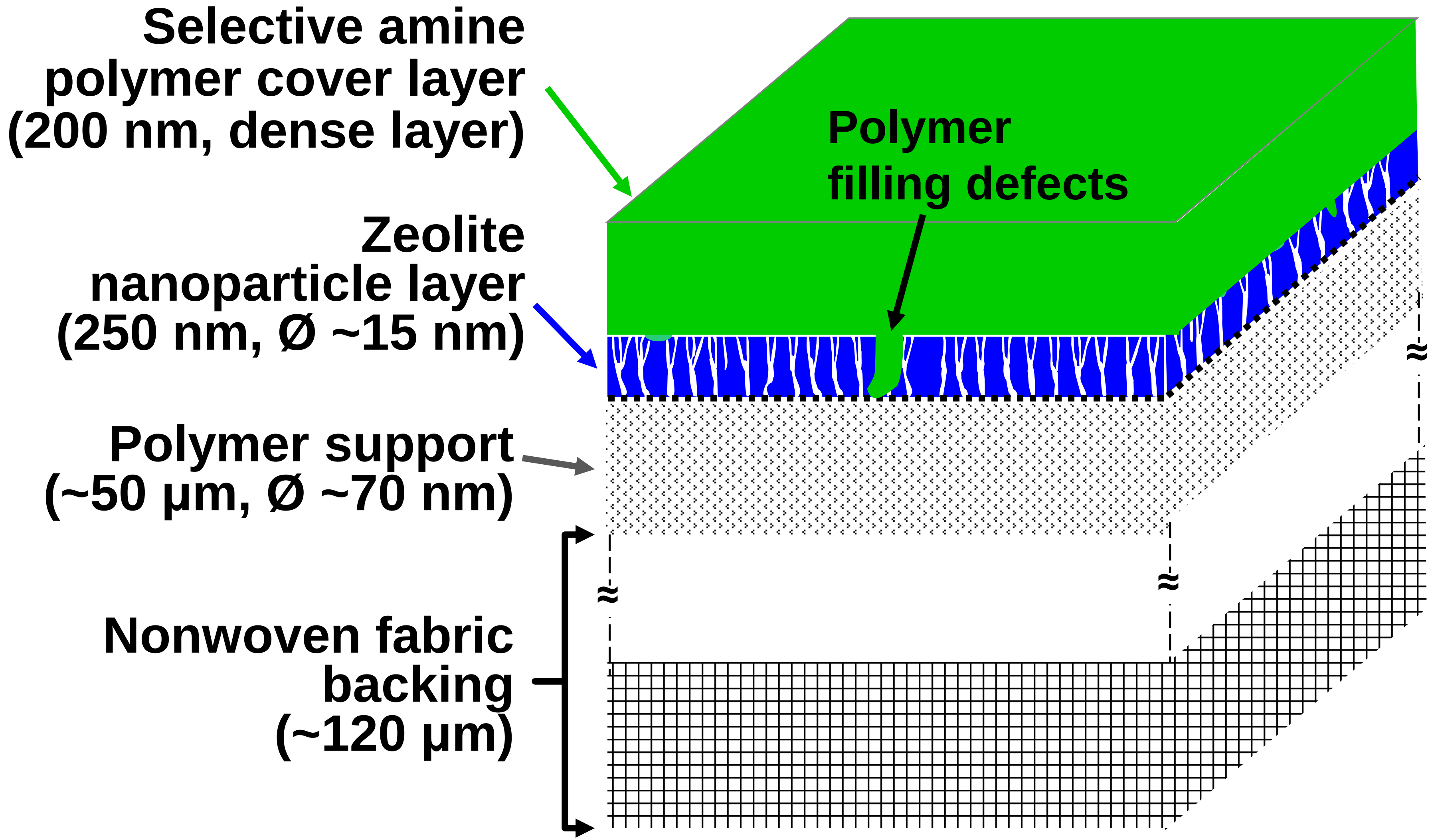


*Air Sweep first used by MTR

- Proposed membrane process eliminates cryogenic distillation (compare to competition)

Approach 1: Selective Amine Polymer Layer / Zeolite Nanoparticle Layer / Polymer Support

High Inorganic Performance and Low-Cost Polymer Processing Benefits



Approach 1: Selective Amine Polymer Layer / Zeolite Nanoparticle Layer / Polymer Support

- **Selective Amine Polymer Layer**
  - Facilitated transport of CO_2 via reaction with amine

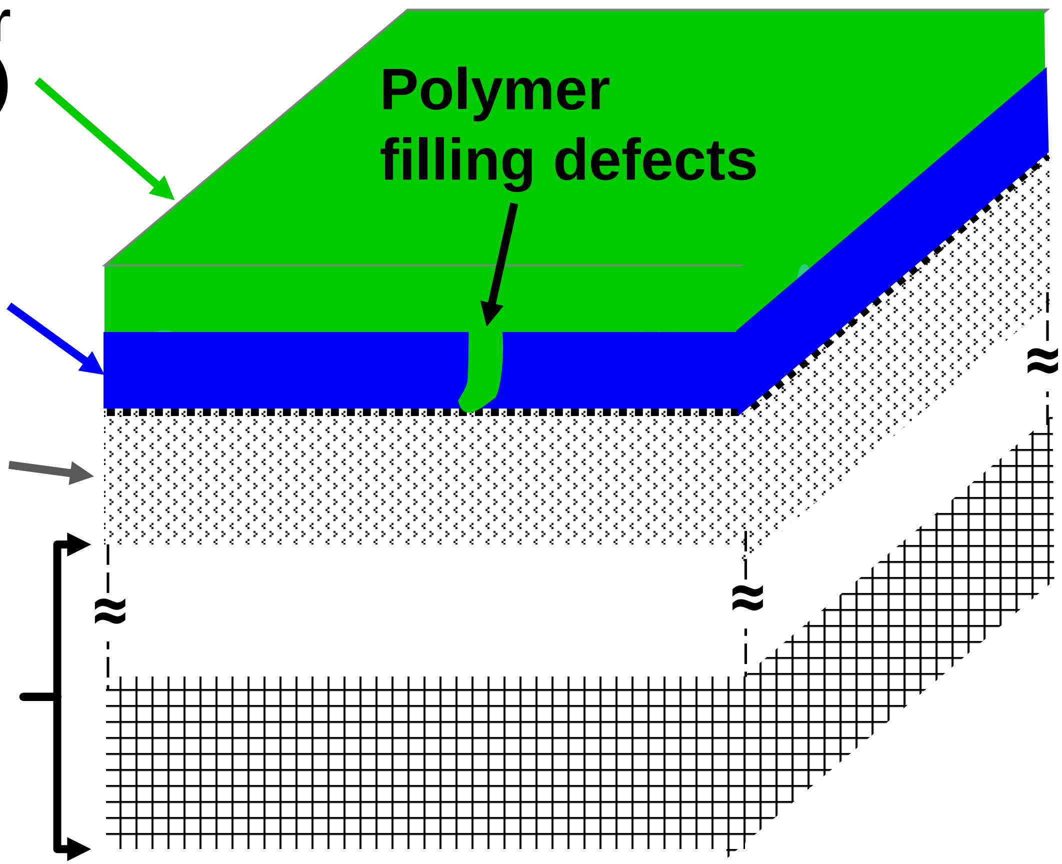
$$CO_2 + R\text{-}NH_2 + H_2O \rightleftharpoons R\text{-}NH_3^+ + HCO_3^-$$

  - High CO_2 permeance and CO_2/N_2 selectivity

- **Zeolite Nanoparticle Layer**
  - Increased porosity
  - Reduced pore size → Thinner selective amine layer
  - Higher CO_2 permeance

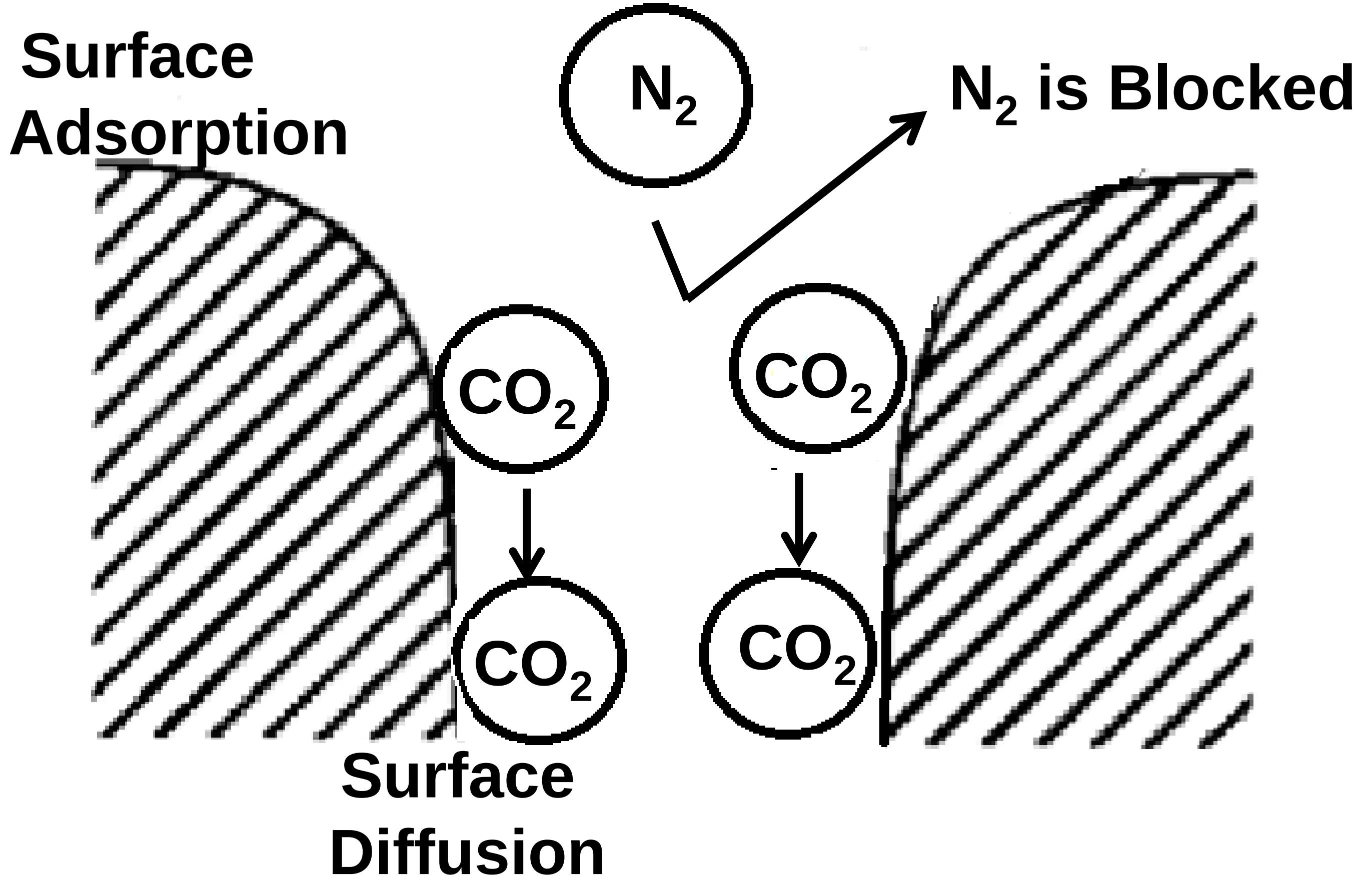
Approach 2: Polymer Caulking Layer / Selective Zeolite Membrane / Polymer Support

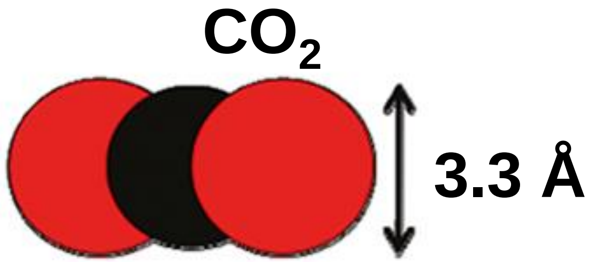
High Inorganic Performance and Low-Cost Polymer Processing Benefits



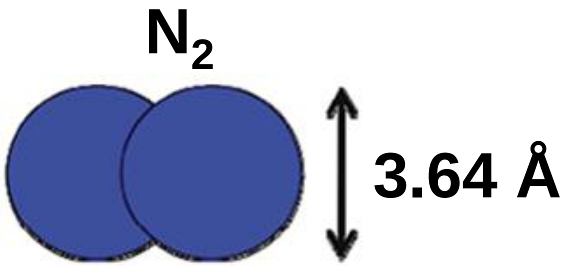
Rapid growth process developed for zeolite membrane for competitive cost

Approach 2: Transport Mechanism through Zeolite





$Q_{CO_2} = -13.67\times10^{-40}$ C m^2

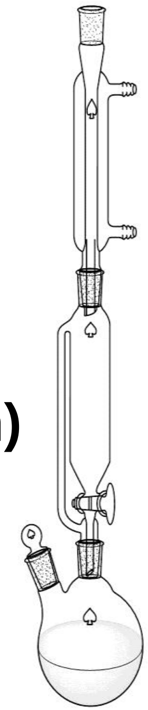


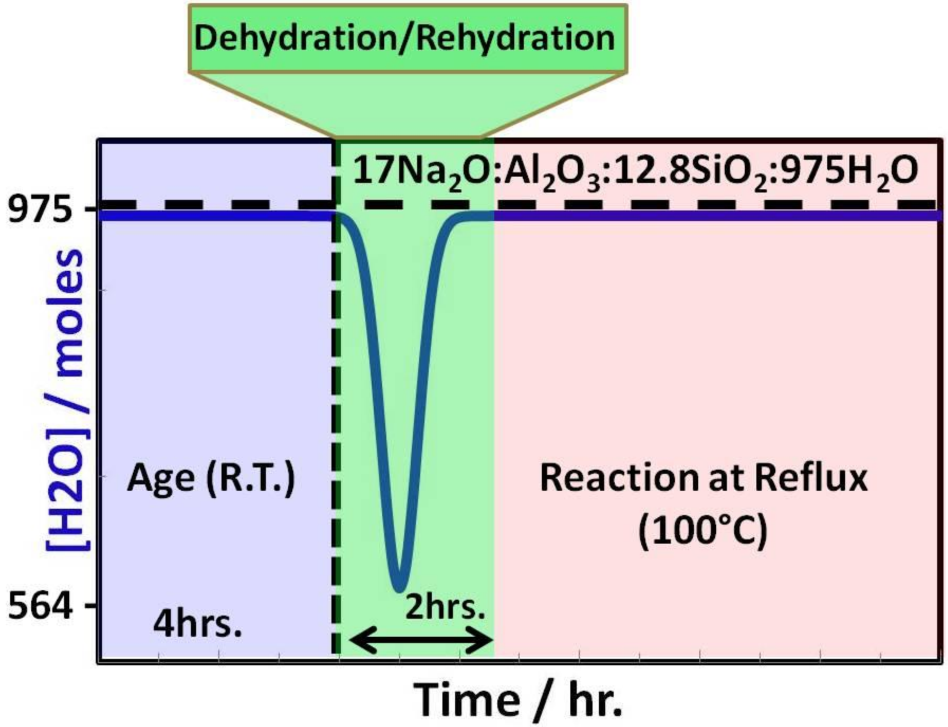
$Q_{N_2} = -4.67\times10^{-40}$ C m^2

Rapid Synthetic Process for Zeolite Powders

Rapid Synthesis

- Open system
- Control water concentration
- Remove H_2O (nucleation)
- Re-add H_2O (crystallization)





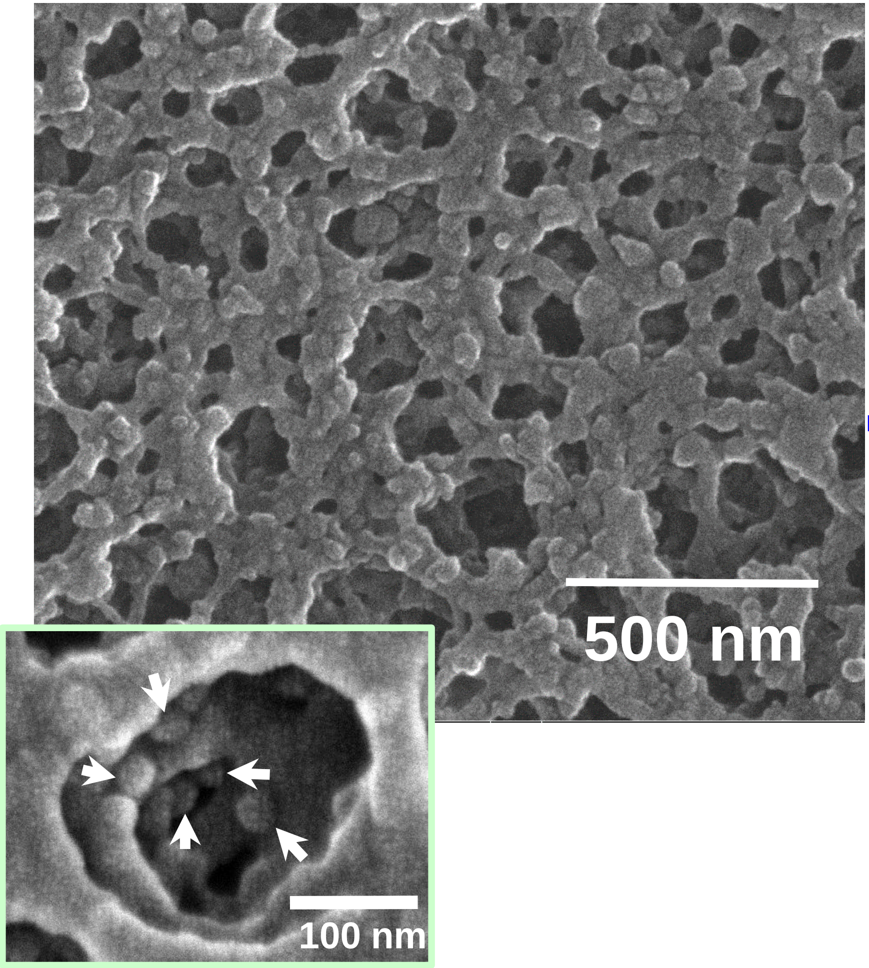
17 Na_2O:Al_2O_3 : 12.8 SiO_2 : 975 H_2O

17 Na_2O:Al_2O_3 : 12.8 SiO_2 : 564 H_2O

Growth Process takes 1 hour compared to 8 hours with conventional method

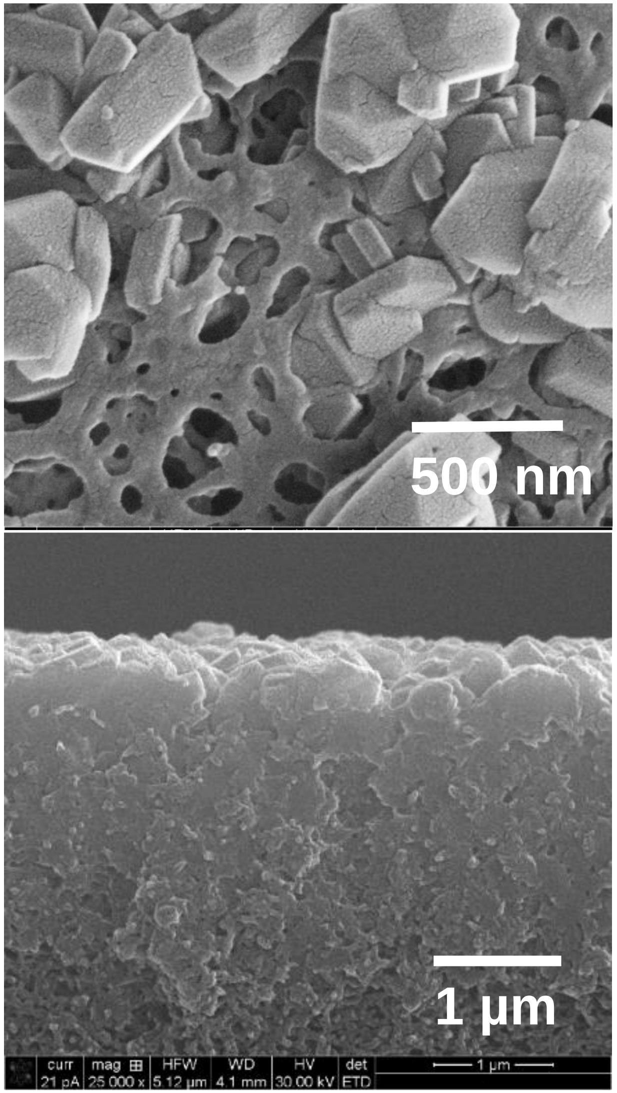
Rapid Synthetic Approach Adapted to Zeolite Membrane

Seed Crystals



1 h growth

Zeolite Membrane



- **Continuous zeolite layer grown WITHIN polymer support**

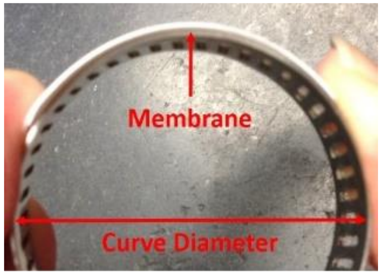
BP3 Accomplishments

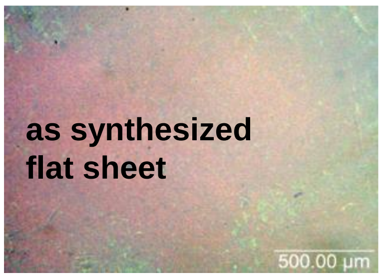
- **Approach 1: Composite Membrane Scaled up and Prototype Modules Fabricated**
  - PES polymer support scaled up to 14” wide for ~2500 feet
  - ZY deposition scaled up to 14” wide for ~1000 feet
  - Membrane scaled up to 14” wide for ~1000 feet
  - 870 GPU with 218 CO_2/N_2 selectivity obtained in flat sheet at 57^oC from lab test
  - ~150 of ~2” diameter by 14” long spiral-wound membrane elements / modules fabricated using rolling machine
  - 820 GPU with ~200 CO_2/N_2 selectivity obtained from modules at 57^oC from lab test
  - Membrane module stable to 1 – 3 ppm SO_2, 3% O_2 and 17% H_2O for 200-h test conducted
  - 3 invention disclosures submitted for membrane composition, process and module design

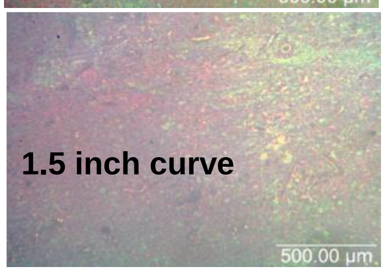
BP3 Accomplishments (continued)

- **Approach 1: Testing with Flue Gas at NCCC**
  - **Good performance targeted for 200-h tests**
    - **810 GPU with ~200 CO_2/N_2 selectivity obtained at 57ºC**
    - **Module tested at NCCC behaved similarly to that in OSU Lab**
    - **Repeatable results from 3 modules tested**
    - **Flue gas contained 0.5 – 5 ppm SO_2, 1.5 – 4 ppm NO_2, 6.6 – 8% O_2 and 17% H_2O**
- **Effects of SO_2 and CO_2/SO_2 Mixture on Amine Carriers Studied by in-situ FTIR**
  - **SO_2 permeated with CO_2**
  - **Amine regenerated by air sweep at 57ºC – Confirmed by in-situ FTIR**
- **Approach 2: Rapid Zeolite Membr. Growth (1 h)**
  - **Bendable zeolite membrane synthesized within PES support**
    - **Potential for roll-to-roll processing**
  - **>2000 GPU CO_2 permeance with ~40 CO_2/N_2 selectivity achieved with dry gas mixture at 25ºC**
  - **Manuscript accepted by *Langmuir***

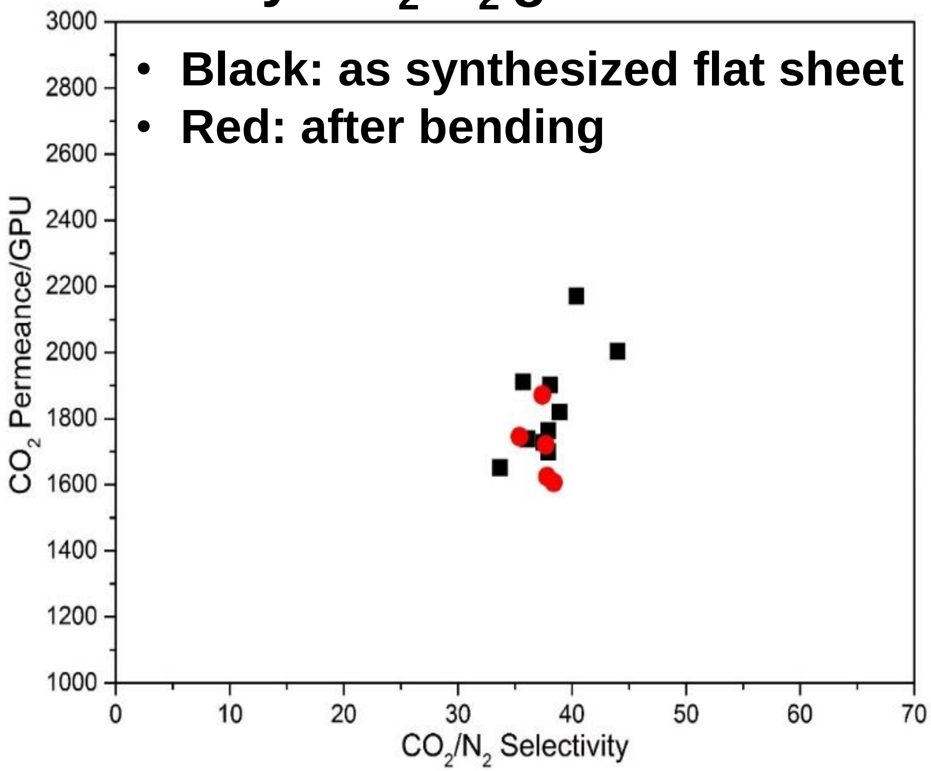
Approach 2: Zeolite Membrane within PES Support

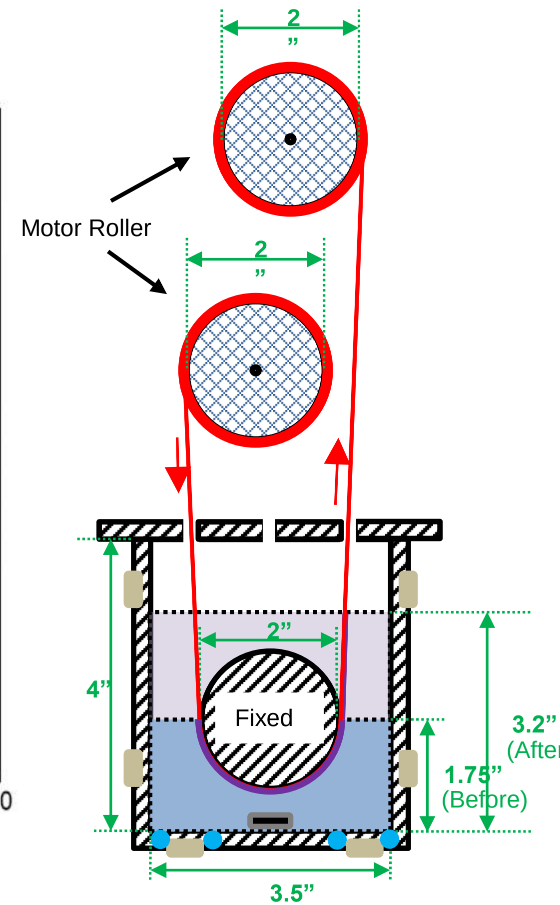






Transport properties with dry CO_2/N_2 gas at 25°C





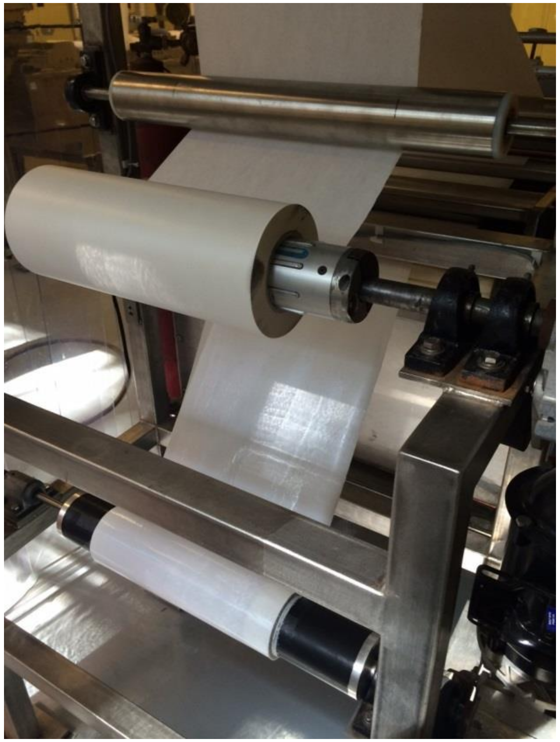
- **Potential roll-to-roll manufacturing**

Membrane Scale-up: Usable for Approaches 1 and 2

Continuous Membrane Fabrication Machine at OSU

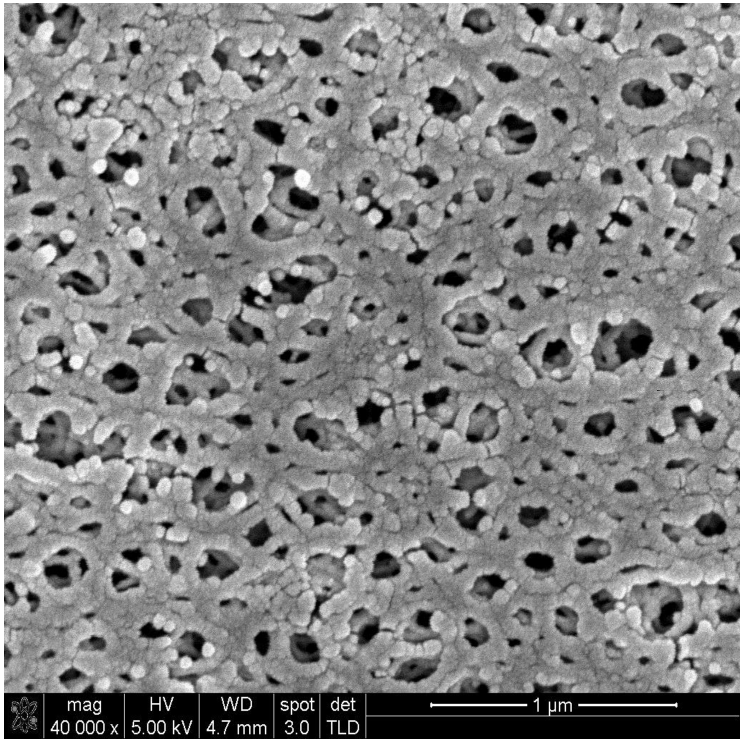
Successful Continuous Fabrication of Affordable PES Support (applicable to Approaches 1 and 2)

Casting Machine



14-inch PES Support

SEM – Top View



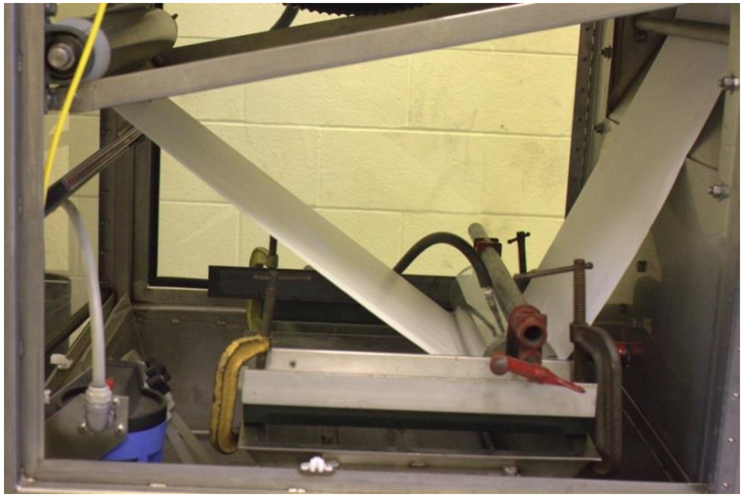
2500 feet fabricated in BP3

- **Manufacturer could not supply PES needed for scale-up**
- **PES synthesized/developed at OSU to resolve supply issue**
- **PES technology being transferred to TriSep**

Scale-up Zeolite-Y Deposition and Amine Coating

14-inch PES Support

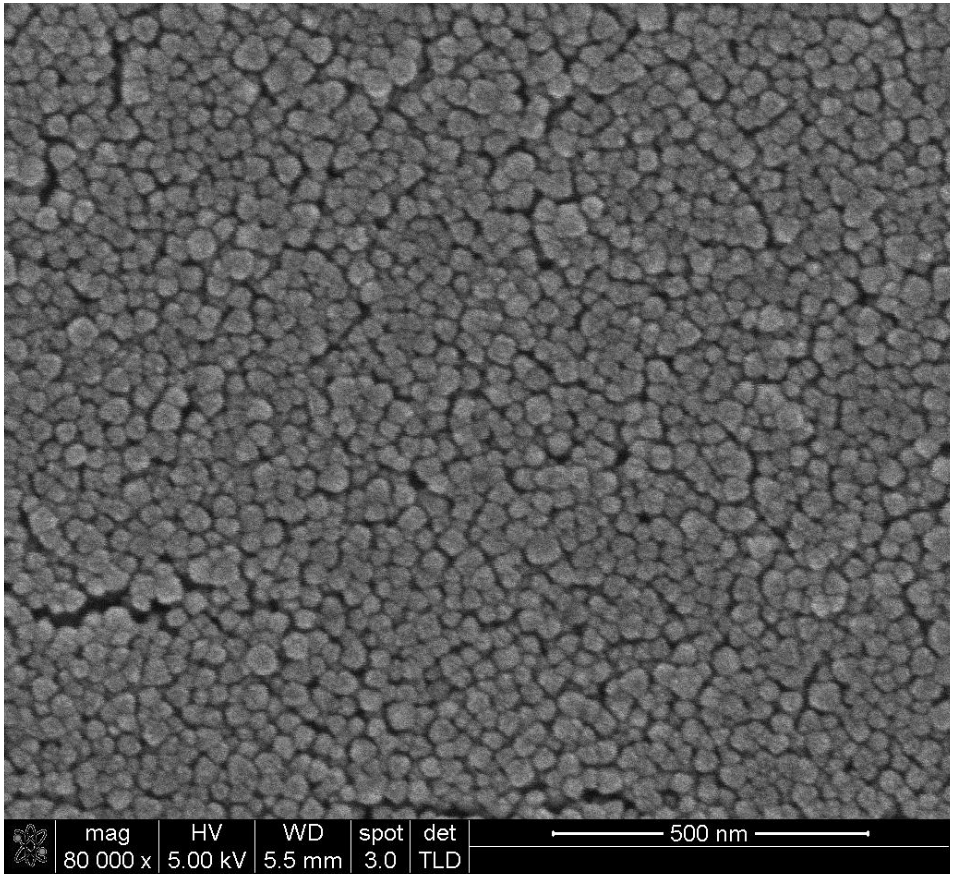
14" ZY Deposition on PES Support



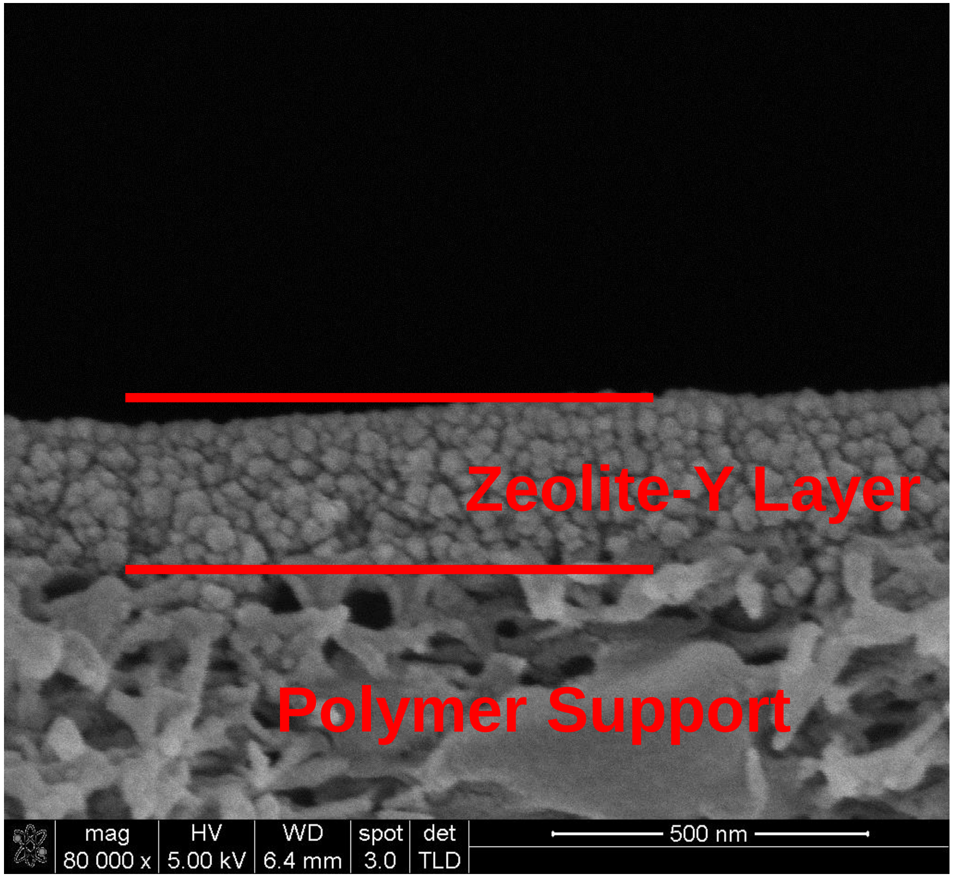
14" Amine Coating on ZY Layer on PES

Approach 1: Zeolite Nanoparticles Deposited on Polymer Support Successfully

Top View

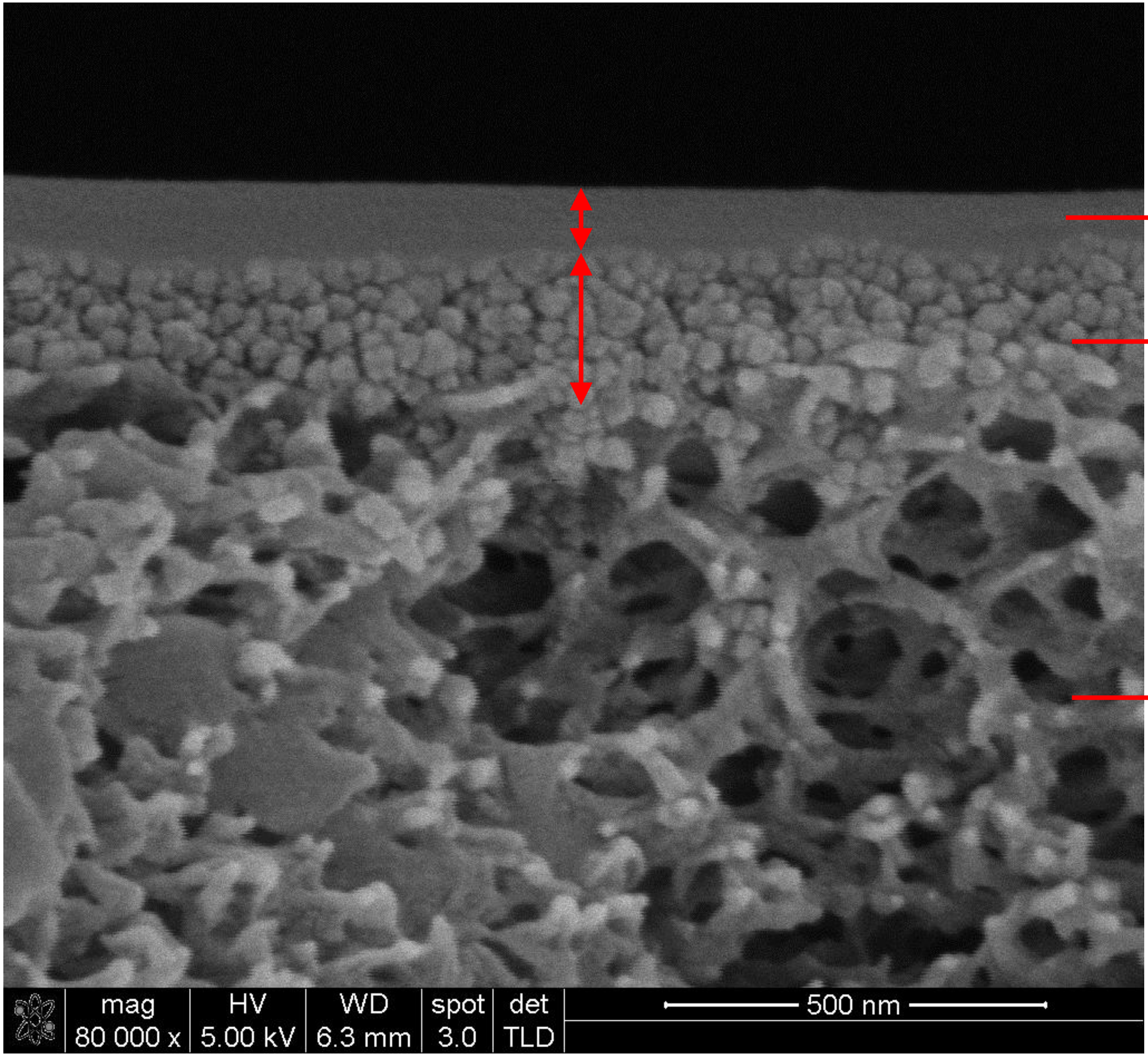


Cross-section



- **High quality deposition with good repeatability**

Amine/Zeolite Seed Layer/Polymer Support



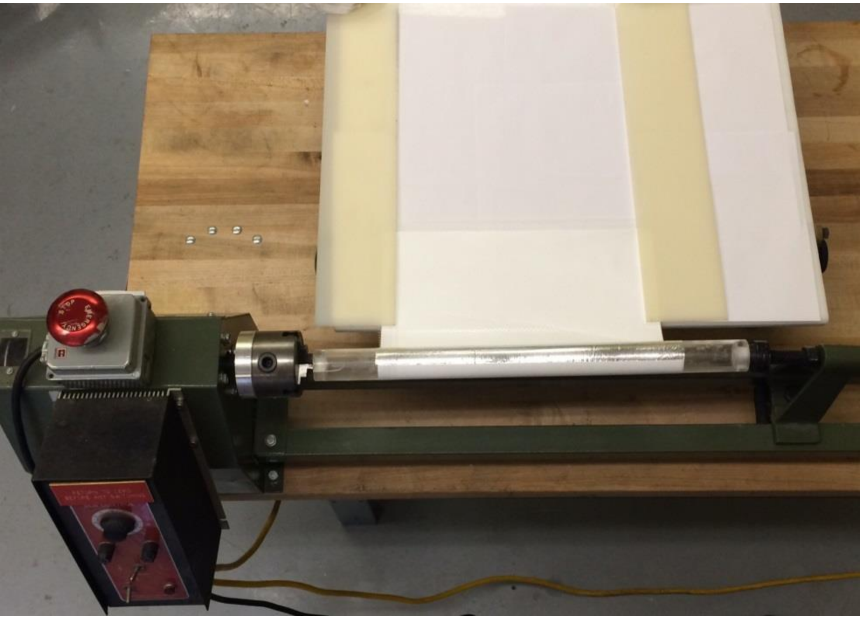
Amine cover layer ~ 185 nm

Zeolite-Y 40 nm seed layer ~ 230 nm

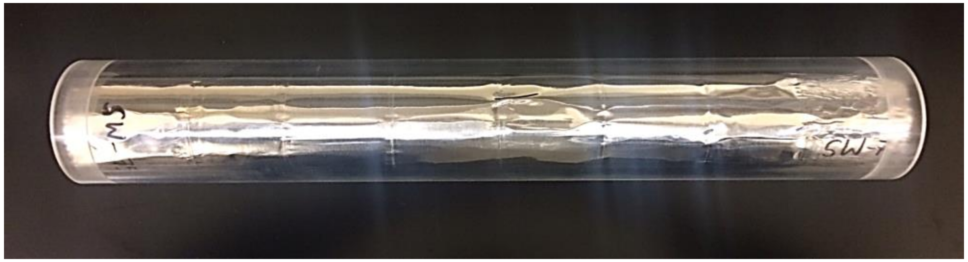
PES support

Membrane Element Fabrication

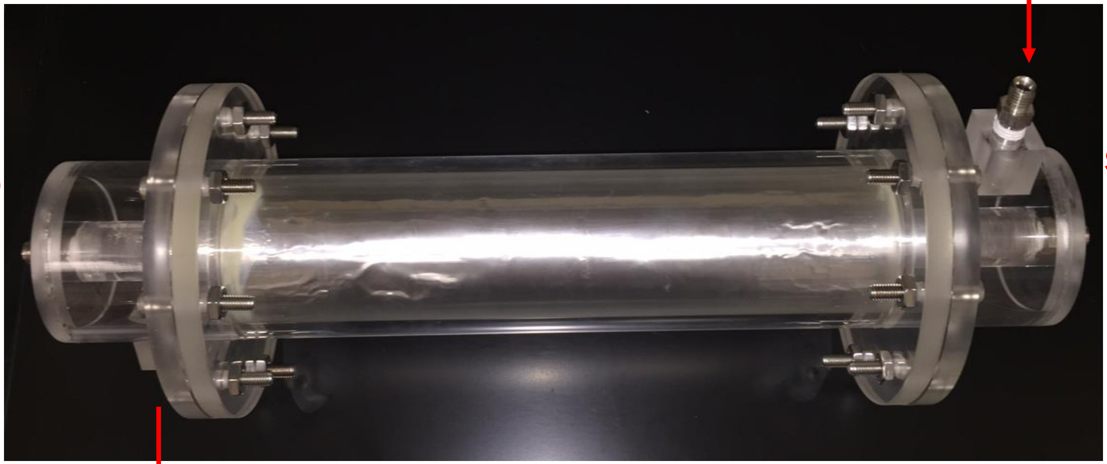
Element Rolling Machine



Spiral-Wound Membrane Element



Membrane Module

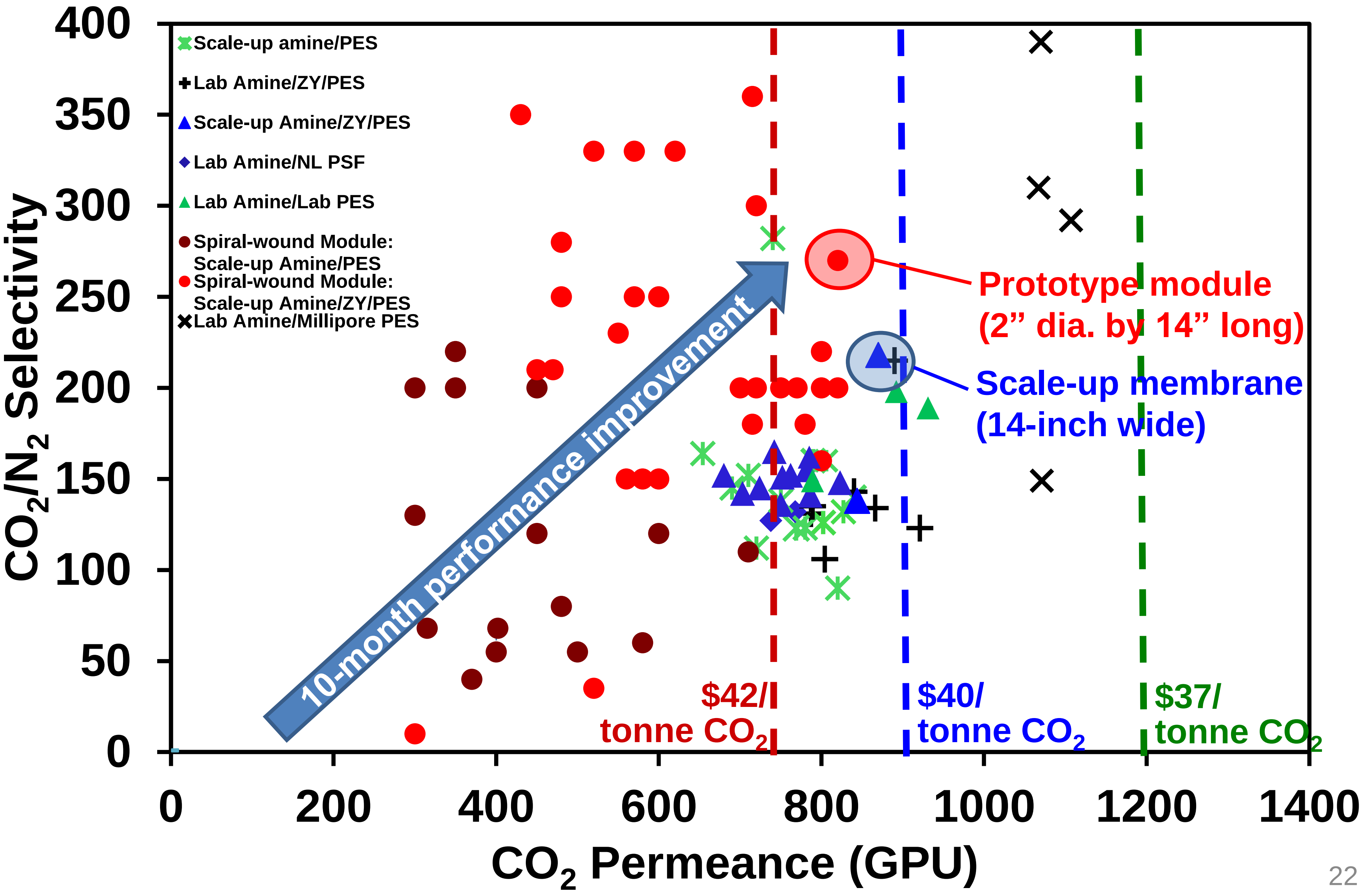


Approach 1: TriSep also Made Elements for us

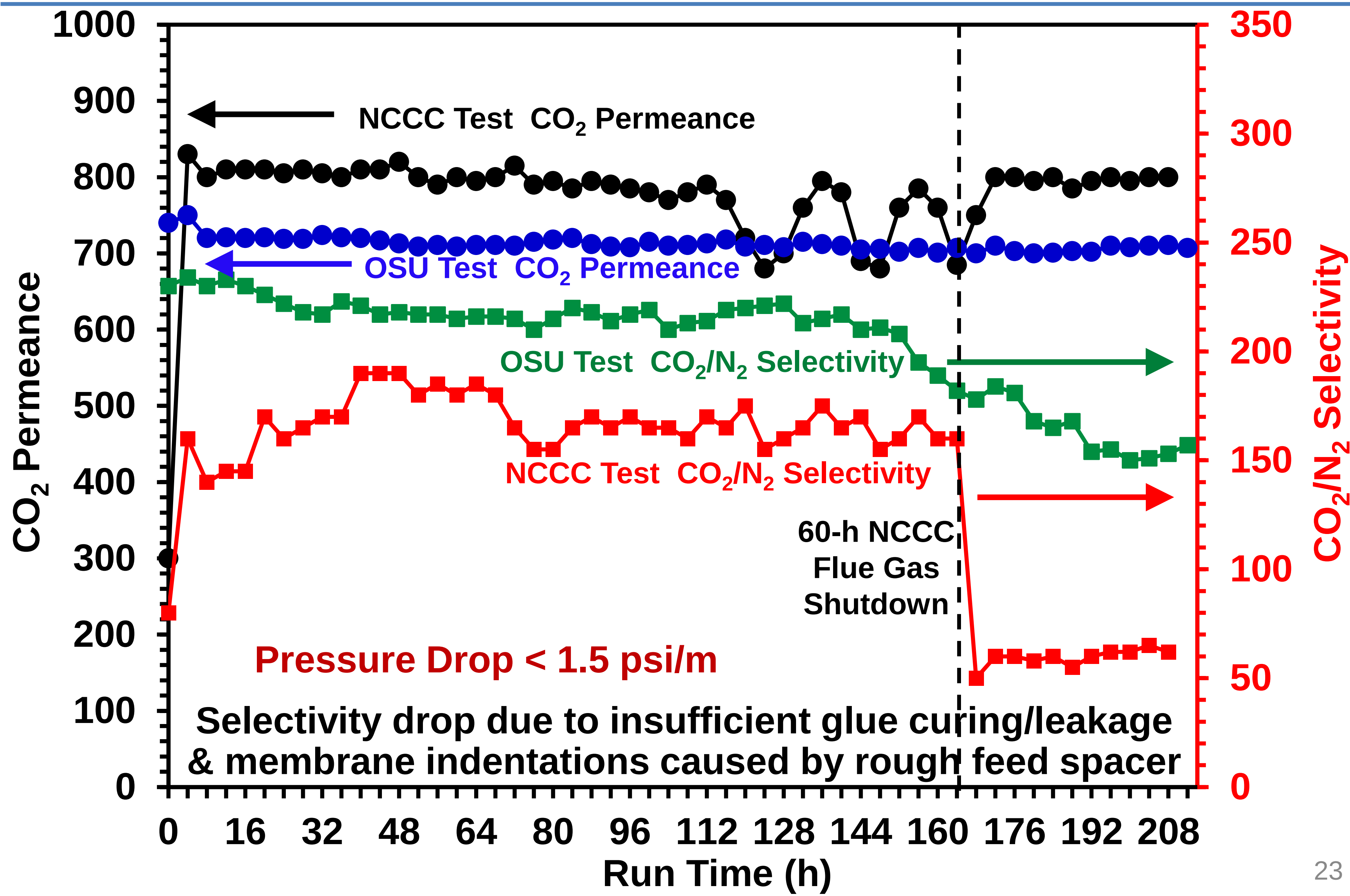
Spiral-Wound Membrane Element Made by TriSep

Membrane Module: Element Made by TriSep in our Housing

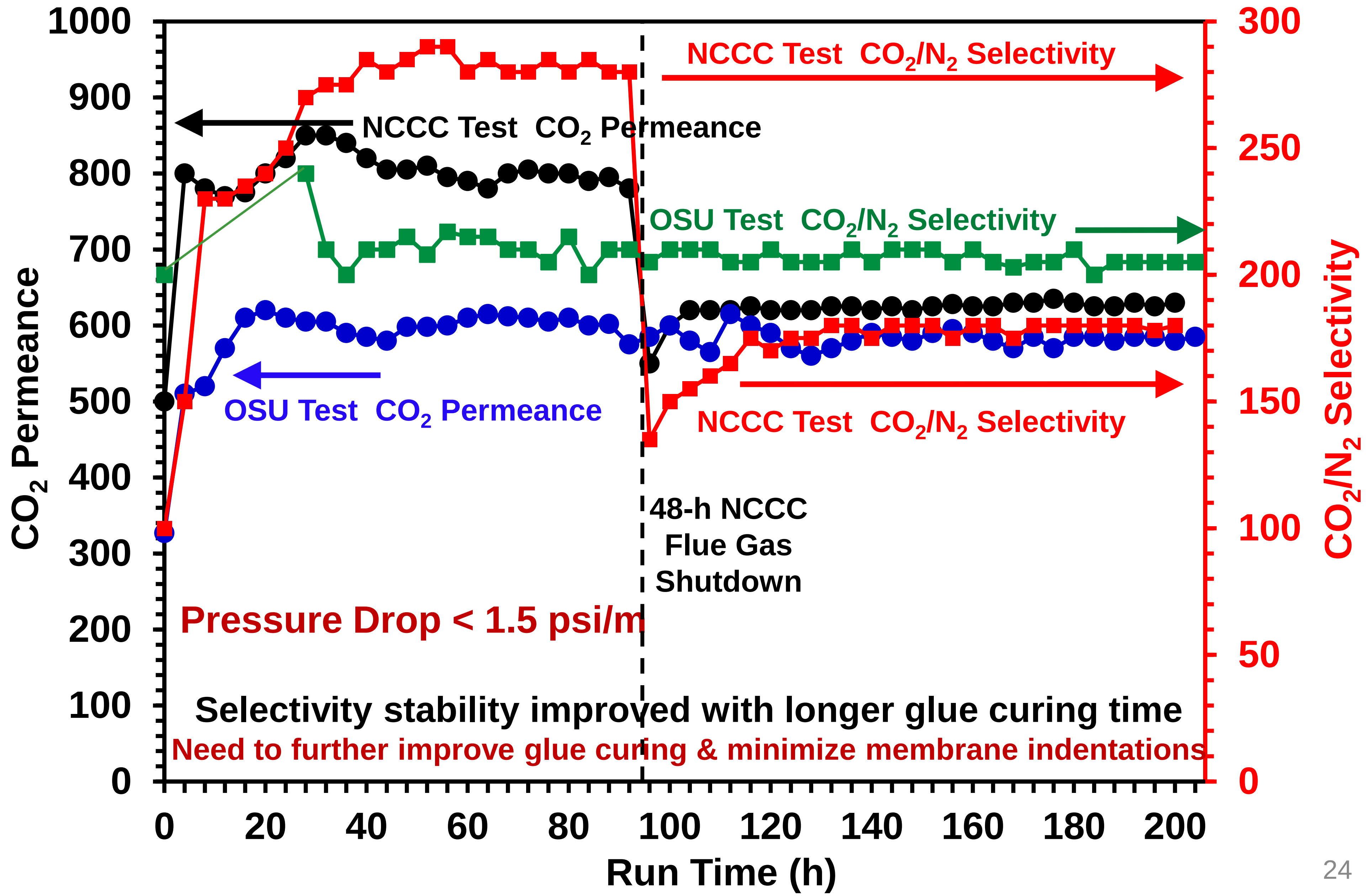
Polymer/Zeolite Composite Membranes Containing Amine Cover Layer: Simulated Flue Gas at 57°C



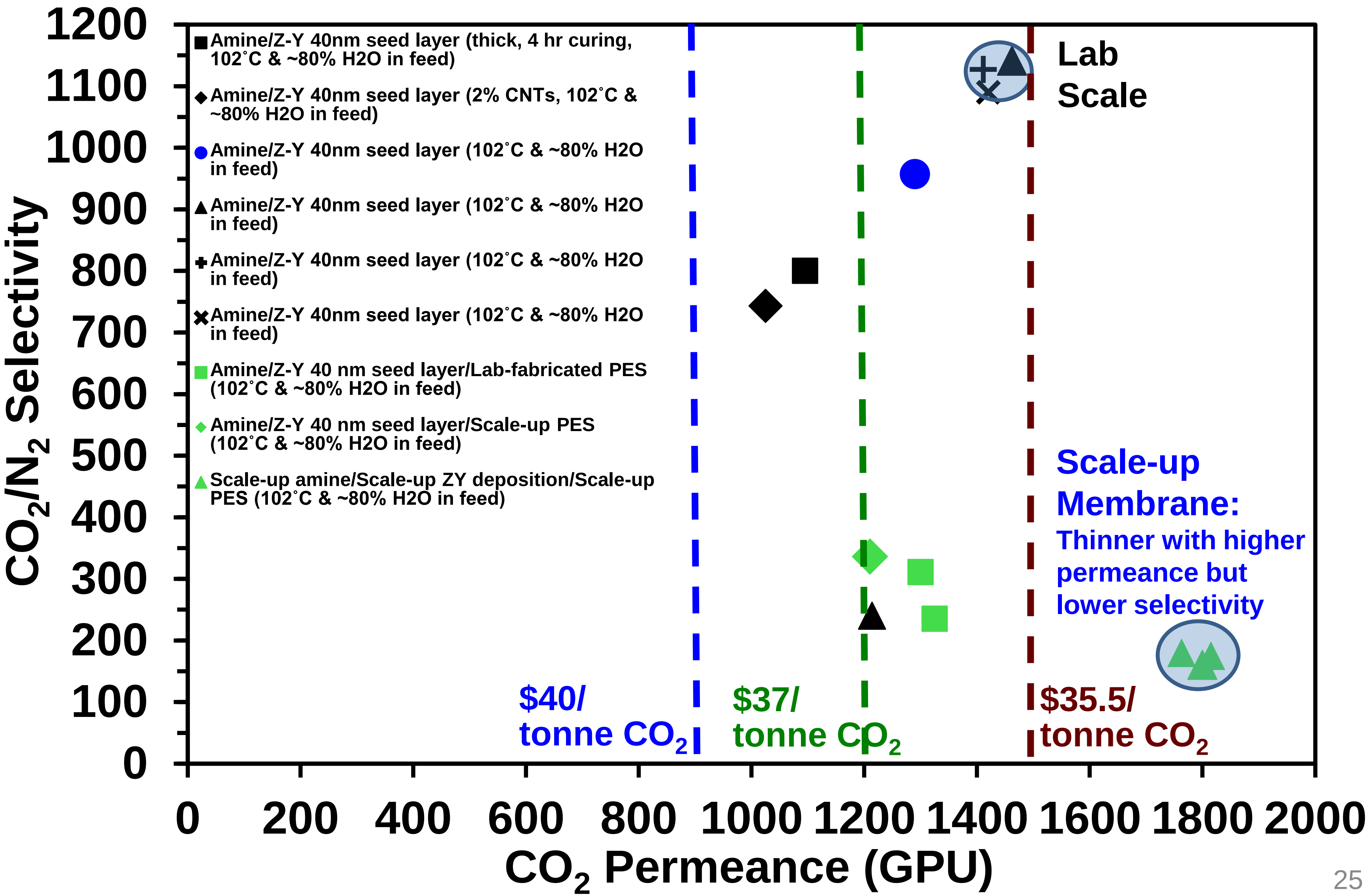
Module Tested at NCCC Behaved Similarly to That in OSU Lab



Module with Longer Glue Curing Time being Tested at NCCC

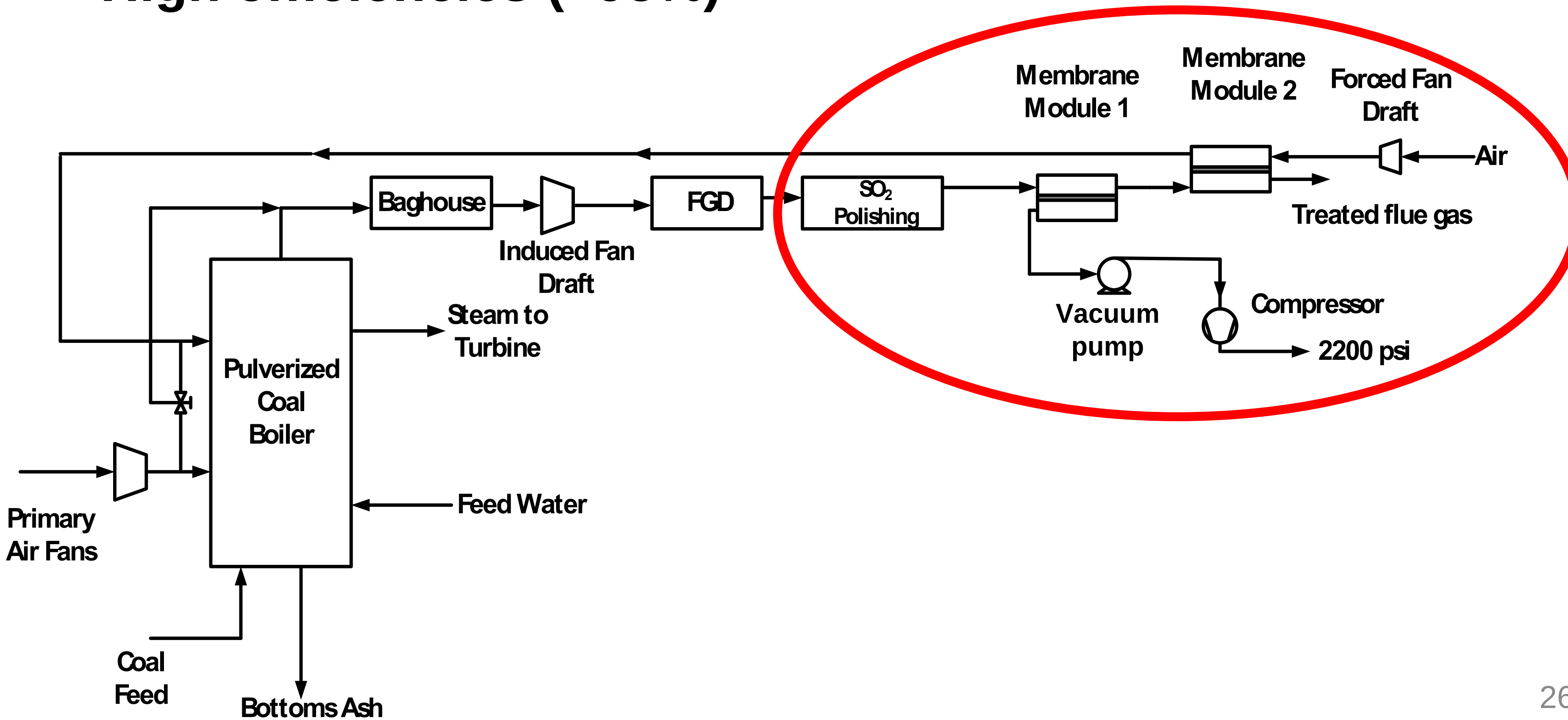


Polymer/Zeolite Composite Membranes Containing Amine Cover Layer: Simulated Flue Gas at 102°C



Approach 1: SO_2 Membrane Mitigation

- **Absorption into 20 wt% NaOH Solution**
  - Polishing step based on NETL baseline document
    - Estimated to be about \$4.3/tonne CO_2 (6.5% COE increase)
  - Non-plugging, low-differential-pressure, spray baffle scrubber
  - High efficiencies (>95%)



Techno-Economic Analysis (applicable to Approaches 1 and 2)

Performed by Gradient Technology

- Preliminary Techno-Economic Analysis (TEA) Based on 2007$ in BP2 for Scale-up Flat-Sheet Membrane Results
  - 870 GPU and 218 Selectivity at 57°C
    - $40.4/tonne CO_2 – Nearly meet DOE target of $40/tonne CO_2
    - 57.2% Increase in cost of electricity (COE)
- NETL Has Reviewed and Provided Invaluable Feedback
- Final TEA Including NETL Feedback under Development
  - Including conversion to 2011$

Plans for Future Testing/Development

- **Complete Testing at NCCC for 200 Hours**
- **Further Improve Glue Curing and Minimize Membrane Indentations for Performance Improvement**
- **Continue Module Fabrication and Testing with Simulated Flue Gas**
- **Update and Finalize Techno-Economic Analysis – Gradient Technology**
- **EH&S Evaluation being Developed by Gradient Technology with AEP/OSU Input**

Acknowledgments

José Figueroa
Great efforts and strong inputs

Tony Wu and Bob Lambrecht, NCCC
Excellent analytical and mechanical supports

DOE/NETL
Financial support