Novel Inorganic/Polymer Composite Membranes for CO_2 Capture

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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, Director of R&D

Gradient Technology

2014 NETL CO_2 Capture Technology Meeting
Pittsburgh, PA, July 29 – August 1, 2014

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 flue gas**
    - **Update techno-economic analysis**
    - **EH&S evaluation report will be 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

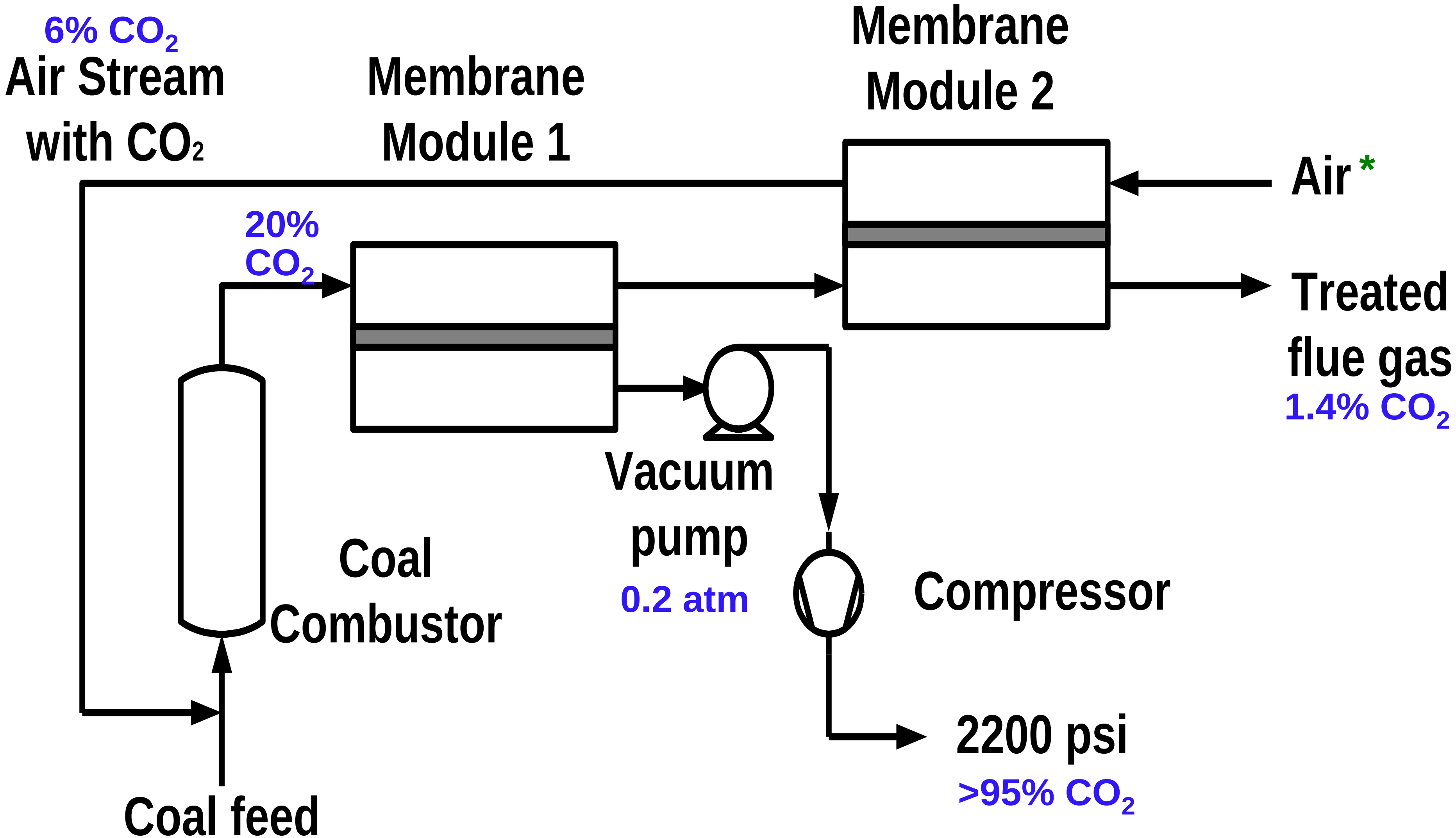
- **Total Budget: 10/01/2011 – 08/31/2015**
  DOE: $3,000K; OSU: $679K; ODOD: $500K

  - **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

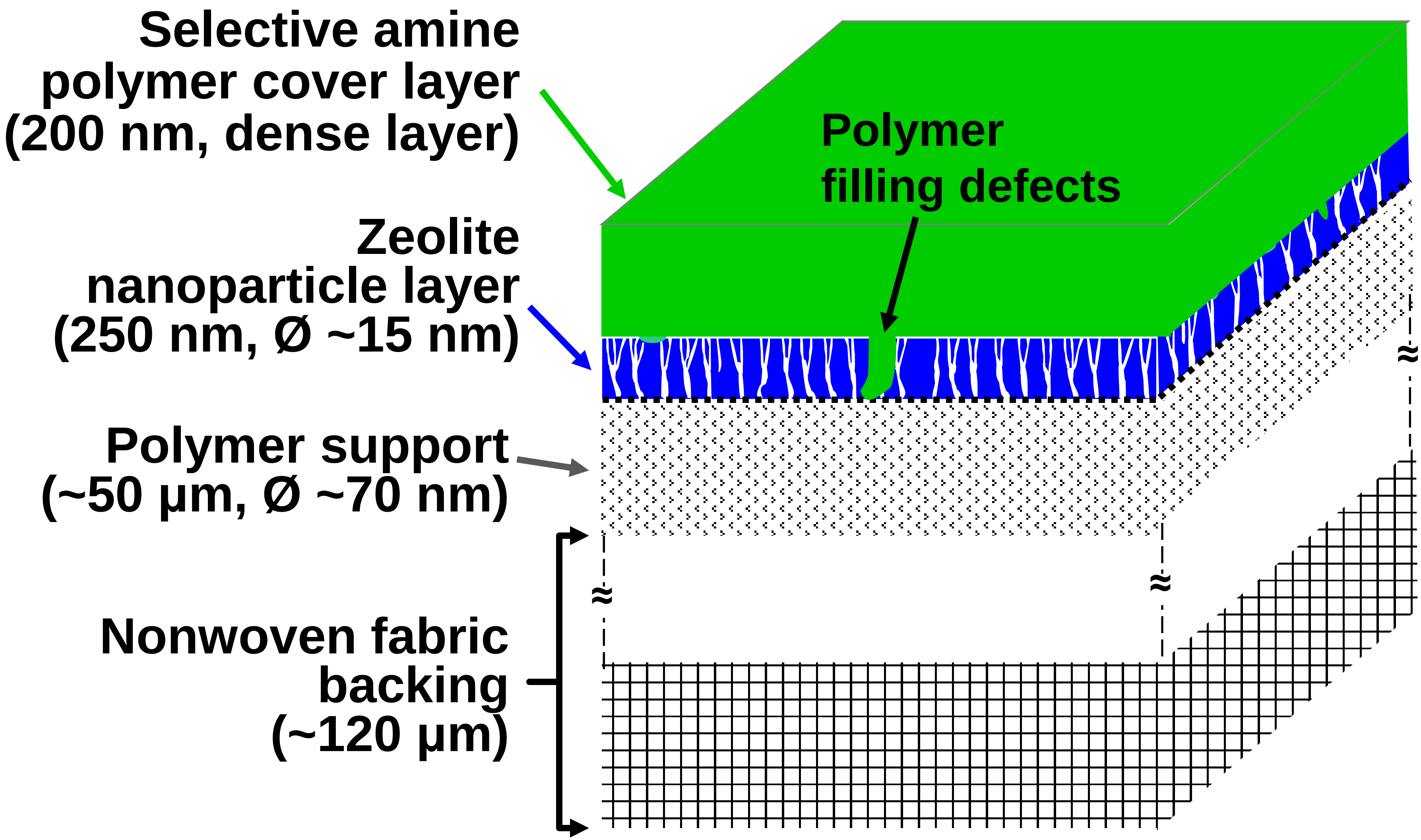
Process Proposed for CO_2 Capture from Flue Gas in Coal-Fired Power Plants



*Air Sweep first used by MTR

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**

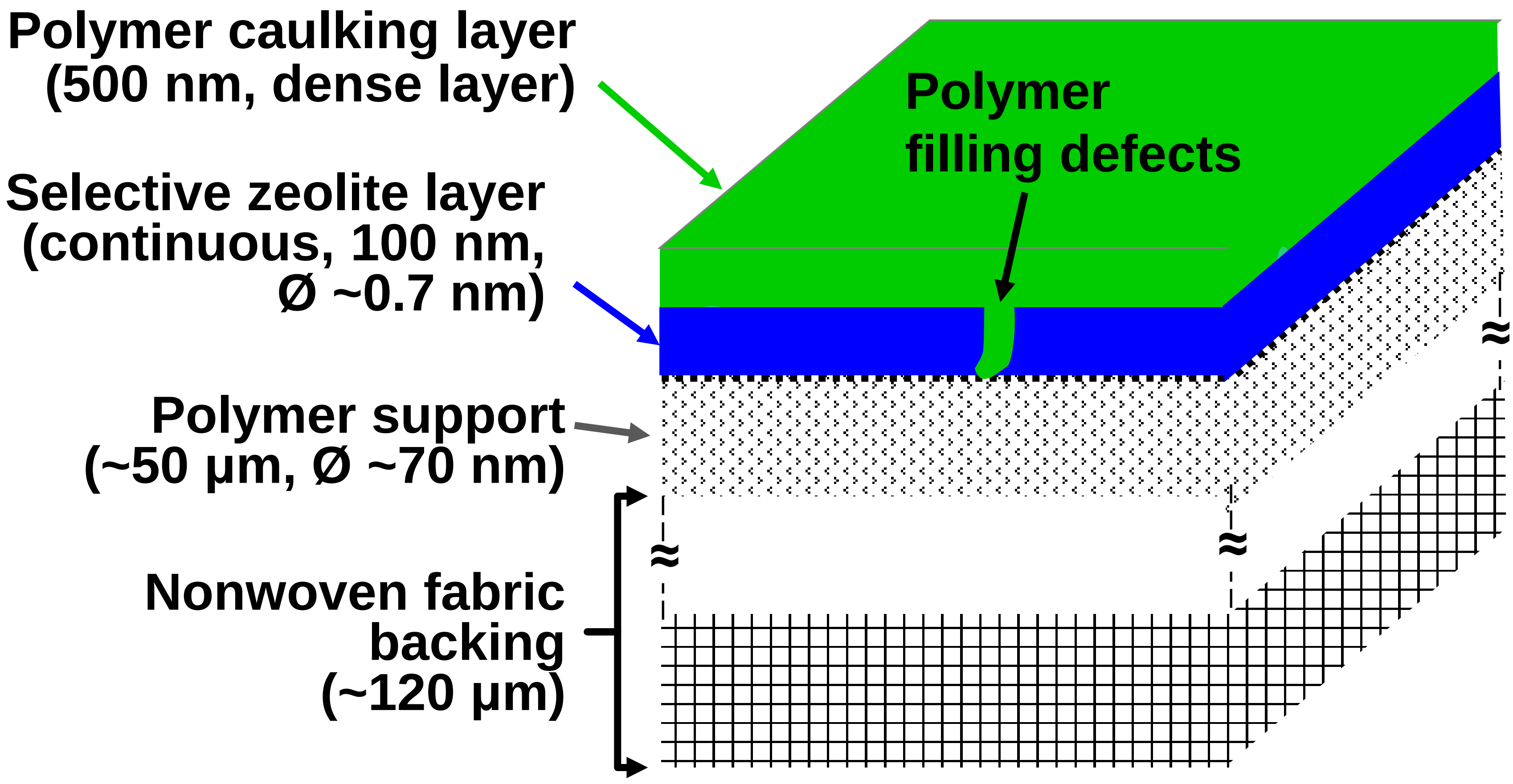
$$CO_2 + R\text{-}NH_2 + H_2O \rightleftharpoons R\text{-}NH_3^+ + HCO_3^-$$

  - **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**

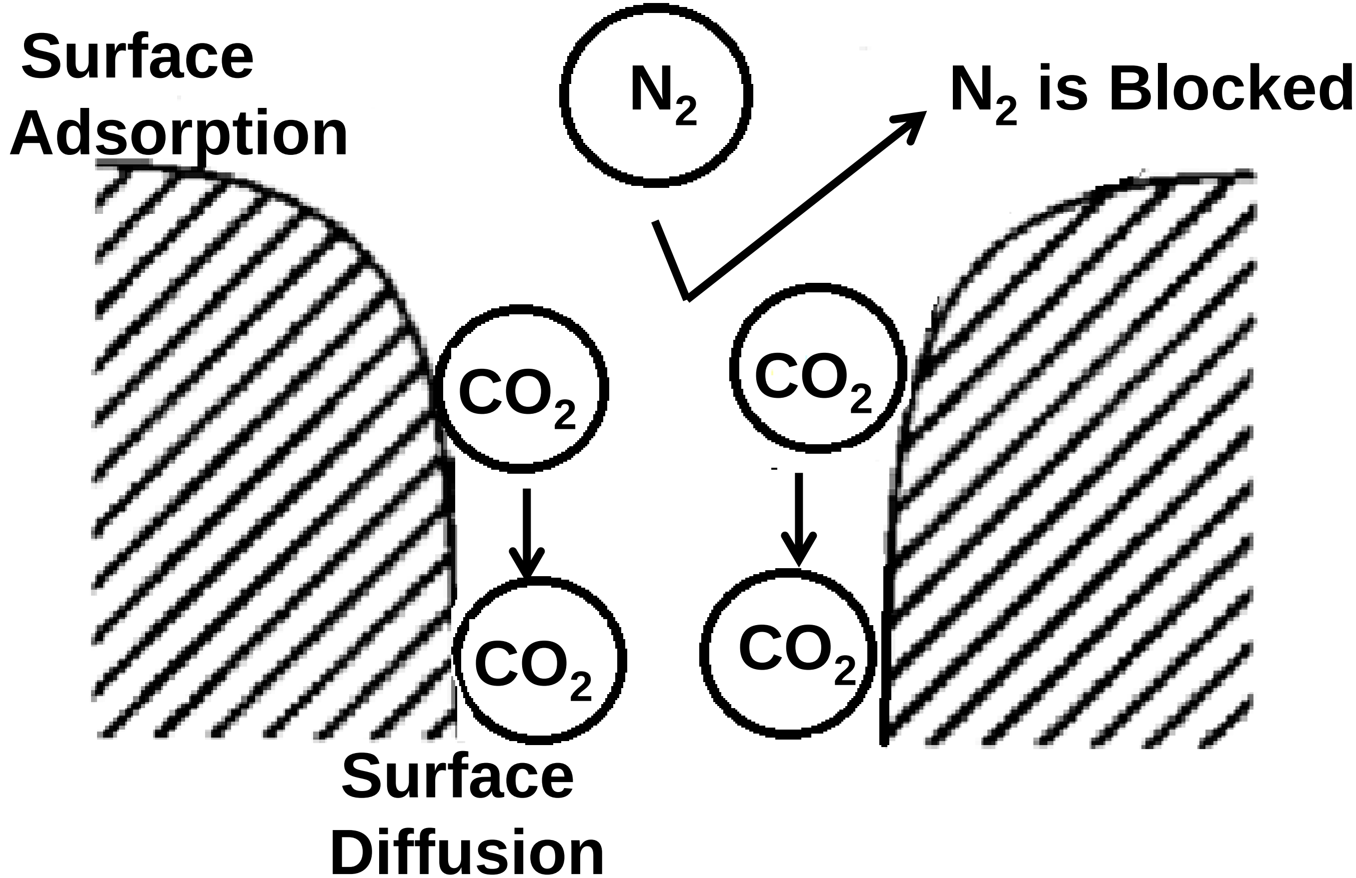
Approach 2: Polymer Caulking Layer / Selective Zeolite Membrane / Polymer Support

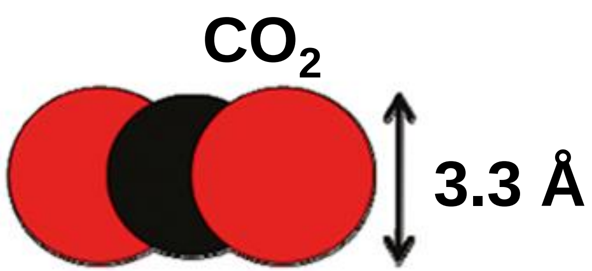
High Inorganic Performance and Low-Cost Polymer Processing Benefits

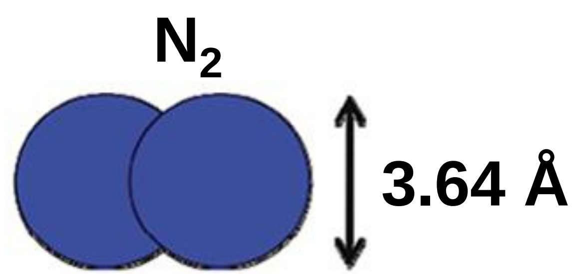


Need rapid growth process for zeolite membrane to be cost competitive

Approach 2: Transport Mechanism through Zeolite







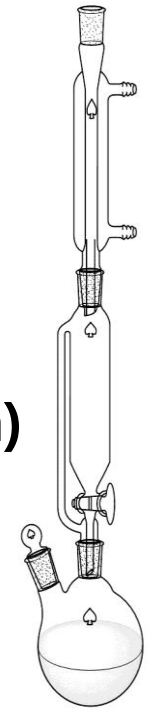
$Q_{CO_2} = -13.67 \times 10^{-40}$ C m^2

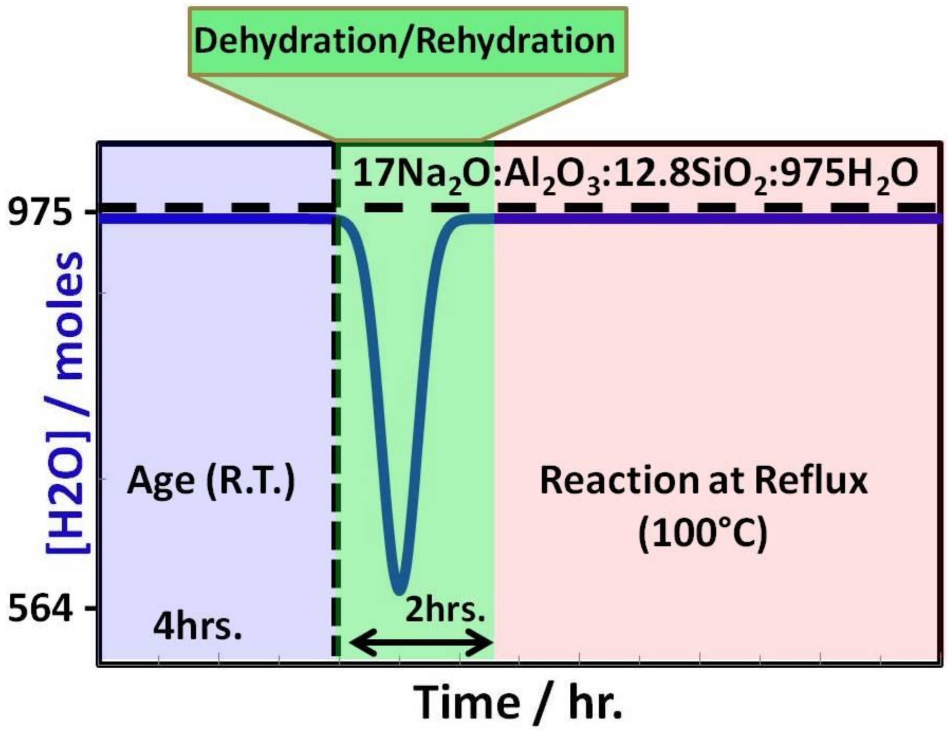
$Q_{N_2} = -4.67 \times 10^{-40}$ C m^2

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

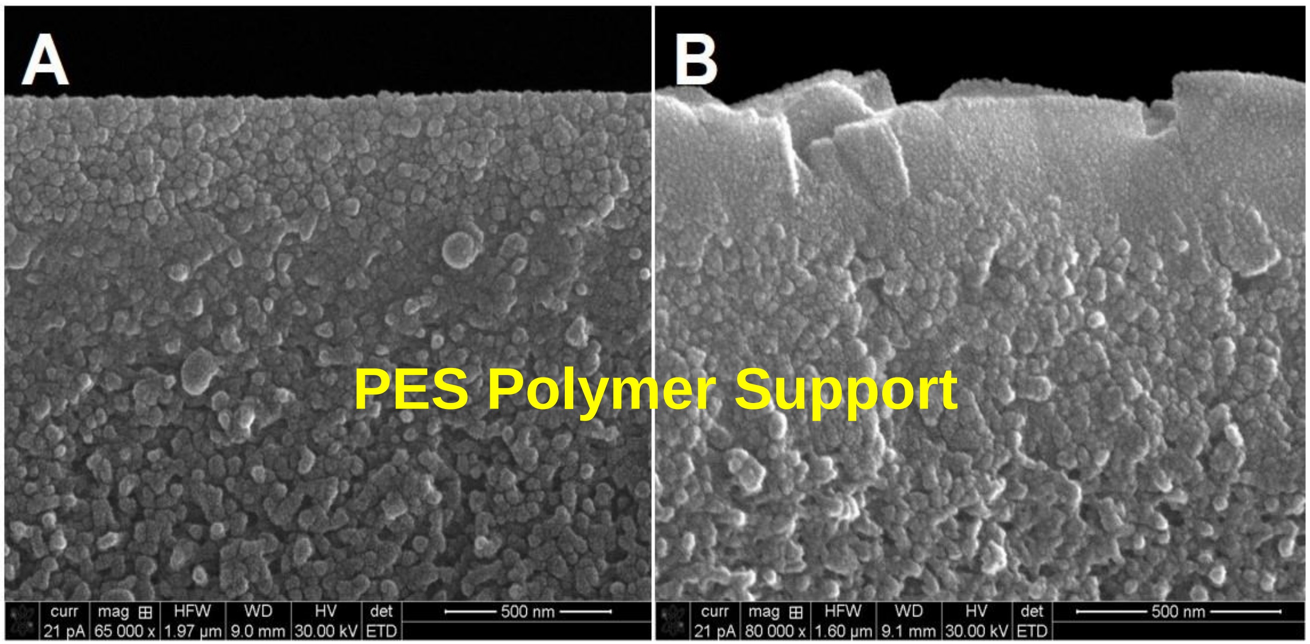
17 Na_2O:Al_2O_3 : 12.8 SiO_2 : 564 H_2O

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

Rapid Synthetic Approach Adapted to Zeolite Membrane

Seed crystals

Zeolite membrane



- **Membrane synthesis process takes 1 hour**
- **Transport studies in progress**

BP1 Accomplishments

- **Approach 1: Zeolite/Amine Polymer Composite Membranes Synthesized and Showed:**
  - 1100 GPU with ~800 CO_2/N_2 selectivity at 102^{o}C
  - 690 GPU with 123 CO_2/N_2 selectivity at 57^{o}C
  - Zeolite/polymer element hand rolled successfully (6” x 6” membrane leaf)

- **Approach 2: Significant Membrane Synthesis Improvements**
  - Discovery of rapid zeolite particle synthesis (< 1 hr vs. 8 hrs)

- **Preliminary Techno-economic Calculations**
  - Techno-economic model developed
  - 690 GPU with ~123 selectivity at 57^{o}C (based on 2007$)
    - ~$43/tonne CO_2

BP2 Accomplishments

- **Approach 1: Zeolite/Amine Polymer Composite Membranes Prepared in Lab Showed:**
  - **1100 GPU with ~140 CO_2/N_2 selectivity at 57^oC**
  - **1460 GPU with >1000 CO_2/N_2 selectivity at 102^oC**
  - **Patent application filed**
- **Approach 1: Composite Membrane Scaled up to Prototype Size**
  - **Membrane scaled up to 14” wide using continuous membrane rolling machine**
  - **844 GPU with ~140 CO_2/N_2 selectivity obtained at 57^oC**
  - **Developed affordable nanoporous polymer support (PES)**
  - **1.8” (1.5” OD central tube) by 14” long spiral-wound membrane elements fabricated using rolling machine**

BP2 Accomplishments (continued)

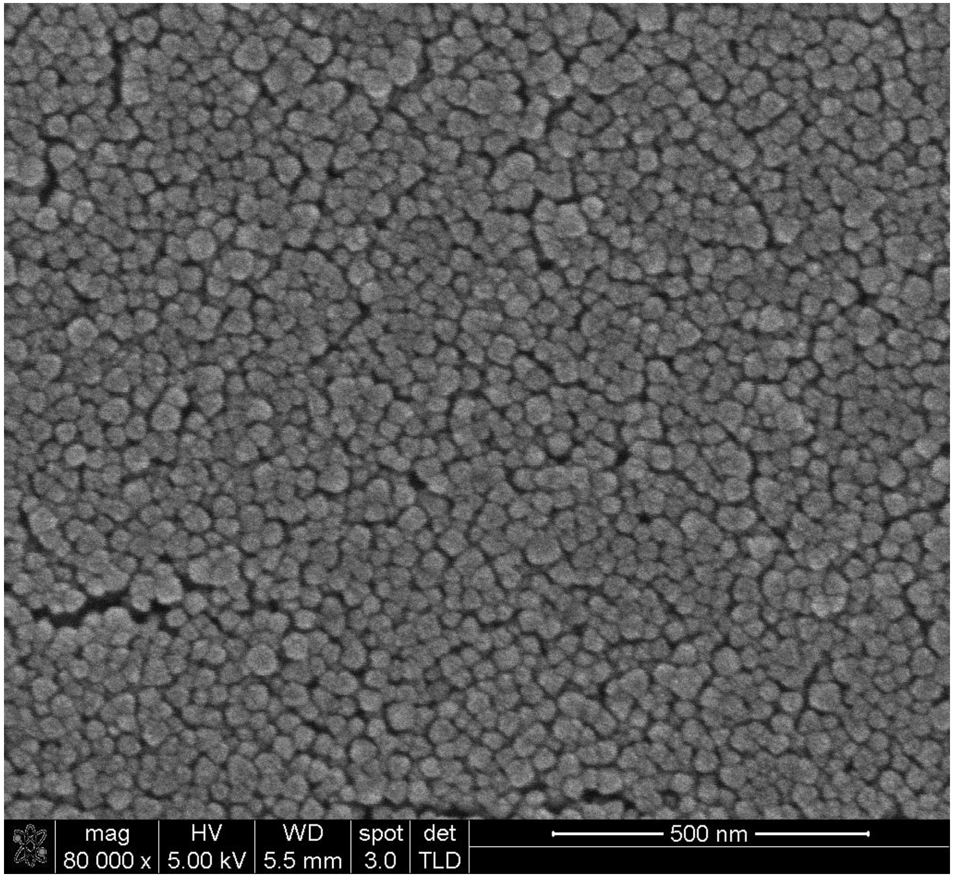
- **Preliminary Techno-economic Calculations showed**
  - **1100 GPU with ~140 selectivity at 57ºC (based on 2007$)**
    - **\$37.5/tonne CO_2 – Exceed DOE target of \$40/tonne CO_2**
    - **52.2% COE increase**

- **Approach 2: Rapid Zeolite Membrane Growth (1 hour)**
  - **Patent application filed**
  - **Published in *Langmuir*, 2014, *30,* 6929-6937**

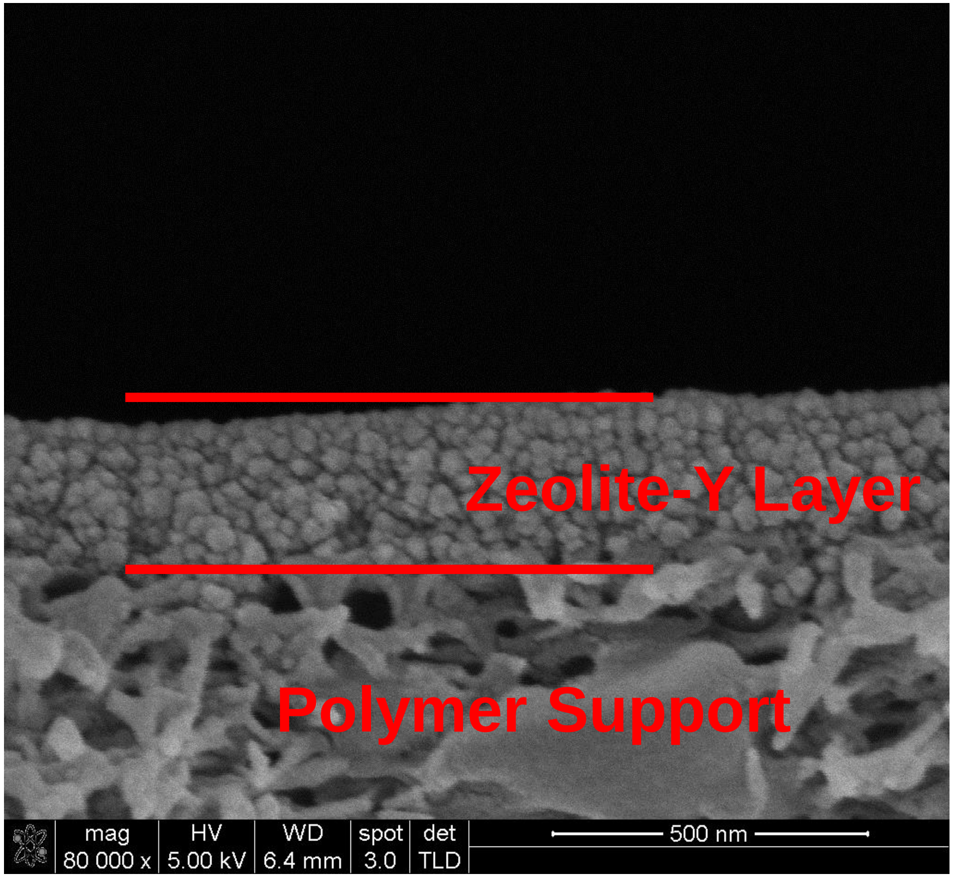
- **Effects of SO_2 and CO_2/SO_2 Mixture on Amine Carriers being Studied by in-situ FTIR**
  - **SO_2 permeated with CO_2**
  - **Membrane performed well**

Approach 1: Zeolite Nanoparticles Deposited on Polymer Support Successfully

Top View

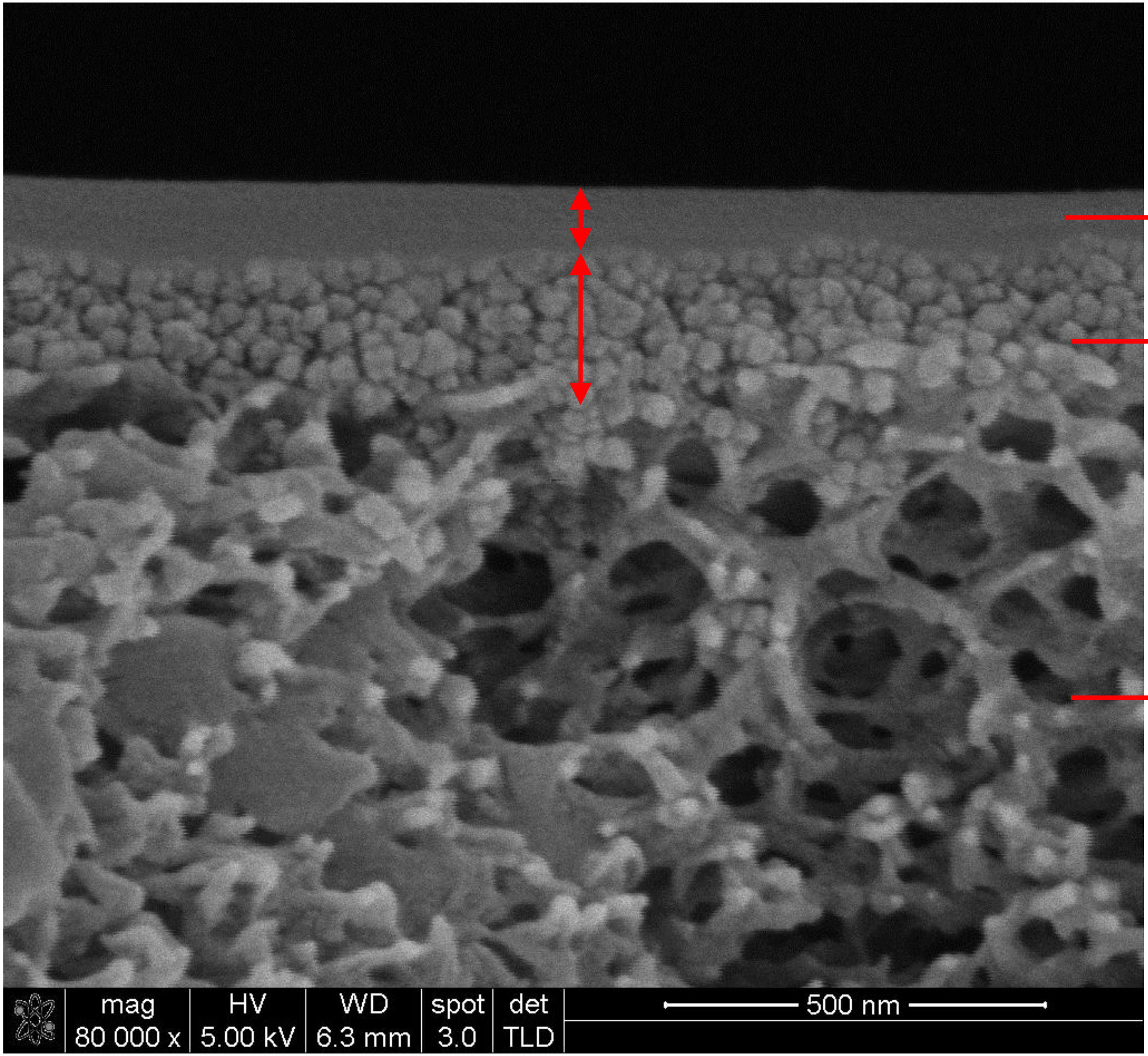


Cross-section



- **High quality deposition with good repeatability**

Amine/Zeolite Seed Layer/Polymer Support



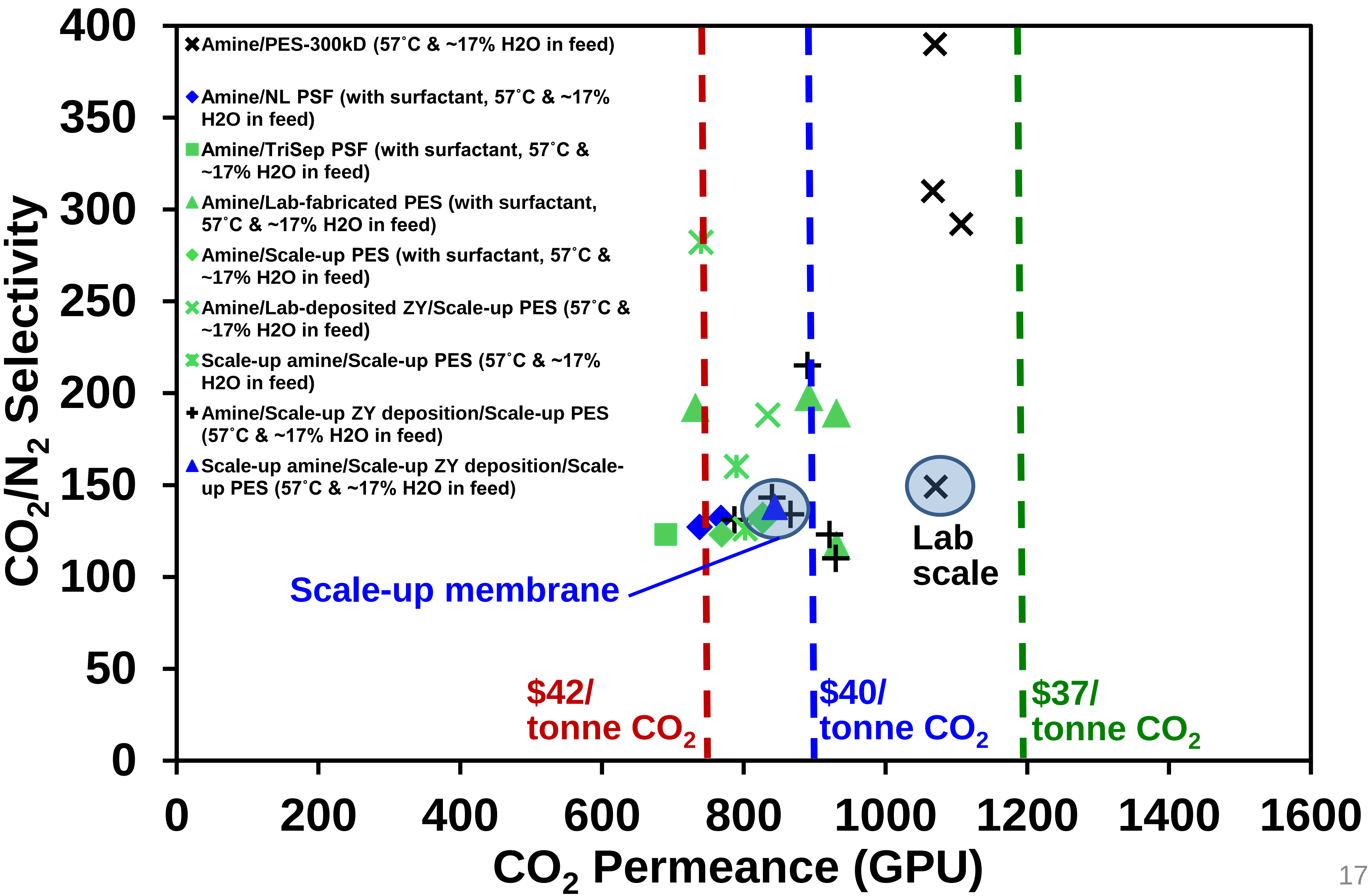
Amine cover layer ~ 185 nm

Zeolite-Y 40 nm seed layer ~ 230 nm

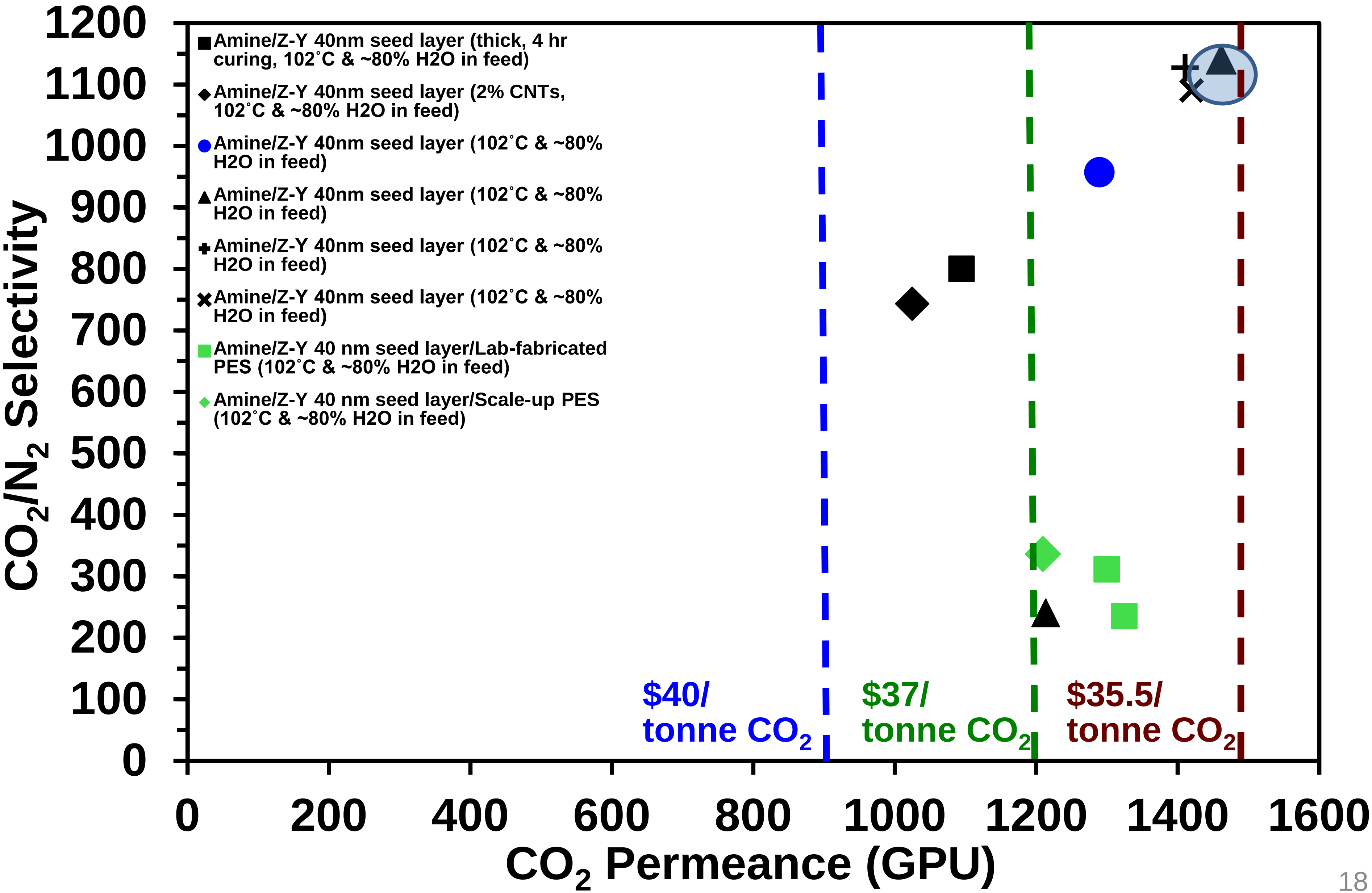
PES support

844 GPU
138 CO_2/N_2 selectivity

Approach 1: Zeolite/Polymer Composite Membranes Containing Amine Cover Layer at 57°C



Approach 1: Lab-size Zeolite/Polymer Composite Membranes Containing Amine Cover Layer at 102°C

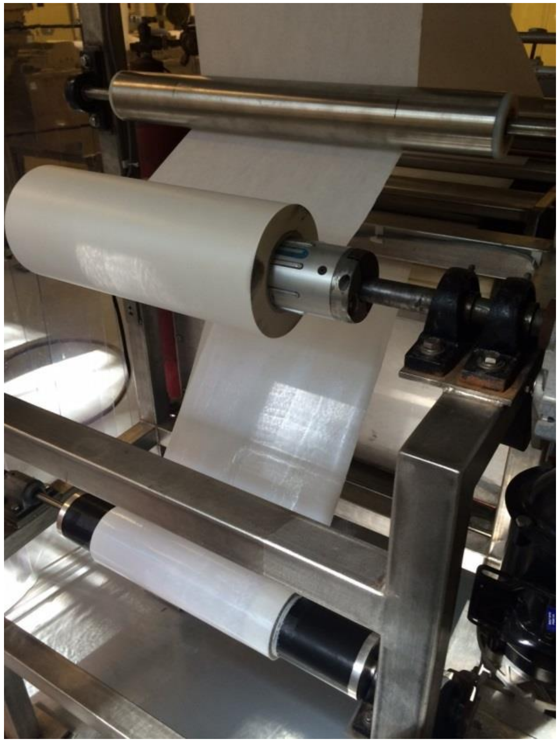


Membrane Scale-up: Usable for Approaches 1 and 2

Continuous Membrane Fabrication Machine at OSU

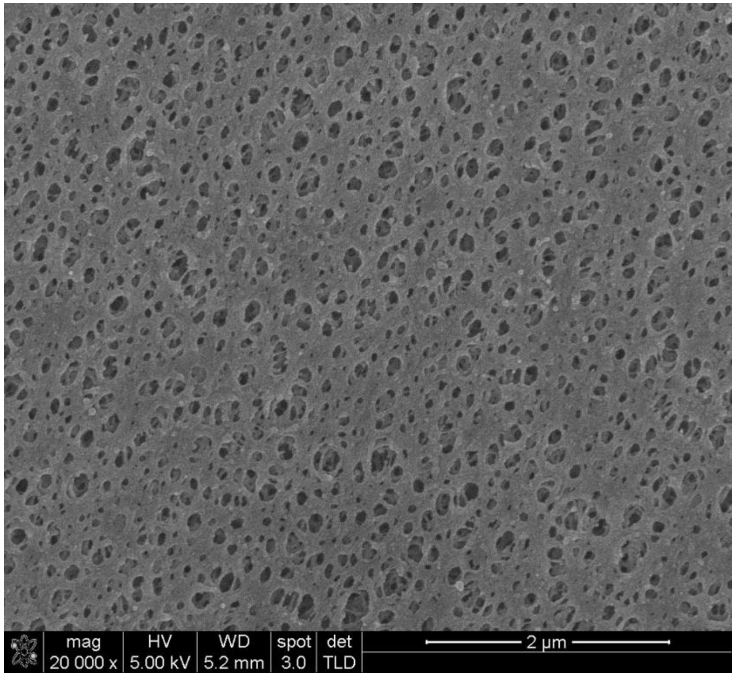
Successful Continuous Fabrication of Affordable PES Support (applicable to Approaches 1 and 2)

Casting Machine



14-inch PES Support

SEM – Top View

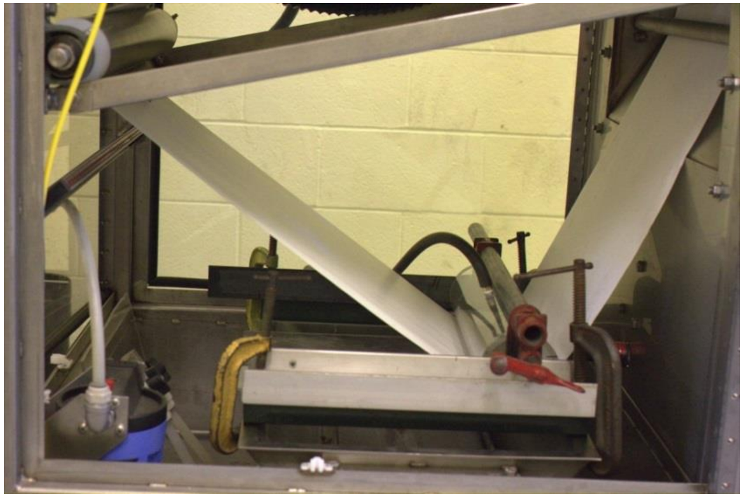


- **Manufacturer could not supply PES needed for scale-up**
- **PES synthesized/developed at OSU to resolve supply issue**
- **Technology transfer to TriSep**

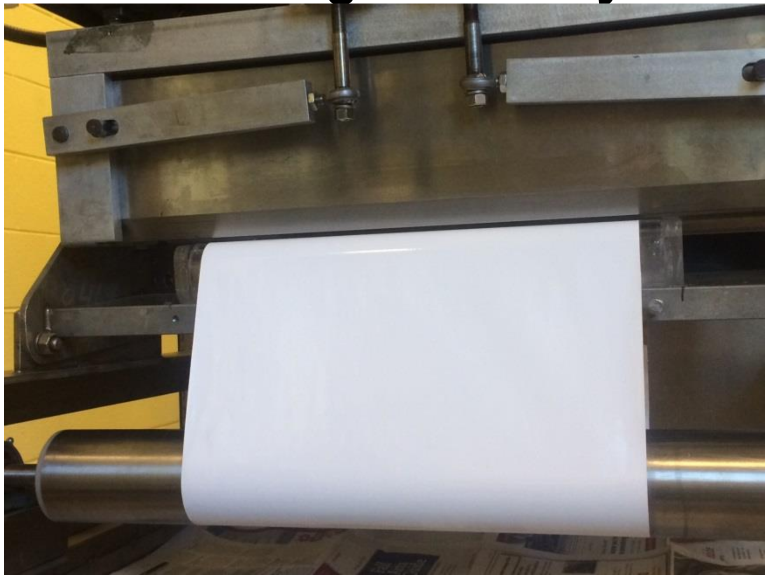
Approach 1: Scale-up Zeolite-Y Deposition and Amine Coating

14-inch PES Support

14" ZY Deposition on PES Support

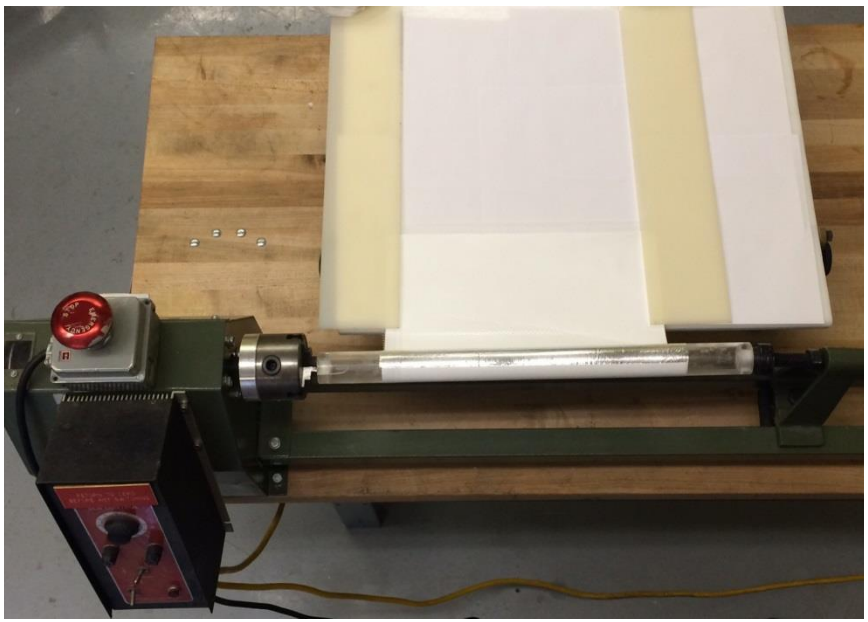


14" Amine Coating on ZY Layer on PES

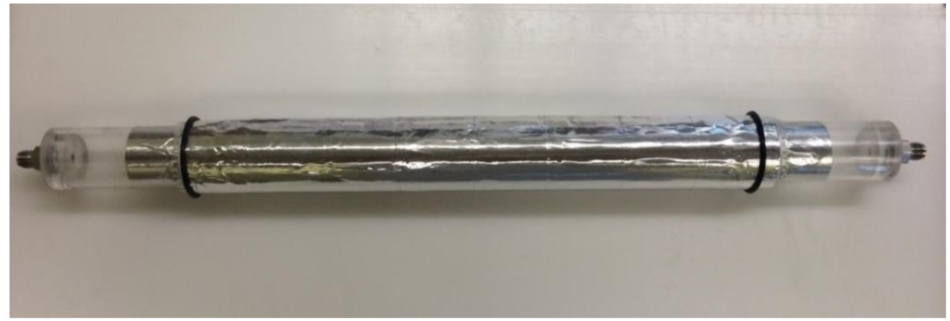


Approach 1: Membrane Element Fabrication

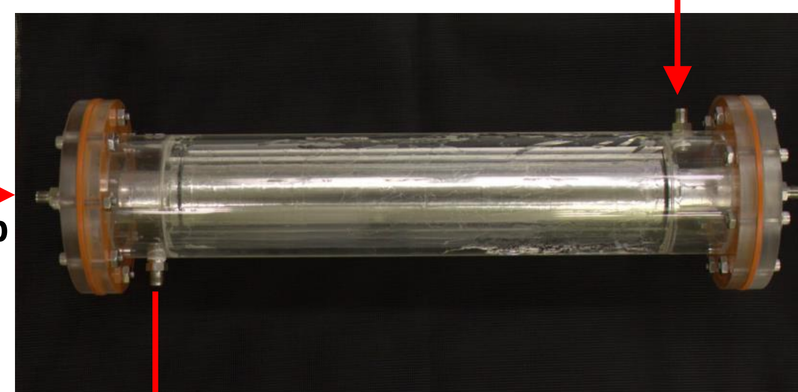
Element Rolling Machine



Spiral-Wound Membrane Element



Membrane Module



Techno-economic Calculations (applicable to Approaches 1 and 2)

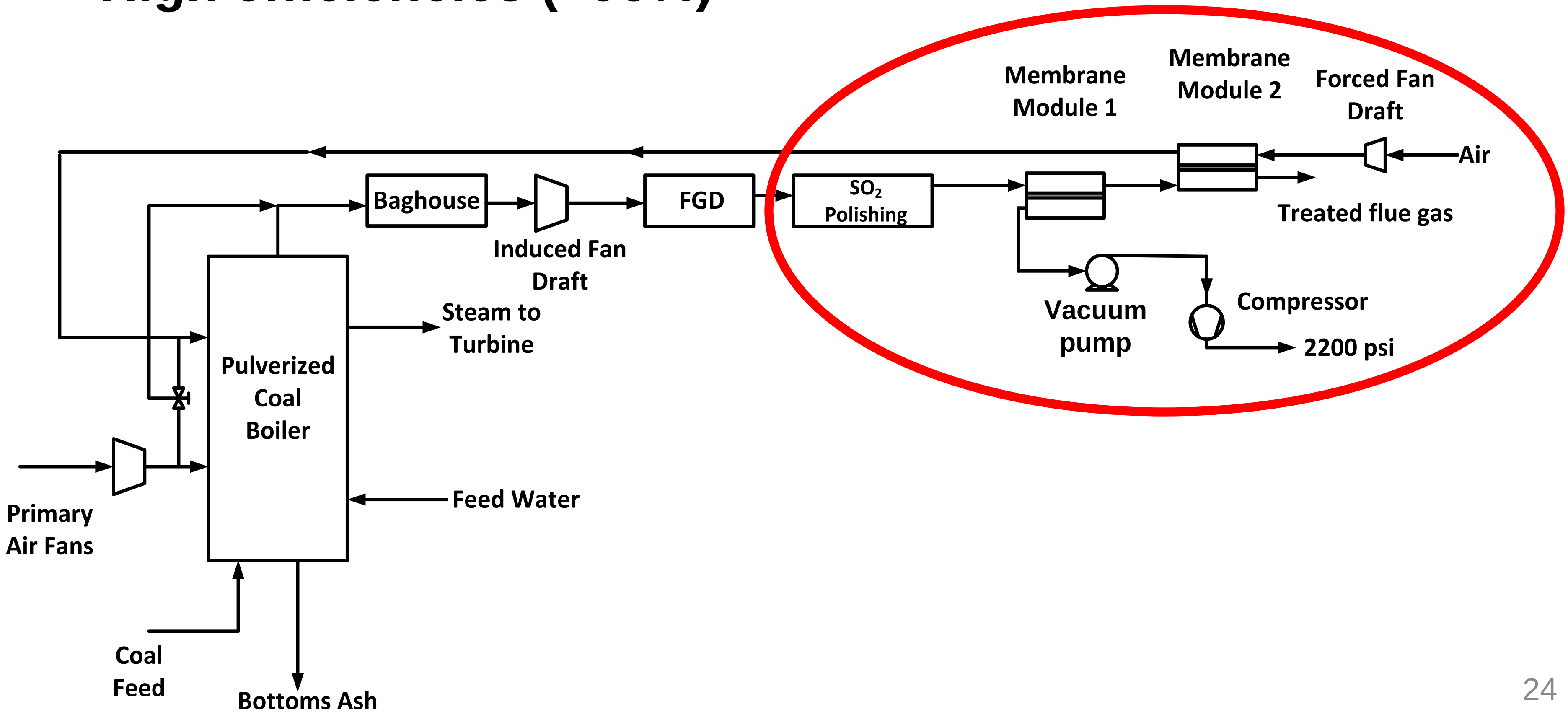
Performed by Gradient Technology (based on 2007$)

- Scaled-up Prototype Results: 844 GPU & 138 Selectivity at 57°C
  - $40.7/tonne CO_2 – Nearly meet DOE target of $40/tonne CO_2
  - 57.7% Increase in cost of electricity (COE)
- Lab Results: 1100 GPU & 140 Selectivity at 57°C
  - $37.5/tonne CO_2 – Exceed DOE target of $40/tonne CO_2
  - 52.2% Increase in COE
- Lab Results: 1460 GPU & >1000 Selectivity at 102°C
  - $35.5/tonne CO_2 – Exceed DOE target of $40/tonne CO_2
  - 48.7% Increase in COE

- If:
  - CO_2 Permeance = 3000 GPU & 140 CO_2/N_2 Selectivity
    - $30.9/tonne CO_2 – Exceed DOE target of $40/tonne CO_2
    - 44% COE increase
- Significantly Lower Cost than Amine Scrubbing

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%)



Plans for Future Testing/Development

- **BP3**
  - 3 prototype modules (each 2 m^2) for testing with simulated flue gas
  - Update and finalize techno-economic analysis
  - EH&S evaluation with Gradient Technology and AEP

- **BP3 Detailed Tasks**

BP3 Detailed Tasks

Task Name	Start	Finish
Task 17: Project Management and Planning	9/1/2014	8/31/2015
Task 18: Further Improved Membrane Synthesis	9/1/2014	8/31/2015
Approach 2: Optimization of rapid zeolite membrane growth	9/1/2014	8/31/2015
Task 19: Membrane Characterization - *SO_2 Mitigation*	10/1/2014	8/31/2015
Task 20: Optimized Prototype Membrane Fabrication	10/1/2014	8/31/2015
Task 21: Optimal Prototype Membrane Characterization	11/1/2014	8/31/2015
Task 22: Prototype Module Fabrication	11/1/2014	5/31/2015
Task 23: Membrane Module Testing	9/1/2014	8/31/2015
Task 24: Use and Refining of the System and Cost Analysis	9/1/2014	8/31/2015
Task 25: Quarterly Progress Reports	11/1/2014	10/1/2015
Task 26: Final Technical Report	6/1/2015	12/1/2015