New Amine-Containing Membranes for CO_2 Capture

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Outline

- CO_2 Capture from Flue Gas in Coal- and/or Natural Gas-fired Power Plants

- CO_2 Capture from <1% CO_2 Concentration Sources, e.g.,
  - Residual flue gas after the primary CO_2 capture system
  - Coal-mine gas streams

Introduction

- **Coal-fired power plants**
  - **40% of global CO_2 emission**
  - **Remain as major energy supply**

- **Membranes for CO_2 capture from flue gas**
  - **System compactness**
  - **Energy efficiency**
  - **Operational simplicity**
  - **Kinetic ability to overcome thermodynamic solubility limitation**

Challenges and Goals

- **High CO_2 Permeance**

$$P_{CO_2} = \frac{J_{CO_2}}{p_{CO_2,f} - p_{CO_2,p}}$$

  - **Reduce Membrane Area**

Thin Membrane Thickness Needed

- **High CO_2/N_2 Selectivity**

$$\alpha_{CO_2/N_2} = \frac{P_{CO_2}}{P_{N_2}}$$

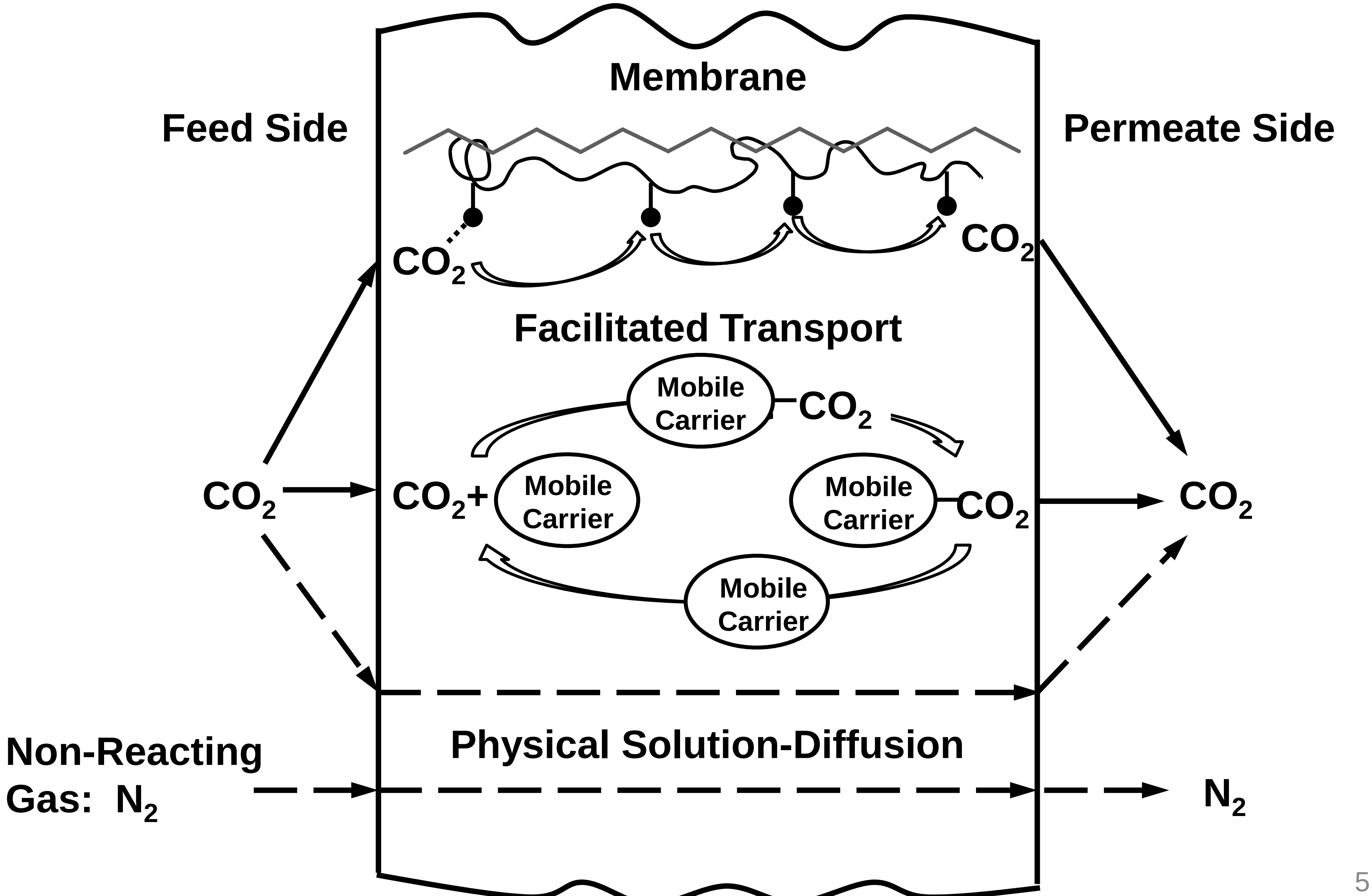
  - **Provide High CO_2 Purity**

High Selective Membrane Material Needed

>700 GPU CO_2 permeance and >140 CO_2/N_2 selectivity at 57°C

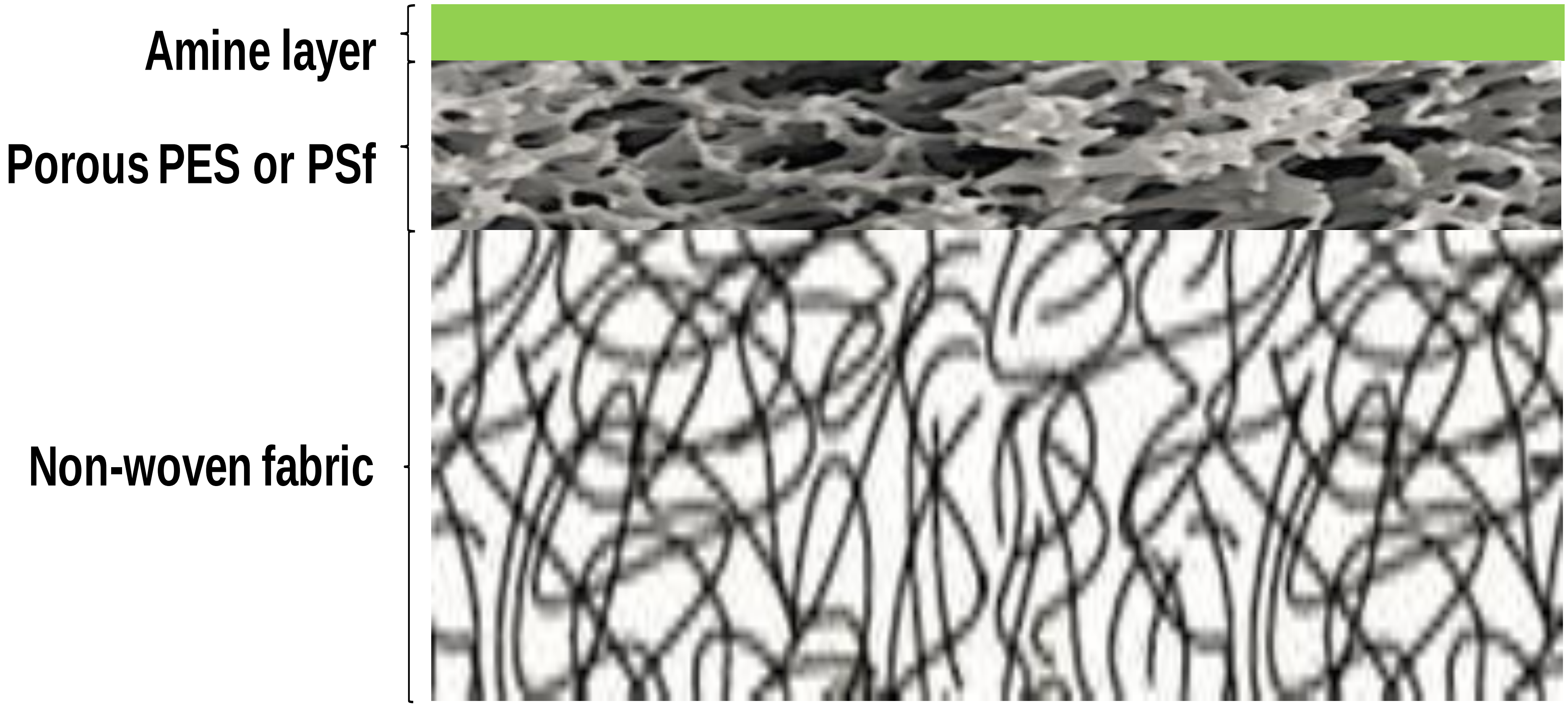
To meet the DOE target < \$40/tonne CO_2 (2007 \$)

Amine Polymer Layer Contains Mobile and Fixed Carriers: Facilitated Transport



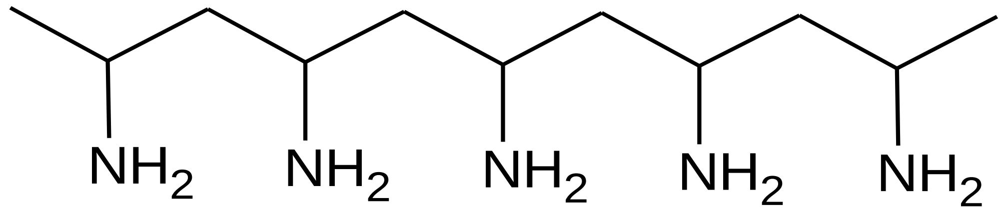
Amine-Containing Polymer Membrane Structure

Simplicity of Membrane for Low Cost



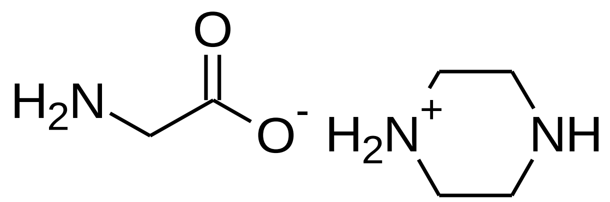
Amine Layer Composition

Fixed-site carrier:



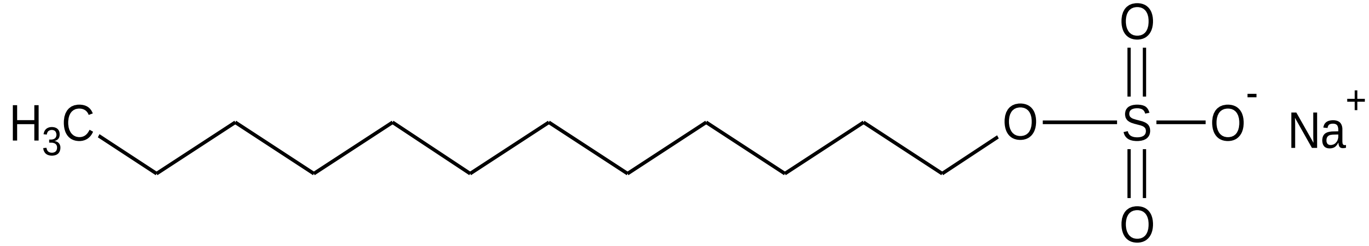
Polyvinylamine (PVAm)

Mobile carrier:



Piperazine glycinate (PG)

Surfactant:



Sodium dodecyl sulfate (SDS)

High-Molecular-Weight PVAm Synthesis

Polymer	Monomer Conc. (wt.%)	Initiator/Monomer Weight Ratio	3 wt.% Polymer Solution viscosity (cp)	Weight Average MW
PVAm (a)	30	0.5/100	486	719,000
PVAm (b)	40	0.14/100	1,400	1,200,000
Lupamin®	N/A	N/A	50	340,000

- **MW measured by Dynamic Light Scattering (DLS)**
- **Lupamin® contains ~66% sodium formate**

High-Molecular-Weight PVAm Synthesized

Viscosity:

3 wt.% commercial PVAm: 50 cp

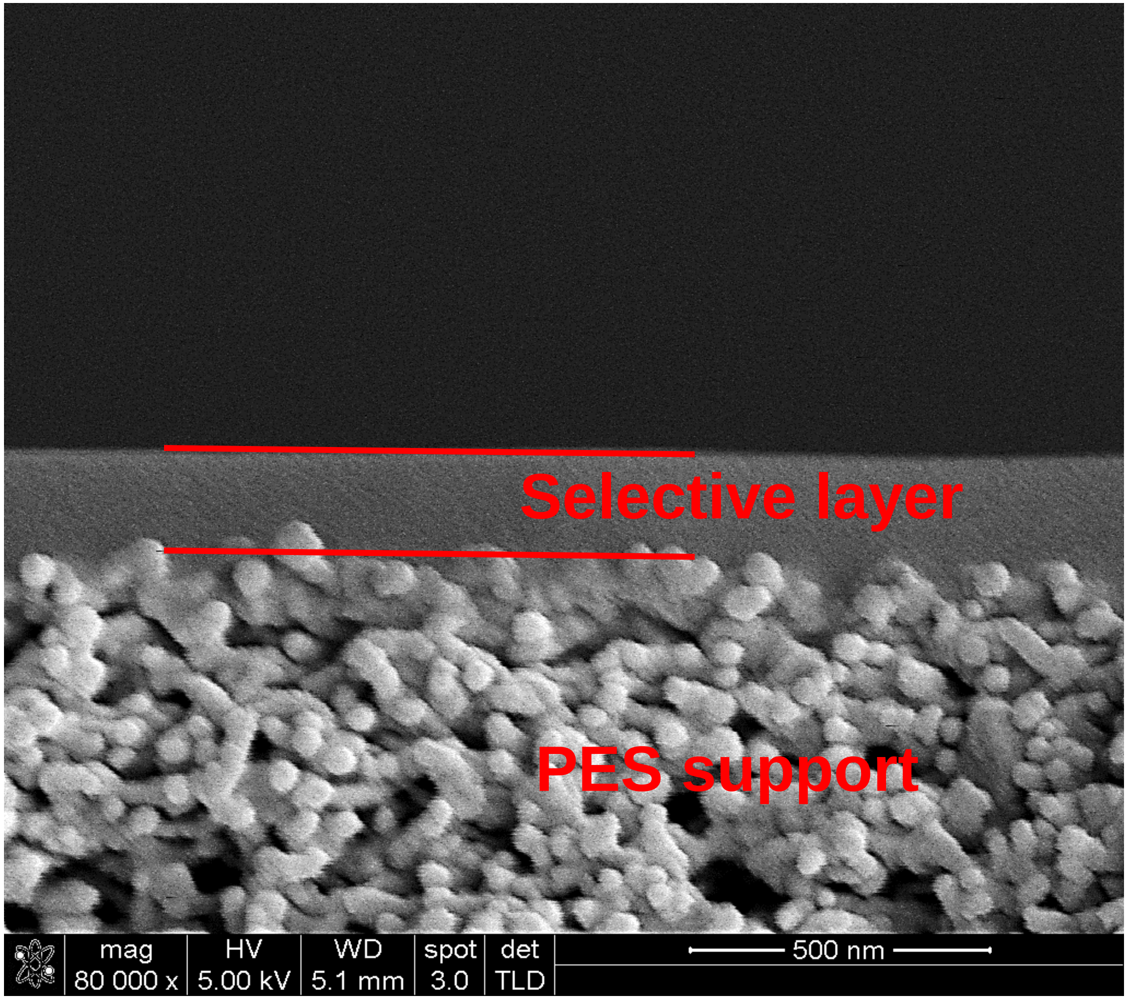
3 wt.% high MW PVAm: 450 – 1950 cp

a) **High viscosity**
   - **Decrease coating solution concentration**
   - **Allow for preparation of thinner membrane**
   - **Improve adhesion to support – less defects**

b) **Low salt amount**
   - **Improve membrane stability**

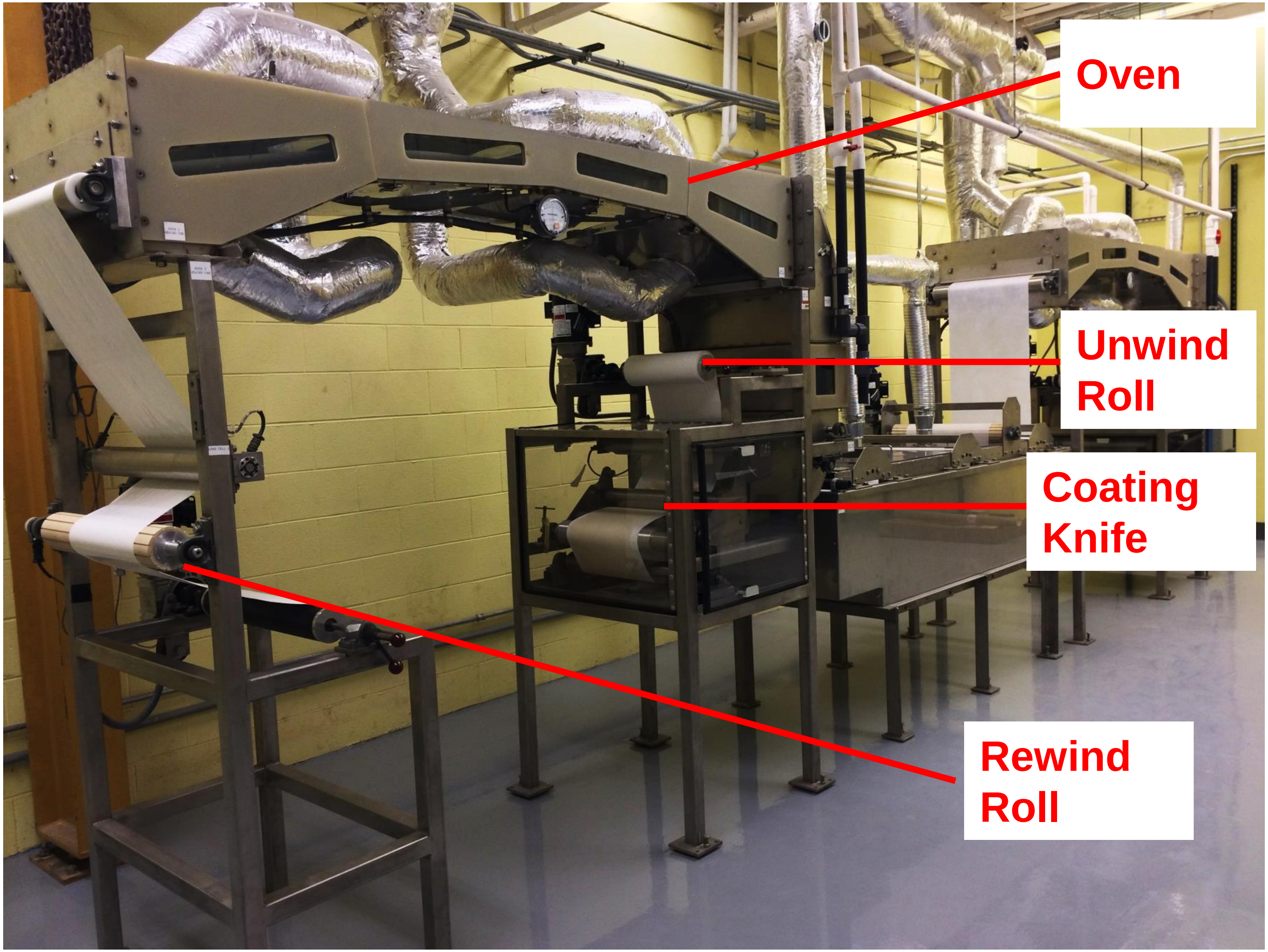
Composite Membrane Synthesized

Selective Amine Polymer Layer on PES Support



Selective layer = 165 nm

Membrane Scale-up: Continuous Roll-to-Roll Fabrication Machine at OSU



Tuning Membrane Thickness

$$l \times \rho_{dry} = 0.5 \times c \times \rho_{sol} \times l_{gap}$$

l: dry membrane thickness (μm)

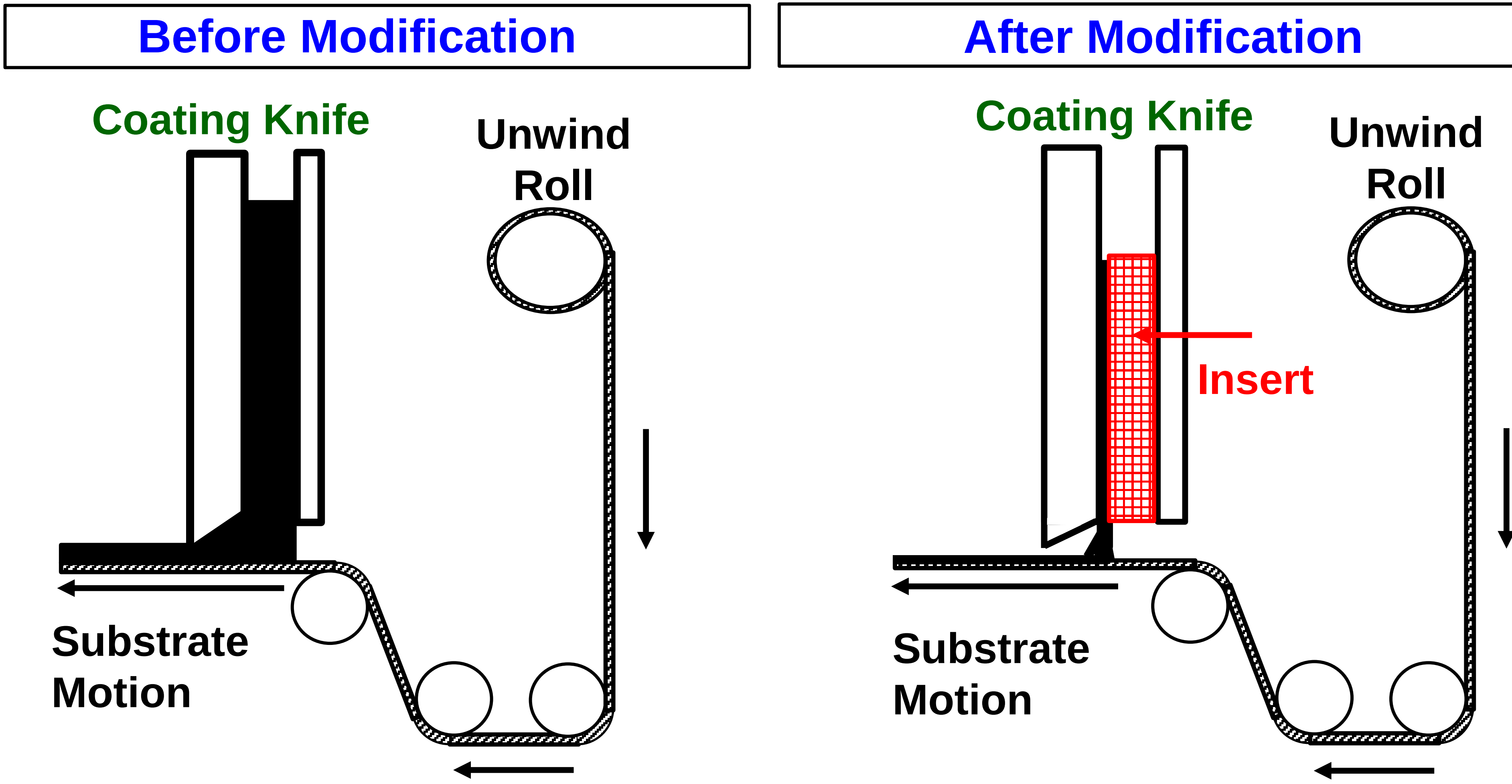
ρ_{dry}: density of dry membrane (g/cm^3)

ρ_{sol}: density of coating solution (g/cm^3)

c: total solid concentration of coating solution (by weight)

l_{gap}: gap setting of coating knife (μm)

Coating Technique Modification: Insert



- A thinner thickness with a higher web speed for a given coating solution supply rate

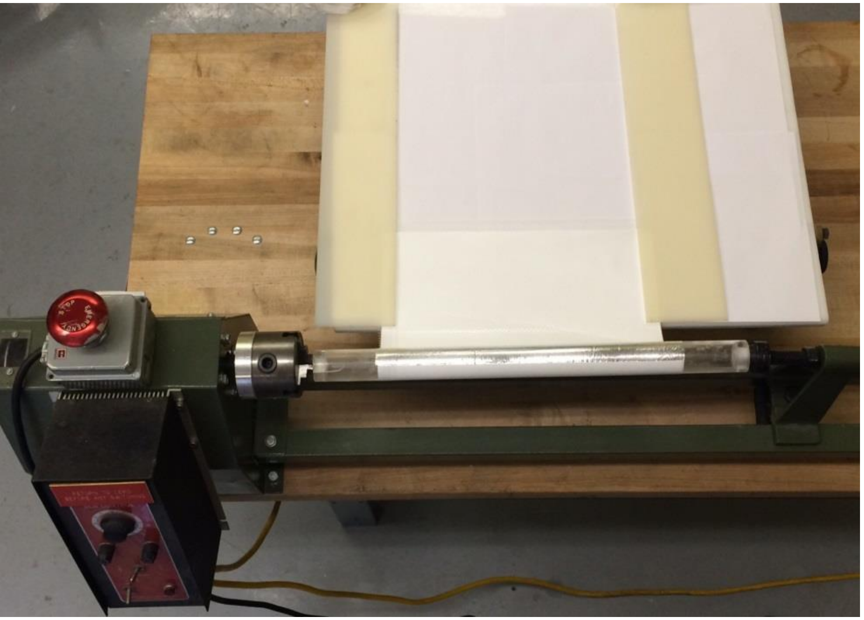
Thin 14”-Wide Amine Coatings on Substrates

Coating knife assembly configuration	Polymer concentration (wt.%)	Viscosity of Coating Solution (cp)	Web speed (ft/min)	Selective amine layer thickness (nm)
Insert with 1-inch flow channel height [a]	1.8	870	3	175
			4	135
			5	115
	2.4	940	3.25	210
			3.5	195
	3	1180	3.5	185
Insert with 2-inch flow channel height [a]	1.5	690	1	230
			2	165
			4	135
	1.8	870	2	220
			3	155
	3.4	1430	1.6	210
			2	178

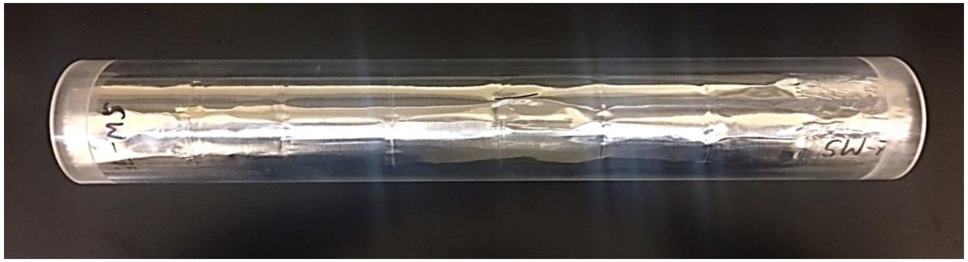
[a] 2.5 mil of flow channel opening

Membrane Element Fabrication

Element Rolling Machine



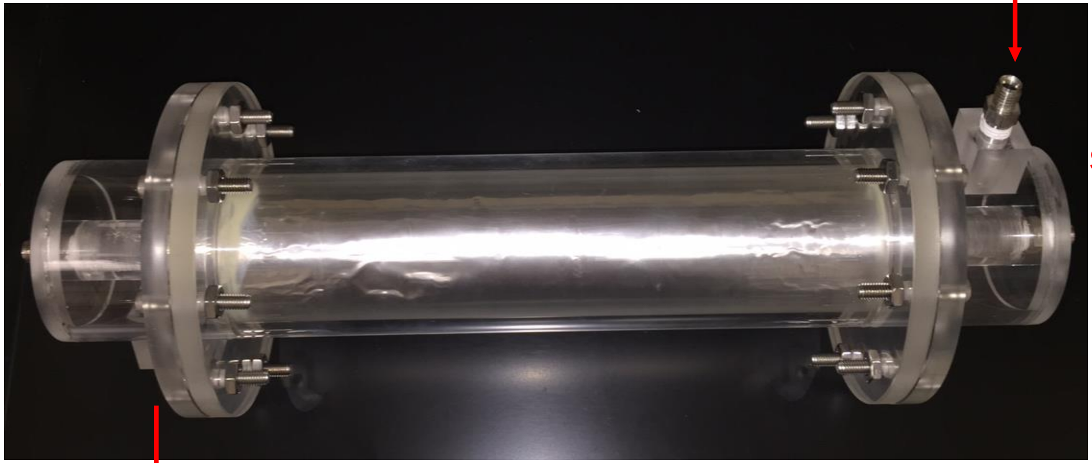
Spiral-Wound Membrane Element



Membrane Module

Feed Inlet

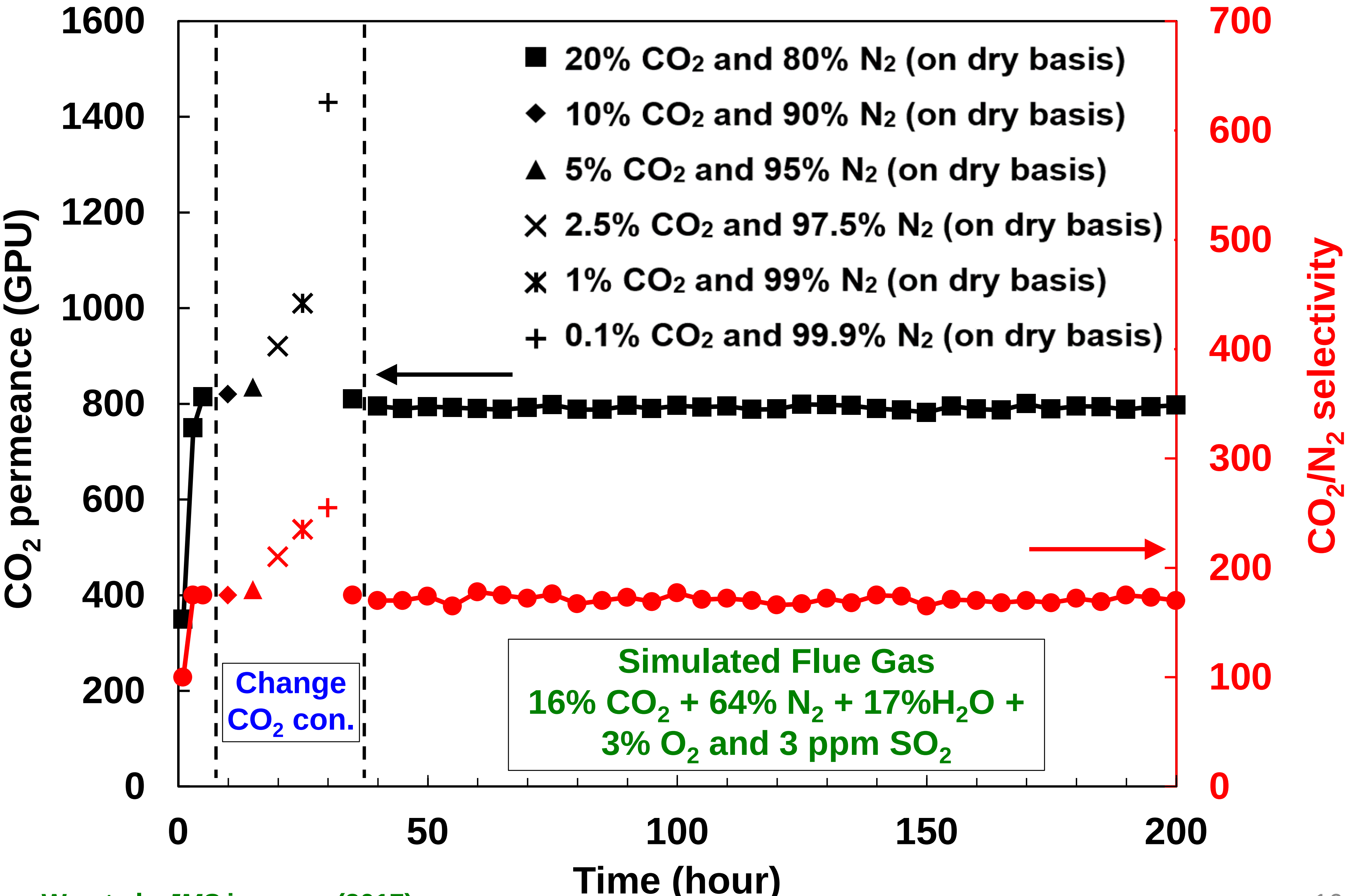
Sweep Inlet



Sweep Outlet

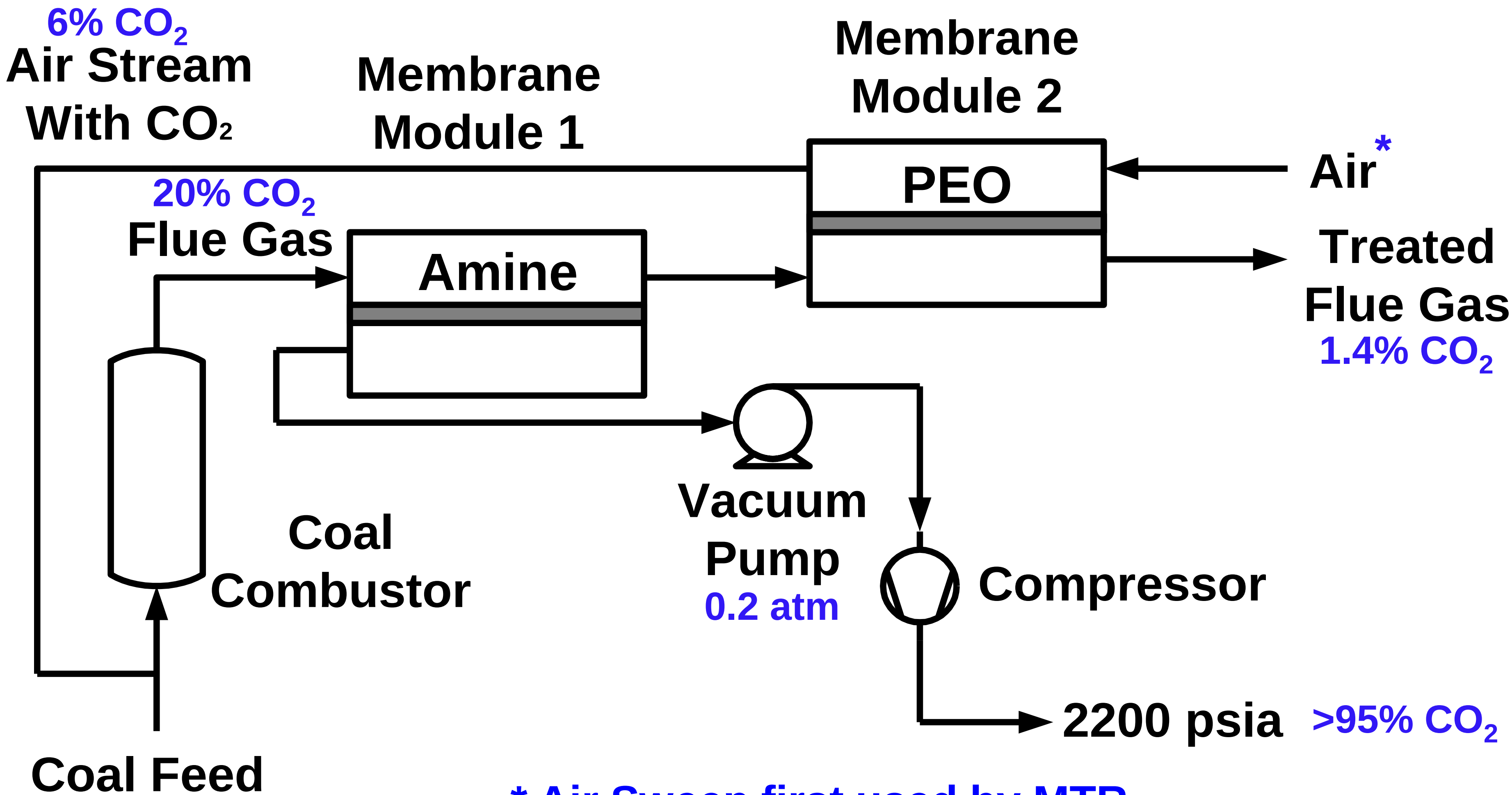
Feed Outlet

Good Membrane Module Stability Obtained



Wu et al., *JMS* in press (2017)

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



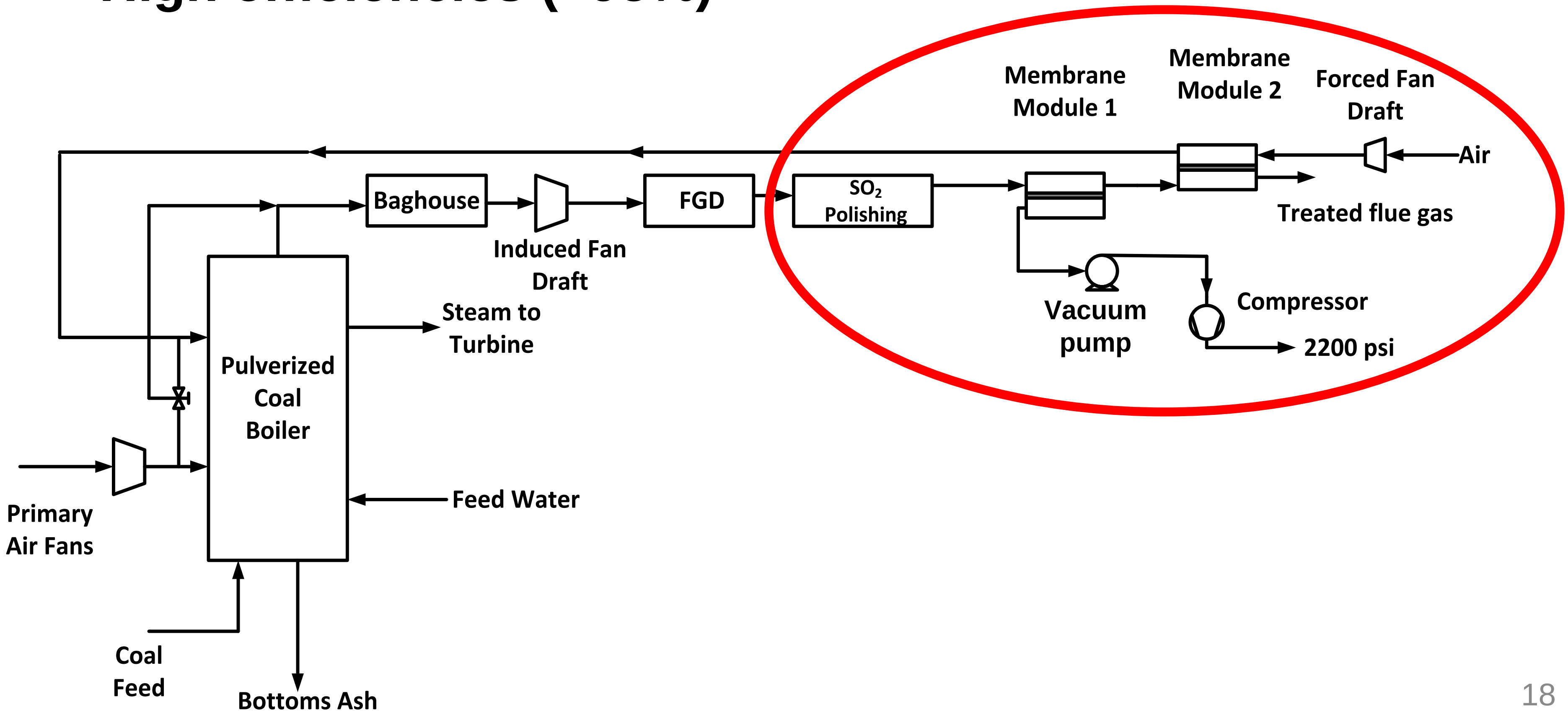
* Air Sweep first used by MTR

- Proposed membrane process does not require cryogenic distillation (compared to competition)

Ramasubramanian et al., *JMS*, *421-422*, 299 (2012)

SO_2 Polishing & Membrane Process

- **Absorption into 20 wt% NaOH Solution**
  - **Polishing step based on NETL baseline document**
    - **Estimated to be ~ \$4.3/tonne CO_2 (in 2007 \$, 6.5% COE increase)**
  - **Non-plugging, low-differential-pressure, spray baffle scrubber**
  - **High efficiencies (>95%)**

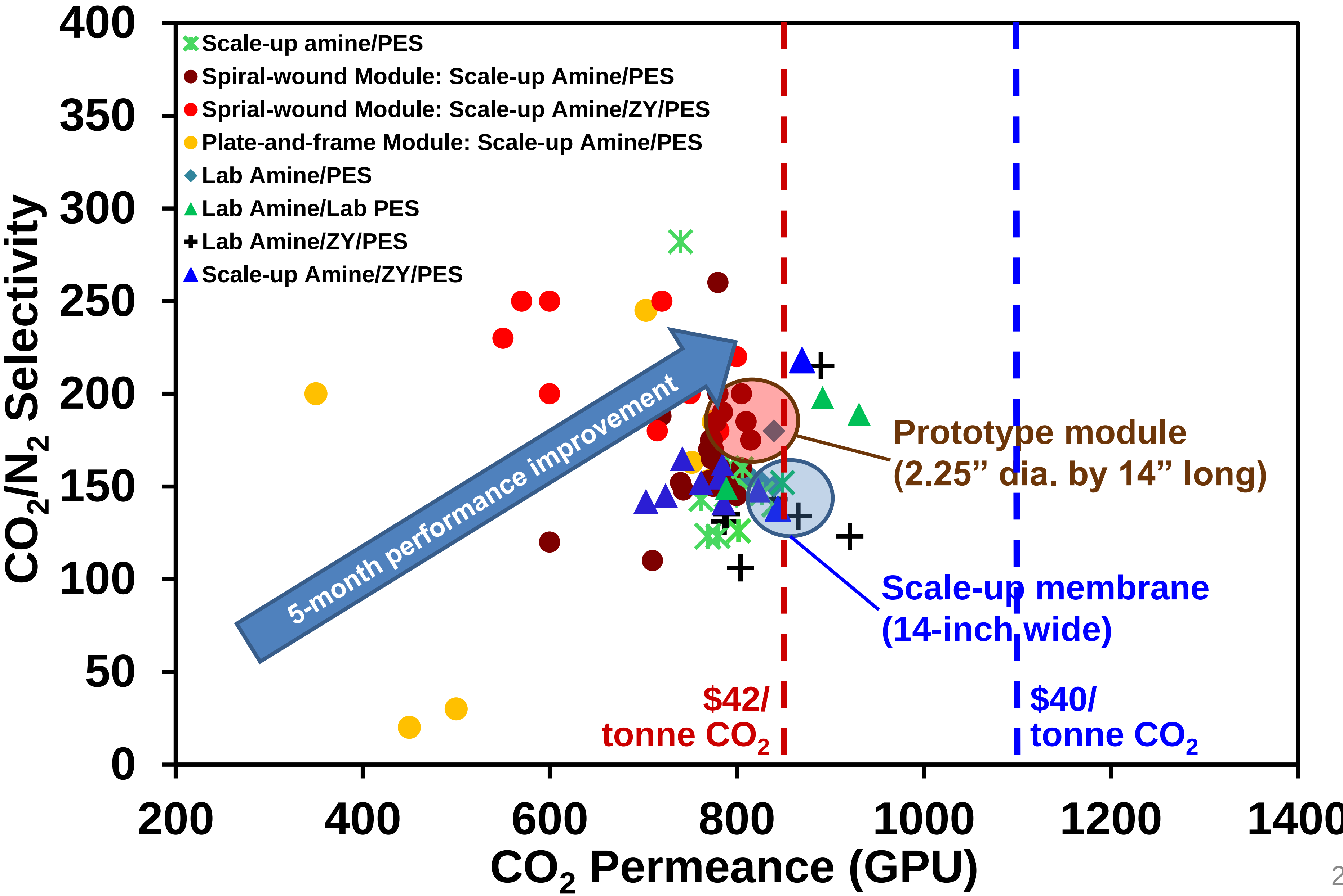


Techno-Economic Analysis

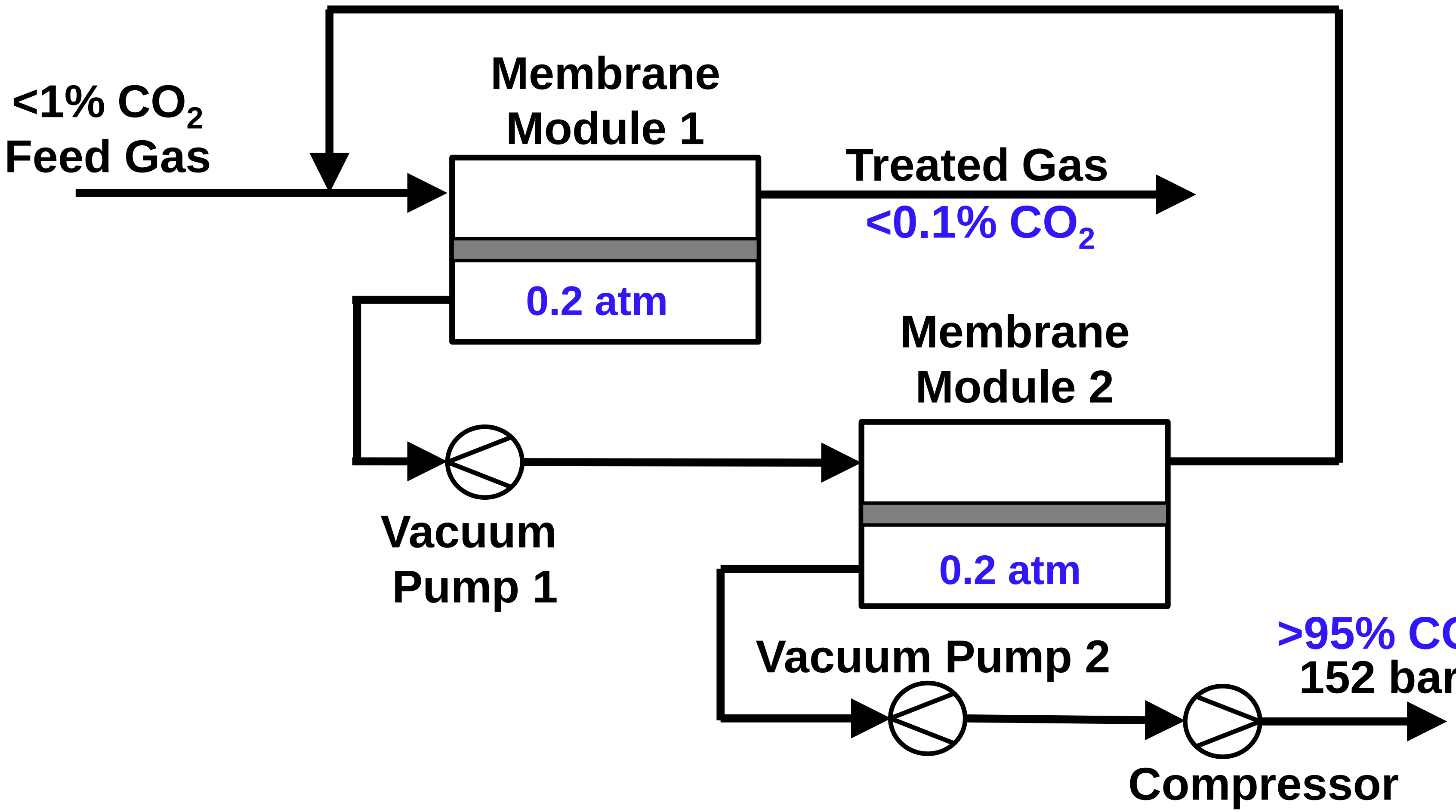
- **Basis: In 2007 dollar**
  - **DOE target: \$40/tonne CO_2 set for 2025**
  - **Include membrane module installation cost**
  - **Also include 20% process contingency**

- **Membrane Results at 57^{o}C**
  - **Amine-containing membrane with >140 selectivity key for stand-alone membrane process**
  - **Membrane process does not require cryogenic distillation**
  - **PEO-containing membrane with 2000 GPU CO_2 permeance and 20 selectivity**

Composite Membranes Containing Amine Cover Layer: Simulated Flue Gas at 57ºC

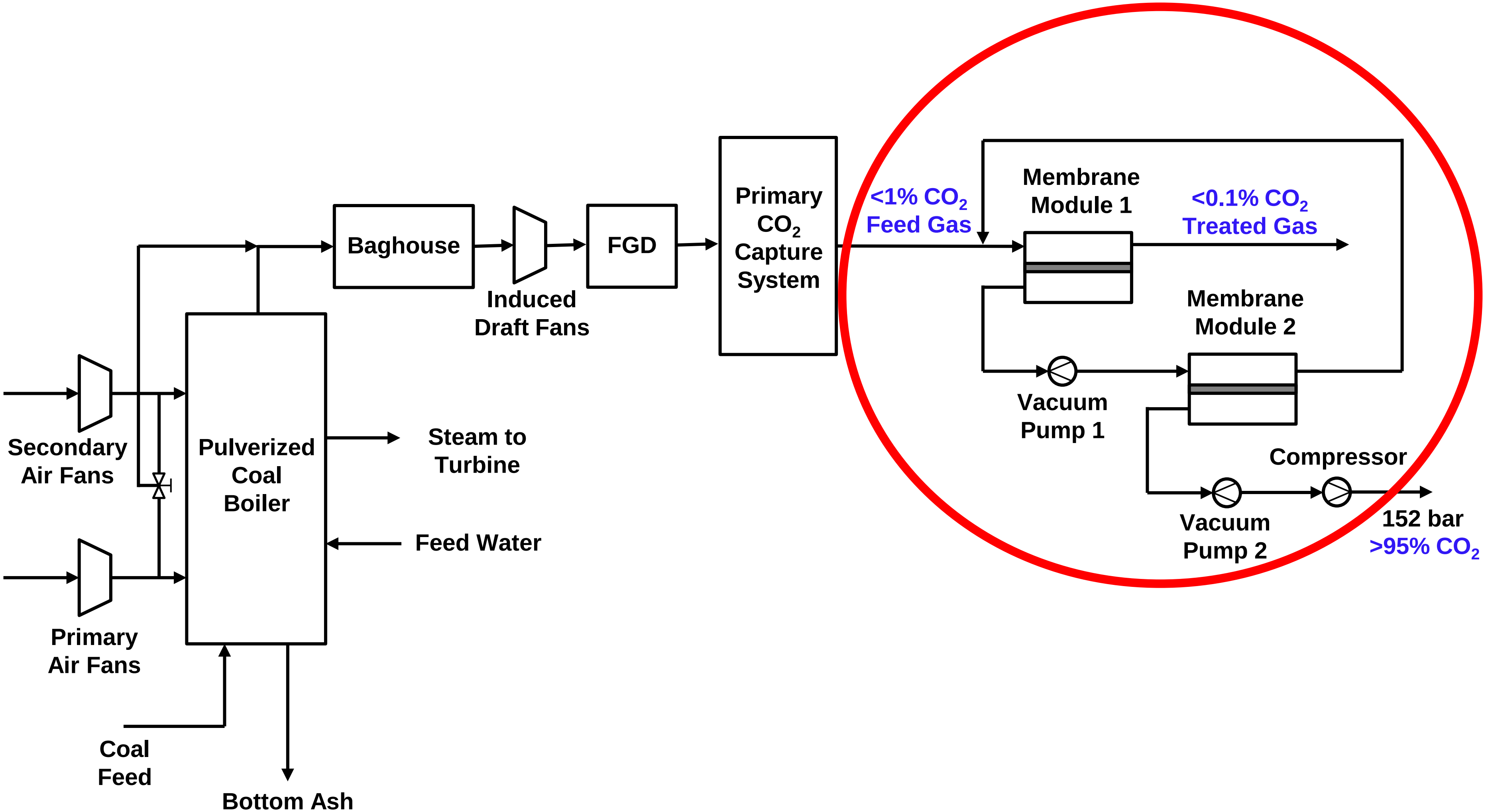


Process Proposed for CO_2 Capture from <1% CO_2 Sources

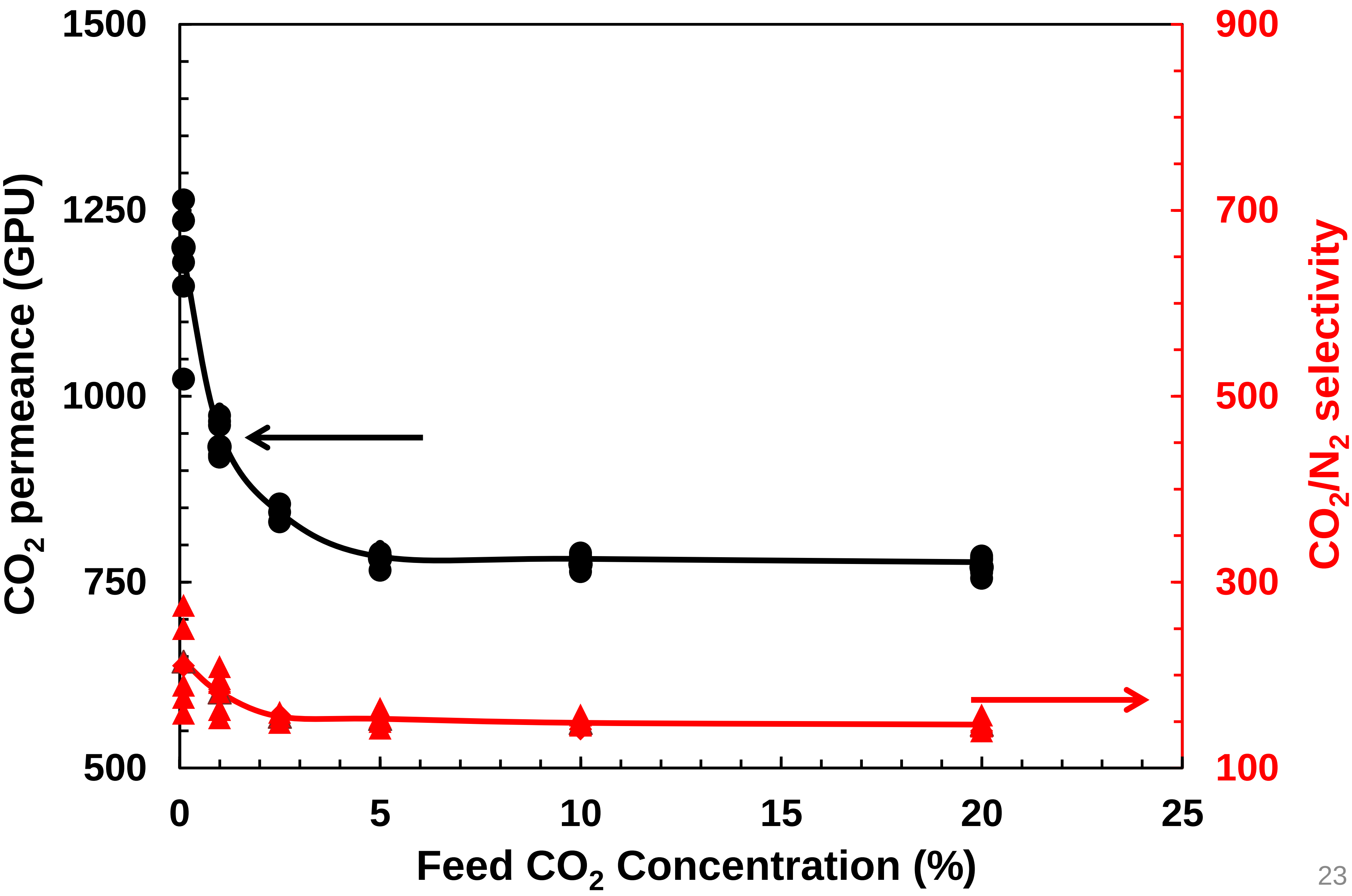


- **Proposed membrane process does not require cryogenic distillation (compared to competition)**

Location of Proposed Technology in Coal-fired Power Plant



Performance Improves as CO_2 Conc. Reduces

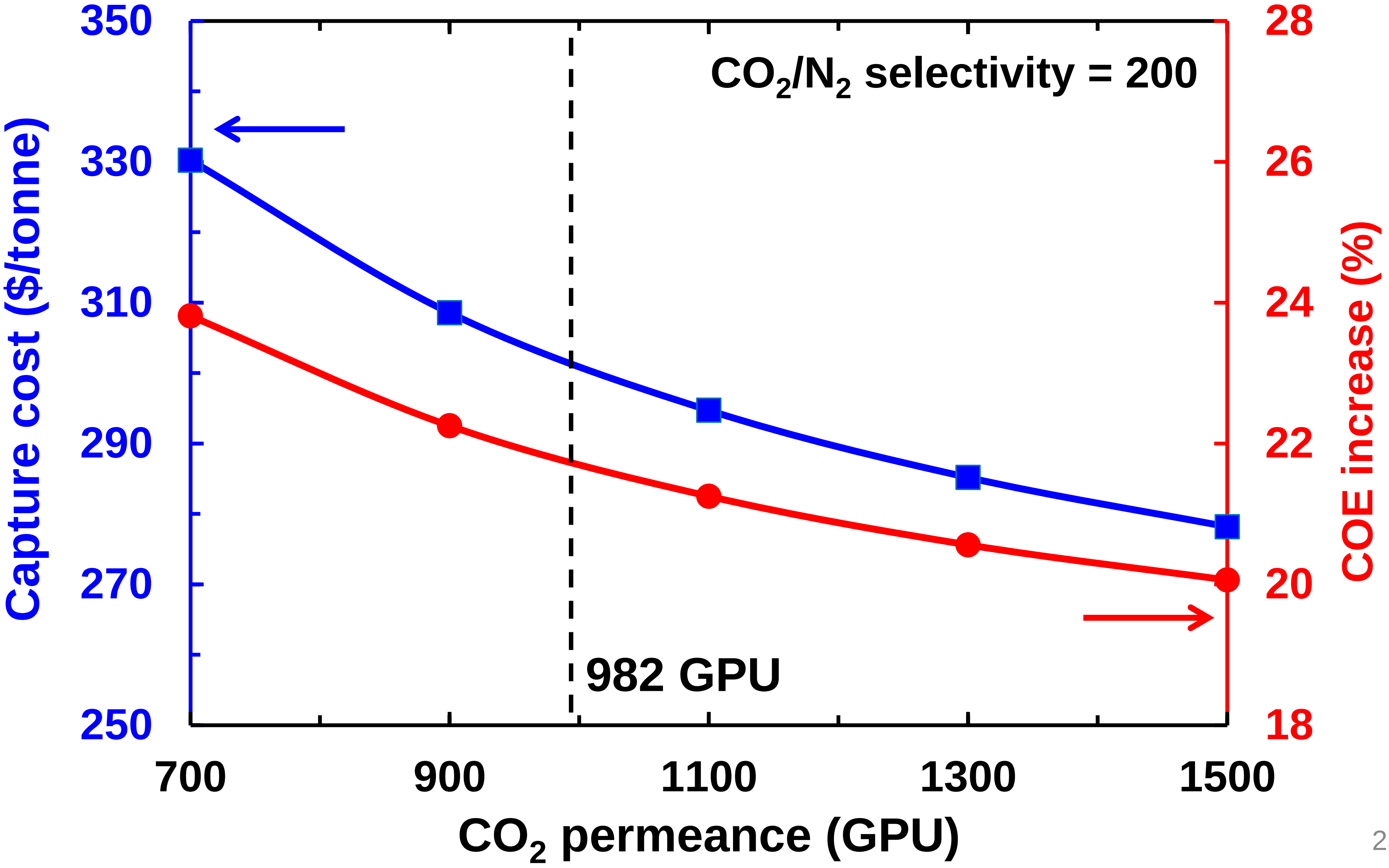


High-Level Techno-Economic Calculations

- **Basis: Membrane Results at 57^{o}C**
  - **982 GPU & 211 Selectivity for 1% CO_2 concentration feed gas**
  - **806 GPU & 173 Selectivity for 20% CO_2 concentration feed gas**
  - **Include Membrane Module Installation Cost and 20% Process Contingency**
  - **In 2011 dollar: NETL Case 12 of *Updated Costs (June 2011 Basis) for Selected Bituminous Baseline Cases***

- **Calculated Cost Results**
  - **32.1 tonne/h of CO_2 captured from 1% CO_2 source**
  - **$107.8 million bare equipment cost**
    - ➢ Membrane 34%, blowers and vacuum pumps 62%, others 4%
  - **1.76 ¢/kWh (1.24 ¢/kWh capital cost, 0.22 ¢/kWh fixed cost, 0.26 ¢/kWh variable cost, and 0.04 ¢/kWh T&S cost)**
    - ➢ COE = 8.09 ¢/kWh for 550 MW supercritical pulverized coal power plant
  - **$302/tonne capture cost ($17.6/MWh × 550 MW/(32.1 tonne/h))**
  - **21.8% Increase in COE (1.76/8.09 = 21.8%)**

Effect of CO_2 Permeance on Techno-economic Analysis Results



Summary

- **CO_2 Capture from Flue Gas**
  - **High-Molecular-Weight PVAm Membrane Synthesized**
  - **Composite Membranes Synthesized in Lab**
    + ~800 GPU with >200 Selectivity at 57°C
  - **Membrane Scaled up Successfully**
  - **Scale-up Membrane Promising for Meeting DOE Cost Target of $40/tonne CO_2 (in 2007 dollar) for 2025**
- **CO_2 Capture from <1% CO_2 Conc. Sources**
  - **Membrane showed 982 GPU with 211 CO_2/N_2 selectivity obtained at 57°C using 1% CO_2 concentration feed gas**
    + 806 GPU with 173 selectivity obtained using 20% CO_2 conc. feed gas due to carrier saturation phenomenon
  - **Performance improves as CO_2 conc. reduces**
  - **High-level techno-economic analysis conducted**
    + Capture cost of ~$302/tonne CO_2 (in 2011 $)
    + 21.8% increase in COE

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– **CO_2-Selective Membranes**

Norman N. Li **Richard Song**

– **Nanoporous Membrane Support**

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– **Free PES Samples**

Purolite Corporation, Bala Cynwyd, PA

– **Free Ion-Exchange Resin Samples**

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Decreasing Emissions Preserves Environment