

Highly Permeable Thin-Film Composite Membranes of Rubbery Polymer Blends for CO₂ Capture



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NETL Research & Innovation Center (RIC)

*2023 FECM/NETL Carbon Management Research Project Review Meeting
Point Source Carbon Capture — Capture from Power Generation (Lab/Bench)*

Aug. 31, 2023



Disclaimer



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Project Overview



- **Project:** High-Permeance Blended Rubbery Membranes
- **Project Period:** 04/01/2021 – 03/31/2026
- **Funding Source:** NETL-RIC Field Work Proposals: Transformational Carbon Capture (2021)
Point Source Capture Technology (2022-2026)
- **Project Objective:** Developing a scalable thin-film composite (TFC) membrane for industrial carbon capture that has a CO_2 permeance $>3,000$ gas permeance unit (GPU) and CO_2/N_2 selectivity of >25 . Both the membrane support and selective material will be optimized for scalability, thermal and chemical stability, and non-aging properties.
- **Project Participants:**



United States Steel

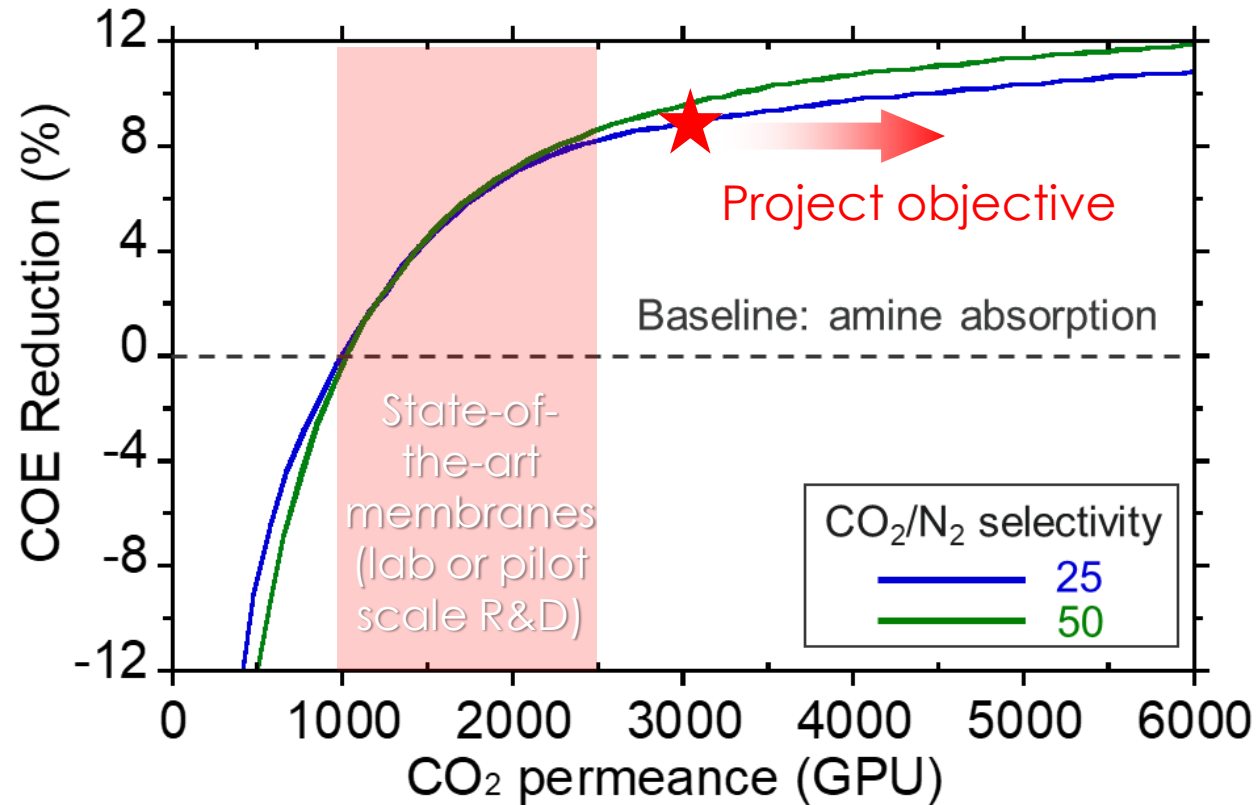
Carnegie Mellon University



CCSI²
Carbon Capture Simulation for Industry Impact



Background: Importance of High-Permeance Membranes



COE: cost of electricity

- Coal flue gas decarbonization: membrane vs. amine absorption
- Two-stage membrane process with air sweep, designed by Membrane Technology and Research (MTR)
- 95% CO₂ purity at a high CO₂ recovery (capture rate) of 90%

For coal flue gas decarbonization, an increase in CO₂ permeance is more important than a further increase in CO₂/N₂ selectivity when the selectivity is above 25.

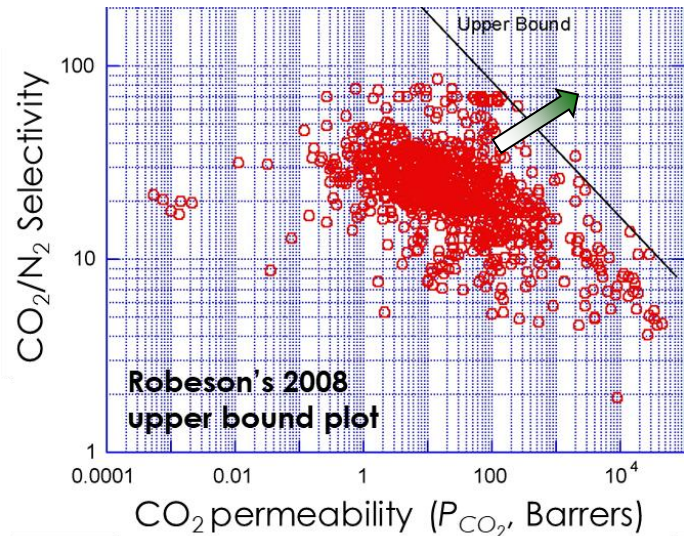
Alex Zoelle et al., [Performance and Cost Sensitivities for Post-Combustion Membrane Systems](#), 2018 NETL CO₂ Capture Technology Project Review Meeting

Background: Achieving High Permeance via Selective Material Optimization and TFC Fabrication

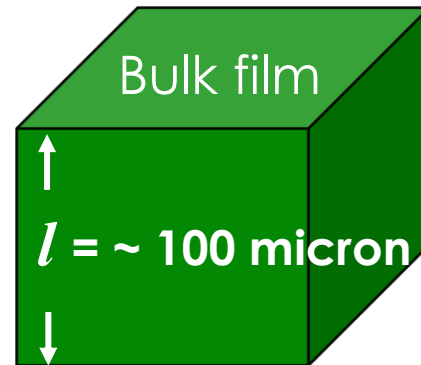
$$\uparrow \text{Permeance} = \frac{\text{Permeability (P) of selective material} \uparrow}{\text{thickness of selective layer} \downarrow}$$

1. Selective material optimization

Permeability/selectivity tradeoff

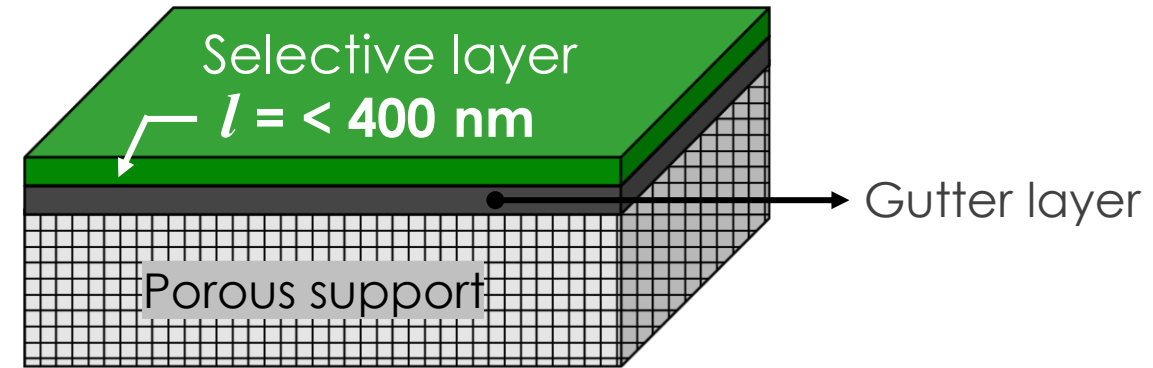


Robeson, J. Membr. Sci. 320 (2008) 390



Thickness reduction

2. TFC membrane fabrication



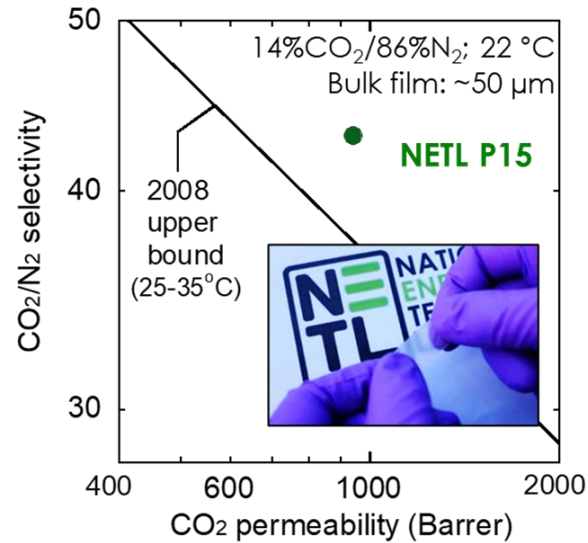
Selective layer ($\ll 1 \text{ }\mu\text{m}$): CO₂/N₂ separation

Gutter layer ($< 500 \text{ nm}$): preventing pore penetration and smoothing porous support

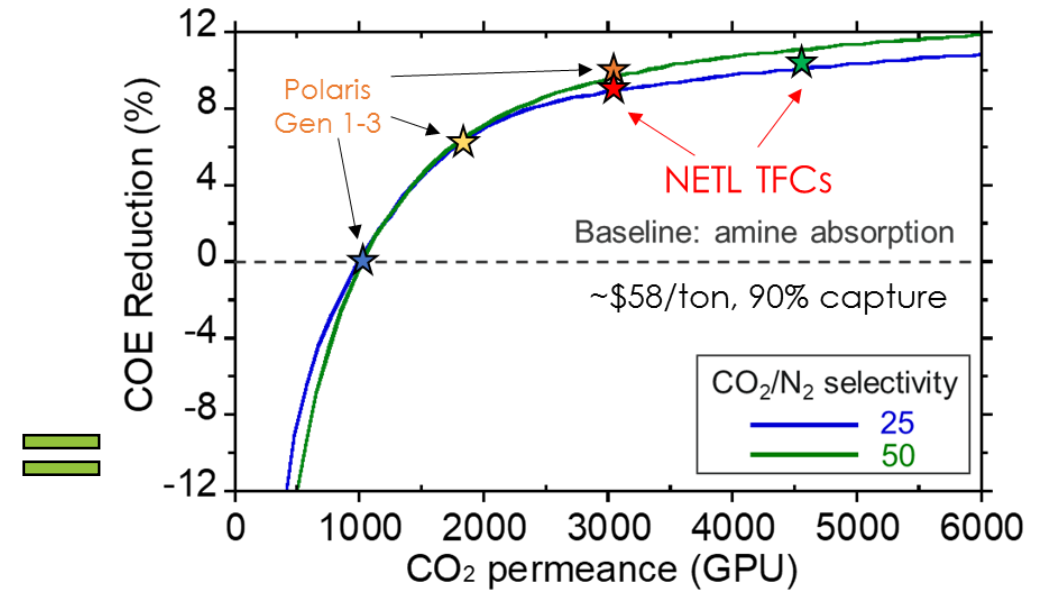
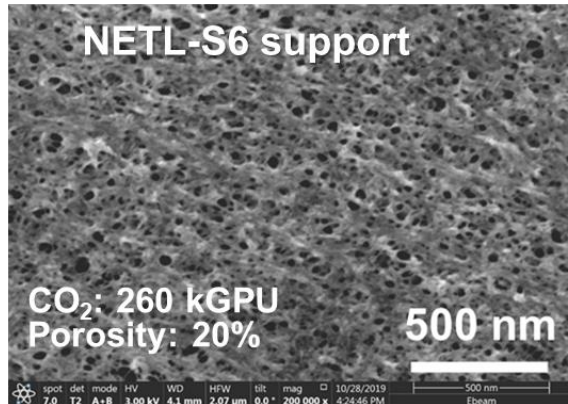
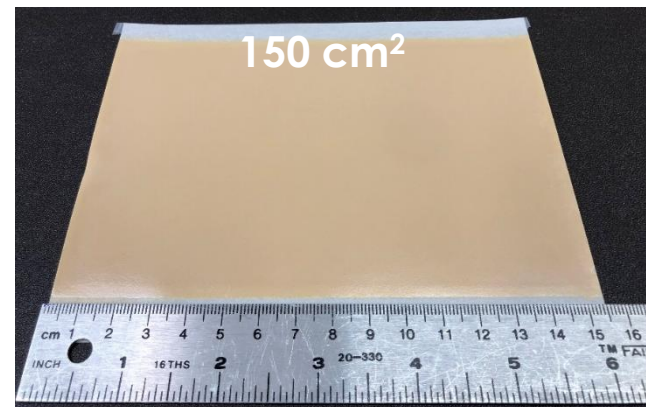
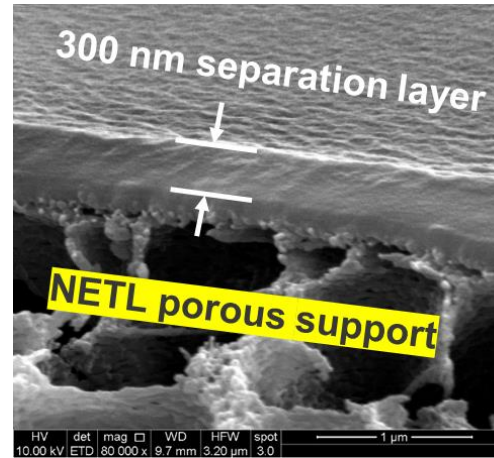
Porous support ($> 20 \text{ }\mu\text{m}$): mechanical reinforcement

Prior Efforts (2019-2022): Successful Bench-Scale Fabrication

High-performance materials



Suitable coating technique



Lower-cost CO₂ capture vs. amine absorption

- Alex Zoelle *et al.*, [Performance and Cost Sensitivities for Post-Combustion Membrane Systems](#), 2018 NETL CO₂ Capture Technology Project Review Meeting
- MTR Polaris membrane performance: Project FE0031591 Technology Sheet, <https://netl.doe.gov/project-information?p=FE0031591>

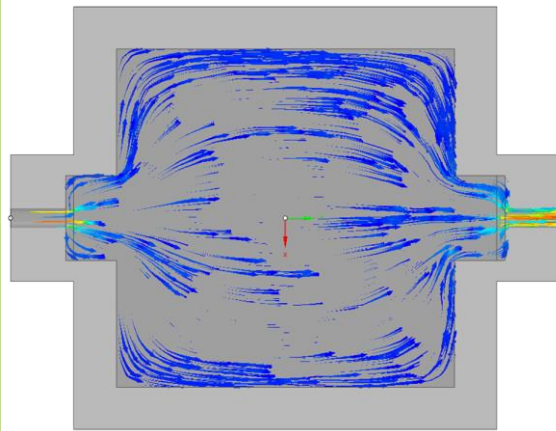
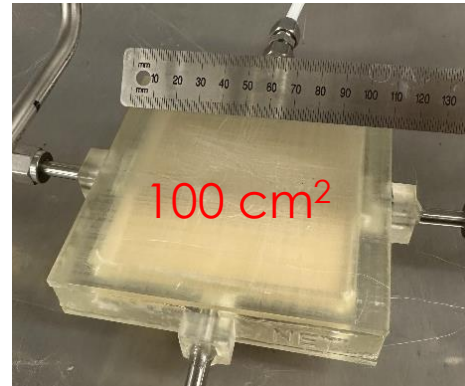
Highlights of 2022-2023 Accomplishments

Field Test @ NCCC

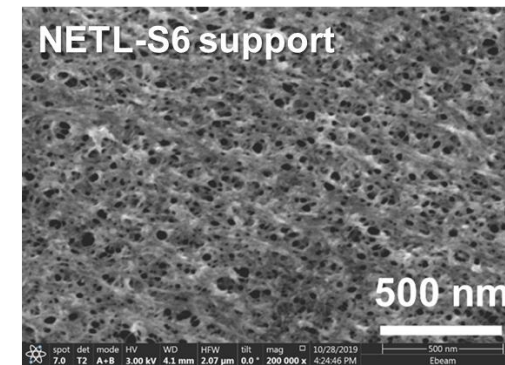
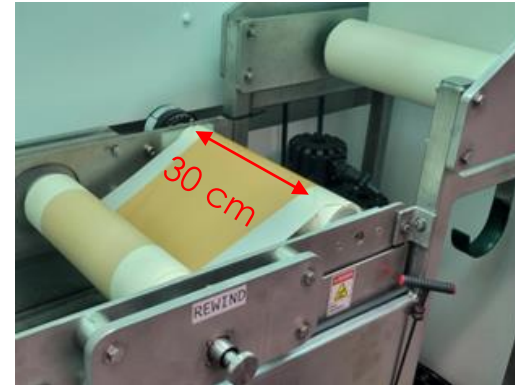


- Oct. 2022 - current
- 6 membranes tested
- >5,000 hours run time

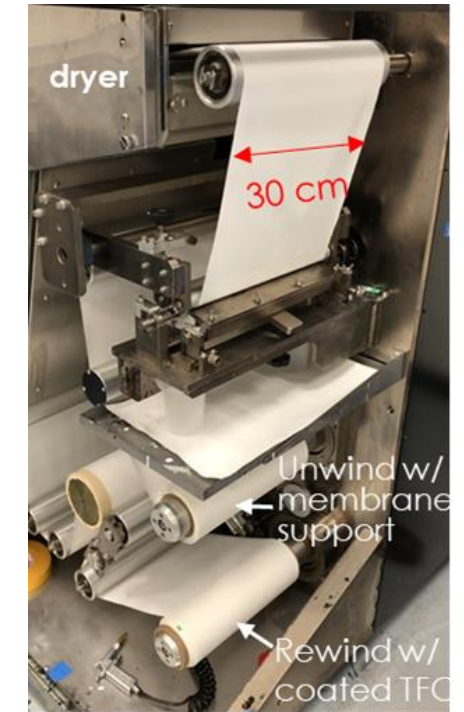
Membrane module design, 3D printing, and optimization



Roll-to-roll scale-up of membrane support



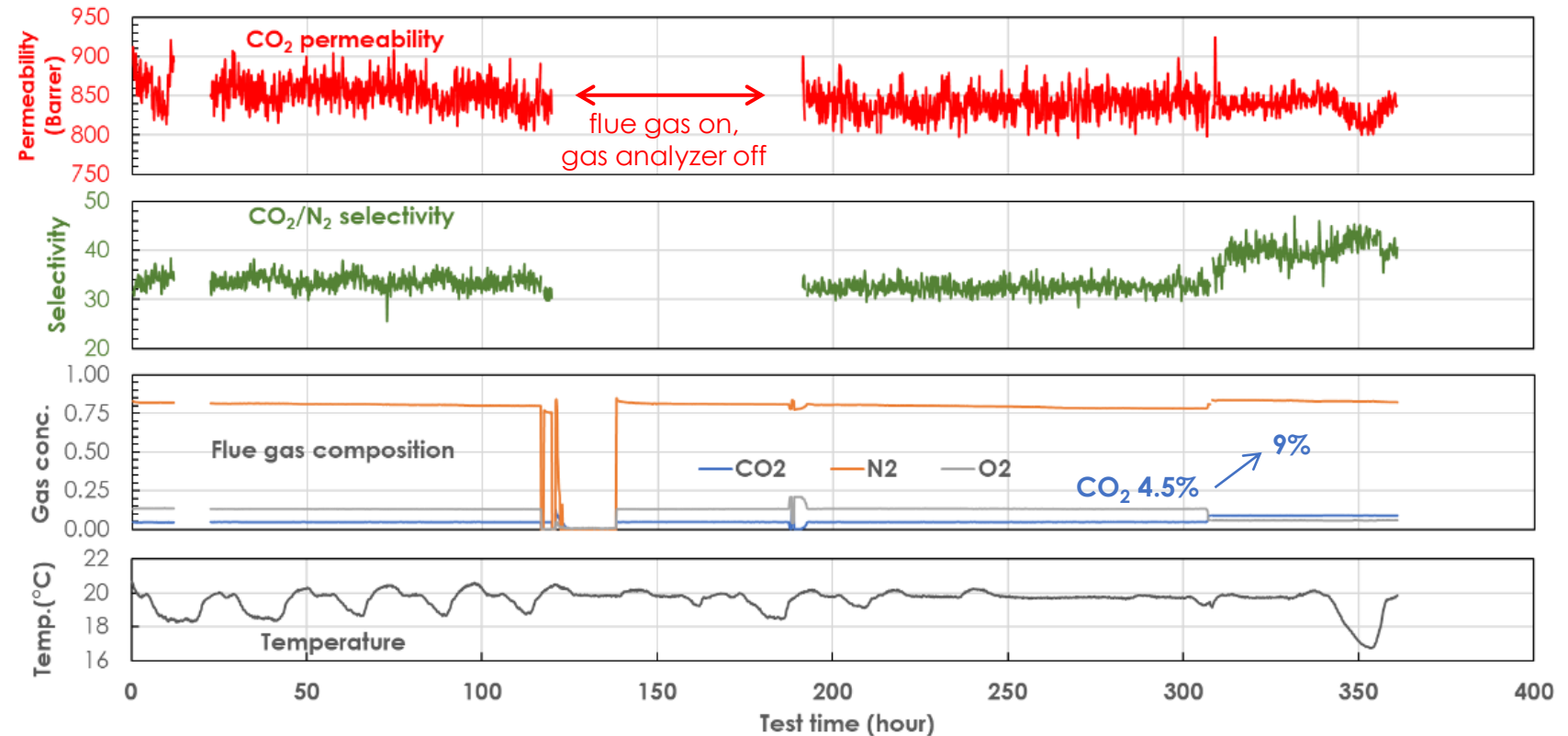
Installation and shakedown of a roll-to-roll thin-film membrane coater



NETL Rubbery Polymer Blend Bulk Films Demonstrating Long-Term Stability in Flue Gas at NCCC

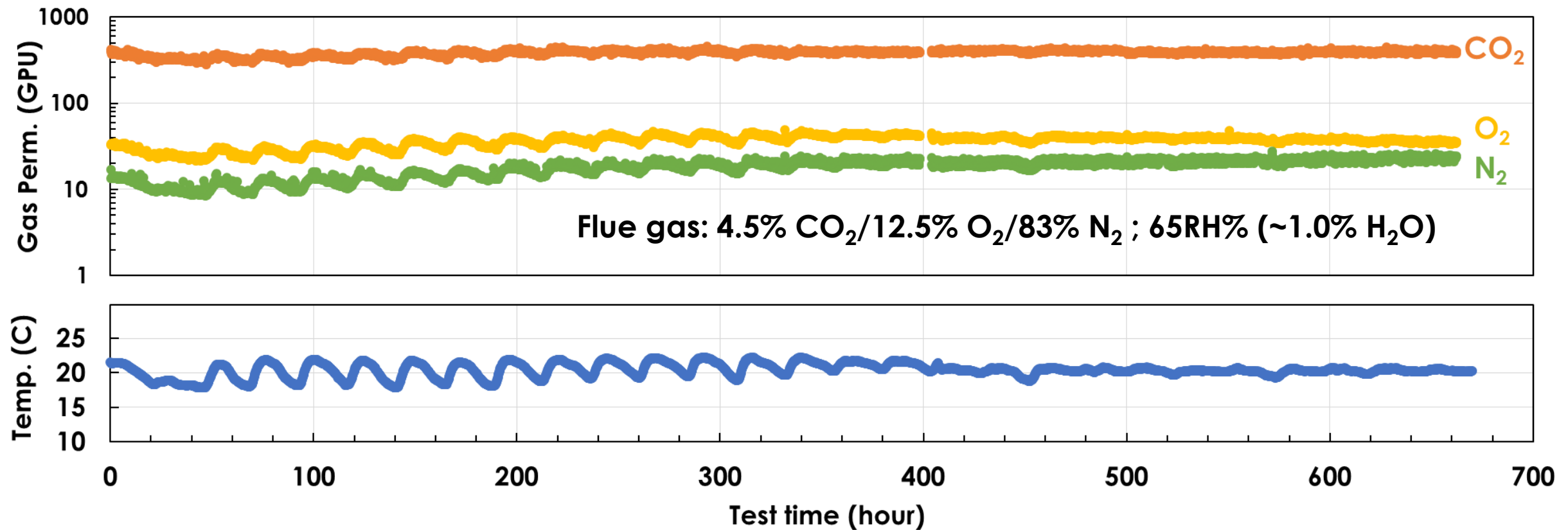


Feed flue gas: 3 atm, 65 RH%, ppm-level NO_x



360-hour field test of a **50 μm** P15 film at NCCC in **natural gas flue gas** with varying CO₂ concentrations of 4.5–9 mol.% at ~20 °C

NETL Rubbery Polymer Blend Thin-Films Demonstrating Long-Term Stability in Flue Gas at NCCC



670-hour (4-week) field test of a **submicron** P15 thin-film composite at NCCC in **natural gas flue gas** with a CO₂ concentration of 4.5 mol.% at ~20 °C

Design, CFD Simulation, and 3D Printing of Plate-and-Frame Membrane Modules

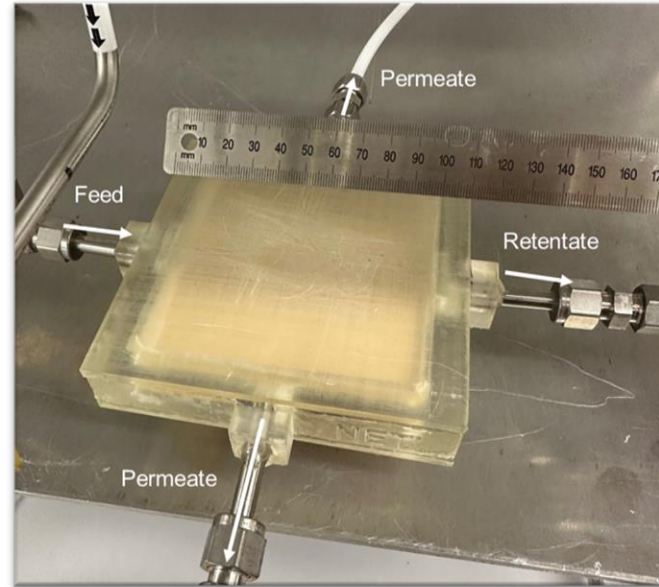


FormLabs 3+
14.5 × 14.5 × 18.5 cm

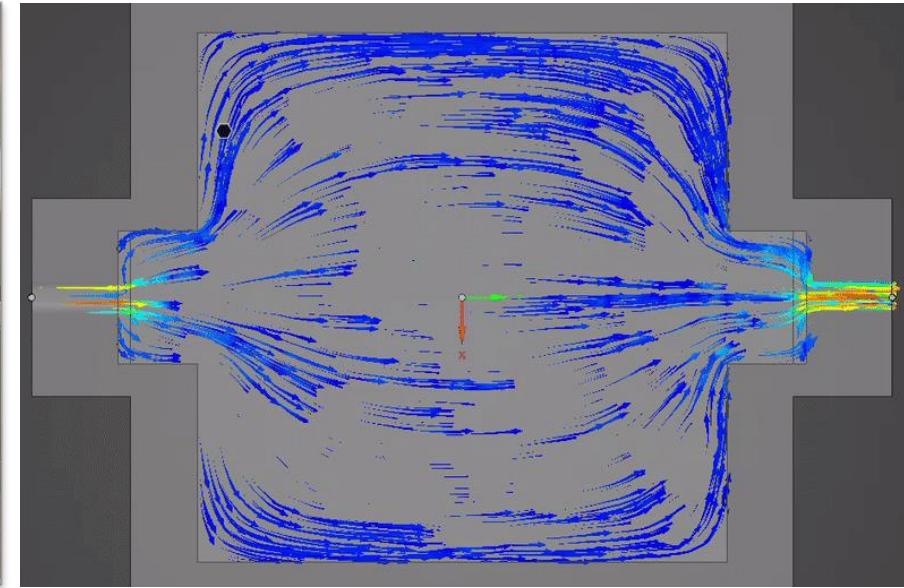
FormLabs 3L
33.5 × 20 × 30 cm



- Good gas tightness resulting from stereolithography (SLA) printing with resin
- High XYZ resolutions: 25 μm

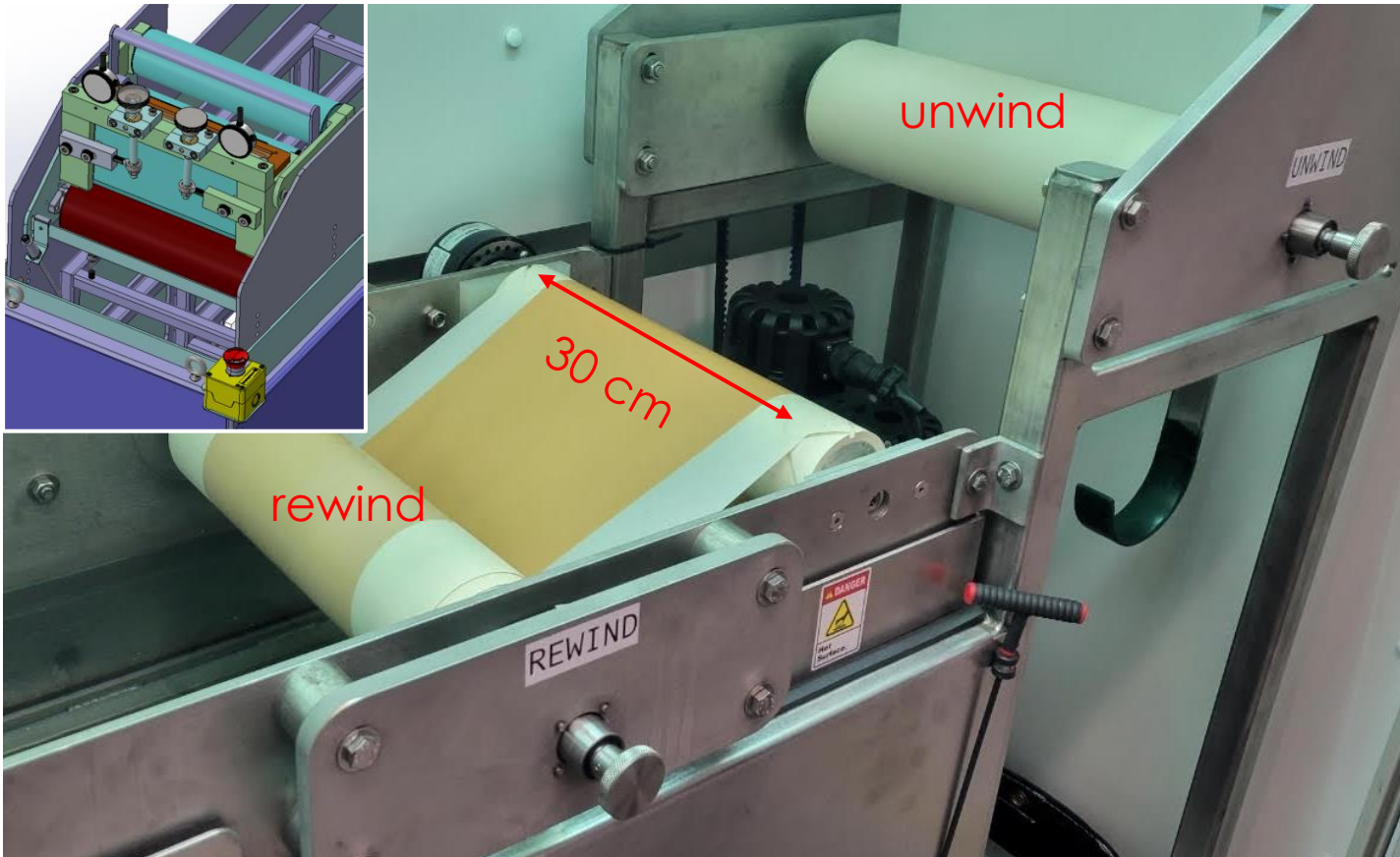


A 3D-printed 100 cm² module prototype being tested in a permeation system

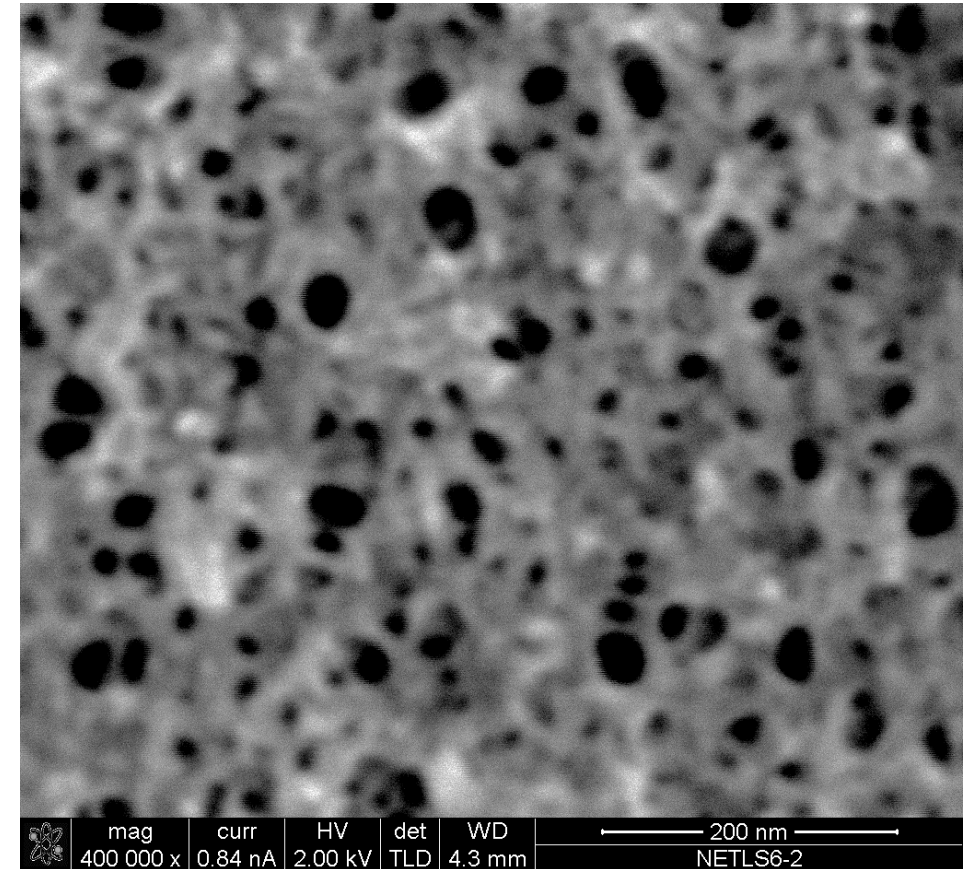


Computational fluid dynamics (CFD) simulation integrated to design modules with optimal flow efficiency

NETL-S6 Membrane Support Scale-Up via Roll-to-Roll Process

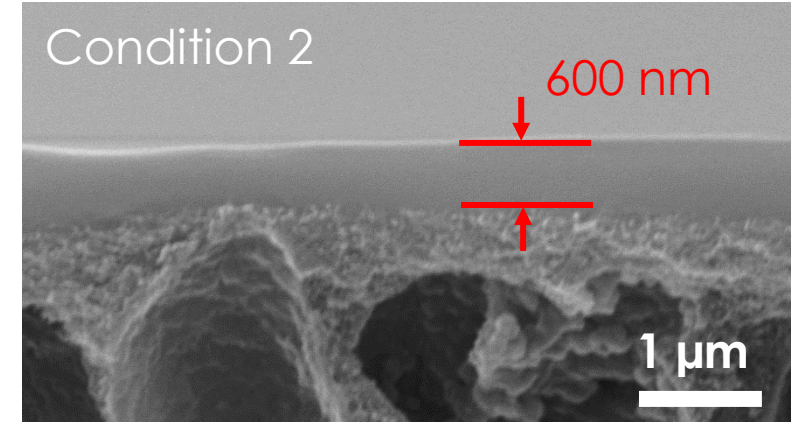
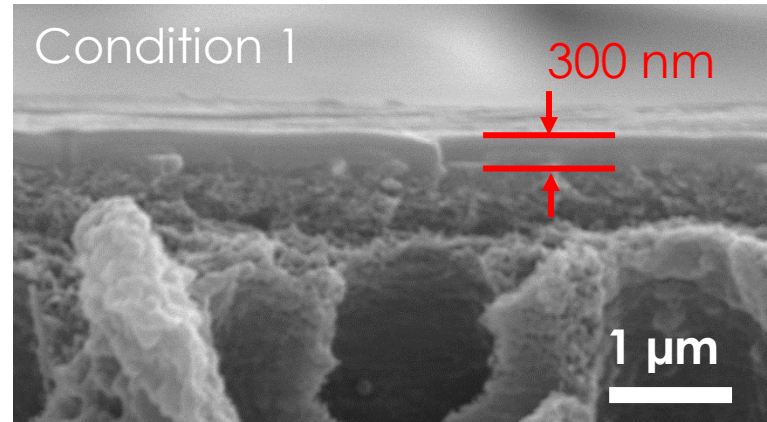
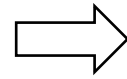


NETL's custom membrane casting machine






Scaled-up membrane's microporous feature

Progress Update on TFC Scale-Up via Roll-to-Roll Process



Roll-to-Roll Thin-Film Coating Machine

- A custom machine ordered in 12/2022 and delivered in 07/2023 
- Installation, shakedown, and EHS approval by 12/2023 
- Optimized roll-to-roll thin-film coating by 03/2024 

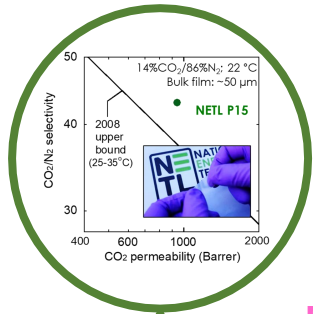
Materials

- P15 polymer scale-up synthesis: 40 g/batch (equiv. 100 m² thin films) 
- NETL-S6 membrane support rolls 

Thin-film coating test run at the vendor's site in 03/2022

R&D Timeline: Project Progress and Future Work

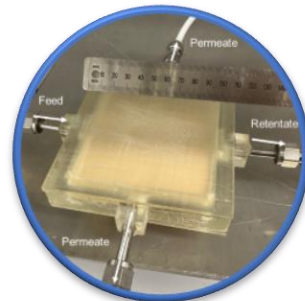
NETL P15 selective material synthesis & optimization



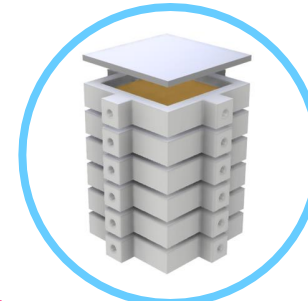
NETL S6 support scale-up via roll-to-roll



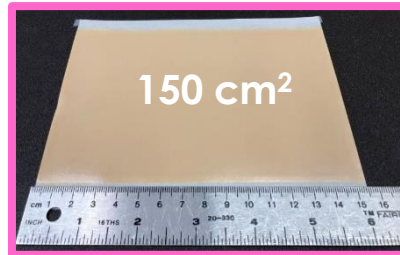
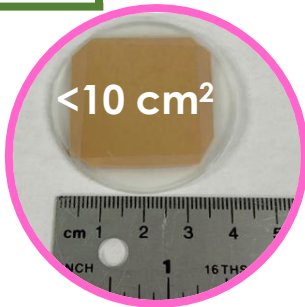
3D printed bench-scale membrane module



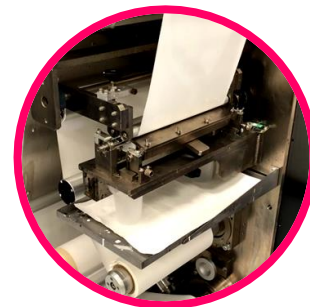
3D printed multi-stacking membrane module



Bench scale TFC fabrication

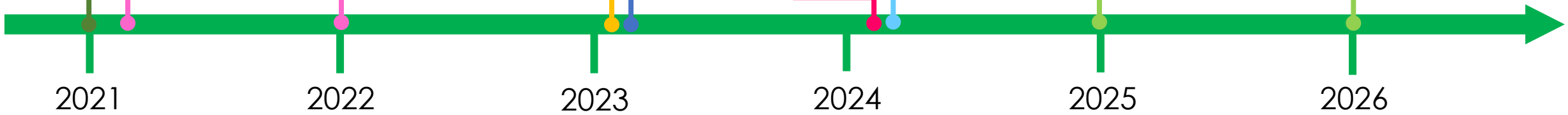


TFC scale-up via roll-to-roll

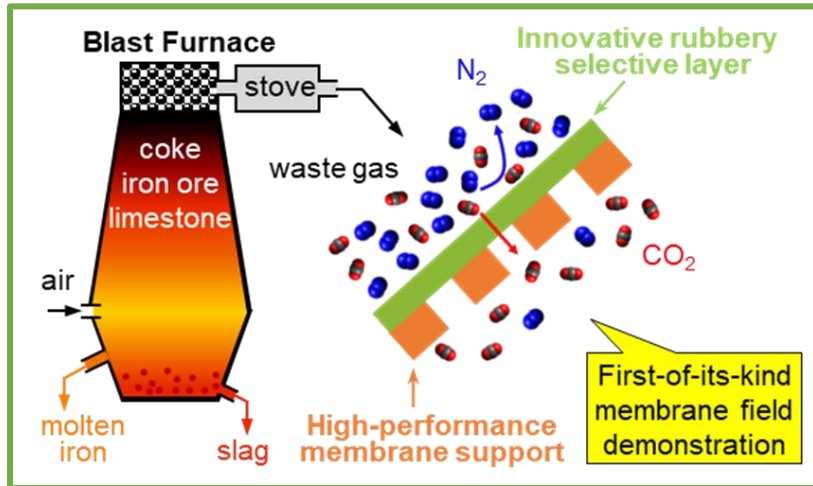


1. Complete long-term field test at U. S. Steel's Edgar Thomson Plant
2. Perform systems and economic analysis by CCSI²

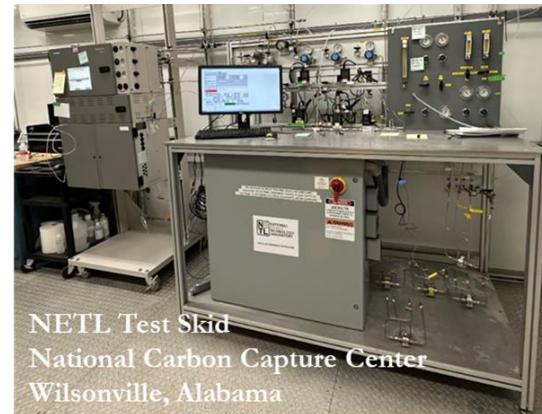
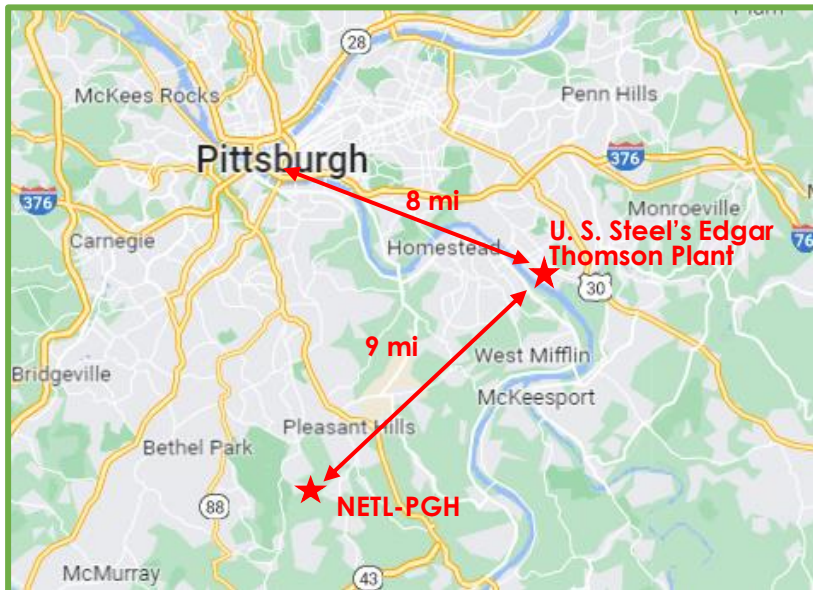
Initiate field test at a commercial steel mill (U. S. Steel's Edgar Thomson Plant)



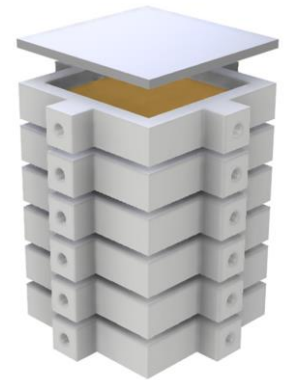
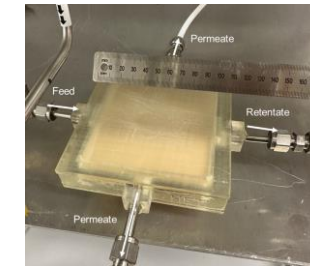
Field Demonstration Preparations in 2024-2025



Collaborate with U. S. Steel for field test using blast furnace waste gas (>20% CO₂) at U. S. Steel's Edgar Thomson Plant, Braddock, PA



Design and construction of membrane testing skid



Module fabrication and lab testing

Acknowledgments



NETL Membrane R&D

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NETL Engineering Team

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Analysis Team from CCSI²

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Benjamin Omell
Eric Grol
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CMU: CFD Simulation

Grigorios Panagakos
Cheick Dosso

U. S. Steel: Field Test Host Site

Brenda Petrilena
Neil Pergar

INL: Material Synthesis

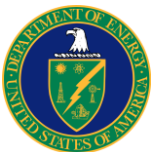
John Klaehn
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NCCC: Field Test Host Site

Tony Wu
Robert Lambrecht
John Carroll
John Cagle
Wayne Isbell

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U. S. Steel



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