Bench-Scale Testing of Monolithic PPI Structured Contactors for Direct Air Capture of CO_2

DE-FE0032094

Dr. Christopher Bertole
CORMETECH, Inc.

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National Energy Technology Laboratory
Carbon Management Project Review Meeting
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Funding and Performance Dates

- Two years total period, in two budget periods.
- Total Federal Share = $1,500,000.
- Cost share = 20%.

BUDGET	Budget Period 1 9/15/2021 – 9/14/2022			Budget Period 2 9/15/2022 – 9/14/2023			Total 9/15/2021 – 9/14/2023		
	Federal Share	Cost Share	Total	Federal Share	Cost Share	Total	Federal Share	Cost Share	Total
Total	$882,681	$220,670	$1,103,351	$617,319	$154,330	$771,649	$1,500,000	$375,000	$1,875,000
Cost Share %	20%			20%			20%		

Project Participants

Georgia Tech

Overall Project Objectives

- Develop a next generation oxide monolith + amine structured contactor for DAC, based on poly(propyleneimine) (l-PPI).

- Refine, with inputs from experimental kinetic, thermodynamic and transport measurements, the following models:
  - (i) Single channel monolith model
  - (ii) DAC process model

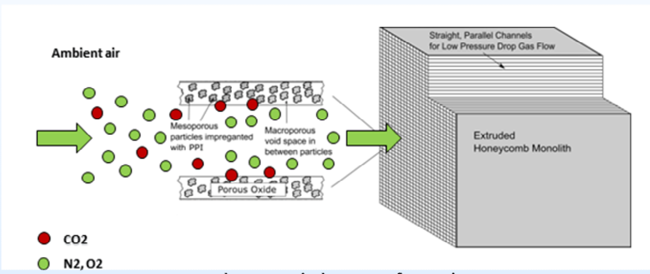
  in order to:
  - (iii) Simulate the impact of substrate textural properties (meso and macro porosity) on DAC performance, and
  - (iv) Enable contactor optimization prior to prototype synthesis and bench-scale testing validation.

- Refine the DAC process TEA and LCA.

Technology Background

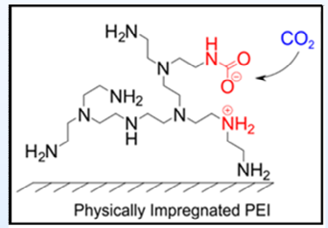
Global Thermostat DAC Platform

1. Moving Large Air Volumes Efficiently



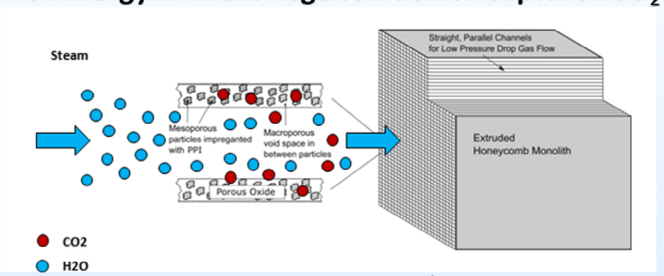
Honeycomb monoliths significantly outperform all other designs, enabling low pressure drop and minimum energy cost

2. Capturing CO_2 Selectively at 400 ppm



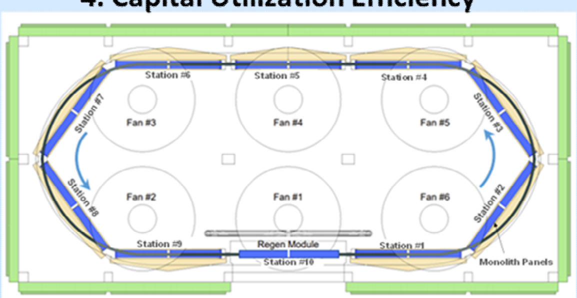
Amine-based polymers, incorporated in proprietary coatings, yield selectivity, capture efficiency, and compatibility with honeycomb monolith approach

3. Energy Efficient Regeneration of Captured CO_2



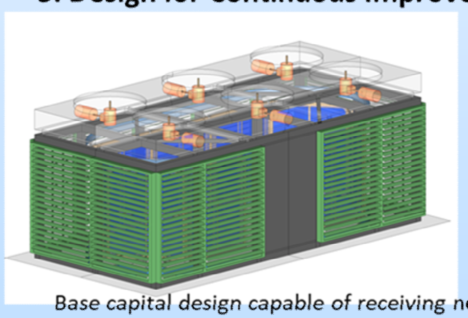
Temperature-Vacuum Swing Adsorption (TVSA) with steam as direct phase-change heat transfer fluid

4. Capital Utilization Efficiency



Process and mechanical movement design enable multi-bed adsorption configuration serviced by one regen module

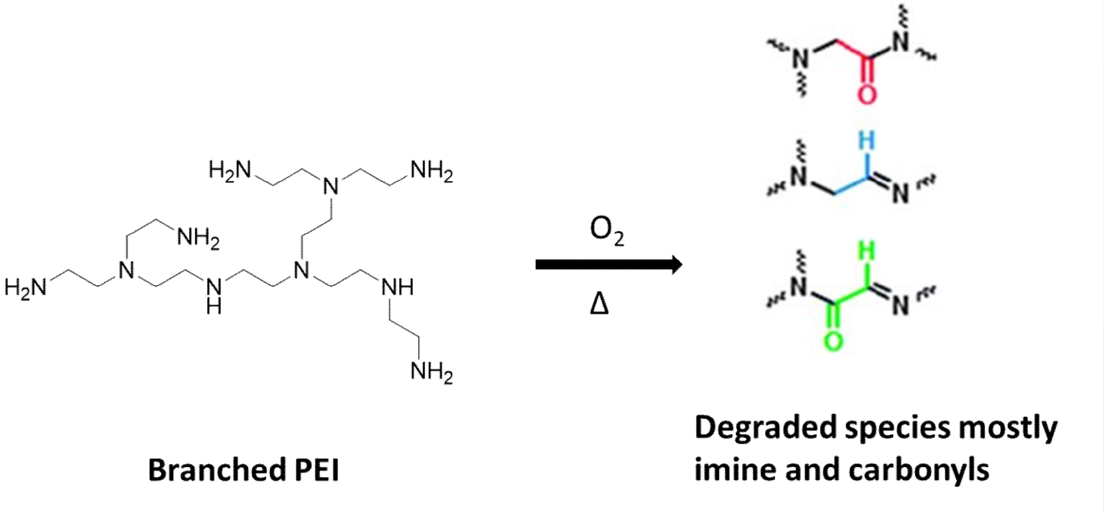
5. Design for Continuous Improvement



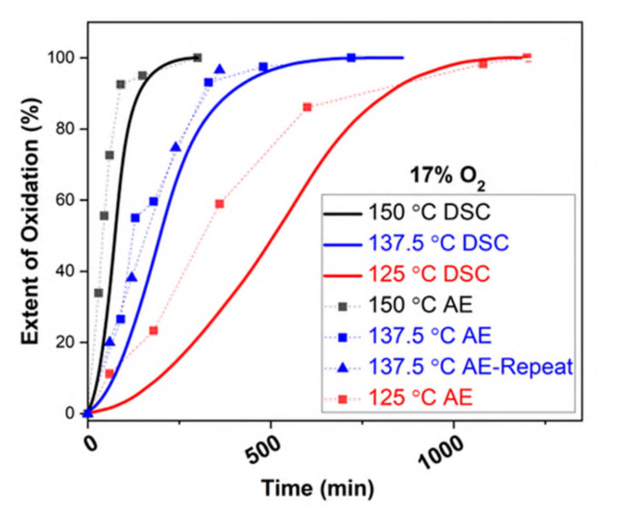
Base capital design capable of receiving new and future generations of improved adsorbent materials to regularly maximize capture capacity and extend plant capital life.

Technology Background
Oxidative Stability of Base Sorbent: PEI

- Poly(ethylenimine) is known to degrade in the presence of O_2.



Phys.Chem.Chem.Phys. 2014, 16, 1529-1535



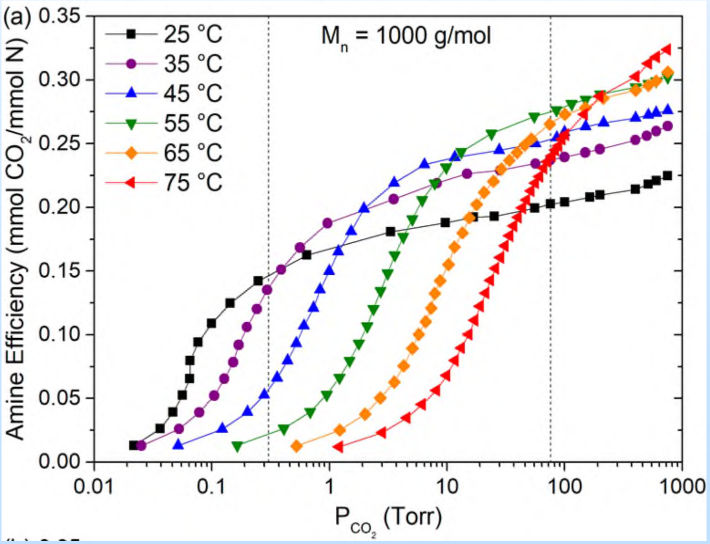
ACS Sustainable Chem. Eng. 2021, 9, 25, 8477–8486

- GT's base DAC process is designed to mitigate high temp exposure.
  - Incorporating a new sorbent with enhanced oxidative stability will improve the on-stream sorbent lifetime in the base GT DAC process, and potentially enable new process paradigms.

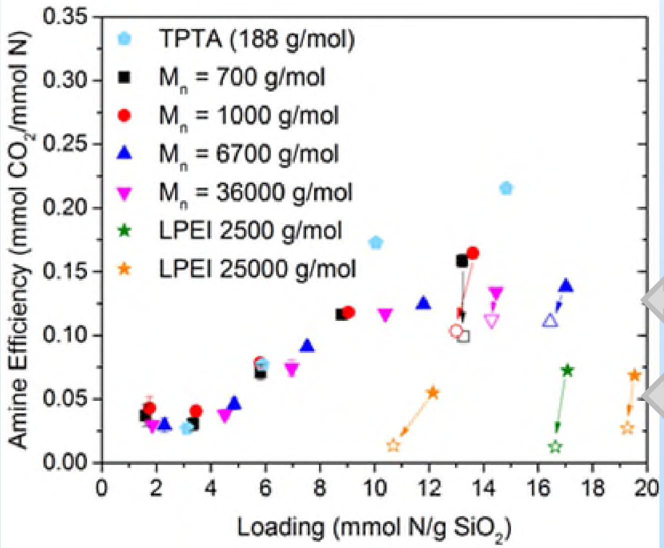
Technology Background
Improved Oxidative Stability Sorbent: PPI

- Poly(ethylenimine) / PEI: $-(NH-CH_2-CH_2)_{n>1}-NH_2$
- Poly(propyleneimine) / PPI: $-(NH-CH_2-CH_2-CH_2)_{n>1}-NH_2$

I-PPI has good CO_2 uptake for DAC.



I-PPI has superior oxidative stability.



Open Symbols:
Post-oxidative exposure
(24h at 110°C in 21% O_2/N_2)

I-PPI

I-PEI

Pang, S. H.; Lively, R. P.; Jones, C. W. ChemSusChem 2018, 11 (15), 2628-2637.

Technology Background
State before Start of Project

- **l-PPI performance under DAC conditions was only known:**
  - for supported powders,
  - under dry feed adsorption,
  - and thermal N_2 desorption conditions.

  Data were not available for monolith l-PPI under "real" process conditions.

- **l-PPI was not a commercially available material.**
  - Cannot order it from a catalog in sufficient quantity to run the bench-scale validation tests for a monolithic form.

Project Steps – BP1

Scale-Up of Linear-Poly(propyleneimine) (l-PPI)

BP1 activities (9/15/2021 – 9/14/2022)

- **Run "initial" bench-scale DAC test for monolithic l-PPI.**
  - Design, build and commission bench-scale test unit for testing.
  - Make sufficient l-PPI to synthesize full-size monolith part (min. 1 kg).
  - Make full-size monolithic l-PPI part, with standard substrate.
  - Complete bench-scale test.
- **Develop predictive tool to optimize substrate for l-PPI.**
  - Establish FEA single-channel monolith model.
  - Measure CO_2 adsorption / desorption equilibria and diffusive transport rates in porous metal-oxide PPI supported materials, for FEA model.
- **Update DAC process model incorporating the novel sorbent/contactor combination and start work on the TEA.**

Project Steps – BP2
Scale-Up of Linear-Poly(propyleneimine) (l-PPI)

BP2 activities (9/15/2022 – 9/14/2023)

- **Optimize the substrate for l-PPI.**
  - Refine and apply the FEA single-channel monolith model to optimize substrate properties and improve performance.
  - Measure CO_2 adsorption / desorption equilibria and diffusive transport rates for the optimized porous metal-oxide PPI supported materials, to refine the FEA single-channel monolith model.
- **Run "optimized" bench-scale DAC test for monolithic l-PPI.**
  - Make optimized substrate and activate full-size monolithic l-PPI part.
  - Complete the bench-scale test.
- **Run oxidative stability testing to validate l-PPI stability.**
  - Update the models (process, single channel monolith) with these data.
- **Finalize the DAC process TEA and LCA for l-PPI.**

Project – Success Criteria

Decision Point	Date	Success Criteria
Completion of BP1	9/14/2022	❑ Adsorption data obtained under DAC relevant conditions for PEI baseline part, under at least two different operating conditions; data consistent with core sorption tester. ❑ Minimum 1 kg of I-PPI. ❑ Capacity of I-PPI > 1.00 (normalized target value basis) on single brick tester. ❑ Optimized substrate for I-PPI: min 20% adsorption capacity improved. ❑ Energy performance calculated from the process model.
Project Completion	9/14/2023	❑ Minimum of 1 full-size I-PPI loaded optimized substrate ready for testing on the single brick sorption tester. ❑ Capacity of I-PPI > 1.20 (normalized target value basis) on single brick tester. ❑ Oxidative stability of I-PPI validated, per State Point Data Table. ❑ Transport data obtained from at least 2 different methods show < 50% variation. ❑ The TEA/LCA show advantages of I-PPI-based DAC systems vs. PEI-based DAC systems.

Project – Risks and Mitigations

- **Risk 1: bench-scale test unit doesn't work properly.**
  - Mitigation: CORMETECH had extensive experience with unit design.
  - **Status: complete.** Data are in good agreement with core test unit.
- **Risk 2: l-PPI produced by sub-contractor is of poor quality.**
  - Mitigation: Global Thermostat set quality specifications for vendor.
  - **Status: complete.** Material produced met quality specifications.
- **Risk 3: only 1kg of l-PPI was produced by sub-contractor.**
  - Achieved target amount (min 1kg), but it's a limited, precious supply.
  - **Status: complete for BP1.** One full-size part has already been made, with ~0.5kg in-process, and the part itself consuming ~0.15kg.
  - **Mitigation: conserve, and reuse, the l-PPI as much as feasible.**

Single Brick Sorption Tester (SBST)
Bench-Scale Test Unit

Test Cycle: Air Adsorption → Vacuum Purge → Steam Injection → Vacuum Purge.

Fully-automated test unit.

Low-range analyzers (inlet, outlet) for air stream analysis.

High-range analyzer for product stream analysis.

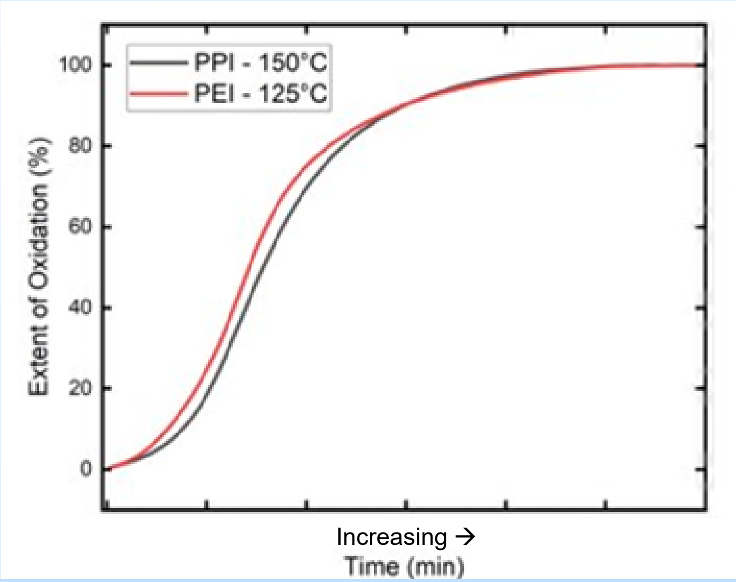
Mass spectrometer for fast transient analysis (steam out); acquired for this project.

Commissioning completed: validated using standard PEI monolith part.

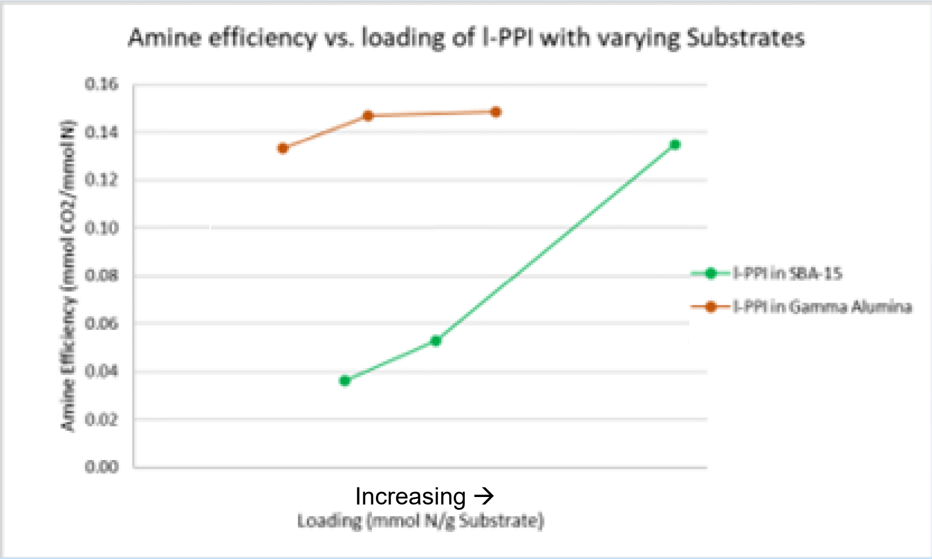
Initial Project Testing of l-PPI

Baseline Data for Large-Batch Validation

- **Initial testing of lab-scale l-PPI selected for scale-up:**
  - Confirmed significant oxidative stability benefit of l-PPI over PEI (+25^{o}C).
  - Confirmed CO_2 adsorption capacity is in expected range.



Isothermal DSC oxidative stability test



CO_2 adsorption capacity test

1kg L-PPI Batch from Vendor
(Subcontracted by Global Thermostat)

Table shows quality assurance tests run by vendor before shipment; all tests passed spec.

Parameter	Method
Appearance	Visual inspection
Average Molecular Weight	Calculated on NMR
Identity	^{1}H-NMR
Identity	ATR-IR
Purity	SEC-HPLC RI-Detection
Metals	ICP-MS
Amine content	Conductometric titration
Drying Loss	Extra Drying at 80°C, 5 mbar

- **GT and GTRC** are performing additional validation tests on a small aliquot of the large batch l-PPI (will be completed by end of BP1).

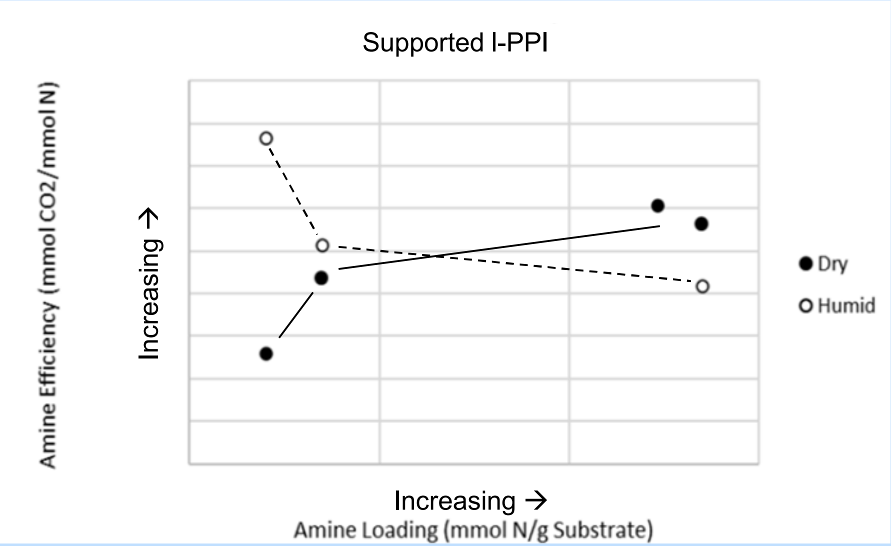
- Data will be compared to previous lab-scale synthesized l-PPI material.

- The data collected to date indicate the large-batch l-PPI is good material.

l-PPI Test Data:
Impact of Adsorption Air Moisture Content

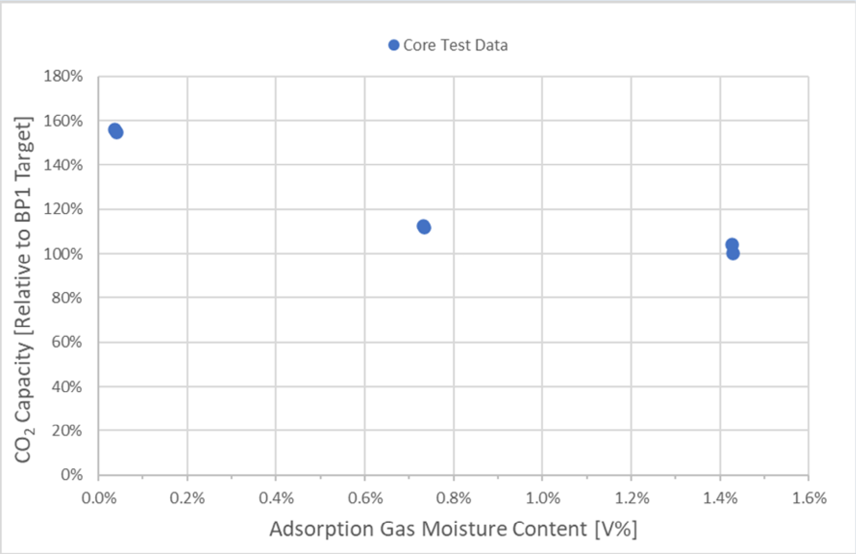
- **Impact of moisture on CO_2 adsorption capacity varies with the PPI loading: promotes at low load, inhibits at higher load.**

Humid TGA data from Global Thermostat



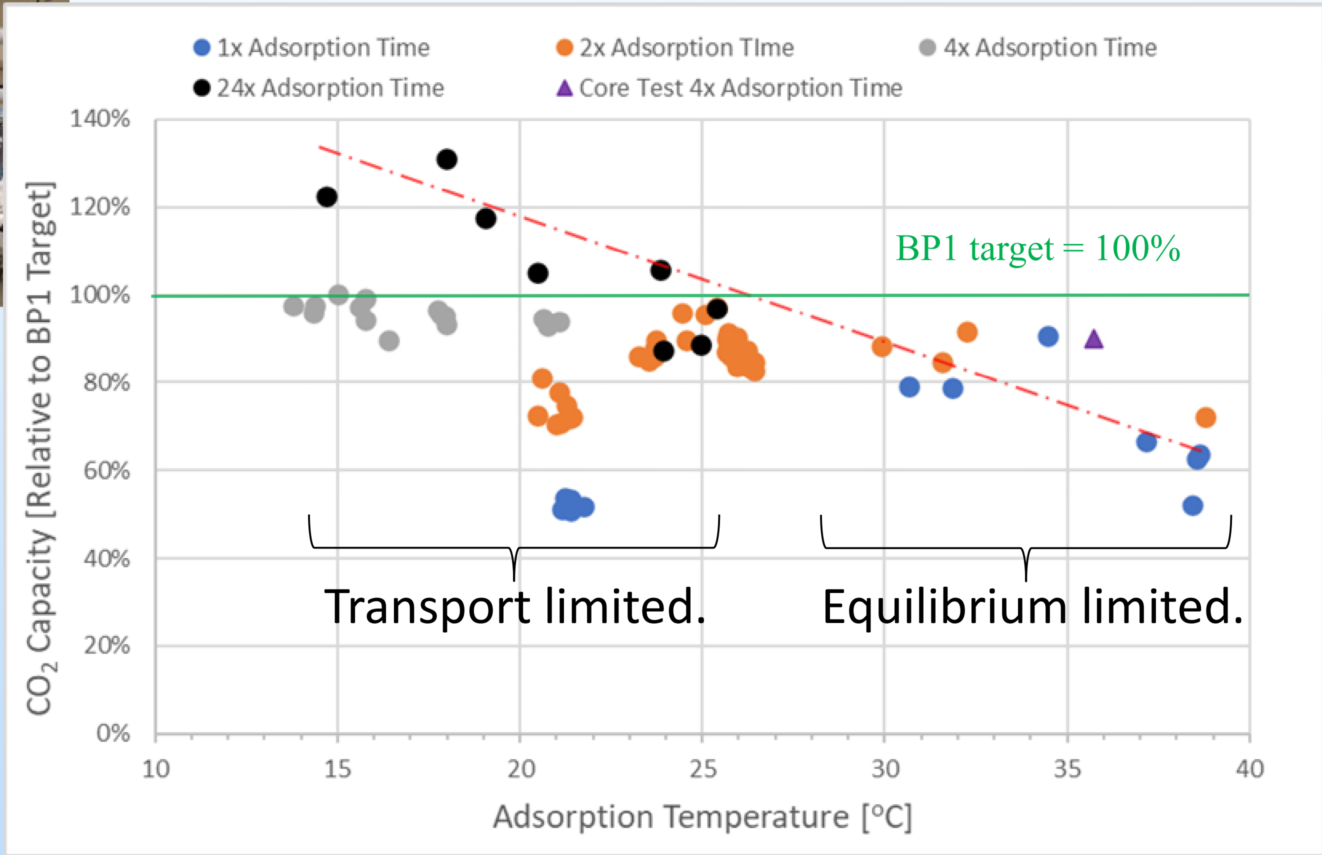
The humid TGA was acquired for this project.

Core sample data from Cormetech



SBST Data for 1-PPI Monolith Part
(Standard Monolith Substrate)

The BP1 performance target has been achieved!
(H_2O content of air feed ranged from 1.0-1.9v%)



Clear opportunity to optimize for PPI:

- Substrate properties
- Amine loading

Core sample data (corrected to same PPI loading) is consistent with SBST data.

Synergy Opportunities

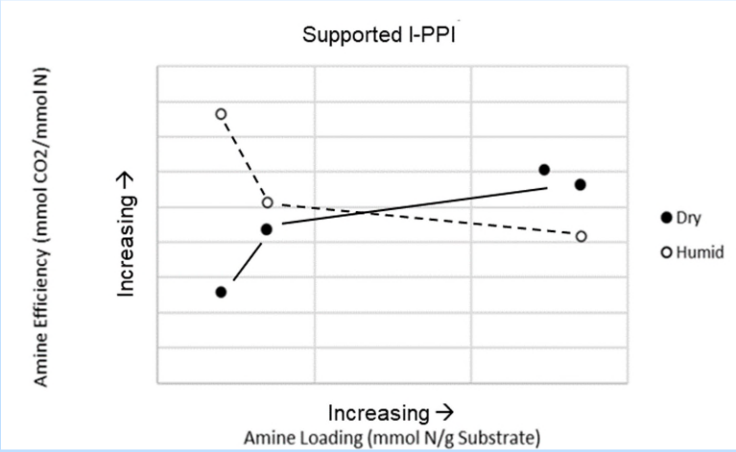
- Fundamentals: Structure / Property Relationships
  - Adsorption/desorption isotherms (Global Thermostat)
  - Diffusive transport (Georgia Tech)
  - Single-channel monolith model (Cormetech)

- Monolith Prototyping
  - Batch and extrude monolith prototypes at Cormetech, with structures optimized for l-PPI (from Fundamentals).

- Monolith Testing
  - Test of optimized l-PPI monolith at Cormetech on SBST.

Adsorption/Desorption
Testing and Model Development

- Measuring CO_2 adsorption isotherms for supported l-PPI under dry and humid conditions.
- Adsorption model → incorporating into the COMSOL single channel monolith model.
- Supports substrate optimization work.



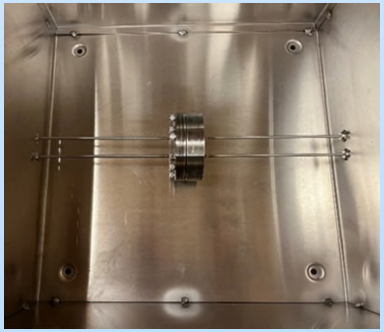
Diffusive Transport
Testing and Model Development

- Measuring CO_2 diffusion rates through l-PPI supported on model and porous substrates.
- Diffusion model → incorporating into the COMSOL single channel monolith model.
- Supports substrate optimization work.

Georgia Tech

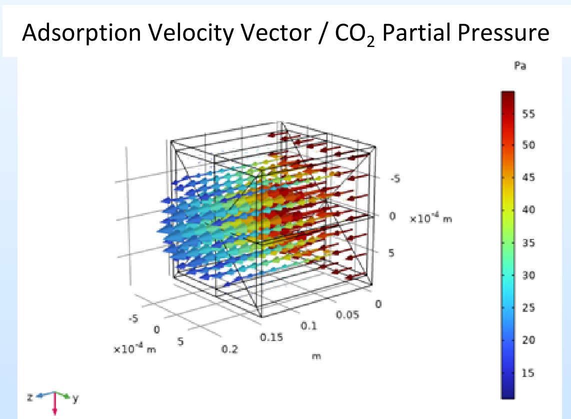
Wicke-Kallenbach membrane diffusion cell

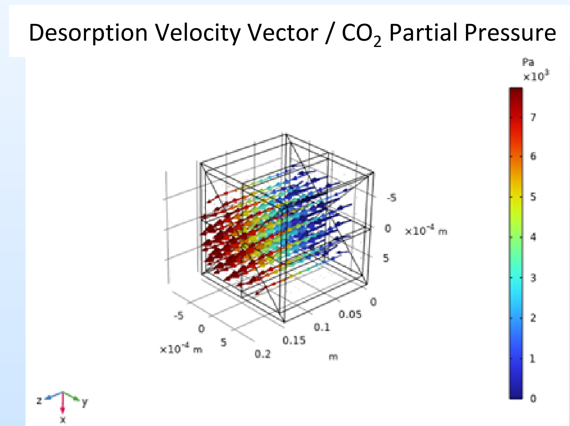





Single Channel Monolith Model
Development and Simulation

- **Model incorporates flow, pressure, temperature, reaction, and transport, with steam as heating medium for desorption.**



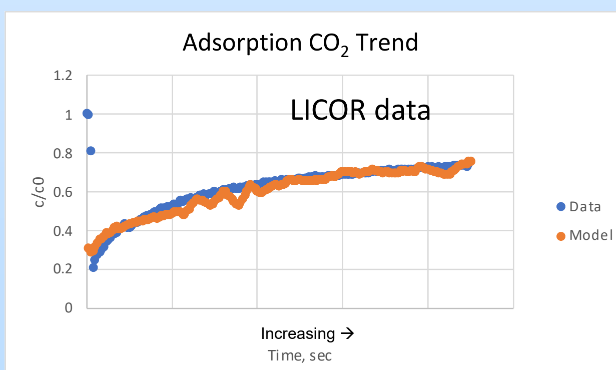


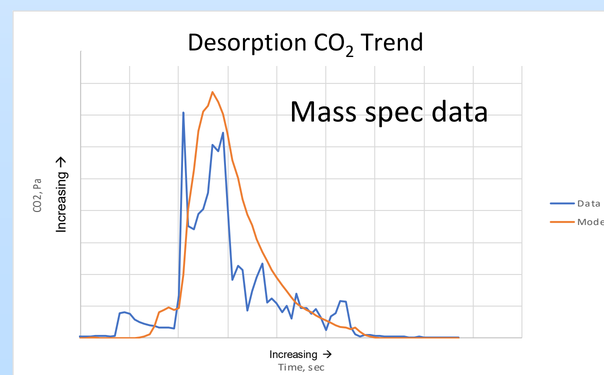
COMSOL platform

Simulation profiles

CORMETECH
RELIABILITY. DELIVERED.

Simulation vs. SBST data





Next Steps
Testing/Development/Commercialization

- In this project:
  - BP1 review meeting is scheduled for August 29, 2022.
  - BP2 work activities:
    - Optimize monolith substrate for l-PPI.
    - Make and test the optimized prototype on the SBST.
    - Run oxidative stability testing for l-PPI and update models.
    - Complete DAC process TEA and LCA for l-PPI.
- After this project:
  - Engineering-scale demonstration for PPI.
    - Depends on feasibility & cost of upscaling l-PPI synthesis.

Summary

- L-PPI supported on a monolithic substrate has been synthesized and tested on the bench-scale, achieving the BP1 CO_2 adsorption capacity target.

- Further work in BP2 will tailor the monolith substrate properties to optimize l-PPI performance.

- Monolithic l-PPI is a promising Next Gen adsorber material for the Global Thermostat DAC process.

Appendix

Organization Chart – Participants

Prime Recipient

CORMETECH
RELIABILITY. DELIVERED.

Christopher Bertole (PI) – Director, Product and Applications Development
Gavin MacInnes – Lead Catalyst Development Engineer
Casey Huten – Lead R&D Technician
Travis Jones – Manager, Product and Applications Development Laboratory
Sam Richardson – R&D Scientist
James Altizer – Director, Product and Manufacturing Development
Colby Burtt – Lead Process Development Engineer

Sub-Recipient

Georgia Tech

Chris Jones – John F. Brock III School Chair & Professor
Ryan Lively – Associate Professor
Antonio Vallace – Postdoctoral Research Fellow

Sub-Recipient

Global Thermostat
The Carbon Negative Solution

Eric Ping – VP, Technology Development
Miles Sakwa-Novak – Director, R&D
Cassandra Hertz – Research Scientist II
Yanhui Yuan – Sr. Development Engineer
Abby Clabaugh – Development Engineer
Joanie Racicot – Research Scientist

Organization Chart – Project Efforts

Prime Recipient

CORMETECH
RELIABILITY. DELIVERED.

- ❑ **Bench-scale test unit (SBST) design, build, and commissioning**
- ❑ **Full-size l-PPI monolith impregnation and CO_2 capacity testing**
- ❑ **Single channel monolith modeling for optimization**
- ❑ **Monolith porous substrate optimization and prototype extrusion**

Sub-Recipient

Georgia Tech

- ❑ **l-PPI validation testing**
- ❑ **CO_2 diffusion rate measurements**
- ❑ **Transport modeling**

Sub-Recipient

Global Thermostat
The Carbon Negative Solution

- ❑ **l-PPI procurement and validation testing**
- ❑ **CO_2 adsorption/desorption measurements**
- ❑ **Adsorption modeling**
- ❑ **l-PPI oxidative stability testing**
- ❑ **TEA and LCA**

Project Schedule – Gannt Chart