Development of Advanced Solid Sorbents for Direct Air Capture

Project Number: DE-FE0031954

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RTI International

U.S. Department of Energy

National Energy Technology Laboratory

Carbon Management and Natural Gas & Oil Research Project Review Meeting

Virtual Meetings August 18-19, 2021

Program Overview

a. Funding: DOE:

   a. $800,000 Cost-Share: $200,502

b. Overall Project Performance Dates:

   a. 10/01/2020 – 03/31/2022

c. Project Participants:

   a. RTI International (Prime)

   b. Mohammed VI Polytechnic University (UM6P)

   c. Creare LLC.

d. Overall Project Objectives:

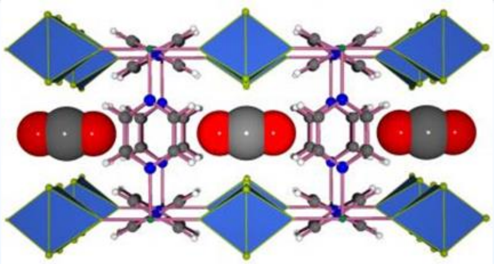
   a. Development of two novel materials: metal organic frameworks (physisorption) and amine-based dendrimers (chemisorption), for direct air capture of CO_2.

   b. Select the best performing material based on technical merit comparison

   c. Scale-up and cost review of the selected candidate

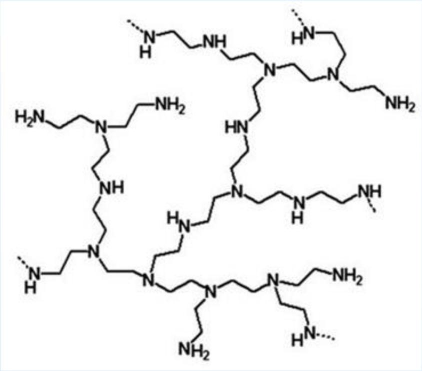
   d. Preliminary process design

Technology Background



Physisorbent Materials
"MOF"

Chemisorbent Materials
"PEI"



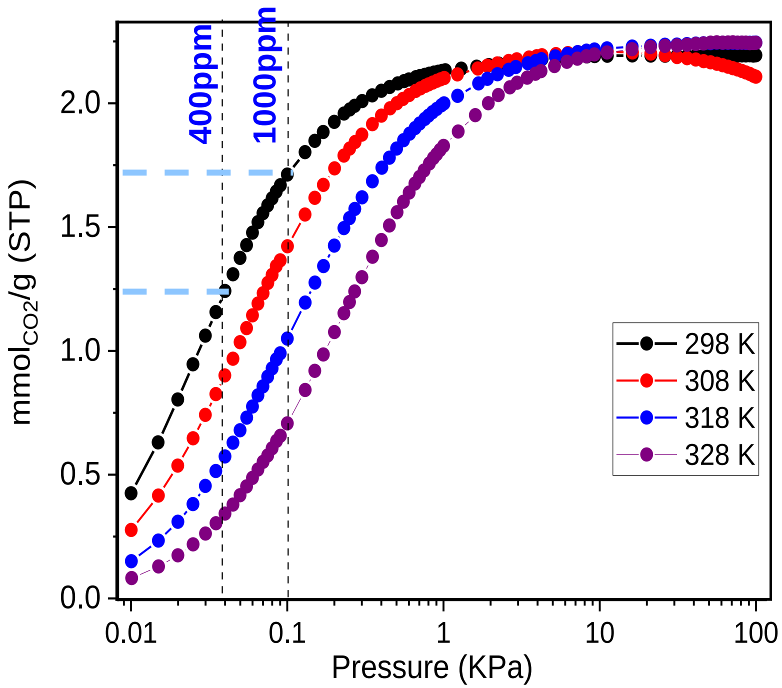
DAC Through Sorbent-Based Processes

- **Performance under DAC conditions**
- **Cost & Scalability**
- **Contaminant's tolerance**
- **Long-term performance**

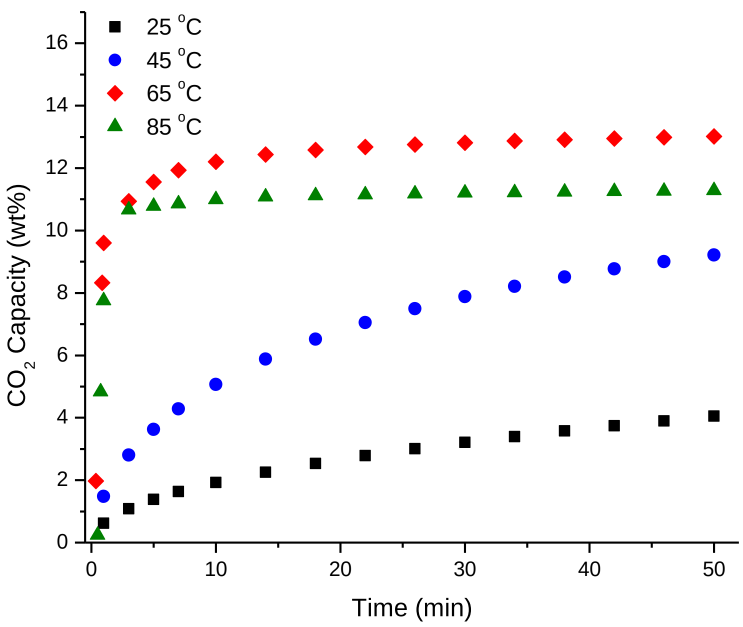
Technology Background

The most significant technical challenge with DAC is the very low atmospheric concentration of CO_2 (currently 415 ppm), thereby requiring sorbents that bind CO_2 strongly and selectively against other components in the air (i.e., nitrogen, water, oxygen, etc.).

Physisorption*: MOF*-Based Sorbent for DAC



Chemisorption*: Amine*-Based Sorbent for DAC

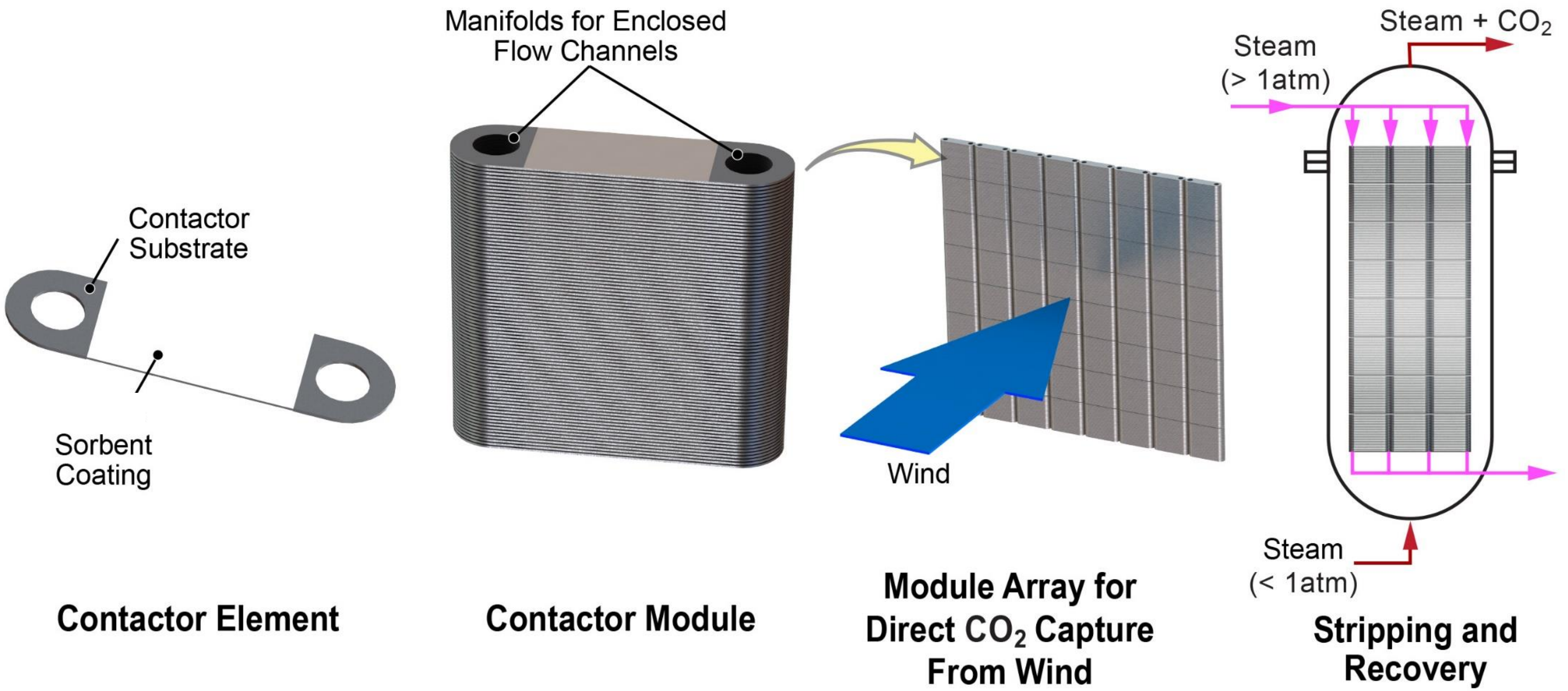


a. **Advantages**: Low-cost sorbents and strongly and selectively bind CO_2

b. **Challenges**: Performance under the presence of contaminants and scale-up

DAC Concept

Innovative contactor and high-performance sorbent will enable a wind-driven process for DAC



Technical Approach/Project Scope

A. Experimental design and work plan

a. Sorbents synthesis, characterization and CO_2 testing using TGA and packed bed reactor at different relative humidity's
b. Air-gas contaminants evaluation
c. Long-term sorbents CO_2 testing
d. CFD simulations of the sorbents
e. Kinetics, heat and mass transfer data for reactor design
f. Sorbent scale-up and cost evaluation
g. Preliminary process design

B. Key milestones

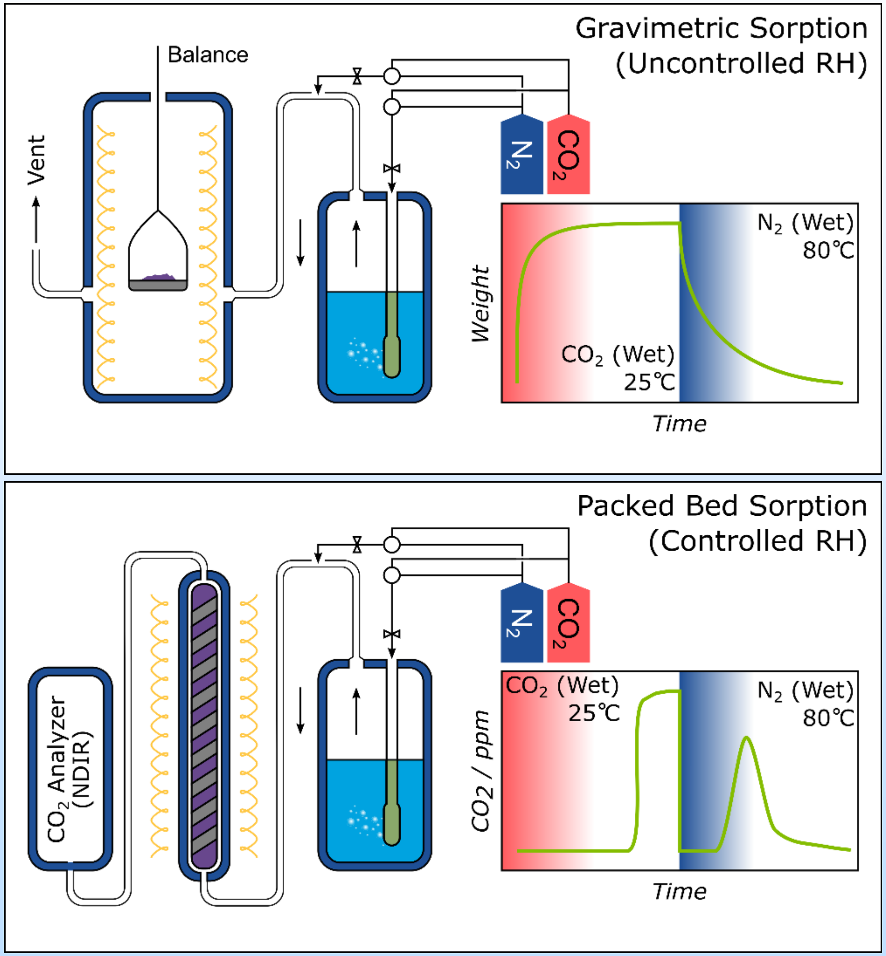
a. Identify one MOF adsorbent and one amine adsorbent for DAC
b. Perform CFD simulations of the MOF and amine adsorbents and validate them with experimental data
c. Select one adsorbent for DAC
d. Demonstrate the scale-up of selected candidate and perform cost review evaluation
e. Perform a preliminary process design

C. Success criteria

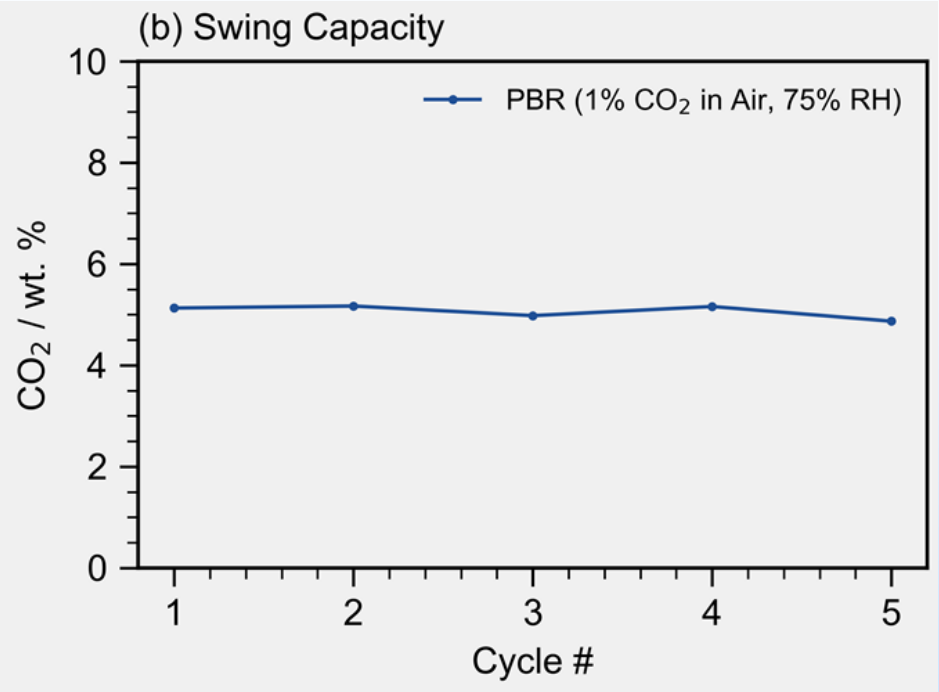
a. Demonstrate that the two novel materials, improve DAC cost, performance, and efficiency.
b. Demonstrate that selected adsorbent has cost-effectiveness, longevity, high CO_2 capacity, improved mass and heat transfer, and integration in a multichannel monolith-type reactor

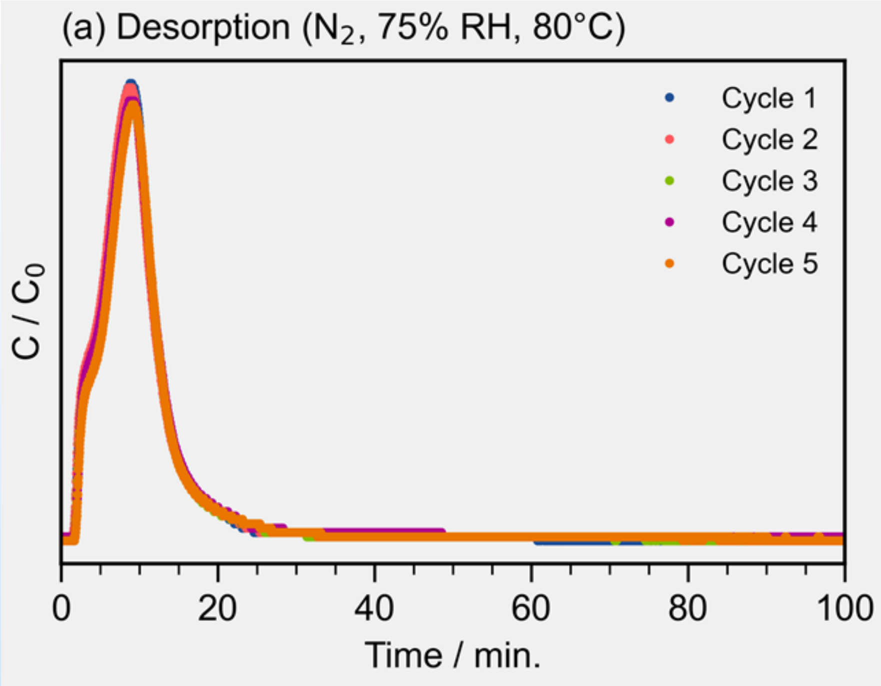
DAC Experimental Set Up

- Thermogravimetic Experiment
  - Wet or Dry conditions
  - Approx. 74% RH
  - CO_2:H_2O uptake estimated
- Packed Bed Experiment
  - Tunable RH (75%)
  - CO_2:H_2O uptake determinable
  - Longer Experiment (3x)
- **Samples activated at 120 °C**
- **Adsorption at 25 °C**
- **Desorption at 80 °C**



Packed Bed CO_2 Capture in MOF_1

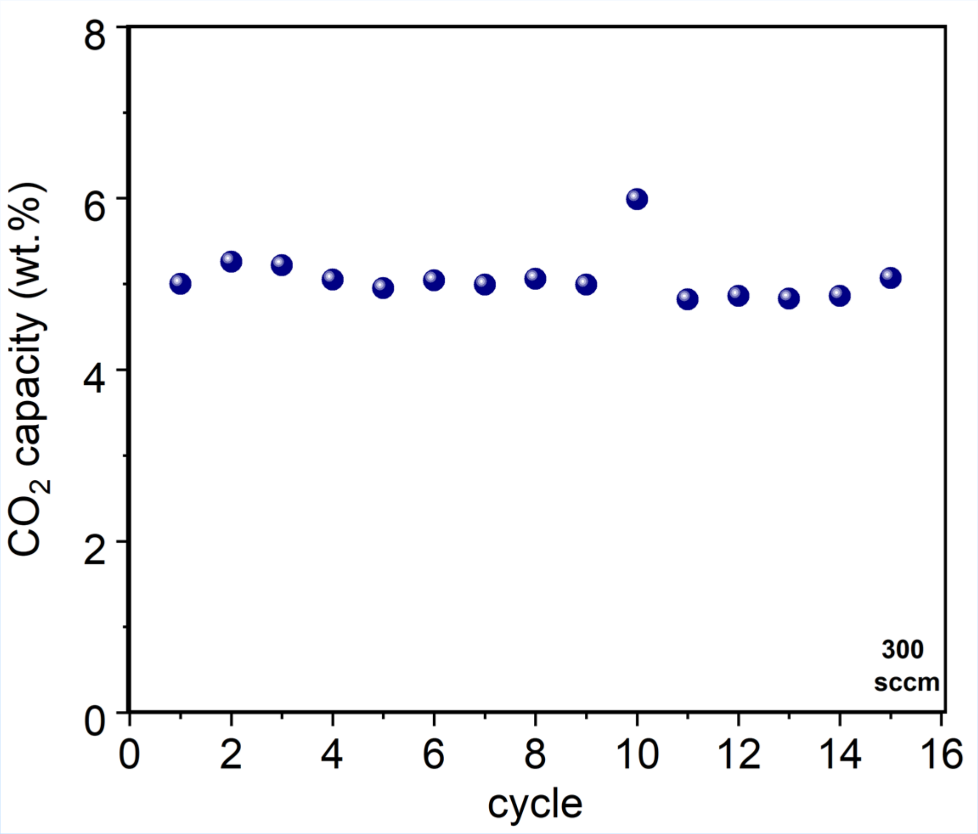


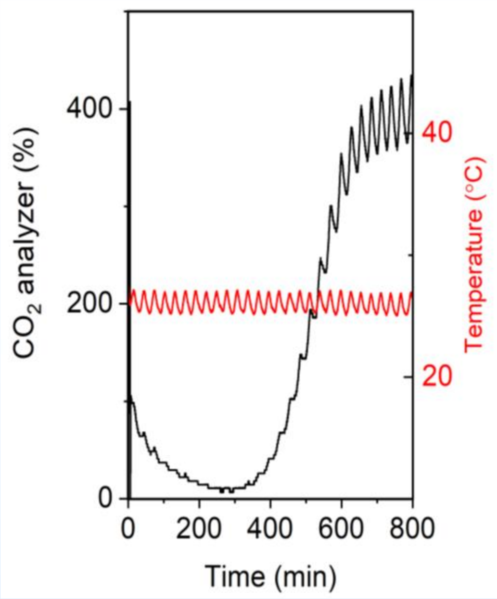


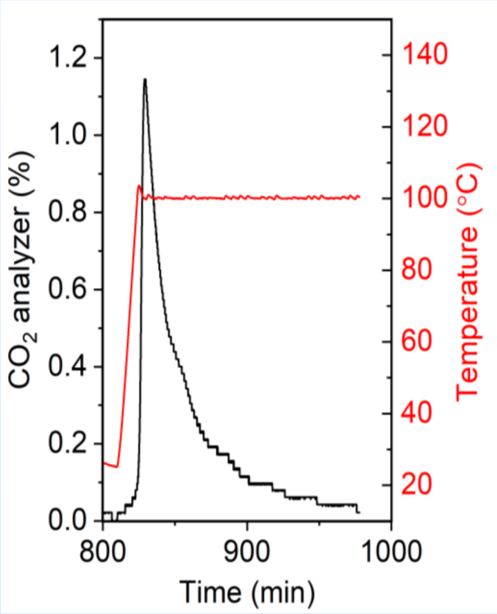
5.1 wt% CO_2 deliverable from 1% CO_2 in Air at 75% RH

Packed Bed CO_2 Capture in MOF_1

Adsorption: Compressed air 25 ˚C (400 ppm CO_2, 1600 ppm water)
Regeneration: N_2 100 ˚C

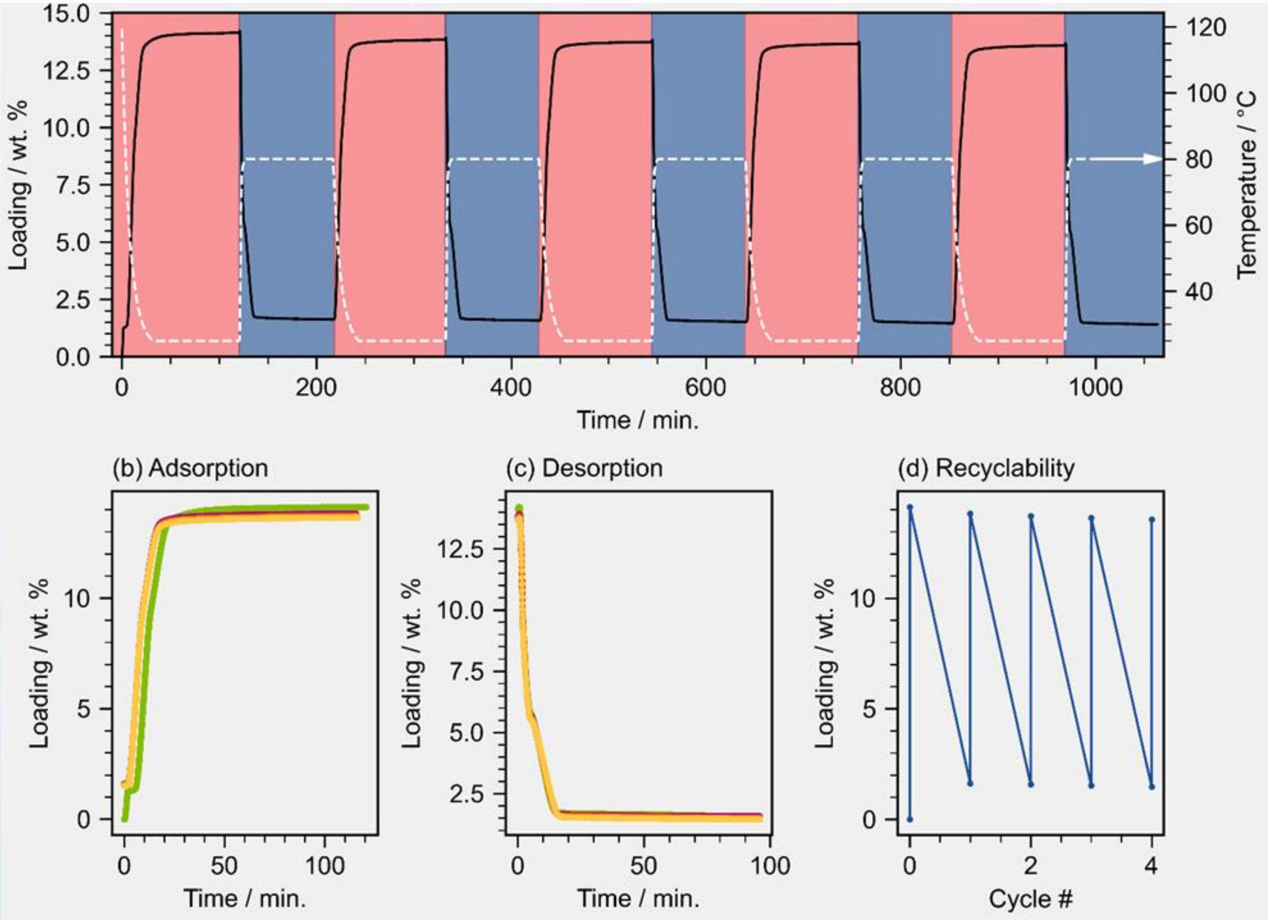






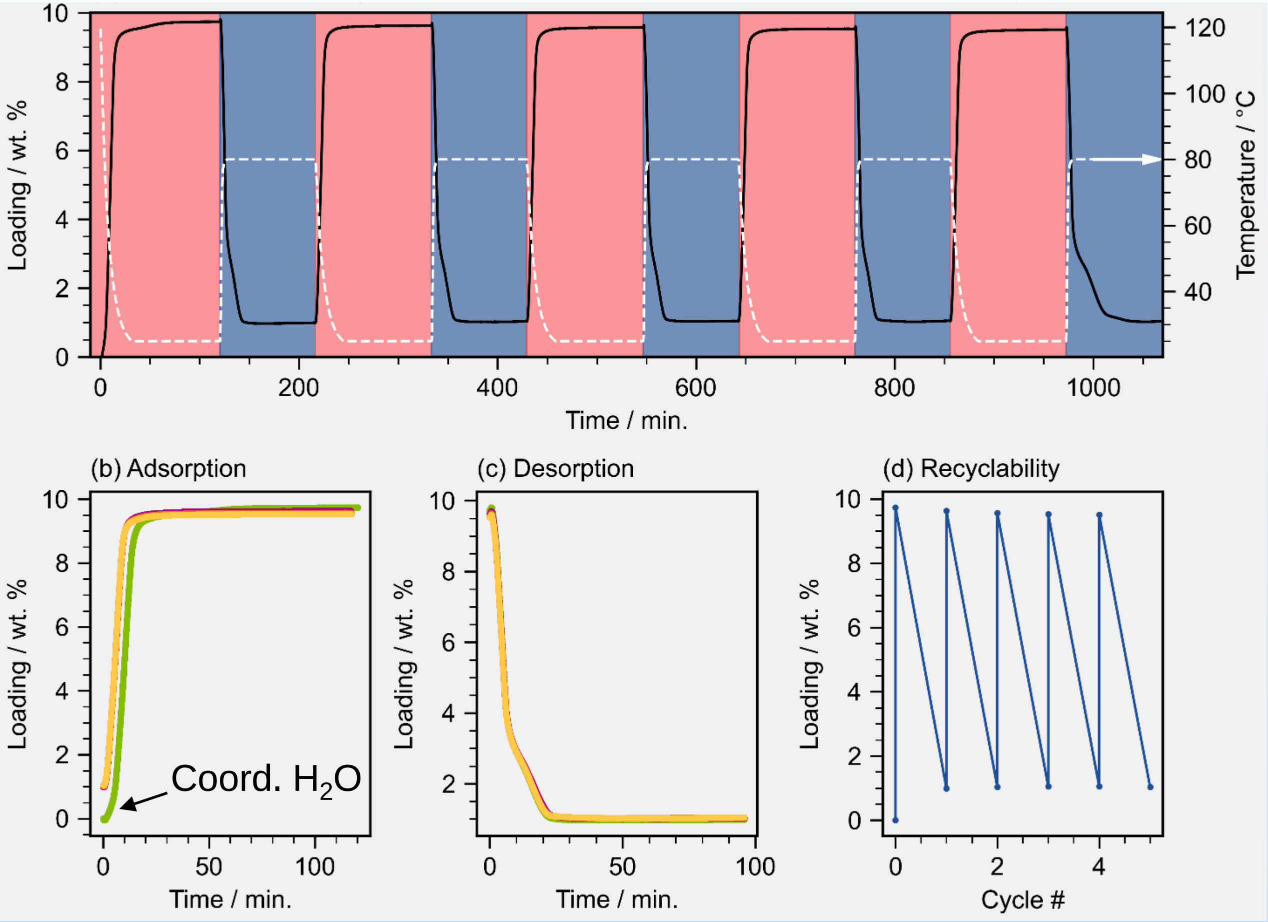
MOF_2 (1000ppm CO_2; 74% RH)

- Adsorption
  - 13.5 wt. %
  - 20 mins
- Desorption
  - 11.9 wt. %
  - 20 mins
- Swing Capacity
  - 0.89
- Cycle time
  - 40 mins



MOF_3 (1000ppm CO_2; 74% RH)

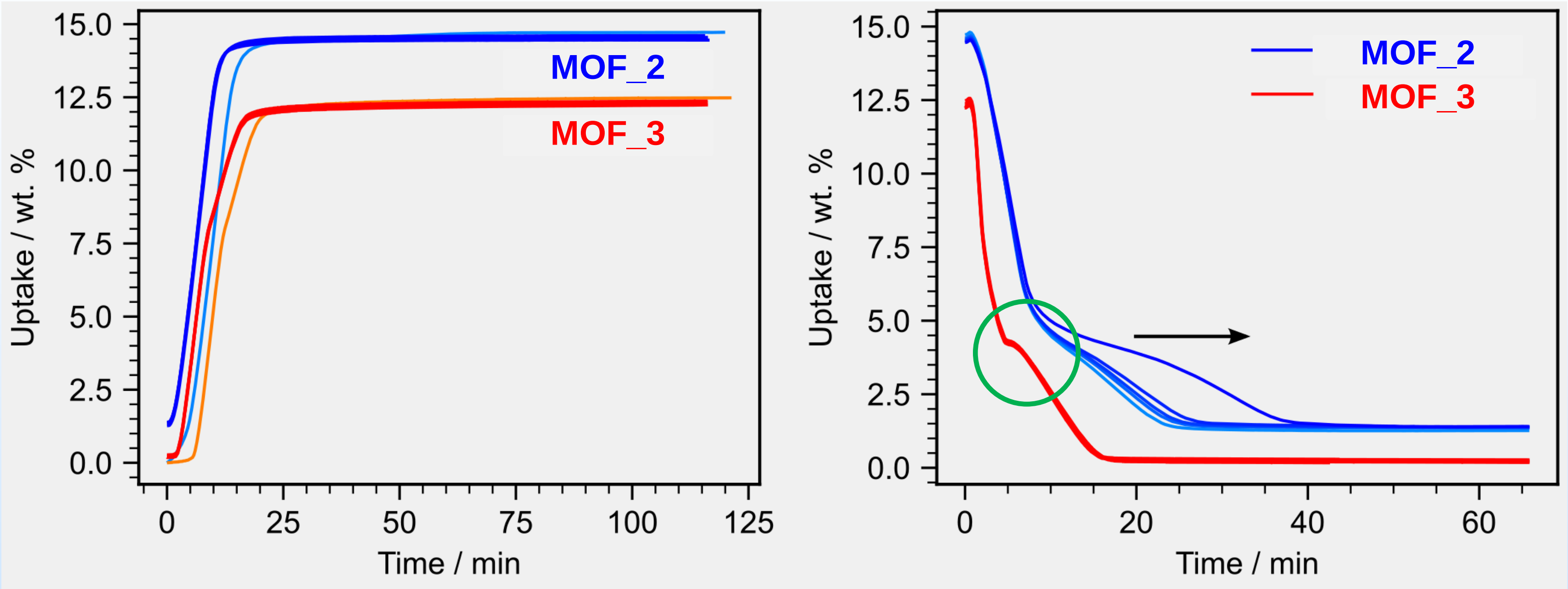
- Adsorption
  - 13.5 wt. %
  - 20 mins
- Desorption
  - 11.9 wt. %
  - 20 mins
- Swing Capacity
  - 0.89
- Cycle time
  - 40 mins



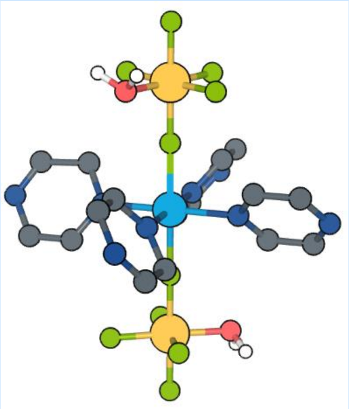
Kinetics under DAC Conditions

Adsorption: 400 ppm, 25 ^oC, 75%RH

Desorption: N2, 80 ^oC, 75%RH



- Both materials exhibit a stepped desorption profile
- **MOF_2** exhibits near complete recycling
- **MOF_3** desorption time increases during cycling



Open metal sites

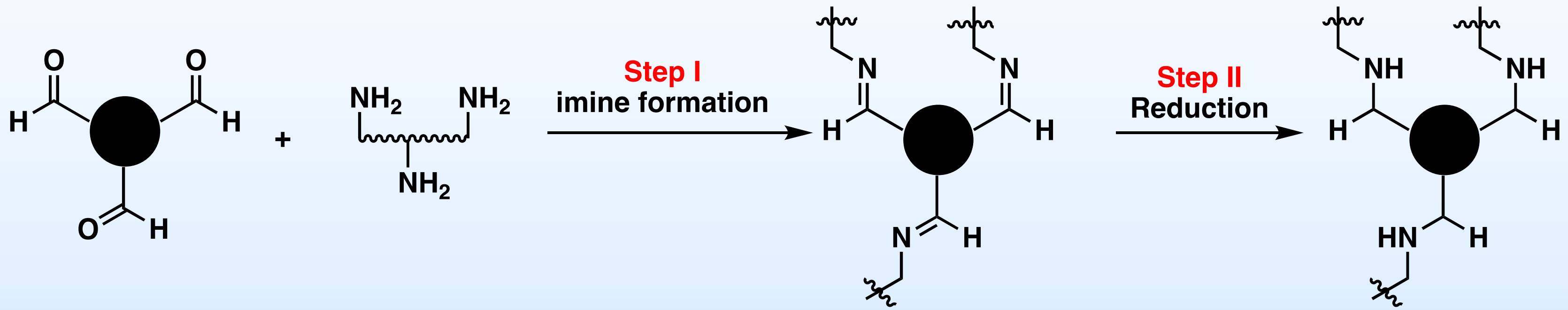
We are in the process of performing DRIFT experiments for these materials to evaluated adsorption competition between water and CO_2 in N_2.

Polyamine *P*-Dendrimer Sorbent Preparation

Two-step's synthesis (reductive amination):

Step-1: Condensation reaction of hexa-aldehyde polyamine (imine formation)

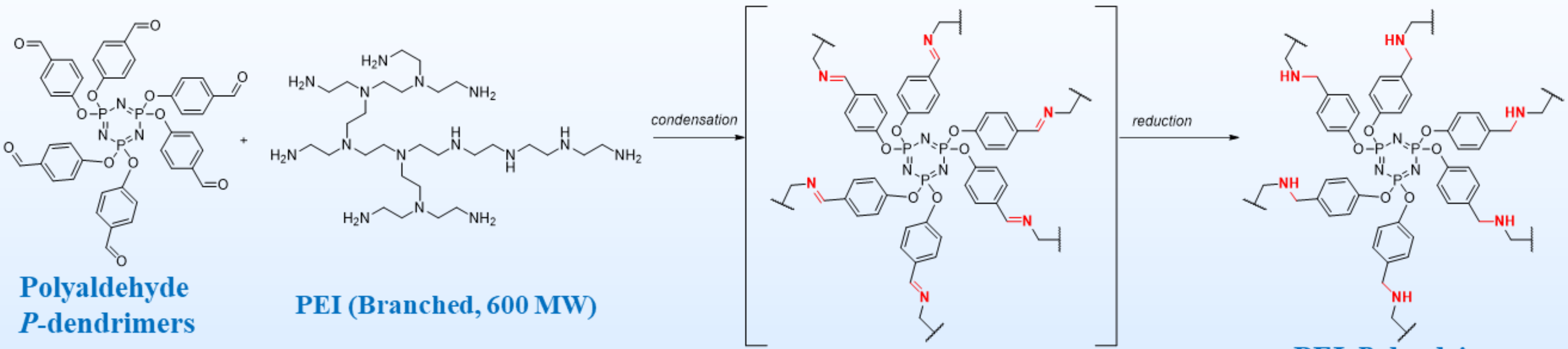
Step-2: Reduction of amine yielding amine



- ❖ ***P*-Dendrimer-based sorbents synthesis and development**
  - ➢ 3 *P*-Dendrimers for DAC were synthesized and tested (short-chain ethylenediamine, 600 MW PEI, and 10,000 MW PEI) and the best performing sorbent was with 600 MW PEI
  - ➢ Determine CO_2 swing capacity and optimal DAC conditions

- ❖ ***P*-Dendrimer-based sorbents evaluation and optimization**
  - ➢ Highest CO_2 loading at 400 ppm
  - ➢ Best CO_2/N_2, CO_2/H_2O selectivity
  - ➢ Fastest kinetics @ lowest temp.
  - ➢ Low regeneration temp.(e.g., 80 ^oC)
  - ➢ Thermal, chemical, physical stability

Polyamine *P*-Dendrimer Sorbent Preparation



Polyaldehyde *P*-dendrimers

PEI (Branched, 600 MW)

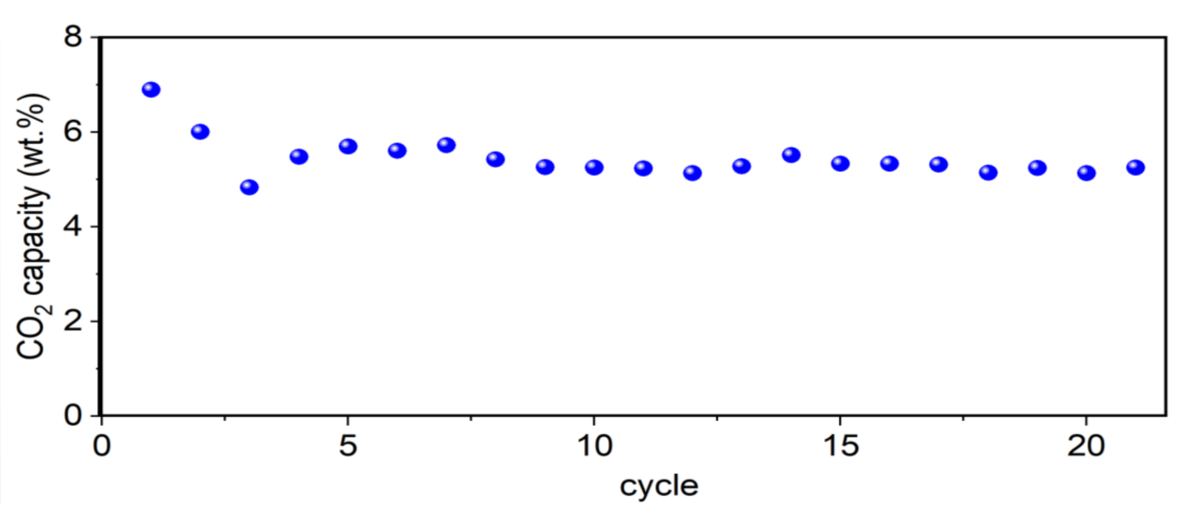
PEI-*P*-dendrimers

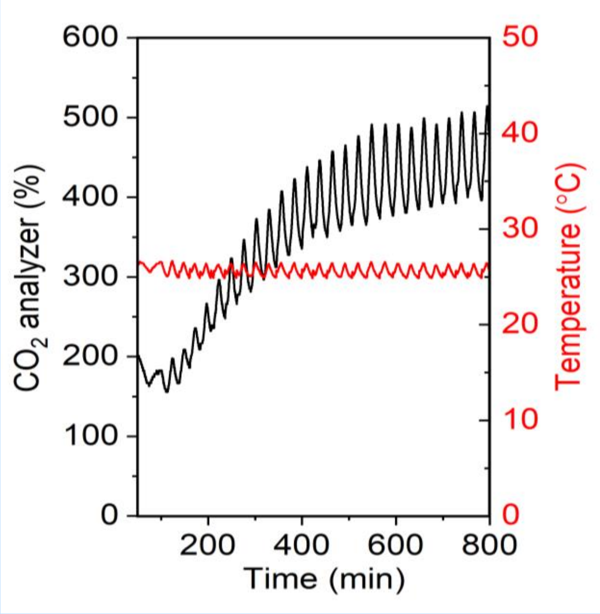
- **Sorbent has been prepared on 50 g scale in 91% yield**
- **Optimized conditions for 1-pot, 2-step reaction:**
  - **2:1 ratio of PEI to *P*-dendrimer**
  - **Condensation solvent: THF**
  - **Reduction solvent: THF/MeOH (2:1)**
  - **Reductant: $NaBH_4$**

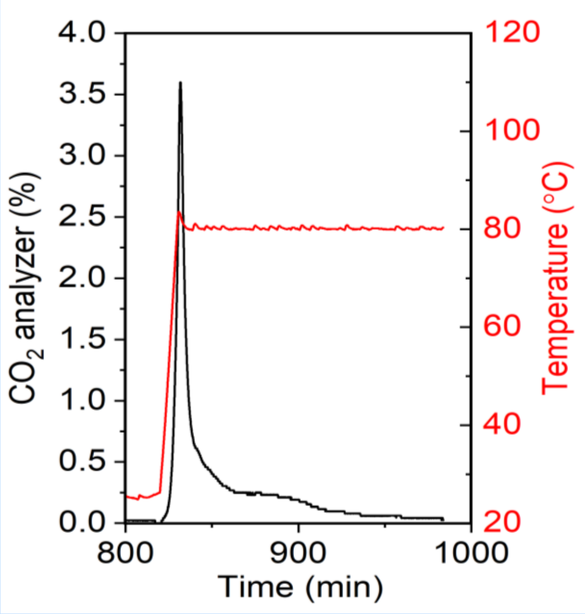
P-Dendrimer Sorbent Performance Under DAC Conditions

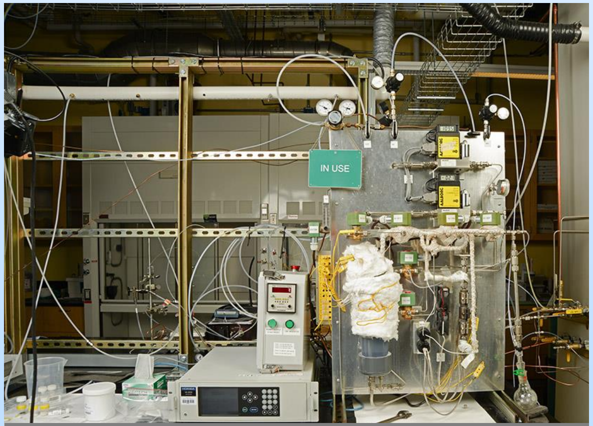
Packed-bed reactor data:

- ***Adsorption*: 300 mL/min compressed air 25 ˚C (400 ppm CO_2, 80% RH)**
- ***Regeneration*: 150 mL/min N_2, 80% RH, 80 ˚C**







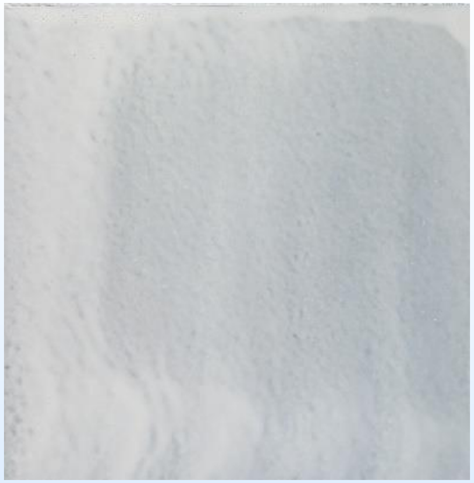


Packed Bed Reactor

P-Dendrimer Coating and Assessment

6 x 6 in. Plate

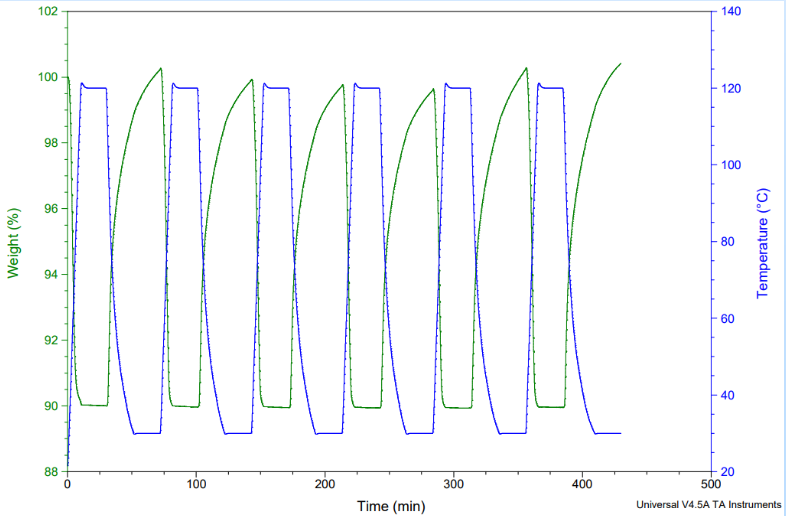
i. Sanding
ii. Primer

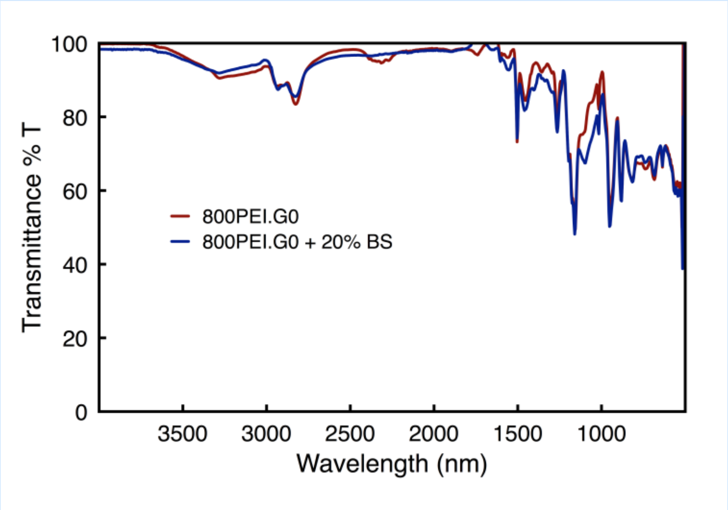


Coating

20 wt% BS + 80 wt% P-dendrimer

11.53 wt.% CO_2 adsorption at 1 bar CO2 and rt. of the coating formulation





Plans for Future Testing & Development

Future testing/development

- ❖ Mass and heat transfer considerations for reactor design
- ❖ Long-term sorbents CO_2 testing
- ❖ Air-gas contaminants evaluation
- ❖ Sorbent scale-up and cost evaluation

After this project

RTI International and its partner Creare have been selected to design, fabricate, and test a bench-scale contactor for DAC.

Summary Slide

- High-capacity, fast kinetics, robust cycling, facile/cheap synthesis procedures and easy scalability are key criteria for selecting DAC material

- Ultra-microporous fluorinated MOFs offer fast sorption kinetics to enable selective capture of CO_2 over both N_2 and H_2O (low %RH), making them prototypal for a previously unknown class of physisorbents that exhibit effective trace CO_2 capture under both dry and humid conditions.

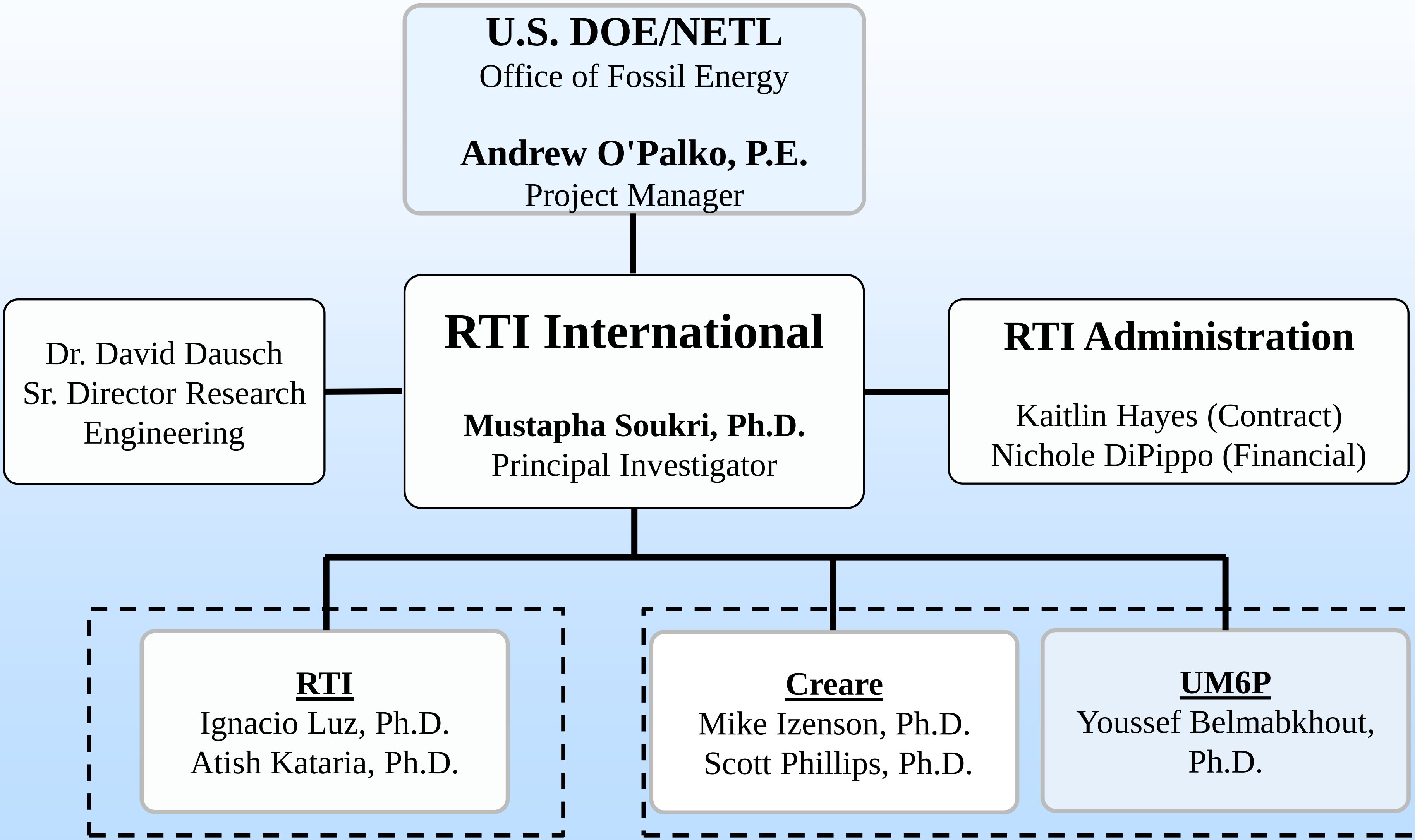
- The *P*-Dendrimer amine-based sorbents were found to perform very well under DAC conditions regardless of the concentration of water vapor in air (e.g., %RH).

→ Novel contactor design and advanced structured material that will capture CO_2 in an energy efficient way with low pressure drop

Appendix

– These slides will not be discussed during the presentation but are mandatory.

Organization Chart



Organization Chart (1)

The Roles of Team Members

Specific Project Roles	Lead Member	Support Member
➢ Project management and planning ➢ MOFs synthesis, characterization and CO_2 testing ➢ P-dendrimers synthesis, characterization and CO_2 testing ➢ Sorbents optimization ➢ Lab-scale reactor CO_2 testing ➢ Long-term sorbents CO_2 testing ➢ Air-gas contaminants evaluation ➢ Sorbent scale-up and cost evaluation ➢ Technology EH&S Risk Assessment ➢ Technology maturation plan	**RTI International**	**UM6P & Creare**
➢ MOFs design and synthesis ➢ MOFs characterization and CO_2 testing	**UM6P**	**RTI International**
➢ CFD simulations of the MOF and P-dendrimer sorbents ➢ Mass and Heat Transfer Considerations for Reactor Design ➢ Kinetics, heat and mass transfer data analysis ➢ Process design and analysis	**Creare**	**RTI International**

Gantt Chart

Project Schedule	2021												2022					
	Q1			Q2			Q3			Q4			Q5			Q6		
Task 1.0: Project Management and Planning	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Task 2.0: Development of MOF-based CO_2 Adsorbents	■	■	■	■	■	■	■	■	■									
Subtask 2.1: MOF-based sorbents synthesis and development	■	■	■	■	■													
Subtask 2.2: MOF-based sorbents evaluation and optimization						■	■	■	■									
Task 3.0: Development of P-Dendrimer Based Adsorbents	■	■	■	■	■	■	■	■	■									
Subtask 3.1: P-Dendrimer-based sorbents synthesis and development	■	■	■	■	■													
Subtask 3.2: P-Dendrimer-based sorbents evaluation and optimization						■	■	■	■									
Task 4.0: Mass and Heat Transfer Considerations for Reactor Design				■	■	■	■	■	■									
Task 5.0: Long-term Performance, Contaminants Testing and Technical Merit Comparison										■	■	■	■					
Subtask 5.1: Multi-cycle performance testing of both sorbents										■	■	■						
Subtask 5.2: Contaminant impact testing in packed-bed reactor											■	■	■					
Task 6.0: Cost Review and Scale-up of Selected Candidate														■	■	■		
Subtask 6.1: Preliminary sorbent production cost review														■	■	■		
Subtask 6.2: kilogram-scale production of selected sorbent														■	■	■		
Task 7.0: Preliminary process design															■	■	■	■
Subtask 7.1 – Preliminary review of process requirements															■	■	■	■
Subtask 7.2 – Preliminary process design															■	■	■	■
Reporting			■			■			■			■			■			■
Milestones									■				■			■		■
Project Meeting		■									■						■	

Project Progress **Reporting**
Milestones **Project Meeting**