Amine Infused ePTFE/SiO_2 Laminate Structured Sorbents as an Advanced Direct Air Capture System
FE0032278

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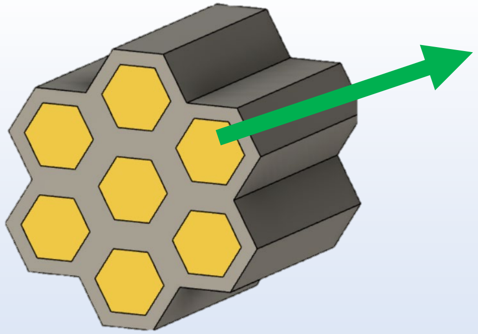
Bench-Scale Research, 4:10-4:25 Monday August 28^{th}

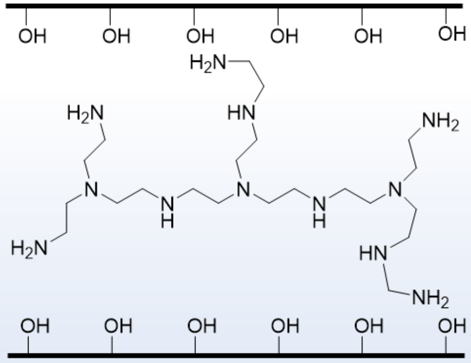
Project Overview

- Funding:
  - Federal share: $1,326,312
  - Cost share: $332,105
- Overall Project Performance Dates
  - 9/1/2023 – 7/31/2025
- Project Participants
  - Georgia Institute of Technology (Jones, Christopher; Realff, Matthew)
  - W.L.Gore & Associates Inc. (Dell, Regina; Beusche, Uwe)

DAC by Solid-supported Amine Sorbents

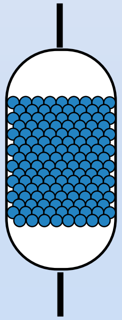
Solid-supported amine sorbents





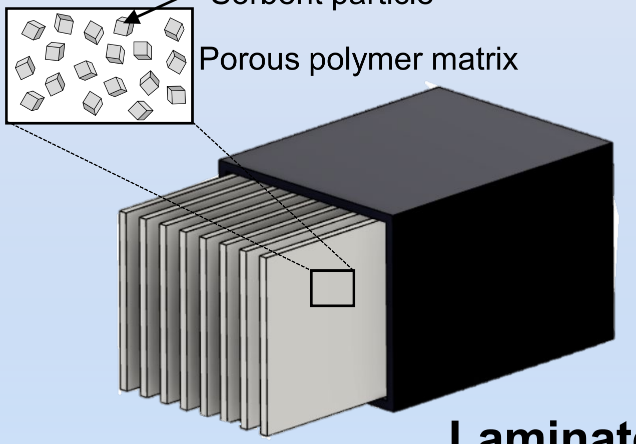
Immobilized amine-bearing polymers

- ❑ **CO_2 adsorption by amine-bearing polymers immobilized on inorganic porous supports**
- ❑ **Requirements for practical DAC applications:**
  - High CO_2 capacity
  - Rapid CO_2 adsorption/desorption kinetics
  - High recyclability under DAC conditions



Fixed bed
lab scale, large pressure drop

This project →



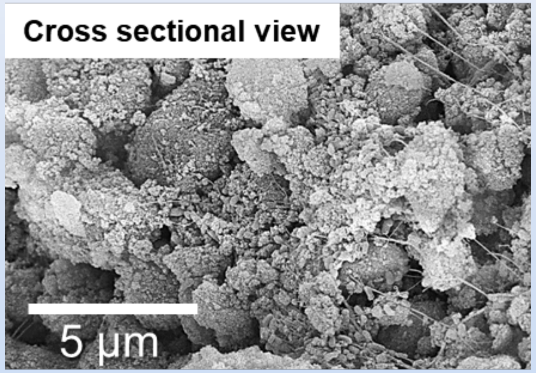
Laminate

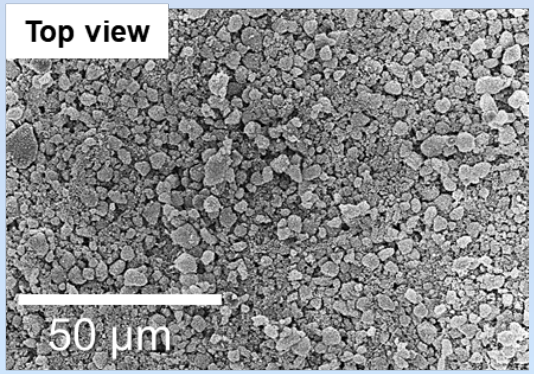
Darunte *et al., ACS Appl. Mater. Interfaces* **2017**, 9 (20), 17042-17050
Lively *et al., Chem. Eng. J.* **2011**, 171 (3), 801-810

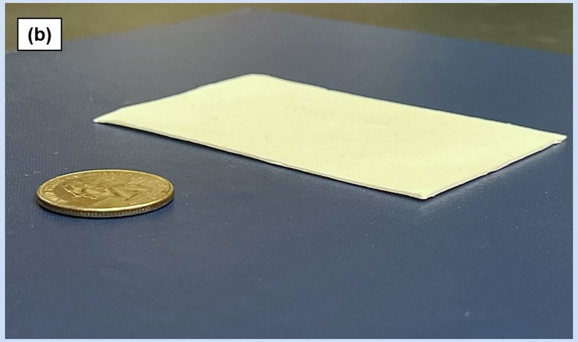
Free Standing Solid-supported Amine Sorbents

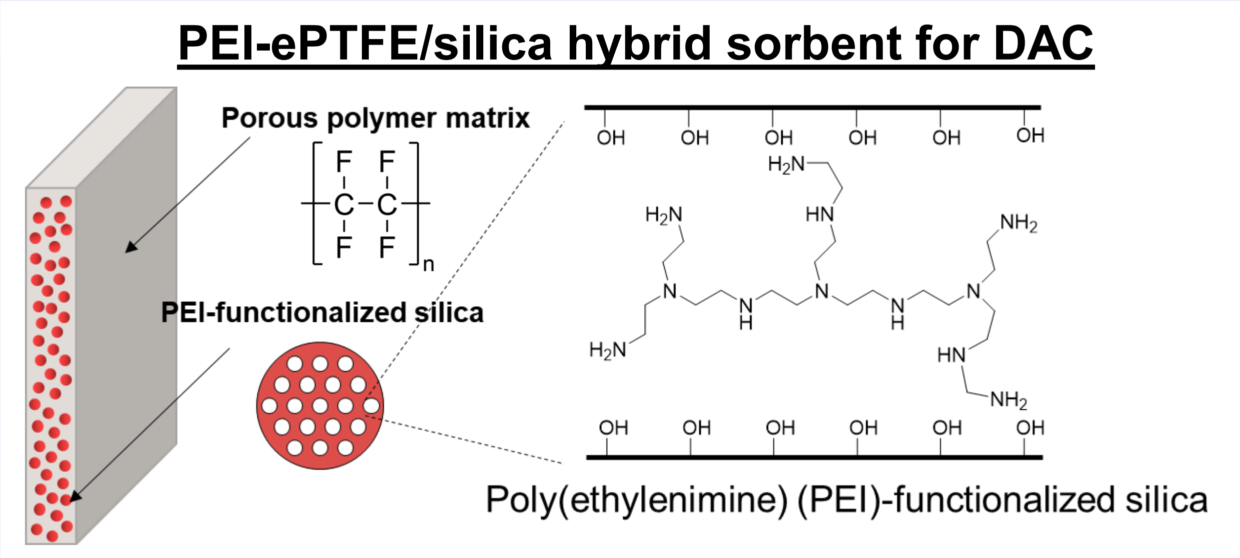
❑ Advantages of polymeric inorganic/organic hybrid sorbents

- High volume-loading of solid adsorbents (silica particles)
- Macroporous polymer – bicontinuous pore network for rapid CO_2 mass transport
- Tunable material properties : thermally stable, tunable porosity & **hydrophobic**

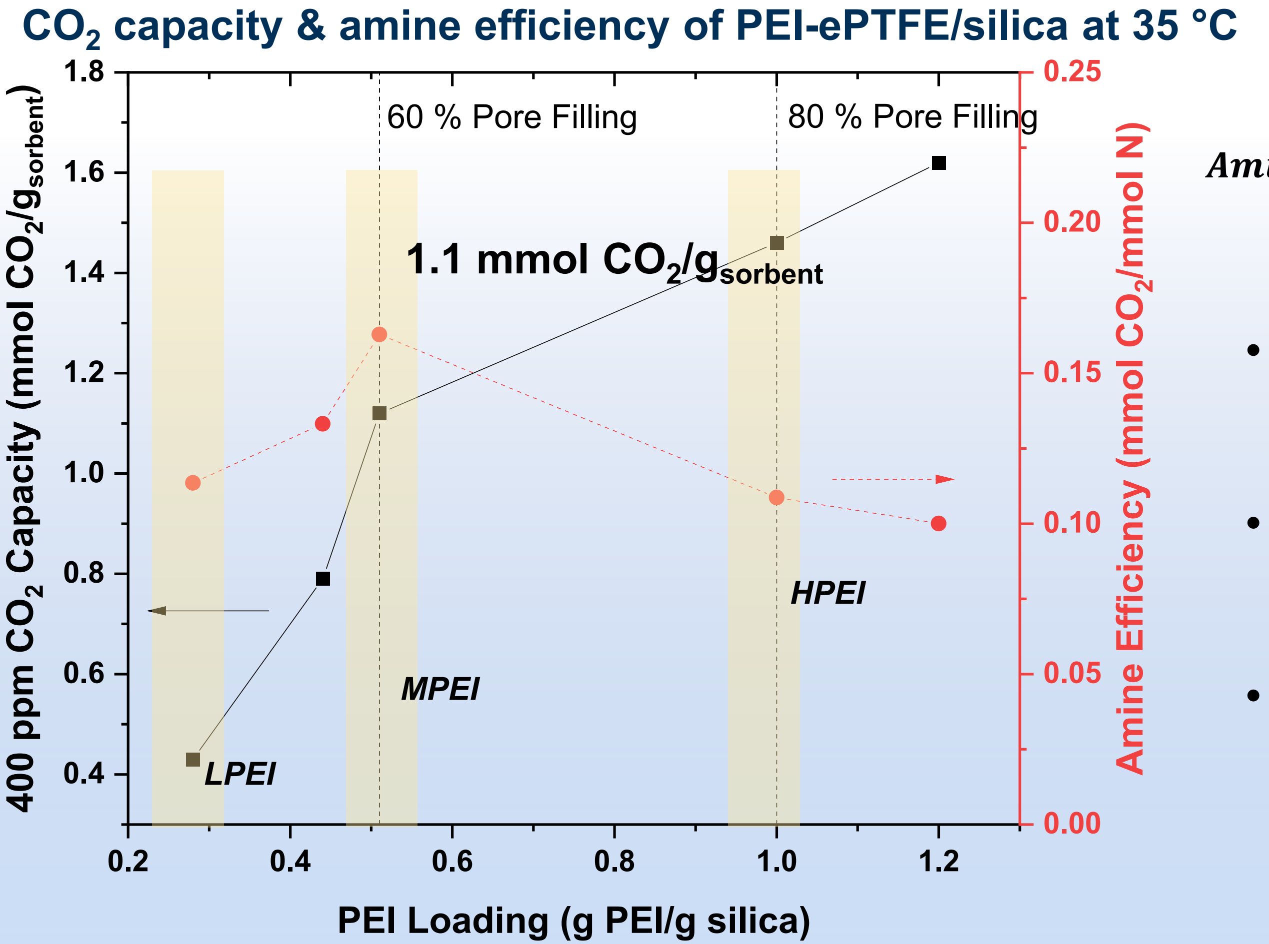








Changes in CO_2 Capacity and Amine Efficiency



$$Amine\ Efficiency\ \left(\frac{mmol\ CO_2}{mmol\ N}\right) = \frac{moles\ of\ captured\ CO_2}{moles\ of\ amine\ sites\ on\ sorbent}$$

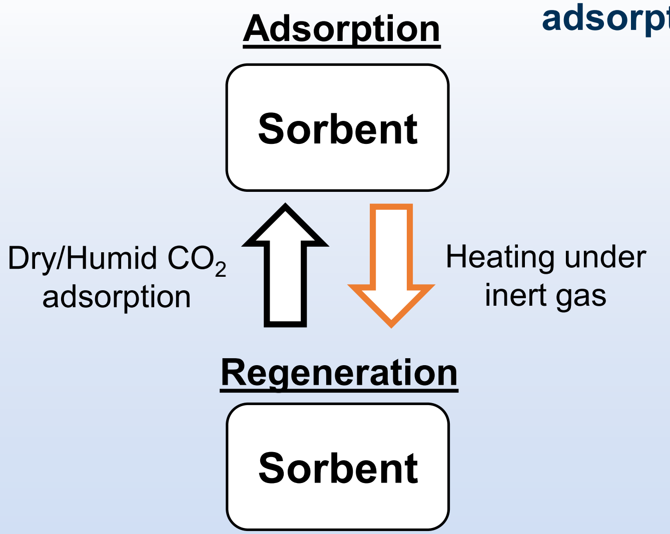
- PEI loading ∝ total number of amine sites ∝ CO_2 capacity of PEI-ePTFE/silica.
- Low PEI loading: interaction of amine sites (-NH_2) with the silica wall (- OH).
- High PEI loading: amine sites with high diffusion limitation.

Single pore view on silica

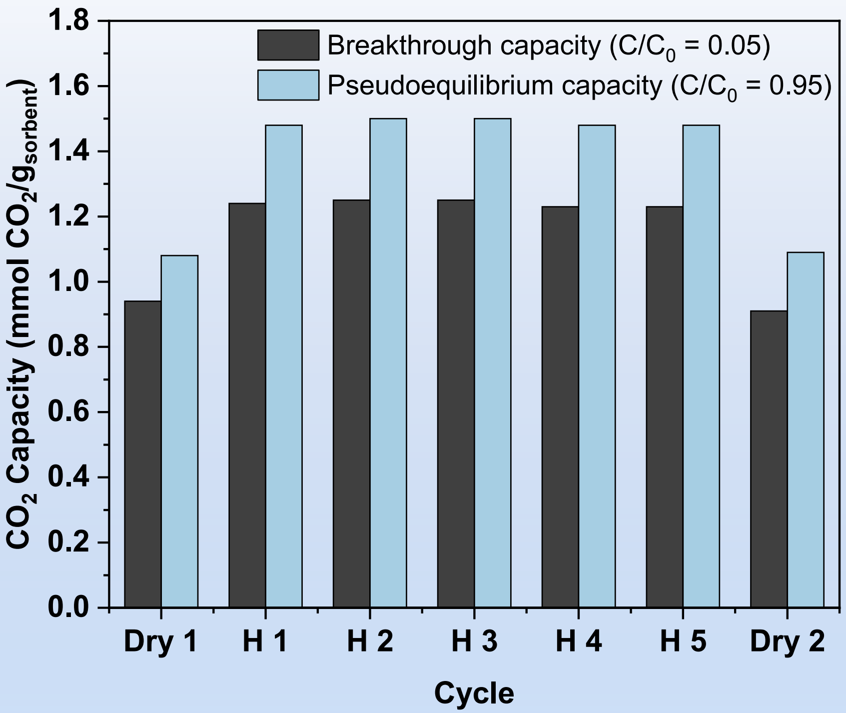
Diffusion limitation as PEI loading ↑

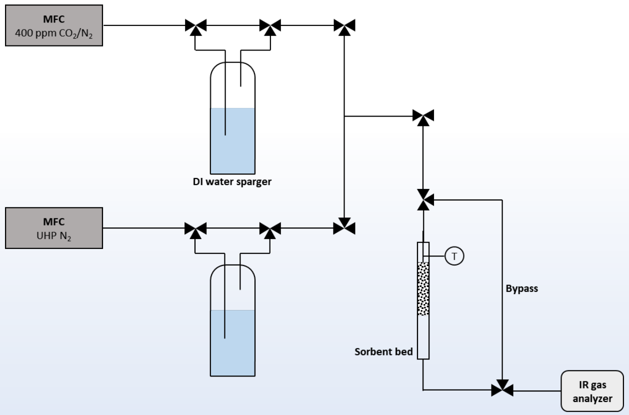
Effect of Moisture on CO_2 Sorption Behavior

❑ Cyclic Humid CO_2 Adsorption/Desorption Study with MPEI-ePTFE/silica



Cyclic dry/humid CO_2 capacities during cyclic CO_2 adsorption/desorption process (Adsorption 35 °C, Desorption 110 °C)





*RH 50% at 35 °C
*Pre-saturation using humid N_2 stream
* Cyclic humid CO_2 adsorption capacity was measured in a custom-built fixed bed configuration

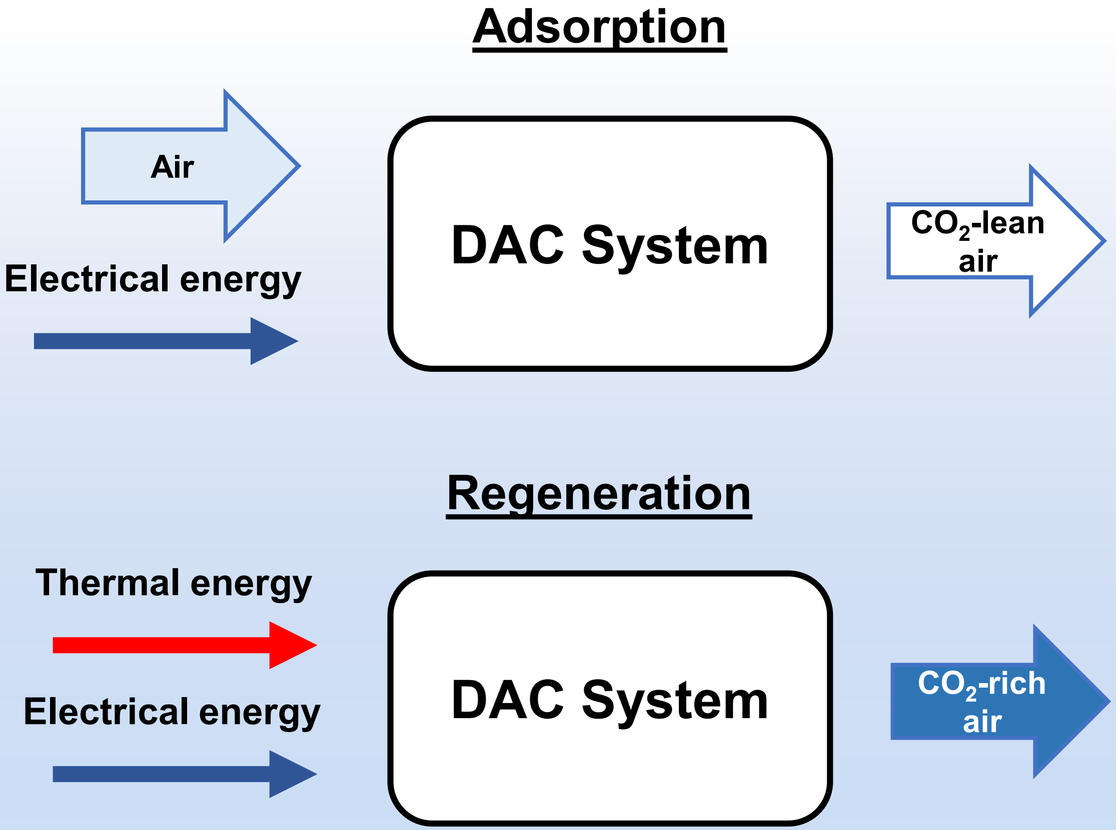
- Possible change in stoichiometry for CO_2 chemisorption by water. (carbamate →bicarbonate)
- Plasticizing effect of water molecules on PEI chain and more amine sites accessible for CO_2 adsorption.

- 37% increase in CO_2 capacity using pre-saturated MPEI-ePTFE/silica sorbent.

→ Release of accessible amine sites allowing more carbamate ions to form and/or bicarbonate.

- Consistent CO_2 capacities under dry conditions were maintained after humid cycles.

Thermal Energy Requirements for Sorbent Regeneration



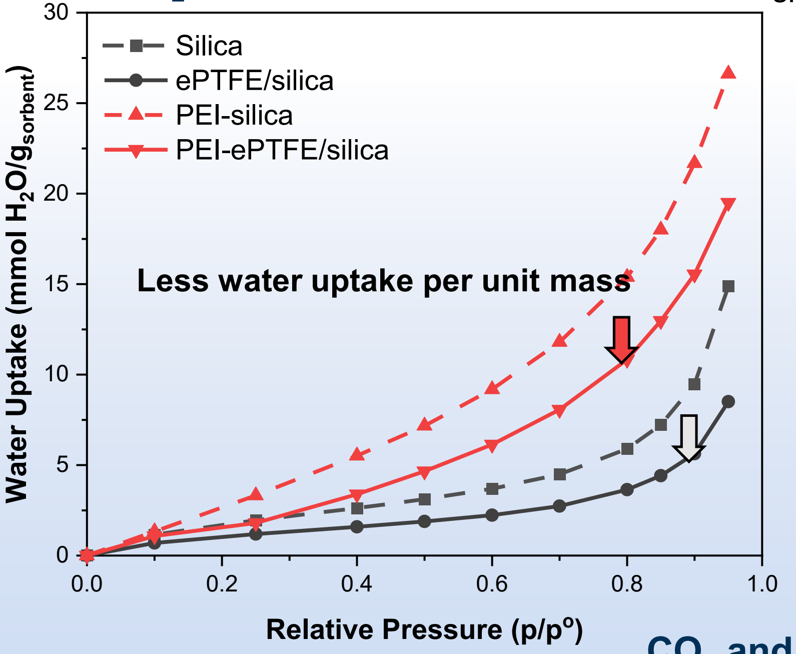
$$\boldsymbol{Q_{regeneration} = Q_{sens} + Q_{des}}$$

$$Q_{sens} = \left(\frac{1}{q_{CO2}} \cdot C_{p,sorb} + C_{p,CO2} + \frac{q_{H2O}}{q_{CO2}} \cdot C_{p,H2O} \right) \cdot \Delta T$$

$$Q_{des} = \Delta H_{CO2} + \frac{q_{H2O}}{q_{CO2}} \cdot \Delta H_{H2O}$$

H_2O Adsorption and Thermal Energy Consumption

H_2O isotherms measured at 35 °C



* Equivalent loading of PEI was loaded onto silica powder sorbent (PEI-silica) for comparison

- Water adsorption is by hydrophilic PEI and silica.
- Hydrophobic polymer domain does not sorb water

→ Less water uptake per unit mass of sorbent material

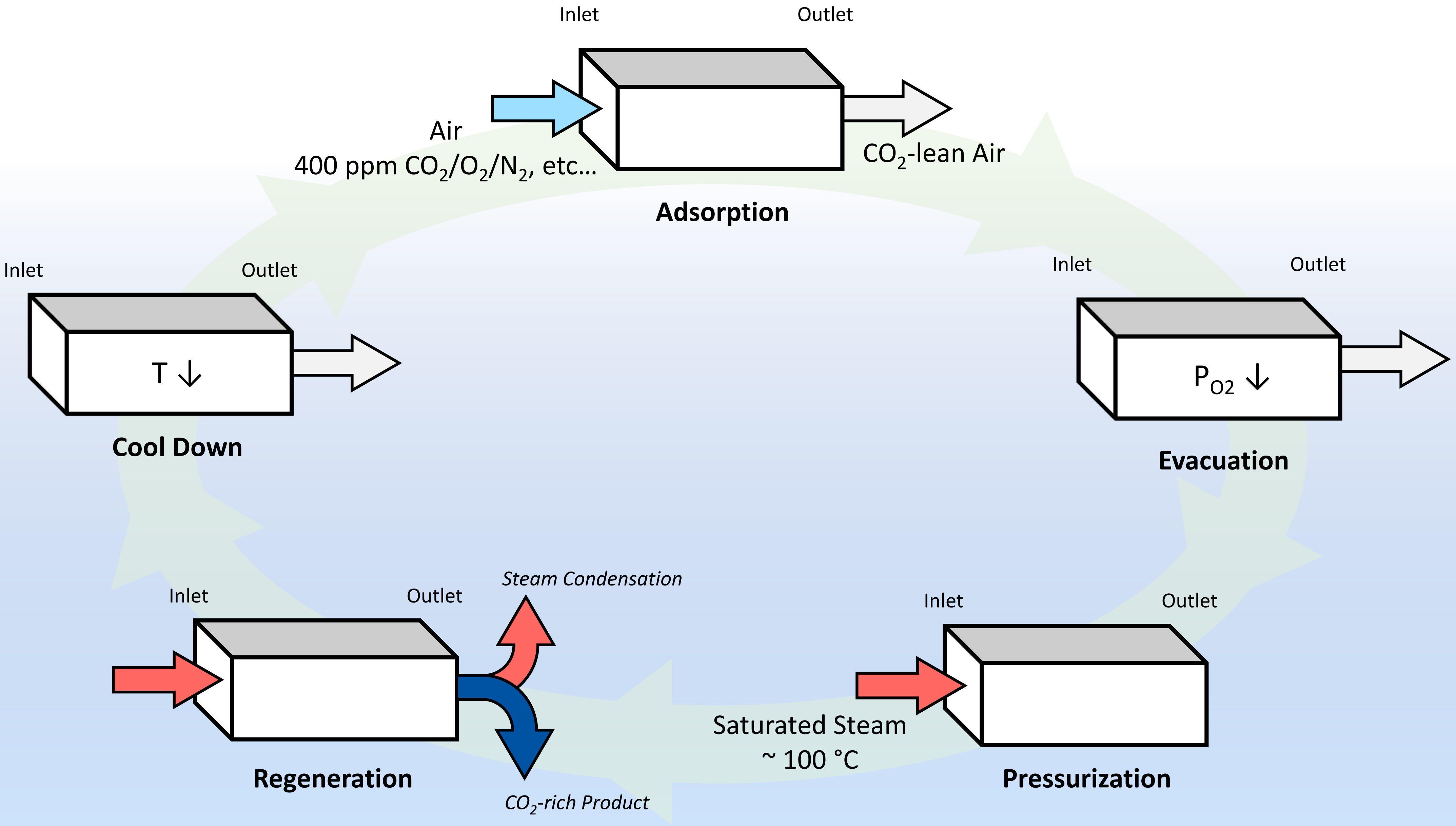
→ Low molar ratio of water to CO_2, q_{H2O}/q_{CO2}

CO_2 and H_2O Capacities of sorbent materials from DAC Literature

Sorbent Material	Humid CO_2 capacity (mmol $CO_2/g_{sorbent}$)	H_2O capacity (mmol $H_2O/g_{sorbent}$)	q_{H2O}/q_{CO2}	Humidity Condition	Reference
PEI-ePTFE/silica	1.5	4.7	3.13	T = 35 °C, 50 %RH	This work
APDES-NFC-FD	0.50	3.0	6.0	T = 30 °C, 60 %RH	*1*
Lewatit® VP OC 1065	1.33	7.23	5.44	T = 35 °C, 60 %RH	*2*
PEI-NFC	1.22	21	17.2	T = 25 °C, 80 %RH	*3*
Amine functionalized resin	0.65	2.66	4.1	T = 35 °C, 36 %RH	*4*
Ph-3-ED/SBA-15	1.45	4.69	3.23	T = 35 °C, 30 %RH	*5*
APS-SBA15	0.52	2.09	4.02	T = 30 °C, 12 %RH	*6*

Y. Min et al. *ACS Appl. Mater. Interf.* **2022**, 14, 40992.

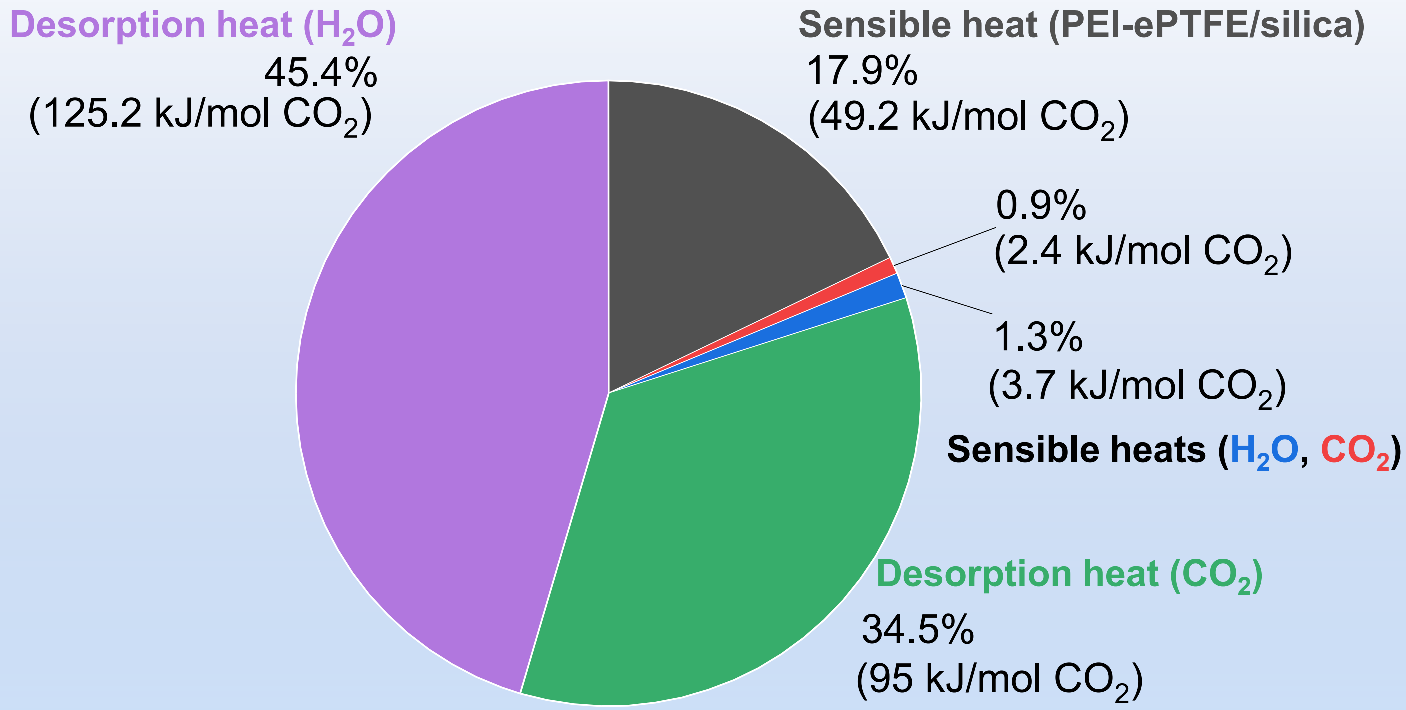
Steam-assisted Temperature Vacuum Swing Adsorption (S-TVSA)



gPROMS^{TM} simulation model

Thermal Energy Requirements for Sorbent Regeneration

Total thermal energy requirement estimation (275.5 kJ/mol CO_2)
PEI-ePTFE/silica



- Water adsorbed during DAC increases thermal energy during regeneration.
- Energetically, *high CO_2 and low water capacity* is preferred.
- Incorporation of hydrophobic polymer can lower the total water uptake, and lower energy burden.

Summary

1. Hierarchical contactor geometry and materials require careful tuning to maximize productivity and minimize energy use.
    a. PEI loading in silica particles
    b. Silica loading in polymer substrate
    c. Polymer substrate in contactor volume
        i. Material thickness
        ii. Material spacing
        iii. Contactor dimensions

2. Water management can be a key issue
    a. Water adsorption/desorption across cycle drives energy use for thermal regeneration strategies
    b. Heat recovery from water management