Gradient Amine Sorbents for Low Vacuum Swing CO_2 Capture at Ambient Temperature

DE-FE0031958

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The University of Akron

U.S. Department of Energy

National Energy Technology Laboratory

Carbon Management Project Review Meeting

August 15 - 19, 2022

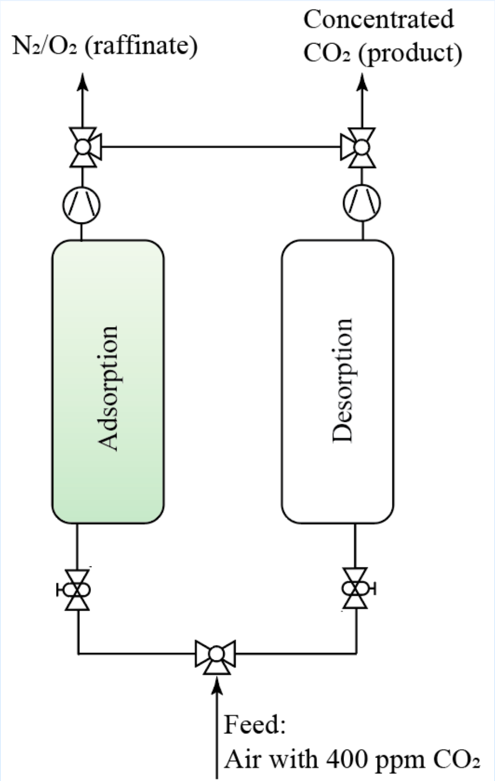
Program Overview

Funding

- Total project funding
  - DoE share: $752,002
  - Cost share: $200, 236

Overall Project Performance Dates

1/1/2021 - 12/31/2022



Project Participants

- PI: Steven. S. C. Chuang, Akron
- Students: J. King, Huhe, S. Billy, S. Starkey, and P. Hollopeter
- Co-PI: Redouane Begag, Aspen
  Nicholas Leventis, Aspen

Overall Project Objectives

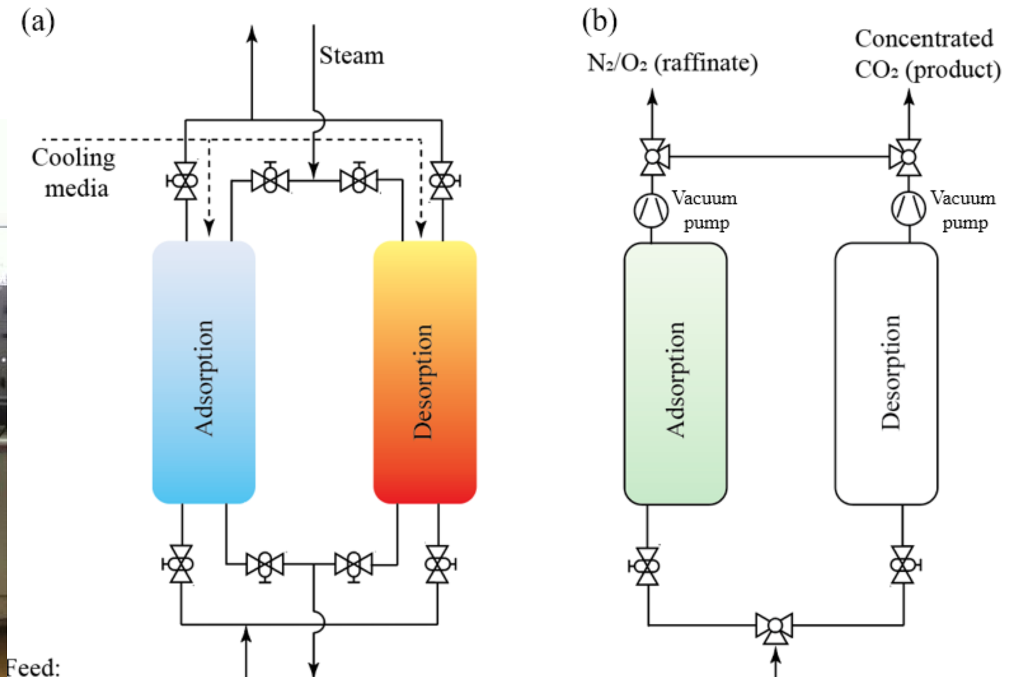
- To develop a novel VSA process by designing, fabricating, and refining the structure of amine sites which can accommodate various climate conditions, testing the low vacuum swing process, evaluating scalability, and cost and life cycle analysis.
- To determine the cost-effectiveness of the proposed technology.

Technology Background

Temperature Swing Adsorption (TSA) Vacuum Swing Adsorption (VSA)

Pilot-Scale
Fluidized Bed Unit

1 meter



Feed:
Air with 400 ppm CO_2

Minimum work needed for separation of mixture with composition 1 and 2:

Feed:
Air with 400 ppm CO_2

$$W_{min} = \Delta G_{mix} = -T\Delta S_{mix} = RT\,(x_1 \ln x_1 + x_2 \ln x_2)$$

T_0 = heating temperature

Lost work: $LW_{TSA} = Q_H\,(1 + \frac{T_0}{20+T_0})$

Separation efficiency: $\eta_{TSA} = \frac{W_{min}}{LW_{TSA}}$

Lost work: $LW_{PSA} = RT\,ln\,(\frac{1\ atm}{P_{VAC}})$

Separation efficiency: $\eta_{PSA} = \frac{W_{min}}{LW_{PSA}}$

Technical advantages:

- Operation at ambient temperature without the input and removal of thermal energy of the sorbent bed.
- Scalable and modular design

Technical challenges

- Identification of amine sites for weakly adsorbed CO_2.
- Production of high purity CO_2 (>99%)
- Fabrication of hierarchical sorbents with a high density of weakly adsorbed CO_2 sites.
- Construction of a low leakage vacuum swing unit.

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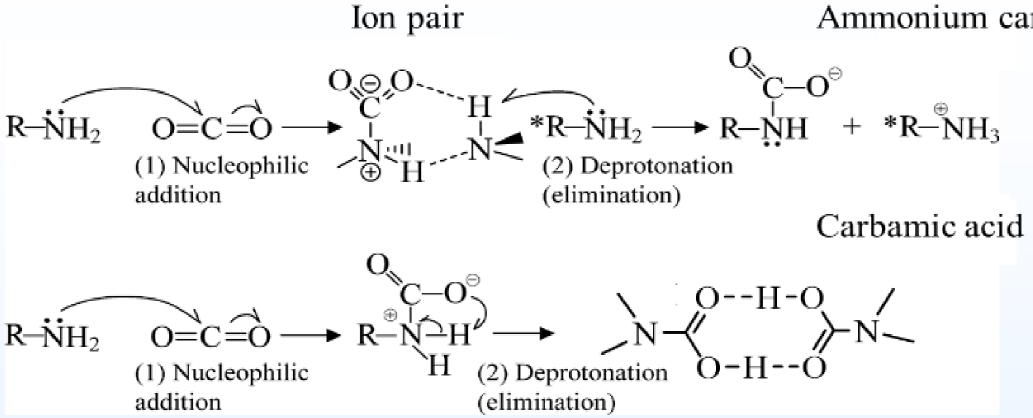
TSA

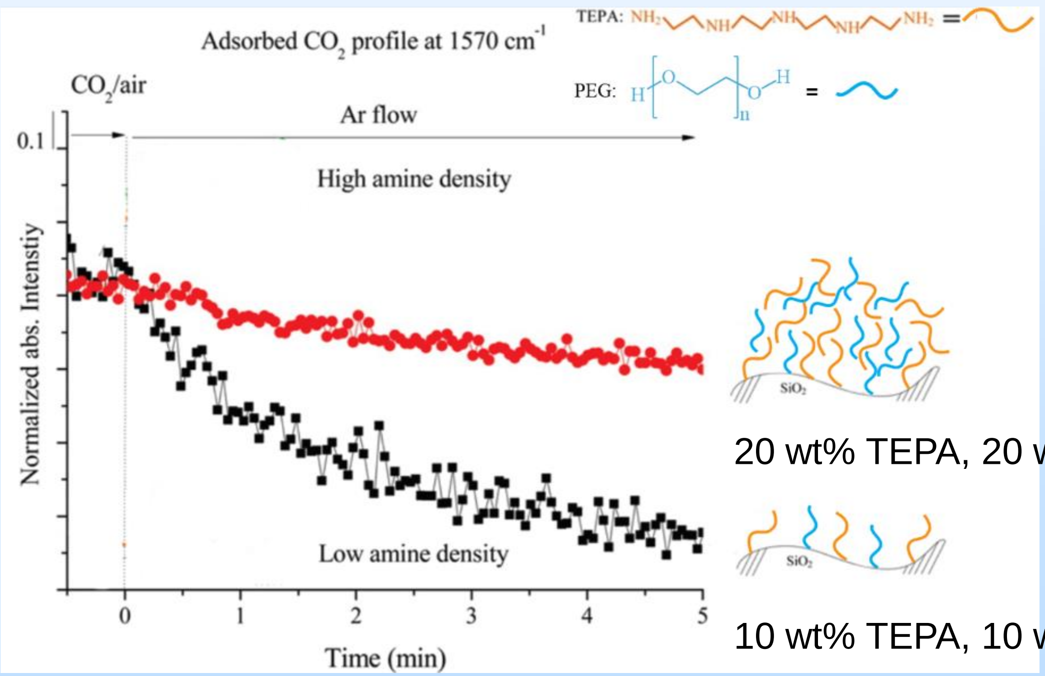
- Sorbent degradation
- Thermal energy

VSA

- Ambient temperature
- Low energy

Technology Background





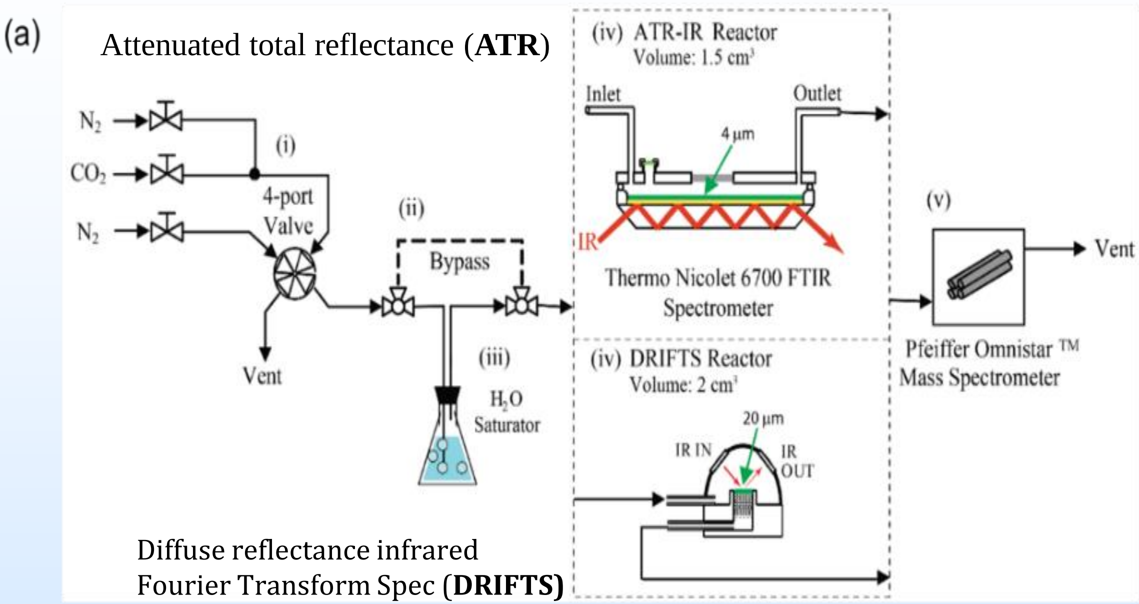
20 wt% TEPA, 20 wt% PEG/SiO_2

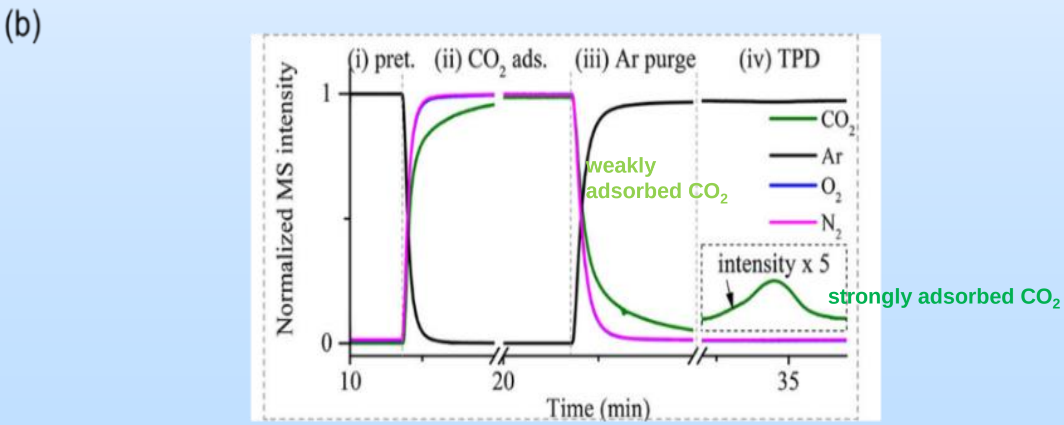
10 wt% TEPA, 10 wt% PEG/SiO_2

IR absorbance of adsorbed CO_2 as a function of time during Ar purge at 150 cm^3/min at 25 ^oC. The slope of the IR decay curve corresponds the rate of desorption of weakly adsorbed CO_2.

Chakravartula S. Srikanth and Steven S. C. Chuang *The Journal of Physical Chemistry C* 2013, 117, 18, 9196-9205

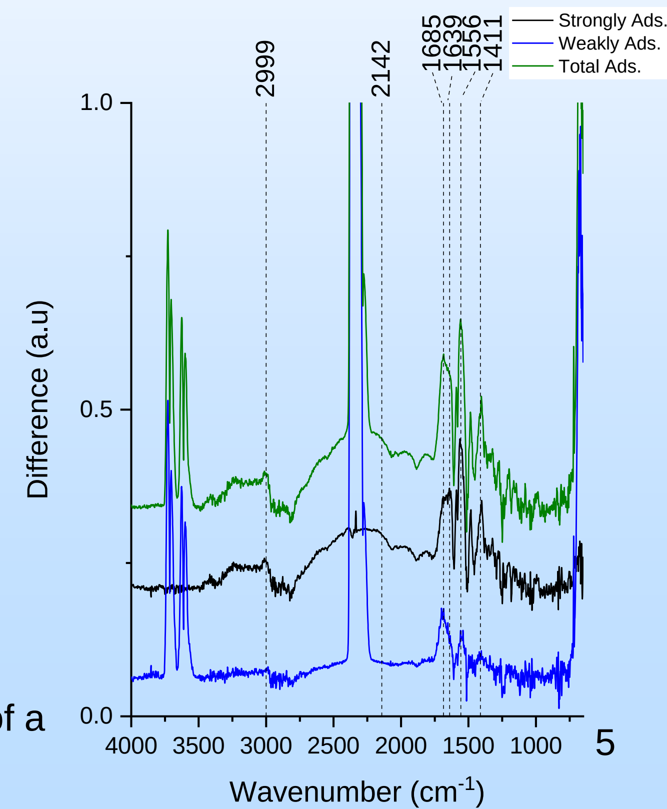
Progress and Current Status of Project





- In situ infrared (IR) spectroscopy coupled with mass spectroscopy (MS) allows simultaneous monitoring the dynamics of adsorption and desorption of strongly and weakly adsorbed CO_2 on amine sorbents.

- The project goal is to populate the porous and stable structure with high density of weakly adsorbed CO_2 sites for the vacuum swing adsorption.



Identification of weakly adsorbed CO_2 sites allows design and preparation of a hierarchically structure of amine sorbent for low vacuum swing adsorption

Technical Approach/Project Scope

a. Experimental design and work plan

- Preparation, characterization, and test of sorbents with weakly adsorbed CO_2 sites
- Fabrication and test of a Kg scale vacuum swing adsorption unit for capture of CO_2 from air.

b.

Task/ Subtask	Milestone Title & Description	Planned completion date	Actual Completion Date	Verification method
4.0	Determination of CO_2 capture capacity and stability (4 -15)	11/01/2021		Quarterly report
5.0	Fabrication of a Kg scale unit. (12-18)	11/01/2021		Quarterly report
6.0	Vacuum swing test (6-18)	02/01/2022		Quarterly report
7.0	Cost Analysis and Life Cycle Analysis.	12/31/2022		Quarterly report

c. Project success criteria

Decision Point	Date	Success Criteria
1	12/1/2021	Both sorbent plates and sorbent particles exhibit the same level in vacuum swing adsorption CO_2 capture capacity. Reaching the target listed in State-Point Data
2	2/1//2022	Completing the construction of the Vacuum Swing Adsorption unit

Risk Management

Description of Risk	Probability	Impact	Overall	Risk Management (Mitigation and Response Strategies)
Financial Risks:				
Commitment to cost-sharing	Low	High	Low	Cost-sharing has been allocated and committed by the U. Akron.
Cost/Schedule Risks:				
Acquiring chemical precursors and component	Medium	High	Moderate	Alternative suppliers
Technical/Scope Risks:				
Equipment maintenance	Moderate	High	Moderate	Regular inspection and calibration
Preparation of Kg scale sorbent	Moderate	Moderate	Moderate	Optimizing the sorbent preparation methods.
Human Resource Risks:				
Availability of manpower to execute project	Moderate	Moderate	Moderate	Recruit domestic undergraduate students as assistants
Continuing employment of each team member	Low	High	Moderate	Incentives for retaining the talents
Management/Planning/ Oversight Risks:				
Capability to coordinate	Low	High	Moderate	Regular and informal meetings and communications
ES&H Risks:				
Environmental	Low	Low	Low	Use of chemicals with low toxicity
External Factor Risks:				
Pandemics	High	High	High	Minimize interpersonal contacts

Progress and Current Status of Project

CO_2 capture capacity for thermal swing adsorption

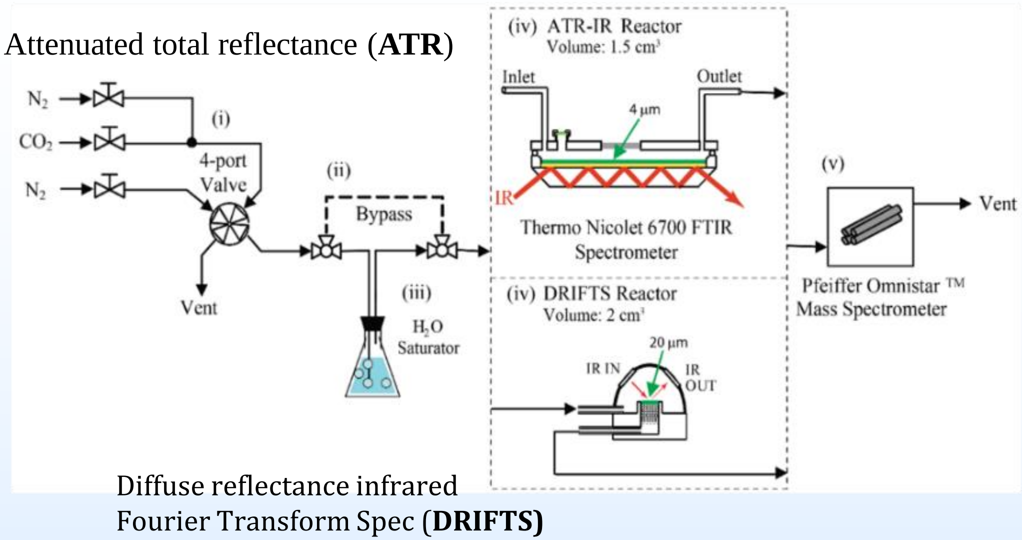
Additional Photos of Samples and Lids

Sample	CO2 Capture	CO2 Capture	CO2 Capture	Avg	Stdev	Name	Ranking
1	1.06	1.12	0.98	1.05	0.07	KD75BMSPA (TMS)	7
2	1.09	1.29	1.11	1.16	0.11	KD75BMSPA	5
3	0.85	1.43	0.98	1.09	0.30	KD75BMSPA	6
4	0.67	1.12	0.92	0.90	0.22	KD75BMSPA (TMS)	10
5	0.66	0.40	0.65	0.57	0.15	KD100BMSPA	16
6	0.47	0.87	0.68	0.67	0.20	KD100BMSPA (TMS)	15
7	1.36	1.34	1.17	1.29	0.10	KD100BMSPA (TMS)	4
8	0.64	0.80	0.74	0.73	0.08	KD100BMSPA (TMS)	13
9	0.69	0.69	0.63	0.67	0.03	KD100BMSPA (TMS)	14
10	0.75	0.77	0.72	0.75	0.03	KD100BMSPA	12
11	1.50	1.18	1.40	1.36	0.17	KD75BMSPA (TMS)	3
12	1.37	1.56	1.32	1.42	0.12	KD75BMSPA	2
13	1.21	1.00	0.77	0.99	0.22	KD100BMSPA	8
14	1.06	0.99	0.72	0.92	0.18	KD100BMSPA (TMS)	9
15	1.49	1.89	1.07	1.49	0.41	KD100BMSPA (TMS)	1
16	0.31	1.24	1.07	0.87	0.50	TPSENA	11

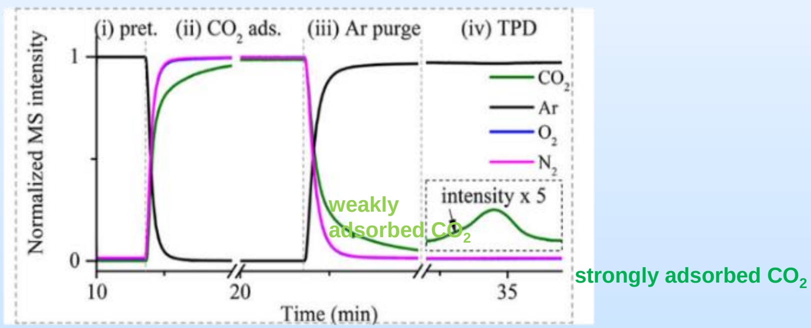
KD100BMSPA: contains 4.92 mmol amine/g
KD75BMSPA: contains 5.96 mmol amine/g

Technology Approach

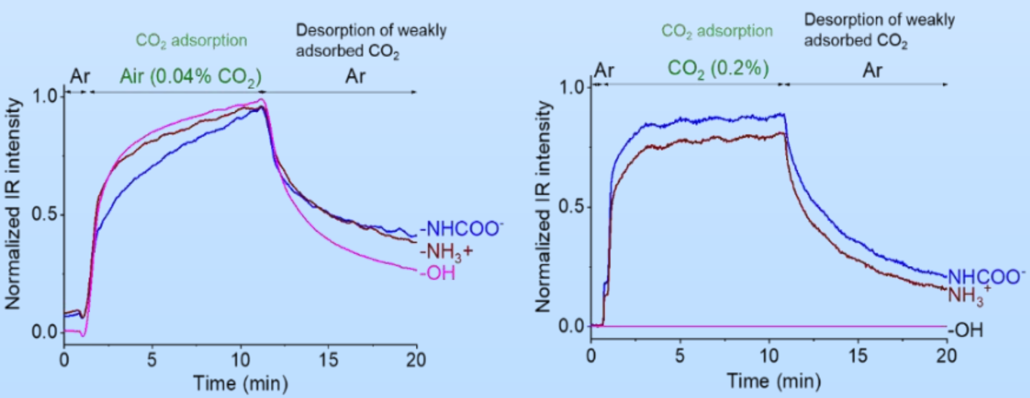
(a)



(b)



(c)

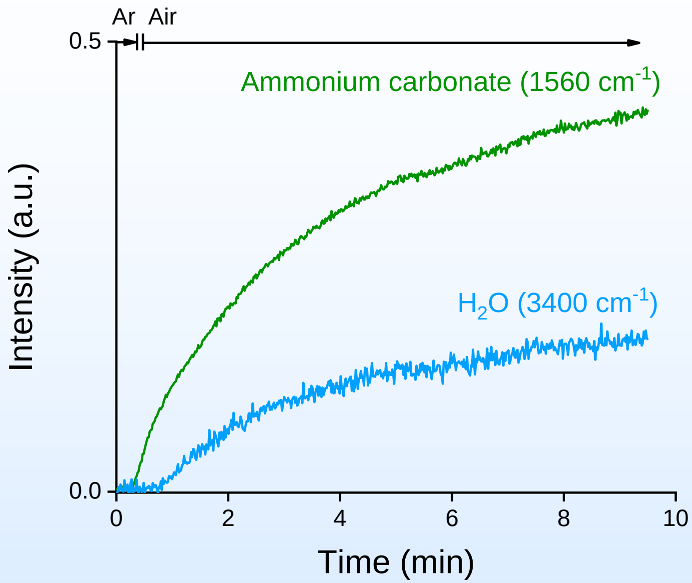


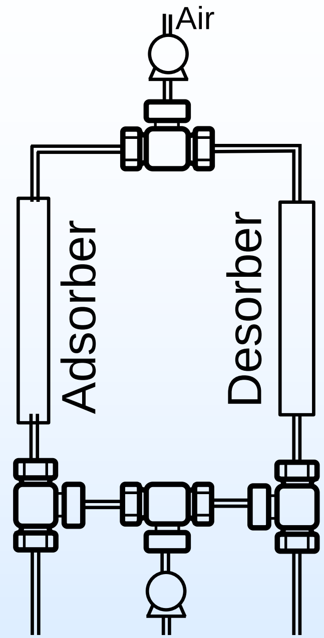
(a) In situ infrared (IR) spectroscopy coupled with mass spectroscopy (MS) allows simultaneous monitoring the dynamics of adsorption and desorption.

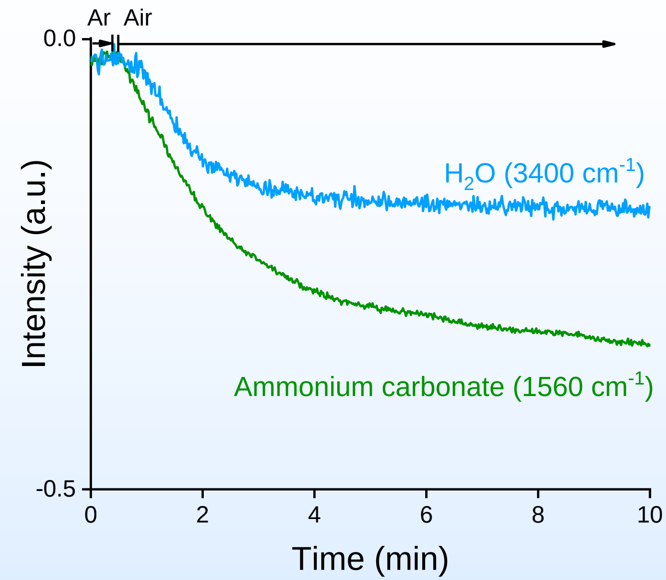
(b) MS profiles of the gaseous effluent from the IR cell during a CO_2 capture cycle: (i) pretreatment, (ii) CO_2 adsorption, (iii) Ar purge to remove weakly adsorbed CO_2, (iv) TPD (temperature-programmed desorption) to remove strongly adsorbed CO_2.

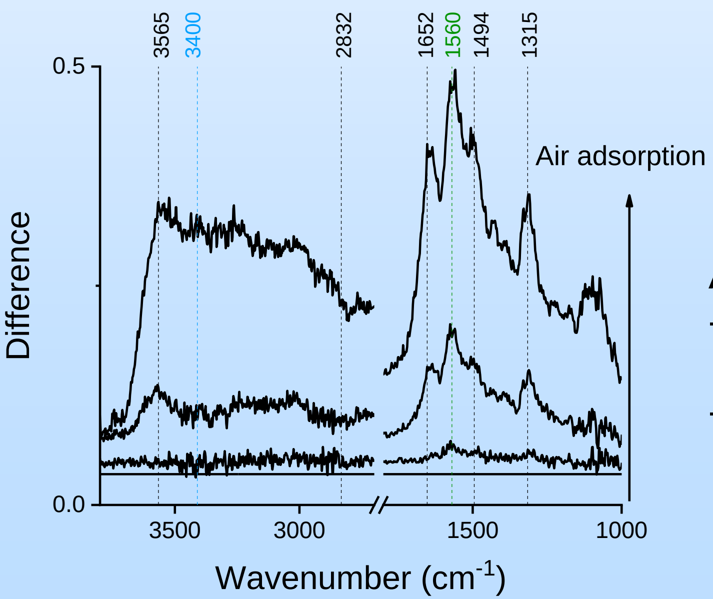
(c) CO_2 capture from air and CO_2 capture from 0.2% CO_2.

Progress and Current Status of Project



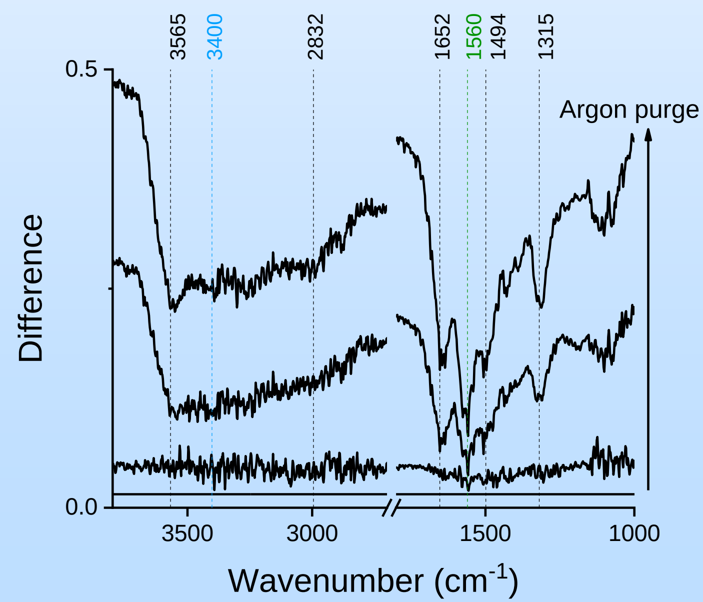






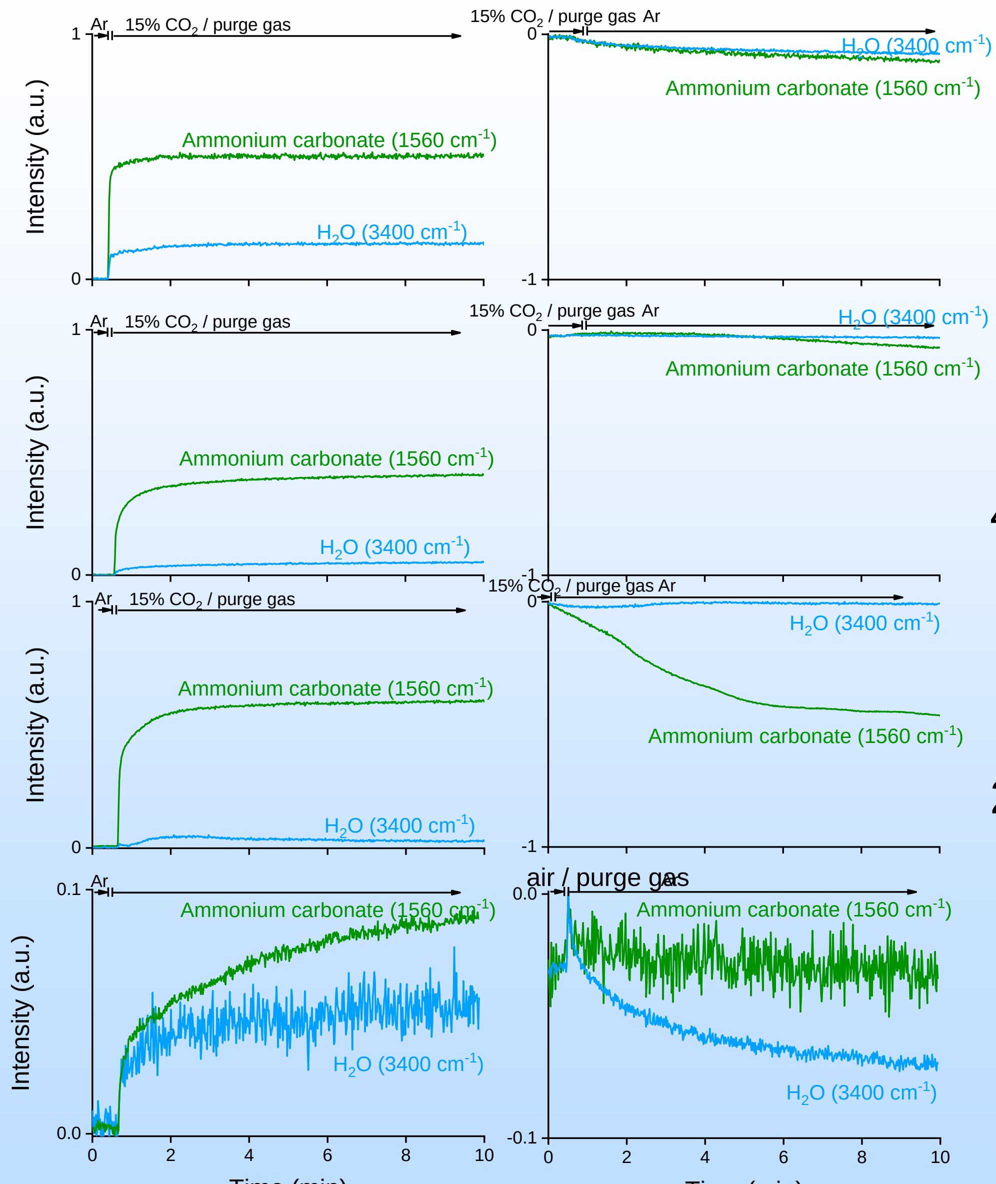
Amine-based sorbents

- CO_2 adsorption prior to H_2O adsorption
- CO_2 desorption prior to H_2O desorption



Progress and Current Status of Project

Control the density of amine sites: Additives, Amino acids, and polyamines



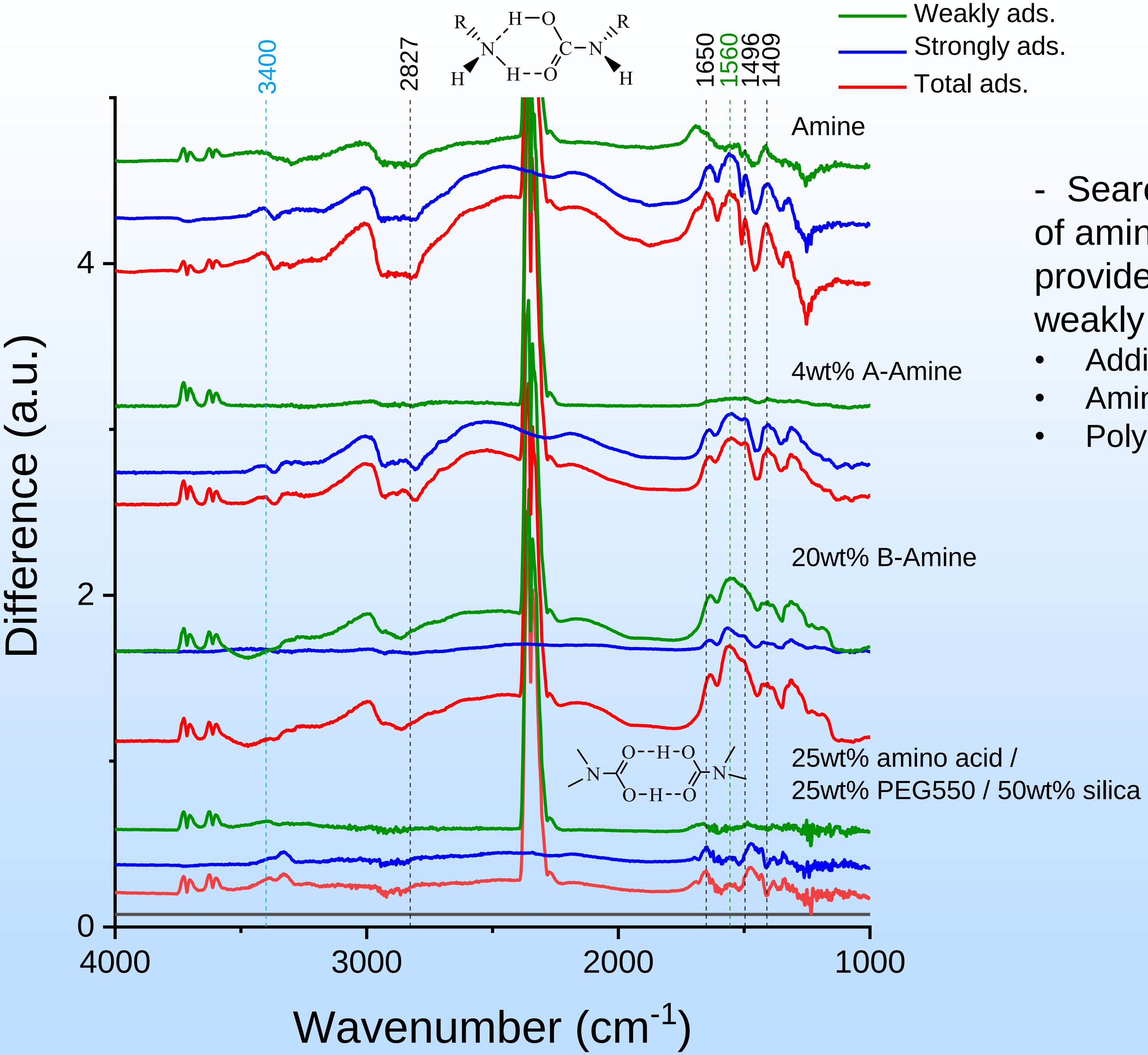
Amine

4wt% A-Amine

20wt% B-Amine

25wt% amino acid/
25wt% C/ 50wt% silica

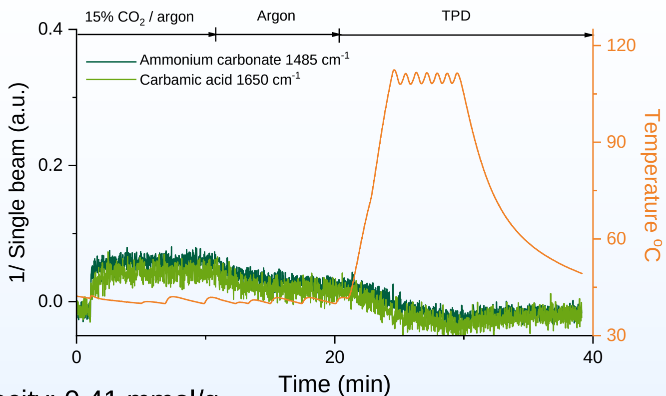
Progress and Current Status of Project



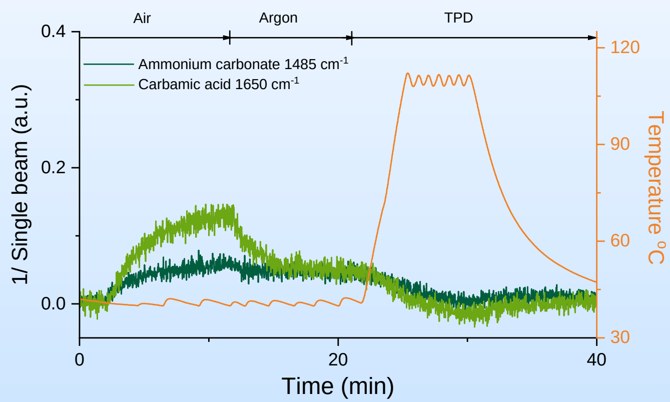
- Search for formulations of amine sorbents which provide a high density of weakly adsorbed CO_2
  - Additives
  - Amino acids
  - Polyamines

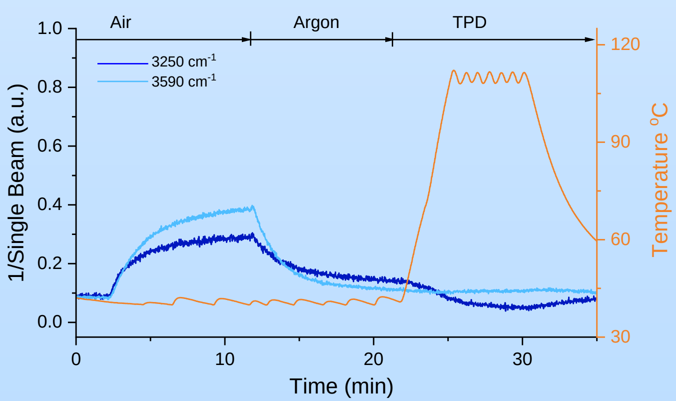
Progress and Current Status of Project

CO_2 Capacity: 0.46 mmol/g

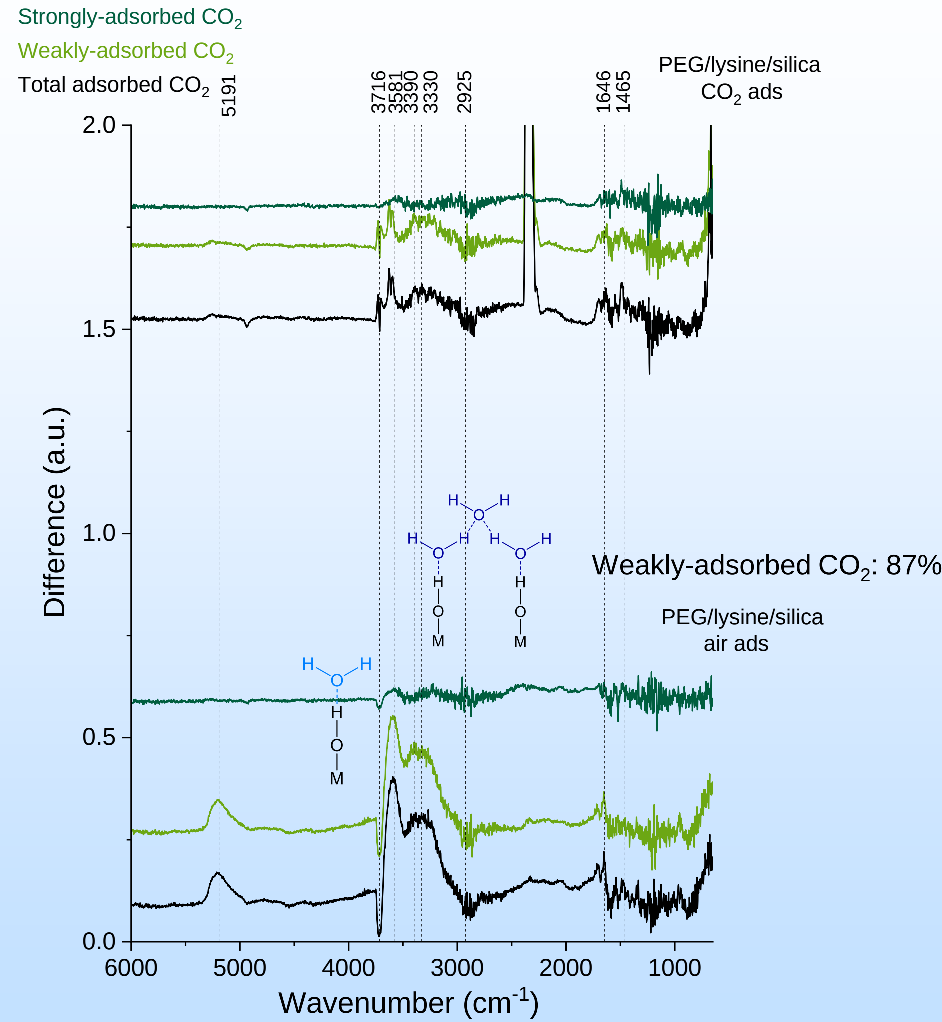


CO_2 Capacity: 0.41 mmol/g





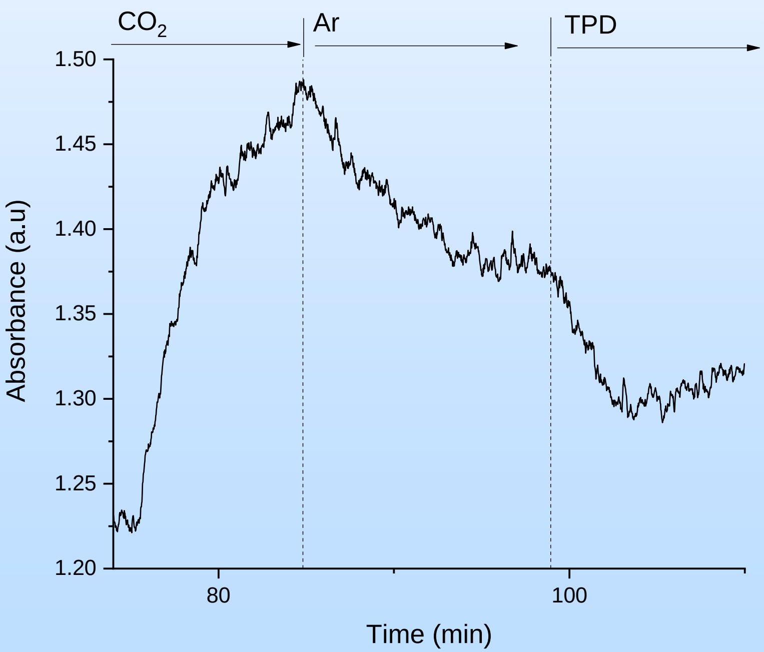
PEG / amino acid / silica (molar ratio: 1 : 1 : 1)



- PEG/amino acid provides both strongly and weakly adsorbed sites for CO_2 and water.
- CO2 capacity and rate from 15% > CO2 capacity and rate from air

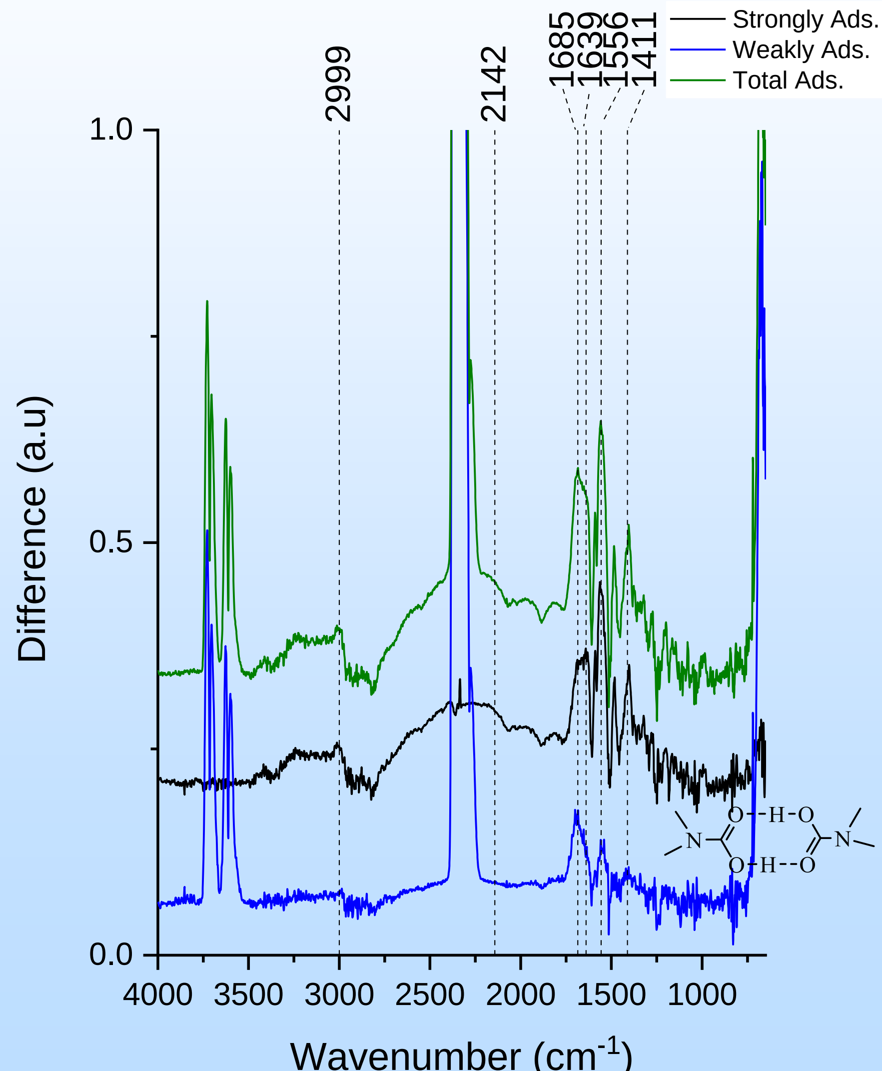
Progress and Current Status of Project

Cross-linked amine film
Approx. 1 mm thick

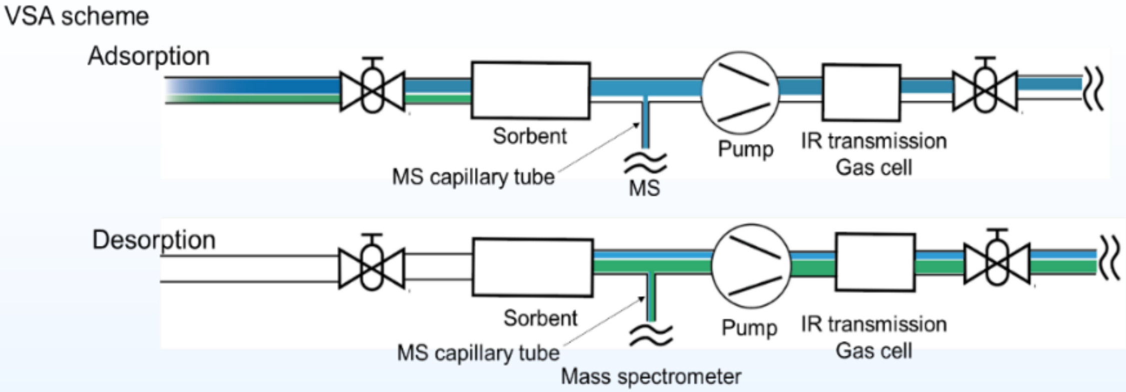


Cross-link amine

- The rate of CO_2 adsorption and desorption
- The density of weakly adsorbed CO_2 sites



Progress and Current Status of Project



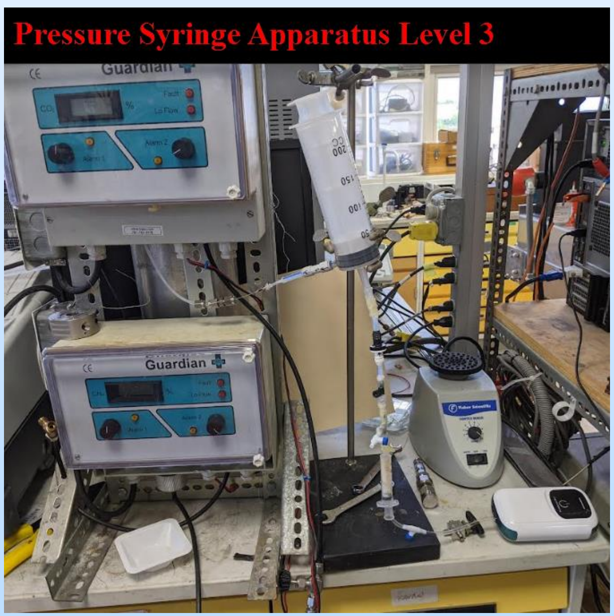
VSA Scheme

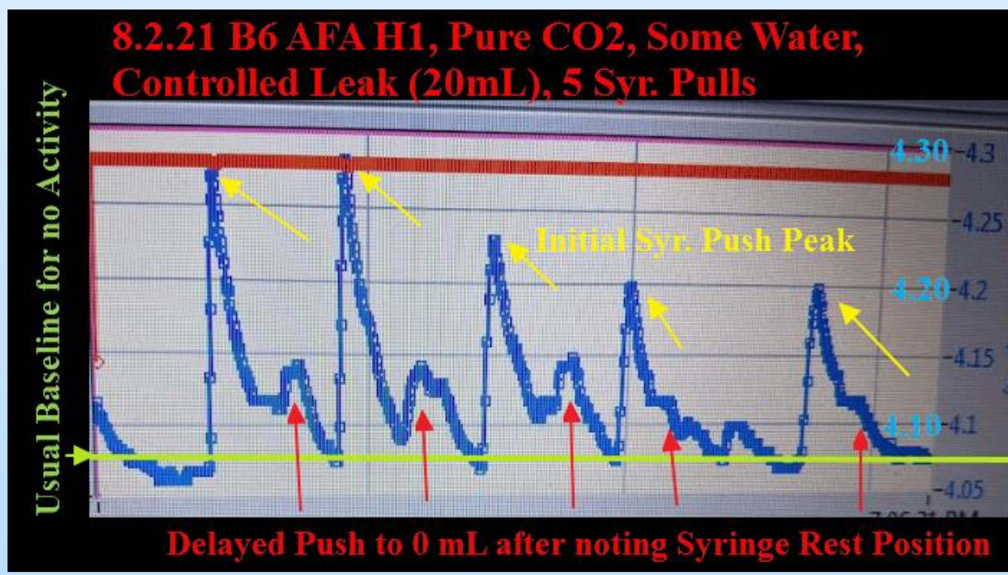
- Adsorption by flowing a 0.04% CO_2 stream over a sorbent bed
- Desorption of weakly adsorbed species by vacuum

Data collection

- Obtaining the concentration profiles of the effluent form the sorbent bed with adsorbed CO_2 under 8 psi vacuum determined by (a) MS before vacuum pump, (b) IR gas cell after vacuum pump.

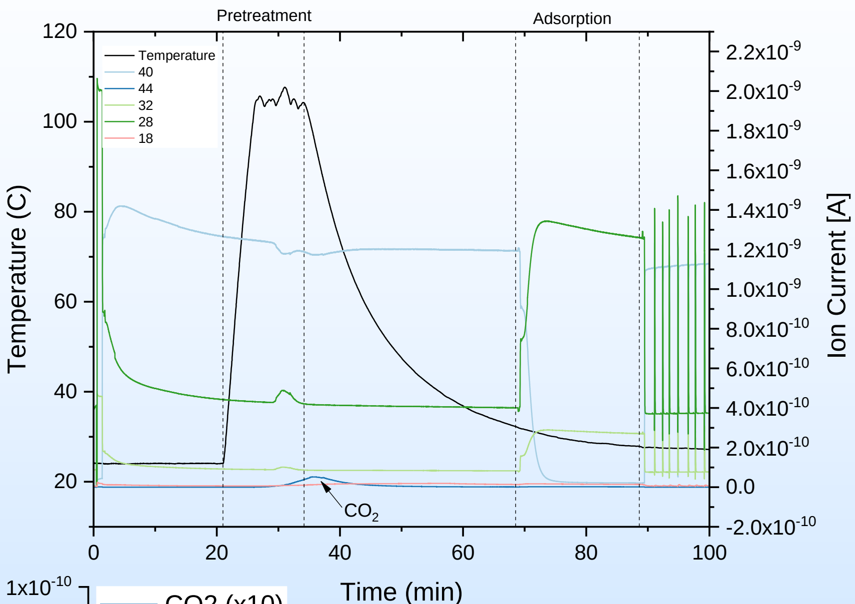
A laboratory scale (5-10 cm^3) VSA unit with a CO_2 sensor



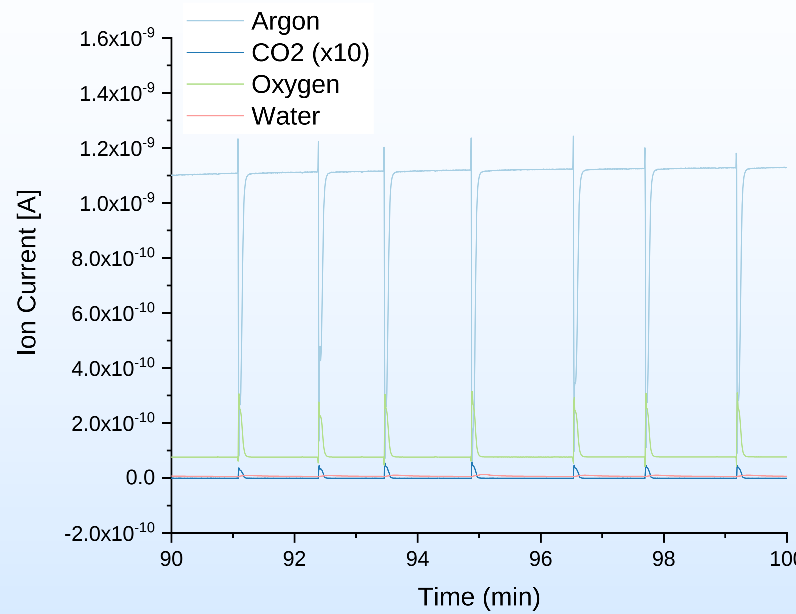


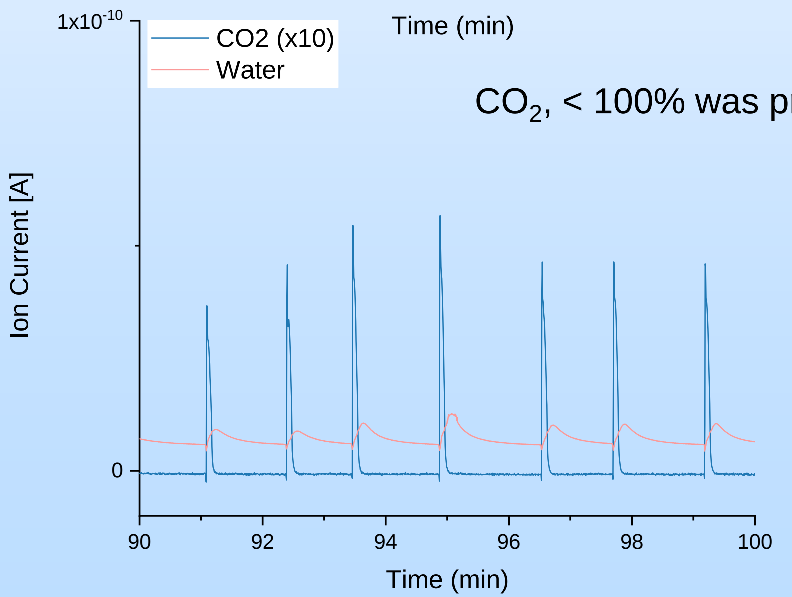
Progress and Current Status of Project

Sample: 40cc TPESNa (E + P)

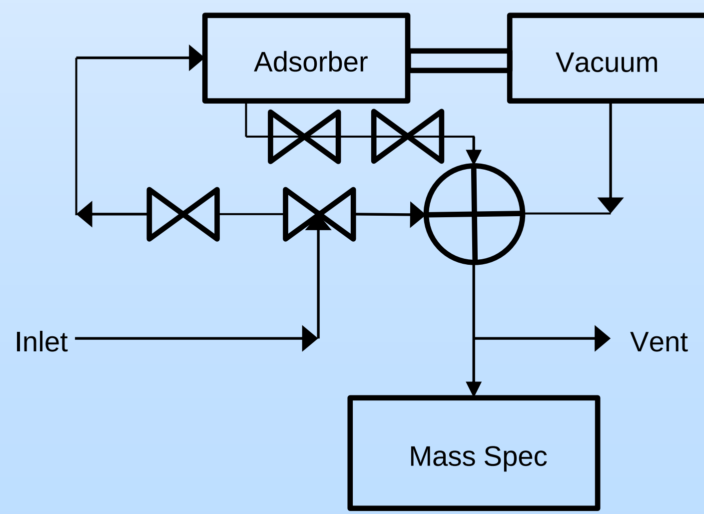


22_02_28 TPESNa (E + P) VSA/D with Mass Spec





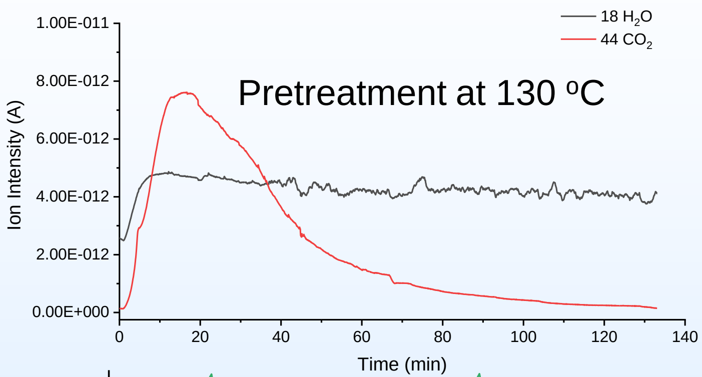
CO_2, < 100% was produced.

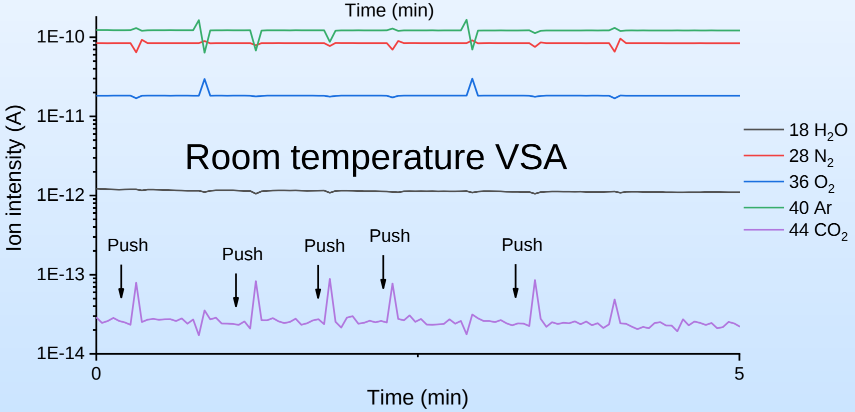


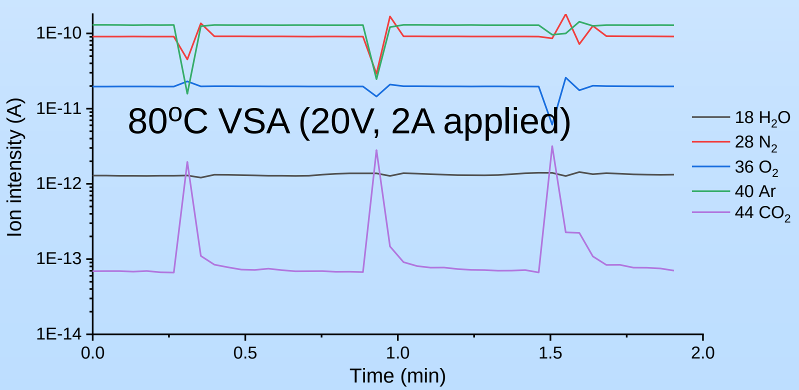
Progress and Current Status of Project

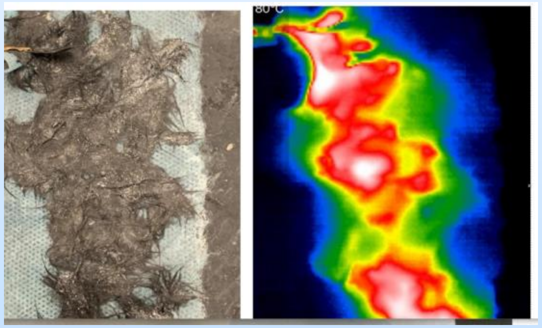
04_03_22 VSA and TSA experiments on carbon heater

Chemicals: Adhesive, Amine, fiber veil.



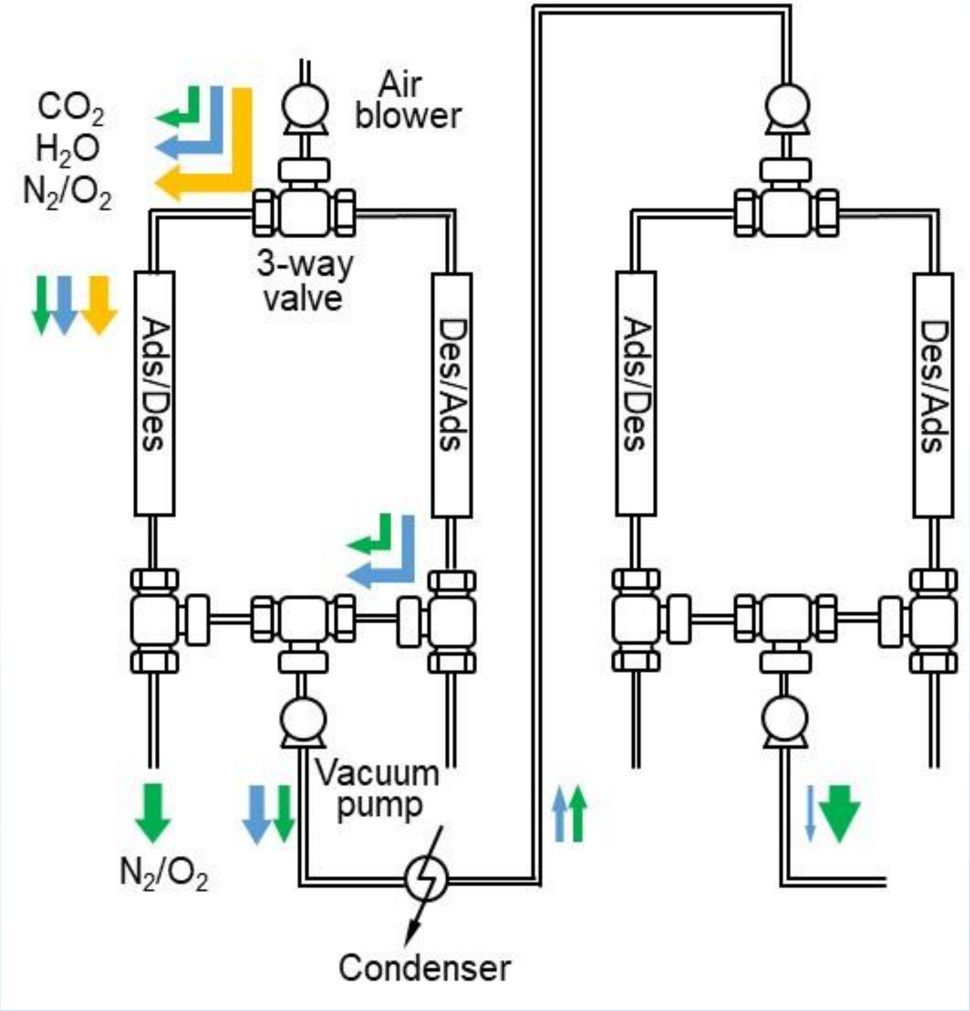






- Concentrated CO_2, > 90%, was produced from VSA at 3 psia.

Scale-up potential – VSA in series



Future testing/development

- Improve the sorbent formulation and monolithic structure
- Integration with automatic control

Summary

Key findings:

- The density of weakly adsorbed CO_2 sites on amine sorbents can be controlled by the types of additives and polyamines.
- Some amine sorbents are able to adsorb CO_2 prior to H_2O; to desorb CO_2 prior to H_2O under flowing inert gas and vacuum.
- Concentrated CO2, > 90%, was produced from VSA at 3 psia.
- Gradient amine layer can be achieved by sequential layer-by-layer deposition of amine-PEG (polyethylene glycol) onto the porous polymer pellet

Lesson learned:

- Fabrication of a laboratory scale VSA (vacuum swing adsorption) unit is highly challenging because of the lack of reliable fittings and valves for holding vacuum.

Future Plan:

- Search for reliable components for building a one-liter VSA unit.
- Fine-tune the formulation of amine sorbents and monolithic structure

Take-away:

- VSA for CO_2 capture is technically feasible.

Teams and Facilities

PI
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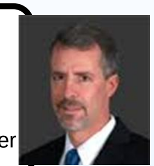
UA leader
Steven Chuang

Aspen
Aerogels, Inc.
George Gould
Chief Technology Officer



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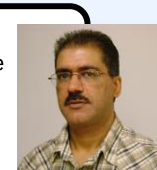

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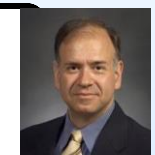

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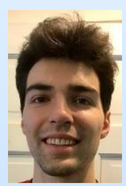
Samantha Starkey



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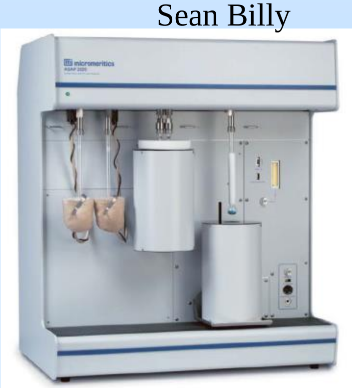
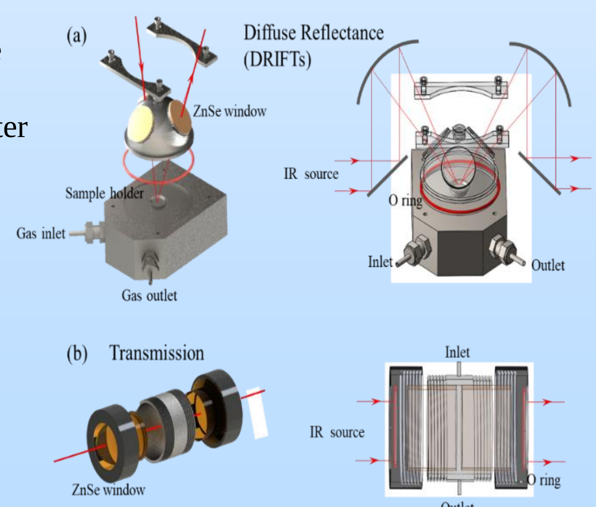


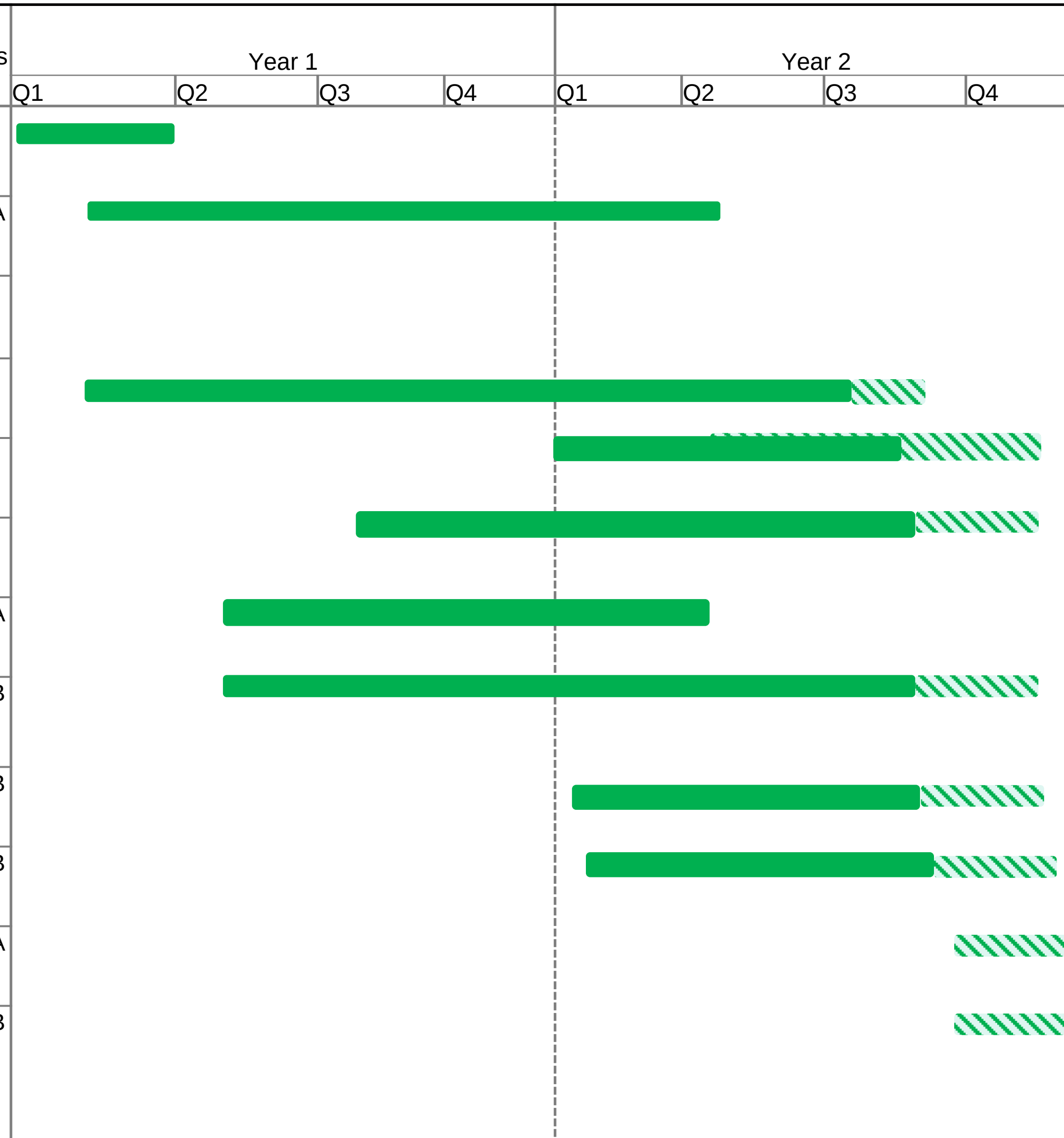


Appendix

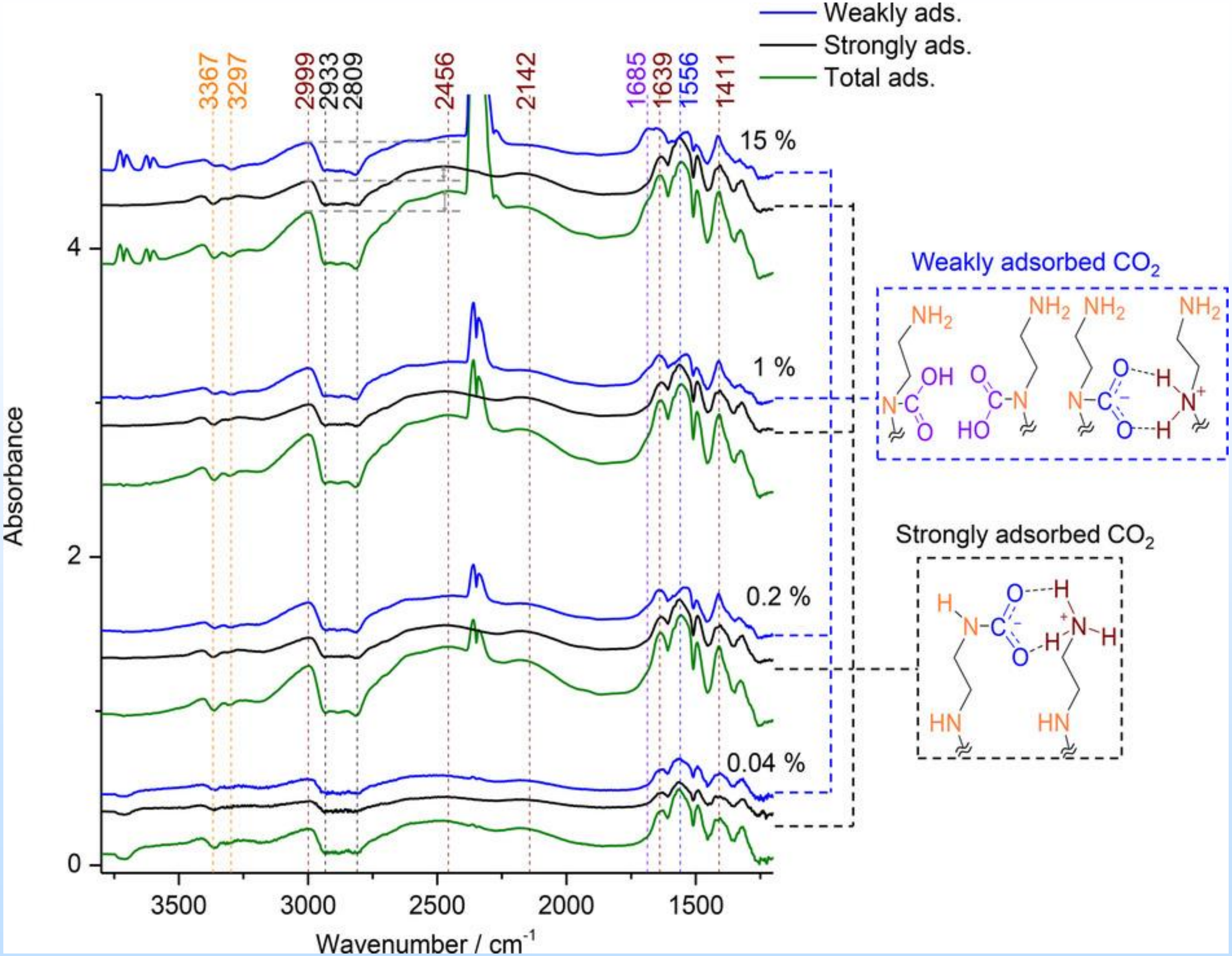
– These slides will not be discussed during the presentation but are mandatory.

Project Timeline

Task name	Assigned resources
Task 1.0 – (UA/Aspen) Program requirements and Project Management	All of team members
Task 2.1– (UA) Fabrication of hybrid sorbents	UA PhD. Student A
Task 2.2 – (Aspen) – Preparation of amine-functionalized aerogel	
2.2.1 – Amine functionalized aerogel (AFA) sorbent further optimization	Aspen Team member
2.2.2 – AFA Bead Fabrication	Aspen Team member
2.2.3 – Small scale AFA bead production (<1kg)	Aspen Team member
Task 3.0 – (UA) Physical characterization of sorbents	UA PhD. Student A
Task 4.0 – (UA) Determination of CO_2 capture capacity and stability (4 - 15)	UA PhD. Student B Team member
Task 5.0 – (UA) Fabrication of a Kg scale unit. (12-18)	UA PhD. Student B Team member
Task 6.0 – (UA) Vacuum swing test (6-18)	UA PhD. Student B
Task 7.0 – (UA/Aspen) Cost Analysis and Life Cycle Analysis.	UA PhD. Student A
Task 8.0 – Report preparation Final TMP, Draft of Final Report	UA PhD. Student B Aspen Team member Aspen Team member



The Nature of Adsorbed Carbon Dioxide on Immobilized Amines during Carbon Dioxide Capture from Air and Simulated Flue Gas



Energy Technology, Volume: 5, Issue: 3, Pages: 510-519, First published: 12 November 2016, DOI: (10.1002/ente.201600685)

Scope of Work

Task 2.0 – Sorbent Preparation and fine-tuning

Subtask 2.1 – Fabrication of hybrid sorbents

Focus on the development of the hierarchical polymer structure to immobilize the sorbent particles.

Subtask 2.2 – Preparation of amine-functionalized aerogel

8 amine-aerogel samples have been prepared.

Task 4.0 – Determination of CO_2 capture capacity and stability

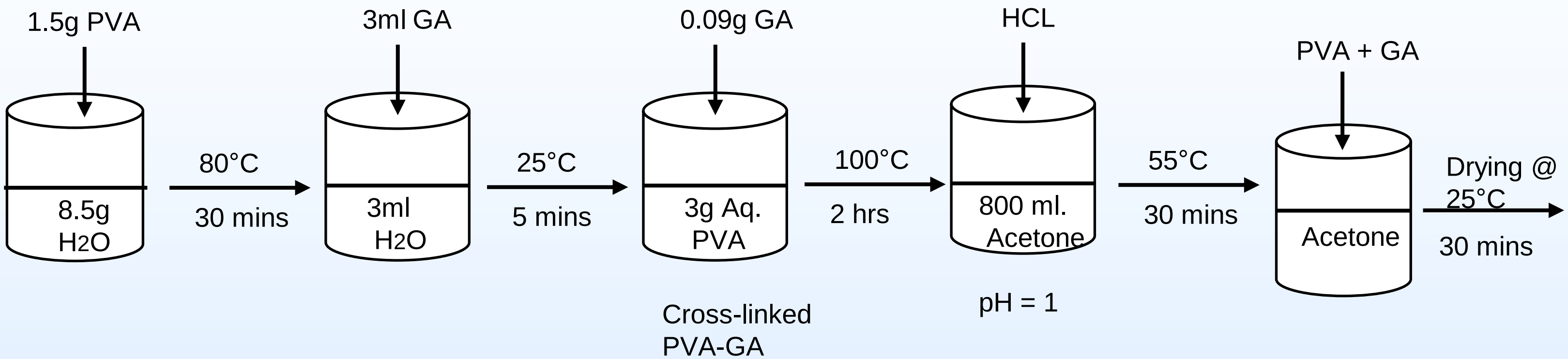
CO_2 capture capacity for thermal swing adsorption have been determined. Investigate the approaches to accelerate desorption of weakly adsorbed CO_2.

Task 5.0 – Fabrication of a kg scale vacuum swing adsorption (VSA) unit

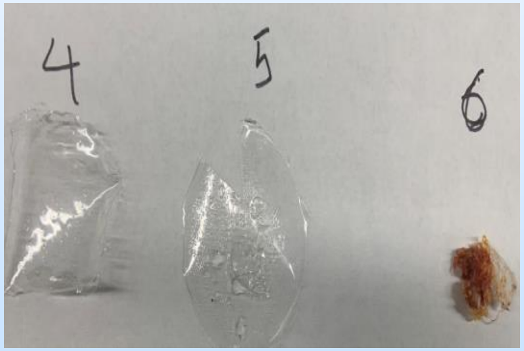
A tubular absorber with vacuum seals have been tested.

Hydrophilic Crosslinked Porous Poly(vinyl alcohol)

Objective: Prepare a porous PVA (Poly(vinyl alcohol))film impregnated with PEI.



PVA + GA+ PEI



*Base = PVA *CL = Crosslinker = Glutaraldehyde

1.5g Base
3ml CL

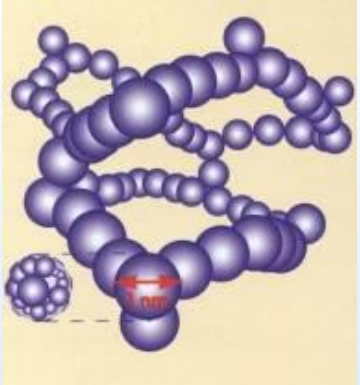
1.5g Base
3ml CL
0.04g PEI
1g Acetone
(pH = 1)

1.5g Base
3ml CL
0.02g PEI
800ml Acetone
(pH = 1)

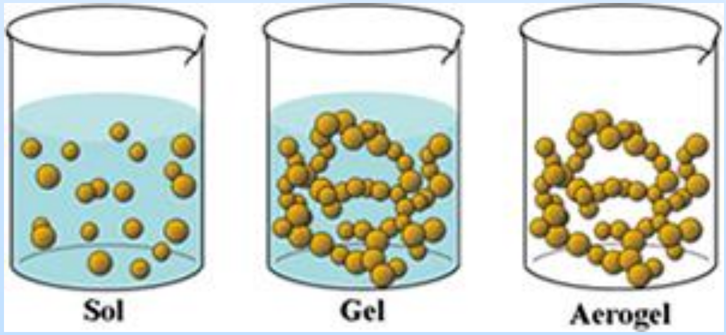
What are Aerogels?

Nanoporous solid with a specific structural morphology……

- Open structure - up to 99% open porosity
- Pore diameters = ~ 10-40 nm on average *(< 1/30,000th the width of a human hair)*
- Nanoporosity slows heat and mass transport, providing record-low thermal conductivity values.



$Si(OR)_4 + 2\ H_2O \rightarrow (SiO_2)_x + 4\ ROH$



…..and the method of production

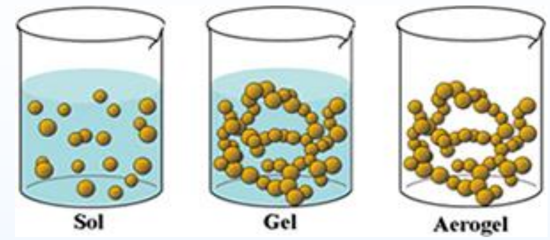
1. Sol-gel Processing
2. Aging
3. Extraction (solvent exchange)
4. Drying (with supercritical fluids)

Scope of Work

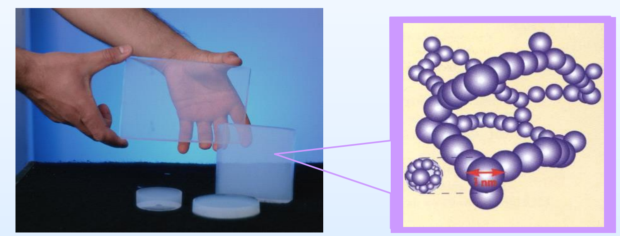
Task 2.0 – Sorbent Preparation and fine-tuning

<u>**Subtask 2.2 – Preparation of amine-functionalized aerogel**</u>

<u>Subtask 2.2.1– Amine Functionalized Aerogel (AFA) Sorbent Further Optimization</u>



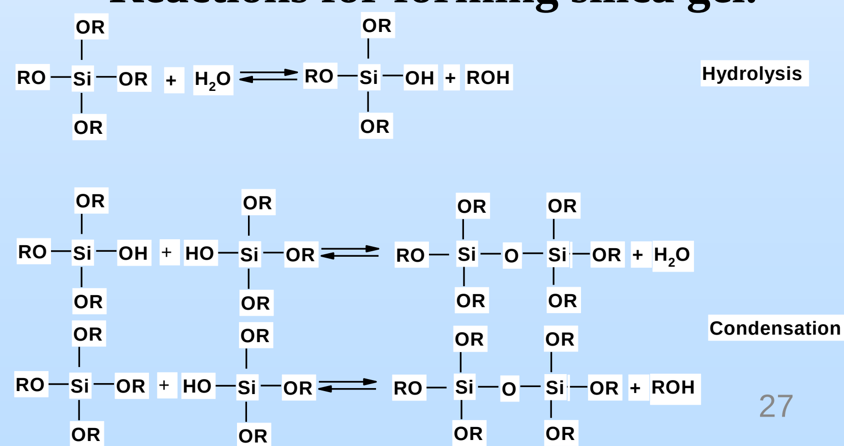
The Recipient will design AFA formulation to maximize hydrophobicity with different primary, secondary and tertiary amines for CO_2 capture. The diamine linker with a secondary amine for weakly adsorbed CO_2 will be incorporated into AFA formulation



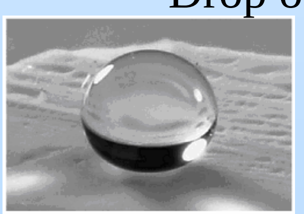
<u>Subtask 2.2.2 – AFA Bead Fabrication</u>

Optimum bead sorbent will be selected and produced for scale-up production to an amount up to 1 kg.

Reactions for forming silica gel.



Drop of water on surface



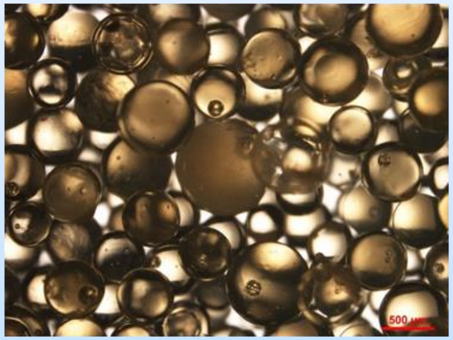
Hydrophobic aerogel monolith

Fiber-reinforced hydrophobic aerogel

AFA Bead Fabrication

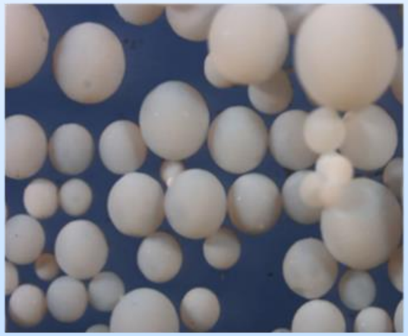
- The optimum AFA formulation will be used to fabricate AFA sorbents in the form of beads.
- The bead size and bead quality will depend on the:
  - Gel time of the AFA sol; and, the
  - Mixing speed and temperature of the “dispersing medium”

Type #1 Sorbent Beads



- Translucent
- 300 – 900 µm
- ~ 0.7 g/cc- packed beads
- S_{BET} = 389 m^2/g
- Ave. Pore diameter = 10 nm

Type #2 Sorbent Beads



- Opaque
- 300 – 1,000 µm
- ~ 0.8 g/cc- packed beads
- S_{BET} = 292 m^2/g
- Ave. Pore diameter = 22 nm

Our results								
Amine	Support	Ads. $t_{1/2}$ /s	Conc. CO_2 %	T_{ads} ^{o}C	CO_2 capacity (mmol/g)	Amine efficiency (mol CO_2/mol N)	Fraction of weakly-adsorbed CO_2	Ref
PEG/lysine (0.3:1)	SiO_2	10.5	15% in Ar	40	0.61	0.18	39%	Link
PEG/lysine (1:1)		-			0.46	0.21	87%	
PEG/lysine (2:1)		-			0.19	0.13	85%	
Glycerol/lysine (1.8:1)		2.7			0.94	0.28	60%	
PEG/lysine (0.3:1)		16.5	Air		0.58	0.17	24.5%	
PEG/lysine (1:1)		-			0.41	0.19	87%	
PEG/lysine (2:1)		-			0.15	0.10	88%	