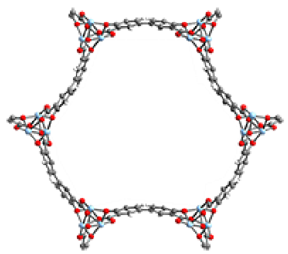
National Energy Technology Laboratory Carbon Capture 2020 Integrated Review Webinar

October 5-7, 2020



Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture

FWP-FP00006194

Jeffrey R. Long

Lawrence Berkeley National Laboratory

Project Overview

Funding

- Total project funding
  - DoE share: $7.4M
  - Cost share: $755k

Project Participants

- PI: Jeffrey Neaton (LBNL)
- Co-PI: Jeffrey Long (LBNL)
- Mosaic Materials (MOF production)
- Svante (System development)
- Electricore (System development)
- CCSI^2 (Process modeling – unfunded)

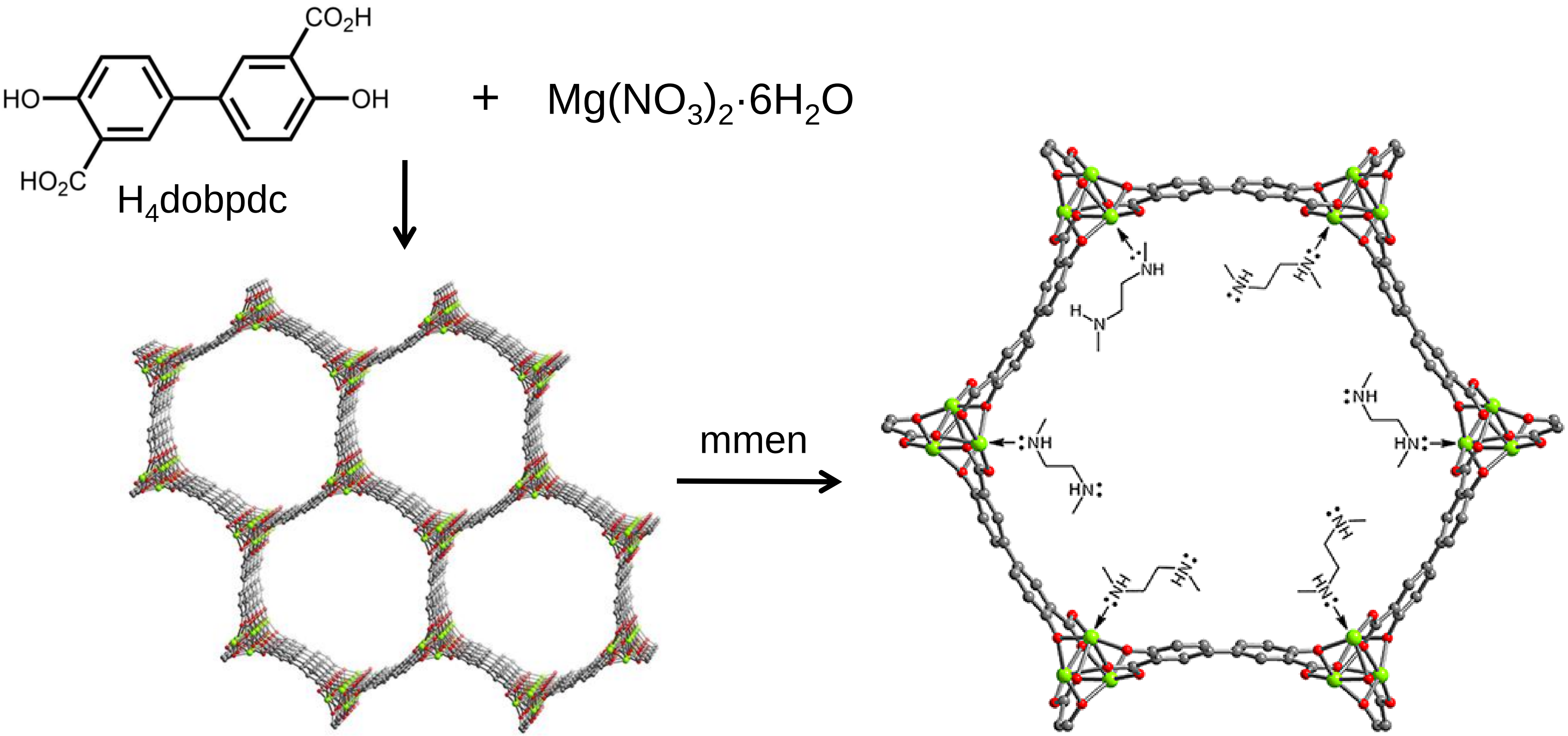
Overall Project Performance Dates

- Project start date: 8/1/2017
- Industrial partners start date: 8/1/2018
- Project end date: 7/31/2021

Overall Project Objectives

Development of a transformational technology based upon a diamine-appended MOF for post-combustion CO_2 capture at a power plant

Technology Background: MOFs for CO_2 Capture

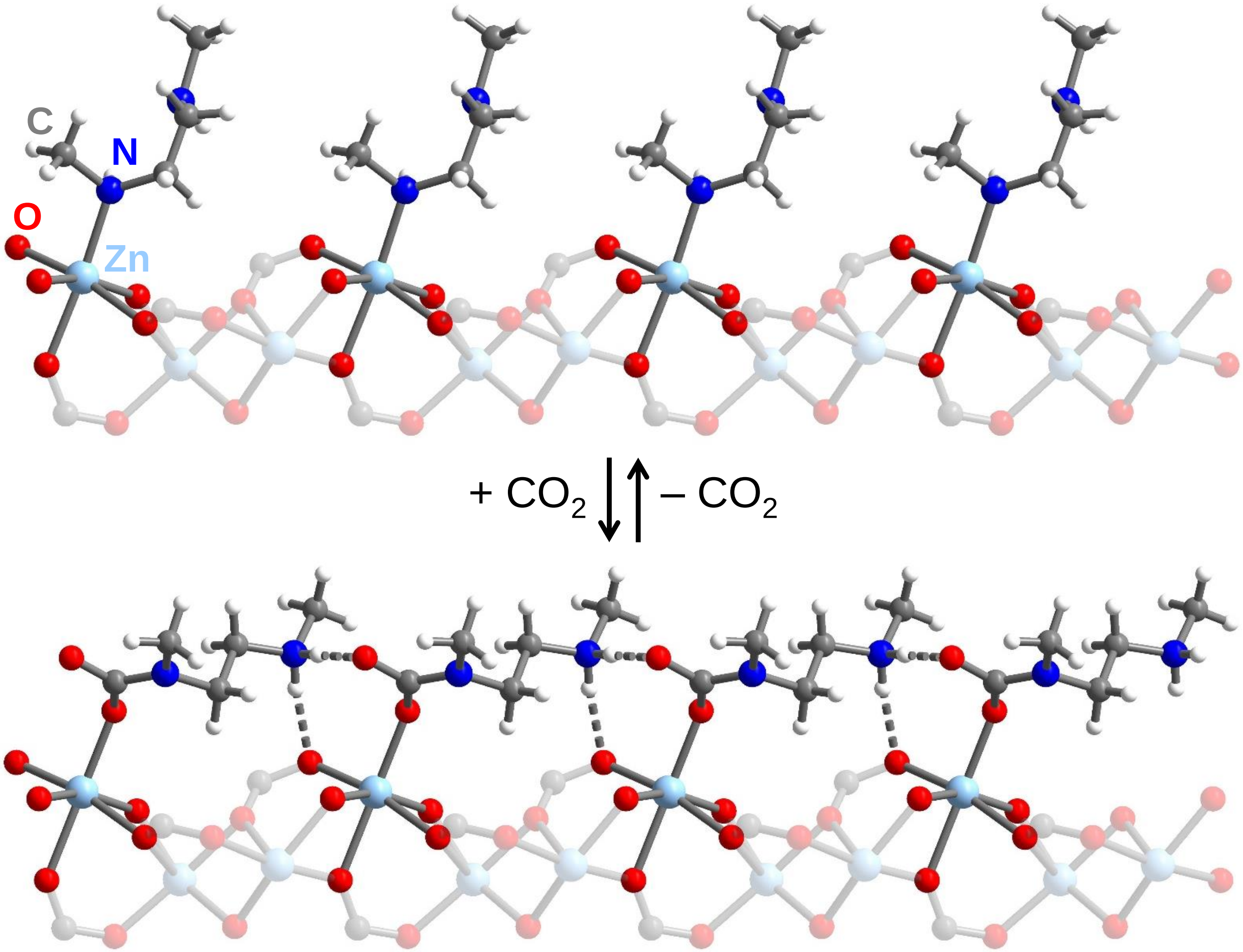


Mg_2(dobpdc) **mmen-Mg_2(dobpdc)**

- MOF channels have a diameter of 18 Å and are lined with open Mg^{2+} sites
- Dangling amines coat periphery of the channel leaving space for rapid CO_2 diffusion

McDonald, Lee, Mason, Wiers, Hong, Long *J. Am. Chem. Soc.* **2012**, *134*, 7056

Cooperative CO_2 Adsorption Mechanism



Siegelman, McDonald, Gonzalez, Martell, Milner, Mason, Berger, Bhown, Long *J. Am. Chem. Soc.* **2017**, *139*, 10526

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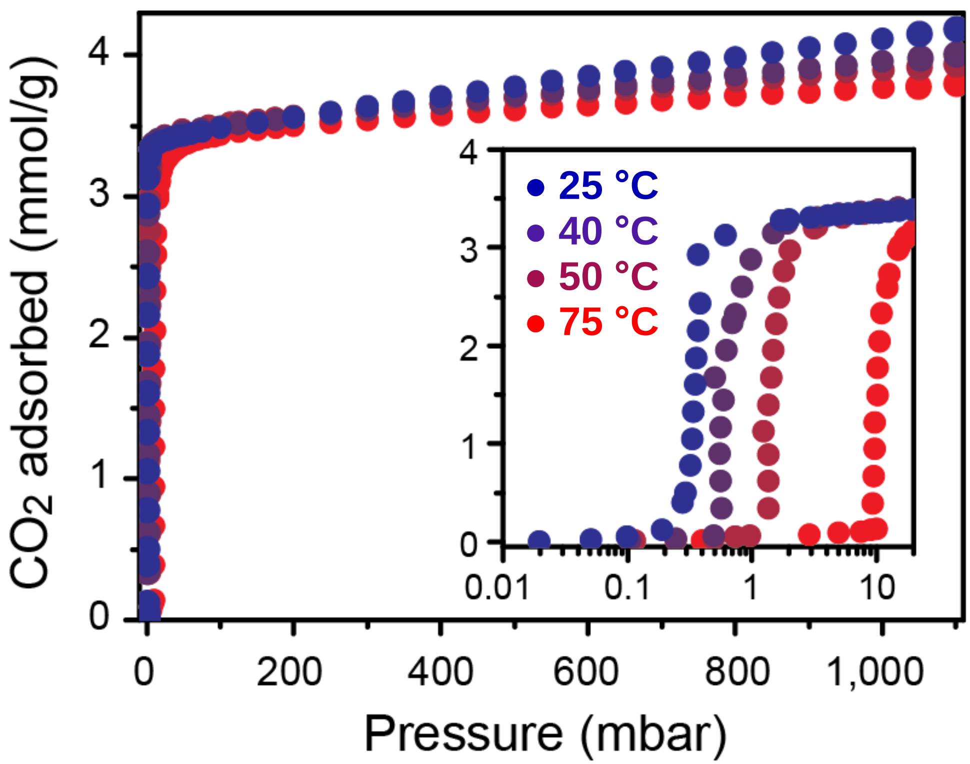
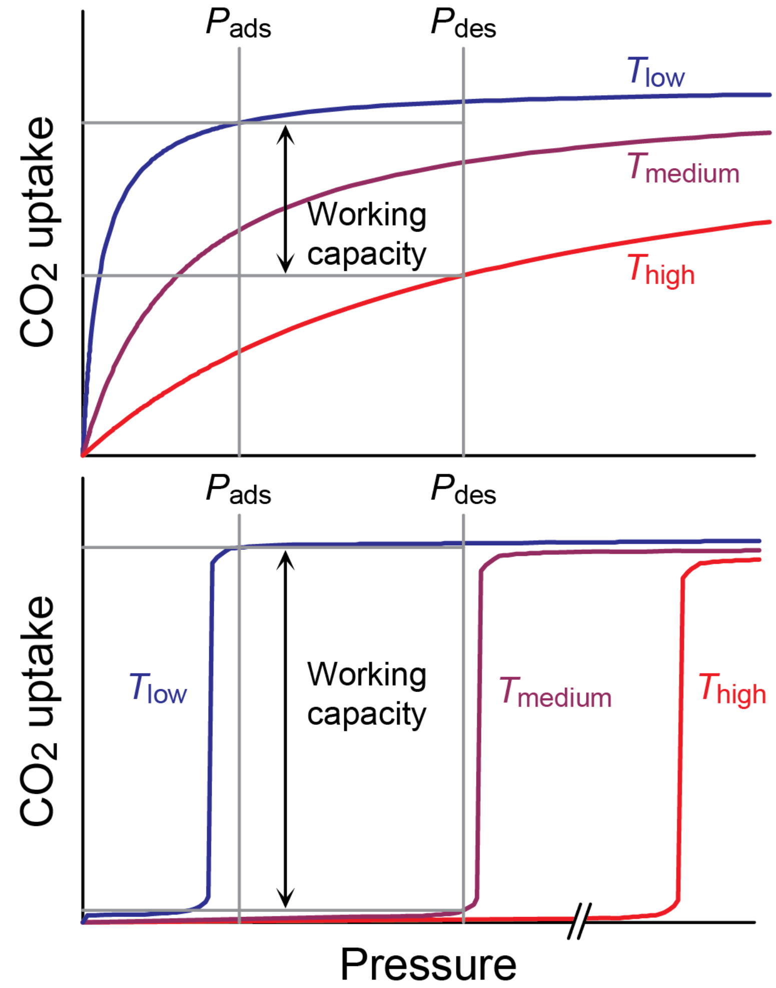
Step-Shaped Isotherms via Cooperative CO_2 Binding

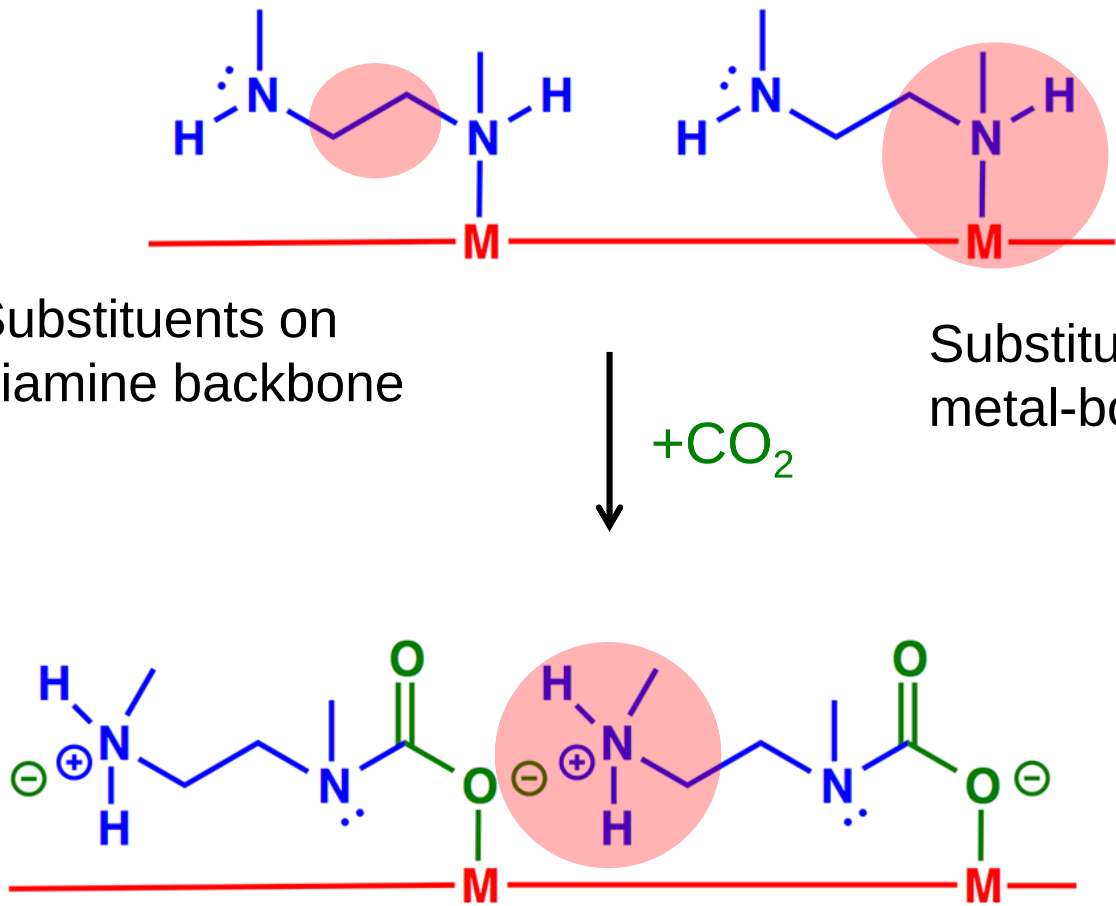




- Very little hysteresis upon desorption of CO_2
- Step shifts rapidly to higher pressure with increasing temperature

McDonald, Mason, Kong, Bloch, Gygi, Dani, Crocellà, Giordano, Odoh, Drisdell, Vlaisavljevich, Dzubak, Poloni, Schnell, Planas, Lee, Pascal, Prendergast, Neaton, Smit, Kortright, Gagliardi, Bordiga, Reimer, Long *Nature* **2015**, *519*, 303

Manipulating the Adsorption Step Position



Substituents on diamine backbone

Substituents on metal-bound amine

Substituents on ammonium-forming amine

Technical and Economic Advantages/Challenges

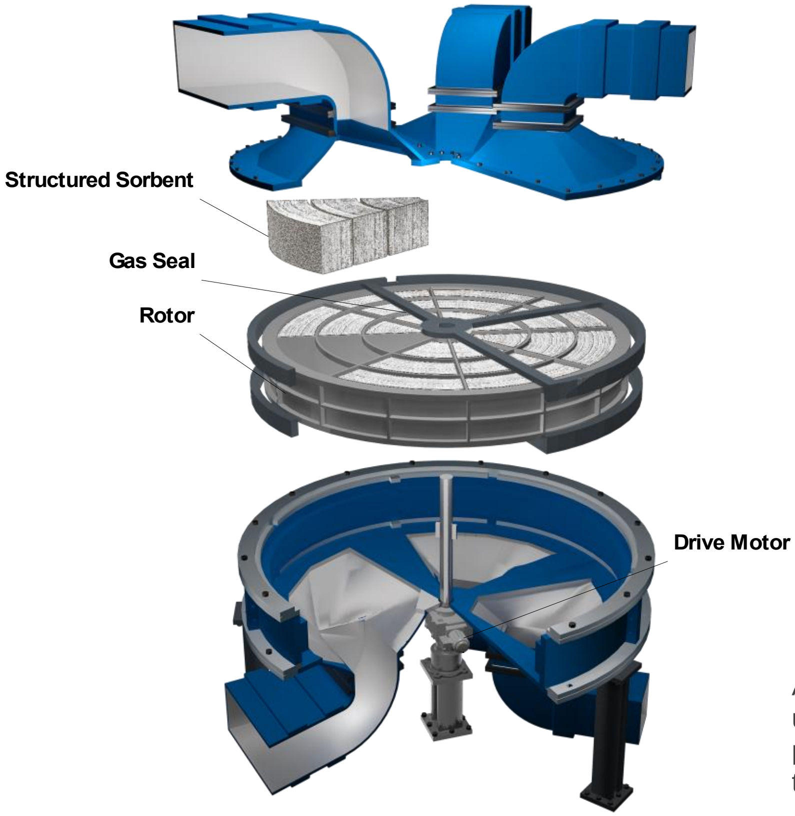
Advantages

- High tunability of amine-appended framework materials
- Large working capacity due to stepped CO_2 adsorption
- High CO_2 selectivity over N_2, O_2, and H_2O
- Molecular level characterization and modeling is possible

Challenges

- Large scale and economical production of materials
- Integration within an appropriate separation platform
- Long-term durability real cycling conditions are unknown
- Determination of optimal process conditions

Objective: Implement Adsorbents in RC-TSA Process



Three simple steps:

60 SECONDS

Step 1: Adsorption

As flue gas passes through the VeloxoTherm™ Adsorbent Structure, CO_2 clings to the adsorbent while the other gases pass through.

Step 2: Regeneration

After the structured adsorbent becomes saturated with CO_2, it is regenerated. Low-pressure steam is used to release the CO_2 from the adsorbent.

Step 3: Cooling

After the CO_2 has been released, air is used to cool the structured adsorbent, preparing it for the adsorption step and the process is started over again.

Svante VeloxoTherm™ is used to perform initial validation experiments on promising materials with RC-TSA process on a single bed

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Technical Approach and Project Scope

LBNL: Materials discovery, synthesis & characterization

- Computational prediction of materials
- Synthesis of amine-appended MOFs (Gen1−Gen3)
- Preliminary stability testing
- Optimize scalable diamine-appended MOF production process

Mosaic: Materials production & scale-up R&D

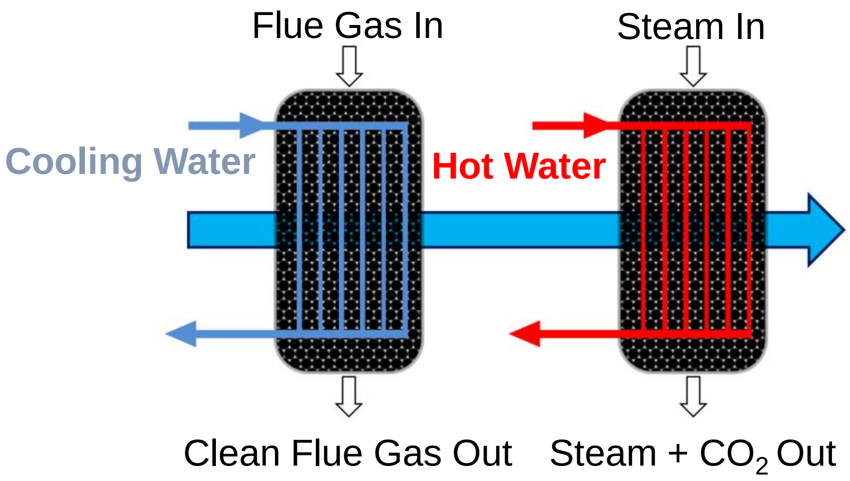
- Interface between LBNL and Svante for process improvements
- Deliver kg-scale batches of material for preliminary testing and demo at NCCC

Svante: Implementation & assessment in real flue gas capture processes

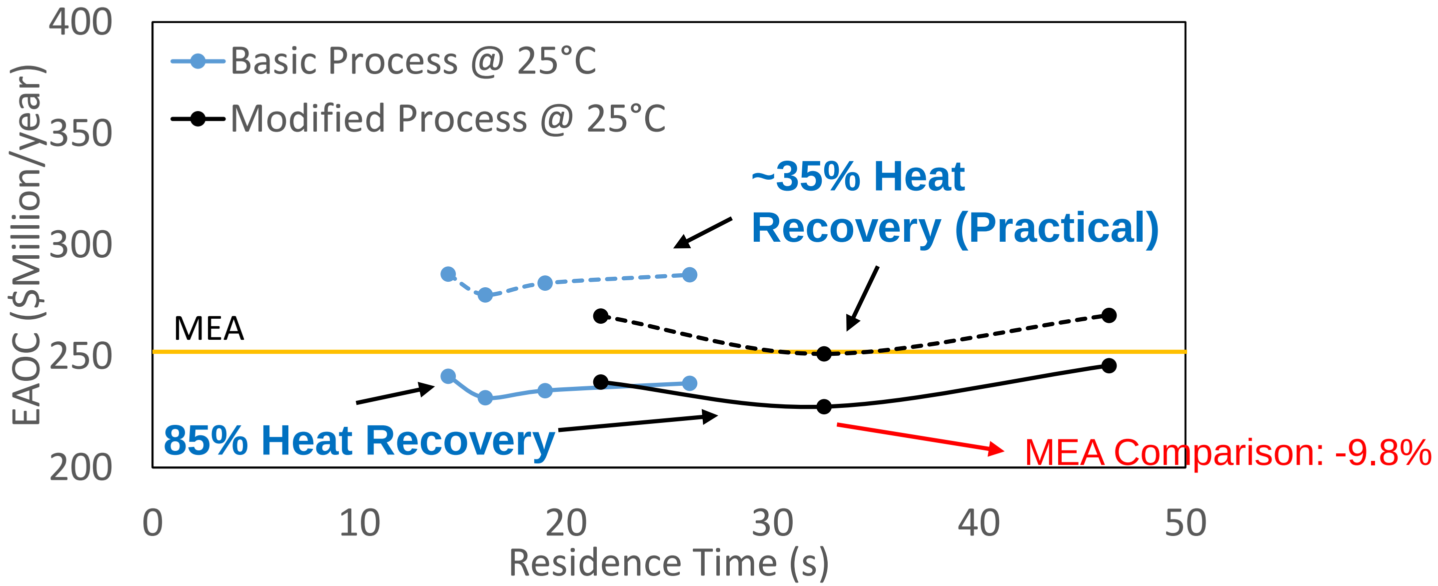
- Formation of structured adsorbent beds
- Process development and testing: powders → VTS → PDU → RPV-RAM
- Process modeling and validation

Goal: Development of transformative carbon capture technologies by the cooperative insertion of CO_2 in amine-appended frameworks

Collaboration with $CCSI^2$



Support from $CCSI^2$ provides computational analysis of step-shaped adsorbents in different CO_2 capture processes to screen various contactor configurations and optimize performance while minimizing cost

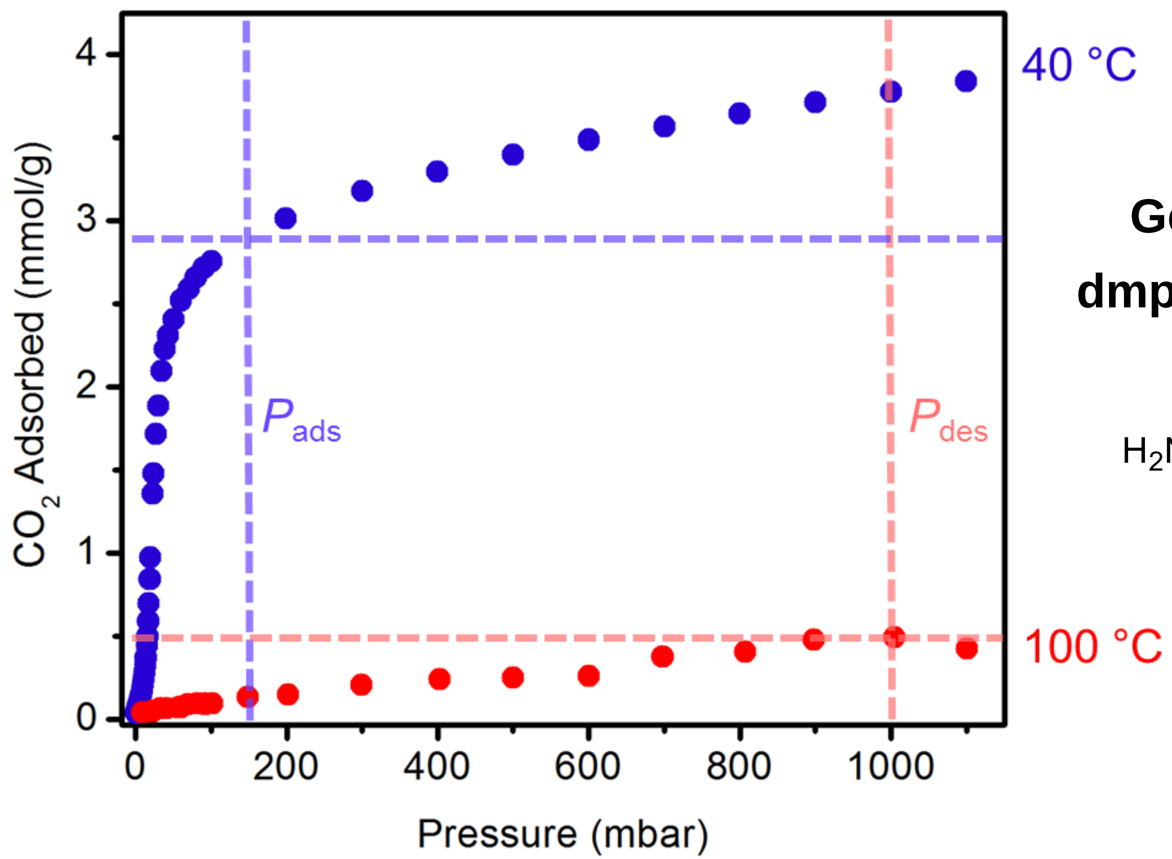


Hughes, Kotamreddy, Ostace, Bhattacharyya, Siegelman, Parker, Didas, Long, Omell, Matuszewski, *manuscript in preparation*

Project Schedule (Year 3)

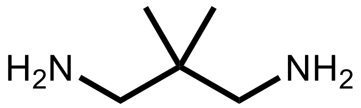
	Tasks
Materials Synthesis	Synthesis & characterization of new diamine-appended MOFs (Gen2 materials) based on test system integration feedback
	Characterization of the effects of water, O_2, SO_x, and NO_x on CO_2 adsorption properties of Gen1 & Gen2 materials
Computation	Search optimal amine-appended MOFs within databases of reported materials
	Prediction of CO_2 binding energies, relative isotherm step position and mechanical strength for amine-appended MOFs
System Testing	Gen1 materials production & process cost model development
	Concept development modeling and testing
	Process & cycle design simulations

Year 2 Recap: Gen1 Material for Scaling and Integration



Gen1 material:

dmpn-Mg_2(dobpdc)



- CO_2 adsorption step positioned for 90% capture from coal flue gas at 40 °C
- 2.4 mmol/g (9.1 wt %) working capacity with only a 60 °C temperature swing

Milner, Siegelman, Forse, Gonzalez, Runčevski, Martell, Reimer, Long *J. Am. Chem. Soc.* **2017**, *139*, 13541

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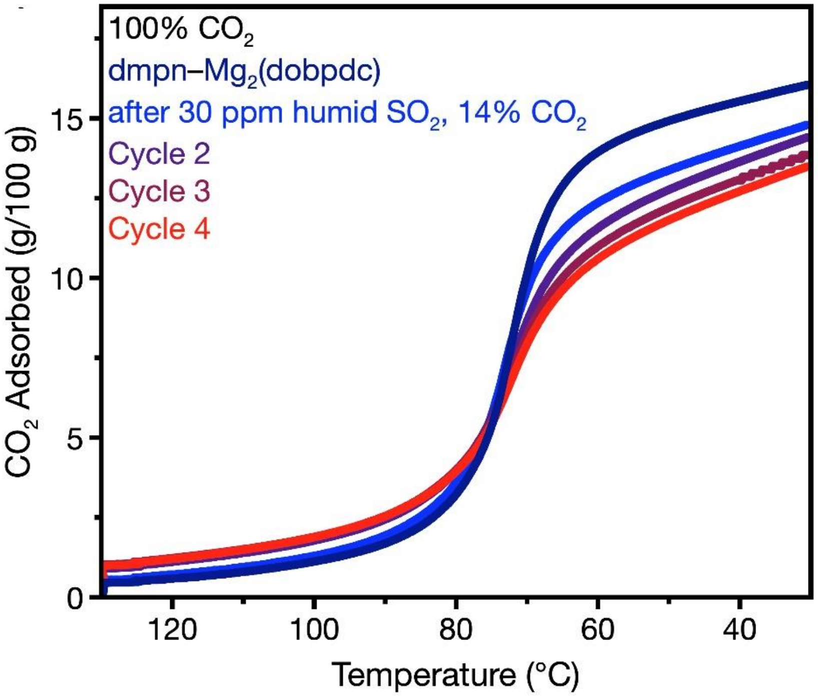
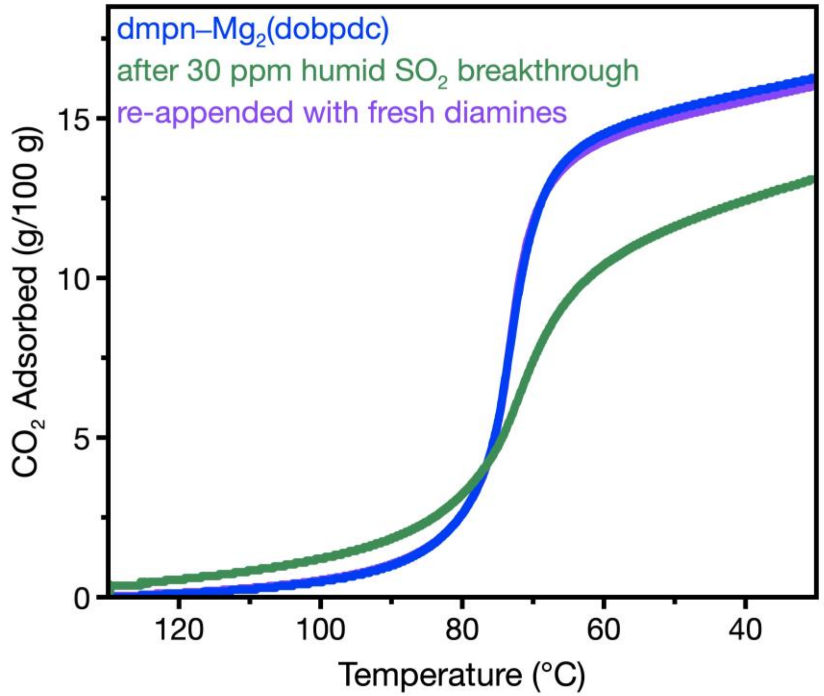
Year 3 R&D: SO_2 Stability and Regeneration of Gen1 Material





- Gen1 material retains 90% of its original CO_2 capacity following saturation with simulated coal flue gas
- Subsequent exposures yield smaller changes in performance
- Stripping and replacing amines recovers full CO_2 capacity in the material

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Year 3: Large Scale Synthesis of Gen1 Material

Objectives for Mosaic Materials

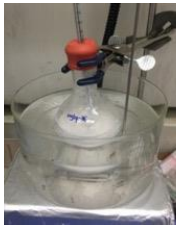
- Produce MOF at the kg scale for use by Svante
- Identify manufacturing improvements at this scale
- Increase scale 3x to reduce variability, increase production

Scale-up involves four steps:

1. MOF synthesis
   Batch reaction of metal salt and organic linker in solvent
2. MOF purification
   Raw product washed and dried to remove impurities and excess solvent
3. Amine loading
   Purified MOF product is impregnated with diamine
4. Activation
   Solvent is removed

These steps are interdependent, such that changes to one can impact the others

Increasing Scales of Synthesis Equipment



LBNL
Gen1
Process

150 mL
Reaction

9 L Reaction
~350 g batches

27 L Reaction
~1 kg btaches

Scale-Up Research and Optimization

Stage 1: Scale-up MOF from 9 L to 27 L scale → success

- All QC metrics met: PXRD after synthesis, N_2 surface area

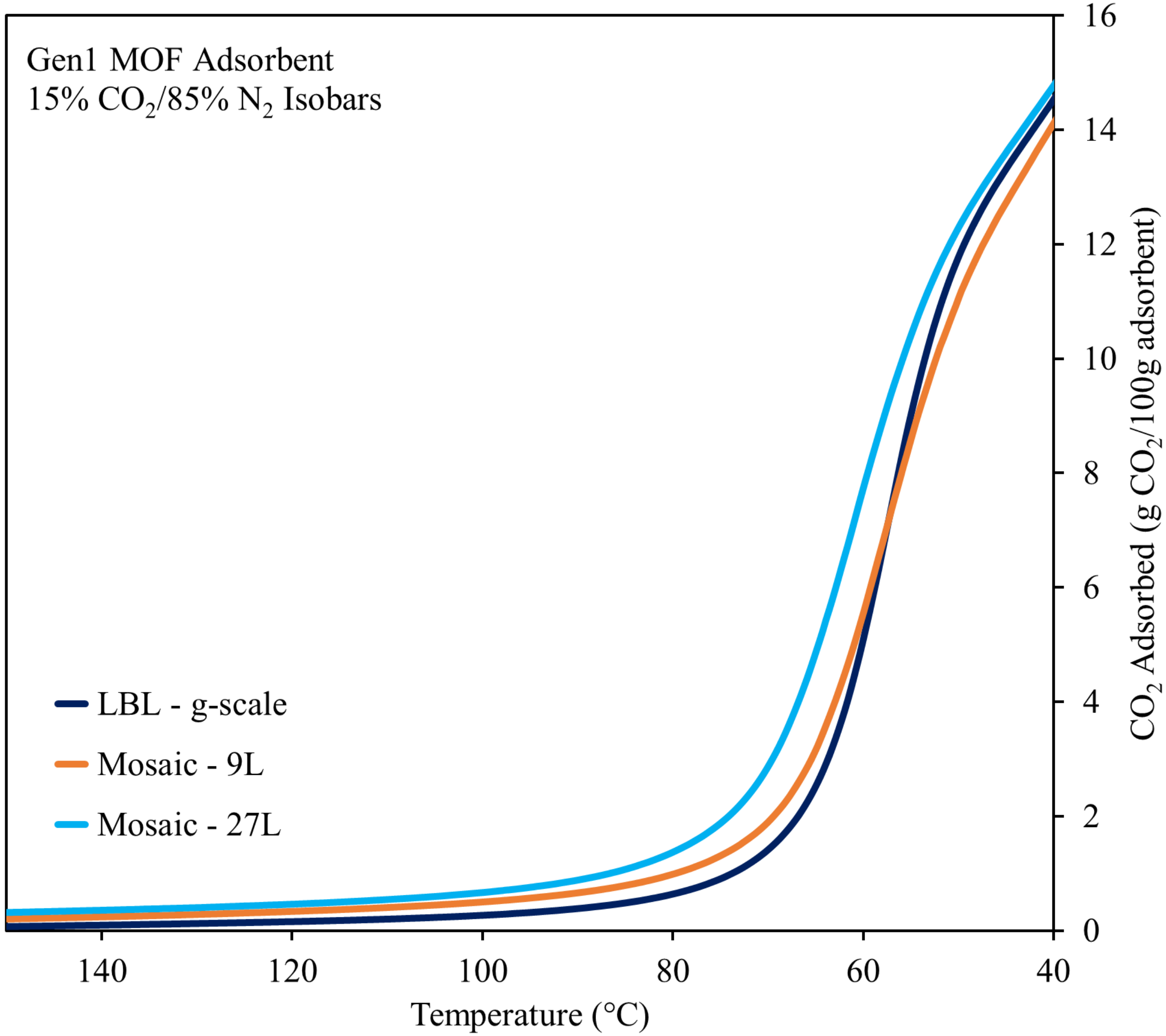
Stage 2: Scale MOF purification and washing → success

- All QC metric met: N_2 surface area

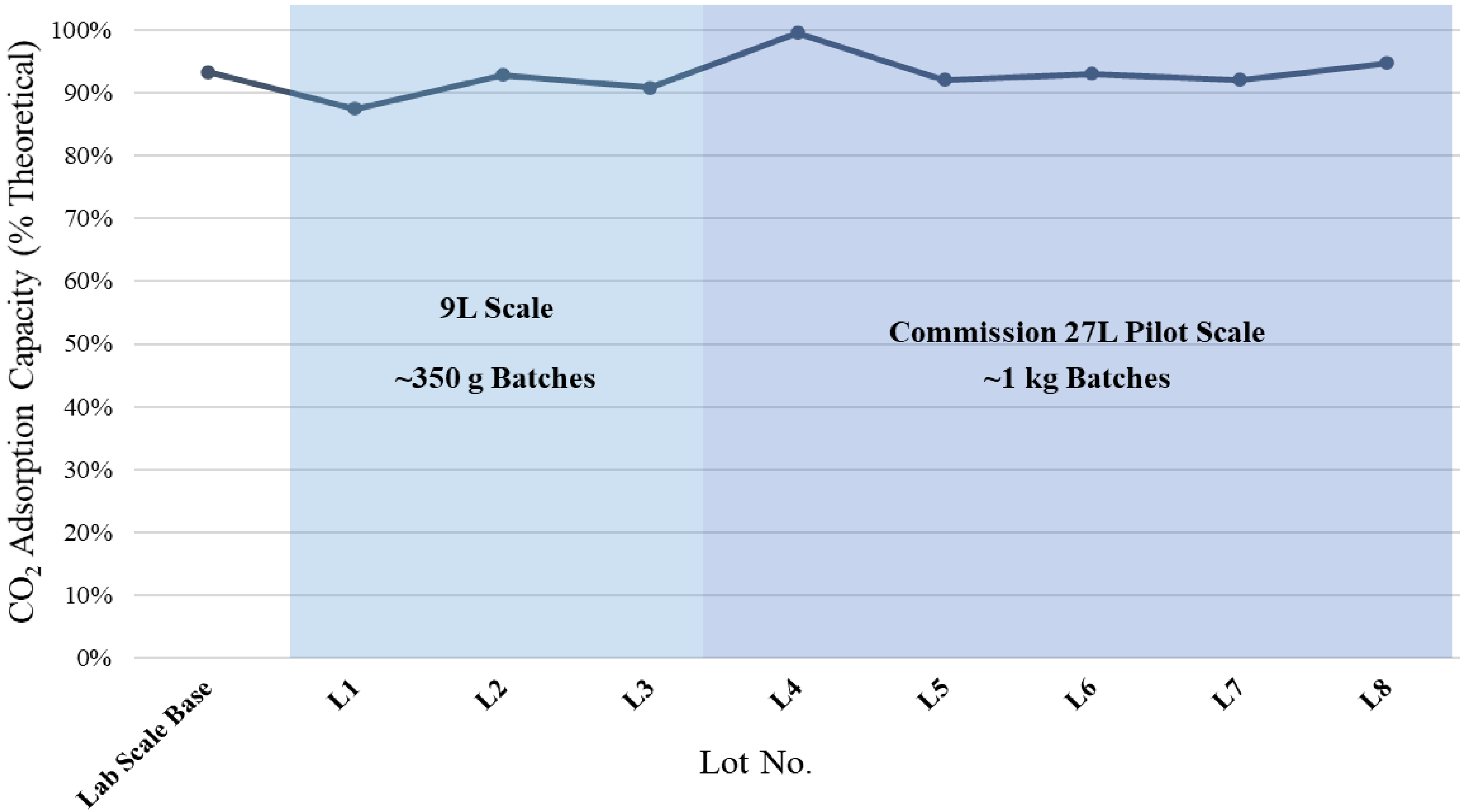
Stage 3: Scale MOF amination from 5 L to 20 L → success

- All QC metrics met: Amine content and CO_2 adsorption capacity via TGA

CO_2 Adsorption Step Retained at Scale



Summary of MOF Manufacturing



- Increased scale: five successful runs with QC metrics met (>80% of g-scale performance), producing >10 kg of Gen1 material to-date

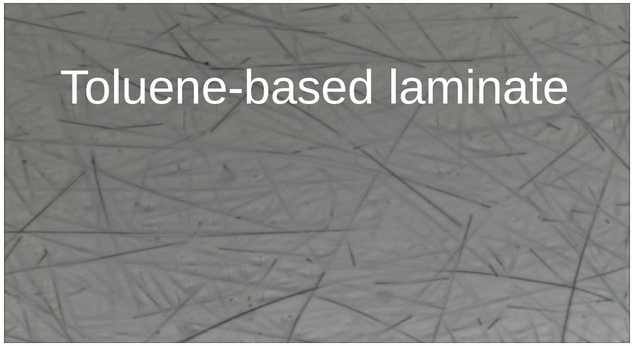
Laminate Coating: Aqueous vs Toluene Slurry

Coating ID	Added diamine	Loading (g/m²)	CO_2 capacity (15% CO_2, 50 °C) (cc/g)
Water based slurry #1	Yes	22.9	28*
Water based slurry #2	Yes	57.35	42.3*
Toluene based slurry	No	95.6	43.5*
MOF powder	-	-	63.5

*CO_2 capacity per g laminate. Based on weight percent, laminate capacity of 43.5 cc/$g_{laminate}$ corresponds to ~62 cc/g_{MOF}.

- First water-based slurry of Gen1 material resulted in low loading and CO_2 uptake
- Improved loading and capacity with second water-based slurry, but slow kinetics observed (see VTS results), loading density still too low
- Toluene-based slurry able to reach the gravimetric CO_2 capacity of the powder and gave the highest loading without the addition of diamine to slurry

VTS Bed Formulation and Testing



Assembled VTS bed under N_2 using toluene-based laminate:

- Bed built at different stages for epoxy curing. With each step, bed kept in nitrogen environment
- Bed kept under positive pressure with nitrogen to ensure driest environment possible

Testing Plan

Evaluate VTS bed performance in adsorption/desorption cycles using the following desorption conditions:

- High temperature CO_2
- Steam

VTS Performance Summary (Water-Based Beds)

	MOF Bed 1 (water-based slurry with added diamine)			MOF Bed 2 (water-based slurry with added diamine)			Target KPI*
	Process with Hot CO_2 (dry)	Process with Steam Day 1	Process with Steam Day 2	Process with Hot CO_2 + 7% moisture	Process with Steam Day 1	Process with Steam Day 2	Process with Steam
Process Baseline Performance							
Cycle Time (s)	**633**	105.5	105.5	407	**100**	105	100
Steam Ratio (kg steam/kg CO_2)	N/A	2.30	2.49	N/A	2.32	2.44	1.40
Productivity (TPD/m³)	Below Detection Limits	1.04	0.97	Below Detection Limits	**2.82**	2.73	10.0
Prod. Purity	N/A	45%	43%	N/A	70.9%	70.9%	90%

Target KPIs to achieve $30/Ton DoE target
Dry feed (16% CO_2), adsorption at 30 °C, desorption using steam in standard process, conditioning with dry N_2

- Hot CO_2 as desorption gas lead to very long cycle time (633 s) due to slow heat transfer between hot gas and adsorbent
- Direct steam desorption enabled significant decrease in cycle time to 100 s

VTS Performance Summary (Toluene-Based Bed)

	Dry feed: MOF Bed 3 (toluene-based slurry bed)	Wet feed: MOF Bed 3 (toluene slurry bed)	MOF Bed 2 (water-based slurry bed)	Target KPI
CO_2 in feed (%)	17.5	17.2	16.7	16
Productivity (TPD/m^3)	4.6	4.2	2.8	10
Product Purity (%)	68.0	66.0	71.0	90

Adsorption at 30 °C, desorption using steam, conditioning with dry N_2

Highest productivity: 4.6 TPD/m^3 with dry CO_2 feed, steam desorption and 60 s cycle time

- Sensitivity tests of several process parameters performed to identify optimal process
- VTS bed with higher loading from toluene slurry preparation significantly increased productivity to 4.6 TPD/m^3, however still lower than target value of 10 TPD/m^3 to reach the $30/ton

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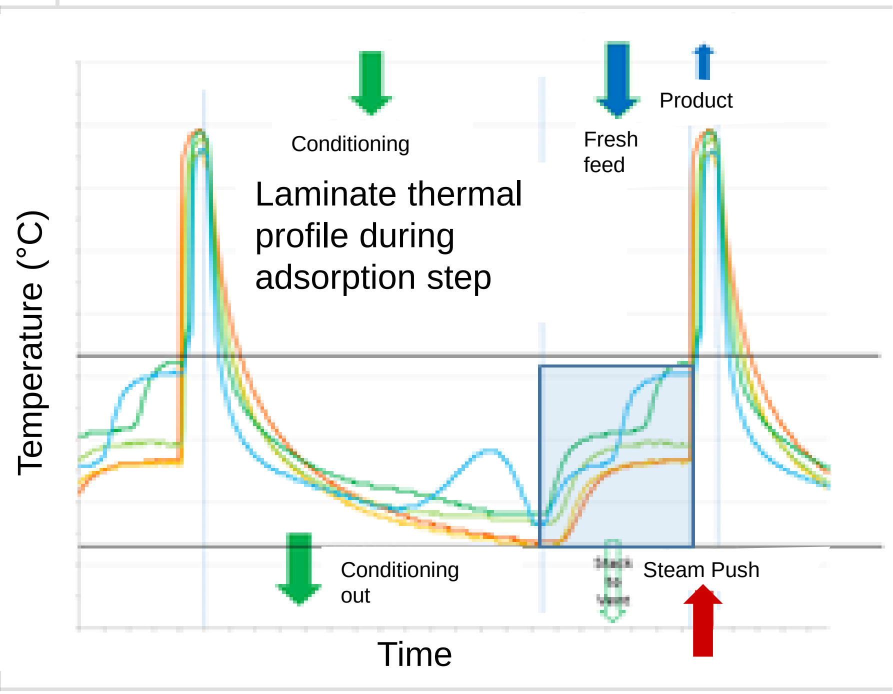
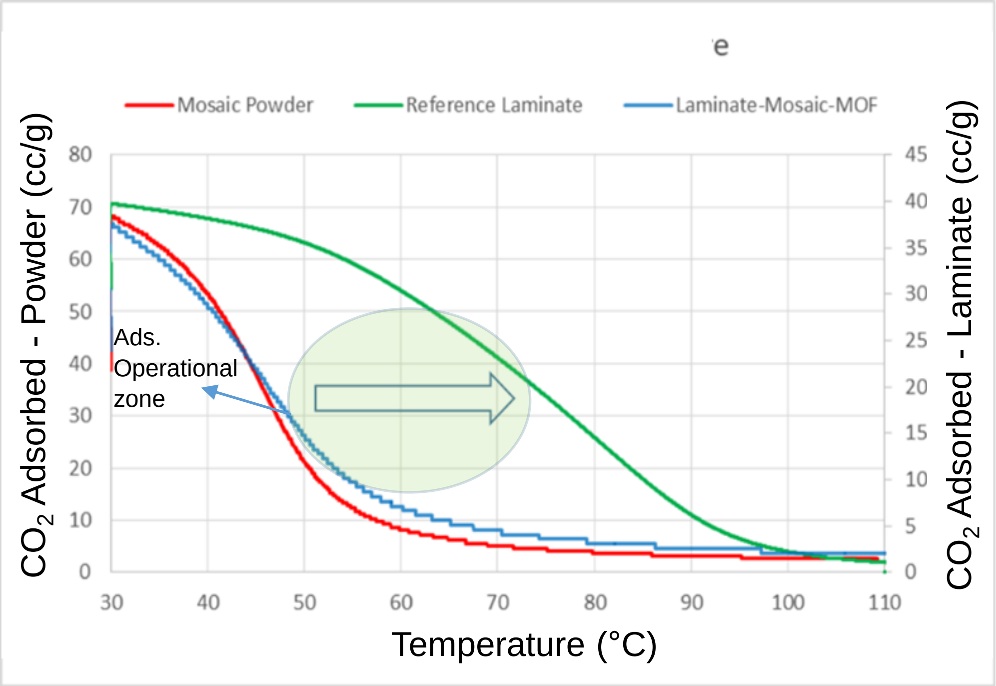
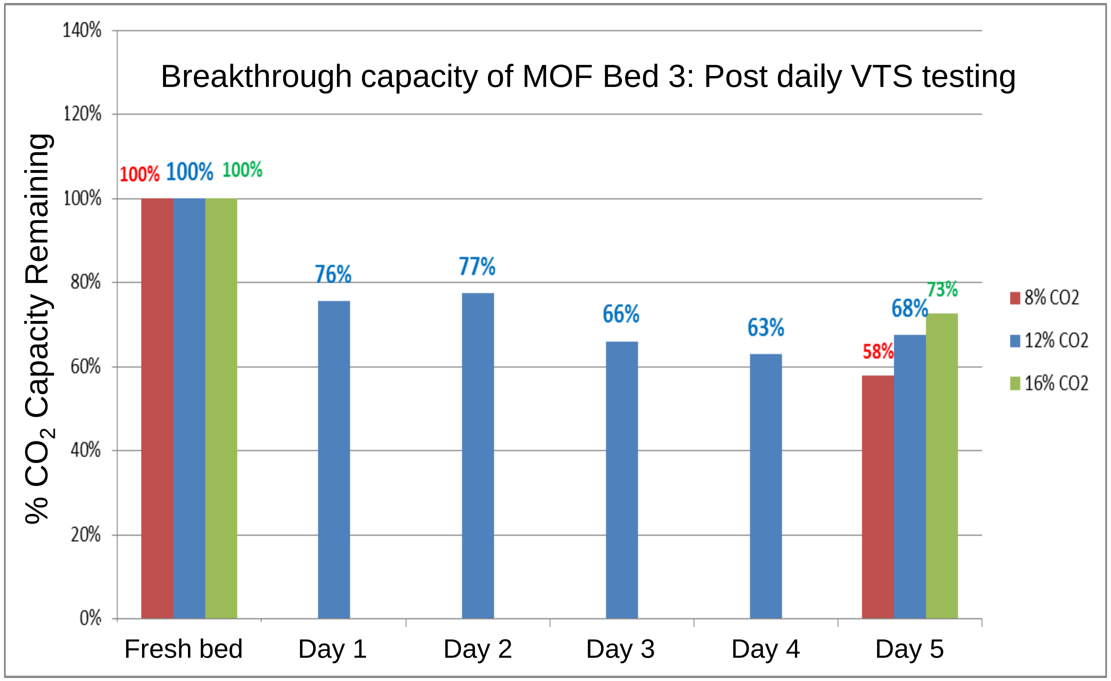
Shifting Step Temperature to Increase Productivity





- Bed temperature increases from 50 to 80 °C during adsorption
- Gen1 material step capacity is outside of operating temperature range
- Shifting material step temperature ~20 °C would result in vastly improved working capacity and productivity

VTS Stability with Steam Process Cycles



- Average reduction in CO_2 uptake is 32% after 5 days testing (12% CO_2)
- Gen1 material subject to degradation when operating with steam

- CO_2 breakthrough used to quantify losses in capacity after each day of testing
- Breakthrough test condition: Adsorption: 8%, 12%, 16% CO_2 in N_2 feed (dry) on fresh bed and after the last process cycle of the day at 40 °C
- Desorption: Dry N_2 gas at 110 °C
- VTS process cycles throughout the day used steam

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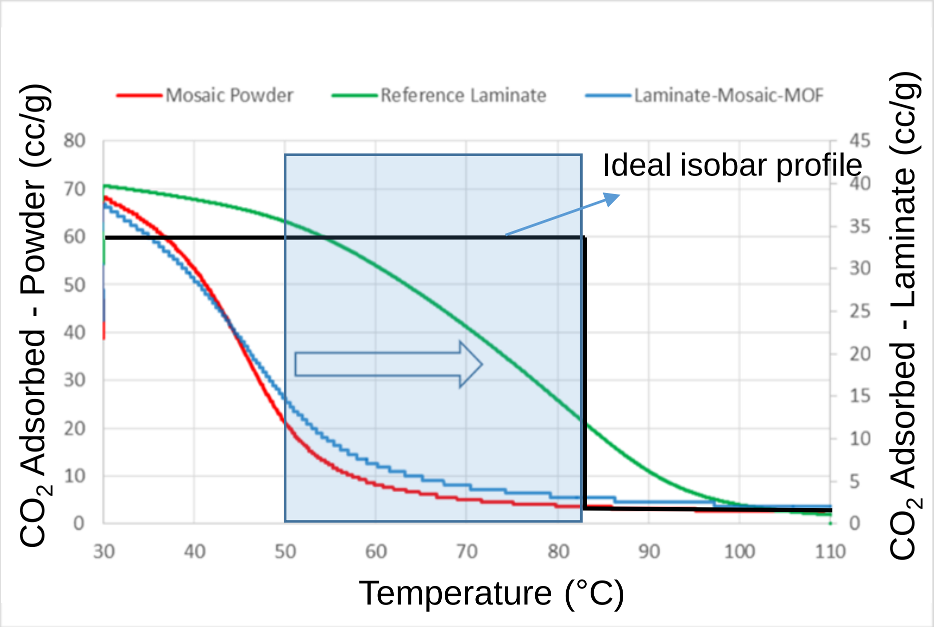
Adsorbent Development Recommendations

Improve water/steam stability: Gen1 material is not water/steam stable owing to diamine loss

Increase CO_2 step temperature

- Isobar step for 15% CO_2 needs to increase from 45 °C to at least 70-80 °C
- Ideal isobar would possess highest capacity at the maximum temperature reached in the bed during adsorption



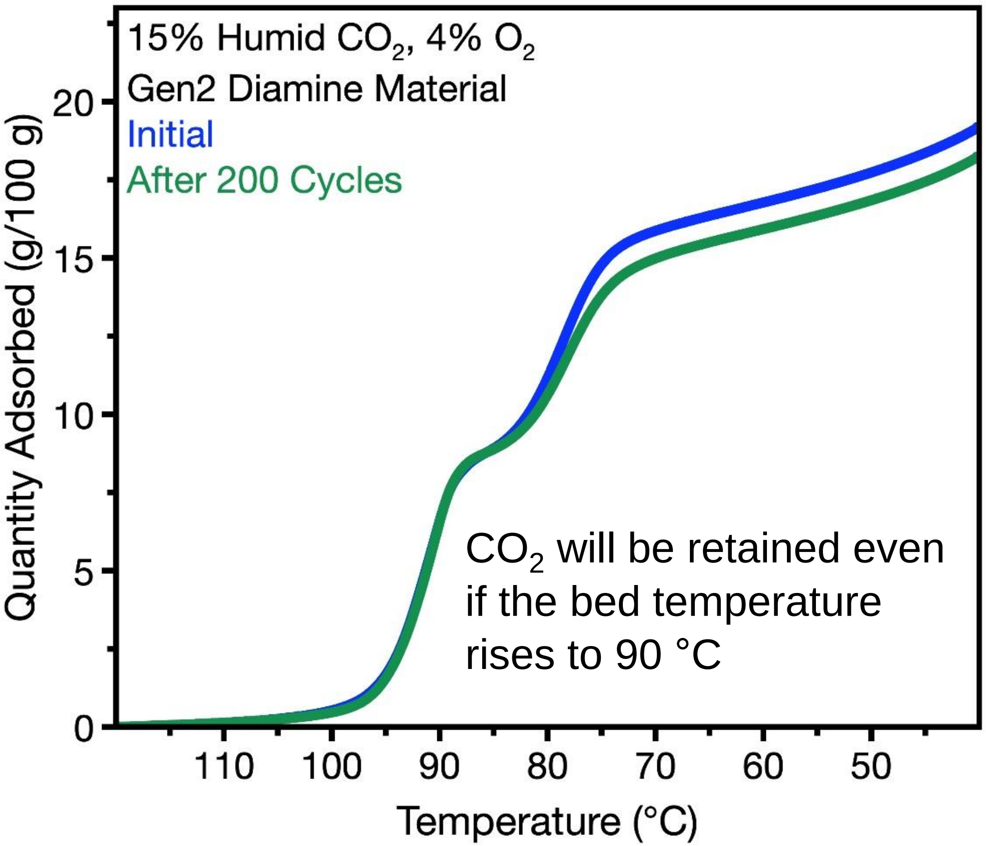
Increase Coating Density: Increasing the adsorbent density would help reach the targeted capacity

Year 3 R&D: Gen2 Material Search

- Heat rise in the bed requires material with higher CO_2 step temperature
- Steam is greatly favored over hot, humid CO_2 as the desorption stream

Increasing Step Temperature:

LBNL identified the best candidate out of 10 diamine-appended MOFs synthesized and screened for cycling stability and CO_2 adsorption temperature



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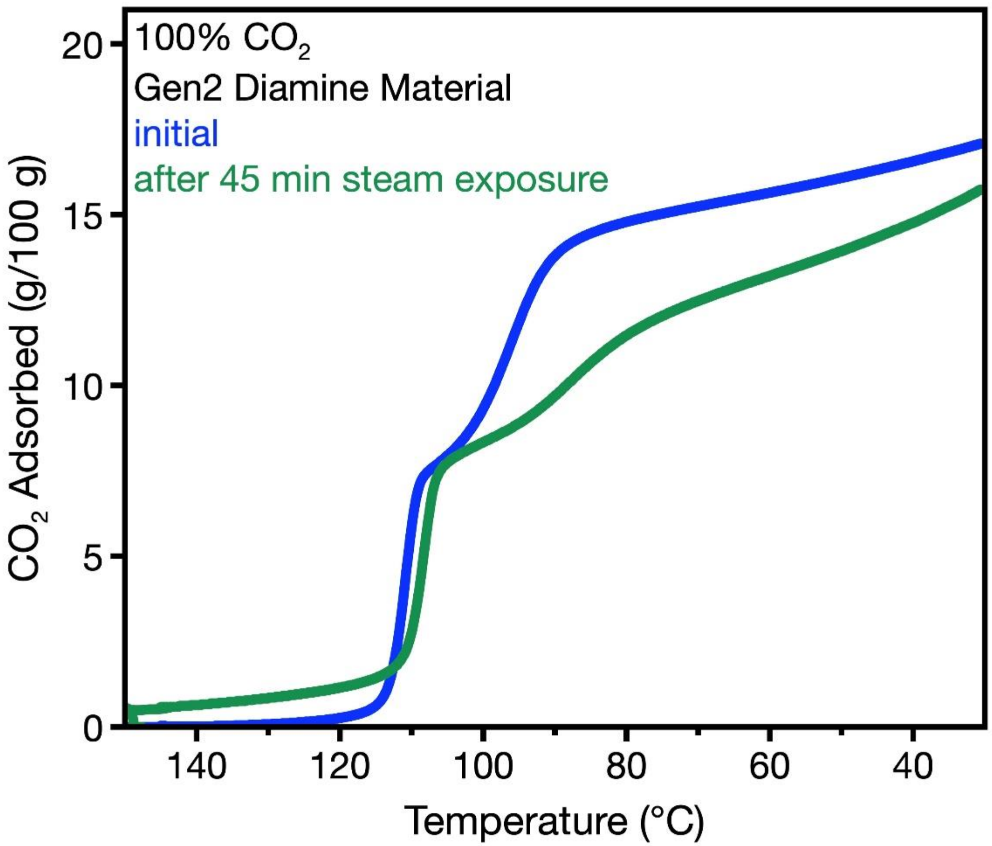
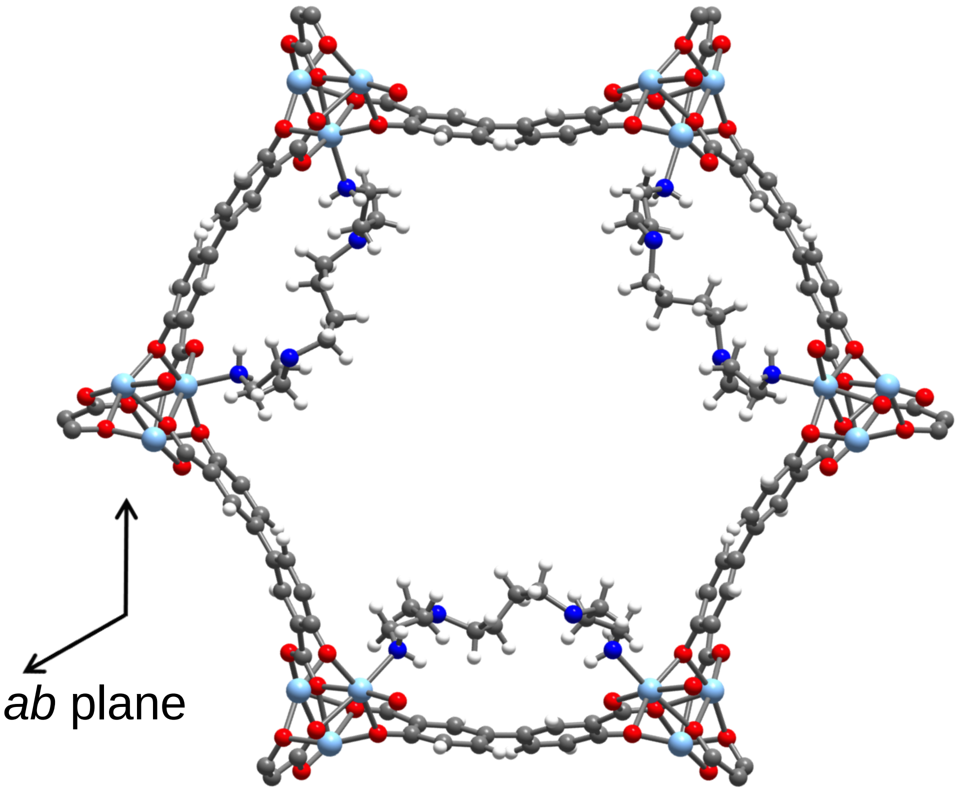
Year 3 R&D: Gen2 Material Search

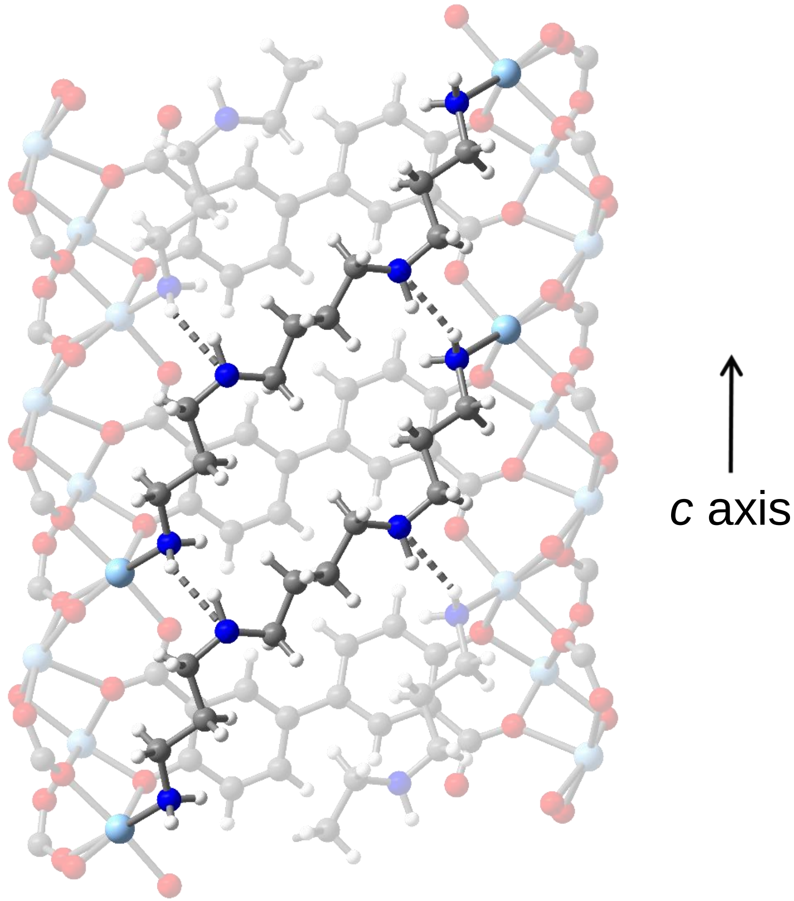


Steam stability:

- Diamine-functionalized materials are unlikely to exhibit long-term steam stability
- Capacity loss in Gen2 diamine material due to significant diamine volatilization

Moving Forward: Tetraamine-Appended Mg_2(dobpdc)

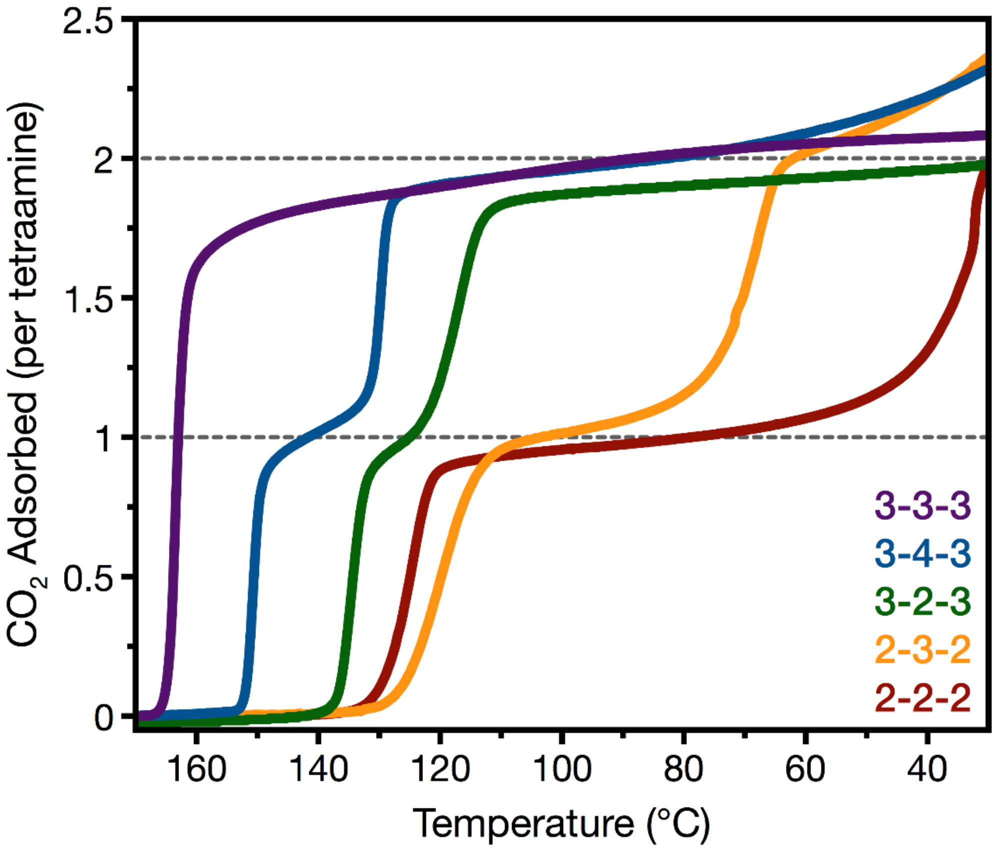




- Binding tetraamines at two metal sites stills allows cooperative CO_2 adsorption
- *Much* greater stability due to reduced volatility and multi-metal coordination

Kim, Siegelman, Jiang, Forse, Lee, Martell, Milner, Falkowski, Neaton, Reimer, Weston, Long *Science* **2020**, *369*, 392

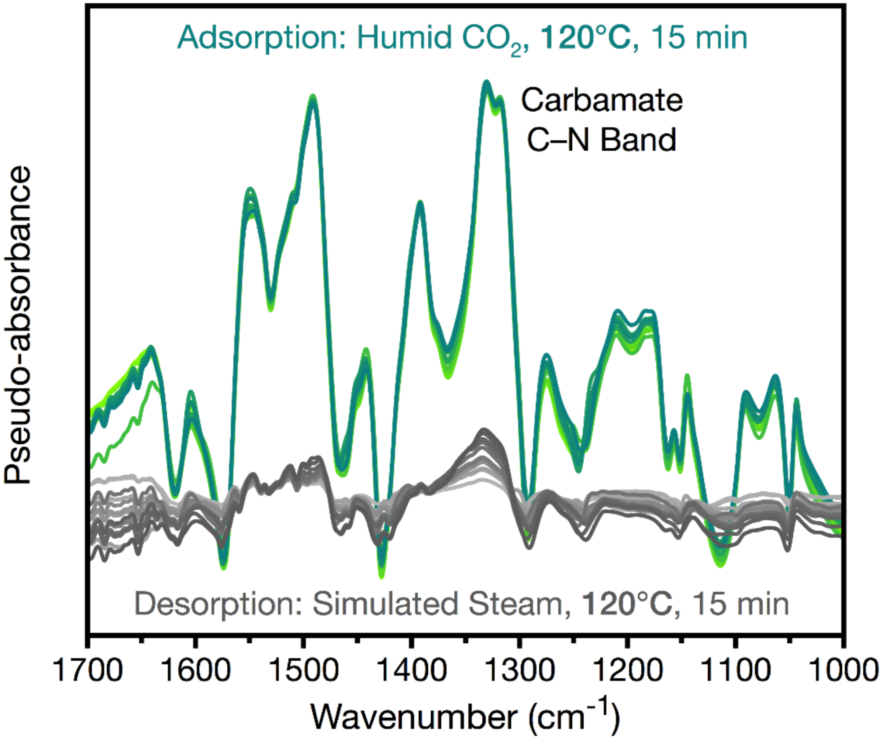
CO_2 Adsorption in Tetraamine–Mg_2(dobpdc)

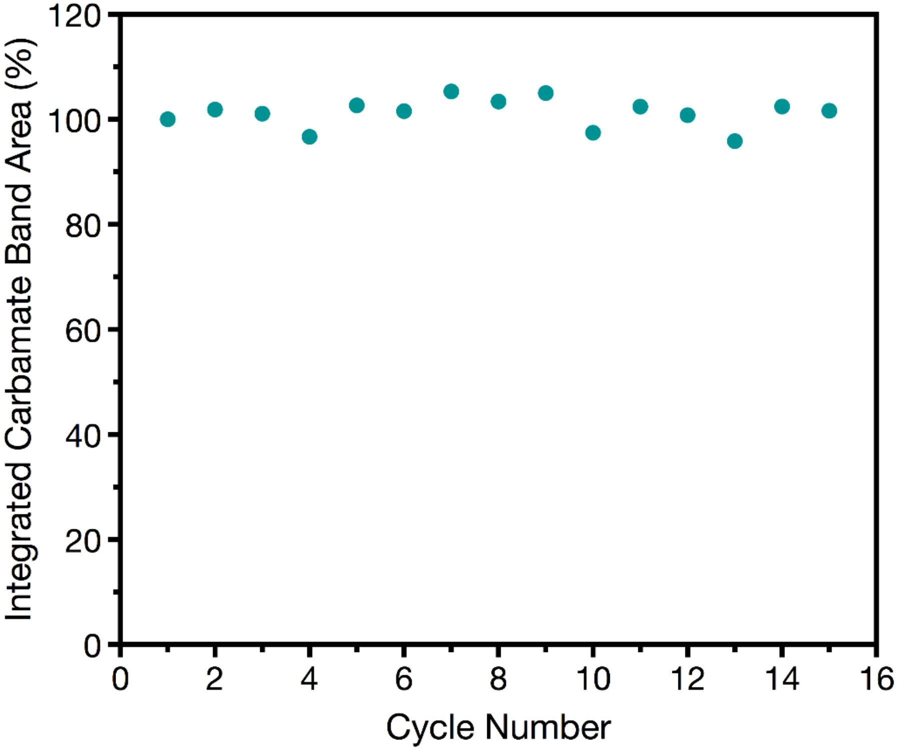


- Step position can be tuned and capture can be achieved at high temperatures
- Double step due to slight energy difference for forming two types of chains

Kim, Siegelman, Jiang, Forse, Lee, Martell, Milner, Falkowski, Neaton, Reimer, Weston, Long *Science,* **2020**, *369*, 392

Stability to Steam Stripping





- Carbamate C-N band indicates cooperative chain formation upon CO_2 uptake
- Exhibits stability to repeated CO_2 stripping via direct steam contact

Kim, Siegelman, Jiang, Forse, Lee, Martell, Milner, Falkowski, Neaton, Reimer, Weston, Long *Science* **2020**, *369*, 392

Plans for Future Testing and Development

Gen2 material scale up and validation

- Gen2 manufacture at kg scale
- Preliminary validation that material satisfies Svante process requirements (VTS bed testing) [Go/Go-No decision point]
- RTSA testing with VTS bed: steam and hot CO_2
- In house multi-bed PDU performance testing: optimize cycle parameters

System testing and optimization

- Gen2 manufacture for multi-bed large scale demonstration campaign
- Planning and refinements to process cycles
- Long-term stability and performance demonstration (500 h) of Gen2 material

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Sara Odom

CCSI^2: West Virginia University
Prof. Debangsu Bhattacharyya
Ryan Hughes

NETL Program Managers
Krista Hill
Andrew Jones (former)
José Figueroa (former)

Appendix Items

Organizational Structure and Management

LBNL Research Team

Jeffrey Long
Materials
(LBNL)

Jeffrey Neaton
Computational
analysis (LBNL)

NETL Project Manager
Krista Hill

Jeffrey Neaton
Lead PI (LBNL)

Managing Director (MD): Stephanie Didas
Administrative Officer (AO): Kenna Eames

Management Team

Partners

Mosaic Materials
MOF production

Svante, Electricore
System development

Svante, Electricore, CCSI² Modeling

- Subcontracts issued:
  - Electricore: 12/18/2019 (previously under Letter subcontract)
  - Mosaic Materials: 10/22/2018
- NDA-MTA-IP agreement executed:12/10/2018

Project Timeline

	Task Descriptions	YR 1	YR 2	YR 3	YR 4
Synthesis & characterization	Synthesis of amine-appended MOFs (Gen1 materials)	■	■		
	Characterization of the effect of water, SO_x, and NO_x on CO_2 adsorption properties of Gen1 materials	■			
	Synthesis of new amine-appended MOFs (Gen2)		■	■	
	Characterization of the effect of water, SO_x, and NO_x on CO_2 adsorption properties of new adsorbents		■		
	Characterization of materials fabricated by industrial partners			■	
	Synthesis and comprehensive characterization for new (Gen3) materials predicted in Year 3				■
	Characterization of materials tested by partners				■
Computation	Search optimal amine-appended MOFs within databases of reported materials	■	■		
	Prediction of CO_2 binding energies for amine-appended MOFs	■			
	Search optimal amine-appended MOFs (Gen2 materials) among computationally designed materials		■		
	Prediction of relative CO_2 isotherm step position		■		
	Extend the material design			■	
	Prediction of mechanical strength for a real process			■	

Project Timeline

	Task Descriptions	YR 1	YR 2	YR 3	YR 4
System Testing	Gen1 materials production for Svante		■	■	
	Concept development, modeling & testing		■	■	
	Process & cycle design simulations		■	■	
	Bench-scale unit design & construction		■	■	
	Gen2 materials production for Svante			■	■
	Comprehensive characterization of all relevant parameters for a real process		■	■	■
	In-house continuous PDU performance testing			■	■
	Bench scale field performance & durability testing			■	■