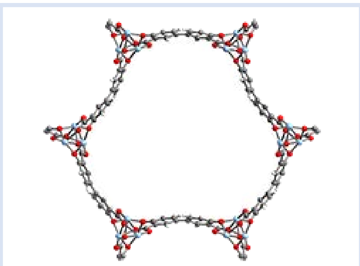
2019 NETL CO_2 Capture Technology Project Review Meeting

August 28, 2019



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

Jeffrey B. Neaton, Jeffrey R. Long, and Maciej Haranczyk

Lawrence Berkeley National Laboratory

NATIONAL ENERGY TECHNOLOGY LABORATORY · BERKELEY LAB LAWRENCE BERKELEY NATIONAL LABORATORY · mosaic materials · inventys · ELECTRICORE POWERING THE FUTURE · CCSI² Carbon Capture Simulation for Industry Impact

Project Overview

Funding

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

Project Participants

- PI: Jeffrey Neaton (LBNL)
- Co-PI: Jeffrey Long (LBNL)
- Co-PI: Maciej Haranczyk (LBNL)
- Mosaic Materials (MOF production)
- Inventys (System development)
- Electricore (System development)
- CCSI[2] (Process modeling – unfunded)

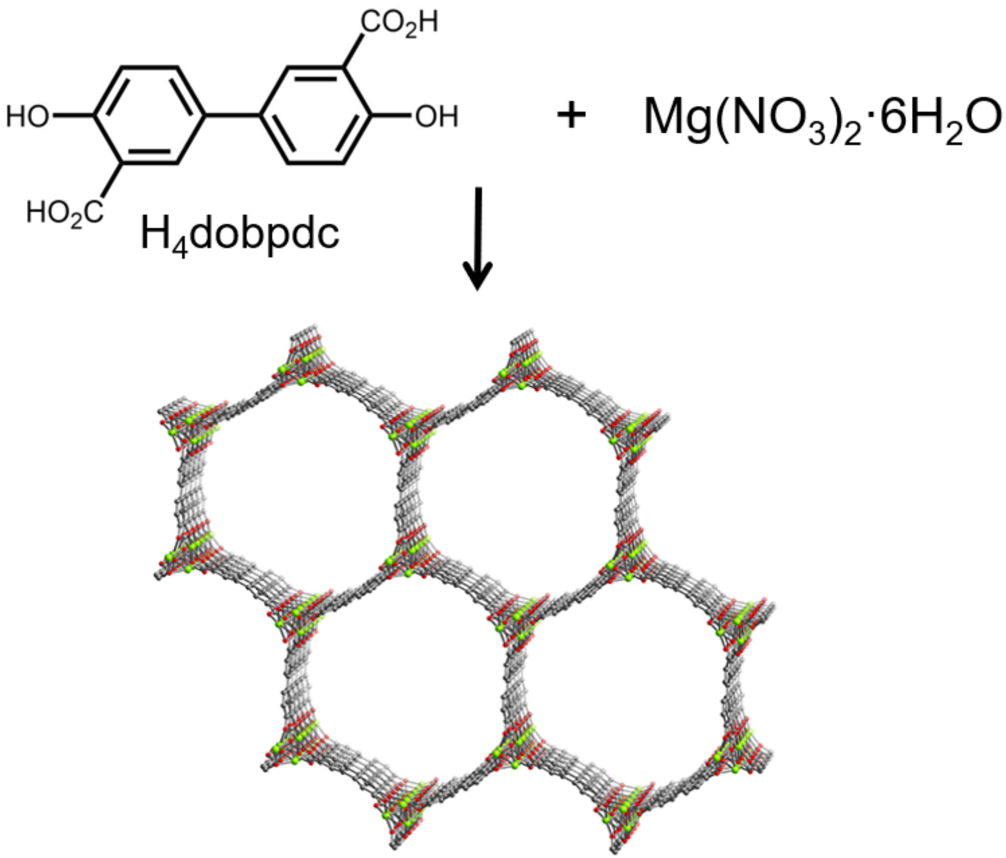
Overall Project Performance Dates

- 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 coal power plant

Technology Background: MOFs for CO_2 Capture



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

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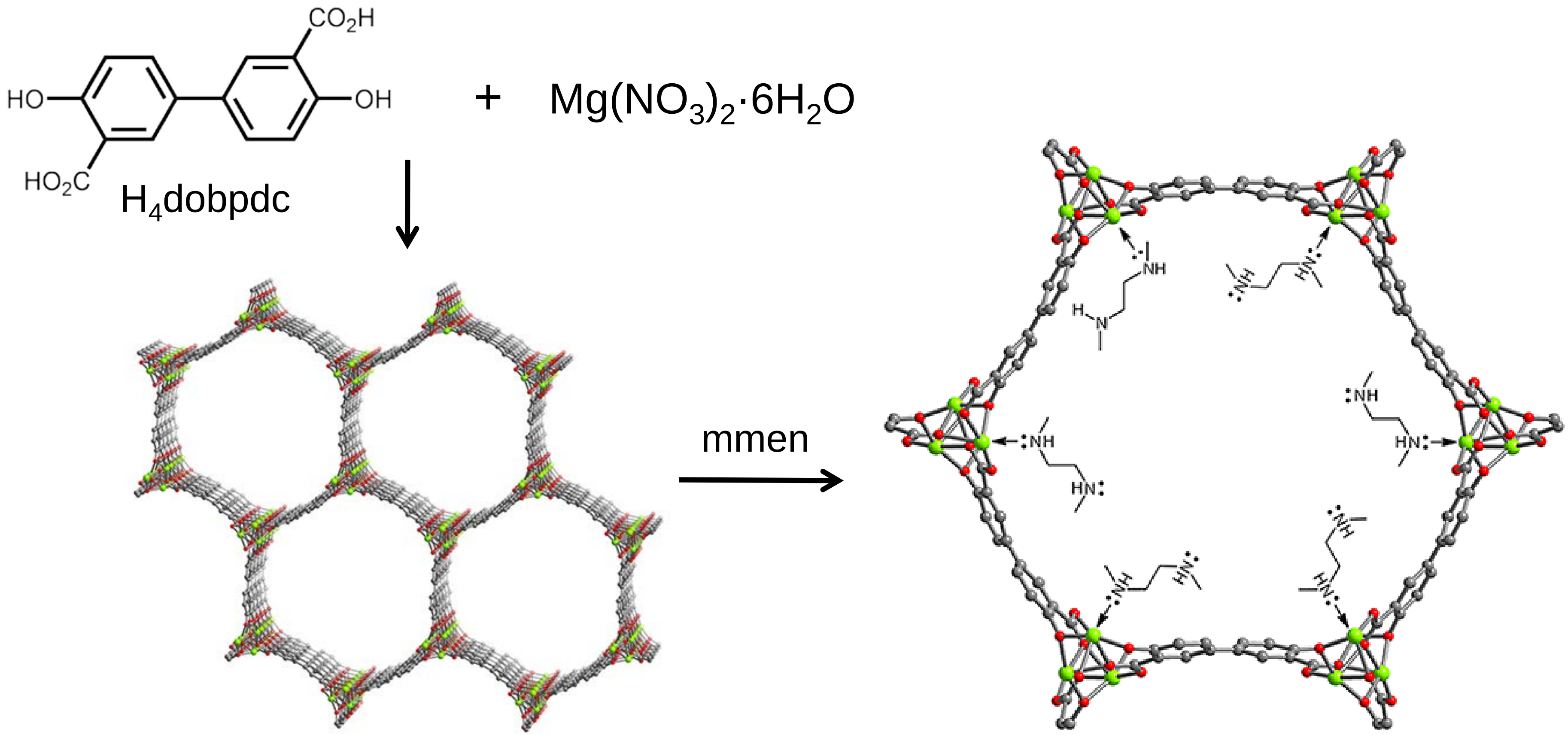

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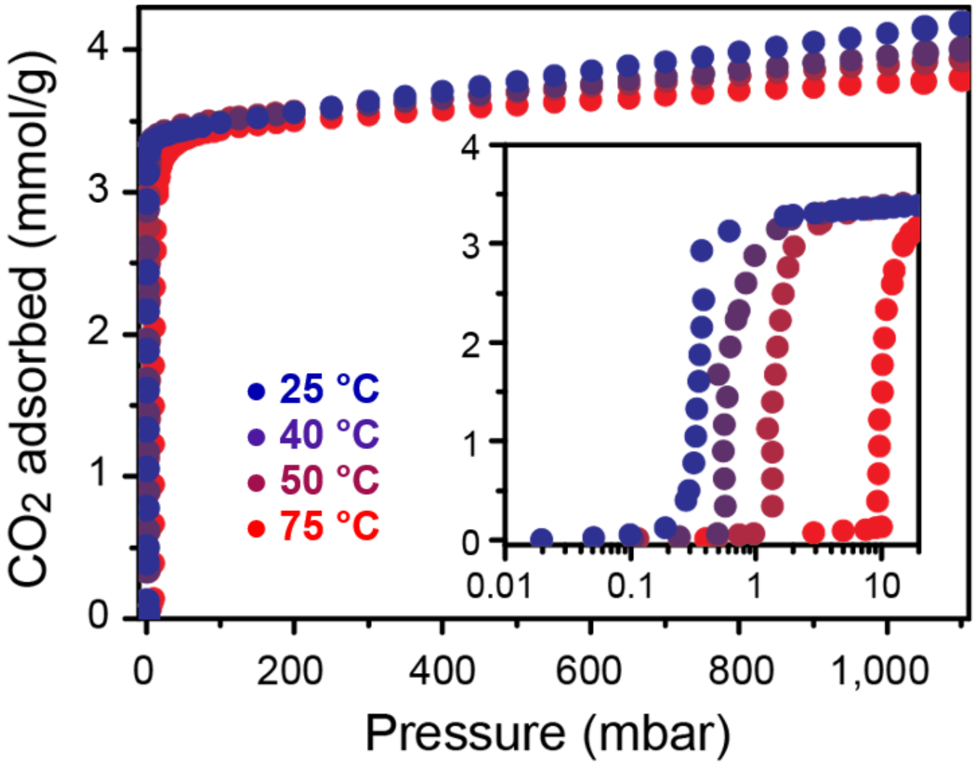
Step-Shaped Isotherms via Cooperative CO_2 Binding



- 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

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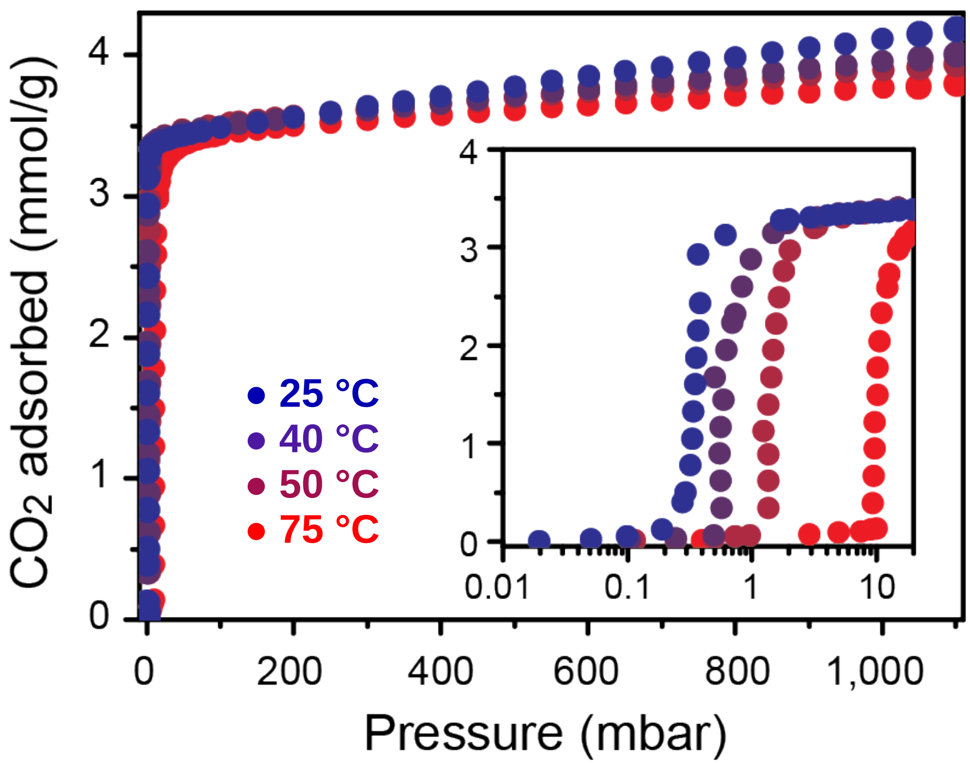

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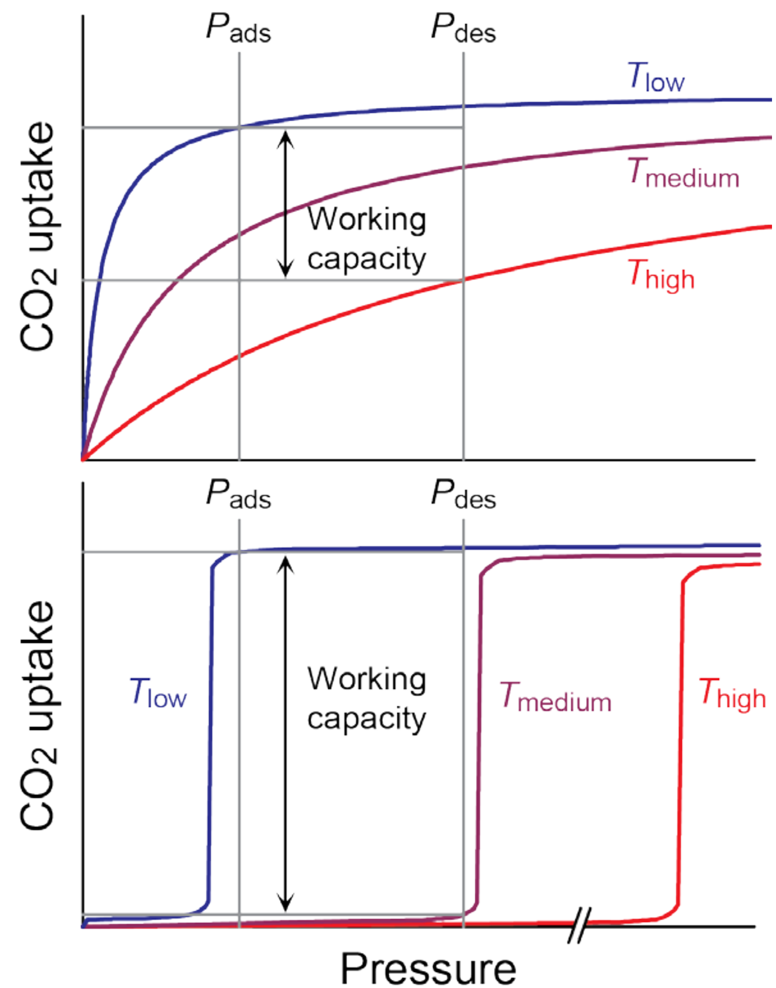

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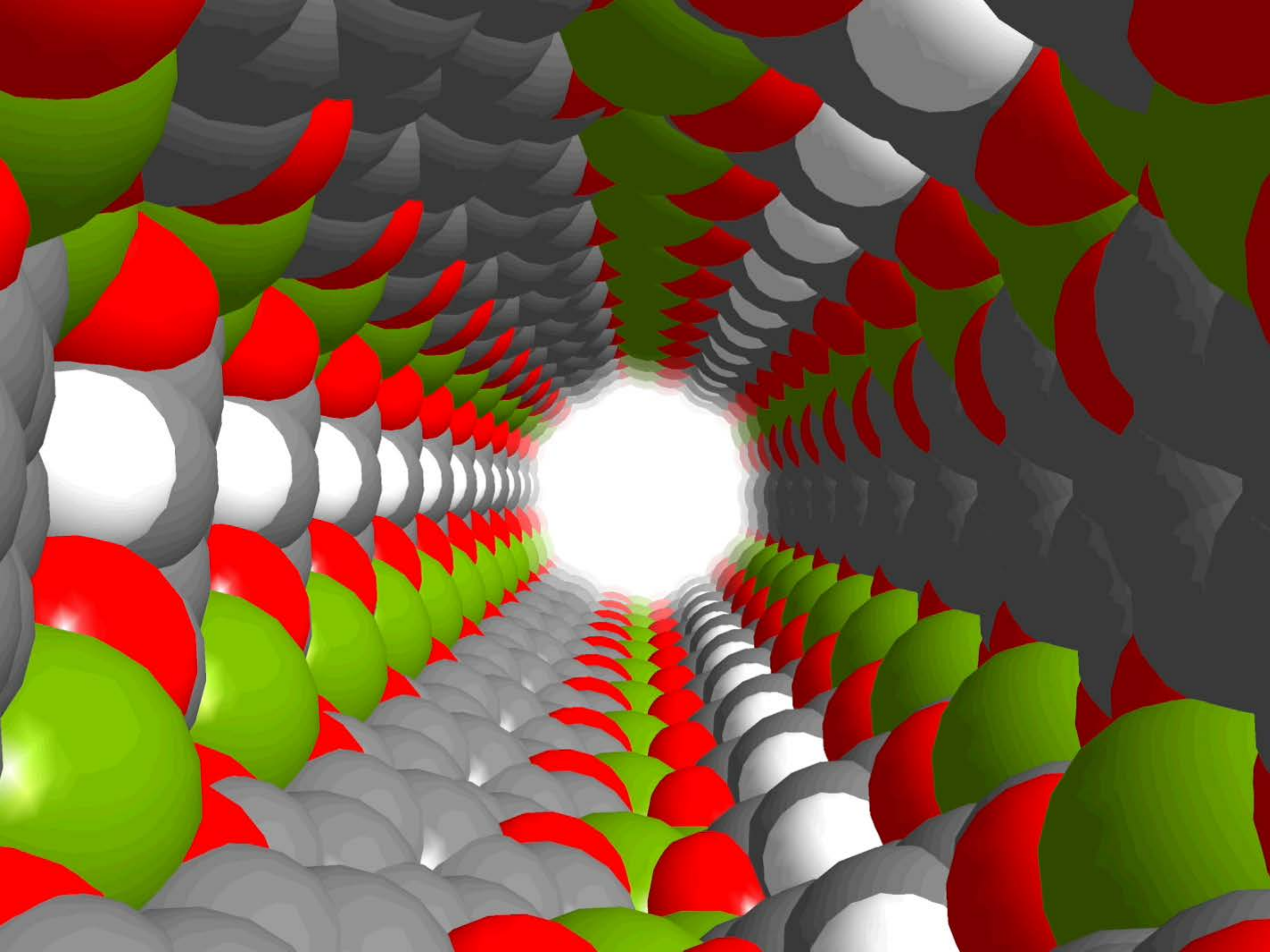
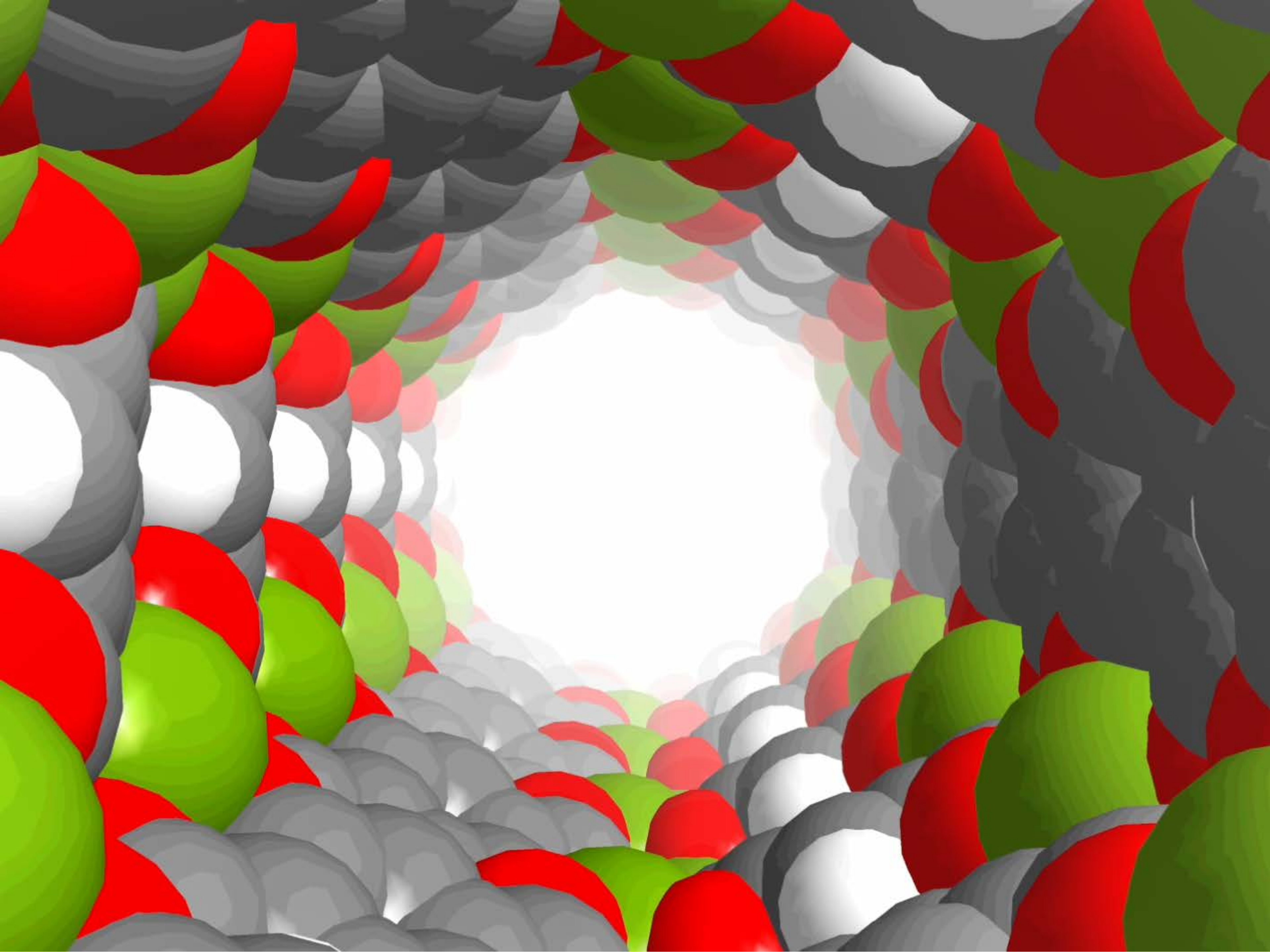
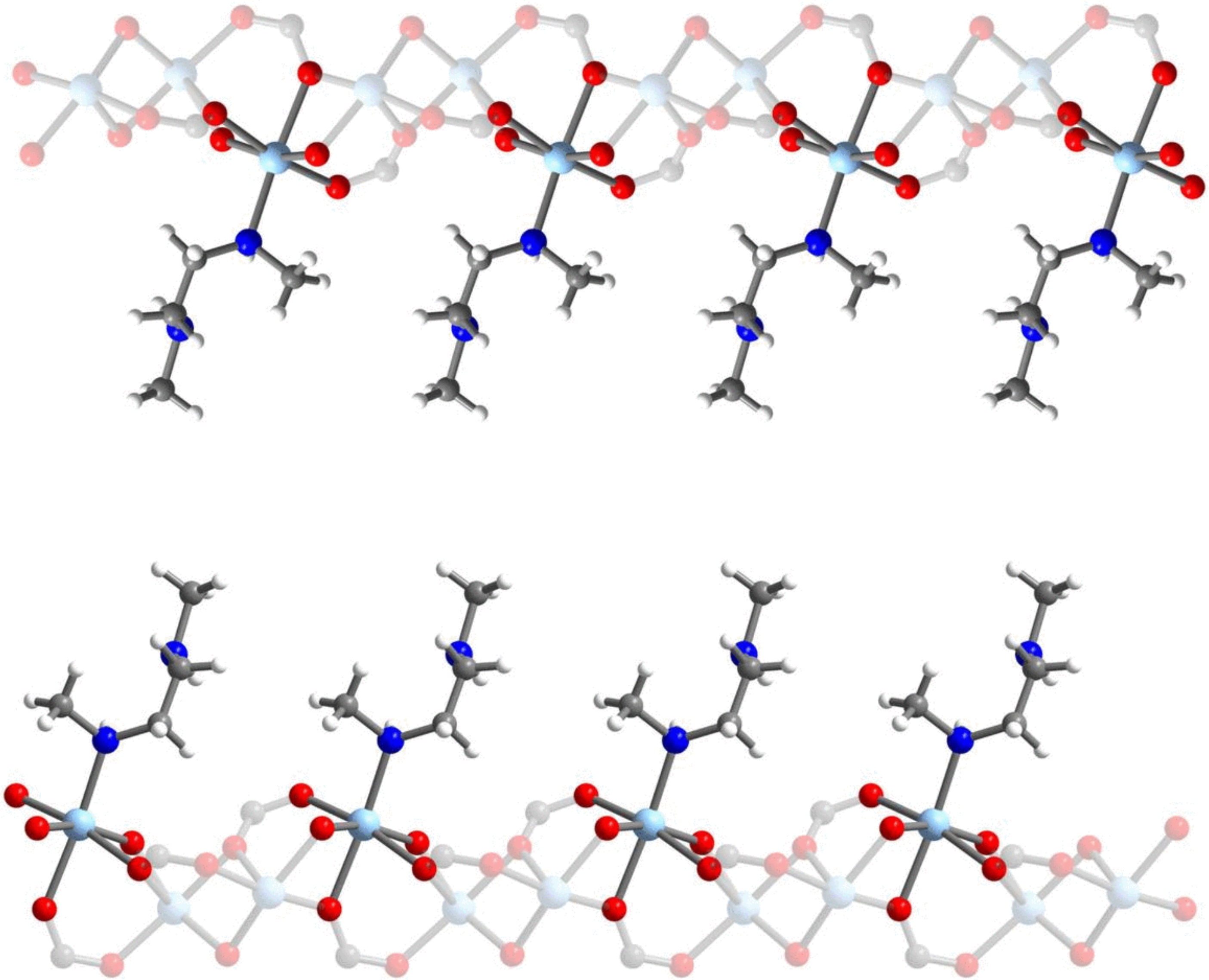
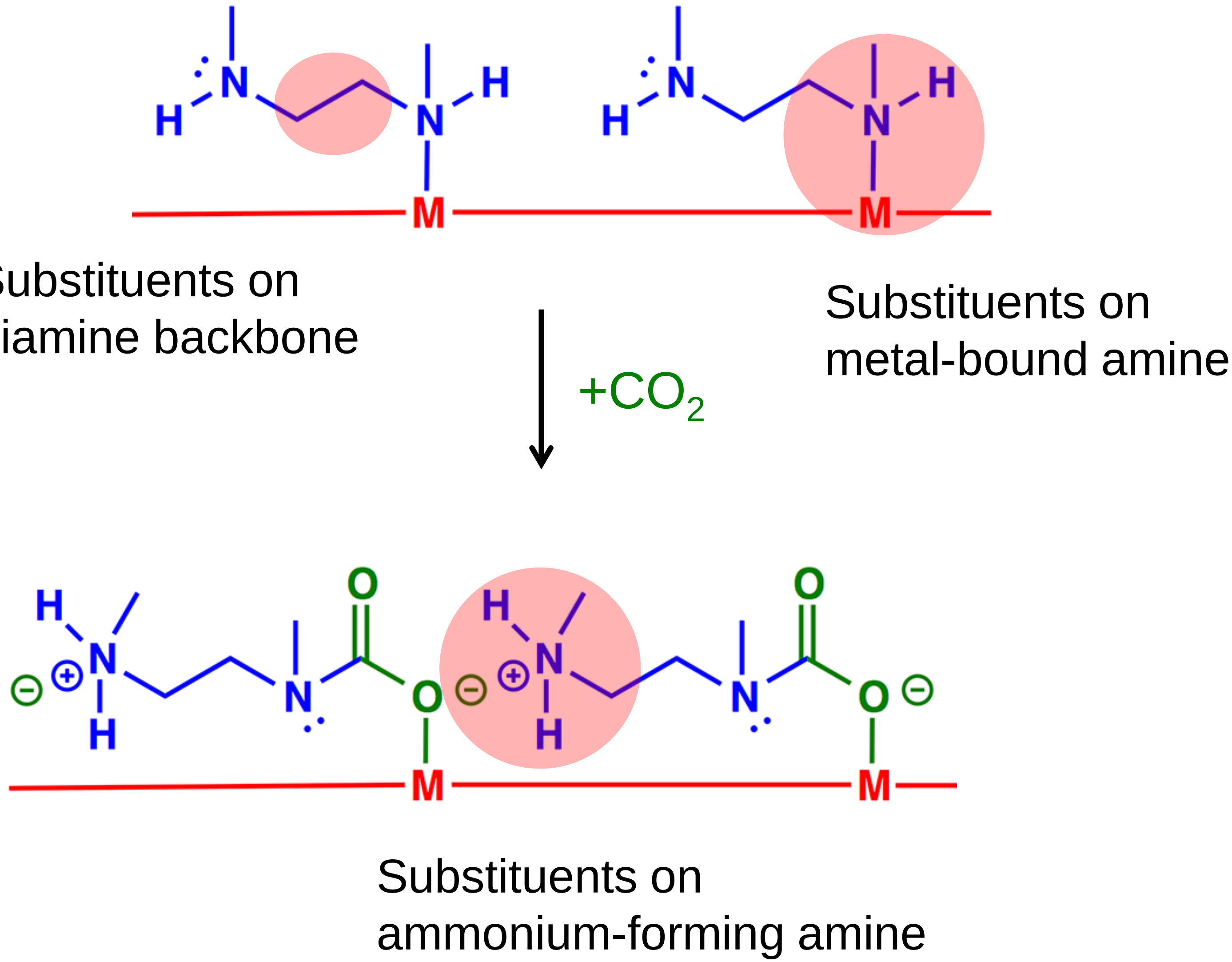






Manipulating the Adsorption Step Position



Technical and Economic Advantages/Challenges

Advantages

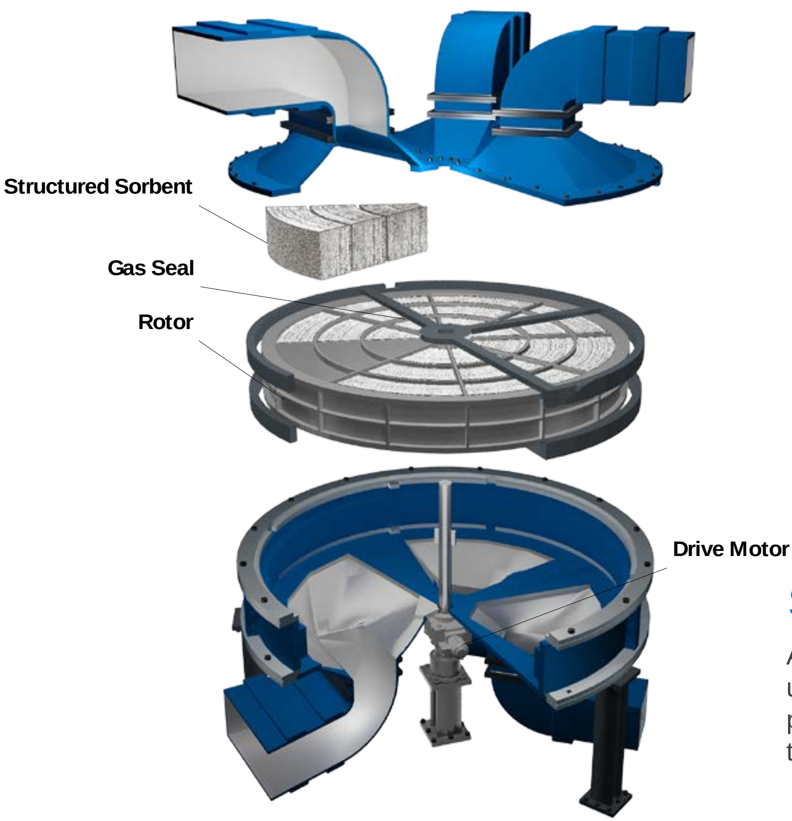
- High tunability of amine-appended framework materials
- Large working capacity due to stepped CO_2 adsorption
- High CO_2 selectivity over N_2, O_2, and H_2O
- Molecular level characterization is possible

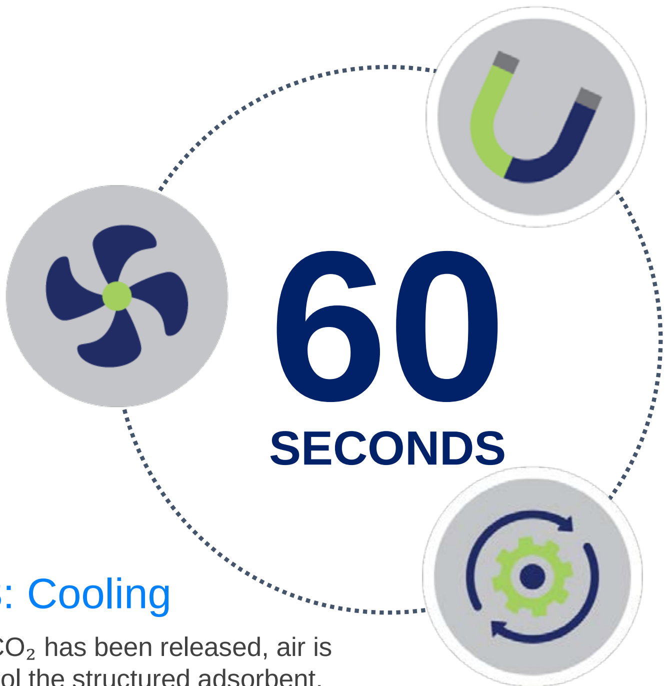
Challenges

- Large scale and economical production of materials
- Durability and chemical stability is unknown
- Reduction of regeneration cost (temperature swing)

Objective: Implement Adsorbents in RTSA Process

THREE SIMPLE STEPS





Step 1: Adsorption

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

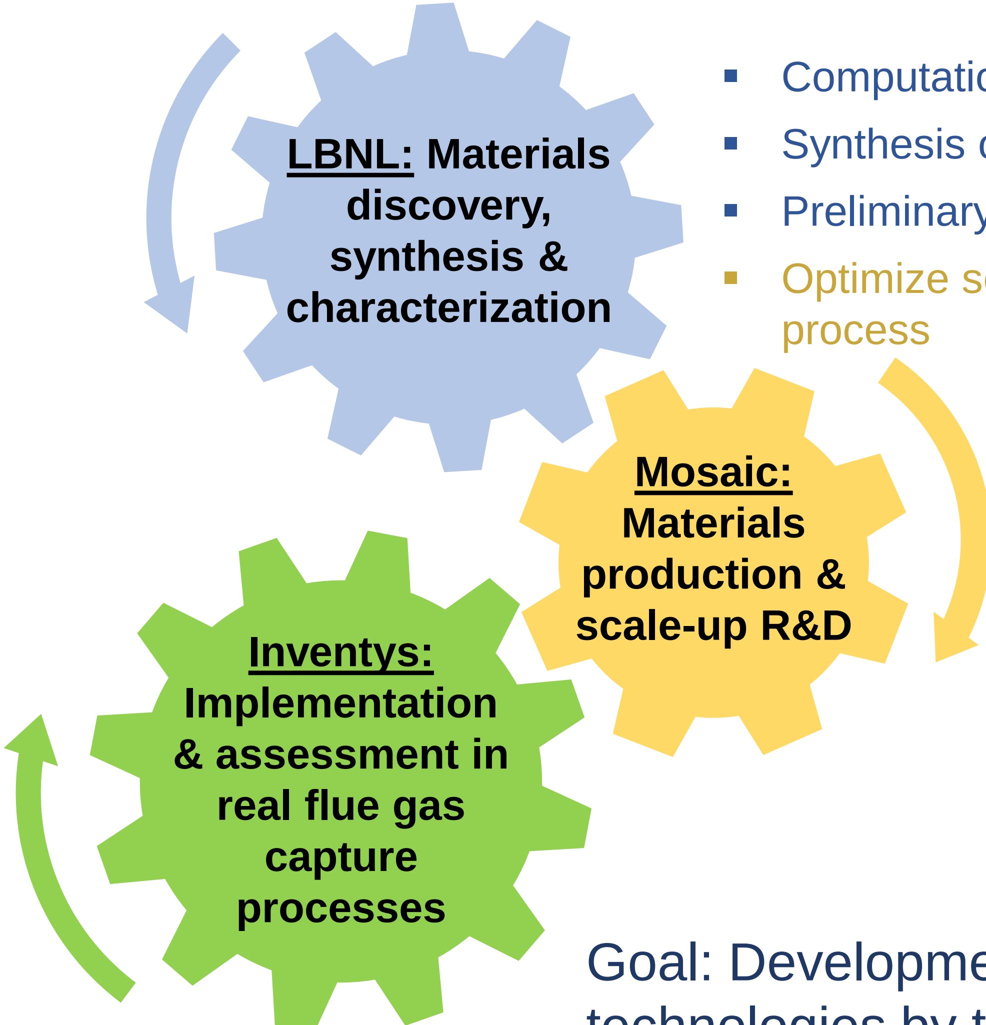
Step 2: Regeneration

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.

Technical Approach and Project Scope



- Computational prediction of materials
- Synthesis of amine-appended MOFs (Gen1−Gen3)
- Preliminary stability testing
- Optimize scalable diamine-appended MOF production process
  - Interface between LBNL and Inventys for process improvements
  - Deliver kg-scale batches of material for preliminary testing and demo at NCCC
  - 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

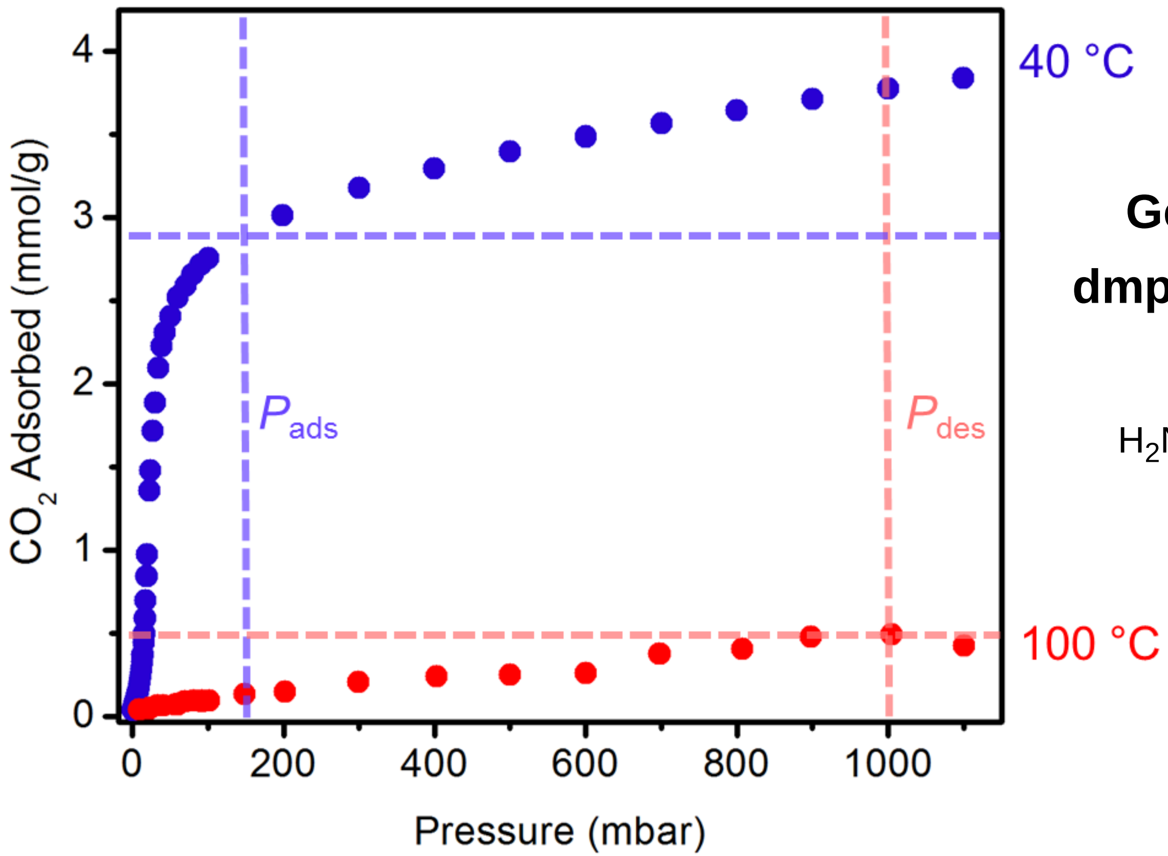
Project Schedule & Key Milestones (Year 2)

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

Project Schedule & Key Milestones (Year 2)

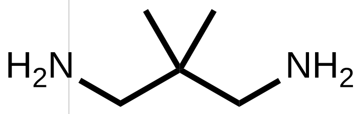
Key Milestones	Status
Gen1 material successfully synthesized at kg-scale and meets CO_2 performance metrics	Complete
Select initial material for VTS-scale single bed testing that demonstrates <5% loss in CO_2 working capacity under cyclic conditions over 5 hours	Complete
Delivery of Gen1 material to Inventys for dynamic VTS testing	Ongoing (2 kg to date)
Create a new material with a working capacity of >3.0 mmol/g (temperature swing <80 °C)	Complete (3.6 mmol/g)

Year 1 Recap: Gen1 Material Identified



Gen1 material:

dmpn-Mg_2(dobpdc)



dmpn

- 2.4 mmol/g (9.1 wt %) working capacity with only a 60 °C temperature swing
- Approximate regeneration energy: 2.4 MJ/kg CO_2

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

Year 2: Large Scale Synthesis of Gen1 Material

Objectives

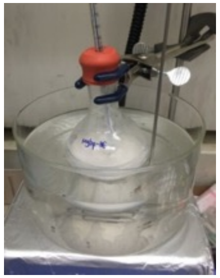
- Research gram to kilogram scale-up method
- Produce MOF at the gram to kilogram scale for use by Inventys
- Identify improvements at kilogram scale

Scale-up involves four distinct steps

- MOF synthesis
  Batch reaction of metal salt and organic ligand in solvent
- MOF purification
  Product is washed and dried to remove impurities and excess solvents
- Amination
  Purified MOF product is impregnated with amines
- Activation
  Solvent is removed

Steps are dependent on each other, and changes to one procedure often effects the others

Increasing Scales of Synthesis Equipment



LBNL Gen1 synthesis

150 mL reaction

1.5 L reaction

10 L reaction

Scale-Up Research & Optimization

- Stage 1: Standardized synthesis of 150 mL reaction volume → success

  All QC metrics met: PXRD after synthesis, N_2 surface area after purification, CO_2 capacity (TGA) after amination, amine content (NMR) after activation

- Stage 2: Scale-up to 1.5 L (100 g theoretical yield) → success

  All QC metrics met: PXRD after synthesis, N_2 surface area after purification, CO_2 capacity (TGA) after amination, amine content (NMR) after activation

- Stage 3A: Scale-up MOF to 10 L scale → success

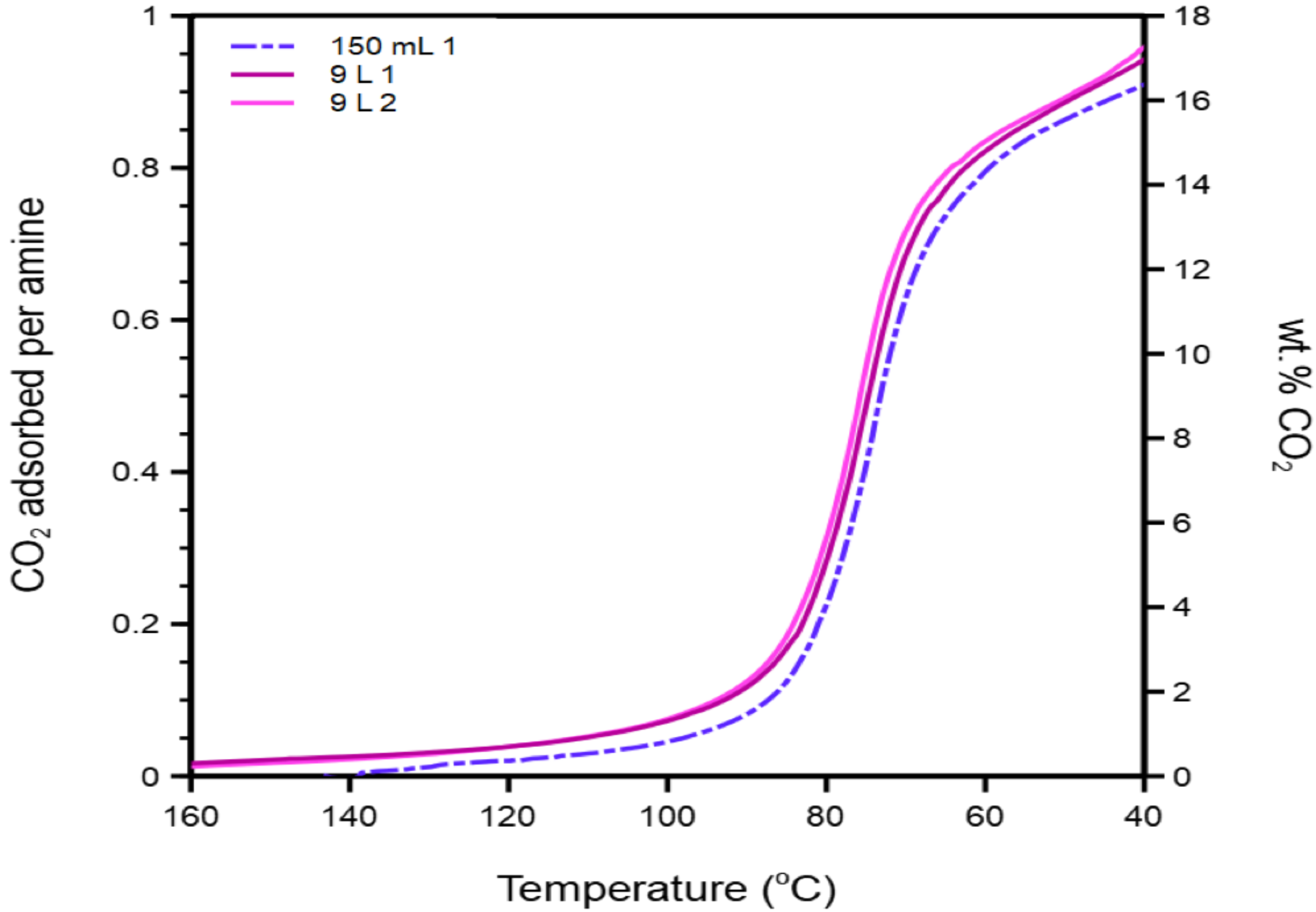
  All QC metrics met: PXRD after synthesis, N_2 surface area

- Stage 3B: Amination and purification combined at 10 L scale → fail

  Amine content and CO_2 adsorption capacity standards not met

  Separating these steps at 10 L scale → success

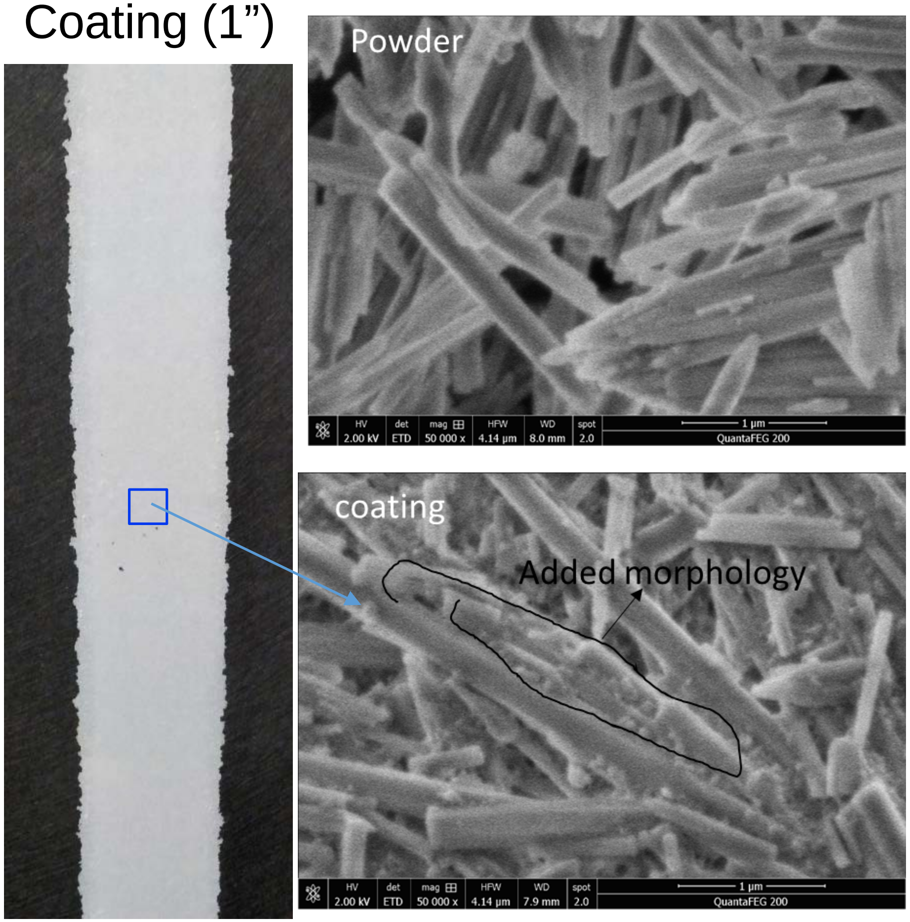
Modified Purification and Amination Procedure

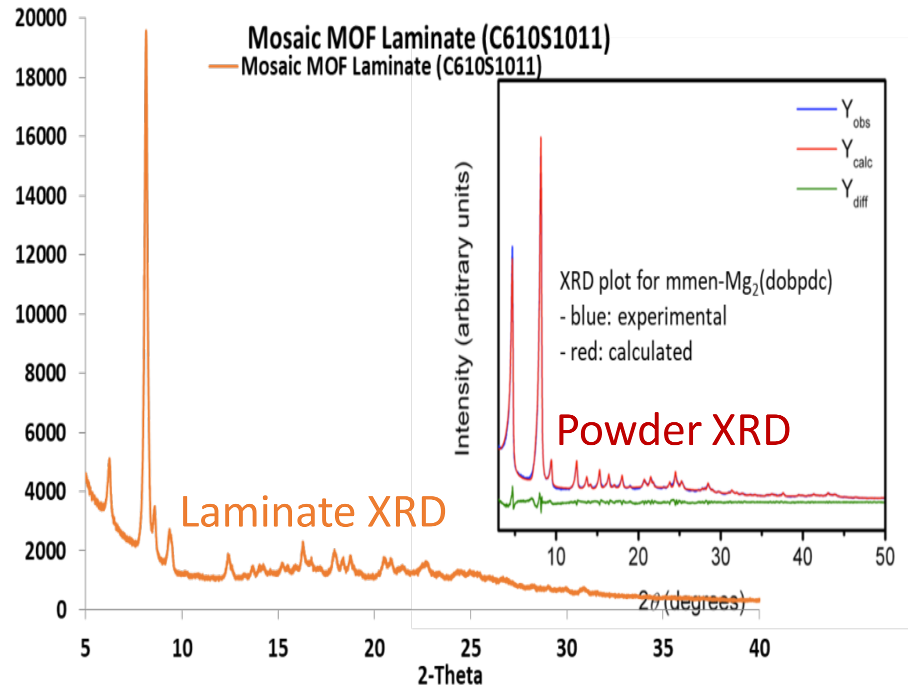


- New procedure separates purification and amination → successful procedure with all quality control metrics met

Gen1 MOF Laminate Formulation

Coating (1”)





- XRD and SEM morphology demonstrate equivalent structure between the powder and laminate. Added morphology found at the laminate surface could be the result of pulverization of the rod-shaped crystals and/or binder addition

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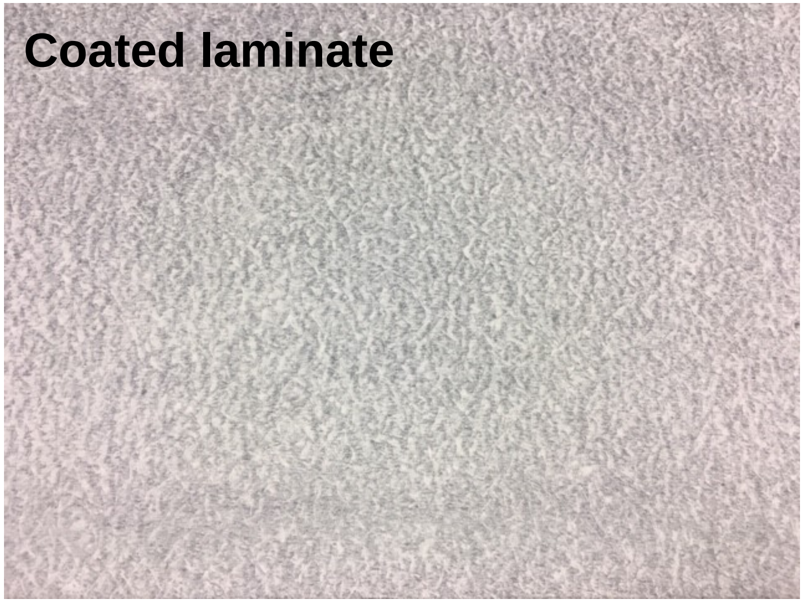
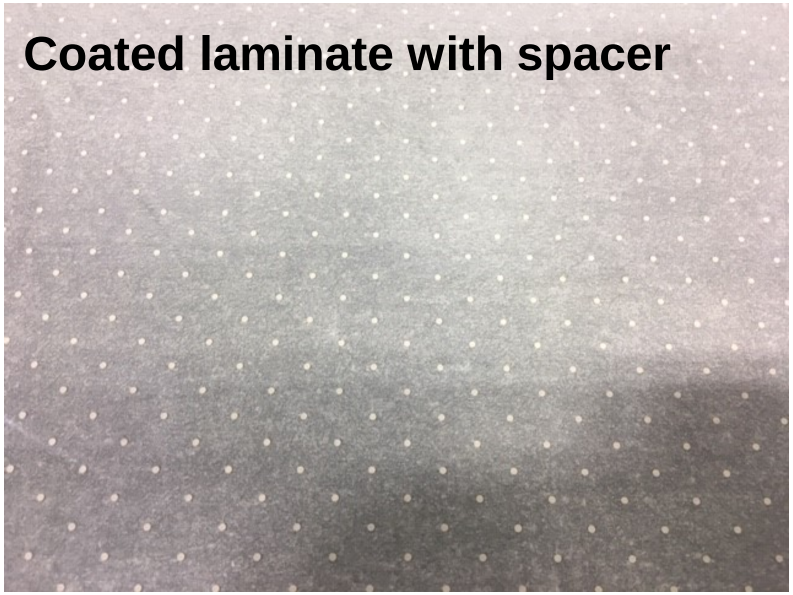
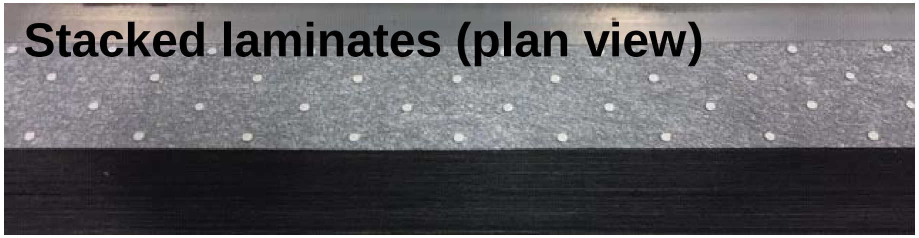
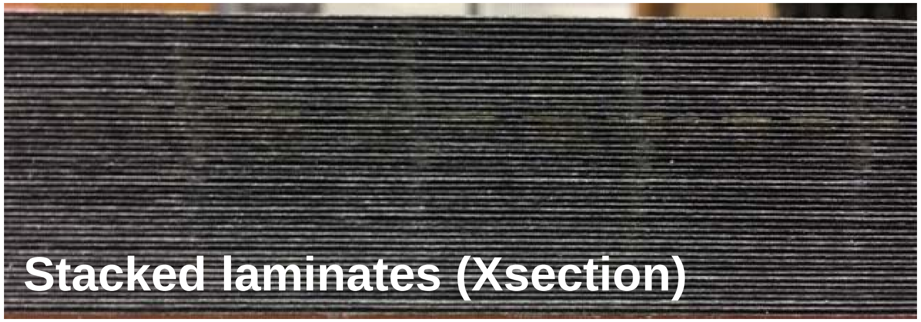
Gen1 Preliminary VTS Bed Produced

inventys





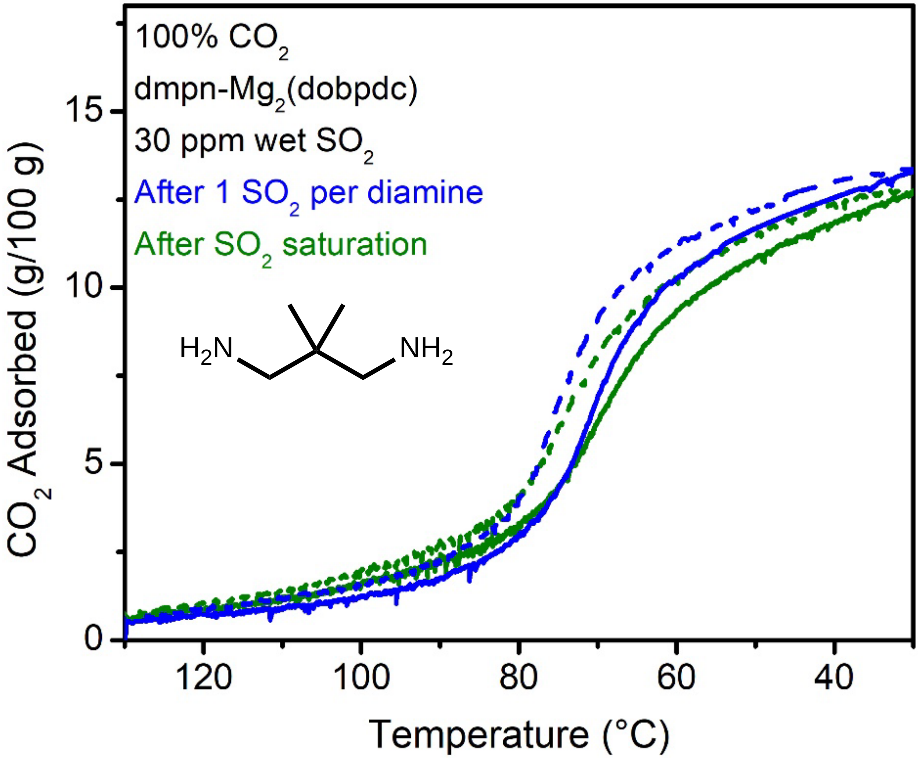




Gen1 MOF VTS Bed Formulation

- Using a new coating technique, Inventys was able to produce enough laminate to build a VTS bed
  - Water based solvent with added diamine was used
    - CO_2 capacity at 50 °C, 15% CO_2 for the laminate >41 cc/g_{MOF} (1.84 mmol/g); working capacity >34.5 cc/g_{MOF} (1.55 mmol/g) for 50 °C/90 °C swing
    - Coating density is 30% of the desired capacity → laminate formulation at full MOF coating density in progress, streamlining material processing between Mosaic and Inventys
- Preliminary VTS bed is a very important milestone which permits testing the full performance of the Gen1 material to rapid-cycling TSA with standard flue-gas concentration and moisture
  - Preliminary kinetics and cycle parameters can be determined
  - Both hot CO_2 and steam will be tested as regeneration gas

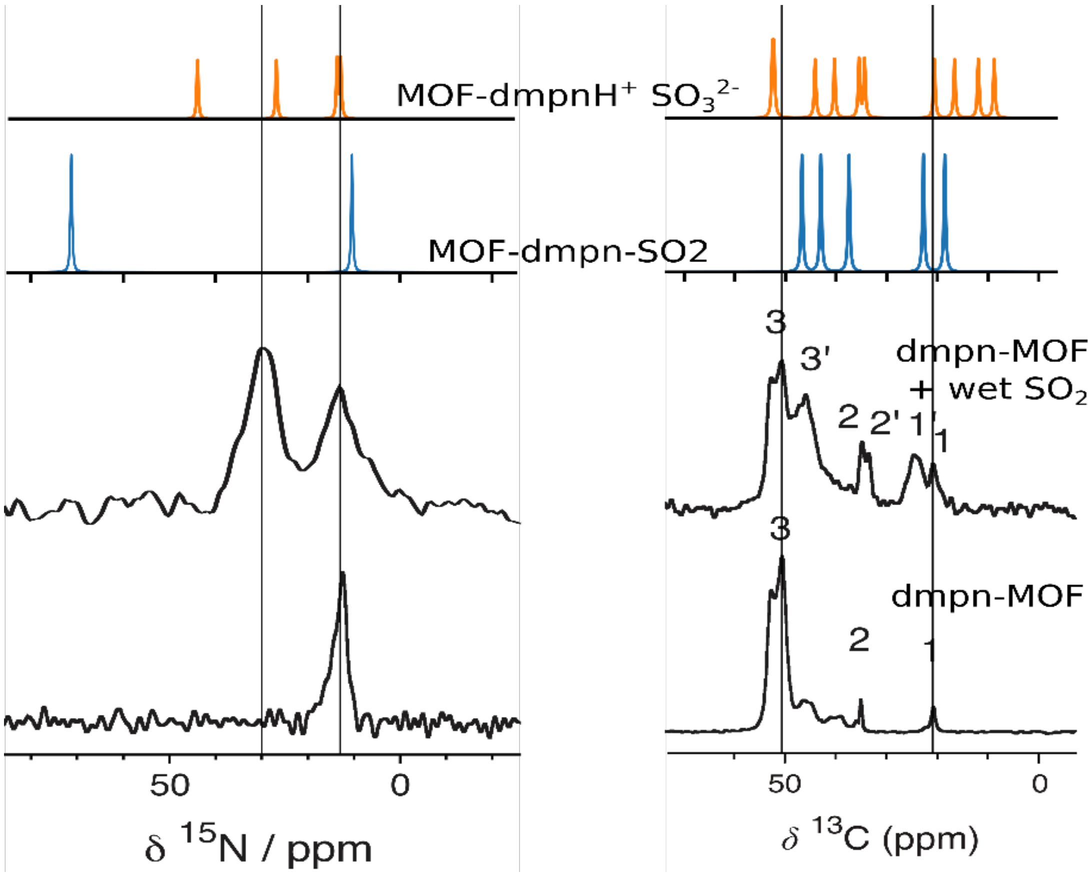
Year 2 R&D: SO_2 Stability and Regeneration



conditions	Gen1 CO_2 capacity retained
1 SO_2 per diamine	79
full SO_2 saturation	77
3 days past SO_2 saturation	77
SO_2 saturation with 14% CO_2	90

- Capacity of 1 SO_2 per diamine obtained from both elemental analysis and SO_2 breakthrough data
- CO_2 capacity does not continually degrade with increased SO_2 exposure time

Understanding SO_2 Adsorption in Gen1 Material



- Solid-state NMR and DFT calculations suggest formation of ammonium sulfites
- Mass spectrometry data also indicates the presence of sulfites

Characterization of SO_2 Adsorption in Gen1 Material

Gen1 initial diamine loading	after humid SO_2 exposure	after collecting CO_2 isobar
98%	98%	89%

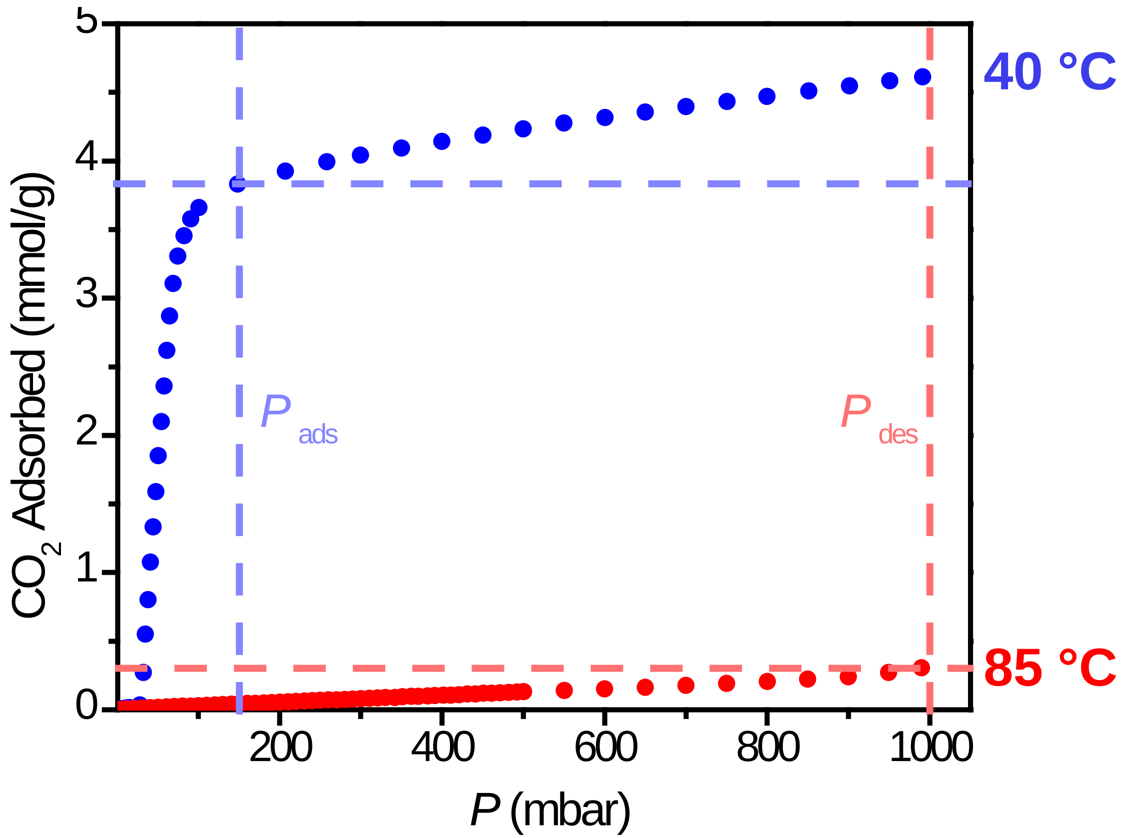
Mechanism of degradation

- Diamine loading shows that diamines are lost during re-activation instead of during exposure

Attempts at regeneration

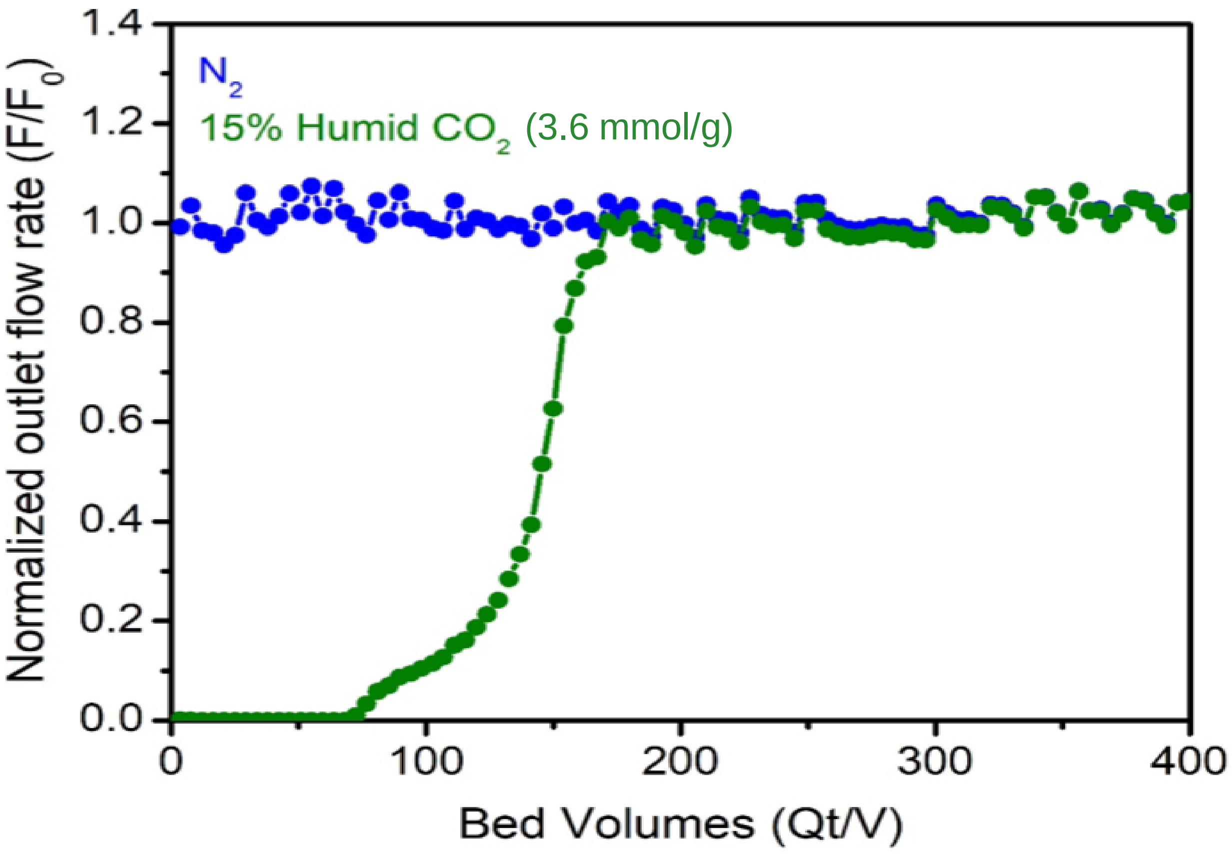
- Ethanol soak, room temperature: removed diamines
- Acetonitrile soak, room temperature: no change
- Acetonitrile soak, 60 °C: removed diamines
- Flowing humid N_2, 4 h at 55 °C: no change
- Flowing humid CO_2, 4 h at 50 °C: no change

Year 2 R&D: Gen2 Material Identified



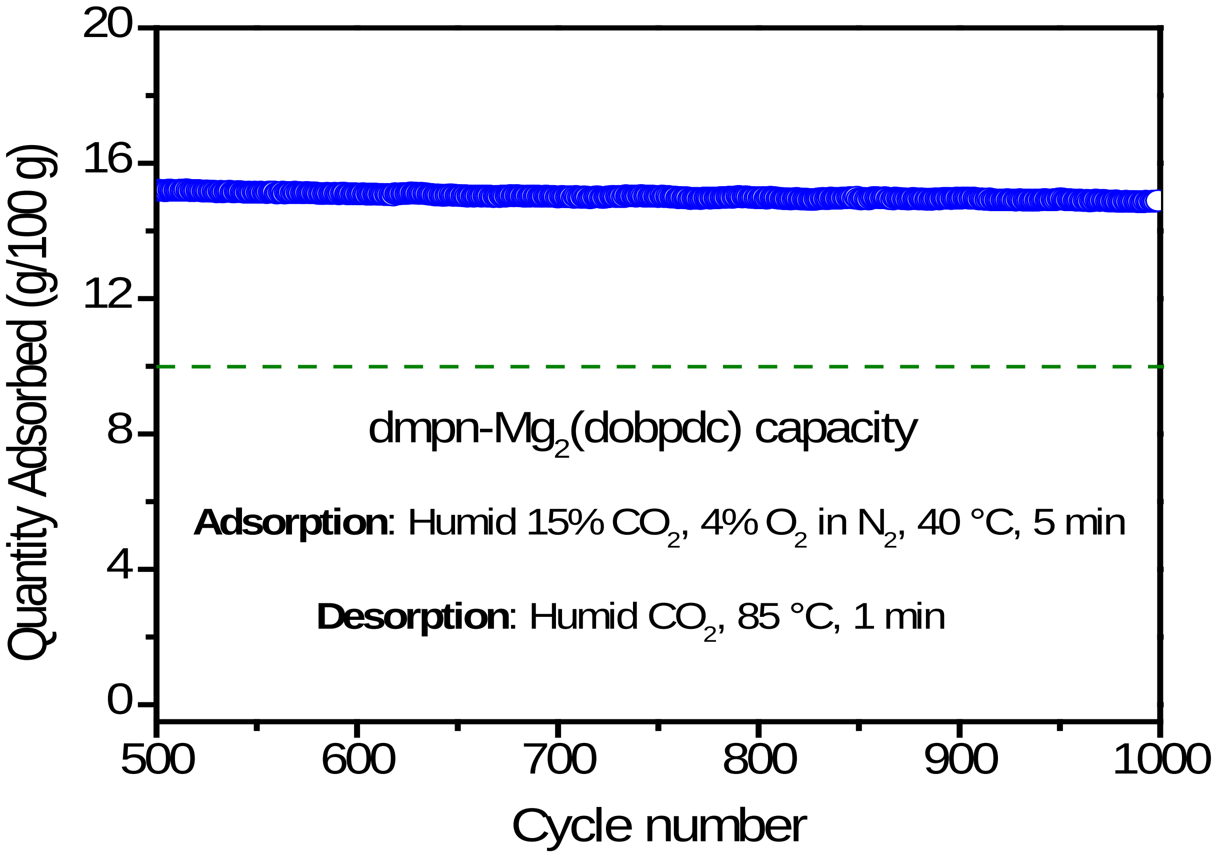
- 3.6 mmol/g (16 wt %) working capacity with only a 45 °C temperature swing
- Approximate regeneration energy: 2.2 MJ/kg CO_2

Gen2: Humid Breakthrough Experiments



- Breakthrough experiments with pre-humidified column and gas stream show sharp CO_2 breakthrough and the expected high capacity

Gen2: 1000 Adsorption/Desorption Cycles



- Stable to 1000 humid adsorption/desorption cycles under simulated coal flue gas conditions (diamine loading after experiment: 99%)
- Gen2 cycling capacity is 50% greater than Gen1 material

Plans for Future Testing and Development

Preliminary system testing of Gen1 material

- Process improvements to large scale manufacturing procedure to better integrate with laminate formulation process
- RTSA testing with VTS bed: steam and hot CO_2
- In house multi-bed PDU performance testing → optimize cycle parameters
- Planning and refinements to design of testing skid at NCCC

Synthesis of improved diamine-appended MOFs (Gen2/Gen3 materials)

- Long term stability assessments of Gen2 material and scale-up evaluation
- Evaluate new diamine-appended MOFs with similar properties of Gen1/Gen2 materials

Further materials improvements

- Use screening database to search for new diamine-appended MOF candidates
- Structure-stability studies of materials (H_2O, SO_x, NO_x) and evaluation of alternate regeneration strategies to recover greater CO_2 capacity

Acknowledgements

LBNL
Prof. Jeffrey Neaton
Prof. Jeffrey Long
Prof. Maciej Haranczyk
Dr. Stephanie Didas
Dr. Alex Forse
Dr. Jung-Hoon Lee
Dr. Jeffrey Martell
Dr. Phillip Milner
Florian Brown-Altvater
Matthew Dods
Surya Parker
Rebecca Siegelman
Eric Taw
Ziting Zhu
Bhavish Dinakar

Mosaic Materials
Dr. Thomas McDonald
Joel Gamoras
Jason Husk
Dr. Graham Wenz

Inventys
Claude Letourneau
Dr. Pierre Hovington
Jeffrey Alvaji
Omid Ghaffari-Nik
Nima Masoumifard
Sabara Rezaei
Matthew Stevenson

Electricore
Deborah Jelen

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

NETL Program Managers
Andrew Jones
José Figueroa (former)