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

## primary project goals

Lawrence Berkeley National Laboratory (LBNL), as part of the Discovery of Carbon Capture Substances and Systems (DOCCSS) Initiative, is developing amine-appended metal-organic framework (MOF) sorbents having step-change adsorption isotherms with larger sorbent working capacities with minor temperature swings for low-energy post-combustion carbon dioxide ($CO_2$) capture.

## technical goals

- Identify, synthesize, and characterize amine-MOF pairs using existing and new computationally designed MOF and amine structures.
- Test the synthesized sorbent materials using simulated flue gas to determine $CO_2$ adsorption and desorption kinetics, tolerance to impurities, and cycling performance.
- Identify the most promising sorbents with realistic potential for implementation in carbon capture.
- Field test the MOF sorbent using actual coal-derived flue gas.

## technical content

LBNL is combining computational and experimental programs to synthesize and characterize amine-appended MOF sorbents for energy-efficient carbon capture. An example of the structure of an MOF with appended amines is shown in Figure 1. These MOF materials show switch-like $CO_2$ adsorption behavior and can be tuned to optimize working capacities under mild regeneration conditions. They exhibit step-change isotherms enabled by a cooperative $CO_2$ adsorption mechanism, as shown in Figure 2. This step-change isotherm allows for larger sorbent working capacities with minor temperature swings, as opposed to the large temperature swings required by traditional amine-based sorbents. The step-change isotherm shows very little hysteresis upon desorption of $CO_2$, and the step shifts rapidly to higher pressure with increasing temperature. Balancing $CO_2$ capture performance and cost is done through vigorous optimization efforts of the amine molecules and pore geometries, combining computational modeling, characterization of molecules, and experiments to evaluate $CO_2$ capture performance.

Diamine-appended MOFs are being identified and synthesized, targeting materials showing step-change or switch-like reversible $CO_2$ adsorption isotherms. Computational modeling is used to identify promising amine-MOF pairs. The computational analysis and measurements of $CO_2$ adsorption behavior provide insight to identify second-generation materials with desired properties. The research team will identify, synthesize, and characterize amine-MOF pairs

### technology maturity
Bench-Scale, Actual Flue Gas

### project focus:
Amine-Appended Metal-Organic Framework Sorbent

### participant:
Lawrence Berkeley National Laboratory

### project number:
FWP-FP00006194

### predecessor projects:
N/A

### NETL project manager:
Andrew Jones
andrew.jones@netl.doe.gov

### principal investigator:
Jeffrey Neaton
LBNL
jbneaton@lbl.gov

### partners:
Mosaic Materials, Svante, Electricore

### start date:
08.31.2017

### percent complete:
55%

using existing and new computationally designed MOF and amine structures. The synthesized sorbent materials will be tested using simulated flue gas to determine $CO_2$ adsorption and desorption kinetics, tolerance to flue gas impurities, and cycling performance, as well as to identify the most promising sorbents with realistic potential for industrial implementation in carbon capture.

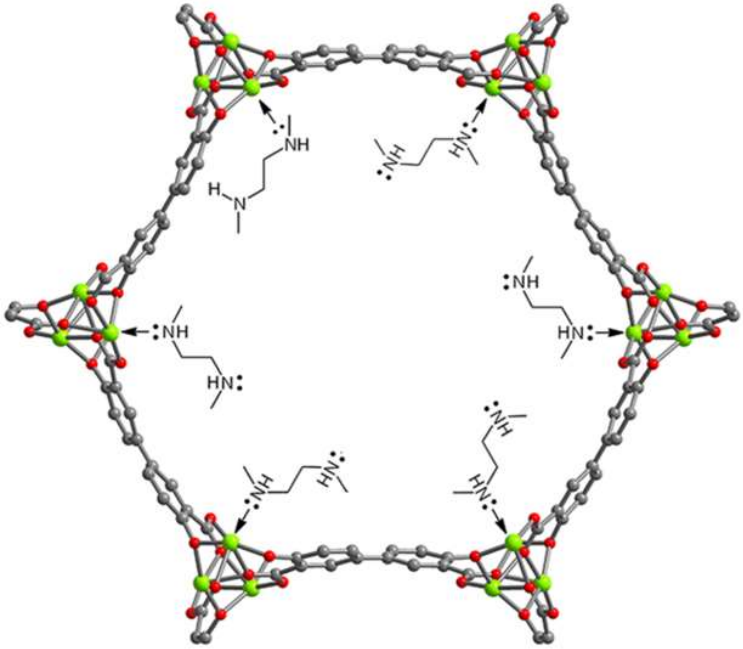

Figure 1: Example of an MOF with appended amines.

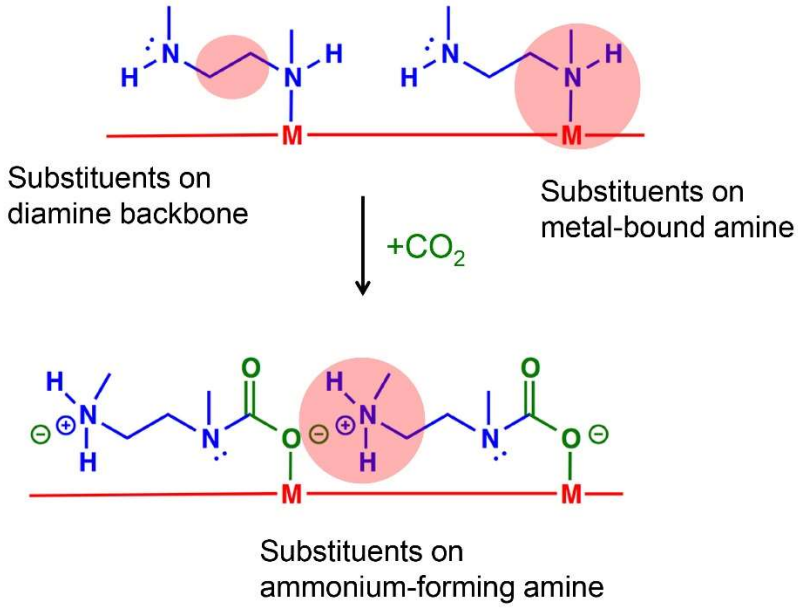


Figure 2: Cooperative $CO_2$ adsorption.

The project is part of DOCCSS, a partnership coupling unique skillsets of national laboratories, industry, and academic institutions to work collaboratively to facilitate discovery, synthesis, performance assessment, and functionalization of new carbon capture materials, and to accelerate the rate at which transformational processes for carbon capture are commercialized. This project includes a combined effort among several entities. LBNL is responsible for materials discovery, synthesis, and characterization. Mosaic Materials is developing materials production protocols and scale-up research and development. Sorbent production scale-up and optimization efforts include evaluating four distinct steps: synthesis of the MOF, purification of the MOF to remove impurities, amination where the purified MOF is impregnated with amines, and activation where the solvent is removed. Svante and Electricore are integrating the diamine-appended

MOFs in a cost-effective $CO_2$ capture system through system development efforts. Svante will perform testing of the sorbent in powder form and in a structured-bed form in their capture test units to confirm performance.

The overall effort will test first-generation (Gen1) materials, continue to develop and synthesize improved diamine-appended MOF (Gen2) materials, and evaluate long-term stability, impurity effects, and alternate regeneration strategies to recover greater $CO_2$ capacity, culminating in field testing using actual coal-derived flue gas.

The sorbent and process parameters are provided in Table 1.

**TABLE 1: SORBENT PROCESS PARAMETERS**

| Sorbent | Units | Current R&D Value | Target R&D Value |
|---|---|---|---|
| True Density @ STP | $kg/m^3$ | 1,560 | 1,560 |
| Bulk Density | $kg/m^3$ | 300 | 300 |
| Average Particle Diameter | mm | N/A | N/A |
| Particle Void Fraction | $m^3/m^3$ | N/A | N/A |
| Packing Density | $m^2/m^3$ | N/A | N/A |
| Solid Heat Capacity @ STP | kJ/kg-K | 1.46 | 1.46 |
| Crush Strength | $kg_f$ | N/A | N/A |
| Manufacturing Cost for Sorbent | $/kg | 4,586 | 3,033 |
| **Adsorption** | | | |
| Pressure | bar | 0.13 | 0.13 |
| Temperature | °C | 50 | 50 |
| Equilibrium Loading | g mol $CO_2$/kg | 2.5 | 2.5 |
| Heat of Adsorption | kJ/mol $CO_2$ | 74 | 74 |
| **Desorption** | | | |
| Pressure | bar | 1 | 1 |
| Temperature | °C | 110 | 110 |
| Equilibrium $CO_2$ Loading | g mol $CO_2$/kg | 0.1 | 0.1 |
| Heat of Desorption | kJ/mol $CO_2$ | 74 | 74 |
| **Proposed Module Design** | | *(for equipment developers)* | |
| Flow Arrangement/Operation | — | Fixed structured beds with rapid cycling | |
| Flue Gas Flowrate | kg/hr | — | |
| $CO_2$ Recovery, Purity, and Pressure | % / % / bar | 90 | 90 / 1 |
| Adsorber Pressure Drop | bar | 0.08 | |
| Estimated Adsorber/Stripper Cost of Manufacturing and Installation | $\frac{\$}{kg/hr}$ | — | |

## Definitions:

***STP*** – Standard Temperature and Pressure (15°C, 1 atmosphere [atm]).

***Sorbent*** – Adsorbate-free (i.e., $CO_2$-free) and dry material as used in adsorption/desorption cycle.

***Manufacturing Cost for Sorbent*** – "Current" is market price of material, if applicable; "Target" is estimated bulk manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

***Adsorption*** – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a $CO_2$ partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

***Desorption*** – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

***Pressure*** – The pressure of $CO_2$ in equilibrium with the sorbent. If the vapor phase is pure $CO_2$, this is the total pressure; if it is a mixture of gases, this is the partial pressure of $CO_2$. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of $CO_2$ is about 13.2%. Therefore, the partial pressure of $CO_2$ is roughly 0.132 atm or 0.130 bar.

***Packing Density*** – Ratio of the active sorbent area to the bulk sorbent volume.

***Loading*** – The basis for $CO_2$ loadings is mass of dry, adsorbate-free sorbent.

***Flow Arrangement/Operation*** – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

***Estimated Cost*** – Basis is kg/hr of $CO_2$ in $CO_2$-rich product gas; assuming targets are met.

***Flue Gas Assumptions*** – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

| Pressure | Temperature | Composition | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | vol% | | | | | ppmv | |
| psia | °F | $CO_2$ | $H_2O$ | $N_2$ | $O_2$ | Ar | $SO_X$ | $NO_X$ |
| 14.7 | 135 | 13.17 | 17.25 | 66.44 | 2.34 | 0.80 | 42 | 74 |

## Other Parameter Descriptions:

***Chemical/Physical Sorbent Mechanism*** – See above.

***Sorbent Contaminant Resistance*** – Flue gas pre-conditioning required in some applications to limit sulfur oxide ($SO_X$) and nitrogen oxide ($NO_X$) in contact with adsorbent material.

***Sorbent Attrition and Thermal/Hydrothermal Stability*** – Thermal stability of the sorbent has been demonstrated for the operating temperature range of the process. Hydrothermal stability for the Gen1 material is insufficient due to water-amine-MOF interactions. Gen2 material development or a change in Gen1 material formulation are being evaluated to minimize the impact of steam on the composite material.

***Flue Gas Pretreatment Requirements*** – To be determined. Initial pilot test on simulated flue gas without $SO_X$ and $NO_X$ supplemented by lab-scale tests and modeling of $SO_X$/$NO_X$ interaction with the sorbent.

***Sorbent Makeup Requirements*** – No makeup, structured sorbent modules do not allow for in-process addition of adsorbent material.

***Waste Streams Generated*** – Condensate water from flue gas pre-conditioning unit with flue gas particulates, solid waste from discarded sorbent modules every two to five years. No makeup liquid amine solution to discard greatly reduces waste streams for solid sorbents compared to liquid amine sorbent technology.

***Process Design Concept*** – Multi-bed structured solid sorbent assembled on rotary contactor for rapid adsorption-desorption cycle. Cycle times are between one to two minutes using rapid thermal swing.

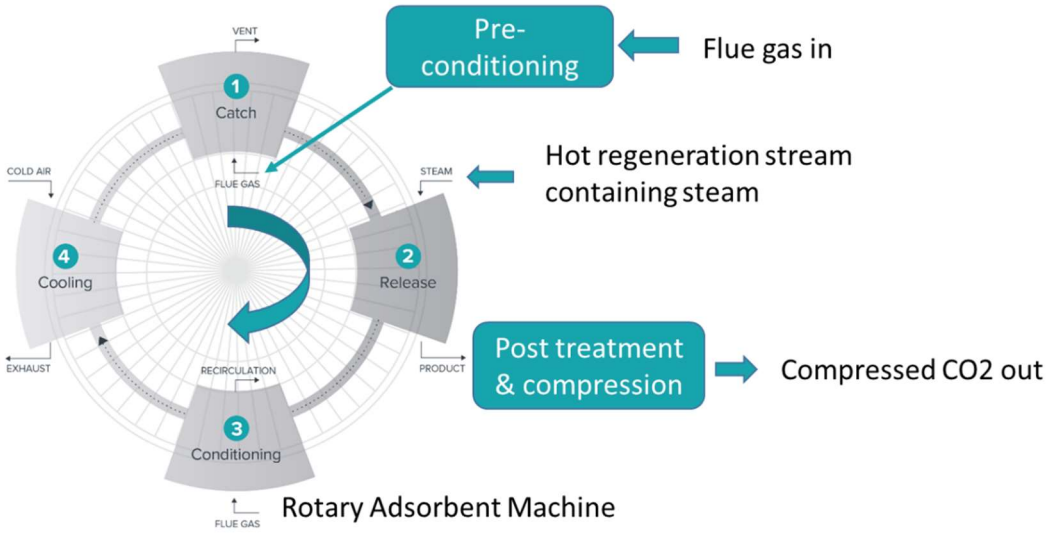


**Figure 3: Rotary adsorbent machine.**

***Proposed Module Design*** – Modules are built to define parallel passageways, enabling large contact area between the solid and the gas while minimizing flow resistance and maximizing volumetric loading of adsorbing material. Modules are typically meter-scale in flow direction, with channels in the millimeter scale.

## technology advantages

- Amine-appended framework materials are highly tunable.
- Sorbent has large working capacity due to step-shaped $CO_2$ adsorption.
- Sorbent has high $CO_2$ selectivity over nitrogen, oxygen, and water.

## R&D challenges

- Large-scale and economic production of materials.
- Durability and chemical stability of these MOFs under actual flue gas.
- Reducing the regeneration cost in temperature swing.

## status

LBNL has identified and synthesized a Gen1 material with a 2.4 mmol $CO_2$/gram working capacity with a 60°C temperature swing. Mosaic Materials successfully synthesized 1 kilogram of Gen1 material that met $CO_2$ performance metrics and was delivered for testing at the Svante test unit.

A screening database has been established to discover new MOFs with similar open metal site distance distributions to the Gen1 material, with three candidate materials of interest identified with potential for greater than 3.0 mmol/gram $CO_2$ uptake. One of these Gen2 materials showed a 3.6 mmol/gram working capacity with a 45°C temperature swing and an approximate regeneration energy of 2.2 MJ/kg $CO_2$. This Gen2 material was stable over 1,000 humid adsorption/desorption cycles under simulated coal flue gas conditions.

## available reports/technical papers/presentations

Long, J., Neaton, J., and Haranczyk, M. “Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture,” Presented at 2019 NETL $CO_2$ Capture Technology Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/J-Long-LBNL-Amine-Appended-MOF.pdf*.

Long, J., Neaton, J., and Haranczyk, M. “Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture,” Presented at the Project Review Meeting, Pittsburgh, PA, August 2019. *https://www.netl.doe.gov/projects/files/2019%20LBL%20DOCCSS%20Project%20Review%20Meeting_08-01-19.pdf*.

Long, J., Neaton, J., and Haranczyk, M. “Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture,” Presented at 2018 NETL $CO_2$ Capture Technology Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/projects/files/J-Long-LBNL-Amine-Appended-MOFs.pdf*.

Long, J., Neaton, J., and Haranczyk, M. “Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture,” Presented at 2017 NETL $CO_2$ Capture Technology Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/projects/files/J-Long-LBNL-Metal-Organic-Frameworks.pdf*.