CALIFORNIA
ENERGY COMMISSION

Energy Research and Development Division

FINAL PROJECT REPORT

Efficient Biogas Upgrading Technology Based on Metal-Organic Frameworks

Gavin Newsom, Governor
August 2020 | CEC-500-2020-054

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Contract Number: PIR-14-021

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ACKNOWLEDGEMENTS

Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the United States Department of Energy under Contract No. DE-AC02-05CH11231.

This project included a significant body of scientific work completed by collaborators in the Long Group at the University of California, Berkeley.

Partners in Sustainability performed the modeling and cost estimation of the aqueous amine scrubber.

PREFACE

The California Energy Commission's (CEC) Energy Research and Development Division manages the Natural Gas Research and Development Program, which supports energy-related research, development, and demonstration not adequately provided by competitive and regulated markets. These natural gas research investments spur innovation in energy efficiency, renewable energy and advanced clean generation, energy-related environmental protection, energy transmission and distribution and transportation.

The Energy Research and Development Division conducts this public interest natural gas-related energy research by partnering with research, development, and demonstration entities, including individuals, businesses, utilities and public and private research institutions. This program promotes greater natural gas reliability, lower costs and increases safety for Californians and is focused in these areas:

- Buildings End-Use Energy Efficiency.
- Industrial, Agriculture and Water Efficiency.
- Renewable Energy and Advanced Generation.
- Natural Gas Infrastructure Safety and Integrity.
- Energy-Related Environmental Research.
- Natural Gas-Related Transportation.

Efficient Biogas Upgrading Technology Based on Metal-Organic Frameworks is the final report for the Cost Reduction for Biogas Upgrading via a Low-Pressure, Solid-State Amine Scrubber project (Contract Number PIR-14-021-02) conducted by Mosaic Materials. The information from this project contributes to the Energy Research and Development Division's Natural Gas Research and Development Program.

For more information about the Energy Research and Development Division, please visit the CEC's research website (www.energy.ca.gov/research/) or contact the CEC at 916-327-1551.

ABSTRACT

An important pathway for California to reach its ambitious climate and environmental goals is to increase the use of biogas produced from waste resources, particularly through upgrading it to renewable natural gas to displace fossil fuel-derived natural gas. The high content of carbon dioxide in raw biogas makes removing it the most cost- and energy-intensive step in the upgrading process. Cleaning and upgrading systems need to be more cost-effective, more energy efficient, and less complex.

This project developed a highly efficient biogas upgrading technology based on novel solid scrubbing materials. Compared to conventional liquid-based scrubbers, the solid-scrubbing technology developed is able to remove biogas more efficiently, resulting in reduced operating cost, and with smaller scrubber volume required, resulting in reducing capital costs. A first-generation of the novel solid materials was developed and manufactured and its ability to purify methane from simulated biogas was validated. The team built and used a simulation tool to predict the performance of the material at scale and design a concept separation process. Technoeconomic assessment of the concept separation process indicates that this technology can reduce operating costs by 38 percent and capital costs by 15 percent compared to aqueous amine scrubbing at commercial scale. Additional development work on the novel solid material and on the separation process, including a field pilot, could lead to commercialization of this technology in four to six years.

Keywords: Adsorbent, biogas, renewable natural gas, metal-organic framework, renewable energy

Please use the following citation for this report:

McDonald, Thomas, Carly Anderson, Zoey Herm, Graham Wenz. 2020. *Efficient Biogas Upgrading Technology Based on Metal-Organic Frameworks*. California Energy Commission. Publication Number: CEC-500-2020-054.

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California has set ambitious climate and environmental goals, including reducing its greenhouse gas emissions by 40 percent below 1990 levels by 2030 through the California Global Warming Solutions Act of 2006: Emission Limit (Senate Bill 32, Pavley, Chapter 249, Statutes of 2016) and achieving carbon net neutrality by 2045 (former Governor Edmund G. Brown's Executive Order B-55-18). One pathway to reach these goals is to increase the use of biogas produced from in-state waste resources to decarbonize California's energy mix.

According to a 2013 assessment of biomass resources in California prepared by the University of California, Davis, total biogas potential is approximately 351 billion cubic feet per year. Resources from which biogas can be produced include woody biomass from forests and agriculture, food waste and the organic portion of municipal solid waste, municipal wastewater, landfill waste, and dairy manure. For biogas to be used in typical natural gas applications like heating, electricity, and transportation fuels, it must first be converted into renewable natural gas (RNG).

Producing RNG from biogas requires extensive cleanup and upgrading. The process begins by removing contaminants harmful to human health and gas pipelines, referred to as the cleanup or conditioning step. Next, the upgrading step removes carbon dioxide (CO_2), which represents 30 percent to 50 percent of most biogas streams, to make the biogas compatible with natural gas equipment and infrastructure. The high carbon dioxide content in raw biogas makes the upgrading step the most cost- and energy-intensive part of the process. There is a need, therefore, to improve the cost-effectiveness, increase the energy efficiency, and decrease the complexity of cleanup and upgrading systems.

Cost-effective and efficient upgrading of biogas to biomethane for injection into California's natural gas storage and transmission and distribution systems will benefit California ratepayers through electricity savings, CO_2 emission reductions, renewable energy expansion, and economic development.

Project Purpose

The purpose of this project was to substantially lower the cost and increase the efficiency of upgrading biogas by using a new CO_2 removal technology developed at the University of California, Berkeley. By offering a low cost, energy-efficient alternative to current upgrading technologies, Mosaic Materials hopes to accelerate market adoption of biogas upgrading at wastewater treatment plants, landfills, and other sites producing biogas in California. The high cost of commercially available upgrading systems and pipeline interconnection costs, particularly in California, make the economics of biogas upgrading difficult in spite of strong state and environmental incentives.

New materials to remove CO_2 from biogas through separation were developed at University of California, Berkeley and commercialized by Mosaic Materials are a type of material called a metal-organic framework (MOF). This framework can be engineered to selectively adsorb (collect condensed gas on a surface) a particular gas over others, in this case CO_2. The Long Research Group at UC Berkeley discovered that adding a chemical called diamine that has a known attraction to CO_2 to a specific group of MOFs created a material with superior CO_2 adsorption properties. However, this material had only been made in small quantities (grams) in the laboratory and had never been used for an industrial separation.

These materials for CO_2 adsorption are unique because they have high capacities for CO_2 and can remove CO_2 using much less energy through a process called pressure swing adsorption or PSA. The process pressurizes biogas and passes it through a vessel or "bed" containing the adsorbent, which acts like a filter. The CO_2 is adsorbed by the filter while the methane in the biogas passes through, producing high purity RNG. Once the material's capacity for adsorbing CO_2 is reached, the pressure is reduced, causing the CO_2 to be released (a process called desorption) and regenerating the material so that it is ready to adsorb CO_2 again. When the desorption pressure is below atmospheric pressure (requiring vacuum), the process is called vacuum-pressure swing adsorption. These processes are designed with two or more beds in parallel so that one bed is always upgrading biogas while the others are regenerating. The CO_2 that was removed from the biogas is sent off to be processed with other waste gas or used for other purposes.

The MOFs explored in this study can be regenerated with smaller changes in temperature and pressure compared to traditional adsorbents systems. This characteristic allows removal of CO_2 using considerably less energy and adsorbent, dramatically reducing the cost of the system. In addition, slight changes in the MOF or amine can shift the pressure at which the CO_2 capacity changes, allowing the adsorbent to be designed for maximum efficiency for a specific separation.

The Mosaic Materials CO_2 separation technology has the potential to reduce the capital and operating costs associated with upgrading biogas by 15 percent and 38 percent respectively relative to traditional amine scrubbing at commercial scale. Like membrane systems and PSA systems using other adsorbents, this technology is easily applied at scales down to 50 standard cubic feet per minute (scfm) of biogas.

Project Process

The primary technical objective of this project was to develop a CO_2 separation system for biogas based on solid MOF adsorbents that would produce RNG at the target purity of less than 2 percent CO_2 and improve the economics of upgrading biogas to RNG at scale. The researchers divided this effort into three main areas: material development, separation process development, and field testing.

Material Development

As the first step in material development, researchers at UC Berkeley studied 30 candidate materials (combinations of MOFs and amines) to evaluate which materials would remove CO_2 from biogas most efficiently. The next step was to increase how much of the material could be made, from a few hundred milligrams to a goal of 5 kilograms (kg). The MOF, a powder, also had to be converted into strong, solid particles that could be loaded into industrial equipment without crushing the MOF's nanoscale (billionth of a meter) pores. Finally, researchers needed to develop techniques to verify the quality of the material at every step in the process.

Separation Process

To develop the separation process, Mosaic Materials built a computer modeling tool to simulate the performance of the first generation (Gen-1) MOF material. Modeling these materials is challenging because they do not behave like typical CO_2 adsorption (adsorption gradually increases with pressure). Instead, these materials display "step-like" or on-off CO_2 adsorption behavior, requiring new models of adsorption behavior. Once the researchers developed the computer model, they performed laboratory testing to determine key material properties and confirm that the model correctly predicted how the MOF would adsorb CO_2 in experiments. Results from these experiments were used to improve and expand the model to predict the performance of the MOF in a full-scale facility. The research team refined the process design by comparing the equipment and operating costs of different versions of the process (for example, varying the operating pressures and amount of adsorbent). Finally, Mosaic Materials completed a technoeconomic assessment of the CO_2 removal process compared to chemical scrubbing systems based on the predicted performance at large scale.

Field Testing

To evaluate the stability of the Gen-1 MOF adsorbent to contaminants, slipstream testing was performed at a partner wastewater treatment site in Davis, California. In these tests, several samples were installed in a slipstream line (pipe) with unconditioned biogas containing 3 percent water and 1,800 parts per million (ppm) hydrogen sulfide flowing through them for up to a month.

Project Results

During this multiyear research project, Mosaic Materials identified two promising MOF adsorbents and scaled production of the most promising MOF-amine combination (the Gen-1 material) from research and development scale (several grams) to pilot production scale (several kg). The researchers selected the Gen-1 MOF adsorbent from an initial list of more than 30 materials based on stability and expected performance over the anticipated range of CO_2 partial pressures. The researchers produced more than 5 kg of MOF with properties consistent with the initial material, showing that there was no performance lost despite scaling-up. Mosaic Materials was also successful in developing a procedure to form the MOF into mechanically strong, high-performing solids with a range of forms and shapes (Figure ES-1). The synthesis and forming processes went through many rounds of optimization to increase throughput and efficiency.

The researchers also developed a first-generation process to separate CO_2 from biogas using the Gen-1 adsorbent over the course of this project. Mosaic's process model incorporates the unique step behavior of the Gen-1 MOF-based solid adsorbent across the range of system temperatures and pressures. Researchers confirmed the validity of the modeling tool using the results of laboratory experiments with the tableted MOF adsorbent. The composition of the product gas and the temperature profile within the adsorbent bed matched the predictions of the model. These bench-scale studies provided insights into how the materials would perform at full-scale, including regeneration requirements, pressure losses, and temperature effects. Not unexpectedly, controlling the adsorbent temperature during the process emerged as a critical design issue. Researchers addressed the thermal management issue in the concept separation process by incorporating a heat exchanger into the vessel containing the adsorbent to cool the material during adsorption and heat it during desorption.

Figure ES-1: Metal-Organic Framework Forms

Metal-organic framework forms produced by Mosaic Materials (left) and tableted Gen-1 metal-organic framework adsorbent (right).

Source: Mosaic Materials, Inc.

The research team created specific models to simulate the vacuum-pressure swing adsorption process for small-scale (50 scfm biogas), and large-scale (2,800 scfm biogas) separation units. The technoeconomic assessment based on these models predicted that the early MOF-based CO_2 separation process can reduce the operating and capital costs associated with CO_2 removal by 38 percent and 15 percent, respectively, compared to chemical scrubbing. Future research will focus on further reducing regeneration requirements and rigorously comparing the process against other technologies.

The researchers also tested the performance of the Gen-1 solid adsorbent by flowing real, untreated biogas over it for up to four weeks at the Davis Wastewater Treatment Plant. The untreated biogas contained impurities (specifically hydrogen sulfide and siloxanes) that could block material pores or degrade the adsorbent. The adsorbent maintained more than 80 percent regenerable CO_2 capacity after constant exposure to the untreated biogas for up to two weeks. Since the contaminants present in unconditioned biogas would not be present at these levels unless there was a failure upstream, this means that (1) the material performance would not be destroyed by a temporary problem with the upstream equipment, and (2) the material is likely to perform well over a longer period at significantly lower levels of impurities. For example, since performance was maintained after two weeks at 1,800 ppm hydrogen sulfide , the material will likely maintain performance over five years at 4 ppm hydrogen sulfide . Mosaic Materials hopes to further test these materials in the field by piloting the separation process in the next few years.

Benefits to California

The Mosaic Materials technology, if successful, could accelerate biogas adoption by reducing the cost of producing pipeline quality natural gas, reducing waste at biogas facilities, and maximizing the energy obtained from biogas production. The benefits of this technology to California investor-owned utility natural gas ratepayers include lower capital and operating costs for production of biomethane that translate into lower costs for ratepayers, accelerated market penetration for biogas, substantial greenhouse gas emission reduction through the use of renewable energy, increased safety of biogas systems, increased energy security through a diversified renewable portfolio, and facilitation of rural development and job creation.

This research also sets the groundwork for additional MOF-based technologies to be used in applications outside the biogas industry. Similar MOF materials can be used to more efficiently remove CO_2 from flue gas or even from air directly. Similar MOFs can be used to separate materials used in making plastics, or remove toxic contaminants such as carbon monoxide. Much of the research done through this project applies to these and other areas.

Technology/Knowledge Transfer

The next step for the Mosaic Materials technology is to further reduce technology risk through field demonstration. This pilot demonstration is expected to occur in one to two years, after which the results could be shared and partnerships with manufacturers could be formed. Potential partners include engineering procurement and construction companies who could help design and produce the equipment, engineering service providers to maintain and operate the equipment, and companies who manufacture biogas conditioning equipment to vertically integrate the Mosaic system as part of a holistic biogas upgrading system. Following the pilot demonstration and formation of strategic partnerships, Mosaic Materials aims to commercialize and sell the novel upgrading system in four to six years.

CHAPTER 1: Introduction

California has set ambitious climate and environmental goals, including reducing its greenhouse gas emissions by 40 percent below 1990 levels by 2030 through the California Global Warming Solutions Act of 2006: Emissions Limit (Senate Bill 32, Pavley, Chapter 249, Statutes of 2016) and achieving carbon net neutrality by 2045 (former Governor Edmund G. Brown's Executive Order B-55-18). One pathway to reach these goals is to decarbonize California's energy mix by using biogas produced from waste resources in-state, which could produce approximately 351 billion cubic feet of gas per year.[1] These resources include forest- and agriculture-derived woody biomass, food waste and the organic fraction of municipal solid waste, municipal wastewater, landfill waste, and dairy manure. For biogas to be used in typical natural gas applications like heating, electricity, and as transportation fuel, it must first be converted into renewable natural gas (RNG).

Producing RNG from biogas requires cleanup and upgrading. Contaminants harmful to human health and pipeline integrity must be removed from biogas—referred to as the "cleanup" or "conditioning" step. After contaminant removal, carbon dioxide (CO_2) (30 percent-50 percent of most biogas streams) must be removed from the biogas for it to be compatible with natural gas equipment and infrastructure, referred to as "upgrading." The high content of CO_2 in raw biogas makes removing it the most cost- and energy-intensive step in the upgrading process. The primary technologies currently used for upgrading biogas to RNG are pressure swing adsorption (PSA) systems using carbon molecular sieves or zeolites, chemical scrubbing systems, water scrubbing systems, and membrane-based systems. The three most commercially applied upgrading technologies—PSA, amine absorption, and pressurized water scrubbing—have comparable levelized costs of energy at high gas throughputs.[2] The advantages and disadvantages of each technology are described in Table 1.

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[1] Williams, R. B., B. M. Jenkins and S. Kaffka (California Biomass Collaborative). 2015. *An Assessment of Biomass Resources in California, 2013 – DRAFT*. Contractor Report to the California Energy Commission. PIER Contract 500-11-020. https://biomass.ucdavis.edu/wp-content/uploads/CA_Biomass_Resource_2013Data_CBC_Task3_DRAFT.pdf

[2] D. M. Ong, R. B. Williams, and S. R. Kaffka. *"Renewable energy resource, technology, and economic assessments. Appendix H – Task 8: Comparative Assessment of Technology Options for Biogas Clean-Up,"* California Biomass Collaborative, University of California, Davis. Energy Research and Development Division Final Project Report. CEC-500-2017-APH, Jan. 2017.

Table 1: Comparison of Current Biogas Upgrading Technologies

Upgrading Technology	Advantages	Disadvantages
Water Scrubbing	• Good technology where wash water is abundant • Able to process large volumes of gas	• Significant water requirements per SCF of biogas treated • Recirculated systems experience biofouling; require energy for CO_2 and H_2S removal • Introduces H_2O and O_2 into gas stream
Chemical Scrubbing	• Higher selectivity than water reduces pumping requirements. • Removes CO_2, H_2S, and halogenated hydrocarbons.	• Solvent degradation requires make-up chemicals; if amines, constitute pollutant • Large steam/heating requirements for solvent regeneration • Cost prohibitive at small scales
Membranes	• Systems scalable by adding or reducing the number of modules online • Efficient at removing water vapor	• Multiple stage systems required to produce > 94% pure methane. • Energy required to heat gas plus compression • Susceptible to fouling, requiring replacement of expensive modules
Standard PSA (carbon molecular sieves, zeolites)	• Simple, mature technology, scalable • No solvents to dispose • Successful at removing multiple compounds present in raw biogas.	• Methane losses due to co-adsorption and bed void volume without recycle • Media performance decreased by H_2O • Mechanical components which may require maintenance
Rapid PSA	• Small system sizes/higher throughputs • Reduced capital costs vs. standard PSA • Simple control interfaces (despite engineering complexity) • Smaller beds → lower pressure drops	• Lower methane recovery relative to standard PSA • Engineering complexity requires vendor maintenance

Source: Mosaic Materials, Inc.

Regardless of the technology selected, biogas cleaning and upgrading costs are high: often more than half of a project's capital costs.[2] Consequently, using biogas to produce RNG remains low despite the large resource potential and increasing demand. Currently, only a fraction of sites that could produce biogas are currently doing so few are actively using the biogas they produce.[3] The United States Department of Agriculture cites a lack of applied research and development in biogas systems as a primary barrier to realizing the full potential of the domestic biogas industry.[4] This project is a critical step in helping lower this barrier, by lowering the cost of implementing a biogas upgrading system.

Any biogas upgrading system must satisfy constraints imposed by the site and natural gas distribution system. This includes the removal of common additional contaminants, including water and hydrogen sulfide (H_2S), as well as source-dependent contaminants including siloxanes and volatile organic compounds. In addition to purity standards, utility-specific heating value standards for the pipeline must be met. While the exact higher heating value requirement is dependent upon injection location and pipeline operator, the requirements for injecting into Southern California Gas Company pipelines (Rule No. 30) are summarized in Table 2.

Table 2: Natural Gas Composition Requirements Distribution Pipeline Injection

Conformity Metric	Required Value
HHV (dry basis)	990-1150 BTU/SCF
Wobbe Index	1279-1385
Total Inerts	< 4 vol%
CO_2	< 3 vol%
O_2	< 0.2 vol%
H_2S	< 4 ppm

Per Southern California Gas Rule No. 30. HHV = higher heating value; Btu = British thermal units; SCF = standard cubic feet.

Source: Mosaic Materials Inc.

Mosaic Materials' technology aims to dramatically reduce the costs of biogas upgrading through a separation process that harnesses the properties of a unique class of metal-organic frameworks (MOFs) developed by the Long Group at University of California (UC) Berkeley. The expanded pore structure of these MOFs allows one diamine (which have a strong affinity for CO_2) to bond at each metal site, at highly regular intervals. The spacing of the diamines within the pores produces a unique mechanism for CO_2 adsorption that creates "step-like" adsorption behavior—the amount of CO_2 adsorbed by the diamine-appended MOF increases or decreases dramatically over a narrow temperature or pressure window. This behavior (described further in Chapter 2) allows these adsorbents to exhibit very large working capacities (approximately 10-16 weight percent CO_2) and to be regenerated with small

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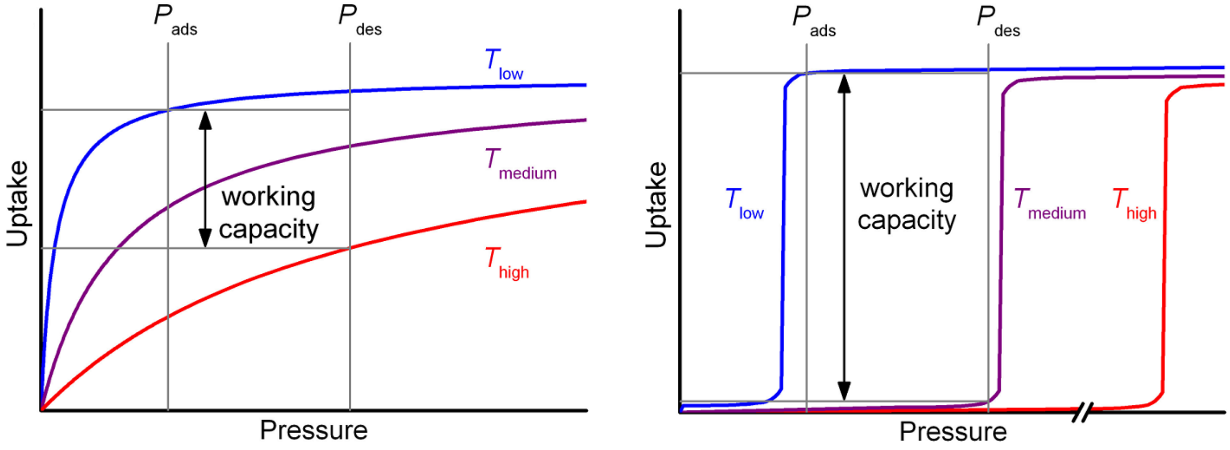
[3] "ABC Biogas 101 Handout", American Biogas Council, https://www.americanbiogascouncil.org/pdf/ABC%20Biogas%20101%20Handout%20NEW.pdf, Accessed 26 April 2018.

[4] "Biogas Opportunities Roadmap", United States Dept. of Agriculture, United States Environmental Protection Agency, and United States Dept. of Energy, Aug. 2014.

changes in pressure or temperature, as shown in Figure 1. In addition, the temperature or pressure at which the "step" in CO_2 adsorption occurs can be readily tuned by changing the diamine used to functionalize the MOF.[5] Mosaic Materials and the Long group at UC Berkeley have identified diamine variants that adsorb CO_2 at full capacity down to very low CO_2 partial pressures (enabling production of high purity RNG, as well as CO_2 capture from dilute sources), and variants that release the entire working capacity upon venting to atmosphere (low regeneration requirements).

Figure 1: Langmuir and Carbon Dioxide Adsorption Isotherms



Langmuir adsorption isotherms exhibited by traditional adsorbents (left) versus the carbon dioxide adsorption isotherms of diamine-appended metal-organic frameworks (right).

Source: T. M. McDonald *et al.*, "*Cooperative insertion of CO2 in diamine-appended metal-organic frameworks*," Nature, vol. 519, no. 7543, pp. 303–308, 2015.

Because of the unique mechanism of CO_2 adsorption, Mosaic's MOF-based adsorbents are also more selective for CO_2 over methane (CH_4) relative to carbon molecular sieves and zeolites. This means less co-adsorption of methane, improving the product (natural gas) recovery rate. These MOF-based adsorbents enable a separation process that combines 1) the selectivity of amine-based chemistry, 2) the scalability of solid adsorbent systems, and 3) drastically reduced energy for regeneration.

A key feature of this family of MOFs is that the location of the step can be selected by changing the diamine-MOF combination. The first technical challenge of this project was to identify the optimal diamine-MOF combination for biogas upgrading based on material stability and performance targets over the range of CO_2 partial pressures anticipated. This effort included synthesis and further characterization of more than 30 candidate materials. For this technology to be successful, the optimal material must be produced at the hundreds of kilogram (kg) to ton scale. Thus, a critical milestone in this development project was demonstrating production at the kg scale, a 1,000 times increase over the initial research and development synthesis procedure which yielded milligrams. For this material to be compatible with industrial processes, the base MOF adsorbent must also be densified into mechanically strong solids (examples shown in Figure 2).

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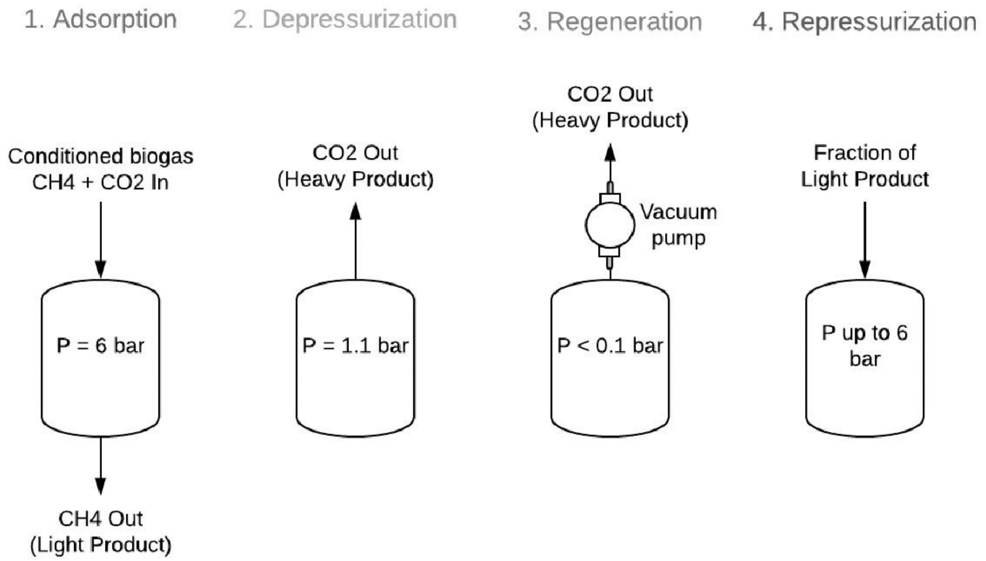
[5] R. L. Siegelman et al., "Controlling Cooperative CO2 Adsorption in Diamine-Appended Mg2(dobpdc) Metal-Organic Frameworks," J. Am. Chem. Soc., vol. 139, no. 30, pp. 10526–10538, 2017.

In addition to the materials challenges, a new separation process based on the MOF adsorbent's unique characteristics had to be developed. To enable continuous removal of CO_2 from biogas using solid adsorbents, vessels containing solid adsorbents are typically run in parallel, such that one bed is constantly removing CO_2 from biogas while the others are regenerated (generally by reducing the pressure or increasing temperature). Over the course of a single PSA cycle, each vessel (or "bed") passes through a series of adsorption, depressurization, regeneration, and re-pressurization steps. A simple example for removing CO_2 from biogas shown in Figure 2. Such processes can be improved by optimizing the adsorption and regeneration temperatures and pressures, adding additional steps (for example equilibrating the pressure of two beds or "rinsing" beds with either product or feed), increasing number of beds, and other cycle modifications.

Figure 2: Vacuum-Pressure Swing Adsorption Cycle



Simplified vacuum-pressure swing adsorption cycle for CO_2 removal from biogas with bed pressure "P" at each step indicated.

Source: Mosaic Materials Inc.

To develop the separation process, simulation models of the process were needed to predict performance at scales. Modeling these materials is challenging because the "step-like" or on-off CO_2 adsorption behavior creates large derivatives in CO_2 loading, leading to convergence issues in numerical solving routines. New models of adsorption behavior were needed. Laboratory testing was done to determine key material properties such as mass transfer and heat transfer coefficients and confirm that the model correctly predicted how the MOF would adsorb CO_2. The information about the material learned from laboratory tests was used to improve and extend the model to predict the performance of the MOF in a full-scale facility (50 standard cubic feet per minute [scfm]-2,800 scfm biogas). The process design was refined by comparing the equipment and operating costs of different versions of the process (for example, varying the operating pressures, amount of adsorbent, etc.). Finally, Mosaic Materials completed a technoeconomic assessment of the best-case CO_2 removal process compared to chemical scrubbing systems based on the predicted performance at large scale (2,800 scfm).

The final technical challenge addressed was evaluating the stability of the solid, optimized MOF adsorbent to contaminants in a real biogas stream. This was accomplished through slipstream testing at a partner wastewater treatment site, the Davis Wastewater Treatment Plant (Davis, California). In these tests, several samples of tableted MOF were installed in a slipstream line (pipe) with unconditioned biogas containing 3 percent water and 1,800 ppm H_2S flowing over them for up to a month.

Mosaic Material's technology will accelerate biogas adoption by reducing the cost of production and upgrading to pipeline quality methane, reduce waste at biogas facilities, and maximize the energy to be obtained from biogas production. The benefits of this technology to California investor-owned utility natural gas ratepayers include lower capital and operating costs for production of biomethane, significant greenhouse gas reduction through the use of renewable energy, increased safety of biogas systems, increased energy security through diversified renewable portfolio, and the facilitation of rural development and job creation.

CHAPTER 2:
Adsorbent Design and Scale-up

Through preliminary process engineering, materials screening, and material stability tests, Mosaic Materials and UC Berkeley selected a Gen-1 diamine-appended MOF for upgrading biogas to pipeline quality methane. For implementation into a realistic adsorption separation scheme, material scale-up and densification was required to manufacture adsorbent materials in a relevant form factor. Mosaic Materials has shown that the CO_2 adsorption performance of the Gen-1 amine-appended MOF was not reduced by scaling up production over four orders of magnitude, from the single gram to kg scale. The three characterization tools (77 Kelvin dinitrogen [N_2] surface area measurement, nuclear magnetic resonance spectroscopy, and thermogravimetric analysis [TGA] adsorption isobars) indicate that the MOFs produced through Mosaic's scale-up MOF synthesis, purification, amination, and densification processes are of consistent quality, and that the CO_2 capacity of the final MOF product is essentially at its theoretical maximum (based on TGA adsorption isobars). Based on the evidence to date, the researchers do not expect the performance of the adsorbent to be negatively impacted by the scale-up process.

Material Selection and Characterization

To improve the efficiency of upgrading crude biogas to pipeline-quality biomethane, new materials with high capacity and selectivity for CO_2 with low regeneration energies are needed. Amine-appended adsorbents are particularly promising candidates in this regard. As with aqueous amine solutions, these materials can bind CO_2 selectively over methane through acid–base chemistry. Further, adsorbents offer the potential to achieve higher cycling capacities with intrinsically lower energy requirements than analogous amine absorbents by eliminating the need to operate at dilute concentrations in aqueous solution.

Screening Diamine-Appended Metal-Organic Frameworks

Recently developed classes of amine-impregnated solid adsorbents exhibiting sigmoidal-shaped (or "step-shaped") CO_2 adsorption isotherms have the potential to reduce the cost and energy usage for CO_2 removal from biogas. The step-shaped isotherm behavior is unique to a specific family of metal-organic frameworks (MOFs) M_2(dobpdc) (M = Mg, Mn, Fe, Co, Ni, Zn; dobpdc^{4-} = 4,4′-dioxidobiphenyl-3,3′-dicarboxylate), developed by the Long Group at the University of California, Berkeley.[6] These materials feature 1-D hexagonal channels of ~18 Angstrom (Å) diameter with octahedral metal(II) sites hosting an appended diamine at each vertex. One end of each diamine binds a metal(II) site lining the pore, leaving the other amine free to initiate chemisorption of CO_2. These materials were found to display cooperative adsorption of CO_2 in which the full working capacity of the material can be achieved through step-like adsorption that proceeds over a very narrow pressure and temperature range. Through spectroscopic and crystallographic studies, this adsorption mechanism was traced to

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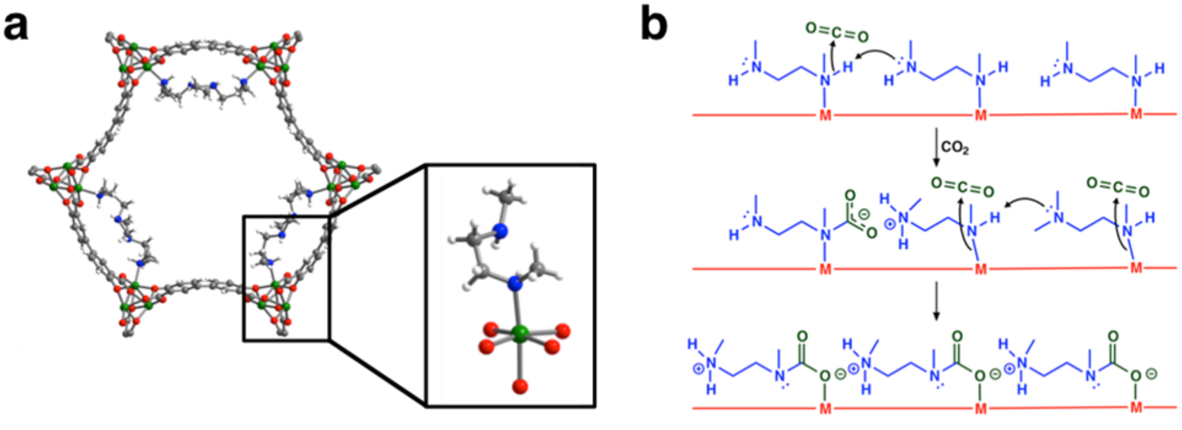
[6] T. M. McDonald et al., "Cooperative insertion of CO2 in diamine-appended metal-organic frameworks," Nature, vol. 519, no. 7543, pp. 303–308, 2015.

insertion of CO_2 into the metal–amine bonds of the framework to form chains of ammonium carbamate extending along the pore axis. Figure 3 illustrates the attachment points of the diamines appended to the metal(II) coordination sites lining the pores (mmen = *N,N′*-dimethylethylenediamine).[7]

Figure 3: Attachment Points of Diamines



a) Structure of mmen-M_2(dobpdc); b) Cooperative CO_2 adsorption mechanism in diamine-appended M_2(dobpdc) frameworks.

Source: T. M. McDonald et al., "*Cooperative insertion of CO_2 in diamine-appended metal-organic frameworks*," *Nature*, vol. 519, no. 7543, pp. 303–308, 2015.

Mosaic Materials sought to design and select a material with a step location for cooperative CO_2 adsorption ideally positioned for biogas upgrading. Using a high-throughput adsorption instrument, CO_2 and CH_4 adsorption properties were analyzed for more than 30 diamine-appended metal–organic frameworks with a variety of metal nodes. Preliminary work during this project determined a target adsorption condition of 6 bar total pressure (30 percent to 50 percent CO_2 in CH_4) at 40 degrees Centigrade (°C). A combined pressure–temperature swing process was assumed, with desorption to occur at the highest desorption pressure and the minimum possible desorption temperature to be optimized through material design. To achieve pipeline-quality biomethane, the candidate material in this case was required to adsorb CO_2 down to pressures below 2 percent of the inlet pressure (6 bar). In the proposed process, $P_{ads} = 0.02(6 \text{ bar}) = 0.12$ bar (Figure 4).

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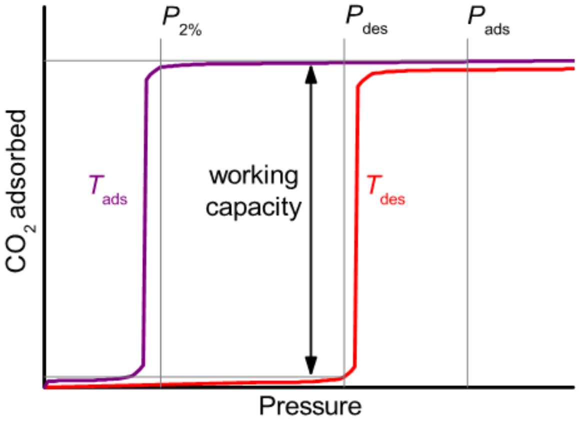
[7] T. M. McDonald et al., "Cooperative insertion of CO2 in diamine-appended metal-organic frameworks," Nature, vol. 519, no. 7543, pp. 303–308, 2015.

Figure 4: Pressure-Temperature Swing Requirement



Combined pressure-temperature swing required to meet <2 percent CO_2 product purity requirement

Source: Mosaic Materials Inc.

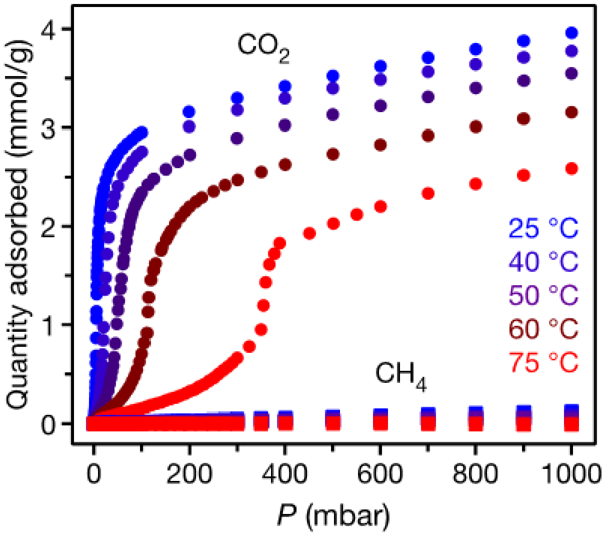
From the 30 diamine-appended MOF materials screened, three candidate materials were identified with CO_2 adsorption properties within the desired range. To select a Generation 1 (Gen-1) adsorbent, TGA cycling experiments with CO_2 and CO_2/N_2 mixtures were conducted for the three candidates to evaluate long-term material stability. The finally selected Generation 1 adsorbent (Gen-1) was found to have the greatest stability to cycling and the lowest projected energy requirement in a biogas upgrading process. Furthermore, the diamine used to prepare Gen-1 is already available at low cost and large scale, facilitating the transition from lab-scale analysis to bench-scale testing and beyond. Characterization of the Gen-1 material is presented below.

Properties of Generation 1 Adsorbent

High-resolution single-component adsorption isotherms at low pressure were collected for the Gen-1 material using an accelerated surface area and porosimetry system (ASAP 2020) volumetric adsorption instrument (Figure 5). The step-shaped CO_2 adsorption isotherms (circles) are indicative of cooperative CO_2 binding. In contrast, the CH_4 isotherms (squares) are nearly flat at pressures up to 1 bar due to the lack of specific binding sites for methane molecules.

The Gen-1 material was found to display exceptional stability to cycling under a variety of conditions. In these experiments, the material was first activated at 150°C under a mixture of CO_2 in N_2 for 30 min to remove any residual solvents. Next, the adsorbent was cooled to the target adsorption temperature of 40°C under the CO_2/N_2 mixture and held isothermal for 10 min to allow the material to saturate with CO_2. The saturated bed was then heated to 100°C for 10 min under a flow of 100 percent CO_2 to desorb the bound gas. The atmosphere in the furnace was returned to the CO_2/N_2 mixture and the sample was cooled to 40°C to begin a new cycle.

Figure 5: Adsorption Isotherms Collected for Generation 1 Material

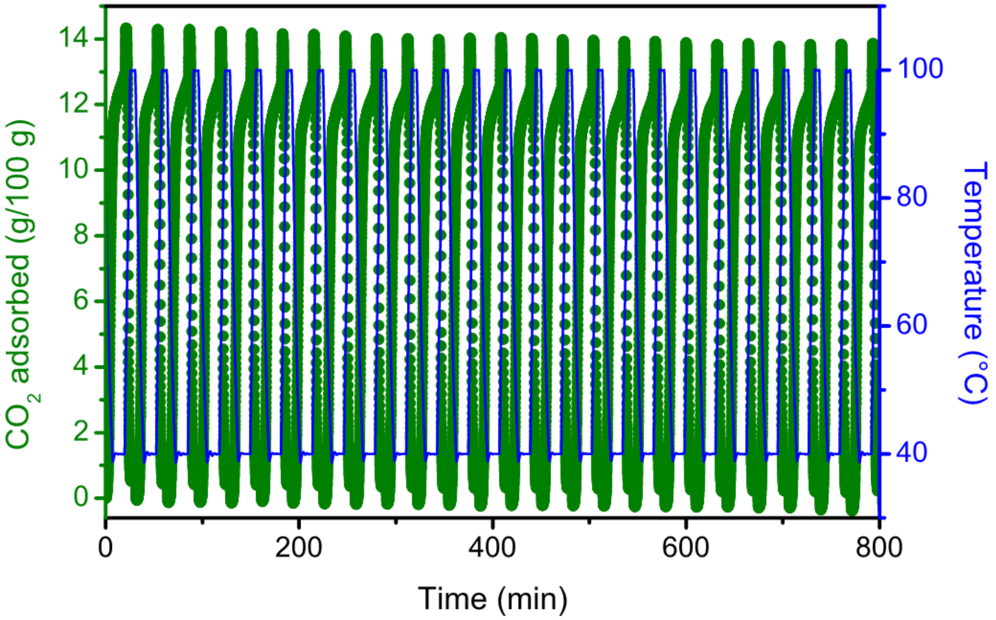


High-resolution, single-component adsorption isotherms for CO_2 (circles) and CH_4 (squares) with the Gen-1 material.

Source: Mosaic Materials Inc.

Thermogravimetric analysis (TGA) cycling experiments can be used to approximate the minimum CO_2 concentration that the framework must adsorb in order to reach the pipeline specification of 2 percent CO_2 in the effluent (in this case, $P_{2\%}$ = 0.02(6 bar) = 0.12 bar). While a mixture of 12 percent CO_2 in N_2 was not available, a mixture of 10 percent CO_2 in N_2 (corresponding to 1.7 percent CO_2 in a 6 bar stream) was used to approximate the desired target minimum partial pressure of CO_2. The cycling results of adsorption at 40°C under 10 percent CO_2 in N_2 with desorption under 100 percent CO_2 at 100°C are shown in Figure 6. A stable CO_2 working capacity of ~9.2 g/100 g was observed. Importantly, the peak CO_2 adsorption in these experiments remained stable and in fact increased slightly for the last few cycles, indicating that lack of full reactivation between cycles, rather than adsorbent decomposition, is responsible for the relative capacity loss of 4.1 percent over 26 cycles (0.16 percent per cycle). It is likely that improved cycling performance can be achieved by a slight increase in the desorption temperature. Longer adsorption periods may also lead to improved working capacity, as the sharp spike in uptake upon switching to 100 percent CO_2 indicates that the material has not yet saturated with CO_2 at the onset of desorption.

Figure 6: Thermogravimetric Analysis Cycling Results



With adsorption under 10 percent CO_2 in N_2 at 40°C and desorption under 100 percent CO_2 at 100°C.

Source: Mosaic Materials Inc.

Generation 1 Adsorbent Scale-up and Densification

For this biogas upgrading technology to be applied successfully, the Gen-1 MOF adsorbent (selected through the screening study) must be produced (1) reliably, (2) in a densified form amenable to an adsorption process, and (3) at a scale relevant to the small demonstration with is a component of the project. At the outset of the project, the synthesis of the Gen-1 MOF was reliable and reproducible at the 1-g scale, and no kind of densification (that is, pelletization, extrusion, or tableting) had been attempted. The results reported here include increasing the scale of Gen-1 MOF production over four orders of magnitude and increasing the output of the tableting to hundreds of grams per day.

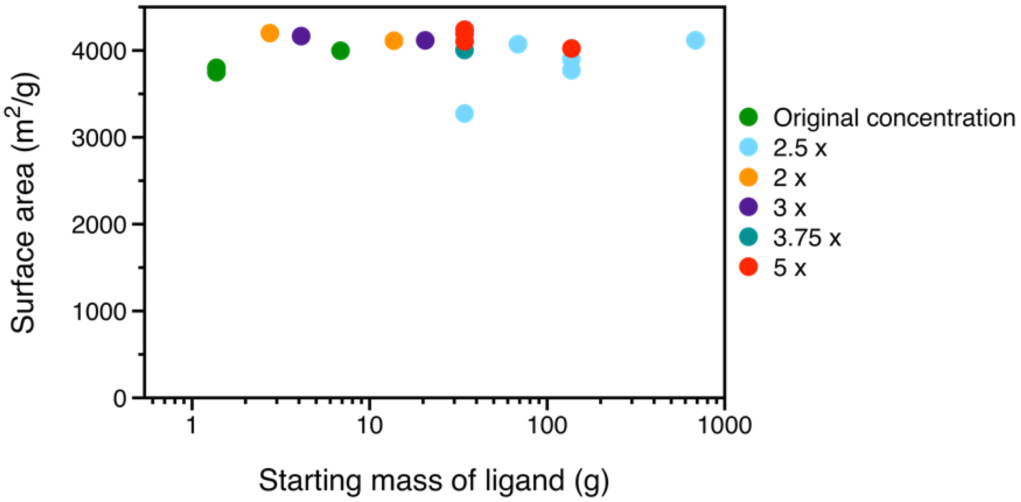
Synthesis of “Bare” Metal-Organic Framework Structure

Importantly, this class of metal-organic frameworks can be produced through a simple hydrothermal synthesis procedure: metal salt and the organic ligand are mixed in solvent, where the reagents self-assemble to form a robust skeletal structure. The metal ions in the MOF structure have only five of their six molecular binding sites coordinated to the organic ligand, leaving one available to bind to one amine group of a diamine molecule. Generally, scaling synthesis such as this is achievable via a linear process, wherein the amount of product made scales with the reaction volume.

Internal surface area is a key metric for evaluating the quality of bare MOF, reported in square meters (m^2) of available surface per gram of MOF as measured via N_2 adsorption at 77 K. Figure 7 presents the surface areas of representative samples of the reactions with the concentration of the limiting reactant indicated (separated by color based on the concentration of the reaction compared to the initial trials). The results are predominantly between 3,600 and 4,000 m^2/g, where 4,100 m^2/g is approximately the theoretical maximum achievable.

Figure 7 shows that it is possible to achieve high quality (>90 percent theoretical surface area) bare frameworks with increased reagent concentrations, reducing both the reaction volume required and the volume of aqueous waste generated.

Figure 7: Representative Sample of Bare Metal-Organic Framework Structures

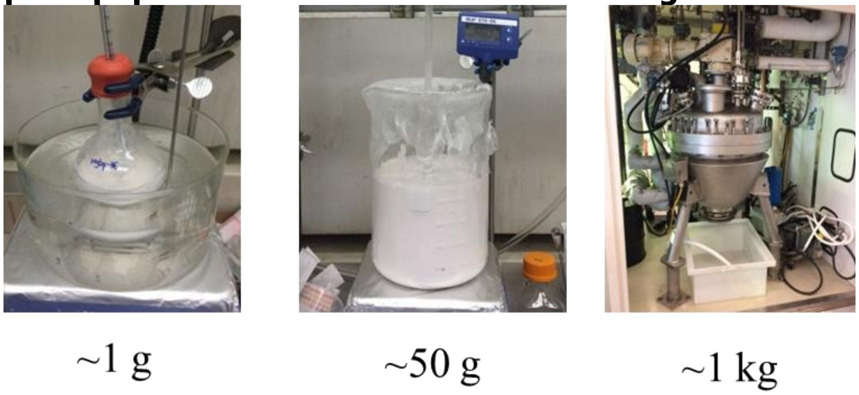


The 77 K N_2 surface area of a representative sample of bare (pre-aminated) metal-organic framework structures undertaken during this project.

Source: Mosaic Materials Inc.

The results in Figure 7 represent a wide range of production scales of the bare framework, from g-scale to kg-scale per batch. Existing Mosaic facilities, using traditional bench-scale techniques, were used to reliably produce g-scale batches of high-quality base framework, shown in the left and middle panels of Figure 8 below. However, to meet the production goals of this project and to demonstrate scalability of this MOF material, large scale syntheses were required. To this end, Mosaic Materials successfully worked with an external toll manufacturer to access larger reactors and processing equipment as a cost and time efficient means for kg-scale MOF production. Comparing the bare MOF surface area from large-scale syntheses were consistent with g-scale syntheses, showing successful technology transfer and the scalability of the MOF used throughout this project.

Figure 8: Sample Equipment Used to Produce Metal-Organic Framework Material



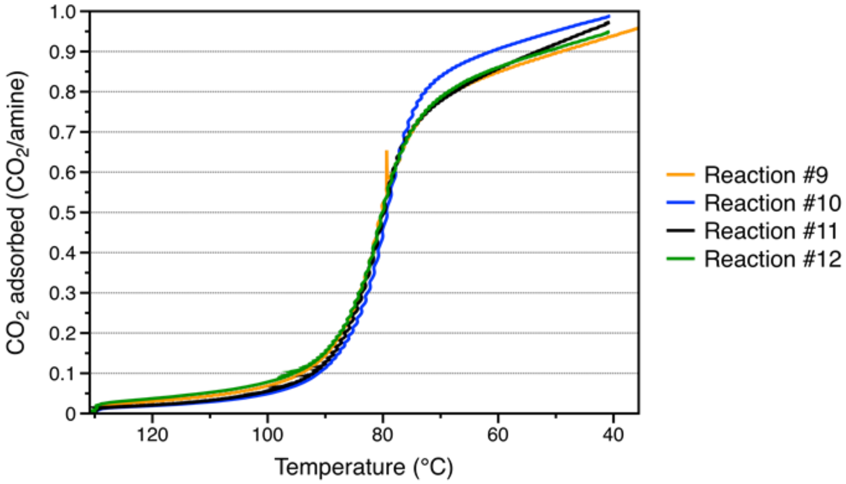
Source: Mosaic Materials Inc.

Amination of the Metal-Organic Framework

Conceptually, the process of adding diamine to the bare MOF scaffold (amination) is straightforward: dissolve the diamine in a solvent, soak the metal-organic framework in that mixture, and filter to recover the aminated MOF. However, the details and subtleties of this procedure create many opportunities for optimization. The ideal conditions are those which generate a MOF with exactly one diamine bound to every open metal site, with little sensitivity to small variations such that the procedure is forgiving to minor changes in handling or operator.

Once the MOF is known to have the correct amine loading, its CO_2 adsorption performance is measured using TGA at isobaric conditions to confirm that the amine is properly bound to the open metal sites of the framework, rather than sitting unbound in the pores. The highly quantitative measure of this is the capacity for CO_2 per gram of MOF, which should be approximately 15 g CO_2) per 100 g MOF. The slightly more qualitative measure is the characteristic step-shaped adsorption behavior that is observed in the TGA trace which is what renders these MOFs so attractive from a biogas upgrading perspective. Figure 9 illustrates these TGA profiles for four aminations showing that for all four MOFs, the quantity of CO_2 adsorbed nearly matches what is expected assuming that the [diamine]:[MOF binding site] ratio is 1. Therefore, Figure 9 shows that the MOFs aminated throughout this project display high CO_2 adsorption performance.

Figure 9: Thermogravimetric Analysis Profiles of Four Aminated Metal-Organic Frameworks



Source: Mosaic Materials Inc.

Tableting of the Diamine-Appended Metal-Organic Framework

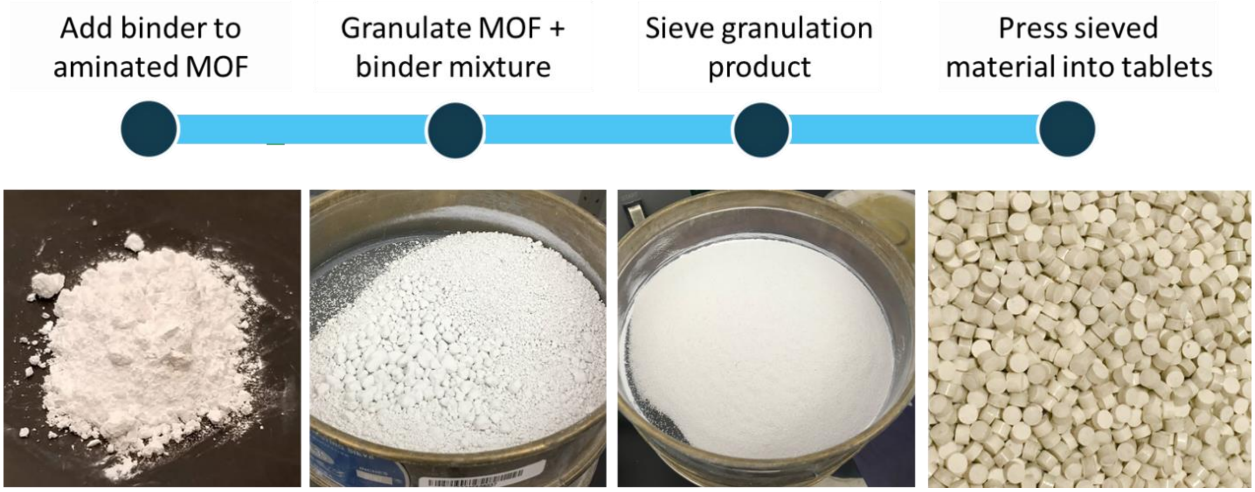
For adsorbents to be used in gas separation processes, either for large-scale biogas upgrading or the small pilot constructed during this project, they must be compacted into appropriately-sized solid forms to prevent excessive pressure drop across the separation bed. Examples of these forms are tablets, extrudates, and spheres. Through a series of engineering planning discussions and bench-scale experimental tests, the form and size determined to be best for this process were 3-mm cylindrical tablets. To create a densified MOF tablet a binder is mixed with the dry MOF powder and then compacted using a pharmaceutical-type tablet press. Here, the research team modified that procedure for rapid generation of pellets without losses in performance.

Large-scale tableting of the aminated MOF introduced new challenges not previously encountered. The sources of these challenges were primarily the powder flowability and the associated yield of tablets, the relationship between which will be explained further below. As in all tableting applications, solid flowability becomes apparent at scale. Therefore, a major challenge associated with scaling up the tableting process was modifying the rheological properties of the powder such that it could flow freely from the feed hopper into the die. This involved extensive development for the process of combining the binder with the MOF ("granulating") and sieving the granulated particles to a mesh size that provided consistent flowed from the hopper into the punch.

The granulation process produces particles (of MOF and binder combined) of a large range of sizes. The range of particle sizes has major implications on the flowability of the mixture fed to the tablet press. One concern is that, if the individual particles are large, the macropores in the pellets produced will be clogged and impede diffusion, or if the particles are small, they may not be strong enough to withstand the mechanical stress of tableting and the MOF framework may collapse. To test this, various size fractions were produced through mechanical sieving. As previously discussed, TGA isobars were used to show that the pellets produced from various particle size ranges maintained their structure and CO_2 capacity. Results from TGA isobars demonstrated that all particle size fractions maintained high adsorption performance, showing that binder did not clog openings to the MOF pores.

The overall workflow of converting the aminated MOF into robust tableted forms is shown in Figure 10.

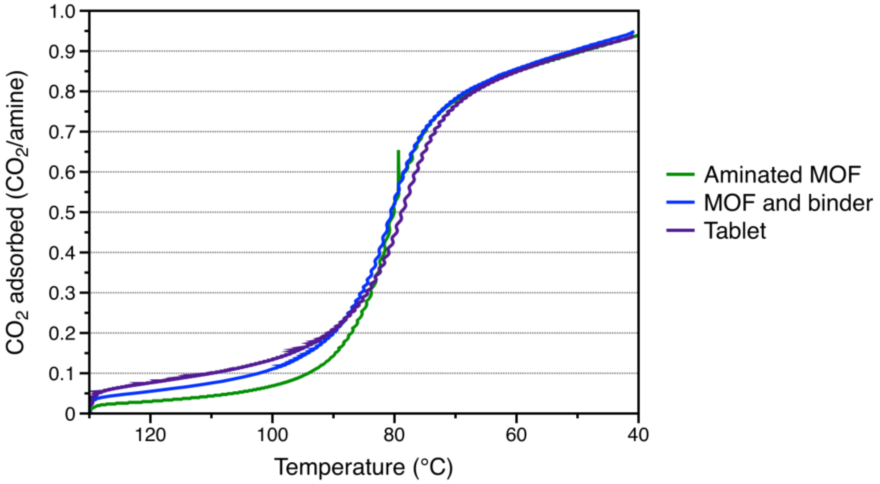
Figure 10: Steps to Convert Aminated Metal-Organic Frameworks into Tablet Form



Source: Mosaic Materials Inc.

At the end of the process, the CO_2 adsorption performance and mechanical stability of the tablets were used as quality metrics for success of the tablet scale-up process. Figure 11 displays the CO_2 adsorption isobars of the as-synthesized aminated MOF, of the aminated MOF after binderization, and of the final tableted product.

Figure 11: Thermogravimetric Analysis Profiles



Profiles of representative aminated MOF (green), mixture of MOF and binder (blue), and a tablet (purple).

Source: Mosaic Materials Inc.

For the tablet and the MOF and binder mixture, the capacities are corrected for the mass of binder. As expected, there is some decrease in the slope of the isobar with additional processing steps, which affects the performance, however the differences are marginal.

Two kg of tableted MOF adsorbent was produced over the course of this project, including multiple charges of material for the bench-scale PSA system described in Chapter 3. The majority of this material (approx. 1.7kg) was produced using the automated single-stage tablet press, which can produce up to 50 g tablets/hr. The tableted MOF has demonstrated consistent performance in more than 1000 realistic vacuum swing adsorption cycles (roughly 160 hours of operation) to date.

CHAPTER 3: Separation Process Design

This chapter describes the design of the separation process for biogas upgrading using the Gen-1 MOF-based adsorbent. Separation processes based on traditional solid adsorbents use process cycles that are tailored to the properties of those adsorbents; these must be re-optimized for these new materials. A process simulation tool was developed using the Aspen software suite to simulate how the Gen-1 material would perform in various vacuum-pressure swing adsorption (VPSA) processes. The simulation tool was validated using breakthrough experiments in the laboratory at bench-scale. The validated model was then expanded to simulate performance of the adsorbent over full cycles at commercial scale, and used to identify efficient, low-cost process configurations. A technoeconomic analyses of the full-scale system performed in parallel indicated that Mosaic's solid-state adsorption system should reduce the operational expenditure associated with biogas upgrading by 38 percent, and capital expenditure by 15 percent, relative to aqueous amine scrubbing with monoethanolamine (MEA). Lastly a bench-scale, commercially available PSA system was retrofitted and used to further optimize the VPSA cycle proposed.

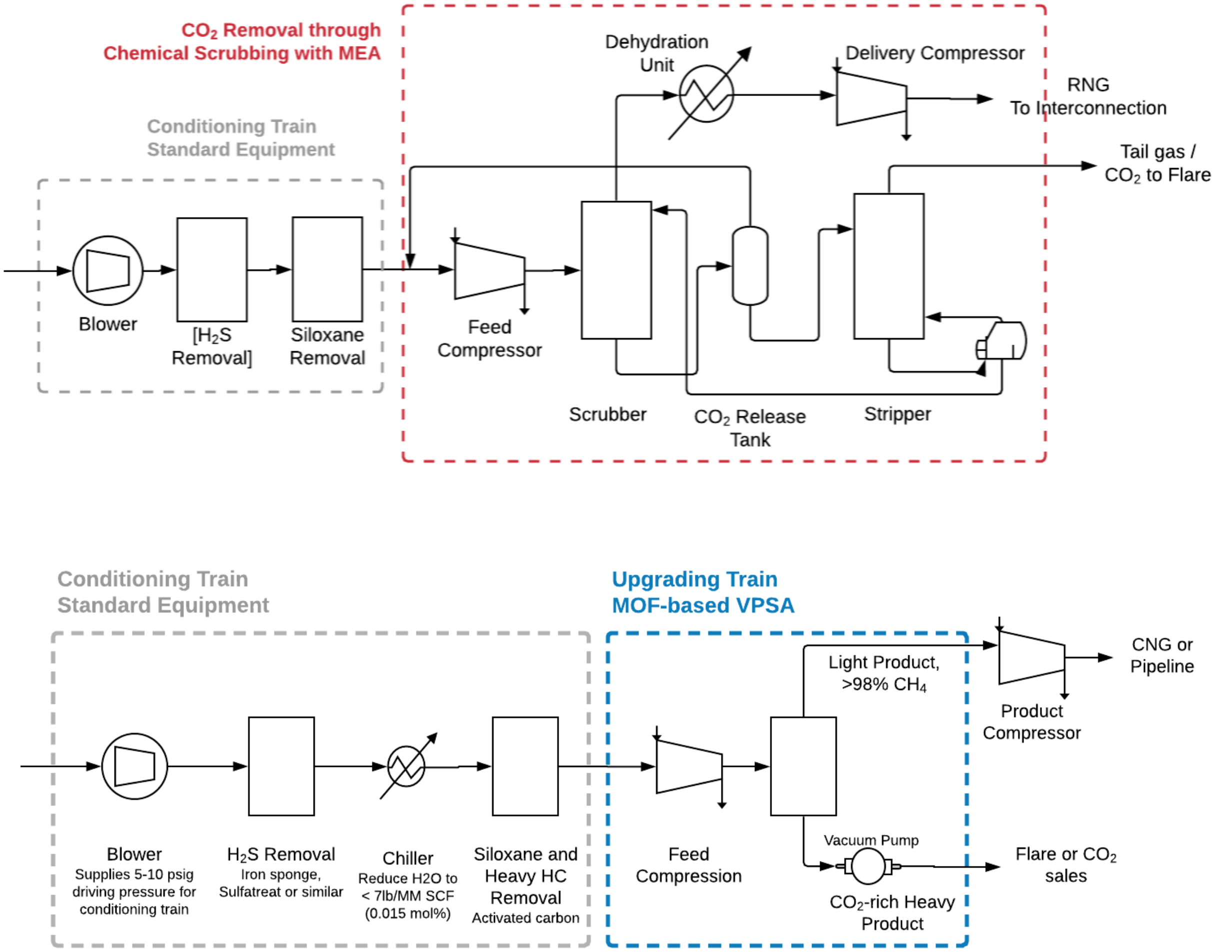
Process Overview and Design Cases

The design and economics of biogas upgrading systems are strongly dependent on the size of the system, the site characteristics, product specifications, and associated utility costs. Potential sites for biogas upgrading include small, distributed facilities such as dairy farms, landfills and wastewater treatment facilities for small to mid-sized towns. Such facilities might produce less than 100,000 standard cubic feet of gas per day (scfd), have limited available utilities (for example, no compressed air or access to high voltage electricity), and little or no on-site engineering support. Alternatively, large landfills and wastewater treatment facilities located in densely populated areas may produce millions of cubic feet per day of biogas, have a wide range of utilities and streams available for heat exchange, and have round-the-clock staffing.

To compare the impact of the technology in these diverse situations, upgrading units for a representative "small-scale" facility, producing 75,000 scfd, and a "large-scale" facility, producing 4 million scfd, were designed and costed. The small-scale facility was sized to process the output of the Davis Wastewater Treatment Plant, who collaborated with Mosaic Materials to facilitate materials stability testing at their site (see Chapter 4). The large-scale facility was sized based on the San Mateo Wastewater Treatment Plant, who kindly provided capacity information and a tour of their facility. The size of the large-scale facility permitted direct comparison of the MOF-based CO_2 separation process developed to a traditional CO_2 removal technology, an amine scrubbing system using MEA. Both MOF-based and MEA separation systems were simulated with the same capacity, feed composition and product requirements.

The general process flow diagram for a biogas upgrading system using 1) an aqueous amine scrubber or 2) the MOF-based solid adsorbents for CO_2 removal is shown in Figure 12.

Figure 12: Flowsheet for Upgrading Biogas to Renewable Natural Gas



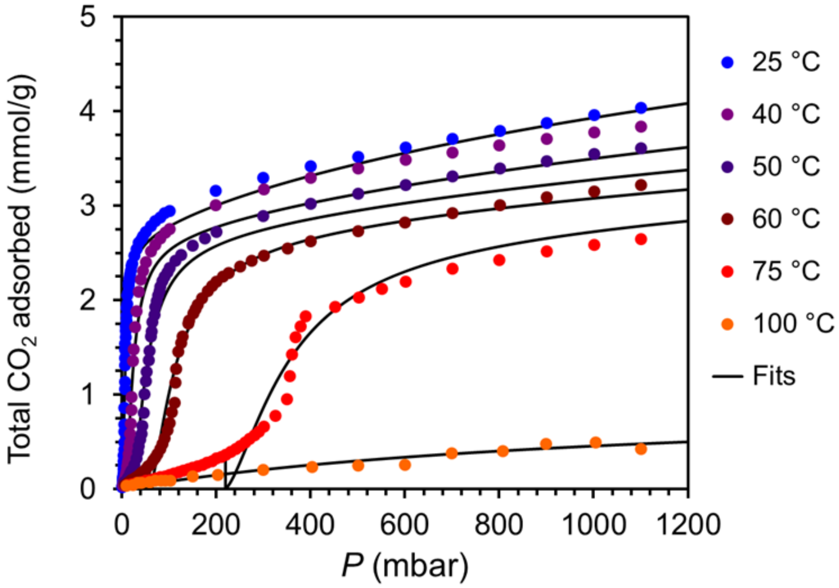
Top: aqueous amine scrubbing; bottom VPSA with MOF-based adsorbents.

Source: Mosaic Materials Inc.

Process Model Development

The Aspen Adsorption simulation package was used to develop finite-element based models of the adsorbent beds investigated in this work. The Gen-1 adsorbent material used throughout this work was highly characterized as described in Chapter 2. A detailed description of the model and governing equations used is included as Appendix A. The adsorption isotherms and model fits for the Gen-1 material that were used to predict the CO_2 performance are shown in Figure 13. One significant advantage of the MOF-based adsorbents, including the Gen-1 adsorbent, over other solid adsorbents is their high selectivity for CO_2 over methane (see Figure 5, Chapter 2).

Figure 13: Carbon Dioxide Adsorption Isotherms



Isotherms for Gen-1 adsorbent (powder) over anticipated process temperatures (markers) and best fits to the data found using the FG-BET isotherm.

Source: Mosaic Materials Inc.

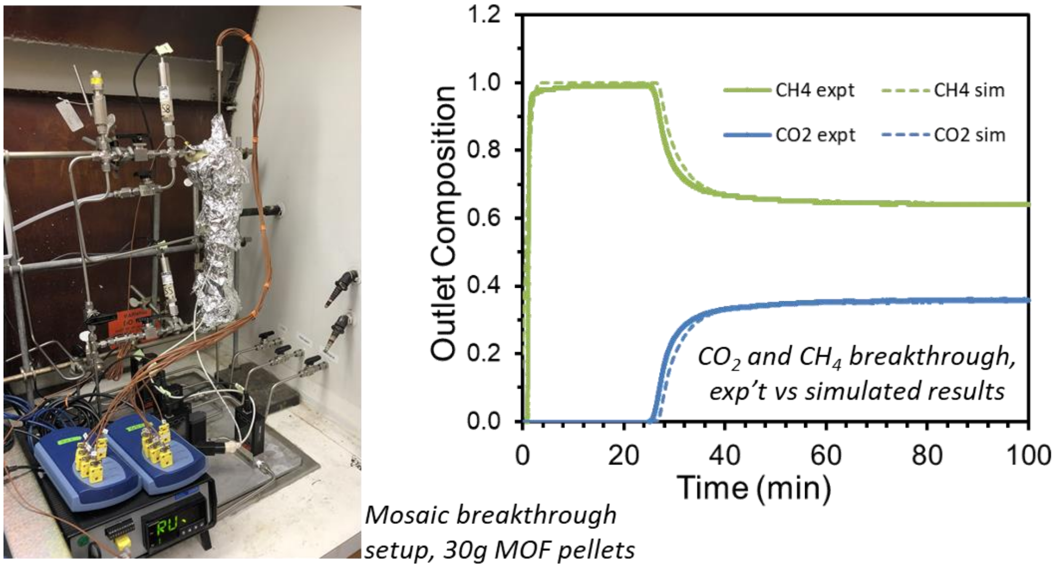
Bench-Scale Testing and Model Validation

The adsorption model described was validated at the bench-scale by comparing the simulation results against data from breakthrough experiments. In brief, a feed gas simulating conditioned biogas was flowed through a "clean" bed of Gen-1 adsorbent tablets while monitoring the product composition until saturation was reached. The apparatus for these tests was a 12-inch section of schedule 40 stainless steel pipe, with an internal diameter of 1.049 inches. This bed was loaded with 25-35 g of pelletized adsorbent. A thermocouple inserted through the middle of the bed tracked and recorded the temperature profile during the runs. As expected, the temperature within the bed increased sharply during breakthrough tests in regions actively adsorbing CO_2.

For each breakthrough test, the experimental data were compared to the model simulations. The CO_2 mass transfer coefficient was determined by adjusting the simulation value until the shape of the CO_2 breakthrough curves matched. As discussed in Appendix A, mass transfer was assumed to be controlled by a linear driving force, proportional to the difference in the adsorbate concentration in the bulk gas and on the surface of the adsorbent. Additional description of the series of experiments run, and comments regarding the effect of flow regime, is discussed in Appendix B.

Overall, good agreement was achieved between the experimentally measured product composition and simulation results over the flow conditions tested. Figure 14 illustrates the fit between experiment and simulation results for a representative breakthrough test with 64 percent CH_4 /36 percent CO_2 at 6 bar and provides a photograph of the breakthrough apparatus used.

Figure 14: Test System and Fit between Model and Results



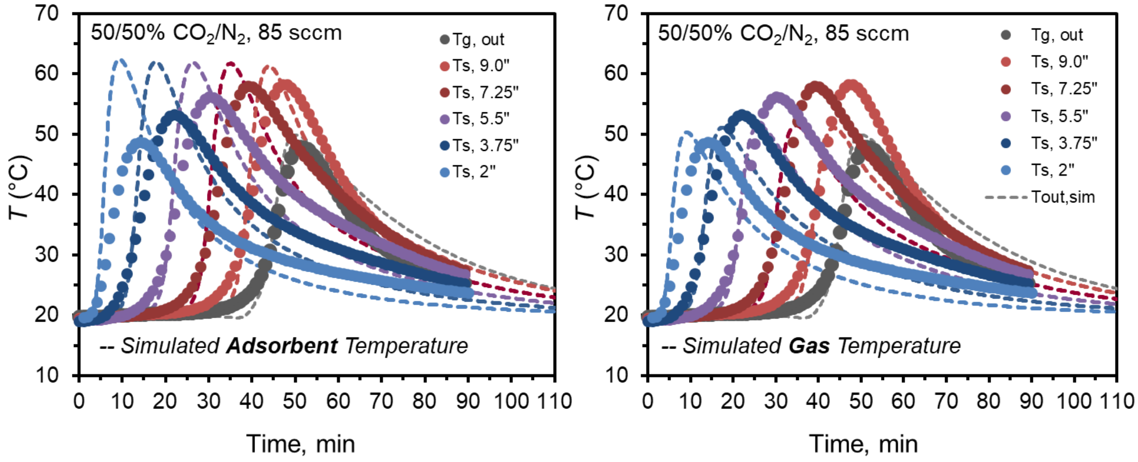
Mosaic breakthrough setup, 30g MOF pellets

Left: breakthrough test system built for this study; right: fit between process model and experimental results in breakthrough testing at 6 bar, 64 percent CH_4/36 percent CO_2.

Source: Mosaic Materials Inc.

The model was also set up to predict the location of the thermal front and axial temperature profiles associated with CO_2 adsorption and heat transfer processes. Heat transfer coefficients (HTC) between the gas and adsorbent, the gas and the bed wall (H_{wall}), and the bed wall and ambient temperature (H_{amb}) were determined by estimating them with Aspen Adsorption's built-in estimating functions, then iteratively adjusting them to improve the fit (Figure 15). The following values to yield the best agreement for the breakthrough setup: *HTC* = 8-10 Watts per meter-Kelvin (W/mK); H_{amb} = *6-8* W/mK, and H_{wall} = *20-50* W/mK (depending on flow rate and other process conditions). Overall, this model accurately predicts the onset of CO_2 breakthrough in the bench-scale unit, and it reasonably describes the temperature profiles in the packed bed.

Figure 15: Adsorbent and Gas Temperature Profiles



Profiles over time during breakthrough experiments, comparison between measured and simulated values.

Source: Mosaic Materials Inc.

Simulation of Full-Scale Process

The bench scale simulation model was next scaled and extended to predict the performance of a VPSA unit at the two design cases: processing either 75,000 scfd (52 scfm) and 4 million scfd (2,800 scfm) of pre-conditioned biogas. In each simulation, sufficient adsorption-desorption cycles were simulated for steady-state operation to be achieved, from 80 to several hundred cycles. The following general assumptions were used for process simulations of full-scale systems:

- Conditioned biogas (simulated as a 64 percent-36 percent CH_4/CO_2 mixture) enters at 40°C.
- The bed is adiabatic.
- The bed is filled with 1.5, 3 or 6 millimeter (mm) spherical pellets; packing density is 60-62 percent (typical of random loose to close-packed spheres).[8]

To regenerate the solid adsorbent and perform multiple cycles, either the partial pressure of CO_2 must be reduced (pressure or vacuum swing adsorption, PSA or VPSA) or the temperature of the adsorbent must be increased. Temperature swing adsorption processes require long regeneration times to accommodate heating the bed to the required temperature, and then cooling it down prior to the next adsorption step. Due to the high CO_2 content of the feed gas (and thus relatively short adsorption periods), the research team focused on PSA/VSA separation processes for this application to enable more rapid cycling of the beds, resulting in smaller bed sizes.

The CO_2 desorption through pressure swing (reducing the partial pressure of CO_2) at below atmospheric pressures can be accomplished 1) through dilution with a sweep gas, 2) pulling vacuum on the bed, or 3) a combination of the two. Purchasing or producing an inert sweep gas on site (for example, N_2) would add significantly to the cost and footprint of the project. If methane were used as a sweep gas, most of the product would be contaminated with CO_2. While air is an inexpensive sweep gas option, the introduction of oxygen into the system containing methane creates a flammable mixture at some compositions and would require additional safety features. The use of sweep gas also reduces the product purity due to the presence of non-product gas occupying the void volume of the adsorption vessels at the start of the adsorption step. The cost and/or logistics associated with producing or purchasing an inert sweep gas were the main deterrent for using this strategy.

Alternatively, p_{CO2} can be decreased by evacuating the gas with a vacuum pump. The pressure that must be attained for CO_2 to desorb is dependent on the adsorbent material and the temperature. Based on the Gen-1 CO_2 adsorption isotherms shown in Figure 13, the bed pressure must be reduced to 100 mbar or less to desorb CO_2 at a bed temperature of 60°C based on the adsorption isotherms.

The target adsorption pressure of 6 bar and vacuum-swing regeneration strategy were determined based on the following inputs:

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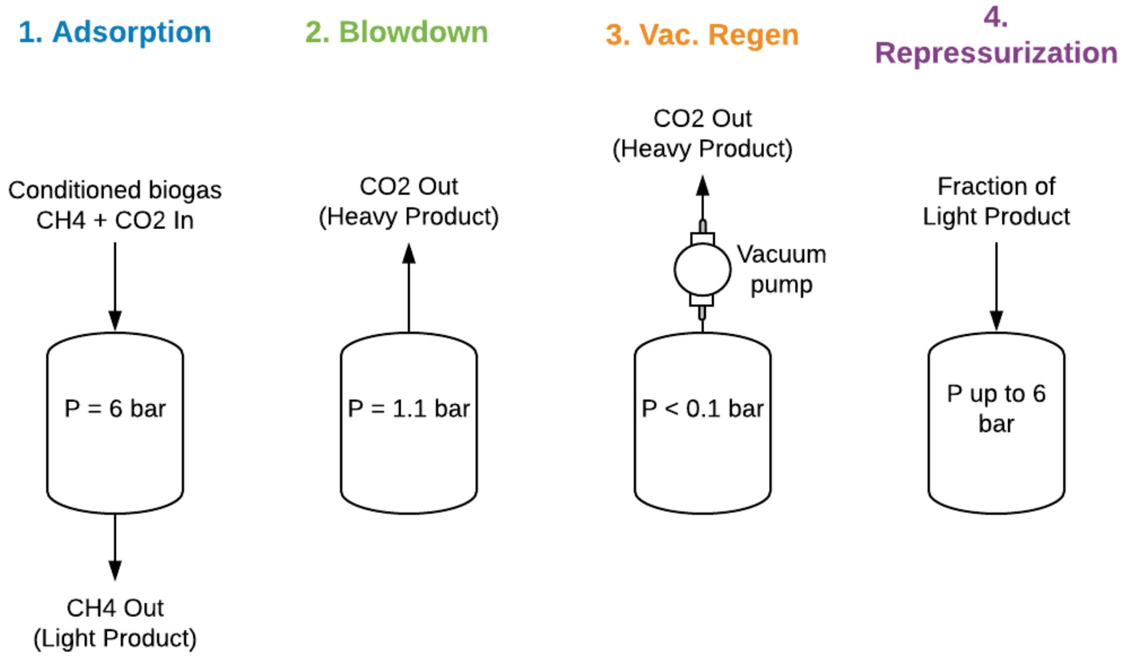
[8] Scott, G. D., & Kilgour, D. M. (1969). The density of random close packing of spheres. Journal of Physics D: Applied Physics, 2(6), 863–866. https://doi.org/10.1088/0022-3727/2/6/311

- Use of air or pure N_2 as a sweep gas is unacceptable. Vacuum would thus be required for regeneration.
- A regeneration pressure of 0.1 bar is achievable with moderate-cost vacuum technology.
- Adsorption pressure and regeneration pressure are set by 1) product purity requirements and 2) adsorbent "step" location.
- To achieve < 2 percent CO_2, p_{CO2} must be ≤ 2 percent of P_{ads} at the bed exit. For example, if a minimum p_{CO2} of 0.12 bar is required at the at exit ($T_{sorbent}$= 60°C), P_{ads} must be ≥ 6 bar. (See Figure 4).

The simple vacuum-pressure swing adsorption cycle shown in Figure 16 was proposed and simulated based on these design constraints. The regeneration step was separated into two steps to increase process efficiency. In the first step, the bed is passively vented by opening a valve and allowing the gas to exit until the bed reaches roughly atmospheric pressure (1.1 bar). In the following step, the bed is evacuated down to the target regeneration pressure with a vacuum pump. Many cycles were simulated back-to-back until cyclic steady-state conditions were achieved (bed temperature and loading profiles remained constant over ten or more cycles).

Figure 16: Vacuum Pressure Swing Adsorption Cycle to Optimize Bed Temperature and Flowrate



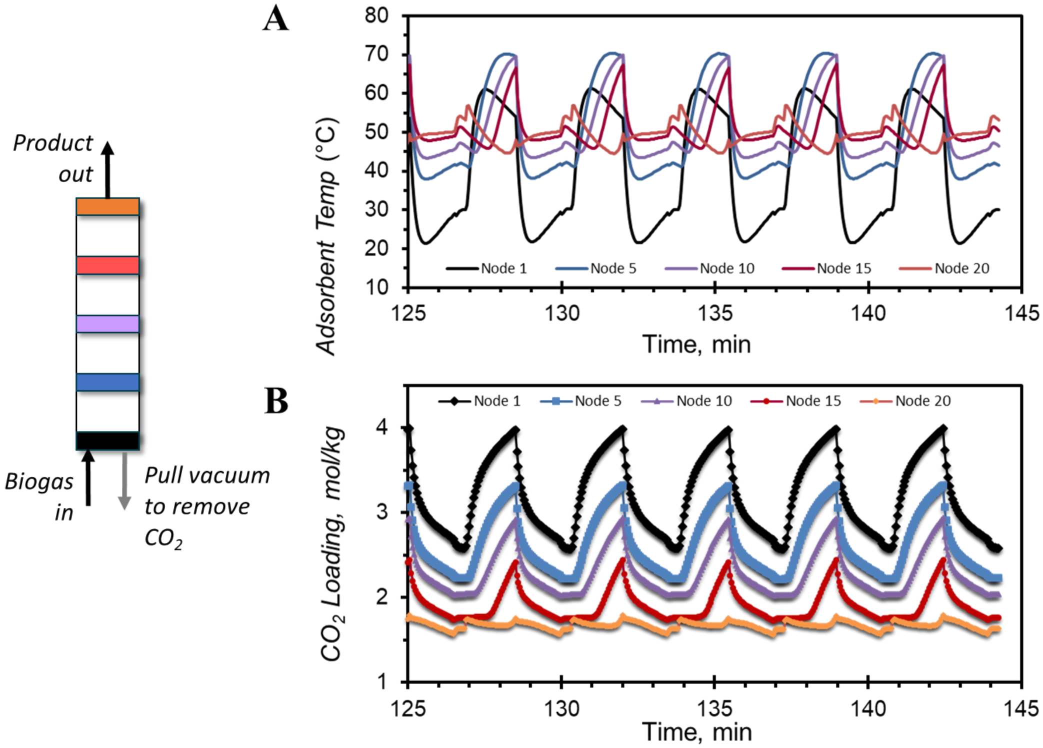
Source: Mosaic Materials Inc.

In these simulations, gas was vented to exhaust during depressurization. For this configuration, the CH_4 recovery was ~ 85 percent for the MOF-based adsorption process developed for this report. Methane recovery could be increased by directing the vent gas to an actively adsorbing bed, either during repressurization or adsorption, at the expense of increasing the overall system size.

Initial simulations were performed with a simple packed bed of adsorbent. However, the simulations showed that uptake of CO_2 by the adsorbent was limited by the adsorbent temperature increase due to the heat of adsorption, reducing the effective working capacity of the adsorbent. Incorporation of an internal heat exchanger (circulating 10 gallons per minute of water as the coolant), modeled as a shell and tube with the adsorbent packed into the tubes, was found to significantly increase the accessible working capacity of the adsorbent. It also rapidly decreased the time for the system to achieve steady state. Simulations were performed with tube diameters from 1 to 4 inches (25 mm to 102 mm). In all simulations, the diameter of the tube diameter was at least 10 times the diameter of the adsorbent pellets to ensure an even flow distribution around the pellets; otherwise, wall effects become significant and channeling may occur. Increasing the diameter of the tubes (while keeping the vessel diameter constant and area occupied by the adsorbent constant) decreases the available surface area for heat exchange, but also reduces the bed fabrication cost (fewer tubes used, fewer welds) and increases the acceptable pellet diameter (decreases pressure drop).

Simulations of this VPSA cycle and bed design predicted that CO_2 could be successfully removed to the desired purity over a range of process conditions. Representative temperature and CO_2 loading profiles at five equally spaced points within a single bed over a few cycles at steady-state are shown in Figure 17 (inlet, outlet, middle, and two equally spaced intermediate points). It is evident from Figure 17 that the inlet of the bed is significantly cooler than later regions of the bed, as it is constantly cooled by the inlet gas. This effect was later observed experimentally in bench-scale cycling tests.

Figure 17: Simulation Results for Vacuum Pressure Swing Adsorption Separation

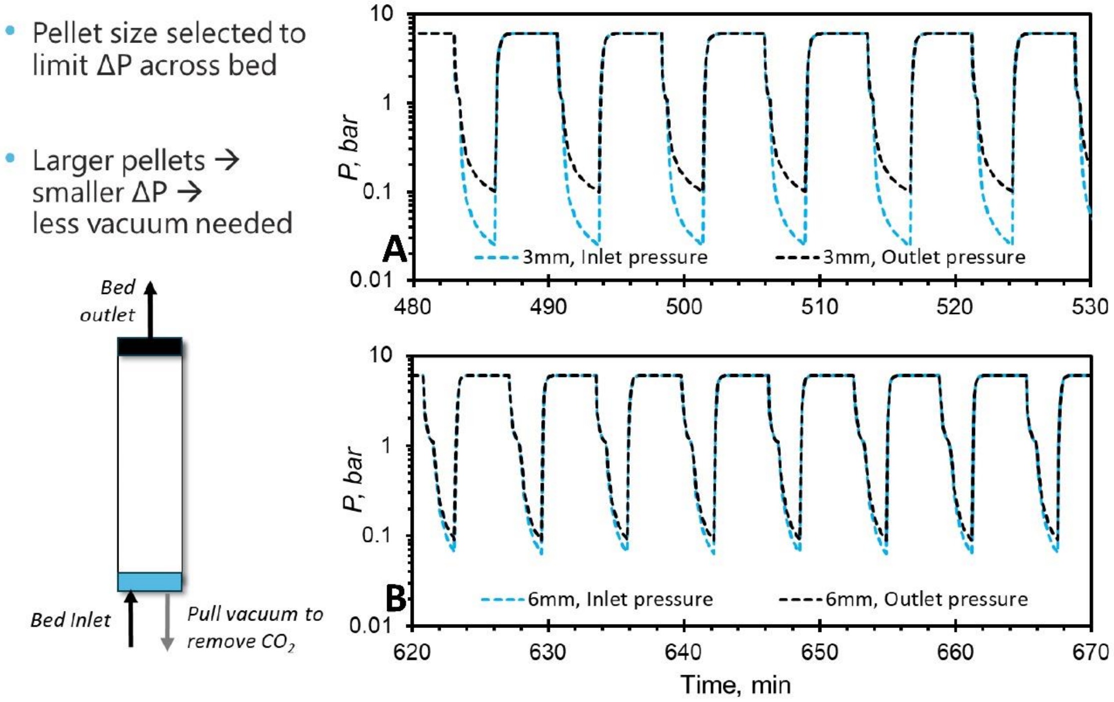


With Gen-1 material and active thermal management: A) adsorbent CO_2 loading and B) temperature at 5 points within the bed during steady-state operation.

Source: Mosaic Materials Inc.

An important consideration in designing the VPSA cycles is the pressure drop across the bed that develops during the vacuum regeneration step. The impact of different adsorbent tablet diameters on the pressure drop across the bed and overall performance was simulated, specifically 1.5, 3, and 6 mm diameters. An example of how the pressure at each end of a large, 6 meter bed evolves when packed with 3 mm or 6 mm pellets in shown in Figure 18. When the bed is packed with 3 mm pellets, the inlet pressure must be reduced to less than 30 millibar (mbar) to achieve a pressure of 100 mbar at the outlet.

Figure 18: Simulated Pressure Drop



Across 6 meter bed (large-scale system) packed with either A) 3 millimeter or B) 6 millimeter diameter tablets.

Source: Mosaic Materials Inc.

Small-Scale System Simulation Results

Once an effective process configuration and rough bed geometry was identified, several rounds of optimization were performed. The first round of optimization was focused on improving model stability and increasing the operating envelope in which throughput and purity specifications could be met. In the second round of optimization runs, the research team focused on increasing the efficiency of the cyclic process by varying the pellet diameter, the heat exchanger geometry and adsorbent location (shell or tube side of system), the size of the vacuum pump(s), and the mass of adsorbent used. The feed temperature, the flow rate of the heat exchanger working fluid (10 gallons per minute), and the vessel length-to-diameter ratio were kept constant. Each process configuration that reached steady-state while meeting the purity requirement was costed to inform future designs.

For the most cost-effective case, the adsorbent beds were the largest portion of the system cost. In the third and final optimization round, the vessel design was varied to identify configurations with lower major equipment costs. The specifications for this system are shown in Table 3.

Table 3: Optimized Adsorbent Bed Parameters, Small-Scale System

Simulation Parameter	Value	Units
Bed height	1.7	m
Bed diameter	0.49	m
Number of internal tubes	31	tubes, 2.5" ID
Mass of adsorbent	75	kg per bed
Adsorption pressure	6	bar
Regeneration pressure	0.1	bar
Vacuum capacity	340	ACFM

ACFM=actual (volumetric) cubic feet per minute; m=meters; kg=kilograms; ID=Inner Diameter.

Source: Mosaic Materials Inc.

Large-Scale System Simulation Results

The optimized conditions for the small-scale system were used as a starting point for the larger separation unit. The cost of the vacuum equipment is the largest contributor to system costs (both capital and operating expenditures) at that scale. The researchers therefore minimized the size of the vacuum requirement while allowing a two-bed cycle to be used. The cost of additional adsorbent beds, and in some cases an additional vacuum pump, outweighed the savings from using smaller vacuum pumps. Table 4 shows the key parameters for the optimized system at large scale.

Table 4: Optimized Adsorbent Bed Parameters, Large-scale System

Simulation Parameter	Value	Units
Bed height	6	m
Bed diameter	2	m
Number of internal tubes	200	tubes, 2.5" ID
Mass of adsorbent	4000	kg per bed
Adsorption pressure	6	bar
Regeneration pressure	0.1	bar
Vacuum capacity	6000	ACFM

ACFM=actual (volumetric) cubic feet per minute; m=meters; kg=kilograms; ID=Inner Diameter.

Source: Mosaic Materials Inc.

Bench-Scale Cycle Optimization Tests

To demonstrate the ability of the scaled Gen-1 adsorbent to perform the separation via the process described above, a commercially available PSA system (PSA 1000, L&C Science) was adapted and configured to run the VPSA cycle at the bench-scale. A series of VPSA cycles with the Gen-1 MOF adsorbent were tested to 1) demonstrate removal of CO_2 to the target purity from a CH_4/CO_2 mixture simulating biogas (from 35 percent CO_2 down to <2 percent CO_2) via a cyclic VPSA process, 2) optimize the concept separation cycle with respect to bed temperature, flowrate (superficial velocity) and pressure, and 3) evaluate the stability of the tableted adsorbent over repeated cycling. As in the simulation and bench-scale validation efforts, the composition of the feed was selected to mimic the biogas at the Davis Waste Water Treatment Plant: 64.5 percent CH_4 and 36.5 percent CO_2.

Materials

The Gen-1 adsorbent material used throughout this work was highly characterized as described in Chapter 2. Physical properties of the Gen-1 MOF adsorbent used in cycle testing are summarized in Table 5 below. CO_2 adsorption isotherms were measured on a sample of these pellets over the operating temperature range, 45-80°C, are included in Appendix A.

Table 5: Physical properties of Generation 1 Metal-Organic Framework Adsorbent

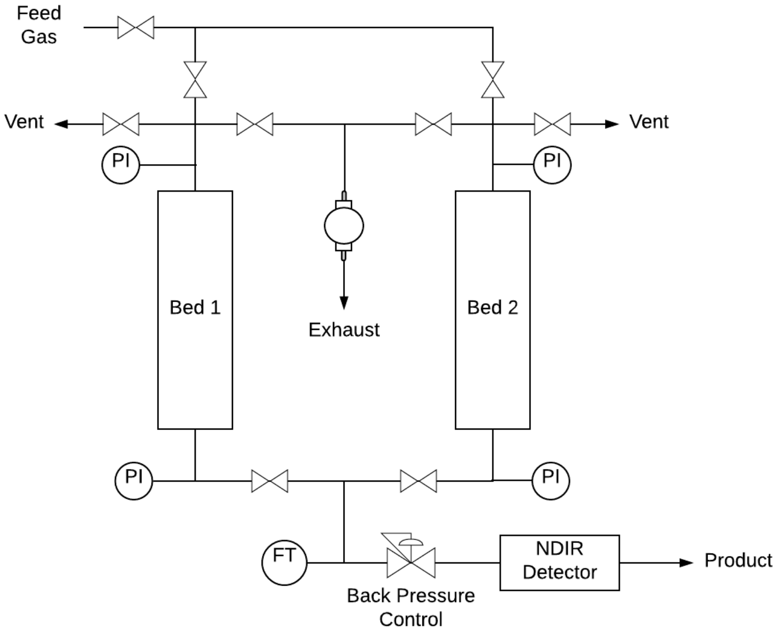
Simulation Parameter	Value	Units
Mass of adsorbent per bed (activated)	120	g
Pellet diameter	3	mm
Average pellet height	2.5	mm
Bulk density	460	g/cm^3

Units: g=grams; mm=millimeters; cm^3=cubic centimeters.

Source: Mosaic Materials Inc.

A simplified schematic of the commercial PSA system used in this test program is shown in Figure 19, and a photograph is included as Figure 20A.

Figure 19: Schematic of Bench-Scale Pressure Swing Adsorption System



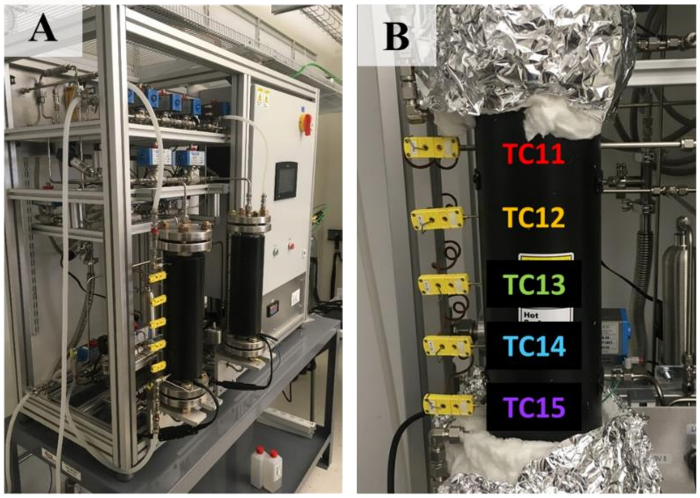
An adapted PSA 1000 from L&C Science was used in this test program. PI = Pressure transducer; FT = Flow transmitter.

Source: Mosaic Materials Inc.

The piping and instrumentation diagram for the system and photographs of the adsorbent beds are included in Appendix C. Gas mixtures from up to three cylinders (N_2, CO_2 and CH_4 for this study) are fed into the manifold, controlled with three mass flow controllers (MFCs) (601CV, Parker). For these experiments, cylinders of pure gases (CH_4, CO_2, N_2) were connected to the manifold. A fourth MFC enabled counter-current flow of purge gas (N_2) during activation or regeneration. The composition of CH_4 and CO_2 in the product gas (gas leaving the active bed) was determined with nondispersive infrared sensors from L&C Science. A system of automated pneumatic valves controlled by the programmable logic controller (Vision^{TM}) and software developed by L&C Science enabled the status of each valve and MFC to be manipulated either manually, or through a pre-set sequence of steps for breakthrough or continuous cycling experiments.

The dual bed cycling system directs flow to and from two custom adsorbent beds, each of which can be packed with up to 260 cc of adsorbent material. The adsorbent beds were fabricated from 316 stainless steel piping, with an OD of 1.660", an ID of 1.380" (3.5 centimeters [cm]), and an active length of 10.5" (27 cm). Beds were wrapped with flexible heaters (5 ft and 250W, Briskheat) beneath the insulation for thermal control and to provide additional heat to the process in some experiments. Each bed contained five welded thermocouples per bed to monitor the temperature profile within the bed, as indicated in Figure 20B and 3C. Temperatures within the beds were also logged by the software.

Figure 20: Commercial Pressure Swing Adsorption System



C

Point	Distance from Inlet, cm
Start of packed bed	0
Thermocouple 1, TC11	2.5
TC12	8.0
TC13	13.8
TC14	19.5
TC15	25
End of packed bed	27

(A) PSA cycling system, including two insulated adsorbent beds (front left) and programmable logic controller screen (on right), (B) one of two adsorbent beds, with location of thermocouples indicated, and (C) table indicating location of each thermocouple relative to the start of packing material (top of column).

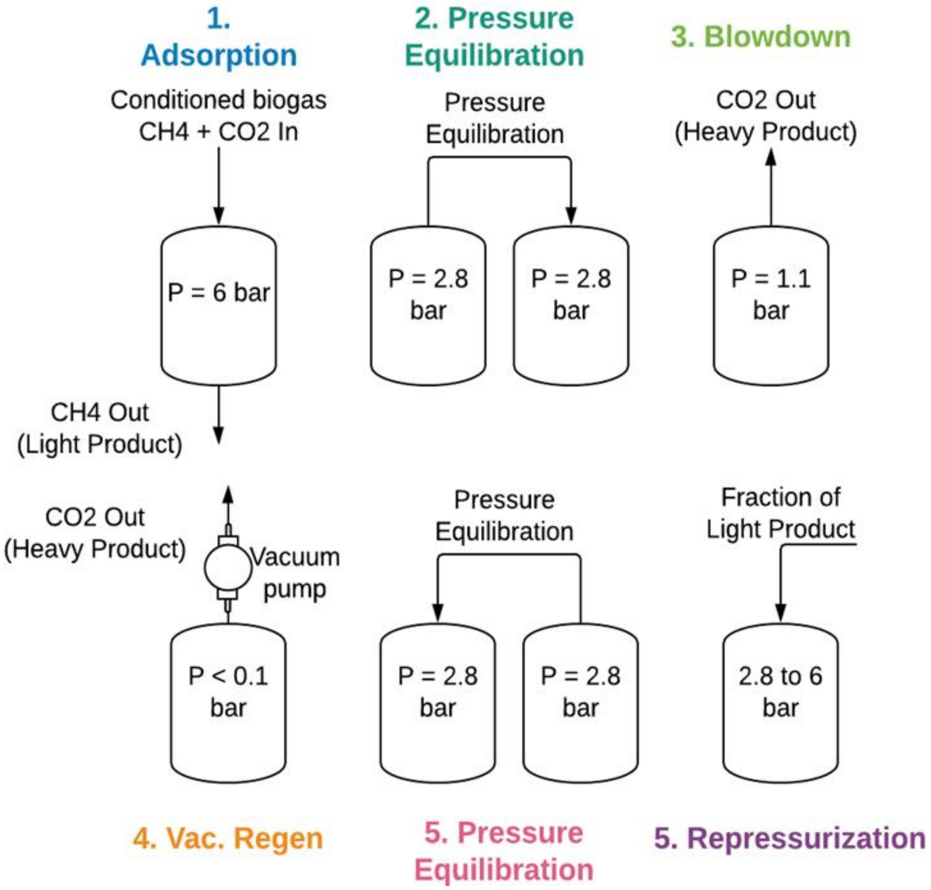
Source: Mosaic Materials Inc.

The pressure within the system was measured using pressure transducers, denoted by “PI” in Figure 19. Bed pressures higher than 1 bar were maintained using a mass flow controller configured as a backpressure regulator, which also measured product flow. A rotary vane vacuum pump with an ultimate pressure of less than 0.1 mbar and pumping speed of 3.5 cubic feet per minute was used to regenerate the bed in vacuum swing experiments. The pressure at each transducer and flow through all MFCs were logged with a programmable logic controller and software developed by L&C Science.

Cycle Programs

The simple VPSA cycle described in Figure 16 was used in initial experiments to optimize 1) the temperature at which the beds were maintained, and 2) the feed flow, which sets the gas superficial velocity through the bed. In these experiments, Bed 1 was packed with the Gen-1 MOF adsorbent, while Bed 2 was packed with glass beads (a non-adsorbent material) as a control. This cycle was improved for pressure optimization experiments by adding a pressure equilibration step at the end of the adsorption period, as illustrated in Figure 21. In this cycle, a line connecting both beds is opened, allowing the pressure between the active bed (at elevated pressure) and the vacuum-regenerated bed to equalize. This greatly reduces the time required to repressurize the regenerated bed. More importantly, it can improve methane recovery as some of the methane occupying the void space of the active bed (and possibly physisorbed during adsorption) is directed to a fresh bed rather than sent to waste.

Figure 21: Vacuum Pressure Swing Adsorption Cycle



Pressure equilibration step used for pressure optimization experiments.

Source: Mosaic Materials Inc.

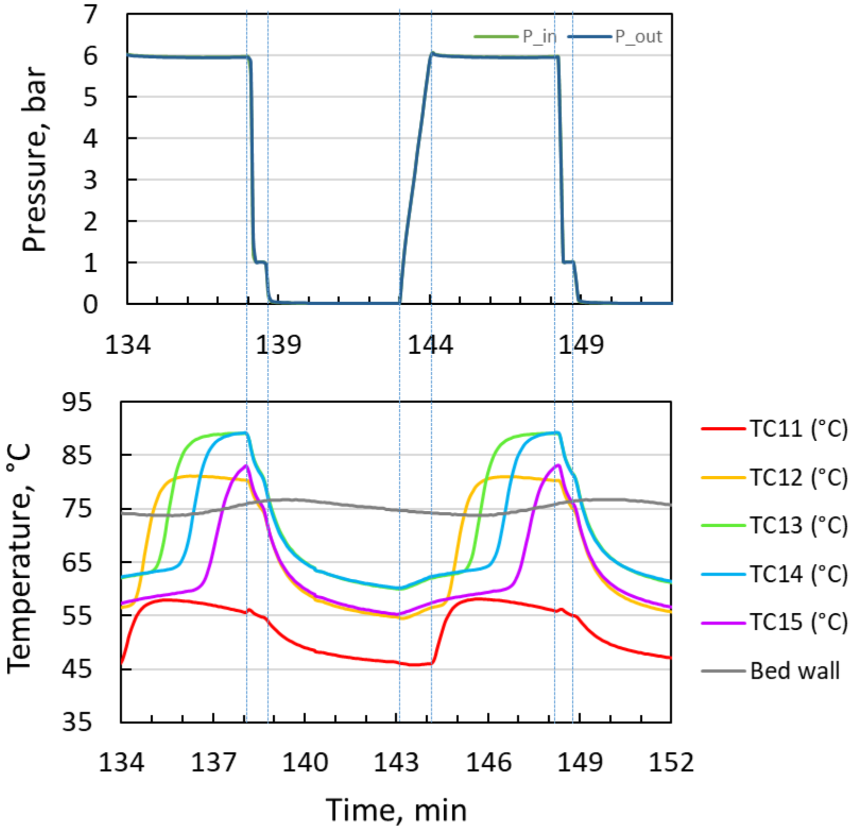
Results and Discussion

Bed Temperature Optimization

The temperature of Bed 1 was set at a constant value between 40 and 80°C (or room temperature, 22°C), and the adsorption step length was adjusted to a value long enough to observe >2 percent CO_2 in the product stream. The average working capacity achieved at steady-state was determined based on the amount of CO_2 fed to the bed before the product CO_2 concentration exceeded 2 percent. Other experimental parameters were kept constant (adsorption: 1500 sccm feed, 63.5 percent CH_4/36.5 percent CO_2, at 6 bar; vacuum regeneration at < 0.02 bar).

As expected from process simulation results, the temperature of the adsorbent and gas within the bed evolves over the course of the cycle—the temperature rises during adsorption, and cools during desorption (regeneration). An example is shown in Figure 22: blue vertical lines indicate a change in step (adsorption at 6 bar, depressurization/vent to exhaust, regeneration under vacuum, and repressurization to 6 bar).

Figure 22: Pressure and Temperature Profiles



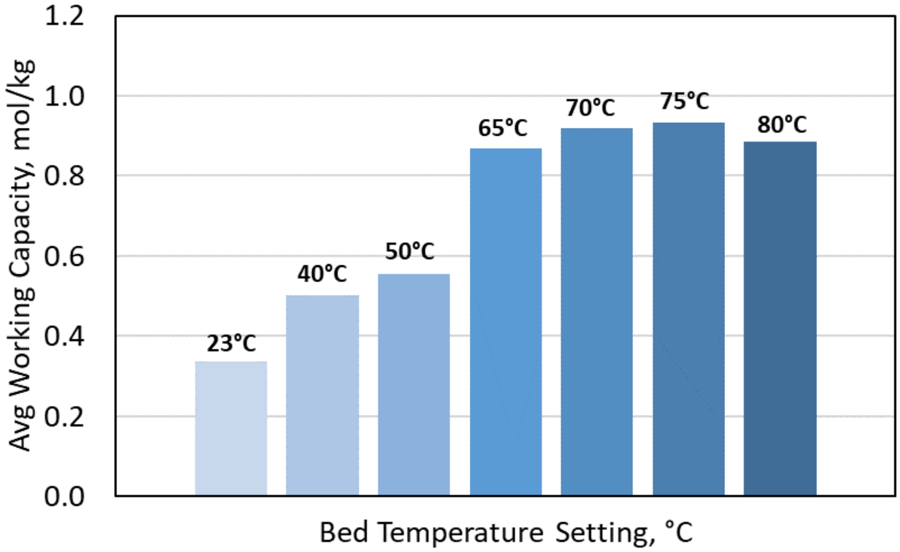
Example of the pressure (top) and temperature (bottom) profiles within a single bed over the course of two VPSA cycles.

Source: Mosaic Materials Inc.

The internal temperatures near the bed inlet and outlet are generally lower than the temperatures in the middle of the bed due to increased heat loss through the bed wall near the large metal flanges used to seal the bed (refer to photographs in Appendix B). In addition, the inlet region of the bed (around TC11) is constantly cooled by the feed gas, which enters near room temperature (20-23°C).

As shown in Figure 23, the accessible working capacity was greatest with the bed wall set at 70°C-80°C. While the driving force for CO_2 desorption (at constant absolute pressure) increases with temperature, it is expected that the adsorbent would be fully regenerated at the end of each cycle based on the temperatures and pressures observed and measured CO_2 adsorption isotherms. However, the increased working capacity at higher temperatures in suggests kinetic effects—that increased temperatures enable deeper CO_2 desorption during vacuum regeneration and subsequently greater available capacity during the next adsorption step.

Figure 23: Average Working Capacity in Temperature Optimization Cycling



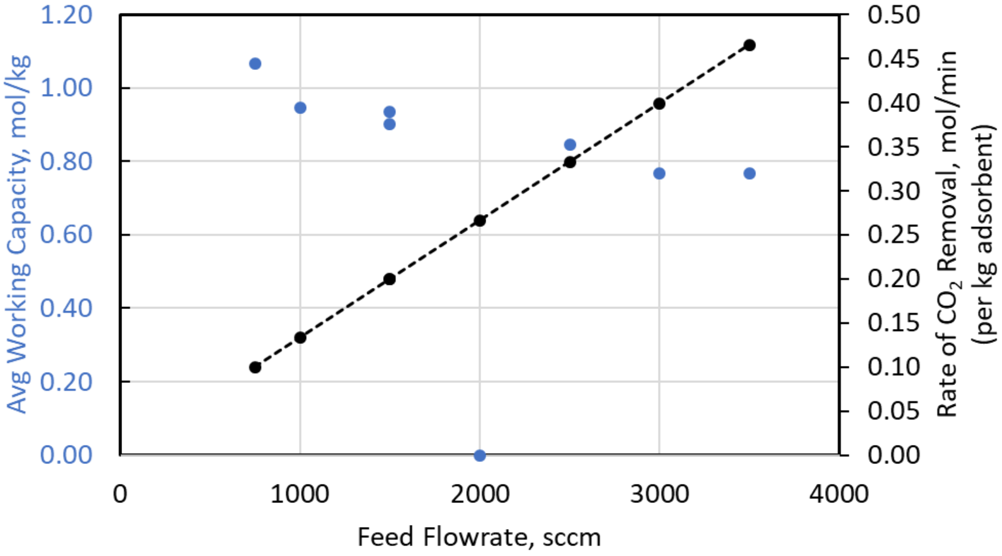
Source: Mosaic Materials Inc.

Superficial Velocity Optimization

A second goal of the cycle optimization test program was to verify the performance of the Gen-1 material at flowrates and superficial velocities that are representative of expected operating conditions. As the flowrate of gas through the test system (with fixed diameter) is increased, the superficial velocity increases and residence time of the gas in the system is decreased. The maximum superficial velocity achieved while meeting the product purity thus informs the minimum adsorbent step time and thus cycle time for a fixed quantity of Gen-1 material.

The effect of gas superficial velocity on performance was assessed by comparing the steady-state working capacities and rate of CO_2 removal achieved at feed flowrates of 750 to 4,000 sccm (Figure 24). These flowrates correspond to superficial velocities of superficial velocities of 15-81 cm/min respectively. At 4,000 sccm, a product purity of >98 percent methane was not obtained, so higher flowrates (superficial velocities above 81 cm/minute) were not tested. As expected, the average working capacity accessed increases with increasing residence time (decreasing superficial velocity). However, the rate of CO_2 removal achieved with the same quantity of adsorbent is higher at increased flowrates (for example, faster cycle times), as shown in Figure 24 (right vertical axis).

Figure 24: Effect of Feed Flowrate



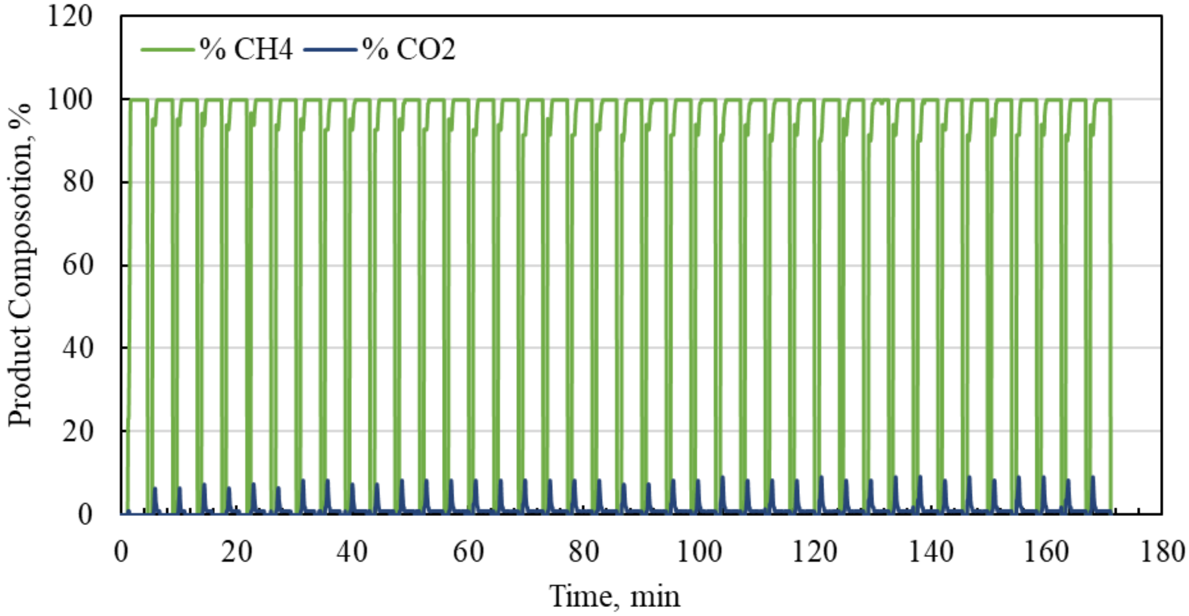
Effects of feed flow rate on the effective working capacity and rate of CO_2 removal by the Gen-1 MOF adsorbent.

Source: Mosaic Materials Inc.

Pressure Optimization

The adsorption pressure was also varied from 4 bar to 8 bar to evaluate the impact of this parameter on process performance. The first set of experiments considered the simple VPSA cycle without pressure equilibration. These tests were used to set the duration of the adsorption step (to just before breakthrough/2 percent CO_2 in product) for subsequent tests performed at that pressure, with pressure equilibration. A representative history plot showing the product CH_4 and CO_2 compositions over 20 VPSA cycles with pressure equilibration is shown Figure 25.

Figure 25: Product Composition Over 20 Vacuum Pressure Swing Adsorption Cycles



Source: Mosaic Materials Inc.

Increasing the feed pressure above 6 bar did not significantly increase the working capacity at low flowrates (1,500 sccm) but did increase it at 3,500 sccm. This is because the superficial velocity decreases with increasing gas pressure, such that the residence time of the gas within the bed is increased at 7 and 8 bar, improving adsorbent utilization. These tests also illustrated that the target product purity (< 2 percent CO_2) can be achieved at reduced feed pressures (4 and 5 bar) if the bed is regenerated under stronger vacuum (10 mbar).

Finally, the addition of a pressure equilibration step reduces the apparent working capacity slightly because some of the CO_2 adsorbed in the previous step is sent to the "clean" regenerated bed. However, the methane that would otherwise be lost in depressurization is also recaptured, and the overall cycle time is decreased. Table 6 reports the average CO_2 concentration of the product, the calculated methane recovery, and overall cycle time for cycles at increasing feed pressures including a pressure equilibration step.

Table 6: Methane Recovery for Vacuum Pressure Swing Adsorption Cycles

Pressure	Feed Flow: 1500 sccm Avg CO_2 in Product	Feed Flow: 1500 sccm Methane Recovery	Feed Flow: 1500 sccm Total Cycle Time, min	Feed Flow: 1500 sccm Avg CO_2 in Product	Feed Flow: 1500 sccm Methane Recovery	Feed Flow: 1500 sccm Total Cycle Time, min
5 bar	< 2%	89%	7.3	< 2%	85%	2.2
6 bar	< 2%	86%	6.8	< 2%	83%	2.6
7 bar	< 2%	85%	8.0	< 2%	81%	2.8
8 bar	< 2%	78%	7.9	< 2%	78%	3.0

Includes a pressure equilibration step. Sccm=standard cubic feet per minute.

Source: Mosaic Materials Inc.

Power Requirements

Power consumption by the system was determined by tallying the power consumption of the process-essential controllers, sensors and rotary machinery (that is, vacuum pump). Taking these items into account, the estimated power consumption for the bench-scale VPSA unit is 0.47 kilowatts, with the breakdown presented in the table below. This does not take into account the equipment required for compression of synthetic biogas feed from atmospheric pressure to the designed adsorption pressure. The energy required to compress 1,500 sccm of synthetic biogas from 1 bar to 6 bar is roughly 10 watts—a small fraction relative to the power usage of the heating and vacuum components of this small-scale system. While the vacuum pump dominates the energy usage of the bench-scale system, the power consumption will not scale proportionally with system size; the vacuum used for regeneration on the bench-scale system is currently oversized for the developed separation process. Moving forward with a true demonstration unit would allow for procuring equipment appropriately sized for the designed process.

Table 7: Power Consumption of Bench-Scale Dual Bed Adsorption Unit

Unit	Power (Watts)
Vacuum Pump	370
Bed Heaters	62
Flow Controllers	18
Sensors (Pressure, composition)	20
Compressed Gases	(10)
Total	470

Source: Mosaic Materials Inc.

The other critical input to determining the minimum cycle time is the time needed to regenerate the adsorbent. A vacuum pump with a 3.5 cubic feet per minute capacity was used to regenerate the adsorbent. In experiments with the vacuum pump running at full capacity, the majority of CO_2 desorption occurs in the first 60 seconds of the regeneration step based on the decrease in adsorbent temperature. Decreasing the vacuum pump speed (and thus power required) such that the same volume of gas is removed over a longer period of time should reduce the overall energy usage of the process while achieving the same extent of CO_2 removal.

CHAPTER 4: Field Testing

The composite diamine-appended MOF adsorbent pellets developed in this project were exposed to a slipstream of raw biogas at the Davis Wastewater Treatment Plant (Davis WWTP) for up to 4 weeks. This raw biogas contained H_2S, siloxanes, and heavy hydrocarbons as well as significant humidity. As exposure time increased, CO_2 adsorption capacity decreased, most likely due to the loss of diamine groups responsible for selective CO_2 adsorption within these materials. However, after 2 weeks of exposure more than 80 percent of the original capacity for CO_2 is retained. Alternative regeneration strategies of higher activation temperatures (150°C) in conjunction with longer times (up to 12 hours) investigated were not able to restore materials to pre-exposure performance. The hypothesized cause of the reduction in CO_2 capacity is diamine loss, supported by nuclear magnetic resonance and TGA. Attempts to reaminate the materials with a fresh solution of diamine were partially successful in restoring CO_2 adsorption capacity, but again not to full pre-exposure levels. These results suggest that a relatively short excursion in contaminant removal processes upstream of the biogas upgrading system would have limited impacts upon diamine-appended MOF adsorbents, mitigating unexpected adsorbent replacement and system downtime.

Contaminant Removal

Adsorbent performance when exposed to common raw biogas contaminants is an important measure of material robustness and the potential to be successfully used for biogas upgrading technology. While it is not common for a single adsorbent to remove all contaminants in raw biogas (for example, H_2S, siloxanes, and higher hydrocarbons [C_3+]), evaluating adsorbent performance in response to contaminant exposure can provide great insights into overall process design and considerations in deployment.

Most of the aforementioned contaminants are commonly removed upstream of the biogas upgrading process by their own treatment schemes. For example H_2S is commonly removed by a lead-lag dual bed adsorption unit using iron-based adsorbents where the gas flows through both beds in series, with the lead bed performing the majority of the removal and the lag bed serving as redundancy for preventing H_2S slippage into the downstream upgrading process. However, when the lead bed is fully saturated it is brought off-line for replacement requiring the full gas flow be processed by the lag bed containing partially saturated adsorbent material. While uncommon, slippage or excursions of this upstream contaminant removal step is possible, exposing the downstream biogas upgrading adsorbent, in this project amine-functionalized MOFs, to the raw biogas stream including contaminants. Therefore, it is of interest to measure the impacts of such a pre-processing excursion upon the CO_2 adsorption performance of diamine-functionalized MOF adsorbents.

Testing Plan

All of the materials discussed here were formed from the optimized methods and materials from Tasks 3 and 4. Specifically, 6 mm composite adsorbent pellets were exposed to raw biogas at the Davis WWTP. Composition of the biogas was determined prior to exposing adsorbent materials to the raw biogas mixture. A gas sample was collected in a sample canister supplied by a previously selected analytical laboratory (ALS Environmental, Simi Valley, California), with the measurement results and methods used reported in Table 8.

Table 8: Biogas Composition at Davis Wastewater Treatment Plant for Slipstream Exposure

Component	Concentration	Testing Method
Methane (CH4)	63.0 (vol %)	Modified EPA Method 3C
Carbon Dioxide (CO2)	35.8 (vol %)	Modified EPA Method 3C
Nitrogen (N2)	0.90 (vol%)	Modified EPA Method 3C
Oxygen (O2)	0.22 (vol %)	Modified EPA Method 3C
Hydrogen Sulfide (H2S)	1800 (ppm)	ASTM D 5504-12
Non-CH4 hydrocarbon	2 (ppm)	EPA Method TO-15-VOC
Equiv. Siloxanes	130 (ppb)	ALS Method AQL - 111

Source: Mosaic Materials Inc.

Due to the toxicity and complexity of the raw biogas and difficulties associated with reproducing the gas composition in a laboratory setting, adsorbent materials were transported to the field site and transported back to the Mosaic laboratory for characterization, performance testing and stability testing following the desired exposure period. The slipstream sample exposure apparatus consisted of ½ inch stainless steel tubing and valves installed upstream of the process flare; specifically across the particulate filter that follows the process coalescer. Figure 26 (top) shows the installed slipstream rig at the Davis WWTP.

The exposure testing rig was sized to hold multiple samples, increasing throughput of sample exposure times. Samples were wrapped in 316 stainless steel mesh to prevent sample contamination and allowing sample segregation within the testing apparatus. A representative sample packet is shown in Figure 26 (bottom).

The flow of the biogas was measured via a soap film bubble flow meter downstream of the second isolation valve with the flow across the sample being throttled via an upstream control valve. For the entirety of the exposure experiments, the flow of raw biogas was controlled to be 200 milliliters/min. The pressure within the line, reported via existing process control sensors at the Davis WWTP was reported to be 0.3 pounds per square inch gauge (15 pounds per square inch absolute) of total pressure.

Figure 26: Slipstream Testing Apparatus at Davis Wastewater Treatment Plant

Installation of slipstream testing apparatus (top); sample of composite metal-organic framework pellets for exposure testing (bottom).

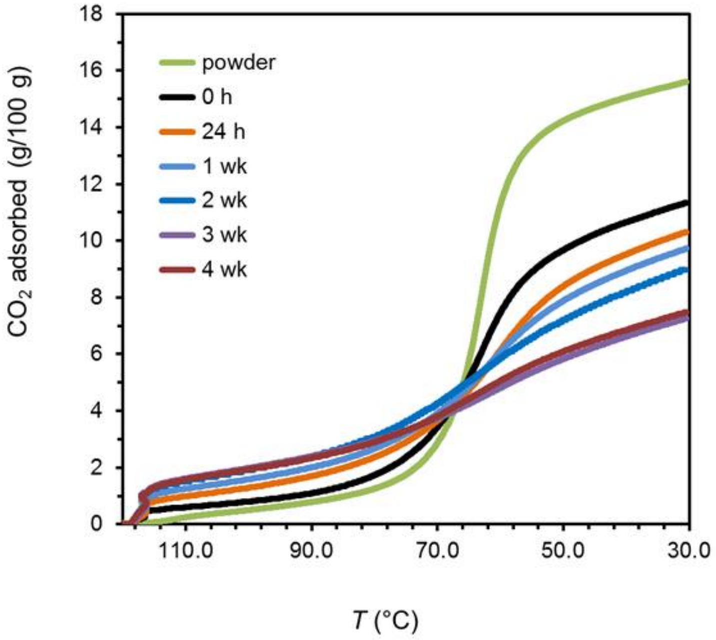
Source: Mosaic Materials Inc.

Field Exposure Testing Results

The initial results for composite adsorbent material slipstream exposure include exposure times from 0 hours (fresh, unexposed) to 4 weeks continuous exposure. As shown in Figure 27, the composite sample (pelletized MOF + binders) shows a reduction in CO_2 adsorption capacity compared to the pure powder adsorption measurement. This result is expected, as composite adsorbent materials exhibit a reduction in adsorption capacity from incorporation of a binder material.

Figure 27 also shows that as biogas exposure time increases, CO_2 adsorption capacity decreases and the step-shape of the adsorption isotherm is broadened. Adsorption capacities of CO_2 at 40°C and 1 bar of pressure for samples measured to-date are reported in Table 9 below. From an adsorbent performance standpoint, the combination of adsorption capacity loss and step-shape broadening is unfavorable as this will lead to a reduced working capacity (material efficiency) and increased regeneration requirements (process energy intensity). However, while there is a slight drop in CO_2 adsorption capacity, more than 80 percent of the original, pre-exposure capacity is retained after 2 weeks, a promising measure of the Gen-1 MOF adsorbent stability. Furthermore, within the samples analyzed to-date, performance degradation plateaus after three cumulative weeks of exposure to the raw biogas; materials exposed for an additional week exhibit no further performance loss.

Figure 27: Thermogravimetric Analysis of Composite Pellets Exposed to Raw Biogas



Source: Mosaic Materials Inc.

Table 9: Adsorption Capacity for Adsorbents Exposed to Biogas

Sample	CO_2 Capacity (g CO_2/100g)
Neat Powder	15.05
0 h	10.39
24 h	9.53
1 wk	8.95
2 wk	8.16
3 wk	6.63
4 wk	6.86

Measured via thermogravimetric analysis at 40°C and 1 bar pressure.

Source: Mosaic Materials Inc.

During the course of this project various regeneration schemes were employed to restore exposed materials to pre-exposure performance levels. Impurities within the biogas stream, like siloxanes and higher hydrocarbons, may adsorb to the surface of the adsorbent structure, impeding CO_2 accessibility to active adsorption sites leading to the performance reduction observed above. Increasing the final temperature during activation prior to CO_2 adsorption may provide the necessary thermal energy to remove these impurities, restoring adsorbent performance. Increasing the activation temperature to 150°C led to slight improvements in overall material performance, however it did not restore the material to the full pre-biogas exposure performance levels. This may be due to removal of contaminant species (such as siloxanes) at the higher temperatures, which are expected to be present in higher concentrations in samples exposed to the raw biogas for longer times. However, due to the low concentrations of these larger adsorptive contaminants, removal leads to minimal gains in material performance. Activation temperatures above 150°C were not tested as volatilization of the diamine components within the MOF pore structure is expected above this temperature, resulting in further reductions in adsorbent performance.

While increasing the activation temperature to 150°C for 60 minutes did not restore the adsorbent performance to pre-exposure levels, increased activation times were also investigated in hopes of further recovery of adsorbent performance. The 4 week sample was selected for this investigation as it will have the highest concentration of any adsorbed contaminants and the largest drop in adsorption capacity, making performance recovery more readily measureable for this strategy. Increasing the activation time from 1 hour to 12 hours has no effect in restoring adsorption capacity, suggesting that the performance lost during exposure to raw biogas may be a result of either contaminants that need higher temperatures for removal, loss of the appended diamine, or physical damage to the MOF structure.

Recalling that selective CO_2 adsorption relies upon metal-bound diamine groups within the base MOF structure, loss of these diamine groups will result in less selective open metal adsorption sites where other adsorbents (for example, water, siloxanes, etc.) can reside, reducing CO_2 capacity. While higher activation temperatures can remove contaminants from these open metal sites, the temperatures needed for this are significantly higher (>200°C) than the metal-bound diamine groups can tolerate (~150°C). To investigate the presence of these bound contaminants, adsorbents were heated to degradation temperatures (>550°C) under an inert atmosphere while tracking the mass changes during the experiment. If additional species within the exposed materials are removed by heating during this experiment, a change in mass at the temperature corresponding to their removal will be observed. Biogas exposed sample exhibits higher mass losses at lower temperatures (<240°C), indicative of removal of additional adsorbed species from metal sites missing diamines. Further detailed discussion can be found in Appendix A.

All samples exposed to the biogas stream show reduced diamine content, supporting the hypothesis that the reduced CO_2 adsorption (cf. Figure 2) is related to diamine loss. But, within this limited data set, diamine content does not directly correlate with adsorption performance loss; for example samples exposed to biogas for 3 weeks show a 36 percent reduction in CO_2 capacity with 13 percent diamine loss. Determining the relationship between diamine loss and adsorption capacity reduction is an ongoing effort.

Small samples of adsorbents exposed to biogas were reaminated in hopes of replacing the diamine lost during biogas exposure. After re-amination the measured amine content was 100 percent theoretical capacity, as measured with nuclear magnetic resonance digestion. Surprisingly, this sample did not exhibit a full recovery of adsorption capacity; the reaminated sample resulted in 90 percent of unexposed capacity. Although the measured amine content was reported to be 100 percent of theoretical loading, it is likely that some of the diamines were not able to displace the species residing on the metal center (i.e. water) but were confined within pores of the adsorbent adding to the elemental correct expected elemental composition, leading to a partial re-amination of the material.

CHAPTER 5: Technoeconomic Analysis

The economics for upgrading of biogas via MOF-based adsorption and traditional aqueous amine absorption with MEA were estimated to benchmark this technology. For both processes, the process was required to produce a biomethane product containing < 2 volume percent CO_2. A large range of process variables (conditions) were investigated to identify process schemes that minimize both capital and operational expenditures. For the MOF-based CO_2 removal the researchers designed and cost upgrading units for both a "small-scale" facility, producing 75,000 scfd, and a "large-scale" facility, producing 4 million scfd. For the MEA scrubbing case, an upgrading unit was designed using Aspen HYSYS at the "large-scale" case of 4 million scfd, enabling direct comparison to the MOF-based adsorption upgrading. Capital and operating expenses for the large-scale, MOF-based upgrading system were found to be lower by 14 percent and 38 percent, respectively.

"Small-Scale" Metal-Organic Framework-Based Carbon Dioxide Separation

Preliminary cost estimates for each of the cases generated in round 2 to identify process conditions leading to the most cost-effective design for CO_2 removal. The process conditions and parameters varied included the pellet diameter, the heat exchanger geometry and adsorbent location (shell or tube side of system), the size of the vacuum pump(s), and the mass of adsorbent used. Capital cost estimates for these systems (major equipment only) are shown in Figure 28. Due to the small-scale (75,000 scfd) of this separation process, traditional cost estimation tools (for example, Aspen Process Economic Analyzer) do not accurately predict the capital costs of common equipment at this scale. In order to evaluate the capital costs associated with the major equipment for the small-scale separation process, a more traditional factor-based approach was implemented.[9]

For the most cost-effective case of the process configurations examined, the adsorbent beds were the largest portion of the system cost. A sensitivity analysis was therefore performed around adsorbent bed configuration targeted to identify cost reductions while still meeting the biogas upgrading goal of < 2 volume percent in the process outlet. In general, adsorbent beds with larger tube diameters and pellet sizes, led to significant capital and operational cost savings. Using larger tube and pellet diameters decreases the pressure drop across the bed, reducing vacuum regeneration requirements. The capital costs associated with the best-case small-scale system are summarized in Table 10.

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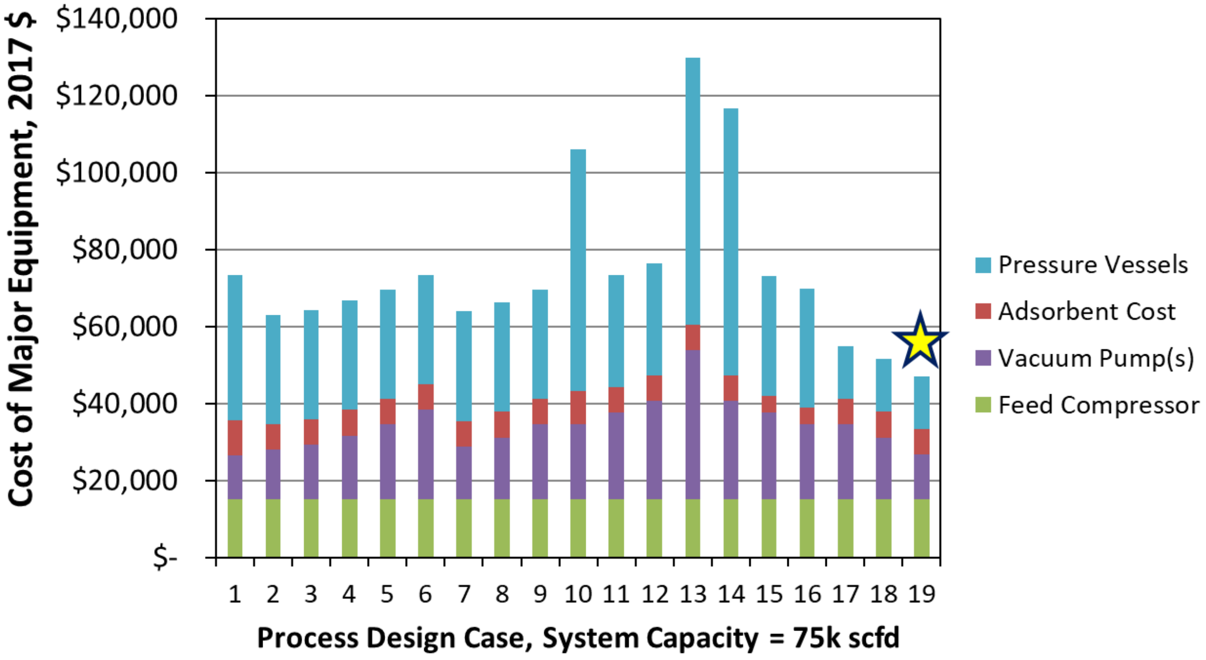
[9] Seider, W. D., Seader, J. D., Lewin, D. R., & Widagdo, S. (2009). Product and Process Design Principles (3rd ed.). John Wiley & Sons, Inc.

Figure 28: Comparison of Major Equipment Costs for Vacuum Pressure Swing Adsorption System



Source: Mosaic Materials Inc.

Table 10: Capital Costs of Metal-Organic Framework-Based Biogas Upgrading

Metric	Cost
Bare Equipment Cost	$71,700
Installed Cost	$175,000
Total Capital Cost	$217,000

Best-case design, 75,000 scfd.

Source: Mosaic Materials Inc.

"Large-Scale" Metal-Organic Framework-Based Carbon Dioxide Separation

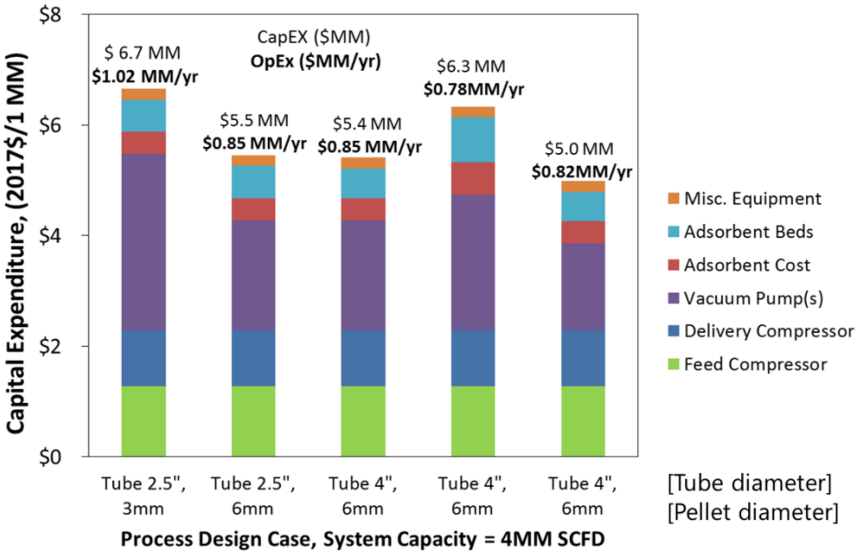
The best-case process configuration for upgrading 75,000 scfd biogas was used as the starting design for a system to upgrade 4 million scfd biogas, representative of volume of gas processed at a centralized biogas collection facility or large-scale municipal treatment center. As with the small-scale case, process conditions and parameters varied included adsorbent pellet diameter, heat exchanger (adsorbent bed) geometry, vacuum pump(s) capacity, and mass of adsorbent used. At this scale, traditional cost estimation tools (for example, Aspen Process Economic Analyzer) could be used to reasonably predict the capital costs of common equipment, enabling direct comparison to the MEA model discussed in the following section. For both the MEA scrubbing and MOF-based adsorption upgrading systems, the following base-line assumptions were made:

- On-site utilities: Cooling water at 77°F (25°C) and electricity, with costs of $0.91/mmBtu and $0.139 kilowatt-hours, respectively.

- Equipment constructed of default materials (i.e. carbon steel) with the exception of equipment in direct contact hot MEA solutions, for which 304 stainless steel was used (Jones, Mcvey, & Friedmann, 2013).
- Final product gas must be pressurized to 20 bar for pipeline injection.
- Installed capital cost (bare module cost) includes delivery, taxes, direct materials and labor for installation.
- Total capital cost includes 5 percent for site development costs, 3 percent contractor fee and 15 percent contingency.

Sample capital cost estimates for possible configurations are shown in Figure 29. At larger system size, the total equipment cost is driven by the vacuum systems rather than the adsorption beds. The equipment capital and operating costs for large-scale MOF-based CO_2 separation designs with varying vacuum requirements are shown in Figure 29. The bottom column labels list the heat exchanger tube diameter, and adsorbent pellet size. Labels on columns correspond to capital expenditures (top label) and annual operating expenditures (bottom label, bold).

Figure 29: Equipment and Operating Costs for Large-Scale Biogas Upgrading Unit



4 million scfd metal-organic framework-based biogas upgrading unit with varying bed configurations.

Source: Mosaic Materials Inc.

As in the small-scale case, capital and operation expenditures decrease with increasing adsorbent bed tube size and adsorbent particle diameter as they result in lower pressure drop across the bed, decreasing the load on the vacuum pump for regeneration. The most economical MOF-based system for biogas upgrading at larger scales had the associated capital costs listed in Table 11.

Table 11: Capital Costs of Best-Case Design

Metric	Cost ($ MM)
Bare Equipment Cost	$3.57
Installed Cost	$5.00
Total Capital Cost	$6.20

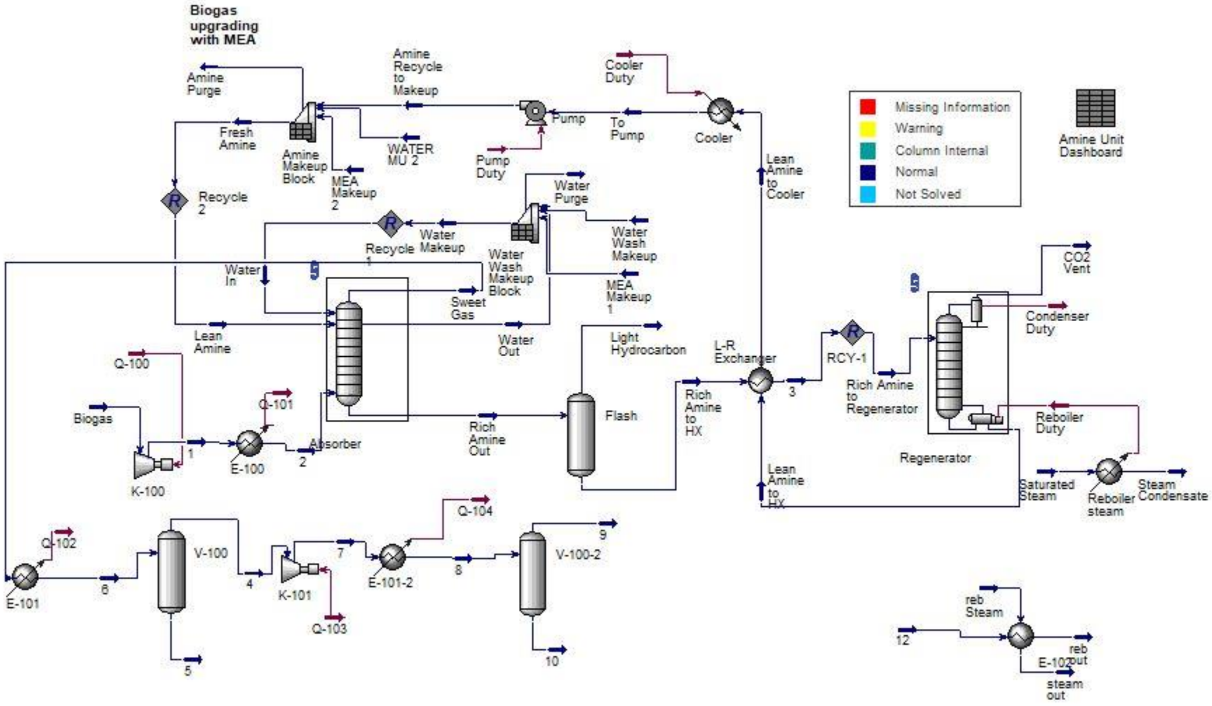
For metal-organic framework-based 4 million scfd biogas upgrading.

Source: Mosaic Materials Inc.

Amine Scrubbing System with Monoethanolamine

The biogas cleanup was simulated in Aspen HYSYS. A process flow diagram of the MEA upgrading system is shown in Figure 30.

Figure 30: Process Flow of Monoethanolamine Absorption-Based Biogas Upgrading



Source: Mosaic Materials Inc.

While there is extensive literature on CO_2 removal from flue gas and natural gas with MEA, there is little data available on biogas upgrading with MEA or other aqueous amines. The key difference between biogas upgrading and natural gas or flue gas upgrading is the higher CO_2 content in biogas. The MEA concentration used in the simulation was 28 weight percent. The maximum MEA loading with CO_2 was 0.50 molar ratio, due to concern about corrosion.[10] The reboiler steam flowrate was adjusted to meet a reflux ratio of 1.9 and the reboiler duty was specified to get a lean amine CO_2 loading of approximately 0.09. The amine circulation rate was then varied to achieve a product gas composition with < 2 vol percent CO_2. Sizing the absorber and regenerator columns was done in an iterative fashion using Aspen HYSYS. The

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[10] Kohl, A. L., & Nielsen, R. L. (1997). Gas Purification (5th Editio). Gulf Professional Publishing.

design process is described greater in detail in Appendix E. Some useful references for understanding how MEA-based processes are affected by process variables are also included in Appendix E.

As with the 4 million scfd MOF-based upgrading case, Aspen Process Economic Analyzer was used to estimate capital costs for both the equipment and installed costs for all equipment except for the boiler and gas dehydration equipment, whose costs were provided from vendor quotes. For an aqueous amine scrubbing system using MEA, sized to handle the same feed flow and composition as the MOF-based case, the associated capital costs are listed in Table 12.

Table 12: Capital Costs of Base Design for Monoethanolamine Biogas Scrubbing

Metric	Cost ($ MM)
Bare Equipment Cost	$3.19
Installed Cost	$5.82
Total Capital Cost	$7.24

Source: Mosaic Materials Inc.

Comparing Monoethanolamine and Metal-Organic Framework-Based Biogas Upgrading

The base case capital and operating costs for the MOF-based upgrading unit and MEA scrubber are shown in Table 13. This analysis did not account for carbon credits that can be obtained for biogas recovery projects, and it does not account for the full project costs (including labor, maintenance, pre-treatment etc.). However, it provides a useful comparison to the MOF-based adsorption process to understand how solid-state amine scrubbers compare to aqueous amine systems in terms of capital and energy-related operating costs.

Table 13: Cash-Flow Comparison of Biogas Upgrading Strategies

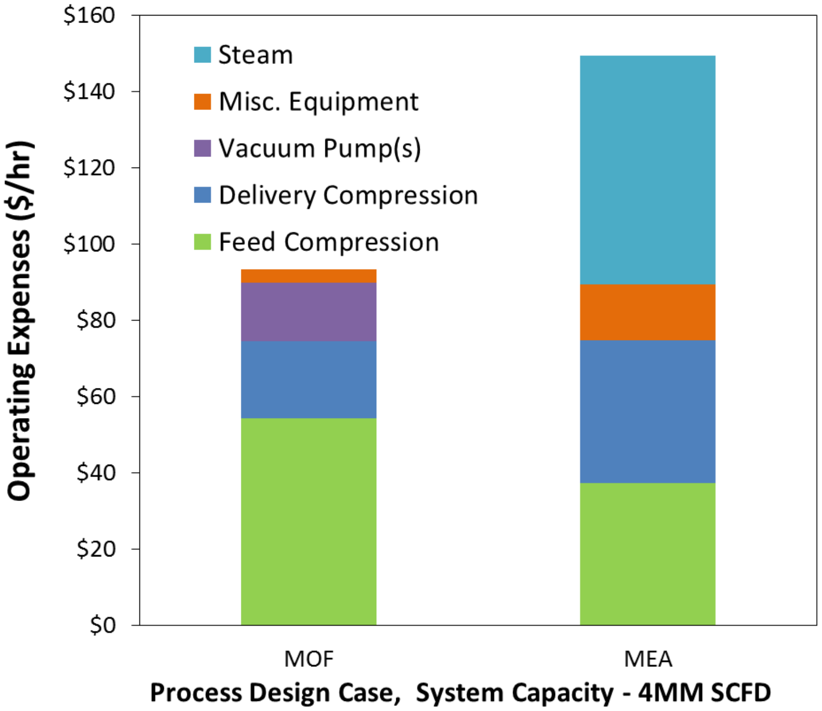
Metric	MEA Aqueous Scrubbing	MOF-based Adsorption
Total Capital Cost ($MM)	7.24	6.20
Operating Cost ($MM/yr)	1.31	0.82

Discounted cash flow comparison of upgrading 4 million scfd biogas with monoethanolamine scrubbing or metal-organic framework adsorption.

Source: Mosaic Materials Inc.

While the complex shell-and-tube adsorbent bed design is a significant capital cost of adsorbent-based upgrading, it is significantly less expensive than the absorption and regeneration (stripping) columns required for MEA scrubbing. Another key difference between the MEA-based and MOF-based processes is higher thermal intensity of the former process, summarized in Figure 31. Steam generation for MEA solvent stripping (regeneration), sourced from natural gas combustion, is a significant fraction of the operating expenditure for the absorption process. The lower regeneration requirements of the MOF-based upgrading results in a 38 percent reduction in operating costs compared to the MEA scrubbing, due to the decreased thermal intensity of the MOF-based process. As the California electrical grid is rapidly becoming decarbonized, the results summarized in Figure 31 suggest the carbon footprint of the MOF-based process can be significantly lower than the MEA process, since it is easier to decarbonize electricity than steam generation.

Figure 31: Operating Expenditures for Metal-Organic Framework-Based Adsorption and Monoethanolamine Scrubbing



Source: Mosaic Materials Inc.

Furthermore, the researchers expect that the economics of removing CO_2 with this technology will be more favorable for small, distributed systems. The capital cost for a 750k scfd MEA-based system was estimated to be $3.7 million—roughly half the cost for a 5 times smaller system. In contrast, the capital costs for MOF-based systems scale much more linearly. Among other advantages, solid-state scrubbing systems do not require a boiler for steam generation.

This analysis indicates that the proposed MOF-based CO_2 separation promises significantly reduced project costs at the 4 million scfd scale. The capital cost of the MOF-based CO_2 removal system is 15 percent lower than the MEA case. Operating costs are reduced by 38 percent for the MOF-based system relative to the MEA scrubbing system. This is including a delivery compressor to deliver the product gas at 20 bar in both cases; if only the energy requirements for the actual separation are considered, the operating costs for the MOF-based system are even lower by comparison. The research team expects costs will come down further with additional improvements to the MOF system design.

CHAPTER 6: Production Readiness Plan

In addition to providing positive climate and environmental benefits, the rapidly growing market for biogas upgrading is an attractive commercial opportunity. Significant progress was made in developing a new MOF-based biogas upgrading technology, which was advanced from a Technology Readiness Level 2 to 4. To fully commercialize this system, additional investment and development work is needed to increase adsorbent production to 2 kg/week while meeting performance targets, beyond which the procedure can be contracted to a toll manufacturer. Further development work on the separation process and system will focus on achieving system cost and performance targets, and de-risking the technology through a field pilot. Mosaic Materials anticipated business model is the manufacture and sale of adsorbent media and possibly licenses to sites using this novel process. Technology providers and engineering companies servicing the wastewater and larger environmental industries will be engaged as partners to design, distribute and service equipment.

Commercial Opportunity

There are many potential biogas production sites located across the United States (Figure 32).[11] The market for biogas upgrading technology is growing rapidly: technology providers predict a compound annual growth rate approaching 30 percent between 2017 and 2022.[12,13] The market is largely driven by government incentives, specifically the Federal Renewable Fuel Standard (RFS) RIN system, which was updated in 2016 to allow biogas to qualify as a D3 or D5 fuel. The value of the gas plus RFS credits associated with 1 mmBtu of gas is currently between $12 to $22/mmBtu for RNG (depending on RIN classification) vs. $3/mmBtu for fossil gas.[14] Significant drivers remain for biogas upgrading in California due to Low Carbon Fuel Standard (LCFS) credits and tightening regulations on waste utilization, and in areas where emissions avoidance is critical.

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[11] "Operational Biogas Systems in the U.S.", American Biogas Council. [Online], Available: http://www.americanbiogascouncil.org/biogas_maps.asp [Accessed June 22, 2018]

[12] Pressure Technologies, Chapeltown, South Yorkshire, UK, Annual Report. Dec. 2017.

[13] "Key Vendors: Acrona Systems, Greenlane Biogas, MT Energie – Research and Markets," Business Wire, August 2, 2016. [Online], Available: https://www.businesswire.com/news/home/20160802005948/en/Global-Biogas-Upgrading-Market-Worth-USD-4.02. [Accessed June 22, 2018].

[14] "RFS/RINs: How to Create your D3/D5 Split for RNG and Biogas Projects," American Biogas Council, Webinar on 2 April 2018. http://www.americanbiogascouncil.org/pdf/ABC%20Webinar%20RFS-RINs%202April2018.pdf.

Figure 32: Biogas Systems in the United States

Wastewater biogas systems (left); all biogas systems (right).

Source: "Operational Biogas Systems in the U.S.", American Biogas Council. [Online], http://www.americanbiogascouncil.org/biogas_maps.asp [Accessed June 22, 2018]

Material Development

From a materials production standpoint, Mosaic's production readiness plan is based on a model in which scale-up R&D is done in house; once a "recipe" is established, a toll manufacturer will be brought in to execute the production. The work flow for material manufacturing is listed below:

- Step 1: Synthesize the MOF (Stainless steel reactor)
- Step 2: Purify MOF product and impregnate the amines that induce the CO_2-capturing mechanism (filter or centrifuge)
- Step 3: Dry the aminated product
- Step 4: Compact the MOF powder into flowable granules (granulator)
- Step 5: Press the granules into tablet forms using a tablet press.

Currently, in-house tablet manufacturing capabilities for Mosaic Materials are roughly 2 kg per month, which is accomplished by working with a local toll facility to perform the synthesis reaction as described in the "scale-up" section. The production cost of making this material is currently ~$8,000/kg, dominated by 1) the personnel needed for material synthesis and pelletization and 2) a precursor that must be custom-ordered since the orders placed are small (~1-3kg). The next goal is to scale-up to reliably produce 2 kg per week of tableted adsorbent. At this rate, Mosaic Materials Inc. can produce the amount of product needed for a pilot scale (10-50 kg) in one to two quarters. The organic ligand and the solvents used during the process account for approximately one third of the cost of the MOF each, both of which will go down substantially at the 2 kg per week scale. Mosaic and others in the adsorbent community are confident current price of approximately $8,000/kg will go down well over an order of magnitude during this process. Other key materials development areas to be addressed for Mosaic to successfully commercialize its biogas upgrading technology include:

- Increasing the scale of the synthesis and formulation process while retaining material performance, with an internal goal of producing 2 kg per week.
- Sourcing feedstocks to reduce the cost of raw materials and take advantage of economies of scale (directly related to scale-up).

- Optimizing the yield of product (MOF adsorbent or precursor) at each step in the synthesis process, reducing solvent, raw material, and overall costs.
- Identifying contractors or toll manufacturers with the necessary equipment and capabilities to produce the adsorbent once the process has been reduced to a standard formula.

Production costs at commercial scale are expected to continue to come down as batch size increases. The production costs of several MOF adsorbents at industrial scale (50,000 kg/year to 2.5 million kg/year) were evaluated by DeSantis et al*.* in 2017.[15] This analysis considered the materials used in each step, the cost of the capital equipment for the step, and the machine and labor operational time to complete each step. The costs of producing a MOF with similar structure to the Gen-1 material at the 2.5 million kg/year scale through solvothermal and aqueous synthesis routes were predicted to be approximately $70/kg and $18/kg respectively. At 50,000 kg MOF/year, the cost of producing the MOF (on a per kg basis) was ~14 percent higher, mainly due to higher rates for raw materials.

Additional improvements to the aqueous method (most similar to Mosaic's synthesis), specifically reducing the ligand-to-metal ratio, reduced costs in their model still further to $11/kg. The primary differences between the MOF evaluated in the that analysis and the aminated MOF variant used in this work are 1) the ligand used, 2) the cost of the diamine used, and 3) the additional process steps of aminating the MOF and subsequent washing to remove excess amine. Based on the trends in DeSantis's model, the additional washing steps will not increase process costs significantly (by more than 5 percent) assuming expensive solvents are not used. The cost of the diamines at scale are expected to add $1.3-$10/kg product to the cost, depending on the diamine used. Lastly, the ligand used to make the MOF for this project is synthesized through an identical route to that analyzed by DeSantis, only with a different (but still commodity) primary chemical feedstock. Thus, it is feasible for Mosaic to eventually achieve an at-scale production cost of $20-30/kg for the Gen-1 adsorbent.

System Development

Mosaic's CO_2 separation system is currently at a technology readiness level (TRL) 4. The research team has demonstrated that the MOF-based adsorbents can continuously achieve the target purity (< 98 percent CH_4) through a cyclic process in the laboratory (Task 7 of this effort). Ultimately, Mosaic must show that the separation system using the adsorbent will upgrade biogas at a lower cost and more efficiently than currently available systems for small-scale biogas upgrading, membrane and traditional PSA systems. Mosaic believes that it can achieve market traction upon meting the key performance and cost targets listed below:

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[15] D. DeSantis, J. A. Mason, B. D. James, C. Houchins, J. R. Long, and M. Veenstra, "Techno-economic Analysis of Metal–Organic Frameworks for Hydrogen and Natural Gas Storage," Energy & Fuels, vol. 31, no. 2, pp. 2024–2032, 2017.

Performance and Cost Targets

- Purity: Outlet CO_2 concentration of ≤ 2 percent CO_2. Concentrations down to ≤1.0 percent can be achieved if necessary due to N_2 content.
- Recovery: Methane recovery of at least 90 percent. Methane recoveries of 80-88 percent are typical for single-stage PSA-based biogas upgrading systems.
- Operational expenditure (OpEx): A specific energy usage rate of ≤ 0.28 kilowatts per scfm gas processed, or 30 percent below the energy used by current technology provider's systems, would make Mosaic's system competitive from an efficiency and OpEx standpoint.
- Capital expenditures (CapEx): Estimates of CapEx for a 100 scfm system range from $350,000-$450,000 for a 100 scfm system.

These metrics will be used as targets to guide Mosaic's development path. The performance of the process relative to other small-scale (50-200 scfm) upgrading technologies, specifically traditional PSA processes, must also be considered going forward. Depending on how the economics of Mosaic's upgrading system compare favorably with current offerings, additional development activities may be pursued. Examples of areas for process improvement affecting both CapEx and OpEx include:

- Reduce vacuum requirements: Building on lessons learned from this project, the amount of vacuum required to remove the entirety of the CO_2 present in biogas in one pass results in the need for a large vacuum pump, which is energy intensive. Strategies to avoid or reduce this load on this expensive piece of equipment will be investigated, such that the overall energy required to regenerate the adsorbent is reduced.
- Add gas recycle for improve methane recovery: Pressure-swing and vacuum-swing adsorption cycles have been proposed that include recycling gas leaving the bed at one or more process steps.[16,17,18]
- Reduce cycle time to reduce capital costs and footprint of system: An area of future technical focus will be to reduce the cycle time of the separation process, further reducing footprint and capital costs.

To advance the technical readiness level of Mosaic's upgrading system and reduce technical risk, demonstration of this technology in the field is critical. Regardless of whether a field pilot or demonstration is performed early or later in the development timeline, Mosaic plans to work closely with engineering partners to bring the process design through the preliminary engineering design (front-end loading [FEL]-2) phase. The detailed design (FEL-3), including drafting and controls schemes, as well as fabrication, will be contracted out to engineering

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[16] M. P. S. Santos, C. A. Grande, and A. E. Rodrigues, "Pressure swing adsorption for biogas upgrading. Effect of recycling streams in pressure swing adsorption design," Ind. Eng. Chem. Res., vol. 50, no. 2, pp. 974–985, 2011.

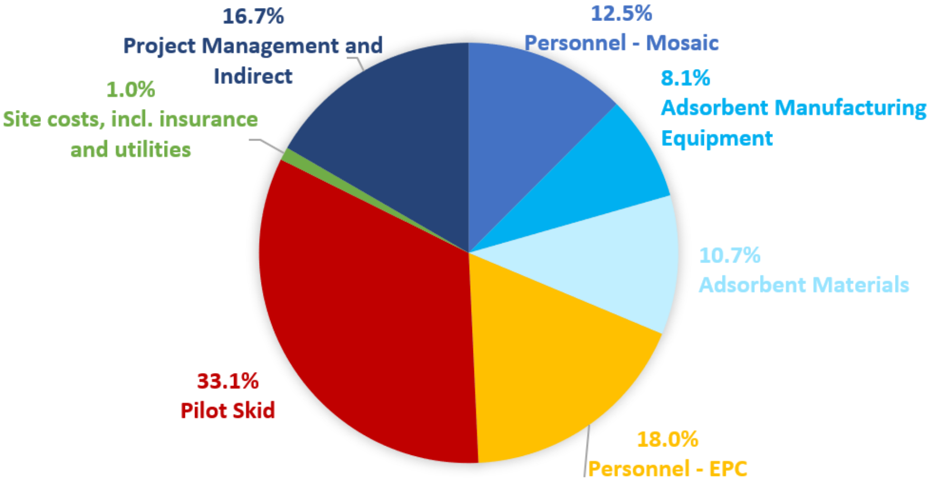
[17] S. Cavenati, C. A. Grande, and A. E. Rodrigues, "Upgrade of Methane from Landfill Gas by Pressure Swing Adsorption," Energy & Fuels, vol. 19, no. 6, pp. 2545–2555, 2005.

[18] B.-K. Na, H. Lee, K.-K. Koo, and H. K. Song, "Effect of Rinse and Recycle Methods on the Pressure Swing Adsorption Process To Recover CO 2 from Power Plant Flue Gas Using Activated Carbon," Ind. Eng. Chem. Res., vol. 41, no. 22, pp. 5498–5503, 2002.

partners. By partnering with well-known engineering procurement and construction (EPC) companies, Mosaic mitigates the risk to the site hosting the demonstration, avoids the need staff specialized engineering personnel early in development, and creates early involvement with future channels or customers for the technology.

Initial cost projections for a 14 scfm pilot project at a specific California wastewater treatment plant were estimated by Mosaic and potential engineering partners. Figure 33 shows the breakdown of the project costs by area. Some items, specifically the adsorbent manufacturing equipment, are expected to be one-time costs. The costs for raw materials to make the adsorbent are based on current cost of adsorbent production at the 1-3 kg scale, and are expected to decrease with scale as previously discussed. The personnel resources needed (mainly in the form of engineering expertise) are also significantly greater for a pilot than expected for subsequent applications, given the current development level of the system, and due to the first-of-its-kind nature. Lastly, the cost estimate in Figure 33 conservatively assumes a cost of $150,000 x 2 for design and fabrication of adsorbent beds for the 14 scfm pilot system, as this is the largest unknown in the process.

Figure 33: Estimated Costs for Pilot Technology Demonstration



Breakdown of costs of upgrading 14 scfm of biogas to renewable natural gas at a wastewater treatment facility in northern California.

Source: Mosaic Materials Inc.

In summary, Mosaic Materials will continue working to achieve cost and performance targets through additional technical development, as well as demonstrate the separation process in a field environment to further reduce risk associated with this technology. Improvement of the CO_2 separation process will be an iterative process of identifying appropriate engineering targets, making process improvements, evaluating the resulting process design, and modifying the path forward appropriately.

Commercialization Plan and Business Model

Mosaic's expected product/service model is the manufacture and sale of adsorbent media to sites using this novel process technology. Another means of getting this innovation to market is licensing the process technology to equipment and engineering providers on an installation or annual basis. Because Mosaic will not be selling integrated systems on its own in the near term, the preferred approach is to partner with upgrading system providers and EPCs to design and provide equipment. This approach also takes advantage of the existing channel to market inherent in these partners.

Large engineering service providers, particularly those serving the wastewater treatment industry, represent a great potential channel for Mosaic's technology to migrate into the biogas upgrading space. Mosaic Materials has initiated conversations with several engineering service providers, and has currently pursuing follow-on grant funding with one such company to pilot the technology. Success on this effort will spur interest from additional EPC partners. Adjacent to this, some of the upgrading technology companies offering PSA systems are also potential channel partners, particularly if the MOF serves as a drop-in replacement for a currently sourced adsorbent within these systems. Mosaic is also working to actively engage these players.

Additionally, Mosaic has started exploring the possibility of creating partnerships with companies where a Mosaic process would be additive to their current offerings, such as companies which manufacture biogas conditioning equipment. An alternate approach to this is partnering with companies producing RNG fueling systems for vehicles, such as Knox Western or WEH, providing a method for them to vertically integrate and provide a holistic solution to a biogas producer.

The next step in de-risking this technology is to demonstrate it in the field under the expected operating conditions. Mosaic expects that pilot will be performed at a wastewater treatment facility producing biogas through anaerobic digestion (Mosaic's target first customer). The research team anticipates treating a flow of 2-15 scfm with the pilot unit. Ideally, the host facility will perform some degree of gas conditioning (for example, iron chloride injection to limit H_2S and activated carbon for siloxane removal upstream of an internal combustion engine or cogeneration unit). An initial pilot unit will use standard processes and equipment to the greatest extent possible (standard vessels, pumps, compressors, analytical equipment, and so on).

The pilot CO_2 removal process equipment will be designed by Mosaic in collaboration with an experienced engineering company, ideally one with specific experience in piloting technology at wastewater treatment plants, to mitigate perceived risk by the host site and to provide external validation of the technology and results. Mosaic expects an initial pilot project to take place over two years: roughly one year for engineering design, and one year of active testing.

CHAPTER 7: Conclusions

The goal of this project was to design and evaluate a solid-state CO_2 removal system for biogas based on a group of metal-organic frameworks (MOFs) with the potential to significantly reduce costs based on CO_2 adsorption properties. During this three-year project, researchers made significant progress in moving this technology from initial research and development scale studies (starting Technology Readiness Level 2-3) to a robust and industrially and commercially viable product. The technology is now at Technology Readiness Level 4 and the MOF-based adsorbent tablets have been used to remove CO_2 from synthetic biogas in cyclic separation experiments in the laboratory. These experiments were run on the 100+ gram scale, and multiple kilograms of adsorbent tablets with consistent strength and adsorption properties produced.

At the start of the project, MOFs had been produced through a time- and material-intensive procedure on the milligram- or gram-scale (quantities roughly the size of a Tic Tac®). From the 30 diamine-appended MOF materials screened, three candidate materials were selected based on CO_2 adsorption properties. The selected Generation 1 adsorbent (Gen-1) was chosen based on its stability, lowest projected energy requirement for regeneration, and raw material costs. The water-based synthesis route for making this MOF was refined and scaled over four orders of magnitude, producing kgs of high-quality material by the end of the project. A procedure for converting the raw MOF into denser solid forms while maintaining its porosity and crystallinity was developed, enabling the MOF adsorbent to be tested in large-scale breakthrough experiments and cycling studies with a commercial pressure swing adsorption (PSA) system for the first time in an industrially relevant form.

A separation process was designed and optimized around the properties of the first-generation tableted MOF adsorbent. To accomplish this, a process simulation tool was developed using Aspen Adsorption to simulate the performance of the Generation 1 (Gen-1) material over a range of vacuum-pressure swing adsorption (VPSA) processes. The simulation tool was validated using breakthrough experiments in the laboratory at bench-scale. The validated model was then extended to simulate performance of the adsorbent at steady state and commercial scale, and used to identify efficient, low-cost process configurations. A techno-economic analyses of the full-scale system performed in parallel indicated that Mosaic's solid-state adsorption system should reduce OpEx associated with biogas upgrading by 38 percent, and CapEx by 15 percent, relative to aqueous amine scrubbing with MEA. Lastly a bench-scale, commercially available PSA system was retrofitted and used to further optimize the VPSA cycle proposed. The Gen-1 tableted MOF adsorbent was shown to effectively remove CO_2 from synthetic biogas to levels below 2 percent over 1000+ cycles, including 300 continuous cycles, without experiencing significant capacity loss.

The Gen-1 adsorbent tablets were also tested for stability against a slipstream of raw biogas at the Davis, California wastewater treatment plant for up to 4 weeks. This raw biogas contained H_2S, siloxanes, and heavy hydrocarbons as well as significant humidity. As exposure time increased, CO_2 adsorption capacity decreased; however, after 2 weeks of exposure more than 80 percent of the original capacity for CO_2 was retained. These results suggest that a relatively short excursion in contaminant removal processes upstream of the biogas upgrading system would have limited impacts upon diamine-appended MOF adsorbents.

Looking ahead, the rapidly growing market for biogas upgrading makes it an attractive commercial opportunity despite the technical hurdles that remain. The next step from the materials production standpoint is to increase adsorbent production to 2 kg/week while meeting performance targets, beyond which the procedure can be contracted to a toll manufacturer. Further development work on the separation process and system will focus on achieving system cost and performance targets, and de-risking the technology through a field pilot. A pilot demonstration of the technology at the Napa Sanitation District Wastewater Treatment Plant is currently planned 2020, potentially leading to full commercialization of this technology in four to six years.

LIST OF ACRONYMS

Term	Definition
Å	Angstrom
ACFM	Actual (volumetric) cubic feet per minute
ASAP	Accelerated Surface Area & Porosimetry system
Bar	Unit of pressure equal to 100,000 Pascals
˚C	Degrees Centigrade
CapEx	Capital expenditures
CFM	Cubic feet per minute
CH_4	Methane
cm	centimeters
CO_2	Carbon dioxide
Davis WWTP	Davis Wastewater Treatment Plant
EPC	Engineering, procurement and construction
˚F	Degrees Fahrenheit
FEL	Front-end loading
FT	Flow transmitter
g	grams
H_2S	Hydrogen sulfide
HHV	Higher heating value
ID	Inner Diameter
kg	Kilogram
kJ	Kilojoule
Mbar	millibar
MEA	Monoethanolamine
MFC	Mass flow controller
mK	Meters-Kelvin
mm	Millimeter
mmBtu	Million British thermal units
MOF	Metal-organic framework

Term	Definition
N_2	Dinitrogen
OD	Outer Diameter
OpEx	Operational expenditure
PI	Pressure transducer
PSA	Pressure swing adsorption
RD&D	Research, development, and demonstration
RFS	Federal Renewable Fuel Standard
RIN	Renewable Identification Number
RNG	Renewable natural gas
sccm	Standard cubic centimeters per minute
scfd	Standard cubic feet per day
scfm	Standard cubic feet per minute
TGA	Thermogravimetric analysis
TRL	Technology readiness level
UC	University of California
VPSA	Vacuum-pressure swing adsorption
WWTP	Waste water treatment plant

APPENDIX A: Metal-Organic Framework-Based Separation Process Simulation Inputs and Structure

Adsorbent Properties

The Gen-1 adsorbent material used throughout this work was highly characterized as part of Task 3, Adsorbent Selection. Adsorbent material properties used as inputs into the adsorption bed model are shown in Table A-1. Note that while a tablet density of 400 kg/m^3 was used in these simulations, later improvements in the formulation process have increased the density of the Gen-1 tablets to roughly 500 kg/m^3.

Table A-1: Generation 1 Adsorbent Properties Used in Bed Simulation

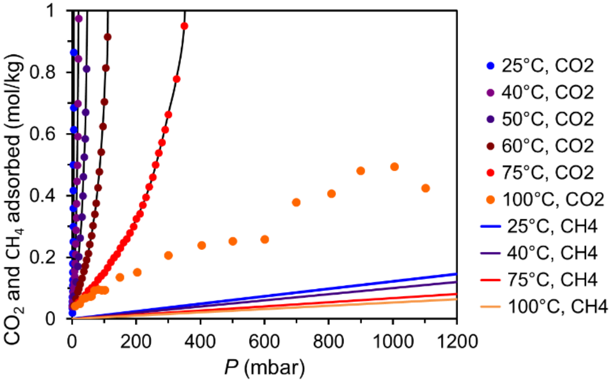
Simulation Parameter	Value	Units
Bulk density	400	kg/m^3
Interpellet void fraction	0.4	
Intrapellet void fraction	0.6	
Solid heat capacity	1.5	kJ/kg-K
Solid thermal conductivity	0.1	W/mK

Kg/m3=kilograms per cubic meter; kJ/kg-K=kilojoules per kilogram-Kelvin ; W/mK=watt per meter-Kelvin .

Source: Mosaic Materials Inc.

Other material properties (adsorption isotherms, heats of adsorption) were determined indirectly from volumetric gas adsorption measurements. Isotherms for methane adsorption by the Gen-1 adsorbent compared to CO_2 are shown in Figure A-1.

Figure A-1: Methane Adsorption of Generation 1 Metal-Organic Framework



Comparison of methane loading (solid lines) to CO_2 loading (markers) at low pressure, highlighting the Gen-1 MOF's high selectivity for CO_2 over CH_4.

Source: Mosaic Materials Inc.

Pressure Drop

The pressure drop across the bed was determined using the Ergun equation, Equation 1 ((Bird, Stewart, & Lightfoot, 2007)).

$$\frac{\partial P}{\partial z} = -\left(\frac{1.5\times10^{-3}(1-\varepsilon_i)^2}{(2r_p\ \psi)^2\varepsilon_i^3}\mu v_g + 1.75\times10^{-5}M\rho_g\frac{(1-\varepsilon_i)}{2r_p\ \psi\varepsilon_i^3}v_g^2\right) \tag{1}$$

Where ε_i is the interparticle void fraction, ψ is the sphericity or shape factor, v_g is the superficial velocity, M is the molecular weight, and ρ_g and μ_g are the gas density and viscosity. This equation combines the description of pressure drop by the Karman-Kozeny equation for laminar flow (terms on the left side) and the Burke-Plummer equation for turbulent flow (terms on the right side). The pressure drop across the bed depends strongly on the superficial velocity, v_g, and the pellet radius, r_p.

Energy Balances and Heat Transfer

In these simulations, an energy balance is performed around each "node" or axial elements ("slices") within the bed. The number of nodes or elements within the bed was set at 50. The temperature was assumed to be uniform in the radial direction. The following terms were considered in the gas-phase energy balance:

- Thermal conduction (axial)
- Convection of energy, accumulation of heat
- Compression or expansion of the gas
- Heat transfer from gas to solid
- Heat transfer to internal wall
- Heat exchange between the gas phase and an internal heat exchanger

The solid-phase energy balance considers:

- Thermal conduction
- Accumulation of heat
- Enthalpy changes in the adsorbed phase
- Heat of adsorption
- Gas-solid heat transfer from gas to solid (expressed in terms of a film resistance, where the heat transfer area is proportional to the area of the adsorbent particles)

At the bench-scale (for example, in breakthrough experiments), heat transfer through the vessel walls to the environment greatly affects the performance of the system. There are three (3) heat transfer coefficients that control the rate of heat transfer between the gas, sorbent and environment:

- Heat transfer between the sorbent and the gas, HTC
- Heat transfer between the gas and the vessel wall, H_{wall}
- Heat transfer between the vessel wall and the ambient environment, H_{amb}

Full-scale adsorption beds are assumed to operate adiabatically, with negligible heat loss to the environment.

Mass Transport

The process simulations used the Lumped Resistance model in estimating the mass transfer resistance. With this assumption, the driving force for mass transfer is taken to be linear, as shown in Equation 2. The mass transfer coefficient for each gas species i, MTC_i, is approximated as the limiting resistance term in the series of resistances to gas diffusion: the external film resistance, macropore diffusion and micropore diffusion. The estimated mass transfer coefficient for each component is thus the sum of individual mass transfer resistances within the system: crossing the gas boundary layer to reach the adsorbent (k_{film}), and diffusion of the gas within the macropores ($k_{macropore}$) and micropores ($k_{micropore}$) of the adsorbent, as shown in Equation 3.

$$\frac{\partial w_i}{\partial t} = MTC_{i,s}(w^* - w) \qquad (2)$$

$$\frac{1}{k_{overall}} = \frac{1}{k_{film}} + \frac{1}{k_{macropore}} + \frac{1}{k_{micropore}} \qquad (3)$$

The overall mass transfer coefficients, MTC_i for this system were determined by adjusting them to best fit the breakthrough data. The shape of the breakthrough curves, and the need to add additional terms to fit the data (for example, axial dispersion), inform which of the resistances is limiting.

Vacuum Regeneration

For cycles with vacuum regeneration, the vacuum pump was modeled as a valve with specified flow coefficient, which restricts the gas leaving the bed to a constant volumetric flow rate (similar to a vacuum pump with set pump capacity). The main difference is that the driving force is the pressure drop between the bed and a specified low pressure condition (for example, 2-5 mbar) on the other side of the valve. For example, a valve coefficient of 0.0065 kmol/bar/s allows roughly 340 ACFM of gas to flow. This arrangement simulates a vacuum pump (with roughly constant capacity and a low ultimate vacuum) working to evacuate the bed directly. By changing the specified valve coefficient, the effective "pump capacity" (size of the pump) can be increased or decreased.

Step Timing

The Aspen Adsorption software package allows the user to define multiple-step cycles and run a specified number of cycles. The criteria for the simulation to exit each step is defined by the user and may be time or event-based. For example, the adsorption step can be specified to continue for 60 seconds, or until the composition of the product gas exceeds 2.00 vol percent CO_2. The following cycle steps and exit criteria were applied within the simulation:

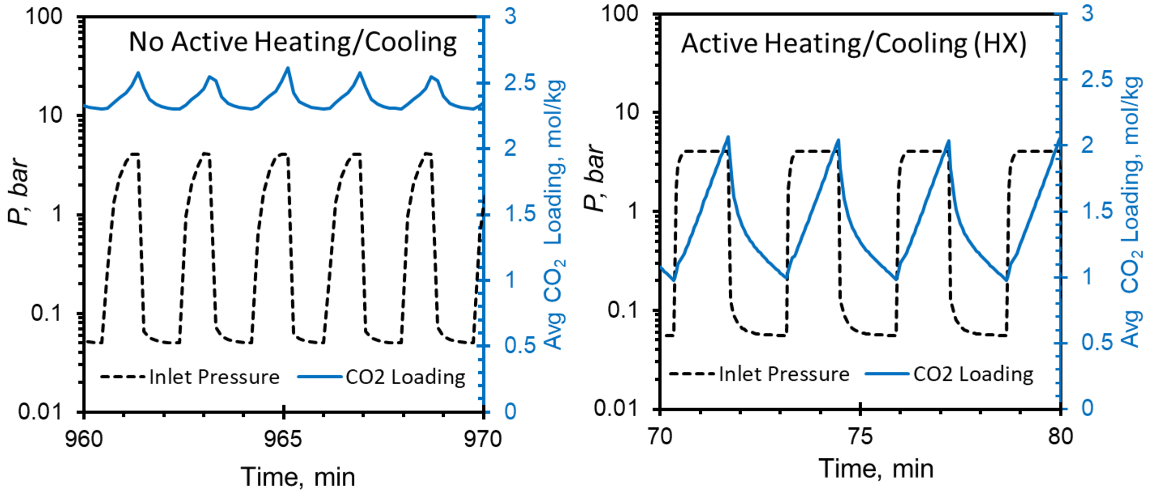
- Adsorption: Feed flows into the bed at a specified flowrate until the concentration of CO_2 in the product gas exceeds 2 percent.
- Depressurization/Vent: Feed and product valves close; gas exits the bed through a separate waste valve (at inlet side of bed) with constant valve coefficient until the pressure falls below 1.1 bar.
- Vacuum regeneration: Feed and product valves remain closed. Gas is evacuated from the bed at a rate controlled by a specified valve coefficient, until the pressure at the outlet of the bed (farthest from the vacuum source) drops below a threshold pressure.

- Repressurization: The waste/vacuum valve closes, and product gas (98 percent CH_4, 2 percent CO_2) is fed into the bed from the feed side until the specified feed pressure is achieved.

Internal Heat Exchanger

An example of the predicted increase in working capacity achieved by incorporating active heating/cooling is shown in Figure A-2. A simple shell-and-tube design was used for the internal heat exchanger: an array of tubes are packed with the adsorbent and a working fluid (in this case water) flows through the external region "shell". During the adsorption and repressurization steps, cooling water at 40°C or less flows through the shell; during the depressurization and vacuum steps, heated water at 75°C flows through the shell. An overall heat transfer coefficient, U, of 25 $W/m^2/K$ is assumed for the heat exchanger.

Figure A-2: Comparison of Average Carbon Dioxide Loading



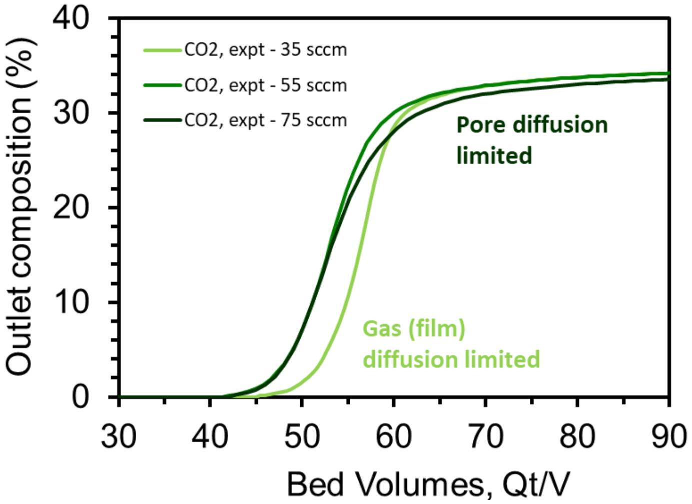
Effective working capacity without active heating or cooling (left), versus incorporating an internal heat exchanger (right).

Source: Mosaic Materials Inc.

APPENDIX B:
Mass Transport Studies

As described in Appendix A, the mass transfer coefficients used in the model are sensitive to the process conditions, including pressure (absolute and partial pressure of CO_2), superficial velocity, pellet diameter, and adsorbent pore structure. The adsorbent properties are constant in all experiments. However, comparing the shape of the breakthrough curves and associated mass transfer coefficients at different flow rates and pellet diameters provides insight into the mass-transfer limitations of the system. The CO_2 breakthrough curves for three tests at different feed flow rates (75 sccm, 55 sccm, and 35 sccm) are overlaid in Figure B-1. A broadening of the curve near saturation indicates that adsorption is limited by diffusion within the solid. As illustrated this figure, the *film resistance*, or the rate of diffusion through the gas film boundary layer to the particle, becomes limiting at low superficial velocities (≤35 sccm, or 8.8 cm/min). At higher superficial velocities and Reynolds numbers, the mass transfer resistance within in the system is limited by events within the adsorption pores: diffusion of the gas molecules within the sorbent pores, or by slow reaction kinetics at the surface (i.e. the CO_2-amine reaction).

Figure B-1: Carbon Dioxide Breakthrough Curves for Different Feed Flows

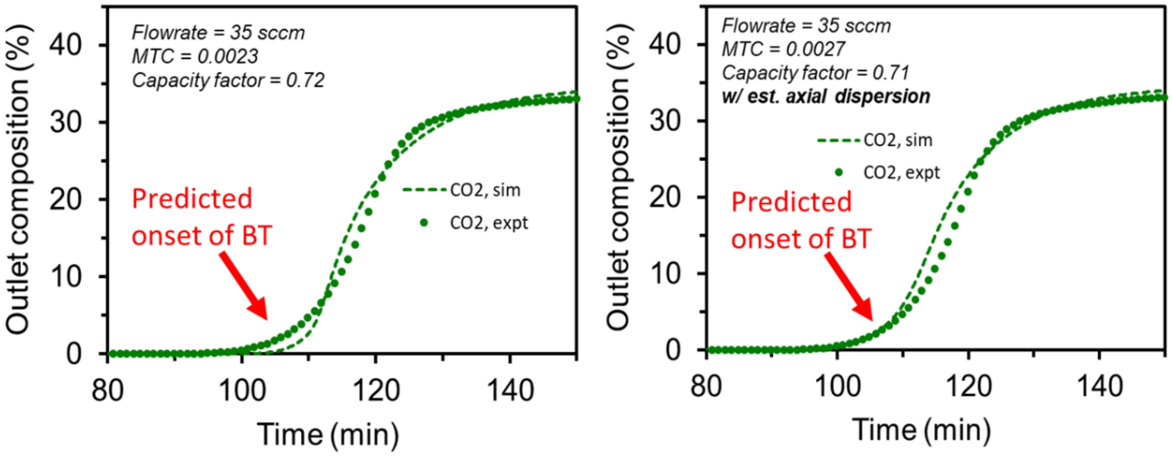


The outlet CO_2 concentration is shown as a function of the number of bed volumes of feed gas treated to allow the curves to be overlaid.

Source: Mosaic Materials Inc.

At low superficial velocities axial dispersion becomes significant. Axial dispersion is diffusion of the gas in both the forward and reverse directions, and results in broadening of the composition profile (often called the mass transfer zone). The effects of axial dispersion were negligible under most conditions tested. However, at flowrates below 55 sccm (Peclet number, $Pe < 30$), the simulation improved with axial dispersion term added to material balance as expected. Simulation results with and without the inclusion of axial dispersion at a flowrate of 35 sccm and 1 bar ($Pe = 16.9$) are shown in Figure B-2.

Figure B-2: Measured and Simulated Breakthrough Curves

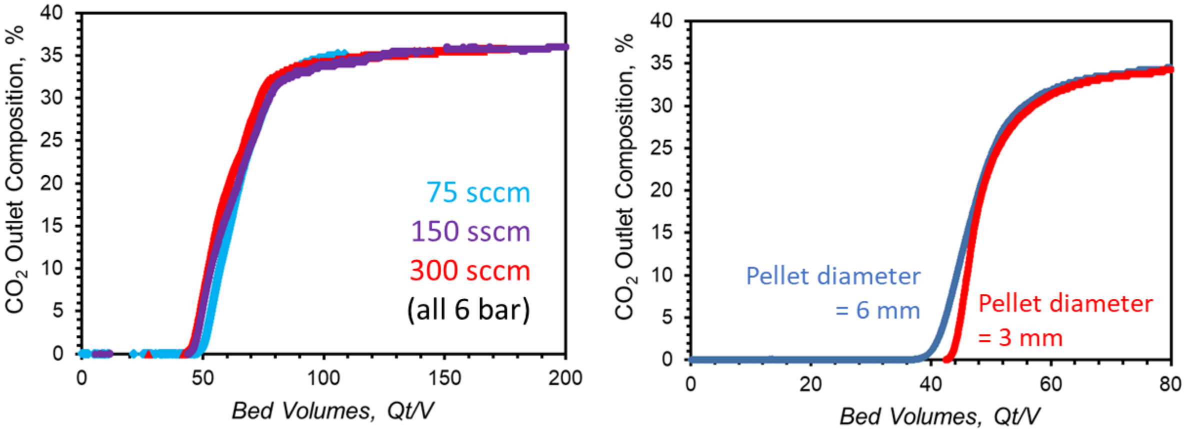


For a low flow condition (Pe<30), shown with and without axial dispersion included in the simulation. Under such conditions, inclusion of axial dispersion is necessary to accurately predict the onset of CO_2 breakthrough.

Source: Mosaic Materials Inc.

At higher flowrates, the resistance to mass transfer within the gas boundary layer is negligible and CO_2 adsorption is limited by diffusion within the adsorbent. This is demonstrated in Figure B-3, left: there is no change in the shape of the breakthrough curve as the flowrate is increased above 75 standard cubic centimeters per minute (sccm), indicating that the limiting mass transfer resistance is independent of flow rate. This resistance increases with increasing pellet size, as is seen by comparing the mass transfer resistance in tests with 6 mm and 3 mm pellets under identical process conditions (Figure B-3, right), suggesting that diffusion through the pores rather than reaction kinetics are limiting.

Figure B-3: Carbon Dioxide Breakthrough Profiles for Generation 1 Adsorption Tablets



Left: CO_2 breakthrough profiles for Gen-1 MOF adsorbent tablets (3mm in diameter) at 6 bar and increasing feed flow rate. Right: CO_2 breakthrough profiles for Gen-1 tablets, 3mm and 6mm in diameter, at the same flow rate (150 sccm).

Source: Mosaic Materials Inc.

APPENDIX C:
Additional Data from Cycling Experiments

In Table C-2, the corresponding superficial gas velocity, V_s at each flowrate and average residence time τ of non-adsorbed gas within the active bed are listed first, followed by the average CO_2 working capacity, Δw_{avg}, and the effective rate of CO_2 removal by the bed at each flowrate tested. In all tests, the feed gas was a 64.5 percent/36.5 percent CH_4/CO_2 mixture at 6 bar, and was cycled through at least 15 VPSA cycles to reach steady state conditions

Table C-1: Results of Bed Temperature Optimization Experiments

Bed Temp.,°C	Time to Reach 2% CO_2 in product, s	Avg working capacity, mol CO_2/kg	$P_{final,regen}$, bar (at PT2), mbar	Temp. at end of bed (TC15), end of vac. regen.,°C	Temp. at bed center (TC13), end of vac. regen.,°C
23	101	0.34	10	22.0	21.5
40	151	0.50	10	33.5	35.5
50	167	0.56	10	38.9	41.6
65	261	0.87	10	51.2	58.3
70	276	0.92	10	52.7	56.2
75	281	0.93	10	56.4	61.3
80	266	0.88	10	59.1	66.4

Source: Mosaic Materials Inc.

Table C-2: Results of Superficial Velocity Optimization Study

Flowrate, sccm	V_s cm/min	τ, s	Δw_{avg} mol/kg	Rate of CO_2 removal, mol CO_2 /kg-min
750	15	42.9	1.07	0.10
1000	20	32.1	0.95	0.13
1500	30	21.4	0.93	0.20
1500	30	21.4	0.90	0.20
2000	40	16.1	0.85	0.27
2500	50	12.9	0.77	0.33
3000	60	10.7	0.77	0.40
3500	71	9.2	0.75	0.47
4000	81	8.0	NA	NA

Source: Mosaic Materials Inc.

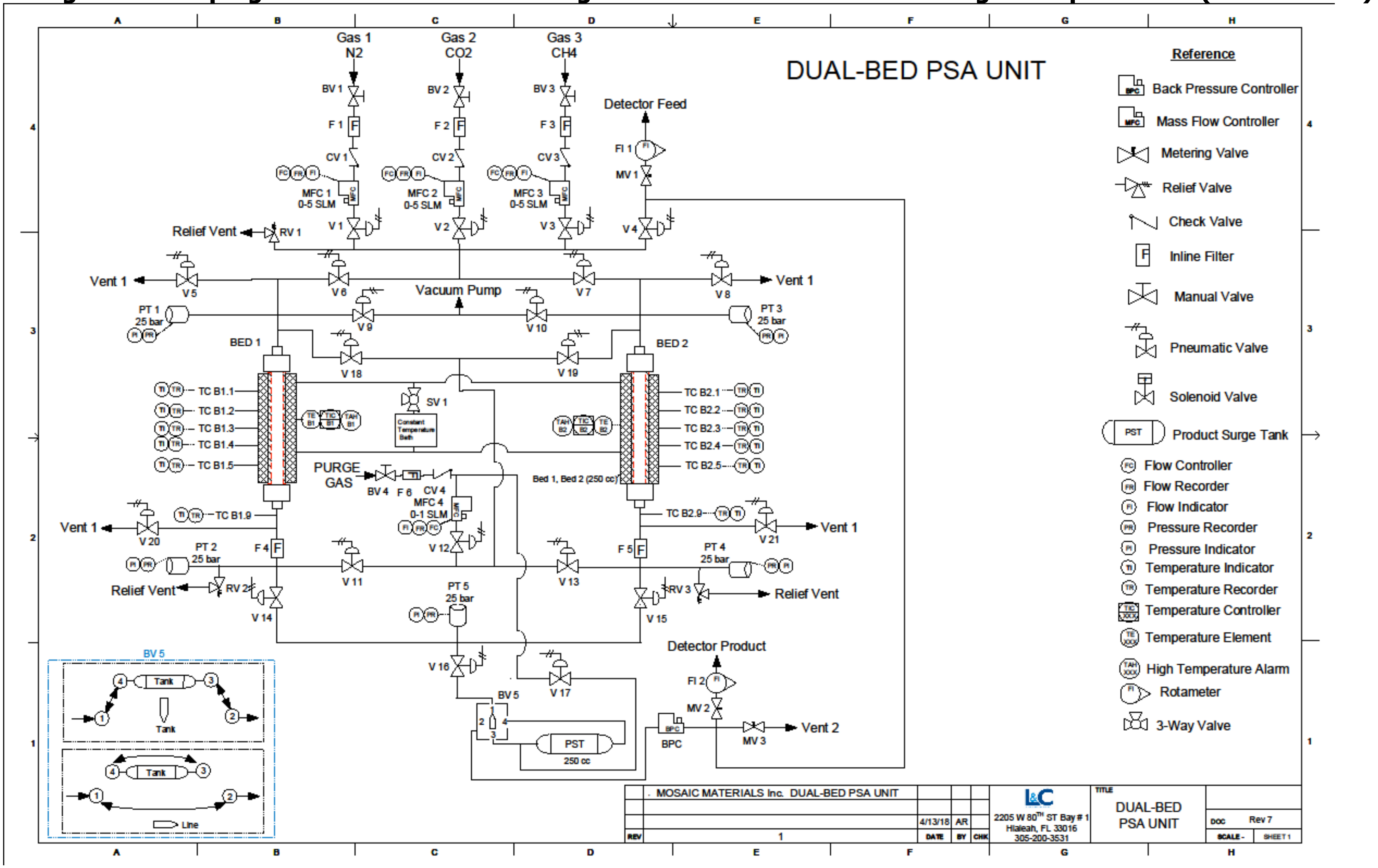
Table C-3: Effect of Varying Feed Pressure on Average Working Capacity, Δw_{avg}, and Bed Use

	1500 sccm			*3500 sccm*	
Pressure	**Time to 2% CO_2, s**	**Δw_{avg}, mol CO_2/kg**		**Time to 2% CO_2, s**	**Δw_{avg}, mol CO_2/kg**
4 bar	174	0.61		-	-
5 bar	199	0.70		60	0.50
6 bar	220	0.77		72	0.59
7 bar	225	0.79		75	0.62
8 bar	210	0.73		86	0.71

Moles CO_2 removed before breakthrough, defined as 2 percent CO_2 in the product stream, simple VPSA cycle.

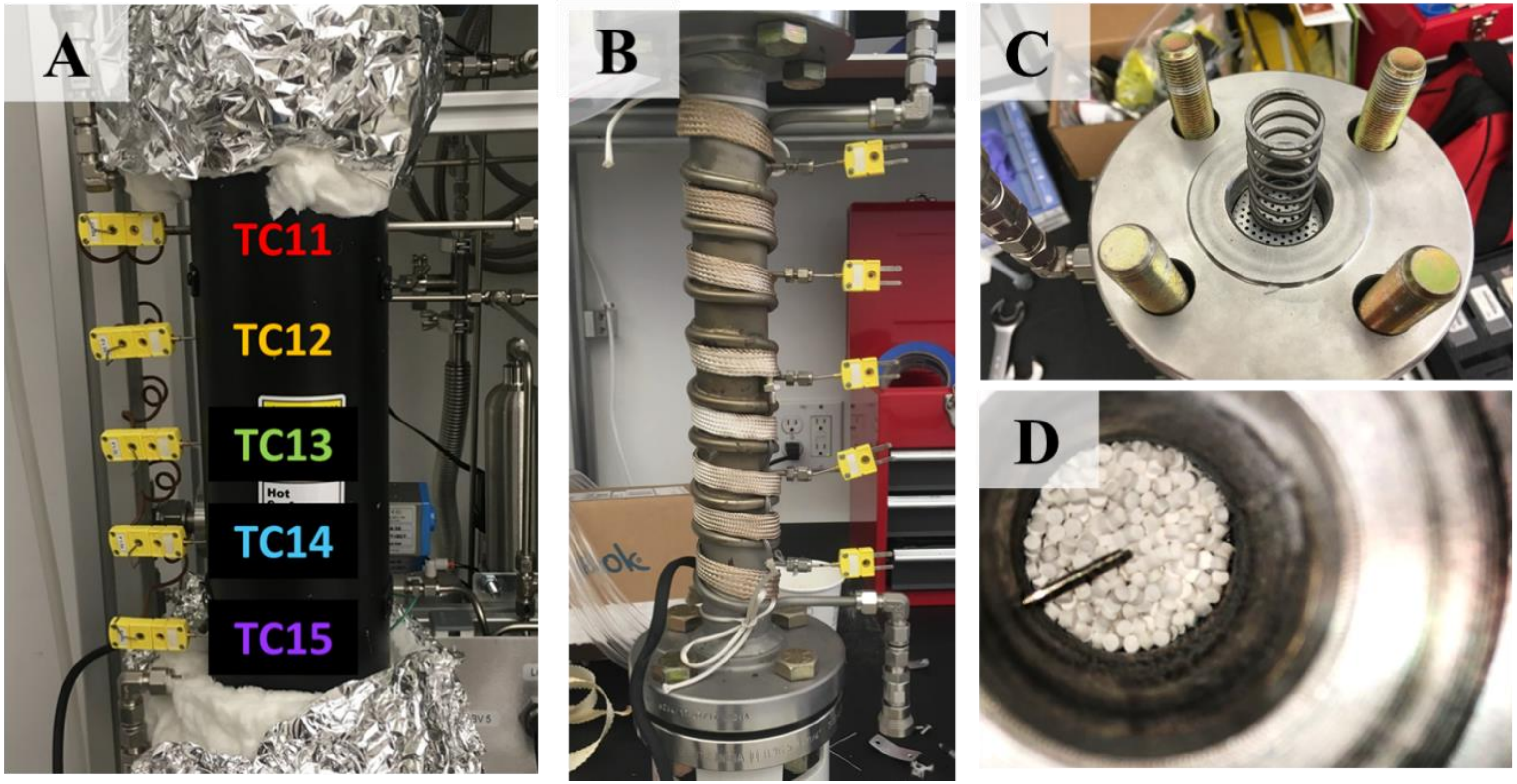
Source: Mosaic Materials Inc.

Figure C-1: Piping and Instrumentation Diagram of Dual Bed Pressure Swing Adsorption Unit (L&C Science)



Source: Mosaic Materials Inc.

Figure C-2: Detail of Adsorbent Beds



(A) Bed 1, packed and loaded into dual bed cycling system, with the location of each thermocouple indicated. (B) Photograph of Bed 1 beneath insulation, showing the heating tape and welded ¼" pipe for heating/cooling fluid. (C) Top view of bed showing screen (with filter pad underneath) used for adsorbent retention. (D) Bed partially loaded with adsorbent, showing how thermocouple extends into center of bed.

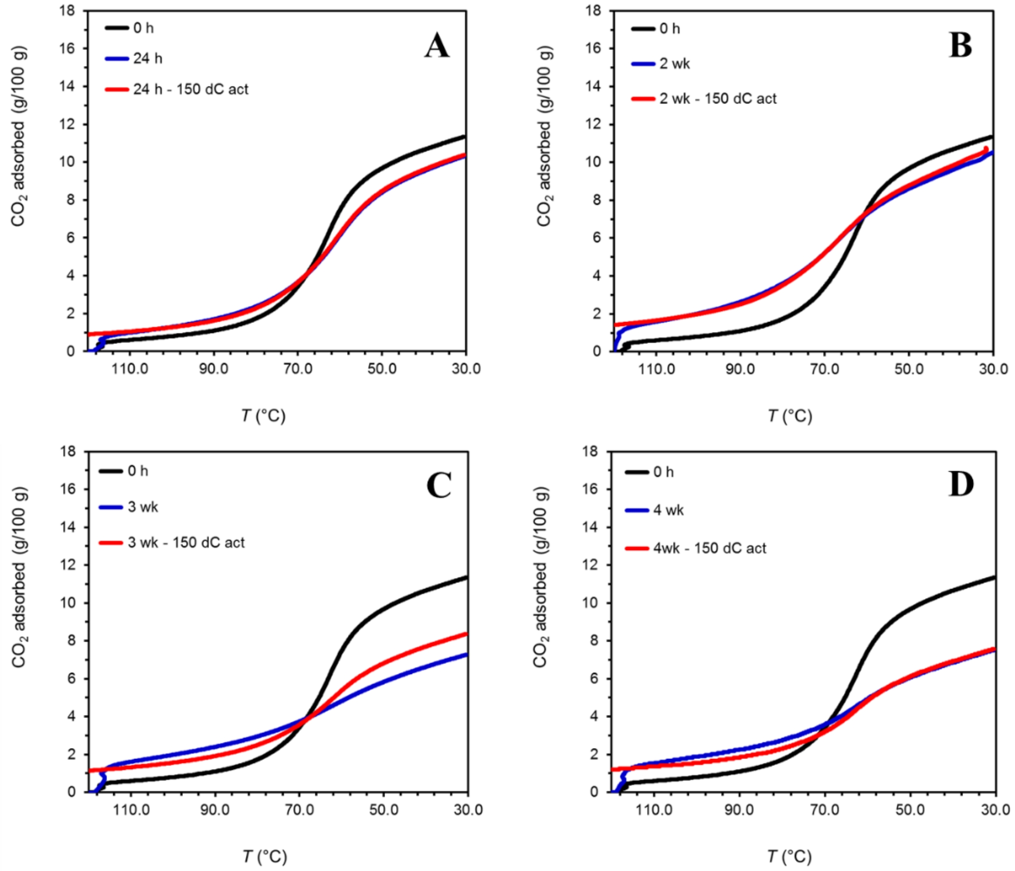
Source: Mosaic Materials Inc.

APPENDIX D: Additional Exposure Testing Data

Investigating High Temperature Activation for Materials Exposed to Raw Biogas

Impurities within the biogas stream, like siloxanes and higher hydrocarbons, may adsorb to the surface of the adsorbent structure, impeding CO_2 accessibility to active adsorption sites. Increasing the final temperature during activation prior to CO_2 adsorption may provide the necessary thermal energy to remove these impurities, restoring adsorbent performance. Figure D-1 summarizes the CO_2 adsorption isobars of composite adsorbents exposed to an activation temperature of 150°C vs 120°C. Activation temperatures above 150°C were not tested as volatilization of the diamine components within the MOF pore structure is expected above this temperature, resulting in further reductions in adsorbent performance.

Figure D-1: Thermogravimetric Carbon Dioxide Adsorption Isotherms



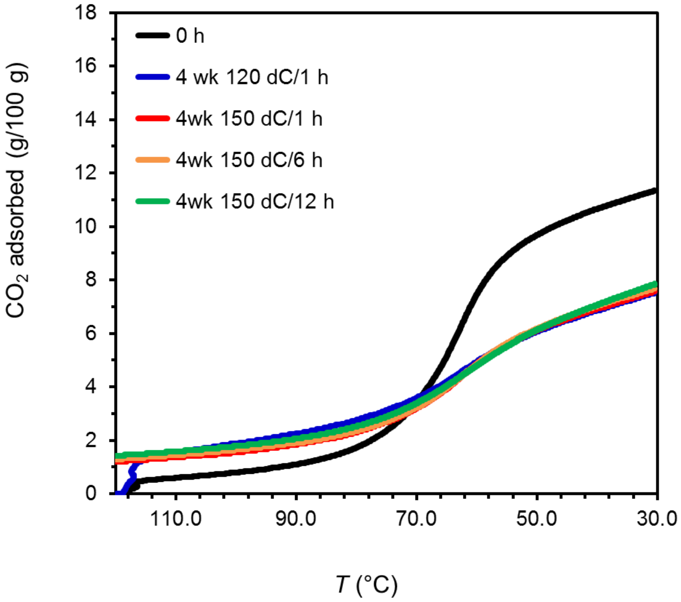
For sorbent materials exposed to varying times of raw biogas. Blue and red traces correspond to final activation temperatures of 120°C and 150°C, respectively, held for 60 minutes.

Source: Mosaic Materials Inc.

Examining the results for 24 hour and 1-week exposure samples show that increasing the activation temperature from 120°C to 150°C following exposure to raw biogas resulted in no recovery of CO_2 capacity. Extending this treatment to materials exposed for 3 and 4 weeks, slight improvements in adsorption isotherm curvature can be seen; the samples activated at 150°C regain a small amount of step behavior, and in the case of the three-week exposure time a slight increase in CO_2 adsorption capacity is observed. This may be due to removal of contaminant species (i.e. siloxanes) at the higher temperatures, which are expected to be present in higher concentrations in samples exposed to the raw biogas for longer times. However, due to the low concentrations of these larger adsorptive contaminants, removal leads to minimal gains in material performance.

While increasing the activation temperature to 150°C for 60 minutes did not restore the adsorbent performance to pre-exposure levels, increased activation times were also investigated in hopes of further recovery of adsorbent performance. Figure D-2 shows the CO_2 adsorption isobars for materials exposed to the raw biogas stream for 4 continuous weeks activated at varying temperatures and times. The 4-week sample was selected for this investigation as it will have the highest concentration of any adsorbed contaminants and the largest drop in adsorption capacity, making performance recovery more readily measurable for this strategy. Isobars for the activation at 120 and 150°C for 1 hour (replicated from Figure D-1.D) are included for reference. It is evident that increasing the activation time from 1 hour to 12 hours has no effect in restoring adsorption capacity, suggesting that the performance lost during exposure to raw biogas may be a result of either contaminants that need higher temperatures for removal, loss of the appended diamine, or physical damage to the MOF structure.

Figure D-2: Thermogravimetric Analysis of Composite Pellets Exposed to Raw Biogas

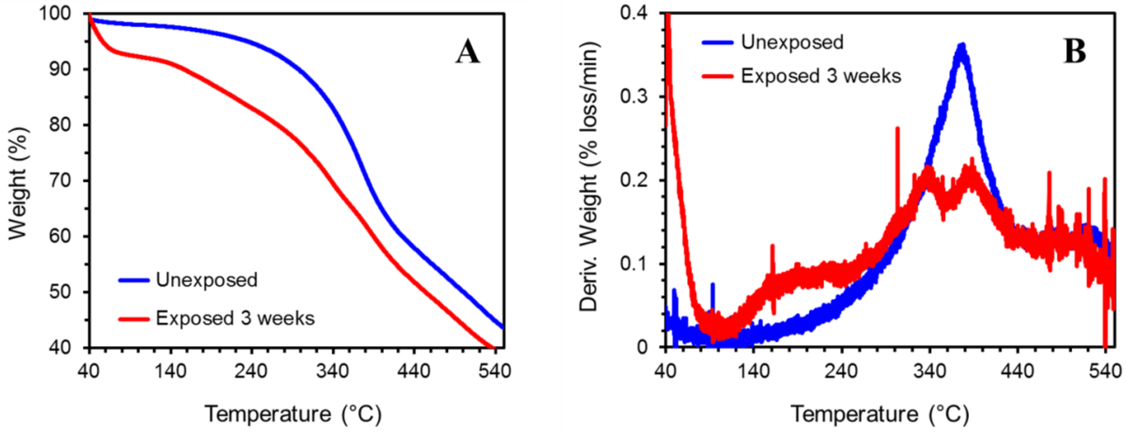


Exposure conducted at Davis Wastewater Treatment Plant for 4 weeks. Samples were activated to 120°C for 1 hour and 150°C for 1, 6, and 12 hours under flowing Argon prior to cooling under pure CO_2 at a rate of 0.5°C/min.

Source: Mosaic Materials Inc.

Recalling that selective CO_2 adsorption relies upon metal-bound diamine groups within the base MOF structure, loss of these diamine groups will result in less selective open metal adsorption sites where other adsorbents (for example, water, siloxanes, etc.) can reside, reducing CO_2 capacity. While higher activation temperatures can remove contaminants from these open metal sites, the temperatures needed for this are significantly higher (>200°C) than the metal-bound diamine groups can tolerate (~150°C). But to investigate the presence of these bound contaminants, adsorbents were heated to degradation temperatures (>550°C) under an inert atmosphere while tracking the mass changes during the experiment. If additional species within the exposed materials are removed by heating during this experiment, a change in mass at the temperature corresponding to their removal will be observed. Results of these experiments are reported in Figure D-3.

Figure D-3: Thermogravimetric Analysis Decomposition of Adsorbents



Unexposed adsorbents (blue) and 3-week (red) adsorbents with (A) relative sample mass, and (B) rate of mass loss for samples as a function of temperature when heated at 1°C /min to 550°C under Nitrogen.

Source: Mosaic Materials Inc.

Both the unexposed and exposed samples exhibit low-temperature mass losses (<100°C) corresponding to weakly adsorbed species (for example, CO_2, water) and a second mass loss (max ~350°C) corresponding to the loss of metal-bound diamines. However, the biogas exposed sample exhibits higher mass losses at lower temperatures (<240°C), indicative of removal of additional adsorbed species from metal sites missing diamines. Additionally, the biogas exposed sample exhibits lower mass losses corresponding to diamine volatilization (centered ~350°C), suggesting lower diamine content relative to unexposed samples.

APPENDIX E:
Modeling of Monoethanolamine Scrubber

A monoethanolamine (MEA) system capable of upgrading 4 million scfd (2,800 scfm) of conditioned biogas was modeled and costed as a baseline using Aspen HYSYS. The absorber is modeled as a column with two sections. The top section is a water-wash where water is sprayed into a single stage column to scrub out any MEA which is carried over in the absorber. This is to ensure that the upgraded biogas contains no MEA. Makeup blocks for MEA and H_2O are included to account for any MEA and H_2O losses in the system, so the flowsheet operates at steady-state.

The feed gas is compressed to 3.6 bar before it is sent to the absorber. This pressure was chosen since a compression ratio of 3.6 is reasonable for a single stage of compression. The trade-off is the cost to compress CO_2 in the feed versus a smaller (but thicker-walled) absorber at higher pressure. The regenerator operates at 2.1 bar and the feed amine to the absorber is 40°C (Addington & Ness, 2010). The methane recovery for the MEA process in both cases is 99.9 percent, not including any losses from the TEG gas dehydration system.

The HYSYS built-in model was used to calculate the recommended column diameter based on pressure drop considerations (hydraulic modeling). The amine circulation rate and the regenerator reboiler duty were varied to reach a CO_2 content of 2.0 vol percent in the product gas. The column height was determined by using 20 stages with a height of 0.25 m per stage for the absorber and 19 stages and 0.2 m per stage for the regenerator (Kister, 1002; Kohl & Nielsen, 1997). The absorber and regenerator are modeled as packed columns filled with ¼" Raschig rings.

The gas which exits the regenerator column is saturated with water at the condenser outlet temperature (assumed to be 35 °C with cooling water in the condenser). To meet the gas pipeline quality specifications (7 lb H_2O/ million SCF), the gas must be dehydrated. To minimize the costs of the dehydration system, the gas is first compressed to 20 bar with a multi-stage compressor, the gas is cooled in a cooling water heat exchanger, liquid water is dropped out in a knockout drum and then the gas is dried in a triethylene glycol (TEG)-based dehydration system. The cost and performance of the dehydration system is based on quotations from Croft Production Systems. The expected water content of the product gas is 3-5 lb/MMSCF. An installation factor of 5.0 was used for the TEG system.

One of the reasons that gas sweetening processes based aqueous amines are energy-intensive is that the amine is regenerated in a column with a steam reboiler. The researchers chose to obtain a vendor quote for a packaged boiler to provide saturated steam at 5 bar (147 °C), rather than trying to simulate the boiler in HYSYS. A quotation was obtained from Hurst Boiler, with gas consumption specified. Electricity consumption for the boiler was neglected. An installation factor of 3.0 was used for the package boiler.

The following references were useful in modeling the MEA scrubbing system:

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Razi, N., Svendsen, H. F., & Bolland, O. (2013). Cost and energy sensitivity analysis of absorber design in CO_2 capture with MEA. *International Journal of Greenhouse Gas Control*, *19*, 331–339. https://doi.org/10.1016/j.ijggc.2013.09.008