MIL-101(Cr)-Amine Sorbents Evaluation Under Realistic Direct Air Capture Conditions

primary project goal

Georgia Tech Research Corporation is investigating the use of hybrid sorbents based on metal-organic framework (MOF, MIL-101(Cr)) materials functionalized with amine groups for the direct air capture (DAC) of carbon dioxide (CO_2) at sub-ambient conditions. The primary goal of the project is to tailor MIL-101(Cr)-based sorbents to overcome technical barriers associated with their application at sub-ambient temperatures/conditions and validate their amenability to practical DAC application. In this direction, the stability of the powder sorbents against adsorption-desorption cycles and oxidative degradation is being determined. MIL-101(Cr) MOFs are being studied alone and in the presence of amines that range in size from small molecules to oligomers. The synthesis and characterization of sorbent materials as powder, fiber, and monolith samples is being conducted. These materials are being tested for CO_2 adsorption performance with air feeds containing 400 parts per million (ppm) CO_2 at sub-ambient conditions above minus 20°C and below 25°C and varied humidity levels. Preliminary models of adsorption and desorption behavior are being developed and used to predict DAC process parameters. Furthermore, the possibility of the deployment of powder sorbents as practical structures for gas-solid contacting (i.e., monoliths and fibers) is being evaluated.

technical goals

- Development of powder MIL-101(Cr) amine sorbents and baseline testing.
- Systematic study of the influence of amine molecular weight on sorbent performance at sub-ambient conditions of varied humidity.
- Investigation of the incorporation of MIL-101(Cr) into fibers and monoliths.
- Computational studies to model adsorption and desorption equilibrium and kinetics of MIL-101(Cr)-amine material.
- Development of adsorption/desorption models used to predict DAC system parameters, including energy consumption, sorbent efficiency, and system size.
- Development of three-dimensional printing procedure for MIL-101(Cr) monoliths.
- Develop an understanding of breakdown pathways and confirm the revolutionary stability of the new solvent using various laboratory techniques.

technical content

Metal organic frameworks (MOFs) are two- or three-dimensional crystalline structures composed of metal nodes coordinated by organic linkers. These hybrid materials have demonstrated great potential for the capture of CO_2, with promising applications, either as CO_2 sorbents themselves or as supports for amine-based CO_2 capture. The use of MOFs, as compared to other commonly used supports (e.g., silica), provides a range of advantages, including:

i. High Brunauer–Emmett–Teller (BET) surface areas.
ii. Tunable pore characteristics.

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Metal-Organic Framework-Based Sorbent for DAC

participant:
Georgia Tech Research Corporation

project number:
FE0031952

predecessor projects:
N/A

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partners:
N/A

start date:
06.01.2019

percent complete:
83%

iii. High pore volume.
iv. High density of open metal sites.
v. Stability under a wide range of conditions.

The last three features are highly desirable for functionalization of the support with amines. MIL-101(Cr) and $Mg_2(dobpdc)_2$ are two MOFs that offer potential to be a tunable platform for practical DAC. However, $Mg_2(dobpdc)$ has been reported to be unstable under humid conditions, and amine-ligated $Mg_2(dobpdc)$ has unsuitable sorption kinetics under DAC conditions. Contrary to this behavior, MIL-101(Cr) has been reported to possess good stability in boiling water, over a variety of pH conditions, and to exposure to sulfur dioxide (SO_2) and nitric oxide (NO). Thus, in this proposed work, the aim is to develop MIL-101(Cr)-based sorbents tailored for deployment under specific DAC conditions. MIL-101(Cr) is a three-dimensional framework with open chromium metal sites that, together with the open space within the porous framework, can provide "loading sites" for various amine species designed for CO_2 capture (Figure 1). The capabilities of this amine-functionalized MOF for CO_2 capture at varied CO_2 concentrations have been demonstrated, with reported CO_2 capacities under DAC conditions as high as 1.35 mmol/g (PEI-MIL-101(Cr)) and 2.8 mmol/g (TREN-MIL-101(Cr)). Although promising candidates as DAC sorbents, prior work evaluating the performance of these materials has focused on CO_2 adsorption at temperatures ranging from 25–100°C and studies of the effect of humidity have been minimal.

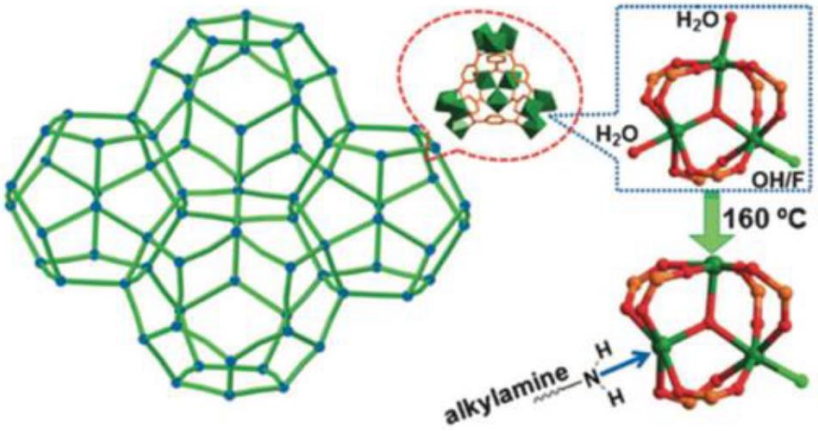

Figure 1: Schematic of amine functionalization of MIL-101(Cr).

The effective removal of carbon from the atmosphere by an air capture technology is known to depend on the specific climate (e.g., temperature and relative humidity [RH]) at a given location, so currently available data are only relevant to hot desert climates. If one considers the temperature spectrum for all the climate regions of the United States in 2019 (Figure 2), the variations in the temperature profiles are noticeable. Furthermore, sub-ambient temperatures (defined herein as temperatures below 20°C) are predominant among these regions for a large portion of the year. From a DAC deployment perspective, the diversity in the profiles reported in Figure 2 would lead to distinct temperatures for CO_2 capture at each of these locations. This would cause significant performance inconsistencies if an identical DAC technology were implemented across these locations. In the proposed work herein, the aim is to investigate the CO_2 adsorption capabilities of MIL-101(Cr)-amine sorbents focusing on this spectrum of overlooked temperatures (-20 to 20°C).

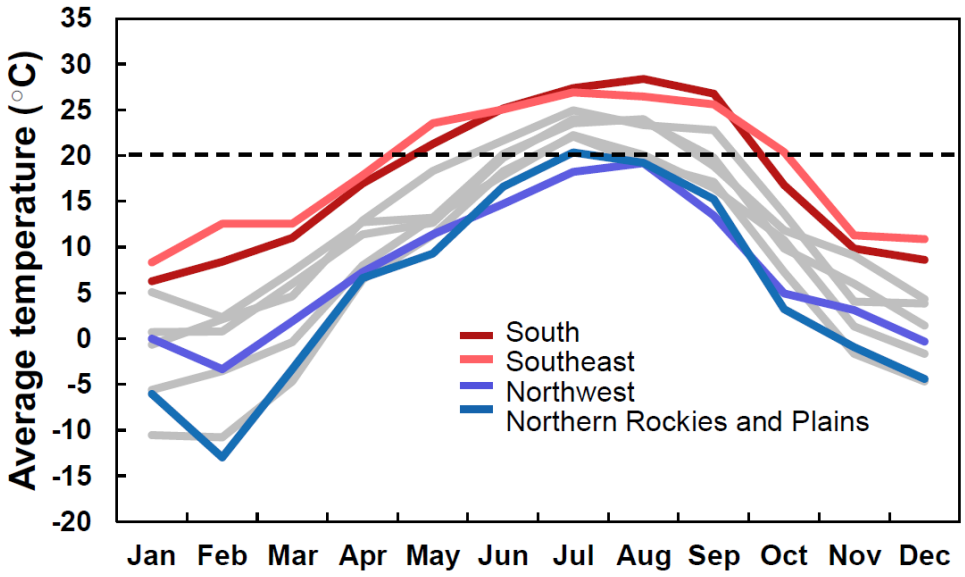

Figure 2: Summary of 2019 average monthly temperatures for U.S. climate regions. Data from the National Climatic Data Center. The gray lines include the following climate regions: Southwest, Ohio Valley, West, Northeast, Upper Midwest.

Separation Mechanism of MIL-101(Cr)/amine [FOA MRC1(b)]

The MIL-101(Cr)-amine hybrid materials follow the zwitterionic mechanism of CO_2 capture. This is the most common mechanism for solid adsorbents, where a zwitterion is formed via the interaction between CO_2 and an amine (process 1 in Figure 3). In the presence of a base, the zwitterion deprotonates to produce a carbamate (process 2 in Figure 3). In dry sorption conditions, a second amine species acts as the base, while in humid conditions, the water or hydroxide group may play this role. In humid conditions, one amine is able to capture up to one CO_2 molecule, improving the theoretical maximum CO_2/N ratio (i.e., amine efficiency) from 0.5 to 1. Under dry conditions, the placement of amines in close proximity (i.e., at high loading) is often used to achieve high amine efficiencies. For both sorption conditions (dry or humid), a sorbent that facilitates the access of CO_2 to the amine sites is required. In this direction, it is anticipated that for CO_2 capture under sub-ambient conditions, the decrease in temperature will increase the rigidity of polymeric amines, leading to high diffusional resistances and therefore compromising the reaction kinetics of CO_2 adsorption. To tackle this challenge, this project proposes a design of the MOF-amine hybrid sorbents where the effect of low molecular weight (LMW) aminopolymers on the CO_2 adsorption capacity and kinetics at sub-ambient conditions will be evaluated. Furthermore, the hypothesis is that the open Cr coordination sites in the MIL-101(Cr) will allow retention of LMW amines (e.g., TREN and tetraethylenepentamine [TEPA]), circumventing issues related to amine losses due to volatility. These losses will also be alleviated by the use of mild desorption temperatures (e.g., as low as 50°C). This approach introduces the idea of sorbent optimization based on DAC deployment location, where the use of LMW amine-based sorbents will be more favorable at ultra-low temperature, while the use of high molecular weight amine-based sorbents would be targeted for elevated temperature operation. The choice of MOF supports is crucial in this design as the absence of open metal coordination sites in silica, alumina, and related supports would preclude use of volatile LMW amines.

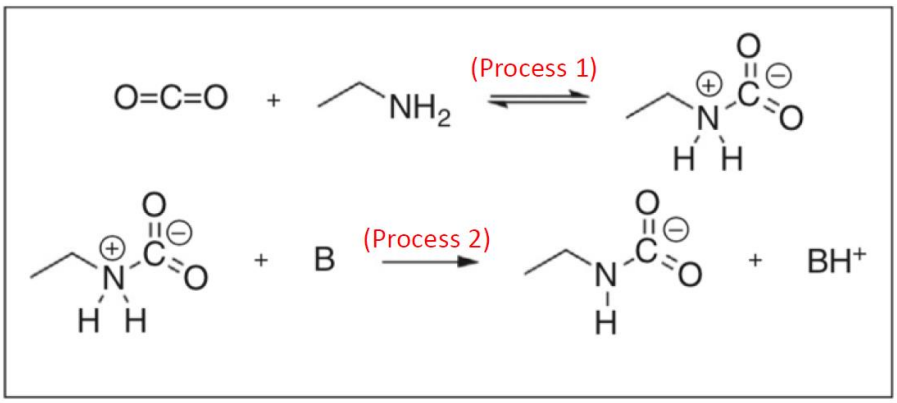

Figure 3: Mechanism of CO_2 capture involving (1) interaction between CO_2 and an amine followed by (2) deprotonation of resulting zwitterion in presence of a base.

Material Compatibility with DAC Conditions

The deployment of solid adsorbents for DAC applications offers a lower energy penalty during the adsorption-desorption process compared to aqueous sorbents, with the sorbents categorized as physisorbents or chemisorbents. At room temperature, physisorbent materials, such zeolite-based adsorbents, have shown appealing CO_2 capacities in pure CO_2 (~135 mg CO_2/g sorbent at 25°C in pure CO_2). However, given the physisorption nature of the uptake and consequential low selectivity between gases, these materials perform poorly at low CO_2 partial pressures, as demonstrated by the isotherms in Figure 4a. In this direction, chemical adsorption of CO_2 to the solid sorbent is more appropriate for DAC application, as it has been shown to be more efficient at extremely low CO_2 concentrations (ca. 400 ppm) (Figure 4a). Chemisorbents can be created by the functionalization of a solid support (e.g., silica, alumina or MOF) by amines. Moreover, functionalizing the support with amines that exhibit optimum adsorbate-adsorbent interaction strength, such as polyethyleneimine (PEI, -65 kJ/mol), provides near-ideal separation efficiency for DAC concentrations in temperature swing adsorption (TSA). In fact, in previous studies using MIL-101(Cr) as CO_2 sorbents at 25°C, it was demonstrated that the CO_2 adsorption performance of MIL-101(Cr) is greatly benefited by functionalization with amines, such as PEI and TREN (Figure 4b).

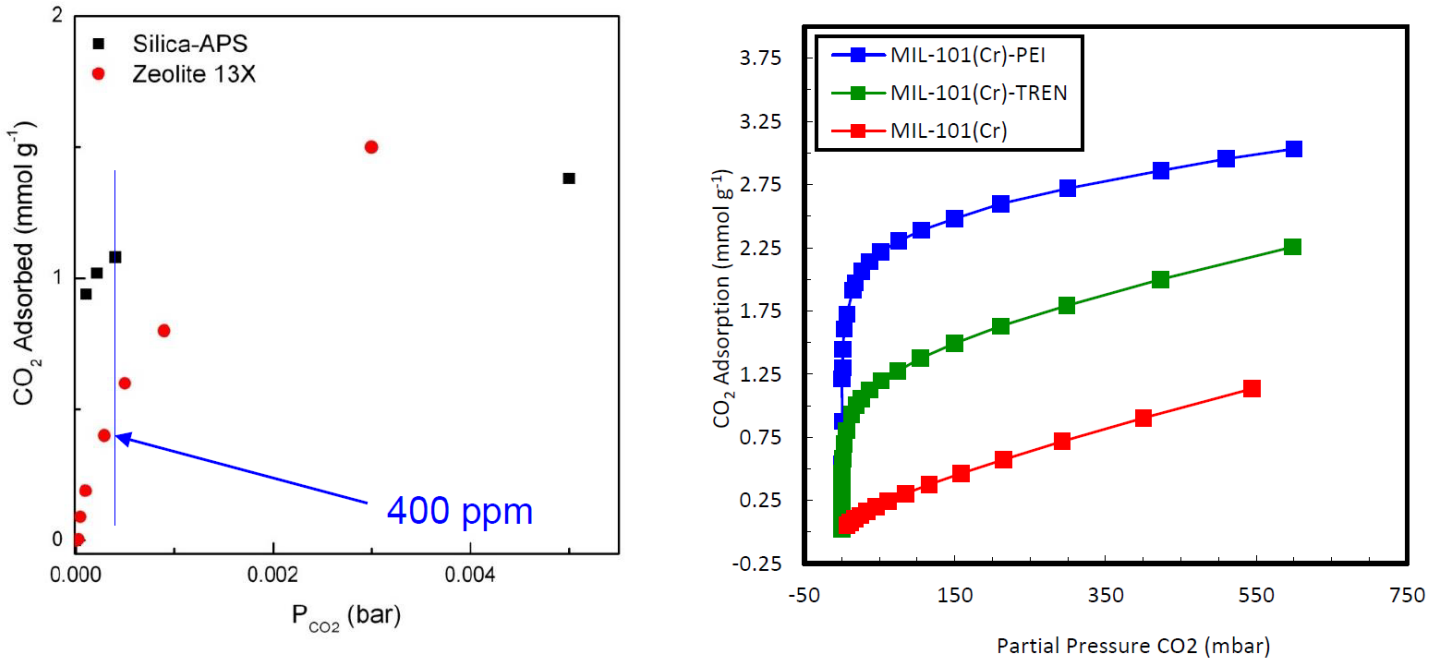

Figure 4: CO_2 adsorption as function of CO_2 partial pressure for: (a) physisorbent (zeolite) versus chemisorbent (silica-APS). (b) Bare MIL-101(Cr), MIL-101(Cr)-TREN (grafted), and MIL-101(Cr)-PEI.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	500 (estimated)	500
Bulk Density	kg/m^3	350 (measured)	350
Average Particle Diameter	mm	Crystal size: 1.5 – 8 x 10^{-4} Fiber diameter: 0.3 – 1.2 Monolith channel opening: 1 -6 (measured)	No change
Particle Void Fraction	m^3/m^3	Fibers: 0.35 (within fiber wall)	No change
Packing Density	m^2/m^3	Fibers: 5,000 – 10,000 (for bundle of fibers in shell and tube configuration)	No change
Solid Heat Capacity @ STP	kJ/kg-K	Crystals: 0.892 Fibers: 0.47 Monolith: 0.84	No change
Crush Strength	kg$_f$	N/A	N/A

Attrition Index	-	N/A	N/A
Thermal Conductivity	W/(m-K)	N/A	N/A
Manufacturing Cost for Sorbent	$/kg	15	15
Adsorption			
Pressure	bar	0.0004 bar CO_2, 1 bar total	0.0004 bar CO_2, 1 bar total
Temperature	°C	-20 to 20°C	-20 to 20°C
Equilibrium Loading	g mol CO_2/kg	1.8 (PEI_MIL-101(Cr)) 2.1 (TEPA_MIL-101(Cr)) (Measured at 25°C)	1 – 4 (at -20°C)
Heat of Adsorption	kJ/mol CO_2	-90	-60
CO_2 Adsorption Kinetics	gmol/time	0.016 mmol/g/min (initial adsorption rate, measured at 25°C)	0.02 mmol/g/min (at -20°C)
Desorption (temperature swing adsorption)			
Pressure	bar	0.005 bar CO_2	0.1 – 1 bar CO_2
Temperature	°C	25 – 60°C	25 – 60°C
Equilibrium CO_2 Loading	g mol CO_2/kg	<0.2 (at 25 – 60°C)	<0.2 (at 25 – 60°C)
Heat of Desorption	- kJ/mol CO_2	40 - 95	60
CO_2 Desorption Kinetics	gmol/time	0.045 mmol/g/min (estimated)	0.1 mmol/g/min (at 25°C) 0.2 mol/g/min (at 60°C)

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

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

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

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

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

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

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

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

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

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

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

Atmospheric Air Feed-Gas Assumptions:

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7 psia	-4 °F	0.04	variable	78.09	20.95	0.93	trace	trace

Chemical/Physical Sorbent Mechanism – Amines in PEI or TEPA react with CO_2 to form ammonium carbamate under the dry condition and potentially also bicarbonate or carbonate in the presence of water

Sorbent Contaminant Resistance – In the targeted ambient air gas stream, oxygen and water can be the contaminants deteriorating the performance of the developed sorbent, However, the effect of the oxygen is assumed to be negligible due to the low operating temperature (from -20 °C to 25 °C). Under 70% relative humidity at - 20 °C, TEPA impregnated MIL-101(Cr) showed promising stability to humidity with ~0.8 mmol of CO_2/g of working capacity.

Sorbent Attrition and Thermal/Hydrothermal Stability – Developed amine-MIL-101(Cr) materials were stable for 15 cycles of temperature swing adsorption and desorption process (from -20 to 25 °C or 60 °C) under dry conditions. Also, during 5 cycles of the breakthrough experiment at -20 °C 70% relative humidity with the same temperature swing process, TEPA impregnated MIL-101(Cr) showed stable working capacity with ~0.8 mmol of CO_2/g of sorbent

Flue Gas Pretreatment Requirements – Targeted air gas stream is directly from the ambient atmosphere

Sorbent Make-Up Requirements – MIL-101(Cr) synthesis requires chromium precursor and terephthalic acid as an organic linker. PEI and TEPA are used to functionalize MIL-101(Cr) for enhanced CO_2 capture performance. To incorporate MIL-101(Cr) into contactors such as fiber and monolith, cellulose acetate (CA) is used as a typical polymer matrix.

Waste Streams Generated – During the sorbent and contactor synthesis steps, chemical solvents such as methanol, hexane, N-methyl-2-pyrrolidone are generated as waste streams. In the CO_2 adsorption process, CO_2 depleted air, high purity CO_2, and water are generated.

Process Design Concept – Process flowsheet shown in Figure 5. Temperature vacuum swing adsorption using fiber or monolith contactor

Proposed Module Design – Fiber and monolith

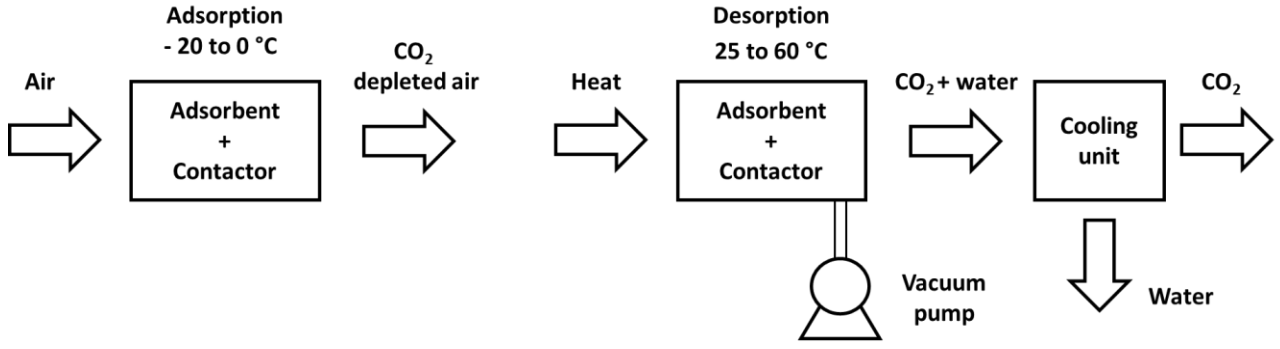

Figure 5: Process Flowsheet/block diagram.

Definitions:

The project is still ongoing and actual parameters from modules are required to estimate economic values.

Cost of Carbon Captured – Techno-economic analysis (TEA) is not a part of this project.

Cost of Carbon Avoided – TEA is not a part of this project.

Capital Expenditures – TEA is not a part of this project.

Operating Expenditures – TEA is not a part of this project.

Calculations Basis – Current R&D values for process parameters sometimes refer to estimates from the paper below, whereas sorbent performance parameters refer to new data generated in this project. Sinha, Anshuman, et al. "Systems design and economic analysis of direct air capture of CO_2 through temperature vacuum swing adsorption using MIL-101 (Cr)-PEI-800 and mmen-Mg_2 (dobpdc) MOF adsorbents." Industrial & Engineering Chemistry Research 56.3 (2017): 750-764.

Scale of Validation of Technology Used in TEA – A TEA is not being performed as part of the scope.

Qualifying Information or Assumptions:

1. Air is considered to have oxygen and nitrogen components in addition to the CO_2 (and 25% relative humidity) and the saturated steam is pure.
2. Ideal gas law and ideal mixtures are assumed for the non-condensable components. Temperature and concentration variations are neglected in the radial direction in the adsorbent film and monolith wall leading to a lumped model in the radial coordinate for these model elements.
3. Adsorbent film thickness is uniform in the axial direction.
4. During the desorption step, condensed water does not penetrate inside the MOF pores due to high flow rate of desorbed CO_2 from the MOF pores in the opposing direction. Thus, heat is conducted into the MOF and wall and is not transferred by diffusion of steam within the MOF phase following steam condensation.
5. Heat loss from the channel is negligible during all steps of the cycle.

technology advantages

- Chemical adsorption of CO_2 to the solid sorbent more efficient at extremely low CO_2 concentrations (ca. 400 ppm).
- Carbon dioxide adsorption performance of MIL-101(Cr) is greatly benefited by functionalization with amines.
- Carbon dioxide uptake at sub-ambient temperatures as low as -20°C enables operation in the temperature range of -20 to 20°C will cover a wide range of deployment locations.
- Regeneration of sorbent occurs at ambient 25°C.

R&D challenges

Carbon dioxide capture under sub-ambient conditions will increase the rigidity of polymeric amines, leading to high diffusional resistances and challenges in the reaction kinetics of CO_2 adsorption.

status

Georgia Tech Research Corporation completed preparation of MOF MIL-101(Cr) powder sorbents. The amine-impregnated MIL-101(Cr) powder show promising CO_2 uptake at -20°C due to enhanced physisorption at cold temperatures. The sorbents' sub-ambient capture capacity of 1.1 mmol/g at -20°C and low regeneration temperature of 25°C is believed to be a physisorption-dominant mechanism. The MIL-101(Cr)-based fiber sorbents were also manufactured and tested, showing 400 ppm CO_2 uptake of 1.2 mmol/g at -20°C. The MIL-101(Cr) was also successfully grown on the surface of cordierite monolith support. The sorbent loading on the monolith and CO_2 uptake optimization are currently being conducted, as is CO_2 adsorption isotherm modeling. Additional work is being conducted to ascertain which contactor is optimum for the DAC application, fiber versus monolith structures. Georgia Tech is continuing to collect CO_2 uptake isotherms, which will support the engineering process analysis for a larger-scale system.

available reports/technical papers/presentations

Christopher W. Jones, Ryan P. Lively, Matthew J. Realff, "MIL-101(Cr)-Amine Sorbents Evaluation Under Realistic Direct Air Capture Conditions," Project Kickoff Meeting presentation, Pittsburgh, PA, December 2020. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11047&filename=MIL-101(Cr)-Amine+Sorbents+Evaluation+Under+Realistic+Direct+Air+Capture+Conditions.pdf*.

Ryan P. Lively, "MIL-101(Cr)-Amine Sorbents Evaluation Under Realistic Direct Air Capture Conditions," Direct Air Capture Kickoff Meeting presentation, Pittsburgh, PA, February 2021. *http://www.netl.doe.gov/projects/plp-*

download.aspx?id=11046&filename=MIL-101(Cr)-Amine+Sorbents+Evaluation+Under+Realistic+Direct+Air+Capture+Conditions.pdf.

Christopher W. Jones, Ryan P. Lively, Matthew J. Realff, "MIL-101(Cr)-Amine Sorbents Evaluation Under Realistic Direct Air Capture Conditions," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Jones.pdf*

Guanhe Rim, Fanhe Kong, Mingyu Song, Cornelia Rosu, Pranjali Priyadarshini, Ryan P. Lively, and Christopher W. Jones," Sub-Ambient Temperature Direct Air Capture of CO_2 using Amine-Impregnated MIL-101(Cr) Enables Ambient Temperature CO_2 Recovery," JACS Au, 2022, accepted.