MIL-101(Cr)-Amine Sorbent Evaluation Under Realistic Direct Air Capture Conditions DE-FE-FE0031952

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Project Overview

➤ Funding

- DOE Funds: \$755,166 (79.73%)
- Cost share (ZCP Sorbent Development, LLC): \$191,482 (20.23%)
- ➢ Funding Period: 10/01/2020-03/31/2022 (no cost extension to 9/2022)
- Project Participants:
 - Georgia Institute of Technology
 - ZCP Sorbent Development, LLC

	FY	2021	FY 2	022	Total		
	DOE Funds	Cost Share	DOE Funds	Cost Share	DOE Funds	Cost Share	
Applicant	\$548,435		\$206,731		\$755,166		
Sub-recipient A, if proposed		\$138,000		\$53,482		\$191,482	
Total (\$)	\$548,435	\$138,000	\$206,731	\$53,482	\$755,166	\$191,482	
Total Cost Share %	20.10%		20.5	5%	20.23%		

Project Overview

- > Overall Project Objectives
 - Explore DAC performance of amine functionalized MIL-101(Cr) MOFs and build models of their adsorption behavior over a wide range of temperatures (-20 °C to 25 °C) and relative humidities (0% – 100%).
 - Develop and test the sub-ambient DAC materials in the forms of composite polymer/MOF <u>fibers</u> and on the surface of or within <u>monoliths</u>. (advance from TRL 2 to TRL 3)

Technology Background

PEI impregnated MIL-101(Cr) MOFs for ambient DAC (Darunte et al., 2016) 25 °C





Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

Aim to investigate the CO₂ adsorption capabilities of MIL-101(Cr)-amine sorbents over wide range of adsorption temperature (-20 to 25 °C) and RH (0 to ~100%) conditions.

Technology Background

Sub-ambient DAC cycles with small T swing (e.g. -20 °C to 25 °C)



- T/VSA using solid sorbents in a structured contactor (fibers or monoliths)
- Heat delivery mode TBD

Innovation: design of sorbents/processes for operation in practical, temperate outdoor adsorption temperature range of -20 to 25 °C, in all humidities.

Technology Background

Sub-ambient DAC cycles with small T swing (-20 °C to 25 °C; Δ T ~ 45 °C)

State-of-the-art at project start:

- 99% of all published DAC studies conducted at $T \ge 25 \text{ °C}$
- >50% of all published DAC studies conducted in absence of humidity
- Warm DAC gives improved kinetics, but requires handling of large water sorption loads

Proposed Innovation:

- Practical, outdoor DAC requires operation at <u>cooler/colder temperatures</u> & in all humidities
- Cool/cold operation may allow for <u>more physisorption</u> as well we <u>less</u> <u>water sorption</u> due to lower humidity, both offer potential for <u>lower</u> <u>desorption energies</u>.

Experimental Design & Work Plan

Characterization of MIL-101(Cr) powder, monolith, and fiber sorbents

Equipment for lab-scale experiments	Equipment for lab-scaleExpected experimental conditionsInformation acquired		ambient CO ₂ adsorption testing with analytical computational studies
Thermo- gravimetric System (TGA)	-20 to 25 °C, dry gas feed	CO_2 equilibrium adsorption and desorption capacities, adsorption and desorption kinetic profiles	Experimental Computational CO, capture performance under sub-
Volumetric System (SAP)	-20 to 25 °C, dry gas feed	CO ₂ adsorption isotherms	ambient conditions modeling
Fixed bed breakthrough System + MS and IR detectors	-20 to 25 °C, humid gas feeds with relative humidity between 0 and ~80%	Breakthrough & equilibrium capacities, adsorption and desorption kinetic profiles	Stability to cycles and oxygen under sub-ambient conditions

Integration of lab goals sub

Project Success Criteria

Milestone	Decision Point	Date	Success Criteria
2	Development of MIL101(Cr)-based fibers and monolith sorbents. MIL-101(Cr) sorbent macrostructures, with at least two different compositions, successfully fabricated and structurally characterized.	Month 9 ↓ Month 24 (extended)	Successful synthesis of MIL-101(Cr)- amine fiber and monolith sorbents.
3	Evaluation of performance and stability of powder MIL-101(Cr)-based sorbents at sub-ambient conditions.	Month 18 ↓ Month 21 (extended)	1-2 MIL-101(Cr)-based powder sorbents identified as promising sorbents at sub-ambient conditions: good compromise between CO ₂ capacity, kinetics and stability (towards multiple cycles and oxygen).
4	Translation of best performing powder MIL-101(Cr)-amine sorbents to fiber and monolith forms.	Month 18 ↓ Month 24 (extended)	Performance of fiber or monolith is at least 75% of the powder performance.
5	Employing models of adsorption and desorption behavior to estimate DAC system performance metrics.	Month 18 ↓ Month 24 (extended)	Adsorption and desorption models represent experimental data and estimated DAC system metrics allow assessment of suitability for next ₈ stage of process development.

Project Risks & Mitigation Strategies

	Ris	sk Rating		
Perceive Risk	Probability	Impact	Overall	Mitigation/Response Strategy
	(Low,	Med, Hig	h)	
Financial Risks:				
Existing equipment failure, replacement funds not in budget	Low	Med	Low	Many experiments will be carried out on existing equipment that is regularly maintained and failure is unlikely.
Cost/Schedule Risks	:			
Delayed hiring of personnel	Med	High	Med	PIs will seek applications for project before notification of award. PIs will seek applicants already at Georgia Tech. (Delays due to slow worker approval)
Delayed delivery of new equipment	Med	High	Med	If new equipment is delayed, existing equipment will be retrofitted with chillers to begin work on the project and limit delays. (Delays due to slow equipment delivery)

	Ris	k Rating						
Perceive Risk	Probability	Impact	Overall	Mitigation/Response Strategy				
	(Low,	Med, Hig	h)					
Technical/Scope Risl	ks:							
Unable to grow MIL-101(Cr) on monolith materials	Low	Med	Low	Previous literature indicates MIL-101(Cr) can be grown on alumina; work can continue if no other monolith materials enable MIL-101(Cr) growth. (Unable to grow due to low compatibility between MIL-101(Cr) and cordierite monolith). Extrusion and <u>3D printing</u> of MIL- 101(Cr) monoliths is also feasible.				
Amine-MIL- 101(Cr) sorbents not stable at low T	Med	Med	Med	Additional amines can be investigated. Previous work has found PEI-MIL-101(Cr) to be stable for adsorption at room temperature and work could continue with PEI only.				
Management, Plann	ing, and Over	sight Risk	S:					
Team collaboration and communication is poor	Low	Med	Low	Jones, Lively, and Realff work together in the same building at Georgia Tech and have successfully worked together before.				
ES&H Risks:								
Accident associated with experimental testing	Low	High	Low	Laboratory designed for adsorption experiments. Gas cylinder management is already in place. Liquid nitrogen is already used and all experimentalists receive proper training. 10				

MIL-101(Cr)_TEPA(30) (400 ppm CO₂ capture at -20 °C)



The amount of weak chemisorption became more significant at lower temperature conditions (thermodynamic effect).

Rim et al., JACS Au, 2022, 2, 380-393.

Cyclic test (400 ppm CO₂ capture at -20 °C (2 h), desorption at 25 °C (2 h))

30 wt% TEPA impregnated MIL-101(Cr) powders



Significant energy savings may be realized for *sub-ambient DAC* via utilization of small T swings enabled by this *weak chemisorption mechanism*.

Rim et al., JACS Au, 2022, 2, 380-393.

Single gas (CO₂ and N₂) adsorption isotherm of 30 wt% amine impregnated MIL-101(Cr) at -20 °C



Sub-ambient DAC fixed bed test (dry and 70%RH at -20 °C)

CO₂ capture capacity (breakthrough experiments)

MIL-101(Cr)_TEPA(30), weak chemisorption dominant

CO₂/H₂O-TPD (0.5 °C/min)

2.5 25 T = -20 °C. drv or 70%RH MIL-101(Cr)_TEPA(30) activated at 60 °C under N2 for 2 h Feed flow rate = 40 sccm60 $C_{CO_{2},0} = 400 \text{ ppm}$ Desorption after 400 ppm CO2 adsorption at 25 °C, 70%RH $MIL-101(Cr)_TEPA(30) = 35 mg$ 400 TPD with 0.5 K/min under 60 SCCM Na $C_{H_{2}O,0} = 870 \text{ ppm}$ (activated at 60 °C for 2 h under N₂) CO₂ adsorption, [mmol_{CO₂}/g_{sorbent}] 20 0.7 0.7 0.7 0.7 H₂O concentration, [mmol/mol] CO₂ concentration, [μmol/mol] CO_2 , [µmol/mol] 20 Pseudo-equilibrium capacity at 95% Co H₂O, [mmol/mol] 40 -60°C TPD Temperature, [°C] 300 15 20 N₂ purge 20 -20 °C 200 10 1.0 100 - 5 -20 0 0.0 0 30 60 90 120 150 180 210 240 Dry Humid Time, [min]

Moisture has positive effect on capacity of sub-ambient DAC with MIL-101(Cr)_TEPA(30)

Rim et al., JACS Au, 2022, 2, 380-393.

Cyclic fixed-bed tests under humid conditions (70% RH at -20 °C) 400 ppm CO₂ adsorption at -20 °C (2 h), desorption at 25 °C (2 h) MIL-101(Cr) TEPA(30)

CO₂ breakthrough curve

CO₂ capture capacity



30 wt% TEPA impregnated MIL-101(Cr) powders (weak chemisorption dominant) <u>can be effectively regenerated at 25 °C even under humid conditions</u>.

Development of Amine MIL-101(Cr)amine <u>Fiber</u> Sorbents

MIL-101(Cr)/CA fiber spinning



Successful fabrication of 50 wt% MIL-101(Cr) fibers of ~ 500 μm diameter High permeance (164,000 GPU) compared to previously reported SiO₂/CA fibers¹

Development of Amine MIL-101(Cr)amine <u>Fiber</u> Sorbents

PEI infused MIL-101(Cr)/CA fiber at -20 °C 400 ppm CO₂



Highest CO₂ adsorption capacity by PEI-MIL-101(Cr) fibers with dual solvent (DS) Stable performance during cycles under dry conditions with mild desorption temperature The PEI-MIL-101(Cr) fibers will be tested under humid conditions in fiber module system.

- Reduction in BET surface area of the monolith proportional to MIL-101 loading
- CO₂ uptake at 400 ppm and -20 °C increased with increased PEI loading





before PEI loading



after PEI loading 18

Sub-ambient CO2 uptake kinetics Temperature-programmed desorption

- Cyclic adsorption experiments: -20 °C in 400 ppm CO₂, 2 h; 60°C in He, 2 h
- 60 °C is enough to regenerate CA/MIL-101-PEI (PEI content: 14.5 N mmol/g MOF)
- Average working capacity: 0.95 mmol g(monolith)⁻¹



Cyclic sorption results

- Breakthrough curves of dry 400 ppm CO₂ at -20 °C
- Pseudo-equilibrium CO₂ sorption capacity comparable to TGA and gas sorption isotherm results





Development of Zeolite <u>Powder</u> Sorbents at <u>Sub-ambient Conditions</u>

13X zeolite TSA process at -20 °C 400 ppm CO₂



Song et al., Ind. Eng. Chem. Res. 2022, in press.

Thermal energy prediction using TSA and TVSA process (4.36 GJ/tCO₂ for TSA) Stable performance of 13X during cyclic TSA experiments in fixed bed system

System Modeling Approach



- The DAC system contains multiple fibers (gray) to adsorb the CO₂, a centered tube (blue) to control the temperature. Air flows through the gas phase (white) and CO₂ is adsorbed onto the fibers
- A complete cycle includes adsorption (~34 min), vacuum (~1 min), desorption (~17 min), and compression (~1 min) steps.
- Mass transfer includes the gas phase, pore phase, and the fiber phase
- Energy balance includes the gas phase, fiber phase, and the tube phase
- Momentum balance includes the gas phase only
- Model equations are developed from the equation of motion and equation of energy for each phase individually
- Langmuir plus linear isotherm (low and high pressure) describes the CO₂ equilibrium of sorbents

Cycle results 30% TEPA, air at -20 °C



- Ambient temperature is -20 °C, and the desorption is at 60 °C
- Sorbent used is MIL-101(Cr)_30wt% TEPA
- Each cycle takes around [40 50] minutes.
- The cyclic steady-state is reached after two cycles of simulation
- The swing capacity is $0.7 \text{ mol-CO}_2/\text{kg-sorbent}$ after two cycles

Performance Metrics

Ambient Temperature: -20 (°C); Desorption Temperature: 60 (°C)										
Material	Cyclic Duration (min)	42	47	52						
DEIDO	Swing Capacity (mol-CO ₂ /kg-sorb)	0.50	0.51	0.51						
PEI30	Production (Ton-CO ₂ /kg-sorb/Year)	0.27	0.25	0.23						
	Swing Capacity (mol-CO ₂ /kg-sorb)	0.52	0.53	0.54						
IEFASU	Production (Ton-CO ₂ /kg-sorb/Year)	0.28	0.26	0.24						

- Shorter cycles lead to
 - Decreased swing capacity
 - Increased production rate

Project Schedule (Key Milestones)

Task/ Subtask	Milestone Title & Description	Planned Completion Date
1	Project Management Plan	Month 1
3.2/4.2/ 6.2	Development of MIL-101(Cr)-based fibers and monolith sorbents. MIL-101(Cr) sorbent macrostructures, with at least two different compositions, successfully fabricated and structurally characterized.	Month 9 ↓ Month 24 (extended)
5/8	Evaluation of performance and stability of powder MIL-101(Cr)- based sorbents at sub-ambient conditions. CO_2 capacities will be measured for at least three sorbent powder types . Cyclic stability and rate of oxidative degradation will be measured for at least 1 sorbent at 3 different conditions.	Month 18 ↓ Month 21 (extended)
9	Translation of most promising powder MIL-101(Cr)-based sorbents to fiber and monolith forms . Developed macrostructures should have CO_2 capacity of at least 75% of the powder sorbent capacity.	Month 18 \downarrow Month 24 (extended)
10	Employ models of adsorption and desorption behavior to estimate DAC system performance metrics; report swing capacity and energy consumption per ton CO_2 .	Month 18 ↓ Month 24 (extended)

Plans for future testing/development/ commercialization

Tasks for future scale-up & testing:

- a. This project
 - -- assess preferred mode of incorporation into structured contactors (**fiber** vs. monolith vs. **3DP monolith**)
 - -- use process model to assess preferred operational conditions
- b. After this project
 - -- assess preferred modes of desorption (T, V, heating modes, etc.)
 - -- use technoeconomic model to find cost minima ²⁶

Plans for future testing/development/ commercialization

Tasks for future scale-up & testing:

- c. Scale-up potential
 - -- sorbent components all commercially available at small scale; assess & develop supply chains for sorbent
 - -- build and test automated low temperature DAC rig

Summary Slides

MIL-101(Cr) powder sorbents

- a. Amine impregnated MIL-101(Cr) powders showed promising CO_2 uptake even at -20 °C due to enhanced weak chemisorption at cold temperatures.
- b. MIL-101(Cr)_TEPA(30) is a preferred sorbent (among the samples we tested) for sub-ambient DAC due to promising adsorption capacity (1.12 mmol/g at -20 °C) and low regeneration temperature, 25 °C (weak chemisorption dominant).
- c. Sub-ambient DAC capacity of MIL-101(Cr)_TEPA(30) was enhanced under humid conditions and stable working capacities (0.82 mmol/g) were obtained over 5 small humid temperature swing cycles (-20 °C <---> 25 °C) showing promising stability to humidity.
- d. This work suggests that significant work on DAC materials that operate at low, sub-ambient temperatures is warranted for possible deployment in temperate and polar climates.

MIL-101(Cr) based fiber sorbents

- a. PEI infused MIL-101(Cr)/CA (cellulose acetate) fiber sorbents with dual solvent method showed promising 400 ppm CO₂ uptake (0.94 mmol/g) at -20 °C.
- b. PEI infused MIL-101(Cr)/CA fiber sorbents will be tested under humid conditions in fixed bed system.

MIL-101(Cr) based 3D-printed monolith sorbents

- a. CA/MIL-101/PEI monoliths have been prepared by a 3D printing technique called solvent-based additive manufacturing (SBAM).
- b. They show hierarchical porosity and comparable CO_2 uptake performance (in terms of MIL-101/PEI content) at sub-ambient conditions with powder sorbents.

DAC modeling

- a. MIL101(Cr)_30% TEPA has higher swing capacity and production rate than MIL101(Cr)_30% PEI at -20 °C air temperature.
- b. Cycle duration optimization leads to decreased swing capacity and increased production rate.
- c. Simulation performance is sensitive to isotherm parameterization and input parameters, requires careful initialization.
- d. Future plans: improve the production rate by productivity optimization, and complete TEA and LCA calculations.

Thanks to:



Fossil Energy and Carbon Management

Lively Group, Realff Group David Elenowitz & Zero Carbon Partners

Jones Group:



- DAC Technology Knowledge Gaps
 Kong et al., *Korean J. Chem. Eng.* 2022, 39, 1-19.
- MIL-101(Cr)-Amine sorbents at cold T.
 Rim et al., *JACS Au* 2022, 2, 380-393.
- Zeolites at cold temperatures
 Song et al., *Ind. Eng. Chem. Res.*2022, in press.



100000 Water vapor at 100% RH (dewpoint) 31,284 ppm Concentration, [ppm] 10000 1239 ppm 1000 Atmospheric CO 100 -40 -30 -20 -10 0 10 20 30 40 Temperature, [°C]

Absolute moisture concentration at dew point

Kong et al., Korean J Chem Eng, 2021



Heat of adsorption at 25 °C



30 wt% loading: weak chemisorption dominant (-40 ~ -65 kJ/mol) 50 wt% loading: strong chemisorption dominant (-95 ~ -110 kJ/mol)

Thermodynamic Separation Efficiency



Lively and Realff, AIChE J., 2016

TSA- for DAC, optimal sorbent has elevated $\Delta H_{ads} > 55$ kJ/mol = Chemisorption

CO₂ Adsorption Kinetics (TGA/DSC)



- Solvent Based Additive Manufacturing
- Cellulose acetate (CA) selected
- Dimethyl acetamide (DMAc) and acetone as solvent
- water as nonsolvent





Phase diagram



As printed monolith



Cross Section

Surface ³⁶

Organization Chart



- School of Chemical & Biomolecular Engineering, Georgia Institute of Technology
 - Primary PI, Christopher Jones: project director and communicate with DOE, developing MOFs powder sorbents and supporting MOFs on monolithic contactors for DAC
 - Co-PI, Ryan Lively: designing and fabricating MOFs bearing fiber sorbents for DAC, process development
 - Co-PI, Matthew Realff: DAC modeling and techno-economic/life cycle analysis
- ZCP Sorbent Development, LLC
 - Provide cost share by directly funding personnel in the project

Gantt Chart

k	m ber			Year 1						Y	Task	Task		
Ta	Tea	Task Description	М	QI	L	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Start Date	End Date
1	CWJ	Project Management, Planning and Reporting	M1											
2		Development of MIL-101(Cr) powder sorbents												
2.1	CWJ	Synthesis of sorbent powder samples											10/01/20	02/28/21
2.2		Baseline testing of powder sorbents											11/01/20	02/28/21
3		Development and preliminary testing of MIL- 101(Cr)-amine fiber sorbents												
3.1		Preparation of MIL-101(Cr) fibers											10/01/20	02/28/21
3.2	RPL	Preparation and characterization of amine loaded MIL-101(Cr) fibers	M2										02/01/21	04/30/22
3.3		Preliminary testing of CO ₂ adsorption performance over MIL-101(Cr)-based fiber sorbents											06/01/21	<mark>04/30/22</mark>
4		Development and preliminary testing of MIL- 101(Cr)-amine monolith sorbents												
4.1	CWI	Synthesis of MIL-101(Cr) on monolith supports											10/01/20	04/31/21
4.2	RPL	Preparation and characterization of amine loaded MIL-101(Cr) monoliths	M2										02/01/21	<mark>07/31/22</mark>
4.3		Preliminary testing of CO ₂ adsorption performance over MIL-101(Cr)-amine monolith sorbents											06/01/21	07/31/22
5		Development of powder MIL-101(Cr)-based sorbents at sub ambient conditions												
5.1	CWJ	CO ₂ adsorption testing of powder MIL-101(Cr)-based sorbent at sub-ambient conditions											12/01/20	10/31/21
5.2		Stability of powder MIL-101(Cr)-based sorbents to humidity	M3										03/01/21	11/30/21

M indicates milestone.

łk	m ber				Ye	ar 1		Year 2				Task	Task
Ta	Tea Mem	Task Description	М	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Start Date	End Date
6		Development of MIL-101(Cr)-amine monolith sorbent via 3D printing											
6.1	CWJ	Development of 3D printing procedure for MIL- 101(Cr) monoliths										10/01/20	03/31/22
6.2	RPL	Testing of CO ₂ adsorption performance for 3D printed MIL-101(Cr)-amine monolith sorbents										05/01/21	<mark>08/31/22</mark>
6.3		Investigation of effect of monolith properties on CO ₂ adsorption performance										09/01/21	09/30/22
7		Build models of the adsorption and desorption behavior of MIL-101(Cr)-amine materials											
7.1		Model equilibrium adsorption behavior										02/01/21	<mark>03/31/22</mark>
7.2	MJR	Model kinetics of adsorption behavior										02/01/21	<mark>03/31/22</mark>
7.3		Model equilibrium desorption behavior										02/01/21	03/31/22
7.4		Model kinetics of desorption behavior										02/01/21	03/31/22
8		Measuring stability of MIL-101(Cr)-based sorbent powders at sub-ambient conditions											
8.1	CWJ	Stability of amine-MIL-101(Cr) sorbents to cyclic operation at sub ambient conditions										10/01/21	03/31/22
8.2		Stability of amine-MIL-101(Cr) sorbents to oxygen	M3									10/01/21	<mark>06/30/22</mark>
9		Translation of best performing powder MIL- 101(Cr)-amine sorbents to fiber and monolith forms											
9.1	RPL	Synthesis and testing of best powder sorbent samples into fiber form										09/01/21	06/30/22
9.2		Synthesis and testing of best powder sorbent samples into monolith form	M4									09/01/21	09/30/22
10		Estimate DAC system performance metrics											
10.1	мір	Determine estimated swing capacity and productivity of adsorbents										10/01/21	<mark>09/30/22</mark>
10.2	MJK	Determine estimated energy consumption per ton CO ₂										10/01/21	09/30/22
10.3		Determine the system cost and life cycle energy inventory for 1 Mton of CO ₂ scale system	М5									10/01/21	<mark>09/30/22</mark>

M indicates milestone.