# Novel Process that Achieves 10 mol/kg Sorbent Swing Capacity in a Rapidly Cycled Pressure Swing Adsorption Process

# primary project goal

The Georgia Institute of Technology developed prototype fiber sorbent modules containing polymeric fibers embedded with metal organic framework (MOF) for use in a sub-ambient rapid-cycle pressure swing adsorption (RCPSA) post-combustion carbon capture process.

## technical goals

- Scaled-up the MOF sorbent.
- Experimentally determined sub-ambient sorption isotherms.
- Spun fibers containing the MOF.
- Constructed the RCPSA system and completed testing of fiber sorbent modules and fiber sorbent modules with phase-change materials.
- Modeled and optimized fiber module operation, as well as flue gas conditioning optimization.
- Prepared an overall system techno-economic analysis (TEA).

## technical content

Georgia Tech Research Corporation developed a process to achieve 10 mole/kg sorbent swing capacity using an RCPSA process. The sorbent system included novel polymeric fibers embedded at high loadings with MOF materials. An example of the fibers is shown in Figure 1. MOFs are known to have good carbon dioxide (CO<sub>2</sub>) capacity and rapid adsorption/desorption kinetics if kept isothermal. The team developed a scalable, modular contactor for the sorbents with high surface area, low pressure drop, and low mass transfer resistance. An encapsulated, stationary phase-change material was incorporated in the hollow fiber sorbents (Figure 2) to maintain isothermal adsorption/desorption. This material has a melting/freezing point equivalent to the system operating temperature. It melts as heat is released upon  $CO_2$  adsorption and freezes as  $CO_2$  is desorbed; therefore, steam and cooling water are not necessary. The system consists of modules containing the hollow fibers.

## program area:

Point Source Capture

## ending scale:

Bench Scale

#### application:

Post-combustion Power Generation PSC

#### key technology:

Sorbents

## project focus:

Pressure Swing Adsorption Process with Novel Sorbent Structured Contactors

#### participant:

Georgia Tech Research Corporation

project number:

FE0026433

predecessor projects: N/A

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percent complete: 100%



Figure 1: MIL-101(Cr)/cellulose acetate fiber sorbents: ~50 wt% MIL-101(Cr); (a) low magnification fiber, (b) zoomed in sub-structure.



Figure 2: Phase-change material in hollow fiber sorbents.

A simplified schematic of the overall CO<sub>2</sub> capture process is shown in Figure 3. The conditioned flue gas is passed through a sub-ambient heat exchanger before entering the PSA unit containing the hollow fiber sorbent modules. The steps of the RCPSA process (pressurization, adsorption, depressurization, desorption) are shown in Figure 4. Sub-ambient conditions increase adsorption selectivity and working capacity.



Figure 3: Process flow diagram.



Figure 4: Pressure swing adsorption process.

The sorbent and process parameters are shown in Table 1.

#### **TABLE 1: SORBENT PROCESS PARAMETERS**

Sorbent	Units	Current R&D Value	Target R&D Value	
True Density @ STP	kg/m <sup>3</sup>	_	_	
Bulk Density	kg/m <sup>3</sup>	1,200	1,200	
Average Particle Diameter (diameter of fiber)	mm	0.8	0.8	
Particle Void Fraction (void fraction of the fiber bed)	m <sup>3</sup> /m <sup>3</sup>	0.4	0.35	
Packing Density	m <sup>2</sup> /m <sup>3</sup>	1,000	2,000	
Solid Heat Capacity @ STP	kJ/kg-K	1,600	1,600	
Crush Strength	kgf	unknown	not specified	
Manufacturing Cost for Sorbent	\$/kg	unknown	30	
Adsorption				
Pressure	bar	2	2	
Temperature	°C	-30	-30	
Equilibrium Loading	g mol CO <sub>2</sub> /kg	10.2	delta (ads-des) =10	
Heat of Desorption	kJ/mol CO <sub>2</sub>	21.5	< 35	
Desorption				
Pressure	bar	0.3	0.3	
Temperature	°C	-30	-30	
Equilibrium CO <sub>2</sub> Loading	g mol CO <sub>2</sub> /kg	1.2	Delta (ads-des) =10	
Heat of Adsorption	kJ/mol CO <sub>2</sub>	21.5	< 35	
Proposed Module Design		(for equipment developers)		
Flow Arrangement/Operation	_	fixed fiber/parallel flow/cyclic		
Flue Gas Flowrate	kg/hr	_		
PSA CO <sub>2</sub> Recovery, Purity, and Pressure [from PSA] (from total process)	%/%/bar	[92/80/1] (90/99.5/60)	[92/95/1] (90/99.9/60)	
Adsorber Pressure Drop	bar	0.1		
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	<u>\$</u> kg/hr	390-480 (process)		

#### **Definitions:**

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Sorbent - Adsorbate-free (i.e., CO2-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, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a  $CO_2$  partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

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

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

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

Loading – The basis for CO<sub>2</sub> loadings is mass of dry, adsorbate-free sorbent.

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

Estimated Cost – Basis is kg/hr of CO2 in CO2-rich product gas; assuming targets are met.

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

		Composition								
Pressure	Temperature	vol%					ppmv			
psia	°F	CO <sub>2</sub>	H <sub>2</sub> O	<b>N</b> 2	<b>O</b> <sub>2</sub>	Ar	SOx	NOx		
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74		

#### **Other Parameter Descriptions:**

Chemical/Physical Sorbent Mechanism – Physisorption.

Sorbent Contaminant Resistance - High, resistant to humid sulfur dioxide (SO<sub>2</sub>) at 50 parts per million (ppm).

**Sorbent Attrition and Thermal/Hydrothermal Stability** – Irreversible sorption of SO<sub>2</sub> and nitrogen dioxide (NO<sub>2</sub>) with little effect on CO<sub>2</sub> capacity.

Flue Gas Pretreatment Requirements – Pressurization, dehydration, cooling.

Sorbent Makeup Requirements - None.

Waste Streams Generated - Clean (100% RH) nitrogen (N2).

Process Design Concept - Discussed above.

## technology advantages

- High working capacity of MOF sorbents.
- High contact area, low pressure drop, and low mass transfer resistance for the modules.
- Sub-ambient conditions increase adsorption selectivity and working capacity.
- The efficiency of the pressure swing cycle was boosted by installing a stationary phase-change material in the fiber sorbents that isothermally melts upon release of sorption enthalpy and conversely isothermally freezes upon CO<sub>2</sub> desorption, requiring no steam or cooling water.
- Improved performance in the presence of flue gas contaminants due to physisorption separation mechanism (as opposed to a chemisorption mechanism).
- Carbon dioxide liquefaction and pumping can be used instead of CO<sub>2</sub> compression.
- Sub-ambient heat exchange and CO<sub>2</sub> liquefaction are commercially demonstrated.

#### R&D challenges

- Scale-up of MOFs.
- Integrating MOF into the fiber to maintain CO<sub>2</sub> capacity.
- Integration of phase-change material into MOF-loaded fibers to maintain near isothermal operation.

- Effective operation of tightly heat- and work-integrated system.
- Monitoring and management of sorbent lifetime over extended operating periods.
- Simulation development for material screening, adsorption process selection, and cost estimation.

#### status

The project was completed on September 30, 2019. Two MOFs were manufactured in large quantities and subsequently converted into adsorbent-loaded fiber materials. These were shown to have more than order-of-magnitude reductions in flue gas pressure drop compared to traditional adsorbent structures. The MOF materials could be composited with glycol-loaded capsules that would freeze and melt during each sorption-desorption cycle, enabling near isothermal operation of the RCPSA. Two mini pilot systems were constructed for testing, and a multi-level simulation for capture mechanisms, thermodynamics, and process-level integration was developed for systems of this technology type. The sub-ambient RCPSA process was estimated to have competitive operating and capital costs via a preliminary TEA based on the experimental data and computational modeling at molecular and process levels.

#### available reports/technical papers/presentations

Lively, R., et al. "Novel Process That Achieves 10 mol/kg Sorbent Swing Capacity in a Rapidly Cycled Pressure Swing Adsorption Process," Presented at the Final Project Meeting, Pittsburgh, PA, September 2019. https://netl.doe.gov/sites/default/files/netl-file/R-Lively-GIT-Rapid-Pressure-Swing.pdf.

Lively, R., et al. "Enabling 10 mol/kg Swing Capacity via Heat Integrated Sub-Ambient Pressure Swing Adsorption," presented at the 2018 NETL CO<sub>2</sub> Capture Technology Meeting, Pittsburgh, PA, August 2018. https://www.netl.doe.gov/sites/default/files/netl-file/K-Walton-GIT-10-MOL-per-KG-Swing-Capacity.pdf.

Lively, R., et al. "Enabling 10 mol/kg Swing Capacity via Heat Integrated Sub-Ambient Pressure Swing Adsorption," presented at the 2017 NETL CO<sub>2</sub> Capture Technology Meeting, Pittsburgh, PA, August 2017. https://www.netl.doe.gov/sites/default/files/event-proceedings/2017/co2%20capture/4-Thursday/R-Lively-GIT-10-MOLKG-Sorbent-Swing-Capacity.pdf.

Lively, R., et al. "Enabling 10 mol/kg Swing Capacity via Heat Integrated Sub-Ambient Pressure Swing Adsorption," presented at the 2016 NETL CO<sub>2</sub> Capture Technology Meeting, Pittsburgh, PA, August 2016. https://www.netl.doe.gov/sites/default/files/event-proceedings/2016/c02%20cap%20review/4-Thursday/R-Lively-GeorgialT-Sub-ambient-Pressure-Swing-Adsorption.pdf.

Lively, R., et al. "Enabling 10 mol/kg Swing Capacity via Heat Integrated Sub-Ambient Pressure Swing Adsorption," Presented at the Project Kickoff Meeting, Pittsburgh, PA, December 2015. https://www.netl.doe.gov/sites/default/files/2017-12/FE0026433-Kickoff-Meeting.pdf.

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Shih, C., J. Park, et al. "*Hierarchical Bayesian estimation for adsorption isotherm parameter determination*" Chem. Eng. Sci. 2020, 2014, 115435

DeWitt, SJA, et al. "*Development of Phase-Change-Based Thermally Modulated Fiber Sorbents*" Ind. Eng. Chem. Res. 2019, 58, 155, 768-5776.

DeWitt, SJA, et al. "Analysis of energetics and economics of sub-ambient hybrid post-combustion carbon dioxide capture." AIChE J. 2021, 67, 11, e.17403

DeWitt, SJA, et al. "*Critical Comparison of Structured Contactors for Adsorption-Based Gas Separations*" Annu. Rev. Chem. Biomol. Eng. 2018 Jun 7;9:129-152.

DeWitt, SJA et al. "*Incorporation of microencapsulated phase change materials into wet-spin dry jet polymer fibers.*" PCT US18/48110; WO 2019/099086.