

Hybridizing Heat-Integrated 3D-Printed Modules with Mass Manufacturable, Low Pressure Drop Fiber Sorbents

primary project goal

Georgia Tech Research Corporation (GTRC), and project partners Oak Ridge National Laboratory (ORNL), ReactWell LLC, and Trimeric Inc., are advancing a fiber sorbent technology for direct air capture (DAC) through optimization of a contactor design to enhance productivity and lower cost. Polyethyleneimine (PEI)-infused cellulose acetate (CA)/silica fiber sorbents previously developed for DAC applications are being housed in 3D-printed modules that provide heat integration and flow control for adsorption of carbon dioxide (CO₂). The hybridization of fiber sorbent technology with modular housing provides several advantages that lead to lower air pressure drops, higher sorbent productivity, and ease of manufacturing and assembly. Budget Period 1 (BP 1) project tasks are to: 1) fabricate the fibers on a large-scale, with a portion woven into laminate-style sheets; 2) design, fabricate, and optimize the hybrid 3D-printed modules 3) conduct long-term cyclic testing at bench scale on the optimal 3D-printed module. BP 2 tasks are to: 1) evaluate the hybrid modules containing the fibers against pressure drop, productivity, purity, and degradation metrics 2) optimize the hybrid system to yield CO₂ purity of at least 95% with a volumetric productivity five times greater than state-of-the-art.

technical goals

- Fabricate the 3D-printed modules and fiber sorbents (GTRC and ORNL).
- Experimentally evaluate the performance of the assembled hybrid modules and further optimize the design (GTRC).
- Complete modeling and a full techno-economic analysis (TEA) and update the model with experimental results (GTRC and Trimeric).
- Test the hybrid modules in a long-term cycling study (ReactWell).

technical content

The overall objective is to research, develop, and evaluate a modular DAC system that is simple and scalable. This system is based on the adsorption of CO₂ into commercial polyamines supported by porous fiber sorbents, which can be produced at kilometer-per-hour scales using the project's pre-pilot spinning line. The project goal is to increase the already-high productivity of these fiber materials via novel 3D-printed modular housing systems that provide easy-to-manufacture and localized heat integration and flow control (Figure 1). This hybridization of fiber sorbent technology with modular housing provides several advantages that lead to lower air pressure drops and higher sorbent productivity, as well as an ease of manufacturing and assembly that is unrivaled by existing and emerging heat-integrated contactor designs.

The design of the modular housing is one of the key enabling features of this new DAC approach, as the manufacturing of the fiber sorbents is a routine practice in the project's facility. The modular housing is being fabricated with the following

program area:

Carbon Dioxide Removal

ending scale:

Bench Scale

application:

Direct Air Capture

key technology:

Sorbents

project focus:

3D-Printed Modules
Integrated with Fiber
Sorbents

participant:

Georgia Tech Research
Corporation

project number:

FE0032129

predecessor projects:

N/A

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Oak Ridge National
Laboratory (ORNL);
ReactWell LLC;
Trimeric Corporation

start date:

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percent complete:

17%

features, at a minimum: (i) a tapered air intake to reduce pressure drop related to entrance effects; (ii) a structured network of heat transfer channels to enable localized cooling and heating during adsorption and desorption, respectively; and (iii) low pressure drop supports for the fiber sorbents (Figure 1). This hybrid manufacturing approach provides a facile method for taking fiber sorbents from lab scale to pilot scale as it dramatically simplifies the fabrication of heat-integrated contactor structures.

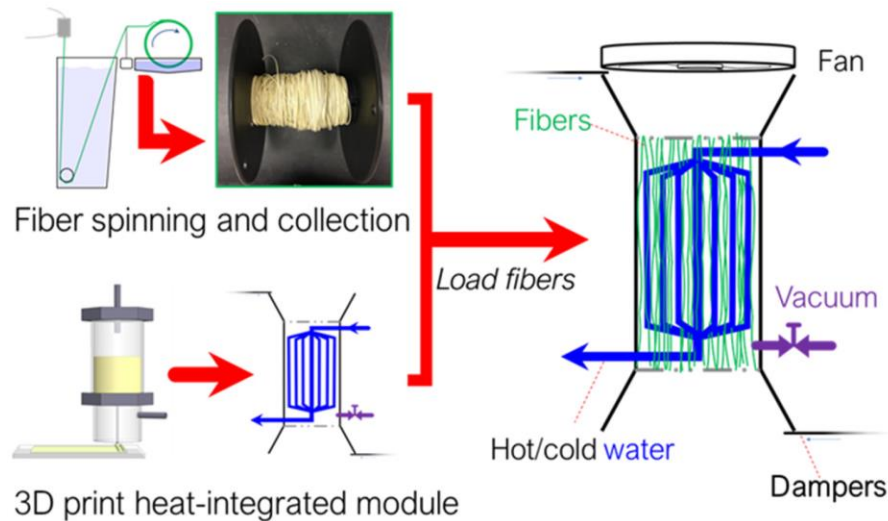


Figure 1: Schematic of proposed technology. The scalability of fiber sorbent spinning (top) is leveraged via novel 3D-printed contactors with internal heating and cooling elements (bottom). The fibers are easily loaded into the contactor without need of glue or epoxy, simplifying manufacturing and driving down costs (right).

This combination of fiber sorbent spinning, re-infusible polyamines, and 3D-printed modular housing provides several advantages that accelerate the translation of DAC materials out of the lab and into the field. Three scalable and modular components are combined into a system that is straightforward to build: (i) the contactor, which provides mechanisms for delivering air, removing/adding heat, and enabling vacuum; (ii) the fiber support, which provides high surface areas and low pressure drops via fiber alignment; and (iii) the active amine adsorbent that is infused into the fiber post-spinning, which enables geography-specific customization in terms of the amine composition and loading. Key challenges in the fabrication of heat-integrated hollow fiber sorbents are avoided, as are difficulties associated with 3D-printing high integrated module devices. Indeed, decoupling the adsorption contactor into two components (the fiber and the novel housing) captures advantages of an all-fiber or an all-3D-printed contactor, but with significant improvements in scalability.

The goal is to create a contactor platform that enables reductions in DAC CO₂ costs to \$100/tonne CO₂. Initial pre-screen TEA estimates from the project team suggests that a pathway to \$100/tonne exists (Figure 2). There are three major cost barriers that are often associated with DAC systems: the fans, the sorbent, and the heat input. Fan costs can be reduced via the creation of low pressure drop structures, which is an objective of this proposal. The sorbent costs can be reduced by rapidly cycling the adsorption system; beyond this, using commodity-scale materials wherever possible and ensuring that the materials have a lifetime of at least one year can further drive down costs. Both of these approaches are being pursued over the course of this project. The final major cost associated with DAC systems is the energy input to desorb the captured CO₂. These are ultimately bounded by the sorption or reaction enthalpy of the adsorbate-adsorbent systems. In the case of heating-induced desorption, avoiding losses associated with poor heat transfer, high thermal masses of contactor materials, and other inefficiencies can reduce the energetic requirements for the CO₂ desorption step. Monoliths are solid contactors composed of parallel channels resembling a honeycomb structure. Monoliths have several advantages over packed beds, such as higher mass transfer rates, good attrition properties, and lower pressure drop, but this is typically balanced against a lower loading of sorbent per unit volume. Monoliths can either be made entirely of the sorbent material, as when the sorbent material is directly extruded with no binder, or with some fraction of sorbent dependent on ratios of binder/sorbent/monolith body, as is the case with many deposition or growth methods (the latter is most common). Laminate-style contactors are essentially simpler forms of monoliths comprised of 1D slits. However, laminates are difficult to make reproducibly. The precision in manufacturing must be quite high to avoid slit bypass effects (less than 5% differences in channel size is required for uniform flow). This level of precision is difficult to scale, and thus laminate-style adsorbents are not often used in gas-separation processes. From a scalability perspective, monoliths are essentially made from high-quality ceramic materials one at a time using high-precision, multi-step robotic equipment.

This process has been commercialized, but the fundamentals of processing ceramics suggest that upper limits on manufacturing rates are being reached and that these rates are likely too low to drive down adsorption contactor costs by an order of magnitude.

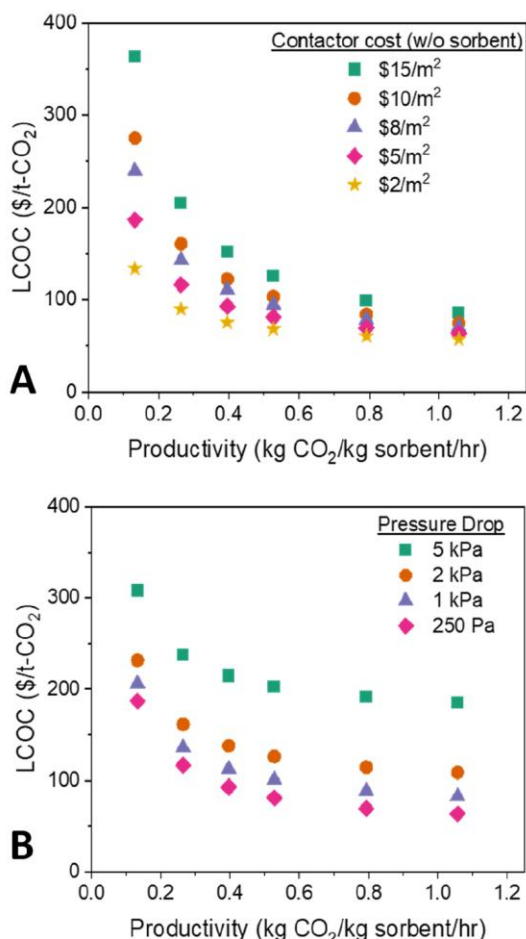


Figure 2: Pre-screen TEA results. Levelized cost of CO₂ capture as a function of productivity and (A) contactor cost or (B) pressure drop. Other parameters are held constant, including one-year sorbent lifetime, -65 kJ/mol heat of adsorption, 300 seconds cycle time, and 100,000 tonne CO₂/year captured.

The project team initially developed polymeric hollow fiber contactors that supported high loadings of CO₂ adsorbents. These materials are highly scalable and facilitated heat-integrated process configurations for post-combustion CO₂ capture. These “hollow fiber sorbents” have several important features that provide solutions to deleterious issues typically associated with post-combustion CO₂, and these solutions have proven to be transferrable to DAC technologies. For instance, CA fiber sorbents containing mesoporous silica impregnated with polymeric amines have been previously developed for DAC applications. In the case of fiber sorbents, the polymeric amines are added to the fibers in a simple, scalable post-spinning infusion step. The porous fiber support allows rapid gas access to the high loadings (~60 wt%) of sorbent particles within the fiber wall. Moreover, the fibers themselves act as structured packing elements, thus allowing for low gas pressure drops (~0.1 pounds per square inch [psi]/foot; Figure 3). This prior work demonstrated the ease at which these materials can be made in large quantities (400 g–1 kg scale per day), and desorption experiments highlighted the ability of these fibers to create CO₂ products that have purities in excess of 98 mol%. The adsorption and desorption chemistry, kinetics, and thermodynamics of the PEI-infused CA/silica sorbents are well understood. Carbon dioxide chemically binds to the PEI located in the silica pores within the CA matrix, and a temperature vacuum swing can be used to desorb the CO₂.

Traditionally, a dense barrier layer is installed on the bore-side of fiber sorbents, preventing mass transport from the shell side of the fibers to the bore, transforming the fibers into integrated “adsorbing heat exchangers.” The fibers are capable of rapid thermal cycles on the order of one to four minutes and have excellent heat management properties (Figure 4). However, the barrier layer addition is the most time-intensive and tedious step of the fiber sorbent fabrication process and prone to defect formation. The contactors proposed here entirely eliminate the need for a barrier layer through advanced 3D-printing technology, thus reducing the time, complexity, and fragility of the contactor manufacturing and assembly process.

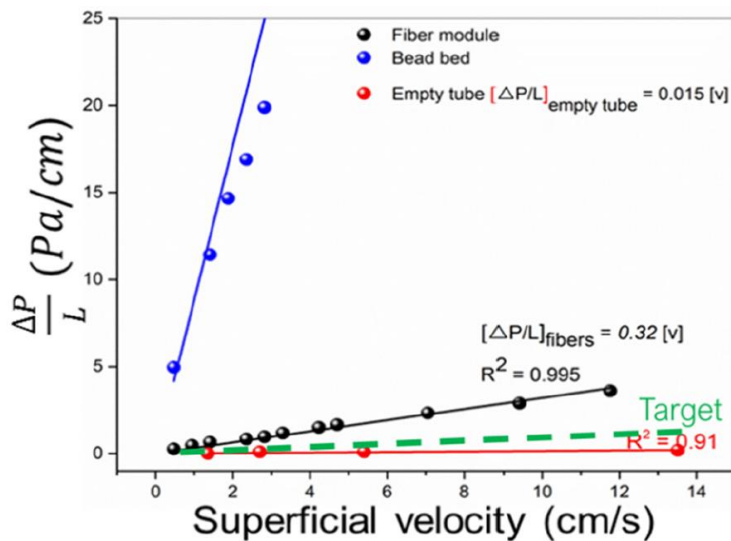


Figure 3: Pressure drop comparison and targets. Target pressure drop for this work is 250 Pa at 3 m/s air speed and is shown by the green line.

In recent years, 3D printing has been used as a method to directly print sorbent-containing monoliths. However, creating internal porosity inside the polymer-adsorbent structure and maintaining high sorbent loadings is a complex task, and the technology is further from scale-up than fiber sorbents. Importantly, printing commercially available polymers is a technologically mature process that has already been scaled up. By hybridizing fiber sorbents and 3D-printed contactors, the most complex aspects of each technology (barrier layer addition of fiber sorbents and internal porosity of 3D printing) are eliminated. Other limitations, including entrance pressure drop, sorbent degradation from direct steam contact, and low productivity due to inefficient heat management, can also be overcome via contactor design.

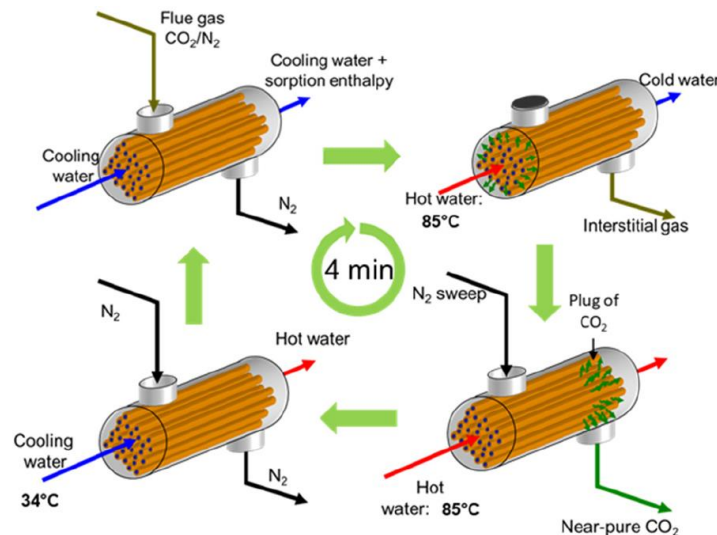


Figure 4: Rapid thermal swing adsorption cycle originally demonstrated for post-combustion CO₂ capture. Cycle times of 2.5–4.0 minutes have been demonstrated experimentally for 10% CO₂.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m ³	—	—
Bulk Density	kg/m ³	—	—
Average Particle Diameter	mm	—	—
Particle Void Fraction	m ³ /m ³	—	—
Packing Density	m ² /m ³	—	—
Solid Heat Capacity @ STP	kJ/kg-K	—	—
Crush Strength	kg _f	—	—
Attrition Index	-	—	—
Thermal Conductivity	W/(m-K)	—	—
Manufacturing Cost for Sorbent	\$/kg	\$3.00	\$1.50
Adsorption			
Pressure	bar	0.0004	0.0004
Temperature	°C	22°C	22°C
Equilibrium Loading	g mol CO ₂ /kg	1.2	1.4
Heat of Adsorption	kJ/mol CO ₂	-65	-65
CO ₂ Adsorption Kinetics	gmol/time	—	—
Desorption			
Pressure	bar	0.003 bar CO ₂	0.3 bar CO ₂
Temperature	°C	110°C	80°C
Equilibrium CO ₂ Loading	g mol CO ₂ /kg	<0.1	0.2
Heat of Desorption	kJ/mol CO ₂	65	65
CO ₂ Desorption Kinetics	gmol/time	—	—
Proposed Module Design		<i>(for equipment developers)</i>	
Flow Arrangement/Operation	—	laminar or shell-tube	
Flue Gas Flowrate	kg/hr	—	
Space Velocity	hr ⁻¹	60000	
Volumetric Productivity	gmolCO ₂ /(hr lab sorber bed)	1.25	
CO ₂ Recovery, Purity, and Pressure	% / % / bar	—	N/A ; 95%, 0.003 50%, 95%, 0.3
Adsorber Pressure Drop	bar	1000 Pa	<500 Pa
Degradation	% capacity fade/cycle	0.1	0.0005
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 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. 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 CO₂ in equilibrium with the sorbent. If the vapor phase is pure CO₂, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO₂.

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

Loading – The basis for CO₂ loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO₂ 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 CO₂ in CO₂-rich product gas; assuming targets are met.

Atmospheric Air Feed-Gas Assumptions – Update values below to describe the air feed-gas pressure, temperature, and composition entering the capture system:

Pressure	Composition						SO _x	NO _x
	CO ₂	H ₂ O	vol% N ₂	O ₂	Ar			
14.7 psia	0.04	variable	78.09	20.95	0.93		trace	trace

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO ₂	>300	100-150—
Cost of Carbon Avoided	\$/tonne CO ₂	—	—
Capital Expenditures	\$/tonne CO ₂	—	—
Operating Expenditures	\$/tonne CO ₂	—	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO₂ captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO₂ avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO₂ captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO₂ captured.

technology advantages

- High sorbents loading in hybrid fibers reduces cycle time.
- Low pressure drop design.
- 3D hybrid fibers are easy to manufacture and assemble, making these suitable for large-scale production.
- Reduce material costs and regeneration heat duty via the use of all-plastic components.

R&D challenges

- Develop sorbent with half-life target equal to one year via non-oxidative internal cooling.

status

GTRC is currently working on fiber fabrication, weaving, and integration into DAC contactors. Fiber bed and woven laminate modeling and validation work are also underway. The design and 3D-printed structure models of the shell-and-tube and plate-and-frame designs are also being developed.

available reports/technical papers/presentations

Ryan P. Lively, David S. Sholl, Matthew J. Realff, Joshua A. Thompson, Anne I. Ryan, Brandon J. Iglesias, “Hybridizing Heat-Integrated 3D Printed Modules with Mass Manufacturable, Low Pressure Drop Fiber Sorbents,” Project kickoff meeting presentation, Pittsburgh, PA, December 2021. <https://www.netl.doe.gov/projects/plp-download.aspx?id=12554&filename=Hybridizing+Heat-Integrated+3D+Printed+Modules+with+Mass+Manufacturable%2c+Low+Pressure+Drop+Fiber+Sorbents.pdf>.