Hollow Fiber Chemisorption Sorbent

primary project goal

The project objective is to provide a viable basic immobilized amine sorbent (BIAS)-based hollow chemisorption fiber sorbent (hollow-CHEFS) demonstrating carbon dioxide (CO_2) capture in diluted environments with a concentration near 400 parts per million (ppm). The hollow-CHEFS target is to achieve a 0.3 mmol CO_2/g capacity that is highly stable over at least three adsorption-desorption cycles. The resulting data will be used to complete a techno-economic analysis (TEA) to evaluate the feasibility of a rapid temperature swing adsorption (RTSA) process using the hollow-CHEFS.

technical goals

- Achieve a CO_2 capture of 0.3 mmol CO_2/g-fiber from simulated air by CHEFS and demonstrate at least three adsorption-desorption cycles.
- Complete a pre-screening analysis for a CHEFS-based rapid temperature swing CO_2 adsorption system.
- Scale-up hollow-CHEFS fabrication and incorporate into a two-fiber module that will be used to evaluate CO_2 capture under ambient air environments.

technical content

Direct air capture (DAC) removes CO_2 directly from the air and is an alternate complementary technology to the capture of CO_2 from large point sources. DAC has the advantage of addressing CO_2 emissions from all sources, including mobile sources, if the technology is operated on a sufficiently large scale. However, air capture presents the technical challenge of developing adsorbents that operate under near-ambient conditions and can extract CO_2 from ultra-dilute sources, 200–600 ppm in concentration. Silica-modified BIASs are promising materials for CO_2 capture from ultra-diluted gas steams such as ambient air. However, a typical BIAS suffers low mechanical strength, low and inefficient heat transfer through a solid bed, and hydrothermal degradation/amine leaching by water vapor.

Over the past few years, the National Energy Technology Laboratory (NETL) has provided the foundational knowledge and technology progress that overcomes the challenges associated with the maturation of BIAS design and application. These include (1) a crosslinked BIAS designed for high stability to water vapor; (2) outstanding CO_2 capture capacity from ambient air; (3) easy scale-up—commercial partner has made 18 kg sorbent at pilot scale; and (4) low energy cost and low waste production for material manufacture and operation. NETL has hollow fiber fabrication and test systems ready for BIAS-based hollow-CHEFS screening. NETL previously (1) synthesized a crosslinked BIAS resistant to organics leaching by precursor fiber sorbent dope solvent; (2) fabricated solid-CHEFS and hollow-CHEFS (Figure 1) for the capture of CO_2; and (3) initiated a non-disclosure agreement (NDA) process with the Georgia Institute of Technology for fiber synthesis scale-up work. Compared to up-to-date literature for immobilized amine sorbent-based fibers, the stability of NETL's pre-functionalized crosslinked material affords a more homogeneous (even amine distribution) and more reliable fiber that is prepared faster and simpler than those prepared by post-infusion.

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
CO_2 Capture from Air with Hollow Fiber Sorbents

participant:
National Energy Technology Laboratory–Research and Innovation Center

project number:
FWP-1022402 (Task 18)

predecessor project:
2020 Carbon Capture FWP

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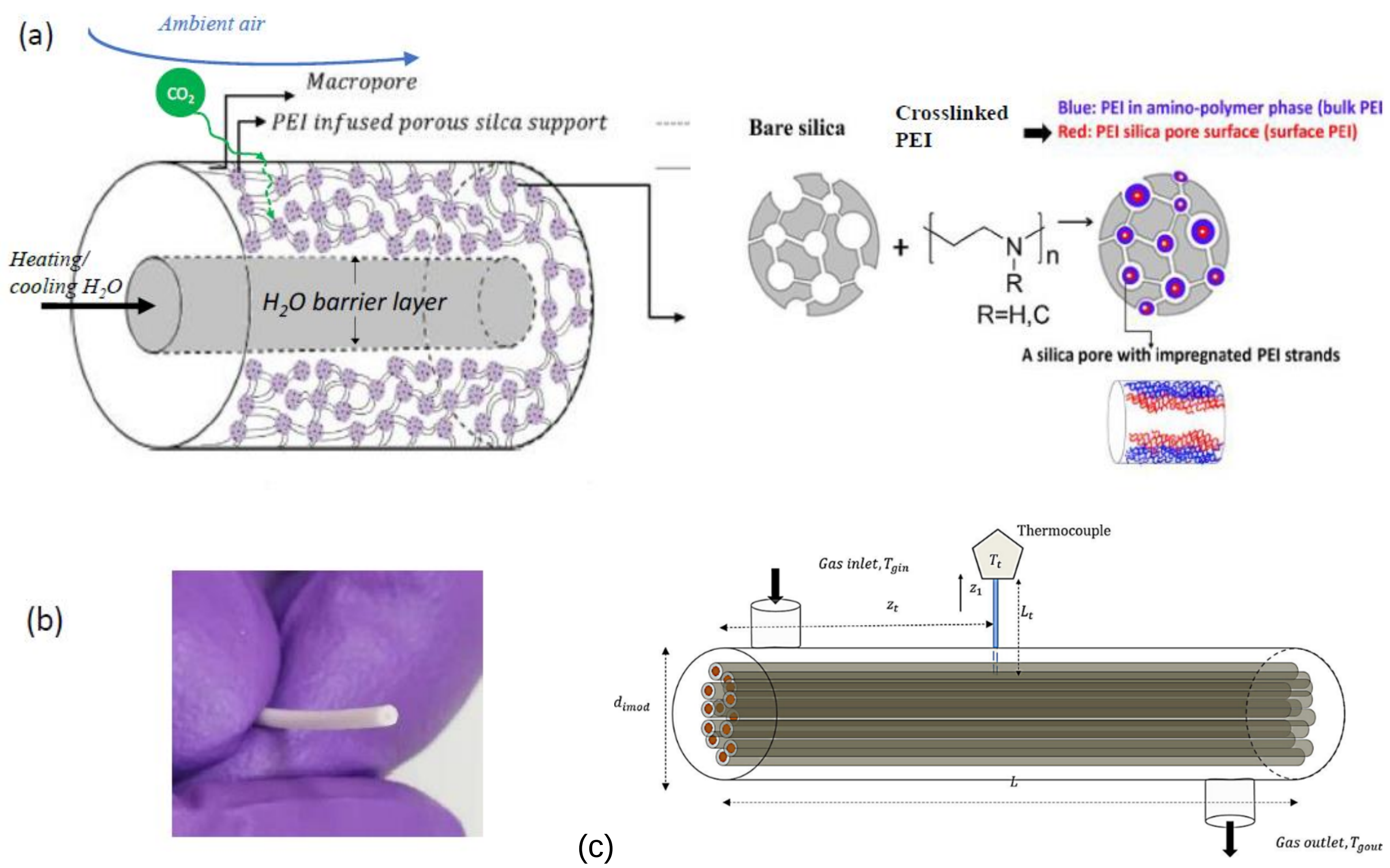

Figure 1: (a) General structure of the BIAS particles and envisioned test setup/CO_2 capture scheme for the hollow-CHEFS, (b) hollow-CHEFS photo image developed at NETL, and (c) schematic of a hollow-CHEFS membrane module[1].

In this project, the previously optimized BIAS is being incorporated into solid-CHEFS to rapidly define, screen, and optimize hollow-CHEFS components and performance. The hollow-CHEFS are complemented through a fabrication, characterization, and performance assessment for ambient air environments. Performance metrics and other information are being used to conduct a TEA of a system using CHEFS. The work is being pursued in two phases. Phase I, "Preliminary Hollow-CHEFS Fabrication and Optimization," comprises the fabrication and characterization of hollow-CHEFS, as well as evaluation under neat environments. Phase II, "Hollow-CHEFS Fabrication Scale Up," includes evaluating the feasibility of a hollow-CHEFS-based RTSA system for CO_2 capture under ambient air environments and scale-up hollow-CHEFS fabrication.

[1] J. Kalyanaraman, Y. Fan, R.P. Lively, W.J. Koros, C.W. Jones, M.J. Realff, Y. Kawajiri, Modeling and experimental validation of carbon dioxide sorption on hollow fibers loaded with silica-supported poly(ethylenimine), Chem. Eng. J., 259 (2015) 737-751.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m³	1.53	1.5
Bulk Density	kg/m³	52	52
Average Particle Diameter	mm	NA	NA
Particle Void Fraction	m³/m³	NA	NA
Packing Density	m³/m³	0.165	<0.2
Solid Heat Capacity @ STP	kJ/kg-K	1.2	1.2
Crush Strength	kg_f	NA	—
Attrition Index	-	NA	—
Thermal Conductivity	W/(m-K)	NA	—
Manufacturing Cost for Sorbent	$/kg	TBD	TBD
Adsorption			
Pressure	bar	1	1
Temperature	°C	35	0-45
Equilibrium Loading	g mol CO_2/kg	0.26	>0.1
Heat of Adsorption	kJ/mol CO_2	32.7	<60
CO_2 Adsorption Kinetics	gmol/g*min	0.019	0.01-0.03
Desorption			
Pressure	bar	1	1
Temperature	°C	105	90-120
Equilibrium CO_2 Loading	g mol CO_2/kg	0.26	<0.1
Heat of Desorption	kJ/mol CO_2	NA	<60
CO_2 Desorption Kinetics	gmol/g*min	0.054	—

Proposed Module Design	Units		*(for equipment developers)*	
Flow Arrangement/Operation	—		Parallel	
Flue Gas Flowrate	kg/hr		NA	
Space Velocity	hr^{-1}		NA	
Volumetric Productivity	$gmol_{CO2}/(hr\ l_{absorber\ bed})$		0.0063	
CO_2 Recovery, Purity, and Pressure	% / % / bar	>90	>95%	1 bar
Adsorber Pressure Drop	bar		low	
Degradation	% capacity fade/cycle		0.0009%	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		NA	

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.

Feed-Gas Assumptions –

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

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Polyethylenimine (PEI) function groups on CHEFS provide chemisorption sites for CO_2 molecules, as shown in Figure 1(a).

Sorbent Contaminant Resistance – Sorbent stability has been reported in previous publications listed below.

Sorbent Attrition and Thermal/Hydrothermal Stability – Sorbent stability has been reported in previous publications listed below.

Flue Gas Pretreatment Requirements – TBD.

Sorbent Make-Up Requirements – TBD.

Waste Streams Generated – N/A.

technology advantages

- The NETL BIAS has shown outstanding performance that offers superior resistance to amine leaching based on a crosslinked amine network. A BIAS-based hollow-CHEFS offers high mechanical strength, low pressure drop, and efficient heat transfer for ambient air carbon capture.
- The hollow-CHEFS offer ease in collecting for transport and disposal and are easy to scale-up.
- Other key advantages over current CHEFS are (1) the fiber's superior stability imparted by the crosslinked amine-epoxy network of the BIAS within, and (2) a single-step spinning approach, where the preparation method avoids a post-amine infusion impregnation step because the stable BIASs are spun directly into the fiber and do not leach their amines.

R&D challenges

- Optimization of BIAS-based hollow-CHEFS composition for diluted CO_2 capture.
- Fabrication of composite hollow-CHEFS and the corresponding large-scale manufacturing.
- Optimization of device and process to fully exploit hollow-CHEFS technology advantages.
- Evaluation of hollow-CHEFS at scales and under environments needed to transfer technology to market.

status

After optimizing mechanical strength and the BIAS formulation recipe for hollow-fiber CHEFS, the project team successfully demonstrated CHEFS possessing a stable CO_2 capture capacity of greater than or equal to 0.3 mmol CO_2/g-fiber over three adsorption-desorption cycles. The optimal solid CHEFS formula is being prepared as a hollow-CHEFS for testing to acquire data for an RTSA process modeling effort. The new dual-layer hollow fiber sorbent concept is being designed for DAC with a lumen-layer polymer coating to act as a water barrier inside the fiber. The lumen layer coating can be performed with the newly spun CHEFS hollow fiber sorbents.

available reports/technical papers/presentations

Wilfong, W.C., et al., "Scale-Up of Immobilized Amine Sorbent Pellets for Landfill Gas Upgrading, Using Benchtop and Pilot Equipment," Powder Technology 395 (2022), 243-254.

Wilfong, W. C.; Kail, B. W.; Howard, B. H.; Wang, Q.; Shi, F.; Ji, T.; Gray, M. L., Steam-Stable Basic Immobilized Amine Sorbent Pellets for CO_2 Capture Under Practical Conditions. ACS Appl. Mater. Interfaces 2019.

Wilfong, W. C.; Kail, B. W.; Howard, B. H.; Fernandes de Aquino, T.; Teixeira Estevam, S.; Gray, M. L., Robust Immobilized Amine CO_2 Sorbent Pellets Utilizing a Poly(Chloroprene) Polymer Binder and Fly Ash Additive. Energy Technology 2017, 5 (2), 228-233.

Wilfong, W. C.; Kail, B. W.; Jones, C. W.; Pacheco, C.; Gray, M. L. Spectroscopic Investigation of the Mechanisms Responsible for the Superior Stability of Hybrid Class 1/Class 2 CO_2 Sorbents: A New Class 4 Category. ACS Appl. Mater. Interfaces 2016, 8 (20),12780-91.

Wilfong, W. C.; Gray, M. L.; Kail, B. W.; Howard, B. H., Pelletization of Immobilized Amine Carbon Dioxide Sorbents with Fly Ash and Poly(vinyl chloride). Energy Technology 2016, 4 (5), 610-619.

Wilfong, W. C.; Kail, B. W.; Gray, M. L., Rapid Screening of Immobilized Amine CO_2 Sorbents for Steam Stability by Their Direct Contact with Liquid H_2O. ChemSusChem 2015, 8 (12), 2041-5.