Direct Air Capture Using Trapped Small Amines in Hierarchical Nanoporous Capsules on Porous Electrospun Fibers

primary project goal

The State University of New York (SUNY)-Buffalo is teaming with Arizona State University (ASU) and Gas Technology Institute (GTI) to develop an innovative sorbent comprised of trapped small amines in hierarchical nanoporous capsules (HNCs) embedded in porous electrospun fibers (PEFs) for direct air capture (DAC). The effective encapsulation of amines in HNCs will enable high sorbent stability and the innovative PEF macroscopic scaffold will allow for fast exposure of sorbent material to air. Research efforts involve the tailoring of both sorbent and PEF materials to achieve a compact system for DAC with high capacities for carbon dioxide (CO_2) at concentrations typically available in air and at near-ambient conditions.

technical goals

- Develop HNCs with trapped small amines sorbents (SUNY-Buffalo).
- Incorporate the sorbent material into PEFs (Arizona State University).
- Test the PEFs with the embedded sorbent material to collect data on CO_2 working capacity and adsorption/desorption rates (SUNY Buffalo).
- Utilize the experimental data obtained to perform high-level process design/analysis.
- Develop an understanding of breakdown pathways; confirm the revolutionary stability of the new solvent using various laboratory techniques.

technical content

An innovative sorbent structure is being designed to directly capture CO_2 from the air using trapped small amines (Figure 1). This technology differs from the sorbents for CO_2 capture at higher CO_2 partial pressure by physical adsorption, in that approximately 400 parts per million (ppm) CO_2 in the air is adsorbed into the HNCs and reacts with trapped amines, following the reactions below:

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Amine Sorbent Embedded in Porous Electrospun Fibers for DAC

participant:
State University of New York (SUNY)-Buffalo

project number:
FE0031969

predecessor projects:
N/A

NETL project manager:
Dustin Brown
dustin.brown@netl.doe.gov

principal investigator:
Miao Yu
State University of New York (SUNY)-Buffalo
Myu9@buffalo.edu

partners:
Arizona State University; Gas Technology Institute (GTI)

start date:
02.01.2021

percent complete:
60%

Dry condition

$$CO_2 + 2RNH_2 \leftrightarrow RNH_3^+ + RNHCOO^-$$

$$CO_2 + 2R_1R_2NH \leftrightarrow R_1R_2NH_2^+ + R_1R_2NHCOO^-$$

Moisture condition

$$CO_2 + R_1R_2NH + H_2O \leftrightarrow \underset{\text{bicarbonate}}{R_1R_2NH_2{}^+HCO_3^-} \leftrightarrow \underset{\text{carbonate}}{R_1R_2NH_2{}^+CO_3^{2-}}$$

$$CO_2 + R_1R_2R_3N + H_2O \leftrightarrow R_1R_2R_3NH^+HCO_3^- \leftrightarrow R_1R_2R_3NH^+CO_3^{2-}$$

Therefore, theoretically, two amine groups can bond with one CO_2 molecule under dry conditions and one amine group with one CO_2 under wet conditions. Small amines enable high amine efficiency (molar ratio of the adsorbed CO_2 to the total amine groups, CO_2/nitrogen [N]) and thus high CO_2 adsorption capacity from the air, while HNCs prevent amine loss and drastically extend amine lifetime. Small-sized (2–5 μm), macroscopic scaffold PEFs allow fast external mass transfer rates and minimize CO_2 adsorption capacity loss via high porosity. In addition, optimized packing of PEFs in a mat (Figure 1) ensures high sorbent packing density while balancing the air flow rate with the energy consumption from the blower.

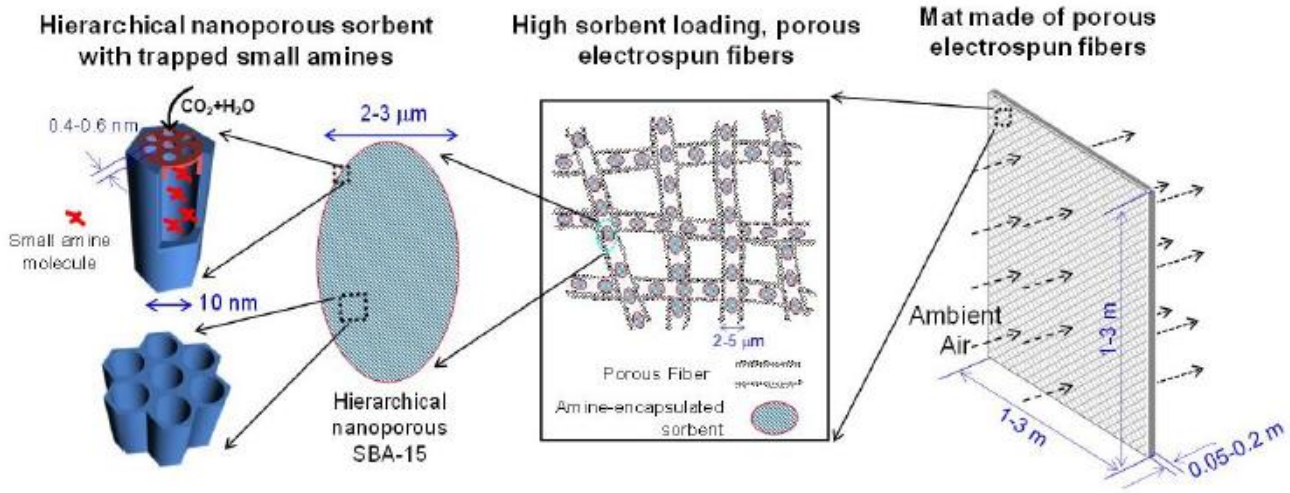

Figure 1: Diagram of the transformational adsorbent for direct capture of CO_2 from air.

These mats are effectively utilized in a process for direct CO_2 capture from the air, as shown in Figure 2. For each operation unit, there are two components: a blower and a sorbent mat equipped with heat exchanger, heating wires, and a hinged cover for mat sealing. Each unit has three operational modes: adsorption, preheat, and desorption. During the process, each unit finishes one operational mode and enters another operational mode. Note that depending on the available sources of energy input, desorption energy can be provided by either electricity or waste heat.

Amine-functionalized sorbents and ion-exchange resins are the promising sorbents reported in the literature for DAC; the former can achieve much higher CO_2 purity (greater than or equal to 98 vol.%) than the latter (less than 5 vol.%). In amine-based sorbents, large surface-area porous substrates are usually used to increase the loading of amines and thus the amine group density; amines with different molecular structures are also used to increase efficiency. The combination of the amine group density and amine efficiency leads to a high CO_2 adsorption capacity. Depending on the interaction between the amines and substrates, three types of sorbents (Types I: physical impregnation; Type II: covalent tethering via silane linkage; Type III: direct covalent tethering via in situ polymerization) can be prepared, as shown in Figure 3.

Figure 4 plots the CO_2 equilibrium capacity versus amine efficiency of the sorbents described above. As shown, the efficiencies are lower than 0.2, far below the theoretical 0.5 (dry condition) and 1 (moisture condition). In the sorbent structure being designed in this project, small amines are featured with fast reaction kinetics and high concentration of amine groups and are expected to have high CO_2 capacity and fast adsorption rate, making them ideal amines for DAC. In addition, small amines typically show high amine efficiency (e.g., diethanolamine [DEA] shows an efficiency of 0.407, very close to the theoretical value [0.5]). In the technology for this project, small amines are loaded and trapped in SBA-15 (a mesoporous form of silica with approximately 10 nm pores and a high surface area of 600–1,000 m^2/g). Assuming 30–50 wt.% amine loading, 0.4–0.6 amine efficiency (in humid air), and four amine groups in one amine molecule (molecular weight: 200 g/mol), the estimated CO_2 capacity of the sorbent is in the range of 3.4–13.3 mmol CO_2/g (Figure 4). This is much higher than reported results, demonstrating the great potential of small amines for DAC.

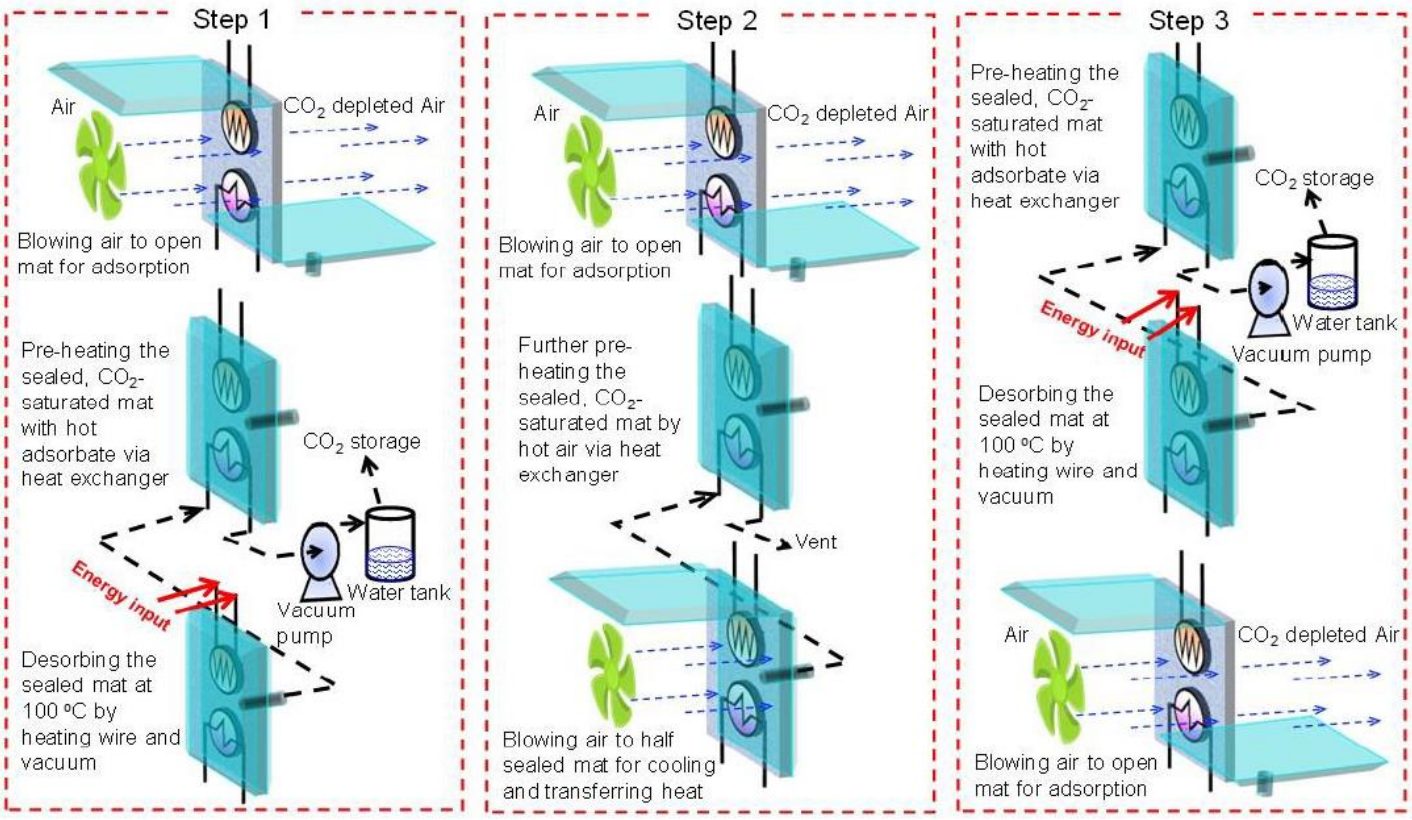

Figure 2: Diagram of the process for DAC.

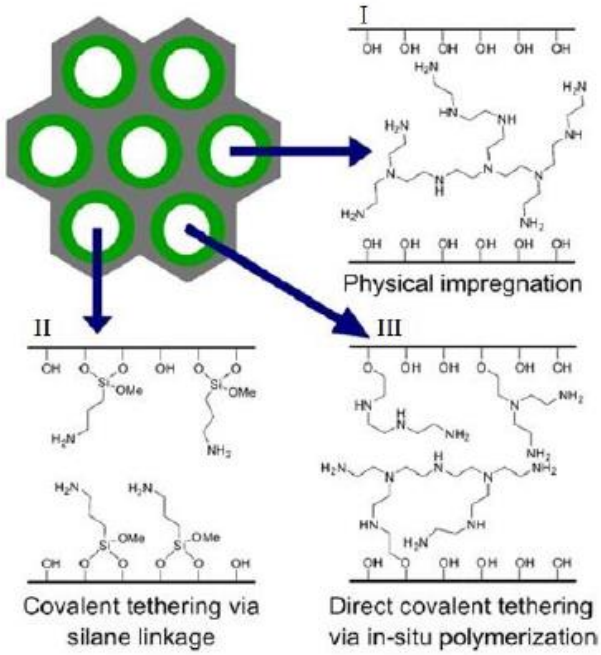

Figure 3: Schematic of three types of amine-based sorbents for DAC.

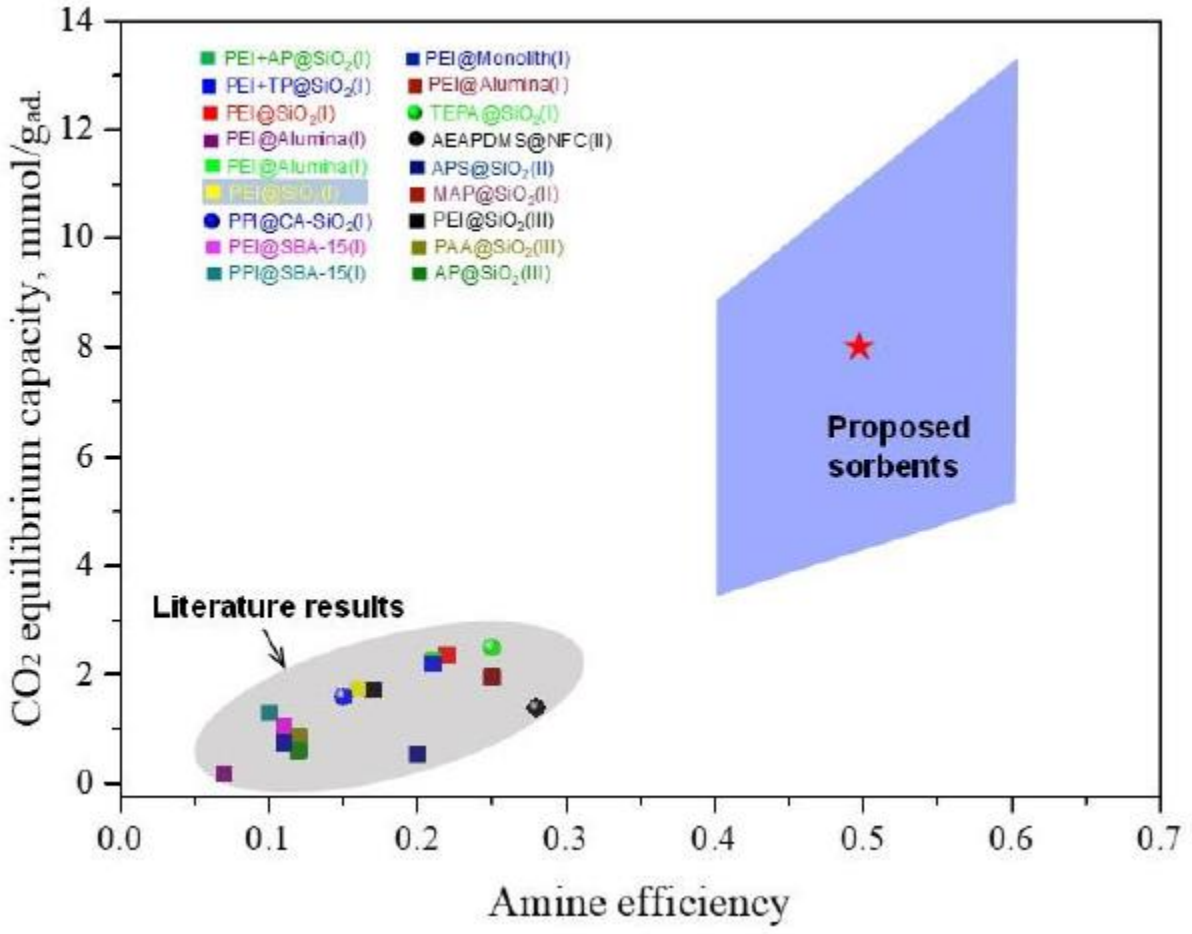

Figure 4: Comparison of reported sorbent materials and projected performance of the proposed sorbent for DAC. Red star represents the average performance of the proposed sorbent.

Small amines, such as monoethanolamine (MEA) and DEA, have been widely used for solvent-based CO_2 capture/removal due to their fast reaction rate with CO_2 and high CO_2 capacity. Small amines on porous substrates exhibited excellent CO_2 adsorption performance: fast CO_2 uptake rate, high amine efficiency (e.g., 0.4–0.6 for DEA), high CO_2 adsorption capacity resulting from the high nitrogen to carbon (N/C) ratio, high primary amine concentration, and low viscosity. However, high volatility of small amines led to severe loss during the sorbent regeneration at high temperature, which significantly restricted their application in sorbent materials. Physically trapped small amines in porous structure using an innovative interfacial reaction process is expected to resolve the amine loss issue.

SUNY-Buffalo recently developed a facile and scalable interfacial reaction process to deposit ultra-thin, microporous coatings on nanoporous substrates for trapping/encapsulating functional species. A mesoporous silica, SBA-15, was used as the porous substrate, and a microporous coating layer of titanium dioxide (TiO_2) was deposited by the liquid-liquid interfacial reaction between ethylene glycol (EG) and titanium chloride ($TiCl_4$) and subsequent calcination to remove the organic compound. Microporous coating pore size can be adjusted by adding different amounts of water in EG and by changing calcination conditions. The microporous TiO_2 coating on SBA-15 was characterized by transmission electron microscopy (TEM), which showed that a continuous, ultra-thin TiO_2 layer (30–50 nm) can be seen on SBA-15 after the coating process. Thermogravimetric analysis (TGA) showed the material was thermally stable to at least 300°C (data not shown). These results clearly showed that hierarchical SBA-15 can be formed by facile interfacial reaction process and can effectively trap functional species. To trap small amines with molecular size of 0.5–0.8 nm, a well-designed interfacial reaction process is applied to form coatings with pores larger than CO_2 (0.33 nm) and H_2O (0.26 nm), but smaller than the amine molecules. Because of the strong affinity of CO_2 with small amines, the adsorption selectivity of CO_2 over N_2 is expected to be high. Studies have shown the CO_2 working capacity is much higher than the amount of N_2 adsorbed. Therefore, very high CO_2/N_2 selectivity can be achieved, and CO_2 purity higher than 99% can be obtained after sorbent regeneration.

HNCs can be fabricated by utilizing interfacial reactions followed by calcination. Depending on metal precursors and organic precursors, a hybrid dense layer with different composition can be formed and subsequently converted into microporous coatings by removal of the organic compound upon calcination. The team fine-tuned coating pore size by changing the calcination conditions and adding different amounts of H_2O into EG; coating pore size was characterized by N_2 adsorption at 77K.

Recently, ASU has developed PEFs embedded with various sorbent materials (metal-organic frameworks [MOFs], zeolites, and resin particles) and applied them for separation applications, including DAC. Matrimid (glass transition point: 320°C) and polystyrene (glass transition point: 100°C) with excellent thermal, mechanical, and chemical stabilities have been used as the PEF materials. PEFs with different porosity, morphologies, and post-synthetic modifications have been prepared. The technique to controllably create porosity on PEFs, called solvothermal polymer additive removal (SPAR), has been demonstrated in a preliminary study of uniaxial electrospinning technique. The mechanical and chemical strength of PEFs embedded with sorbent materials can also be improved by a cross-linking process that has been previously demonstrated. In previous work, PEFs embedded with ion-exchange resin have been demonstrated for DAC application by moisture swing adsorption and showed the highest cycle capacity with an uptake rate of 1.4 mmol CO_2.

TABLE 1: ATMOSPHERIC AIR FEED-GAS CONDITIONS

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

Chemical/Physical Sorbent Mechanism – Trapped amines inside the hierarchical nanoporous capsules react with low concentration of CO_2 (~400 ppm) in the air for high-capacity CO_2 capture.

Sorbent Contaminant Resistance – Resistance of the sorbent to trace sulfur oxide (SO_X) and nitrogen oxide (NO_X) is not clear at this stage, but resistance to other components is expected to be good.

Sorbent Attrition and Thermal/Hydrothermal Stability – Sorbent attrition is not clear at this stage. The thermal/hydrothermal stability of the sorbent is expected to be excellent under DAC operation.

Flue Gas Pretreatment Requirements – Particulate removal from air using filters is required to prevent sorbent mat from plugging.

Sorbent Make-Up Requirements – There are no sorbent make-up requirements for the process. The sorbent is expected to have a lifetime of five years before it needs to be replaced.

Waste Streams Generated – Depleted air stream and condensed liquid water.

Proposed Module Design – Please refer to Figure 2.

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	$/tonne CO_2	311	—
Cost of Carbon Avoided	$/tonne CO_2	—	—
Capital Expenditures	$/tonne CO_2	24	—
Operating Expenditures	$/tonne CO_2	259	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

TABLE 3. COST ASSESSMENT OF THE SORBENT TECHNOLOGY

Line	Items	Units	Value
1	Major Equipment (blower, heat exchanger, vacuum pump, and compressors) Cost	$	506,921
2	Projected Lifetime of the Equipment	years	15
3	Major Equipment Annual Costs (= line 1/line 2)	$/year	33,795
4	Utility Costs for Major Equipment (compressor, heater, vacuum)	$/year	776,480
5	Total Major Equipment and Utility (= line 3+line 4)	$/year	810,275
6	CO_2 Capture Rate	tonne/hr	0.3425
7	Major Equipment and Utility Cost Per Tonne CO_2 Produced	$/tonne CO_2	270
8	Cost of PEF Embedded with HNC Sorbent Particles	$/tonne CO_2	13.0
9	Total Capital Costs (total of lines 7 and 8)	$/tonne CO_2	283
10	Total Operating & Maintenance Costs (10% of line 9)	$/tonne CO_2	28.3
11	Total CO_2 Production Costs (total of lines 9 and 10)	$/tonne CO_2	311

Table 3 indicates that the estimated sorbent DAC cost of **$311/tonne** of CO_2 captured is only 44% of Climeworks' sorbent technology (~$700/tonne). Note that the lower cost is mainly due to the high CO_2 adsorption capacity[1,2] of this project's sorbent, as Sholl et al.[3] also reported that the CO_2 capture cost in DAC would decrease by 43–46% when the CO_2 adsorption capacity of the sorbent is doubled. Further analysis indicates this project's CO_2 capture cost could decrease to **$169/tonne** if waste heat is used for desorption instead of electricity. A more comprehensive cost assessment will be performed at the end of the project during the high-level design and analysis based on the experimental data and kinetic parameters collected.

1. Wurzbacher, J. A., Gebald, C., Piatkowski, N. & Steinfeld, A. Concurrent Separation of CO_2 and H_2O from Air by a Temperature-Vacuum Swing Adsorption/Desorption Cycle. *Environ. Sci. Technol.* **46**, 9191–9198 (2012).
2. Wurzbacher, J. A., Gebald, C. & Steinfeld, A. Separation of CO_2 from air by temperature-vacuum swing adsorption using diamine-functionalized silica gel. *Energy Environ. Sci.* **4**, 3584–3592 (2011).
3. Kulkarni, A. R. & Sholl, D. S. Analysis of Equilibrium-Based TSA Processes for Direct Capture of CO_2 from Air. *Ind. Eng. Chem. Res.* **51**, 8631–8645 (2012).

Calculations Basis – The operational process (Figure 2) was translated into a compact process design (Figure 5) and modeled in ASPEN using the project team's preliminary experimental data, projected sorbent performance, and literature data for capital cost and energy calculation.[4,5] Three groups of sorbent mats are included in the design, and each group has six steps to finish one cycle.

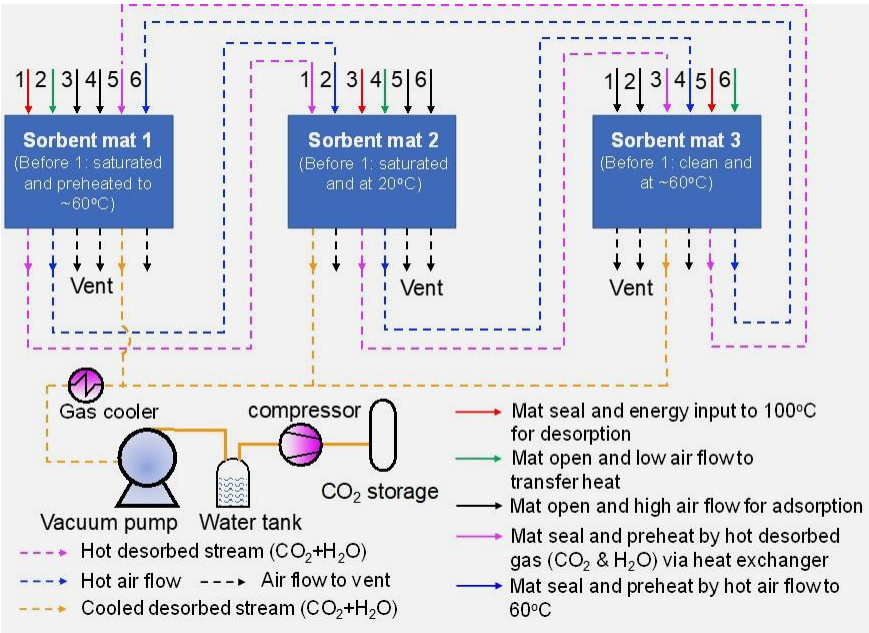

Figure 5: Proposed process flow for DAC.

4. Wurzbacher, J. A., Gebald, C., Brunner, S. & Steinfeld, A. Heat and mass transfer of temperature–vacuum swing desorption for CO_2 capture from air. *Chem. Eng. J.* **283**, 1329–1338 (2016).
5. Peters, M. S. & Timmerhaus, K. D. *Plant design and economics for chemical engineers*. (McGraw-Hill Press, 1991).

Scale of Validation of Technology Used in TEA – The basis for the cost assessments is 3,000 tonnes captured CO_2/year (3,000 tonne/year was selected for this preliminary cost assessment to be compared to published data on the Climeworks technology[4]).

Qualifying Information or Assumptions – In the assessments, the lifetime for the PEF fiber sorbent was assumed to be five years. The other capital equipment was assumed to have a 15-year operating life. The total annual operating and maintenance costs were assumed to be 10% of the total capital costs.

technology advantages

- Small amines with molecular weight less than or equal to 200 g/mol trapped in HNCs enable fast reaction kinetics, high amine efficiency, and high CO_2 sorption capacity for dilute CO_2 (~400 ppm) in the air.
- Thin coating with molecular-sized pores (0.4–0.6 nm pores) effectively prevents small amines from leaking during the heat regeneration process and thus achieving good sorbent stability.
- Innovative macroscopic scaffold with small fiber size (2–5 μm) and porous features allows high sorbent loading and fast and effective exposure of sorbent material to the air.

R&D challenges

- Amine Loading and Sealing: Developing effective amine loading and sealing processes on samples with microporous coating; conducting amine loss evaluation.
- PEFs Loaded with Sorbent: Optimizing electrospinning conditions to incorporate sorbent materials; characterizing composite sorbent structure.

status

SUNY-Buffalo has prepared coated SBA-15 by pore filling and precursor loading via vapor condensation and liquid-phase preparation methods. Microporous coating deposition processes, based on both vapor condensation and liquid filling, were developed; crystal violet (CV) rejection suggested that microporous coatings with pore sizes smaller than 1.3 nm

were successfully deposited; and O-xylene uptake indicated less than 0.7-nm coating pores were formed under optimized coating preparation conditions. Further studies are being conducted to modify samples with microporous coating by molecular layer deposition in order to fine-tune the coating pore size, and CO_2 sorption performance evaluation will be conducted on the newly prepared sorbents that are incorporated in PEFs.

available reports/technical papers/presentations

Miao Yu, “Direct Air Capture Using Trapped Small Amines in Hierarchical Nanoporous Capsules on Porous Electrospun Hollow Fibers,” Direct Air Capture kickoff meeting presentation, Pittsburgh, PA, February 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11097&filename=Direct+Air+Capture+Using+Trapped+Small+Amines+in+Hierarchical+Nanoporous+Capsules+on+Porous+Electrospun+Hollow+Fibers.pdf*.

Miao Yu, Bin Mu, Shiguang Li “Direct Air Capture Using Trapped Small Amines in Hierarchical Nanoporous Capsules on Porous Electrospun Hollow Fibers,” Project kickoff meeting presentation, Pittsburgh, PA, April 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11099&filename=Direct+Air+Capture+Using+Trapped+Small+Amines+in+Hierarchical+Nanoporous+Capsules+on+Porous+Electrospun+Fibers.pptx*.

Miao Yu, Bin Mu, “Direct Air Capture Using Trapped Small Amines in Hierarchical Nanoporous Capsules on Porous Electrospun Hollow Fibers,” NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Yu.pdf*