Gradient Amine Sorbents for Low Vacuum Swing Carbon Dioxide Capture at Ambient Temperature

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Amine-Based Aerogel Sorbents for DAC

participant:
University of Akron

project number:
FE0031958

predecessor projects:
N/A

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partners:
Aspen Aerogels Inc.

start date:
01.01.2021

percent complete:
67%

primary project goal

The University of Akron, in partnership with Aspen Aerogels Inc., is developing novel solid sorbent materials that can be regenerated in a low vacuum swing adsorption (VSA) process with greater performance than current state-of-the-art materials for the capture of carbon dioxide (CO_2) from air.

technical goals

- Prepare amine-functionalized aerogel.
- Fabricate and test a hierarchical structure of gradient amine sorbent on carbon fiber.
- Construct a VSA test apparatus.
- Conduct sorbent characterization and performance testing.
- Conduct high-level process design and analysis to evaluate feasibility of applying the new sorbents in a direct air capture (DAC) system.

technical content

A hierarchical structure of gradient amine sorbent, which allows CO_2 to adsorb in the form of weakly adsorbed CO_2, will be constructed in bead form. The weakly adsorbed CO_2 can then be regenerated from the sorbent by applying a low vacuum. The novel sorbent allows VSA to be operated at ambient temperature without a significant energy demand, eliminating the energy-intensive heating and cooling cycle in temperature swing adsorption (TSA) processes. Operation at ambient temperature also eliminates the possibility of thermal degradation of sorbents, leading to a prolonged lifetime of the sorbent and minimizing maintenance costs to provide a cost-effective approach for DAC.

To mitigate the corrosive nature of liquid amine sorbents and solvent loss, and to enhance the rate of adsorption/desorption, immobilization of organic amine on high surface area/porous solid has been shown to hold a great promise for replacing the liquid amine process. Many studies have suggested the mechanism of CO_2 adsorption/desorption on solid amines resembled that of CO_2 adsorption in liquid amines. The overall reactions involved in the adsorption/desorption process can be described by the following:

$$2\ R_1R_2NH + CO_2 \leftrightarrow R_1R_2NH_2^+ + R_1R_2NCOO^- \text{ (carbamate ion) (1)}$$

$$R_1R_2NH + H_2O + CO_2 \leftrightarrow R_1R_2NH_2^+ + HCO_3^- \text{ (bicarbonate) (2)}$$

$$R_1R_2NH + CO_2 \leftrightarrow R_1R_2NCOO^-H^+ \text{ (carbamic acid) (3)}$$

In absence of water (H_2O) vapor, one mole of CO_2 reacts with two moles of amine to form carbamate by reaction (1); in presence of H_2O vapor, one mole of CO_2 reacts with one mole of amine to form bicarbonate by reaction (2). Recently infrared spectroscopic studies conducted by the University of Akron (Akron), as well as a number of in-depth spectroscopic studies, have shown that CO_2 adsorbs on the immobilized amine (i.e., solid amine) as carbamic acid and ammonium carbamate ions (i.e., the same type of carbamate ion as the liquid organic amine in the aqueoussolution). Because of an insufficient amount of adsorbed H_2O and the lack of mobility of amine sites, bicarbonate was produced at a negligible level on immobilized amine.

Development of Pellets for TSA with Fixed Bed and Fluidized Bed

Akron has developed a number of immobilized amine sorbents for TSA processes. Collaboration with Aspen Aerogels (Aspen) led to the development of a robust sulfur-resistance sorbent for TSA. Akron has also developed a sorbent for fixed and fluidized beds. The infrared spectra in Figure 1 shows these sorbents containing primary amine at 3,297 and 3,355 cm^{-1}. The secondary amine at 3,297 cm^{-1} capture of these sorbents and their CO_2 binding energy, as well as their resistance to degradation, are strongly dependent on many factors, such as the type of amine (i.e., primary, secondary, and tertiary) and their loading, overlapped with the asymmetric vibration of the primary amine. The sulfur resistant amine (KD-SRE) sorbent containing Aspen's hydrophobic aerogel produces a smaller water band in the 3,100–3,700 cm^{-1} region. These results show Aspen's amine-functionalized aerogel is able to impart hydrophobicity to the amine sorbent. The carbon dioxide adsorbed in the form of ammonium ions at 1,668 cm^{-1} and carbamate ion at 1,510 cm^{-1}. Evacuation of adsorbed CO_2 at 8 pounds per square inch (psi) at 25℃ for three minutes by vacuum led to a decrease in the infrared intensity of adsorbed CO_2, indicating a weakly adsorbed CO_2, which may be removed without heating. More than 60% of adsorbed CO_2 has to be removed from the temperature program desorption (TPD). The sorbent is then returned to the initial state, as shown by its infrared spectra, which exhibited the same feature as the initial spectra. The key feature of TSA sorbents is the requirement of heating to desorption temperature for sorbent regeneration.

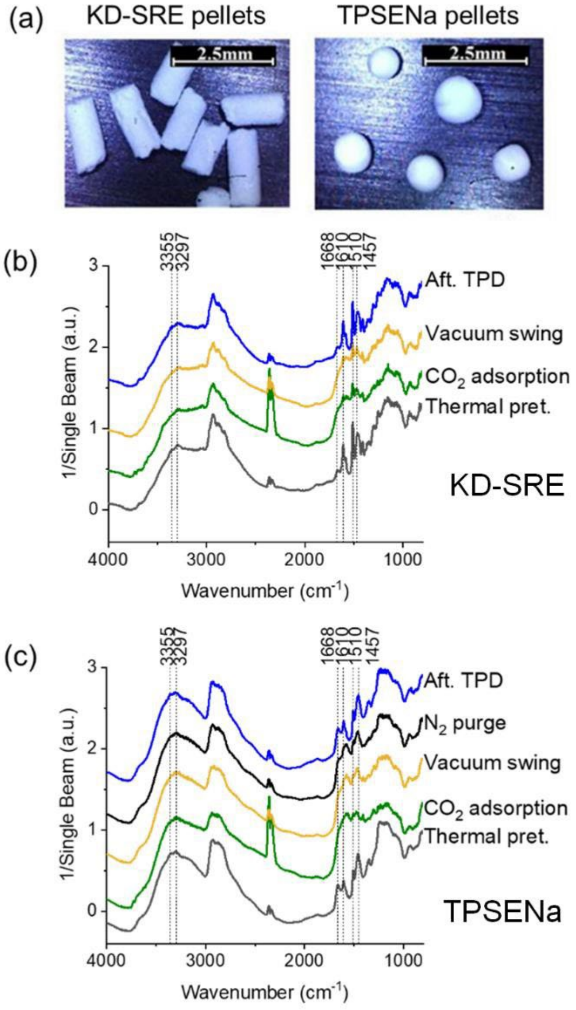


Figure 1 (a) KD-SRE pellets: a sulfur-resistant amine sorbent prepared by incorporation of TPSENa with Aspen's aerogels; TPSENa pellets: a high attrition-resistance sorbent that contains tetraethylenepentamine (TEPA), polyethylene glycol (PEG), epoxy, Na_2CO_3, and SiO_2; (b) (c) infrared spectra.

Vacuum Swing Adsorption

Akron devised a vacuum swing CO_2 capture process for the sorbent that allows CO_2 to adsorb in the form of weakly adsorbed CO_2. Figure 2 compares Akron's VSA process with the TSA process. VSA significantly simplifies the process by eliminating the highly energy-intensive heating and cooling process. Operation at ambient temperature further eliminates the possibility of thermal degradation of the amine sorbents.

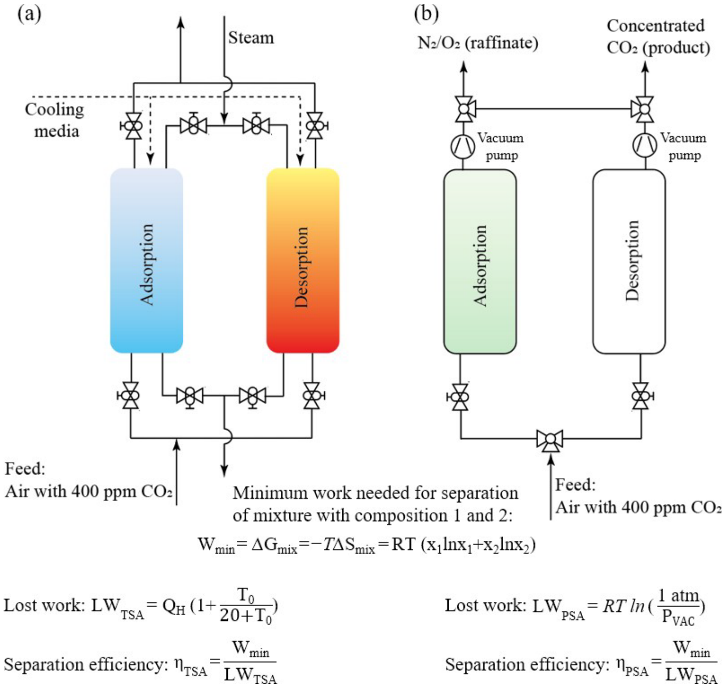
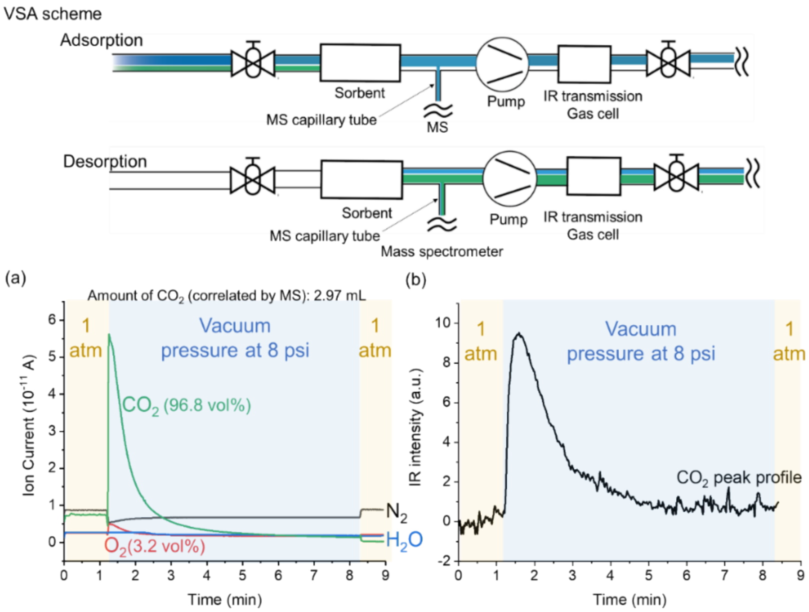


Figure 2 Temperature swing adsorption versus vacuum swing adsorption. (T_0 = heating temperature).

Thermodynamics for TSA and VSA

Minimum work (Wmin) for separation of CO_2 from air is the same for both TSA and PSA. The thermodynamic efficiency of the processes are determined by lost work temperature swing adsorption (LW_{TSA}) and lost work pressure swing adsorption (LW_{PSA}). The absence of thermal energy term (Q_H) in the separation efficiency of the pressure swing adsorption (ηPSA) equation leads to lost work being greater than that of the TSA (ηPSA > ηTSA). LW_{PSA} is a result of using a mechanical pump to evacuate gaseous species to drive the desorption of weakly adsorbed CO_2. Lowering the pressure from 1 atm (760 torr) to 8 psi (413 torr), LW_{PSA} = 1,563 kJ/mol of gas, the operation efficiency can vary from more than 90% to less than 80%, depending on the level of vacuum. Therefore, decreasing the solid volume (i.e., the amount of gas to be evacuated) in the VSA unit can increase the efficiency of the VSA system; however, it will affect the kinetics of adsorption and desorption, as well as the pressure drop of the air flow during CO_2 adsorption. Akron has also observed a 2–3°C drop in temperature during CO_2 desorption of weakly adsorbed CO_2 and then a return to the initial sorbent bed temperature under argon purge, revealing the sorbent bed adsorbs the energy from the ambient. Thus, it is essential to incorporate highly thermal co-conductive materials in the sorbent to facilitate the heat transfer and desorption.

Figure 3 illustrates the VSA results on previous TSA sorbents that were selected for their high capacity of weakly adsorbed CO_2 for the preliminary study. In a typical VSA, CO_2 adsorption was carried out by flowing CO_2-containing stream over the sorbent bed. Instead of heating for sorbent regeneration and collection of both weakly and strongly adsorbed CO_2 with steam or purge gas, VSA removes weakly adsorbed CO_2 at ambient temperature with low pressure. In this specific experiment, closing the inlet valve of the sorbent bed and applying the low pressure at 8 psi led to the removal of weakly adsorbed CO_2. (Note that 1 atm=14.7 psi) Figure 3(a) shows the mass spectrometer (MS) composition profile of the gaseous stream during evacuation of weakly adsorbed CO_2 on a KD sorbent (an amine-functionalized aerogel prepared by Aspen Aerogels Inc.). Figure 3(b) shows the infrared profile of gaseous CO_2 emitted from the vacuum pump. The infrared profile of CO_2 is broader than the MS profile of CO_2 because of the transportation lag resulting from the gaseous line and the vacuum pump. The MS profile showed a highly concentrated CO_2 mole fraction of 96.8%, with a low concentration of nitrogen (N_2) and oxygen (O_2), as determined by the areas under their corresponding MS profiles in Figure 3(a), demonstrating the technical feasibility of VSA using sorbent with weakly adsorbed CO_2.



Profile of CO_2, O_2, N_2 and H_2O form quadrupole mass analyzer during vacuum swinging

IR intensity profile of CO_2 peak measured by gas phase transmission cell after the vacuum pump

Sample	Capture capacity (mmol/g)	Weakly adsorption percentage	
		Vacuum swinging	N_2 purge
TPSENa	3.4	18.84%	24.76%
KD-240-24-9B sorbent	2.0	55.55%	/

Figure 3. VSA Scheme—Adsorption by flowing a 0.04% CO_2 stream over a sorbent bend; desorption of weakly adsorbed species by vacuum. The concentration profiles of the effluent form adsorption bed under 8 psi vacuum determined by (a) MS before vacuum pump, (b) infrared gas cell after vacuum pump. (1 atm=14.7 psi)

CO_2 Capture VSA Unit

The need for processing a large volumetric flow of air with a dilute concentration of CO_2 around 420 parts per million (ppm) presents a monumental challenge to the development of a sustainable and cost-effective CO_2 capture process. The current liquid monoethanolamine (MEA) technology is cost-effective for separation of CO_2 from natural gas in liquefaction and ammonia synthesis processes because of the value of their end products. This technology, when applied for capture of CO_2 from coal-fired power plants, increases the cost of electricity by more than 70%. Application of MEA technology to a dilute stream is not economically feasible in the foreseeable future. In spite of extensive research and development on immobilized (i.e., solid) amines and their attractive features, the employment of solid amines in TSA CO_2 capture has not been successful because of sorbent degradation and low CO_2 capture capacity. In addition, the cost of energy-intensive heating and cooling in TSA is nearly insurmountable.

Recent studies conducted by Akron have shown that amine sorbents aiming at TSA CO_2 capture consists of strongly and weakly adsorbed CO_2. The availability of weakly adsorbed CO_2 to be removed under a purge gas flow and vacuum at ambient temperature for sorbent regeneration provides a unique opportunity to utilize low vacuum for a VSA CO_2 capture process.

Figure 4 illustrates the approach to develop a cost-effective VSA CO_2 capture process. Figure 4(a) show a cascade VSA process consisting of two VSAs in a series, which allows concentrated CO_2 from the first VSA to be further concentrated in the second VSA. Air stream will be diverted to parallel VSA units for semi-continuous processing, where one VSA unit will be operated at the adsorption stage and the other unit will be operated at the desorption stage (i.e., under vacuum). Preliminary estimation showed that a 1-kg VSA unit will be able to process 200 liters per minute for five minutes for CO_2 adsorption to saturate amine sites at ambient condition (room temperature and one atm).

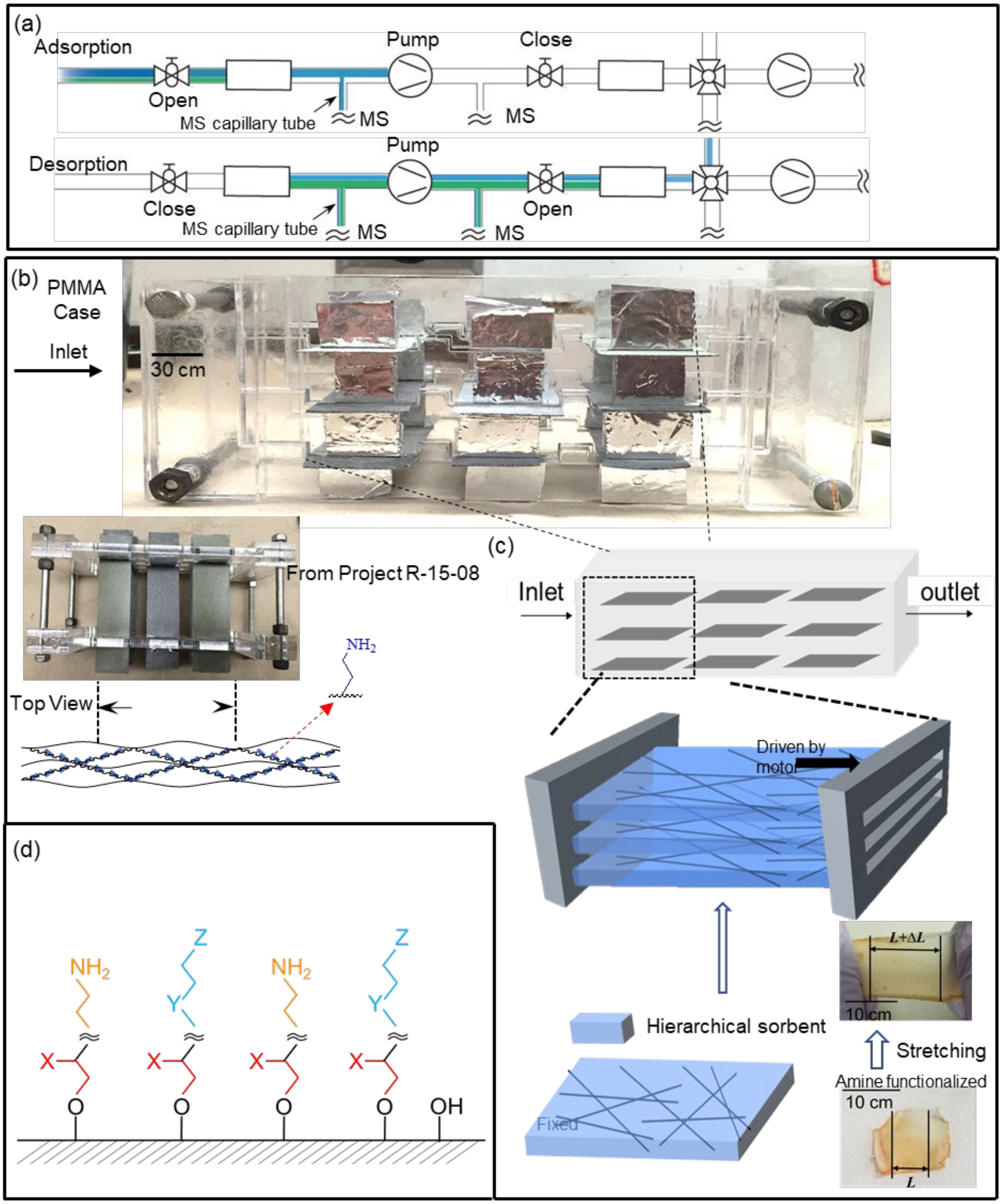


Figure 4. Vacuum swing adsorption for CO_2 capture from air (a) VSA scheme, (b) a VSA unit with sorbent plates in a plexiglass (i.e., PMMA) case, (c) the arrangement of sorbent plates in a parallel configuration, (d) the structure of amine sites for weakly adsorbed CO_2. X, Y, and Z denote different types of functional groups.

Figure 4(b) shows the CO_2 VSA unit Akron has designed and built on plexiglass (i.e., Poly(methyl methacrylate): PMMA). This unit was previously built for an electrically heated TSA process and consists of a set of monolithic rectangular plates of sorbent with dimensions of 20 cm x 10 cm x 0.1 cm, shown in Figure 4(c)/(d). The new sorbent plates manufactured with a low-cost carbon fiber provides mechanical strength. Amine sorbent particles were adhered on the carbon fiber with a porous adhesive. The use of parallel sorbent plates allows for the processing of a large volume of air flow with a minimum pressure drop and diffusion limitation. Porous polymer with a surface area greater than 350 m^2/g will be used to support the amine sites, shown in Figure 4(d). Akron has prepared sorbent pellets at kg-scale for previous TSA CO_2 capture processes. This preparation method, which was tuned for mechanical strength for a fluidized bed operation, are being tuned for high surface area since the sorbents in VSA are stationary. Immobilized amine and specific additives will eliminate the migration of amine sites during long-term VSA operation. In summary, the VSA process will allow use of low energy air blower to bring air to contact with VSA sorbent and allow use of low vacuum for collecting weakly adsorbed CO_2.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	910	<800
Bulk Density	kg/m^3	270	260
Average Particle Diameter	mm	0.1	2
Particle Void Fraction	m^3/m^3	0.32	0.5
Packing Density	m^2/m^3	0.7	0.5
Solid Heat Capacity @ STP	kJ/kg-K	2.36	2.2
Crush Strength	kg_f	N/A	N/A
Attrition Index (wt% change at 1.4 x fluidization	-	<0.01%	—
Thermal Conductivity	W/(m-K)	N/A	N/A
Manufacturing Cost for Sorbent	$/kg	100	50
Adsorption			
Pressure	bar	1	1
Temperature	°C	25	25
Equilibrium Loading	g mol CO_2/kg	0.7	1
Heat of Adsorption	kJ/mol CO_2	51	45
CO_2 Adsorption Kinetics at the first 3 sec	gmol/sec	1.1	1.1
Desorption			
Pressure	bar	0.1	0.1
Temperature	°C	25	25
Equilibrium CO_2 Loading	g mol CO_2/kg	0.6	0.8
Heat of Desorption	kJ/mol CO_2	51	45
CO_2 Desorption Kinetics at 1 atm	gmol/time	To be determined	0.1

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.

Atmospheric Air Feed-Gas Assumptions:

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	77 °F	0.04	variable	78.09	20.95	0.93	trace	trace

technology advantages

- Amine-functionalized aerogels have high CO_2 working capacity, low energy sorbent regeneration, high moisture resistance, and long stability over 500 adsorption-desorption cycles.
- Operates at ambient temperature.
- Scalable and modular design.

R&D challenges

- Identification of amine sites for weakly adsorbed CO_2.
- Production of high-purity CO_2 (greater than 99%).
- Fabrication of hierarchical sorbents with a high density of weakly adsorbed CO_2 sites.
- Construction of low leakage vacuum swing unit.

status

The project team developed an amine-functionalized aerogel that was tested in multiple adsorption/desorption cycles in a laboratory-scale (5–10 cm^3) VSA unit. The simultaneous monitoring of the aerogel sorbent using in situ infrared and MS was completed to understand the adsorption and desorption kinetics for both the strongly and weakly adsorbed CO_2. Fabrication and scale-up of a 1-liter VSA unit is currently in progress. Preparation for impregnation of amine-based aerogel into monolith structures is also currently in progress.

available reports/technical papers/presentations

Steven Chuang, "Gradient Amine Sorbents for Low Vacuum Swing CO_2 Capture at Ambient Temperature," Direct Air Capture Kickoff Meeting Presentation, Pittsburgh, PA, February 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11068&filename=Gradient+Amine+Sorbents+for+Low+Vacuum+Swing+CO2+Capture+at+Ambient+Temperature.pdf*.

Steven Chuang, "Gradient Amine Sorbents for Low Vacuum Swing CO_2 Capture at Ambient Temperature," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Chuang.pdf*