Curbing the Greenhouse Effect by Carbon Dioxide Adsorption with Zeolite 13X

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The removal of carbon dioxide (CO_2) from industrial emissions has become essential in the fight against climate change. In this study, we employed Zeolite 13X for the capture and recovery of CO_2 in a flow through system where the adsorbent was subjected to five adsorption-desorption cycles. The influent stream contained 1.5% CO_2 at standard conditions. The adsorbent bed was 1 in. in length and 1 in. 3/8 in dia., and was packed with 10 g of the zeolite. Temperature swing adsorption (TSA) was employed as the regeneration method through heating to approximately 135 °C with helium as the purge gas. The adsorbent capacity at 90% saturation was found to decrease from 78 to 60$g_{CO_2}/kg_{Zeolite13X}$ after the fifth cycle. The CO_2 capture ratio or the mass of CO_2 adsorbed to the total mass that entered the system decreased from 63% to only 61% after the fifth cycle. The CO_2 recovery efficiency ranged from 82 to 93% during desorption, and the CO_2 relative recovery, i.e., CO_2 desorbed for the nth cycle to CO_2 adsorbed for the first cycle, ranged from 88 to 68%. The service life of the adsorbent was determined to be equal to eleven cycles at a useful capacity of 40$g_{CO_2}/kg_{Zeolite13X}$.
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Introduction

Increasing amounts of greenhouse gases (GHGs) in the atmosphere are becoming a detriment to the health and welfare of every living organism, the natural landscape, and even our way of life. The combustion of fossil fuels used in electric generation poses an intrinsic environmental responsibility to the world. It then becomes vital that technologies are continually developed to reduce the amount of GHGs in the atmosphere.

The intergovernmental panel on climate change (IPCC) indicates that carbon dioxide (CO_2) as the most significant GHG produced as a result of human activities.[1] For this reason, the amount of CO_2 emissions must be reduced in order to meet the global treaty on CO_2 reduction.[1] Commercial CO_2 capture technologies that exist today, such as sequestration by direct injection into geologic or oceanic sinks, or monoethanolamine (MEA) chemical solvent absorption, are very expensive, energy intensive and unsustainable.[2,3] Adsorption by molecular sieves (zeolites), then, becomes a viable alternative because of the reusable nature of the adsorbents used.

In the long-term, if fossil fuels continue to be used as the primary fuel, power plants utilizing CO_2 capture and storage technologies could become effective net sinks of CO_2.[4] Scrubbing CO_2 from industrial flue gases through adsorption with zeolites will assist in alleviating the amount of GHGs that enter the atmosphere by concentrating the scrubbed gas through the regeneration of the adsorbents. Typical flue gases consist of approximately 17% CO_2, 79% N_2, and 4% O_2 with trace amounts of SO_2 and NO_x.[1] A number of zeolite based adsorbents used for CO_2 capture exist, including ZSM-5-30, ZSM-5-50, ZSM-5-80, ZSM-5-280, HiSiv 3000, H-Y-5.1, H-Y-30, H-Y-80, HiSiv 1000, NaY-10, NaY, 5A, and 13X[5]. Zeolite 13X molecular sieve has shown a high-work-

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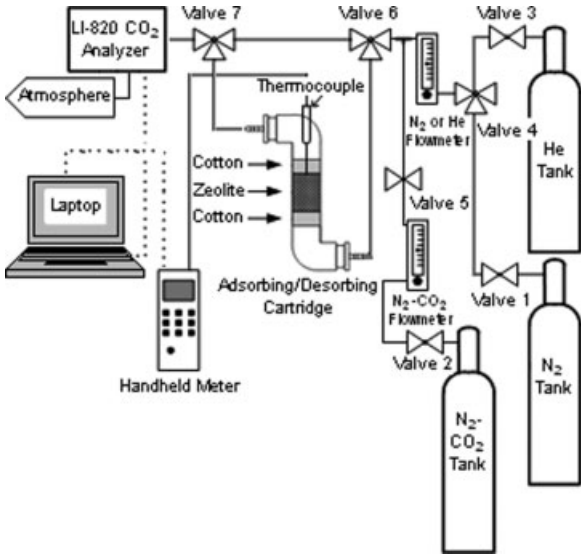

Figure 1. Single-bed temperature swing adsorption unit.

ing capacity for CO_2, and low-purge requirements.[1] In addition, this adsorbent exhibits preferential adsorption of CO_2, and can be utilized for the separation of CO_2 from gas mixtures, including mixtures containing N_2, H_2, and He[6]. In one report by Chue et al.,[7] high-purity CO_2 (~99%) could be produced by Zeolite 13X from a gas stream containing 84% N_2 and 16% CO_2.

A variety of cyclic adsorption processes are used commercially for adsorbent regeneration, including pressure swing adsorption (PSA), vacuum pressure swing adsorption (VPSA), and thermal or temperature swing adsorption (TSA). In PSA and VPSA processes, the adsorbent is regenerated by decreasing the total or partial pressure, while the feed and regeneration temperatures are kept approximately equal. In TSA processes, the temperature of the adsorbent is increased to remove the adsorbate, while the feed and regeneration pressures are kept approximately equal.[8] The regeneration method of choice for many zeolite molecular sieves is PSA,[8–11] although some experiments have employed a combined pressure and temperature swing adsorption (PTSA) process. Harlick et al.[12] investigated the expected working capacity (EWC) for PSA, TSA, and PTSA cycles, which is the difference in the amount adsorbed at the feed pressure, and the regeneration pressure obtained from an adsorption isotherm. It was determined that the largest EWC values were under high-pressure gradient PSA cycles, or high thermal and pressure gradient PTSA cycles. In addition, the results indicated that particular TSA and PSA cycle conditions would result in higher EWC's, with an increase in feed temperature.[12]

The objective of this work is to develop a process in which CO_2 is scrubbed from a gas stream containing approximately 1.5% of CO_2 using Zeolite 13X undergoing a TSA operation, where adsorption occurs at ambient temperature and bed regeneration occurs at high-temperatures with continuous purge feed. The system will be tested over five cycles of adsorption and desorption in order to determine the adsorbent bed's regeneration and recovery efficiency. The parameters that will be investigated include adsorbent capacity, the CO_2 capture ratio, the CO_2 recovery efficiency, the CO_2 relative recovery and the service life of Zeolite 13X.

Materials

The materials used include a scrubber made of a copper cartridge that serves as the adsorption/desorption bed, two flow meters (Fischer, NJ) (see Figure 1; size 2 flow meter for N_2 or H_2: max. flow = 846(N_2)/1297(H_2) mL/min, size 1 flow meter for N_2 and CO_2: max. flow = 85(N_2)/75(CO_2) mL/min), four two-way and two three-way valves (Fischer, NJ), 3/8 in. tubing (Nalgene, NY), various faucet connectors (4 ½ in. FIP to 3/8 in. FIP; 8 1/2 in. FIP to 1/2 in. FIP; 1 3/8 in. FIP to 3/8 in. FIP by BrassCraft, MI), a LI-820 CO_2 Gas Analyzer (LI-COR inc., NE), a Laptop computer (Toshiba), a 75%N_2–25% CO_2 gas mixture (Welco, NJ), Medipure Nitrogen (Welco, NJ), Helium (Airgas, PA), spherical Zeolite 13X APG (Air Purification Grade): 8 × 12 beads (UOP, IL) used without pretreatment, heating tape (1 in. × 24 in.) (Fischer, NJ), and a thermocouple fitted with a handheld meter and pipe plug fitting (Omega, CT). The physical properties of Zeolite 13X are listed in Table 1.

Process Description and Theoretical Equations

The process employed a single-bed temperature swing adsorption unit (Figure 1 and a detailed description in Appendix A) is described briefly as follows: (1) adsorption at ambient temperature, and (2) bed regeneration at high-temperatures with continuous purge feed.

In the first step, the adsorbent bed is subjected to a CO_2-N_2 gas stream of approximately 1.5% CO_2 at standard temperature and pressure (298 K, 1.0 atm). A tank of N_2-CO_2 gas (75%-25%), which is similar to industrial flue gas composition, and a tank of N_2 were used to develop this concentration of 1.5% CO_2. The volumetric flow rate of CO_2 was measured using two flow meters placed upstream of the bed. The CO_2 effluent concentration of the system was measured with the LI-820 CO_2 analyzer that reads a maximum CO_2 concentration of 20,000 ppm_v. A termination limit was arbitrarily set to 90% the influent concentration.

Once 90% of the influent concentration is reached, the second step initiates the retrieval of CO_2 through the regeneration of the adsorbent bed through stepwise heating from 20 to 135 °C, and purging with helium gas (helium was used

Table 1. Physical Properties of Zeolite 13X APG

Property	*Value*
SiO_2 to Al_2O_3 ratio	2.5
Bulk Density (kg/m^3)	641
Spherical Particle Diameter (mm)	2.0
Surface Area (m^2/g)	720
Porosity (cc/g)	0.28

[a]Data obtained from manufacturer (UOP, IL).

due to its inert characteristics, ensuring that it will not be adsorbed to the polar cation sites of Zeolite 13X). In order to keep the effluent CO_2 concentration below the 20,000 ppm_v analyzer bound, the temperature of the zeolite bed was closely regulated; hence, the requirement of stepwise heating. The temperature of the bed was slowly raised until the rate of CO_2 effluent concentration reached 15,000 ppm_v, at which point the heating tape was turned off, and the adsorbent bed was allowed to cool. The heating tape was turned back on when the CO_2 concentration fell to 12,000 ppm_v. After several such heating steps, the heating tape was allowed to stay on for the rest of the desorption cycle, and kept at a maximum temperature of 135 °C. The desorption cycle was terminated when the effluent CO_2 concentration reached 130 ppm_v, as described in Appendix A (Section 5: "Desorption Step").

Adsorption at Ambient Conditions

During the adsorption phase, the measured CO_2 concentration was imported into an MS Excel graph. The total mass absorbed m_A, and the total mass that has entered m_{tot}, through the system were calculated using Eqs. 1 and 2

$$m_{\text{tot}} = Q \times t_{90} \times \rho_{CO_2} \tag{1}$$

where m_{tot} is the total CO_2 mass passing through scrubber at time t_{90}, g; Q is the volumetric flow rate of CO_2, L/min; t_{40} is the time at 90% concentration, min, ρ_{CO_2} is the density of CO_2 during adsorption, g/L.

On a graph of CO_2 concentration (ppm_v) vs. time (min), the area above the curve represents the amount of CO_2 adsorbed onto Zeolite 13X, while the area below the curve represents the amount of CO_2 that has not been adsorbed. Equation 2 allows for the calculation of the mass adsorbed m_A, at any time t, from the ratio of the adsorbed area (A_t) on the total area (A_{tot}), which is then multiplied by the total mass that has entered the system m_{tot}, calculated in Eq. 1.

$$A_{tot} = C_{\text{inf}} \times t \qquad A_t = \int_0^t (C_{\text{inf}} - C)dt \qquad m_A = \frac{A_t}{A_{\text{tot}}} \times m_{\text{tot}} \tag{2}$$

where m_A is the mass adsorbed at time t, g; A_{tot} is the total area at time t, ppm_v min; A_t is the area above the curve at time t, ppm_v min; C is the concentration of CO_2 at time t, ppm_v, and C_{inf} is the influent concentration of CO_2, ~15,000 ppm_v.

$R_{capture}$ is defined as the capture ratio or ratio of m_A on m_{tot}, or A_t on A_{tot}, as defined in Eq. 3 and illustrated in Figure 2

$$R_{\text{capture}} = \frac{A_t}{A_{\text{tot}}} \tag{3}$$

$R_{capture}$ = capture ratio or ratio of the mass CO_2 adsorbed by the bed, at 90% C_{inf}, to the total amount of CO_2 that entered the system.

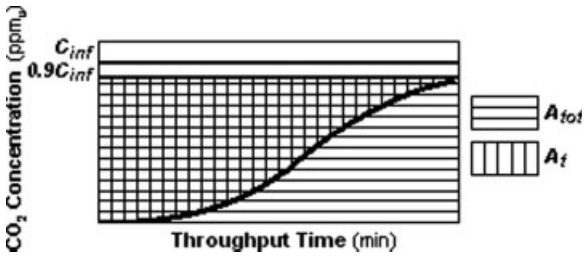

Figure 2. Capture ratio.

Another parameter used to determine the quality of the adsorbent is its capacity, S_{cap} defined here

$$S_{\text{cap}} = \frac{m_A}{m_{\text{media}}} \tag{4}$$

S_{cap} is the capacity of adsorbent bed at 90% C_{inf}, $g_{CO_2}/kg_{adsorbent}$, and m_{media} is the mass of adsorbent used, kg.

Both $R_{capture}$ and S_{cap} are primarily used to compare the efficiency of Zeolite 13X after one or several cycles.

Desorption Under Heating and Continuous Purge Feed

Again, the measured CO_2 concentration during the desorption step was imported into MS Excel. Equation 5 was used to determine the mass desorbed m_D, by taking the sum of the incremental masses over 1-s time increments for the duration of the regeneration process

$$m_D = \sum_{i=1}^{n} Q_D \times \rho_{DCO2,i} \times \Delta t \tag{5}$$

or

$$m_D = Q_D \times \Delta t \times \sum_{i=1}^{n} \rho_{DCO2,i} \tag{6}$$

The temperature ranged from 20 to 135 °C, and the density was calculated from Eqs. 7 and 8 for each 1-s time increment using the temperature and concentration data entries T_i and $C_{D,i}$ collected during the desorption step

$$\rho_{DCO_2,i} \frac{P_{DCO_2,i} \times MW}{R \times T_i} \tag{7}$$

and,

$$P_{DCO_2,i} = C_{D,i} \times P \tag{8}$$

where n is the duration of desorption step, min; m_D is the mass desorbed, g; Q_D is the volumetric flow rate of CO_2 during desorption, L/min; $\rho_{DCO_2,i}$ is the incremental CO_2 density during desorption, g/L; Δt is the time increment, min; $P_{DCO_2,i}$ is the incremental CO_2 partial pressure during desorption, atm; MW is the molecular weight of CO_2, g/mol; R is the universal gas constant, μL-atm/mol-°C; T_i is the incremental adsorbent bed temperature, °C; $C_{D,i}$ is the incremental CO_2 concentration during desorption, ppm_v, and P is the standard atmospheric pressure, atm. The recovery efficiency per cycle, S_{rec}, was obtained from the following equation

Table 2. Characteristics of Adsorbent and Operating Parameters (Base Case Conditions)

Adsorbent	Zeolite 13X
Bed Weight (g)	10 ± 0.0018
Bed Length (cm)	2.54
Bed Diameter (cm)	3.18
Influent CO_2 Concentration (ppm_v)	15,000 ± 100
Termination Concentration (ppm_v)	90% Influent ~ 13,500
Desorption Termination Conc. (ppm_v)	130 ± 10
CO_2 Flow Rate [Adsorption] (L/min)	0.01269
CO_2 Flow Rate [Desorption] (L/min)	1.015
Adsorption Temperature (°C)	20
Regeneration Temperature Range (°C)	20–135
Adsorption Total Pressure (atm)	1
Regeneration Total Pressure (atm)	1

$$S_{\text{rec}} = \frac{m_D}{m_A} \tag{9}$$

S_{rec} is the recovery efficiency per cycle.

The relative recovery per cycle, or recovery relative to fresh zeolite S_{rel}, was obtained from Eq. 10

$$S_{\text{rel}} = \frac{m_D}{m_{A1}} \tag{10}$$

where S_{rel} is the relative recovery per cycle, and m_{A1} is the mass adsorbed during the first cycle at 90% C_{inf}, g.

Results and Discussion

Five cycles of CO_2 adsorption and desorption using Zeolite 13X were performed in this study. The system characteristics, shown in Table 2, were kept constant throughout all five cycles. The results of multiple cycles of adsorption and desorption using Zeolite 13X are shown in Figures 3, 5 and Table 3. The adsorption curves observed in this study for Zeolite 13X (Figure 2) are similar to those observed by Siriwardane et al.[2,6] Upon the introduction of the CO_2-N_2 gas mixture to molecular sieve 13X, the effluent concentration dropped to 0 ppmv for approximately 12–14 min. The initial capacity is 78 $g_{CO_2}/kg_{Zeolite13X}$, and is slightly lower than the 92 $g_{CO_2}/kg_{Zeolite13X}$ reported by Siriwardane et al.[6] for a gas mixture containing N_2 (85.2%) and CO_2 (14.8%). This is expected because the adsorption step in this experiment was terminated before complete saturation could be achieved, i.e., 90% the influent concentration. Figure 2 also shows that the time to reach 90% saturation decreases with each successive cycle. This behavior is attributed to a residual of CO_2 that was not removed from the adsorbent during the desorption period.

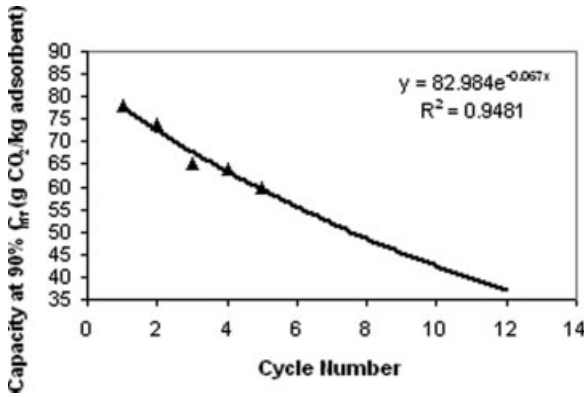

Figure 4. Capacity at 90% C_{inf} verse cycle number.

A plot of adsorbent capacity versus number of cycles is shown in Figure 4. The presence of residual causes the capacity of Zeolite 13X to decrease with each successive cycle starting at 78 and ending with 60 $g_{CO_2}/kg_{Zeolite13X}$ resulting in a 23% decrease; Siriwardane et al.[2] report that the working capacity of Zeolite 13X decreases from approximately 264 to 176 $g_{CO_2}/kg_{Zeolite13X}$ (a 33% drop), with two cycles for their adsorption of CO_2 on 13X at 22 °C and 250 psi. Figure 3 shows the change in capacity at 90% influent concentration with each cycle. An extrapolation of the exponential trendline to a useful capacity of 40 $g_{CO_2}/kg_{Zeolite13X}$ corresponds to approximately 11 cycles (zero capacity corresponds to 200 cycles).

The capture ratio, shown in Table 3, remained nearly constant, varying between 63% (1st Cycle) to only 58% (3rd Cycle) across the five cycles. This indicates that it is possible for 13X to continue to adsorb approximately 60% of CO_2 that passes through the bed for several cycles, although the time to reach the adsorption termination concentration and

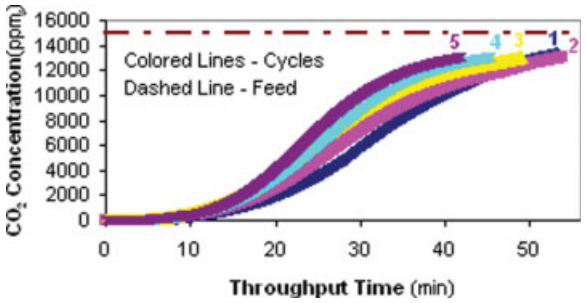

Figure 3. Multiple cycle results of adsorption.

[Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

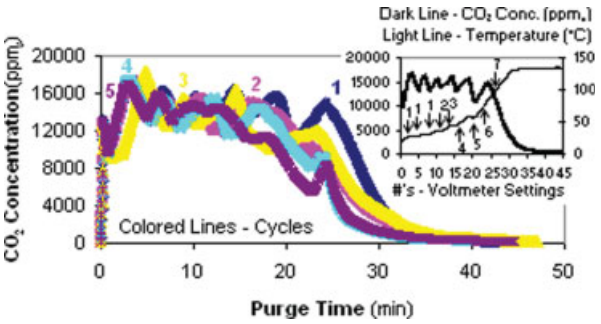

Figure 5. Multiple cycle results of desorption: temperature variance of the first cycle (insert).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 3. Summary of Experimental Results

Zeolite 13X								
Cycle	Adsorption Time (Min)	Desorption Time (Min)	CO_2 adsorbed m_A (g)	Capacity S_{cap} ($g_{CO2}/kg_{Zeolite13X}$)	Capture Ratio $R_{capture}$ (%)	CO_2 desorbed m_D (g)	CO_2 Recovery S_{rec} (%)	CO_2 Relative Recovery S_{rel} (%)
1	53	45	0.781	78	63	0.690	88	88
2	54	45	0.740	74	59	0.608	82	78
3	49	47	0.655	65	58	0.612	93	78
4	45	42	0.642	64	61	0.555	86	71
5	42	45	0.597	60	61	0.532	89	68

amount adsorbed will decrease with each cycle. Studies with additional cycles need to be conducted in order to fully establish whether this ratio will remain constant.

The desorption curves, shown in Figure 5, demonstrate a rather constant percent CO_2 recovery efficiency S_{rec}, ranging from 82 to 93% across the five cycles and averaging 88%, which is clearly higher than the recovery of 67% reported in Chou et al.[1] who utilized dual- and three-bed processes, and different system parameters, i.e., a higher adsorption pressure of 5.5 atm, and a regeneration pressure of 0.05 atm. The desorption temperature change with time for cycle 1 is also shown in the insert of Figure 5.

The desorption termination concentration was approximately 130 ppm_v in all experiments. However, in preliminary studies (results not shown), the desorption period was extended until the CO_2 effluent reached 10 ppm_v, instead of 130 ppm_v, which doubled the desorption time to 80 min and yielded a recovery of about 88%. Furthermore, desorption to 0 ppm_v is expected to remove all of the captured CO_2; however, this would result in an extremely long desorption period, making full regeneration impractical.

The amount of CO_2 desorbed per unit weight of zeolite, as a function of purge time, is shown in Figure 6. The total mass desorbed per unit weight of Zeolite 13X decreases across the five cycles, from 69 to 53 $g_{CO_2}/kg_{Zeolite13X}$. Decreases in the amount of CO_2 adsorbed would result in the decrease in the amount of CO_2 desorbed, in keeping with the termination concentration limit (130 ppm_v) for the desorption step.

The relative recovery, S_{rel}, shown in Table 3, represents the most important defining quality of molecular sieve 13X in this experiment within the bounds placed on the concentrations, i.e., adsorption and desorption termination limits. As expected, the recovery decreases from 88 to 68% across the five cycles, which demonstrates the decrease in the amount of CO_2 desorbed in correlation to the mass adsorbed in the first cycle, and can be considered the maximum relative amount of CO_2 that can be adsorbed under the conditions specified in this experiment.

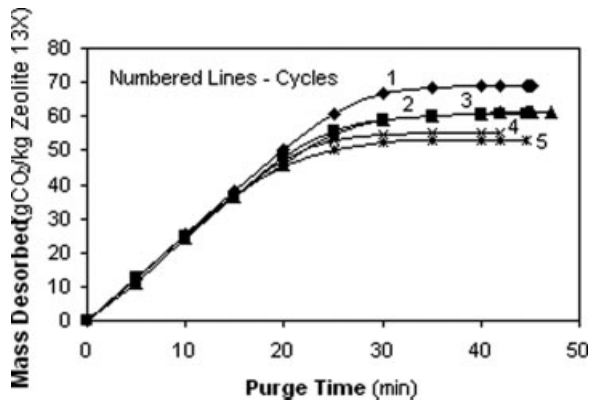

Figure 6. Amount of CO_2 desorbed during regeneration vs. purge time.

Conclusions

In this study, a single-bed temperature swing adsorption process was employed to determine the ability of Zeolite 13X to capture CO_2 preferentially from a mixed CO_2-N_2 gas stream and undergo regeneration in a TSA cyclic process. The CO_2 capacity of 13X was taken at 90% saturation (or 90% C_{inf}) during the adsorption step and regeneration of the adsorbent was shortened at an effluent concentration of 130 ppm_v during the desorption step. The capacity (S_{cap}) at 20 °C and a CO_2 partial pressure of 0.015 atm decreased, which was expected. In addition, CO_2 was desorbed efficiently with a relative recovery (S_{rel}) that was high (over 68%), and almost unchanged after several adsorption-desorption cycles.

It can be concluded that Zeolite 13X shows promise as an adsorbent with substantial capacity for CO_2 uptake, based on the average CO_2 recovery (S_{rec}) of 84% after five cycles in a TSA cyclic process. To further establish 13X as the best adsorbent for the system parameters defined in this experiment, future work will test our system using other adsorbents. Nevertheless, the above results for 13X illustrate its potential as an effective adsorbent for the selective separation of CO_2 from a CO_2-N_2 gas stream at a medium or industrial scale from flue gas exhaust or other greenhouse gas emissions, and may have important applications in the pressing areas of sustainability and climate change mitigation. Experiments at higher concentrations may confirm the suitability of this technology as an economically sustainable CO_2 capture system.

Acknowledgments

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Appendix A: Experimental Procedure

1. Valve Control

a. Valve 1 controls the flow of influent coming from the nitrogen tank alone.

b. Valve 2 controls the flow of influent coming from the nitrogen-carbon dioxide mixture tank alone. When zeroing, this valve must be closed.

c. Valve 3 controls the flow of influent coming from the helium tank alone.

d. Valve 4 is a three-way valve that allows for flow to the system from either the helium tank or the nitrogen tank. During the adsorption step, this valve is opened toward the nitrogen tank, and during the desorption step, to the helium tank.

e. Valve 5 is a valve that allows or restricts the flow of the nitrogen-carbon dioxide tank to the system. During adsorption, this valve is open and during desorption, this valve is closed.

f. Valve 6 is a three-way valve that allows flow to the analyzer or to the adsorption bed. This valve must be opened to the analyzer side when calibrating.

g. Valve 7 is the valve that allows or restricts the flow to come into contact with the adsorbent, on the effluent end of the copper cartridge. When calibrating, this must remain closed.

2. Initial Preparation

Turn on the computer. Open the "Start" menu, go to "All Programs", and click on LI-820. A green light should appear on the analyzer to indicate that it is on.

Measure out approximately 10 grams of Zeolite 13X; record this weight to four significant digits past the decimal. Finish this step as quickly as possible. It is important to place the adsorbent into the cartridge as soon as possible to minimize the risk of adsorption of carbon dioxide from the atmosphere.

Open the adsorbing cartridge and place a ball of cotton on the holding pins. Load the 10 grams of adsorbent into the cartridge after the cotton. Place another ball of cotton in the cartridge after the adsorbent bed. Close and seal the cartridge using Teflon tape. Connect the thermocouple probe to the bed. This is done by carefully inserting the probe into the pipe plug located at the top of the absorbing cartridge. Connect the probe to the thermocouple handheld meter. Turn on the handheld meter and open the Thermolog program under the "Start" menu in the "All Programs" list. If the thermocouple is properly set to the handheld meter, the program will display the current temperature. Make certain that the thermocouple is reading on the Celsius temperature scale and that entries for the data-log occur every 1-s.

3. Calibration

Before beginning the calibration, make sure valve 7 is closed (down position), that valve 6 is open to the analyzer side (up position), and that valve 4 is set to receive flow from the nitrogen tank (up position). On the LI-820 window, click the "Connect" icon. Open the nitrogen tank valve 1 and set the nitrogen flow meter to 140 mm with the steel ball. Go to "View" on the LI-820 window, and select "Calibration". Click on zero and then click "OK" to zero the gas concentration. When completed, open valve 2 and set the CO_2-N_2 mixture flow meter to a height of 92 mm with the steel ball. Wait at least 2 min, and then type in 15,000 into the box for the "Span Value" and click "OK".

4. Adsorption Step

When the reading is close to the span value ($\pm$ 150 ppm_v), begin recording the CO_2 concentration data by clicking the "Start Logging" icon. Enter a file name (Exp. '£'—'date'—ads. cycle '£') and select "Save". In addition, begin data-logging with the Thermolog program. In the LI-820 program, a graph can be viewed to see the real-time run in its entirety as the CO_2 concentration is being recorded. Go to "View" on the window toolbar and select "Charting". In this window, a time of 60 min should be entered with the y-axis minimum and maximum values of zero and 16,000 ppm, respectively—click "Start" to begin charting. When the red line appears on the graph, record the CO_2 concentration, which will represent the *initial influent concentration*. Turn valve 6 to allow the flow from the N_2-CO_2 and N_2 tanks to the bed (down position), and turn valve 7 to allow the flow from the bed to the analyzer (up position). Finish the adsorption step when the concentration of CO_2 reaches 90% the *initial influent concentration*. Click "Stop" on the charting graph and click the "Stop Logging" icon on the LI-820 window. Stop data-logging with the thermocouple program and save the graph (Exp. '£'—'date'—ads. cycle '£'). Close valve 2. Turn valve 6 to restrict the flow through the bed (down position) and turn valve 7 (down position). This concludes the first run of the adsorption step.

5. Desorption Step

Leave the nitrogen tank valve 1 open to allow N_2 to flow through the system, the goal of which is to clear the system of CO_2. Wait until the concentration of CO_2 drops down to approximately 20–40 ppm_v and close valve 1. Turn valve 4 to the down position, allowing flow from the helium tank to the system. Set the helium tank flow meter to a height of 113 mm with the steel ball. Begin data-logging with the LI-820 and the thermocouple program. A new file should be created for the logging of the CO_2 concentration for this step, as well as for the thermocouple program (Exp. '#'—'date'—des. cycle '#'). For the charting sequence in the LI-820 program, set the y-axis to 20,000 ppm_v and the x-axis to 60 min. Turn valve 6 to allow the He gas flow to the system (down position), and turn valve 7 to allow flow from the bed to the analyzer (up position) (Note: This represents time zero $t = 0$ min, of the desorption step). The concentration of CO_2 will reach a peak and then abruptly drop to approximately 10,000 ppm_v. At this point, turn the heating tape on by setting the voltmeter to a setting of 1 and turn it off again when the CO_2 concentration reaches 15,000 ppm_v. When the concentration of CO_2 falls to 12,000 ppm_v, reset the heating tape to a setting of 1, until the concentration reaches 15,000 ppm_v again. Repeat this cycle several more times, until it is clear that a temperature difference will not rapidly cause a sharp increase in the concentration of CO_2. When this is evident, turn on the heating tape by setting the meter to 2. The concentration will increase and then, eventually, decrease, at which point the voltmeter should be set to 3, and gradually increased to higher voltmeter settings with every drop in the concentration, which occurs around every 3 min, to a maximum setting of 7 (see insert of Figure 2). Eventually, the temperature of the bed will reach 135 °C, which is to remain constant for the remainder of the cycle. When a concentration of 130 ppm_v is reached, turn off the heating tape, close valve 3. Stop data-logging with the LI-820 and the Thermolog programs. Turn valve 6 to restrict flow through the bed (up position), and turn valve 7 to allow flow from the tanks to the analyzer (down position).

6. Begin New Cycle

Repeat steps 3 through 5, excluding the re-spanning of the concentration.

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