

## **Report**

GTI ENERGY PROJECT 22688

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# **Transformational Molecular Layer Deposition Tailor-made Size-sieving Sorbents for Post-combustion CO<sub>2</sub> Capture**

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## Executive Summary

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This report summarizes the bench-scale tests conducted at the National Carbon Capture Center (NCCC) under U.S. Department of Energy (DOE) project DE-FE0031730 titled "Transformational Molecular Layer Deposition Tailor-made Size-Sieving Sorbents for Post-Combustion CO<sub>2</sub> capture." The objective of this project was to develop a transformational molecular layer deposition (MLD) tailor-made size-sieving sorbent integrated with a pressure swing adsorption (PSA) cycle schedule that can be installed in new or retrofitted into existing pulverized coal (PC) power plants for CO<sub>2</sub> capture with a cost of electricity at least 30% lower than a supercritical PC power with CO<sub>2</sub> capture, or approximately \$30 per tonne of CO<sub>2</sub> captured, and with it being ready for demonstration by 2030.

In this project, the project team member at the State University of New York at Buffalo (UB) developed a transformational Ti-13X sorbent by employing MLD or atomic layer deposition (ALD) technology to passivate the strong adsorption sites of conventional 13X zeolite. This treatment increased the CO<sub>2</sub> working capacity and CO<sub>2</sub>/N<sub>2</sub> separation selectivity, while also reducing the CO<sub>2</sub> heat of adsorption and improving tolerance to water vapor and flue gas contaminants. Meanwhile, the University of South Carolina (USC) developed a proprietary PSA cycle schedule for CO<sub>2</sub> capture from flue gas. This process requires far fewer number of adsorption beds (relative to conventional adsorption processes), thereby reducing the CO<sub>2</sub> capture cost. By combining the advantages of the Ti-13X sorbent and the proprietary PSA cycle, a bench-scale skid was designed and constructed. The skid was extensively tested at USC including comparison between 13X and Ti-13X and effects of water vapor on CO<sub>2</sub> capture performance. During these tests, greater than 90% CO<sub>2</sub> capture efficiency with >95% CO<sub>2</sub> dry-basis purity was achieved for the Ti-13X adsorbent. The skid was then moved to NCCC for testing with actual coal flue gas or actual natural gas boiler flue gas modified to replicate the CO<sub>2</sub> concentrations found in coal flue gas, natural gas combined cycle (NGCC) and industrial flue gases. GTI Energy led the field tests at the NCCC.

A three-bed PSA system loaded with approximately 2 kg of Ti-13X sorbent was installed in NCCC's laboratory-scale test unit, where testing was first conducted using simulated coal-fired flue gas (15.7 vol% CO<sub>2</sub>, wet basis). Under a feed flow rate of 13 standard liters per minute (SLPM) and a vacuum pressure of 5 kPa, the system achieved a CO<sub>2</sub> dry-basis purity of 96.3 vol% and a CO<sub>2</sub> capture efficiency of 92.6%. Good long-term and dynamic stabilities were demonstrated over a 1,000-hour test. Parametric tests indicated: 1) the CO<sub>2</sub> dry-basis purity remained constant while CO<sub>2</sub> capture efficiency decreased with increasing vacuum pressure; 2) the H<sub>2</sub>O vapor concentration had minimal impact on CO<sub>2</sub> capture performance; and 3) higher feed flow rates and CO<sub>2</sub> concentrations resulted in slightly higher CO<sub>2</sub> dry-basis purity but lower capture

efficiency. When testing simulated natural gas combined cycle (NGCC) flue gas (5 vol% CO<sub>2</sub>, wet basis), under a vacuum pressure of 15 kPa and a feed flow rate of 18 SLPM, the system achieved a CO<sub>2</sub> dry-basis purity of 85.6 vol% and a CO<sub>2</sub> capture efficiency of 31.1%. Tests were then conducted for simulated industrial flue gas (24 vol% CO<sub>2</sub>, wet basis). Under a mild vacuum pressure of 20 kPa and a feed flow rate of 8 SLPM, the system achieved a CO<sub>2</sub> dry-basis purity of 96.4 vol% and a CO<sub>2</sub> capture efficiency of 70.5%. The performance also remained highly stable during a 200-hour test. Testing results indicate the Ti-13X/PSA technology is promising for CO<sub>2</sub> capture at coal-fired power or industrial plants where the CO<sub>2</sub> concentrations are higher than 10 vol%.

In summary, the Ti-13X/PSA bench-scale skid was tested for over eight months under multiple test campaigns at NCCC with different types of flue gases. During these tests, the Ti-13X adsorbent did not undergo regeneration, demonstrating good stability. This good stability enables continuous, reliable PSA operation while reducing energy consumption, maintenance and operational costs.

Following these successful tests at NCCC, future plan after the current project is to design and build an engineering-scale Ti-13X/PSA CO<sub>2</sub> capture system, conduct tests at coal-fired power or industrial plants, and demonstrate a continuous, steady-state operation for a minimum of two months.

## 1. Introduction

As a promising adsorbent material for post combustion CO<sub>2</sub> capture, 13X zeolite has been widely investigated in PSA <sup>[1]</sup>. 13X is particularly attractive due to its high CO<sub>2</sub> adsorption capacity, low cost, and commercial availability as a low attrition formed material <sup>[2]</sup>. Gas adsorption in 13X zeolite is inherently heterogeneous, involving both physisorption and chemisorption sites that are thermodynamically distinct <sup>[3-4]</sup>. Physically adsorbed CO<sub>2</sub> can be readily regenerated under mild pressure swing conditions, whereas chemisorbed CO<sub>2</sub> requires much more energy for regeneration. Moreover, the chemisorption sites occupy pore volume within the zeolite cages and induce strong polarization of extra-framework cations, which in turn suppresses the physisorption of CO<sub>2</sub> <sup>[5]</sup>. Therefore, suppressing CO<sub>2</sub> chemisorption in 13X zeolite while preserving or enhancing physisorption is critical to lowering the CO<sub>2</sub> capture cost in the PSA-based CO<sub>2</sub> capture process.

ALD/MLD techniques have been applied to tailor the gas separation properties for zeolites <sup>[6-8]</sup>. To permanently weaken the chemisorption strength of 13X zeolite, our team member at UB employed ALD and MLD to passivate the chemisorption sites, thereby producing a novel adsorbent, Ti-13X. In the ALD/MLD process, vapor-phase precursors undergo self-limiting surface reactions, resulting in the deposition of conformal, nanometer-scale coatings.

Meanwhile, team member at USC developed a proprietary PSA process for CO<sub>2</sub> capture from flue gas. This new PSA process requires far fewer numbers of adsorbent beds, thereby reducing the CO<sub>2</sub> capture cost <sup>[9]</sup>. By combining the advantages of the Ti-13X sorbent and the proprietary PSA process, a bench-scale skid was designed and constructed. The skid was extensively tested at USC. During these tests, greater than 90% CO<sub>2</sub> capture efficiency with >95% CO<sub>2</sub> dry-basis purity was achieved for the Ti-13X adsorbent. The skid was then moved to NCCC for testing with actual coal flue gas or actual natural gas boiler flue gas modified to replicate the CO<sub>2</sub> concentrations found in coal flue gas, NGCC and industrial flue gases. GTI Energy led the field tests at the NCCC.

The goal of the testing at NCCC is to achieve DOE's Carbon Capture performance goal of 95% CO<sub>2</sub> purity. The main scope of work at NCCC was as follows:

- Complete system installation and on-site system shakedown;
- Perform parametric tests and identify operational conditions for the continuous steady state run;
- Complete a continuous, steady-state operation for a minimum of 200 hours, gather data necessary for further process scale-up; and
- Remove the skid from the testing site.

## 2. Materials and Experimental Method

### 2.1. Ti-13X internal modification mechanism

Due to its large pore size of 0.74 nm, 13X zeolite permits  $\text{TiCl}_4$  (molecular size: 0.5 nm) to access its internal micropores and interact with hydroxyl defects throughout the framework, instead of reacting solely to the crystal exterior. Since hydroxyl defects occupy the same framework sites as chemisorbed  $\text{CO}_3^{2-}$  species<sup>[3-4]</sup>, reaction of  $\text{TiCl}_4$  with these defects is expected to inhibit the formation of  $\text{CO}_3^{2-}$ , as shown in Figure 1. ALD modification could polarize  $\text{Na}^+$  cations and/or create steric hinderance that limit interactions between  $\text{Na}^+$  and physisorbed  $\text{CO}_2/\text{N}_2$ , thereby decreasing quadrupole interactions and lowering adsorption enthalpy and affinity.

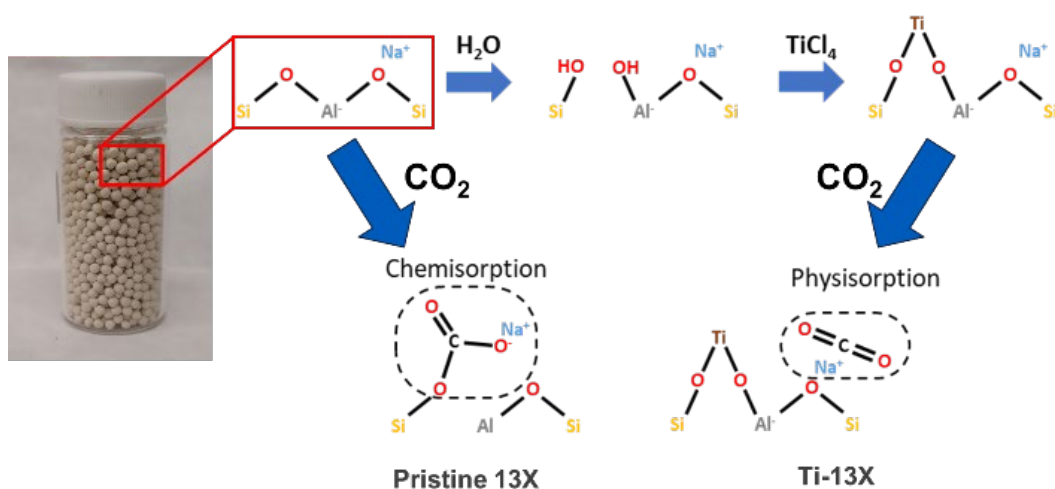


**Figure 1.** Schematic of the 13X zeolite functional group modification via ALD.

### 2.2. Ti-13X sorbent fabrication procedure, apparatus and characterizations

Ti-13X sorbent was fabricated using a home-built ALD system (Figure 2) using commercial 13X zeolite.



**Figure 2.** A home-built ALD system.

The ALD treatment included following steps:

- 1) Pristine 13X was purged with N<sub>2</sub> and degassed at 250°C for 12 h to remove physically adsorbed gases and moisture;
- 2) The reactor was cooled to the ALD reaction temperature of 100, 150, or 200°C;
- 3) TiCl<sub>4</sub> vapor was dosed for 2 h;
- 4) The reactor was evacuated, purged, and evacuated again for 60, 5, and 120 min, respectively;
- 5) H<sub>2</sub>O vapor was dosed for 1 h;
- 6) The reactor was evacuated, purged, and evacuated again for 60, 5, and 120 min, respectively; and
- 7) Steps 3-6 were repeated for the desired number of ALD cycles.

Sorbent surface morphology was characterized by Focused Ion Beam Scanning Electron Microscope (FIB-SEM) on a Hitachi SU-70. X-ray diffraction (XRD) patterns were collected on a Rigaku Ultimate IV using a Cu K $\alpha$  source (0.154 nm) at an x-ray power of 40kV/44mA. X-ray photoelectron spectroscopy (XPS) was performed using an AXIS Ultra DLD system (Kratos Analytical) equipped with a monochromatic Al K $\alpha$  source (1.5 keV) at a 45° incident angle. An electron gun was used during the XPS measurements for charge neutralization. Ar<sup>+</sup> ions accelerated at 4 keV were used for surface sputtering and depth profiling. XPS Peak 41 software was used for curve fitting using mixed Gaussian-Lorentzian functions, with a Shirley-type background subtraction. Under these conditions, the estimated sputtering speed rate was ~1 nm/min. This rate was determined from calibration measurements on a SiO<sub>2</sub>/Si interface, in which an oxide layer was grown on a Si wafer and its thickness was evaluated by XPS before and after successive sputtering steps.

A similar etching speed is expected for the zeolite samples examined in this study. Scanning electron microscopy (SEM) images were obtained on a Zeiss AURIGA Crossbeam system to observe the morphology of pristine 13X and Ti-13X. Nitrogen adsorption isotherms at 77K were measured using a 3Flex Physisorption Station by Micromeritics Instrument Corporation. Prior to adsorption measurement, all samples were degassed under vacuum at 350°C for 4 h with a heating ramp rate of 1°C/min.

### 2.3. PSA process

The flowsheet for the PSA technology is shown in Figure 3. This system was designed to capture  $\geq 90\%$  CO<sub>2</sub> with  $\geq 95$  vol% CO<sub>2</sub> dry-basis purity. In this process, water vapor in the feed is removed upstream of the PSA unit by incorporating two desiccant wheels, which are regenerated via a simple concentration swing using the PSA light product and

ambient air, without the need for external heating <sup>[10-11]</sup>. The numbered process streams shown in Figure 3 are identified in Table 1.

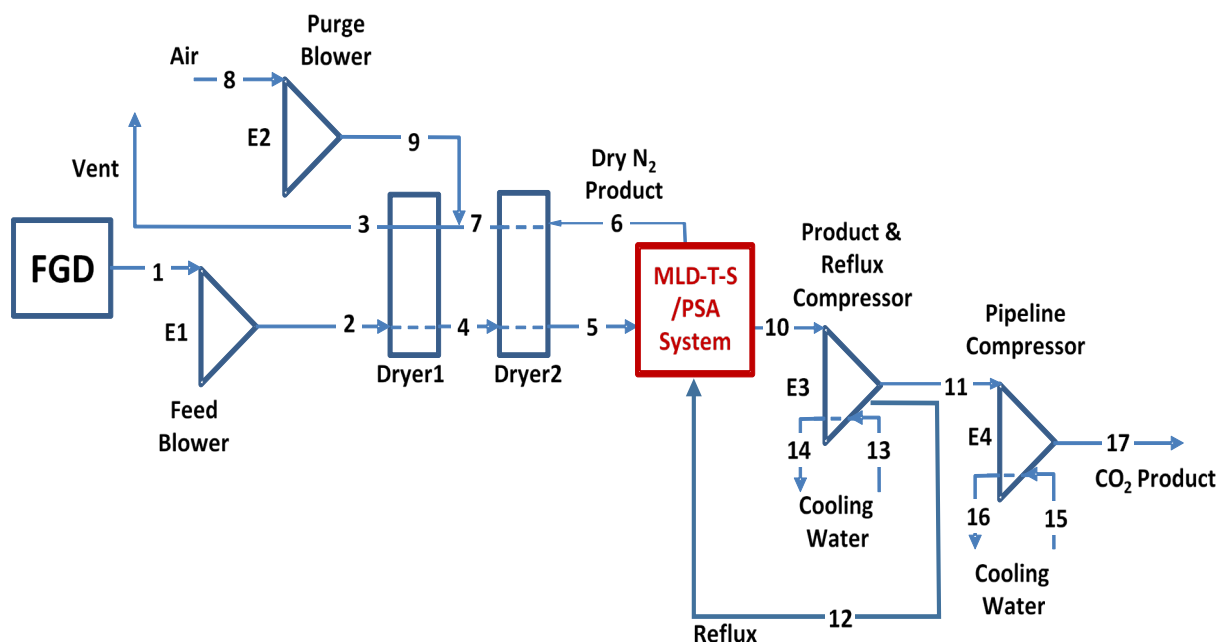


**Figure 3.** USC patented flowsheet for CO<sub>2</sub> capture from wet flue gas.

**Table 1.** Stream number and identify for the PSA process flow sheet in Figure 3.

| Stream No. | Stream identity                                                                                                  |
|------------|------------------------------------------------------------------------------------------------------------------|
| 1          | Flue gas from FGD unit to feed blower                                                                            |
| 2          | Compressed flue gas from feed blower to dryer 1                                                                  |
| 3          | Wet ambient air from dryer 1 to atmosphere vent                                                                  |
| 4          | Partially dried flue gas from dryer 1 to dryer 2                                                                 |
| 5          | Dried flue gas from dryer 2 to PSA system                                                                        |
| 6          | Dry N <sub>2</sub> light product from PSA system to Dryer 2                                                      |
| 7          | Wet N <sub>2</sub> product from dryer 2 to atmosphere vent                                                       |
| 8          | Ambient air from atmosphere to purge blower                                                                      |
| 9          | Compressed ambient air to dryer 1                                                                                |
| 10         | CO <sub>2</sub> heavy product from PSA system to product and reflux vacuum pump suction inlet                    |
| 11         | CO <sub>2</sub> heavy product from product and reflux vacuum pump discharge outlet to pipeline compressor        |
| 12         | CO <sub>2</sub> heavy product from product and reflux vacuum pump discharge outlet to PSA system as heavy reflux |
| 13         | Cooling water into product and reflux vacuum pump                                                                |
| 14         | Cooling water out from product and reflux vacuum pump                                                            |
| 15         | Cooling water into pipeline compressor                                                                           |
| 16         | Cooling water out from pipeline compressor                                                                       |
| 17         | Compressed CO <sub>2</sub> product from pipeline compressor to storage                                           |

Figure 4 shows the 3-bed-7-step PSA cycle operated at the NCCC with the following cycle steps: feed, heavy reflux (HR), equalization down (EqD), countercurrent depressurization (CnD), light reflux (LR), equalization up (EqU) and light product pressurization (LPP).

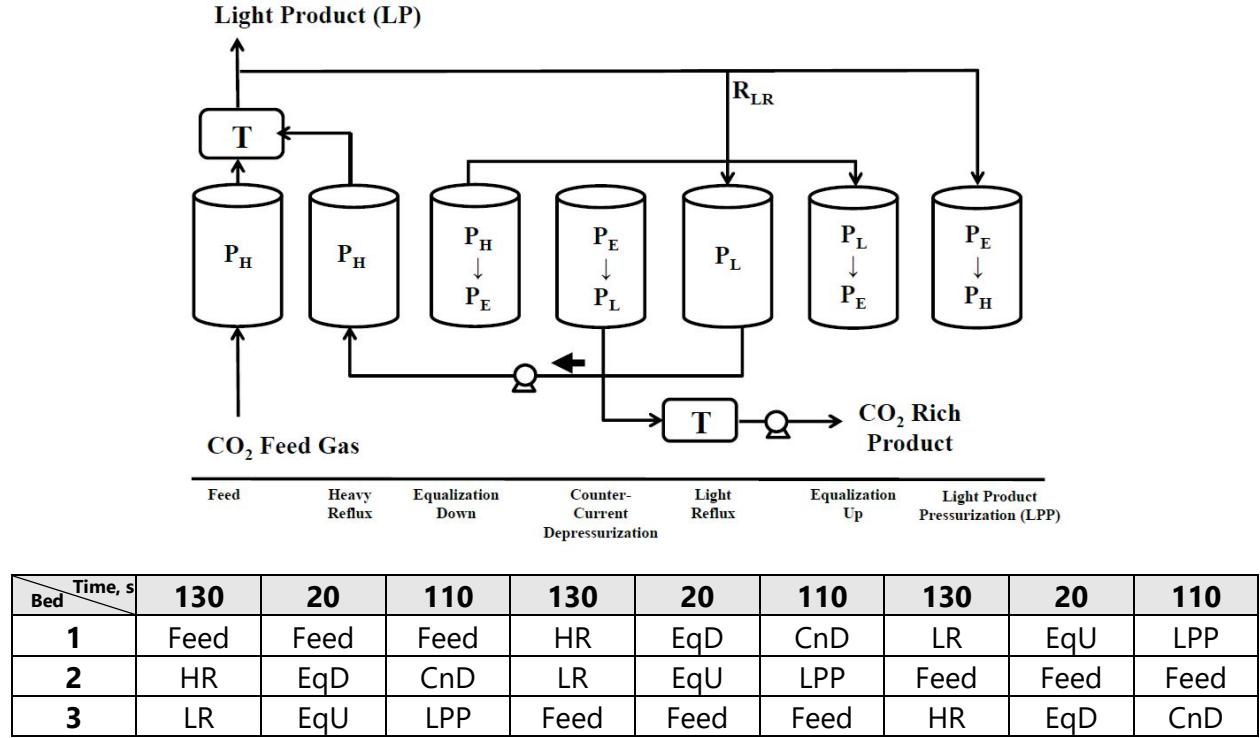


**Figure 4.** Schematic of the 3-bed-7-step PSA system bed interconnect diagram and cycle step sequence table with cycle step times indicated.

## 2.4. CO<sub>2</sub> capture performance measurement

$$CO_2 \text{ dry basis purity} = \frac{x_{CO_2,p}}{x_{CO_2,p} + x_{N_2,p} + x_{O_2,p}}$$

Where  $x_{CO_2,p}$ ,  $x_{N_2,p}$ ,  $x_{O_2,p}$  are the CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> mole fractions in the product stream, respectively.

$$CO_2 \text{ capture efficiency} = \frac{f_p \times x_{CO_2,p}}{f_f \times x_{CO_2,f}}$$

Where  $f_p$  and  $f_f$  are the product and feed flow rate, respectively, and  $x_{CO_2,f}$  is the CO<sub>2</sub> mole fraction in the feed gas.

$$CO_2 \text{ capture rate} = \frac{f_p \times x_{CO_2,p}}{m}$$

Where  $m$  is the mass of the sorbent.

### 3. Results and Discussion

#### 3.1. Ti-13X sorbent characterization

The Ti-13X samples were denoted as x-Ti-yC, where x represents the number of ALD cycles and y denotes the ALD temperature (in °C). SEM image of 1-Ti-100C is shown in Figure 5A, in which 3-5  $\mu\text{m}$  13X zeolite crystals and binder are clearly observed.

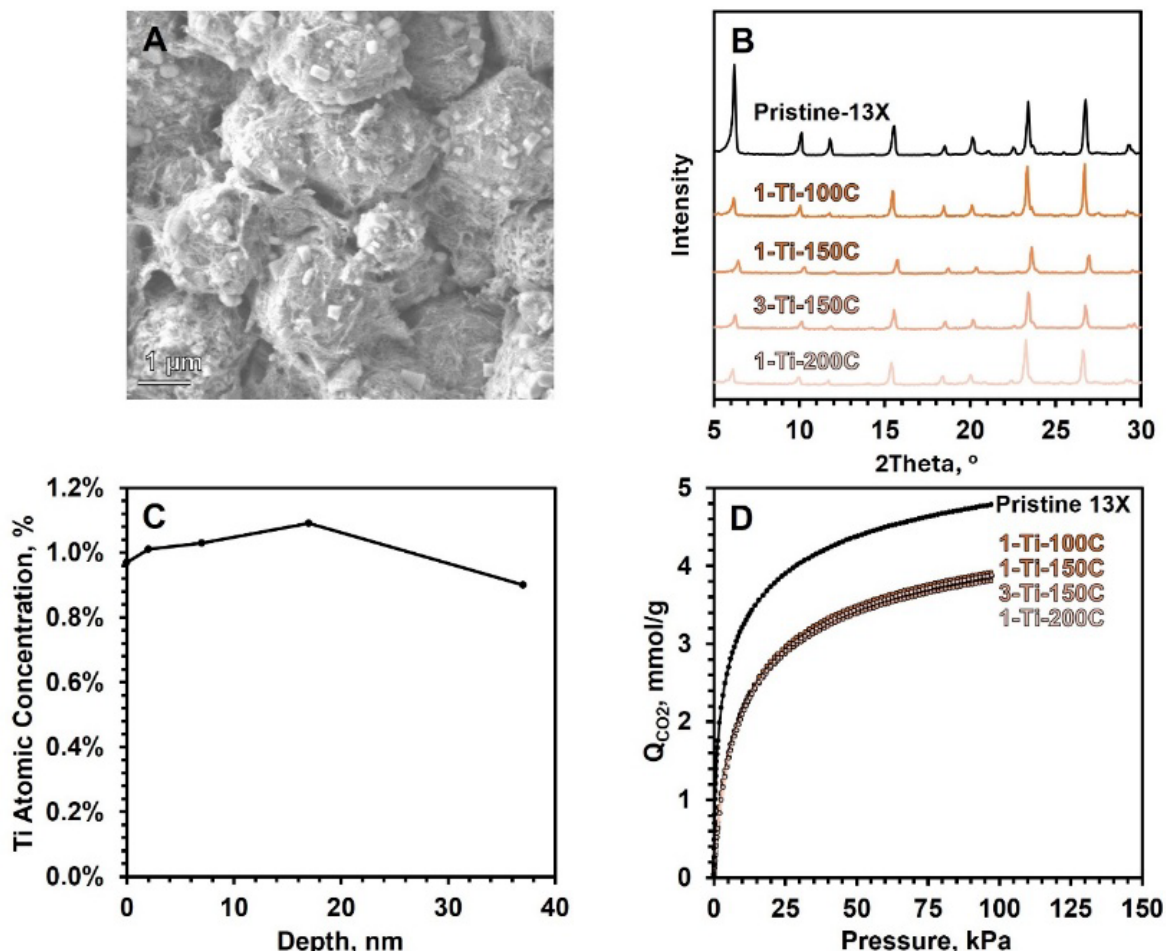


**Figure 5.** (A) SEM images of 1-Ti-100C samples. (B) XRD patterns of pristine 13X and various Ti-13X samples. (C) XPS Ti atomic concentration depth profile of 1-Ti-100C. (D) 30°C CO<sub>2</sub> isotherms of pristine 13X and various Ti-13X samples.

XRD patterns of pristine 13X and the Ti-13X samples are shown in Figure 5B. No new diffraction peaks or peaks shifts were observed, indicating that ALD has a negligible effect on zeolite structure and the faujasite framework is preserved. The Ti atomic content of the Ti-13X samples was measured by Energy-Dispersive Spectroscopy (EDS). A clear increase in Ti atomic percentage is observed with increasing ALD reaction temperature and with an increase in the number of ALD cycles from one to three (Table 2). To evaluate the homogeneity of ALD modification, Ti atomic percentage depth profile was measured via XPS on 1-Ti-100C and are shown in Figure 5C. The Ti atomic

percentage measured by XPS was close to the value obtained by EDS (~1.3% vs. ~1.4%) and exhibited minimal variation with depth, indicating that  $\text{TiCl}_4$  efficiently diffused throughout the 13X structure and reacted with hydroxyl functional groups across the framework.

Nitrogen adsorption isotherms at 77K were collected for pristine 13X and the Ti-13X samples to evaluate their textural properties. The Brunauer-Emmett-Teller (BET) surface area and micropore area of pristine 13X and Ti-13X samples are summarized in Table 2. After one ALD cycle, the BET area decreased by approximately 15%. This reduction is almost entirely attributable to a loss of micropore area, indicating that  $\text{TiCl}_4$  diffused into the 13X micropores and reacted with exposed hydroxyl defects. No systematic trends in surface area or microporosity were observed with increasing ALD cycle number or reaction temperature.

**Table 2.** BET and micropore area via 77K  $\text{N}_2$  isotherms and atomic concentrations via EDS of pristine 13X and Ti-13X.

| Sample       | BET area, $\text{m}^2/\text{g}$ | Micropore area, $\text{m}^2/\text{g}$ | Ti atomic %       |
|--------------|---------------------------------|---------------------------------------|-------------------|
| Pristine 13X | 506                             | 453                                   | N/A               |
| 1-Ti-100C    | $411 \pm 26^a$                  | $377 \pm 22^a$                        | $1.41 \pm 0.15^a$ |
| 1-Ti-150C    | 442                             | 374                                   | 2.51              |
| 3-Ti-150C    | 400                             | 353                                   | 4.97              |
| 1-Ti-200C    | 436                             | 382                                   | 4.12              |

<sup>a</sup> Standard deviation was calculated via analysis of four samples.

$\text{CO}_2$  adsorption isotherms measured at 30°C for pristine 13X and Ti-13X samples are shown in Figure 5D. Only minor differences in  $\text{CO}_2$  adsorption behavior were observed among the Ti-13X samples. These results indicate that variations in elemental composition and textural properties arising from changes in ALD temperature or cycle number do not translate into measurable differences in  $\text{CO}_2$  adsorption performance. This suggests that  $\text{TiCl}_4$  may react with hydroxyl groups throughout the framework during the first ALD cycle but fails to find hydroxyl sites within the micropores in subsequent ALD cycles. Clearly, additional Ti-OH units are either inaccessible to  $\text{TiCl}_4$  or are not present within the super cages after the first ALD cycle. Based on these observations, the 1-Ti-100C was selected for further investigation, as it utilized the mildest reaction conditions and exhibited the lowest Ti atomic percentage among the Ti-13X samples.

### 3.2. Ti-13X QA/QC testing

Ti-13X sorbent was fabricated following the previously described experimental procedure. For each batch, quality assurance/quality control (QA/QC) testing was conducted using passing criteria of  $\text{CO}_2/\text{N}_2$  selectivity >60 and a  $\text{CO}_2$  working capacity

>0.8 mmol/g. As shown in Figure 6, 23 batches of Ti-13X adsorbent were prepared, and ~3.6 kg adsorbent had met the QA/QC requirements.

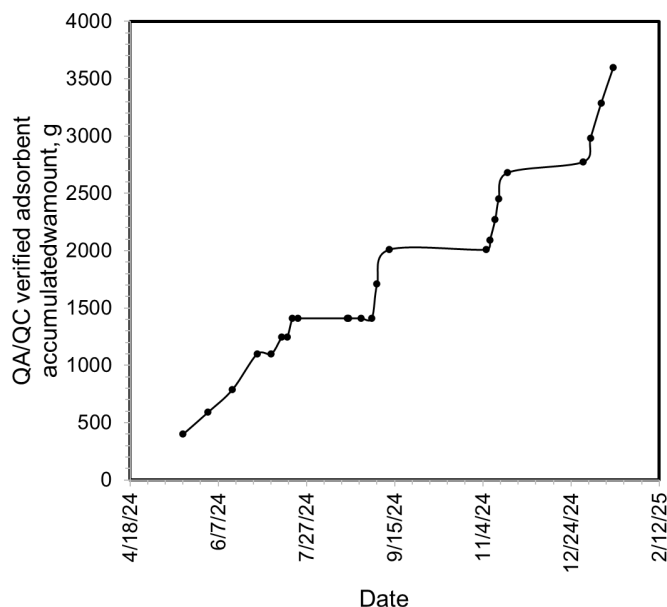


**Figure 6.** Status of accumulated sorbent passing the quality assurance/quality control process.

### 3.3. Testing results of the Ti-13X obtained at USC's lab

By combining the advantages of the Ti-13X sorbent and the proprietary PSA cycle, a bench-scale skid was designed and constructed at USC. Prior to the NCCC test campaign, a series of laboratory experiments were conducted at USC to evaluate the impact of different moisture levels on sorbent performance. All tests were conducted under identical operating conditions, including an operating temperature of 40°C, a feed CO<sub>2</sub> concentration of 16 vol%, a total feed flow rate of 12.93 SLPM, sorbent inventory of 2.22 kg, and a vacuum desorption pressure of 5 kPa. Under these baseline conditions, the effect of feed moisture on CO<sub>2</sub> capture performance was evaluated through Runs 1-4, followed by a regeneration step and a post-regeneration performance check in Run 5. Testing results are shown in Table 3.

**Table 3.** Experimental results of 3-bed PSA testing at USC.

| Run | H <sub>2</sub> O concentration, % | CO <sub>2</sub> capture efficiency, % | CO <sub>2</sub> dry-basis purity, % |
|-----|-----------------------------------|---------------------------------------|-------------------------------------|
| 1   | 0                                 | 89.4                                  | 95.5                                |
| 2   | 1                                 | 88.7                                  | 95.1                                |
| 3   | 0.42                              | 87.6                                  | 95.2                                |
| 4   | 0.05                              | 86.0                                  | 95.4                                |
| 5   | 0                                 | 95.7                                  | 93.6                                |

Run 1 served as the dry baseline test, in which the feed contained no moisture. Under these conditions, the sorbent achieved a CO<sub>2</sub> capture efficiency of 89.4% and a CO<sub>2</sub> dry-basis purity of 95.5 vol%. This run established a reference point for evaluating

the effect of moisture and provided a benchmark for assessing sorbent recovery after regeneration.

Run 2-4 introduced moisture levels of 1%, 0.42%, and 0.05% H<sub>2</sub>O vapor, respectively, and each run was operated continuously for 24 hours. Compared with the dry baseline, the presence of moisture led to a modest decline in CO<sub>2</sub> capture efficiency, decreasing from 89.4% in Run 1 to 88.7-86% across the moist runs. This trend reflects competitive adsorption between H<sub>2</sub>O and CO<sub>2</sub> on the sorbent surface. Despite the reduction in capture efficiency, the CO<sub>2</sub> dry-basis purity remained largely unchanged (95.1-95.5 vol%), indicating that moisture had little influence on desorption selectivity under the applied vacuum conditions. Following Run 4, the sorbent underwent regeneration at 200°C under vacuum.

Run 5, conducted under after the regeneration, achieved a CO<sub>2</sub> capture efficiency of 95.7%, notably higher than the dry baseline in Run 1. Although the CO<sub>2</sub> dry-basis purity decreased slightly to 93.6 vol%, the significant recovery and even improvement of capture efficiency indicates that regeneration at 200°C is sufficient to fully regenerate the sorbents, the residual moisture or adsorbed intermediates accumulated during the 24-hour tests were effectively removed during regeneration.

Overall, these results show that moderate moisture levels in the feed lead to a small but consistent reduction in CO<sub>2</sub> capture efficiency, while the CO<sub>2</sub> dry-basis purity remains essentially unaffected by the presence of water under the applied vacuum desorption conditions. In addition, the post-regeneration performance indicates that heating the sorbent to 200°C under vacuum is sufficient to fully regenerate the sorbents.

### **3.4. PSA skid delivered and installed at NCCC's LSTU**

After successful testing at USC's lab, the skid was delivered to NCCC for testing with actual coal flue gas or actual natural gas boiler flue gas modified to replicate the CO<sub>2</sub> concentrations found in coal flue gas, NGCC and industrial flue gases. GTI Energy led the field tests at the NCCC.

Figure 7 shows the setup of the PSA skid installed at NCCC's Lab-Scale Testing Unit (LSTU). A slipstream of flue gas from a natural gas boiler was directed to the PSA skid as the feed gas. Pure CO<sub>2</sub> was blended with natural gas boiler flue gas to simulate coal-fired and industrial flue gas compositions. The incoming flue gas was first passed through a chiller to reduce its moisture content to approximately 1%. The dried gas was then compressed and delivered to the adsorption bed for PSA operation. The entire process sequence—including valve actuation, step timing, and data acquisition was controlled through a dedicated LabVIEW program, which continuously logged all operating parameters in real time. A vacuum pump installed downstream of the sorbent beds provided the required desorption pressure, while the CO<sub>2</sub>-enriched product stream was collected in a pressurized product tank. Gas phase composition was continuously

monitored using a residual gas analyzer. Two additional gas chromatographs were used to perform detailed compositional analyses of both the product and exhaust streams.

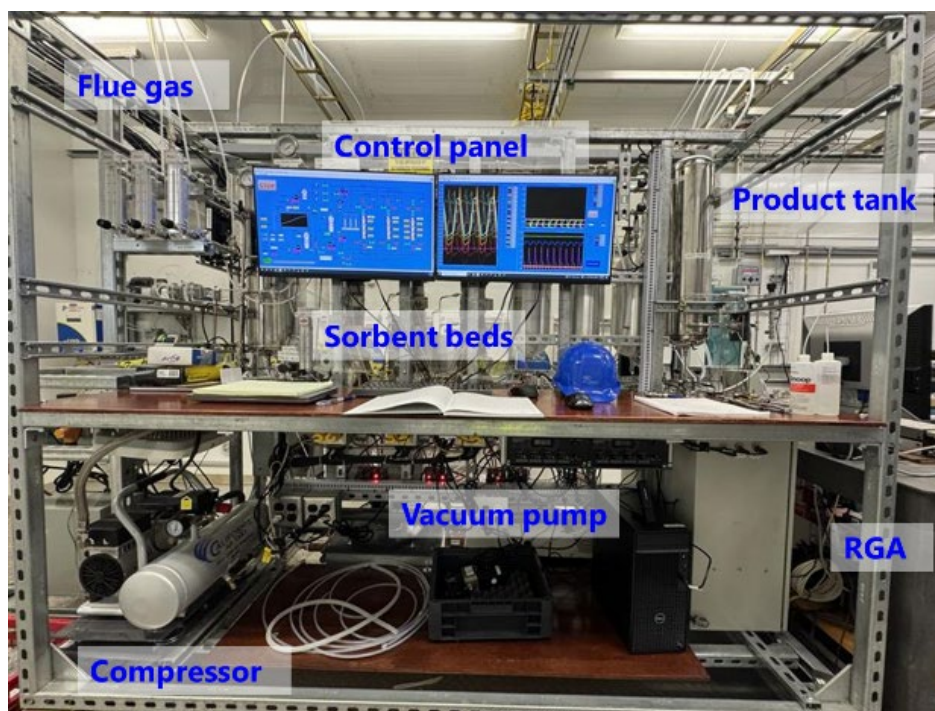


**Figure 7.** PSA skid delivered and installed in the Lab-scale test unit at NCCC.

### 3.5. Simulated flue gases via CO<sub>2</sub> blending at NCCC

This project was initially intended to test coal-fired flue gas. However, due to the unpredictable availability of coal-fired flue gas at NCCC, an alternative approach was implemented. NCCC can provide natural gas boiler flue gas, which is diluted with air to reach a CO<sub>2</sub> concentration of approximately 4.5 vol% (dry basis). After discussion with DOE, the decision was made to inject pure CO<sub>2</sub> into the diluted natural gas boiler flue gas to create simulated coal-fired flue gas. The gas composition of NCCC's natural gas boiler flue gas and the simulated coal-fired flue gas are shown in Table 4.

**Table 4.** Composition of NCCC's diluted natural gas boiler flue gas and simulated coal-fired flue gas.

| Gas              | NCCC diluted natural gas boiler flue gas | Simulated coal-fired flue gas | Simulated industrial flue gas |
|------------------|------------------------------------------|-------------------------------|-------------------------------|
| CO <sub>2</sub>  | ~4.5 vol%                                | 15.7 vol%                     | 24.0 vol%                     |
| O <sub>2</sub>   | ~13.1 vol%                               | 11.7 vol%                     | 10.3 vol%                     |
| NO <sub>2</sub>  | 3-4 ppm                                  | 2.6-3.5 ppm                   | 2.4-3.2 ppm                   |
| H <sub>2</sub> O | 1.0 vol%                                 | 0.5-1.0 vol%                  | 0.5-1.0 vol%                  |
| N <sub>2</sub>   | Balanced                                 | Balanced                      | Balanced                      |

## 3.6. Coal-fired flue gas testing at NCCC

### 3.6.1. Long-term testing

A 1,000-hour test campaign was conducted at NCCC to evaluate the PSA system performance and sorbent stability. The results are shown in Figure 8.

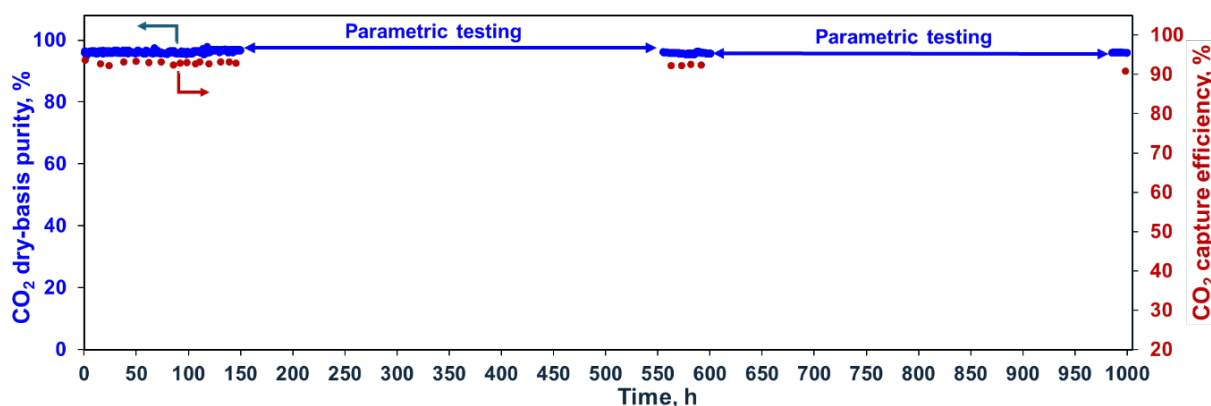


**Figure 8.** 1,000-hour testing at NCCC with simulated coal flue gas.

During the initial 165-hour, the system operated under the following conditions: feed gas composition of 15.7 vol% CO<sub>2</sub>, 0.5 vol% H<sub>2</sub>O, 11.7 vol% O<sub>2</sub>, and balanced N<sub>2</sub>, flow rate of 13 SLPM, temperature of 35°C, feed pressure of 106.2 kPa, and vacuum level of 5 kPa. Under these conditions, the PSA system consistently exhibited CO<sub>2</sub> dry-basis purity of ~96.4 vol% and a CO<sub>2</sub> capture efficiency of 92.6%, meeting the technical goals of >95 vol% CO<sub>2</sub> dry basis purity and >90% capture efficiency. From 166 to 550 hours, a series of parametric tests were conducted by varying feed gas composition, flow rate, and vacuum level to evaluate the CO<sub>2</sub> capture performance under different operating conditions. Between 550 and 600 hours, the original operating conditions were reinstated, and the system achieved the initial performance, indicating no degradation in sorbent properties. From 601 to 980 hours, additional parametric tests were conducted to reduce the CO<sub>2</sub> production cost. Finally, between 981 and 1,000 hours, the system was back to the original operating conditions again, and a similar performance was observed, further confirming the stability of the sorbent properties over the entire duration of testing. It is important to note that no sorbent regeneration was performed throughout the entire 1,000-hour test period.

During the 1,000-hour testing, a total of 13 shutdowns and startups were intentionally conducted to evaluate the dynamic stability of the sorbent system. A summary of these shutdown/restart events is provided in Table 5. After each shutdown and restart, the system was able to recover to its original performance within a few PSA cycles, indicating the strong dynamic operability of the sorbent and operational robustness of the PSA system.

**Table 5.** Shutdown and restart events for dynamic operation evaluation.

| Event No. | Shutdown/restart description                                 |
|-----------|--------------------------------------------------------------|
| 1         | System shutdown for 10 minutes and restart at 5-hour         |
| 2         | System shutdown for 20 minutes and restart at 25-hour        |
| 3         | System shutdown for 3 hours and restart at 50-hour           |
| 4         | NCCC's LSTU power outage for 3 hours at 75-hour              |
| 5         | NCCC outage for 2 weeks                                      |
| 6         | System shutdown for 6 hours and restart at 220-hour          |
| 7         | Flue gas loss for 10 hours and restart at 325-hour           |
| 8         | Flue gas loss for 3 hours and restart at 350-hour            |
| 9         | NCCC's LSTU power outage for 15 hours at restart at 410-hour |
| 10        | Flue gas loss for 2 hours and restart at 525-hour            |
| 11        | System shutdown for 24 hours and restart at 600-hour         |
| 12        | System shutdown for 24 hours and restart at 715-hour         |
| 13        | System shutdown for 24 hours and restart at 860-hour         |

### 3.6.2. Parametric tests

Figure 9 shows the effect of vacuum level on CO<sub>2</sub> capture performance. During the tests, the feed gas composition was fixed at 15.7 vol% CO<sub>2</sub>, 11.7 vol% O<sub>2</sub>, and 0.5 vol% H<sub>2</sub>O, balanced N<sub>2</sub>, with a total flow rate of 13 SLPM. The feed gas temperature and pressure were maintained at 35°C and 1.06 bara, respectively.

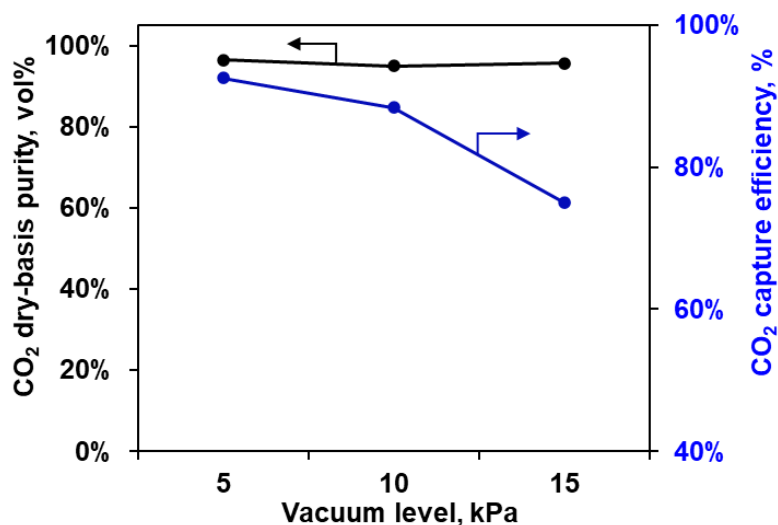


**Figure 9.** Effect of vacuum level on CO<sub>2</sub> capture performance.

As the vacuum level increased from 5 kPa to 10 kPa, and then to 15 kPa, the CO<sub>2</sub> dry-basis purity of the product stream remained nearly constant at approximately 96 vol%. In contrast, the CO<sub>2</sub> capture efficiency decreased from 92.6% to 88.4% and then to 75%.

In addition to capture efficiency, the CO<sub>2</sub> capture rate-defined as the amount of CO<sub>2</sub> captured per unit mass of sorbent per day-was also calculated. The capture rate decreased correspondingly from 2.55 to 2.43 and finally to 2.06 kg CO<sub>2</sub>/kg sorbent/day as the vacuum level increased. These results indicate that increasing vacuum pressure has a substantial impact on CO<sub>2</sub> capture efficiency and capture rate, while having little effect on CO<sub>2</sub> dry-basis purity.

Figure 10 shows the effect of H<sub>2</sub>O concentration on CO<sub>2</sub> capture performance under otherwise identical operating conditions. The feed gas composition was fixed at 15.7 vol% CO<sub>2</sub>, and 11.7 vol% O<sub>2</sub> and balanced N<sub>2</sub>, with a total flow rate of 13 SLPM. The feed temperature and pressure were maintained at 35°C and 1.06 bara, respectively, while the vacuum pressure was held constant at 15 kPa.

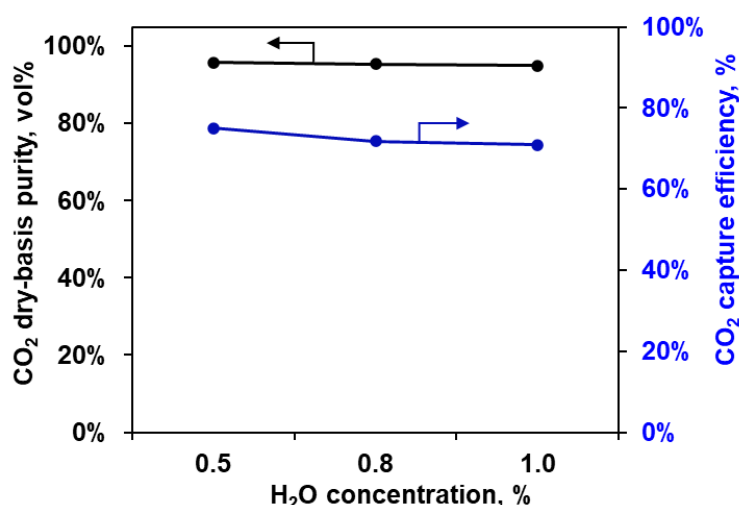


**Figure 10.** Effect of H<sub>2</sub>O concentration on CO<sub>2</sub> capture performance.

As the H<sub>2</sub>O concentration increased from 0.5 vol% to 0.8 vol% and then to 1.0 vol%, the CO<sub>2</sub> dry-basis purity of the product stream remained constant at approximately 96 vol%. In contrast, the CO<sub>2</sub> capture efficiency slightly decreased, declining from 75% to 71.8% and then to 70.9%. The CO<sub>2</sub> capture rate decreased from 2.06 to 1.97 and finally to 1.95 kg CO<sub>2</sub>/kg sorbent/day.

Figure 11 shows the effect of feed gas flow rate on CO<sub>2</sub> capture performance under otherwise constant operating conditions. The feed gas composition was fixed at 15.7 vol% CO<sub>2</sub>, 11.7 vol% O<sub>2</sub>, and 1.0 vol% H<sub>2</sub>O, balanced N<sub>2</sub>. The feed temperature and pressure were maintained at 35°C and 1.06 bara, respectively, while the vacuum level was held constant at 15 kPa. As the feed gas flow rate increased from 8 SLPM to 10.5 SLPM and then to 13 SLPM, the CO<sub>2</sub> dry-basis purity of the product stream remained nearly unchanged at approximately 96 vol%. However, the CO<sub>2</sub> capture efficiency decreased from 90.6% to 83.2% and then to 75%. The CO<sub>2</sub> capture rate increased from 1.53 to 1.83 and further to 2.06 kg CO<sub>2</sub>/kg sorbent/day with increasing feed gas flow

rate. These results indicate that increasing feed gas flow rate significantly enhances CO<sub>2</sub> capture rate at the expense of capture efficiency, while having little impact on CO<sub>2</sub> dry-basis purity.

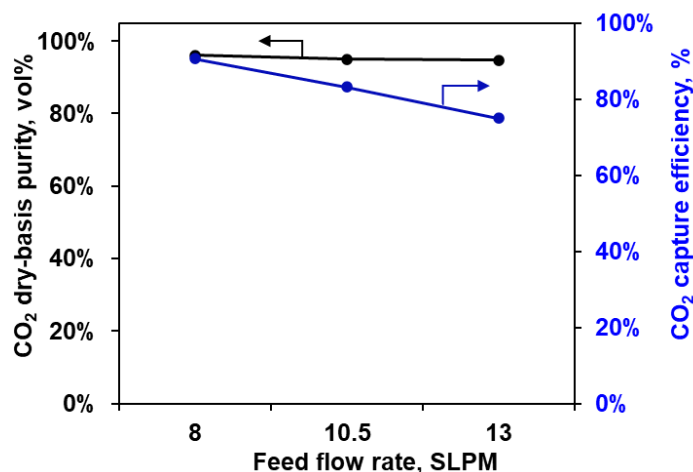


**Figure 11.** Effect of feed flow rate on CO<sub>2</sub> capture performance.

Figure 12 shows the effect of feed CO<sub>2</sub> concentration on capture performance under otherwise constant operating conditions. The feed gas flow rate was held constant at 8 SLPM, and the vacuum pressure was maintained at 15 kPa. The feed gas contained 11.7 vol% O<sub>2</sub> and 1.0 vol% H<sub>2</sub>O, balanced N<sub>2</sub>, with the feed temperature and pressure fixed at 35°C and 1.06 bara, respectively. The CO<sub>2</sub> concentration in the feed gas varied from 15.7 vol% to 24.0 vol% and then to 25.6 vol%. Across the range of feed CO<sub>2</sub> concentrations, the CO<sub>2</sub> dry-basis purity of the product stream remained stable at approximately 96 vol%. In contrast, the CO<sub>2</sub> capture efficiency decreased from 90.6% to 69.3% and then to 66%, while the CO<sub>2</sub> capture rate increased from 1.53 to 1.96 and then slightly decreased to 1.88 kg CO<sub>2</sub>/ kg sorbent/day.

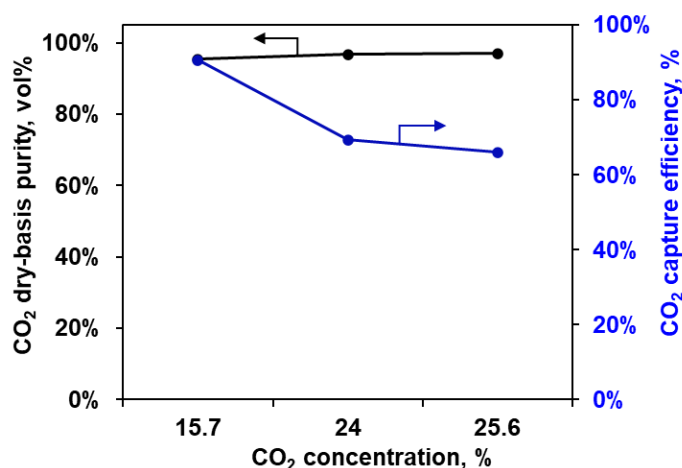


**Figure 12.** Effect of feed CO<sub>2</sub> concentration on CO<sub>2</sub> capture performance.

### 3.7. Simulated industrial flue gas testing at NCCC

#### 3.7.1. Parametric testing

Figure 13 shows the effect of vacuum level on CO<sub>2</sub> capture performance using simulated industrial flue gas. The feed gas flow rate was maintained at 8 SLPM, with a composition of 24.0 vol% CO<sub>2</sub>, 10.3 vol% O<sub>2</sub>, 1.0 vol% H<sub>2</sub>O, and balanced N<sub>2</sub>. The operating temperature and feed pressure were fixed at 35°C and 1.06 bara, respectively. As the vacuum pressure increased from 15 kPa to 20 kPa and then to 25 kPa, the CO<sub>2</sub> dry-basis purity of the product slightly decreased from 97.2 vol% to 96.1 vol% and further to 92.5 vol%. The CO<sub>2</sub> capture efficiency decreased from 84.4% to 70.3% and then to 60%. Correspondingly, the CO<sub>2</sub> capture rate decreased from 1.96 to 1.82 and finally to 1.55 kg CO<sub>2</sub>/kg sorbent/day as the vacuum level increased.

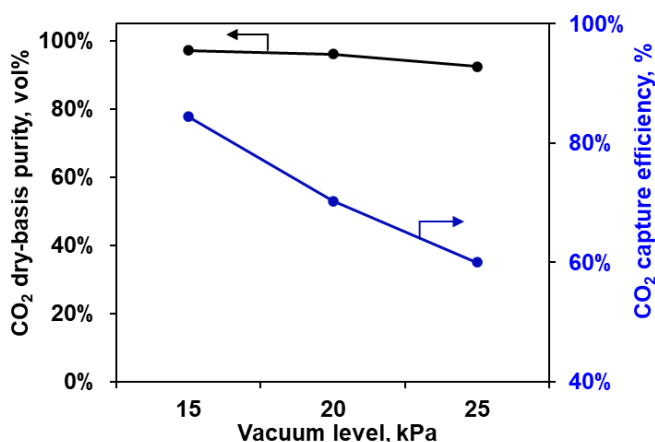


**Figure 13.** Effect of vacuum level on industrial flue gas CO<sub>2</sub> capture performance.

#### 3.7.2. Long-term testing

A 200-hour continuous CO<sub>2</sub> capture test using simulated industrial flue gas was conducted to investigate the long-term stability. The system was operated under the following conditions: a feed gas composition of 24.0 vol% CO<sub>2</sub>, 10.3 vol% O<sub>2</sub>, and 1.0 vol% H<sub>2</sub>O, balanced N<sub>2</sub>, a feed flow rate of 8 SLPM, feed pressure of 1.06 bara, temperature of 35°C, and vacuum pressure of 20 kPa. The system achieved a CO<sub>2</sub> dry-basis purity of 96.4 vol% with a CO<sub>2</sub> capture efficiency of 70.5%, indicating promising capture performance. Throughout the 200-hour test, both the CO<sub>2</sub> dry-basis purity and CO<sub>2</sub> capture efficiency remained stable, as shown in Figure 14. These results show the robust long-term stability of the sorbent under industrial flue gas conditions. It is also worth noting that since the test campaign began at NCCC in April 2025 and continued through December 2025, no sorbent regeneration was carried out. After each test campaign, the system was simply shut down and later restarted for the next campaign, without any special reactivation procedures applied to the sorbent during the shutdown.

periods. This clearly indicates the robustness and long-term durability of the sorbent under realistic operating conditions.

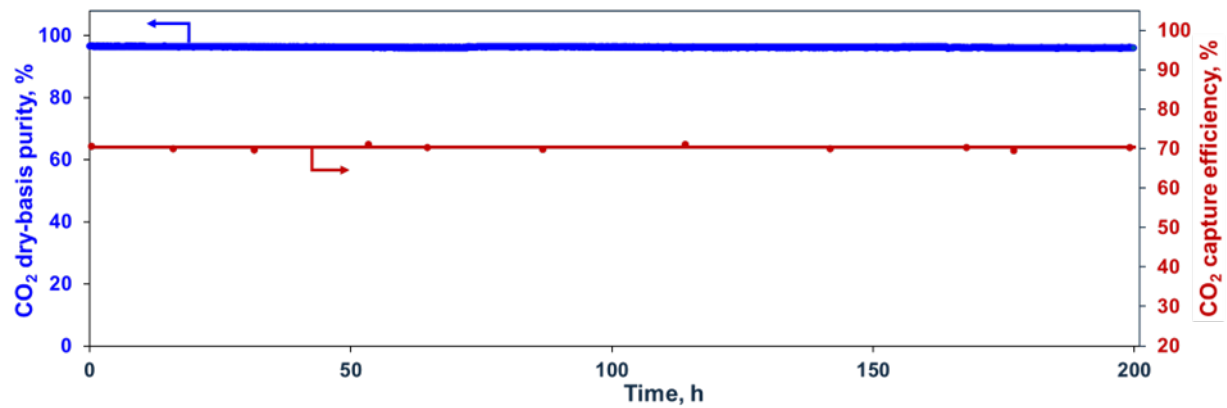


**Figure 14.** Long-term testing results over a 200-hour campaign at NCCC using simulated industrial flue gas.

#### 4. Summary and future steps

- UB developed a transformational Ti-13X zeolite using ALD to passivate strong adsorption sites in conventional 13X zeolite. Compared with pristine 13X zeolite, Ti-13X exhibited improved CO<sub>2</sub> capture performance, including higher CO<sub>2</sub> working capacity, increased CO<sub>2</sub>/N<sub>2</sub> selectivity, improved regenerability, and greater tolerance to water and contaminants.
- USC developed a proprietary PSA cycle concept for flue gas CO<sub>2</sub> capture that significantly reduces the number of required adsorption beds and overall capture cost.
- A bench-scale PSA skid using the Ti-13X sorbent was designed and constructed.
- GTI Energy led field testing at the NCCC. For simulated coal fired flue gas, the system achieved a CO<sub>2</sub> dry-basis purity of 96.3 vol% and a CO<sub>2</sub> capture efficiency of 92.6%, with stable operation over 1,000 hours.
- For simulated industrial flue gas, the system achieved a CO<sub>2</sub> dry-basis purity of 96.4 vol% and a CO<sub>2</sub> capture efficiency of 70.5%, with stable operation over 200 hours.

Future steps would include the following:

- Design and build an engineering-scale Ti-13X/PSA CO<sub>2</sub> capture system; and
- Conduct tests at coal-fired power or industrial plants, and demonstrate a continuous, steady-state operation for a minimum of two months.

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## List of Acronyms

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| Acronym | Description                                   |
|---------|-----------------------------------------------|
| ALD     | Atomic layer deposition                       |
| BET     | Brunauer-Emmett-Teller                        |
| CnD     | Countercurrent depressurization               |
| DOE     | Department of Energy                          |
| EDS     | Energy-dispersive spectroscopy                |
| EqD     | Equalization down                             |
| EqU     | Equalization up                               |
| FGD     | Flue gas desulfurization                      |
| FIB-SEM | Focused ion beam scanning electron microscope |
| GTI     | GTI Energy                                    |
| HR      | Heavy reflux                                  |
| LPP     | Light product pressurization                  |
| LR      | Light reflux                                  |
| LSTU    | Lab-scale testing unit                        |
| MLD     | Molecular layer deposition                    |
| NCCC    | National Carbon Capture Center                |
| NGCC    | Natural gas combined cycle                    |
| PC      | Pulverized coal                               |
| PSA     | Pressure swing adsorption                     |
| QA/QC   | Quality assurance/quality control             |
| RPI     | Rensselaer Polytechnic Institute              |
| SEM     | Scanning electron microscope                  |
| SLPM    | Standard liter per minute                     |
| UB      | The State University of New York at Buffalo   |
| USC     | University of South Carolina                  |
| XRD     | X-ray diffraction                             |
| XPS     | X-ray photoelectron spectroscopy              |

**END OF REPORT**