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A realistic study of the applicability of Zeolite 13X as a sorbent for Point Source Capture

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In this study, the sorption capabilities of zeolite 13X were evaluated for the Point Source Capture (PSC) of CO_2 *using multiple Surface Measurement Systems sorption instruments. Experiments were conducted at 15%* CO_2 *as a common flue gas concentration using the DVS Carbon Advanced and Breakthrough Analyzer (BTA) Frontier systems. Under dry conditions Zeolite 13X demonstrates efficient* CO_2 *capture with 20 wt% average uptake. Gravimetric experiments under humid conditions emphasized the complex nature of the competitive adsorption of water and* CO_2 *on 13X, and thus the preferential adsorption of water over* CO_2*. BTA experiments provide true co-sorption data, which revealed the extensive impact water has on* CO_2 *uptake, with water occupying adsorption sites and significantly reducing* CO_2 *uptake even at low relative humidity levels. This study demonstrates that for a comprehensive sorbent analysis for post combustion applications, prospective materials must be evaluated under both dry and humid conditions.*

Introduction

In 2024, the global temperature anomaly surpassed 1.5°C, a direct result of anthropogenic activities and increased greenhouse gas (GHG) emissions.[1] The consumption of fossil fuels has made CO_2 the leading GHG, with atmospheric concentrations rising to 421.20 ppm in 2024.[2] In order to meet the global temperature limit of 2° outlined in the Paris Agreement (2015), responsible and effective removal technologies must complement the ongoing replacement of fossil fuels. [3]

As such, the 2015 UN Climate Change Conference predicted that carbon capture and storage will play a significant role in mitigating CO_2 emissions and facilitating the decarbonization of the industrial sector.[4] **Direct Air Capture (DAC)** removes CO_2 directly from the atmosphere (around 400ppm concentration) at a high energy cost. This differs from **Point Source Capture (PSC),** which targets the removal of CO_2 from industrial effluent streams, such flue gas which has a CO_2 concentration of 15%.[5, 6]

Currently, the most mature CO_2 capture process is amine scrubbing, but amine regeneration is an energy intensive process due to its high temperature requirement. The use of amines has also resulted in significant equipment corrosion.[7] Solid sorbents, such as polymers, activated carbon, zeolites and metal organic frameworks (MOFs) provide an attractive alternative for the next generation of CO_2 capture technologies due to their promise of energy efficiency, decreased environmental impact and lower operating costs.

Such sorbents have a high affinity for CO_2 and once saturated can be regenerated by applying heat, vacuum or other methods to release the captured CO_2, which can then either be stored or utilized. Some, but not most, have been shown to achieve significant CO_2 uptake and stable performance over multiple regeneration cycles, making them ideal candidates to replace liquid amine adsorption on account of their efficiency and scalability.

Zeolites are highly porous solid sorbents with a large surface area and strongly interacting cages or counterions that can enable high CO_2 uptake. As such, they are particularly attractive candidates due to their CO_2 capacities at low pressures and their ability to achieve high CO_2 selectivity.[8]

Zeolite 13X is a prototypical material often used as a benchmark for adsorbent post combustion carbon capture due to its large selectivity of CO_2 over N_2.[9] 13X is a sodium-exchanged aluminosilicate with a faujasite topology and an effective pore size of around 0.9-1.0 nm. It is a cost effective, highly stable and widely available material used in industrial gas separations such as oxygen production, gas drying or desulfurization. Due to its high uptake for CO_2, resulting from its well-defined pore structure, it was investigated for its capture in post combustion conditions in flue gas streams. However, zeolite 13X also has a strong affinity for water which means that CO_2 adsorption is inhibited in real-world humid conditions as water competes and occupies the micropores. As such, it is generally not a prime adsorbent candidate for PSC.

In this study, we aim to evaluate zeolite 13X for PSC at the lab scale. The DVS Carbon Advanced and BTA Frontier are utilized to analyze its applicability as a carbon capture sorbent material under real world post-combustion conditions of 15% CO_2 concentration influenced by humidity.

Materials and Methods

Zeolite 13X was sourced from Zeochem as binderless pellets of 1.2-1.4 mm diameter.

Isothermal, time-resolved uptake and kinetics experiments were performed using 20 mg (3 pellets) of sample at target temperatures of 25, 50 or 85°C on a DVS Carbon Advanced instrument, shown in Figure 1. The uptakes of CO_2 and water were measured gravimetrically using a high-resolution low-mass UltraBalance (0.01 µg sensitivity) in a temperature-controlled incubator (±0.01°C resolution). Gas compositions were adjusted by blending a saturated H_2O stream in N_2 and pure CO_2 with dry N_2 and were equally split between a sample and reference chamber. A total flow rate of 200 sccm, with 100 sccm over the sample, was maintained to achieve the desired concentrations. Relative humidity (RH) was monitored with a capacitive sensor. Similarly, CO_2 concentration was monitored with the SMS patented Speed of Sound (SOS) technology. Prior to sorption, the sample was activated *in situ* at 300°C under a flow of pure N_2 for 5 hours. Each step was considered equilibrated when the rate of mass change (*dm/dt*) was equal to 0.002 %/min.

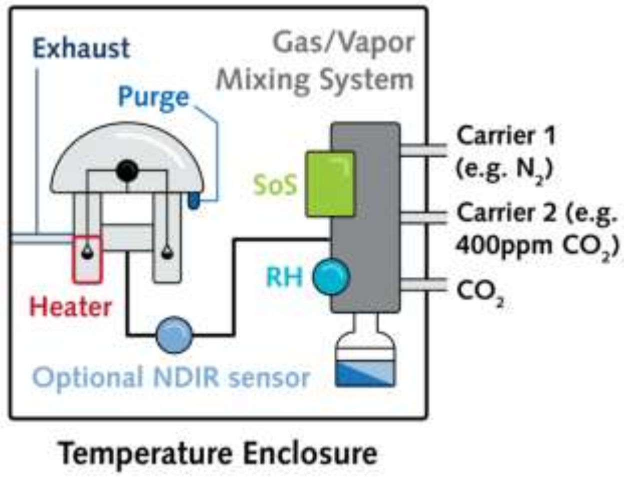


Figure 1: Schematic of the DVS Carbon Advanced.

Breakthrough experiments were completed in the BTA Frontier, a self-contained breakthrough instrument which accurately controls concentrations of water and CO_2 over a packed bed, indicated by Figure 2. A silanized glass column of 4 mm inner diameter was packed with zeolite 13X pellets (263 mg), held in place with quartz wool. All breakthrough experiments were carried out under a temperature of 25°C and a total flow rate of 50 sccm, maintained by 6 mass flow controllers (MFC's).

Firstly, the pressure drop was verified to be negligible over the column before the sample was activated *in situ* at 300°C (in a control oven of accuracy ±0.2°C) under a flow of pure N_2. The concentration of CO_2 is monitored at the column outlet (C) when a flow of constant concentration (C_0) is put through the inlet. Initially, as gas flows through the sorbent, the material captures CO_2 and nothing is seen at the outlet (C/C_0 is close to 0.) Over time, the sorbent material becomes increasingly saturated, leading to the "breakthrough" point, where the concentration of gas passing through the material begins to rise. The curve then steepens, reflecting the mass transfer zone closely related to the sharpness of the front through the column, which is largely a result of sorption kinetics.

The equilibrium time marks the point where the sorbent is fully saturated, and the gas concentration at the outlet matches the inlet concentration (C/C_0 close to 1.) A mass balance is then performed to calculate the total CO_2 uptake. A blank experiment is carried out to account for the dead volume of the column, which is then subtracted from the results to obtain accurate uptakes. While the BTA frontier measures both inlet and outlet flow rates, and flow change effects can be considered negligible in the low concentrations used in experiments. Outlet H_2O and CO_2 concentrations were measured respectively with a capacitive RH sensor and an NDIR sensor.

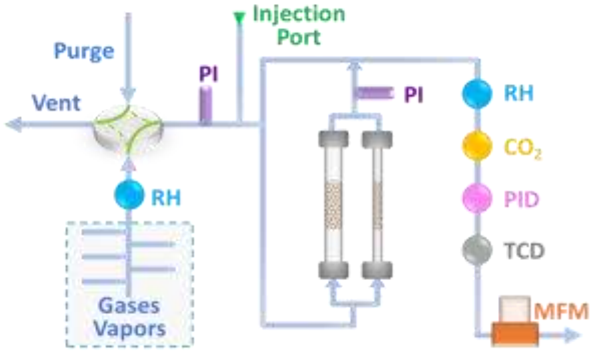


Figure 2: Schematic of the BTA Frontier.

Preliminary textural characterization of zeolite 13X was performed using a volumetric BET analyzer. The sample was activated at 300°C for 12 hours before nitrogen isotherms were collected within the relative pressure range (p/p_0) of 0.01-0.99 at 77K and 298K using liquid nitrogen as the coolant.

Results

Textural Characterization

To textually characterize the 13X sample, N_2 isotherms were collected at 77K and 298K, shown in Figure 3. At 77K, the sample shows a Langmuir Type I profile, characteristic of a microporous material with an uptake at saturation of approximately 30wt%. A calculated BET area of 706.1 m^2/g is consistent with previously reported literature values.[10] At ambient temperature, the isotherm follows a Henry's law regime, and uptake decreases to 1%. From these results, it can be concluded that N_2 is not adsorbed significantly onto 13X at higher temperatures due to the intrinsically weak interaction between the N_2 molecule and the surface of the zeolite at this temperature.[11, 12] This confirms that the N_2 carrier gas used in this study does not significantly compete for adsorption sites on 13X and does not influence subsequent CO_2/H_2O co-adsorption measurements.

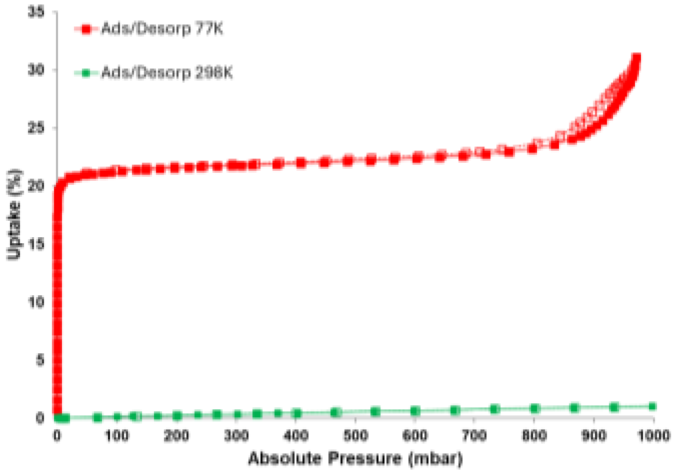


Figure 3: N_2 Isotherm of 13X at 77K (-196°C) and 298K (25°C)

Single Component Gravimetry

To firstly assess the potential of 13X for post combustion capture, single component CO_2 isotherms were recorded. The sample was pre-treated at 300°C before individual isotherms of CO_2 recorded in a carrier gas (N_2) at 25, 50 and 85°C are shown in Figure 4.

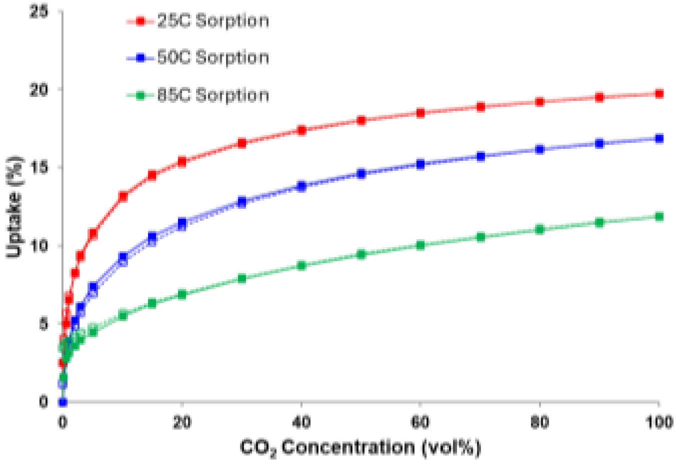


Figure 4: CO_2 Isotherm of zeolite 13X at 25, 50 and 85°C

The isotherm shows a Langmuir Type I isotherm with a high uptake below 20% CO_2 which plateaus as saturation is approached, indicating 13X is reasonably effective at capturing CO_2 at post-combustion conditions. Uptake of CO_2 decreases as expected with increasing temperatures. The desorption curves closely match the adsorption curves, indicating minimal hysteresis and good reversibility.

Other than N_2, the most common contaminant in the PSC process is water. The presence of water in post combustion gas can potentially compete with the adsorption of CO_2 on solid sorbents. [14]

The isotherms of single component water uptake at 25, 50 and 85°C are shown as a function of RH in Figure 5 a) and as a function of volume gas composition (vol %) in Figure 5 b). Note that while the CO_2 isotherm is presented as a function of CO_2 volumetric concentration (vol%) of a total pressure of 1 bar, the water isotherm is shown as a function of relative humidity (RH %) and can vary from 0% to 100%. At 100% RH the gas composition by volume of water is around 3 vol %.

The water experiments show a Type II isotherm, characterized by a steep initial uptake at low RH before a gradual loading increase until RH levels of 80% are reached. As higher RH levels were reached a final steep uptake was observed. These observations are consistent with Type II profiles commonly reported for hydrophilic zeolites, suggesting a mechanism of initial filling close to the cation (Na^+) sites, followed by multilayer growth and eventual pore filling.[15, 16]

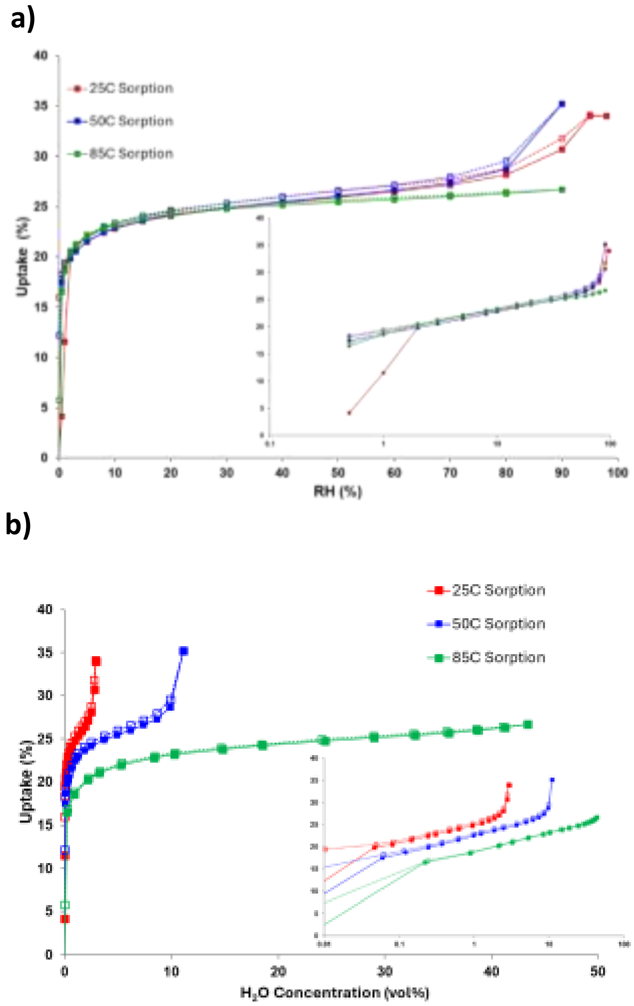


Figure 5: H_2O Isotherms of zeolite 13X at 25, 50 and 85°C plotted against RH (a) and absolute pressure (b)

Comparison of both isotherms highlights that 13X has a significantly higher affinity and uptake for water over CO_2, indicating water may compete and occupy potential CO_2 adsorption sites on 13X in post combustion streams. Langmuir (K_L) coefficients determined by fitting a Langmuir model are 500 times larger for water than CO_2.

Complementary to single component isotherms, single point sorption experiments were performed at 15% CO_2 and 5% RH, indicated by Figures 6 and 7 respectively. The CO_2 uptake was calculated to be 3.31 mmol/g, and the water uptake 11.9 mmol/g. These experiments can indicate the adsorption capacity and rate of uptake at atmospheric conditions.

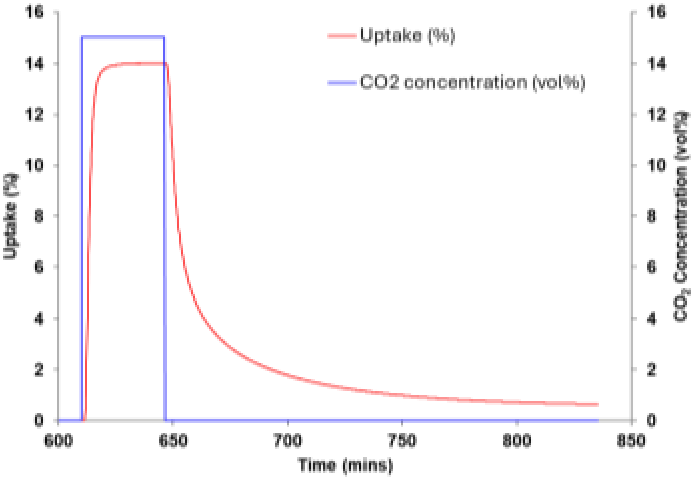


Figure 6: Single step sorption of Zeolite 13X at 15% CO_2, 25°C

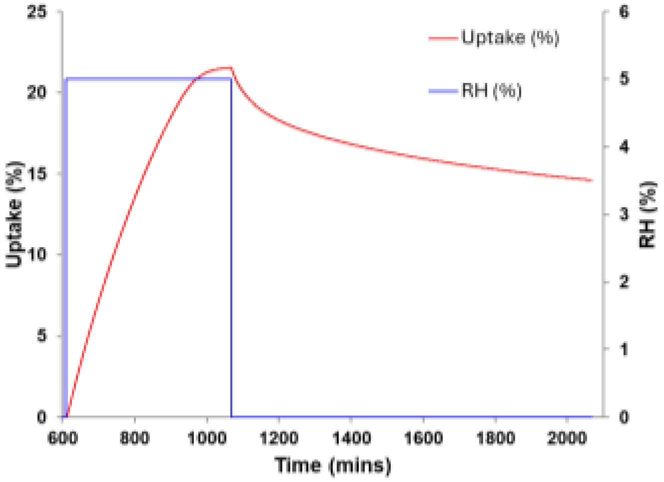


Figure 7: Single step sorption of zeolite 13X at 5% RH, 25°C

An interesting observation from these experiments is that the overall kinetics and mass transport of water sorption are slow compared to CO_2. This may allow kinetic driven, rather than equilibrium driven separation processes within zeolite 13X.

Multi-Component Gravimetry

To further assess the performance of 13X under realistic post-combustion conditions a series of CO_2-water co-adsorption experiments were performed. Multi-component gravimetry experiments enable the simultaneous total competitive adsorption between CO_2 and water and the influence of pre-adsorbed species on uptake to be assessed.

Firstly, CO_2 isotherms were collected at a relative humidity of 1% and 5%, with CO_2 concentration varied from 0-90% at 25, 50 and 85°C. Figure 8 shows the 25°C co-sorption isotherms plotted against the CO_2 single component isotherm collected at 25°C. Higher temperature results are omitted for clarity but show the expected trend of decreasing uptake with increased temperature, in accordance with the exothermic nature of adsorption. In these experiments, the sample was weighed under dry conditions after being fully activated. Water vapor was then introduced and allowed to equilibrate before CO_2 was introduced. The CO_2 isotherm was therefore recorded after an initial water adsorption step, and as such, the non-zero mass uptake observed at 0% CO_2 corresponds to water adsorption.

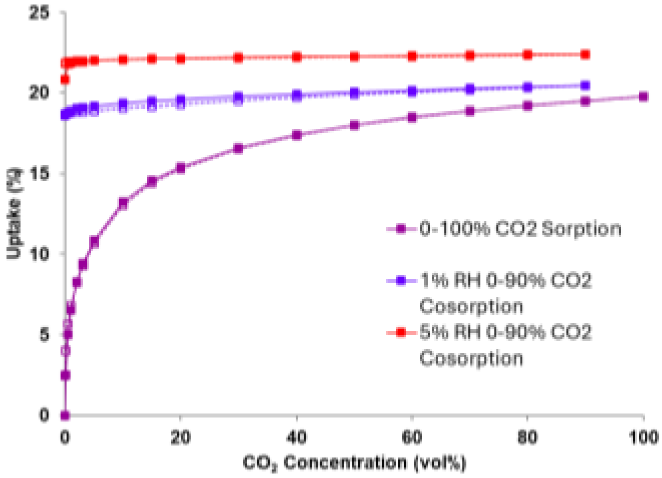


Figure 8: 1% RH 0-90% CO_2 co-sorption, 5% RH 0-90% CO_2 co-sorption and 0-100% CO_2 sorption isotherms, all at 25°C

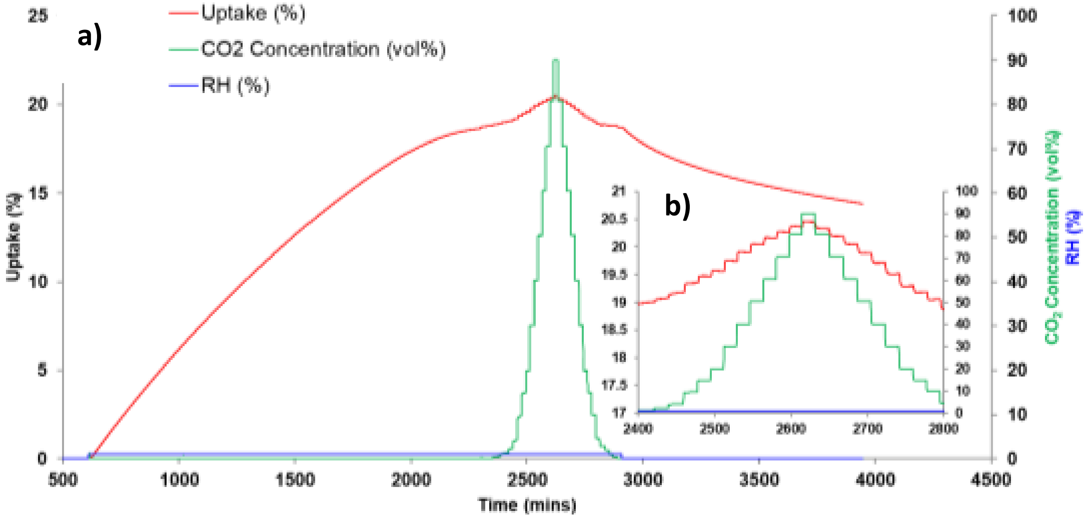


Figure 9: Kinetic plots of 1% RH 0-90% CO_2 co-sorption experiments.

The uptake of both co-sorption isotherms is notably greater than the single component CO_2 isotherm, indicating the strong affinity of zeolite 13X for water even at low relative humidities. As RH decreases from 5% to 1%, a decrease in total uptake is also observed. Contrasting to the single component CO_2 isotherm, the co-sorption isotherms do not display a Langmuirian Type I shape and instead appear as straight lines with high initial adsorption, followed by negligible increase. This suggests that while water initially adsorbs quickly, the presence of humidity competes with and limits CO_2 adsorption on zeolite 13X. The clear difference between the 1% and 5% RH conditions suggests that under intensive desiccation conditions, zeolite 13X could be a successful PSC material.

Figure 9 indicates the kinetic profile of the 1% RH, 0-90 vol% CO_2 experiment and supports the isotherm data. Introduction of humidity resulted in substantial initial mass increase, reflecting the strong affinity of zeolite 13X for water. Small increases in mass under high CO_2 concentrations can also be seen in Figure 9b, which could be small quantities of CO_2 adsorbing. This is supported by the much faster kinetics of these steps, in comparison to the slower kinetics seen for water adsorption processes, although true multicomponent data is needed to confirm these findings.

Conversely, water isotherms collected at a fixed background CO_2 concentration of 15 vol%, were subsequently performed at 25, 50 and 85°C, reflecting post combustion flue gas compositions, Similarly, the sample was first activated and weighed under dry conditions. The background CO_2 was then introduced and allowed to equilibrate prior to introducing humidity, as such the non-zero uptake at 0% RH corresponds to CO_2 adsorption. Figure 10 shows this co-sorption water isotherm compared to the single component water isotherm, both at 25°C.

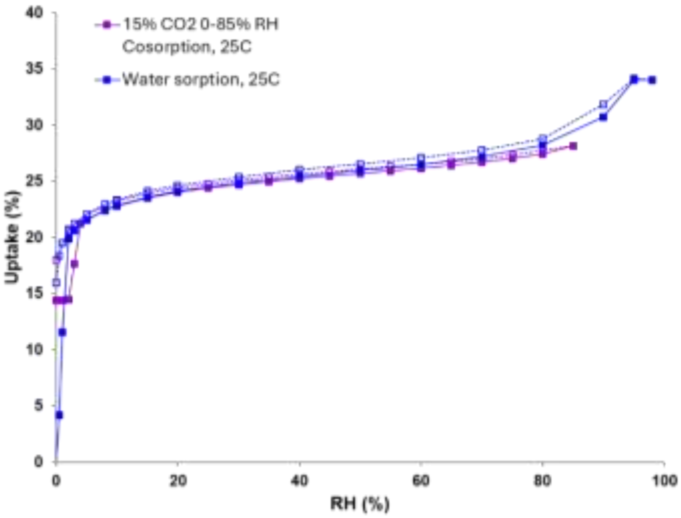


Figure 10: 15% CO_2 with 0-85% RH co-sorption (purple) and single component H_2O sorption isotherm (blue), both at 25°C

Comparing the two plots shows almost identical isotherms. In contrast to Figure 8, it is evident that pre-adsorbed CO_2 does not prevent water adsorption in zeolite 13X. Instead, comparison of these isotherms further suggests that water competes and replaces CO_2 due to its ability to form significantly stronger bonds with the zeolite's sodium cationic sites. Due to the close resemblance between co-sorption data and the single component water isotherm, it can be concluded that the uptake of zeolite 13X under these conditions resulted from water adsorption.

To complement these findings, a single step sorption experiment at 15% CO_2 and 5% RH was performed, shown in Figure 11. CO_2 and water are introduced simultaneously in this experiment. Water is measured in RH, corresponding to a partial pressure of 1.5 mbar, compared to 150 mbar of CO_2. Thus, considering the different sorption kinetics of CO_2 and water established by the single component single step isotherms, the initial fast mass uptake can be primarily attributed to CO_2 adsorption, followed by a slower uptake of water. As such, this experiment confirms kinetic driven post-combustion capture could be achieved using zeolite 13X.

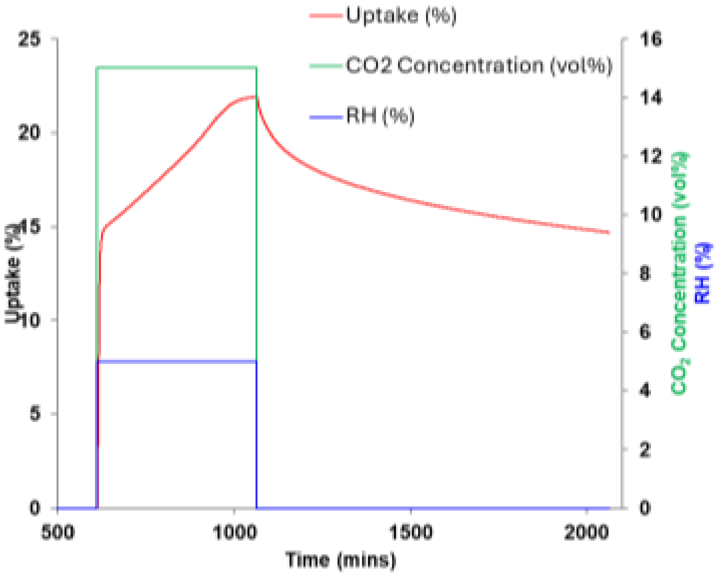


Figure 11: Single step sorption experiment at 15% CO_2 and 5% RH at 25°C

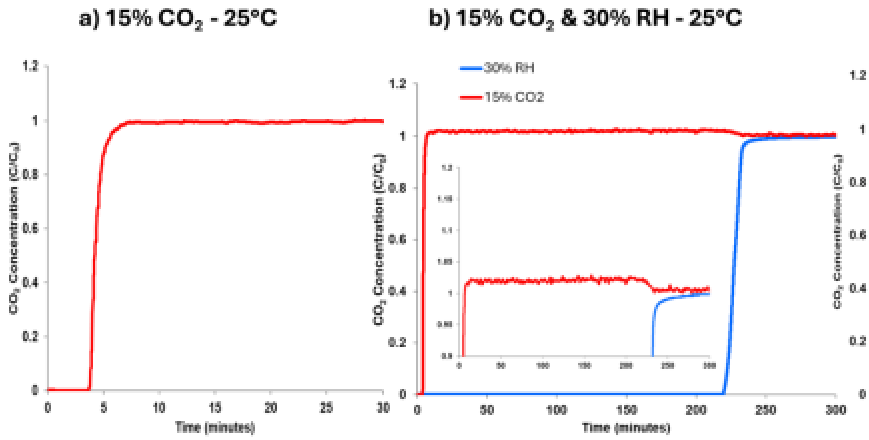
To conclude, Figures 8, 9, 10 and 11 collectively indicate the preference of zeolite 13X for water adsorption over CO_2, thus indicating substantial limitations for its application as a sorbent for carbon capture in humid conditions.

Multi-Component Breakthrough

The BTA Frontier is an essential tool for evaluating solid sorbent candidates for PSC. It provides critical insights into the total capacity, usable capacity (the time before significant breakthrough occurs) and the kinetics of the sorption process, all of which are essential for evaluating the performance of sorbent materials in carbon capture applications. More importantly, it provides true multicomponent data under dynamic flow conditions in both dry and humid regimes and allows evaluation and therefore optimization of the regeneration process. This analysis is crucial for understanding the real influence of humidity on PSC performance in zeolite 13X.

Figure 12 a) shows a breakthrough curve obtained from the BTA Frontier at 15 vol% CO_2 concentration and temperature of 25°C and a flowrate of 50 sccm Figure 12 b) and c) overview the same 15% CO_2 breakthrough when the inlet flow also contains a RH of 30 and 60%, respectively. The experiment at 30% shows a markedly different breakthrough curve to pure CO_2. Similarly, the CO_2 front has passed through the column after saturating it. However, the CO_2 concentration rises above the inlet concentration while water is saturating the column. The same effect, with a slight increase in CO_2 concentration, is also observed when tested with 60% RH. As the water front passes through the column, it is preferentially adsorbed onto zeolite 13X and thus displaces the previously weakly adsorbed CO_2. As such, the displaced CO_2 is added to the inlet stream of CO_2 resulting in a notably larger outlet value. Under 60% RH, the observed displacement of CO_2 occurs much faster than under 30% RH, indicating higher humidity levels increase water sorption and therefore the replacement of CO_2 in the pores of zeolite 13X.

Figure 13 shows the integration of the BTA data to obtain the equilibrium uptake of CO_2 and H_2O. When there's no humidity present, CO_2 uptake is in good agreement with the previous single component results from DVS (3.31 mmol/g).



increasingly occupying adsorption sites as humidity

Figure 12: Breakthrough curves of zeolite 13X at 15% CO_2 and 25°C at (a) 0% RH, (b) 30% RH and (c) 60% RH.

The data shows that as humidity increases to 30% and 60% RH, the uptake of CO_2 drops to very low levels of 0.19 and 0.1 mmol/g, respectively. The uptake of water at this humidity reaches values around 14 mmol/g and 16 mmol/g at 30% RH and 60% RH, in close accordance with the gravimetric data (13.7 mmol/g at 30% RH and 14.5 mmol/g at 60% RH). This indicates strong competitive water adsorption behavior, where water molecules preferentially occupy the adsorption sites on zeolite 13X, effectively fully inhibiting the adsorption of CO_2.

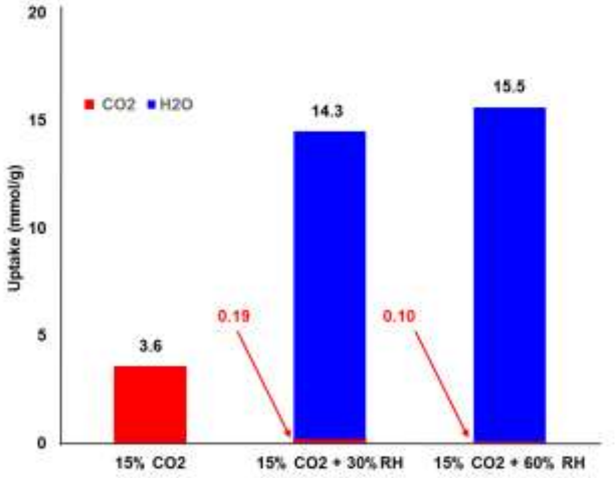


Figure 13:: Uptake of CO_2 and H_2O by zeolite 13X at a concentration of 15% CO_2, with varying relative humidity levels at 0%, 30% and 60%, all completed at a temperature of 25°C.

Overall, the breakthrough results indicate that increasing humidity levels reduce the CO_2 adsorption capacity of zeolite 13X, with water vapor

Conclusion

The investigation of zeolite 13X as a carbon capture sorbent material has demonstrated its advantages and limitations for Point Source Capture applications. Effective carbon capture in these conditions requires a sorbent material that adsorbs significant levels of CO_2 in real world humidity conditions.

The findings of this study from the DVS Carbon Advanced precise gravimetric analysis and the BTA Frontier's dynamic breakthrough testing indicate zeolite 13X exhibits strong CO_2 adsorption capabilities, particularly at low concentrations below 10%. However, co-adsorption studies revealed that humidity significantly hinders zeolite 13X's application as a sorbent. Water vapor competes and preferentially adsorbs on sorption sites, thus drastically reducing the efficiency of zeolite 13X in real-world scenarios. The advanced techniques used in this study provided further valuable insights into the kinetics, mass transport and diffusion capacity of zeolite 13X, emphasizing the necessity for further research to optimize its performance under a variety of environmental conditions. As climate change mitigation efforts grow in the following years, comprehensive analysis of materials like zeolite 13X will be crucial in developing effective technologies to reduce CO_2 emissions and successfully transition to a net-zero future.

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