

# Analysis of Dynamic CO<sub>2</sub> Capture over 13X Zeolite Monoliths in the Presence of SO<sub>x</sub>, NO<sub>x</sub> and Humidity

Qasim Al-Naddaf<sup>1</sup>, Shane Lawson<sup>1</sup>, Ali Rownaghi<sup>1</sup>, and Fateme Rezaei<sup>1</sup>

<sup>1</sup>Missouri University of Science and Technology

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## Abstract

In this investigation, CO<sub>2</sub> capture performance of zeolite 13X monoliths with 600 and 800 cpsi in presence of SO<sub>2</sub>/NO impurities under dry and humid conditions were evaluated and compared with that of 13X beads. Dynamic breakthrough tests demonstrated a drastic reduction in CO<sub>2</sub> capture capacity and deterioration of kinetics under dry-clean conditions, whereas, upon switching the feed from a clean gas to contaminated gas which contained SO<sub>2</sub> and NO, different adsorption performance was observed. Specifically, in dry-contaminated mode, the adsorbents retained their capture capacities with comparable kinetics to that of dry-clean feed conditions, however, in humid-contaminated mode, the adsorbents experienced improved CO<sub>2</sub> uptake and CO<sub>2</sub>/N<sub>2</sub> selectivity, albeit at the expense of deteriorated kinetics. These findings indicate that the presence of SO<sub>2</sub> and NO contaminants, especially SO<sub>2</sub> contaminants, lead to dramatic changes in the adsorption performance of zeolite 13X monoliths, indicating the importance of evaluating adsorbent materials under realistic conditions.

## Introduction

Addressing climate change requires significant efforts to curtail greenhouse gas emissions, in particular anthropogenic CO<sub>2</sub> as well as acidic SO<sub>2</sub> and NO, to keep the average increase in global temperature below 2 °C and to achieve negative emissions by the year 2100. Although a significant amount of recent research has developed innovative technologies for SO<sub>2</sub>, NO, and CO<sub>2</sub> capture from large-point sources, such as affluent post-combustion streams,<sup>1-3</sup> the amine scrubbing method, which is plagued by inherent drawbacks including poor recyclability, deterioration of equipment, energy requirements as high as 4.2 GJ/tonne CO<sub>2</sub>, and poor performance in the presence of SO<sub>2</sub> or NO,<sup>4-7</sup> remains the benchmark technology. In that regard, developing cost-effective and more efficient capture strategies is essential to addressing the impending issue of climate change.

In recent years, adsorption, a technique wherein target gases are physically (physisorption) or chemically (chemisorption) adhered to a selective medium, has cemented itself as an alternative to amine scrubbing technology for CO<sub>2</sub> capture.<sup>8,9</sup> To bring adsorptive CO<sub>2</sub> capture technology one step closer to large-scale implementation, adsorbent materials are required to be shaped into practical contactors that not only demonstrate low mass and heat transfer resistances but also address the operational challenges such as attrition and pressure drop. Honeycomb monoliths with uniform channels and thin walls are considered suitable configurations for this purpose. To date various CO<sub>2</sub> adsorbents including zeolite 13X, activated carbon, and metal-organic frameworks (MOFs) have been shaped into monolithic structures and their CO<sub>2</sub> capture performance has been investigated.<sup>10-12</sup>

While much is known about the performance of CO<sub>2</sub> adsorbents under binary feed conditions (dry CO<sub>2</sub>/N<sub>2</sub> feed), the multicomponent data is quite scarce, especially under realistic feed conditions, where trace contaminants like SO<sub>x</sub> and NO<sub>x</sub> are present. To date, most studies have focused solely on examining the zeolite

stability in the presence of these species, or have focused only on equilibrium adsorption of each species, but have not compared clean and contaminated feeds to one another under dynamic conditions.<sup>13,14</sup> For example, Deng et al.<sup>13</sup> showed that zeolite 13X has a high affinity towards SO<sub>2</sub> on account of its dipole moment, and predicted that this would lead to reduced CO<sub>2</sub> adsorption in multicomponent streams, however, it has yet to be studied how the presence of multiple species impacts CO<sub>2</sub> adsorption on zeolite 13X. Moreover, these effects are likely to be further complicated by the presence of water, which is known to co-adsorb alongside CO<sub>2</sub> under clean-feed conditions and reduce the adsorption capacity. For example, our recent study<sup>12</sup> demonstrated that pre-humidifying zeolite 13X monoliths before exposure to CO<sub>2</sub> leads to competitive adsorption between the two gases and a reduction in CO<sub>2</sub> uptake of 60-80%. Other studies have demonstrated similar effects of humidity on CO<sub>2</sub> adsorption in zeolite 13X materials,<sup>15,16</sup> however, no study yet exists which isolates the combined influences of SO<sub>x</sub>, NO<sub>x</sub>, and H<sub>2</sub>O on CO<sub>2</sub> adsorption in zeolite 13X.

Aiming at addressing this question, we embarked on a study to systematically investigate the CO<sub>2</sub> adsorptive performance of zeolite 13X in both honeycomb and bead forms under various simulated flue gas conditions. We primarily addressed relative CO<sub>2</sub> adsorption changes imparted by competitive/cooperative adsorption of flue gas impurities. Two self-standing commercial zeolite 13X monoliths, with 600 and 800 cells per square inch (cpsi) cell density and beads with particle size of 1.6 mm were used in this work. Multicomponent breakthrough runs were conducted with a simulated flue gas consisting of 10%CO<sub>2</sub>/1000 ppm SO<sub>2</sub>/1000 ppm NO/balance with N<sub>2</sub> under dry and humid conditions and the effect of feed conditions on CO<sub>2</sub> capture performance of 13X samples were investigated accordingly.

## Experimental Section

### Materials Synthesis and Characterization

All ultra-high pure and mixed gases were purchased from Airgas. The crystallinity of zeolite samples was investigated by X-ray diffraction (XRD) measurements on a PANanalytical X'Pert multipurpose X-ray diffractometer with a scan step size of 0.02°/step at the rate of 147.4 s/step. The textural properties were evaluated by N<sub>2</sub> physisorption isotherms at 77 K on a Micromeritics (3Flex) instrument. Prior to the measurements, the adsorbents were degassed under vacuum for 6 h at 350 °C on a Micromeritics Smart VacPrep system. The Brunauer-Emmet-Teller (BET) and non-local density functional theory (NLDFT) methods were used to estimate the surface area and pore size distribution (PSD), respectively. Thermogravimetric analysis (TGA) experiments were carried out to determine the amount of zeolite in each sample. Therein, the temperature was ramped at 15 °C/min from 25 °C-700 °C in 60 mL/min air.

### CO<sub>2</sub> and N<sub>2</sub> Adsorption Isotherm Measurements

Pure gas adsorption isotherms for CO<sub>2</sub> and N<sub>2</sub> were obtained on a volumetric gas analyzer (3Flex) at 25 °C. Prior to measurement, the samples were degassed using the conditions from N<sub>2</sub> physisorption. The isotherms were then used to estimate the ideal selectivity values using ideal-adsorbed solution theory (IAST). Additionally, TGA was also used to measure the CO<sub>2</sub> uptake capacity of fresh samples and used samples (after breakthrough tests) using a 10% CO<sub>2</sub>/N<sub>2</sub> gas mixture at 25 °C and flow rate of 60 mL/min. Before the uptake runs, samples were degassed at 350 °C under N<sub>2</sub> with a flow rate of 40 mL/min for 1 hr.

### Multicomponent Breakthrough Tests

The breakthrough experiments were performed using the setup described in our recent work.<sup>12</sup> The multicomponent adsorption tests were carried out at 1 bar and 25°C in a stainless-steel breakthrough column with an inner diameter of 3.2 cm and a length of 15 cm. Four experimental conditions were investigated: dry-clean, humid-clean, dry-contaminated, humid-contaminated. Under dry conditions, 10% CO<sub>2</sub>/N<sub>2</sub> (dry-clean) or 10%CO<sub>2</sub>/1000 ppm SO<sub>2</sub>/1000 ppm NO/ N<sub>2</sub> (dry-contaminated) gas mixtures were sent through the bed with a flow rate of 100 mL/min whereas, under humid conditions, the sample was first pre-humidified by sending a water-saturated He flow at 100 mL/min to the bed for 30 min. The He stream was humidified by passing the gas through a bubbler before entering the column. Before the breakthrough runs, the adsorbent was regenerated *in-situ* at 350 °C for 3-6 h under He flow at 100 mL/min and then cooled down to 25 °C to

start the test. The concentration of gas mixture in the outlet stream was measured using a mass spectrometer (BELMass). **Table 1** summarizes the geometric characteristics of the adsorbents for the three samples. Notably, the weights were not held constant across sample runs. This was necessary to completely pack the bed. Because the samples contained different infill percentages, the amount necessary to achieve 7.5 cm of bed packing changed between samples.

**Table 1.** Characteristics of the adsorption column for three samples.

Sample	Adsorbent Weight (g)	Bed Height (cm)	Bed Diameter (cm)	Pressure Drop (bar)
1.6 mm 13X-beads	50	7.5	3.2	0.264
Monolith - 600 cpsi	27	7.5	3.2	0.178
Monolith - 800 cpsi	42	7.5	3.2	0.192

## Results and Discussion

### Materials Characterization

The crystallinity of the zeolite adsorbents was confirmed by XRD (**Figure 1a**). As evident, the major characteristics peaks observed in these spectra were consistent with those of zeolite 13X powder,<sup>17</sup> indicating that the crystallinity was not affected during either the extrusion or pelletization processes. It is also worth noting here that, in the monoliths several of the minor diffractive indices exhibited greater intensities compared to the zeolite beads. This could have possibly been attributed to variation between the sources used to manufacture the zeolite or slight differences in the hardening procedures. From the TGA experiments (**Figure 1b**), it was also shown that the monoliths exhibited a greater weight loss (20%) compared to the beads (10%) below 300 °C. This further suggested that the monoliths contained higher amount of organic components than the beads, because the weight loss in both samples could likely be attributed to removal of additional moisture, and the elevated loss in the monoliths indicated that a greater quantity had been adsorbed. Instead, the monoliths' weight loss exhibited a smooth profile which was nearly parallel to that of the beads and is indicative of the removal of a single species.<sup>18</sup> The difference in weight loss could also be explained in terms of zeolite content which is lower in the monoliths (90 wt%) relative to binderless beads.

**Figure 1.** (a) XRD profiles and (b) thermogravimetric analysis curves for 1.6 mm beads, 600 and 800 cpsi monoliths.

The N<sub>2</sub> physisorption isotherms and pore size distributions are shown in **Figure 2** while the textural properties of the samples are summarized in **Table 2**. In the N<sub>2</sub> physisorption profiles (**Figure 2a**), all three 13X adsorbents displayed type I isotherm with H4 hysteresis, suggesting microporous nature of the materials and also the presence of slit-type mesopores formed during the formulation process.<sup>19</sup> These differences were further evident in the pore distributions (**Figure 2b**), where significant reductions in pore volume were observed from the monoliths to the beads. It is also worth noting here that the honeycomb monoliths also exhibited slight mesoporosity at ~4 nm pore diameter. As we reported recently,<sup>12</sup> this could have been caused by the binder removal process, which burns out the organic components and produces a hierarchal pore structure.

**Figure 2.** (a) N<sub>2</sub> physisorption and (b) NLDFT pore distributions for beads, 600 and 800 cpsi monoliths.

As shown in **Table 2**, the BET surface areas were found to be 662, 548, and 571 m<sup>2</sup>/g for the binderless beads, 600 cpsi monolith and 800 cpsi monolith samples, respectively. The surface areas of the monoliths ~ 83% of that of binderless beads which is due to lower zeolite content of the monoliths (i.e., 90 wt%). These differences in surface area were to be expected from TGA, XRD, and N<sub>2</sub> physisorption, which all suggested the monoliths' formulation process decreased the number of accessible pores. This was further supported by the monoliths' slight (8-9%) reduction in micropore volume from the monoliths. Nevertheless, it is worth noting that the differences in pore volume between the three samples were, overall, small. For this reason, they could all be considered comparable in further testing.

**Table 2.** Textural properties of 13X zeolite beads and 600 and 800 cpsi monoliths.

Adsorbent; Zeolite-13X	$S_{\text{BET}}$ [ $\text{m}^2/\text{g}$ ]	$V_{\text{micro}}$ [ $\text{cm}^3/\text{g}$ ]	$V_{\text{meso}}$ [ $\text{cm}^3/\text{g}$ ]	$d_p$ [nm]
1.6 mm Beads	662	0.32	0.04	1.2, 4.0
600 cpsi Monolith	548	0.26	0.06	1.4, 4.1
800 cpsi Monolith	571	0.28	0.05	1.3, 3.4

### CO<sub>2</sub> and N<sub>2</sub> Adsorption Isotherms

**Figure 3** illustrates the CO<sub>2</sub> and N<sub>2</sub> adsorption isotherms obtained at 25 °C for the three adsorbents. In agreement with data for the powdered zeolite,<sup>20</sup> all adsorbents exhibited a high affinity toward CO<sub>2</sub> and negligible capacity for N<sub>2</sub>. At 1 bar and 25 °C, CO<sub>2</sub> adsorption capacities reached to 4.5, 5.1, and 5.1 mmol/g for the beads, 600 cpsi, and 800 cpsi monoliths, respectively, (**Figure 3a**), while N<sub>2</sub> adsorption capacities of 0.2, 0.4, and 0.4 mmol/g, respectively, were observed at the same conditions. The lower adsorption capacity of the beads could be correlated to their formulation which limited their active sites accessibility upon processing, despite having higher surface area and pore volume. Nevertheless, the differences in adsorption capacity between the two configurations were overall small and, therefore, the beads could still be considered an acceptable analogue for testing of multicomponent CO<sub>2</sub> adsorption.

**Figure 3.** Pure gas adsorption isotherms of (a) CO<sub>2</sub> and (b) N<sub>2</sub> for beads, 600 and 800 cpsi monoliths at 25 °C.

The theoretical selectivity for 10% CO<sub>2</sub>/N<sub>2</sub> in the pressure range of 0-1 bar was calculated by the IAST method, as shown in **Figure 4**. A decreasing trend with pressure was observed for the three adsorbents with almost identical values ranging from 720 to 150. Notably, all three samples exhibited the same selectivity values, even though the monoliths exhibited higher adsorption capacities. This was attributed to the fact that, although the beads may have reduced in adsorption capacity from the monoliths, the reductions in adsorption uptake were the same for both CO<sub>2</sub> and N<sub>2</sub>. In turn, this caused the CO<sub>2</sub> selectivity value to remain consistent with that for the monoliths. Chue et al.,<sup>21</sup> who studied zeolite 13X pellets in a pressure swing adsorption process for CO<sub>2</sub> removal from flue gas, reported similar selectivities for zeolite 13X at 1 bar and 10% CO<sub>2</sub>. Effectively, this indicated that the zeolites examined here could be considered representative analogues for materials used in industrial separation processes.

**Figure 4.** Theoretical CO<sub>2</sub>/N<sub>2</sub>selectivity curves estimated from adsorption isotherms for beads, 600 and 800 cpsi monoliths.

### Multicomponent Breakthrough Experiments

To evaluate the materials' performance for CO<sub>2</sub>adsorption under multicomponent conditions, four modes of operation were considered: dry-clean, humid-clean, dry-contaminated, and humid-contaminated. The breakthrough profiles are shown in**Figure 5** while the corresponding breakthrough data is located in **Table 3**. The profiles from the blank experiments as well as the desorption profiles are also shown in **Figure S1**, **Supporting Information** and **Figure S2**, **Supporting Information**, respectively. As was expected, pre-exposing the samples to humidity under clean conditions led to a significant reduction in CO<sub>2</sub> breakthrough time ( $t_{5\%}$ ), on account of the competitive adsorption behavior which exists between these two molecules on zeolite 13X.<sup>12,16</sup> In turn, this led to losses in CO<sub>2</sub> adsorption capacity for all samples from dry to humid conditions. These effects were especially present in the case of the beads (**Figure 5a-b**), where a 65% reduction in  $t_{5\%}$  and a 10% decrease in CO<sub>2</sub>adsorption capacity ( $q_{95\%}$ ) from 2.0 to 1.8 mmol/g occurred from the dry to the humid experiments. This corresponded to a 66% reduction in the bead's CO<sub>2</sub>/N<sub>2</sub>selectivity from 138 to 48. In the monoliths, however, the breakthrough time was only reduced by ~19% in the 600 cpsi sample (**Figure 5c-d**) and 47% in the 800 cpsi sample (**Figure 5e-f**). For the 600 cpsi sample, this corresponded to a reduction in CO<sub>2</sub> adsorption capacity of 2.2 to 1.9 mmol/g, as well as a reduction in CO<sub>2</sub>/N<sub>2</sub> selectivity

of 77 to 54.4. Similarly, the 800 cpsi sample experienced a loss in CO<sub>2</sub> capacity of 1.8 to 1.6 mmol/g, with a reduction in selectivity of 99 from dry to 77 humid modes of operation. These observations were in agreement with both our recent report as well as other literature for dry versus humidified CO<sub>2</sub> adsorption on zeolite 13X and were to be expected.<sup>12,20,22,23</sup> As we detailed therein, the greater reductions in breakthrough time for the beads and 800 cpsi monolith compared to the 600 cpsi monolith could be attributed to differences in particle mass transfer. Namely, the 600 cpsi monolith's larger channels did not throttle the gas and allowed enough time for CO<sub>2</sub> and water to diffuse through the dense walls. In the beads and 800 cpsi monolith, however, adsorbate diffusion occurred through particles and the CO<sub>2</sub> broke through faster than the adsorbent could saturate. A similar effect was also likely present with water, as it readily adsorbed on the closest accessible pores, and further increased the rate dependence for CO<sub>2</sub> adsorption on particle mass transfer.

Moreover, investigation of breakthrough widths revealed that the adsorption dynamics was also impacted by water, with the wavefronts becoming broader under humid-clean conditions. Such a result was in agreement with our recent work,<sup>12</sup> which showed that pre-humidified zeolite 13X samples exhibit broader adsorption wavefronts, on account of the increased dependence on molecular mass transfer caused by saturation of the outer adsorbent layer. The dynamic CO<sub>2</sub> adsorption capacities of 13X zeolite beads estimated at  $t_{50\%}$  were found to be 2.0 and 1.8 mmol/g under dry and humid conditions, respectively, whereas, for the 600 and 800 cpsi monoliths, these values were calculated to be 2.2 and 1.9 mmol/g and 1.8 and 1.6 mmol/g, respectively. Overall, these results indicated that the competitive CO<sub>2</sub>/water adsorption occurred independent of adsorbent geometry, as all three samples experienced a ~10% reduction in  $q_{50\%}$  from dry to humidified conditions. Such a result was to be expected, as the competitive adsorption for CO<sub>2</sub> and water on zeolite 13X is dependent on the adsorbent pore size and adsorbate molecular diameter, which are both independent of the bulk structural packing.<sup>12,16</sup>

**Figure 5.** Breakthrough profiles for CO<sub>2</sub>, He, H<sub>2</sub>O and N<sub>2</sub> under dry-clean and humid-clean modes for (a-b) beads, (c-d) 600 cpsi, and (e-f) 800 cpsi monoliths.

**Table 3.** Summary of breakthrough parameters for zeolite 13X samples under four modes of operation.

Run	Sample	$t_{5\%}$ (min)	$t_{50\%}$ (min)	$t_{95\%}$ (min)	Breakthrough			CO <sub>2</sub> /N <sub>2</sub> Selectivity
					Width (min)	$q_{50\%}$ (mmol/g)	$q_{95\%}$ (mmol/g)	
Dry-clean	Beads	149	179	222	73	1.6	2.0	138
Humid-clean	Beads	54	94	203	150	0.8	1.8	48
Dry-contaminated	Beads	184	216	305	121	1.9	2.7	154
Humid-contaminated	Beads	199	245	351	152	2.2	3.2	177
Dry-clean	600 cpsi	73	94	134	61	1.6	2.2	77
Humid-clean	600 cpsi	59	79	116	57	1.3	1.9	54.4
Dry-contaminated	600 cpsi	87	111	160	73	1.8	2.7	102
Humid-contaminated	600 cpsi	97	131	185	88	2.2	3.1	118
Dry-clean	800 cpsi	111	147	175	64	1.6	1.8	99
Humid-clean	800 cpsi	58	94	156	98	1.0	1.6	77

Run	Sample	$t_{5\%}$ (min)	$t_{50\%}$ (min)	$t_{95\%}$ (min)	Breakthrough			CO <sub>2</sub> /N <sub>2</sub> Selectivity
					Width (min)	$q_{50\%}$ (mmol/g)	$q_{95\%}$ (mmol/g)	
Dry-contaminated	800 cpsi	113	149	193	80	1.6	2.0	104
Humid-contaminated	800 cpsi	115	157	229	112	1.7	2.4	115

In the next step, a multicomponent gas mixture containing CO<sub>2</sub>/SO<sub>2</sub>/NO/N<sub>2</sub> was used to characterize the adsorption behavior of the 13X zeolite monoliths and beads under both dry and humid conditions. **Figure 6** displays the concentration fronts for the three adsorbents collected during dry-contaminated and humid-contaminated breakthrough runs. It should also be noted that SO<sub>2</sub> adsorption did not break through the bed in any experiment. On the other hand, He broke through almost immediately, while N<sub>2</sub> and NO<sub>2</sub> broke through at ~10 min for all samples and exhibited sharp breakthrough wavefronts under both dry and humidified conditions. This was attributed to the low affinity of 13X towards He, N<sub>2</sub> and NO, but high affinity towards SO<sub>2</sub>. Namely, Deng et al.<sup>13</sup> reported that zeolites have a high affinity towards SO<sub>2</sub> compared to N<sub>2</sub>, NO, and CO<sub>2</sub> because SO<sub>2</sub> is the only molecule which contains a permanent dipole moment. In turn, this increases the Henry's Law constant for SO<sub>2</sub> compared to the other compounds and promotes greater adsorption on zeolites. In comparison, the Henry's Law constants for NO and N<sub>2</sub> are much lower and, because of this, these species do not adsorb in high quantities on zeolite 13X, as further demonstrated by their rapid breakthrough times. On the other hand, because the SO<sub>2</sub> concentration in the stream was so low, and the zeolite affinity towards the gas was so high, SO<sub>2</sub> saturation was never achieved and the gas was not detected. It is also worth noting here that, similar to CO<sub>2</sub>, the pre-humidification likely reduced the overall SO<sub>2</sub> adsorption capacity, as water also exhibits a permanent dipole moment and should compete with SO<sub>2</sub> on zeolite.<sup>24</sup> However, given the low SO<sub>2</sub> concentration relative to H<sub>2</sub>O, it is impossible to say for certain whether or not its capacity was reduced under humidified conditions. This being the case, because the goal of the study was to examine CO<sub>2</sub> adsorption behavior in the presence of SO<sub>2</sub>, N<sub>2</sub>, and NO, and not focusing on the adsorption behavior for the contaminant species, the experiments were terminated after CO<sub>2</sub> saturation was observed. For reference, the SO<sub>2</sub> desorption profiles are displayed in **Figure S3, Supporting Information**.

As evident from **Figure 6**, introduction of the acidic contaminants produced significantly longer CO<sub>2</sub> breakthrough times for all three adsorbents under both dry and wet conditions. This caused the CO<sub>2</sub> adsorption capacity to increase by 0-20% in the dry experiments and by ~100% in the wet experiments. This also corresponded to an increase in CO<sub>2</sub> selectivity of 5-30% across the dry experiments for the various samples, whereas the selectivity increased by 50% or more between the humidified-clean and contaminated runs. These increases in adsorption capacity were to be expected from established literature for multicomponent adsorption, which illustrates the promotional effect of SO<sub>2</sub> for CO<sub>2</sub> capture.<sup>25</sup> This may be attributed to the promotional effect of the acidic contaminants towards CO<sub>2</sub>, which becomes more pronounced in the presence of water, on account of the formation of carbonate species. Specifically, under dry operation, the acidic SO<sub>2</sub> increase the sorbents basicity by reacting with the slightly basic Na<sub>2</sub>O species, to produce oxygen atoms which share free radicals. In turn, this causes the contaminants to act as chemisorbents and increases the overall affinity towards CO<sub>2</sub>,<sup>14</sup> but also degrades the zeolitic alumina. Under humid mode, however, the Na<sub>2</sub>O readily reacts with water to form NaOH, which then bonds to the oxygen free radicals in the SO<sub>2</sub>, to produce species which do not interact with the Al<sub>2</sub>O<sub>3</sub> centers. These free electrons can then react with CO<sub>2</sub> to form carbonate, similar to the promotional mechanism of water on CO<sub>2</sub> for amine-modified solids<sup>4</sup> or the promotional effect which occurs between SO<sub>x</sub>, NO<sub>x</sub>, CO<sub>2</sub>, in other solid adsorbent systems.<sup>25,26</sup>

**Figure 6.** Breakthrough profiles for CO<sub>2</sub>, He, H<sub>2</sub>O, NO, SO<sub>2</sub>, and N<sub>2</sub> under dry-contaminated and humid-contaminated modes for (a-b) beads, (c-d) 600 cpsi and (e-f) 800 cpsi monoliths.

Comparison of CO<sub>2</sub> concentration profiles obtained under each mode of breakthrough experiments are pre-

sented in **Figure 7**. It can be observed that the breakthrough time was shortened significantly in the humid bed as a result of competitive adsorption of CO<sub>2</sub> and water, however, when SO<sub>2</sub> and NO were present, a reverse trend was observed and total dynamic adsorption amount was enhanced. Such cooperative adsorption occurred across all three samples examined in this study and became further exacerbated under humid-contaminated conditions. Considering the shape of wavefronts, the zeolite 13X beads (**Figure 7a**) exhibited the sharpest breakthrough front under dry-clean conditions, however, exhibited nearly double the breakthrough width under both humidified modes, on account of the competitive CO<sub>2</sub>/water adsorption behavior. In comparison, the dry-contaminated mode did not increase the breakthrough width nearly as much as the humidified modes of operation. However, the additional chemisorption still broadened the profile by 65% from the dry-clean run. Both the 600 cpsi (**Figure 7b**) and 800 cpsi (**Figure 7c**) monoliths experienced similar changes in wavefront broadness across the different modes, however, the increases in front width were much less compared to the beads. This was attributed to the monoliths' higher rate of film mass transfer compared to the beads, which is a well-established benefit of using monolithic contactors.<sup>27</sup> Between the two monolith samples, the 800 cpsi sample experienced greater increases in front width from the dry-clean to the other modes compared to the 600 cpsi monolith. As discussed previously, this was attributed to the increased kinetic dependence on molecular mass transfer which occurs at elevated cpsi monoliths, leading to more bead-like behavior.<sup>12,16</sup>

**Figure 7.** Comparison of CO<sub>2</sub> breakthrough profiles under four modes of operation for (a) beads, (b) 600 cpsi monolith, and (c) 800 cpsi monolith.

After breakthrough tests, TGA runs were conducted over the used samples to investigate the degree of CO<sub>2</sub> capacity loss after exposure to impurities. **Figure 8** compares the CO<sub>2</sub> uptake capacities of the three adsorbents after each mode of breakthrough runs with that of fresh materials. As can be seen, the differences in CO<sub>2</sub> adsorption between the fresh, dry-clean, and humid-clean samples were, overall, marginal. Notably, the dry-clean samples all exhibited slightly lesser CO<sub>2</sub> adsorption from the fresh and humid-clean samples, however, these losses were only ~8% and could have been caused by slight changes in intraparticle bonding from the repeated heating and cooling of the samples. On the other hand, the losses in adsorption capacity for the dry-contaminated runs could not be discounted, as the beads, 600, and 800 cpsi monoliths exhibited 38%, 58%, and 14% losses in CO<sub>2</sub> adsorption capacity, respectively. As previously discussed, these sizable losses could likely be attributed to decomposition of the sodium centers after reaction with the acid gases. Following the humidified-contaminated runs, however, the losses in CO<sub>2</sub> capacity were only marginal, as the reductions in CO<sub>2</sub> adsorption capacity were only 25%, 14%, and 11% for the beads, 600 cpsi monolith, and 800 cpsi monolith, respectively. On the basis of these results, it was concluded that water can act as a protective barrier during CO<sub>2</sub> adsorption on zeolite when SO<sub>x</sub>/NO<sub>x</sub> are present, as it allows the acid gases to react with hydroxide clusters instead of decomposing the alumina centers.

**Figure 8.** Comparison of CO<sub>2</sub> adsorption capacity of the materials before and after breakthrough experiments for beads, 600 and 800 cpsi monoliths.

#### 4. Conclusions

This study reports on CO<sub>2</sub> adsorption behavior of zeolite 13X monoliths and beads under dry and humid conditions using both clean and contaminated simulated flue gas feeds. As reported herein, zeolite beads and monoliths experienced substantial drop in CO<sub>2</sub> breakthrough time after being saturated with humidity, on account of the competitive adsorption which exists between CO<sub>2</sub> and water. On the other hand, a cooperative effect was observed when SO<sub>2</sub> and NO were introduced alongside the presence of water. In those experiments, water led to the formation of NaOH clusters which reacted with the acid contaminants to produce chemisorbents. In turn, this gave rise to enhanced CO<sub>2</sub> adsorption capacity via carbonate formation on the additional active sites. This being stated, all samples exhibited broader breakthrough fronts in the contaminated runs compared to the clean-mode experiments, as a result of added chemisorption because, although it did provide additional sites for CO<sub>2</sub> adsorption, the mechanism for chemisorption was likely slower than that of physisorption, as it relied on the reaction kinetics instead of mass transfer alone. Therefore, this study concluded that zeolite materials – including binderless beads and 600 cpsi, and 800 cpsi monoliths –

perform better under multicomponent flue gas conditions from an adsorption capacity standpoint, but exhibit slightly slower mass transfer kinetics. Moreover, this study indicated the importance of examining adsorbent materials under realistic conditions for successful implementation in scaled-processes and emphasized the need for performing cyclic adsorption-desorption experiments using multicomponent streams.

### Author Information

Corresponding Author

\*Email: rezaeif@mst.edu

ORCID: 0000-0002-4214-4235

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