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ADSORPTION REVERSIBILITY OF SO2, NO2, AND NO ON 13X AND 5A ZEOLITES

by

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ABSTRACT

The adsorption reversibility of gasses that are typically found in flue gas for coal based power plants, such as SO_2, NO_2, and NO, onto 13X and 5A zeolites was presently investigated. The four individual gas mixtures containing these species consisted of 74 ppm NO (balance He), 74 ppm NO_2 (balance He), 42 ppm SO_2 (balance He), and 500 ppm SO_2 (balance N_2), which were also consistent with the values that are found in flue gas. Another gas, 15.03 mol% CO_2 (balance N_2), was also used in this work to evaluate the role of exposing SO_2 to the zeolite on their adsorption behavior toward CO_2. The study included single cycle thermogravimetric analyses (STGA) with all gas mixtures, multiple cycle thermogravimetric analyses (MTGA) with the mixture containing 500 ppm SO_2, and consecutive CO_2 breakthrough studies through an adsorption bed containing 1 to 1.5 g sample of zeolites before and after saturating the samples to 500 ppm of SO_2. All runs were executed at 70 ºC during exposure to SO_2, NO_2 and NO and CO2, while during regeneration with nitrogen, the role of temperature is also investigated when possible. The absolute pressure was kept at 1 atm. Results show that NO and NO_2 showed limited, but very reversible, behavior toward to both 13X and 5A. In the case of SO_2 however, the results show that SO_2 has a very negative effect on 13X, adsorbing irreversibly. Nitrogen purge at temperatures of even 450 ºC were not sufficient to remove and desorb the SO_2 from the 13X. A completely different result was observed with the 5A, where SO_2 did not display any observable irreversible adsorption upon it. A simple purge of nitrogen at 70 ºC overnight was sufficient remove most of the

SO_2 from the 5A zeolite. These results conclusively show that 5A could be used as a good candidate for an effective guard layer to protect the better, 13X zeolite, placed downstream for CO_2 capture.

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CHAPTER 1

INTRODUCTION

It has widely been suggested that present forms of energy generation is resulting in global climate change. Worldwide, the energy sector relies strongly on the combustion of fossil fuels for the generation of electricity. Carbon dioxide is the largest greenhouse gas constituent of flue gas, about 15% by volume (DOE, 2007). Consequently, current forms of power generation has resulted in a significant release of carbon dioxide into the atmosphere. Atmospheric concentrations of carbon dioxide have increased at an average rate of approximately 10.8 ppm/decade from the year 1955 to 2015, resulting of today values of around 400 ppm (Stocker, 2013). Despite alternative energy research, combustion is still forecasted to be responsible of 28% of the power generated in the year 2030 (Owens, 2012).

Important efforts have been given to the development of technologies that specifically address carbon capture, that is, to the separation of carbon dioxide from flue gas to avoid its release into the atmosphere. The utilization of absorption via alkanolamines has been one solution offered to deal with this problem. Absorption via alkanolamines is well known and a commercially established technology in the industry of natural gas sweetening (Conway, 2015) and could, eventually, also be implemented in carbon capture (Conway, 2015). However, there are key traits rendering amine absorption unattractive that include, just to mention a few, its strong dependence on steam generation that result in significant parasitic losses, the corrosive nature of alkanolamines, the costs associated with the removal of vapor from the enriched carbon dioxide product stream, the constant need of makeup alkanolamines and the inherent toxicity of alkanolamines that presents health hazards risks to workers (Arunkumar, 2011). Safer technologies that have also been proposed for carbon capture has been processes that rely on adsorption principles such us pressure swing adsorption (PSA) or temperature swing adsorption (TSA). These technologies only require electricity for regeneration (via vacuum) and do not involve any chemical reaction between adsorbents and adsorbates. To date, zeolites have shown to be the most effective materials for CO_2 capture via adsorption (Arunkumar, 2011), and amongst these, 5A and 13X have been most extensively studied for CO_2 capture (Dirar, 2013). Being made of a microporous alumina-silicate structure containing positive cations (Yang, 1987), zeolites are always excellent candidates for physisorption of molecules with dipoles and quadrupoles, in particular CO_2, at intermediate and low pressures. Despite their similarities, they do have structural differences that lead to differences in exposure to their microstructure and behavior toward carbon dioxide. While the micropores of both 5A and 13x possess cations (Kärger, 1992) 5A zeolite has a Linde Type A structure with calcium cations whereas sodalite cages link to 6 other neighboring sodalite cages through all of its 4 member rings. In contrast, 13X zeolite has a faujasite structure wherein sodalite cages link to only 4 to four of its neighboring sodalite cages via half of its eight 6-member rings.

However, other gasses such as nitrogen dioxide (NO_2), nitrogen monoxide (NO) and sulfur dioxide (SO_2) are also present as combustion products of (DOE, 2007) flue gas and even if present in low concentrations they can still undergo irreversible interactions with the zeolite that may significantly compromise the performance of the PSA or TSA process. SO_2 may react through irreversible chemical reactions (Cotton, 1999), but to date, little or no research on the reversibility of SO_2, NO_2, and NO upon zeolites is available.

In the present work, two zeolites, 5A and 13x, will be tested to infer their reversibility and carbon dioxide working capacity upon exposure to $NO_{2,}$ NO, and SO_2,. The reversibility of these gases of 13x and 5A will be analyzed through various methods that include single-cycle thermogravimetric analysis (STGA), multi-cycle thermogravimetric analysis (MTGA), and breakthrough studies.

CHAPTER 2

MATERIALS AND METHODS

2.1 MATERIALS

5A and 13X zeolite samples were used in the present study including a 5A zeolite in pelletized form and a 2-µm 13X zeolite crystal powder provided by Grace Davison and a 13X zeolite (Oxysiv-5XP) provided by Honeywell UOP. All gases utilized for the experimentation were purchased from Airgas and include pure N_2 and He (both UHP grade), and mixtures containing 74 ppm NO (balance He), 74 ppm NO_2 (balance He), 42 ppm SO_2 (balance He), 500 ppm SO_2 (balance N_2) and 15.03% by volume CO_2 (balance N2).

2.2 THERMOGRAVIMETRIC ANALYSES

A Perkin-Elmer TGA-7 thermogravimetric analyzer (TGA) was used to measure the dynamic adsorption and desorption behavior of different gasses on 5A or 13X zeolites. A schematic of the experimental apparatus is displayed in Figure 2.1. Three different gases are feed into the TGA apparatus during one run as depicted in the figure. Both the balance gas and the purge gas consist of pure nitrogen while the feed gas may also be pure nitrogen, or any of the mixtures previously mentioned. The balance gas is sent directly to the chamber at the upper part of the TGA wherein the electronic balance is located to protect it from getting in direct contact with gas species present in the feed gas. The feed gas and the purge gas are sent into the chamber containing the sample of zeolite to achieve adsorption and desorption of the species present in the feed onto the sample. The purge gas is also used during the pre-purge and activation steps carried out on the sample. The feed and purge gasses access the TGA through the bottom and once inside move upward toward the sample to then meet and mix with the balance gas leaving the balance chamber at some place above the sample to leave the TGA toward the exhaust. Each gas line is connected to an individual rotameter that is set to provide a flow rate of 80 cc/min. The lines of the feed gas and the purge gas are connected to individual solenoid valves located downstream the rotameters. These solenoid valves are opened and closed alternatively via an electronic timer (Chrontrol by Chrontrol Inc.) that control either the feed or the purge gas to go into the TGA at any given time. The

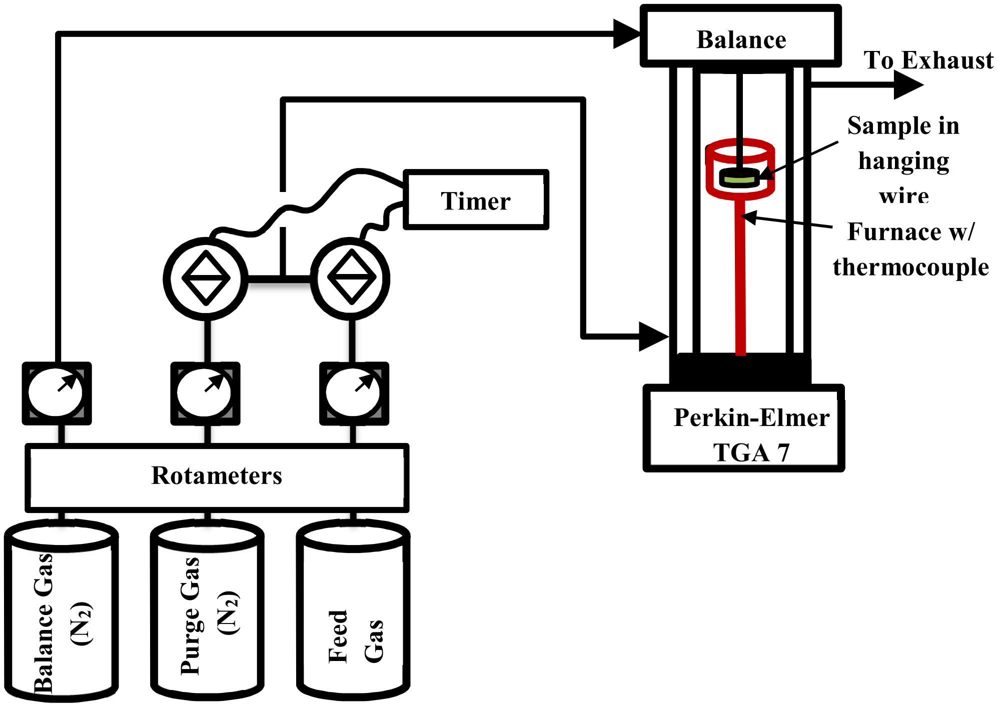

Figure 2.1 Schematic of The Adsorption-Desorption Cycling Experimental Apparatus, Depicting a Thermogravimetric Analyzer, An Electronic Valve Timer and Balance Purge

electronic timer allows these valves open and close in a cyclic fashion or as desired by the user.

About 10-20 mg of sample is used in each run. In the case of 5A, the samples consisted of ground sample of the pelletized 5A provided by Grace Davison. In the case of 13X, the samples consisted of the 2-μm 13X zeolite crystal powder provided by Grace Davison. All samples were pre-purged and activated prior to any run. The pre purge step was done to remove any traces of water in the feed lines, while the activation step was done to remove any traces of water adsorbed in the sample. The pre-purge step consisted in keeping the sample at room temperature overnight or at least 12 h under purge gas flow. The activation step consisted in maintaining the pre-purged sample at 50, 100, 250, and 350 ºC for a soaking periods of 30, 30, 120 and 240 min, respectively, using ramping rates of 3.30 °C/min between soaking periods. At the end of the last soaking period, the temperature was brought down to 70 ºC, which was the temperature set for the runs carried out in all TGA analyses.

Two different TGA analyses were carried out onto the activated sample. The first TGA analysis consisted of a single cycle (STGA) wherein the activated sample undergoes an exposure step followed by a regeneration step. During the exposure step, the sample is exposed to feed gas for a period of 120 min at 70 °C. During the regeneration step the exposed sample is under purge gas sequentially at soaking temperatures of 70, 350 and 450 ºC for a period of 120, 60 and 120 min respectively, using ramping rates of 3.30 °C/min between soaking periods. The feed gas in these runs was pure nitrogen or any of the gas mixtures. The second TGA analysis consisted of a multiple cycle (MTGA) wherein the activated sample undergoes 24 cycles at 70 ºC, each cycle consisting of 30 min of adsorption time with feed gas and 30 min of desorption time with purge gas. The feed gas in these runs was only the gas mixture containing 500 ppm of SO_2.

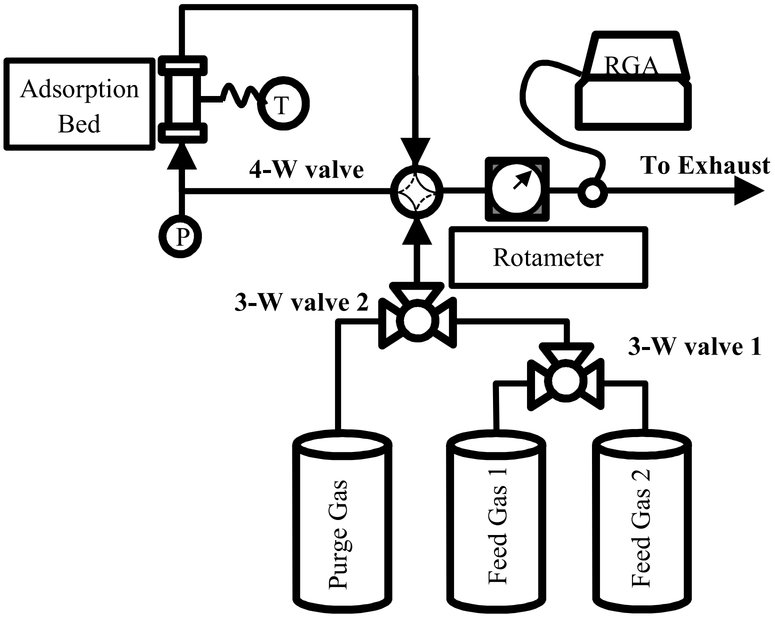

Figure 2.2. Schematic of the Adsorption Breakthrough Setup.

2.3 BREAKTHROUGH STUDIES

An adsorption bed containing a sample of zeolite was used to carry out breakthrough runs with the mixtures containing SO_2 or CO_2 onto 5A or 13X zeolites. In the case of 5A, the samples consisted of pelletized 5A sample provided by Grace Davison. In the case of 13X, the samples consisted of the Oxysiv-5XP provided by Honeywell UOP. The masses of the 5A and 13x Oxysiv-5xp zeolite were measured at 1.00 g and 1.57 g, respectively. The schematic of the experimental apparatus is displayed in Figure 2.2.

The purge gas was nitrogen gas, while the feed gas was a mixture containing either 15.03 % CO_2 (feed gas 1) or 500 ppm of SO_2 (feed gas 2) onto 5A or 13X zeolites. The feed was selected with the aid of a 3-way valve. Once past this first 3-way valve, a second 3-way valve connected the common feed line and purge line to select whether the chosen feed gas or the purge gas is run through the bed. From this second 3-way valve the now common gas line continued into a 4-way valve. This 4-way valve would direct gas to two different paths. The first path would allow the purge of feed gas to go through the adsorption bed, return back to the 4-way valve, then out to a volumetric flowmeter, then through a port connected to microcapillary leading to a residual gas analyzer (RGA) by Stanford Research Systems and then finally to the exhaust. The RGA allows the concentration of the feed gas to be followed in time during a breakthrough. The second path would direct purge or feed gas directly to the volumetric flowmeter, the RGA, and out of the system as exhaust. While this is happening, the adsorption bed is in a closed loop. The purpose of the four-way valve was to choose and set a small volumetric flow rate to values below 200 cc/min for both purge and feed gases without contaminating the bed. The volumetric flow rate was chosen small to avoid any significant backpressure within the adsorption bed and to keep its pressure near 1 atm during breakthroughs. The adsorption bed, which consisted of 3/8 inch stainless steel tubing ant contained less than two grams of sample. The bed was wrapped with a heat tape connected to a 2A variac by Staco Energy Co. for activation and regeneration of the sample up to 350 °C and for temperature control at 70 °C during runs. A thermocouple (T) and the pressure gauge (P) are attached to the adsorption bed for pressure and temperature determination.

Prior to any run, the purge gas flowrates was set approximately 40 mL/min. The feed gas volumetric flow for the 15.03% CO_2 was set at 17 cc/min. In contrast, because of the much lower concentrations and to allow a breakthrough run within a reasonable time, the feed gas volumetric flow for the 500 ppm SO_2 gas mixture was set at 149.3 cc/min for the 5A and 191.0 cc/min for the breakthrough of 13x. Then the newly placed sample was activated under nitrogen purge at 100 °C for an hour and then at 350 °C overnight for a minimum of at least twelve hours. Once activation is over the bed temperature was let cool down to 70 ºC still under nitrogen purge.

Each sample was subjected to five consecutive CO2 breakthrough runs. In the First one, the feed gas containing the CO_2 was feed into the adsorption bed containing the just activated sample until breakthrough is complete. This run is termed is labeled as the "Pre-SO_2 Exposure: Run 1." The sample in the bed is regenerated again overnight at 350 ºC and with nitrogen purge repeating the same procedure followed during the activation and then cool back to 70 °C still under nitrogen purge.

The second breakthrough with CO_2 is carried in identical fashion as the first one. This second run is labeled "Pre-SO_2 Exposure Run 2." The sample in the bed is regenerated again overnight at 350 ºC and with nitrogen purge once more and then cool back to 70 ºC still under nitrogen purge. Feed gas containing the SO_2 is now feed into the adsorption bed (still at 70 ºC) and as soon as the full breakthrough of the SO_2 is complete, the feed gasses are switched and a third breakthrough CO_2 in identical fashion as the previous two. This third run is labeled as "Post-SO_2 Exposure: Initial." The sample is then purged with nitrogen at 70 ºC overnight or a duration of at least 12 hours with no regeneration at 350 ºC taking place.

The fourth breakthrough run with CO_2 is executed, on the purged zeolite, to completion. This fourth run is labeled "Post SO_2-Exposure: N_2 Purge." Next, the sample undergoes a last regeneration overnight at 350 ºC and with nitrogen purge and then cool back to 70 ºC still under nitrogen purge. The fifth and final breakthrough run with CO_2 is carried out, once again, to CO_2. The RGA would record the partial pressure response. The fifth and final run of the breakthrough studies would be labeled, "Post – SO_2 Exposure: Regenerated.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 SINGLE CYCLE THERMOGRAVIMETRIC STUDIES

The first experimental procedure would be the single cycle TGA on the 13x zeolite. The key reason for using a ground zeolite or a homogeneous powder is the adsorbent will be placed into the sample pan and the constituent's exposure to the zeolite's porous surface will be increased.

"Figure 3.1," depicts how the change in temperature and time affect the weight of the 13x zeolite. The weight is calculated as the ratio of the change in weight divided by the regenerated weight of the sample and converted to a percentage. The results suggest adsorption of each constituent due to the increase in mass within the first 120 min. of the experiment. The nitrogen purge gas flow is initiated at 120 min and once the 13x comes into contact with the nitrogen purge gas a decrease in mass is observed for the feed gasses of 15.03% by volume CO_2 and 500 ppm SO_2. The nitrogen purge would continue until 240 min. Three gasses, 42 ppm SO_2, 74 ppm NO, and 74 ppm NO_2, do not demonstrate significant desorption. However, during the nitrogen purge, the 13x zeolites exposed to these gases increase in weight overtime. One possible reason for the increase after the adsorption of flue gas constituent are water adsorption within the TGA. The TGA contains a glass column, and the connection to the TGA from the steel tubing was a synthetic rubber tubing. Either the seals, or the porous tubing could still allow water into the TGA column. The water would continue to adsorb to the zeolites surface because of the dipoles of the water molecule (Yang, 1987).

At the time of 240 min., the electro-thermal heat source would begin to increase the zeolite to a temperature of 350 °C. Once the temperature reached 350 °C, the desorption of the respective flue gas constituent decreased the weight of the 13x zeolite. This decrease is shown throughout all 5 flue gas constituents. After an extended period of 60 min., at a temperature of 350 °C, the flue gas constituents of NO_2, NO_x, and CO2 all return to a value of approximately zero. Although SO_2 at a concentration of 42 ppm returns to approximately zero, the % weight difference is even greater than NO_2, NO_x, and CO_2. At a feed gas concentration of 500 ppm, SO_2 will not desorb completely at a temperature of 350 °C after the adsorption of SO_2 at 70 °C.

For reversibility purposes, the 13x zeolite would be electro-thermally heated to a temperature of 450 °C. To ensure the effects of the exposure of the 13x zeolite to a high temperature of 450 °C were detected. The zeolite was held at the maximum temperature for a duration of 120 min. The temperature had little effect on all of the gas mixtures, especially with respect to the determination of reversibility. The most significant decrease witnessed was associated with the 500 ppm SO_2.

In summary, the single cycle TGA depicted a possible irreversible interaction between SO_2 and 13x zeolite. Although the concentration of 42 ppm was miniscule in magnitude, the higher concentration of 500 ppm SO_2 did not completely desorb to approximately zero like all other constituents. This can be inferred by the percent (%) difference in weight of the 13x zeolite never reaching approximately 0%. This suggests an interaction with the 13x zeolite and SO_2 may not be able to be overcome by regeneration in a cost effective manner due to energy expenditures (Arunkumar, 2011).

Although an irreversible interaction with flue gas constituents is suggested, the other gasses NO_2, NO_x, and CO_2 all demonstrate reversibility. The comparison suggests, the energy requirement of regeneration would be smaller than that of SO_2 (Arunkumar, 2011) The concentrations of the reversible flue gas constituents, NO_2, NO_x, and CO_2, are all represented similar to that of flue gas from fossil fuel energy production (DOE, 2007).

5A was another zeolite tested in the exact same manner as the 13x zeolite. The same procedure was applied to the 5A zeolite. However, the results demonstrate, the 5A sample would return to, at least, the approximate initial regenerated weight when exposed to 350 °C during regeneration. The results also depict the change in weight obtaining a negative value upon the sample reaching a temperature of 450 °C for all five flue gas constituent mixtures. The results suggest, the 5A will interact with the flue gas constituents reversibly, unlike the 13x zeolite.

Although the 5A zeolites imply more reversible interaction with 500 ppm SO_2, the 5A would still depict the sample hypothetical interaction with water throughout the TGA column. The 42 ppm SO_2, 74 ppm NO, and 74 ppm NO_2 would all demonstrate slight increases in weight during the nitrogen purge. Once again, this could be caused by the interaction of water due to lack of a seal, or diffusion of water into the TGA system.

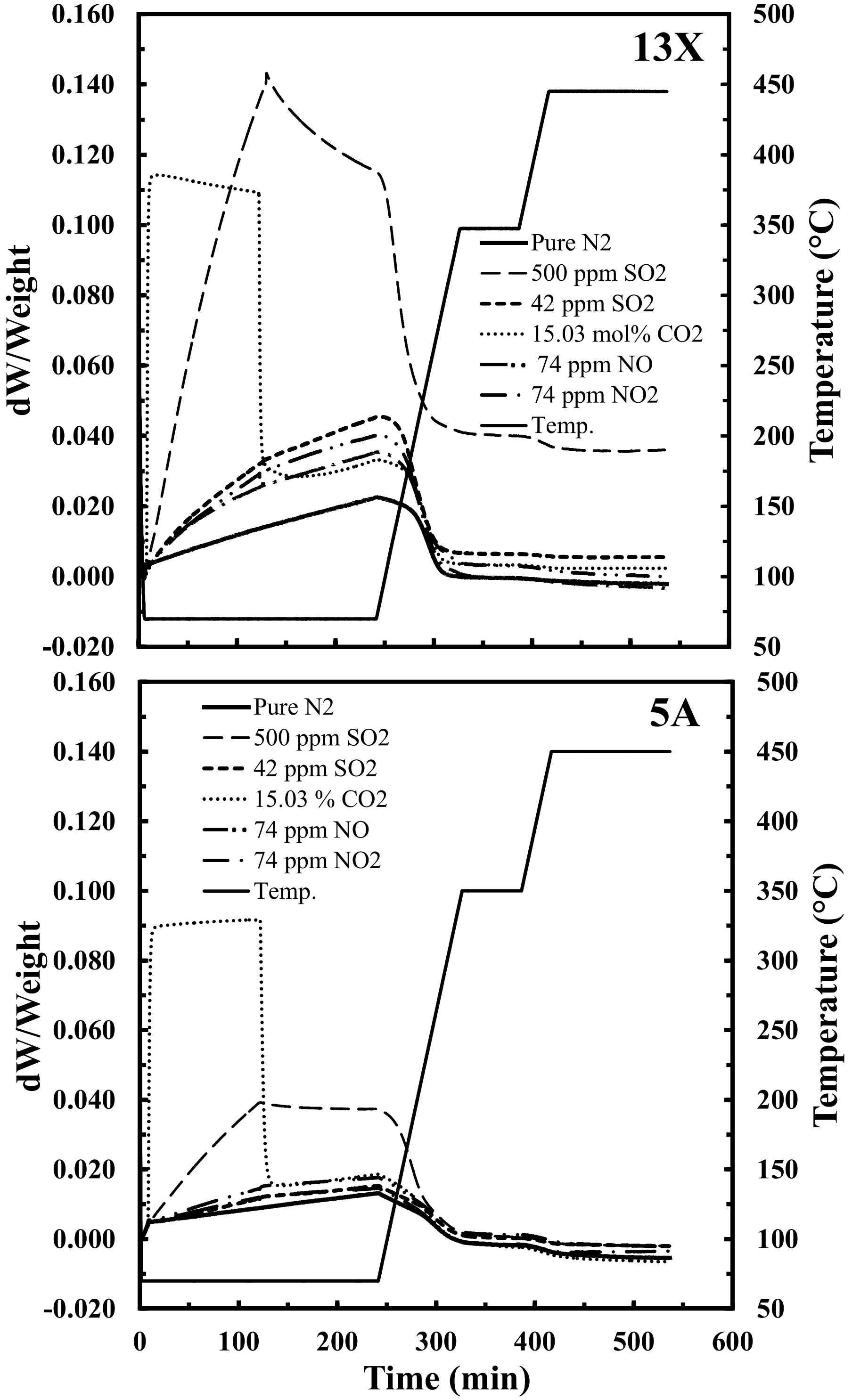

Figure 3.1 STGA Runs for Different Feed Gasses on 13X and 5A. The Sample is in Contact with Feed Gasses up During First 120 minutes and then in Contact with N_2 Purge Gas thereafter while Temperature of Sample Changes on Time as Indicated.

3.2 MULTICYCLE THERMOGRAVIMETRIC ANALYSIS OF SULFUR DIOXIDE ADSORPTION FOLLOWED BY NITROGEN PURGE OF 13X ZEOLITE, 5A ZEOLITE, & SILICA GEL

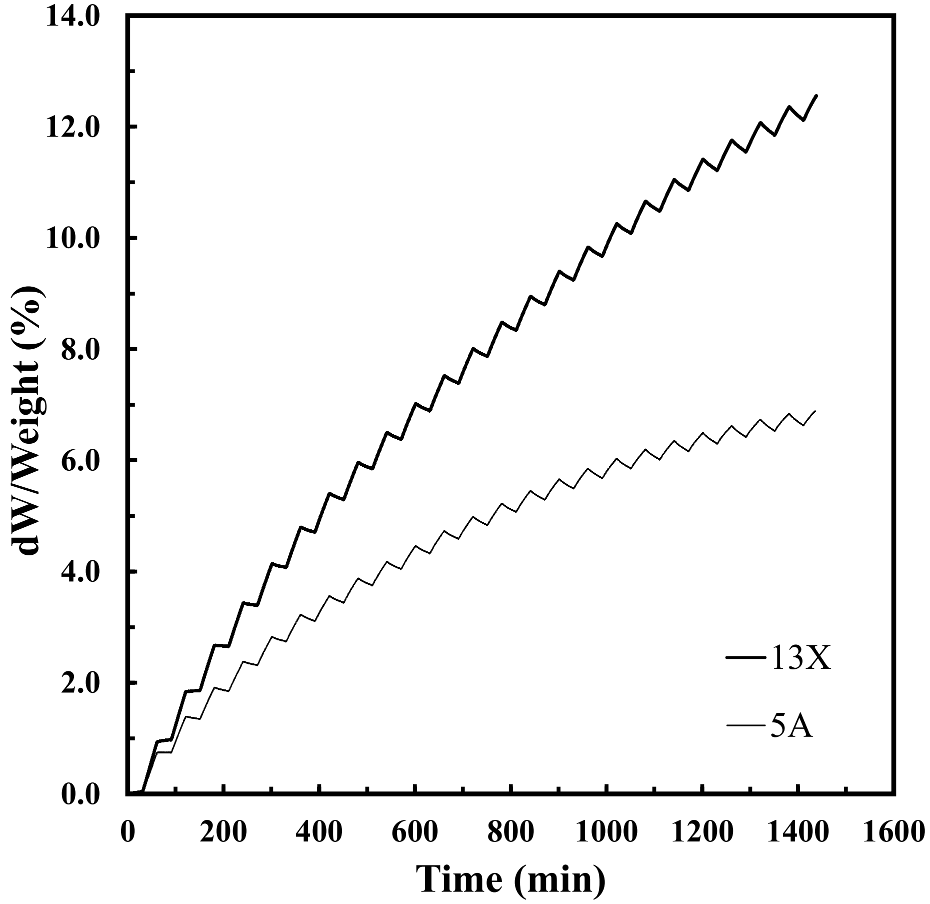

Figure 3.2 MTGA Runs of 500 ppm SO_2 Feed Gas and N_2 Purge Gas on 13X and 5A. Each of the 24 TGA Cycles Consisted of 30 min with the 500 ppm SO_2 Feed Gas and 30 min with the N_2 Purge Gas

Multicycle TGA would be utilized to further indicate the possibility an irreversible process was present within the adsorption of SO_2 upon 13x and 5A zeolites. A cycle would last a duration of 60 min. For the first 30 min. the respective zeolite would be exposed to SO_2 at a concentration of 500 ppm. For the last 30 min. the zeolite would be exposed to a pure nitrogen purge gas within the TGA. The results are illustrate below in “figure 3.2.

The behavior of both adsorbents varies drastically. The loading is the amount of moles of SO_2 adsorbed per mass of adsorbent (Kärger, 1992). The first adsorbent cycling to discuss is SO_2 cycling of the 5A zeolite. Although the zeolite does not plateau immediately, the results indicate the loading finally meets loading capacity under the experimental conditions. Over time the 5A zeolite will remain in a steady state of adsorption and desorption. This implies the SO_2 adsorption upon the 5A zeolite is reversible.

Unlike the 5A and silica gel, the 13x zeolite would not plateau and continued to form a positive linear increase in loading after each cycle. The results indicate a possibility that the SO_2 adsorption upon the 13x zeolite to not be reversible. However, the loading could keep increasing and plateau eventually, but after 1440 min. this is highly unlikely. The weigh also increases in linear fashion overtime after approximately 800 minutes of cycling. The Multicycle TGA implies again the irreversible interaction of SO_2 with the 13x zeolite.

3.3 EFFECTS OF SULFUR DIOXIDE EXPOSURE UPON 13X AND 5A ZEOLITE CARBON DIOXIDE MASS BREAKTRHOUGH

The final experiment, exploring the reversibility of the zeolites was a mass breakthrough within a single bed temperature swing adsorption (TSA) system. Assuming the respective zeolite is reversible the same capacity for CO_2 adsorption will be able to be exhibited despite zeolite's exposure to SO_2. The experiment would initially run two mass breakthroughs of the zeolite unexposed to SO_2. Then the zeolite would be forced to reach working capacity with adsorption of SO_2. Once exposed to SO_2, the experiment used three manners of desorbing the SO_2 from the zeolite. The first, CO_2 would directly compete with the SO_2 for pores of the adsorbent (Bhadra, 2011). For this CO_2 flow would be introduced directly after adsorption of SO_2. The second step, after exposure, would be a nitrogen gas purge over a duration greater than 12 hours. The nitrogen purge allows for desorption of a competing adsorbate (Bhadra, 2011). The third step involved a regeneration at 350 °C with nitrogen purge gas. Theoretically, the temperature increase would cause desorption of SO_2 adsorbate in a process of regeneration. If not, the results suggest too much energy will be required (Augustine, 2015).

The first mass breakthrough involved SO_2 adsorption upon 13x zeolite. After the five trials were completed, the data was analyzed for the ratio of concentration of CO_2 (C/C_0) versus time. The results are demonstrated in "figure 3.3."

From the dimensionless concentration of gas exiting the single bed TSA system, the concentration increases rapidly at the time the 13x adsorbent capacity is achieved for the available physisorption sites. The results suggest after the 13x zeolite's exposure to SO_2 the adsorbent loses capacity regardless of the method for causing SO_2 desorption. The "Post SO_2 Exposure: Initial" run would have less capacity than any of the other trials. The "Post SO_2 Exposure: N_2 Purge" demonstrated an increase in adsorbent capacity, but did not recover completely to the adsorbent capacity of "Pre-Exposure: Run 1" or "Pre-Exposure: Run 2." The results demonstrate, even after the overnight regeneration at a temperature of 350 °C, the 13x zeolite would not allow for complete desorption of SO_2. The capacity decreased and consequently the load associated with the lesser adsorbent capacity was achieved in a quicker duration.

Although the working capacity has been shown to decrease little information is known for the chemical interaction of SO_2 within 13x zeolite pores. A possible explanation could be the chemical reactions, which may occur exothermically and spontaneously with species of the TSA system (Atkins, 2010). Water and other gases can interact within the zeolite bed after combustion processes (Wang, 2009). The 13x zeolite framework possesses sodium cations, bound to an oxygen, which also binds to the framework of the zeolite (Meier, 2007). The SO_2 could possibly form a bisulfite complex with the interaction of the oxygen (Cotton, 1999). The bisulfite complex would be bound to the aluminum upon the zeolite framework. This is only a hypothesized explanation for the irreversibility of the 13x zeolite.

The final zeolite tested for the effects of SO_2 adsorption was the 5A zeolite. The 5A zeolite was tested in the same manner as the 13x zeolite in all 5 trials. The results are shown below, and suggest, the 5A zeolite can desorb SO_2 reversibly. The "Pre-Exposure: Run 1" and the "Pre-Exposure: Run 2" demonstrate equivalent working capacity when compared to the "Post-Exposure: Regenerated" CO_2 mass breakthrough. The results imply the regeneration overnight at 350 °C will cause SO_2 occupied adsorption sites to desorb SO_2. The 5A zeolite, after exposure to SO_2 would maintain 94.59% of the initial CO_2 capacity after regeneration and in comparison to "Pre-SO_2 Exposure: Run 1." The SO_2 will desorb because the heat of adsorption is not too high for the regeneration to overcome (Yang, 1987). Another deduction which can be made from the results is there is not any chemical mechanism developing too large of a heat of adsorption. The data implies, unlike the 13x zeolite, the heat of adsorption may be viable for implementation in CO_2 capture. “Figure 3.3” depicts the results for both zeolite mass breakthrough and “Table 3.1” demonstrates the difference in breakthrough times between both zeolites.

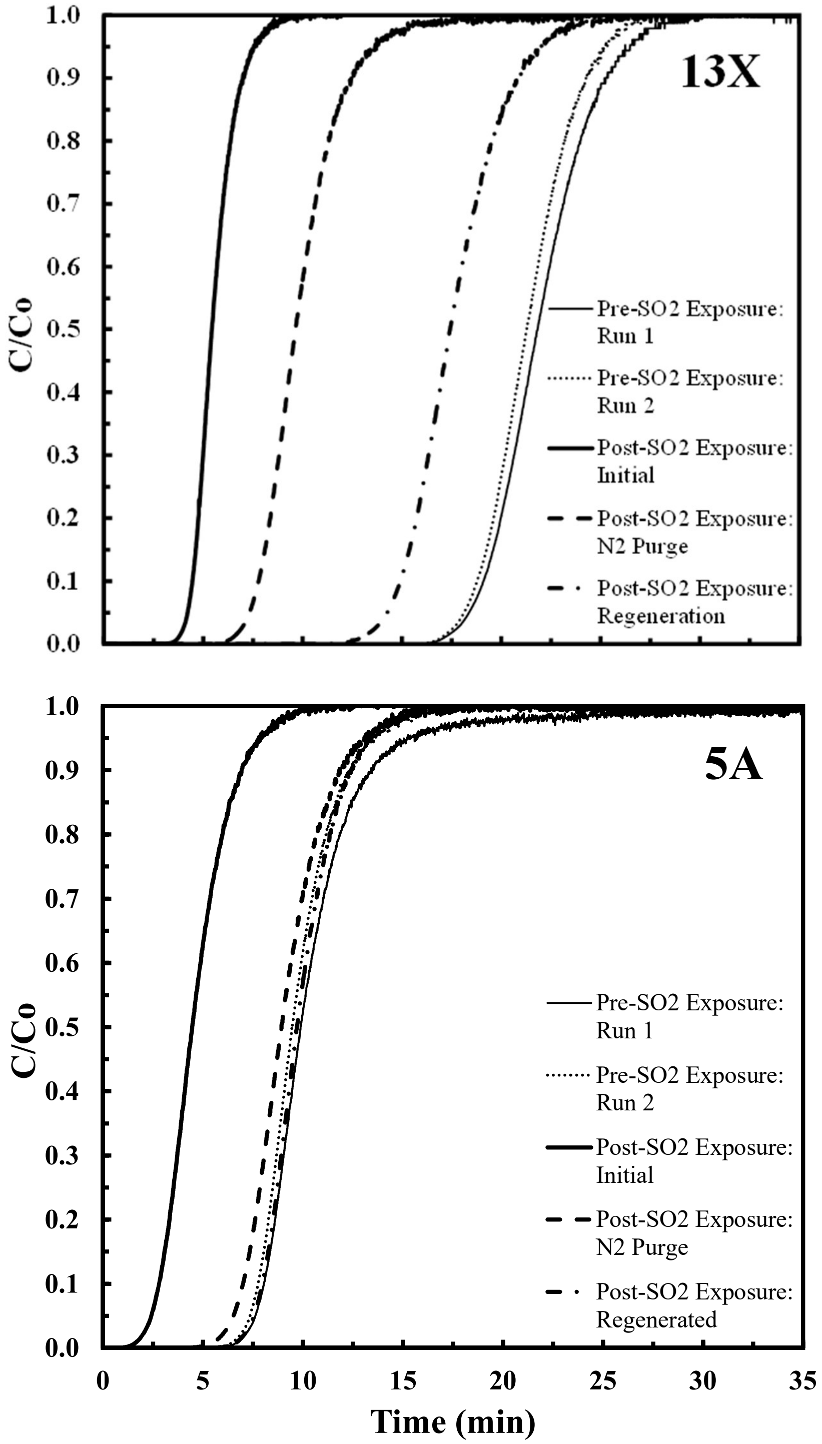

Figure 3.3 Five Breakthrough Consecutive Runs of 15.03 mol% CO_2 ppm on 13X and 5A Showing the Role Saturating the Sample with 500 ppm of SO_2 on the Adsorptive Capacity of the Sample Toward CO_2. Breakthroughs Took Place on the Sample Sequentially in the Same Order as Shown in the Legend from Top to Bottom. Further Details are Given in the Experimental.

Table 3.1. Breakthrough times for the runs shown in Figure 3.3 and their value relative to that of the first breakthrough run.

BT Run	13X		5A	
	Time (min)	Relative to Run1 (%)	Time (min)	Relative to Run1 (%)
1. Pre-SO_2 Exposure: Run 1	22.02	100.00	10.53	100.00
2. Pre-SO_2 Exposure: Run 2	21.39	97.14	9.81	93.16
3. Post-SO_2 Exposure: Initial	5.59	25.39	4.69	44.54
4. Post-SO_2 Exposure: N_2 Purge	9.94	45.14	9.24	87.75
5. Post-SO_2 Exposure: Regenerated	17.69	80.34	9.96	94.59

CHAPTER 4

CONCLUSION

The experimentation was to determine if the constituents contained in power plant production of flue gas from fossil fuels were reversible upon the 5A zeolite and the 13x zeolite. Due to previous research being limited on reversibility, three experiments all converged to a unanimous conclusion for the 13x zeolite. The results for single cycle TGA analysis, multi-cycle TGA analysis, and the simulated single bed TSA mass breakthrough imply the flue gas constituent SO_2 is irreversible with respect to adsorption upon the 13x zeolite. The inorganic chemical mechanism could be a reason for the irreversibility, but more research is necessary for a definitive cause. However, other flue gas constituents NO_2, NO_x, and CO_2 are all depicted as reversible adsorbates upon the 13x zeolite from the results of the single cycle TGA.

As for the 5A zeolite, the adsorption of all flue gas constituents appeared to be reversible. The regeneration at 350 °C, over a period of greater than 12 hours, with nitrogen purge gas demonstrated the desorption of SO_2 and all other flue gas mixtures in the experimentation. The desorption of SO_2 can be inferred due to the 5A zeolites mass breakthrough occurring between the time intervals of the first two mass breakthroughs and the behavior depicted in the various TGA studies. In summary, the 5A could be utilized as a guard layer for the more effective 13x zeolite in carbon capture.

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