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Effect of Flue Gas Impurities on CO₂ Capture Performance from Flue Gas at Coal-fired Power Stations by Vacuum Swing Adsorption

Jun Zhang, Penny Xiao, Gang Li, Paul A. Webley*

*Department of Chemical Engineering, Monash University, Wellington Road, Clayton, Victoria, 3800, Australia
CO2CRC – Cooperative Research Centre for Greenhouse Gas Technologies*

Abstract

CO₂ capture from major stationary emission sites has been studied widely with the increasing realization of the negative impact of greenhouse gas emissions on climate change. In terms of capture technology, solvent scrubbing, membrane processes and adsorption processes are the major contenders with the latter making significant progress over the last decade due to both improved adsorbent and process design and operation. As is well known, capturing CO₂ from flue gases at coal-fired power stations by pressure/vacuum swing adsorption is complicated by the existence of significant amounts of water, SO_x, NO_x and other impurities, which are detrimental to most commercial CO₂ selective-adsorbents. Conventional adsorption-based CO₂ capture processes rely on using a pre-treatment stage to remove water, SO_x and NO_x, which adds considerably to the overall cost. In contrast, we report here an adsorption process developed in our laboratory which directly tackles the untreated flue gas without a separate pre-treatment stage by using a propriety multiple-layered bed comprising different adsorbents. The species CO₂, H₂O, SO_x and NO_x are processed in the same column within different function layers optimized according to adsorption properties and process conditions. A fully programmable logic controller (PLC) automated three-column pilot plant was built to perform the study with real-time control and data acquisition conducted through Human Machine Interface/Supervisory Control and Data Acquisition (HMI/SCADA) system. Through running continuous experiments, the effects of impurities on process performance such as CO₂ purity, recovery and process power are investigated and reported. This is the first in-depth report of the performance of adsorption based capture plants in the presence of impurities found in real flue gas streams.

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Keywords: carbon dioxide capture, flue gas, vacuum swing adsorption, impurity

1. Introduction

With the increasing recognition of the importance/feasibility of CO₂ capture and storage (CCS) in mitigating global warming, great efforts have been made in the academic, engineering, and political sphere to further our

* Corresponding author. Tel.: +61-3-9905-3445; fax: +61-3-9905-5686.
E-mail address: paul.webley@eng.monash.edu.au.

understanding of details and role of this technology [1-5]. In addition to cryogenic process, solvent scrubbing and membrane technology, pressure swing adsorption has attracted much attention, with recent focus on new adsorbent materials and new cycle developments [6-8]. Pressure/vacuum swing adsorption, as a widely utilized technology in the gas separation/purification industry, shows great potential in CO₂ capture from coal fired power stations (post-combustion capture) because of its promise of low energy consumption and system simplicity. Extensive investigations have been undertaken in applying adsorption technology to post-combustion CO₂ capture. These efforts include materials preparation and characterization, cycle design, process optimization, the effect of impurities, the results of pilot experiments and so on [9-12]. The presence of several impurity gases (SO_x/NO_x/H₂O) greatly complicates the CO₂ separation processes. SO₂ is reported to have reactions with basic sites on adsorbent materials. NO can be oxidized to NO₂ /N₂O₃/N₂O₅ and eventually react with the adsorbent [13-15]. The pressure-swing reversible adsorption capacity for these species is very small [9,10,12]. Much research has been done on the adsorption/desorption of SO_x/NO_x on activated carbon fibre, activated carbon, ZSM and other zeolites, especially with dry gas. To protect the main CO₂ adsorption layer, pre-layers need to be placed in the column. The concept of multiple layers is well established and applied in the industrial gas separation/purification area [16-17]. The interactions of CO₂/H₂O/SO_x/NO_x in typical flue gas with adsorbents are quite complex. Systematic work needs to be done to gain a better understanding of these interactions and their effect on the process performance.

In this study, we focus on the effect of water vapour on the pressure/vacuum swing adsorption process, especially the influence of water vapor in the product purge gas. In addition, we report the adsorption behaviour of SO_x/NO_x/CO₂/H₂O/O₂/N₂ multiple mixtures in a simple breakthrough column as a starting point of a more systematic R&D project currently in progress. Such experiments not only help our understanding of the fundamental of impurity adsorption on adsorbent performance but also provide valuable process design and equipment selection reference data. The adsorbents chosen in this study are CDX (an alumina/zeolite blend), alumina and NaX zeolite as these adsorbents will be either the pre-layer for water adsorption or the main CO₂ adsorption layer in the packed bed. This study follows on from previous work conducted through the Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC) at Monash University in which a pilot scale VSA process was operated with dry flue gas and a single-column system was operated with wet flue cycle [7, 8, 18]. The objective of the current study was to understand the adsorption and desorption of water in CO₂ capture process from flue gas emitted from coal-fired power stations. Engineering solutions developed during this study formed the basis for designs of adsorption-based demonstration plants to be operated at an actual power station in 2009.

2. Experimental Work

Systematic experiments investigating the effects of flue gas impurities were conducted. Water isotherms were measured on an IGA (Intelligent Gravimetric analysis) apparatus and CO₂ isotherms were measured using a modified Micromeritics ASAP2010 volumetric gas adsorption analyzer. SO₂ and NO isotherms on a dry basis have been reported and were not measured in our laboratories. However, the adsorption behaviour of these gases under wet conditions was studied. A simple breakthrough type of apparatus (column diameter 30mm with a length of 280mm) was used to measure simple breakthrough of SO₂/NO/CO₂ under wet conditions. In each experiment, the CO₂/H₂O/NO/N₂/O₂/SO₂ mixture gas was passed through the column and after breakthrough, wet argon gas (wet gas mimicking the real process condition) was used to desorb the column. A HORIBA multiple gas analyzer was used for analysis and data were transmitted to a computer for logging.

To investigate the effect of water on a realistic multiple-bed VSA process, full cycle experiments with wet gas were conducted in our 3-bed VSA pilot plant. Details of the apparatus have been reported earlier [8]. To equip the apparatus for operation with wet fed gas, a feed gas bubbler was added. Blended CO₂/air mixtures were saturated through the bubbler and fed to the adsorption columns. Process control and data acquisition were performed by GEFANUC PLC and Citect SCADA/HMI. The role of water for different adsorbent layering and different cycles were examined and are discussed below.

3. Results and discussions

3.1 Water Isotherms on Alumina F-200 and zeolite NaX

Water isotherms were measured on Alumina F-200(BASF) and zeolite NaX(UOP) and CO₂/N₂ isotherms were also measured on NaX. The water isotherms on both alumina and zeolite exhibit the well-known Type IV isotherm (Figure 1) and are represented by the BET model in our simulation work. The adsorption of CO₂/N₂ (Figure 2) are represented with dual-site Langmuir model.

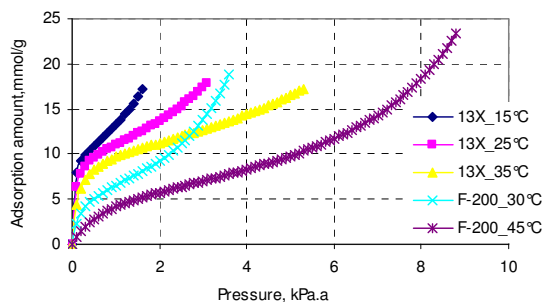


Figure. 1. Water isotherms on 13X and F-200 Alumina

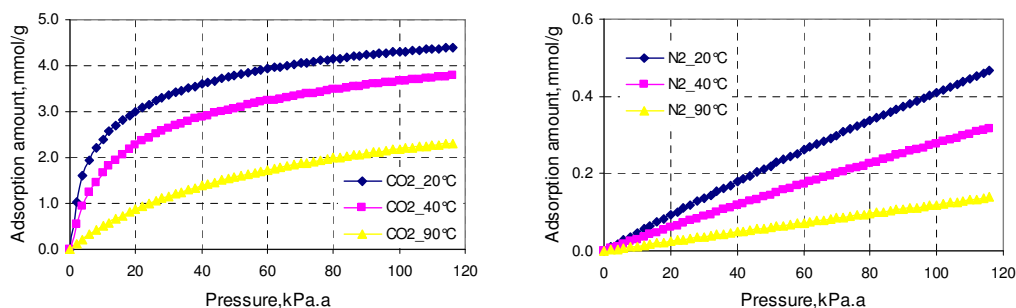


Fig. 2. CO₂ and N₂ isotherms on 13X zeolite

Figure 1 shows that both 13X and F-200 Alumina have good water adsorption capacity with F-200 alumina showing superior at higher humidity levels. This is directly relevant to flue gas conditions in which high relative humidities at elevated temperatures are not uncommon. The CO₂ and N₂ isotherms on NaX zeolite show good CO₂/N₂ selectivity even up to 90°C.

3.2 Cyclic Adsorption Experiments with wet flue gas – Single layered Adsorbent

3.2.1 NaX Zeolite

The most widely used adsorbent for CO₂ capture is zeolite NaX. As a starting point in our studies, the beds were packed with NaX and the VSA process was tested under wet flue gas conditions. A 6-step conventional VSA cycle was run [7] to cyclic steady state using a variety of feed conditions. It was of particular interest to investigate the movement of the water adsorption zone in the beds. It is well known that water adsorption excludes CO₂ from the adsorption sites and hence could potentially remove all separation capacity of the adsorbent. In all cases the feed concentration of CO₂ was 13%. When the water percentage is low (bubbler set at a temperature of 20°C), the water front can be stabilized within the bed and the process still is able to capture CO₂ at relatively high purity (70%) and recovery although an increase in power is inevitable due to the need to evacuate water. However, when the water vapor percentage is high (35~40°C saturated), the water front steadily migrates through the column and breakthrough can be clearly seen by observing the corresponding temperature profiles. Thermocouples T1 to T7 are located in the bed from the bottom (feed) to the top (CO₂ free product), separated by approximately 10 cm. Figures 3 and 7 shows these temperatures one and seven days after startup. On day one, a temperature swing of 15°C is

observed at locations T3 to T7. This indicates CO₂ adsorption and desorption at these locations. The smaller temperature swing at T1 and T2 corresponds to water adsorption and desorption. On day 7 the temperature change within the main section of the bed has decreased to less than 5°C indicating that the water front has moved slowly through the column and reduced the CO₂ adsorption capacity. Figure 5 shows a 20-hr trend change for T5 at day 7. It clearly shows the temperature swing attenuation over the 20 hour period due to migration of water to this location and subsequent CO₂ adsorption reduction. Eventually, the water front moved to T7 (top of the column) and reached breakthrough. From a power consumption perspective more energy is consumed in the vacuum pump in the presence of water vapour and the specific power consumption for CO₂ capture is increased. Purity and recovery drop significantly with propagation of the water front until no separation of CO₂ is possible.

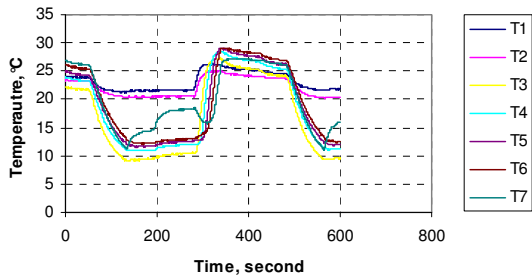


Figure 3. Temperature profile on day 1

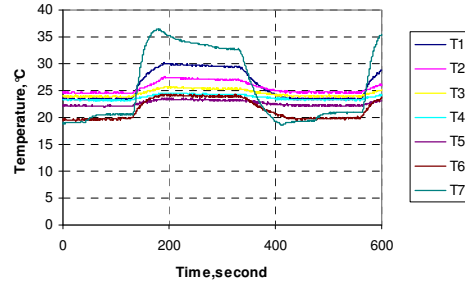


Figure 4. Temperature profile on day 7

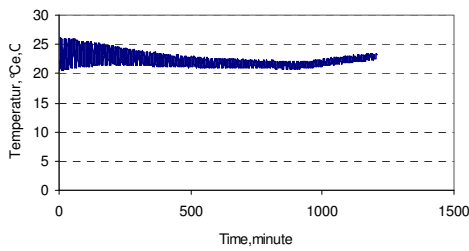


Figure 5. Temperature profile at T5 on day 7 over a 20 hour period

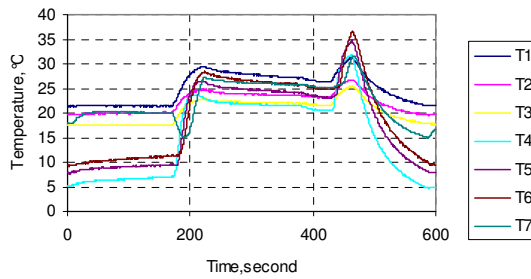


Figure 6. 9-step cycle temperature swing profile

The mechanism of water migration is related to the water isotherm and the relative extents of feed and countercurrent purge. At low water humidity, water adsorption is within the favourable “Langmuir” zone of the isotherm (see Figure 1) and the water front does not move significantly into the column. Sufficient countercurrent vacuum flow is produced to regenerate the adsorbent and hence arrest the migration of the water zone. A simple model to predict the position of the zone has been developed by Wilson et al. [19]. At higher levels of water in the feed, the water front moves further into the column and a proportionally greater ratio of column now becomes saturated with water greatly reducing CO₂ capacity and hence vacuum countercurrent flow. In addition, the water isotherm is now unfavourable leading to a spreading pattern during adsorption. The vacuum level achieved in our experiments (6–7 kPa) was not low enough to desorb sufficient CO₂ gas to stabilize the water front. Lower vacuum level and higher column temperature would be among possible solutions to prevent the breakthrough of water as such conditions create more countercurrent CO₂ flow and desorb additional water from the adsorbent. Prediction and control of the movement of water as a function of water concentration and process conditions is therefore key to successful operation of the process.

3.3 Multiple layer adsorbent column experiments

3.3.1 NaX-CDX multiple layered bed

CDX Alumina, (a commercially available blend of NaY and Alumina), is a potential candidate for handling SO_x/NO_x, as well as water. The adsorbent beds were layered with CDX at the feed end followed by NaX in a 30/70 split by weight. The conventional 6-step cycle without purge was used as before with a high level of water fed to the system (35–40 °C saturated). After 5 days of continuous operation, the water front had migrated to the center of the column. The product CO₂ purity dropped from 66.68% to 46% and the recovery decreased from 65% to 20%. Eventual water breakthrough occurred as before.

3.3.2 NaX-F200, 6-step and 9-step experiments with water

A third set of experiments were performed with an alumina/NaX multi-layered bed. In these experiments F-200 alumina and NaX (40/60 split) was loaded into the columns and a more powerful oil vacuum pump was used to provide deeper vacuum capability. A 6-step cycle (as above) and a 9-step cycle was used and a vacuum level of 3–4 kPa was achieved. For high humidity feed levels, both cycles sustained more than one week running time (>3,000 cycles) at which stage the water front was found to be stabilized at around the middle of column without breakthrough. The results are summarized in Table 1. As shown in Table 1, product purity from the 9-step cycle with product purge (vs the 6-step cycle with no purge) does not change substantially although only a small purge flow was used (16% of the product flow). Higher recovery was achieved in the 9-step cycle due to extended evacuation time. The specific power consumption for the 9-step cycle is surprisingly lower than the 6-step cycle. The reason is related to the change in CO₂ concentration in the bed after product purge and subsequent change in the pumpdown profile during evacuation. Additional product purge would ultimately increase the required pumpdown power.

Careful examination of Figure 6 shows that the temperature rise at thermocouples T1 to T4 is small for the first 200s indicating that the water zone has penetrated to this point. Beyond T4 the temperature rise is larger indicating CO₂ adsorption is still taking place. A temperature “spike” is observed at approximately 450s – this is the result of the high CO₂ concentration product purge which re-adsorbs to the bed during the purge step. The purge gas used is “wet” resulting as it does from the CO₂ product removed in a previous cycle. The 6-step cycle and 9-step cycle experiments indicated that with proper purge, product purity can be increased and the water front can be controlled with proper layering, though the purge gas needs to be optimized in terms of purge ratio and purge pressure.

3.4 Simulations

To further guide understanding of the process, numerical simulations were conducted using our in-house simulator MINSAs (Todd et al.[20]). Different cycles and conditions were simulated. The results are summarized in Table 2.

Table 1. 6-step and 9-step experiments results

Temperature	35 °C	35 °C	45 °C
Cycle	6-step without purge	9-step with purge	9-step with purge
Adsorbents	F-200, zeolite 13X	F-200, zeolite 13X	F-200, zeolite 13X
Feed pressure,kPa.a	1.4	1.4	1.4
Vacuum pressure,kPa.a	3	3	3
Inlet compositions	CO ₂ -13% H ₂ O-0.05%	CO ₂ -13% H ₂ O-0.05%	CO ₂ -13% H ₂ O-0.07%
CO ₂ in waste gas	3.85%	4.25%	3.36%
Product purity	89.63%	98.90%	98.90
Recovery	74.9%	78.5%	82.7%
Power, kW/TPD	8.43996	6.57668	7.62

Table 2 Simulation performances

	6-step cycle without purge	9-step cycle with purge
Feed gas temperature, °C	41.5	35~40
Feed CO ₂ purity	15%~16%	15~16%
Product purity	86.1%	90%
Recovery	60%	62%
Evacuation time, second	100	120
Power, kW/TPD	12.39	10.41

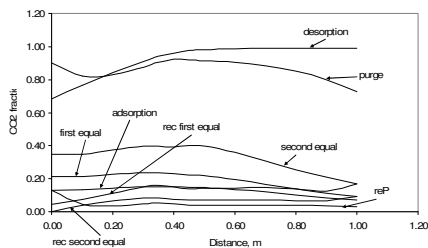


Fig. 7 CO₂ concentration profile

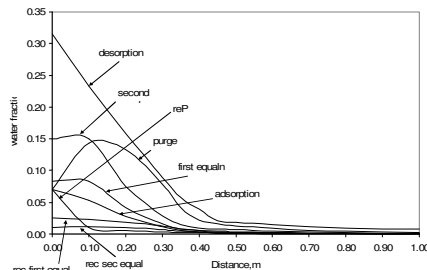


Fig.8. H₂O concentration profile

These simulations greatly assist the elucidation of profile data since detailed concentrations can be calculated, such as CO₂ and water axial concentration profiles at different steps (shown in Figures 7 and 8). From those results, it is found that with 40% F-200 in the adsorber column, the water front can be stabilized within the alumina layer at 3kPa and produces reasonable purity and recovery even at a high humidity level.

The simulations performed in this study agree reasonably with experimental results although exact numerical agreement is extremely difficult to achieve given the large number of input parameters and the strong dependence of the results on detailed competitive adsorption of the species. In addition, the simulation is based on adiabatic operation while the laboratory data are generated at non-isothermal conditions. A significant amount of heat transfer is observed especially through the connecting flanges. In addition, greater pressure drop (as large as 2kPa) on the vacuum line is found in the experiment than predicted by simulation due to various flow elements – flow meter, control valve, dust filter and solenoid valve which all contribute. As a result, the simulation overpredicts CO₂ product purity which is extremely sensitive to pressure drop in the system.

3.5 SO₂/NO breakthrough experiments

In this study, breakthrough experiments (20°C) of SO₂ and NO were performed on both zeolite 13X (5 LPM, 90 ppm SO₂, 45ppm NO in wet CO₂) and CDX (10 LPM, 50ppm SO₂, 250 ppm NO). These are candidate adsorbents for the main layer and prelayer as discussed above. The SO₂/NO concentrations used reflect expected values in the flue gas after the flue gas has passed through a water wash tower. As can be seen from Figure 9(a), SO₂ breakthrough time was very short (a few seconds) surprisingly and NO breakthrough is much slower. Similar roll-up phenomena as reported in the literature was observed as the SO₂ concentration rapidly increased to a much higher

level than in the feed gas [11,13]. The reason is that more competitive water adsorption is taking place and relatively weaker adsorbed SO₂ was desorbed in the breakthrough. Such an effect also occurs for O₂ as shown in Figure 9(b) though CO₂ adsorption was not much significantly affected. The desorption curves (Figure.10) indicated slow desorption of SO₂ and a quick desorption of NO and O₂. CO₂ desorption is delayed due to its high uptake and non-linear isotherm. SO₂ concentration initially drops quickly but is then maintained for a long time due to its great capacity and adsorption bonding. However, a NO desorption roll-up spike was observed, which may be caused by the complex interactions of SO₂/O₂/H₂O/NO/NO₂. From Figure.10, when combining the NO and O₂ desorption together, it is found that NO concentration sudden increases - this may be because of the sudden drop of O₂ concentration, which greatly reduces the oxidization of NO to NO₂, however, more detailed experiments need to be done to investigate this mechanism. For CDX alumina, a combination of alumina and NaY (more hydrophobic than 13X), similar breakthrough roll-up effects for SO₂ and O₂ were observed. During desorption, NO roll-up effect was also observed. Overall, SO₂/NO can be adsorbed and desorbed under ambient conditions though the partial desorption of SO₂ is very slow.

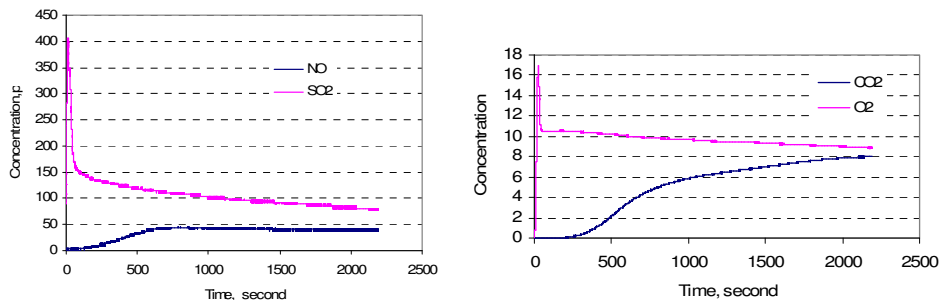


Figure 9. 13X mixture gas breakthrough curve

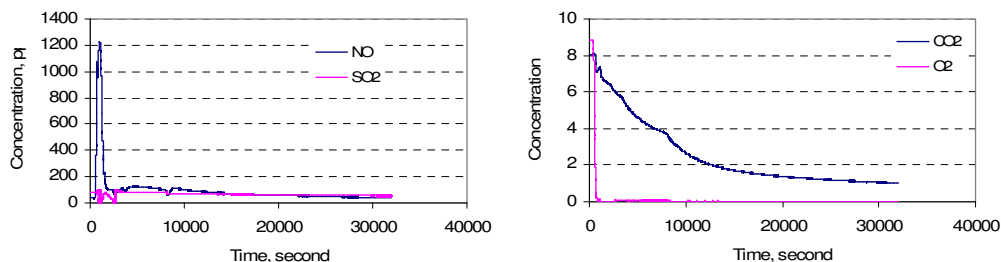


Fig. 10. 13X desorption curve

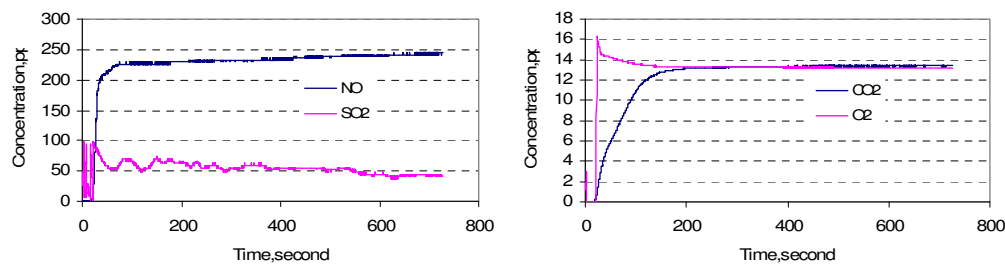


Fig.11. CDX Alumina breakthrough curve

4. Conclusions

This study confirms the applicability of multiple layer columns to tackle flue gases with CO₂/H₂O/O₂/N₂/SO₂/NO.

Through continuous full cycle experiments and simulation, it is found that the water front can be managed by using a combination layer of alumina and 13X, and reasonably good performance was observed at steady state. Single layered adsorbents, such as 13X, can not stabilize the water front under high humidity feed conditions. Vacuum level is also found to be one of the most important factors in controlling the counter current flow and equilibrium desorption of water. A vacuum level lower than 3kPa is preferred to promote higher CO₂ purity and recovery. The movement and position of the water front was inferred by examination of the thermal profiles in the column during operation. It was seen that wet product gas purge has little effect on the purge process as the humidity level for this stream is low. With proper management of purge ratio, good product purity and recovery are achievable.

In SO₂/NO mixture gas breakthrough experiments, it was found that H₂O produces roll-up effects for SO₂ and O₂ for both 13X and CDX Alumina. Such effects may also contribute to the quick breakthrough of SO₂ in the adsorbents studied. NO desorption is closely related with O₂ concentration in the gas mixture. Also it is found that SO₂ desorption is slow due to its great capacity and chemical adsorption and NO can be desorbed fairly quickly. However, more fundamental work needs to be done to better understand the mechanism of those interactions and more cycle work needs to be done to test the long term running effects of those gases on process performances and adsorbent structures.

Acknowledgement

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