Competition of CO₂/H₂O in Adsorption Based CO₂ Capture

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

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

Abstract

All flue gases contain water vapour along with carbon dioxide, nitrogen, etc. Vacuum Swing Adsorption (VSA), which has been successfully studied for post-combustion dry CO₂ capture in our group, is strongly affected by the overwhelming competitive adsorption of water vapour on CO₂ adsorbents. In this study, breakthrough experiments have been conducted to measure the single/binary adsorption isotherm data of CO₂ and water vapour on zeolite 13X and a proprietary alumina-based adsorbent alumina CDX to study the competitive adsorption effect on each other. The CO₂ adsorption data are well represented by the Dual site Langmuir isotherm equation. Based on the above understanding, a single column multilayered VSA unit was used with a guard-bed layer of superior desiccant and a main layer of 13X to simultaneously remove water (3-4% by volume) and capture CO₂ (10-12%) at 30 °C within the same process. In this study, activated alumina CDX was selected as the appropriate pre-layer. Furthermore, we have investigated the effects of operating parameters on the multilayered CO₂/H₂O VSA performance. The water front was accurately located in the bed and the interaction of CO₂ and water vapour indicates a clear indication of a water loaded zone and a CO₂ loaded zone. The result demonstrates that water front has been successfully held in the pre-layer and CO₂ product purity of 76.9 % and purity of 67 % were achieved for the double layered single column CO₂/H₂O VSA.

© 2009 Elsevier Ltd. Open access under CC BY-NC-ND license.

Keywords: Carbon Dioxide; Water Vapour; Pressure Swing Adsorption; Layered Bed; Thermal Front.

1. Introduction

Carbon dioxide is the major greenhouse gas emitted as a result of human activities especially power generation. There have been world wide efforts to mitigate and control the CO₂ emissions from these activities including improvement in generation efficiency, reduction in energy use, use of renewables, and carbon capture and storage. Carbon capture and storage relies on effective capture technologies to enrich the CO₂ in the flue gas stream to >90% prior to compression and storage. One technology for capturing CO₂ is the use of adsorption processes. Over the past few years, we have experimentally investigated the capture of CO₂ from synthetic dry air-CO₂ blended gas

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

doi:10.1016/j.egypro.2009.01.148
streams containing 10-12% CO₂ by our VSA (vacuum swing adsorption) process and achieved good technical performance (CO₂ purity > 95% and recovery > 80%) [1]. These results are largely achieved with zeolite13X adsorbents which is the most common commercial adsorbent used for separating CO₂ from dry simulated flue gases. However, most flue gas streams under consideration for post-combustion carbon capture are highly humid. Since water adsorption on zeolite 13X and many other polar adsorbents is much stronger than CO₂ adsorption, the effect is to displace CO₂ and reduce the adsorbent’s capacity for CO₂ capture [2]. There have been a large number of studies examining the removal of CO₂ and water vapour from gas streams using adsorption processes. However, most of these studies are confined to ppm levels of CO₂ and saturated water vapour for air purification systems [3,4]. Since zeolite 13X has a large adsorption capacity for water, our preliminary one-bed VSA experiments directly used 13X as the sole adsorbent for wet CO₂ flue gas streams containing 3.4% (vol.) of water vapour at 30 °C. The result of these experiments indicated a relatively low purity (59% CO₂) and recovery (68%) [5]. It is readily apparent that water adsorption on 13X is too strong to allow the adsorbent be effectively regenerated under the VSA conditions. Activated alumina and silica gel on the other hand are common adsorbents used in industries for removing water vapour in pre-PSA and pre-cryogenic separation processes [4,6,7]. The adsorption amount of water on these materials increases linearly with the adsorptive partial pressure. Therefore, binary adsorption of CO₂/H₂O has been investigated in this study on a benchmark adsorbent alumina CDX which has a near linear adsorption isotherm for water. In addition, a double layered VSA bed system was proposed and tested to study the simultaneous adsorption and desorption of water and CO₂ in the same VSA column under a variety of process conditions.

2. Experimental

2.1. Materials and isotherm measurement

Isotherms of water vapour on zeolite 13X were measured at 25 °C from 0 to 3 kPa by a gravimetric apparatus (IGA-002 Intelligent Gravimetric Analyzer system manufactured by Hiden Isochema, Ltd. (UK)). The isotherms of single water vapour and binary CO₂/H₂O adsorption isotherms on activated alumina CDX (a special type of alumina and NaY mixture, from BASF) were measured by the gravimetric/volumetric method at 30 °C with a custom-built breakthrough apparatus. For binary gas measurements, the CO₂ pressure was fixed at 105.3 kPa while the water partial pressure was increased stepwise once reaching equilibrium at each step by bubbling the CO₂ through a temperature controlled bubbler set at a variety of set points depending on the desired water concentration. The isotherms of dry CO₂ and N₂ on these materials were measured by a volumetric apparatus (ASAP 2010 Gas Adsorption Analyzer (Micromeritics, USA)) at different temperatures over the pressure range of 0-118 kPa. Surface area and pore size distribution of the adsorbents were also measured with the same apparatus by conducting liquid nitrogen adsorption tests at 77K. All samples were activated by heating up to 350 °C under vacuum condition for 24 hr prior to each experiment. The physical properties of zeolite 13X and alumina CDX are listed in Table 1.

Table 1. The physical properties for experimented materials

<table>
<thead>
<tr>
<th>Property</th>
<th>alumina CDX</th>
<th>Zeolite 13X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shape of adsorbent</td>
<td>Spherical</td>
<td>Spherical</td>
</tr>
<tr>
<td>Diameter [mm]</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Bulk density [kg/m³]</td>
<td>670</td>
<td>640.7</td>
</tr>
<tr>
<td>Total pore vol [cm³/g]</td>
<td>0.48</td>
<td>0.27</td>
</tr>
<tr>
<td>Avg pore dia [nm]</td>
<td>4.223</td>
<td>2.44</td>
</tr>
<tr>
<td>BET surface area [m²/g]</td>
<td>441.7</td>
<td>445.5</td>
</tr>
<tr>
<td>Crush strength (kg)</td>
<td>4</td>
<td>-</td>
</tr>
</tbody>
</table>

2.2. Equipment set-up

The VSA system employed for our preliminary tests consists of one adsorption bed constructed from 3 mm thick stainless steel with an internal diameter of 49mm and height of 560mm. The feed system includes a humidifier and a
feed tank, waste tank, product tank and vacuum pump (Fig. 1(a)). Eleven thermocouples (T type) are located axially from the entrance to the exit of the bed as shown in Fig. 1(b). As described earlier [5], pressure transducers (S902, accuracy < 1% of reading, MKS), flow meters (EJA115, Yokogawa, Japan), carbon dioxide analyzers (Ir1507, intrinsic error < 0.1% CO₂, Servomex) and a number of thermocouples are located in the feed line, waste line and vacuum line to measure pressures, flow-rates, CO₂ concentration and temperatures during the period of processing; a number of pressure regulators are equipped in the inlet system to control inlet/outlet pressures. Heating tape and tubular heating elements are equipped on the inlet pipeline and also the external wall of the VSA column to control the feed gas temperature and prevent water vapor condensation. The entire system is insulated by ceramic fiber cloth and nitrile rubber. Solenoid valves are installed in the pipelines for operating different VSA cycle steps and the whole process is controlled by Advantech® software and hardware. Compressed dry air enters the humidifier (water bubbler) where wet air at different humidity is achieved by controlling the heating temperature. Then the wet air mixes with pure CO₂ (from liquid CO₂, Linda gas) to generate synthetic flue gases in the feed tank. The temperature and the partial pressure of the humid gases are analyzed by in situ hydrometers (HMT330, ±0.05% full scale, VAISALA, Finland).

Figure 1. Diagram of the CO₂/H₂O VSA apparatus: (a) lab setup, photographed before being wrapped by heating elements and insulation materials; (b) positions of the thermocouples plugged along the column.

2.3. VSA cycle design and operation

In this experiment, the temperatures for the feed gas and column are all controlled at 30 °C. This corresponds to a saturated moisture content of 3.4% water in the feed line (at 118 kPa). The inlet CO₂ concentration is controlled to 10-11% in both dry and wet gas streams. The pressure for the inlet gas stream is 118 kPa and the flow-rate is 70 L/min. 200 g of activated alumina CDX, was placed into the bottom layer of the adsorption bed – the estimated length of this layer is 158 mm. This is equivalent to an overall prelayer mass fraction of 0.28 and the height of the prelayer just exceeds the position of thermocouple T3. The remainder of the bed is filled with zeolite 13 X (485 g) which fills the bed with an additional 402mm of adsorbent.

In our 1-bed experiments, a simple three step VSA cycle including only adsorption, desorption and repressurization (Fig. 2) was designed for investigating the adsorption/desorption capacities of water vapour and CO₂ component in the pre-layer and main layer. We emphasize that this is not a cycle one would use in commercial CO₂ capture plants since the latter would involve additional steps such as pressure equalization, product purge, etc. The goal in our 1-bed tests was simply to evaluate appropriate layering and adsorbent schemes. For this reason, detailed multi-bed cycles are not necessary. The detailed operation for each step is as follows. In step 1, the adsorption step,
the feed gas passes through the adsorption column from the bottom to the top. The step time was fixed at 45 s for all the experiments in this study based on the given flow rates, valves and piping system, the size of the beds and the need to utilize the maximum bed length for CO2 adsorption without breakthrough. These conditions were established as being appropriate in our earlier study [5]. In step 2, the countercurrent evacuation step, the adsorbed components (mainly CO2, H2O and a small co-adsorbed amount of N2 and O2) are desorbed from the adsorbents by the vacuum pump. The step time was initially set at 112 s and then reduced to 100 s and 80 s for investigating the effect of desorption time on the performance of the CO2/H2O VSA and the propagation of the water front. This is based on a compromise between cycle scheduling constraints as well as reasonable kinetics of desorption and vacuum pump capacity. In step 3, the re-pressurization step, the bed is re-pressurized to atmospheric pressure with waste gas from the top of the bed. This step time was fixed at 3 s.

Figure 2. Three step cycle design for CO2/H2O VSA with double-layered column: Step 1, adsorption; Step 2, evacuation; Step 3, re-pressurization

The concentration of H2O in the column was monitored in situ by a hydrometer at every thermocouple position of the column. All the experimental data were automatically collected and stored by a PC. The performance of the CO2/H2O VSA was characterized by product (CO2) recovery, purity and unit productivity [5].

3. Results and Discussion

3.1. Effect of adsorbents

Working capacity is the major criteria for adsorbent selection which is defined as the difference between the adsorption loading at the feed partial pressure (adsorption step in VSA operation) and the vacuum partial pressure (evacuation step). As can be seen from Fig 3, the isotherms of CO2 on both of the materials are of type I. The loadings of CO2 show a sharp rise in the low pressure region and then level off above 20 kPa. The full range adsorption capacity of CO2 on zeolite 13X is almost twice of that on alumina CDX. However, the loading of N2 on alumina CDX is as low as 0.093 mmol/g at 106.09 kPa and 303.15 K, which is two thirds of the 13X one. Although N2 loading is insignificant compared to CO2 at the same partial pressure, it must be recalled that N2 is the major component of the post-combustion flue gases. Its partial pressure ranges from nearly 100 kPa at feed conditions to deep vacuum compared to approximately 12~2 kPa for CO2. The co-adsorption of nitrogen therefore leads to a noticeable reduction of CO2 product purity. Our measured CO2 isotherms are well characterized by the Dual site Langmuir equation [8]:

\[ N = M_s \frac{BP}{1 + BP} + M_o \frac{DP}{1 + DP} \]  \hspace{1cm} (1)

\[ B = b_0 \exp\left(\frac{-Q_B}{RT}\right); D = d_0 \exp\left(\frac{-Q_D}{RT}\right) \]  \hspace{1cm} (2)
where \( P \) is the gas pressure, and \( B, D, b_0 \) and \( d_0 \) are constants. \( Q_B \) and \( Q_D \) are the heats of adsorption for adsorption on the two types of sites, \( R \) the gas constant and \( T \) the temperature. \( M_B \) and \( M_D \) represent the maximum monolayer adsorption on the two types of sites. The units for the above parameters are listed in Table 2 along with the fitting results of the model. The adsorption heat of CO\(_2\) on 13X is slightly higher than that of alumina CDX.

![Figure 3. Adsorption isotherms of CO\(_2\) and N\(_2\) onto zeolite 13X and alumina CDX at different temperatures. Dashed lines represent curve fitting by dual-site Langmuir model. Lines represent model fitting by dual site Langmuir equation, in which solid ones stand for 13X and dashed ones for alumina CDX at corresponding temperatures.](image)

Table 2. Parameters of the dual site Langmuir equation for CO\(_2\) adsorption isotherms.

<table>
<thead>
<tr>
<th>Asorbent</th>
<th>( M_B ) (g/mole/kg)</th>
<th>( b_0 ) (1/kPa)</th>
<th>( Q_B ) (J/g-mole)</th>
<th>( M_D ) (g/mole/kg)</th>
<th>( d_0 ) (1/kPa)</th>
<th>( Q_D ) (J/g-mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite 13X</td>
<td>2.5440</td>
<td>8.00E-7</td>
<td>-32725.1</td>
<td>2.4185</td>
<td>3.93E-8</td>
<td>-33048.1</td>
</tr>
<tr>
<td>alumina CDX</td>
<td>1.2100</td>
<td>2.10E-7</td>
<td>-33685.7</td>
<td>2.2042</td>
<td>1.40E-7</td>
<td>-28440.1</td>
</tr>
</tbody>
</table>

At ambient temperature, it is known that water adsorption is solely a function of relative humidity regardless of slight variations of the temperatures [7]. Therefore, this observation allows us to compare the isotherms of water on 13X and alumina CDX in this case. As can be seen from Fig. 4(a), the initial water adsorption on zeolite 13X shows an extremely steep increase to 11.2 mmol/g at 1.47% R.H. (relative humidity) i.e. 0.0465 kPa, and then quickly levels off and has a slight rise at near saturation pressure which can be explained by the pore filling theory in micropores. The heat of adsorption of water on 13X is reported as 51.7 kJ/mol [3] due to the strong interaction between Na\(^+\) cations and polar water molecules. Its isotherm shape more closely resembles Type I than Type II. On the other hand, the adsorption of water on alumina CDX is of the “BET” shape, a typical type II isotherm. This suggests that there is a steady and quick increase of water loading from 4.05 mmol/g at low R.H. of 4.04% (0.171 kPa) to 24.1 mmol/g at high R.H. of 99% (4.20 kPa). Meanwhile, a moderate hysteresis loop is also observed indicating the existence of mesopores in alumina CDX, which has been confirmed by the results of liquid nitrogen adsorption. The latter indicates that this adsorbent presents a very broad pore size distribution ranging from 0.8 nm up to 40 nm. In this study, saturated water vapour was fed into the column while the lowest partial pressure observed was 0.44 kPa (referring to Fig. 6(a) in later sections) so the equilibrium working capacity of alumina CDX for water adsorption/desorption is around three times of that of zeolite 13X. However, it must be pointed out that this value
may change in a real VSA process due to temperature variation and insufficient time to reach equilibrium conditions [9]. Therefore, the effect of water adsorption/desorption kinetics deserves careful investigation in a future study.

Figure 4. (a) Adsorption and desorption isotherms of water vapour on zeolite 13X at 298.15 K and on alumina CDX at 303.15K in which solid squares of variant colours denote data of different runs. Results of different runs were presented in the same graph to show the repeatability of the measurement. (b) Binary adsorption isotherm of CO₂/H₂O alumina CDX at 303.15K with trend lines added. Carbon dioxide is kept at constant pressure of 105.3 kPa.

Regarding the binary CO₂/H₂O adsorption on alumina CDX as shown in Fig. 4(b), the CO₂ loading is dramatically reduced from 2.3 mmol/g under dry conditions to 0.33 mmol/g in the presence of 2.79 % R.H. (0.118 kPa) of water. Thereafter, CO₂ adsorption remains almost constant with increasing water humidity, which may be explained by the hydration interaction of CO₂ and adsorbed water on adsorbent surface [10]. Although we were not able to measure the desorption isotherm, we may still infer that the VSA working capacity of CO₂ on CDX is negligible in this study. It means low concentration of water can largely displace CO₂ adsorption. On the contrary, the loading of water on CDX shows little dependence on the CO₂ atmosphere. As reported earlier, the equilibrium adsorption capacity of CO₂ on 13X beads decreased by 99% in the presence of H₂O [5]. Therefore, it is necessary to use a pre-layer of adsorbent with excellent water working capacity for effective CO₂/H₂O VSA processes.

3.2. VSA Performance

The desired product in the VSA process is high purity CO₂. However, as water is the heavy component and cannot be permitted to break through the column, it is recovered as a by-product during regeneration. During the adsorption step, water is adsorbed by the bottom layer i.e. the pre-layer of the column and CO₂ is adsorbed by the 13X main layer. The light components N₂ and O₂ quickly penetrate the column and flow through to the waste line. As the thermal front is always closely related to the adsorption/desorption process (which involves large enthalpy changes [11]), one can readily use thermal information to infer H₂O and CO₂ mass transfer fronts in this study. From Fig. 5(a), we can see that there are two temperature waves propagate along the column with time in the case of wet CO₂ feed with 112 s of evacuation. The narrow and sharp front in the pre-layer characterized by T0, T1 and T2 is caused by water adsorption/desorption. However, the thermal front of water adsorption only reaches T2 which means T3 (the last thermocouple in the pre-layer) is still dry at the end of adsorption. This is further supported by the data of gas phase water vapour concentration as shown by Fig. 6(b). The second broad temperature wave

![Figure 4a](image1.png)

![Figure 4b](image2.png)
occurring in the 13X layer is attributed to CO$_2$ adsorption heat. The wave peaks at T8 in order to properly retain the heat of adsorption in the column and prevent CO$_2$ breakthrough.

Figure 5. Temperature profiles along the column. (a) during the adsorption step of CO$_2$/H$_2$O VSA with 112 s desorption time; (b) at the end of adsorption step and at the end of evacuation step in the case of dry CO$_2$ VSA and CO$_2$/H$_2$O VSA with desorption time of 112 s and 80 s. The first point at the position of 0 bed length is the inlet temperature. The second point along the bed is thermocouple T0.

During the evacuation step, water and CO$_2$ are desorbed from the column along with some weakly adsorbed N$_2$ and O$_2$ and gases from the void spaces. A typical pump down curve is shown in Fig. 6(a), where the CO$_2$ and H$_2$O mole fractions increase with decreasing partial pressures. At the end of the desorption step, the CO$_2$ partial pressure reaches 1.70 kPa and the H$_2$O partial pressure reaches 0.44 kPa. It must be noted that the CO$_2$ product purity increased after the vacuum pump compared with the values recorded in Fig. 6(a) because water is condensed and trapped in the vacuum pump as the pressure rises to atmospheric conditions.

Figure 6. (a) Pump down curve in terms of partial pressure and mole fraction during the 112 s evacuation step of CO$_2$/H$_2$O VSA; (b) Gas phase water front in the double layered VSA column at the end adsorption step for cycles with different desorption time: 112 s, 100 s and 80 s. The dashed line represents the boundary between the two layers.

Due to the fixed feed condition in this study, the major parameters influencing desorption are the evacuation time and hence the final vacuum pressure. In Fig. 5(b), the temperature change of the column through a cycle with evacuation time of 112 s is larger than that with 80 s. Longer evacuation time provides opportunities to attain deeper
vacuum levels and enhance CO₂ regeneration compared to shorter evacuation times. As a result, there is more CO₂ adsorbed/desorbed in cycles with longer evacuation times. The CO₂ product recovery and purity are reduced with a decrease of evacuation time as well as increase of vacuum pressure for the H₂O/CO₂ VSA process.

It should be emphasized that water desorption is largely affected by the counter current internal purge of CO₂ and other weakly adsorbed gases coming from the top of the column, in addition to the evacuation time and vacuum pressure. As we can see from Fig. 6(b), the steady state water front (at the end of adsorption step) moves deeper into the column as evacuation time decreases. In the worst case — 80 s desorption, water has already reached T3, almost the boundary between the two layers. This result is parallel to the propagation result of the thermal front caused by water in Fig. 5(b).

4. Conclusion

A laboratory VSA unit was used to study experimentally the capture of carbon dioxide from humid flue gases with a double layered adsorption column. Preliminary binary experiments showed that water could easily displace carbon dioxide adsorption in this study. Higher working capacity of water under VSA conditions is desired for selecting adsorbents for the pre-layer while zeolite 13X still remains one of the best commercial adsorbents for carbon capture by VSA. Appropriately longer evacuation time and deeper vacuum level are essential for keeping the water front in the pre-layer and maintaining a higher product carbon dioxide recovery. Finally, the double layered single bed CO₂/H₂O VSA has obtained successful results with 76.9 % CO₂ recovery and 67 % purity. Future work will examine carbon dioxide capture from flue gases with higher water content at elevated temperatures and tests on a full multi-column VSA.

Acknowledgements

The project is financially supported by Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC). We would also express our grateful thanks to Mr Barry Hooper for his review and technical support.

References