Production of high purity CO₂ from air using solid amine sorbents

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Abstract

For CO₂ capture from air on a supported amine sorbent, the effects of water co-adsorption and steam purge on the CO₂ working capacity and energy requirement for CO₂ desorption are studied. Working capacities are studied by fixed bed operation for changing temperature, pressure and amount of steam purge. Results show that for pressure-temperature swing adsorption a temperature above 100 °C and a pressure below 200 mbar as desorption conditions are required to maximize CO₂ working capacity and reduce energy requirement for desorption. Co-adsorption of water reduces energy requirement due to an increased CO₂ working capacity. Application of a steam purge increases the CO₂ working capacity and hence reduces sorbent inventory required. However, the net energy requirement per kilogram CO₂ does not decrease due to the latent heat of water. Concluding, steam purge regeneration for air capture does not reduce opex but might reduce capex.

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1. Introduction

CO₂ concentrations in the atmosphere have been steadily increasing from 250 ppm in pre-industrial era to more than 400 ppm today (Metz et al., 2005) due to anthropogenic emissions. The IPCC report (IPCC, 2014) showed that reducing CO₂ concentrations in the atmosphere is necessary to stay within the 1.5 °C temperature increase limits (Williamson, 2016).

In literature and industry CO₂ capture is often performed using amine compounds. Compared to aqueous amine CO₂ capture – commonly used in flue gas CO₂ capture – solid amine sorbents have the advantages of lower heat capacity, higher CO₂ capacity and lower energy requirement of CO₂ amine contacting. The last point being of major importance since at 100% capture efficiency 1400 m³ of air at normal conditions have to be processed to capture 1 kg of CO₂. Another advantage of solid amine sorbents is the high selectivity for CO₂. Adsorption of CO₂ from air using solid amine sorbents have been described in literature (Belmabkhout et al., 2010; Wurzbacher et al., 2011; Choi et al., 2011a; Sculley and Zhou, 2012; Brilman et al., 2013; Lu et al., 2013; Liu et al., 2014).

Regeneration methods of solid amine sorbents and production of high purity CO₂ from air has been given less attention. An overview of regeneration studies has been given by Bollini et al. (2011). Regeneration studies often result in low purity CO₂ due the use of inert purge media (Choi et al., 2011b; Zhao et al., 2017; Schönny et al., 2017). Lower purity CO₂ can be used for algae growth (Brilman et al., 2013) or greenhouse cultivation. High purity CO₂ is required for CO₂ utilization options such as the production of methanol (Bos and Brilman, 2015; Martens et al., 2017). The underground storage of CO₂ also requires CO₂ with a high purity. Moreover, air captured CO₂ can open opportunities to produce renewable fuels and chemicals independent of locations of point sources of CO₂.

Production of high purity CO₂ can be done by applying a temperature or pressure swing adsorption without purge flow (Pirngruber and Leiniekugel-le Cq, 2013; Goepert et al., 2011). Moreover, CO₂ recovery can be increased by use of a steam purge (Li et al., 2010b; Sandhu et al., 2016; Pröll et al., 2016; Fujiki et al., 2017). Additionally, Sandhu et al. (2016) showed increased desorption kinetics with the use of steam. Wurzbacher et al. (2012) and Stuckert and Yang (2011) demonstrated the production of high purity CO₂ from air. The energy required for regeneration for CO₂ capture from air is discussed by Elfving et al. (2017) using isotherm based working capacities.

The stability of amine sorbents during steam regeneration has been questioned in literature. Sakwa-Novak and Jones (2014) showed leaching of PEI from the sorbent. Also Hammache et al. (2013) found reduction of capacity of PEI based sorbents due to steam regeneration. Chakkitisilp et al. (2011) concluded that PEI-alumina based sorbents are suitable for steam regeneration in contrast to PEI-silica based sorbents. Isenberg and Chuang (2013) showed that copper ions from the steam boiler degraded a TEPA based amine sorbent. Li et al. (2010a) discussed degradation...
because of structural changes of the sorbent due to steam regeneration. However, work by Yu et al. (2017) showed no issues with 48 h exposure to steam for the Lewatit VP OC 1065 sorbent used in this study. Therefore, we have fair confidence that this sorbent can be used in steam regeneration conditions. Additionally, it was shown by Yu et al. that the sorbent is stable in pure CO_2 up to 120 °C and that oxygen induced degradation starts at 70 °C. Furthermore, stability in N_2 was proven up to 150 °C (Yu et al., 2017).

In this paper, the regeneration methods of solid amine sorbents are studied using a fixed bed setup. However, conventional fixed bed reactors have too high pressure drop leading to excessive cost for air sorbent contacting (Yu and Brilman, 2017). Therefore, for large scale Direct Air Capture (DAC) applications we envision a shallow radial flow fixed bed adsorption reactor combined with a moving bed desorber reactor (Yu, 2018). For smaller scale operations the adsorption and desorption step might be performed in the same vessel because of operation simplicity.

Energy consumption of regeneration options based on experimental data will be discussed in this paper. Especially, the influence of a steam purge on the desorption energy requirement is studied. Next to that, the effect of co-adsorption of water during the adsorption on the working capacity and energy requirement is studied.

2. Materials and methods

2.1. Materials

The sorbent used in this study is the commercial sorbent Lewatit VP OC 1065 from Lanxess. The sorbent has a support of spherical polystyrene beads with primary benzyl amine functional units. The commercial sorbent is selected because in parallel adsorber development studies the sorbent is needed at kilogram scale (Yu, 2018). Moreover, this sorbent shows good CO_2 capacity at air capture conditions (Yu and Brilman, 2017). More details about the sorbent and adsorption isotherms can be found in previous work (Veneman et al., 2015; Driessen et al., 2018; Bos et al., 2018a). Water adsorption capacity and the effect of humidity on the CO_2 adsorption capacity was reported by Veneman et al. (2015).

2.2. Experimental setup

The setup used is discussed in previous work (Bos et al., 2018b). However, three changes have been made. First, the 0–50 vol.% CO_2 analyser is replaced by a 0–2 vol.% [LI-COR LI-840A] and a 0–15 vol.% [Sick Maihak Sidor S700] CO_2 analyser for increased accuracy at low partial pressures of CO_2. The 0–2 vol.% analyser is used during adsorption and the 0–15 vol.% CO_2 during desorption and regeneration. Second, a gas humidifier is added to the system to be able to perform co-adsorption experiments of CO_2 with water. Gas humidity is measured using humidity sensors [Galltec LKK3.05.FI01. C05.00GC] in the inlet and outlet. Third, a steam injection system is installed. Liquid water is injected by a syringe pump to an inline heater where the steam is generated. The amount of steam injected and the injection rate are controlled by the syringe pump. For convenience a schematic overview of the setup is given in Fig. 1. In this study the fixed bed reactor was filled with 53.6 g of wet Lewatit sorbent as supplied by the manufacturer for all experiments. After removal of pre-adsorbed moisture and CO_2 this equals about 30.4 g of dry sorbent. The amount of pre-adsorbed of moisture and CO_2 for the batch of sorbent used is determined using TGA analysis. The dry sorbent mass is used for normalization of the sorbent loading.

2.3. Experimental method

Desorption capacity measurements are performed in three steps. In the first step, the adsorption is performed at 20 °C with simulated air of 400 ppm of CO_2 in nitrogen until the sorbent equilibrium capacity is reached. Also, experiments are performed with 5000 ppm of CO_2 allowing for faster successive adsorption – desorption cycles in the experiments. Additionally, 5000 ppm might represent CO_2 levels in enclosed environments such as submarines or spacecraft’s (Schladt et al., 2007). Therefore, these experiments are relevant for reducing CO_2 concentrations in such enclosed environments. The adsorption step is performed until the equilibrium capacity of the sorbent is reached.

After completion of the adsorption step, the second step, desorption, is performed. First the heater is switched on directly followed by the vacuum pump. The steam purge – when applied – is applied as soon as the reactor temperature is above the boiling point of water to prevent condensation of water on the sorbent. Condensation of water on the sorbent and into the pores will effect the adsorption rate in the consecutive adsorption step. In screening experiments it was seen that liquid water on the sorbent significantly reduced the adsorption rate in a consecutive adsorption step unless the sorbent was fully dried prior adsorption. For this reason, rapid heating by condensing steam on the sorbent is not possible and heating by steam can only be applied indirectly. The desorption step is run until the CO_2 concentration – mixed with the dilution stream (see Fig. 1) – in the analyser is below 0.05 vol% CO_2.

The final step is to fully regenerate the sorbent by purging nitrogen at 100 °C to ensure a clean sorbent for the next adsorption. It should be noted that this step is only performed to fully clean the sorbent for the next adsorption step. In an industrial process only the adsorption and desorption will be performed, since the use of purge gas is too expensive and will lead to dilution of the CO_2 produced.

2.4. Error analysis

All experiments are performed with the same batch of sorbent. This ensured quick successive screening of the working capacities for various conditions during desorption. In Fig. 2 the adsorption capacity of CO_2 is analysed for signs of sorbent degradation and repeatability of adsorption experiments. As shown, no sign of degradation is seen over more than 60 experiments with varying desorption conditions. However, it should be noted that during earlier screening experiments – which are not included in the results presented here – degradation of the sorbent was seen when operating at temperature above 120 °C during desorption and regeneration. These results are in line with data presented by Yu et al. (2017) and therefore high temperatures should be prevented. The adsorption experiments show great reproducibility as the average adsorption loading is 1.64 ± 0.03 mol kg⁻¹ for the 5000 ppm CO_2 dry adsorption experiments. The adsorption experiments at 400 ppm show the same reproducibility as the standard deviation (1.06 ± 0.03 mol kg⁻¹) is equal to the standard deviation for 5000 ppm. The equilibrium loading itself is lower because it is a function of the CO_2 partial pressure (Bos et al., 2018a). Another measure of the reliability of the experiments is the loading after regeneration. With perfect mass balance closure this loading should be zero. As seen in Fig. 2 the CO_2 loading after regeneration approaches zero and therefore shows great accuracy.

Whereas for CO_2 the mass balance closure in the experiments is excellent, the closure of the mass balance for water is less good. The closure of the mass balance for H_2O is 79.0% on average. Source of the poor mass balance closure is the limited accuracy of the relative humidity sensors used. The accuracy of the sensors ranges from ±3%RH at 10 – 40 °C and 30 – 80%RH to ±8%RH at 90 °C.
and < 30% RH. Especially, during desorption the accuracy of the relative humidity sensors is too low because of high temperature and low relative humidity caused by the dilution flow needed for good CO₂ mass balance closure. As will be shown in the results section, despite the uncertainty in the water balance, the trends in the CO₂ recovery in the presented data are beyond the uncertainty due to the water balance. Conclusions in this article are therefore not influenced by this imperfect closure of the H₂O mass balance.

All the error bars shown in the study present one standard deviation (68% confidence interval) unless mentioned otherwise. The error in loading shown in the results section is the error in mass balance of the experiment, that is the loading after regeneration. The error in the energy requirement for desorption is determined by propagation of the errors in the experimental values. The main contributors to the error in energy requirement are the errors in the working capacity of both CO₂ and – if present – H₂O. For the
cases with low working capacity and high loading after regeneration consequently a large relative error in working capacity is found. This might result in large error – up to 25% – in the energy requirement for desorption, as seen in the results section.

2.5. Energy calculations

In the results section the energy requirement for desorption of CO₂ from the solid amine sorbent is shown. The calculations are given in more detail below. Included in the evaluation are the sensible heat of the sorbent, CO₂, water and the reaction heat of CO₂ and adsorbed water. Next to that, the latent heat of water for steam generation and the compression energy required for the vacuum production are included.

First of all, the sensible heat of the sorbent (\(Q_{\text{sensible,sorbent}} \, [\text{J/kg} \text{CO}_2]\)) is calculated using Eq. (1). Where \(T_{\text{des}}\) and \(T_{\text{ads}}\) are the desorption and adsorption temperature respectively. The amount of sorbent to capture one kilogram of CO₂ is calculated by the experimental working capacity \(\Delta q_{\text{exp}}\) and the molar mass of CO₂ \(MW_{\text{CO}_2}\).

\[
Q_{\text{sensible,sorbent}} = \frac{1}{\Delta q_{\text{exp}}} \cdot MW_{\text{CO}_2} \cdot C_{\text{p,sorbent}} \cdot (T_{\text{des}} - T_{\text{ads}}) \tag{1}
\]

The sensible heat of the CO₂ (\(Q_{\text{sensible,CO}_2} \, [\text{J/kg} \text{CO}_2]\)) is calculated by Eq. (2):

\[
Q_{\text{sensible,CO}_2} = C_{\text{p,CO}_2} \cdot (T_{\text{des}} - T_{\text{ads}}) \tag{2}
\]

The energy required for the desorption reaction of CO₂ (\(Q_{\text{reaction heat}} \, [\text{J/kg} \text{CO}_2]\)) is given by Eq. (3) and is calculated by dividing the reaction heat \(\Delta H\) by the molar mass \(MW_{\text{CO}_2}\). Similar, the energy required for desorption of H₂O is found. The ‘reaction heat’ for H₂O is equal to the vaporization enthalpy (Veneman et al., 2015).

\[
Q_{\text{reaction heat}} = \frac{\Delta H}{MW_{\text{CO}_2}} \tag{3}
\]

The amount of energy needed to heat the co-adsorbed water or steam purge – when used – is determined by the sensible heat of the sorbent, CO₂, water and the reaction heat of CO₂ given in more detail below. Included in the evaluation are the sensible heat of the CO₂, water and steam purge. If applicable the combination of both is used.

\[
\frac{Q_{\text{sensible,H}_2O}}{MW_{\text{H}_2O}} = m_{\text{H}_2O} \left[ C_{\text{p,H}_2O} \cdot (T_{\text{sat}} - T_{\text{des}}) + C_{\text{p,steam}} \cdot (T_{\text{des}} - T_{\text{sat}}) \right] \tag{4}
\]

\[
Q_{\text{latent,H}_2O} = m_{\text{H}_2O} \cdot \Delta H_{\text{vap,H}_2O} \tag{5}
\]

The amount of H₂O per kilogram of CO₂ (\(\frac{m_{\text{H}_2O}}{kg_{\text{H}_2O}/kg_{\text{CO}_2}}\)) can be found by Eq. (6). The molar ratio H₂O : CO₂ is defined by Eq. (7) when using humid feed gas and by Eq. (8) when applying a steam purge.

\[
m_{\text{H}_2O} = \frac{\text{ratio H}_2O : \text{CO}_2}{MW_{\text{H}_2O}/MW_{\text{CO}_2}} \tag{6}
\]

\[
\frac{\text{ratio H}_2O : \text{CO}_2}{MW_{\text{H}_2O}/MW_{\text{CO}_2}} = \frac{\Delta q_{\text{H}_2O,exp}}{\Delta q_{\text{CO}_2,exp}} \tag{7}
\]

In the case of steam purge the ratio H₂O : CO₂ can be determined using the volume of H₂O (\(V_{\text{H}_2O,exp}\)) added during the experiment. In Eq. (8) \(\rho_{\text{H}_2O}\) is the density of H₂O and \(m_{\text{sorb,exp}}\) the amount of sorbent used during the experiment.

\[
\frac{\text{ratio H}_2O : \text{CO}_2}{MW_{\text{H}_2O}/MW_{\text{CO}_2}} = \frac{V_{\text{H}_2O,exp} \cdot \rho_{\text{H}_2O} \cdot MW_{\text{H}_2O}^{-1}}{\Delta q_{\text{CO}_2,exp} \cdot m_{\text{sorb,exp}}} \tag{8}
\]

For the creation of vacuum adiabatic compression (Green and Perry, 1997) is assumed and the required energy is calculated by Eq. (9). The efficiency of compression \(\eta\) is assumed to 0.75 and the ratio of \(C_p/C_v\) is \(k = 1.3\) (Partington, 1921). In Eq. (9), \(P_1\) is the suction pressure of the compressor whereas \(P_2\) is the discharge pressure which is assumed to be 1.5 bar.

\[
Q_{\text{adiabatic compression}} = \frac{1}{\eta} \frac{k}{k-1} \frac{1}{MW_{\text{CO}_2} \cdot RT_{\text{desorption}} \cdot \left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}}} - 1 \tag{9}
\]

Symbols and values used in the equations above are summarized in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
<th>Meaning</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_{\text{p,CO}_2})</td>
<td>0.85</td>
<td>kJ kg⁻¹ K⁻¹</td>
<td>CO₂ heat capacity</td>
<td>Linstrom and Mallard (2018)</td>
</tr>
<tr>
<td>(C_{\text{p,H}_2O})</td>
<td>4.18</td>
<td>kJ kg⁻¹ K⁻¹</td>
<td>H₂O heat capacity</td>
<td>Linstrom and Mallard (2018)</td>
</tr>
<tr>
<td>(C_{\text{p,sorbent}})</td>
<td>1.58</td>
<td>kJ kg⁻¹ K⁻¹</td>
<td>Sorbent heat capacity</td>
<td>Sonnleitner et al. (2017)</td>
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<tr>
<td>(C_{\text{p,steam}})</td>
<td>2.05</td>
<td>kJ kg⁻¹ K⁻¹</td>
<td>Steam heat capacity</td>
<td>Linstrom and Mallard (2018)</td>
</tr>
<tr>
<td>DAC</td>
<td></td>
<td></td>
<td>Direct air capture</td>
<td>Lanxess (2016)</td>
</tr>
<tr>
<td>(d_p)</td>
<td>0.7</td>
<td>mm</td>
<td>Average particle diameter</td>
<td></td>
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<tr>
<td>(d_r)</td>
<td>13</td>
<td>mm</td>
<td>Reactor diameter</td>
<td></td>
</tr>
<tr>
<td>(k)</td>
<td>1.3</td>
<td></td>
<td>Ratio of (C_p/C_v)</td>
<td>Partington (1921)</td>
</tr>
<tr>
<td>(m_{\text{H}_2O})</td>
<td></td>
<td>kg(\text{H}_2O)/kg(\text{CO}_2)</td>
<td>mass of H₂O per kilogram of CO₂</td>
<td></td>
</tr>
<tr>
<td>(m_{\text{sorb}})</td>
<td>30.4</td>
<td>g</td>
<td>Dry sorbent mass</td>
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<tr>
<td>(MW_{\text{CO}_2})</td>
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<td>kg mol⁻¹</td>
<td>Molar mass CO₂</td>
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<tr>
<td>(MW_{\text{H}_2O})</td>
<td>0.018</td>
<td>kg mol⁻¹</td>
<td>Molar mass H₂O</td>
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<tr>
<td>(P)</td>
<td></td>
<td>Pa</td>
<td>Pressure</td>
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<tr>
<td>(\text{PTSA})</td>
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<td>Pressure temperature swing adsorption</td>
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<tr>
<td>(Q)</td>
<td></td>
<td>J kg(\text{kg}_{\text{CO}_2})</td>
<td>Energy requirement</td>
<td></td>
</tr>
<tr>
<td>(r)</td>
<td></td>
<td>m</td>
<td>Reactor radius</td>
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<tr>
<td>(R)</td>
<td>8.314</td>
<td>J mol⁻¹ K⁻¹</td>
<td>Gas constant</td>
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<tr>
<td>(R_H)</td>
<td></td>
<td>%</td>
<td>Relative humidity</td>
<td></td>
</tr>
<tr>
<td>(T)</td>
<td></td>
<td>K</td>
<td>Temperature</td>
<td></td>
</tr>
<tr>
<td>(V_{\text{H}_2O})</td>
<td></td>
<td>m³ s⁻¹</td>
<td>Volume flow of steam injection</td>
<td></td>
</tr>
</tbody>
</table>

Greek Symbols:

\(\Delta H\) \quad \text{kJ mol}⁻¹ \quad \text{Reaction heat}

\(\Delta v_{\text{H}_2O}\) \quad \text{kJ mol}⁻¹ \quad \text{H}_2\text{O vaporization enthalpy}

\(\Delta Q\) \quad \text{kJ mol}⁻¹ \quad \text{Work capacity}

\(\eta\) \quad \text{kJ kg}⁻¹ \quad \text{Compressor efficiency}

\(\rho_{\text{H}_2O}\) \quad \text{kg m}⁻³ \quad \text{H}_2\text{O density}

References:

3. Results and discussion

3.1. PTSA dry adsorption

One of the ways to produce high purity CO₂ is desorption without the use of a purge medium. The effect of pressure and temperature on the working capacity is shown in Fig. 4 for pressure temperature swing adsorption (PTSA) operation without any purge flow during desorption. Example profiles for temperature and loading during a desorption experiment at 200 mbar and a bed temperature set-point of 100 °C are given in Figs. 3. As seen in Fig. 3, the temperature at the wall is significantly higher than the set point temperature. The reason for this is the fact that the power input via the heating coil around the reactor is controlled by the temperature. The reason for this is the fact that the power input via the heating coil around the reactor is controlled by the temperature. This implicates that not all experiments have reached their equilibrium capacity as soon as the CO₂ concentration is below 0.05 vol.% (including dilution) and the desorption step was stopped. Additionally, it can be seen that the two experiments with the highest pressure at 91 °C have a very small working capacity. This is in line with isotherm predictions, as the isotherm predicts a loading above 1.6 mol kg⁻¹ when considering 100% CO₂ and a pressure above 700 mbar at 91 °C. The small working capacity observed might be due to some residual nitrogen present in the reactor from the adsorption step. Moreover, the loading reached falls within the accuracy of the isotherm. It can be concluded that in order to reach reasonable working capacities low pressure (<300 mbar) at 116 °C or really low pressure (<100 mbar) at 91 °C have to be used.

The energy evaluation using Δq₂₀₀ in Fig. 5 confirms the need for high temperature and low pressure to increase working capacity and thereby lowering the energy requirements. The experiments with a low working capacity at 900 s in Fig. 4 show high energy requirement in Fig. 5. Major reason is the increased amount of sorbent needed to capture one kilogram of CO₂. With increased sorbent mass, the sensible heat for the sorbent increases linearly. It can be seen in Fig. 4 that for the experiments with low working capacity the error is larger than the working capacity itself. Consequently, in Fig. 5 considerable error bars for the experiments with low working capacity are found due to error propagation.

Pressures below 200 mbar are needed to have a energy requirement for desorption below 10 MJ/kgCO₂. Moreover, if the CO₂ concentration is 400 ppm also a higher temperature is needed. At 91 °C the 400 ppm experiments lead to high energy requirements due to the low working capacities. However, the energy requirement might easily be halved by extending the desorption phase and reaching the final working capacity instead of the working capacity at 900 s. As shown in Fig. 4 the working capacity at 400 ppm is significantly increased from 900 s to the final capacity, especially at 91 °C. Moreover, the achieved adsorption loading of 1.1 mol kg⁻¹ is at 20 °C and under absolute dry conditions. Lowering the temperature or increasing the relative humidity will somewhat more variation in the data for the final loading. This might be an effect of slower desorption kinetics at lower temperature. The definition of working capacities used in this article are visualized in Fig. 3. Δq₆₀₀ is the working capacity 600 s after the start of the desorption operation. The working capacity is the difference between the adsorption loading and the loading after desorption, in this case after 600 s. Analogue is Δq₉₀₀ the working capacity after 900 s of desorption operation. When the CO₂ concentration – mixed with the dilution stream, see Fig. 1 – in the analyser is below 0.05 vol.% the desorption is stopped. The capacity at this time is defined as residual loading q₉₀₀ with final working capacity (Δq₉₀₀).

In Fig. 4 the working capacities as a function of pressure and temperature are shown. First, experiments with 5000 ppm of CO₂ are performed leading to an adsorption loading around 1.6 mol kg⁻¹. Additionally, experiments with 400 ppm of CO₂ – resulting in an adsorption loading of 1.1 mol kg⁻¹ – are performed at those pressures leading to a positive working capacity. As seen, the final loading after desorption is independent of the adsorption loading. Although, it seems that for the 91 °C experiments there is

\[ T_{\text{avg}} = \frac{2\pi \int_0^r T(r) rdr}{\pi d_r^2} \]  

Fig. 4. Experimental working capacities as a function of temperature and pressure (on x-axis in mbar) reported after 600 s (Δq₆₀₀), 900 s (Δq₉₀₀) and at the end (Δq₉₀₀) of the experiment. Δq₆₀₀, Δq₉₀₀ and Δq₉₀₀ are shown. Note the break in x-axis in the adsorption stage to give more emphasis to the desorption stage.

Fig. 3. Example loading and temperature profiles versus time. Set point temperature 100 °C for the bed temperature (Tₑₑₑ – 116 °C) and pressure 200 mbar. The definition of the working capacity after 600 s (Δq₆₀₀), 900 s (Δq₉₀₀) and at the end (Δq₉₀₀) are shown. Note the break in x-axis in the adsorption stage to give more emphasis to the desorption stage.
increase the adsorption loading and thereby the working capacity (Veneman et al., 2015). However, in an air capture process the environmental conditions will determine the adsorption conditions and thus cannot be optimized separately. Pre-treating air is too costly because of the enormous amount of air – minimal 1400 m$^3$ – to be processed to capture one kilogram of CO$_2$. A temperature higher than 116°C might increase working capacities even more. However, increasing the temperature above 120°C may lead to degradation of the sorbent (Yu et al., 2017). Therefore, it can be concluded that in order to reach sufficient high working capacities without the use of a purge gas, the air capture equipment should be able to reach a pressure below 200 mbar and temperatures higher than 100°C during the desorption step. Otherwise, energy requirement for desorption might significantly increase.

### 3.2. PTSA humid adsorption

As mentioned in the previous section, the incoming air during CO$_2$ air capture will be humid and water will co-adsorb on the sorbent. Moreover, the CO$_2$ equilibrium capacity is increased by co-adsorption of H$_2$O. Both of these effects are described by Veneman et al. (2015). In Fig. 6 the increase in CO$_2$ capacity and co-adsorption of H$_2$O is confirmed. With increasing relative humidity in the gas feed, both the CO$_2$ and H$_2$O capacity are increased. The CO$_2$ working capacity after 900 s is increased by two effects with increasing relative humidity. To illustrate, the adsorption capacity is increased by 0.4 mol kg$^{-1}$ at 79%RH compared to 0%RH. Secondly, because of the temperature of the adsorption temperature above 120°C, it can be concluded that in order to reach sufficient high working capacities without the use of a purge gas, the air capture equipment should be able to reach a pressure below 200 mbar and temperatures higher than 100°C during the desorption step. Otherwise, energy requirement for desorption might significantly increase.

5000 ppm experiments. Although the co-adsorption of water raises an energy penalty for the adsorption enthalpy and sensible heat of water, the total energy requirement reduces because of the increased working capacity of CO$_2$. When considering the error bars the decreasing trend with increasing relative humidity is less pronounced. However, an energy saving compared to dry adsorption is seen for all relative humidities. For the 400 ppm experiment the reduction of energy requirement is more clear. Even though the ratio H$_2$O to CO$_2$ is significantly higher. The increased ratio is a result of a reduced CO$_2$ working capacity with constant H$_2$O working capacity. From 44%RH onwards the total energy requirement remains constant due to increasing ratio of H$_2$O to CO$_2$. This is a

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**Fig. 5.** Energy requirement for desorption for the experimental conditions presented in Fig. 4 calculated with the working capacity after 900 s. Other includes sensible heat of CO$_2$ and compression energy. Error bars show the propagated experimental error.

**Fig. 6.** Experimental working capacities for CO$_2$ and H$_2$O reported after 600 s ($\Delta q_{600}$), 900 s ($\Delta q_{900}$), at the end ($\Delta q_{fin}$) and residual capacity ($q_{res}$) as function of the adsorption at 20°C and RH on x-axis and 400 or 5000 ppm of CO$_2$. Desorption at 500 mbar and $T_{avg} = 116^\circ$C. Error bars show the loading after regeneration.

**Fig. 7.** Energy requirement for desorption for the experimental conditions presented in Fig. 6 calculated with the working capacity after 900 s. In the reaction heat bar the ratio H$_2$O:CO$_2$ [mol mol$^{-1}$] – see Eq. (7) – is given. Other includes sensible heat of CO$_2$ and H$_2$O and the compression energy. Error bars show the propagated experimental error.
result of the fact that the working capacity of H$_2$O is increasing faster compared to the working capacity of CO$_2$. From this, it can be concluded that the co-adsorption of H$_2$O does not lead to an increased energy penalty and, on the contrary, even might reduce the energy requirement. An energy reduction is clearly shown for 400 ppm experiments. Moreover, water will be co-harvested from air during air capture of CO$_2$ using a solid amine sorbent and will be a secondary product.

3.3. Steam purge with dry adsorption

3.3.1. Amount of steam

Steam is often used as a purge medium to produce pure CO$_2$ because it is easily separated from CO$_2$ by condensation. Therefore, in this work the effect of the amount of steam injected (in kg$_{steam}$/kg$_{sorbent}$) during desorption is evaluated in Fig. 8. Three stages of desorption can be identified in the figure. First, the heating stage is seen for $t = 0$–250 s. In this phase only the heating elements are switched on and the bed temperature is increased. This stage could be considered a temperature swing adsorption. As seen in Fig. 8A, little desorption is occurring at $T_{avg} = 91 \degree C$ which is in line with isotherm predictions at 91 \degree C and 100% CO$_2$. A slight decrease in loading can be observed in Fig. 8B due to the higher reactor temperature. The second stage is seen after approximately 250 s when the vacuum pump and water injection are started. A decrease in loading is seen due to the decrease in CO$_2$ pressure with total pressure. The third stage starts at approximately $t = 600$ s where a strong decrease in loading is observed as a result of reduced partial pressure of CO$_2$ due to the steam injected. This peak is not instantaneous because of the residence time of the water and steam in the evaporation system.

Using a steam purge does not always lead to a positive effect on the working capacity as seen in Fig. 8. Steam amounts up to 0.03 kg kg$^{-1}$ even have a slight negative effect on the working capacity, when compared to the 0 kg kg$^{-1}$ PTSA experiment. An explanation can be found in the water capacity of the sorbent. Because the adsorption is performed with dry feed gas as soon as steam is injected it adsorbs on the sorbent. Veneman et al. (2015) showed adsorbed water will increase the CO$_2$ capacity and hence a negative effect on the working capacity is seen for water volumes up to 0.03 kg kg$^{-1}$. Another effect of the adsorption of water is that it will not lower the partial pressure of CO$_2$ in the reactor. Veneman et al. (2015) showed that the water capacity on the sorbent is a function of relative humidity. Evaluating the maximum relative humidity in the reactor – 41% and 29% respectively – a water capacity of 3.9 and 2.6 mol kg$^{-1}$ was found for the conditions of $T_{avg} = 91 \degree C$ & $P = 300$ mbar and $T_{avg} = 116 \degree C$ & $P = 500$ mbar respectively. These capacities correspond to 0.07 and 0.05 kg kg$^{-1}$ of steam added. Consequently, adding more than 0.05 kg kg$^{-1}$ of steam at 116 \degree C would reduce the CO$_2$ partial pressure and accordingly the loading. In Fig. 8B this effect is confirmed as from 0.07 kg kg$^{-1}$ onward a significant improvement in working capacity is seen. However, for the low temperature the 0.07 kg kg$^{-1}$ line unexpectedly has an improved working capacity. This might be an effect of the radial temperature gradient inside the reactor resulting in lower maximum relative humidity locally. Moreover, the local partial pressure of H$_2$O can be reduced due to desorbing CO$_2$ also resulting in lower relative humidity.

The energy requirement for desorption as a function of the amount of steam added is shown in Fig. 9. The absolute amount of energy required is not reduced by introducing the steam purge. The latent heat for evaporation of water raises the energy requirement significantly. Therefore, it is important to reduce the ratio H$_2$O:CO$_2$ as defined in Eq. (8) and shown on the inside of the x-axis in Fig. 9. The ratio can be lowered by adding less water or by increasing the working capacity of CO$_2$ with the same amount of water. However, the working capacity for CO$_2$ can only be increased by increasing the temperature or reducing the pressure. Practically, the temperature cannot be increased because of stability issues (Yu et al., 2017). Moreover, reducing the pressure would also lower the relative humidity and thereby the adsorption of water. As discussed above this should improve the effectiveness of the purge. Reducing the amount of steam added reduces the CO$_2$ working capacity as displayed in Fig. 8. Hence, reducing the amount of steam at the current pressure is not an option. Therefore, the amount of water should be minimized while the CO$_2$ working capacity is maximized. This effect is clearly seen in Fig. 9 as the 0.10 kg kg$^{-1}$ case of the 116 °C experiments has the lowest energy requirement for the highest temperature. Adding more water will not increase CO$_2$ working capacity and hence is a waste of energy. On the other hand, for the 91 °C case increasing the water amount above 0.13 kg kg$^{-1}$ might increase the CO$_2$ working capacity even more and thereby reduce energy requirement.

Comparing PTSA and steam purge, it should be noted that although the total energy requirement is not reduced the temperature level of the heat requirement can be reduced. Since, the total pressure of the system is reduced the latent heat of water can be supplied by low temperature heat. The boiling point of water at 300 and 500 mbar is 69 and 81 °C respectively, which is significant.

![Fig. 8. Effect of the amount of steam purge added (kg$_{steam}$/kg$_{sorbent}$) at an injection rate of 1 kg$_{steam}$/h on the desorption rate and working capacity. Adsorption at 5000 ppm, 20 °C and 0%RH.](image-url)
lower than the reactor temperature. Thereby, a reduction of energy requirement at a higher temperature level can be achieved. This opens extra opportunities for heat integration and thereby options for energy savings on process level. Moreover, by using the steam purge the working capacity is increased which means that less sorbent is required to capture the same amount of CO₂. This results in smaller adsorption equipment and thereby possibly a reduction in associated capex costs. The reduction depends on the balance between the capex cost of the steam generator and for the combined sorbent and reactor cost.

### 3.3.2. Injection rate

The effect of the injection rate of steam on the working capacity is shown in Fig. 10. It can be seen that the injection rate does not have an effect on the final loading. Only the 0.07 kg kg⁻¹ at 2.0 kg h⁻¹ injection has a slight increase in working capacity. A clear effect of the residence time of the water in the evaporation system can be seen by the ‘breakthrough’ of the steam purge.

The difference in breakthrough between 2.0 and 1.0 kg h⁻¹ and 1.0 and 0.5 kg h⁻¹ is approximately 100 and 200 s respectively. Because the working capacity of CO₂ is not affected by the injection rate the energy requirement for desorption will not change with the injection rate. It can be concluded that injection rate is mainly influencing the time needed for desorption. Thereby, a higher injection rate increases equipment productivity.

### 3.4. Steam purge with humid adsorption

In the previous section it was concluded that the ratio of water and CO₂ should be reduced to have a reduction in energy requirement when applying a steam purge. Moreover, in Section 3.3.1 it was shown that the steam injected partly adsorbs on the sorbent. However, since water will co-adsorb from air during air capture of CO₂ it is expected that less steam will adsorb. This might effectively reduce the amount of steam needed to increase the working capacity of CO₂. In Fig. 11A the effect of the amount of steam purged is shown for an adsorption feed gas with 66%RH. In Fig. 11B the corresponding water loading is shown. Looking at the figures it can be seen that indeed the adsorption of the steam

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**Fig. 9.** Energy requirement for desorption as a function of the amount of steam purge added (in kgsteam/kgsorbent) injected. The CO₂ working capacity at 900 s in Fig. 8 is used. The ratio H₂O:CO₂ [mol mol⁻¹] – see Eq. (8) – is shown inside of the x-axis. Other includes sensible heat of CO₂ and H₂O and the compression energy. Error bars show propagated error.

**Fig. 10.** The effect of the injection rate of steam (kgsteam/h) on the working capacity for two injection amounts (in kgsteam/kgsorbent). Adsorption at 5000 ppm, 20 °C and 0%RH. Desorption at 500 mbar and Tavg = 116 °C.

**Fig. 11.** Effect of the amount of steam purge added (in kgsteam/kgsorbent) at an injection rate of 1.0 (kgsteam/h), Tavg = 116 °C and 500 mbar on the desorption rate and working capacity. Adsorption at 5000 ppm, 20 °C and 66%RH.
purged is reduced, as now both the 0.02 and 0.03 kg kg\(^{-1}\) experiments have an positive effect on the working capacity. In contrast to the results with 0%RH adsorption feed gas shown in Fig. 8, where a positive effect was only seen from feeding 0.05 kg kg\(^{-1}\) of steam or more. However, the increase of working capacity by adding 0.03 kg kg\(^{-1}\) is only limited to 0.1 mol kg\(^{-1}\) and might not justify the cost involved in installing extra equipment.

The lines in Fig. 11B imply that the steam injected is adsorbed first and then desorbed again (when the injection is stopped). This would imply an extra energy penalty for the desorption of water. However, in our opinion this is unlikely to happen. At the 116 °C and 500 mbar the maximum relative humidity is 29% corresponding to a loading of 2.6 mol kg\(^{-1}\) according to literature (Veneman et al., 2015). Therefore, it is far-fetched that a loading of 7 mol kg\(^{-1}\) is actually reached despite local variations in pressure and temperature. The equilibrium capacities for water exceeding the 2.6 mol kg\(^{-1}\) as displayed in Fig. 11B should most likely be attributed to inaccuracies involved in determining the water mass balance.

The effect of the steam purge on the energy requirement is shown in Fig. 12. Adding a steam purge does increase the working capacity of CO\(_2\), but the total energy requirement is not reduced. The counteracting effects of energy required for desorption of co-adsorbed water and the increase in the working capacity for CO\(_2\) is already discussed in Section 3.2. Comparing the effect of steam purge for dry and humid adsorption it can be seen that the effect on the working capacity in case of humid adsorption is reduced. As an example, for the 0.1 kg kg\(^{-1}\) experiment at 900 s the increase in working capacity by the addition of steam is reduced from 0.75 to 0.45 mol kg\(^{-1}\) when comparing for the dry and humid adsorption experiments. The effect of the steam purge is reduced and as a consequence a reduction of energy requirement is not achieved.

In Fig. 13 the working capacity of CO\(_2\) as a function of the steam purge added is shown for adsorption using 400 ppm of CO\(_2\). As shown the desorption capacities of CO\(_2\) are more or less equal to the capacities for the 5000 ppm experiments. This means the working capacity for CO\(_2\) is significantly reduced as the adsorption loading is much lower for the 400 ppm experiments compared to the 5000 ppm experiments. Similar to the 5000 ppm an effect of the steam purge is seen from 0.03 kg kg\(^{-1}\) of steam purge added. Looking at the energy requirement for desorption in Fig. 14 it is seen that the energy requirement is higher for the 400 ppm adsorption because of the reduced working capacity. Again, the application of the steam purge does not reduce the total energy requirement. However, as discussed in Section 3.3.1 the temperature level of the heat required is reduced and equipment productivity increased because of the increase in CO\(_2\) working capacity.

3.5. Multi cycle experiment

All experiments up to this point have been performed using a clean sorbent, where all previously adsorbed CO\(_2\) and H\(_2\)O is removed by a deep regeneration step at the end of the previous experiment using a hot nitrogen purge. Of course, in an envisaged industrial process the regeneration step should be removed because it is cost and equipment inefficient. Therefore, experi-
ments have been performed without this deep regeneration step. After the first desorption step, a new adsorption is directly started using the same conditions. In Fig. 15 it is shown that the CO₂ working capacity is reaching a constant value. Also all the measured desorption CO₂ working capacities are equal. This confirms that the working capacity found for the first cycle is relevant for the following cycles. Due to a lower measurement accuracy, the working capacities of H₂O show more variation. However, after the first cycle the adsorption working capacities of H₂O show constant values. Therefore, these adsorption capacities are used in the energy evaluation below. Note that the desorption working capacity of H₂O for the steam purge experiment is higher because of the steam injected.

In Fig. 16 the energy requirement for desorption is shown using the average final working capacities from Fig. 15. Once again, it can be concluded that adding a steam purge does not reduce the energy requirement. Moreover, by comparing the 500 mbar experiment shown here and shown in Fig. 7 it can be seen that the energy requirement is larger when using the final working capacity instead of the average value. This is a result of the increased ratio of H₂O to CO₂. When obtaining high H₂O to CO₂ ratios in the product gas, a water condensation step prior to recompression of the gas should be considered when upscaling the process.

4. Conclusion

High purity CO₂ can be produced from air using solid amine sorbent. The high purity CO₂ can be produced by applying either a pressure temperature swing or by purging steam. In case of a pressure temperature swing operation a temperature above 100 °C and a pressure below 200 mbar should be reached in order to maximize CO₂ working capacity and reduce the energy requirement for desorption. Co-adsorbed water will increase the CO₂ working capacity and, counter intuitive, reduce the energy requirement for desorption.

Application of a steam purge during desorption will increase the sorbent CO₂ working capacity. However, the energy requirement for desorption per unit of CO₂ remains approximately constant (or increases) due to latent heat for water evaporation. On the other hand, the sorbent mass required to capture a kilogram of CO₂ reduces. This implies a reduction in equipment size and consequently in capex costs.

The global minimum of the energy requirement should be found by an optimization of the complete system including the adsorption and desorption conditions, cycle times and equipment sizes.

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