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Adsorption of CO₂ and H₂O on supported amine sorbents

Rens Veneman^{a*}, Wenyng Zhao^b, Zhenshan Li^b, Ningsheng Cai^b, Derk W.F. Brilman^a

a. Sustainable Process Technology Group, Green Energy Initiative, Faculty of Science and Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

b. Key Lab for Thermal Science and Power Engineering of MOE, Department of Thermal Engineering, Tsinghua University, Beijing 100084, Peoples Republic of China

Abstract

In this work we have evaluated the H₂O and CO₂ adsorption characteristics of Lewatit VP OC 1065 in view of the potential application of solid sorbents in post combustion CO₂ capture. Here we present single component adsorption isotherms for H₂O and CO₂ as well as co-adsorption experiments. It was concluded that the sorbent material shows a high affinity in the adsorption of H₂O. The adsorption of CO₂ alone does not prevent the co-adsorption of large quantities of water and additional measures are necessary to prevent this from negatively affecting the energy demand of the process.

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1. Introduction

Application of carbon capture and storage (CCS) at fossil fuel burning plants is, among other alternatives, a technically feasible method to significantly reduce the global anthropogenic emission of CO₂. However, using the current state-of-art technology, this would result in an increase in the cost of electricity (COE) by 40% mainly due to high cost of carbon capture [1]. This increase in COE is a major hurdle in deployment and the development of a more cost effective capture technology is a main objective in CO₂ capture research. The conventional capture

*Corresponding author. Tel.: +31 53 489 4418, Fax.: +31 53 489 4718
E-mail address: R.Veneman@utwente.nl

process utilizes a mixture of amine molecules, typically MEA, and water to selectively absorb CO₂ from flue gases. Already at low temperatures, CO₂ dissolves in this absorption liquid (or solvent). By contacting the CO₂ containing gas with this solvent in an absorber column, the absorption liquid ‘captures’ the CO₂. Subsequently, the liquid with the dissolved CO₂ is transported to a second column, the desorber. Here, the liquid is heated, which causes the solvent to release the CO₂ again. This supplies a stream of pure CO₂, which is compressed and stored, while the regenerated solvent is pumped back to the absorber column to capture more CO₂.

The main cost driver of the process is the high energy demand, mainly associated with heating the aqueous amine solution from the absorption temperature to the desorption temperature. Applying supported amine sorbents may offer a low-cost capture technology. The operational costs associated with the thermal energy input of the amine scrubbing process make up around 44% of the total CO₂ capture costs. A large part of this energy requirement is associated with heating of the aqueous amine solution from the absorption temperature to the desorption temperature and with the evaporation of solvent in the desorber column. Replacing H₂O as solvent by a solid support greatly reduces the energy required for CO₂ capture as; (1) the evaporation of water is inhibited and (2) the energy required for heating the sorbent up to the desorption temperature is much lower due to the lower heat capacity of solid supports compared to water.

Supported amine sorbents (SAS) consist of a high internal surface-area support (e.g. silica’s, polymers, zeolites) with amine functional groups immobilized on or grafted to its surface [2]. The key strengths of this type of sorbents material include high CO₂ capacities [3], fast CO₂ uptake rates, a low heat of adsorption and relatively mild regeneration conditions compared to other chemical sorbents [3, 4].

Supported amine sorbents are tolerant towards the presence of water in the CO₂ containing gas i.e. the CO₂ capacity does not degrade in presence of H₂O. In many cases H₂O was even found to promote the CO₂ capacity [2, 5-8]. This is an important strength of these type of sorbents since flue gas contains as much, if not more H₂O, than CO₂. Still, these sorbent materials also capture significant amounts of H₂O under conditions relevant for post-combustion CO₂ capture. Franchi et al. [6] reported an adsorption capacities for DEA on pore expanded MCM-41 of 5.37 mol/kg at 28% RH, and Xu et al. [9] measured the adsorption capacity for PEI on MCM-41 to be 2.45 mol/kg and 3.01 mol/kg at 26% relative humidity (RH) and at 31% RH respectively. The sorption capacities reported for H₂O in these studies surpass the capacities measured for CO₂. Also other materials considered for applications in post-combustion capture as a sorbent or support material (13X, silica supported amines, carbons, etc..) are all known to capture large quantities of H₂O under flue gas conditions [10].

In terms of sorbent stability, the process may benefit from the co-adsorption of some of the water present in flue gas. The presence of water during sorbent regeneration suppresses the undesired formation of urea [5, 11-14]. Drage et al. [13] observed CO₂ induced deactivation of a PEI impregnated silica supported amine sorbents at temperatures above 135°C. The loss of adsorption capacity was attributed to the bonding of CO₂ into the PEI polymer through the formation of a urea type linkage. Sayari et al. [5] reported that water vapour greatly improved the stability of this type of sorbent material. It was observed that the formation of urea could be completely be reversed by adding steam via hydrolysis of such groups. Even at a relative humidity as low as 0.4% urea formation was strongly inhibited. Desorption was performed here using a N₂ as a sweep gas. Therefore, higher partial pressures of water might be needed to prevent urea formation in case the sorbent material was to be regenerated in an atmosphere containing higher concentrations of CO₂.

Although the adsorption of small quantities of water might prevent CO₂-induced sorbent deactivation, the adsorption of large quantities of water could severely affect the energy demand of the process. In the desorber column temperatures are high and H₂O partial pressure are envisioned to be low [3]. Hence a large part of the co-adsorbed water will be released again in the desorber column. In addition to the heat required to desorb the captured CO₂, also energy is required to release the co-adsorbed water, resulting in an increase in the parasitic heat demand for capture. The role of water in this process is complex, as the H₂O present in flue gas (1) interferes with the CO₂ adsorption mechanism [6, 9] and affects (2) the sorbent stability [5, 11-14] as well as (3) the process energy demand. However, the number of studies on the H₂O adsorption by supported amine sorbents is limited. Moreover, there is not yet a clear strategy on how to deal with the co-adsorption of water on a process scale. The aim is to identify the most convenient way to deal with water in this adsorption based capture process. In this work we set the arbitrary goal of capturing no more than 0.25 moles of H₂O per mole of CO₂ captured. This would increase the energy demand of the process with no more than 0.25 GJ/t of CO₂ captured which we deem acceptable (assuming the heat of adsorption of water on the sorbent is equal to the heat of condensation).

2. Experimental

2.1 Material

The sorbent material used in this study is Lewatit® VP OC 1065 (Lanxess). It is a polystyrene based ion exchange resin (IER) containing primary benzyl amine units [15]. The resins are spherical shaped beads with a diameter between 0.47 and 0.57 mm. The materials' pore volume, pore surface area and average pore size are 27 cm³/g, 50 m²/g and 25 nm respectively.

2.2 CO₂ and H₂O capacity measurements

The experimental work focusses on measuring adsorption capacities for CO₂ and H₂O at temperatures and partial pressure relevant for post combustion CO₂ capture.

A NETSZCH STA 449 F1 Jupiter thermal gravimetric analyzer (TGA) was used to assess the CO₂ adsorption capacity of the sorbent material. In a typical adsorption experiment around 15 mg of sorbent was placed inside the TGA furnace. The sample was heated up to 80⁰C in N₂ to desorb any pre-adsorbed CO₂ and moisture. The temperature was kept constant until the sample mass stabilized. Then, the sample was cooled down to the desired adsorption temperature after which CO₂ was fed to the TGA furnace. The uptake of CO₂ by the sorbent sample results in an increase in the sample mass. The sorbent CO₂ uptake, in mole.kg⁻¹ sorbent, was calculated from the weight change of the sample during adsorption. Typically, after 4 hours of adsorption time the change in the sample mass was minimal (<0.01 mol/kg/hr) and the measurement was stopped. The adsorption experiments were performed at different temperatures and CO₂ partial pressures to obtain the data required to construct an adsorption isotherm. Desired gas compositions were obtained by mixing high purity (grade 5.0) N₂ and high purity (grade 5.0) CO₂. The specific configuration of the TGA equipment limited the CO₂ concentration to a maximum of 80vol% of CO₂ at 1 atm.

The H₂O adsorption capacity of the sorbent material was measured in a custom built packed bed reactor equipped with a humidifier column, two humidity meters and an infrared CO₂ gas analyzers. The humidity meters (Hygrosens FF-20MA-INT-TE0) continuously measured the temperature and relative humidity of the gas entering and leaving the reactor (detection range: T=-30..70C, RH=0..100%). The CO₂ analyzer (SIDOR, SICK MAIHAK) was used to monitor the CO₂ concentration in the outlet gas of the packed bed column (detection range: 0..15vol%). Two JULABO F32 water baths were used to control the temperature of the adsorber and the temperature of the H₂O saturation columns. The CO₂ and H₂O concentrations in the column inlet gas were controlled by mixing a flow of high purity (grade 5.0) N₂ and a high purity (grade 5.0) CO₂ flow with a third pre-saturated flow of N₂. The flow rates were controlled using three BROOKS mass flow controllers. After mixing of the three gas flows the humidity of the gas was measured. All of the gas lines were heated to temperatures just above the dew point of the gas mixture to prevent condensation of H₂O in the gas lines.

In a typical H₂O adsorption experiment around 10 gr of dried sorbent material was loaded into the column. After closing the reactor, the reactor was heated up to 80⁰C while flushing the column with N₂ (500 ml/min) to desorb any remaining CO₂ and H₂O. The reactor was subsequently cooled and when the desired adsorption temperature was reached, the N₂ flush was stopped and the H₂O containing gas (500-1000 ml/min) was fed to the column. The experiment was stopped when the inlet partial pressure of H₂O was equal to the outlet partial pressure of H₂O within the error margin of the humidity meters. CO₂/H₂O co-adsorption experiments were performed in a similar manner.

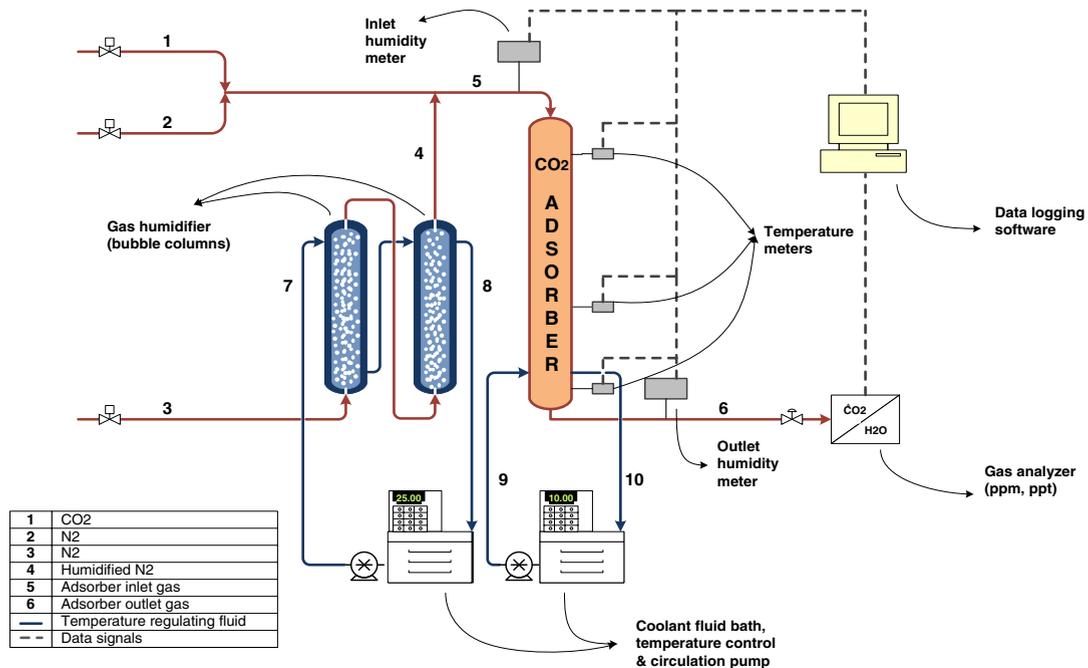


Figure 1: Fixed bed setup schematic

3. Results

The experimental results obtained from the TGA apparatus provided CO₂ adsorption capacities at different adsorption temperatures and CO₂ partial pressures. Figure 2 shows the measured adsorption isotherms at 303.15, 313.15, 343.15, 353.15 and 373.15 for CO₂ on Lewatit VP OC 1065.

The CO₂ highest capacity observed in the measurements performed was 2.95 mol/kg resin measured at 306K in 70 vol% of CO₂. Alesi et al. reported that the maximum theoretical amine loading is expected to be in the order of 6.7 mol N/kg resin [15] for this type of IER. A CO₂ loading of 2.95 mol/kg then corresponds to a amine efficiency of 0.44 mol CO₂ per mol N₂, which is typical for these kind of sorbent materials.

One of the most important parameters in this capture process is the sorbent's cyclic operating capacity. This parameter will for a large part determine the heat demand of the process. Especially the partial pressure of CO₂ and the temperature during sorbent regeneration have a large impact on this cyclic adsorption capacity. Since we are aiming here to produce a high purity CO₂ product gas, the sorbent will be regenerated in an atmosphere with a high CO₂ content. This regeneration method has our preference over alternative regeneration methods like vacuum swing adsorption or steam regeneration [3]. Under the adsorption conditions relevant for post-combustion CO₂ capture and sorbent regeneration at 140°C at a CO₂ partial pressure of 80 kPa, the sorbent material can cyclically capture 1.8 mol/kg.

Based on the experimental data, the isosteric heat of adsorption was calculated using the Clausius–Clapeyron equation. The adsorption heat of 87 kJ/mol lies in the range typical for CO₂ adsorption by amine molecules [8, 17].

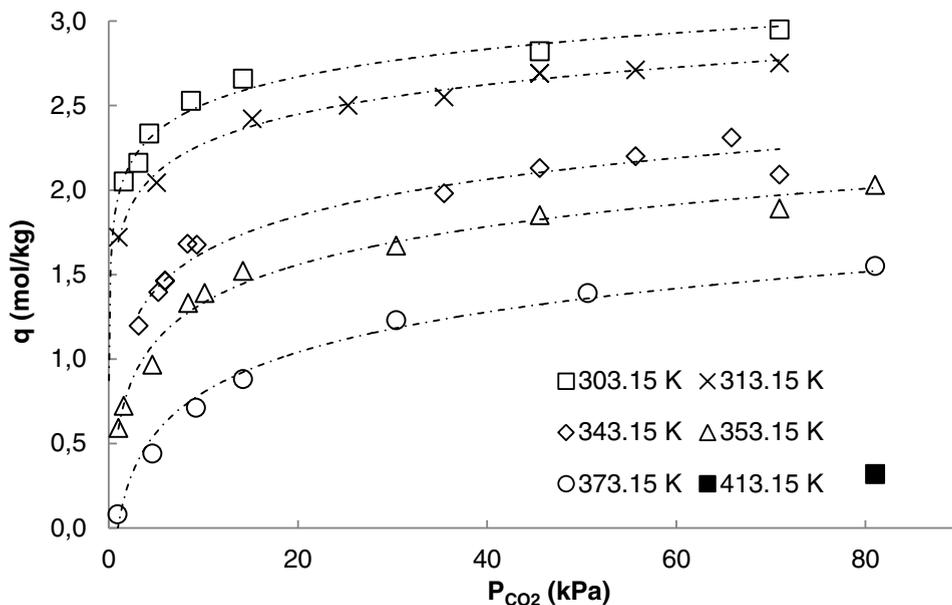


Figure 2: CO₂ adsorption isotherms for Lewatit VP OC 1065 at 30°C, 40°C, 80°C, 100°C and the measured capacity of the sorbent at 140°C and a CO₂ partial pressure of 80 kPa.

Figure 3 shows the measured H₂O adsorption capacities at different relative humidities. As a reference, the adsorption capacities of DEA on pore expanded MCM-41 (5.37 mol/kg at 28%RH, [6]) and PEI on MCM-41 (2.45 mol/kg and 3.01 mol/kg at 26%RH and 31%RH respectively, [7]) were plotted in the same graph as well as the H₂O sorption capacity of Zeolite 13X and SiO₂ gel. The highest observed H₂O sorption capacity for Lewatit VP OC 1065 was 12,5 mol/kg at a relative humidity of 95%. At these high levels of saturation, water condenses inside the pores of the sorbent material and this high H₂O loading approaches the H₂O capacity for a completely filled pore space of 14.4 mol/kg respectively. Based on the experimental data, the isosteric heat of adsorption was calculated using the Clausius–Clapeyron equation. The adsorption heat of 43 kJ/mol is close the condensation heat of water which suggest that indeed condensation/pore filling occurs at higher relative humidities.

Analysis of the pore volume distribution showed that the sorbents' micropore volume was minimal (0.003272 cm³/g) and more than 95% of the pore volume is attributed to pores larger than 10 nm. Hence, pore filling will most likely not be the main mechanism for H₂O uptake in the humidity range from 10%RH to 60%RH. Moreover, polymeric resins with a poly (styrene-divinylbenzene) matrix were found to have a very limited H₂O capacity (<1 mol/kg) at relative humidities lower than 60%RH [18, 19] due to the hydrophobic nature of the material. The relatively high H₂O capacities (5.8 mol/kg at 60%RH) observed for Lewatit VP OC 1065 might therefore be attributed to the presence of amine molecules on the pore surface increasing the affinity towards the adsorption of water. Figure 3 also shows the H₂O adsorption capacity for other sorbent materials studied for their application in post combustion CO₂ capture. The adsorption capacities of DEA on pore expanded MCM-41 (5.37 mol/kg at 28%RH, [6]) and PEI on MCM-41 (2.63 mol/kg and 3.24 mol/kg at 26%RH and 31%RH respectively, [7]) are in the same order as the capacities measured for the IER and also both well above the targeted working capacity even at relatively low saturation levels of around 30%RH. The adsorption capacities observed for Zeolite 13X under the same conditions are even higher than that of Lewatit VP OC 1065 and the MCM-41 based supported amine sorbents shown in the graph. Especially at relative humidities below 60%RH, Zeolite 13X shows much higher adsorption capacities for water than the sorbent studied here. This is most probably attributed to the smaller pore sizes of 13X, compared to the sorbent studied here, in which pore filling occurs at lower relative humidities. It is also important to mention here that the H₂O capacity of the sorbent material is only a function of the relative humidity. Hence all data presented in Figure 4 fall onto one curve that is the curve presented in Figure 3 for Lewatit VP OC 1065.

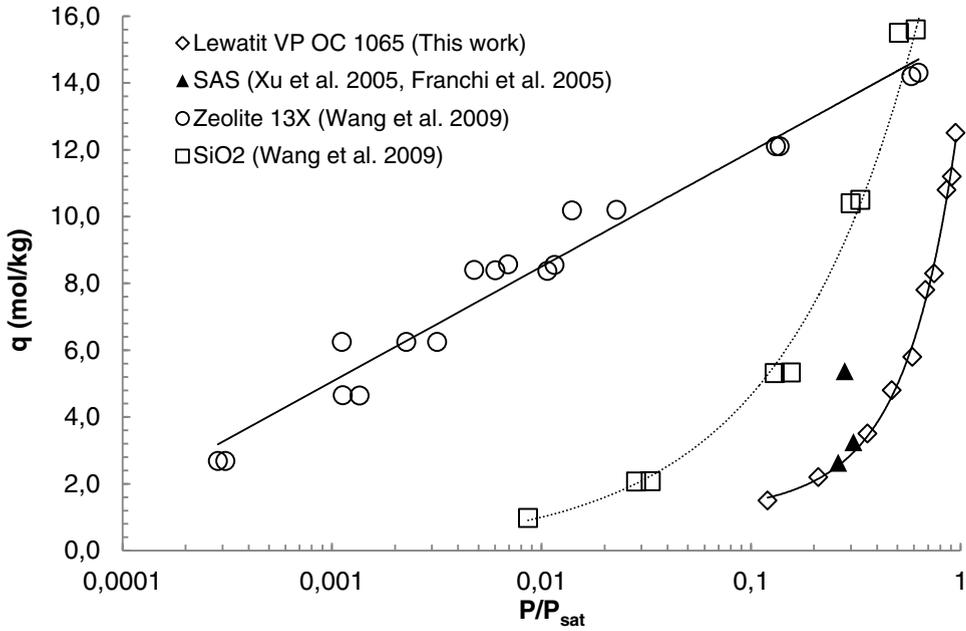


Figure 3: H₂O capacity as a function of the relative humidity for Zeolite 13X, silica gel, Lewatit VP OC 1065 and sorbents prepared by Franchi et al. [6] and Xu et al. [7]. The data shown for Lewatit was measured at temperatures between 20 and 80°C

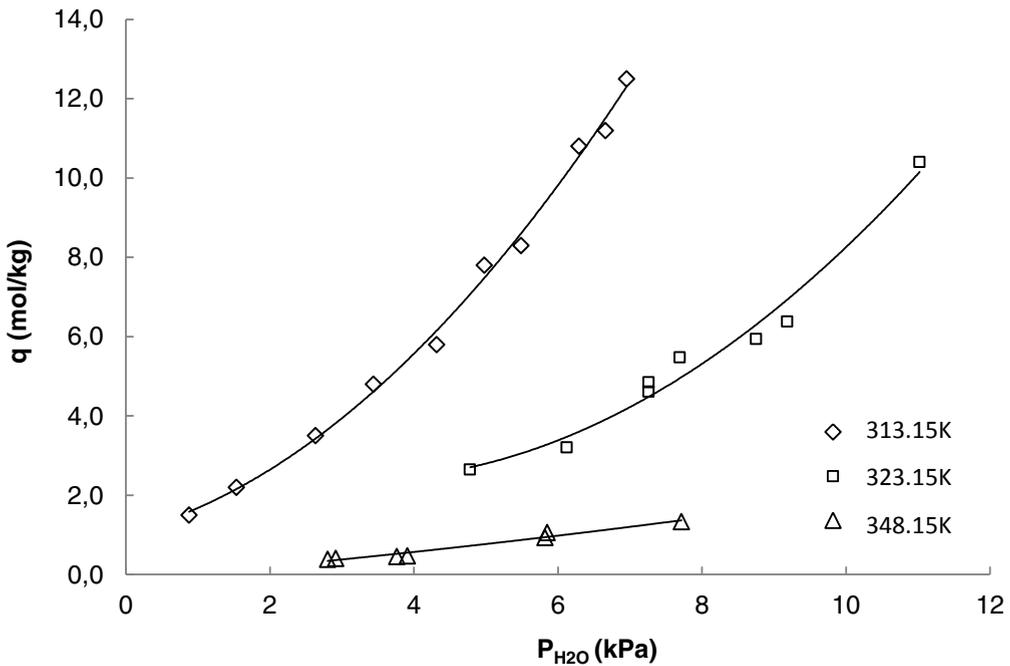


Figure 4: H₂O adsorption isotherms for Lewatit VP OC 1065 at 40°C, 50°C and 75°C.

The dewpoint of flue gas is around 47°C before entering the adsorber column which corresponds to a saturation level of 67% RH at the gas inlet temperature. Under these conditions this sorbent material is capable of adsorbing around 8 mol H₂O/kg. These high saturation capacities lead to the following important conclusion regarding the co-adsorption of water in the sorbent based process: The adsorption of H₂O in the adsorber column of the post combustion capture process is not limited by the equilibrium capacity of the sorbent material under adsorption conditions. Instead, the H₂O working capacity is supply limited, i.e. the sorbent will adsorb practically all H₂O entering the column given there is enough contact time. This is not only true for this particular sorbent. Any sorbent with a H₂O capacity higher than its CO₂ capacity will adsorb practically all water entering the adsorber. This includes also Zeolite 13X. Even if the adsorption temperature is increased to, say, 100°C in order to lower the relative humidity in the column, the H₂O equilibrium capacity will still be around 1.5 mol/kg which is far above the targeted capacity and will hence not lead to a lower (parasitic) H₂O working capacity. Moreover, a higher adsorption temperature will lower the CO₂ working capacity.

The development of a sorbent that does not bind water would solve the issue entirely. It needs to be stressed however that this sorbent should have a saturation capacity not higher than 0.5 mol/kg at relative humidities around 70-90% RH. In case the saturation capacity is higher than 0.5 mol/kg, the H₂O co-adsorption will still be limited by the inlet molar flow of H₂O and the resulting H₂O working capacity of this 'hydrophobic' sorbent will then be effectively the same as for Lewatit VP OC 1065 or Zeolite 13X.

One way to prevent the co-adsorption of large quantities of water is by lowering the relative humidity of the incoming flue gas. Lowering the dewpoint of the flue gas to 15°C would lower the amount of water adsorbed to ~0.25 mol/mol CO₂ adsorbed. This requires 0.2 GJ of cooling duty per tonne of CO₂ captured in addition to the 0.25 GJ/t of heat required to desorb the co-adsorbed water.

It is clear that CO₂ and H₂O do not bind to the sorbent in the same way, considering the large difference in heat of adsorption and capacity. Still, the presence of H₂O could influence the sorption of CO₂ through for example physical interaction between CO₂ and H₂O or shielding of amine active sites by H₂O. Figure 5 shows the CO₂ adsorption capacities for Lewatit VP OC 1065 under dry and humid conditions. The presence of water does not seem to have a detrimental effect on the CO₂ capacity; the CO₂ capacities are even little higher in the measurements with water present. This is phenomenon has been noticed before for supported amine sorbents [6, 20-22] and is usually attributed to the interference of H₂O in the adsorption mechanism. Water can act as a free-base, resulting in the formation of bicarbonate in presents of water vapor whereas carbamate is formed when water is not present. This changes the reaction stoichiometry; in the presence of water one amine group could theoretically react with one CO₂ molecule whereas two amine molecules are required to bind one molecule of CO₂ under dry conditions. Alesi et al. also observed the formation of carbamate on Lewatit VP OC 1065 [15]. In these co-adsorption experiments, the water capacity was not significantly affect by the presence of CO₂.

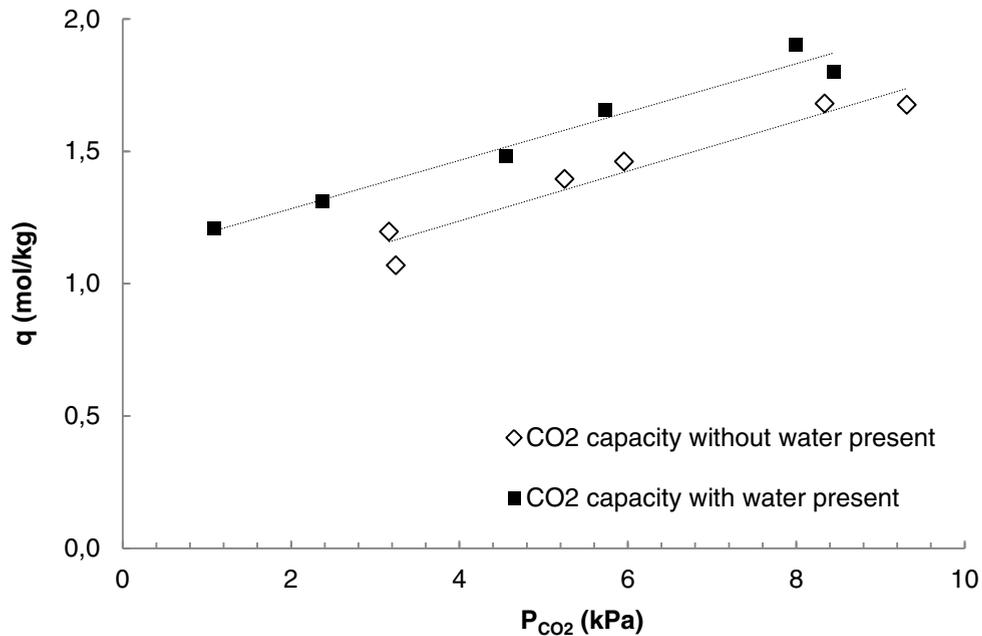


Figure 5: CO₂ capacities for Lewatit VP OC 1065 measured in the fixed bed at different CO₂ partial pressures and at 70°C in presence of water (6 kPa) and under dry conditions.

4. Conclusion

In this work we have evaluated the H₂O and CO₂ adsorption characteristics of Lewatit VP OC 1065 in view of the potential application of solid sorbents in post combustion CO₂ capture. Based on the experimental results presented here we conclude that:

- Lewatit VP OC 1065 can adsorb much more (4-5 times) H₂O than CO₂ under adsorption conditions relevant for post-combustion CO₂ capture.
- The equilibrium water capacity seems to be only a function of the relative humidity in the gas phase; all data point measured here fall onto one curve when the capacity is plotted against the relative humidity in the gas phase.
- The presence of water in the gas phase does not seem to negatively impact the CO₂ adsorption capacity.
- Due to high equilibrium capacities, the adsorption of H₂O in the adsorber column of the post combustion capture process is not limited by the equilibrium capacity of the sorbent material under adsorption conditions. Instead, the H₂O working capacity is supply limited, i.e. the sorbent will adsorb practically all H₂O entering the column given there is enough contact time.
- One way to prevent the co-adsorption of large quantities of water is by lowering the relative humidity of the incoming flue gas. Lowering the dewpoint of the flue gas to 15°C would lower the amount of water adsorbed to approximately 0.25 mol/mol CO₂ adsorbed. This requires 0.2 GJ of cooling duty per tonne of CO₂ captured in addition to the 0.25 GJ/t of heat required to desorb the co-adsorbed water.

Acknowledgement

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