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Evaluation of Postcombustion CO2 Capture by a Solid Sorbent with Process Modeling Using Experimental CO2 and H2O Adsorption Characteristics

Jan Wilco Dijkstra,[*,†][ORCID] Stéphane Walspurger,[†] Gerard D. Elzinga,[†] Johannis A.Z. Pieterse,[†] Jurriaan Boon,[†] and Wim G. Haije[‡]

[†]ECN, Energy research Centre of The Netherlands, P.O. Box 1, 1755 ZG, Petten, The Netherlands

[‡]Process and Energy laboratory, Technical University of Delft, Leeghwaterstraat 39, 2628 CA Delft, The Netherlands

ABSTRACT: A combined experimental and modeling study was performed to evaluate the relation between sorbent characteristics and process performance for solid sorption postcombustion CO_2 capture. A pulverized coal (PC) and a natural gas combined cycle (NGCC) power plant were considered, addressing CO_2 and H_2O sorption. The measured isotherms for PEI/silica sorbent were implemented in an equilibrium-based flow sheeting model. The PC regeneration heat demand is 3.9 GJ/ton CO_2 captured. This is lower than that of the NGCC and, though a direct comparison is not valid, similar to a literature MEA case. Solid sorption systems hold the promise to be energetically superior to MEA: a 2-fold increase in CO_2 adsorption capacity (to 4.4 mmol/g) yields a regeneration heat demand of 3.3 GJ/ton, even when accompanied by a similar increase in H_2O adsorption capacity.
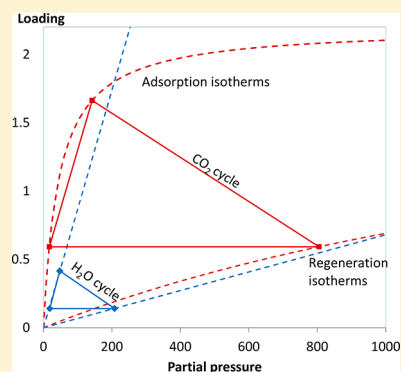
1. INTRODUCTION

CO_2 capture at large point sources such as coal or gas fired power plants using postcombustion technology offers, compared to oxy-combustion and precombustion technology, the advantage of low impact on the primary process and an option for retrofit on existing facilities. Besides issues related to the large volumetric flow rates to be treated, the energy requirement for regeneration of the solvent enabling >90% recovery of sufficiently pure CO_2 (>95%) is high, in the range of 3.2 to 4.2 GJ/tCO_2 for most of the aqueous alkanolamines-based technologies.[1] Corresponding efficiency loss results in a significant increase of the cost of electricity and calls for more efficient and less energy-intensive novel capture technologies. In addition, when using amine-based capture systems, the amine and its degradation products could be emitted into the air. This necessitates a substantial makeup stream and has negative environmental impacts.[2] A technology that uses a solid phase sorbent with low vapor pressure and high stability could facilitate the technology introduction at large scale by decreasing environmental concerns.

In this framework, adsorption processes based on the use of solid sorbents for selective removal of CO_2 have been the focus of intensive R&D efforts for the past decade. In particular, a NETL study pointed at a reduction of regeneration energy by up to 50% requirement when solid material with sufficiently high CO_2 capacity is used in an appropriately designed reactor system.[3] Veneman et al. estimated that solid sorbent systems using a sorbent with a CO_2 working capacity of at least 2 mmol/g would allow 30−40% reduction in energy requirement compared to a MEA scrubbing system. This indeed results from the lower sensible heat required to heat up a circulating solid mass, compared to the sensible heat required for raising the aqueous amine solvent temperature.[4]

The capture process considered here makes use of a porous solid sorbent able to capture CO_2 from power plant flue gases and release the CO_2 when exposed to elevated temperatures, that is, temperature swing adsorption (TSA). A wide range of research is currently conducted on improving sorbents as well as on process development. The direct relation between both is seldom considered; nevertheless the two are largely connected. Furthermore, in literature, the role of water during adsorption is largely neglected, especially in process design. For this paper, a method has been developed which allows for easy evaluation of relationships between sorbent properties, optimal process conditions, and process performance in capturing CO_2 with solid sorbents, while accounting for the role of water sorption. It considers capture in both natural gas and pulverized coal (PC) fired power plants and gives insight into the optimal process conditions and required heat for regeneration in relation to the sorbent properties.

As a reference case, amine (MEA) scrubbing is used. It must be noted that a comparison with amine scrubbing is not a fair comparison for two reasons. First, the development status of amine scrubbing is much higher than solid sorption, making the uncertainties in process performance much lower. Next, for

amine scrubbing, the level detail is much larger and more phenomena can be accounted for, making that the results of MEA are more accurate. Nevertheless, a comparison can be considered valuable in terms of quantifying the potential of immobilized amines and identifying the relative advantages and disadvantages of each technology.

The solid sorbent capture process can make use of various types of adsorption and regeneration reactor types. Veneman et al. make use of trickle flow fluid bed absorber.[5,6] Pröll proposes a double loop multistage bed system.[7] Yang and Hoffman evaluate both a bubbling fluidized bed adsorber and a four-stage fluidized bed adsorber design, each equipped with cooling pipes inserted into the fluidized bed.[8] Krutka et al. report on a 1 MW pilot scale multistage bubbling bed adsorber with a bubbling bed regenerator.[9] Khongprom et al. proposed a circulating fluidized bed adsorber with riser as the adsorber, and a bubbling bed regenerator integrated in the downcomer.[10] Tarka et al. evaluated a fluidized bed adsorber as well as novel design consisting of multiple radial flow fixed bed reactors.[11] Kim et al. evaluate a cooled moving bed reactor.[12] Pirngruber et al. evaluate three types of reactors: fluidized bed and both adiabatic as well as isothermal fixed bed reactors.[13] While the exact type and design of the reactors is of great importance for large scale processes, when evaluating the relation between sorbent properties and capture process performance the reactor performance can be largely simplified, for example, by considering them as ideal-counter-current or cross-flow reactors, which will be the approach of this study. This allows for a better understanding of the basic characteristics of the material, without the impact of sorption kinetics and mass- and heat transfer limitations related to a specific reactor design and choices in the design of such a reactor. After obtaining these basic insights, in a next stage the reactor concept, design, and the minimization of mass- and heat transfer limitations can be considered.

A number of studies indicate that solid sorbents have the potential of using 2 to 2.5 times less energy for regeneration than aqueous phase scrubbing.[14,15] Nevertheless, it is important to consider the relation between the solid material performances and a full scale process design including evaluation of the operating conditions and performance. Next to joint work by Yang and Hoffman,[8] work by Kim et al.,[12] Pirngruber et al.,[13] and Veneman et al.[4] consider this very important aspect. Equally important, as results from recent insights show, is to take into account the contribution of steam adsorption on the regeneration heat in the cycle design.[16−18] Steam is known to have two important effects. It will increase the capacity for CO_2 uptake but it will also evaporate during regeneration of the sorbent thus increasing the heat required for regeneration. The amount being released during regeneration may be limited by the water capacity of the sorbent, but also by the water present in the flue gas. This study will take these effects into account in designing the absorption/regeneration cycle.

A number of materials have been proposed and developed for CO_2 removal from flue gas, with different affinity for CO_2. Notably activated carbons,[19,20] zeolites,[21,22] and certain types of metal organic frameworks are well-known CO_2 physisorbents with relatively low adsorption enthalpies, resulting from London dispersion forces (physisorption).[23−25] Physisorbents, however, suffer from limited capacity at low CO_2 partial pressure and limited CO_2/N_2 selectivity.[26,27] Even more important, the CO_2 capacity of physisorbents such as zeolites is strongly affected by the presence of water vapor, which tends to accumulate on the sorbent and decrease CO_2 capacity when regeneration conditions are kept mild.[28−30] Hence the use of zeolites in regenerative processes requires extra facilities for thorough dehydration of flue gases.[31,32]

This study focuses therefore on chemisorbents; supported amines, more specifically, polyethylenimine (PEI) have been selected as an example material. These supported amine materials are highly selective sorbents that chemically bind CO_2. Among supported amines, polyamines have several advantages such as low volatility, easy preparation, and general availability.[33,34] Xu et al. reported a PEI supported on ordered mesoporous silica MCM-41 with CO_2 adsorption capacity increased by up to 40% in wet flue gas compared to dry flue gas, pointing at a beneficial use of these materials in the presence of water.[35] Other authors have found similar improvements in uptake performance in the presence of moisture when PEI was supported on polymer-based supports, which has been ascribed to bicarbonate formation.[14,15,36,37] In addition, it has been demonstrated that moisture avoids the deactivation of PEI supported materials,[38] and helps to recover high purity CO_2.[39]

The mechanism of water in promoting CO_2 adsorption capacity on solid sorbents has recently been discussed by Zhao et al.[40] Although water coadsorption with CO_2 on PEI-silica had been identified in earlier studies,[35] no adsorption isotherm data were found in the literature, urging us to measure the isotherms experimentally before using these as input for the present modeling study. The study aims at identifying the role of water in relation to process conditions in a real-scale system using models and experiments, rather than studying the fundamentals of the interaction of water and CO_2 on sorbents. Therefore, an approach is chosen to measure the sorption capacities in relevant (wet) conditions for CO_2, and for water separately and assuming that these are not correlated that is, no enhancing or competitive effects. Sorption capacities can be measured by both TGA as well as breakthrough experiments. For multicomponent gas mixtures containing water, breakthrough experiments were expected to be of a more practical approach than equilibrium adsorption capacity obtained by TGA measurements. Very similar to other recent contributions,[31] adsorption data based on breakthrough capacities were considered as a practical first estimation, whereas true thermodynamic equilibrium data would be required for further detailed modeling.

This study evaluates the relation between sorbent properties, process conditions, and process performance at the industrial scale, addressing CO_2 sorption and identifying the impact of water sorption on supported PEI sorbents. The approach chosen uses experimental determination of sorbent isotherms, combined with equilibrium-based thermodynamic modeling of the absorption/regeneration cyclic process. This approach allows the acquisition of basic insight into the system for a large operating range and without the influence of mass and heat transfer limitations related to a specific reactor design. After this, it is possible to move to a next stage where the effects of sorption kinetics, mass, and heat transfer, and reactor design to minimize these effects, are considered. The present study gives a clear indication under which operating conditions these kinetic, mass, and heat transfer effects are to be determined experimentally, thereby significantly reducing the experimental effort and avoiding iterations based on early choices in reactor design and operation. This objective of this study is to therefore to identify the main contributions to the regeneration heat and to identify optimal process conditions as set by the character-

istics of the material, and also to set targets for material development.

2. METHODOLOGY

2.1. Sorbent Preparation. A commercial porous silica (Vpore, 5 mm spheres crushed and sieved to 0.245−0.425 mm, pore volume 0.90 cm^3/g, pore mean diameter 8.5 nm) and commercial polyethylenimine (PEI) with a number-average molecular mass of 600 g/mol were used for the preparation of the sorbent. The weight ratio silica/PEI was 65:35. The silica support was poured in a solution of PEI in methanol (weight ratio PEI/methanol was 1:8) and stirred for 30 min. The solvent was evaporated from the resulting slurry under reduced pressure (0.5 bar) at 65 °C as described elsewhere.[36] The actual loading of the final material assessed by weighing was found to be in the range 35 ± 2 wt %. The impregnated material was further characterized by N_2 physisorption experiments from which the remaining pore volume determined by the Gurvich method was 0.16 cm^3/g.

2.2. Sorbent Testing. The dried solid (about 5 g) was homogeneously diluted by a factor 30 with SiC (Gimex, 0.300−0.425 mm) and placed in a glass fixed bed reactor (inner diameter 14 mm, bed height 23−35 cm. SiC was used in these experiments to extract as much as possible heat from the adsorber thus obtaining a near isothermal adsorption process. In all adsorption experiments the temperature rise due to adsorption heat release was found to be limited to less than 3 °C. The low surface area SiC used in the experiment was found to have both insignificant CO_2 and H_2O uptake capacities for CO_2 and H_2O partial pressures below of 0.15 bar (<0.002 mmol/g at 60 °C). The experimental setup was equipped with a set of mass flow controllers, pressure controllers, and temperature controllers. The reactor was heated externally by a three-zone oven. Online gas detection was carried out using an infrared detector (Midac FTIR I1803). Adsorption and desorption data obtained by breakthrough experiments were used to determine both CO_2 and H_2O adsorption capacities. The sample was pretreated by heating at 135 °C under nitrogen, which was found to be a sufficiently high temperature to desorb CO_2 and water that could be present on the solid. This in fair agreement with previous work.[38] Then, the sample was cooled down to the selected adsorption temperature under nitrogen and several adsorption/desorption cycles were carried out with various N_2/CO_2/H_2O flows. The temperature was 60 °C for adsorption and 135 °C for desorption which was found to be a suitable temperature for thorough regeneration while preventing thermal degradation of the sorbent as seen in literature.[38] Methane breakthrough experiments carried out with an empty reactor, with SiC only, and with SiC and sorbent confirmed that methane was not adsorbed on the sorbent, and methane was therefore used as a tracer. In a typical breakthrough experiment 5% methane was added to the feed further consisting of nitrogen and either up to 20% of CO_2 or up to 9% of H_2O. After measuring the outlet concentration of the reactor until complete breakthrough, the capacity calculations were based on the time difference between the CO_2 or water breakthrough curves (ranging typically between 2 and 10 min for CO_2 and between 30 and 100 min for H_2O) and methane breakthrough onset (less than a minute on stream). This method allowed determination of adsorbent capacities accurately, taking gas phase accumulation terms into account by considering the inert breakthrough point.

2.3. Experimental Determination of CO_2 and Water Isotherms. CO_2 adsorption experiments were carried out at CO_2 partial pressures between 0.025 and 0.2 bar at adsorber bed temperatures of 60, 80, 90, 100, 110, and 120 °C, at ambient total pressure. Each point (partial pressures and temperature) was measured in triplicate, in order to get a more reliable breakthrough time. The breakthrough point was calculated considering the inert breakthrough point to compensate for dead volume of the bed. The steam partial pressure was maintained at 0.038 bar while N_2 and 5% CH_4 were used as inert for balancing the gas mixture. The regeneration was always carried out at 135 °C with a mixture of N_2 (98.7%) and steam (1.3%, to prevent from deactivation). The sorbent overall capacity loss during this experiment was checked by repeating standard CO_2 adsorption experiments at the start and at the end of the series using different CO_2 partial pressures and was found to be below 5% over 60 cycles.

H_2O adsorption experiments were carried out at H_2O partial pressures between 0.01 and 0.089 bar at adsorber bed temperatures of 60, 70, 80, and 90 °C. N_2 and 5% CH_4 were used as inert for balancing the gas mixture. The regeneration was always carried out at 135 °C with dry N_2 (100%). The overall CO_2 capacity loss of the sorbent during this experiment was found to be smaller than 2%.

3. SYSTEMS DESCRIPTION AND MODELING

3.1. Approach. The solid sorbent capture system is depicted in Figure 1. CO_2 is captured by a circulating solids
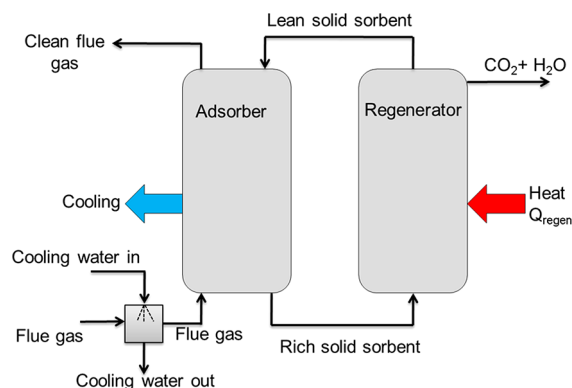

Figure 1. Schematic of solid sorbent CO_2 capture.

stream and is released by means of a temperature swing adsorption (TSA) cycle. Simulated flue gas from the PC or NGCC power plant containing mainly N_2, O_2, CO_2, and H_2O is fed into an adsorber in which the gas stream is brought into contact with the solid stream. A countercurrent reactor, for example, a multistage fluidized bed or moving bed adsorber are envisaged. Both CO_2 and water are adsorbed on the solid, yielding a clean, mostly CO_2-free gas. The adsorber needs to be cooled to prevent excessive temperature rise due to exothermic adsorption. The rich solid sorbent is transported to the regenerator for the endothermic desorption of CO_2 and water, at an elevated temperature. A cross-flow mode reactor such as a bubbling bed is foreseen. Heat is supplied to increase the temperature to regeneration conditions. The CO_2/H_2O product is exported and available for compression, drying, and subsequent underground storage.

Figure 2 gives a schematic representation of the reference MEA liquid solvent capture system. Flue gas is fed to the
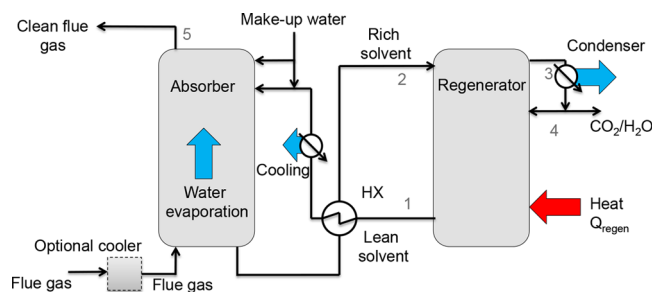
Figure 2. Schematic of reference solvent CO_2 capture.

absorber, where most of the CO_2 is absorbed leaving a clean gas. The sorption heat released increases the solvent temperature and leads to endothermic evaporation of water which allows for control of the absorber temperature. The rich solvent is heated in a lean/rich solvent heat exchanger (HX), before being fed to the regenerator. In the regenerator, the increased temperature leads to desorption of CO_2 and evaporation of water, which is partially condensed out in the condenser. A makeup water stream compensates for the water evaporation in both columns.

3.2. Solid Sorbent System Modeling. The solid sorbent system has been modeled using a gas/solid equilibrium model using experimental data. The sorbent sorption characteristics for both CO_2 and H_2O resulting from the experiments, as discussed in section 2 are implemented as isotherms in the model to determine the amount of adsorbed CO_2 and water. The CO_2 sorption isotherm is described with a Langmuir model characterized by the maximum capacity q_{max}, heat of adsorption Δh_{CO2}, and pre-exponential factor $B_{0,CO2}$ (eq 5). The water sorption isotherm is described using a linear relation with the water partial pressure, using the water adsorption coefficient K_{H2O}, and the heat of sorption Δh_{H2O} (eq 7). Both the CO_2 and water heat of sorption are used for modeling isotherms and heat effects in the Aspen Plus calculations.

The regenerator has been modeled assuming equilibrium between the gas and solid outlet streams. This is, as a first approach, in accordance with a regenerator concept consisting of a bubbling fluidized bed, using a CO_2/H_2O product recycle for fluidization. The regenerator is modeled assuming ideal cross-flow between the solid stream and the gas stream: that is, the outlet (lean) solid stream is assumed to be in CO_2 and H_2O equilibrium with the outlet gas CO_2/H_2O stream.

For the adsorber ideal counter-current flow between sorbent and gas is assumed. The rich sorbent is assumed to be in equilibrium with the feed flue gas stream, and the solid flow rate is adjusted to exactly load the sorbent to fully CO_2 saturated conditions. At the lean side of the adsorber, equilibrium between the outlet clean gas stream and the lean sorbent is assumed. The clean gas CO_2 outlet concentration and thus the relative amount of CO_2 captured is thereby directly related to the loading of the lean sorbent. The loading of the sorbent can be influenced by the regenerator temperature. For all cases, the CO_2 capture target is set at 90%. This is achieved by adjusting the regenerator temperature. Both the absorber and regenerator work at atmospheric pressure. Using an equilibrium and ideal counter-current approach is likely to give an optimistic performance result, but allows for an easy assessment of the relation between sorbent characteristics and process performance.

Since the sorbent flow rate is adjusted to match the optimal sorbent loading with respect to CO_2, water sorption results from the conditions set by CO_2 sorption. In the design procedure, the feed gas water inlet partial pressure and lean sorbent loading of H_2O are fixed by the flue gas cooler specifications and regeneration conditions required for meeting the product specifications for CO_2, respectively. For water sorption, two possible limitations can be distinguished as illustrated in Figure 3. In Figure 3a, the mass flow of water present in the gas limits the water uptake. Consequently, the lean sorbent is in equilibrium with the outlet gas flow, and the rich sorbent is not saturated with water. Alternatively, in Figure 3b, the sorbent capacity limits the water uptake. As a consequence, the sorbent is fully saturated and the gas cannot be dried to lean sorbent conditions. Through a preliminary mass balance evaluation, the model is programmed to discriminate between the two possible limitations and proceeds with the calculations accordingly.

The sorbent system model has been implemented in the flow sheeting tool Aspen Plus[41] for setting up mass and heat balances with a flexible structure. The adsorber and regenerator have been modeled using mass and enthalpy-balance envelopes, also referred to as *constructs*,[42] Figure 4. Constructs are combinations of standard unit operations models (heaters, mixers, separators, etc.) allowing modeling complex processes, with the advantage of giving a breakdown of the different contributions in energy demand. Input to the model are the flue gas specifications, CO_2 capture ratio (amount of CO_2
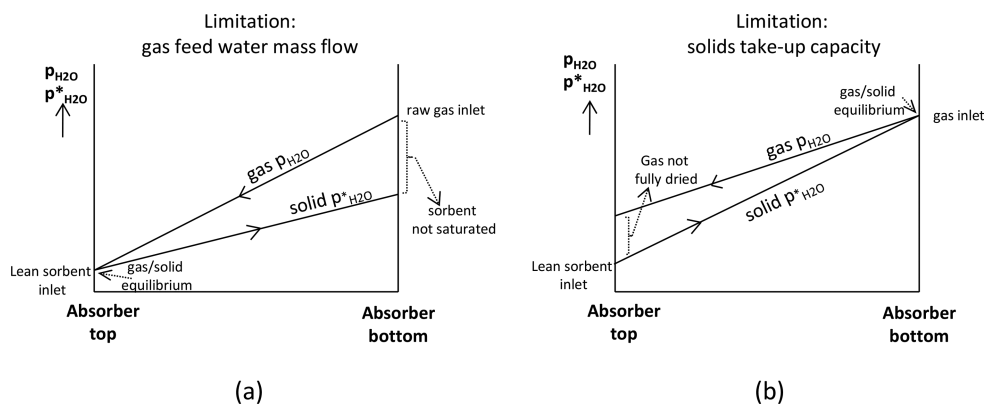

Figure 3. Illustration of the two possible limitations for water take-up in the absorber. X-axis: the relative position in the absorber. Y-axis: water gas partial pressure p_{H2O}, or the p^*_{H2O} equilibrium water partial pressure corresponding with the water loading of the sorbent.
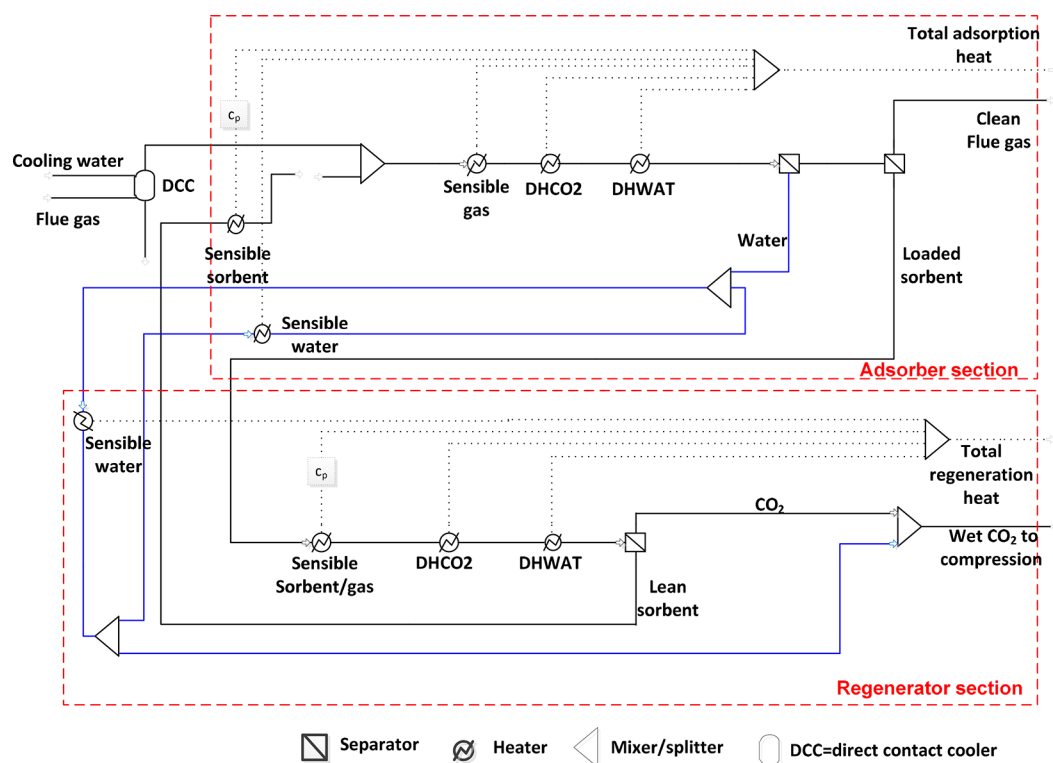
Figure 4. Structure of the Aspen Plus model of the solid sorbent CO_2 capture system.

captured relative to the adsorber CO_2 inlet flow rate), adsorber/regenerator operating temperature and pressure, and experimental sorbent sorption characteristics.

Assumptions made in the model are the absence of heat leak to the environment, a uniform temperature of the solids for all streams. The model uses the "IDEAL" set for thermodynamic models available in Aspen Plus. Adsorbed CO_2 and water are modeled as being vapor phase, water for a part of the model as a separate vapor stream. The solid sorbent stream was modeled as pure SiO_2. Since the heat capacity of PEI on silica is significantly different from pure silica, a correction for specific heat in the sensible heat stream is applied. Recent experimental data by Quang et al. of PEI on silica was used for estimating the correction factor by linear interpolation of the specific heat as a function of PEI loading.[43] The effective c_p used is 1.40 kJ/kg·K, which is almost double the value of pure silica. The model focuses on the main contributor to the energy penalty for CO_2 capture which is the total regeneration heat, and does not address the power requirements for blowers and pumps, the effects of pressure drop on these power requirements. This needs to be accounted for in a next evaluation stage, which involves detailed reactor design and optimization. CO_2 compression is outside the system boundaries considered.

Figure 4 depicts the model implementation in Aspen Plus in which the process streams are indicated by solid lines, and heat streams are indicated by dashed lines. The inlet stream is the flue gas from a coal or natural gas fired power plant, the outlet streams are the depleted flue gas stream to the stack (clean flue gas) and the CO_2-rich product stream (wet CO_2 to compression). For modeling purposes, the closed circuit of circulating sorbent is cut at the adsorber inlet transferring enthalpy and mass flow rate.

Flue gas feed is first cooled in a direct contact cooler (DCC). Here cooling water is sprayed in the flue gas streams, which

cools the flue gas and condenses out a significant part of the water in the flue gas. The lean sorbent is cooled to the adsorber temperature and mixed with the flue gas. Next, the model has three heater blocks describing the heat of adsorption (both CO_2 and H_2O) and the sensible heat of cooling the sorbent and gas to the adsorber temperature. Then in a separator block the amount of adsorbed water is split off and sent to the regenerator as a separate water vapor stream. In the last separator block of the adsorber the loaded sorbent stream is separated from the clean gas. The amount of CO_2 and water adsorbed are calculated using the sorption isotherms, adsorber conditions, the lean loading of the sorbent and the amount of CO_2 and water in the flue gas as described above.

The loaded sorbent stream is fed to the regenerator, where three heaters calculate the heat of desorption (CO_2 and H_2O) and the sensible heat of the heating the sorbent and gas to the regenerator temperature. The CO_2 and water desorbed are split off and mixed resulting in the wet CO_2 stream by compression. The amount of CO_2 and water are calculated based on the experimental isotherms and regenerator conditions. The resulting wet CO_2 product stream is exported. Any water not desorbed from the sorbent is returned to the adsorber.

The model results are presented by the total heat required for regeneration of the sorbent (total regeneration heat) and a breakdown thereof obtained from the unit operation blocks described above:

total regeneration heat

$$= \text{sorption heat}_{CO_2} + \text{sorption heat}_{H_2O} + \text{sensible heat}$$

(1)

Here the sensible heat is the heat involved in heating the sorbent from the adsorber to the regenerator temperature. In the calculations, the specific heat of adsorbed water and CO_2

are neglected, which is estimated to give a 10% underestimation of the latent heat.

The flue gas compositions for the inlet of the CO_2 capture unit have been taken from recommended values for evaluation of CCS technologies as set by the European Benchmarking Task Force (EBTF).[44] Two cases are considered (i) flue gas from a natural gas fired combined cycle (NGCC) and (ii) flue gas from an advanced supercritical pulverized bituminous coal (PC) power plant. A third case has been added for the comparison with the MEA reference system, see the next paragraph.

3.3. Reference MEA System Breakdown Analysis. For the purpose of a breakdown comparison with MEA scrubbing a separate third case was defined, also for a pulverized coal power plant, but different from the PC case. This case, the Sanpasertparnich case, is based on a literature modeling study by this author.[45] It must be noted that a direct comparison between the solid sorbent modeling and MEA is not valid, because the MEA model is a much more detailed one and it incorporates reaction kinetics and possibly mass transfer, whereas these are not accounted in the solid sorbent model. Therefore, the solid sorbent model is likely to be optimistic with respect to the magnitude of the regeneration heat, specifically in the underestimation of the contribution of the sensible heat. Nonetheless, a comparative assessment is made in order to assess the differences with the results available at this stage in the development.

The data set used for the MEA system was for a conventional liquid amine scrubbing process incorporating a water wash section at the top of the absorber column to cool down the column and to prevent amine losses due to mechanical entrainment and evaporation. It uses a 30% MEA solution in water (lean/rich loading 0.213/0.452 mol_{CO_2}/mol_{MEA}) as the capture solvent and captures 90% CO_2 from the flue gas of a bituminous coal fired pulverized coal power plant with a CO_2 content of 14.97%. The absorber works at atmospheric pressure (1.0135 bar). The regenerator is operated at a pressure of 1.09 bar and has a reboiler working at a temperature of 123 °C with a heat requirement 587.9 MW_{th} (4.29 GJ/ton captured). The regeneration heat demand for this reference is higher than that of state of the art as listed in the EBTF report[44] (3.7 GJ/ton captured) and that of novel capture systems. However, among numerous works on modeling of amine systems published, this is one of the few studies presenting a complete set of stream data for all streams in the capture process, which is necessary for making a breakdown of capture energy requirements and understanding the underlying effects.

Feed flue gas specifications for the Sanpasertparnich case are listed in Table 1. The differences in flue gas composition compared with the PC case from the EBTF report are minor.

The sensible heat of gases is neglected, as is the impact of CO_2 on the specific heat of the liquid phase. The specific heat

of MEA was taken from the literature,[46] as well as the properties for water and steam.[47] The heat of CO_2 sorption in MEA applying the van 't Hoff equation (eq 2) to the top conditions for absorber and regenerator, respectively, assuming gas/liquid equilibrium. The adsorption heat was found to be −78 kJ/mol CO_2, which is in agreement with the literature value measured by calorimetry of −82 kJ/mol.[48]

$$\Delta h_{r,CO_2\,in\,MEA} = -R\left(\frac{1}{T_5} - \frac{1}{T_3}\right)^{-1} \ln\left(\frac{p_{CO_2,5}}{p_{CO_2,3}}\right) \quad (2)$$

The required heat for regeneration in the reboiler is broken down according to the contributions resulting from the simplified enthalpy balance over the regenerator, for which the stream numbers are indicated in Figure 2.

$$Q_{regen} = \text{reaction heat} + \text{sensible heat}_{MEA}$$
$$+ \text{evap heat}_{H_2O,regen} + \text{sensible heat}_{H_2O,reflux} \quad (3)$$

$$Q_{regen} = \phi_{CO_2,3}\Delta h_{r,CO_2} + \phi_1 c_{p,MEA}(T_1 - T_2) + \phi_{H_2O,3}\Delta h_{evap,H_2O} + \phi_4 c_{p,water}(T_1 - T_2) \quad (4)$$

The right-hand terms are for the contributions of (i) the reaction heat for absorption of CO_2 in the amine solution (ii) the sensible heat for heating up the amine solution between the regenerator rich feed temperature and the regenerator lean product temperature and (iii) the heat for evaporation of water in the absorber and (iv) the sensible heat for heating up regenerator reflux water from the reflux.

4. RESULTS

4.1. Experimental CO_2 and H_2O Sorption Data. The study aimed at evaluating the relative effect of CO_2 and water sorption on efficiency rather than optimization of the material for maximum CO_2 capacity. The material used in the experiments was therefore prepared by a simple impregnation procedure of a commercial silica having a high mesoporous volume with commercial polyethylenimine (PEI). A material with 35 wt % PEI loading showing a breakthrough capacity of about 2.2 mmol/g at 150 mbar CO_2 in preliminary experiments, was selected for this study. The material was subjected to a series of breakthrough experiments with various CO_2 partial pressures at various temperatures, while testing at regular interval the breakthrough capacity in a standard breakthrough experiment at 60 °C. The water feeding rate was kept constant all the time in adsorption mode as well as in regeneration steps to prevent degradation of the polyamine as indicated by previous work.[39] Throughout the whole measurement campaign the deactivation of the material was less than 5%, as measured by repeated standard breakthrough experiments with a CO_2 partial pressure of 150 mbar. CO_2 capacity at CO_2 partial pressure in the range 0.025 to 0.2 bar was obtained by breakthrough experiments at temperatures between 60 and 120 °C (Figure 5).

At 60 and 80 °C, breakthrough capacities decrease with increasing pressure and are even lower than at 90 °C at equal CO_2 pressure. The nature of possible mechanisms for this has been summarized in a recent review.[49] A comparative analysis of the breakthrough curves at 60 and 90 °C did not reveal any broadening of the breakthrough curve that is typically found when significant mass transfer limitation exists. Therefore,

Table 1. Feed Flue Gas Data for the Three Cases Considered

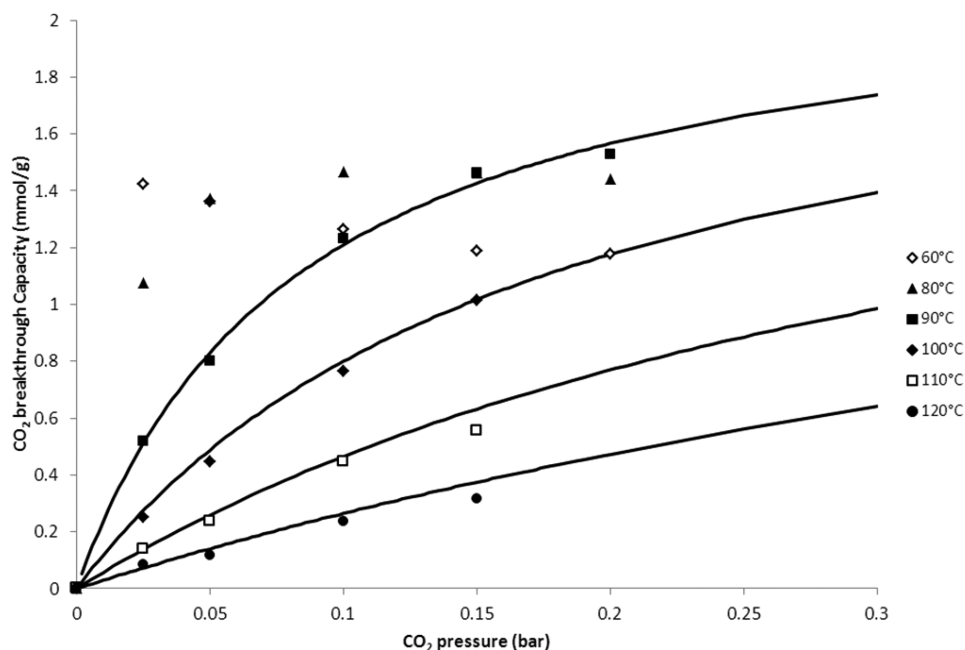| case	gas composition (mol %) and flow rate.	conditions
PC case	13.73% CO_2, 9.73% H_2O, 72.855% N_2, 3.65% O_2, Ar 0.05% 781.77 kg/s.	50 °C, 1.016 bar
NGCC case	3.96% CO_2, 8.38% H_2O, 74.38% N_2, 12.39% O_2, Ar 0.89%, 665.3 kg/s.	86.8 °C, 1.013 bar
Sanpasertparnich case	14.97% CO_2, 6.1% H_2O, 76.5% N_2, 2.3% O_2, 0.04% others. 725 kg/s	45 °C, 1.0135 bar.

Figure 5. CO_2 breakthrough capacity of 35 wt % PEI supported on silica at temperatures between 60 and 120 °C. The solid lines represent the best fit obtained for the Langmuir adsorption model.

Table 2. Langmuir K_{CO2} Parameter Obtained Experimentally at Various Temperatures, with Associated Confidence Interval

temp (°C)	K_{CO2} (1/bar)	estimated error (95%) (1/bar)
90	12.15	±0.44
100	5.34	±0.19
110	2.35	±0.091
120	1.22	±0.077

hampered accessibility due to pore clogging under the effect of polymer rearrangement as an effect of temperature for instance may be excluded from the list of potential causes. Formation of bicarbonates by the reaction between CO_2, coadsorbed water and carbamate species, that are probably formed as a result of CO_2 reaction with PEI, may play a role in the behavior

observed for $T < 80$ °C. The present study however does not provide sufficient experimental data to investigate these mechanisms in more detail.

Only the experimental data obtained at higher temperature (90 °C and higher) were used and all fitted with a Langmuir adsorption model which was found to describe the chemisorption process very well. The modeling results will not be totally accurate in the extrapolated region. This approach however allows for determining the optimal operating temperature and can therefore be used to decide whether further refinement of the isotherm description is advised. The Langmuir parameter K_{CO2} in eq 5 and the associated 95% confidence interval were calculated using the method of least-squares for each temperature. Results are listed in Table 2.

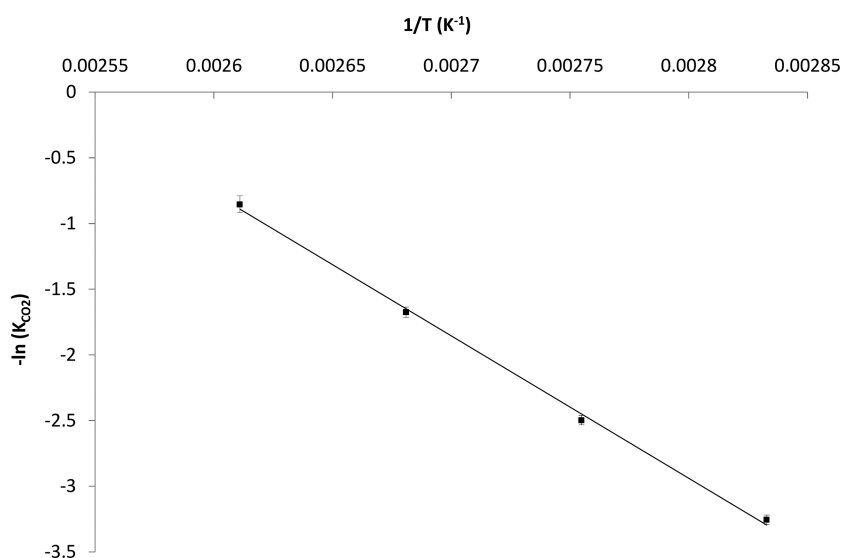The CO_2 sorption is described with a Langmuir isotherm:

Figure 6. Van't Hoff plot for CO_2 sorption on 35% PEI/silica, $\Delta h_{CO_2} = 90 \pm 5$ kJ/mol.
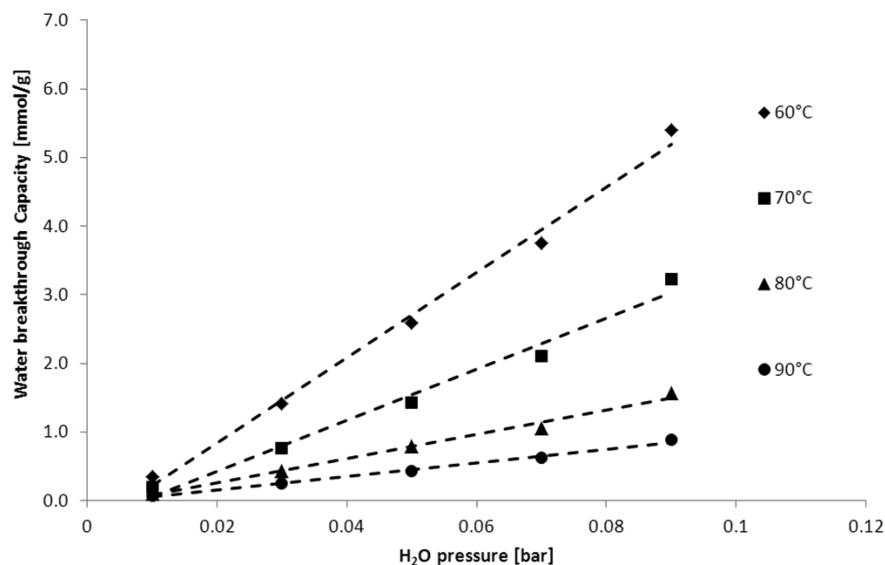
Figure 7. H_2O breakthrough capacity of 35 wt % PEI supported on silica at temperatures between 60 and 90 °C. The dashed lines represent the best fit obtained for a linear adsorption model.

$$q_{CO_2} = \frac{K_{CO_2} p_{CO_2}}{1 + K_{CO_2} p_{CO_2}} q_{max,CO_2} \quad \text{with}$$

$$K_{CO_2} = B_{0,CO_2} \exp\left[\frac{-\Delta h_{CO_2}}{RT}\right] \tag{5}$$

The resulting Langmuir K_{CO_2} parameters for each temperature were used to estimate the adsorption enthalpy Δh_{CO_2} and the pre-exponential factor B_0 according to the van 't Hoff equation (eq 6).

$$\Delta h_{CO_2} = R \frac{d \ln K_{CO_2}}{d\frac{1}{T}} - \ln B_{0,CO_2} \tag{6}$$

From Figure 6, the adsorption enthalpy calculated by this method was $\Delta h_{CO_2} = -90 \pm 5$ kJ/mol and was used as input for the modeling of the CO_2 removal process.

A similar experimental campaign was carried out to determine the water adsorption isotherm of the 35 wt % PEI supported on silica. Since for silica based materials strong affinity with water was known[50] it was important to check whether the water coadsorption was mostly related to the support material choice. Therefore, in a preliminary experiment the water capacity of the bare silica support was determined by a breakthrough experiment at temperatures between 60 and 90 °C with water partial pressure between 10 and 90 mbar. The results indicated that the breakthrough capacity of silica was below 1 mmol/g for all conditions screened in this experiment. In comparison, Figure 7 displays the water breakthrough capacity of 35 wt % PEI supported on silica.

Although the result of the preliminary experiment indicated that silica support has clear capacity for water, the comparison of breakthrough capacities between bare silica and PEI impregnated silica revealed that most of the water capacity is indeed induced by the presence of PEI for temperatures below 80 °C. The plot of water breakthrough capacity as a function of the water partial pressure exhibited a linear correlation in the pressure range considered herein, for all temperatures. The water uptake data obtained has been used to fit a linear adsorption model.

$$q_{H_2O} = K_{H_2O} \cdot p_{H_2O} \quad \text{with}$$

$$K_{H_2O} = B_{0,H_2O} \exp\left[\frac{-\Delta h_{H_2O}}{RT}\right] \tag{7}$$

The K_{H2O} in eq 7 and the associated 95% confidence interval were calculated using the method of least-squares for each temperature. Results are listed in Table 3.

$$\Delta h_{H_2O} = R \frac{d \ln K_{H_2O}}{d\frac{1}{T}} - \ln B_{0,H_2O} \tag{8}$$

Table 3. K_{H2O} Parameter Obtained Experimentally at Various Temperatures, With Associated Confidence Interval

temp (°C)	K_{H2O} (mmol/g/bar)	estimated error (95%) (mmol/g/bar)
60	56.0	±3.2
70	32.4	±2.8
80	16.3	±1.6
90	9.32	±0.79

K_{H2O} parameters for temperatures between 60 and 90 °C were put in eq 8 for the calculation of water adsorption enthalpy (see also Figure 8). This resulted in an enthalpy $\Delta h_{H2O} = -60 \pm 8$ kJ/mol, that was used as input parameter for the CO_2 removal process modeling.

Table 4 summarizes the experimental parameters that were used as input for the modeling study described in the next paragraphs. As discussed above, the presence of water is known to increase the capacity for CO_2. In the current work, this effect was not quantified. Instead, the adsorption parameters for CO_2 have been determined in the presence of steam, both during the adsorption and the regeneration steps in an approximation of the conditions that the sorbent will experience in the fluidized bed cycles currently under investigation.

4.2. Modeling Results. The water content in the flue gas is of obvious importance when considering a sorbent that coadsorbs water and CO_2. The amount of water in the flue gas can be decreased by cooling in the direct contact cooler
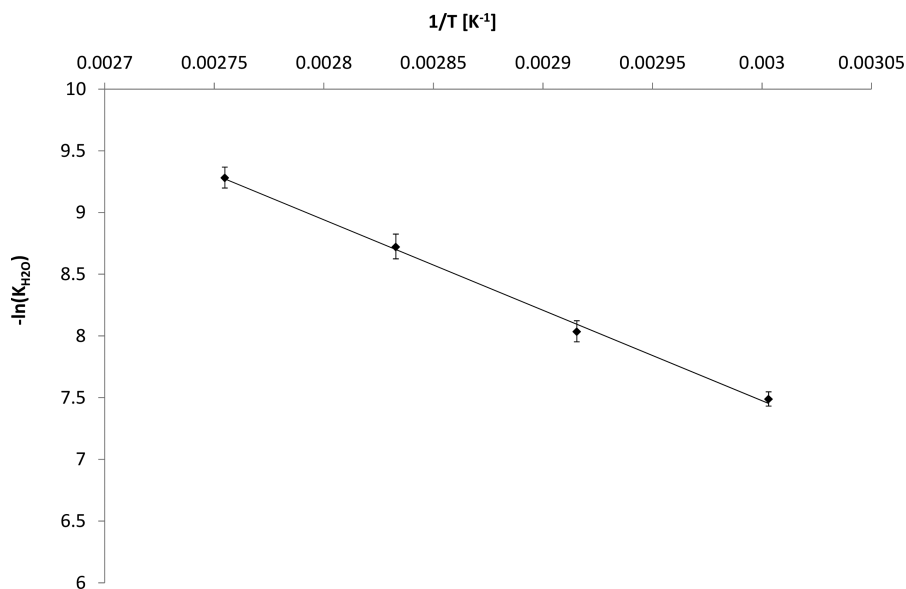
Figure 8. Van't Hoff plot for H_2O sorption on 30% PEI/silica $\Delta h_{H_2O} = 60 \pm 8$ kJ/mol.

Table 4. Adsorption Parameters Derived from Experimental Data

		CO_2	H_2O
adsorption enthalpy	kJ mol^{-1}	91	60
pre-exponential factor B_0	CO_2: bar^{-1} H_2O: mmol g^{-1} bar^{-1}	1.25×10^{-12}	1.61×10^{-13}
maximum loading q_{max}	mmol/g	2.2	n.a.

(DCC) upstream of the adsorber. In a first approach we assessed the impact of temperature of this direct contact cooler on the regeneration heat and on the amount of cooling water required, which is presented in Figure 9. The adsorber temperature was fixed at 81 and 66 °C for the PC and NGCC case, respectively (these values are derived from the optimal regeneration heat duty detailed below). A minimum in the regeneration heat is observed at very high cooling water flow rates because the cooling water also takes up CO_2. This lowers the CO_2 concentration in the flue gas, which makes that effort in terms of regeneration heat to capture the CO_2 in the solid sorption system is increased. Achieving very low temperatures requires excessive amount of cooling water. For the cases evaluated in this paper, the direct contact cooler outlet temperature was chosen as 32.2 °C. This value is equal to the condensate outlet temperature in the steam turbine and is a reasonable compromise between reduction in regeneration heat and the amount of cooling water required. Introducing this cooling water reduces the regeneration heat required by approximately 7% for the PC case, and 20% for the NGCC case.

Figure 10 shows the impact on total regeneration heat and a breakdown thereof according to eq 1 for the PC case. The heat of desorption of CO_2 is the largest contribution, followed by that of the sensible heat for heating the sorbent from the adsorber to the regenerator temperature, and the heat of
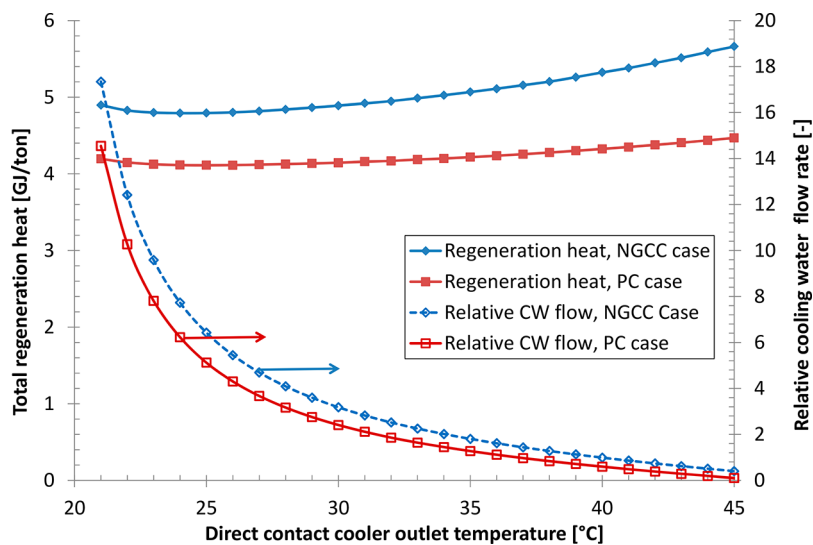

Figure 9. Variation of direct contact cooler temperature, impact on regeneration heat demand and required cooling water (CW) flow rate (relative to the flue gas mass flow rate).
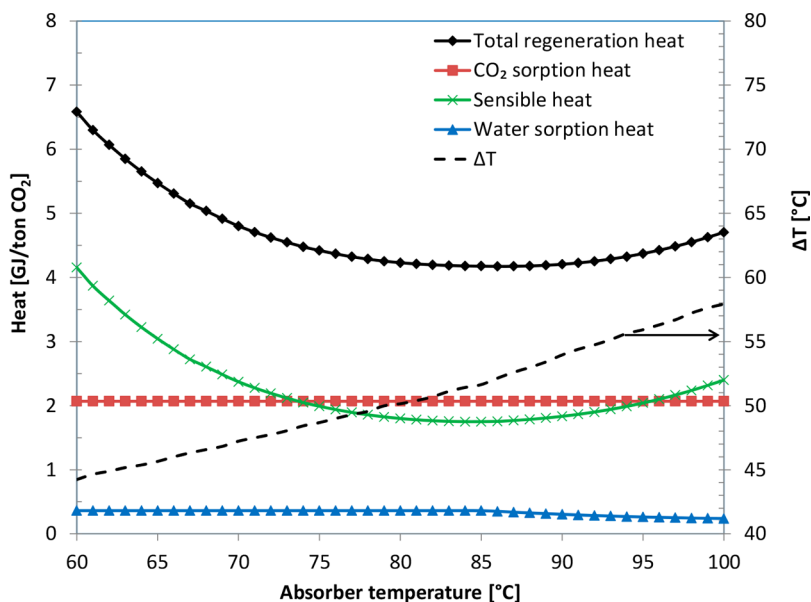
Figure 10. Breakdown of regeneration heat and adsorber/regenerator temperature difference (ΔT) as a function of adsorber temperature. PC case.

sorption of water. The global contribution of the heat of CO_2 sorption is not dependent on the adsorber temperature because of the specification of 90% CO_2 capture. The contribution of water sorption is low and constant because the model shows that the amount of water in the flue gas is limiting the water take-up rather than the sorbent water capacity. The sensible heat contribution and thus the total regeneration heat goes through a minimum as a result of the increasing solids flow rate and decreasing adsorber/regenerator temperature difference. The resulting total regeneration heat has a minimum value of 4.17 GJ/ton CO_2 captured. The optimum is at 86 °C adsorber temperature with a 52 °C temperature difference, resulting in a regenerator temperature of 138 °C.

The total regeneration heat and breakdown thereof for the NGCC case (Figure 11) is different from that of the PC case. At low adsorber temperatures the contributions of CO_2 sorption heat and sensible heat are of a similar value. The
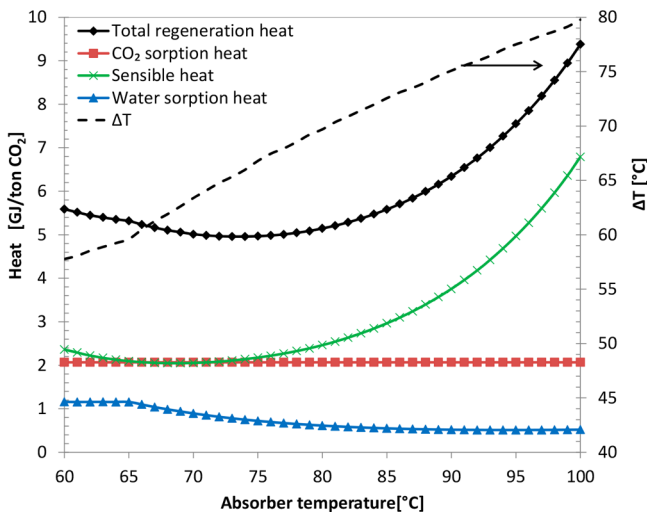
contribution of water is much higher than in the PC case because more water is present in the feed relative to the amount of CO_2. At low temperatures the amount of water in the flue gas is limiting the water take-up and the contribution of water is constant. Above 65 °C the sorbent capacity is limiting the water take-up and the contribution of water decreases. The total regeneration heat again passes through a minimum, with a value of 4.96 GJ/ton CO_2 captured at 73 °C adsorber temperature. The temperature difference amounts to 64 °C, which results in a regenerator temperature of 138 °C. The desorption heat increases significantly at temperatures above 85 °C. This is caused by the large increase in solids flow rate, as a result of a much lower cyclic capacity.

Figure 12 and Figure 13 provide graphic representations of the solid sorbent capture process for both the PC and the NGCC case. The dashed lines are the isotherms for CO_2 and water (dashed lines) at the optimum operating temperatures as discussed above. The operating line represented with a solid

Figure 11. Breakdown of regeneration heat and adsorber/regenerator temperature difference (ΔT) as a function of adsorber temperature. NGCC case.
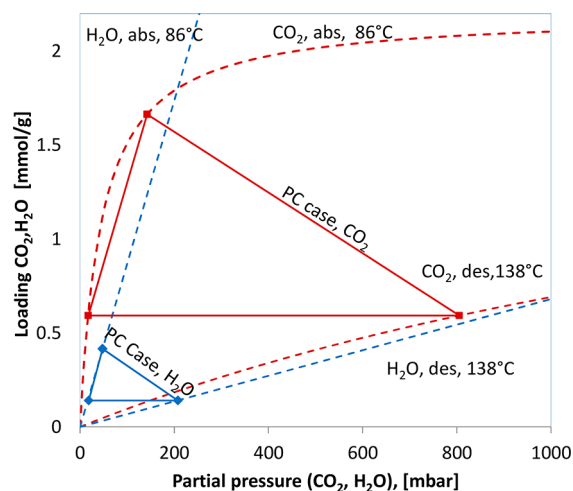

Figure 12. Solid sorption process for the PC case. Solid lines: In/outlet conditions of absorber and regenerator. Dashed lines: sorption isotherms for CO_2 and water.
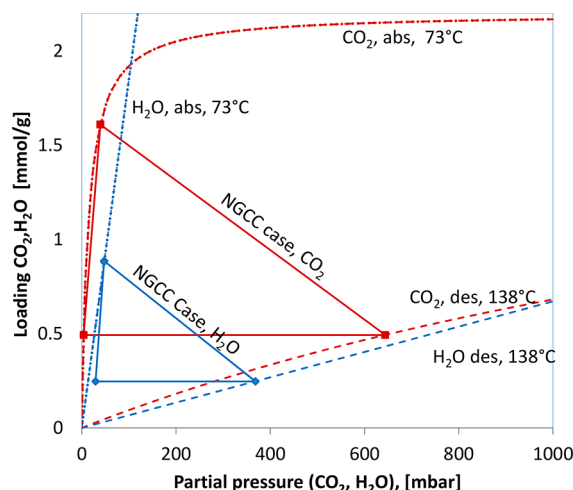
Figure 13. NGCC case at the optimum temperature. Solid lines: In/outlet conditions of absorber and regenerator. Dashed lines: sorption isotherms for CO_2 and water.
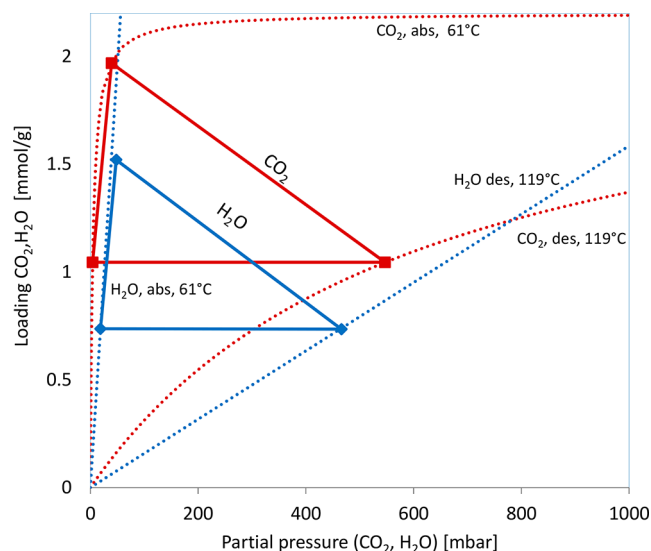

Figure 14. NGCC case at the low absorber temperature. Solid lines, in/outlet conditions of absorber and regenerator; dashed lines, sorption isotherms for CO_2 and water.

plotted lines represent the cyclic process connecting the points for respectively the regenerator gas/lean solids outlet (high temperature, high partial pressure), absorber rich solids inlet/flue gas inlet (low temperature, medium partial pressure), and absorber clean gas outlet/lean solids inlet. For CO_2 this line interconnects with the equilibrium line as a result of the design strategy equilibrium at the regenerator and absorber gas outlet and choosing the solid circulation rate for full saturation of the loaded sorbent. The water line not always intersects with the equilibrium line, as discussed earlier for Figure 3. For Figure 12 and Figure 13, the water operating line is below the equilibrium line for the lean solid inlet/clean gas outlet point. This is in accordance with the mode in Figure 3b, in which the amount sorbent cyclic capacity is limiting the water take-up. This makes that the clean gas is cannot be dried until the partial pressure corresponding with lean sorbent conditions.

Comparing the NGCC and PC case it can be seen that the cyclic capacity for CO_2 is higher for the PC case, caused by the higher CO_2 partial pressure in the feed flue gas. Also, the PC case has a much lower cyclic capacity of water, which is predominantly caused by the lower H_2O/CO_2 ratio in the PC feed flue gas. In the NGCC case, the flue gas contains more water than the PC case, but the direct contact cooler effectively reduces the flue gas water content from 9.73% for the NGCC case and 8.38% for the PC case to 4.7% for both cases. This makes the relative amount of water compared to the CO_2 be significantly higher for the PC case. The higher feed gas CO_2 partial pressure in the PC case causes the cyclic capacity to be higher, the required temperature difference at optimum conditions to be lower, and the cyclic capacity for water sorption to be lower.

For a low temperature operation of the NGCC case, for example, at 61 °C as is shown in Figure 14, a different limitation is observed as compared to the NGCC case presented in Figure 13. Here the situation of Figure 3a is observed, in which the amount of water in the feed gas limits water loading of the sorbent, and where consequently the rich sorbent is not fully loaded (compared to the loading corresponding with the feed gas water partial pressure).

The cyclic capacities, the difference between the rich and lean capacity, for both CO_2 and water for varying adsorber temperature are depicted in Figure 15. The cyclic capacities for

both CO_2 and water have an optimum. With increasing adsorber temperature the CO_2-rich capacity is decreased. On the other hand, it has been shown that the regenerator/adsorber temperature difference also increases with increasing adsorber temperature, resulting in a lower CO_2 lean capacity. This together explains the optimum in the CO_2 cyclic capacity observed. It is seen that the cyclic capacity of water is significantly lower for the PC case, which is related to the ratio of CO_2 partial pressure and water partial pressure which is significantly higher for the PC case.

Finally, Table 5 presents a summary of the process characteristics of the solid sorption system for the PC and NGCC cases, both working at their optimal adsorber temperatures.

Further materials research aims at developing sorbents with improved characteristics, for example an increased CO_2 capacity or lower water capacity (as mentioned above, optimization of the sorbent was not within the scope of the present work). To evaluate the impact of potential improvements to sorbent characteristics on the process, case studies have been carried out for the PC case varying the sorption capacity by changing the value of pre-exponential factor B_0 for water and the for CO_2 maximum capacity $q_{max,CO2}$, since both parameters have a direct impact on the rich sorbent loading. Since the capacity of CO_2 and water might be related, scenarios have also been evaluated where an improvement in CO_2 capacity leads to an increase in water capacity and vice versa. Figure 16 shows that increasing the CO_2 capacity by a factor 2 is much more effective in terms of reducing the regeneration heat requirement than reducing the water capacity by a factor 2. However, while increasing the CO_2 capacity the water capacity of a sorbent could also increase. Even by doubling both values, a significant improvement is obtained. Doubling the CO_2 capacity and reducing the water capacity gives the largest reduction of the regeneration heat, with 23% and 30% for, respectively, the PC and NGCC case. Obviously the effect of water capacity is the strongest for the NGCC case. For several PC cases the effect of water capacity is negligible, because the amount of water in the feed gas remains limiting, even in a case of a 50% reduction in H_2O capacity.
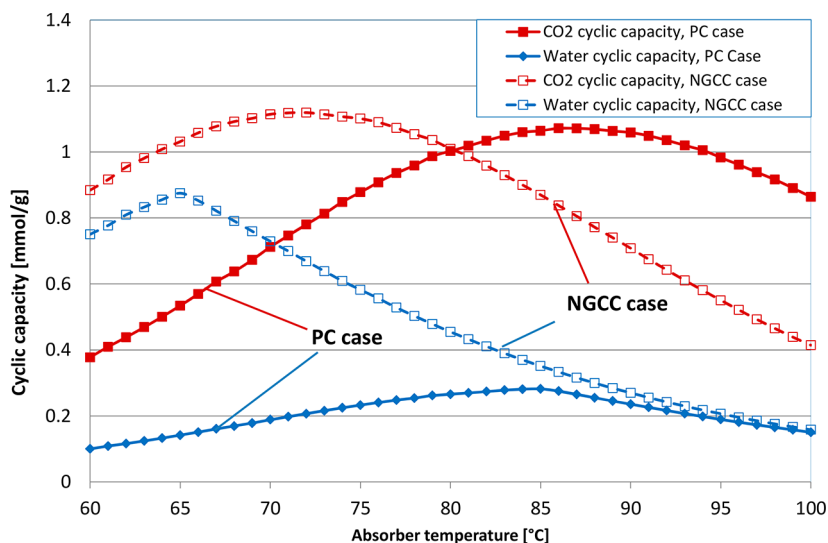
Figure 15. Cyclic capacity of CO_2 and water sorption as a function of adsorber temperature. PC and NGCC case.

Table 5. Main Solid Sorbent Capture System Results at Optimum Conditions. Compositions in mol %

	PC case	NGCC case
flue gas after direct contact cooler	32.2 °C. 14.0% CO_2, 4.7% H_2O	32.2 °C. 3.9% CO_2, 4.7% H_2O
lean sorbent	138 °C, 0.59 mmolCO_2/g, 0.14 mmolH_2O/g, 2943 kg/s	138 °C, 0.49 mmolCO_2/g, 0.25 mmolH_2O/g, 708 kg/s
rich sorbent	86 °C, 1.66 mmolCO_2/g, 0.41 mmolH_2O/g	73 °C, 1.60 mmolCO_2/g, 0.87 mmolH_2O/g
clean gas	86 °C. 1.7% CO_2, 1.8% H_2O	73 °C. 0.4% CO_2, 2.9% H_2O
CO_2 product	138 °C, 79.5% CO_2, 20.5% H_2O	138 °C, 63.3% CO_2, 36.4% H_2O
CO_2 capture rate	90%	90%
regeneration heat	4.17 GJ/ton CO_2 captured	4.96 GJ/ton CO_2 captured

4.3. Comparison with Reference MEA Absorption. The breakdown comparison between the MEA absorption and solid sorption, taking the starting points of the Sanpasertparnich case, is presented in Figure 17. This is done using the measured solid sorbent capacity as well as a case with a 200% increase in CO_2 and water capacity. Adding up the individual contributions from MEA sorption from Sanpasertparnich et al. gives a total regeneration heat that is 8% higher than the reported total regeneration heat by the authors in the same reference. This difference cannot be attributed to the inaccuracy of a single parameter from the underlying stream data and is likely due to a combination of inaccuracies. The optimal operating temperatures for the solid sorption system are 82 °C for the adsorber and 132 °C for the regenerator. The total regeneration heat for the solid sorption system was found to be 4.26 GJ/ton$_{CO2}$, lower than that for MEA for the same flue gas composition (4.13 GJ/ton$_{CO2}$).[45] It is in the range of 3.7−4.3 GJ/ton reported for MEA in general.[44,45] However, for a case with a 200% increase in CO_2 and water capacity the regeneration heat is reduced to 3.31 GJ/ton (at optimum temperatures of 90 and 142 °C for the absorber regenerator respectively).

From Figure 17 we can obtain a more detailed comparison of the underlying contributions of the total regeneration heat for the PC and NGCC case. A significant difference is observed in the contribution of the heat of evaporation (MEA) and

desorption (solid sorbent). For MEA, a large amount of water is evaporated in the regenerator, while the amount of water being desorbed in the regenerator of the solid sorbent systems is relatively limited. Even taking into account the fact that the heat of evaporation (relevant for the MEA case) is lower than the heat of adsorption (relevant for the solid sorbent system), the amount of water being adsorbed or evaporated appears to be dominant, causing the solid sorption system to have a much lower contribution in the regenerator heat demand. The amount of sensible heat in reflux water in the MEA system proved to be insignificant.

Finally, there is the contribution of the sensible heat of current solid sorbent. Here, one has to consider the temperature lift, sorbent/solvent mass flow rate, and specific heat of both systems. The heat exchanger present in the MEA system exchanges heat between rich and lean solvent, effectively reducing the MEA solution temperature lift required in the regenerator to only 16 °C. Heat exchange between solid streams has, in taking a conservative approach, not been assumed in the system solid sorbent process design. The temperature lift is therefore around 50 °C, equal to the full temperature difference between adsorber and regenerator. The mass flow of solid sorbent depends on the (cyclic) capacity. It is significantly higher for the MEA than for solid sorbents (MEA 4536 kg/s, solid sorbent 3215 kg/s, 200% capacity solid sorbent 1545 kg/s). The specific heat of the solid sorbent (1.4 kJ/kg.K) however is significantly lower than that of the MEA solution (3.8 kJ/kg·K). The low specific heat of the sorbent is concluded to be an important asset of solid sorbents and compensates in a large part for the effects of higher temperature difference.

To assess the ultimate impact on the electrical efficiency of a power plant, not only the heat demand for sorbent/solvent regeneration, but also the temperature level thereof is of importance.[51] The temperature level of the heat demand for the solid sorption system is 138 °C, whereas is it is 123 °C for the reference MEA system. The temperature level of the solid sorption system is less favorable, but the effect is expected to be small.

If in the solid sorbent system a rich/lean heat exchanger would be introduced, the contribution of the sensible heat could be substantially lower. This would involve the introduction of a solid/solid heat exchanger, which is not a
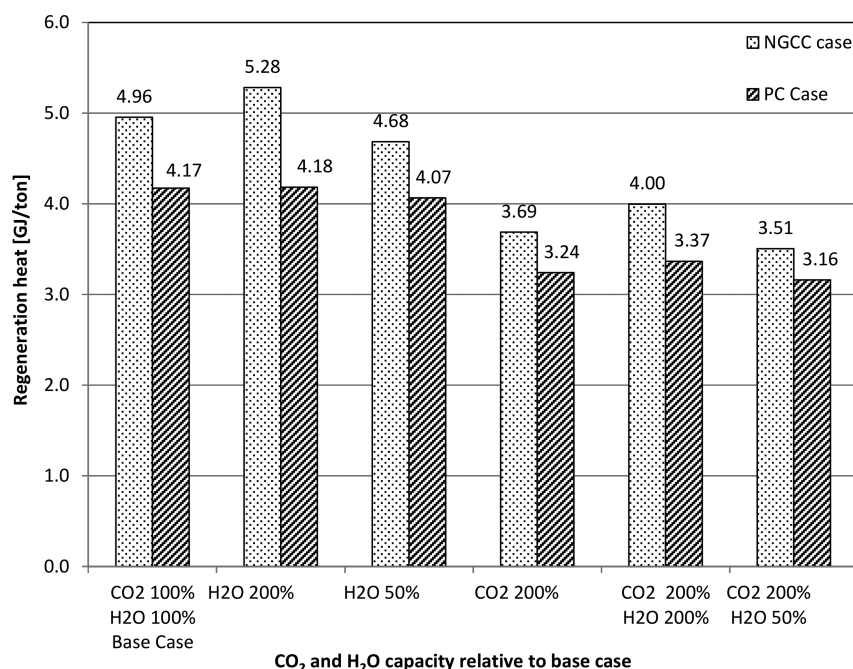
Figure 16. Potential for improvement by varying CO_2 and water sorption parameters ($q_{max,CO2}$ and $B_{o,water}$, respectively). Values of Table 4 were set to 100%).
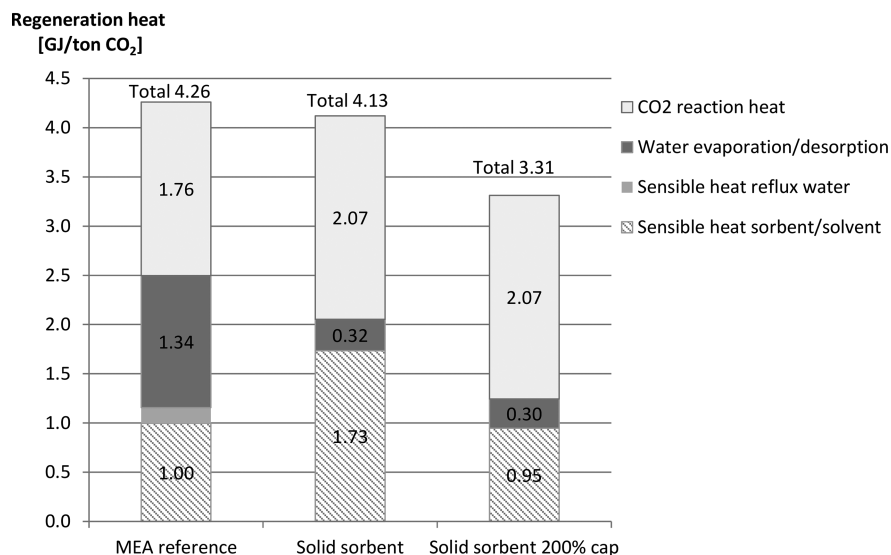

Figure 17. Breakdown of regeneration heat for MEA reference and solid sorption capture system for PC. Sanpasertparnich case.

standard technology. In the limiting case of full thermal integration of the rich and lean stream the contribution of the sensible heat would disappear and the resulting regeneration heat would be lowered to 2.37 GJ/ton$_{CO2}$, independent of sorbent capacity.

5. DISCUSSION

The performance of a supported PEI sorbent for postcombustion CO_2 capture critically depends on the adsorption characteristics, for CO_2 as well as for water. Corresponding adsorption isotherms are lacking from literature and were therefore measured. The choice of experimental method for the determination of adsorption parameters that are relevant for such a modeling study is not trivial. Especially in the case of chemisorption, in which two consecutive reactions (carbamate

formation and bicarbonate formation) contribute to the total adsorption capacity, and in which strong mass transfer limitations may occur, using equilibrium data might not be the most obvious experimental technique. In the present study, however, breakthrough capacity analysis was found to be implemented easily and to give a good estimate of the uptake capacity of CO_2 and water using a realistic gas mixture. Note that the breakthrough capacity data do not suffice as a mechanistic study of the adsorption of CO_2 and water during the different process steps, but rather should be interpreted as a preliminary screening of the system with respect to the sorption characteristics and their impact on process performance. Evaluation of the adsorption mechanism remains an objective for further study. The fairly large CO_2 adsorption enthalpy of 91 + 5 kJ/mol derived from the experimental study was

comparable to values found in previous studies on related materials and may be attributed to the highly exothermic formation of carbamate. For instance, Knowles et al. gave a typical range of 70−90 kJ/mol for PEI supported materials,[52] Satyapal et al. found an adsorption enthalpy of 94 ± 8 kJ/mol in an early study on similar materials,[53] and other recent studies confirm that these values are commonly found for CO_2 chemisorption on secondary amines.[54] Our experiments were carried out at rather high adsorption temperature (60−120 °C) and high regeneration temperature (135 °C), conditions which are in accordance with the optimal application range as seen in the modeling results. In contrast, when lower adsorption temperatures are used, carbamate reaction with excess adsorbed water molecules leading to the formation of bicarbonate species becomes the dominating uptake mechanism, resulting in lower adsorption enthalpies, as was also found in literature.[14,55] In the present experiments, the water adsorption experiments revealed that the adsorption capacity decreased considerably when the temperature approached 100 °C. In contrast, when the adsorption temperature was as low as 60 °C, water accumulated on the sorbent, with capacity reaching up to 5 mmol/g. The water adsorption capacity was found to be described best by a linear dependency with the steam partial pressure for all temperatures tested. The corresponding adsorption enthalpy was calculated at $\Delta h_{H_2O} = 60 \pm 8$ kJ/mol which is 40% higher than the adsorption of water on silica found by Ng et al.[50] consistent with a higher affinity of water with the PEI polymer phase in comparison with silica surface indicative for chemical reactions to bicarbonate and carbamate species. The isotherms were fitted using experimental data above 90 °C. For the PC case the optimal temperature found in the modeling is 86 °C. Only a minor extrapolation is used and the isotherm is therefore sufficiently accurately described. For the NGCC case however the optimal temperature is 73 °C, which makes that for these design the isotherm used significantly extends in the extrapolation temperature region. For a more accurate description of this case a more detailed description of the sorption including water–CO_2 interaction is advised.

The main advantage of a solid sorbent is the much lower energy involved with water evaporation in the regenerator. Regenerating a 30% MEA in water solution unavoidably involves evaporating a significant amount of water. For solid sorbents the amount of adsorbed water is limited, and therefore, also the amount of water desorbed and the water regeneration energy involved. To limit the amount of water adsorbed, a direct contact cooler in the feed flue gas proved to be effective, reducing the amount by roughly a factor 2. The positive impact of direct contact cooling is also known for MEA systems[56] but in that case it is primarily related to the decrease of the rich solvent temperature, which increases the rich solvent loading. In the present study one important assumption was that the adsorber is designed such that ideal counter-current flow regime may be assumed. The outlet flue gas composition is assumed to be in equilibrium with the lean sorbent stream, the rich sorbent stream in equilibrium with the inlet flue gas. This allows reaching high capture ratio and high cyclic loading.

The results of the sensitivity study underline the need to focus sorbent development work primarily on achieving higher CO_2 capacity in order reduce the heat requirement for the capture process, and the results show that an increase in water capacity may be acceptable as a side effect. The system modeling results show that solid sorbent technology, with

currently available nonoptimized solid sorbents, is modeled to be in the same range of published data on MEA sorption. A substantial benefit over state-of-the art reference MEA can be obtained for sorbents with a CO_2 capacity of over 4.4 mmol/g, which is a factor 2 improvement over the nonoptimized sorbent used in this study. This then would lead to an overall regeneration energy in of 3.3 GJ/ton CO_2.

Achieving such a capacity can be considered a realistic goal. Our preliminary work on (nonoptimized) poly(methyl methacrylate) supported PEI sorbents shows potentially much higher capacities for PMMA based sorbents compared to PEI/SiO$_2$. In Table 6 sorbents are compared for their cyclic

Table 6. Results of CO_2 Breakthrough Capacity Screening of Nonoptimized PEI−PMMA and PEI/SiO$_2$ Sorbents.

	CO_2 breakthrough capacity [mmol/g]	
	35 wt % PEI/SiO$_2$	45 wt % PEI−PMMA
15%CO$_2$/80 °C	1.5	2.3
41%CO$_2$/80 °C	1.6	2.4
41%CO$_2$/45 °C	1.7	3.0

breakthrough capacities under the flue gas conditions as well as at higher CO_2 concentration in the presence of 1 vol % water. On the other hand the use of PMMA will increase the overall heat capacity of the sorbent to some extent.

Also in the literature, authors have reported much higher CO_2 (equilibrium) capacities than used in this study. For example Xu et. al,[57] Son, Choi et al.[58] and Gray et al.[14] have reported CO_2 capacities of respectively 3.8, 3.06, and 3.5 mmol/g.

The specific heat of a solid sorbent is much lower than MEA, and proved to be an important advantage of solid sorbents. This advantage should be maintained and is advised to be a strong point of attention when preselecting sorbents for development and screening.

Some challenges and opportunities in solid sorbent technology could also be identified in this study. In the adsorber design, a counter-current regime was assumed. The reactor design for achieving this, while taking into account sufficient mass transfer properties and contact time between gas and solids, as well as a low adsorber pressure drop, might be challenging. The heat duty in the adsorber is significant, so heat management is also identified as a point of attention. Finally, a comparison with the reference case showed that the absence of heat exchange between the rich and lean streams is a primary drawback of solid sorbent technology. If it would be possible to introduce lean solid/rich solid heat exchange, a major reduction in heat requirement will result. Indeed in ref 59 it was shown that the energy requirement of a system with solid/solid heat exchange is dominated by the sorption heat rather than by the contribution of sensible heat.

6. CONCLUSIONS

A combined system modeling and experimental approach was used to design and evaluate a solid sorbent for CO_2 capture in postcombustion applications. The experimental determination of CO_2 and H_2O adsorption revealed that coadsorption of water is a serious issue that must be taken into consideration for process evaluations, especially when the adsorption process is carried out at low temperature, favoring significant water adsorption.

The sorption isotherms were implemented in an equilibrium-based ideal-countercurrent flow-sheeting model, obtaining the relative contributions of sensible heat, CO_2, and H_2O sorption heat to the heat demand for CO_2 capture and obtaining basic insights in the impact of operating conditions: flue gas type and operating temperature. The modeling results showed clearly that a proper choice of operating conditions, in particular the adsorber temperature, is crucial to optimize the regeneration heat demand. An optimum for the regeneration heat was found for 82 °C if implemented in a PC power plant translating into a regeneration heat of 4.2 GJ/ton CO_2 captured. This is lower than for the NGGC case, which has a regeneration heat of 5.0 GJ/ton CO_2 captured. The results were compared with literature modeling data for amine scrubbing using MEA at a PC power plant. Though the results cannot be directly compared due to differences in modeling approach, it is seen that the calculated regeneration heat is similar, but that the underlying contributions are fundamentally different. For the solid sorption system the contribution of water evaporation is largely reduced. Solid sorbents have a much lower specific heat, but the absence of a lean/rich heat exchanger results in a high required temperature difference, causing the contribution of the sensible heat to be still somewhat higher. The contribution of the heat of adsorption of CO_2 is the most important, and higher than that of the reference MEA. If a solid/solid heat exchanger would be introduced in the solid sorption system the regeneration heat could potentially be lowered significantly, to a value of 2.4 GJ/ton$_{CO2}$ captured independent of sorbent capacity.

In a PC power plant the amount of water available in the flue gas was found to always limit the water uptake in the adsorber. In the NGCC case this is also the case at low flue gas temperatures, whereas at high flue gas temperatures the sorbent is saturated and the limitation is in the sorbent water adsorption capacity. Important is cooling of the flue gas in a direct contact cooler, reducing the water content of the flue gas resulting in a reduction in regeneration heat with around 7% for the PC case, and 20% for the NGCC case.

A sensitivity study toward the potential of improved sorbents showed the solid sorbent CO_2 capture process might be effectively improved to more competitive systems with sorbents having a higher CO_2 capacity. A significant reduction in regeneration energy to a competitive value 3.3 GJ/ton$_{CO2}$ is predicted for sorbent materials with a doubling of non-optimized capacity used in this study to 4.4 mmol/g, even if this is accompanied by a doubling of the water capacity.

AUTHOR INFORMATION

Corresponding Author
*Tel. +31-224-56 8238. Fax. 31-224-56 8489. E-mail: dijkstra@ecn.nl.

ORCID
Jan Wilco Dijkstra: 0000-0002-9398-6600

Notes
The authors declare no competing financial interest.

ABBEVIATIONS AND SYMBOLS

ads	adsorption
B_0	pre-exponential factor in sorption equation
C_p	specific heat [J/mol.K]
CO_2	Carbon dioxide
DCC	Direct Contact Cooler
ΔT	adsorber/regenerator temperature difference [K]
des	desorption
EBTF	European Benchmarking Task Force
evap	evaporation
gas	gas stream
h	specific enthalpy [J/mol]
H_2O	water, water vapor
K	sorption coefficient [mmol/g/bar]
max	maximum
MEA	monoethanolamine
NGCC	natural gas combined cycle power plant
PC	pulverized coal power plant
PEI	polyethylenimine
p	pressure [bar]
q	sorbent capacity [mmol/g]
R	gas constant [J/mol.K]
r	reaction
s	sorption
T	temperature [K]
Δh_{ads}	enthalpy of adsorption [J/mol]
ϕ	molar flow rate [mol/s]

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