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In this publication the reaction is experimentally investigated in an indirectly operated reactor at different technically relevant but so far not investigated operating conditions. This in particular means the thermal charging and discharging of the storage at low water vapor pressures under different heating and cooling loads induced by a heat transfer fluid. The experiments revealed that the reaction gas handling not only affects the operating range of the storage but has also a significant influence on its thermal capability. Especially at low vapor pressures operational limits of the system have been identified and could be contributed to the effective reaction rate of the unmodified reaction material which is in the relevant operating range very sensitive to small changes of the local reaction conditions.

Highlights

Development of a novel indirectly heated reaction bed for thermochemical energy storage

Experimental demonstration of thermal charging and discharging at low vapor pressures (1.4 – 20 kPa)

Experimental study of the reaction at various heating and cooling loads of the heat transfer fluid

Identification of operational limits under some technically relevant boundary conditions

Thermochemical Energy Storage with $CaO/Ca(OH)_2$ – Experimental investigation of the thermal capability at low vapor pressures in a lab scale reactor

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Abstract

The reversible reaction of calcium hydroxide ($Ca(OH)_2$) to calcium oxide (CaO) and water vapor is well known in the context of thermochemical energy storage. Cheap material costs, a theoretically very high energy density and the potentially wide temperature range of the reaction imply that the storage system could be beneficial for many high temperature processes. For example the system could be applied to store and reutilize industrial waste heat or as an alternative storage solution in future concentrated solar power plants.

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1. Introduction

Thermochemical energy storage by means of the reversible gas solid reaction of calcium hydroxide ($Ca(OH)_2$) to calcium oxide (CaO) and water vapor offers several advantages. Firstly, calcium hydroxide is a cheap industrial mass product abundantly available all over the world. Secondly, the enthalpy of reaction is high which leads to high possible energy storage densities. Thirdly, the charge and discharge temperature of the reaction can theoretically be adapted in a wide range (approx. 300 – 650 °C). Thus the application of the system could potentially be beneficial for many high

temperature processes such as the storage and reutilization of industrial waste heat or as an alternative storage solution in future concentrated solar power plants [1, 2].

The reaction system has been examined in many studies but the majority of the studies focus on the thermal analysis of small sample masses. Already in 1979 Rosemary and his colleagues demonstrated cycle stability of the reaction for 1171 cycles [3]. Until today different research groups derive kinetic equations from de- and rehydration experiments carried out in thermogravimetric devices [4-6]. Beyond that other groups focus on the modification of the material in order to adapt the reaction temperature [7], enhance the reaction rate [8], or improve powder bed properties [9].

Besides these investigations on the material level, reports on experiments with lab scale reactors are scarce. Schaube et al. demonstrated the operation of a fixed bed reactor where the material is in direct contact with a gas mixture of air and water vapor [10]. Pardo et al. carried out the reaction in a fluidized bed reactor using a mixture of $Ca(OH)_2$ and 70 wt% inert easy to fluidize particles [11]. Yan et al. recently reported experiments with 400 g of material in a fixed bed set up. They analyzed the hydration reaction at different vapor pressures but the reactor concept did not allow the recovery of the released heat. Furthermore the dehydration reaction was driven by an electrical heating jacket [12].

All of these concepts have their special advantages and are worth investigating since at the current state of development an optimal reactor design is not available. However, some process applications require an indirectly heated concept. For example, if the heat transfer fluid of the process is liquid or a direct contact of the flue gas and the storage material could cause impurities. In both cases thermal energy has to be transferred via a heat exchanging surface that separates the reaction from the heat transfer fluid – a so called indirect concept. An additional advantage of this concept is that the reaction temperature can be adapted independently from the power output of the reactor. This in conclusion leads to more flexible operating modes and thus could extend process integration possibilities.

However for indirectly heated reactor concepts there is even less experimental data available. Ogura et al. were the first who demonstrated a concept where the heat released during the exothermic reaction was transferred via a heat exchanger to an air flow at ambient temperature [13]. The dehydration step though was still performed in a furnace. The first concept in which not only the discharging but also the charging step was driven by an indirect coupling of the reaction bed with a heat transfer fluid was presented from our group in a previous publication [14]. On one hand the reactor showed good performance especially for the discharge at reaction gas pressures of 100 kPa and higher. On the other hand the design of the reaction bed limited the operating range of the reactor. Particularly at low vapor pressures (e. g. 10 kPa) the performance during charging and discharging was significantly limited. We mainly contributed this limitation to the mass transfer of the reaction gas due to the low permeable reaction bed and its height of 200 mm.

Nevertheless, as soon as energy efficient process integration is considered, the operation of the storage system at low vapor pressures is of high technical relevance. There are two main reasons for that. Firstly, the dehydration at lower vapor pressures results in a lower reaction temperature. As a consequence we can use lower grade heat to charge the storage. Secondly, the hydration at lower vapor pressures requires only a reduced evaporation temperature. Therefore the enthalpy of evaporation can more likely be supplied by waste heat available from the process.

Fig. 1 shows the experimentally obtained equilibrium lines of the reaction system $Ca(OH)_2/CaO$ from Schaube [4] and Samms [15] as well as the theoretical equilibrium line based on thermochemical values from Barin [16]. In addition reported onset temperatures, determined in thermogravimetric measurements from Schaube [4] and Matsuda [17] are displayed as well as the results of equilibrium measurements performed by Halstead [18] in an appropriate test bench. It is obvious that within the important operating range for indirect concepts at low vapor pressure (marked as grey area), the results vary significantly. This may be on one side contributed to differences in the used material but on the other side also the measurement principle itself (e. g. dynamic or static) might have an influence.

In order to investigate the reaction for thermochemical storage under technically relevant operating conditions, we designed a novel reaction bed with minimized mass transfer limitations but a sufficient mass of reactive material to investigate thermal capabilities. With this reactor we performed several charging and discharging experiments at low vapor pressures and analyzed the influence of different heating and cooling loads induced by a heat transfer fluid. The operating conditions for the kg-scale experiments presented in this study are marked in Fig. 1 by the red triangles for the dehydration and the red squares for the hydration. For the analysis of the results, the experiments in lab-scale were complemented by thermogravimetric measurements in mg-scale with the same material.

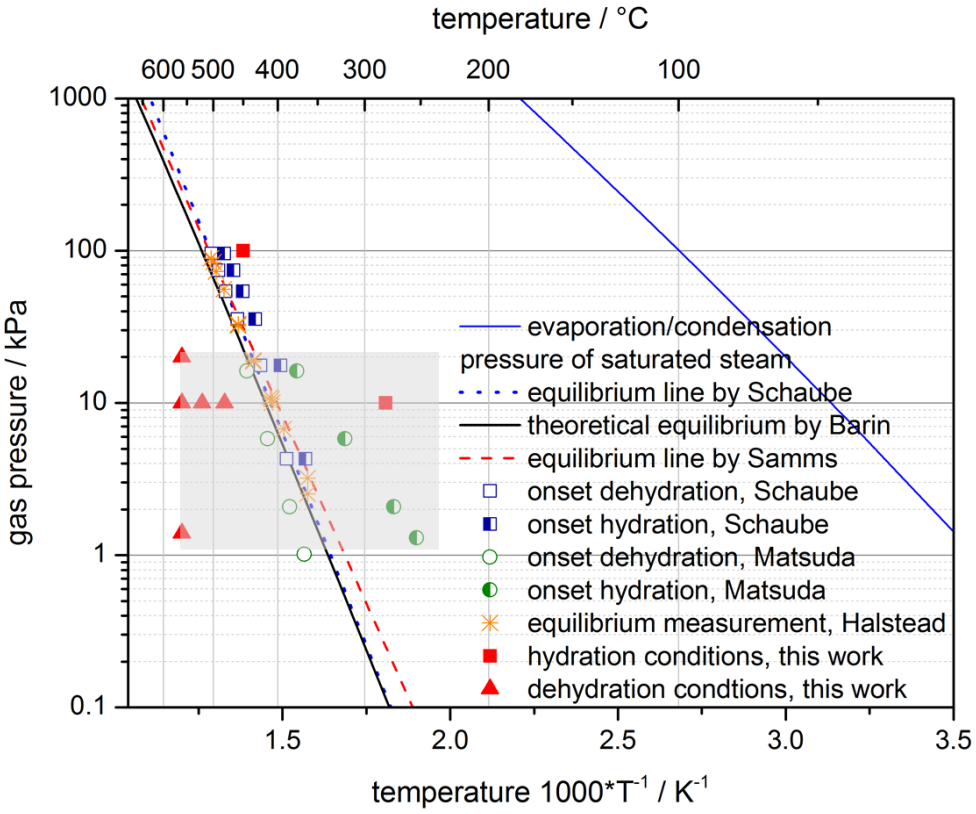


Fig. 1 *Thermodynamic equilibrium lines for the $Ca(OH)_2/CaO$ reaction system and operating conditions of the performed experiments; evaporation/condensation pressure of saturated steam*

2. Experimental Set Up

2.1 Reactor

The aim of the reaction bed development was to analyze the performance of the storage material for a wide operating range. The main limitations that are generally contributed to the reactor (not to the material) are mainly caused by the low permeability and the poor thermal conductivity of the bulk material. Bearing in mind to minimize these limitations without affecting the material properties we derived two important design constraints for the novel reactor. First of all, the reaction gas should only pass through a very thin layer of storage material. Secondly, the furthest distance between a single particle and the heat exchange surface should be short. Both design constrains would in principle lead to a very small mass of reaction material. In contrast a representative mass of reaction material is mandatory, in order to be able to operate the material according to the later application as thermochemical storage and to allow for both: a proper analysis of the thermal capability of the reaction and the analysis of the impact of the indirect heating or cooling.

Taken all design constraints into account it is obvious that the reactor has to offer a reasonable compromise between a reactor for investigations and a reactor for thermochemical energy storage. For this purpose, we choose a single heat exchanger plate as the basis for our reaction bed (see Fig. 1, top). In this concept, the heat transfer fluid, air, flows inside the plate while the storage material lies on the plate. The plate is on both sides surrounded by a metallic frame of 10 mm height. The inner sides of the frame measure 150 mm in width and 1600 mm in length giving us 0.48 m² heat exchange surface. Consequently the reactor offers a cubic volume of 4.8 l (2.4 l on each side of the plate) for the storage material (see Fig 2., bottom left). A gas permeable metallic filter (pore size is 5 µm) placed over the powder material and screwed to the frame encases the reaction bed (see Fig 1., bottom right). The large filter area allows for a negligible pressure drop between the powder material and the reaction gas supply.

Fig. 2 *Top: heat exchanger plate used as reactor; bottom left: storage material filled into the frame; bottom right: filter plate to encase the reaction bed*

The heat exchanger plate with the encased bed on both sides is mounted into a pressure resistant casing pipe. Fig. 3 shows a sectional view of the whole set up including important dimensions and positions of the measurement instruments. To observe the reaction progress seven thermocouples $\delta_{1\text{-}7}$ (type K, ± 0.4 % X T) are located in the middle of the beds height, at a vertical distance of 5 mm to the heat exchange surface. In the horizontal direction of air flow the distance between each measurement point is 200 mm with the first point 200 mm away from the beginning of the reaction bed. Additional thermocouples measure the air temperature directly at the air in- ($\delta_{Air,in}$) and outlet ($\delta_{Air,out}$) of the plate. Furthermore a pressure sensor p_1 (PPA-35XHTT, Keller Ges. für Druckmesstechnik mbH, ± 0.8 kPa) measures the gas pressure in the reaction chamber.

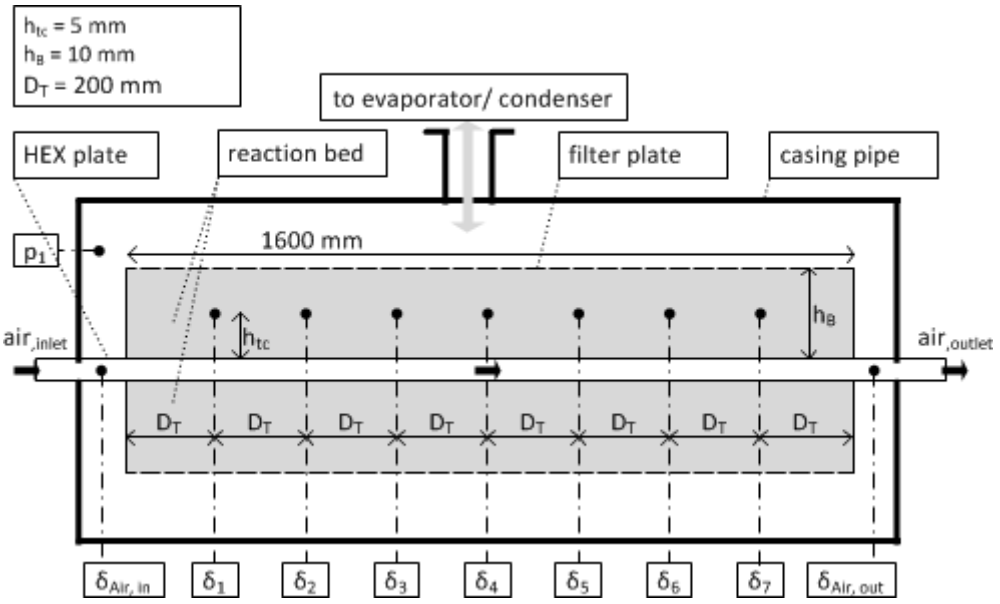


Fig. 3 *Sectional view of the reaction bed in the casing pipe including important dimension and positions of thermocouples and the pressure sensor*

2.2 Material

All experiments presented in this paper we performed with $Ca(OH)_2$, product type "Sorbacal®H", supplied by Rheinkalk GmbH/Lhoist group. Based on the products data sheet the purity of the material is approximately 98 % the specific surface area is 19 m²/g and the d_{50} is 5.5 µm.

2.3 Test bench

Fig. 4 shows the schematic process flow diagram of the test bench. The test bench was designed to operate the reactor under different thermal load conditions and at a wide range of vapor pressures. Therefore it was most important to be able to adjust the thermal power of the heat transfer fluid and the vapor pressure in the reaction chamber independently of each other.

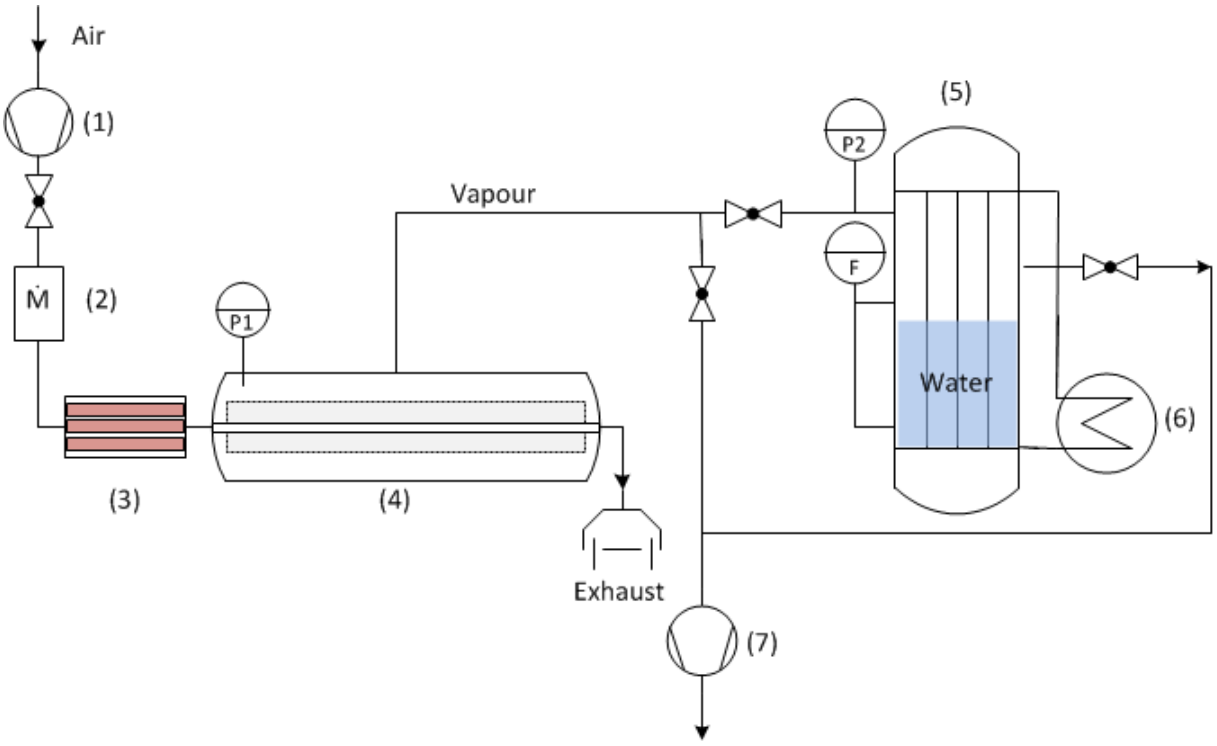


Fig. 4 *Layout of the test bench*

Heat transfer fluid supply

Due to the required temperatures, ambient air is used as heat transfer fluid in the experiments and is supplied by a compressor (1). The air volume flow can be adjusted with a mass flow controller (2) (Bronkhorst, digital flow controller, ± 0.4 %) before it splits up and enters three parallel electrical heating units (3). Each heating unit has an electrical power of 2 kW and preheats the air to a maximum temperature of 600 °C. After these heating units the air flows merge again in a diminishing pipe. This diminishing pipe is equipped with a controllable auxiliary heating to ensure a homogenous air temperature at the reactor inlet.

Reaction gas handling

During an ongoing reaction we must either remove water vapor from or supply it to the reaction bed. To realize this, a tube bundle heat exchanger (5) and a vacuum pump (7) are connected to the reactor. With the vacuum pump inert gases are removed from the system ensuring a pure vapor atmosphere. The tube bundle heat exchanger operates as condenser or evaporator depending on the direction of reaction. A thermal oil flows inside the tubes of the bundle. The oils inlet temperature can be tempered between 3-160 °C by a thermostatic bath (6). On the shell side is liquid water (for condensation or evaporation) and the water temperature can be kept constant during experiments because the thermal oil takes up the heat of condensation or supplies the heat of evaporation. Accordingly the evaporation/condensation pressure in the system can be varied between 0.7 - 618 kPa and be kept constant during an ongoing reaction. A pressure sensor at the outlet flange measures the pressure in the evaporator/condenser and the change of the water level is measured with a filling level meter (Vegaflex 65, ± 2 mm). By means of this value we can monitor the reaction and calculate its conversion.

2.4 Experimental procedure

For all experiments presented in this paper only one batch of the material described in 2.2 is used. In total 2.4 kg are filled in the reactor, equally distributed on each side of the heat exchanger plate.

Before every experiment the whole set up is evacuated to 0.5 kPa ± 0.3 kPa and afterwards all valves are closed. The reactor is preheated to a set starting temperature with the air volume flow and additional auxiliary heating cables attached to the casing pipe. Simultaneously we adjust the vapor pressure for the experiment in the condenser/evaporator by the thermostatic bath. As soon as the pressure in the condenser/evaporator and the temperatures in the reaction bed stay constant an experiment can be started.

The different operating conditions were shown above (compare Fig. 1). From the equilibrium line for water and saturated steam (blue solid line in Fig. 1) the operating temperature of the condenser/evaporator at the required pressure can be determined. Besides the different temperatures, in some experiments the volume flow of the heat transfer fluid has also been varied. The volume flows as well as an overview of all parameters of each presented experiment is given in Table 1.

Thermal charging procedure (Dehydration)

At the beginning of each dehydration only $Ca(OH)_2$ is in the reactor and the set up is preheated to a temperature below the equilibrium temperature of the reaction at the adjusted vapor pressure. To start the experiment the valve between condenser and reactor is opened and simultaneously the air inlet temperature is increased to the set dehydration temperature (marked with red triangles in Fig. 1). The induced heat load drives the dehydration reaction. Accordingly water vapor comes out of the reaction bed and condenses in the condenser. When no further increase of the water level is observed the dehydration is finished.

Thermal discharging procedure (Hydration)

At the beginning of every hydration experiment only CaO is in the reactor and the set up is preheated to a set starting temperature (marked with red squares in Fig. 1) below the equilibrium temperature of the adjusted evaporation pressure. To start the experiment the valve between reactor and evaporator is opened. In that moment water vapor streams into the reaction chamber and initiates the exothermic hydration reaction. The air flow takes up the heat of reaction as long as the reaction proceeds. The experiment is finished as soon as the temperature in every region of the reaction bed has reached its starting value.

Tab. 1 *Parameters of all experiments presented in this study*

Experiment	$T_{air,\ initial}$ / °C	$\dot{V}$ / $\frac{Nm^3}{h}$	$T_{dehydration}$ / °C	$p_{condenser/\ evaporator}$ / kPa	T_{water} / °C
Dehydration					
A	400	20	560	10	45
B	400	12	560	10	45
C	400	12	520	10	45
D	400	12	480	10	45
E	400	12	560	19.9	60
F	400	12	560	1.4	12
Hydration					
G	280	20	-	8.7	43
H	280	16	-	8.7	43
J	280	12	-	8.7	43
M	450	12	-	100	100

2.5 Thermogravimetric analysis

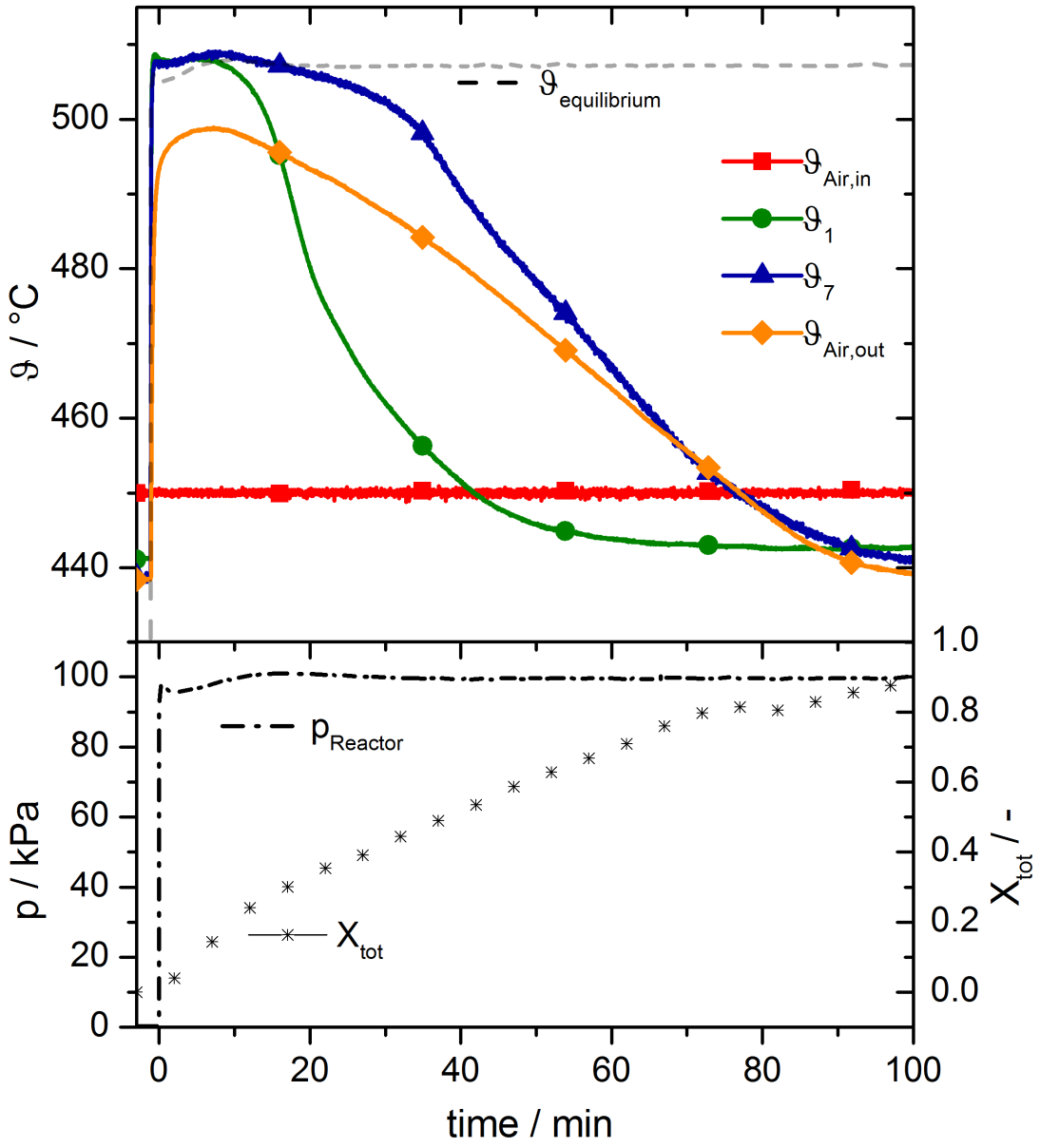
To compare some results observed in the reactor a small sample mass (10 mg) of the same batch has additionally been analyzed in the thermogravimetric analysis (TGA). For these experiments a NETZSCH simultaneous thermal analysis (STA 449 F3 Jupiter ®) was used, equipped with a molar humidity generator (MHG32). The atmosphere during the measurements was inert using nitrogen, or a mixture of nitrogen and water vapor as purge gas (surrounds the sample) and pure nitrogen as the protective gas. The pressure inside the furnace was ambient pressure at ~97 kPa and a volume flow of 100 ml/min of purge gas was used. The bottom of the furnace was heated to 120 °C and a protection gas volume flow of 20 ml/min nitrogen was supplied, in order to protect the thermo-balance of condensation drops. The furnace design does not allow the mixing between the purge and protective gases, thus the protective gas flow does not affect the concentration of humidity inside of the furnace. With this set up we were able to conduct isothermal hydration and dehydration experiments in the TGA at vapor pressures comparable to the conditions in the reactor.

3. Results and Discussions

3.1 Set in operation

In order to prove the correct function of the reactor and the measurement equipment a hydration experiment at an evaporation pressure of 100 kPa according to the procedure as described in 2.5 was performed.

Fig. 5 shows the results of the experiment. We keep the air inlet temperature $\delta_{Air,in}$ (red solid line) constant at 450 °C during the experiment. At t = 0 min we open the valve between evaporator and reactor thus the pressure in the reactor rises to 100 kPa (black dash dotted line). Consequently the temperatures in the reaction bed δ_1 (green solid line) and δ_7 (blue solid line) jump up to a maximum of 507 °C. This temperature accords to the theoretical equilibrium temperature (grey dashed line) which was calculated by the measured pressure and the respective correlation given by Samms et al. [15] (compare Fig. 1). We also observe a reaction front along the flow direction of the air. Close to the air inlet the cooling of the reaction bed is maximal due to the largest temperature difference between the bed and the air. Thus the reaction proceeds quickly and 10 min after the initiation the temperature δ_1 drops again. This indicates that a major part of the material is already converted in this region and the heat released by the reaction decreases. In contrast in the rear region of the reactor the temperature between the bed and the air flow is small in the beginning. As a consequence the reaction proceeds slower indicated by the constant temperature plateau which is hold for 25 min. As more and more material has reacted in this part also the temperature δ_7 starts to drop. After 100 min the bed reaches its initial temperature again indicating that no more heat is released. Accordingly, a conversion of 95 % (black cross dots) is measured at this time. The Difference before and after the reaction between air inlet temperature and temperatures inside the reaction bed are contributed to radiative heat losses inside the reaction chamber, that have been minimized but cannot be completely removed.



242 **Fig. 5** *Hydration experiment at 100 kPa and a starting temperature of 450°C*

3.2 Thermal charging

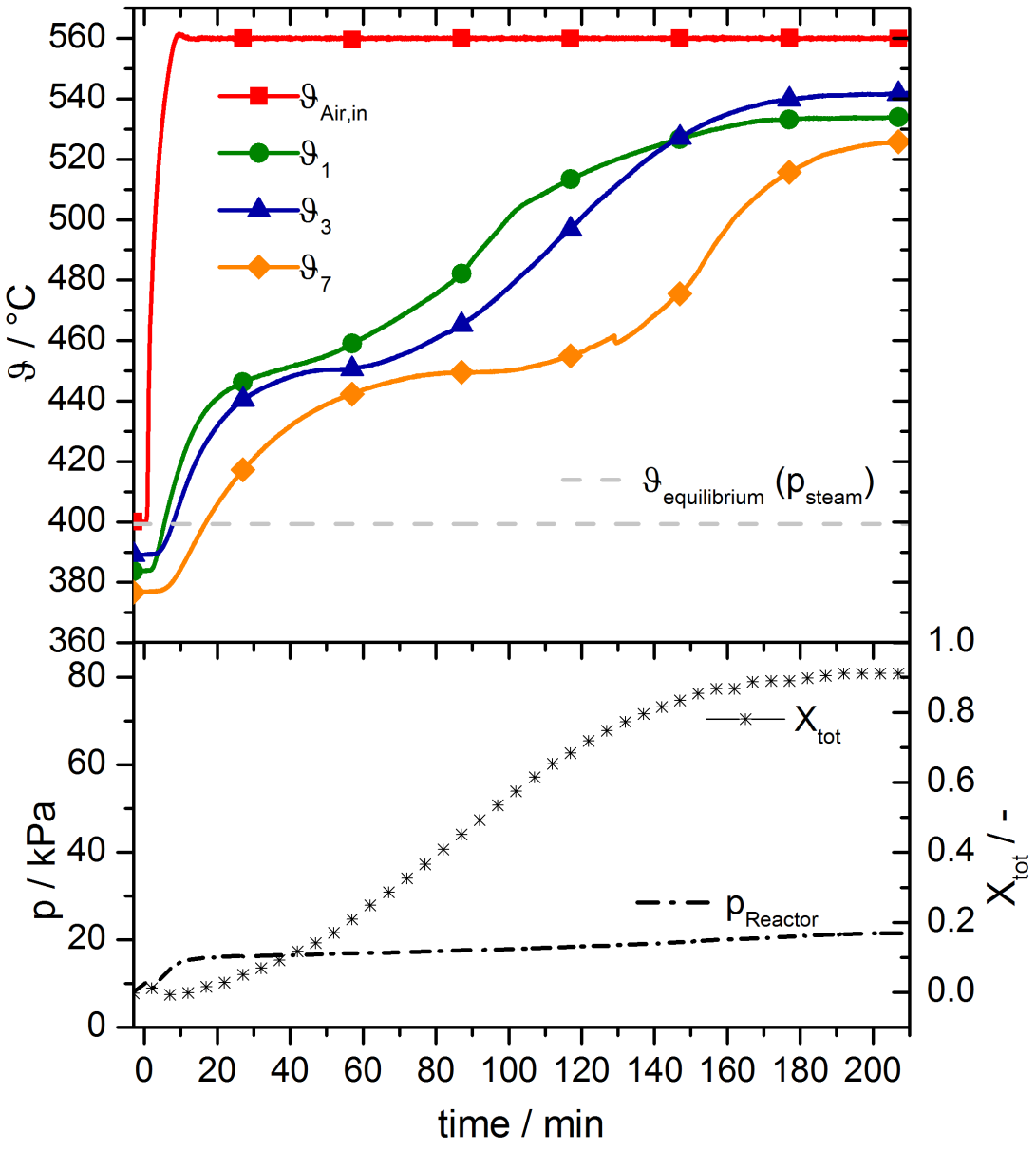


Fig. 6 *Dehydration experiment at 10 kPa and a dehydration temperature of 560 °C*

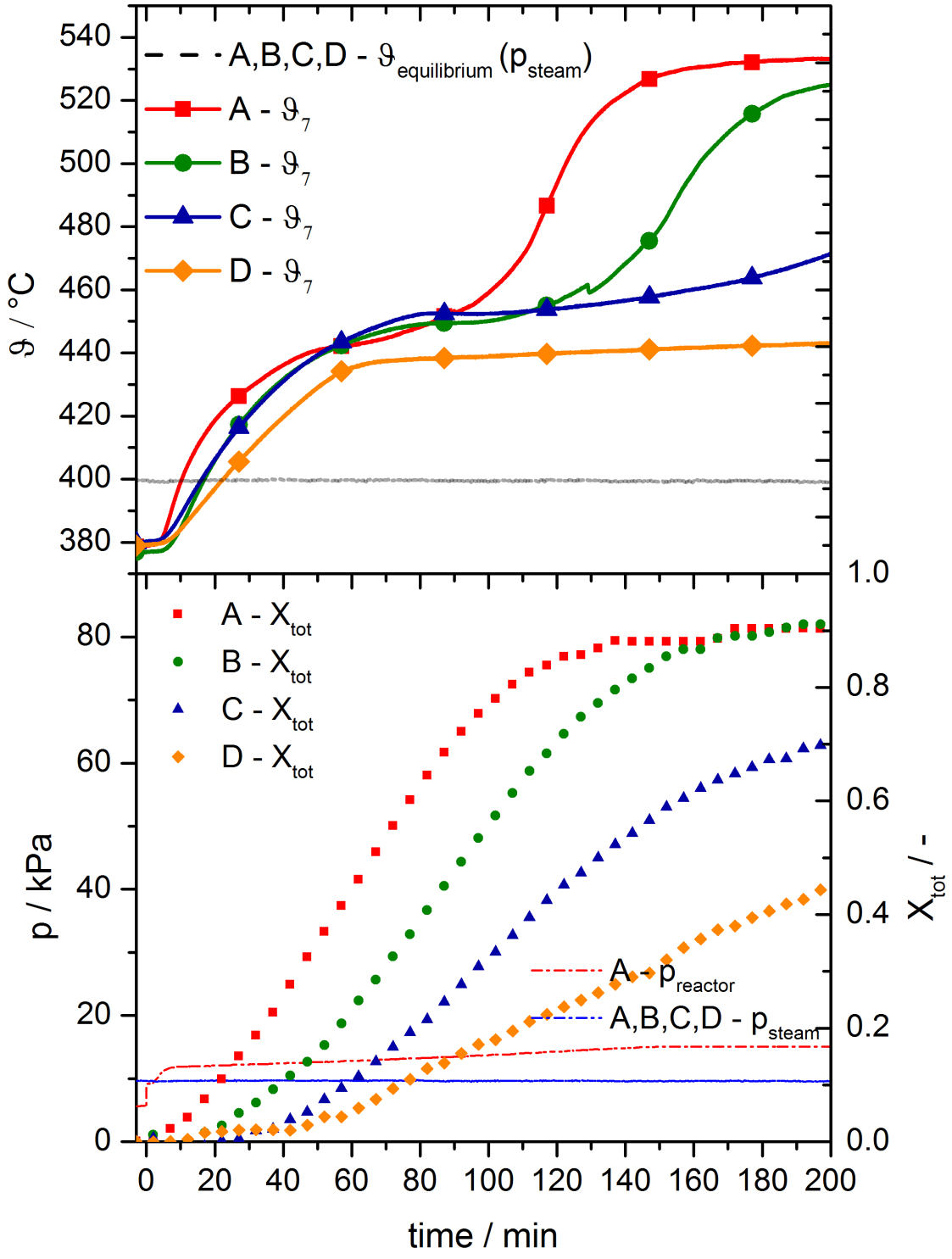
A reference dehydration experiment has been performed with a preheating temperature of 400 °C and a condensation pressure of 10 kPa (condensation temperature 45 °C). Fig. 6 shows the temperature, pressure and conversion trends. At t = 0 min the air inlet temperature starts to rise up to the set dehydration temperature of 560 °C (red solid line). Exemplarily the temperatures δ_1 (green solid line) δ_3 (blue solid line) and δ_7 (orange solid line) positioned in the front, middle, and rear region (compare Fig.2) of the bed are plotted. Within the first 30 min the material temperatures increase to 445 °C due to the incoming heat flux. At a temperature of 445 °C a significant change occurs in the slope of the temperature trend. In particular in the middle (δ_3) and rear region (δ_7) of the bed a temperature plateau can be observed. The temperature plateau indicates that the heat input from the heat transfer fluid is completely absorbed by the endothermic reaction. Accordingly during this

time we also observe that the conversion trend (black cross dots) shows a constant rate indicating the ongoing reaction with a constant thermal charging power. After 120 min almost 80 % of the material is converted thus the heat input in the rear region slowly becomes larger than the amount of heat which is still absorbed by the endothermal reaction. Consequently the material temperature rise again until after 200 min a conversion of 96 % is reached and all bed temperatures reach their constant maximum. What might seem controversy is that the temperature plateau lies at 445 °C while the equilibrium temperature at the condensation pressure of 10 kPa is 400 °C (grey dash dotted line). This significant distance to the theoretical equilibrium temperature was further analyzed with a variation of thermal power of the heat transfer fluid.

Variation of heat load of the heat transfer fluid

In order to analyze the influence of the thermal power of the heat transfer fluid on the dehydration reaction, we performed the dehydration experiments at a condensation pressure of 10 kPa with 4 different thermal heat fluxes into the reaction bed. The results are shown in Fig. 7. Experiment A (red curves) runs with a 60 % higher volume flow than the reference experiment B (green curves) but with the same dehydration temperature of 560 °C. Experiment C (blue curves) and D (orange curves) run with the nominal volume flow but at reduced dehydration temperatures of 520 °C respectively 480 °C (compare Table 1. for all parameters). The conversion curves show that the influence of the heat flux into the bed directly correlates with the speed of conversion. With the largest heat flux we receive the shortest dehydration time (red squares – experiment A), whereas smaller heat fluxes prolong the dehydration times (B, C, D).

Fig. 7 also shows the temperature trend of δ_7 for every experiment. We can see that independently from the heat flux into the bed, the material temperatures increase within the first 30 min. This indicates that initially the reaction speed is so slow that the incoming heat flux is larger than the thermal energy absorbed by the reaction. However a constant temperature plateau develops at temperatures above 440 °C for all experiments. In general, a temperature plateau region during dehydration is characterized by an equilibrium state between the thermal energy absorbed by the endothermic reaction and the heat flux delivered by the heat transfer fluid. It is remarkable that in the experiments A, B and C the plateau lies at the same temperature of 445 °C independently of the heat flux into the reaction bed. This supports the hypothesis of a limitation that is due to material intrinsic properties which in turn would lead to a serious limitation of the operating range of this thermochemical storage: In contrast to the hydration experiment at 100 kPa (compare Fig. 5) where the operating range can be basically derived from the equilibrium line, the measured plateau temperature of 445 °C for these experiment is around 45 K higher than the value predicted by the equilibrium line. Only in experiment D the plateau temperature is slightly lower at 440 °C - but at the same time the charging power seems not anymore of technical relevance due to its long dehydration time. In order to further analyze this important aspect for the operation flexibility of a thermochemical energy storage based on Ca(OH2), we performed additional experiments by thermogravimetric analysis.



293 **Fig. 7** *Dehydration experiments at 10 kPa at different heat loads of the heat transfer fluid*

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Dehydration at 10 kPa in the TGA

The experiments in the TGA were performed according to the procedure described in 2.6 and conditions comparable to the reactor experiments. The main differences to generally reported TGA data for Ca(OH)2 are isothermal measurement conditions at very low gas pressures. Seven different dehydration experiments at a humid atmosphere inside the furnace of 10 kPa and isothermal temperatures between 400 °C and 450 °C were conducted. Each temperature was remained constant for 1 hour while the mass change was measured.

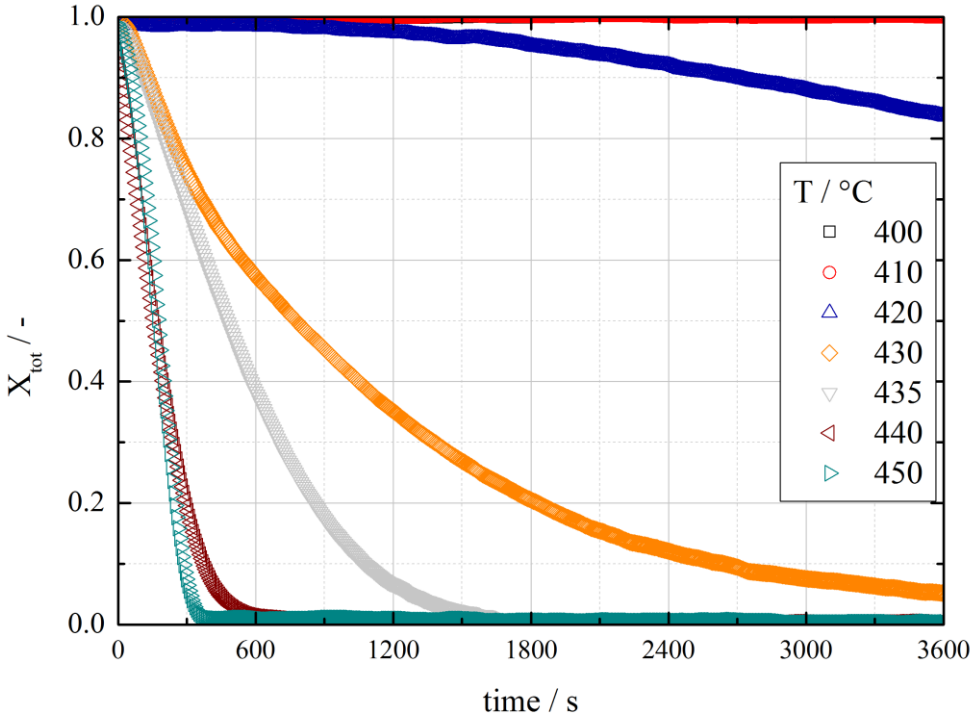


Fig. 8 *Effect of the temperature on the dehydration reaction of Ca(OH) at a vapor pressure of 10 kPa*

Fig. 8. shows the conversion trend of $Ca(OH)_2$ to CaO at different isothermal measurements. It can be observed that at 400 °C and 410 °C no mass change occurs within 1 hour. At 420 °C a small mass change was measured, while at 430 °C the rate of conversion changes significantly but conversion is still incomplete after 1 hour. At 435 °C we reach full conversion after 30 min - but with only a slight increase of 5 K to 440 °C the dehydration time is reduced to less than 10 min. A further increase to 450 °C does not result in a significantly faster conversion.

The results from the thermogravimetric analysis accord to what was observed in the reactor. Below a temperature of 440 °C the reaction rate is rather slow thus the heat flux into the reaction bed is always higher than the thermal energy absorbed by the reaction. As a consequence the reaction bed heats up sensible. When we exceed 440 °C the reaction becomes so fast that the heat flux into the reaction bed is completely absorbed by the endothermic reaction. Consequently a constant temperature plateau forms. With regard to a later application of $Ca(OH)_2$ as thermochemical storage, it can be concluded that the unmodified material possesses a kind of tipping point: at a condensation

pressure of 10 kPa (corresponding to a condensation temperature of 45 °C) a charging temperature of at least 445 °C is required to achieve technically relevant charging times (less than two hours).

Variation of condensation pressure

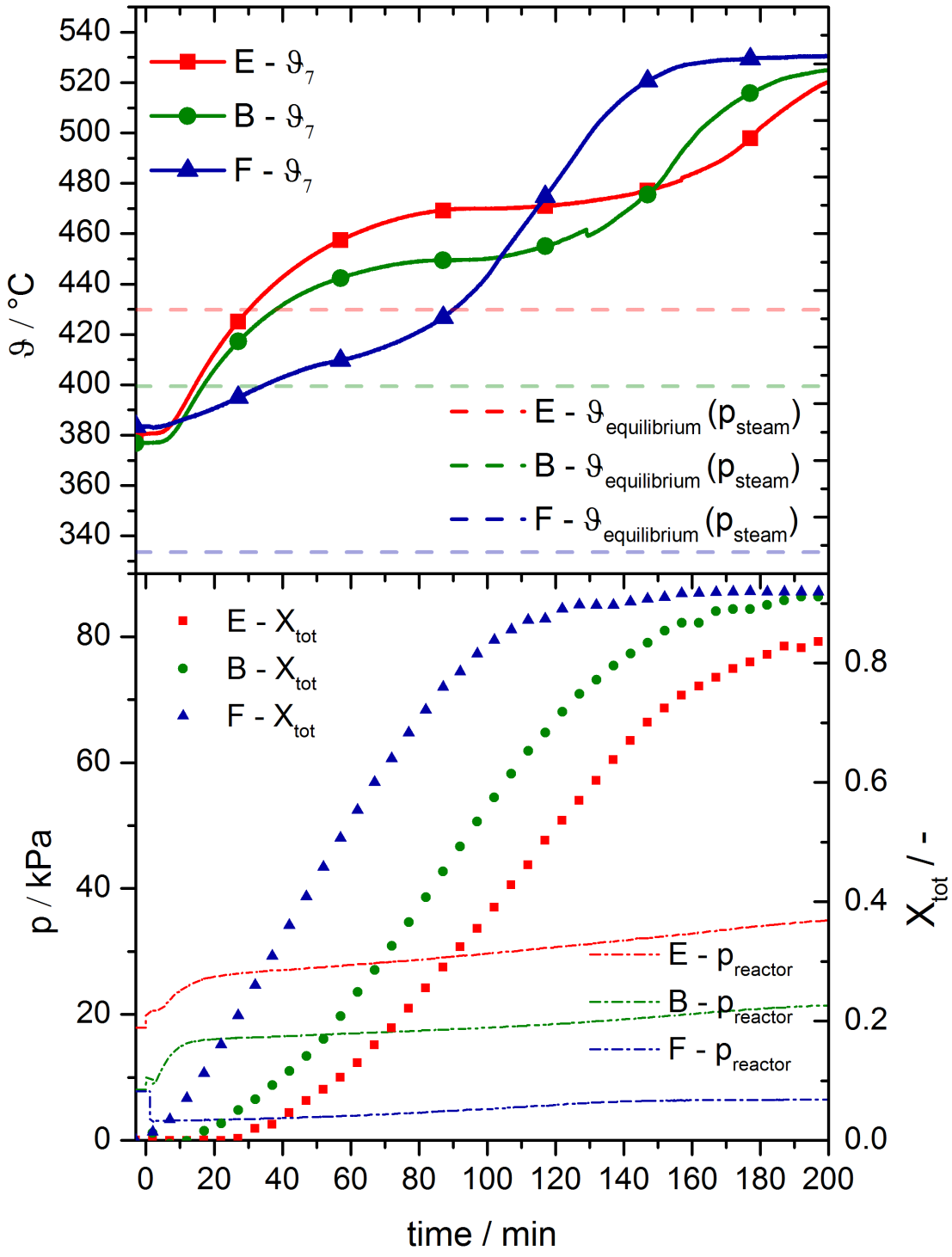


Fig. 9 *Dehydration experiments at 1.4, 10 and 20 kPa and a dehydration temperature of 560 °C*

In order to examine the influence of the condensation pressure on the dehydration time and the charging temperature we performed experiments at three different condensation pressures but at the same heat load induced by the heat transfer fluid. Experiment B (green line) is the reference dehydration experiment at 10 kPa while experiment E (red line) is performed at 20 kPa and experiment F (blue line) is performed at 1.4 kPa. Each experiment was run with the nominal volume flow and the air inlet temperature was increased to 560 °C. From the conversion curves we can clearly see, that the lower the condensation pressure the faster we reach full conversion. For example for experiment F 80 % is converted after 80 min while for experiment B 80 % conversion is achieved in 120 min, respectively in 180 min for experiment E.

Even more interesting are the plotted temperature trends for the rear region of the bed. We can see that for the experiments at 10 kPa and 20 kPa the temperature trends are qualitatively similar. The material heats up sensible in the beginning until the reaction becomes as fast that we reach an equilibrium state between heat influx into the reaction bed and the thermal energy absorbed by the reaction (indicated by the constant temperature plateaus). In all cases we observe that the above discussed temperature difference to the theoretical equilibrium temperature (red, green and blue dashed line) is required. However the difference tends to be smaller for higher dehydration pressures: the difference is 35 K at 20 kPa, 45 K at 10 kPa and more than 50 K for 1.4 kPa (compare Fig. 9). But even though a smaller temperature difference to the equilibrium is required at 20 kPa the dehydration temperature at which reasonable reaction rates can be realized is already 465 °C. From a process integration point of view this means energy at a higher temperature is required to charge the storage. If the condensation pressure is lower the dehydration can be performed faster and at lower temperatures which would be favorable for the integration of the storage system (lower charging temperatures are required). However it must be taken into account that a lower condensation pressure might require an additional cooling load for the condenser.

3.3 Thermal Discharge

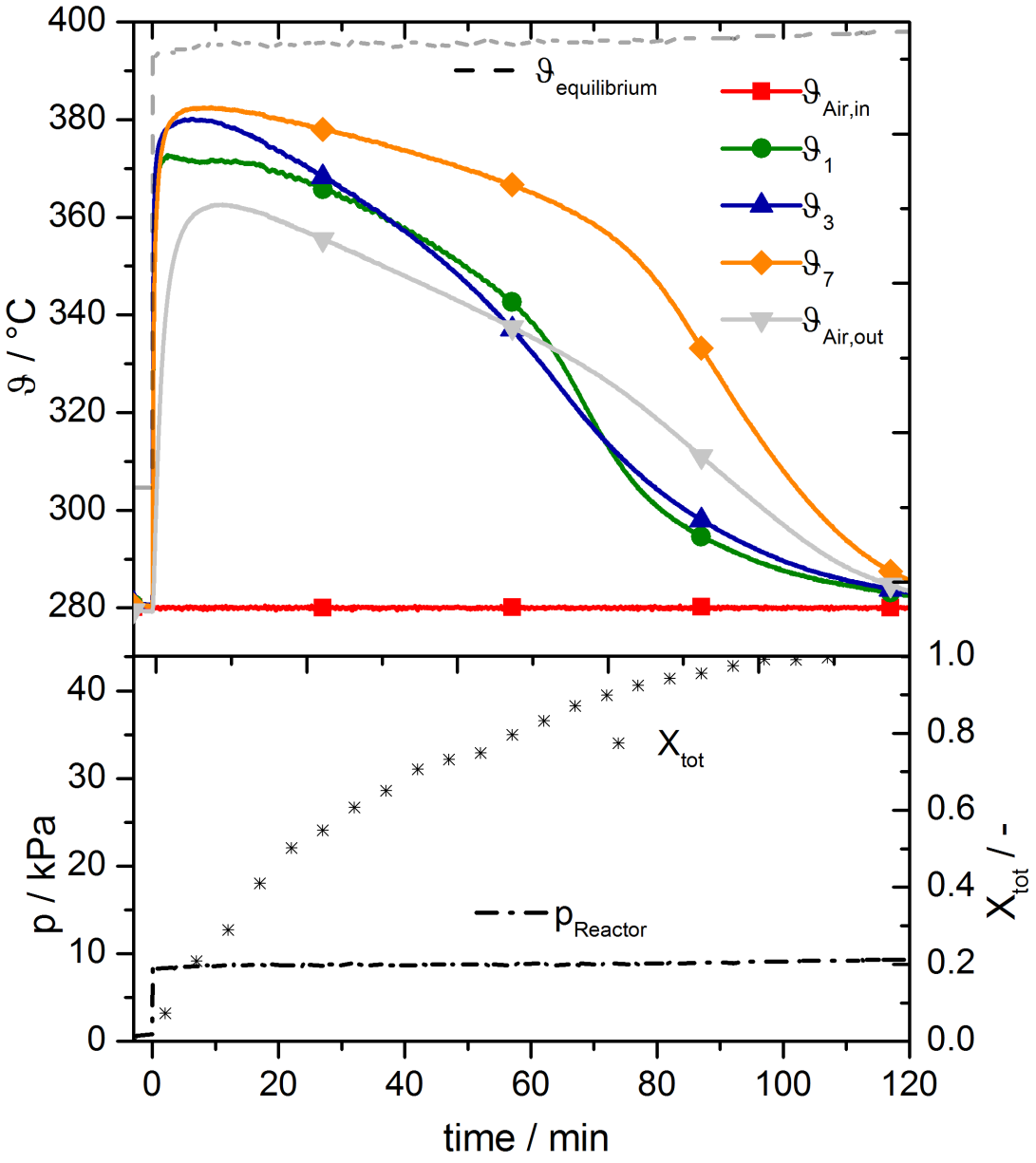


Fig. 10 *Hydration experiment at 8.7 kPa and a starting temperature of 280 °C*

Fig. 10 shows a reference experiment for the thermal discharging. The initial temperature was set to 280 °C and the evaporator was tempered at 43 °C. At min 0 the valve between evaporator and reactor is opened and the pressure in the reactor increases to ~8.7 kPa (compare black dash dotted line in Fig. 10). In the moment when the vapor enters the reactor the bed temperatures escalate (compare δ_1, δ_3 and δ_7 in Fig. 10) due to the heat released by the exothermic reaction. It seems that in the front (δ_1) and middle region (δ_3) of the bed the temperatures reach slightly lower maxima than in the rear region (δ_7). This can be ascribed to the higher cooling load of the reaction bed closer to the air inlet where the temperature difference between bed and the incoming air is maximal.

In the rear region the temperature in the bed reaches a maximum of ~383 °C and stays constant for approximately 20 min. In contradiction to the discharging experiment at 100 kPa (compare Fig. 5), in this case, at lower vapor pressures, a deviation of the plateau temperature from the equilibrium line of 15 K is observed. Since it is lower than the theoretical equilibrium temperature of the reaction (grey dashed line) one could dedicate this observation again to the reaction rate at given conditions: Initially, at the beginning of the experiment, the rate of reaction is high since the temperature difference between the start temperature of 280 °C and the theoretical equilibrium temperature of 398 °C is large. As a consequence more heat is released by the exothermic reaction than removed by the heat transfer fluid which leads in turn to increasing temperatures. The increasing temperature directly leads to a deceleration of the reaction rate. In contrast to the reference experiment at 100 kPa, at lower vapor pressure the deceleration of the heat release seems more pronounced since the temperature predicted by the theoretical equilibrium line is in this case not reached.

Variation of cooling load of the heat transfer fluid

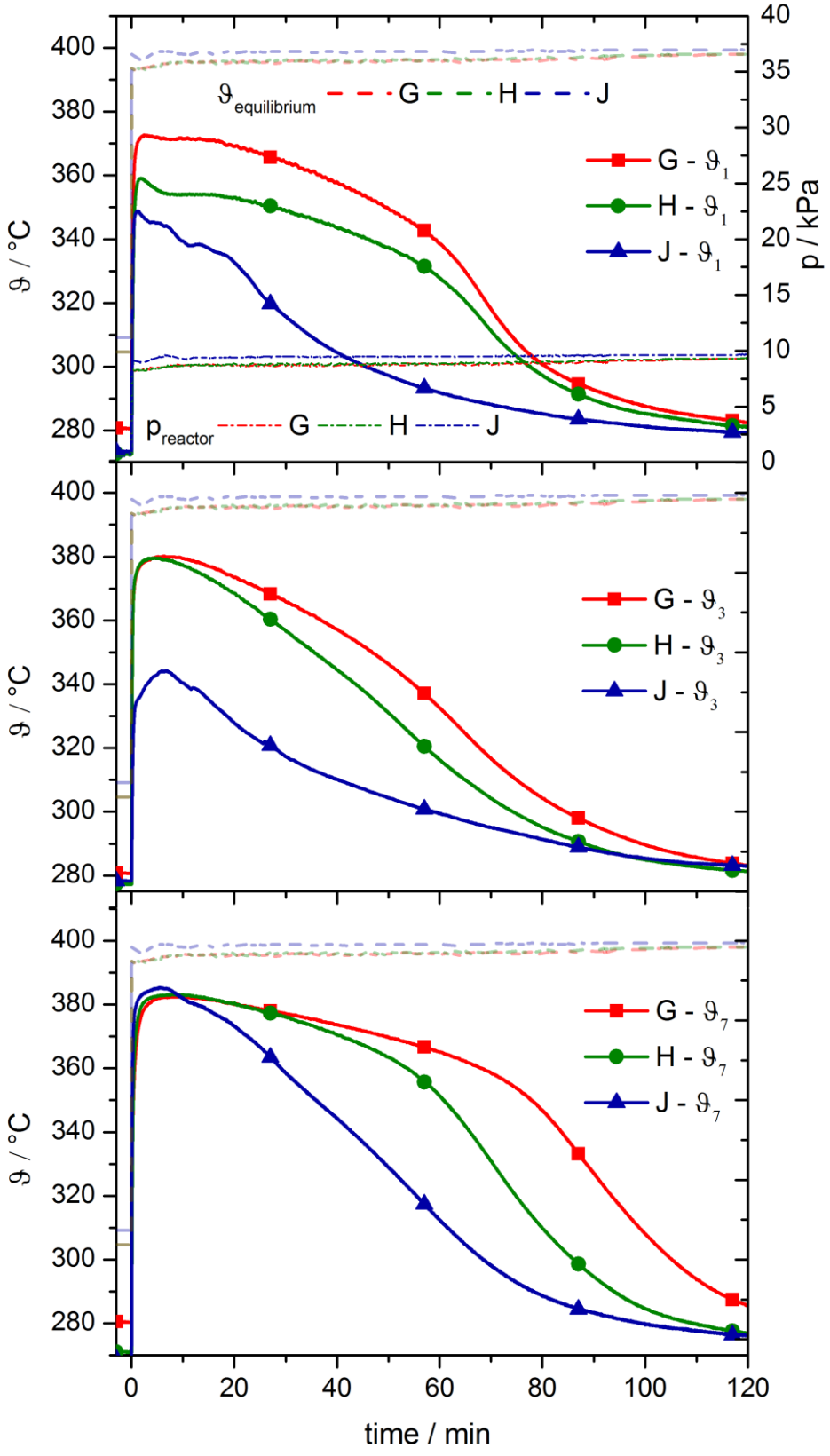
To analyze the influence of different cooling loads on the discharge temperature experiments at three different volume flows of the heat transfer fluid have been conducted. The results are shown in Fig. 11. Experiment G (red solid lines) was run with the nominal volume flow of 12 Nm^3/h while in the experiments H (green solid line) and J (blue solid line) the volume flow was increased to 16 Nm^3/h and 20 Nm^3/h. In all cases the air inlet temperature was set to 280 °C and the exothermic reaction was induced by a gas pressure of 8.7 kPa. The temperature trends in the front (δ_1), middle (δ_3) and rear region (δ_7) of the bed are plotted.

In particular in the front region of the reaction bed (compare δ_1, first diagram of Fig. 11) the reached temperatures directly correlate with the volume flow of the heat transfer fluid, respectively the cooling load of the reaction bed. The experiment with the highest cooling load shows the lowest temperature maximum of ~350 °C (blue curve). Whereas the experiment with the medium cooling load (green curve) shows a kind of plateau at ~355 °C and a clear temperature plateau lies at 370 °C for the experiment with the lowest cooling load (red curve). Again, temperature plateaus indicate an equilibrium state between the heat released due to the exothermic reaction and the heat taken up by the heat transfer fluid. Closer to the equilibrium temperature the reaction decelerates thus less heat is released. Accordingly the plateau for lower cooling loads is at higher temperatures. If the cooling load increases, the temperature plateau arises at lower temperatures, since at temperatures further away from the equilibrium temperature, the reaction rate accelerates. This trend can be observed in the first diagram of Fig. 11 even though the experiment with the highest cooling load (blue) reaches rather a peak than a plateau.

In the middle region of the reactor (δ_3, second diagram Fig. 11) we observe that the material temperature for the experiment with the highest cooling load still remains below 350 °C while for the other two experiments the same maximum temperature of 380 °C is reached. In the rear region of the reactor (δ_7) the same maximum temperature of around 380 - 383 °C is reached for all experiments. At this position the temperature difference between the reaction and the heat transfer fluid is rather small since the heat exchange takes first place in the front and later in the middle region of the reactor. However, still the maximum temperature is approximately 15 K below the thermal equilibrium.

Since for these experiments, the inlet temperature was kept constant, the temperature difference between the reaction and heat transfer fluid was generated by the exothermic reaction itself. In

contrast to physical storages, in this case a high local heat flux is characterized by a reaction at a lower temperature level (compare values for highest heat flux at the front region). Consequently, one can conclude that this leads in turn to an optimization question for the later application of the thermochemical storage: for low vapor pressures, high power densities directly reduce the quality (temperature level) of the discharged thermal energy. Additionally, comparable to the charging experiments, a material intrinsic tipping point seems to limit the maximum reaction temperature at 8.7 kPa to around 15 K below the theoretical equilibrium. To investigate this hypothesis additional isothermal hydration experiments have been conducted by TGA.



408 **Fig. 11**: *Hydration experiments at 8.7 kPa under different cooling loads of the heat transfer fluid*

Hydration at 8.7 kPa in the TGA

To support the findings observed in the reactor we examined the rate of reaction under comparable operating conditions in the thermogravimetric analysis. Before every hydration cycle, $Ca(OH)_2$ was dehydrated under nitrogen atmosphere. The hydration experiments were performed at a water vapor pressure of 8.7 kPa and at different isothermal temperatures between 390 °C and 110 °C. The hydration temperature was reduced about 10 K in each following cycle.

Fig. 12 shows the conversion trends for the experiments. We can see that for temperatures between 391 °C (theoretical equilibrium is 398 °C) and 367 °C almost no material has reacted after one hour. At 357 °C approximately 30 % of the material is hydrated after 1 hour while at 347 °C almost 80 % is hydrated within the first 20 min. At a temperature of 337 °C we achieve 80 % of conversion within 10 min while at temperatures below 300 °C the conversion accelerates only slightly.

One can conclude that at temperatures above 360 °C the rate of reaction is rather slow while at temperatures below 350 °C the rate of reaction quickly accelerates. Consequently, one can state that the tipping point for a technically relevant discharge reaction of the Ca(OH)2 with a vapor pressure of 8.7 kPa (corresponding to an evaporation temperature of 43 °C) is at around 350 °C. This value is around 48 K below the theoretical discharge temperature according to the equilibrium line.

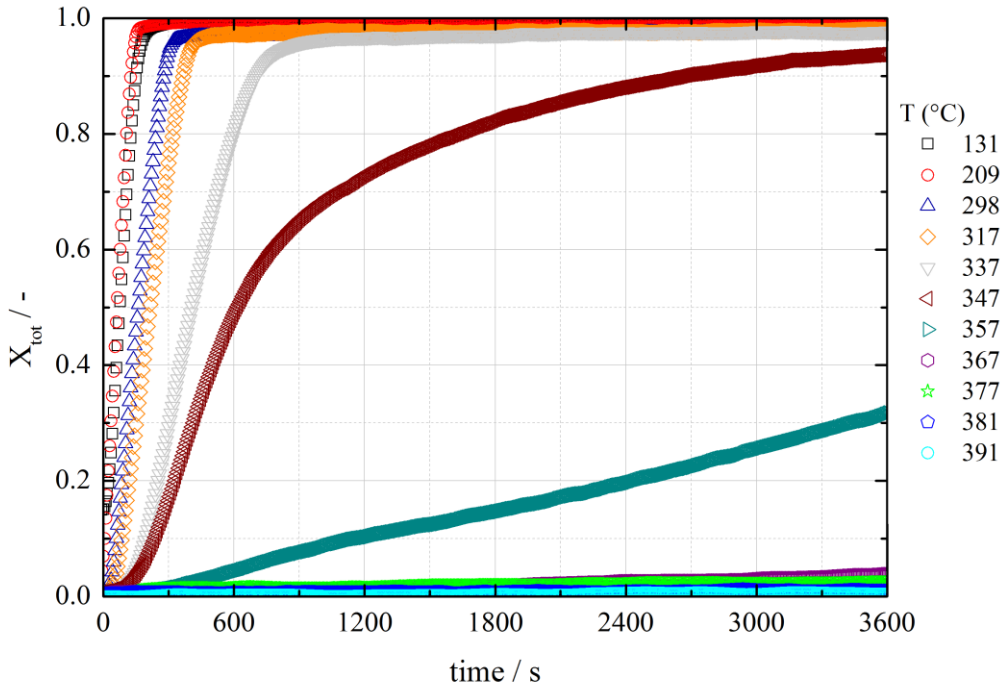


Fig. 12 Effect of the temperature on the hydration reaction of CaO at a gas pressure of 8.7 kPa

4. Conclusions

This study presents a newly designed indirectly heated reaction bed for 2.4 kg of calcium hydroxide storage material. The reactor design was especially dedicated to investigate the reaction at low vapor pressures and under different thermal loads induced by the heat transfer fluid.

Thermal charging and discharging at technically relevant operating conditions were experimentally demonstrated at vapor pressures between 1.4 kPa and 20 kPa. It can be stated that the operation of the storage system at low vapor pressures is possible. This not only enhances process integration possibilities (gas handling) but could also increase the overall storage efficiency of the thermochemical system. However, the experiments revealed that the operating range of the calcium hydroxide system is partially limited due to the effective reaction rate of the storage material at low vapor pressure. For example for the thermal charging at 10 kPa (condensation at 45 °C) a technically relevant minimum temperature of 445 °C was identified which is around 45 K higher compared to the theoretical values. For the discharge at 8.7 kPa (evaporation at 43 °C) a maximum temperature of only 383 °C could be reached which is 15 K below the theoretical value. However for high discharge powers a reaction temperature below 350 °C should be maintained during the discharge process. For process integration studies as well as evaluations of $Ca(OH)_2$ as thermochemical energy storage, this limited operating range at low water pressures has to be taken into account. Further studies will complement the technically relevant operation range of $Ca(OH)_2$ for higher vapor pressures.

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Nomenclature

HEX	heat exchanger
TGA	thermogravimetric analysis
P	pressure
T	temperature
t	time
δ	temperature measurement point, thermocouple
$\dot{V}$	volume flow
X	conversion