Heat transformation based on CaCl$_2$/H$_2$O – Part A: closed operation principle

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Abstract

Thermochemical systems based on gas-solid-reactions enable both storage of thermal energy and its thermal upgrade by heat transformation. Thus, they are an interesting and promising option in order to reutilize industrial waste heat and reduce primary energy consumption. In this publication an experimental analysis of the reaction system calcium chloride and water vapor is presented. The endothermic dehydration reaction is used in order to charge the storage at 130 °C while the reverse reaction leads to a discharging at 165 °C. Thus, a thermal upgrade by 35 K could be demonstrated and main limitations by heat and mass transfer were analyzed. Whereas this part focusses on a closed operation principle, the associated part B deals with the open operation utilizing air as purge gas.

Nomenclature

Abbreviations:

HI	1st hydration step anhydrous CaCl$_2$ to CaCl$_2\cdot$0.3H$_2$O
HII	2nd hydration step CaCl$_2\cdot$0.3H$_2$O to CaCl$_2\cdot$1H$_2$O
HIII	3rd hydration step CaCl$_2\cdot$1H$_2$O to CaCl$_2\cdot$2H$_2$O
HTF	heat transfer fluid
tot	total, over all

Symbols

$c_{p,HTF}$	specific heat capacity (J kg^{-1} K^{-1})
h	step of hydration (mol H$_2$O / mol CaCl$_2$)
$\Delta_R H$	enthalpy of reaction
$\dot{M}$	mass flow (kg s^{-1})
p	pressure (kPa)
$\dot{Q}$	heat flux (W)
ρ_E	energetic storage density (kWh m^{-3})
s	distance (mm)
T	temperature (K)
t	time (h)
X	conversion (-)

| 1 | z | vertical position in reaction tube (m) |
| 2 | ϑ | temperature, thermocouple (°C) |

1. Introduction

In Germany more than 50 % of the primary energy is used for thermal purposes [1]. Besides space heating and warm water, the biggest amount of heat is needed as process heat. Especially the chemical industry is important in this context since it is one of the most energy consuming industrial sectors [1]. In order to further reduce energy consumption and CO_2-emissions thermal energy could in principle be integrated into the processes. However, approx. $4{,}76 \cdot 10^{17}$ J waste heat (not used thermal energy) is released from industrial processes every year [2]. There are mainly two process related reasons for the limited re-utilization of waste heat:

- Fluctuation in heat source and demand
- Low temperature level of waste heat [2][3]

In general, in order to tackle both aspects, two different technologies are needed On the one hand the time dependent fluctuation has to be buffered by thermal energy storage. On the other hand a heat pump is needed to perform a thermal upgrade so reintegration of the waste heat is possible at the required temperature.

Thermochemical systems based on gas-solid-reactions exhibit the potential to do both, thermal storage and upgrade within one single process. Hereby, a reversible reaction
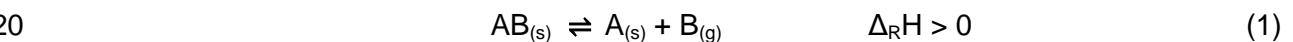
$$AB_{(s)} \rightleftharpoons A_{(s)} + B_{(g)} \qquad \Delta_R H > 0 \qquad (1)$$

is used. During the endothermic reaction the storage is charged, whereas discharging takes place through the exothermic reaction. This storage function has been demonstrated in a 10 kW scale by Schmidt et al. with the reaction system CaO/H_2O [4]. In order to perform the chemical heat pump function the gas pressure has to be changed between charging and discharging process. Several materials are discussed as chemical heat pump systems, e.g. metal hydrides or ammoniates, hydroxides and hydrates [5][6]. If hydrogen or ammonia is used as gaseous reactant a second solid is needed to store it. Water vapor, in contrast, can easily be condensed at moderate pressures. Kato et al. analyzed a chemical heat pump with MgO/H_2O as reaction system [7]. Due to kinetic limitations an application of this reaction requires further material improvements. Alternative reactions with water vapor are salts which form hydrates. These materials are suggested for seasonal storage in domestic applications [8]. The reaction of calcium chloride with water vapor

$$CaCl_2 \cdot 2H_2O_{(s)} \rightleftharpoons CaCl_{2(s)} + 2H_2O_{(g)} \qquad (2)$$
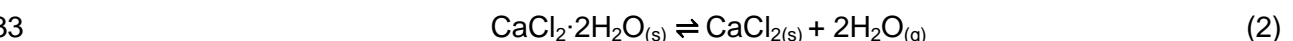
is also suitable for application at higher temperatures as it exhibits complete reversibility, thermal and cycling stability and reasonable kinetics at temperatures up to 200 °C [9][10]. Therefore, this material was chosen for further analysis in a lab scale reactor in order to demonstrate the principle of thermal storage and upgrade in one single unit.

2. Experimental

The schematic sketch of the test bench is shown in Fig. 1. Since the process concept is based on a closed system the reactor (1) is connected with a condenser/evaporator (2).

1 Therefore, the gaseous reactant water is condensed or evaporated depending on the
2 operation mode. Thus, the conversion can be easily determined from the liquid level in the
3 heat exchanger (2). The whole set-up is evacuated before operation, decreasing the
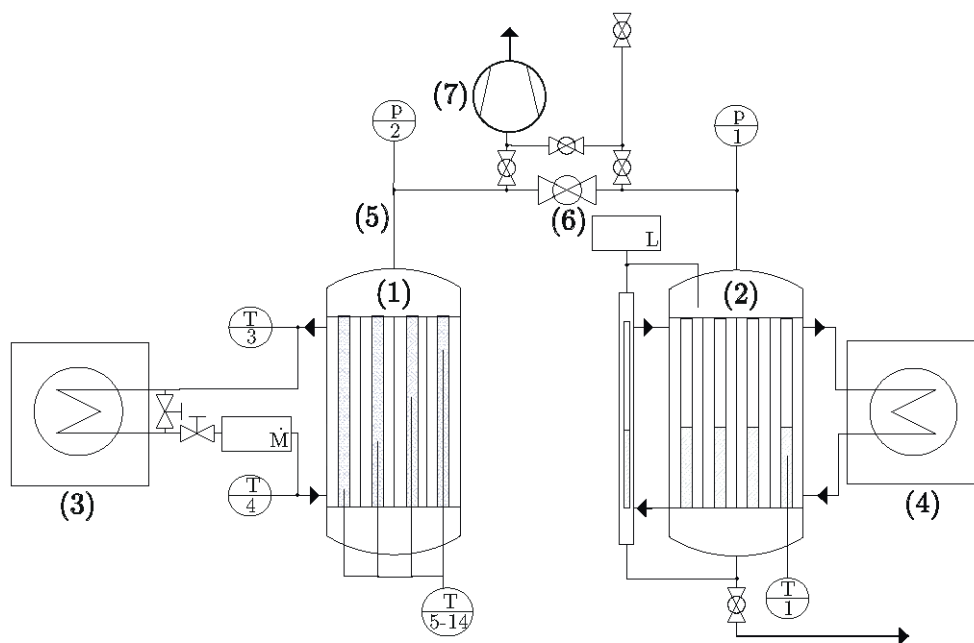4 absolute pressure to about 2 kPa.

5
6 *Fig. 1: Schematic sketch of the test bench in lab scale including (1) the reactor, (2) the condenser/evaporator, (3)*
7 *thermostatic bath for the reactor, (4) thermostatic bath for the condenser/evaporator, (5) connecting tube, (6)*
8 *valve, (7) vacuum pump.*

9

2.1. Reactor

11 The permeability of the material with regard to the gaseous reactant is one important
12 parameter and needs to be analyzed. To do so, a temperature measurement in different
13 positions inside the reaction bed can be used to derive a rough estimate about the local
14 reaction conditions. Therefore, a tube bundle heat exchanger is used as reactor enabling a
15 long and thin reaction bed. The reaction material is filled into the upright tubes and tempered
16 inside the shell. Here, a heat exchanger with 31 tubes with a diameter of 9 mm and a length
17 of 400 mm is used (see Fig. 3, left). At the bottom of the tubes a lid including thermocouples
18 is placed which closes the reactor and the whole system. On top of the tubes a filter is placed
19 and the connection to the evaporator/condenser unit is mounted. Thus, the reaction gas is
20 removed and supplied from the top of the reactor. Heat transfer oil (Petro Canada, Purity FG)
21 is flowing through the shell of the reactor tempering the reaction bed through a thermostatic
22 bath (Unistat 430, Huber Kältemaschinen GmbH).

23 The reaction bed can be modified by introducing fixed gas channels (see Fig. 3, right). These
24 are made of a wire mesh filter material with a mesh size of 100 µm. It is rolled to a thin tube
25 with a diameter of 1 mm. These fixed gas channels enable a good gas transport along the
26 tube.

1
2 *Fig. 2: Tube bundle heat exchanger, used as reactor (left) and its modification with fixed gas channels made of*
3 *thin wire mesh (right).*

4   2.2.   Material

5   Calciumchloride dihydrate from Macco Organique/ Magnesia (4155) is used in all
6   experiments. The purity is specified with 97 %. The particle size distribution has been
7   determined by a Mastersizer 3000 (Malvern Instruments) as a dry dispersion in air. The
8   intermediate particle size of the material is about 200 µm.

9   2.3.   Gas supply

10 To supply the reaction bed with the reaction gas water vapor a second tube bundle heat
11 exchanger is used ((2) in Fig. 1). The apparatus is identical to the reactor but water is
12 condensed and evaporated in the tubes. Again, the shell is tempered using heat transfer oil
13 (Mobiltherm 600, Mobil) and a thermostatic bath (Lauda TW 220). With this set-up gas
14 pressures between 0.8 kPa and 101.3 kPa are possible.

15

2.4.   Measurement instrumentation

Through the bottom lid of the reactor ten thermocouples (type K) with a tolerance of ±1.5 K are inserted into the reaction bed. They are placed in the radial center of ten different tubes at different vertical positions (see Fig. 4).
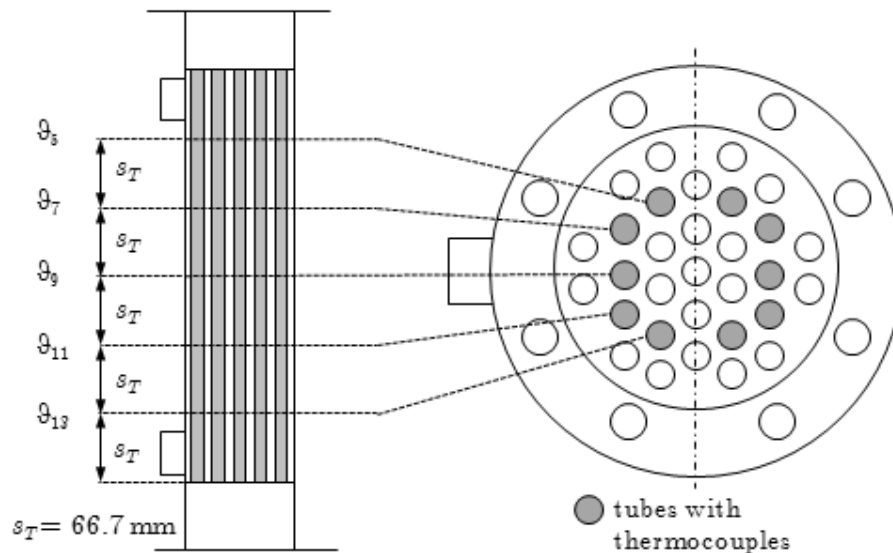

Fig. 3: Positions of thermocouples in the reaction bed. The thermocouples ϑ_6, ϑ_8, ϑ_{10}, ϑ_{12}, ϑ_{14} are at analog positions (mirrored at the symmetry plane).

The in- and the outlet temperature of the thermal oil in the reactor as well as the water temperature in the condenser/evaporator is determined by thermocouples, too.

The water level in the condenser/evaporator is determined with an accuracy of ± 1.5 mm (Vegaflex 61, VEGA Grieshaber KG). From this the conversion of the reaction is calculated.

The gas pressure in the system is measured by a pressure sensor (PAA-35XHTT, Keller Ges. für Druckmesstechnik mbH) with an accuracy of ± 0.8 kPa . There are two pressure sensors placed in the set-up: one on top of the reactor and one on top of the condenser/evaporator. The mass flow of the thermal oil tempering the reactor is measured by a mass flow meter (Coriolis, F-Series, Emerson Process Management GmbH) with an accuracy of ± 0.0697 kg min^{-1}.

2.5.   Experimental procedure

The reactor is filled with approx. 700 g calcium chloride dihydrate. Before starting the experiments, the whole set-up is evacuated to approx. 2 kPa ± 1 kPa using the vacuum pump (Hena 25, Pfeiffer Vacuum GmbH, (7) in Fig. 1). The evaporator/condenser (2) is tempered in order to reach the requested vapor pressure. The starting temperature of the reactor is set by the heat transfer oil with a mass flow of 2 kg min^{-1}. As soon as thermal equilibrium is reached the valve (6) is opened to initiate the reaction. The experiment ends when thermal equilibrium is reached again.

The experimental conditions are summarized in Fig. 5. Here, the gas pressure and the inlet temperature of the heat transfer oil tempering the reactor are indicated by the squares and

1 triangles. For dehydration low vapor pressures (2 kPa to 3 kPa) are chosen in order to
2 decrease the charging temperature of the thermochemical storage. Thus, the water vapor
3 generated by the reaction is condensed at these pressures. The reactor is tempered to
4 150 °C and 130 °C. In order to discharge the storage at higher temperatures the reverse
5 reaction is performed at higher pressures (approx. 100 kPa). The temperature of the reactor
6 is varied in these experiments between 160 °C and 185 °C. Lower temperatures than this
7 result in deliquescence of the hydrate. This is indicated by the red line in Fig. 5. Therefore,
8 the feasible temperature and pressure range is very small. This is why accurate tempering of
9 the reaction material is necessary in order to preclude the salt from dissolving in its own
10 crystal water.

11 As the first reaction cycle might significantly differ from the following [9], only the second
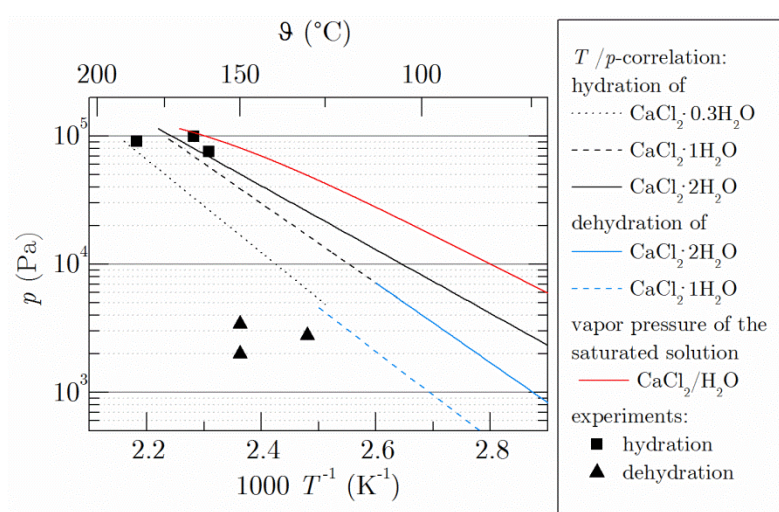12 cycles are analyzed in this publication.

13
14 *Fig. 4: Reaction lines for the hydration and dehydration of calcium chloride and its hydration steps* [9]. *Squares*
15 *and triangles indicate the reaction conditions of the experiments in the reactor.*

16

3. Results and Discussion

3.1.   Thermal charging

19 The dehydration reaction of calcium chloride dihydrate was performed at 150 °C. Fig. 6
20 shows the experimental results. The indicated gas pressure was measured at the top of the
21 reaction bed. As soon as the valve to the condenser is opened (t = 0 h) the pressure drops to
22 about 2 kPa. This initiates the endothermic dehydration reaction and the temperatures in the
23 reaction bed drop. The trends of the temperatures indicate the multiple steps of the
24 dehydration reaction. This is in good agreement with the thermodynamic characterization of
25 the material, that has been published before [9]. The first minimum indicates the dehydration
26 from dihydrate to monohydrate, the second one from monohydrate to the anhydrous calcium
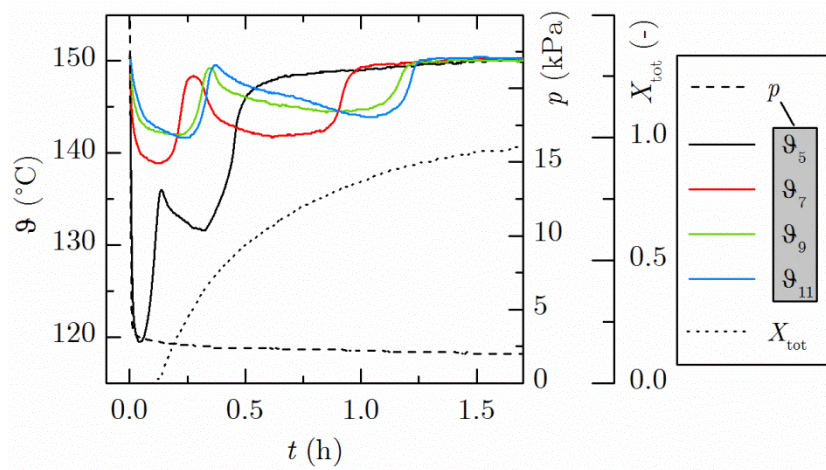27 chloride.

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Fig. 5: Dehydration reaction of calcium chloride dihydrate at 150 °C without a modification of the reaction bed.

But the temperatures in the reaction bed do not change simultaneously. The thermocouple ϑ_5 (black curve) is positioned at a height of z = 0.33 m. Therefore, it is only covered by a little amount of material. At this position the lowest temperature of 120 °C is reached. After about 45 min the temperature rises to 150 °C indicating the end of the reaction in this region of the reaction bed. Thus, the top part of the packed bed reacts faster and at lower temperatures than in the lower regions. This happens due to the low gas permeability of the packed bed of solid material. During dehydration, water vapor is generated which needs to be removed from the packed bed. At the top of the tubes the pressure is approx. constant, mainly influenced by the temperature in the condenser. Thus, the lower regions in the packed bed exhibit a higher gas pressure due to the pressure drop produced through the gas flow through the bed. This can be confirmed by an experiment performed with a modified bed. Here, fixed gas channels are introduced into the fixed bed. Fig. 7 shows the experimental results of a dehydration reaction at the same conditions but with a modified reaction bed. The inserted thin tubes of wire mesh function as fixed gas channels, enabling a good axial gas flow in the reactor tubes. The second right ordinate refers to the conversion that has been calculated from the amount of water collected in the condenser. The conversion curve indicates the end of reaction after approx. 0.5 h. Thus, the reaction time is decreased to one third of the reaction time of the unmodified bed. The temperature at all heights of the fixed changes simultaneously. Thus, a simultaneous reaction can be observed.
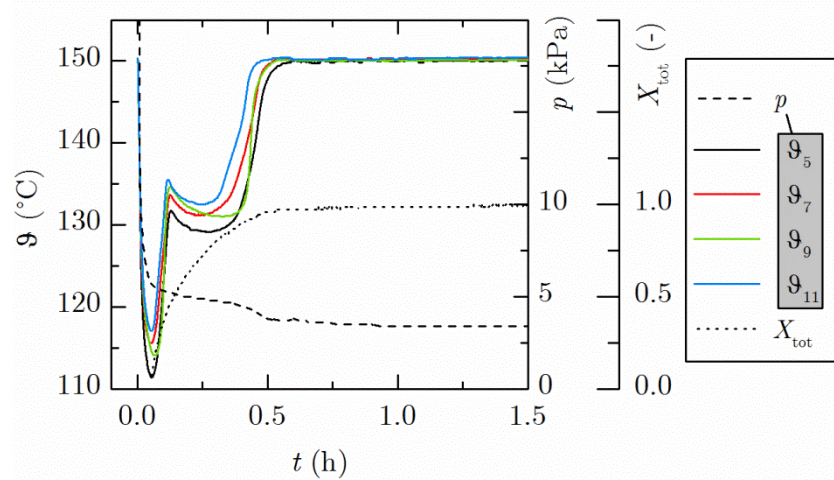
Fig. 6: Dehydration reaction of calcium chloride dihydrate at 150 °C with fixed gas channels as a modification of the packed bed

The aim of heat transformation with gas-solid-reactions is to maximize the temperature difference between charging and discharging. In previous experiments (not shown here), it was analyzed that the low gas permeability of the solid material prohibits a lower charging temperature than 150 °C. However, this strong limitation can be overcome by using these fixed gas channels. Thus, a lower charging temperature is possible. Fig. 8 shows the experimental temperature curves during dehydration at 130 °C. Complete conversion can be observed after approx. 1 h. Compared to dehydration at 150 °C the reaction time doubles. Due to the temperature dependence described by Arrhenius the reaction rate decreases at lower temperatures. But this kinetic effect couples with a thermodynamic one: the reaction generates lower gas pressures at lower reaction temperatures. Therefore, the driving force for the gas transport though the fixed bed is reduced. This results in another raise of overall dehydration time. Nevertheless, a charging of the thermochemical energy storage is technically demonstrated at a temperature of 130 °C with reasonable effective reaction rates.
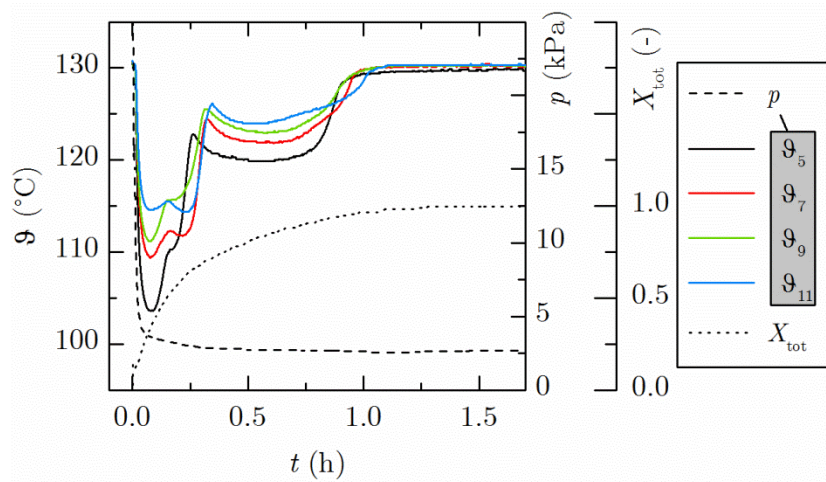

Fig. 7: Dehydration reaction of calcium chloride dihydrate at 130 °C with fixed gas channels

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The temperatures in the reactor show the characteristics discussed before. Although fixed gas channels were introduced into the reaction bed, a small axial gradient is visible. In contrast to dehydration at 150 °C the thermocouple ϑ_{11} shows a higher temperature than ϑ_5. The deeper the position of the thermocouple the higher is the measured temperature. This effect can be explained by the van't Hoff dependence of the reaction. The temperature and gas pressure of the reaction are coupled through the relation $\ln(p) \propto T^{-1}$. Through this logarithmic dependence at smaller gas pressures a small change in pressure has a higher influence on the reaction temperature that at higher pressures. This effect becomes apparent comparing Fig. 6 and Fig. 7.

In closed mode lower charging temperatures are hard to reach. This would require a sufficient pressure difference between the reaction bed and the condenser leading to a lower temperature of condensation and a lower overall pressure. However, these boundary conditions are not interesting for the addressed application as a cooling of the condenser below ambient temperature would be required. Therefore, the lowest temperature for the thermal charging process is 130 °C in a closed mode operation. Therefore, in the associated paper of Bouche et al. an open operation mode was investigated. The open operation mode utilizes air as purge gas in order to decrease the mass transfer limitations discussed above.

3.2.   Thermal discharging

In order to release the thermal energy from the storage at higher temperatures the hydration reaction is performed at higher vapor pressures. Fig. 9 shows the experimental results at a vapor pressure of 75 kPa. The reactor was tempered to 160 °C before reaction. If the reaction gas is introduced into the reaction bed, the temperatures rise up to 185 °C due to exothermal reaction. This temperature relates to the equilibrium of the first step in hydration reaction (HI), the formation of $CaCl_2 \cdot 0.3H_2O$ [9]. This corresponds to 15 % of the overall conversion. After this reaction step is completed the temperatures drop to about 167 °C. At the present gas pressure this relates to the equilibrium temperature of the reaction from $CaCl_2 \cdot 0.3H_2O$ to monohydrate (HII). In this reaction step 35 % of the overall reaction is converted. Thus, the second step corresponds to a bigger part of the overall reaction. Furthermore, it takes place at a lower temperature resulting in a smaller difference to the temperature of the heat transfer fluid. This leads to a lower heat transfer and the reaction time of step HII is longer than the one of HI. A third temperature level is reached after 50 % of the conversion is reached. The temperature of approx. 163 °C corresponds to the equilibrium temperature of the hydration from monohydrate to dihydrate (HIII) at 75 kPa. During this last reaction step the temperature difference between the reaction bed and the heat transfer fluid adds up to 3 K. Therefore, the overall reaction takes more than 3.3 h until full conversion is reached.
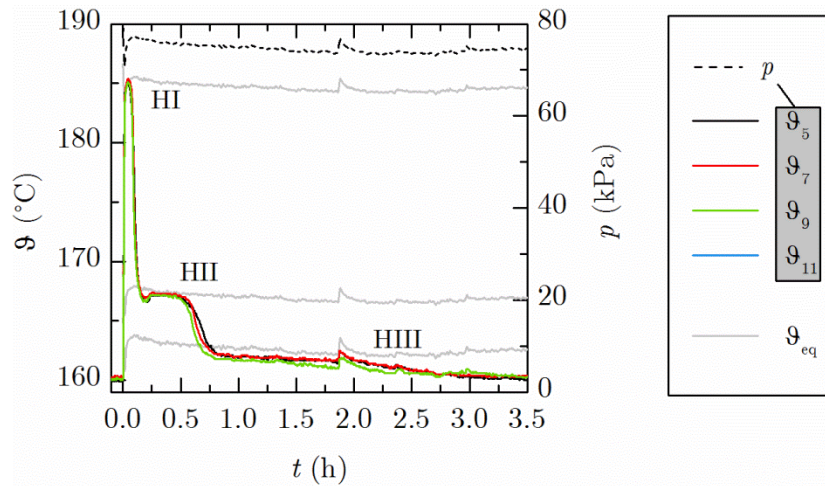
Fig. 8 : Hydration of calcium chloride at a temperature of 160 °C and a vapor pressure of 75 kPa

Although no fixed gas channels were introduced into the solid material, the whole material reacts simultaneously. At any time the same temperatures were detected at every measuring point. Therefore, the pressure loss of the incoming gas does not influence the reaction at higher pressures. Thus, the gas permeability is not a limiting factor for hydration reaction. The conversion rate is mostly limited by the heat transfer.

In order to reach higher conversion rates the gas pressure is increased to approx. 100 kPa. As can be seen in Fig. 4 at this pressure deliquescence might occur. Thus, the reaction temperature needs to be adapted. Choosing 165 °C the hydration can take place without dissolving. Fig. 10 shows the results of this experiment. The temperature of solid follows the three steps of the reaction (HI, HII and HIII) as described before. In this case, these temperature levels have a higher difference to the temperature of the heat transfer fluid. Thus, the heat of reaction is removed faster and the overall reaction consequently requires only approx. 1.5 h. The gas pressure during this experiment is highly influenced by the fast reaction. It drops as the reaction starts and reaches the set value of 100 kPa after about 60 % of the reaction is completed.
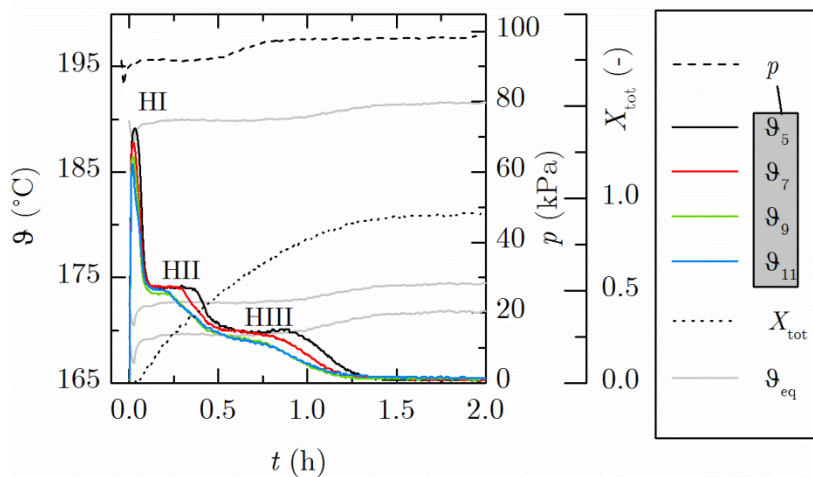

Fig. 9: Hydration of calcium chloride at a temperature of 165 °C and a vapor pressure of 100 kPa

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In all experiments for the hydration of $CaCl_2$ the maximal temperatures directly relate to the multiple steps of reaction. For a maximal temperature difference between charging and discharging of the thermochemical storage a limitation to only one reaction step (HI) is necessary. At a vapor pressure of 100 kPa an equilibrium temperature of 190 °C can be expected. If the solid is tempered to 180 °C this reaction can take place completely without further reaction to monohydrate and dihydrate (see Fig. 11). Assuming a charging temperature of 130 °C this leads to a thermal upgrade of 50 K. In this case the conversion is reduced to 15 % at most, though.
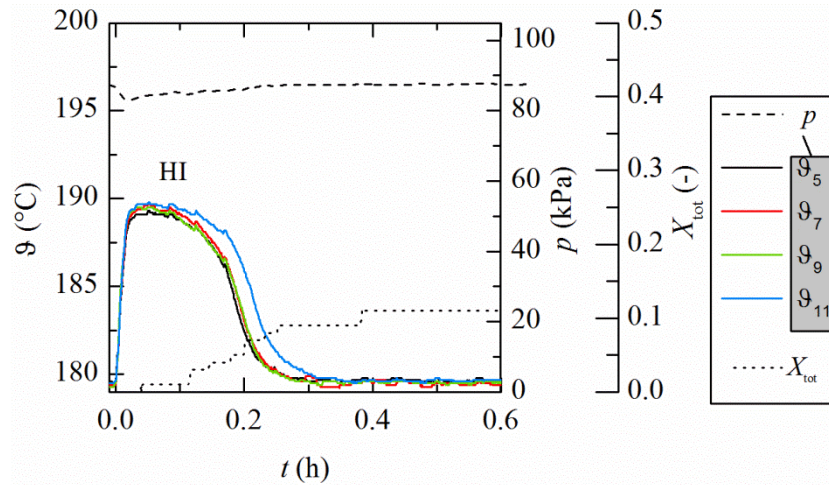

Fig. 10: Hydration of calcium chloride at a temperature of 180 °C and a vapor pressure of 100 kPa

3.3.   Changes with cycling

Although cycling stability over 20 cycles was demonstrated before [9], the fixed bed changes considerably after several hydration and dehydration reactions. Fig. 11 shows the cycled material. On the one hand the particles agglomerate into highly porous solid structures. On the other hand bridges and channels are formed. The mean particle size of 200 µm does not change significantly during dehydration. But after three cycles of de- and rehydration a very broad particle size distribution is obtained. As can be seen in Fig. 11 big agglomerates in the size of few cm are formed, that easily decompose into smaller particles. This may lead to a change of the local thermophysical properties, e.g. the effective thermal conductivity and permeability of the reaction bed. These changes are highly anisotropic and depend on stochastic effects. Therefore, a homogeneous distribution of the reaction enthalpy is limited.
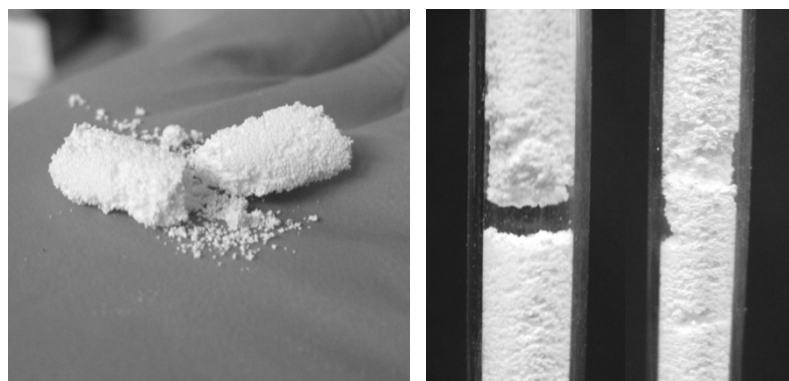

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Fig. 11: Agglomerates, bridges and channels in the cycled calcium chloride reaction bed

1

2 As a consequence not only the chemical properties considering thermodynamics and
3 reaction kinetics should be addressed in cycling experiments but also the potentially
4 changing macroscopic properties of packed beds.

5 Fig. 12 shows the overall conversion calculated by the water level in the evaporator and the
6 heat flux transferred by the thermal oil for four hydration experiments with the same filling.
7 The heat flux has been calculated by

8
$$\dot{Q}_{HTF} = \dot{M}_{HTF} \cdot c_{p,HTF} \cdot \Delta T_{HTF} \tag{3}$$

9 with the mass flow of the thermal oil $\dot{M}_{HTF}$ = 2 kg min^{-1}, the specific heat capacity
10 $c_{p,HTF}$ = 2364.75 J kg^{-1} K^{-1} and the temperature difference ΔT_{HTF} between the inlet and the
11 outlet of the reactor (maximum 8 K). Considering the error of measurement the heat flux is
12 given with an accuracy of ±101 W.

13 All experiments were performed at the same conditions (hydration: ϑ_{HTF} = 165 °C,
14 p_{H2O} = 100 kPa; dehydration: ϑ_{HTF} = 130 °C). Comparing the different cycles, differences in
15 the conversion and heat flux curves can be observed. But no clear trend for a de- or increase
16 of the rate of reaction or thermal power can be identified. Consequently, the changes in the
17 reaction bed may decline or improve the performance of such a system. But a degradation of
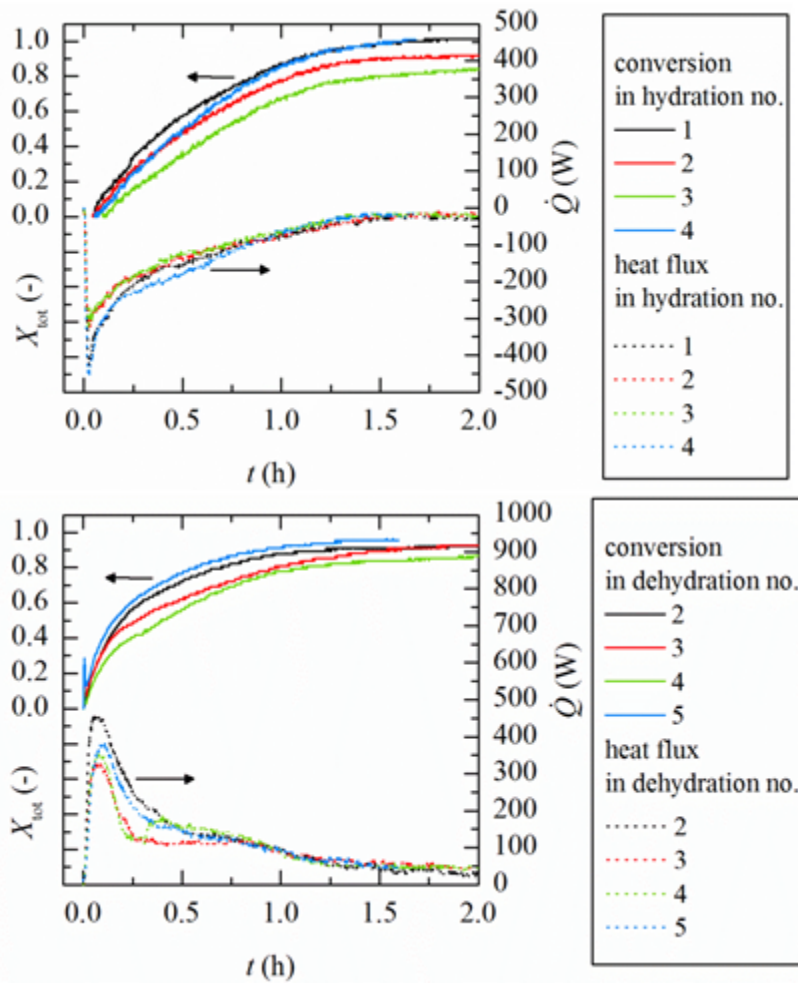18 the thermal power of the thermochemical system is not observed comparing the first cycles.

Fig. 12: Overall conversion and transferred heat flux during hydration cycles at a vapor pressure of 96 kPa and a starting temperature of 165 °C (above) and during dehydration cycles at a starting temperature of 130 °C

3.4.   The potential of thermal upgrade using CaCl$_2$/H$_2$O

The energetic storage density of the thermochemical storage material CaCl$_2$ and H$_2$O$_{(g)}$ is approx. 216 kWh m^{-3}, assuming a void fraction of 0.5. Using water vapor with a pressure of 100 kPa the discharging can be performed at 165 °C, while charging can take place at 130 °C. Thus, a thermal upgrade of 35 K is possible using this system if full conversion from anhydrous CaCl$_2$ to dihydrate is realized. The multiple steps of the reaction limit the possible temperature lift between charging and discharging. If only one reaction step is used, e.g. the reversible hydration to CaCl$_2$·0.3H$_2$O, discharging can be conducted at 180 °C. This increases the possible thermal upgrade to 50 K, but it reduces the storage density. Fig. 13 summarizes these possible modes of operation comparing temperature lift and storage density. Depending on the requirements of the thermochemical storage the reacting amount of water should be adapted. The higher the maximal level of hydration the higher the storage density on the one hand but the lower the temperature lift on the other hand. The theoretical limit is reached for the reaction to hexahydrate. In this case no thermal upgrade can be performed.
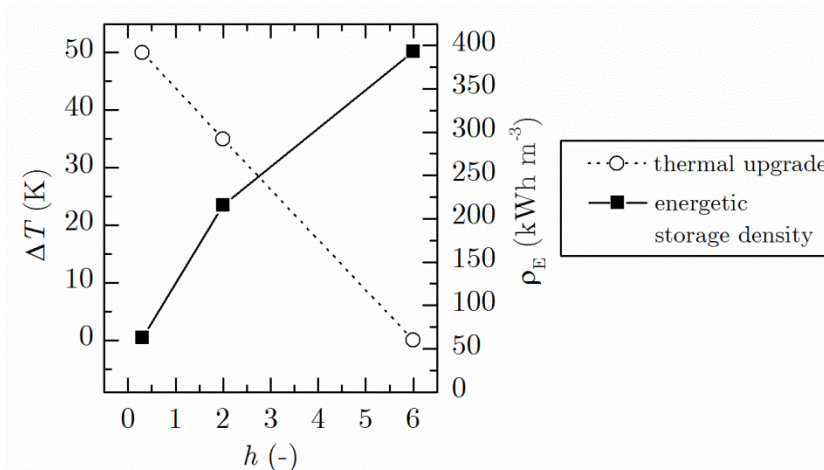
Fig. 13: Energetic storage density (ρ_E) and temperature lift (ΔT) of the heat transformation for different modes of operation of the reaction system $CaCl_2/H_2O$ with respect to different level of hydration (h)

These values are upper limits for that material. If the whole set-up (e.g. reactor and condenser) is taken into account, the storage density is obviously smaller. Compared to physical storage systems, e.g. sensible or PCM storage, the required system complexity is clearly higher and consequently the differences between material related and system related values might be higher. However, the possibility to combine thermal storage with a thermal upgrade that has been demonstrated in this paper might compensate the higher complexity.

To increase the thermal upgrade between charging and discharging of the system either hydration needs to take place at higher temperatures or dehydration at lower ones. Due to the low melting temperature of calcium chloride dihydrate the hydration temperature cannot be increased. Dehydration temperature could be decreased if mass transport limitations can be overcome. One approach to improve mass transfer is to conduct a constant flow of (dry) air through the fixed bed. Thus, an open operation mode should enable lower charging temperatures and consequently a higher temperature lift of the heat transformer. The results of the dehydration process in an open operation are described in the associated paper by Bouché et al.

4. Conclusions

The experimental results demonstrate the functionality of thermal energy storage and transformer using water vapor and calcium chloride. Different limitations occur during charging and discharging process: Macroscopic mass transport retards the dehydration reaction at low vapor pressures. Using gas-channels this limitation can be overcome. At higher gas pressures such as 100 kPa the permeability of the packed bed is not limiting. In this case, heat transport becomes the more important factor. Small temperature differences between reaction and tempering and the low thermal conductivity of the solid are the reasons for this limitation. A further analysis of these and other reaction effects is given by Molenda [11].

In general, it can be concluded that salt hydrates offer interesting options for the utilization of thermochemical systems in thermal processes. These systems are especially promising to reduce industrial waste heat due to thermal upgrade possibility. The reaction system $CaCl_2$

14

/H_2O is not optimal due to its multiple steps of reactions and deliquescence. But it is reasonable reference material to demonstrate the process and understand the limitations.

Acknowledgements

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