SHC 2012

Hydration and dehydration of salt hydrates and hydroxides for thermal energy storage - kinetics and energy release

Holger Urs Rammelberg[a*], Thomas Schmidt[a], Wolfgang Ruck[a]

[a]Institute of Environmental Chemistry, Faculty Sustainability, Leuphana University of Lueneburg, Scharnhorststrasse 1/13, 21335 Lueneburg, Germany

Abstract

Hydration and dehydration of $Ca(OH)_2$ / CaO, $CaCl_2 \cdot 6\ H_2O$ / $CaCl_2$ and $MgCl_2 \cdot 6\ H_2O$ / $MgCl_2 \cdot 2H_2O$ were investigated as heat storage materials. The reaction rates, released power of the hydrations in dependence on water vapour pressure and the conversion of the dehydration in dependence on heating rate are discussed.

Keywords: Hydration; dehydration; TGA; DSC; reaction enthalpy

1. Introduction

Thermal energy storage drives the change towards the use of renewable energy resources and energy efficiency. It can be applied for the use of waste heat and solar thermal. Solar thermal systems work at temperatures between 120°C (space heating and hot tap water) and up to 600°C (CSP plants), where thermal energy storage is a key component [1]. In comparison to most commonly used water or molten salt storage, thermochemical storage materials provide ten times or higher storage capacities per mass or volume and the ability to store heat for longer times without the need of insulation [2]. Recently published results state $MgCl_2 \cdot 6\ H_2O$ and $CaCl_2 \cdot 6\ H_2O$ to be useful for space heating and hot tap water [3] and $Ca(OH)_2$ for higher temperature levels [4]. We reported earlier about our studies in $MgCl_2 \cdot 6\ H_2O$ as pure and composite materials [5] and about our cycle stability measurements with $MgCl_2 \cdot 6\ H_2O$, $CaCl_2 \cdot 6\ H_2O$ and $Ca(OH)_2$ [6].

---

* Holger Urs Rammelberg.: tel.: +4941316771768 ; fax: +4941316772822 .
E-mail address: Rammelberg@leuphana.de.

In this paper we discuss detailed TGA/DSC investigations of hydration and dehydration reaction of salt hydrates and hydroxides. The main issues addressed in this paper are the kinetics and the reaction enthalpy of water release and uptake as well as the released power in dependence on water vapor pressure and temperature.
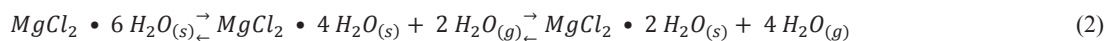
2. Materials and methods

$MgCl_2 \bullet 6\ H_2O$ (p.A.) and $Ca(OH)_2$ (p.A.) were obtained from Merck and $CaCl_2 \bullet 6\ H_2O$ (reinst Ph. Eur.) was purchased from Lohmann Laborservice. All materials were used as received.

TGA/DSC measurements were performed with around 10 mg of material. We used a TGA/DSC1 (Mettler) to analyze heat fluxes and changes in sample mass during hydration and dehydration experiments. The humidity of the mixture gas was measured at the oven outlet and used for calculation of the water vapour partial pressure inside the TGA/DSC oven. The temperature program used for dehydration of the samples prior to the hydration was set to ramp up with 1, 5 or 10 °C/min, and then to cool down with -5°C/min. The hydration process was conducted at 30 °C or 35 °C and switched on after a settling time of 5 min to start the hydration of the sample. The moist nitrogen gas flow was varying from 25 – 150 ml, corresponding to a water vapour pressure in the oven ranging from 12-22 hPa during hydration. Integration of the hydration heat fluxes over time was done manually using the Mettler Toledo STARe Software 9.30b and 11.00a. [5]

3. Results and discussion

3.1. Dehydration

The dehydration of $Ca(OH)_2$, $CaCl_2 \bullet 6\ H_2O$ and $MgCl_2 \bullet 6\ H_2O$ has been studied with a heating rate of 1 K/min (Figure 1) and a heating rate of 4 or 5 K/min (Figure 2) under nitrogen atmosphere. The dehydration of $CaCl_2 \bullet 6\ H_2O$ to $CaCl_2$ and $MgCl_2 \bullet 6\ H_2O$ to $MgCl_2 \bullet 2\ H_2O$ starts already at room temperature and proceeds in 3 and 2 reaction phases, respectively. The respective decomposition phases are:

$$CaCl_2 \bullet 6\ H_2O_{(s)} \underset{\leftarrow}{\rightarrow} CaCl_2 \bullet 4\ H_2O_{(s)} + 2\ H_2O_{(g)} \underset{\leftarrow}{\rightarrow} CaCl_2 \bullet 2\ H_2O_{(s)} + 4\ H_2O_{(g)} \underset{\leftarrow}{\rightarrow} CaCl_{2(s)} + 6\ H_2O_{(g)} \quad (1)$$

$$MgCl_2 \bullet 6\ H_2O_{(s)} \underset{\leftarrow}{\rightarrow} MgCl_2 \bullet 4\ H_2O_{(s)} + 2\ H_2O_{(g)} \underset{\leftarrow}{\rightarrow} MgCl_2 \bullet 2\ H_2O_{(s)} + 4\ H_2O_{(g)} \quad (2)$$

$$Ca(OH)_{2(s)} \underset{\leftarrow}{\rightarrow} CaO_{(s)} + H_2O_{(g)} \quad (3)$$

For each reaction phase, acceleration with increasing temperature is observed in the respective initial phases, followed by a decline with advancing conversion. The overall dehydrations are completed after about 2 hours at temperatures below 140°C, respectively, which is consistent with similar investigations in our laboratory [7],[8] and of Zondag et al. [9], 2010 for $MgCl_2 \bullet 6\ H_2O$ and somewhat lower than reported by other groups [10], [11], [12], [13]. We applied a heating rate of 1 K/min, which is significantly lower than heating rates that have been applied by other groups. Furthermore, we used a flow of dried nitrogen instead of humidified gas for dehydration reactions. This can contributes to the lower dehydration temperatures in this work compared to literature results. The dehydration of $MgCl_2 \bullet 2$ H_2O and the irreversible decomposition side reaction (eq. 4) were running side by side [11].
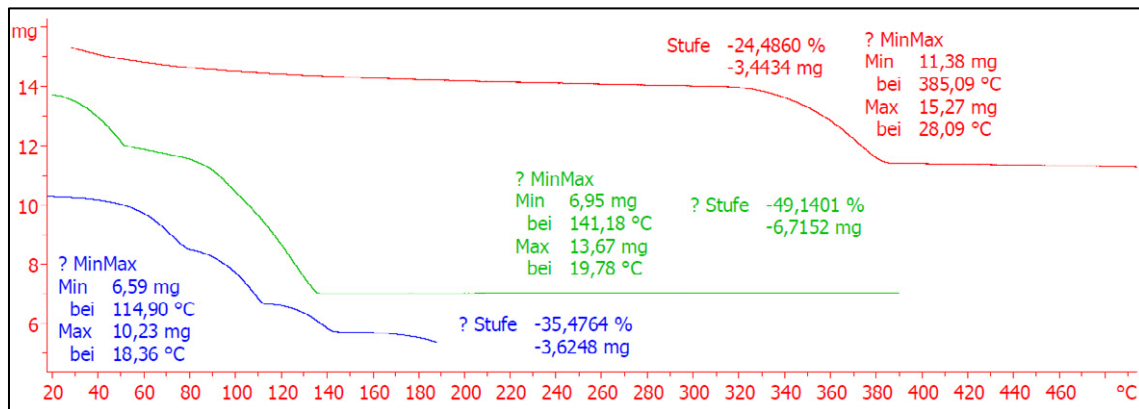
$$MgCl_2 \bullet 2\ H_2O_{(s)} \rightarrow MgClOH \bullet H_2O_{(s)} + HCl_{(g)} \quad (4)$$
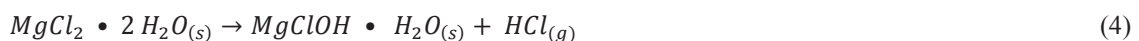
Fig. 1. Dehydration TGA - measurements of $Ca(OH)_2$ (red), $CaCl_2 \cdot 6 H_2O$ (green) and $MgCl_2 \cdot 6 H_2O$ (black). Heating rate 1 K/min
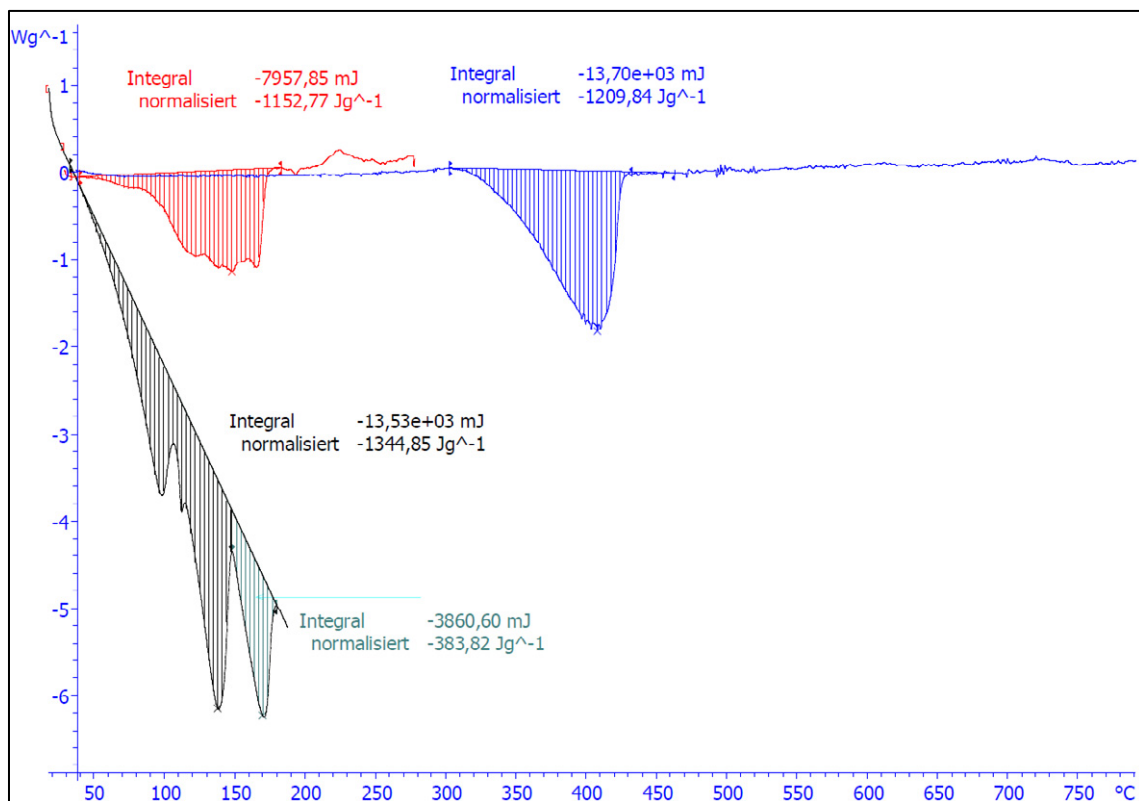
Fig. 2. Dehydration DSC - measurements of $Ca(OH)_2$ (blue), $CaCl_2 \cdot 6 H_2O$ (red) and $MgCl_2 \cdot 4 H_2O$ (black). Heating rate: $Ca(OH)_2$ and $MgCl2 \cdot 4 H_2O$: 5 K/min and $CaCl_2 \cdot 6 H2O$: 4 K/min

The dehydration of $Ca(OH)_2$ to CaO, however, starts at a temperature around 300 °C and is completed at around 420°C under the applied conditions, which is again lower than reported by others [14]. The obtained overall reaction enthalpies are 1209 J/g for $Ca(OH)_2$, 1153 J/g for $CaCl_2 \cdot 4 H_2O$, and1344 J/g

for $MgCl_2 \cdot 6 H_2O$. The decomposition of $MgCl2 \cdot 2 H_2O$ according to (4) starting from 149 °C showed a reaction enthalpy of 383 J/g. The conversion and the first derivation of the dehydration of calcium hydroxide are shown in Figure 3 at different heat rates. With the heat rate by 1 K/ min the conversion is at 98 % finished at 387 °C, by 5 K/ min at 412 °C and by 10 K/min at 438 °C. Also the temperature of the highest reaction rate is shifting from 372°C with 1 K/min over 398 °C with 5 K/min to 428 °C with 10 K/min.
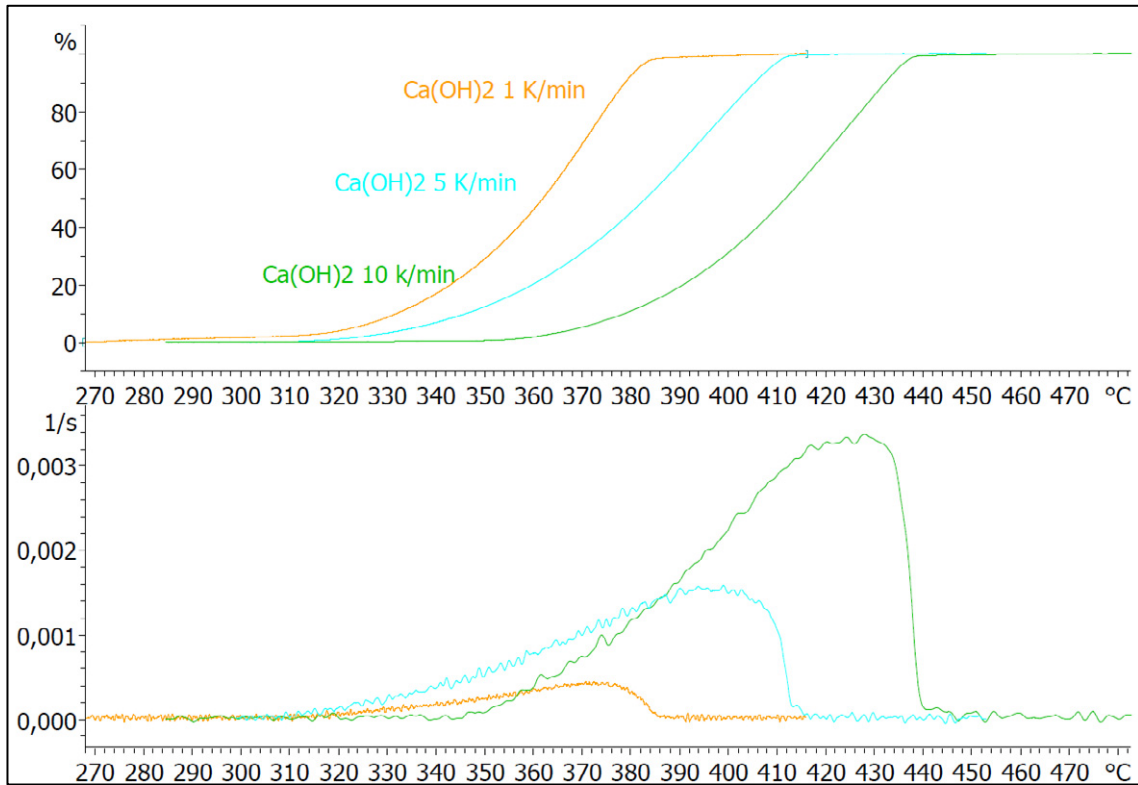

Fig. 3. Conversion and first derivation of the dehydration of $Ca(OH)_2$.

The shift of the conversion temperature is caused by "overheating" of the material above the stable range. Similar effects are shown in Figure 4 for calcium chloride hexahydrate and Figure 5 for magnesium chloride hexahydrate. Firstly, there is a temperature shift as before the $Ca(OH)_2$. Secondly, the conversion shows for $CaCl_2 \cdot 6 H_2O$ two phases and for $MgCl_2 \cdot 6 H_2O$ three phases.

When a heating rate of 1K/min is applied, the first dehydration phase of $CaCl_2 \cdot 6 H_2O$ to $CaCl_2 \cdot 4 H_2O$ is completed at 63 °C at 30 % conversion. The second phase (dehydration to the anhydrite) is completed at 142 °C. The first derivation shows for the heating rate of 1 K/min still in the beginning of the dehydration a high reaction rate until a conversion of 22 %, which is going down to a minimum reaction rate by a conversion of 30 %. After this the reaction rate is increasing smoothly from 40 % conversion to a conversion of 90 %. For the heating rate of 10 K/min there is a temperature shift of the first heating rate peak at 46 K and for the second heating rate at 18 K.
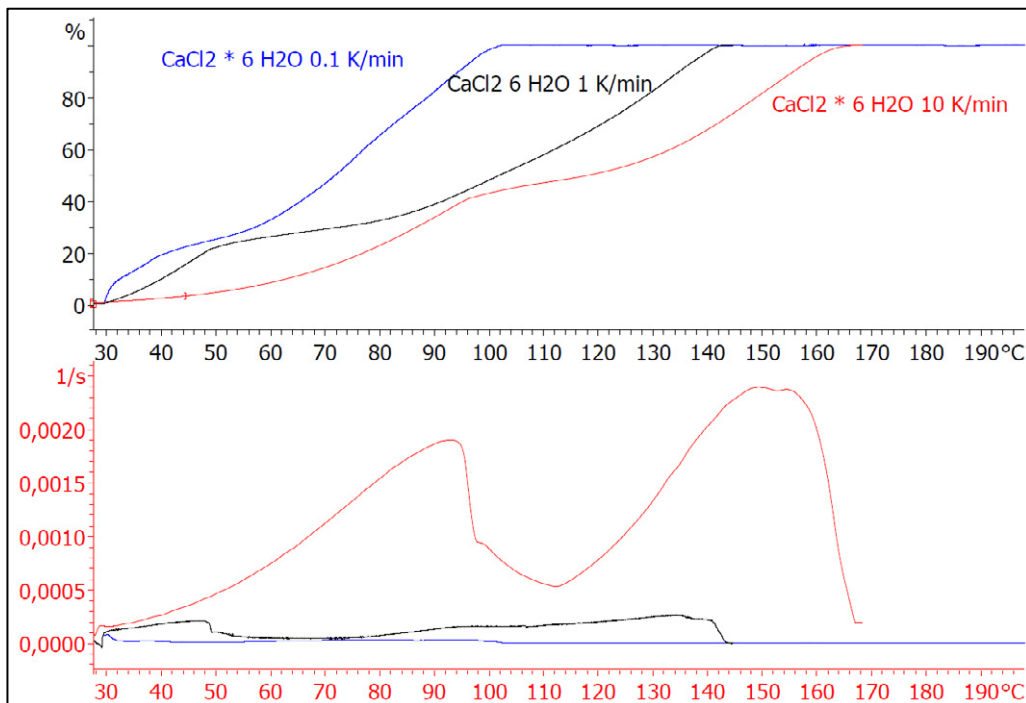
Fig. 4. Conversion and first derivation of the dehydration of $CaCl_2 \cdot 6 H_2O$
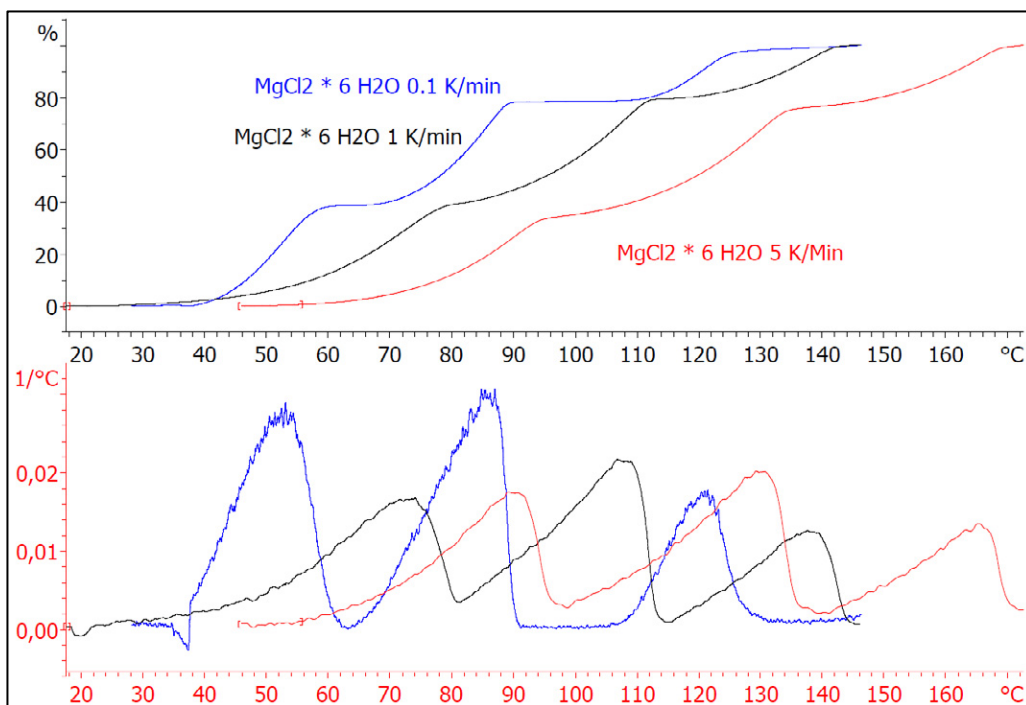

Fig. 5. Conversion and first derivation of the dehydration of $MgCl_2 \cdot 6 H_2O$

With a heat rate of 10 K/min the conversion phase one appear to prolong to a conversion of 48 % at 116°C, which formally corresponds to the release of three water molecules. Further investigations are required to check if the trihydrate is formed or if the effect is caused by overlapping of two consecutive reaction phases. The second phase is the dehydration to the anhydrite, which is completed at 167°C.

Magnesium chloride hexahydrate shows three phases. With a heating rate of 1K/min the first conversion phase is going to the tetrahydrate at 82°C and the second conversion phase to the dehydrate at 116°C. Hereafter the third phase is following to the temperature of 145°C. This phase is probably a summary of the dehydration to the monohydrate and the decomposition to magnesium hydroxy chloride. [11] With higher heating rate the conversion phases are prolonged to higher temperatures. The first phase at a conversion of 34 % is overlapping with the second phase of conversion before the dehydration to the tetrahydrate is finished. The second phase is overlapping with the third phase before the dehydration to the anhydrate was finished, too. The heating rate of $MgCl_2 \cdot 6 H_2O$ shows for the heating rate of 1 K/min and 5 K/min very similar only 16 - 22 K shifted heating rate peaks, which indicate, that for low heating rates all reactions take place in similar way but only to lower temperatures.

3.2. Hydration

The rehydration of the obtained CaO, $CaCl_2$ and $MgCl_2 \cdot 2 H_2O$ is shown in Figure 6. Each material shows an induction period. After this period, the reaction rates of the rehydration of $MgCl_2 \cdot 2 H_2O$ and $CaCl_2$ are roughly constant over a broad range of conversion, followed by a distinct decline.
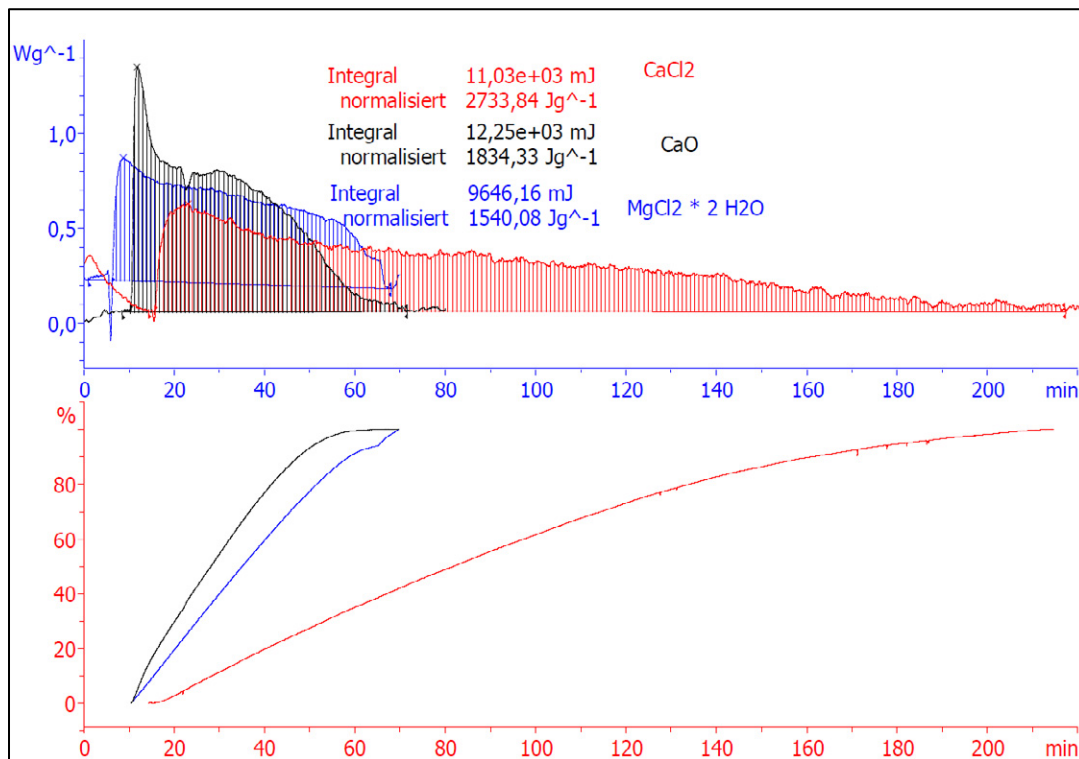

Fig. 6. TGA / DSC measurement of the rehydration of CaO (black), $CaCl_2$ (red) and $MgCl_2 \cdot 2 H_2O$ (blue) at 30 °C with water vapour pressure of 19 hPa. Enthalpies are normalized to dehydrated substances.

The rehydration of CaO shows a clear decline of the reaction rate with progressing conversion. Under the applied conditions (30°C, $p(H_2O) = 20$ hPa), the dehydration of CaO was already completed within 65 min. $CaCl_2$ was completely hydrated after 75 min. The respective specific reaction enthalpies are 1823 J/g CaO, 2629 J/g, $CaCl_2$ and 1551 J/g $MgCl_2 \cdot 2\ H_2O$. Neither the TGA signals of each material nor the DSC signals show any distinction of the reaction phases, which have been identified in the hydration curves.

A huge difference in conversion time of magnesium chloride and calcium hydroxide with both at t = 58 min on one hand and calcium chloride with t = 128 min on other hand is found. Thus, the reaction rate of magnesium chloride and calcium hydroxide is much higher than that of calcium chloride.

3.3. Peak power

The peak power has been determined in dependence on the applied water vapour pressure (Figure 7). A linear relationship can be anticipated for lower vapour pressures. For both CaO and $MgCl_2 \cdot 2\ H_2O$ an optimum water vapour pressure of ca. 19 hPa has been found. A linear relationship between peak power and water vapour pressure can be identified at lower water concentrations. However, at higher water vapour pressures, the peak power is slightly decreased. The water vapour pressure range below 12 hPa remains to be investigated.

The devolution of the peak power in dependence on the humidity indicates that at least two different effects play a role. At lower concentrations of water vapour, the reaction rate and thus the peak power is proportional to the water vapour pressure. The rate-limiting phase is therefore correlated with the amount of water molecules available. At higher water vapour concentrations, a saturation is observed in the case of $MgCl_2 \cdot 2\ H_2O$. For CaO, the peak power even drops slightly at higher concentrations. This can only be explained by a change of the rate-limiting phase, since the reaction rate is directly coupled with the power of the heat release. However, further investigations are needed to identify the reason for this change (material-intrinsic or extrinsic effect, such as heat or mass transfer).
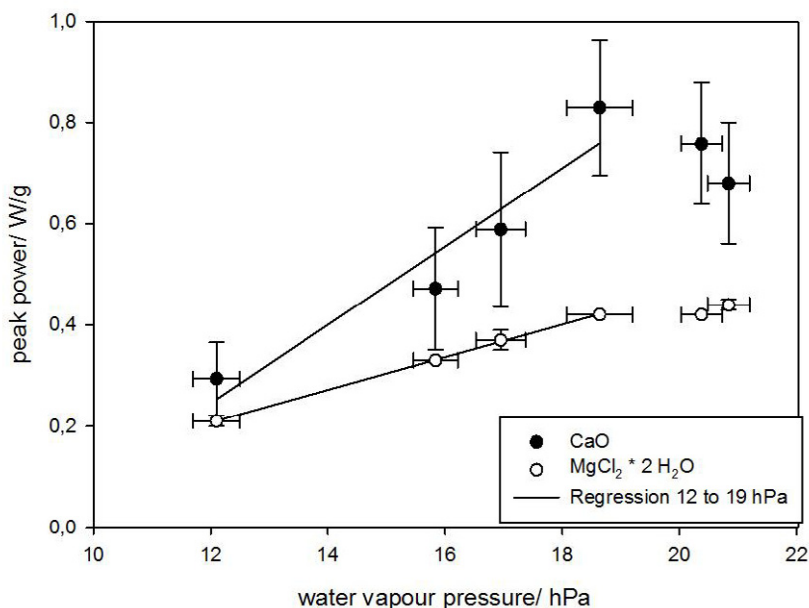

Fig. 7. Dependence of the peak power on the water vapour pressure

4. Conclusion and outlook

The dehydration onset temperature and the temperature with the maximum heating rate depend of the heating rate. The heating rate seems to have some influence on the decomposition pathway for magnesium chloride, although it has to be proven by structural characterization of the intermediate states. In comparison with literature temperature our dehydration temperatures are most lowly caused in our lower heating rate. The heat storage at lower temperature is essential for $MgCl_2 \cdot 6\ H_2O$ to avoid irreversible decomposition. The peak power of the hydration of $MgCl_2 \cdot 2\ H_2O$ and CaO strongly depends on the water vapour pressure.

Acknowledgement

References

[1] Gil A, Medrano M, Martorell I, Lázaro A, Dolado P, Zalba B et. al., State of the art on high temperature thermal energy storage for power generation. Part 1-Concepts, materials and modellization, Renewable and Sustainable Energy Reviews, 2010, 14, 31-35.

[2] Fisch N, Bodmann M, Kühl L, Saße C and Schnürer., H, Wärmespeicher. BINE Informationsdienst, 4th edition, Bonn 2005.

[3] van Essen V M, Cot Gores J, Bleijendaal L P J, Zondag H A, Schuitema R and van Helden W G J Characterisation of salt hydrates for compact seasonal thermochemical storage, Proceedings of the ASME 3rd International Conference on Energy Sustainability, July 19-23, San Francisco, California, USA, 2009.

[4] Schaube F, Wörner A and Müller-Steinhagen H, High temperature heat storage using gas-solid reactions. Conference proceedings of the EFFSTOCK 11th International Conference on Energy Storage, June 14-17, Stockholm, Schweden, 2009.

[5] Opel O, Rammelberg H U, Gérard M and Ruck W, Thermochemical Storage Materials Research - TGA/DSC-Hydration Studies, prepared for International Conference on Sustainable Energy Storage 2011, February 21.-24., Belfast, Ireland 2011.

[6] Rammelberg H U, Opel O, Ross S, Ruck W, Hydration and Dehydration of CaO/ Ca(OH)$_2$ and CaCl$_2$ / CaCl$_2$ * 6 H$_2$O– TGA/ DSC studies, 6th International Renewable Energy Storage Conference IRES 2011, 28-30 November 2011, Berlin, Germany.

[7] Gerard M, Eignung von Salzen in thermochemischen Energiespeichern - Bestimmung der Wärmespeicherkapazität und weiterer spezifischer Materialparameter mittels Dynamischer Thermogravimetrie-Differenzkalorimetrie, Master Thesis, Leuphana University Lüneburg, Germany, 2011.

[8] Ross S, Eignung mesoporöser Materialien als Trägermatrizen zur Optimierung der chemischen Wärmespeicherfähigkeit hygroskopischer Salze, Master Thesis, Leuphana University Lüneburg, Germany, 2011.

[9] Zondag H A, van Essen V M, Bleijendaal L P J, Kikkert B W J and Bakker M, Application of MgCl$_2$•6H$_2$O for thermochemical seasonal solar heat storage, 5th International Renewable Energy Storage Conference IRES 2010, 22-24 November 2010, Berlin, Germany.

[10] Behrendt F, Kerskes H; Bertsch F; Mette B; Wörner A and Schaube F, Thermochemische Energiespeicher, Chem. Ing. Techn., 2011, 83, 2014-2026.

[11] Heide K and Eichhorn H J, Die thermische Zersetzung des MgCl$_2$ • 6 H$_2$O unter dynamischen Bedingungen - ein Beitrag zur kinetischen Analyse nichtisothermer Festkörperreaktionen., Journal of Thermal Analysis, 1975, 7, 397-409.

[12] Iyimen-Schwarz Z and Lechner M D, Thermochemica Acta, 1983, 68, 349.

[13] Sugimoto K; Dinnebier R E and Hanson J C; Structures of three dehydration products of bischofite from in situ synchrotron powder diffraction data (MgCl$_2$ nH$_2$O; n = 1, 2, 4), Acta Cryst. B, 2007, B63, 235-242.

[14] Schaube F; Tamme R and Wörner A. High Temperature Thermochemical Heat Storage for Concentrated Solar Power Using Gas–Solid Reactions. Journal of Solar Energy Engineering, 2011, 133, 031006-1.