THERMOCHEMICAL STORAGE MATERIALS RESEARCH - TGA/DSC-HYDRATION STUDIES

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ABSTRACT

Thermal energy storage is regarded as an enabling technology with a variety of applications, especially regarding energy efficiency and usage of renewable and waste heat. Thermochemical storage materials, in this aspect, provide much higher storage capacities per mass or volume compared to sensible or latent heat storage, often by a factor of 10 or more compared to water storage, the most often used storage type [1]. Moreover, thermochemical storage materials can store the heat for infinite time without insulation and are regarded as a key technology for heat transport and long term storage, although short term storage concepts presently seem to be more feasible in terms of economy [2]. However, as with latent heat storage materials too, the storage design has to meet a number of key parameters, the power density and cycle efficiency as well as cycling stability being of highest importance in addition to the storage capacity. In order to assess these key parameters, a method for TGA/DSC measurements of hydration and dehydration processes has been developed. Using this method, properties of thermochemical storage materials that are making use of hydration/dehydration processes can be determined directly. We were able to investigate power densities dependent on water vapour partial pressure and layer thickness, as well as maximum storage efficiencies and cycling stability of various materials and composites.

NOMENCLATURE

Q	Heat, J
Q_0	Amount of heat released during the first hydration concerning cycling stability , J
ϑ	Temperature, °C
ε	Cycle efficiency, %

BACKGROUND, AIM AND SCOPE

Thermochemical heat storage materials (TCM) have been subject of research for quite a long time. Since water as a reactant, as it is non-toxic, less corrosive and ubiquitous, and can be stored in its liquid form at ambient temperatures, provides certain advantages over carbon dioxide, ammoniac and hydrogen, for example, research is more or less focused on adsorption and desorption of water and hydration/dehydration processes. First qualitative descriptions of the underlying reactions can be found published in the 1820's [e.g. 3]. Reversible chemical reactions, which could be useful for thermochemical heat storage, have been studied since the 1930's [4, 5]. First theoretical considerations on a possible use as a thermochemical heat store can be found published in the 1980's [6], whereas system designs first appeared in the early 1990's, for example as an application to store solar heat in the concept of steam-process based electricity production for a lunar base, using calcium hydroxide as TCM [7]. Later, different systems have been described using adsorption/desorption of water on zeolites [8] and the concept of a thermochemical heat pump [9] using magnesium hydroxide. In 2006, van Helden presented a concept for the seasonal storage of solar heat using TCM [10], basically following the concept of a thermochemical heat pump.

Whereas zeolite systems can be regarded to be more or less functional, TCM storage using salts and salt hydrates is still in development. Key questions are still the appropriate basic process design, which has to be fitted to the targeted applications, and materials research to optimize key parameters as there

are cycling stability, power density and storage efficiency, whilst storage capacity is of course still one of the most important factors. These key parameters, too, are to be weighted differently, depending on the system design and application.

In any case, recently published material indicates that for certain temperature levels and applications only a small number of materials have been successfully tested, $MgCl_2 * 6 H_2O$ and $CaCl_2 * 6 H_2O$ being most promising for temperature levels useful for space and water heating [11] and $Mg(OH)_2$ and $Ca(OH)_2$ for higher temperature levels > 500 K [12, 13]. Whilst $Ca(OH)_2$ shows good reactivity and overall behaviour, whilst being only relevant for high-temperature heat storage, $Mg(OH)_2$ and the hydrated sulphates more or less showed less sufficient reactivity in the hydration process. The chloride salt hydrates on the other hand, whilst showing good reactivity under all circumstances, are known to be quite corrosive and show a certain tendency to over-hydrate, developing a gel-like consistency which significantly hinders the ability to store and release heat [11]. Moreover, when using $MgCl_2 * 6 H_2O$, care is to be taken, as the material shows thermal decomposition releasing HCl above certain temperatures. Whereas different sources state that thermal decomposition of $MgCl_2 * 6 H_2O$ starts at temperatures above 130-140°C, our own observations during first experiments (not published) at low pressures, which are considered interesting due to possible better water uptake, as well as easier water evaporation [14], show slight acid formation even at lower temperatures around 115°C. Therefore, a method has been developed to systematically conduct hydrations/dehydration measurements using TGA/DSC on hydrated salts and other materials. Particularly composites, which are considered as providing possible solutions to over-hydration as well as power density and cycling stability/thermal decomposition issues and potentially helpful in optimizing materials for different applications, are investigated.

MATERIALS AND METHODS

EXPERIMENTAL SETUP

A TGA/DSC1 (Mettler) has been used to analyze heat fluxes and changes in sample mass during hydration and dehydration experiments. The Mettler TGA/DSC1 provides the opportunity to introduce two different reaction gases into the TGA/DSC oven in addition to the purge gas. We used $CaCl_2$ and silica gel-dried nitrogen as purge gas at a flow rate of 50 ml/min. The gas flow was controlled by a gas box providing 2 independent mass flow controllers connected to the TGA/DSC control. In addition to the purge gas flow, we used a separate nitrogen flow humidified via a thermostatised gas bubbler flask as the reaction gas with variable flows, varying from 25 – 150 ml/min. 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.
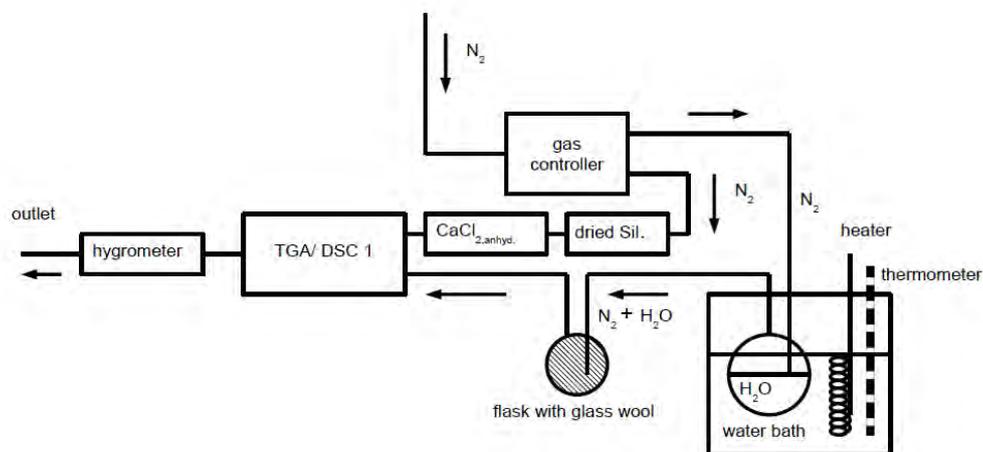

Figure 1: Experimental setup

This setup, shown in figure 1, allowed an investigation of hydration characteristics in addition to the dehydration of several thermochemical storage materials like $MgCl_2*6\,H_2O$, $Ca(OH)_2$, Zeolites and composite materials.

PREPARATION OF COMPOSITE MATERIALS

Composite materials as discussed in this paper were prepared from $MgCl_2 * 6\,H_2O$ (p.A., Merck) and graphite (p.A., Merck), copper (p.A., Merck), zeolite A and sand, respectively. For this purpose, portions of approximately 250 mg of $MgCl_2 * 6\,H_2O$ were mixed using mortar and pestle with similar amounts of the additive. The zeolite A was purchased from Süd Chemie AG, Moosburg, Germany. The sand used was sieved at < 250 µm before use. Grain size distribution analysis revealed a > 80% contribution of 125 – 250 µm grain size. The amounts of $MgCl_2 * 6\,H_2O$ in the composites were calculated from Mg measurements using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) at 285.213 nm after sonication of the composite in 10 mL hydrochloric acid (37%) for 30 min and subsequent filtration and dilution to 100 mL.

PEAK POWER DEPENDENCY ON WATER VAPOUR PRESSURE AND AMOUNT OF SAMPLE USED

In order to assess the dependency of the hydration reaction of $MgCl_2 * 6\,H_2O$ on water vapour pressure and the amount of sample used, measurements of the hydration heat fluxes of samples of 2.5, 5, 7.5 and 15 mg mass were taken out at different moist nitrogen flows ranging from 25 – 150 mL / min, corresponding to a water vapour pressure in the oven ranging from 12-22 hPa during hydration at 35°C. The temperature program used for dehydration of the samples prior to the hydration was set to ramp up from 35°C to 130°C at 1°C / min, and then to cool down at -5°C / min to 35°C. Data handling was done using the Mettler Toledo STAR^e Software 9.20.

INFLUENCE OF HEATING RATES AND ADDITIVES ON THE DEHYDRATION TEMPERATURES

Influences of graphite, zeolite, copper and sand on the dehydration reaction were investigated using a temperature program starting at 25°C and heating up to 200°C at 1°C / min. For a $MgCl_2$: Graphite – composite, we used 0.1°C / min and 5°C / min in addition to the measurements with 1°C / min heating rates. The onset, peak and offset temperatures of the different dehydration stages were obtained using the Mettler Toledo STAR^e Software 9.20.

CYCLING STABILITY

Investigations on the cycling stability of the TCM materials and material composites were done by multiple measurements of the integrated hydration heat fluxes of one sample during consecutive dehydration/hydration cycles. The hydration process was conducted at 35°C. The moist nitrogen gas flow was set to 125 mL/min and switched on after a settling time of 5 min to start the hydration of the sample. For dehydration, the same temperature program as for the peak power measurements was used. The amount of sample used was around 10 mg. Integration of the hydration heat fluxes over time was done manually using the Mettler Toledo STAR^e Software 9.20.

RESULTS AND DISCUSSION

During method development, problems were observed regarding residual water in the reaction chamber, leading to lower energy recovery rates due to re-hydration during cool down of the TGA/DSC-oven and a heat flow of > 0 at the start of the hydration measurements, which rendered proper integration of the peak difficult. Care must be taken to ensure the use of proper dried nitrogen as a purge gas and avoid leakage in the gas supply system.

Measured heat storage capacities of the investigated materials were within range of data available in the literature, showing around 1400 kJ/kg for $Ca(OH)_2$ and 940 kJ/kg for $MgCl_2*6\,H_2O$ [11, 14]. Heat

recoveries were > 90% in our measurements. Peak power measurements showed high possible power densities of the materials investigated, up to 6 W/g during dehydration and 2 W/g during hydration of $Ca(OH)_2$ and CaO, respectively. CaO as a tendency shows a faster hydration compared to $MgCl_2*2\ H_2O$. Because of the need to optimize $MgCl_2$ – based materials for applicability and feasibility, whilst being considered of highest relevance for space heating and warm water thermal energy storage [11], we will concentrate on showing and discussing results obtained using this TCM.

During dehydration of $MgCl_2 * 6\ H_2O$, three distinguishable steps are observed, where the material looses two water molecules on each of the first two steps and one water molecules on the third step. Thermal decomposition was not observed below 130°C using TGA/DSC measurements. If heated to temperatures above 130°C, the third step equal to the loss of one more water molecule can be observed, as well as thermal decomposition, starting at around 130°C, when slow heating rates of about 0.1°C / min are used.

Unlike the dehydration, the hydration of $MgCl_2$-hydrates shows no distinguishable discrete stages of hydration at 35°C, but a broad peak with slightly decreasing heat flux during the hydration time of approximately 50 minutes, dependent on sample size and water vapour partial pressure. The hydration TGA/DSC graph is shown in figure 2.

The graph shows influences of occurring overhydration, as the heat flux does not return to the bottom line and the sample mass keeps increasing as long as the moist gas is flowing into the reaction chamber (in this measurement, 20 min settling time was used until the moist gas was switched on). The water taken up from the moist gas can cause additional steps to occur in dehydration measurements if starting below 30°C.
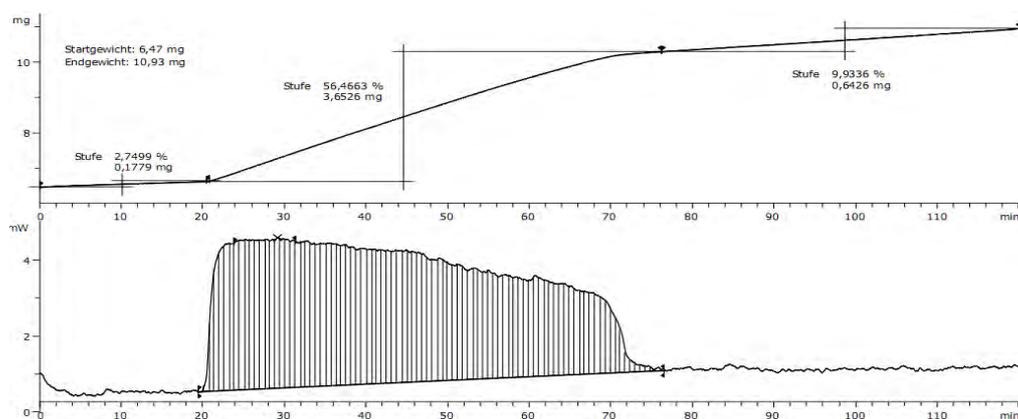

Figure 2: Hydration TGA/DSC plot of $MgCl_2 * 2\ H_2O$ to $MgCl_2 * 6\ H_2O$ (35°C, p(H_2O) ~ 2 kPa)

We were able to observe a dependency of the peak power on water vapour partial pressure in the reaction chamber, as well as on the thickness of the layer, varied by using different amounts of the samples (figure 3). The highest peak power was observed using an initial amount of 5 mg of $MgCl_2 * 6\ H_2O$, corresponding to a thickness of the layer of approximately 2 mm. The lower peak power of the 2.5 mg sample is due to a higher influence of heat dissipation which must be regarded as a possible source of errors using this method, the lower peak power of the 7.5 mg and 15 mg samples are due to the higher thickness of the layers. The error bars show variation in resulting water vapour partial pressures using the described setup as well as the variation of several hydration/dehydration cycles using the same sample. As can be seen from the two measurements using 5 mg of $MgCl_2 * 6\ H_2O$, the repeatability of the hydration experiments may depend on different levels of compression of the samples when introduced into the alumina crucible.
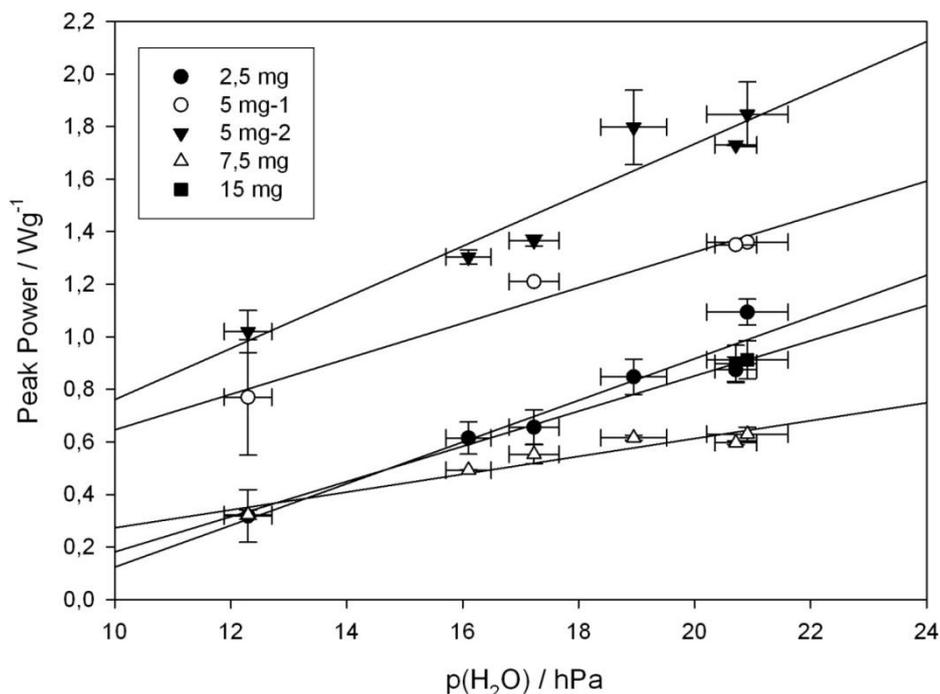
Figure 3: Dependency of the peak heat flux observed during hydration of $MgCl_2 * 2\ H_2O$ on water vapour partial pressure and sample size.

INFLUENCE OF HEATING RATES AND ADDITIVES ON THE DEHYDRATION TEMPERATURES

Additives are considered to be helpful in the development of PCM to enhance power density by increasing thermal conductivity (graphite, nanoparticles [15, 16, 17], copper), or acting as a supporting agent, enhancing structure stability of the TCM (zeolites, other materials [18]). It is well known, that the heating rates used in TGA/DSC measurements show a strong influence on the observed temperatures, at which the dehydration reactions occur. If higher heating rates are used, observed reaction temperatures shifted upwards for two possible reasons: either heat conductivity of the material or the kinetics of the reactions itself are limiting.

Figure 4 is showing observed reaction temperatures of the dehydration of $MgCl_2 * 6\ H_2O$ and a $MgCl_2 * 6\ H_2O$: graphite composite when heated to 200°C at different rates.

The addition of graphite shows the highest reduction in observed reaction temperatures at a rate of 5°C / min. The temperature ranges in which the reactions occur are lowered by 10-15°C, showing a possible influence of the heat conductivity of the material together with an effect possibly caused by the lower amounts of $MgCl_2 * 6\ H_2O$ used (10 mg and 6.9 mg, respectively). The influence of the added graphite naturally decreases with lower heating rates, as both effects, heat transfer and kinetic hindrance, are of lower importance at lower heating rates. At 0.1°C / min, the addition of graphite does not lead to a further reduction in the observed peak temperatures, but still sharpening of the peaks can be observed. At this very low heating rate, the material reveals dehydration temperatures below 100°C, which is an interesting fact regarding possible applications connected to CHP plants, where heat at a temperature of 90-95°C can be stored to make electricity production more flexible.
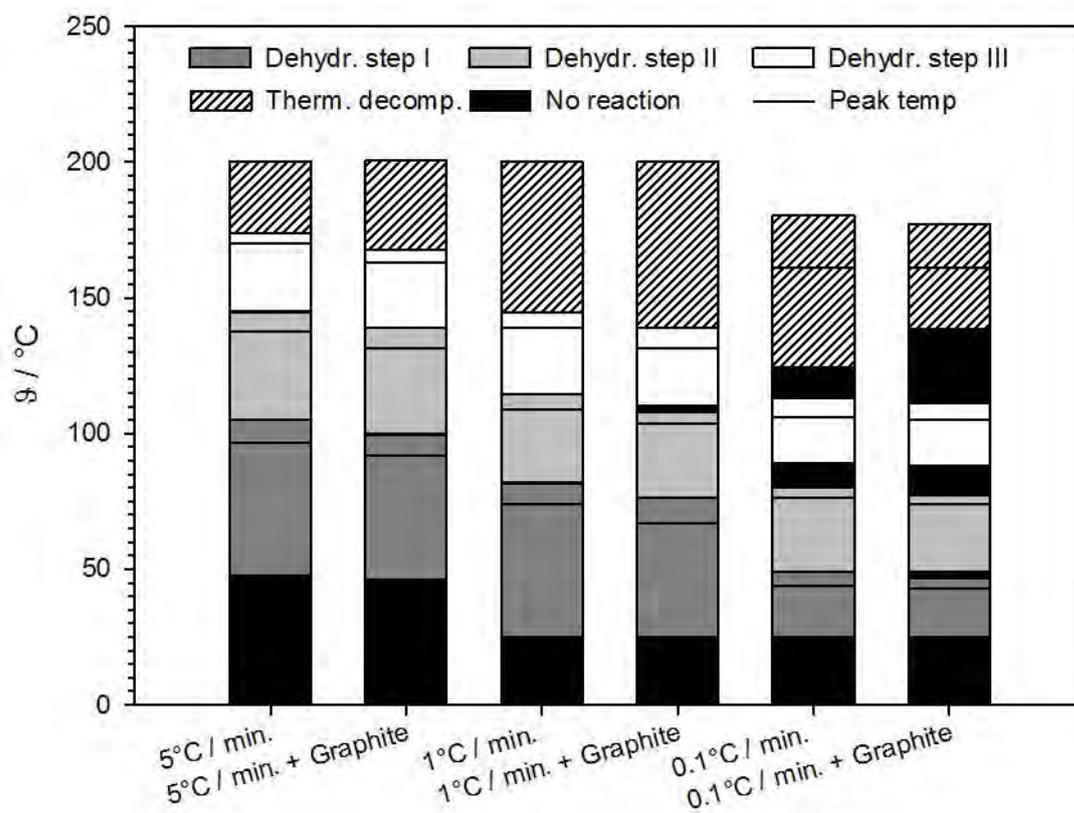
Figure 4: Reaction temperatures observed during dehydration of $MgCl_2 * 6 H_2O$ and a $MgCl_2 * 6 H_2O$: graphite composite (1 : 0.45) at different heating rates, 25 – 200°C.

Also, at a heating rate of 0.1°C / min, the occurrence of thermal decomposition can be clearly observed using TGA/DSC at temperatures above 125°C, reaching its peak at 160°C. This is an important finding, as it explains the more or less parallel occurrence of beginning thermal decomposition together with the third dehydration step in most published material [e.g. 19]. When working under vacuum, the temperatures at which the different reactions occur are lowered further [20], leading to observable acid formation at even lower temperatures then 125°C.

It is hardly possible to investigate a higher number of samples using a heating rate of 0.1°C, because of the long time needed for a single TGA/DSC run of 30h. Therefore, with these results in mind, we investigated other possible additives using 1°C / min heating rate.

Figure 5 shows the obtained results using different additives. Sand and zeolite were used as possible structure supporting agents, whereas copper and graphite could act as ingredients that are able to enhance heat conductivity. However, an influence of higher heat conductivity of the materials cannot be clearly deduced from these measurements, as the addition of sand shows results very similar to those adding an equivalent amount of copper to the sample. The graphite composite contains a higher amount of $MgCl_2 * 6 H_2O$, possibly accounting for higher observed reaction temperature at 1°C / min heating rate. In contrast, the zeolite composite shows a different behavior. Whilst the observed peak temperatures are similar to those obtained by using copper and sand as additives, zeolite is altering the peak shape, leading to a more peak tailing in contrast to the fronting observed in other experiments.

A comparison of peak heat fluxes during dehydration step II, which shows the highest heat flux of the three observed steps, normalized to $MgCl_2 * 6 H_2O$ content (Figure 6), shows, that reactivity of pure $MgCl_2 * 6 H_2O$ is more or less comparable to the zeolite and copper composites.
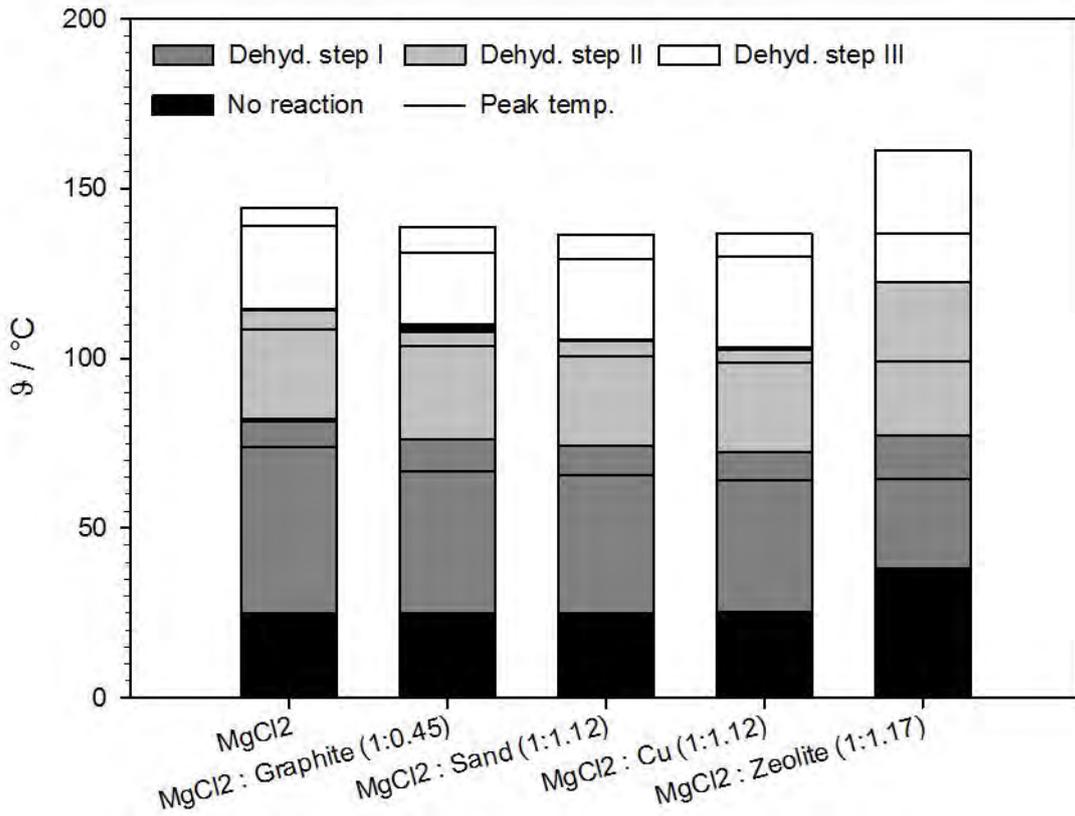
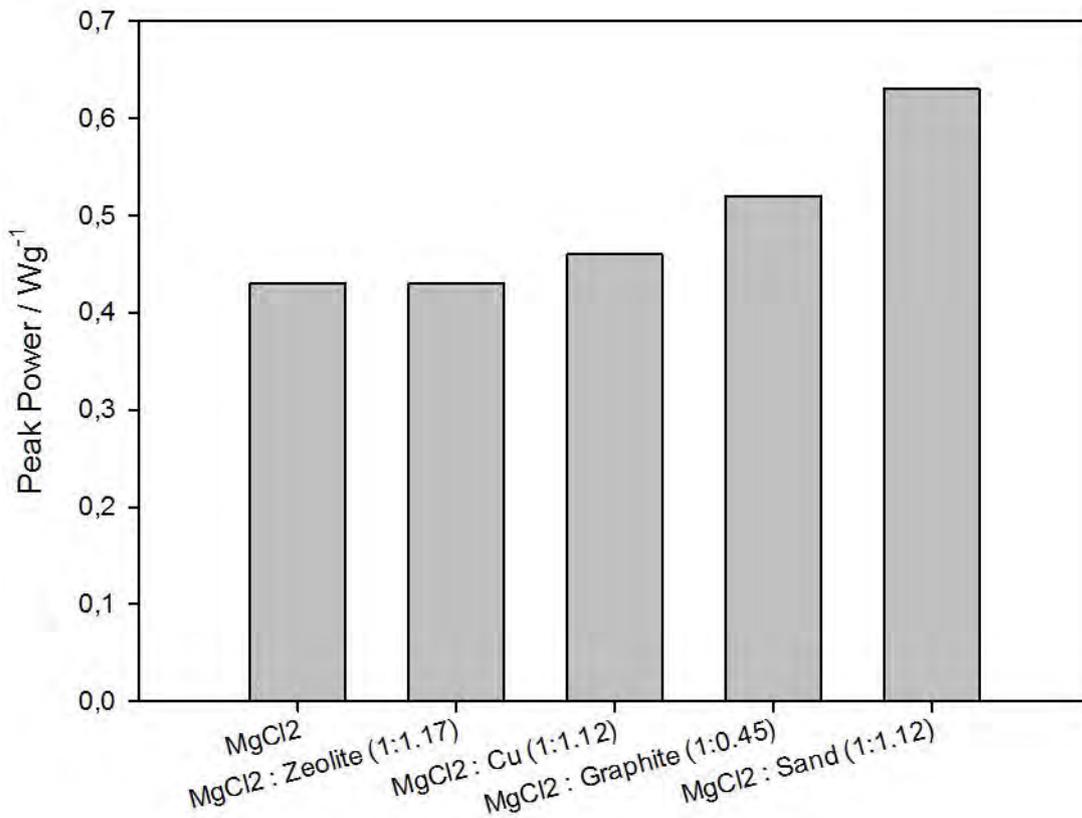Figure 5: Influence on observed reaction temperatures of different additives.

Figure 6: Peak heat fluxes observed during dehydration (step II) of the different composites, normalized to $MgCl_2 * 6\ H_2O$ content.

Here as well, an influence of the heat conductivity of the material cannot be clearly seen, as copper and graphite seem to enhance the reactivity of the sample, but the sand composite, surprisingly, shows highest reactivity, possibly due to a more porous structure of the composite sample compared to the other materials.

CYCLING STABILITY AND CYCLE EFFICIENCY

$MgCl_2 * 6 H_2O$ is known to develop a gel-like structure due to overhydration, which hinders further water uptake, leading to a possibly reversible decrease of the reactivity of the TCM. Furthermore, thermal decomposition could lead to an irreversible loss in reactivity.

We decided to investigate cycling stability of the zeolite composite in comparison to pure $MgCl_2 * 6 H_2O$ closer, as the zeolite composite, compared to the other samples, seems to enhance the characteristics of the sample in such a way, that the third dehydration step (step III), during which a beginning thermal decomposition is likely to take place, is occurring at higher temperatures compared to the other samples, whereas peak temperatures of step I and II are similar to those of the other composites and the heat fluxes obtained are comparable to pure $MgCl_2 * 6 H_2O$.

During cycling, both materials show a linear decrease of the amount of heat generated during rehydration (Figure 7). After 25 cycles, $MgCl_2 * 6 H_2O$ has a 40% lower heat output during hydration compared to the first cycle. The 26th, 27th cycle and 28th cycle show a sudden drop by another 10%. The reactivity of the sample was recovered to 80% after grounding using mortar and pestle, indicating that overhydration plays the major role in the decrease of reactivity of $MgCl_2 * 6 H_2O$.
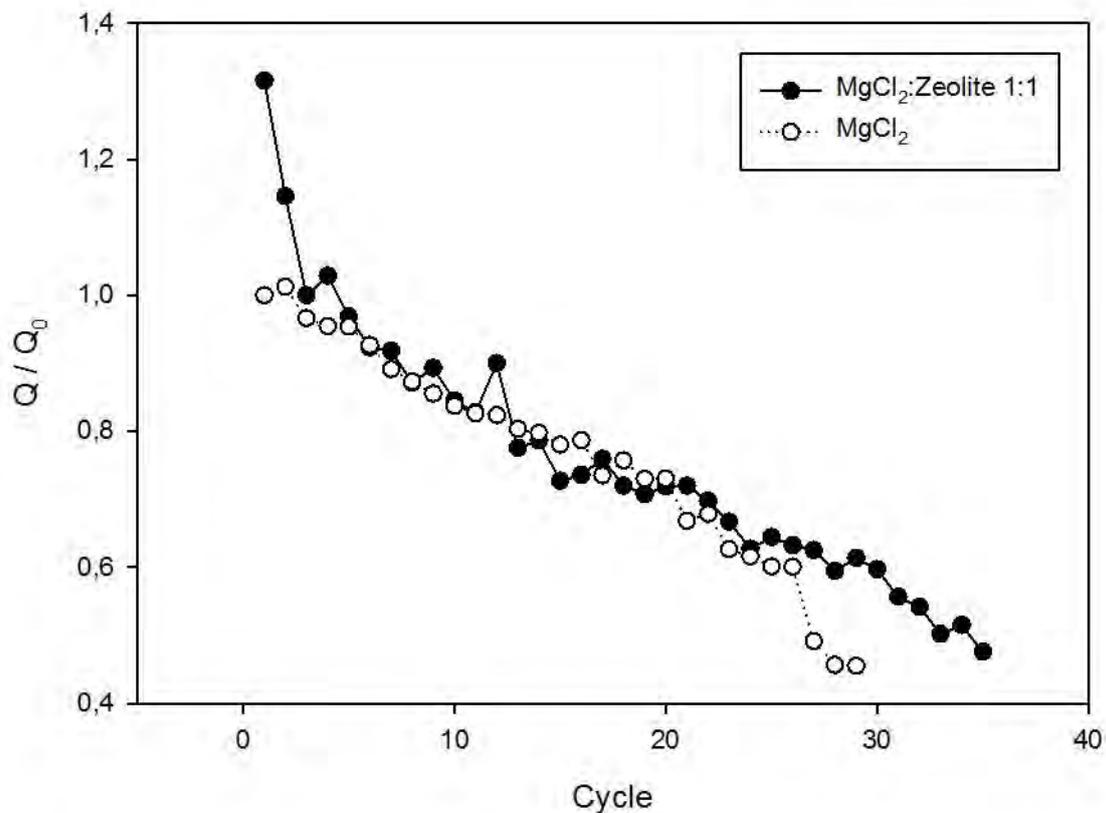

Figure 7: Decrease in reactivity of $MgCl_2 * 6 H_2O$ and a zeolite composite, respectively, during subsequent hydration/dehydration cycles. The amount of heat released during hydration of the sample was measured.

The zeolite composite shows a similar linear decrease, but up to the 35th cycle, no sudden additional drop in the reactivity was observed. Water adsorption on the zeolite during hydration accounts for a higher heat output during the first 2 cycles, but the dehydration temperature used (130°C) was not sufficient to desorb the additionally adsorbed water.

Zeolite A, therefore, shows a certain effect as a structure supporting agent, but the actual results are not indicating a practicable use as an additive for $MgCl_2 * 6 H_2O$, as dehydration temperatures for $MgCl_2 * 6 H_2O$ should not exceed 120°C to avoid thermal decomposition. At these temperatures, the used zeolite A acts as a more or less inert material, where thermal storage capacity is concerned. The structure stabilizing effect possibly can be enhanced using improved methods to prepare the composite, for example wet impregnating and evaporation, as well as possibly better suited zeolites then zeolite A.

Also, further work must be done in testing composites using different additives. In a first screening, we found a recovery of around 90% of the energy stored in the transition of $MgCl_2*6 H_2O$ -> $MgCl_2*2 H_2O + 4 H_2O$ during rehydration using a $MgCl_2 * 6 H_2O$: Graphite (1:1) composite (figure 8) and a per-cycle decrease of 1-3 % in reactivity or heat storage capacity, respectively. The plot shows, that the per-cycle reduction in reactivity is decreasing with an increasing number of cycles. It is still necessary, though, to investigate the cycling stability of the graphite and other composites using a number of cycles at least similar to those used for investigation of pure $MgCl_2 * 6 H_2O$ and the zeolite composite, as shown in figure 7. Furthermore, switching off the moist nitrogen earlier or later can be used to investigate methods to avoid overhydration by controlled hydration of the material in real applications.
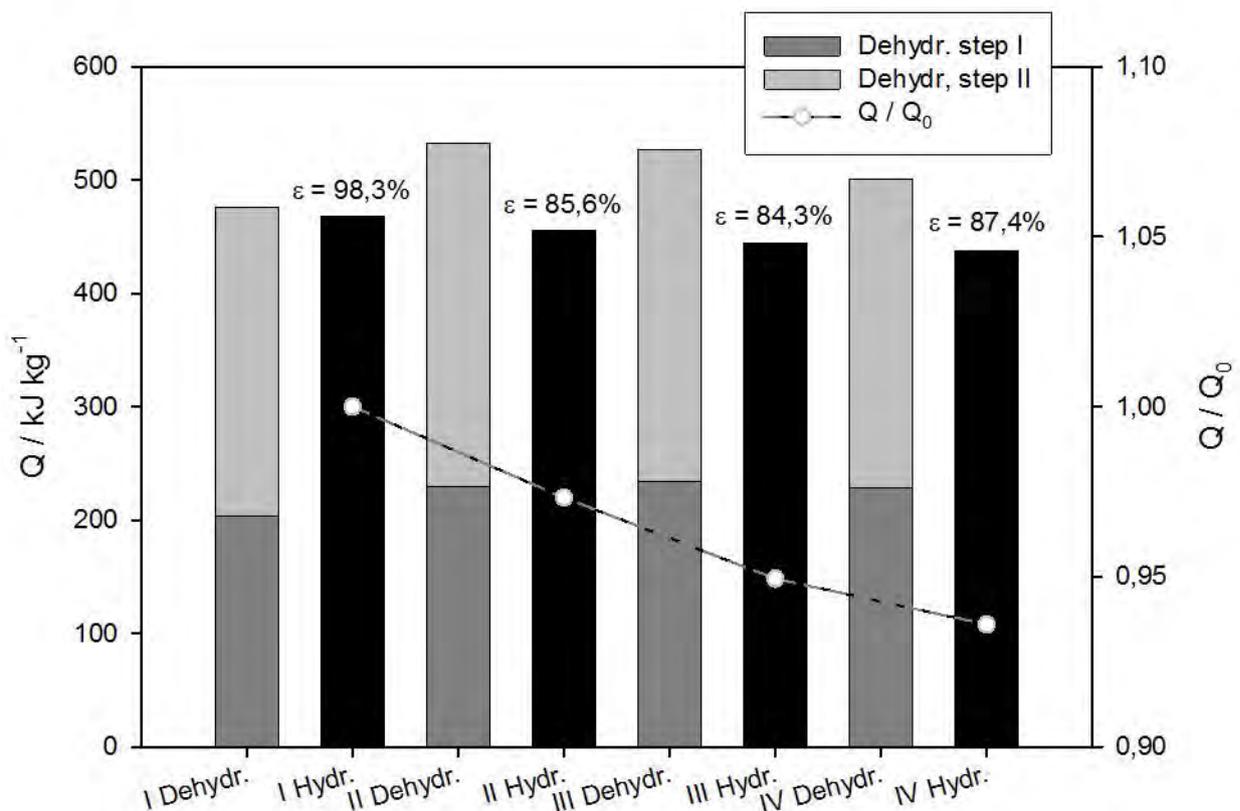

Figure 8: Heat quantities during dehydration and hydration, cycle efficiency and cycling stability using the transition of $MgCl_2 * 6 H2O$ -> $MgCl_2 * 2 H_2O + 4 H_2O$ of a $MgCl_2 * 6 H_2O$: Graphite (1:1) composite.

CONCLUSION AND OUTLOOK

The described method has been shown to be useful for rapid screening of possible TCM and composite materials. This way, hydration as well as dehydration characteristics of possible TCM materials, power density and cycling stability can be pretested before designing a laboratory scale reactor fitted to the desired application.

The results indicate, that it is possible to use $MgCl_2 * 6 H_2O$ as a TCM at temperatures below 100°C, which is relevant to a number of applications, for example heat storage for space heating and warm water applications and in combination with CHP plants. We made clear, that thermal decomposition is taking place at temperatures above 125°C and may be overlapping with the last dehydration step leading to the monohydrate salt. This is clarifying the ambivalent situation pictured in the available literature due to fast heating rates used in most TGA/DSC measurements, causing bias in the available data.

For the moment it remains unclear, if additives could help in using the full potential of $MgCl_2 * 6 H_2O$ by separating the thermal composition of the material from the third dehydration step, leading to the monohydrate salt, which would add another 10-20% in theoretically available storage capacity.

It was shown, though, that additives can have various influences on the reaction characteristics of TCM and $MgCl_2 * 6 H_2O$ in particular and should be studied in detail. Our investigations only mark a starting point for systematic studies regarding this subject.

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