Mixed salts in thermochemical heat storage applications

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1 Introduction

Thermochemical heat storage systems are based on storage materials that release heat when binding a solvent into their chemical structure in a reversible reaction. Due to their usually low material costs and availability, salts are an attractive option as storage material choice. However, while many different salt hydrates may theoretically be considered to be used as thermochemical heat storage materials, many of them show undesirable properties in practical applications. Low melting points, thermal instability and strong hygroscopy, which may lead to agglomeration, irreversible decomposition or deliquescence, are possible properties that lower the cycle stability of salts. Furthermore heat storage density and reaction temperatures need to be put into consideration when choosing a material. (N'Tsoukpoe, Schmidt, Rammelberg, Watts, & Ruck, 2014) (Visscher, 2004) Among the most promising materials concerning their heat storage density are calcium and magnesium chlorides. However, magnesium chloride shows low cycle stability and decomposes above 120 °C. (Rammelberg, Opel, Ross, & Ruck, 2011) Additionally magnesium chloride is prone to overhydrating and turning into a gel like substance (Zondag et al., 2010). Calcium chloride hexahydrate has a low melting point (T_M = 29°C) causing agglomeration at dehydration. (Behunek, Bachorec, & Fiala, 2006)

Material properties can be attempted to be improved in various ways:

- By addition of carrier materials as impregnated matrices (Druske, et al., 2014) (Druske, et al., 2013) (Korhammer, Druske, Fopah-Lele, Rammelberg, Wegscheider, & Opel, 2016) this however leads to a lower energy storage density of the system,
- Compression of the storage material into granular or pellet form to counter uncontrolled accumulation (Kerskes et al., 2011),
- Process control to avoid overhydration by limiting of the water vapor pressure during the discharge process. This reduces the risk of agglomeration, melting and deliquescence. (Rammelberg, Opel, Ross, & Ruck, 2011),
- Creating material mixtures and compounds (Druske, et al., 2014) (Druske, et al., 2013) (Rammelberg, Myrau, Schmidt, & Ruck, 2013).

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An attempt was made to improve said material properties by mixing different sulfate-, chloride- and bromide-salts and comparing their test results to those of related untreated materials. In a second step the hydration behavior of the most promising materials were investigated in large-scale experiments.

2 Methodology

2.1 Material selection

The untreated salts were dissolved in distilled water at a ratio of 1g to 10ml. The solutions were then mixed at calculated ratios such as 2:1 or 1:1 mol and the mixed salt crystals were grown from the liquid in a desiccator for optimal crystal growth and stored in the desiccator. 53 different chlorides, sulfates and bromides of potassium, strontium, calcium, magnesium and zinc (Lohman GmbH, Ph Eur.) were first analyzed by TGA/DSC for their energy storage density and stability over 2 cycles of dehydration and hydration. Of the 53 different mixtures 2 materials qualified for further testing for stability over 25 cycles and lab-scale experiments.

2.2 TGA/DSC measurements

By combined thermogravimetric analysis and differential scanning calorimetry (TGA/DSC), the mass change and heat energy sorption behavior of 10mg salt samples were monitored during the dehydration and hydration cycles. (Opel et al., 2011) The water vapor for hydration methods was produced by variant nitrogen flows through a water bubble flask. For the initial preselection of the materials the samples were dehydrated first at 100°C with a heating rate of 1K min^{-1}, followed by a hydration step with a water vapor pressure at 10 for 30 minutes, 17 for 45 minutes and 20mbar for 45 minutes. Afterwards they were dehydrated again with T_{max} = 200°C with a heating rate of 5K min^{-1}. (N'Tsoukpoe, Schmidt, Rammelberg, Watts, & Ruck, 2014), (Druske, et al., 2014), (Druske, et al., 2013) The hydration/dehydration cycle was repeated once after that. Materials which showed unstable behavior or low energy storage capabilities during this step were discarded from further research. The 25 cycle stability measurements consisted of a dehydration with a heating rate of 1K min^{-1} and a maximum temperature of 120°C, followed by a hydration with a water vapor pressure at 15mbar. The energy storage density was normalized by the weight of the dry salt, which did not equal an anhydrated salt in case of the 25 cycles measurements.

2.3 Lab-scale experiments

The TGA/DSC analysis is a good prescreening method to narrow down the amount of materials to consider for use in the battery systems. However, those systems operate on a different scale for which the TGA/DSC results may not apply. Therefore tests with mixed materials in an upscaled setup are required. For the lab-scale experiments the temperature changes within 20g samples of salt mixtures were measured during exposure of the sample to water vapor. The samples were dried beforehand at 120°C in an oven and cooled in a desiccator. The apparatus consisted of a reaction vessel, a tube with a metal mesh containing the sample secured between filter paper and wool. The reaction vessel is supplied with water vapor from a reservoir bottle filled with distilled water. The water vapor within the setup was created with heating by ambient air and at a total pressure between 20 to 30mbar. The dehydrated water was condensed into a water collection vessel from which the water can be returned into the reservoir bottle. The temperature within the apparatus was monitored online by two thermal elements: T_{H2O} measuring the temperature of the water vapor, T_{sample} measuring the temperature within the salt sample as seen in Figure 1.

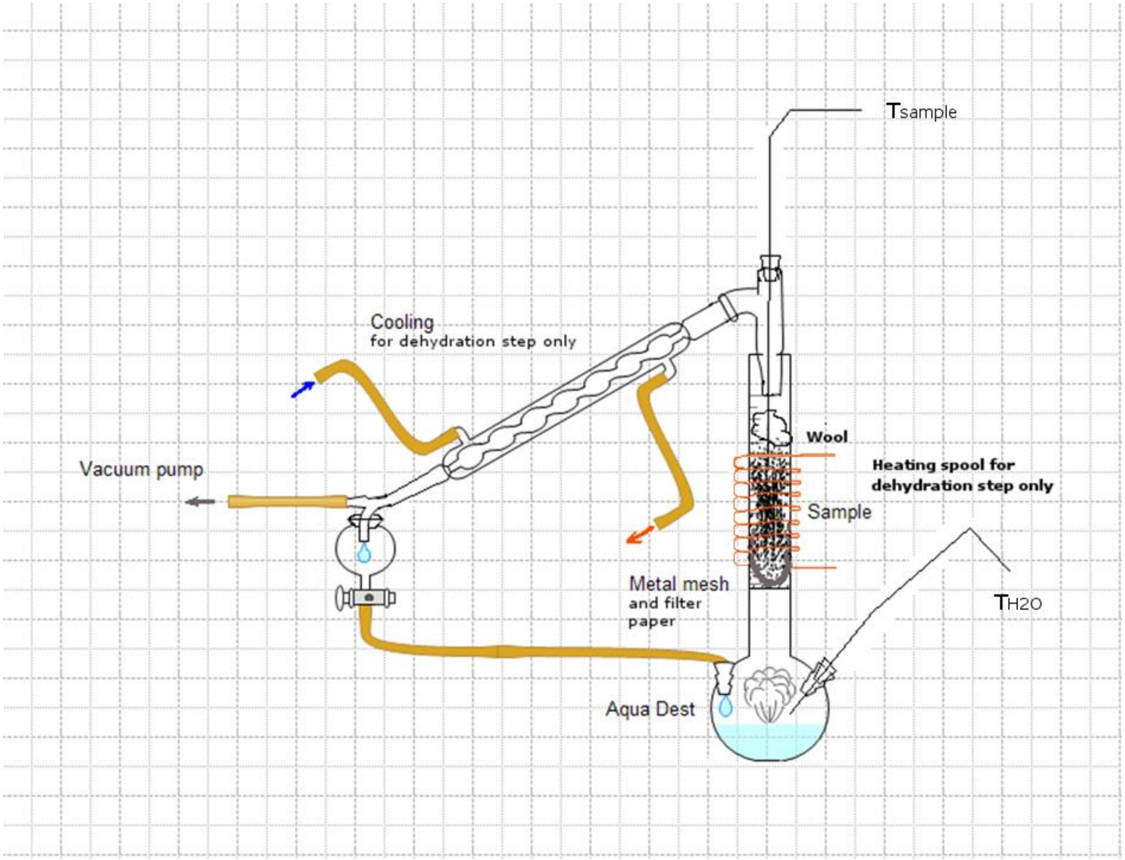

Figure 1 Experimental setup for the lab-scale experiments. The dried sample is exposed to water vapor generated by the vacuum pump lowering the pressure in the apparatus.

3 Results

3.1 TGA/DSC measurements

Used salt hydrates for TGA/DSC measurements were stored in a desiccator over silica gel to stabilize the hydration levels in dried atmosphere.

As seen in Table 1 the chloride mixtures reached the highest energy storage density, observed for the sample {$2MgCl_2 : CaCl_2$}. The {$2MgCl_2 : KCl$} and the {$CaCl_2 : 2ZnCl_2$} mixtures showed the best cycle stability among the chlorides, however for the hydrated phase of the {$CaCl_2 : 2ZnCl_2$} sample a low melting point of $T_M < 25°C$ was observed and the material was extremely deliquescent. The bromide sample {$SrBr_2 : 2LiBr$} combined a good cycle stability with a high energy storage density. However the high material costs of LiBr and $SrBr_2$ limit its use as storage materials. Therefore the latter two salt hydrate mixtures mentioned above were not used for further lab-scale experiments. The sulfate mixtures failed the prescreening due to low cycle stability combined with low energy storage density.

Table 1 The 4 materials with the best TGA/DSC prescreening results. ΔHp measured at hydration after dehydration at T_{max} = 200°C, normalized to the dry salt.

Material	ΔH_P (dry salt) [Jg^{-1}]
$2\ MgCl_2 : 1\ CaCl_2$	3330
$2\ MgCl_2 :1\ KCl$	1020
$1\ CaCl_2 : 2\ ZnCl_2$	1320
$1\ SrBr_2 : 2\ LiBr$	2140

Of those 4 materials the {$2MgCl_2 : KCl$} and {$2MgCl_2 : CaCl_2$} mixtures were chosen for the 25 cycle analysis and the lab-scale tests, since the materials are of low cost and literature research implied high stability of the materials (Rammelberg H. U., 2016) (Rammelberg, Myrau, Schmidt, & Ruck, 2013). The results of the cycle stability test of {$2MgCl_2 : KCl$} are shown in Figure 3 and Figure 3.

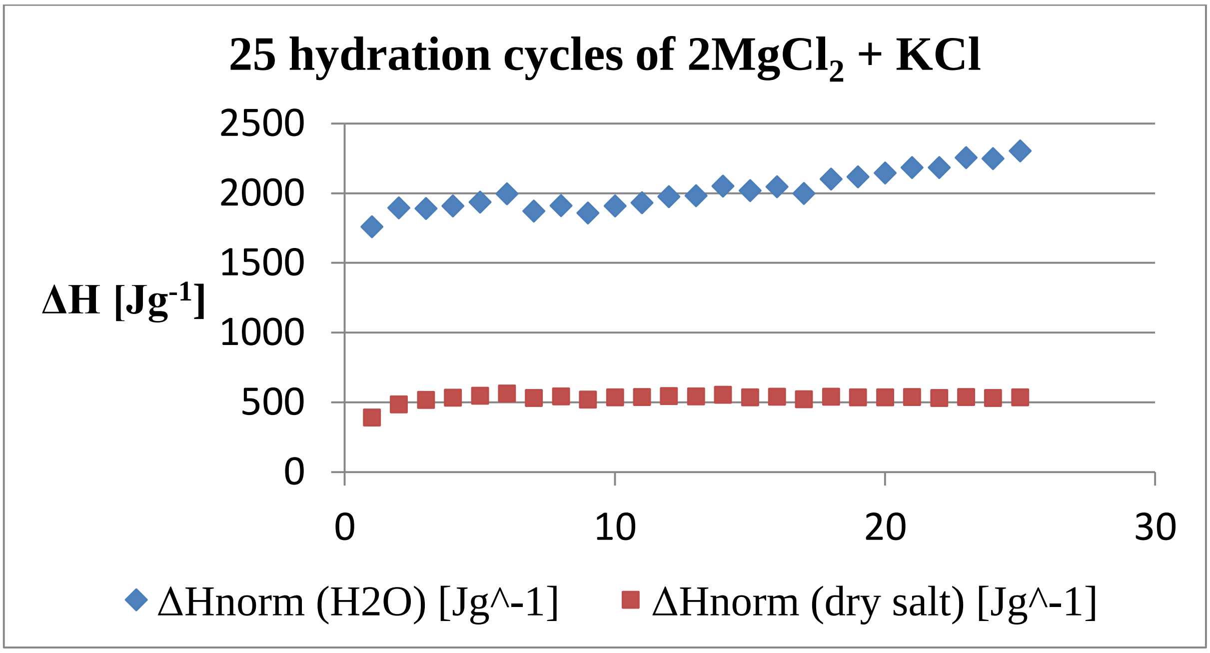

Figure 2 The 2MgCl2 + KCl mixture remained stable over all 25 cycles. The first low water release was reasoned by the low water vapor pressure stabilization in the desiccator during storing as mentioned above. The following hydrations therefor showed a higher hydration level, which in turn increased water release during the next dehydrations.

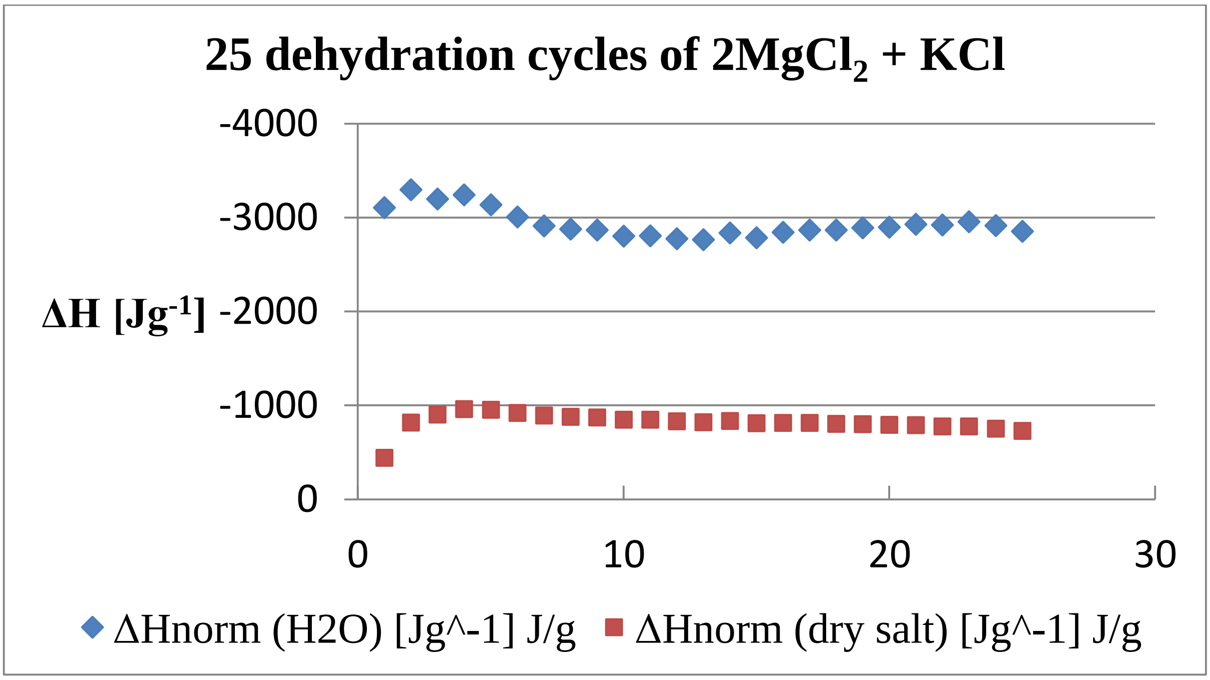

Figure 3 Dehydration enthalpies of the {2MgCl2 : KCl} salt mixture for 25 cycles normalized to H2O and dry salt respectively. The normalized enthalpies show a good stability over all cycles, however there is a light decline in the enthalpy normalized to the dry salt.

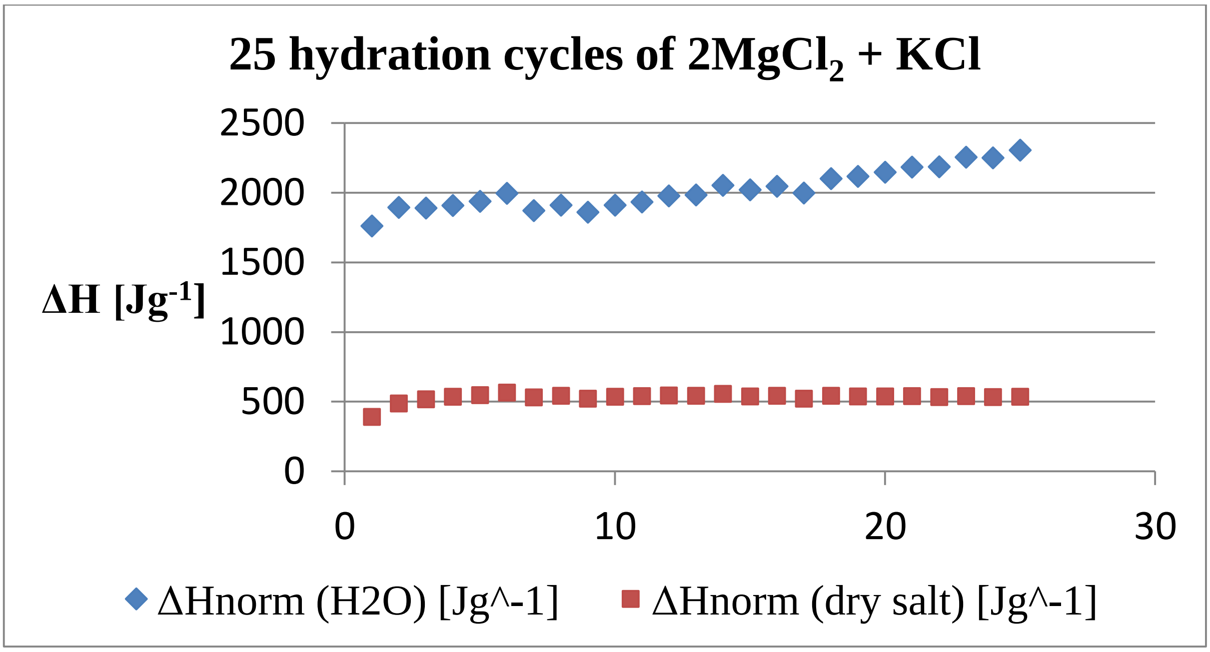

Figure 4 Hydration enthalpies of the {2MgCl2 : KCl} salt mixture for 25 cycles normalized to H2O and anhydrate respectively. The enthalpies normalized to water show a light incline over the cycles.

The results of the cycle stability test for the {$2MgCl_2$ + $CaCl_2$} mixture is given in Figure 5 and Figure 6. The hydration enthalpies show some incline over the cycles. The energy storage density is at a comparable level while the dehydration enthalpy is higher than that of the {$2MgCl_2$: KCl} mixture.

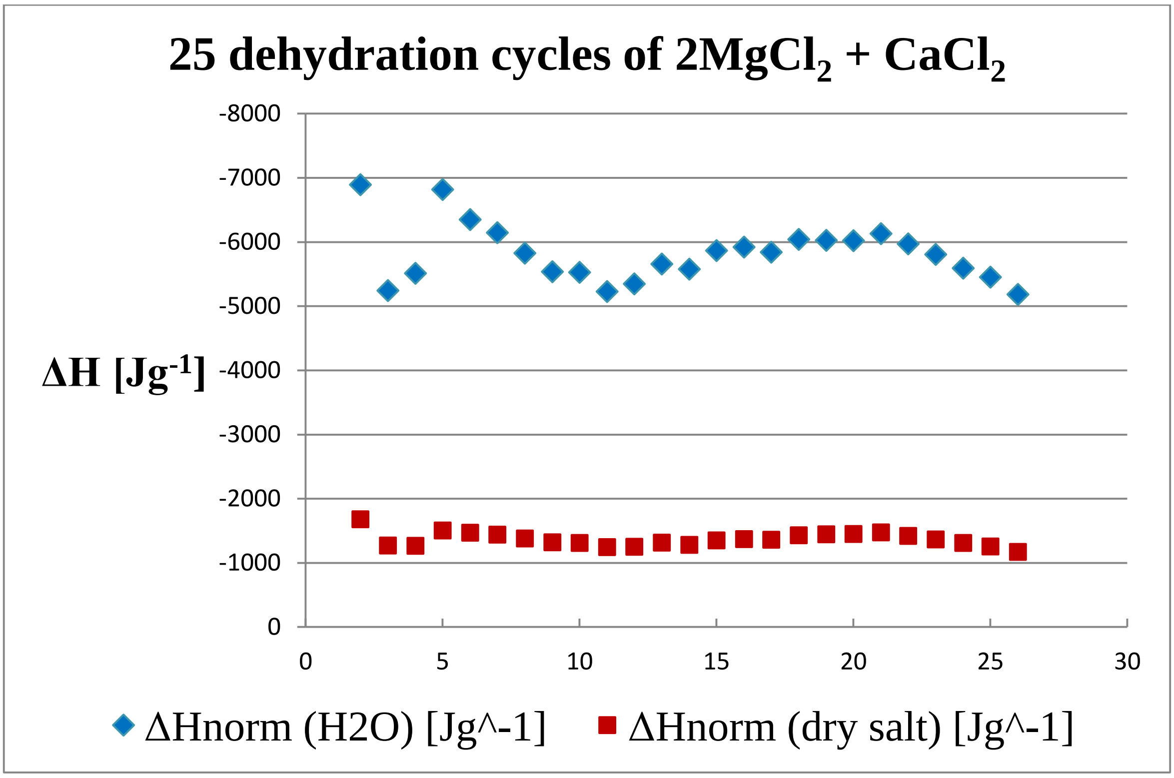

Figure 5 Dehydration enthalpies of the {2MgCl2 : CaCl2} salt mixture for 25 cycles normalized to H2O and dry salt respectively. The enthalpies normalized to the dry salt show a good stability with only a slight decline after 20 cycles.

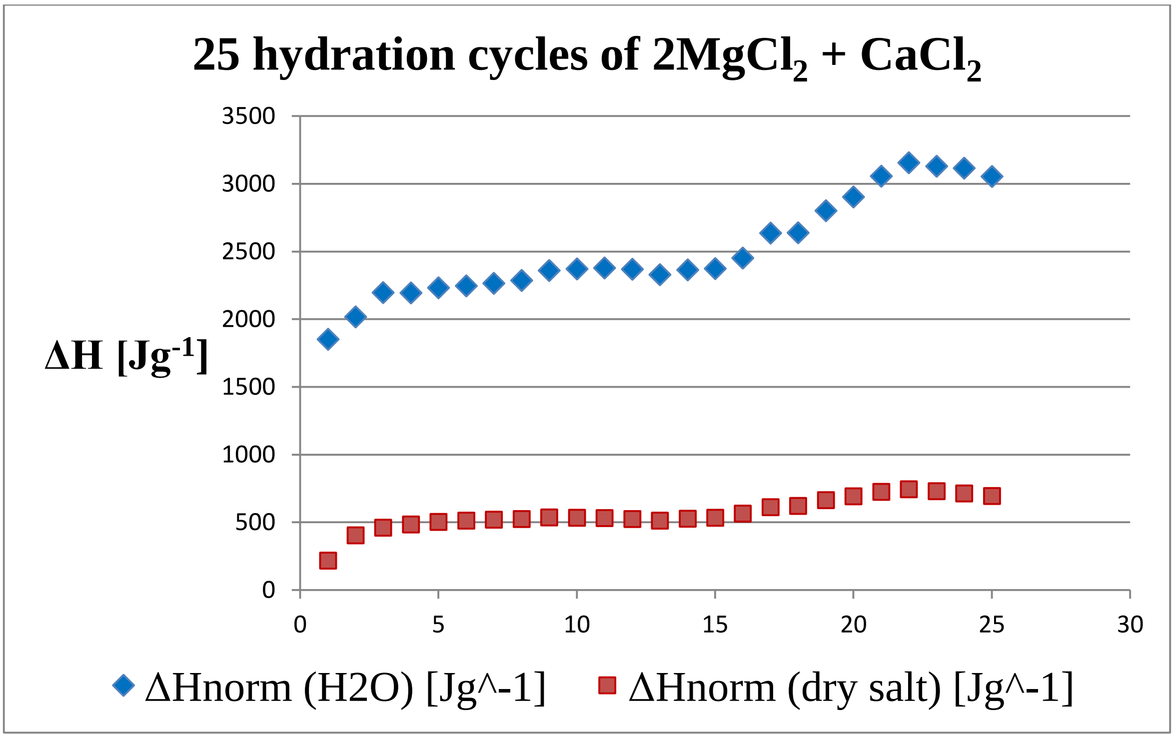

Figure 6 Hydration enthalpies of the {2MgCl2 : CaCl2} salt mixture for 25 cycles normalized to H2O and anhydrate respectively. The enthalpies normalized to water show a strong incline after the 15th cycle. This incline can be seen in the enthalpies normalized to the dry salt as well.

3.2 Lab-scale experiments

In the lab-scale apparatus the {2MgCl$_2$: KCl} mixture reached a maximum temperature of $T_{2MgCl2+KCl\ max}$ = 86°C within 3 minutes after exposure to water vapor. After 30 minutes it had cooled down to $T_{2MgCl2+KCl\ 0,5h}$= 63,3°C, after 1 hour to $T_{2MgCl2+KCl\ 1h}$= 47,3°C as shown in Figure 7. In comparison a sample of MgCl$_2$ reached a maximum temperature of $T_{MgCl2\ max}$ = 84,8°C within 1 minute of exposure to water vapor and cooled down to $T_{MgCl2\ 0,25h}$ = 30,8°C after 15 minutes.

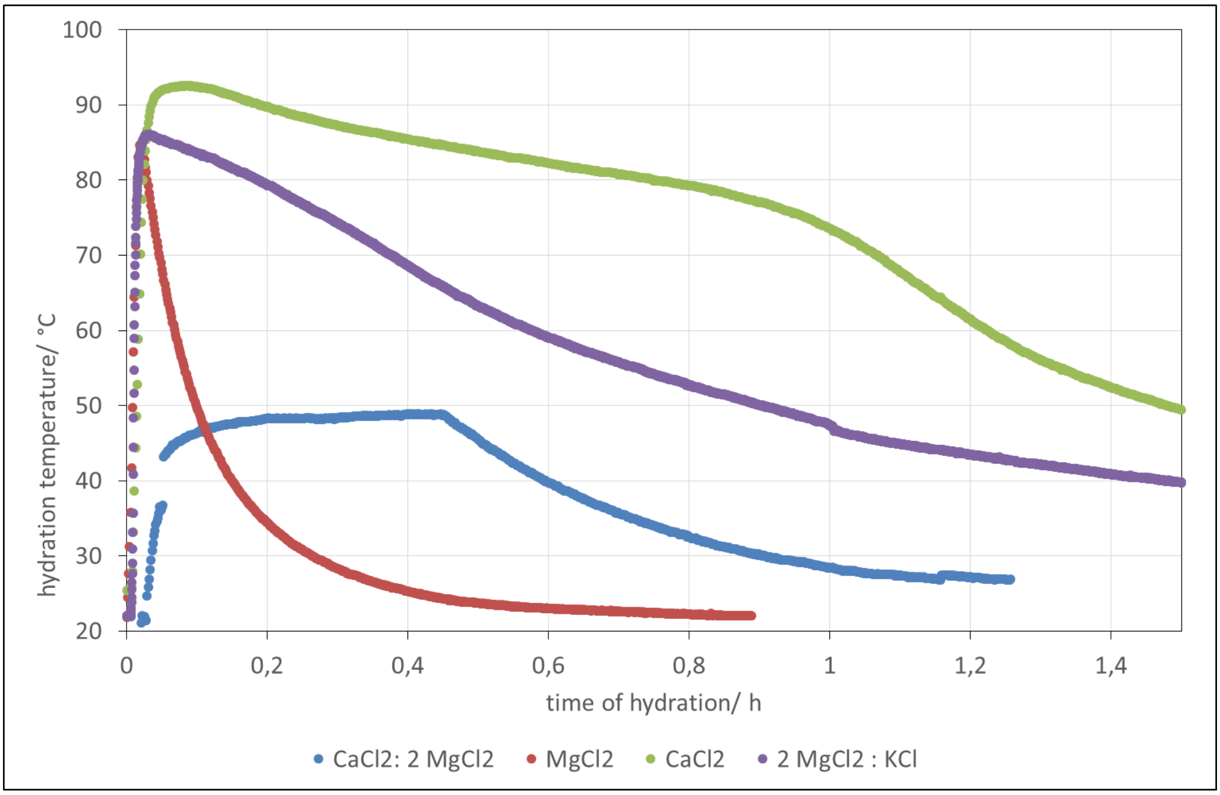

Figure 7 The first hydration of the {2MgCl2 : KCl} and {2MgCl2 : CaCl2}samples in the labscale aperture. TH2O representing the temperature of the water vapor,. The salt temperature reached its peak at T2MgCl2:KCl max= 86°C T2MgCl2:CaCl2 max= 48,9°C, TMgCl2 = 84,8°C and TCaCl2 = 92,6°C

Untreated CaCl$_2$ reached a maximum temperature of $T_{CaCl2\ max}$ = 92,6°C within 5 minutes of exposure to water vapor (T_{H2O} = 24,6°C). After 1 hour it had cooled to $T_{CaCl2\ 1h}$= 73,5°C, to to $T_{CaCl2\ 1,5h}$= 49,4°C after 90 minutes. The {2MgCl$_2$: CaCl$_2$} mixture reached a maximum temperature of $T_{2MgCl2+CaCl2\ max}$= 48,9°C within 14 minutes of exposure to water vapor in the apparatus (T_{H2O} = 24,3°C). After 1 hour the temperature had dropped to $T_{2MgCl2+CaCl2\ 1h}$ = 28,4°C.

4 Discussion

Compared to the untreated $MgCl_2$ the {$2MgCl_2$: KCl} mixture shows improved cycle stability in mg scale and an improved heat storage capacity in the lab-scale test.

The water vapor may have caused an agglomeration in the sample of untreated $MgCl_2$, which blocked the material partially from further hydration and stopped the reaction, which then led to a fast cooling of the sample.

Over 25 cycles the {$2MgCl_2$: $CaCl_2$} mixture shows an incline in heat storage capacity, which speaks for a delayed thermal activation of the material. It can be observed as well, that the heat storage capacity of the mixture at temperatures of $T_{max} < 120$°C is at the same level as that of the {$2MgCl_2$: KCl} mixture. The {$2MgCl_2$: $CaCl_2$} mixture shows only improvement in heat storage capacity compared to the $MgCl_2$ but not to the $CaCl_2$. However the temperature used to dry the untreated salts before the experiment was lower than the activation temperatures from literature (Kerskes et al., 2011) as seen in Table 2. This indicates that the untreated material may have been exposed to higher temperatures already before the experiment and that heating the {$2MgCl_2$: $CaCl_2$} mixture to $T_{max} = 200$°C instead of $T_{max} = 120$°C before discharge may yield improved results. Therefore a test for cycle stability for both untreated materials as well as for the two mixed materials will be necessary in the future to validate these results.

Table 2 Reversible reactions and reaction temperature intervals of MgCl2 and CaCl2 hydrates as tested by (Kerskes et al., 2011)

Reaction	Temperature interval [°C]
$MgCl_2·6H_2O \leftrightarrow MgCl_2·H_2O + 5H_2O$	100 – 130
$CaCl_2·6H_2O \leftrightarrow CaCl_2·H_2O + 5\ H_2O$	150 – 200

5 Conclusion

The TGA/DSC analyses are a good tool to narrow the search down for materials to be used in lab-scale analysis. The results from the tests with the lab-scale apparatus indicate an improvement of the heat storage capacity for the {$2MgCl_2$: KCl} mixture but further experiments are necessary to prove an increased cycle stability in larger scale.

While an improvement of the properties of the {$2MgCl_2$: $CaCl_2$} mixture could not be verified, tests with a higher dehydration temperature may give better results.

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