CALORIMETRIC INVESTIGATION OF TWO FACTORS INFLUENCING THE MAXIMUM STORAGE CAPACITY OF CALCIUM CHLORIDE HEXAHYDRATE

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Abstract. CaCl\textsubscript{2}·6H\textsubscript{2}O is a salt hydrate that is attractive as phase change material (PCM). However, in literature, different values are indicated for its melting enthalpy. Here, two possible influence factors on the maximum storage capacity of CaCl\textsubscript{2}·6H\textsubscript{2}O are investigated via differential scanning calorimetry (DSC): deviations of the water content from the stoichiometrically correct concentration and different basic raw materials used in the preparation process. While both influence factors are found to have a considerable impact on the maximum storage capacity of CaCl\textsubscript{2}·6H\textsubscript{2}O, the influence of deviations of the water content is more important than that of the basic raw materials.

1. Introduction
Latent heat storages with phase change materials (PCM) are attractive for thermal energy storage (TES) [1]. CaCl\textsubscript{2}·6H\textsubscript{2}O is a salt hydrate that is attractive as PCM due to its comparably high melting enthalpy (190.8 J g\textsuperscript{-1} indicated by Lane [2]). Additionally, it is “among the most economical PCMs” [2]. Due to its popularity, it has been often investigated in the past with, amongst others, its melting enthalpy determined several times. This leads to a plethora of values present in literature for the melting enthalpy of CaCl\textsubscript{2}·6H\textsubscript{2}O. Exemplarily, two of the most popular reviews on PCM, written by Zalba et al. [3] and Cabeza et al. [4] were consulted. Zalba et al. [3] indicate melting temperatures in a range between 29 and 30 °C while for the melting enthalpy the range is between 171 and 192 J g\textsuperscript{-1}. In the review of Cabeza et al. [4], published 8 years later, the range for the melting temperature is identical, however, the indicated values for the melting enthalpy are between 171 and 296 J g\textsuperscript{-1}. These examples show that, while there are only small deviations in the values for the melting temperature, considerable differences exist for the melting enthalpy of CaCl\textsubscript{2}·6H\textsubscript{2}O.

This observation was already generally documented for salt hydrates in 1983 by Guion et al. [5]. As sources for the observed deviations, Guion et al. [5] cite amongst others “trivial errors in transcription, or in conversion between different systems of units”. While these errors cannot be quantified, the focus of this work is on two further sources of deviations of melting enthalpy values: the influence of deviations from the stoichiometrically correct water content and of different basic raw materials.

CaCl\textsubscript{2}·6H\textsubscript{2}O is hygroscopic and does not melt congruently but semicongruently. These two aspects render CaCl\textsubscript{2}·6H\textsubscript{2}O a notoriously difficult candidate to be reliably measured via differential scanning calorimetry (DSC) relying on small sample sizes in the range of 10 µl [6]. To suppress the formation...
of CaCl$_2$·4H$_2$O associated with the semicongruent melting of CaCl$_2$·6H$_2$O and obtain reliable calorimetric data for CaCl$_2$·6H$_2$O via DSC, all measurements are carried out with 0.1 wt% Ba(OH)$_2$ as nucleating agent (following the recommendation by Rudaleviciene [7]).

In this work, instead of the melting enthalpy, the maximum storage capacity is used to compare different samples. The maximum storage capacity represents the enthalpy difference over a certain temperature range including the phase change. Therefore, it is better suited to compare samples which contain impurities and thus have an enlarged temperature range over which the phase transition takes place.

The first part of the investigation focusses on the influence of deviations from the stoichiometrically correct water content on the maximum storage capacity of CaCl$_2$·6H$_2$O. The aim of the second part of the investigation is to assess the influence of different basic raw materials on the maximum storage capacity of CaCl$_2$·6H$_2$O. All of the data was obtained experimentally via DSC measurements.

2. Materials and methods

2.1. Phase diagram and melting behaviour

According to Lane [2], CaCl$_2$·6H$_2$O composed of 50.66 wt% CaCl$_2$ melts at 29.6 °C with a melting enthalpy of 190.8 J g$^{-1}$. The same author states that CaCl$_2$·4H$_2$O composed of 60.63 wt% CaCl$_2$ melts at 45.3 °C. Thereby, CaCl$_2$·4H$_2$O is polymorphic with three different crystal phases: $\alpha$, $\beta$, and $\gamma$. A partial phase diagram of CaCl$_2$ + H$_2$O is shown in Figure 1.

![Partial phase diagram of CaCl$_2$ + H$_2$O adapted from [8]; point P is the peritectic point; point IC is the incongruent melting point.](image)

Figure 1. Partial phase diagram of CaCl$_2$ + H$_2$O adapted from [8]; point P is the peritectic point; point IC is the incongruent melting point.

CaCl$_2$·6H$_2$O melts semicongruently. Upon heating of solid CaCl$_2$·6H$_2$O, the peritectic temperature is reached at 29.45 °C (point IC in Figure 1). Upon further heating, a liquid solution is formed and $\alpha$ CaCl$_2$·4H$_2$O crystallises until the liquidus is reached at 32.78 °C. In this temperature gap of 3.33 °C, a maximum of 9.45 wt% $\alpha$ CaCl$_2$·4H$_2$O can crystallise. It is only after heating above the liquidus temperature of 32.78 °C that a liquid solution with the composition of CaCl$_2$·6H$_2$O is obtained. [2] A further interesting point, the peritectic point (point P in Figure 1), is located at a concentration of 49.62 wt% CaCl$_2$ [2]. For this concentration, no CaCl$_2$·4H$_2$O crystallises, making it potentially attractive to be used as PCM.

The term “semicongruent melting” implies that CaCl$_2$·4H$_2$O crystallises during the melting of CaCl$_2$·6H$_2$O, which is correct in theory, but is rather not the case in application relevant time intervals.
It was shown that CaCl$_2$·4H$_2$O forms e.g. in DSC measurements during cooling due to the considerable amount of supercooling associated with the typically small sample size [6]. Due to its higher density the crystalline CaCl$_2$·4H$_2$O sinks to the bottom of the crucible leading to a CaCl$_2$·H$_2$O solution with higher water content than CaCl$_2$·6H$_2$O. During the subsequent heating cycle, after melting, a droplet with vertically different densities is obtained. This behaviour along with the statistical nucleation behaviour introduces a high randomness into DSC measurements carried out on CaCl$_2$·6H$_2$O.

A possible solution is to measure multiple DSC samples of the same concentration to obtain more reliable arithmetic mean values of calorimetric data [9]. A different approach was suggested by Rudaleviciene [7] who investigated different amounts of four known nucleating agents for CaCl$_2$·6H$_2$O, and found that the addition of 0.1 wt% Ba(OH)$_2$ reliably suppresses the formation of CaCl$_2$·4H$_2$O while least affecting the melting enthalpy. Therefore, in this work, 0.1 wt% Ba(OH)$_2$ was also added to all of the CaCl$_2$·6H$_2$O samples to obtain reliable calorimetric data on CaCl$_2$·6H$_2$O via DSC with negligible effect on the melting enthalpy.

2.2. Sample preparation

The majority of the samples was prepared using CaCl$_2$·2H$_2$O and adding deionised water to obtain the targeted sample concentration, e.g. a water content of 49.34 wt% for the stoichiometrically correct CaCl$_2$·6H$_2$O. For each sample, the water content was checked three times with the moisture analyser HR 83 from Mettler Toledo to obtain a meaningful arithmetic mean value for the water content. The resulting measurement uncertainties were calculated according to the Eurachem / Citac Guide CG 4 [10] and are indicated for a coverage factor of 2 (95% confidence interval).

2.2.1. CaCl$_2$ + H$_2$O samples

To investigate the influence of the water content on the maximum storage capacity of CaCl$_2$·6H$_2$O, six CaCl$_2$ + H$_2$O samples were prepared. Since CaCl$_2$·6H$_2$O is known to be hygroscopic, besides CaCl$_2$·6H$_2$O, five CaCl$_2$ + H$_2$O samples with a higher water content than that of CaCl$_2$·6H$_2$O were prepared. Thereby, CaCl$_2$·2H$_2$O from Merck KgaA was used along with deionised water to prepare the six CaCl$_2$ + H$_2$O samples. An overview of the samples is provided in Table 1, where the water content with the combined measurement uncertainty (95% confidence interval), the standard deviation, and the resulting CaCl$_2$ concentration are listed.

| CaCl$_2$ + H$_2$O sample | H$_2$O / wt%  | sd(H$_2$O) / wt% | CaCl$_2$ / wt% |
|--------------------------|---------------|-----------------|---------------|
| C1                       | 51.09 ± 0.12  | 0.03            | 48.91         |
| C2                       | 50.73 ± 0.10  | 0.00            | 49.27         |
| C3                       | 50.37 ± 0.11  | 0.02            | 49.63         |
| C4                       | 50.04 ± 0.10  | 0.01            | 49.96         |
| C5                       | 49.73 ± 0.10  | 0.00            | 50.27         |
| **C6**                   | **49.35 ± 0.10** | **0.01**       | **50.65**     |

2.2.2. CaCl$_2$·6H$_2$O samples

To investigate the influence of different basic raw materials on the maximum storage capacity of CaCl$_2$·6H$_2$O, the three basic raw materials listed in Table 2 were chosen.
Table 2. Overview of manufacturers, product names, product numbers, batch numbers, and product specifications of the basic raw materials used to prepare the different CaCl$_2$·6H$_2$O samples.

| Manufacturer       | Product name                                      | Product number | Batch number | Product specification          |
|--------------------|---------------------------------------------------|----------------|--------------|--------------------------------|
| Merck KGaA         | Calcium chloride dihydrate for analysis EMSURE®ACS, Reag. Ph Eur | 102382         | A07463826 03 | Assay (complexometric) 99.0 – 102.0% |
| VWR Chemicals      | Calcium chloride hexahydrate ≥97%, GPR Rectapur®   | 22311.297      | 14J200025    | Min. 97%                       |
| TETRA Chemicals    | Technical grade calcium chloride flakes           | /              | BR400000     | CaCl$_2$ concentration > 77%   |

Two of the basic raw materials listed in Table 2 are of laboratory grade, from Merck KGaA and VWR Chemicals. The third basic raw material is of technical grade from TETRA Chemicals. Thereby, the basic raw materials are twice CaCl$_2$·2H$_2$O (even if the product name from TETRA Chemicals does not indicate this directly) and once CaCl$_2$·6H$_2$O. Depending on the manufacturer, the product specifications presented in Table 2 are quite varying. From the three basic raw materials, four different CaCl$_2$·6H$_2$O samples were prepared.

To prepare a CaCl$_2$·6H$_2$O sample with a purity as high as possible to serve as reference sample, CaCl$_2$·6H$_2$O crystals were grown from a parent solution containing 45 wt% CaCl$_2$ and 55 wt% H$_2$O. The basic raw material that was used to prepare the parent solution was “calcium chloride dihydrate for analysis” from Merck KGaA. CaCl$_2$·2H$_2$O from Merck KGaA was chosen since it was the basic raw material with the highest purity (cf. Table 2). The parent solution was left overnight in a laboratory refrigerator set at 5 °C. The grown CaCl$_2$·6H$_2$O crystals were dried using filter paper, which was, however, not enough to remove all of the parent solution. Consequently, the dried CaCl$_2$·6H$_2$O crystals were melted and the excess water was evaporated using a magnetic stirring plate with the temperature set at 150 °C and under constant stirring until the stoichiometrically correct water content was reached.

Two samples were prepared from the CaCl$_2$·2H$_2$O basic raw materials from both Merck KGaA and TETRA Chemicals by adding deionised water. One sample was prepared from the CaCl$_2$·6H$_2$O basic raw material from VWR Chemicals by adjusting its water content to match the stoichiometrically correct content. Indeed, after melting a sample of CaCl$_2$·6H$_2$O from VWR Chemicals, it was found that the water content was 50.04 wt% and thus deviated from the stoichiometrically correct water content. Hence, the excess water was evaporated analogously to the case with the grown CaCl$_2$·6H$_2$O crystals.

An overview of the four CaCl$_2$·6H$_2$O samples with the determined water content, the corresponding measurement uncertainties and standard deviations is provided in Table 3.

Table 3. Overview of the four CaCl$_2$·6H$_2$O samples, the manufacturer of the corresponding basic raw materials, and the water content (H$_2$O). Additionally, the standard deviation (sd(H$_2$O)) obtained for three measurements per sample is indicated.

| CaCl$_2$·6H$_2$O sample | Manufacturer          | H$_2$O / wt% | sd(H$_2$O) / wt% |
|-------------------------|-----------------------|--------------|-----------------|
| Grown                   | Merck KGaA            | 49.37 ± 0.11 | 0.02            |
| Merck                   | Merck KGaA            | 49.33 ± 0.11 | 0.02            |
| VWR                     | VWR Chemicals         | 49.35 ± 0.12 | 0.03            |
| Tetra                   | TETRA Chemicals       | 49.33 ± 0.12 | 0.03            |
The water contents listed for the four CaCl$_2$$\cdot$6H$_2$O samples in Table 3 demonstrate that for each sample, the water content corresponds to that of the stoichiometrically correct water content of 49.34 wt% of CaCl$_2$$\cdot$6H$_2$O within the indicated measurement uncertainties. Additionally, the obtained standard deviations show a high reproducibility of the determination of the water content via moisture analyzer. It can therefore be concluded that possible differences in melting enthalpy and maximum storage capacity are not due to differences in the water content but arise from the grade differences, i.e. impurities present in the basic raw materials.

2.3. Calorimetric measurements

All of the calorimetric measurements were carried out with a DSC Q2000 from TA Instruments. The DSC Q2000 was calibrated with indium. The manufacturer, TA Instruments, indicates an accuracy of 1 - 2% for the heat of fusion in the temperature range from -50 to 350 °C for the single point indium calibration [11]. The accuracy of the enthalpy curves determined with the used DSC device has been approved in various comparative studies, such as the round robin test of octadecane within IEA SHC Task 42 / ECES Annex 24 and its continuation Task 42 / Annex 29 [12]. Based on the participation in the ECES Annex 24 and our experience, the enthalpy can be measured with our DSC with an estimated relative uncertainty of ±5% [13]. However, it has to be considered, that these ±5% represent the deviation from the “real value” and apply in the case of a single measured DSC sample. In contrast, here, the combined measurement uncertainty with a coverage factor of 2 (95% confidence interval) will be provided (the latter calculated as recommended by Eurachem / Citac Guide CG 4 [10]) for arithmetic mean enthalpy values determined for several DSC samples. The temperature uncertainty was determined by measuring indium again after the temperature calibration. With a coverage factor 2, assuring a 95% confidence interval, it amounts to ±0.1 K. A constant stream of nitrogen (50 ml min$^{-1}$) was applied as flushing gas during the measurements.

Liquid samples with a mass of 11-14 mg (weighing accuracy 0.01 mg) were introduced in hermetically sealed alodined aluminium crucibles and measured with a heating/cooling rate of 2 K min$^{-1}$. The melting enthalpy can be determined from DSC thermograms. However, it has to be considered that it is only meaningful to indicate the melting enthalpy for pure substances [6]. For salt hydrates, e.g. an excess water content leads to an enlarged temperature interval over which the phase transition occurs. In that case, the phase transition is not only composed of the melting process but additionally of a solution process due to the excess water. Then it is recommended to indicate the enthalpy over a certain temperature range containing the phase transition. Here, the maximum storage capacity is used to compare multiple samples. Typically, a temperature range of 15 K is chosen to indicate the maximum storage capacity since it is a temperature range used for phase change materials in applications [8]. The maximum storage capacity over a temperature range of 15 K is designated as $\Delta h_{15K}$.

To determine an appropriate temperature interval to indicate the maximum storage capacity, the enthalpy representation of calorimetric measurements can be consulted [13]. Figure 2 shows representative enthalpy curves of a sample of CaCl$_2$$\cdot$6H$_2$O containing 0.1 wt% Ba(OH)$_2$ for the second heating/cooling cycle measured via DSC at a heating/cooling rate of 2 K min$^{-1}$. The heating and cooling curves were shifted to a common zero point at 40 °C. Despite the presence of 0.1 wt% Ba(OH)$_2$ as nucleating agent, some supercooling persists due to the small sample size. Therefore, a temperature range between 25 and 40 °C is selected to indicate the maximum storage capacity, only based on the enthalpy curve during heating. This temperature range is the same one as in our previous work on CaCl$_2$$\cdot$6H$_2$O [9].
3. Results and Discussion

3.1. Influence of deviations of the water content

For each of the six \( \text{CaCl}_2 \cdot \text{H}_2\text{O} \) samples, \( \text{3 DSC samples} \) were measured at a heating/cooling rate of 2 K min\(^{-1}\). The results for the maximum storage capacity along with the combined measurement uncertainty with a coverage factor of 2 (95% confidence interval) and with the corresponding standard deviation are listed in Table 4.

| \text{CaCl}_2 \cdot \text{H}_2\text{O} \text{ sample} | \Delta h_{15K} / \text{J g}^{-1} | \text{sd}(\Delta h_{15K}) / \text{J g}^{-1} | \delta(\Delta h_{15K}) / \% |
|---|---|---|---|
| C1 | 171 ± 7 | 1 | -26 |
| C2 | 183 ± 8 | 1 | -21 |
| C3 | 196 ± 8 | 1 | -15 |
| C4 | 209 ± 9 | 2 | -10 |
| C5 | 218 ± 9 | 1 | -6 |
| C6 | 232 ± 9 | 1 | 0 |

The highest value for the maximum storage capacity is \( (232 ± 9) \text{ J g}^{-1} \), determined for sample C6 corresponding to \( \text{CaCl}_2 \cdot 6\text{H}_2\text{O} \). This sample serves as reference sample and the deviation in maximum storage capacity of each \( \text{CaCl}_2 \cdot \text{H}_2\text{O} \) sample is indicated in Table 4 relative to that sample. It can be seen that a deviation in the water content of around 1 wt\% leads to a decrease in maximum storage capacity of about -15%. This difference in maximum storage capacity is determined between sample C6 and sample C3, representing the peritectic point. The largest deviation is -26% for sample C1 with a water content 1.74 wt\% higher than that of \( \text{CaCl}_2 \cdot 6\text{H}_2\text{O} \). The results show that seemingly small deviations in the water content can lead to considerable decreases in the maximum storage capacity of \( \text{CaCl}_2 \cdot 6\text{H}_2\text{O} \).
3.2. Influence of different basic raw materials

For each of the four CaCl$_2$·6H$_2$O samples, 3 DSC samples were measured at a heating/cooling rate of 2 K min$^{-1}$. The results for the melting enthalpy and the maximum storage capacity along with the combined measurement uncertainty (95% confidence interval) and with the corresponding standard deviations are listed in Table 5.

Table 5. Overview of the melting enthalpy ($\Delta h_m$) and maximum storage capacity ($\Delta h_{15K}$) determined for the four CaCl$_2$·6H$_2$O samples containing each 0.1 wt% Ba(OH)$_2$ as nucleating agent. Additionally, the standard deviations are provided for $\Delta h_m$ and $\Delta h_{15K}$ by $\text{sd}(\Delta h_m)$ and $\text{sd}(\Delta h_{15K})$, respectively. $\delta(\Delta h_{15K})$ indicates the difference in $\Delta h_{15K}$ relative to the reference sample “Grown”.

| CaCl$_2$·6H$_2$O sample | $\Delta h_m$ / J g$^{-1}$ | $\text{sd}(\Delta h_m)$ / J g$^{-1}$ | $\Delta h_{15K}$ / J g$^{-1}$ | $\text{sd}(\Delta h_{15K})$ / J g$^{-1}$ | $\delta(\Delta h_{15K})$ / % |
|-------------------------|--------------------------|-------------------------------------|-----------------------------|---------------------------------------|---------------------------|
| Grown                   | 201 ± 8                  | 1                                   | 235 ± 9                     | 1                                     | 0                         |
| Merck                   | 198 ± 8                  | 1                                   | 234 ± 10                    | 2                                     | 0                         |
| VWR                     | 200 ± 8                  | 1                                   | 235 ± 10                    | 1                                     | 0                         |
| Tetra                   | 173 ± 8                  | 2                                   | 204 ± 8                     | 1                                     | -13                       |

From the results listed in Table 5, it can be seen, that the CaCl$_2$·6H$_2$O reference sample “Grown” has the largest value for both the melting enthalpy and the maximum storage capacity, i.e. (201 ± 8) J g$^{-1}$ and (235 ± 9) J g$^{-1}$, respectively. However, the values for the melting enthalpy and the maximum storage capacity for the other two CaCl$_2$·6H$_2$O sample of laboratory grade, “Merck” and “VWR”, coincide with the values of the sample “Grown” within the respective measurement uncertainties. Only the sample “Tetra” prepared from a technical grade basic raw material shows a decrease in maximum storage capacity of -13% relative to the reference sample “Grown”.

3.3. Impact on literature values

The results obtained for both investigations show that the water content seems to have a higher influence on the maximum storage capacity of CaCl$_2$·6H$_2$O than the basic raw material used in the preparation process. Therefore, it is crucial when measuring CaCl$_2$·6H$_2$O to assure that is has the stoichiometrically correct water content or at least to be aware of the magnitude of the deviation. With the CaCl$_2$·6H$_2$O purchased from VWR Chemicals, it was determined, that even for readily purchased CaCl$_2$·6H$_2$O, deviations from the stoichiometrically correct water content can exist.

Especially the decrease in maximum storage capacity due to a deviation of the water content from the stoichiometrically correct water content of CaCl$_2$·6H$_2$O shows how differences in melting enthalpy values in literature can originate. Combining both influence factors, i.e. water content and basic raw material, even larger deviations in maximum storage capacity from laboratory grade CaCl$_2$·6H$_2$O can be expected. Therefore, it is recommended to researchers to analyse the composition of the measured salt hydrates and to indicate such relevant information in published articles. Reviews containing melting enthalpy data on salt hydrates should also contain such information. Additionally, researchers collecting data for a review should make sure to only use original measured data and not data from existing reviews to minimise amongst others transcription errors.

4. Conclusions

CaCl$_2$·6H$_2$O is a salt hydrate that is attractive as PCM. However, a multitude of different values for its melting enthalpy exists in literature, leading to the question of possible origins of these deviations.

In this work, two possible influence factors on the maximum storage capacity of CaCl$_2$·6H$_2$O were investigated: deviations from the stoichiometrically correct water content and different basic raw materials used in the preparation process. An amount of 0.1 wt% Ba(OH)$_2$ was added as nucleating agent to each investigated sample to counteract the difficulties associated with the semicongruent melting of CaCl$_2$·6H$_2$O. All of the measurements were carried out via DSC. The enthalpy value that
served to compare the different samples was the maximum storage capacity over a temperature interval of 15 K including the phase transition.

It was found that seemingly small deviations in the water content have a considerably impact on the maximum storage capacity of \( \text{CaCl}_2\cdot6\text{H}_2\text{O} \). For a deviation of about 1.7 wt% in the water content, a decrease in the maximum storage capacity of -26% compared to stoichiometrically correct \( \text{CaCl}_2\cdot6\text{H}_2\text{O} \) was determined. Using a technical grade basic raw material to prepare \( \text{CaCl}_2\cdot6\text{H}_2\text{O} \) instead of laboratory grade was found to lead to a decrease of -13% in the maximum storage capacity. Therefore, it can be stated that both investigated influence factors can be at the origin of deviating melting enthalpy values found for \( \text{CaCl}_2\cdot6\text{H}_2\text{O} \) and hence for other salt hydrates in literature.

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