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Characterization of microencapsulated and impregnated porous host materials based on calcium chloride for thermochemical energy storage

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HIGHLIGHTS
• Attempts have been made to stabilize calcium chloride-based materials.
• Impregnation and microencapsulation methods are applied.
• Stability, kinetics and energy density are investigated.
• Combined TGA-DSC methods and microscopic observation are employed.
• Microencapsulation improved stability and kinetics but not energy density.

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TGA-DSC

ABSTRACT

Thermochemical heat storage in salt hydrates is a promising method to improve the solar fraction in the built environment. The major concern at this stage is liquefaction followed by washing out of active material and agglomeration into large chunks of salt, thus deteriorating the diffusive properties of the porous salt hydrate structure. In this work, specific attention is given to the methods to stabilize a sample salt hydrate. Attempts have been made to stabilize calcium chloride by impregnation in expanded natural graphite and vermiculite, and by microencapsulation with ethyl cellulose. The effect of these stabilization methods on the performance of the material, such as kinetics and energy density, is investigated. Characterization of the materials is carried out with combined Thermo-Gravitational Analysis (TGA) and Differential Scanning Calorimetry (DSC) methods and microscopic observation, in order to evaluate the improvements on the basis of three subjects: reaction kinetics, heat storage density and stability. Within the boundary conditions for thermochemical energy storage as presented in this work, microencapsulated calcium chloride showed high multicyclic stability, compared with pure and impregnated materials, that liquefy upon hydration under the given conditions. Microencapsulated material remains stable over multiple cycles and at the same time shows the faster kinetics, but has a lower volumetric energy storage density.

1. Introduction

In Europe, energy consumption for domestic purposes accounts for almost 40% of the total energy demand [1]. Therefore, a significant potential to reduce greenhouse gas emissions exists by the reduction in fossil fuel consumption in this sector. Energy storage is a key step to shift to low carbon energy sources, which are inherently intermittent. Solar energy, as one of the most exploitable renewable energy sources, is available more than required in residential houses during summer, while the demand cannot be met during winter. A solution is to store excess of solar energy in summer by a so-called thermal battery which can be discharged to provide heat for the residential demand in winter [2].

A promising method is heat storage in ThermoChemical Materials (TCMs), by which heat can be stored in a compact and quasi loss-free way over a long time. In the sorption heat storage process, heat is stored into an endothermal dissociation reaction (charging), and at a later time, the energy can be retrieved from the reverse exothermal reaction (discharging). In the built environment, heat generated by a solar collector during summer can be employed to desorb water from the material. The energy stored in this way can be released during winter by introducing water vapor to the dehydrated material. For low
temperature sorption heat storage, adsorption of water vapor on sorption materials [3] and hydration of salt hydrates [4,5] are frequently studied. Based on theoretical energy storage density, salt hydrates (such as calcium chloride) are better candidates compared to sorption materials (such as zeolite) [6]. It should be noted here that the physical phenomenon of fixation or capture of water vapor (sorbate) by sorbent is defined under the term sorption, however the expressions “thermochemical” and “sorption” are used differently by authors [7].

In recent years, intense research has been performed on innovative system design for integrating the sorption heat storage concept into an overall system, and lab or pilot scale setups are developed and tested [8]. Several Prototypes are built based on zeolite [9] [10] and some salt hydrates, such as magnesium chloride [11] and strontium bromide [12]. More can be find in the extensive reviews on sorption heat storage, which are done to summarize state of the art on systems and reactors for building applications [13] and advancements at material and prototype for long-term low-temperature applications [14].

Both open and closed systems are investigated for long-term thermal storage of solar energy [15]. In an open system, both sorbate and energy are exchanged between the system and the environment, while in a closed system, only energy is exchanged between the system and the surrounding environment. The open system concept seems more promising for seasonal heat storage because of robustness and low cost [16]. In open systems, mass transfer is the main limitation to achieve a good system performance [17]. Therefore, the mass transfer phenomena occurring locally in the reactor, and hence the material reaction, are critical parameters for the global performance of the system [18]. For instance, low stability of material can lead to formation of a non-diffusive layer around the material grains locally in the reactor, and hence a limited vapor transport into the thermochemical material. Therefore, performance of the system (with such unstable material) drops after couple of de/re-hydration cycles.

The major concern regarding the stability of salt hydrates is liquefaction followed by washing out of active material and agglomeration into large chunks of salt, thus deteriorating the diffusive properties of the material porous structure. These features make the material unfit for application in a thermochemical heat storage system, since stability is required for many cycles. Stability could in principle be guaranteed when overhydration can be prevented. However, this means restricting the conditions to which the reactor material is exposed during storage. This is hard to accomplish without the use of energy and technology to prevent either low temperatures or high humidity values from occurring in the system. Apart from additional costs, this will make the system more complicated. Furthermore, in case of failures like leakages in the reactor wall or power outage, stability of the material cannot be guaranteed. Therefore, the focus of this work is on the stabilization of the material. Calcium chloride, as one of the promising salt hydrates [4] with known properties, is chosen, in order to test and evaluate some of the stabilization methods on the material.

Microencapsulation is another approach for the stabilization of salt hydrates, although it is not so common in the context of thermochemical energy storage. In this approach (salt hydrate) particles are enveloped with a second inherently stable material to prevent coalescence or agglomeration. Recently, there is a growing interest in the microencapsulation of inorganic Phase Change Materials (PCMs) [30]. However, a critical difference exists between encapsulation of TCM and PCM. In TCM, it is essential that water can escape through the encapsulation material, while it is not the case for PCM. The microencapsulation of CaCl₂ hydrates has been reported by Cuypers et al. [31]. It is claimed that both the physical stability and reaction kinetics can be enhanced, however it still needs to be approved by more elaborate experiments.

In this work, specific attention is given to the stability of calcium chloride-based materials, since it is a serious concern as discussed. Attempts have been made to stabilize calcium chloride by impregnation in expanded natural graphite and vermiculite, and by encapsulation with ethyl cellulose. The effect of these stabilization methods on the performance of the material, such as kinetics and energy density, is investigated. Characterization of the materials is carried out with combined Thermo-Gravitational Analysis (TGA) and Differential Scanning Calorimetry (DSC) methods, in order to evaluate the improvements on the basis of three subjects: reaction kinetics, heat storage density and stability.

2. Materials and methods

2.1. Calcium chloride

Calcium chloride is one of the promising salt hydrates for thermochemical heat storage for common building applications [32]. A reversible chemical gas-solid reaction can be employed that involves CaCl₂, according to the de/re-hydration reaction of CaCl₂·xH₂O(s) + heat → CaCl₂·(x−y)H₂O(s) + yH₂O(g). A review on the use of calcium chloride in applied thermal engineering is done in [33]. The interest for calcium chloride has been triggered by: easy availability and subsequently low price (0.1–0.4 €/kg [34]), high capacity for water uptake and energy storage density, relatively better chemical stability than other salt hydrates, low corrosiveness and non-toxicity. Furthermore, the material dehydrates at low temperature (below 100 °C), which makes it suitable for the applications.

The reference water vapor pressure of 1.3 kPa is chosen, being the saturation water vapor pressure at 10 °C, which is a typical borehole (humidity generator) temperature in the Dutch climate [11]. The equilibrium loading of CaCl₂ at a vapor pressure of 1.3 kPa at different discrete temperatures is taken from the phase diagram of calcium chloride [35] shown in Fig. 1. The equilibrium loading at two temperatures (20 °C and 30 °C) is also measured in the experiments.
(explained in the next sections) and shown in the figure. The data are well fitted with a power function as shown in the figure, which will be used in the results section. It should be noted that the equilibrium loading curve for the solid state (the part below the aqueous solution line) should have a step function shape. These steps should be visible at 6, 4, 2, 1 and 0 state of hydration values. Therefore, the real equilibrium loading can be express by the step function, however a pseudo-equilibrium loading can be express by the extrapolated function.

The hydration reaction steps for known states of hydration for calcium chloride (an-, mono-, di-, tetra- and hexahydrate) with the reaction enthalpies are presented in Table 1. During the hydration process, after a certain state of hydration liquefaction occurs, which is caused by the depression of the melting point upon water uptake. This is caused by the highly hygroscopic nature of the material. In practice, this means the formation of an aqueous solution instead of a solid state material. Dehydration of such overhydrated solution yields an agglomerated bulk of solid material, instead of the initial powdery porous form. Agglomeration is an undesirable behavior of the material as TCM, because it prevents or decelerates the subsequent water uptake process. Therefore, most thermochemical storage studies do not intend to use calcium chloride in pure form [33]. A solution for this problem is the use of additional materials, which helps to stabilize the physical structure of the material. However, this can decrease the energy storage density and/or reaction rate.

2.2. Composite materials

Four calcium chloride-based materials are studied as presented in Table 2: pure salt (P), calcium chloride impregnated in expanded graphite (G), calcium chloride impregnated in vermiculite (V) and encapsulated calcium chloride powder (E). The samples are identified on basis of the dry calcium chloride content, all over the work, instead of the gross mass. The impregnated samples are noted with 1 as once impregnated and 2 as twice impregnated.

The pure salt (Sigma-Aldrich 499609) is used in powder form and the estimated state of hydration for the material in the container is two moles of water per mole of calcium chloride (CaCl₂·2H₂O). However, due to the hygroscopic nature of the material, the water uptake after being taken out of the container and exposed to the room conditions is fast. The initial state of the calcium chloride for experiments is therefore not defined accurately. Because of this, samples are dehydrated at high temperature (150°C) at the beginning of each experiment.

The encapsulated material is produced by spray-drying a solution of calcium chloride and ethyl cellulose in a solvent mixture composed of ethanol alcohol and water [31]. The resulting formed particles are composed of a calcium chloride dihydrate core and an ethyl cellulose shell. The respective mass fractions of calcium chloride and ethyl cellulose are 80 wt% and 20 wt%. Ethyl cellulose is a hydrophobic material, i.e. swelling with water is practically negligible, and is highly permeable for water vapor. This material is mostly used in pharmaceutical applications especially for coating, and has thermal stability up to its melting point (around 165–173°C) [37], which makes it stable for the application.

The remaining two materials consist of salt impregnated into porous structures of vermiculite and expanded graphite. Vermiculite mainly consist of aluminium, iron and magnesium silicates minerals. Heat treatment of this material provides a porous and layered structure, having a large surface area per unit of volume. Vermiculite (Agra M4-Seedo) with a packed density of around 111 kg/m³ and a particle size smaller than 2 mm is used. The expanded graphite has also a layered structure with a high porosity, and is obtained by exposing graphite to high temperatures. A plate of expanded natural graphite (Sigraflex Thermophit L-sheet) with a density of 92 kg/m³ is used to cut cylinders of 20 mm diameter and 9 mm thickness. A high internal porosity of around 95% is calculated, based on the density of pure graphite (2150 kg/m³).

Before impregnation, the host materials are submersed in ethanol alcohol, overnight in order to remove any dirt and enhance the salt content. However, for vermiculite, the attempt to remove impurities by alcohol actually reduced the uptake of salt, so the method was abandoned. Impregnation was carried out by submerging the host materials in a saturated aqueous solution of calcium chloride over a night in order to deposit the salt in the pores of the matrix. Then the water was removed in two thermal steps, first at 90 °C overnight, and then at 190 °C in a convection stove. Subsequently, the samples are cooled down in a desiccator in order to protect them from moisture in the ambient.

The samples under the name V2 and G2 were impregnated twice, to increase the salt content. The second impregnation is done with the same method, and result in a considerable increase in the salt content of the samples. A different impregnation technique was also tested by submerging the host materials in molten calcium chloride salt at 800 °C. This method was however abandoned, because it resulted in a decrease in salt content instead of an increase, as well as in agglomeration of the salt.

For the pure and encapsulated materials, the volumetric bulk density is directly measured with a micro balance in a crucible with known volume. The materials are filled into the crucible without applying any force to compress the material, same as the samples used in the experiments. It is assumed that the state of hydration of the samples is CaCl₂·2H₂O. The calculated standard deviation is less than 7%. For the impregnated materials, the volumetric density is calculated based on the density of calcium chloride and the host materials in solid state from literature, and salt content (mass of active material to total mass of sample). The salt content can be calculated based on weighing the samples before and after the impregnation procedure, or based on the experimental results from the TGA (explained in Section 2.4). The porosities are calculated by comparing the presented densities to the theoretical densities.

2.3. TGA-DSC experiments

The characterization of TCM is based on measurement data, obtained through the methods of Thermo-Gravitational Analysis (TGA) and Differential Scanning Calorimetry (DSC). A Simultaneous Thermal

<table>
<thead>
<tr>
<th>Code</th>
<th>Synthesis method</th>
<th>Passive material</th>
<th>Salt content [wt%]</th>
<th>Density [kg/m³]</th>
<th>Estimated porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>Pure</td>
<td></td>
<td>100</td>
<td>660</td>
<td>0.7</td>
</tr>
<tr>
<td>G1</td>
<td>Impregnation</td>
<td>Expanded graphite</td>
<td>73</td>
<td>300</td>
<td>0.9</td>
</tr>
<tr>
<td>G2</td>
<td>Impregnation</td>
<td>Expanded graphite</td>
<td>87</td>
<td>600</td>
<td>0.7</td>
</tr>
<tr>
<td>V1</td>
<td>Impregnation</td>
<td>Vermiculite</td>
<td>68</td>
<td>320</td>
<td>0.9</td>
</tr>
<tr>
<td>V2</td>
<td>Impregnation</td>
<td>Vermiculite</td>
<td>86</td>
<td>600</td>
<td>0.7</td>
</tr>
<tr>
<td>E</td>
<td>Encapsulation</td>
<td>Ethyl cellulose</td>
<td>80</td>
<td>190</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Analysis (STA) apparatus (Netzsch STA 449 F3 Jupiter) connected to a Modular Humidity Generator (MHG ProUmid) is used, which allows for simultaneous measurement of both the mass change (TGA) and the heat release/uptake (DSC) of a sample. The STA apparatus consists of a thermally controlled environment (furnace), which is subjected to a pre-defined temperature program. Sample is situated in an aluminium crucible located in the furnace, with a typical sample mass of 5–20 mg. An empty crucible is located just beside the sample crucible as reference for the DSC measurement. The crucibles are assumed to be subject to identical conditions. Both crucibles are positioned on a sample holder, which is mounted on a balance. The humidity generator provides an air flow with a controlled flow rate, temperature and humidity. The air flow is from top to the bottom of the furnace. A schematic view of the setup is shown in Fig. 2.

The TG signal shows the weight change of a sample during an experiment, with respect to the initial mass, as measured with the balance. The temperature of each crucible is measured with a thermocouple attached at the bottom of each platform on which the respective crucible is situated. The temperature difference between the sample crucible and the neighboring reference crucible is recorded. The temperature difference serves as a measure for the heat flux towards or from the sample. The DSC signal is a measure for the heat flow to or from the sample: negative values indicate exothermic reactions, positive values indicate endothermic reactions; the direction of exothermic values is indicated on the respective axis. Generally, hydration and thus mass gain, implies an exothermic reaction, whereas dehydrolization implies an endothermic reaction.

The aerodynamic drag and buoyancy forces also affect the TG signal. As the temperature in the furnace changes, the density of the air changes, thus affecting the buoyancy and drag forces acting on the crucibles and crucible holder, resulting a change in the measured weight. Temperature change in the furnace can also affect the DSC signal. As the two crucibles are not located at the exact same place, the temperature change at the two locations can be sensed slightly different, which leads to an inaccurate DSC reading. However, these effects are reproducible in different experiments, therefore they can be cancelled out by conducting a so-called empty crucible run. In an empty crucible run, both crucibles are empty and are subject to the exact same conditions (temperature program and humidity) as the original sample measurement. Then as a post processing step, the empty run signals are subtracted from the original sample run signals. In addition, empty runs are also used to estimate the measurement uncertainties.

Experiments are conducted under an air atmosphere with a vapor pressure of 1.3 kPa and flow rate of 100 ml/min. The temperature program used in the experiments is shown in Fig. 3, and some definitions are introduced. The initial heating is implemented for the sample to completely dehydrate and reach anhydrous state at a maximum temperature of 150 °C.

In literature, the performance of the material under investigation is usually studied with TGA and DSC methods. These methods are mostly used to evaluate the water release and energy gain of materials during the dehydration reaction, because it is a faster reaction, therefore, the results can be more accurate. However, the rehydration reaction is an important part of the cycle in which overhydration might happen. If the water vapor transport in the material. Therefore, the hydration reaction of the material is of high interest in this work. The focus is on stabilization of the material during the hydration reaction without decreasing the kinetics and energy density significantly.

2.4. Data post processing

In order to evaluate the performance of the materials, TG and DSC signals can be converted to performance indication factors, such as loading (or state of hydration), conversion, conversion rate, and reaction enthalpy. For instance, TG and DSC signals for an endothermic dehydration process are as shown in Fig. 4. The TG signal shows the mass at each time (mi), which drops from the initial mass (mf0) to the final value (mf1). The DSC signal shows the power with which the heat is absorbed by the sample, which is positive for endothermic reactions. As the temperature in the furnace changes, the density of the air flow will change slightly, which affects the TG and DSC measurements. Therefore, a correction factor is used to estimate the measurement uncertainties. In theory, the baseline (BL) should have a value of approximately zero. The deviation of the DSC signal from the baseline indicates the occurrence of a chemical process, involving thermal effects.

The sample mass, used in the figures and tables, represents the mass of the active material in a sample (the calcium chloride content). The salt content of the impregnated material is determined by weighing the samples before and after the impregnation. For encapsulated material, it is determined to be 80% by the ratio of active to passive material (4:1) used in the synthesis process. In addition, the salt content of each sample can be determined by the experimental results, by comparing the calculated equilibrium loading based on measurements and the theoretical equilibrium loading from Fig. 1. This method gives results that are accurate within 1% of active material. The loading L, or state of hydration, is the mole of water NHO2 per number of calcium chloride NCaCl2 crystal units, and can be calculated by:

\[
L = \frac{N_{\text{HO2}}}{N_{\text{CaCl2}}} = \frac{m_{\text{HO2}}M_{\text{CaCl2}}}{m_{\text{HO2}}M_{\text{CaCl2}}}
\]

where \(m_{\text{HO2}}\) is the mass increase of the sample starting from the anhydrous state due to the absorption of water, and \(m_{\text{CaCl2}}\) is the mass of the anhydrous salt and only considers the active material in the sample (calcium chloride salt content); \(M_{\text{HO2}}\) and \(M_{\text{CaCl2}}\) are the molar mass of water and calcium chloride, respectively. The anhydrous state is recognized when the TG signal is more or less constant in time at high temperatures. In addition, under the conditions applied during the experiments, the loading eventually exceeds hexahydrate state. Apparent loading would therefore be a more suitable term to be used instead of loading.

An important parameter in the material investigation is the conversion \(\alpha\). The conversion ranges between 0 and 1 and is used to describe the progress of a reaction. In the case of hydration, for instance,
the conversion $\alpha$ changes from 0 for dry sample to 1 for fully hydrated sample. Conversion can be calculated based on the measured sample mass via TG:

$$\alpha_{TG}(t) = \frac{m(t) - m_i}{m_f - m_i} \tag{2}$$

where $m$ is the mass of the sample at a certain moment in time $t$, and $m_i$ and $m_f$ are the initial mass and the final mass of the sample, respectively. Conversion can also be calculated based on the measured energy change of the sample via DSC:

$$\alpha_{DSC}(t) = \frac{\int_0^t (DSC(t) - BL(t)) dt}{\int_0^t (DSC(t) - BL(t)) dt} = \frac{I_{tot}-I}{I_{tot}} \tag{3}$$

where $I_{tot}$ is the total integrated area under the DSC signal curve from the beginning to the time $t$, and $I_{tot}$ is the total integrated area under the DSC signal curve (as shown in Fig. 4). In this work, the conversion of hydration reaction is calculated based on the TG signal $\alpha_{TG}$, which can also be presented based on loading as:

$$\alpha = L/L_f \tag{4}$$

where $L$ is the loading at a certain moment in time and $L_f$ is the final loading value.

Based on the assumption that the hydration reactions can be described by a linear driving force (LDF) model, the rate of conversion ($dx/dt$) can be written as:

$$\frac{dx}{dt} = k_{LDF} \gamma \tag{5}$$

where $k_{LDF}$ is the kinetics coefficient in $[s^{-1}]$, and $\gamma$ is the linear driving force, which can be written in dimensionless form as:

$$\gamma = \frac{I_{eq}(t) - L(t)}{L_f} \tag{6}$$

where $I_{eq}$ is the equilibrium loading at each time (derived from the equilibrium line as presented in Fig. 1).

The enthalpy of reaction is determined through the energy change during a reaction. The stoichiometry of the reaction itself is identified through the mass change, used to calculate the change of state of hydration. Host materials are assumed to be inert to water vapor and not participate in hydration reactions. The reaction enthalpy is the energy released per mole of CaCl$_2$ and can be obtained by:

$$\Delta h = \frac{\Delta H}{N_{CaCl_2}} \tag{7}$$

where $\Delta H$ is the released heat, as measured in the STA apparatus, which can be calculated by integrating the heat flow over the course of a reaction, according to:

$$\Delta H = \int_0^T [DSC(t) - BL(t)] dt = \int_0^T Q dt \tag{8}$$

3. Results

Different samples are compared in terms of kinetics, energy density, and stability. These criteria are investigated through the water adsorption and energy exchange of the materials during the de/re-hydration reaction, which are measured by the TGA and DSC methods. A typical experimental result is shown in Fig. 5 as a function of time and temperature. A de/re-hydration of a 7 mg encapsulated CaCl$_2$ sample subjected to a water vapor pressure of 1.3 kPa is shown versus time and temperature. The temperature program starts from the temperature of the high temperature isotherm (150 °C), decreases at a rate of 1 °C/min and finally stabilizes at the temperature of the low temperature isotherm (20 °C in this case).

The hydration reaction starts at a temperature of around 80 °C and continues during the temperature decrease and the low temperature isotherm. During hydration, an almost stable state at the temperature around 40 °C can be seen in both TG and DSC signals. It is recognizable in the TG signal as a semi-stable step at around 40 °C, and in the DSC signal it appears like a peak (it is a dip in energy release toward 0 mW) at around 40 °C. This semi-stable state is calculated to be almost
CaCl\textsubscript{2} \cdot 2\text{H}_2\text{O}. The hydration reaction continues also during the isotherm, till finally, the state of loading in the sample reaches the final value of 12.3 mol H\textsubscript{2}O/mol CaCl\textsubscript{2} and the energy release (DSC signal) reaches 0 mW.

The dehydration reaction is much faster than the hydration reaction, and starts when temperature starts to increase. The mass of the sample decreases because of the water desorption from the sample. The mass reaches to a stable state after the temperature rises above 80 °C and continues till around 105 °C. This stable state is calculated to be CaCl\textsubscript{2} \cdot 2\text{H}_2\text{O}. The dehydration continues after the temperature increases above 100 °C till 120 °C.

It should be noted that in theory the equilibrium temperature of the state CaCl\textsubscript{2} \cdot 2\text{H}_2\text{O} at the water vapor pressure of 1.3 kPa is around 62 °C. However, dihydrate state is not reached at this temperature during dehydration, because of the kinetics limitation. It is also not reached during hydration, as the hydration kinetics is even slower than dehydration. In general, the difference between the hydration and dehydration curves is because of the difference in the kinetics and the fact that the measurement is perform far from equilibrium.

Similar experiments are performed on different samples from the four materials mentioned in Table 2. The experimental results are post processed and used to evaluate the performance of the material in respect to the reaction kinetics, heat storage density and stability.

3.1. Kinetics

Kinetics characteristics of the rehydration reaction for the four materials are expressed in terms of conversion and conversion rate. The conversion of samples upon hydration is calculated based on the apparent loading calculated by Eq. (4). The data concerns the second rehydration in the experiments, since it is established that the material’s behavior changes during the first cycle, which therefore is not representative [32]. During the first hydration of samples with granular powder form, the grain structure is lost and the material is agglomerated. Therefore, the resulting sample shows different kinetics features in the second hydration than the sample in initial form. This effect, represented by the difference between the first and second hydration, is also a measure for the stability of the material, which is discussed further later in Section 3.3.

Fig. 6 shows the water loading and the absolute mass of water as a function of time for hydration of several samples with different sizes. As can be seen, the conversion rate decreases as the sample mass increases. This implies that the sample weight affects the conversion rate. Therefore, samples with similar masses should be used, in order to compare the kinetics of different materials. This suggests that the hydration reaction is a diffusion-limited process. The ratio between diffusion and intrinsic reaction rate, expressed as the Damköhler number \( D_a \) [38], is expected to decrease as sample size decreases. It is thoroughly discussed by Lan et al. [39] using a model based on direct numerical simulation for TGA experiment. It is concluded that small samples are the best representation of the actual hydration reactions. Specially, since the TG signal from the STA apparatus is accurate enough, smaller samples are favourable for the kinetics study. However, the accuracy in the determination of the enthalpy of reaction for the energy density study (based on the DSC signal) might be critical.

In addition, the effect of the sample mass on the conversion rate can also be caused by the limited moisture flow towards the samples. Since a large sample simply takes up more water, it can lead to a slower water uptake relative to the sample mass. In order to check that, a test is done with a large sample of encapsulated calcium chloride material with a sample mass of 15 mg at different flow rates of 100, 200 and 300 ml/min. It is observed that by increasing the air flow rate, the reaction rate is increased by about 10–20%. It suggest that the moisture supply has an effect, but still is not the main limitation factor limiting the reaction progress.

In spite of the different conversion rates, all the samples reach the same loading (around 12.3 mole of water per mole of salt) after a long enough period of time (depending on the sample size). This is an apparent loading, since the sample is in solution and it is not in crystal form any more. In the subsequent analysis, conversion rates of the materials are calculated, based on the measured masses during the initial three hours of the rehydration reaction, and are compared. During this period, the materials reach at least the tetrahydrate state, depending on the sample mass. The impregnated materials are compared to both pure and encapsulated salt.

Fig. 7 shows the conversion rate vs. time and loading for the impregnated graphite in comparison with the pure and encapsulated calcium chloride. For impregnated graphite, the conversion rate as a function of time is similar to that of pure salt. In terms of vapor diffusion, the host structure does not enhance the material’s characteristics, for small samples. A dip is visible at the loading of 2 mol H\textsubscript{2}O/mol CaCl\textsubscript{2}, in case of encapsulated material, while for the other two it is at around 1 mol H\textsubscript{2}O/mol CaCl\textsubscript{2}. But in all the cases these dips happen at almost the same time (around 0.6 h) and temperature (about 40 °C). This can be caused by the temperature program, and the fact that temperature decreases during the first one hour. This effect will be discussed further later in this section.

Fig. 8 shows the conversion rate vs. the time and loading of the impregnated vermiculite in comparison with the pure and encapsulated calcium chloride. Because of the higher sample masses compared to the previous set of experiments, the dips are less pronounced. The impregnated vermiculite sample shows conversion rates in between values for pure and encapsulated materials during the initial stage of the process. Therefore, vermiculite seems to slightly improve the diffusive properties of the material. In general, the encapsulated material shows the fastest rehydration among all the materials. However, it should be noted that the grain size of the encapsulated material is much smaller...
than the one of pure calcium chloride.

Part of the hydration process takes place under non-isothermal conditions, which means that the equilibrium loading alters over time until the lower isotherm is reached. The hydration of calcium chloride under 1.3 kPa initiates as the temperature falls below 80 °C (see Fig. 5). The lower isotherms during the experiments are 20 °C and 30 °C, so the equilibrium loading changes between the start of the reaction and the moment at which the lower isotherm is reached. In order to see the effect, the driving force is calculated based on Eq. (6) and compared with the conversion rate.

Fig. 9 shows the conversion rate (left axis) and the driving force \( \gamma \) (right axis) as a function of loading for different sample masses of the encapsulated material. As can be seen, the conversion rate shows a strong dependency on sample size. For lighter samples, the conversion rate in general is higher and the shape of the conversion rate is more pronounced than for heavier samples. Smaller samples show a more pronounced profile for the conversion rate as a function of hydration state. In addition, a distinct dip is observed at the dihydrous state \((\text{CaCl}_2 \cdot 2\text{H}_2\text{O})\), despite the positive driving force. However, the driving force for the small samples is low, which leads to a slower reaction. For the large sample with a sample size of 14 mg, the reaction rate is almost constant. This is caused by the diffusion limitation. From a hydration state around 3–4, the conversion rate has reached a maximum and decreases slightly with increasing hydration.

The kinetics coefficient \( k_{LD} \) can be calculated by Eq. (5). The kinetics coefficient is shown in Fig. 10 as a function of loading and sample mass for pure and encapsulated samples. It is concluded that the linear driving force model cannot adequately describe the reaction kinetics in details for small samples, because the kinetics coefficient is varying with loading. Specially, at the beginning of the process, where the temperature decreases. The largest values for the kinetics coefficient can be found in this segment, which can be caused by a higher activity because of higher temperature. The maximums for the kinetics coefficient of the samples of the pure material happen at lower loadings (Fig. 10) compared to the encapsulated material (Fig. 10). During the isotherm segment, a more or less constant kinetics coefficient can be seen for both the materials.

The average conversion rates and kinetics coefficients are evaluated and compared in Fig. 11 for the pure and encapsulated materials and lower isotherm temperature of 20 and 30 °C. There is a general
decreasing trend with increasing sample mass for both conversion rate and kinetics coefficient. The conversion rate and kinetics coefficient for encapsulated material are slightly higher compared to the ones for pure material with the same sizes. The average kinetics coefficients are in the order of $10^{-3}$ s$^{-1}$ and $10^{-4}$ s$^{-1}$ for small and large sample sizes, respectively. Effect of the reaction kinetics on the performance of the system is discussed further in Section 4.

3.2. Energy storage density

The energy storage density is studied for the four calcium chloride-based materials. The energy release for each sample during hydration from anhydrous to hexahydrate state is determined. The simultaneous thermal analysis method allows the estimation of the energy per mole of calcium chloride and per mole of absorbed water. Storage density values are compared to literature values. The measured thermal power from all samples is integrated over time, from the loading of 0 to 6. The released energy is calculated by integration of the thermal power over time between the DSC signal curve and the baseline in the domain where loading ($L$) is between 0 and 6 [mol H$_2$O/mol CaCl$_2$].

In Fig. 13, the enthalpy of the hydration reaction from anhydrous to hexahydrate state is shown for samples of the materials with different masses. The calculated enthalpies seem independent of the sample mass. The energy densities per kilogram and cubic meter of material are summarized in Table 3. The energy densities are based on gross material mass (not the salt content). The material densities, which are used in order to calculate the energy densities, are small scale sample densities from Table 2. As expected, the pure material has the highest energy density, because of the highest salt content. The energy density of impregnated vermiculite is the highest among the composite materials. The energy density of the encapsulated material is the lowest. The gravimetric energy density of the encapsulated material is 80% of the pure material, which is the same as the salt content weight percentage of the encapsulated material.

Enthalpies of different steps of the hydration reaction per mole of
pronounced in samples with poor conductivity compared to the metallic calibrants. Moreover, because of the larger density of metallic calibrants, the volume for the calibration samples is smaller than for the salt samples. In addition, the process of melting and solidification of the calibration samples is much quicker than the hydration of salts (a few minutes versus time spans in the order of ten hours). All these effects result in a larger heat loss to the flow in the furnace compared to the heat flux sensed at the bottom of the crucible with the thermocouple.

Another reason for the underestimation in the measured enthalpies can be the differences in heat transfer-related properties between the investigated samples and the employed calibrants. The samples used for calibration of the setup are made of Gallium, Indium, Tin, Bismuth and Zinc. The investigated samples mainly consist of a salt, having a typical thermal conductivity in the order of 1 [W/m K] [40], whereas the calibration materials, which are metals, have conductivities in the order of 40–80 [W/m K]. The dimensionless Biot number is a suitable parameter to evaluate the temperature distribution in a physical object having a characteristic length \( l \) and heat conductivity \( k \) that exchanges heat with a fluid flow with a convective heat transfer coefficient \( h \). A low Biot number represents a fast spread of heat inside the object, and hence indicates a uniform temperature distribution in the object. On the other hand a low Biot number is an indication for non-uniform temperature distribution in the object. A comparison is made between the Biot number for a typical calibrant and a typical TCM sample. Assuming the same convective heat transfer coefficient for spherical samples with similar masses, the Biot number for the calibrant is then in the order of hundred times larger than the one calculated for the TCM sample. Therefore, a more elaborate study on the sensitivity of the apparatus to the conductivity of the calibrant is advised. Also, more detailed knowledge about the thermal processes inside the furnace or around the sample would provide useful insight and will help defining future experiments. Furthermore, non-uniformity of hydration states throughout the sample leads to an inaccuracy in the enthalpy measurement. Therefore, smaller sample size should lead to a higher accuracy. However, using smaller sample sizes lead to a smaller energy release which will be harder to measure.

3.3. Stability

Stability of the materials is investigated, based on STA experiments and microscopic observations. Multi-cycle STA experiments have been conducted on the pure and encapsulated salts. The released heat during hydration between anhydrous and hexahydrous state as a function of cycle number is shown in Fig. 15. The released heat does not vary significantly over ten to eleven cycles, apart from slight random fluctuations. For the pure material, the second and third cycle are missing.

adsorbed water are shown in Fig. 14, for samples of the pure and encapsulated materials. The experimental values are generally lower than the literature values. The discrepancy is in the order of 15–30%. The only value which is not underestimated, is the heat release between monohydrated and dihydrous state.

The measured values show a general underestimation compared to the literature value. The cause for the underestimation can be explained in various ways. As discussed before, it is found that the hydration of the investigated materials is a non-uniform process over the whole sample. Since the thermocouple is located at the bottom of the crucible containing the sample, it senses the temperature of the bottom part of the sample more than the temperature at the top, because of poor conductivity. In other words, the part of the released heat from the reaction occurring at the top of the sample is less effectively transferred to the bottom of the crucible (near the thermocouple) compared to the reaction occurring at the bottom of the sample. This phenomena is more

Table 3

<table>
<thead>
<tr>
<th>Material</th>
<th>( \Delta h ) [kJ/molCaCl(_2)]</th>
<th>( \Delta h ) [MJ/kg]</th>
<th>( \Delta h ) [GJ/m(^3)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>290 ± 50</td>
<td>2.6 ± 0.5</td>
<td>1.7 ± 0.5</td>
</tr>
<tr>
<td>G</td>
<td>300 ± 20</td>
<td>2.0 ± 0.2</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>V1</td>
<td>260 ± 20</td>
<td>1.6 ± 0.2</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>V2</td>
<td>260 ± 25</td>
<td>2.0 ± 0.2</td>
<td>1.2 ± 0.1</td>
</tr>
<tr>
<td>E</td>
<td>290 ± 40</td>
<td>2.1 ± 0.4</td>
<td>0.4 ± 0.1</td>
</tr>
</tbody>
</table>

Fig. 13. Energy densities of the hydration reaction from anhydrous to hexahydrous state for samples of the materials with different masses.

Fig. 14. Enthalpies of hydration reaction for different state of hydration for samples of the pure and encapsulated materials.

Fig. 15. Measured storage capacity upon hydration from anhydrous to hexahydrous state over multiple cycle numbers; lower temperature isotherm is 30 °C and the vapor pressure is 1.3 kPa.
because the hexahydrous state was not reached.

To show the behavior of samples hydrating under high humidity and subsequently dehydrating, photographs from the samples are taken during the de/re-hydration process. Experiments are carried out in a transparent chamber with controlled humidity and temperature under a microscope (Zeiss SteREO Discovery V20). More details on the setup are available in [41].

A qualitative description of the phenomena, occurring under excessive humid conditions, can be seen in the pictures. First, the fresh samples are placed on a glass plate and exposed to humid environment (approximately 2 kPa at 80 °C) in order to hydrate them. After this period of hydration, the samples are exposed to dry environment (approximately 0.5 kPa at 80 °C) in order to dehydrate them. Then, the samples are rehydrated again under the same condition as the first hydration. The hydration process under the stated conditions takes a day, and the dehydration process is finished within two hours.

The pictures of hydration, subsequent dehydation and subsequent rehydration of the pure salt sample are shown in Fig. 16a. During the first hydration of the pure salt sample with granular powder form, the grain structure is lost and the resulting solution droplets allow the material to coalesce and form a bigger droplet. Dehydration of this droplet results in the formation of an agglomerated piece of dry salt. The resulting agglomerated salt shows different kinetics features than the salt in initial granular form. This effect is discussed later in this section.

The pictures of hydration, subsequent dehydation and subsequent rehydration of the impregnated graphite sample are shown in Fig. 16b. The impregnated expanded graphite first shows overhydration of the contained salt. This is seen by the change in color of the top of the sample. The fresh sample contains relatively dry calcium chloride, which appears as white spots. Deliquescence of the salt results in formation of transparent solution and allows it to flow out of the sample, a process also referred to as washing out. Subsequent dehydration of the sample leads to a structure which is similar to the dehydrated pure salt. However the structure of the graphite host matrix in the middle (probably with a part of salt content still inside) is left intact but softer, as it is vulnerable to mechanical force. After dehydation, the sample appears to be whiter than it was initially, before hydration. This means that salt has escaped from inside the graphite to the surface. The washing out effect of salt from the host matrix is an undesired process, which cannot be observed in the STA experiments, since the sample is contained in a cup, retaining all the original material.

The pictures of hydration, subsequent dehydation and subsequent rehydration of the impregnated vermiculite sample are shown in Fig. 16c. A similar process is observed for the impregnated vermiculite sample as the impregnated graphite sample. Additionally, the structure of the vermiculite host matrix is distorted after hydration and a paste-like mixture is formed.

The pictures of hydration and subsequent dehydation of the encapsulated salt sample are shown in Fig. 17. The top row shows the fresh sample as taken from the storage container (left) and the sample after being exposed to humid conditions for approximately one day (right). The sample seems to be expanded after hydration. This process is however poorly visible in the two stills, taken at the beginning and end of the process. In the right picture, a yellow line was drawn along the circumference of the fresh sample on the left and copied to the hydrated sample on the right in an attempt to visualize the expansion. The bottom row shows the glass plate after wiping the hydrated encapsulated material off the glass. A few drops of liquid were still

Fig. 16. Hydration, subsequent dehydation and subsequent rehydration of pure and impregnated materials; during hydration (frames 1–4), the sample is exposed to a vapor pressure of roughly around 2 kPa; during dehydation (frames 4–6), the sample is exposed to a temperature of around 80 °C and a vapor pressure of roughly around 0.5 kPa; during rehydration (frames 6–4) the same condition as the first hydration is applied again.

Fig. 17. The top row shows the fresh sample of encapsulated material as taken from its storage container (left) and the sample after being exposed to humid conditions for approximately one day (right). The sample seems to be expanded after hydration. This process is however poorly visible in the two stills, taken at the beginning and end of the process. In the right picture, a yellow line was drawn along the circumference of the fresh sample on the left and copied to the hydrated sample on the right in an attempt to visualize the expansion. The bottom row shows the glass plate after wiping the hydrated encapsulated material off the glass. A few drops of liquid were still
attached to the glass and the glass was then exposed to a temperature around 80°C. The remaining of salt can be recognized as small white spots on the glass. The encapsulated material also shows washing out of material, but to a smaller extent than the impregnated materials. In terms of stability, the encapsulated material shows the best properties. The agglomeration effect of the pure salt can be also detected in STA experiments. This effect in pure salt is compared with encapsulated salt and shown in Fig. 18. The samples are inserted in the set-up in granular form. After initial dehydration, all samples are hydrated to values beyond the hexahydrous state, which implies that deliquescence has occurred. Presumed agglomeration of the resulting solution in the crucible would lead to dehydration into a cake-like structure, as is observed in the pictures in Fig. 16a. During the first hour of hydration of the pure salt sample, a clear decline is observed in the conversion rate between first and second cycle. In the first cycle, the sample still has its granular form, however, in the second cycle it has agglomerated. From the second cycle onwards, material behavior is well reproducible. For the case of encapsulated material, it can be seen that the agglomeration is avoided, as the first and second cycles are exactly similar.

Only during the first minutes of the experiments, the conversion rate has similar values for both the first and second cycle: a steep increase is observed. It is expected that this is caused by reactions on the material’s surface. The total surface of the grains is bigger and can therefore prolong the steep increase of the conversion rate. After one hour of hydration, the conversion rates for both first and second cycle take on similar values. An explanation is that the outer layer of the grains reaches a higher state of hydration in an early stage, a process expected as a result of the non-uniformity of the process. The hydrated outer layers consequently may agglomerate and thereby obstruct the diffusion of water further into the material, and the process becomes limited by diffusion of water molecules into the salt.

Fig. 18. First and second cycles of hydration of pure and encapsulated materials.

4. Discussion

As explained, attempts have been made to stabilize calcium chloride by impregnation in expanded natural graphite and in vermiculite, and by encapsulation with ethyl cellulose. In order to achieve a higher energy storage density in a composite material, higher density of the composite material (combination of higher salt content and lower density of inert material) is favourable. The densities of twice impregnated materials and encapsulated material are 91% and 29% of the density of the pure material. Characterization of the calcium chloride-based thermochemical materials is carried out on the basis of three subjects: reaction kinetics, heat storage density and stability.

Kinetics of the reaction, and hence performance of the material, is significantly affected by sample size. Since the kinetics is important to the global performance of the thermochemical heat storage system, it is important to find the optimum pellet size for the material being used in the real system. A small pellet size leads to a fast reaction in the material bed, and hence, higher power and efficiency. A large pellet size leads to a lower pressure drop over the material bed, and hence, higher COP. The average kinetics coefficient of the hydration reaction is calculated for the pure and encapsulated materials based on the LDF model. The kinetics coefficient shows dependency on the sample size, however the dependency is smaller for large samples. The average kinetics coefficient is roughly in the order of $10^{-5} s^{-1}$ and $10^{-4} s^{-1}$ for small (about 2 mg) and large (about 20 mg) sample masses, respectively. Based on the investigation performed in previous work [42], the average kinetics coefficients for the relatively fast hydration reaction of zeolite is around $10^{-2} s^{-1}$. So the average kinetics coefficients for small and large samples of calcium chloride-based materials are approximately one and two orders of magnitude lower, respectively. Based on the parametric study done on the performance of the systems with different reaction rates in previous work [42], it is still possible to achieve a high efficiency, in spite the relatively slow reaction. However, the residence time of the water vapor flow into the reactor needs to be longer, in order to provide enough time for the absorption reaction of water to the material. This should be done by either a lower flow rate through the system, which leads to a lower power, or a bigger reactor. This can be done by taking special measures in the design of the system and the process. However, the optimization problems for material grain size and the process design should be solved simultaneously, for which more investigation is necessary.

The energy storage density is studied for the four calcium chloride-based materials. The energy density is calculated based on the enthalpy of the hydration reaction for each material being dehydrated at a temperature of 150 °C and being hydrated at a vapor pressure of 1.3 kPa and temperature of 20 °C. Based on the measured enthalpy (around 300 kJ/molCaCl$_2$), it can be estimated that a system operating under these conditions can provide a temperature lift of around 22 °C. However, for a system intended for domestic purposes, a higher output temperature is needed (around 60 °C). Therefore, the inflow temperature needs to be increased to above 40°C in order to achieve the required outflow temperature which can be realized by an air-to-air heat exchanger in the system. Having an elevated inlet temperature to the reactor means that the material bed reacts at the elevated temperature, during most of the discharge process. Only during the initial part of the discharge process, the temperature is below the elevated inlet temperature, when the material bed still needs to be heated up. Therefore, it is important to study reaction enthalpy of thermochemical materials at elevated temperatures.

Stability of the materials is investigated, based on STA experiments and microscopic pictures. Multi-cycle STA experiments have been conducted on the pure and encapsulated salts. The released heat does not vary significantly over ten to eleven cycles. However, based on the pictures of hydration and subsequent dehydration of samples, it can be seen that the grain structure is lost and a solution is formed on hydration of the pure and impregnated materials. Dehydration of this
solution results in the formation of an agglomerated piece of dry salt. This makes the pure and impregnated materials unfit for the application, unlike the encapsulated material. However, the stability of materials at low temperatures around ambient temperature (for example 20 °C, which is used here) is only an issue during the initial part of the discharge process, when the temperature is below the elevated inlet temperature, as explained above. This period is in the order of hours depending on the configuration of the system, while the overhydration of the material is much slower. This suggests that the overhydration problem can be tackled with innovative solutions. For instance, the inflow can contain less humidity during this starting period or a more stable material can be placed at the top layer of the reactor. Nevertheless, these measures might lead to a more complicated and more expensive system. In addition, it should be noted that the material might face the overhydration condition anyway, if a failure such as leakage occurs in the system.

5. Conclusions

In general, a strong relation between conversion rate and sample mass is observed. This suggests that the hydration reaction of calcium chloride is a diffusion-limited process. The hydration reaction rate for impregnated materials is similar to that of pure salt. Interestingly, the encapsulated sample shows the highest rehydration among all the materials. In general, it seems that the kinetics of the hydration reaction of the calcium chloride based materials can be expressed by the LDF model, only for large samples (larger than 10 mg).

The calculated enthalpies per mole of material seem unaffected by the sample mass. The volumetric energy density of the encapsulated material (about 0.4 GJ/m³) and twice impregnated vermiculite (about 1.2 GJ/m³) material are, respectively, the lowest and the highest among the studied composite materials. The volumetric energy density of the twice impregnated graphite material is not measured experimentally, but it is expected to be the highest among all the materials (roughly around 1.5 GJ/m³).

The impregnated samples show overhydration, allowing the contained salt to be washed out. Subsequent dehydation of the sample leads to an agglomerated structure similar to the dehydrated pure salt, which reduces vapor transport through the structure. The structure of the graphite host matrix (probably with a part of the salt content still inside) is left intact, unlike the vermiculite sample, which is distorted after hydration and a paste-like mixture is formed. It has been seen that the agglomeration is avoided in the encapsulated material.

A method is developed to evaluate the agglomeration effect in STA experiments by comparing the first and second cycles. The samples are inserted in the setup in granular form. After initial dehydation, all samples are hydrated to values beyond the hexahydrite state, which implies that deliquescence has occurred. During the subsequent dehydation, agglomeration of the solution in the crucible is expected, which will lead to form a cake-like structure. During the first hour of the second hydration of the pure salt, a clear difference is observed in the conversion rate between first and second cycle. In the first cycle, the sample still has its granular form. However, in the second cycle it has agglomerated, causing a reduction of the conversion rate. From the second cycle onwards, material behavior is well reproducible. For the case of encapsulated material, it seems that the agglomeration is avoided, as the first and second cycles are exactly similar.

Within the boundary conditions for thermochemical energy storage as presented in this work, microencapsulated calcium chloride showed high multicyclic stability, compared with pure and impregnated materials, that liquefy upon hydration under the given conditions. Microencapsulated material remains stable over multiple cycles and shows the fastest kinetics. The only disadvantage of the currently used encapsulation methodology is the resulting low energy storage density. Future work regarding material development is directed to enhancement of the energy storage density, while maintaining the positive attributes (stability and fast reaction kinetics). In addition, it is important to evaluate the performance of the material at larger scales (in the order of couple of tens of kg) in terms of its practicability and future perspectives for real systems.

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