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CHARACTERIZATION OF SALT HYDRATES FOR COMPACT SEASONAL THERMOCHEMICAL STORAGE

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ABSTRACT

This paper describes the characterization of four salt hydrates as potential thermochemical material for compact seasonal heat storage in the built environment. First, magnesium sulfate was investigated in detail using TG-DSC apparatus. The results of this study revealed that magnesium sulfate is able to store almost 10 times more energy than water of the same volume. However, the material was unable to take up water (and release heat) under practical conditions. A new theoretical study identified three salt hydrates besides magnesium sulfate as promising materials for compact seasonal heat storage: aluminum sulfate, magnesium chloride and calcium chloride. These salt hydrates (including magnesium sulfate) were tested in a newly constructed experimental setup. Based on the observed temperature lift under practical conditions, it was found that magnesium chloride was the most promising material of the four tested salt hydrates. However, both calcium chloride and magnesium chloride tend to form a gel-like material due to melting or formation of a solution. This effect is undesired since it reduces the ability of the material to take up water again. Finally, it was observed that performing the hydration at low-pressure will improve the water vapor transport in comparison to atmospheric pressure hydration.

INTRODUCTION

In the Netherlands a large part of the domestic primary energy consumption (~65%) is used for space heating and domestic hot water preparation [1]. This heat demand can be reduced by energy saving measures (e.g. improved insulation and heat recovery). A substantial part of the remaining heat demand can be fulfilled by using renewable energy sources such as solar energy.

The heat demand in summer can be completely fulfilled using solar heat, but in winter the heat demand exceeds the solar supply. To accommodate this difference in time between the solar energy surplus in summer and the energy demand in winter, a seasonal thermal storage is needed. Traditionally water is used for storing solar heat (e.g. solar boiler) for short time periods, however, long-term heat storage will require a large water tank (>50 m^3) that is often too large to be placed inside a building. As an alternative, it is possible to store energy by means of chemical processes, making use of the reversible reactions: $C + heat \leftrightarrow A + B$

During summer, the thermochemical material (TCM) dissociates under influence of solar heat into components A and B, which are stored separately. In the winter, the two components (A and B) react to form the original TCM while releasing the stored solar heat. No reactions occur as long as the two components are stored separately, which means that thermo chemical storage can be used for loss-free storage and transportation of heat

Not all TCMs are suitable for seasonal solar heat storage in the built environment. Besides common conditions such as low costs, safely and reliable operation, TCMs have to be non-poisonous, non-corrosive, must have sufficient energy density and have reaction temperatures that can be reached by a medium temperature solar collector. These requirements are fulfilled by a large number of salt hydrates [2]. Four salt hydrates were investigated at ECN on their potential for compact seasonal heat storage in the built environment: $MgSO_4.7H_2O$, $Al_2(SO_4)_3.18H_2O$, $CaCl_2.2H_2O$ and

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$MgCl_2.6H_2O$. In the present paper, the results of these experiments are discussed.

TCM HEAT STORAGE SYSTEM

A salt hydrate has to be able to store and release solar heat under practical conditions. These conditions are determined by the heat storage system. The TCM heat storage system is shown in Fig. 1:

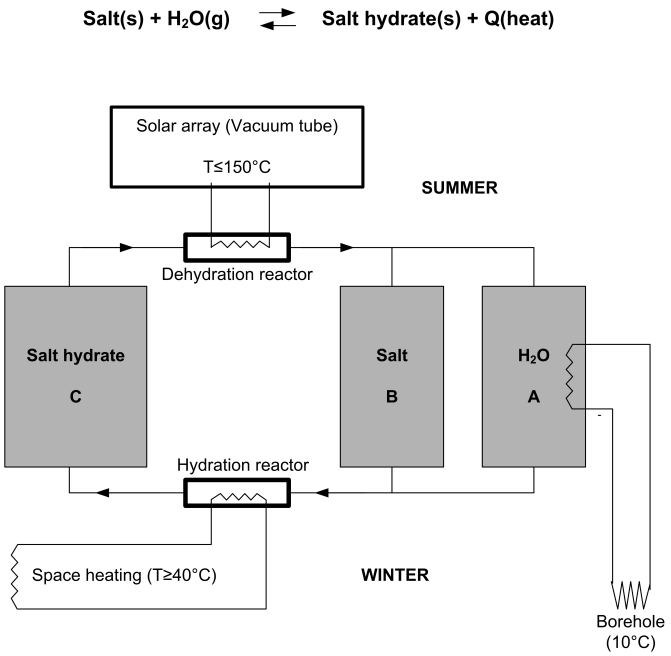


Fig. 1: Schematic overview of TCM heat storage system

The heat storage system consists of 3 storage vessels: vessel C containing the salt hydrate, vessel B containing the (dehydrated) salt and vessel A containing the water vapor in condensed form. During the summer, the salt hydrate is transported to the dehydration reactor that is heated by a vacuum collector array (vacuum tube). The hot dehydrated salt is fed to vessel B and the water vapor to vessel A, where it condenses. During the winter, water vapor is produced by means of heat from a borehole, which is assumed to be at a constant temperature of 10°C. Both the water vapor and the salt are separately transported to the association reactor. Inside the reactor the dry salt reacts with water vapor to form the original salt hydrate while releasing the stored solar heat. This heat can be used for space heating, for example for floor heating, which normally operates at maximum inflow temperatures of 40°C. It means that the material should be able to hydrate and release heat at these temperatures.

DETAILLED CHARACTERIZATION OF MAGNESIUM SULFATE: MAIN RESULTS

A first theoretical study at ECN on which material is most suitable for compact seasonal heat storage identified magnesium sulfate ($MgSO_4.7H_2O$) as most promising material [2] using the following reversible reaction:

$$MgSO_4.7H_2O(s) + \text{heat} \leftrightarrow MgSO_4(s) + 7H_2O(g) \quad (1)$$

The material was selected based on low costs, non-toxicity, non-corrosivity and high theoretical energy density: the theoretical energy density associated with reaction (1) is 2.8 GJ/m^3, which offers a more compact way of storing energy for the same volume in comparison to water (0.25 GJ/m^3 at temperature range of 25-85°C)[1]. Based on the results of this theoretical study, it was decided to further analyze the potential of $MgSO_4.7H_2O$ as TCM for compact seasonal heat storage.

Reaction (1) suggests that the hydration and dehydration is a single step process, but in literature several accounts were found that indicate the formation of stable intermediates. However, these published results are at some points conflicting on which intermediates are formed [3-5]. To investigate which intermediates are formed it was decided to examine both hydration and dehydration of magnesium sulfate anew.

The hydration and dehydration processes were investigated using differential scanning calorimetry (DSC) and thermo gravimetric analysis (TG). TG involves the measurement of the mass change as function of temperature or time and DSC involves the measurement of heat (enthalpy) changes as function of temperature or time, in which both are subjected to a predefined temperature program. The main application of TG-DSC is to identify steps in dehydration and hydration processes, determination of enthalpy of transition and identification of melting of a material. The measurements were performed on samples in the range of 10-50 mg. A typical TG-DSC result for dehydration of $MgSO_4.7H_2O$ is shown in Fig. 2:

[1] The energy density was calculated based on the crystal density of hydrate ($MgSO_4.7H_2O$).

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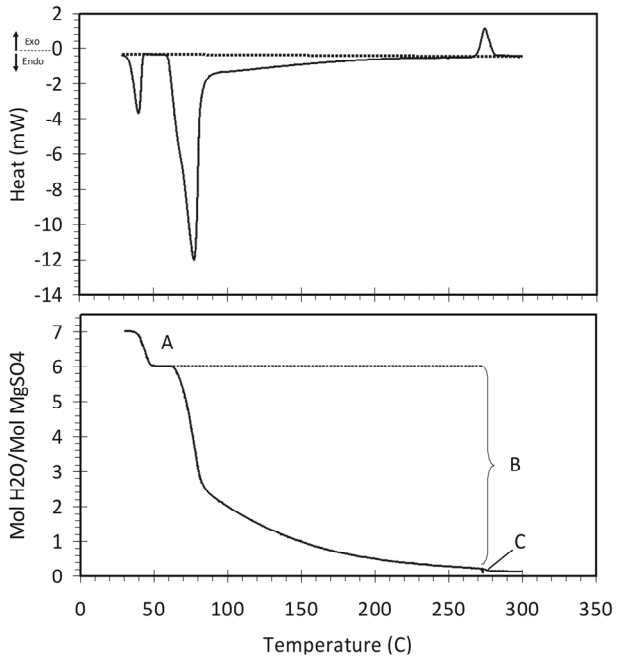


Fig. 2: A typical TG-DSC curve for dehydration of $MgSO_4.7H_2O$. Top part of the Figure is the DSC curve; the bottom part of the Figure is the TG curve. A particle size distribution of 38-106 μm was used.

The TG curve shows that the dehydration proceeds in three distinct steps indicated with letters A, B and C in Fig. 2. During the first step in the range of 25-55°C, $MgSO_4.7H_2O$ releases one mole of water to form $MgSO_4.6H_2O$. This dehydration step is a single step process. Next, $MgSO_4.6H_2O$ gradually losses 5.9 moles of water when the sample is heated to 265°C. The gradual loss of water suggests that the dehydration of $MgSO_4.6H_2O$ proceeds through several single steps in series instead of one overall single step. Unfortunately, it was not possible to clearly identify any intermediates formed during dehydration step B. Finally, the last water molecules are dehydrated at a temperature near 275°C resulting in the formation of $MgSO_4$.

As can be seen from the DSC curve (top part of Fig. 2), each step is accompanied with a peak in the DSC curve, which indicates that heat is either stored (negative value) or released (positive value) during dehydration. The enthalpy of reaction can be determined by integrating the area under each peak. The second dehydration step (B) shows the largest area under the DSC peak, which corresponds to an energy density of 2.2 GJ/m^3. Additionally, most of the energy can be stored below 150°C: a temperature that can be reached by a vacuum tube solar collector (see above). It means that the second dehydration step (B) is most interesting for compact seasonal heat storage.

Interestingly, the final step in the dehydration of $MgSO_4.7H_2O$ (step C) is accompanied with a heat release, indicating an exothermic process, which is unexpected since dehydration is an endothermic process (see also DSC peaks associated with peaks A and B in Fig 2.). This exothermic final transition to anhydrous $MgSO_4$ was also found by Ruiz et al [5], who suggested that the final transition includes an exothermic recrystallization of an amorphous precursor. X-ray diffraction measurements were carried out to investigate Ruiz's suggestion. The results of the XRD experiments are shown in Fig. 3.

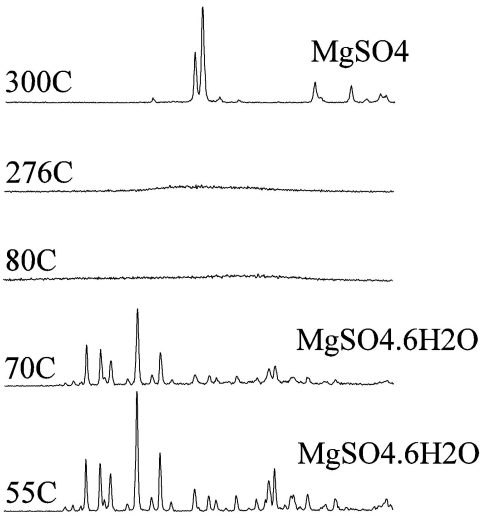


Fig. 3: XRD analysis of the dehydration of $MgSO_4.7H_2O$, where the sample was heated from 25°C to 300°C at 1°C/min.

No peaks were observed in the temperature range of 80°C to 276°C indicating that an (unknown) amorphous phase is formed during the dehydration of $MgSO_4.6H_2O$. The X-ray diffraction measurements show that the material recrystallizes above 276°C. This observation confirms the suggestion by Ruiz et al [5] that the exothermic process during the last dehydration step is due to recrystallization of an amorphous precursor.

The dehydrated material ($MgSO_4$) was subsequently exposed for 16 hours to a nitrogen-water vapor atmosphere at atmospheric pressure inside a TG-DSC apparatus to investigate the water uptake. The initial experiments were performed at 25°C using a water vapor pressure of 2.3kPa, which corresponds to the water vapor saturation pressure at 20°C. The results of these measurements are shown in Fig. 4.

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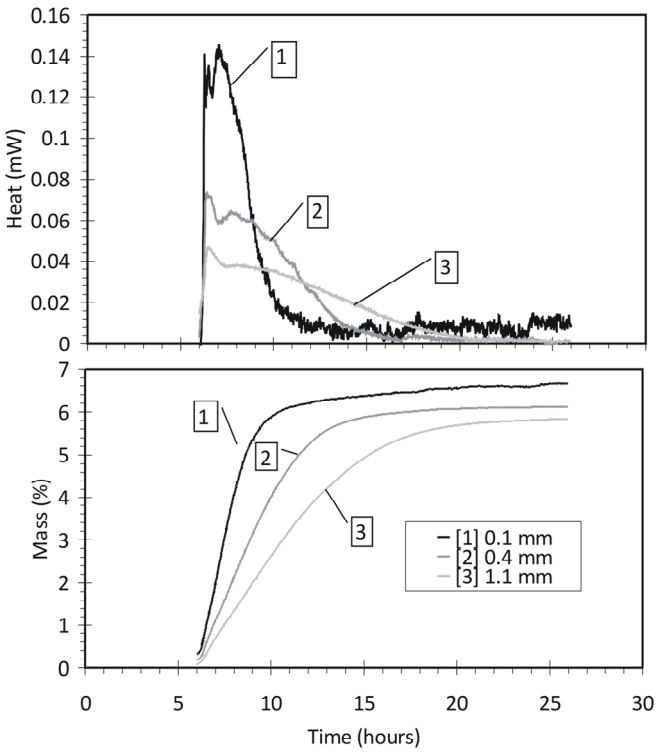


Fig. 4: The effect of layer thickness on the hydration of $MgSO_4$ at 25°C when exposed to a N_2-H_2O atmosphere with P_{H2O}=2.3 kPa. Top part of the Figure is the DSC curve; the bottom part of the Figure is the TG curve. A particle size distribution of 38-106 μm was used and sample masses of 5, 10 and 50 mg were used.

The material is able to take up 6 moles of water, but the speed of the water uptake strongly depends on the layer thickness of the sample: a thicker layer significantly reduces the hydration rate. This result indicates that the water vapor transport through the material is a limiting factor.

From the DSC measurements (Top part of Fig. 4), the energy density of the hydration reaction was determined to be 1.8 GJ/m^3. It means that almost 86% of the stored solar heat can be released during the hydration reaction. However, these experiments were performed at 25°C and in a future TCM heat storage system, the material should also be able to release (more) heat at T≥40°C. Fig. 5 shows the experimental TG-curve of hydration of $MgSO_4$ carried out at 50°C:

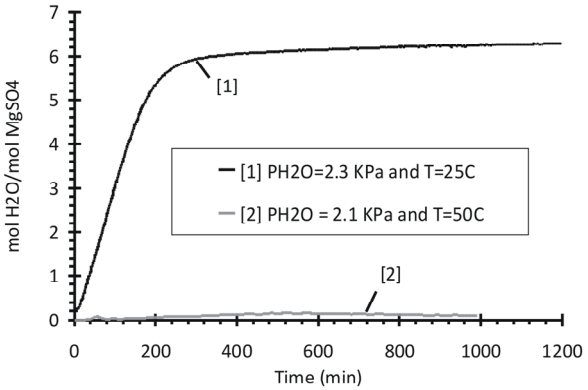


Fig. 5: Mass (TG) as function of time for hydration of MgSO4 with particle size distribution of 38-106μm and a sample mass of 10 mg.

The result shows that $MgSO_4$ is unable to take up water at 50°C, which also means that no heat is released. It should be noted that under practical conditions, the water vapor pressure is equal to the saturation water vapor pressure at 10°C (from the borehole, see also Fig. 1) corresponding to 1.3 kPa. The higher water vapor pressure used in the hydration experiments should be favorable for the water uptake [6]. The fact that the material is unable to take up water at higher water vapor pressures indicates that the application of magnesium sulfate as TCM for compact seasonal heat storage under atmospheric pressure is quite problematic.

DETAILLED MATERIAL SELECTION FOR COMPACT SEASONAL HEAT STORAGE IN THE BUILT ENVIRONEMENT

Since magnesium sulfate was unable to take up water under practical conditions it was decided to investigate other promising salt hydrates. Magnesium sulfate was selected based on results from a first theoretical study on promising materials for compact seasonal heat storage in the built environment. However, this study investigated a limited amount of carbonates, hydroxides and hydrates. In order to acquire a more complete overview of possible candidate materials for compact seasonal heat storage in the built environment, it was decided to perform a second theoretical study [7]. This study included all known absorbents (hydrates, ammoniacates, ethanolates, etc.) and adsorbents (zeolites, silica gel, etc.). The materials were selected based on energy density, costs, toxicity, temperatures that can be achieved and taking into account the various hydration steps (depending on the available information). The theoretical study identified three salt hydrates besides magnesium sulfate as most promising for compact seasonal heat storage:

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Reaction:	Theoretical Energy density [2](GJ/m^3)
$MgCl_2.H_2O(s) + 6H_2O(g) \leftrightarrow MgCl_2.6H_2O(s)$	2.5
$CaCl_2\ (s) + 2H_2O(g) \leftrightarrow CaCl_2.2H_2O(s)$	1.1
$AlSO_4(s) + 6H_2O(g) \leftrightarrow AlSO_4.6H_2O(s)$	1.9
Heating up water (ΔT=60°C)	0.25

Table 1: Selected salt-water vapor reversible reactions with corresponding energy densities

EXPERIMENTAL SETUP FOR CHARACTERIZATION OF FOUR PROMISING SALT HYDRATES

The detailed characterization of magnesium sulfate was performed at atmospheric pressure (see above). It was found that the material was unable to take up water under practical conditions. A possible solution is to hydrate the material under low-pressure conditions, which could enhance the diffusion of the water vapor to the material and thereby improve the water uptake. A newly build closed fixed bed experimental setup was able to perform the hydration experiments under practical conditions at low pressure. This experimental setup is shown in Fig. 6:

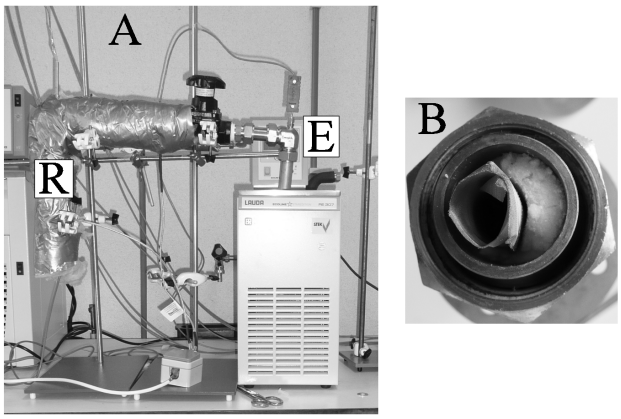


Fig. 6: Fixed bed reactor setup for characterizing the four selected salt hydrates. R denotes Reactor, E denotes Evaporator

The experimental setup consists of a fixed bed reactor and an evaporator. The fixed bed reactor shown in Fig. 6A is capable of storing 40 grams of dehydrated salt. In the centre of the fixed bed reactor a cylindrical metal mesh (aperture size 40μm and diameter 1 cm) is placed that acts as a vapor channel to facilitate the water transport to the salt during hydration (see also Fig. 6B). The fixed bed reactor is connected to an evaporator ('E' in Fig. 6A). The evaporator is immersed in a thermostat bath to control the temperature of the water inside the evaporator. A vacuum pump system consisting of a pressure sensor and two diaphragm vacuum pumps is used to evacuate the system to a minimum pressure of 2.8 mbar. The temperature inside the reactor and the evaporator during the experiments is monitored by K type thermocouples. The data from the thermocouples is digitized using a data acquisition unit and subsequently stored on a PC.

An advantage of using the fixed-bed reactor setup instead of TG-DSC measurements is that a larger sample can be used: 0-40 g instead of 10-50 mg. In this way, the hydration behavior of the four salts can be studied under more realistic conditions

HYDRATION OF FOUR PROMISING SALT HYDRATES UNDER PRACTICAL CONDITIONS

All four salt hydrates were dehydrated inside an oven prior to the experiments. The oven was programmed to heat up the samples from room temperature to 150°C with 1°C/min. The heating rate was chosen based on the magnesium sulfate dehydration experiments performed in the TG-DSC apparatus [6,8]: for heating rates >1°C/min the water vapor transport out of the material was insufficient, which resulted in melting of higher hydrates still present in the sample. To avoid this melting of the material, it was decided to restrict the heating rate to 1°C/min.

The dehydrated salt from the oven was placed inside the fixed bed reactor to examine the hydration behavior. The hydration was performed under two different conditions: first, both reactor and evaporator were at 25°C and second, the reactor was at 50°C (using a heating cable) and the evaporator at 10°C. In the latter case, the salts are tested under practical conditions as was done with magnesium sulfate at atmospheric pressure using the TG-DSC apparatus (see above). Fig. 7 shows the results of these experiments for the four salt hydrates under investigation:

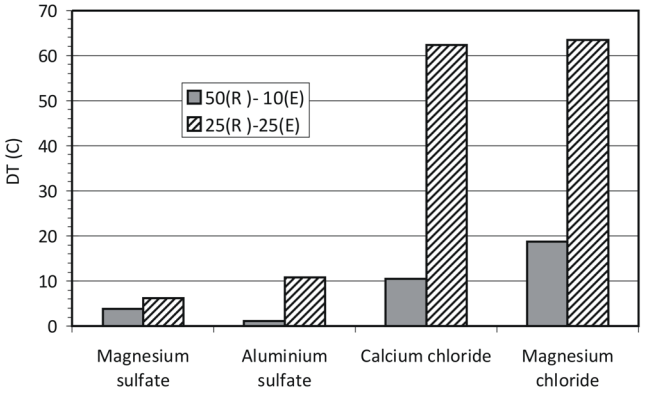


Fig. 7: Measured maximum temperature increase (DT) for the four salt hydrates tested in the fixed bed reactor. R denotes reactor temperature, E denotes evaporator temperature. The setup was evacuated to 2.8 mbar prior to the experiments.

[2] The theoretical energy density was calculated using the crystal density of the salt hydrate

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The results show a clear difference between hydration behavior of the sulfates and the chlorides: higher temperature lifts can be achieved using the chlorides under identical conditions. Based on the observed temperature lift, it seems that magnesium chloride is the most promising material for compact seasonal heat storage However, during the experiments it was observed that calcium chloride and magnesium chloride tend to form a gel-like material, which is due to the melting of the material during hydration or the formation of a solution:

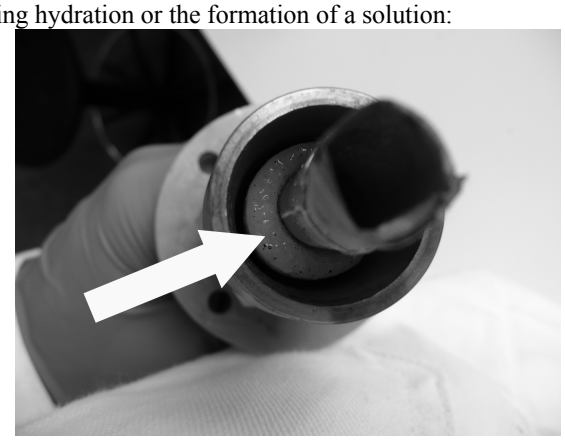


Fig. 8: Formation of a gel-like material after hydration of calcium chloride indicated with the arrow.

This is an undesirable effect since it reduces the bed porosity of the material and the ability to take up water again. It means that this problem has to be solved before using the chlorides as TCM for compact seasonal heat storage.
The hydration results for magnesium sulfate in Fig. 7 show that a small temperature lift (4°C) was observed under practical conditions at low-pressure. Under atmospheric pressure conditions, magnesium sulfate was unable to take up water (and release heat) under practical conditions. The fact that a small temperature increase was observed at low pressure, suggests that the vapor transport in the system is improved.

CONCLUSION

Four salt hydrates were investigated for their potential as TCM for compact seasonal heat storage application. These four salt hydrates were magnesium chloride, calcium chloride, aluminum sulfate and magnesium sulfate. The characterization was mainly performed using a TG-DSC apparatus and a newly constructed fixed bed reactor. The results suggest that a reduction in system pressure leads to an improvement in water vapor transport in the system. Based on the measured temperature lift under practical conditions, it was concluded that magnesium chloride is the most promising salt hydrate of the four selected salts. However, both hygroscopic chlorides under investigation tend to form a gel-like material during the hydration experiments, which is a problem for further water uptake. Once this problem is solved, it is recommended to use magnesium chloride as TCM for compact seasonal heat storage in the built environment.

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