

Characterization of the sorption process in thermochemical materials for seasonal solar heat storage application

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Characterization of the sorption process in thermochemical materials for seasonal solar heat storage application

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1. Introduction

The heat demand for dwellings in summer can be completely covered by solar heat, but in winter the heat demand exceeds the solar supply. For a low-energy house, a solution is to store the excess of solar energy in summer, and to use it to meet the heat demand in winter. Water is traditionally used for storing heat (e.g. solar boiler), but seasonal heat storage requires large water tanks (> 40 m³) that are too large to be placed inside an average family house. An alternative option is to store heat by means of chemical processes using a reversible reaction in thermochemical materials (TCM). Such thermochemical heat storage has a 5 to 10 times higher energy storage density than water, with the additional benefit that, after charging, the heat can be stored for a long time without losses. With thermochemical materials, the entire heating demand of a low-energy house could be met using a storage volume of 4 to 8 m³, that is charged during summer by solar collectors. Because of the amount of material required for implementation in the built environment, safety and low cost of the TCM materials are important aspects. Previous theoretical and experimental studies at ECN identified magnesium sulfate heptahydrate (MgSO₄·7H₂O) and magnesium chloride hexahydrate (MgCl₂·6H₂O) as promising materials for seasonal heat storage in the built environment, based on their high energy density, suitable temperature range, low cost and inherent safety. Solar heat provided by solar thermal collectors with a temperature below 150°C can be used to dehydrate the hydrates during summer, while during winter the dehydrated materials can be hydrated again with low water vapor pressure (13 mbar) provided by means of the evaporation of water by a borehole at 10°C, releasing the heat again. A representation of the practical conditions used during the dehydration and hydration reactions of the salt hydrate material is presented in fig. 1.

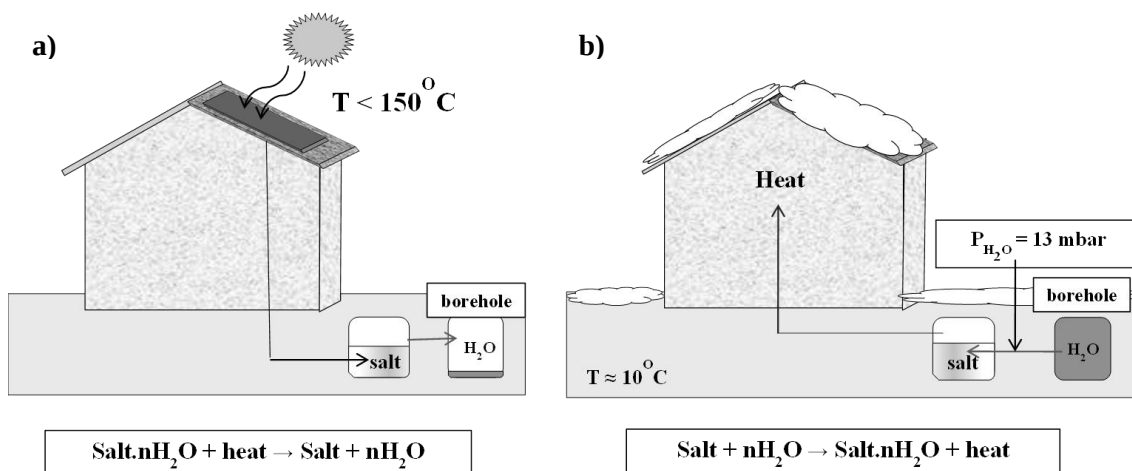


Figure 1 : Representation of the practical conditions of the (a) dehydration and (b) hydration reactions taking place in the seasonal heat storage system based on the water vapor sorption process in salt hydrates

During previous experiments performed in small scale reactors, the salt hydrates have shown promising characteristics, but their efficiency for a long term storage can still be improved. An identification and optimization of the material properties (structure, composition) and the heat- and vapor transport is required in order to develop adequate salt hydrate materials for the seasonal heat storage application. The present work focusses on the study of the water vapor sorption process in these salt hydrates on the nano- (crystal level) and the micro-scale (grain level) of the material.

2. Materials and method

This paper will focus on the dehydration process on the levels of a single crystal, grain and powder bed (fig. 2) to establish the effect of the structure and material properties on the heat- and vapor transport under the conditions corresponding to a seasonal heat storage.

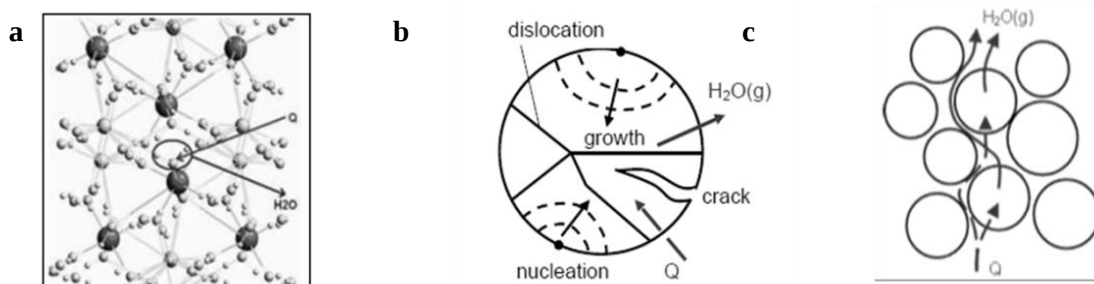


Figure 2 : Representation of the heat and mass transfer processes during dehydration of a powder bed at (a) crystal, (b) grain and (c) powder bed scales. The dashed red lines indicate the heat flow and the solid blue lines the vapor flow.

2.1 Studied materials

Firstly, two reference materials ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) having a well-established and well-documented water vapor sorption process, have been investigated under seasonal heat storage conditions on large monocrystals of 2-5 mm, synthesized by a slow evaporation of saturated aqueous solution of each material, and on samples of commercial powder sieved at 100-200 μm . Additionally, these experiments have been extended to sieved powders samples (100-200 μm) of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, which are promising for long-term heat storage.

2.2 Characterization techniques

Microscopic observations on monocrystals were carried out by *in-situ* optical microscopy to identify the textural changes of the materials occurring in the dehydration reaction. *In-situ* X-ray diffraction (XRD) analyses were performed on sieved powders to identify the composition and microstructure changes of the materials during the process. In addition, a parallel kinetic study was performed by thermal analysis to identify the dehydration reaction steps with their corresponding kinetics and reaction enthalpies. Two thermal analysis techniques were used in this work, differential scanning Calorimetry (DSC) and Thermogravimetry (TG) analysis. These analyses have been carried out in parallel in a simultaneous thermal analyses (STA) apparatus on samples of 10 mg of sieved powders placed in aluminum cups. TG analysis involves the measurement of the mass change as a function of temperature or time, and DSC involves the measurement of heat enthalpy changes as a function of temperature or time, while in both techniques the test material is subjected to a predefined temperature program. All these experimental measurements were carried out under a moist air flow of 100 ml/min fixed with a water vapor pressure of 13 mbar (± 0.2 mbar), and the dehydration took place with a heating rate of $0.5^\circ\text{C}/\text{min}$ until 150°C .

3. Results and discussion

3.1 Study on the references materials

The results obtained for each dehydration reaction of the two reference materials $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ are presented independently in this paragraph and a comparison of their behavior is made.

3.1.1 Lithium sulfate monohydrate $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$

The result of the thermal analysis (TG-DSC) experiments and *in-situ* XRD measurements performed on lithium sulfate monohydrate are shown respectively in fig. 3a and 3b. The transition temperature, the enthalpy of reaction and the energy density obtained from the DSC measurement have been compared with the reaction enthalpy and energy density calculated from the NBS data [1] for the corresponding reaction of dehydration. All these data are listed in Table 1.

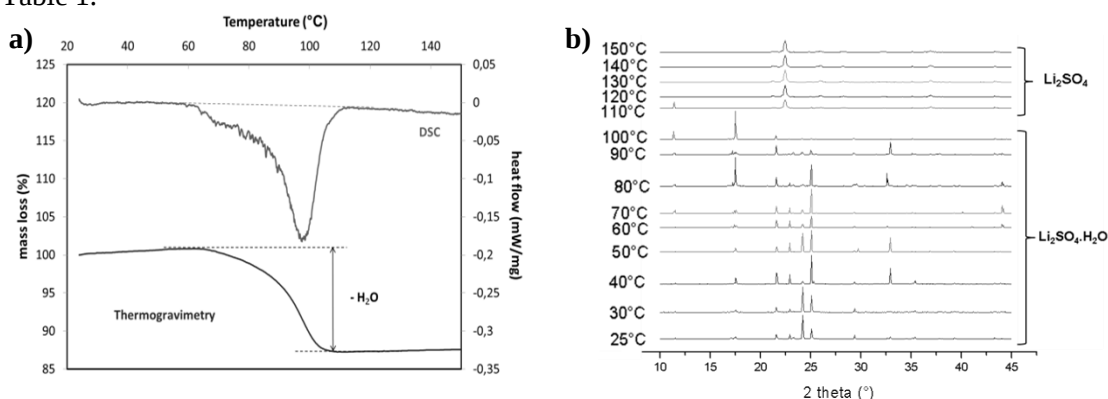


Figure 3 : TG and DSC curves of the dehydration process of (a) $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and (b) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ sieved powder (100-200µm) under a water vapor pressure of 13 mbar with a heating rate of 0.5°C/min

The dehydration reaction of the lithium sulfate monohydrate occurs in one step with a mass loss of $14.0 \pm 0.5\%$ as shown on the TG curve (fig. 3a). This corresponds to the loss of one water molecule to form the crystalline anhydrous phase Li_2SO_4 as shown by *in-situ* XRD measurement (fig. 3b). This mass loss is accompanied by a wide asymmetric endothermic peak on the DSC signal (fig. 3a) between 62°C and 112°C, which corresponds to a heat storage density of 0.71 GJ/m^3 (table 1). This is only 72 % of the literature value for the heat storage capacity of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

Dehydration reaction	NBS data [1]		Experimental data			
	$\Delta_r H$ [kJ/mol]	Energy density GJ/m^3	$T_{\text{transition}}$ (°C)	$\Delta_r H$ [kJ/mol]	Energy density GJ/m^3	Storage capacity
$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O} (\text{s}) \rightarrow \text{Li}_2\text{SO}_4 (\text{s}) + \text{H}_2\text{O} (\text{g})$	57.18	0.99	97	41.01	0.71	72 %

Table 1 : Transition temperatures and enthalpies and energy densities values obtained for the dehydration process of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ under a water vapor pressure of 13 mbar with a heating rate of 0.5°C/min.

The dehydration reaction of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ has been studied in parallel by optical microscopy on a monocrystal under the same conditions of experiments. The results are presented in fig.4. This reaction occurs as a random nucleation process of the new phase on the surface of the crystal. The nuclei grow homogeneously forming spherical opaque areas. Due to the contraction of the crystal related to the formation of the new phase, cracks are formed (turning the material opaque). This phenomenon can be explained by the fact that the material structure at the molecular level keeps a similar arrangement (monoclinic) with a simple compaction of the crystal lattice when the water molecule is removed from the crystal structure of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. This compaction creates the cracks in the microstructure of the material at the grain level to maintain the initial volume occupied by the material.

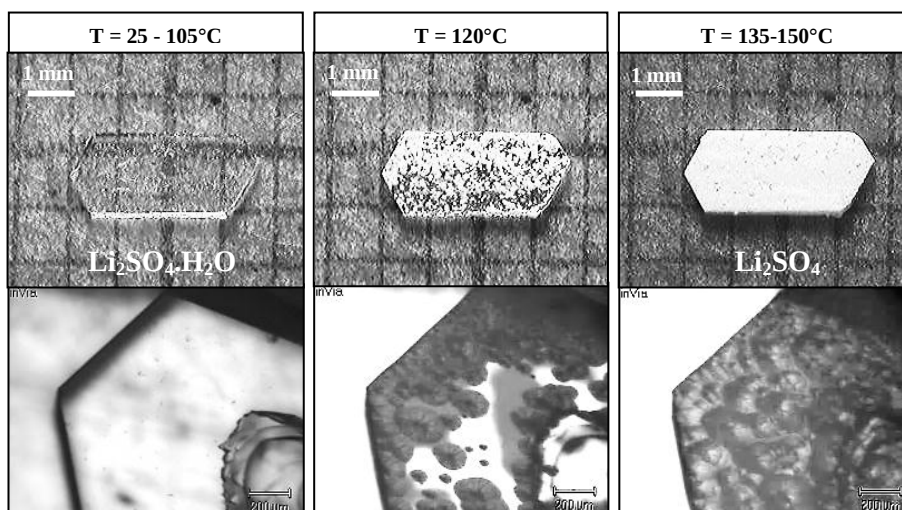


Figure 4 : In-situ microscopic observations of the dehydration process of a $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ monocrystal under a water vapor pressure of 13 mbar with a heating rate of $0.5^\circ\text{C}/\text{min}$

By comparison of the results obtained by thermal analysis (fig. 3a) and by microscopic observation (fig. 4), it can be observed that the temperature range of the dehydration reaction of $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ is shifted to higher values ($105\text{--}135^\circ\text{C}$) when the experiment is performed on a monocrystal instead of a powder. The dehydration reaction taking place in the monocrystal is slower than in the experiment performed on the powder sample. This phenomenon can be explained by a better diffusion of the water vapor through a powder than through the bulk of the monocrystal material. A large number of studies in the literature already showed for $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ a similar influence of the particle size and the crystallinity on the kinetic of reaction [2].

3.1.2 Copper sulfate pentahydrate $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$

The result of the thermal analyses (TG-DSC) experiments and *in-situ* XRD measurement performed on copper sulfate pentahydrate are shown respectively in fig. 5a and 5b. The copper sulfate pentahydrate dehydrates in two consecutive steps under these measurements conditions. For both steps, a loss of two water molecules can be identified by a mass loss on the TG curves of $14.0 \pm 0.5\%$ in the respective temperature ranges of $30\text{--}58^\circ\text{C}$ and $65\text{--}94^\circ\text{C}$. These mass losses are accompanied by well-defined endothermic peaks in the DSC signal, indicating two phase changes in the material during the dehydration process. *In-situ* XRD measurements performed on $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ sieved powder under the same measurement conditions (fig. 5b) confirmed the thermal analysis results by observation of new crystalline phases of $\text{CuSO}_4\cdot 3\text{H}_2\text{O}$ and $\text{CuSO}_4\cdot \text{H}_2\text{O}$.

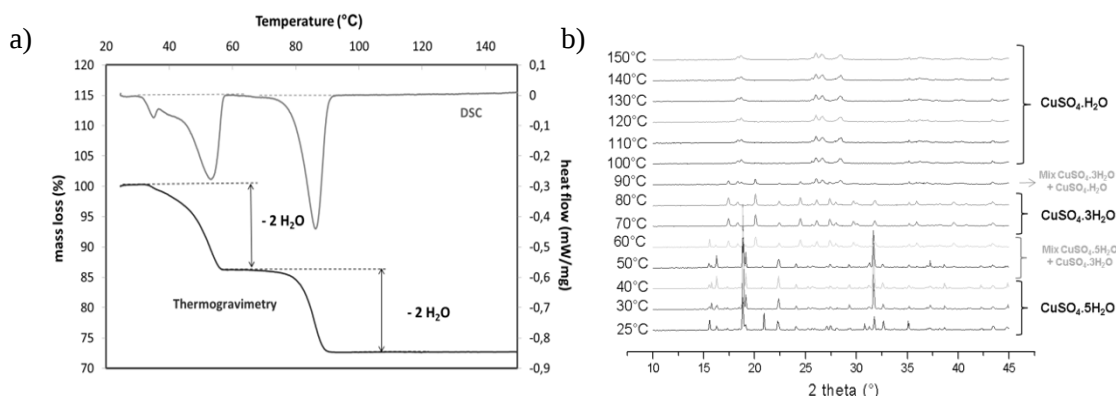


Figure 5 : In-situ XRD diffractograms of the dehydration process of (a) $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ and (b) $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ sieved powder ($100\text{--}200\mu\text{m}$) under a water vapor pressure of 13 mbar with a heating rate of $0.5^\circ\text{C}/\text{min}$

The transition temperature, the enthalpy of reaction and the energy density of the two chemical reactions taking place during the dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ have been compared with the reaction enthalpy and energy density calculated from the NBS data [1] for the corresponding reaction of dehydration. The energy density values presented in this table have been calculated with the density and molar mass values of the initial phases of each reactions (2.284 g/cm^3 for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 2.68 g/cm^3 for $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$). All these data are listed in Table 2.

Dehydration reactions	NBS data [1]		Experimental data			
	$\Delta_r H$ [kJ/mol]	Energy density GJ/m^3	$T_{\text{transition}}$ (°C)	$\Delta_r H$ [kJ/mol]	Energy density GJ/m^3	Storage capacity
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} (\text{s}) \rightarrow \text{CuSO}_4 \cdot 3\text{H}_2\text{O} (\text{s}) + 2\text{H}_2\text{O} (\text{g})$	111.68	1.02	52	89.07	0.81	79 %
$\text{CuSO}_4 \cdot 3\text{H}_2\text{O} (\text{s}) \rightarrow \text{CuSO}_4 \cdot \text{H}_2\text{O} (\text{s}) + 2\text{H}_2\text{O} (\text{g})$	114.82	1.44	86	89.44	1.12	77 %

Table 2 : Transition temperatures and enthalpies and energy densities values obtained for the dehydration process of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ under a water vapor pressure of 13 mbar with a heating rate of 0.5°C/min .

As shown in the table 2, the two chemical reactions observed during the dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ present similar values of reaction enthalpies of 89 kJ/mol for a release of the two water molecules. However, by comparison of the energy densities, the first reaction has a lower value of 0.81 GJ/m^3 than the second reaction which reaches a value of 1.12 GJ/m^3 . The calculation of the energy density take into consideration the variation of density of the material, hence a direct influence of the crystal lattice variation, while the enthalpy of reaction corresponds to the energies of the species formed and released during the reaction. These results signify that at the molecular level, the release of the two water molecules observed for each chemical reaction requires more or less the same amount of energy and the difference of crystal lattice reorganization observed by *in-situ* XRD measurement during these two reactions, does not have a relevant effect. However, this parameter influences the reactions at the grain level. Microscopic observations on monocrystals performed under the same conditions of experiments (fig.6) show that the nucleation-growth process of the crystalline phase $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ observed during the first reaction of the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ dehydration differs strongly from the process in $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. The nuclei of the new phase $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ appear on preferential sites of the crystal and progress in the crystal along a preferential direction where the removal of first two water molecules is facilitated. Cracks are also formed during this process by compaction of the lattice structure in the material in preferential direction, creating an additional porosity, as is apparent from the loss of transparency in the monocrystal. These cracks increase further during the second removal of the two water molecules to form the phase $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, due to a further rearrangement of the microstructure of the material.

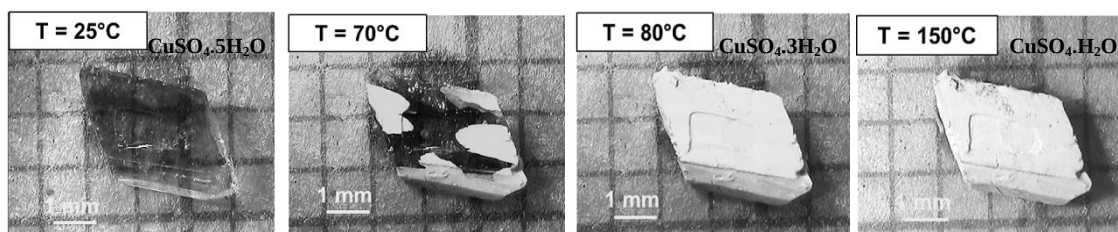


Figure 6 : In-situ microscopic observations of the dehydration process of a $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ monocrystal under a water vapor pressure of 13 mbar with a heating rate of 0.5°C/min

Similar to the study performed for $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, the kinetics of reaction in the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ dehydration are influenced by the particle size and the crystallinity of the material. By comparison on the thermal analysis curves and the microscopic observations on monocrystals, it can be observed for the first step in the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ dehydration, that the temperature range of reaction is shifted to higher temperature ($62\text{--}82^\circ\text{C}$). The diffusion through the powder sample is better than through the monocrystal. The dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ shows a total heat storage

density of 1.93 GJ/m^3 under seasonal heat storage conditions, which corresponds to 78 % of the total theoretical storage capacity of this material. This material presents promising characteristic for seasonal heat storage. However, the environmental toxicity of this material is a considerable negative characteristic for its integration in a residential environment.

3.2 TCM for seasonal heat storage

In this paper, the dehydration reactions of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ have been only studied on powder samples by thermal analyses (TG-DSC) and *in-situ* XRD measurements, since the preparation of monocrystals of these two materials still needs some improvement. The thermal analyses carried out in this work, reproduce the same type of experiments performed on these two TCM materials in previous studies [3,4,5] with a slower heating rate to identify the kinetics of reaction of these material under well-controlled conditions representative for seasonal heat storage. The *in-situ* XRD measurements performed under the same experimental conditions, bring additional information on the changes in structure and composition of the material during the dehydration reaction. The results obtained for each material will be presented separately in this paragraph due to the large differences in behavior observed for these two materials during the related experiments.

3.2.1 Magnesium sulfate heptahydrate $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

The dehydration reaction of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ under the conditions of the seasonal heat storage releases around six molecules of water in three different steps of reaction as shown on the TG curves in fig. 7a. The first dehydration step takes place between 30 and 45°C involving a mass loss accompanied by an well-defined and symmetric endothermic reaction on the DSC curve corresponding to the phase transition of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ to $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ as confirmed by the *in-situ* XRD measurements in fig. 7b.

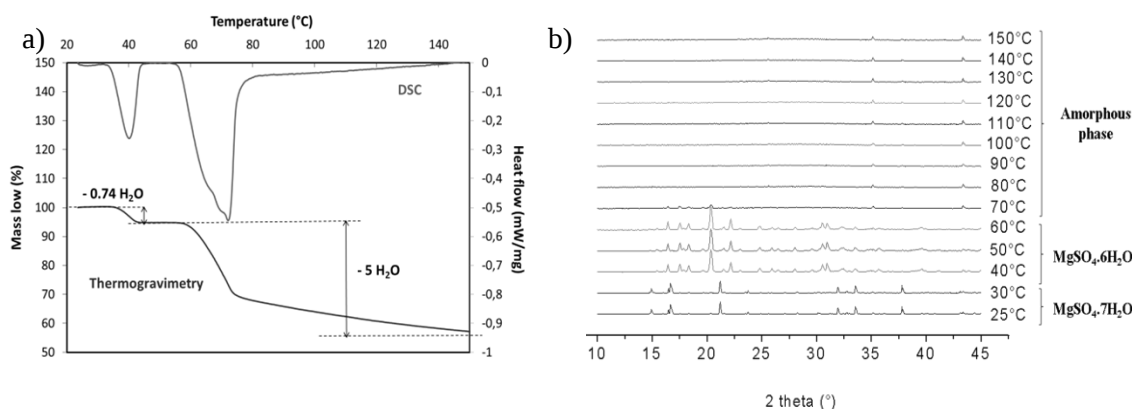


Figure 7 : (a) Thermal analyses (TG-DSC) curves and (b) *in-situ* XRD diffractograms taken every 10 $^\circ\text{C}$ of the dehydration process of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ sieved powder ($100\text{-}200\mu\text{m}$) under a water vapor pressure of 13 mbar with a heating rate of $0.5^\circ\text{C}/\text{min}$

The mass loss observed for this first transition step corresponds to a release of only 0.74 molecules of water which means that 25% of the initial powder was already converted to $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ before the measurement. This phenomenon can be explain by the fact that the transition of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ to $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ starts at low temperature nearby the ambient conditions ($25\text{-}30^\circ\text{C}$) and the initial powder has been sieved under these conditions. The values of reaction enthalpy and energy density presented in the table 2 show that the 0.74 water molecules of the initial product releases 0.29 GJ/m^3 which corresponds to an energy density of 0.39 GJ/m^3 for one molecule of water. Therefore, the heat storage capacity of the material for this reaction is within 95 % of its theoretical capacity. This high value indicates a fast conversion rate of the material for this first chemical reaction.

Dehydration reactions	NBS data [1]		Experimental data			
	ΔrH [kJ/mol]	Energy density GJ/m ³	$T_{\text{transition}}$ (°C)	ΔrH [kJ/mol]	Energy density GJ/m ³	Storage capacity
$\text{MgSO}_4 \cdot 6.74\text{H}_2\text{O}(\text{s}) \rightarrow \text{MgSO}_4 \cdot 6\text{H}_2\text{O}(\text{s}) + 0.74\text{H}_2\text{O}(\text{g})$	59.88 (7→6)	0.41	39	42.97 (0.74) 58.07 (1)	0.29 (0.74) 0.39 (1)	95 %
$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}(\text{s}) \rightarrow \text{MgSO}_4 \cdot \text{H}_2\text{O}(\text{s}) + 5\text{H}_2\text{O}(\text{g})$	275.75	2.37	72	249.88	1.83	77 %

Table 3 : Transition temperatures and enthalpies and energy densities values obtained for the dehydration process of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ under a water vapor pressure of 13 mbar

The second step of the dehydration reaction of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ present an abnormal behavior comparing to the previous dehydration reactions observed in this paper. The total mass loss of this reaction has been quantify at 38.32 % of the total mass which corresponds to a loss of around 5 additional molecules. The *in-situ* XRD measurements show that the new phase formed in this reaction is amorphous and any of the compositions found in the literature [6] are formed as intermediate phases. This observation have been explained in the literature [2,7] by a slow rate of reaction for this material at 13 mbar which indicates a slow reorganization of the lattice structure in the material forming a disordered microstructure similar to glass. Nevertheless, this second reaction presents an energy density of 1.83 GJ/m³, which means that under these measurement conditions only 77 % of the theoretical heat storage capacity of the dehydration reaction $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ to $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ was found. The total heat storage capacity obtained for the dehydration of $\text{MgSO}_4 \cdot 6.74 \text{H}_2\text{O}$ to the amorphous phase with a monohydrate composition reaches 2.12 GJ/m³ which corresponds to 80 % of the total expected value. This high value of energy density identifies $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ as an interesting TCM material for seasonal heat storage. However, previous studies at ECN [3,4] showed that this material does not provide sufficient temperature lift during the rehydration reaction under practical conditions for seasonal heat storage.

3.2.1 Magnesium chloride hexahydrate $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

The previous studies carried out on $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ have shown that this material has promising potential as TCM material for seasonal heat storage in term of energy density and temperature release [3,5]. However, this material presented some limitations for long term storage due to instability or decomposition of the material in certain ranges of temperature. At ambient temperature, overhydration of the material has been commonly observed and when this overhydrated phase is dehydrated, a impervious layer is formed in the reactor, limiting the water vapor transport though the powder bed of material. In addition, at a temperature 150°C, the material is decomposed in MgOHCl , involving a release of hydrochloric acid vapors. This reaction reduces the quantity of active material over time and can induce corrosion of the external elements of the heat storage system. In order to determine the range of temperature over which $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ remains stable and to find the kinetics of the dehydration reaction for this material, thermal analysis (TG-DSC) and *in-situ* XRD measurements have been carried out under conditions relevant for seasonal heat storage. The results presented in fig. 8 show that between 30°C and 65°C, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ remains in solid phase. This result confirms the results obtained from other experimental studies [8] indicating that $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ remains in solid state for a temperature above 30°C in combination with a water vapor pressure of 13 mbar.

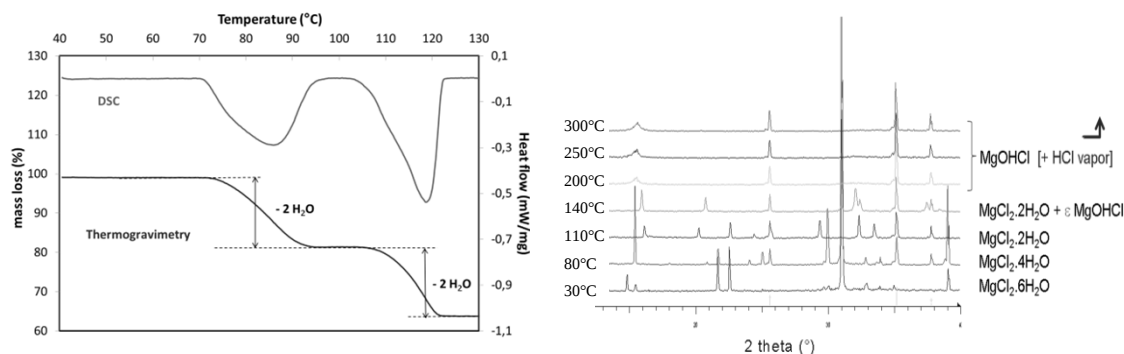


Figure 8 : (a) Thermal analyses (TG-DSC) curves and (b) *in-situ* XRD diffractograms taken every 10°C of the dehydration process of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ sieved powder (100-200 μm) under a water vapor pressure of 13 mbar with a heating rate of 0.5°C/min

The material is dehydrated in two consecutive steps with a loss of two water molecules for each step between 75-95°C and 105-123°C as shown on the TG curve in fig.8a. These two mass losses are accompanied by two corresponding endothermic peaks on the DSC curve in fig. 8a, corresponding to the formation of the lower hydrated phases $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$, as shown by the *in-situ* XRD measurements in fig. 8b. The final material seems to keep a stable composition of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ until 130°C as observed on TG-DSC results. At 140°C, the *in-situ* XRD measurements show that the material is decomposed in MgOHCl . Therefore, as conclusion of these experiments, the seasonal heat storage system based on the reversible water vapor sorption reaction of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ requires operating between 40°C and 130°C to keep a stable material during long term cycling. For the two dehydration steps of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in this range of temperature, the transition temperatures, the enthalpies of reaction and the energy densities have been identified and compared with the literature data to quantify the heat storage capacity of this material. The values are listed in table 3.

Dehydration reactions	NBS data [1]		Experimental data			
	$\Delta_r H$ [kJ/mol]	Energy density GJ/m ³	$T_{\text{transition}}$ (°C)	$\Delta_r H$ [kJ/mol]	Energy density GJ/m ³	Storage capacity
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} (\text{s}) \rightarrow \text{MgCl}_2 \cdot 4\text{H}_2\text{O} (\text{s}) + 2\text{H}_2\text{O} (\text{g})$	116.37	0.89	85	102.61	0.79	89 %
$\text{MgCl}_2 \cdot 4\text{H}_2\text{O} (\text{s}) \rightarrow \text{MgCl}_2 \cdot 2\text{H}_2\text{O} (\text{s}) + 2\text{H}_2\text{O} (\text{g})$	135.61	1.27	118	117.41	1.10	87 %

Table 3 : Transition temperatures and enthalpies and energy densities values obtained for the dehydration process of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ sieved powder under a water vapor pressure of 13 mbar with a heating rate of 0.5°C/min

As shown in the table 3, the first dehydration reaction presents a lower reaction enthalpy and energy density than the second reaction. The enthalpy of the first reaction (102.61 kJ/mol) corresponds to 87 % of the one of the second reaction (117.41 kJ/mol). However, this is reduced further to 72 % when the energy densities are compared, which is related to expansion of the material on water uptake. The total energy density of 1.89 GJ/m³ obtained for the dehydration $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ under the practical conditions of the seasonal heat storage corresponds to 88% of its theoretical value. This value is higher than the values observed for all the sulfate hydrates materials studied in this paper under the same experimental conditions. It seems that $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ presents a higher storage capacity. Therefore, this material is seen as the most promising TCM material for seasonal heat storage application.

4. Conclusions

The characterization of the dehydration reaction by thermal analyses (TG-DSC), *in-situ* XRD measurements and microscopic observations on monocrystals for the two reference materials

$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ have showed that different processes involved at molecular and grain levels influenced the heat and vapor transport in the materials. The reorganization of the lattice structure and the release of water molecules induce a compaction at the molecular level which directly influences the grain level by the formation of cracks in the material. However, the studies on the two reference materials and the two TCM materials selected in this study, show that the behavior of each material is different and an individual study of the process is required.

The dehydration studies carried out in this paper on the two TCM materials $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ have shown interesting characteristics for seasonal heat storage application. However the high energy density value of 2.12 GJ/m^3 of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ should be treated with caution. Parallel studies at ECN showed that this material does not provide sufficient temperature lift during rehydration under the practical conditions of seasonal heat storage. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, which has a lower energy density of 1.83 GJ/m^3 , is the most interesting material for seasonal heat storage application due to his high storage capacity compared to the sulfate hydrates, as observed during each step of its dehydration. Nevertheless, a seasonal heat storage system based on the water vapor sorption process in $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ should be carefully set with a restricted operating temperature range between 40 and 130°C to avoid the problems of instability and decomposition of this material as observed in previous studies.

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