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# MATERIAL RESEARCH ON SALT HYDRATES FOR SEASONAL HEAT STORAGE APPLICATION IN A RESIDENTIAL ENVIRONMENT

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## ABSTRACT

Water vapor sorption in salt hydrates is a promising method to realize seasonal solar heat storage in the residential sector. Several materials already showed promising performance for this application. However, the stability of these materials needs to be improved for long term (30 year) application in seasonal solar heat storages. The purpose of this article is to identify the influence of the material properties of the salt hydrates on the performance and the reaction kinetics of the sorption process. The experimental investigation presented in this article shows that the two salt hydrates  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  can store and release heat under the operating conditions of a seasonal solar heat storage in a fully reversible way. However, these two materials show differences in terms of energy density and reaction kinetics.  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  can release heat with an energy density of around  $0.80 \text{ GJ/m}^3$  within 4 hours of rehydration at  $25^\circ\text{C}$ , while  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  needs around 130 hours at the same temperature to be fully rehydrated and reaches an energy density of  $1.85 \text{ GJ/m}^3$ . Since the two salts are dehydrated and hydrated under the same conditions, this difference in behavior is directly related to the intrinsic properties of the materials.

**Keywords:** Seasonal solar heat storage,  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , material characterization, energy density

## 1. INTRODUCTION

A promising concept for seasonal solar heat storage in the residential sector is based on reversible water vapor sorption into crystalline salt hydrates. During summer, the salt hydrate can store heat by dehydration of the salt with an ambient air flow heated up by vacuum tube solar collectors. During winter, the salt releases the stored heat by rehydration of the dried salt bed with a moist air stream. Such thermochemical heat storage has a 5 to 10 times higher energy storage density than sensible heat storage in a water tank ( $0.25 \text{ GJ/m}^3$ ), with the additional benefit that, after charging, the heat can be stored for a long time without losses [1]. Additionally, many salt hydrates are available in large quantity at low cost and have non-toxic and non-corrosive properties suitable for implementation in a residential environment. Moreover, these materials can store and release heat under the operating conditions of a seasonal solar heat storage system (solar collector temperature up to  $150^\circ\text{C}$  for dehydration, water vapour pressure about 13 mbar during hydration, corresponding to air saturated with water by evaporation from a borehole at  $10^\circ\text{C}$ ) [2].

In a theoretical study on Thermo Chemical Materials (TCM) carried out at the Energy research Center of the Netherlands (ECN), several salt hydrates such as

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  showed a promising performance for seasonal heat storage application [2]. However, subsequent experimental studies showed that the material stability of these salt hydrates needs to be improved for application in a seasonal heat storage [3-5] over a period of 30 years. To develop adequate sorption materials for this application, a material investigation under typical dehydration conditions in a seasonal heat storage was previously performed at ECN. The aim of this study was to identify the influence of the material properties and the operating conditions on the kinetics of the dehydration process [4]. This study was carried out on two reference salt hydrate materials  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  which have a well-documented structure and dehydration behavior [6-8], and also on two promising materials for seasonal heat storage,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . As a conclusion of this study, it was shown that the dehydration of each material is governed by different processes at the molecular and grain levels. This is due to the different intrinsic material properties (structure, composition) of each salt hydrate, influencing the heat and vapor transport in the material. Another experimental study investigated a complete dehydration-hydration cycle for  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  [9]. It was shown that the operating conditions of the system (temperature  $T$  and water vapor pressure  $p(\text{H}_2\text{O})$ ) also

influence the stability of the materials and the kinetics during the sorption process.

The present paper shows experimental results on structure, mass and reaction enthalpy during a complete sorption cycle for the reference materials  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . These experiments were carried out to complete the materials study and to be able to compare these materials with each other and with the literature.

## 2. MATERIALS AND METHODS

In order to compare the results of this study with the previous studies, commercial powder samples of  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  (Sigma-Aldrich) and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (Merck), sieved at 100-200  $\mu\text{m}$ , were studied by thermal analysis and *in-situ* X-ray diffraction (XRD) under the operating conditions of a seasonal heat storage. These operating conditions were applied for the two characterization techniques and defined as follows. The dehydration was carried out between 25°C and 150°C with a heating rate of 1°C/min followed by a plateau for 3 hours at 150°C to stabilize the composition of the dehydrated material. Next, the rehydration of the material was performed with a slow cooling at 1°C/min until 25°C and subsequently left in an isothermal mode at 25°C. The water vapor conditions were controlled by a humidification system setting the water vapor pressure at a constant pressure of 13 mbar (+/- 0.2 mbar) and a constant flow velocity of 100 ml/min (+/- 2 ml/min).

XRD analyses were performed, using a Bruker D8 Advance with a MRI oven with  $\text{Cu K}\alpha 1 + \text{K}\alpha 2 = 1.5418 \text{ \AA}$  radiation, to characterize the evolution of the composition and the micro-structure of the material during the cycling process. In parallel, thermal analysis was performed to identify the heat storage capacity and the reaction kinetics of the reversible sorption process of each material. 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 Analysis (STA) apparatus (Netzsch STA 409 PC Luxx). Powders samples of 10 mg and aluminum cups of 25  $\mu\text{l}$  without lids were used for these analyses.

In order to get relevant enthalpy data from this study and minimize the experimental errors, the DSC signal was calibrated in the STA apparatus under the operating conditions used during the experiment ( $p(\text{H}_2\text{O}) = 13 \text{ mbar}$ , heating rate = 1°C/min). Additionally, an effort was made to carry out the calibration in the temperature range of 25-150°C, where the (de)hydration reactions proceed. Biphenyl ( $T_{\text{fusion}} = 79^\circ\text{C}$ ) was used as low temperature calibration standard, in addition to the conventional high temperature calibration standards

(indium,  $T_{\text{fusion}} = 156^\circ\text{C}$ ; tin,  $T_{\text{fusion}} = 231^\circ\text{C}$ ; bismuth  $T_{\text{fusion}} = 271^\circ\text{C}$ ; zinc,  $T_{\text{fusion}} = 420^\circ\text{C}$ ) in order to calibrate the STA apparatus in this entire temperature range [10]. The DSC calibration used in this study is based on a fitting of the experimental data of these materials (figure 1) in the STA apparatus.

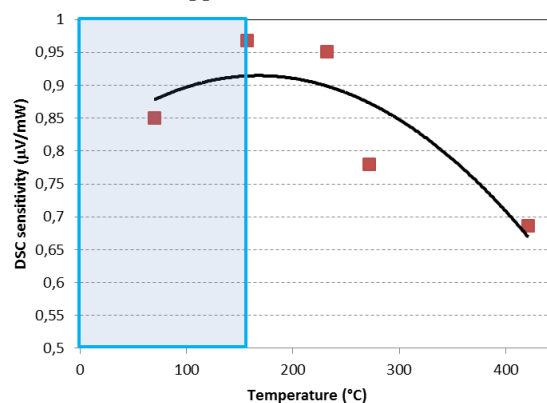


Fig. 1 DSC calibration under  $p(\text{H}_2\text{O}) = 13 \text{ mbar}$  and heating rate = 1°C/min - red dots: experimental data, black line = exp. calibration fitting with a polynom order 2.

## 3. RESULTS AND DISCUSSION

### 3.1 Lithium Sulfate

Figure 2 presents the thermal analysis results obtained for the cycling test performed on  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  powder. During the dehydration process, the TG curve showed a mass loss of  $14.0 \pm 0.5\%$ , corresponding to the loss of one water molecule. XRD analysis confirmed that, during the reaction, the crystalline salt hydrate  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  (JCPDS file 72-2320,  $P2_1$ ,  $a = 5.4553 \text{ \AA}$ ,  $b = 4.869 \text{ \AA}$ ,  $c = 8.1761 \text{ \AA}$ ,  $\beta = 107.34^\circ$ ) is fully dehydrated into the crystalline anhydrous phase  $\text{Li}_2\text{SO}_4$  [4] (JCPDS file 20-0640,  $P2_1/a$ ,  $a = 8.2414 \text{ \AA}$ ,  $b = 4.9533 \text{ \AA}$ ,  $c = 8.474 \text{ \AA}$ ,  $\beta = 107.9^\circ$ ), maintaining a similar lattice structure (monoclinic) with shrinkage of the lattice parameters. A wide endothermic peak in the DSC signal related to the reaction indicated that this reaction is a slow process taking place in the temperature range 60-115°C, with a peak at 103°C.

During the rehydration process, the crystalline phase of  $\text{Li}_2\text{SO}_4$  (JCPDS file 20-0640) was slowly rehydrated into the initial crystalline phase  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  (JCPDS file 72-2320), maintaining a monoclinic lattice framework with a re-expansion of the lattice parameters. The rehydration reaction of the material, characterized by the large exothermic peak on the DSC signal, started when the temperature of the system gets below 33.5°C and proceeded progressively for 5 hours when the system is left at 25°C and  $p(\text{H}_2\text{O}) = 13 \text{ mbar}$ .

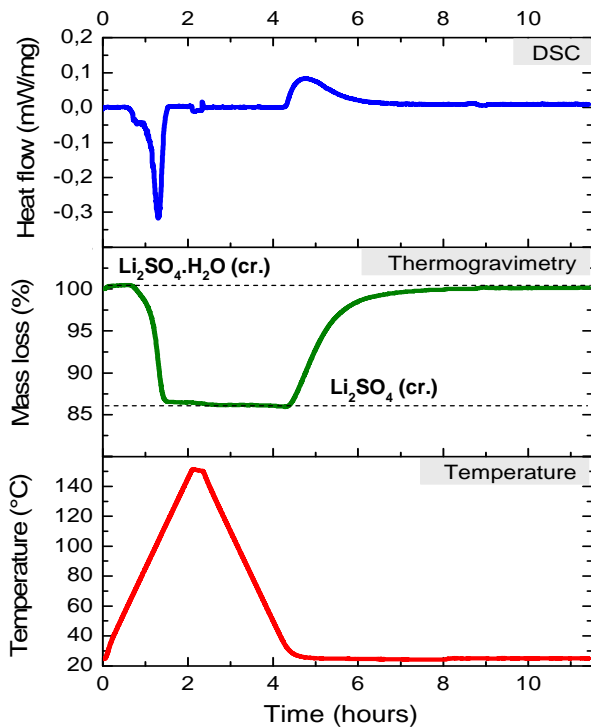
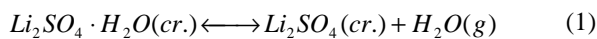


Fig. 2 Thermal analysis of the reversible sorption process of  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  powder (10 mg, 100-200  $\mu\text{m}$ ) under  $p(\text{H}_2\text{O}) = 13$  mbar

It can be concluded from these results that the sorption process of  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  is reversible under the operating conditions of a seasonal heat storage, and can be described by the following equation.



The experimental reaction enthalpy  $\Delta_r H$  and crystal energy density  $E_v(\text{cr.})$  for dehydration and hydration were calculated from the DSC peaks to quantify the performance of  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  as a TCM. In figure 3, these values are compared with the theoretical data calculated from the National Bureau of Standards (NBS) data [11]. All these data were calculated based on the molar mass of  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  of 127.96 g/mol and a density of 2060  $\text{kg}/\text{m}^3$ .

	NBS data	dehydration	hydration
$\Delta_r H$ - kJ/mol	57.18	51.24	47.84
$E_v(\text{cr.})$ - $\text{GJ}/\text{m}^3$	0.92	0.82	0.77

Fig. 3. Reaction enthalpy and crystal energy density values calculated for the reversible sorption process of  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  (100-200  $\mu\text{m}$ , 10 mg) under  $p(\text{H}_2\text{O}) = 13$  mbar.

These results indicate that  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  is able to store and release heat with an average crystal energy density of  $0.80 \text{ GJ}/\text{m}^3$  under typical operating conditions for a seasonal heat storage. These experimental reaction enthalpy data are lower than the theoretical value calculated from the NBS data. Also, it can be observed that the hydration energy density is slightly lower than the dehydration energy density. The difference in these values may be explained either by the change in structural properties of the material or by experimental artifacts. Structural modifications (grains expansion cracks) are caused by the change in lattice structure in the material during the sorption process [4]. On the other hand, experimental artifacts may be due to the calibration needing further improvement. Finally, due to the slow reaction kinetics characterized by wide peaks in the DSC profile, a certain inaccuracy is introduced in the definition of the baseline and the peak integration.

### 3.2 Copper Sulfate

Figures 4 and 5 present the thermal analysis results for  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  powder under the operating conditions of seasonal heat storage as a function of temperature and of time.

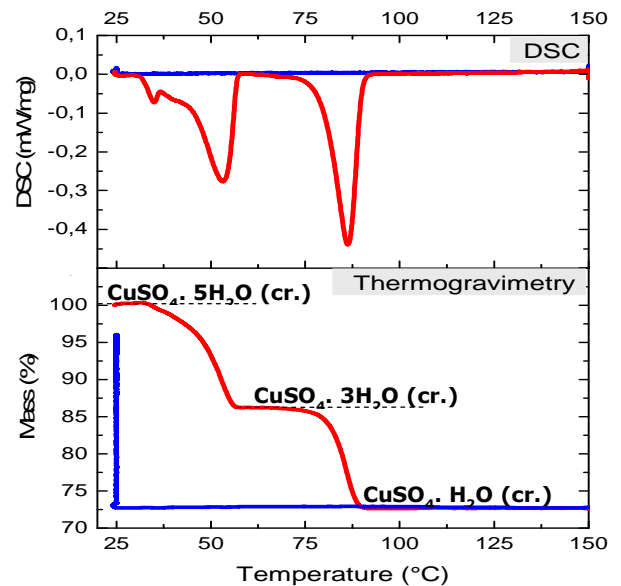


Fig. 4 Thermal analysis results of the reversible sorption process of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  powder (10 mg, 100-200  $\mu\text{m}$ ) under  $p(\text{H}_2\text{O}) = 13$  mbar. Red is dehydration, blue is rehydration.

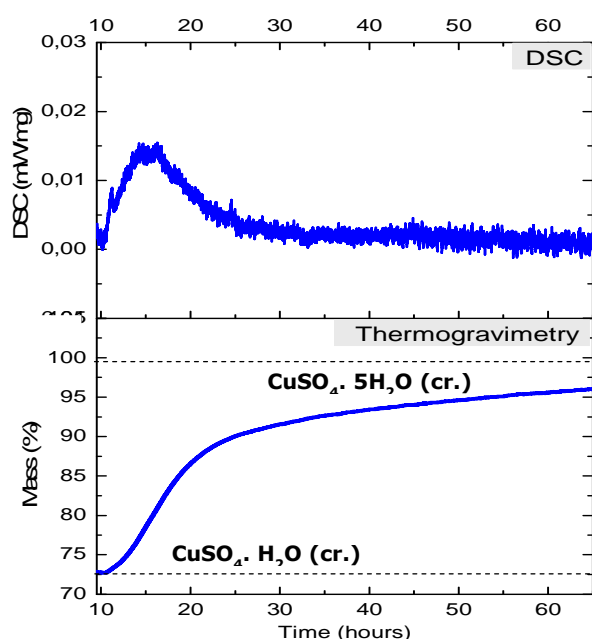
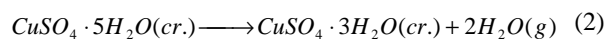


Fig. 5 Thermal analysis results of the isothermal rehydration process at 25°C and  $p(H_2O) = 13$  mbar, of the pre-dried sample of  $CuSO_4 \cdot 5H_2O$  (initial mass of 10 mg, 100–200  $\mu m$ ).

The dehydration process of the material proceeded in two consecutive chemical reactions.

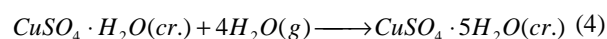


For both steps, a loss of two water molecules was identified by a mass loss of  $14.0 \pm 0.5\%$  on the TG curve in figure 3. XRD measurements [4] indicated that the first mass loss corresponds to the dehydration of the crystalline salt hydrate  $CuSO_4 \cdot 5H_2O$  (JCPDS file 77-1900, P-1,  $a = 6.1224 \text{ \AA}$ ,  $b = 12.7223 \text{ \AA}$ ,  $c = 5.96810 \text{ \AA}$ ,  $\alpha = 82.35^\circ$ ,  $\beta = 107.33^\circ$ ,  $\gamma = 102.60^\circ$ ), having a triclinic crystal lattice structure, into the monoclinic crystalline phase  $CuSO_4 \cdot 3H_2O$  (JCPDS file 076-0777,  $C_c$ ,  $a = 5.5920 \text{ \AA}$ ,  $b = 13.0290 \text{ \AA}$ ,  $c = 7.3410 \text{ \AA}$ ,  $\beta = 97.05^\circ$ ). The second mass loss corresponded to a consecutive dehydration of the crystalline phase  $CuSO_4 \cdot 3H_2O$  into the triclinic crystalline phase  $CuSO_4 \cdot H_2O$  (JCPDS file 80-03892, P-1,  $a = 5.037 \text{ \AA}$ ,  $b = 5.170 \text{ \AA}$ ,  $c = 7.578 \text{ \AA}$ ,  $\alpha = 108.62^\circ$ ,  $\beta = 108.39^\circ$ ,  $\gamma = 90.93^\circ$ ). These two phase changes, also evidenced by two well-defined endothermic peaks in the DSC signal in figure 3, took place in the respective temperature ranges of 30–60°C and 65–95°C, with peaks at 58°C and 92°C. The first endothermic peak showed an atypical shape with a slower kinetic on the beginning of the peak. This

phenomenon is characteristic of the formation of cracks in the material, as observed by microscopic observation during the first step of dehydration in a previous study [4]. The second peak had a more symmetrical shape, indicating that the formation of cracks during the first step of dehydration helps the diffusion of water vapor in the second reaction step.

Unlike the dehydration, the rehydration of  $CuSO_4 \cdot H_2O$  proceeded in a single step reaction with very slow kinetics. The TG profiles in figures 3 and 4 show that the reaction started when the temperature of the system reaches 25°C and continued for 130 hours before a full rehydration of the material is realized.

Additionally, a single exothermic peak on the DSC signal (figure 4) indicated a single step process for the rehydration reaction. *In-situ* XRD measurements showed that the crystalline phase  $CuSO_4 \cdot H_2O$  (JCPDS file 80-03892) was directly rehydrated in the initial crystalline phase  $CuSO_4 \cdot 5H_2O$  (JCPDS file 77-1900) without formation of other intermediate crystalline phases. The reaction can be described by the following equation.



This phenomenon can be explained by the fact that under the operating conditions for seasonal heat storage, the material shows very slow kinetics for the rehydration reaction. Therefore, the crystalline phase  $CuSO_4 \cdot H_2O$ , having a triclinic crystal structure will preferentially keep a similar lattice framework by forming directly the crystalline phase of  $CuSO_4 \cdot 5H_2O$  during the rehydration reaction instead of forming intermediate phases such as  $CuSO_4 \cdot 3H_2O$  (monoclinic structure) which would require an even longer time of reaction.

The experimental reaction enthalpy  $\Delta_r H$  and the crystal energy density  $E_v(cr.)$  were also calculated from the DSC peaks to quantify the performance of  $CuSO_4 \cdot 5H_2O$  as a TCM. These values are compared in figure 6 with the theoretical data calculated from the NBS data [11]. All these data were calculated with the molar mass of  $CuSO_4 \cdot 5H_2O$  of 249.69 g/mol and a crystal density of 2284 kg/m<sup>3</sup>.

	NBS data	dehydration	hydration
$\Delta_r H$ - kJ/mol	226.5	202.0	201.9
$E_v(cr.)$ - GJ/m <sup>3</sup>	2.07	1.85	1.84

Fig. 6 Reaction enthalpy and crystal energy density values calculated for the reversible sorption process of  $CuSO_4 \cdot 5H_2O$  (100–200  $\mu m$ , 10 mg) under  $p(H_2O) = 13$  mbar.

It can be concluded from all of these results that the sorption process of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is a fully reversible process under seasonal heat storage conditions. The material is able to store and release heat under those system conditions with an average crystal energy density of  $1.85 \text{ GJ/m}^3$ . Once again, this experimental energy density value is lower than the theoretical value calculated from the NBS data due to the influence of experimental artifacts during the measurement (calibration, results interpretation) and possible modifications of the material structure (grains expansion, cracks) during the sorption process.

#### 4. CONCLUSIONS

The experimental investigation performed in this study shows that the two salt hydrates  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  can store and release heat under the operating conditions of a seasonal solar heat storage in a fully reversible way. However, these two materials show differences in terms of energy density and reaction kinetics.  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  can release heat with an energy density of around  $0.80 \text{ GJ/m}^3$  within 4 hours of rehydration at  $25^\circ\text{C}$ , while  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  needs around 130 hours at the same temperature to be fully rehydrated and reaches an energy density of  $1.85 \text{ GJ/m}^3$ . Since the two salts are dehydrated and hydrated under the same conditions, this difference in behavior is directly related to the intrinsic properties of the materials.

It can be concluded from this study, that the sorption process of a salt hydrate material is depending on the intrinsic properties (crystal structure, thermodynamic) of this material. Therefore, a general kinetic model of the sorption process in salt hydrates material will require information on these material properties.

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