

Investigations of ZnSO_4 hydrates for solar heat storage applications

Konrad Posern¹, Kirsten Linnow², Christian Kaps¹ and Michael Steiger²

¹ Bauhaus-Universität Weimar, Chair of Building Chemistry, Weimar (Germany)

² University of Hamburg, Inorganic and Applied Chemistry, Hamburg (Germany)

Abstract

The reversible hydration of $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ to $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ is a promising way to store solar heat, due to the high enthalpy of hydration from $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ to $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ of $\Delta_{\text{hyd}}H_{6/7} = -58.3$ kJ/mol. The hydration behavior was investigated by using isothermal calorimetry at different constant humidities. A lower limit of 70 % RH was chosen which is slightly below the equilibrium humidity for the hydration from $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ to $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, thus, $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ was expected as the hydration product. The upper limit of 85 % RH was chosen below the deliquescence humidity of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, therefore, the heptahydrate was the expected hydration product in this case. It turned out that neither the hydration to $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ at 70 % RH nor the formation of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ at 75 % RH was achieved whilst a water content above 7 mol H_2O per mol ZnSO_4 indicated the formation of a solution at 80–85 % RH. The heat of reaction was found to be significantly smaller than the enthalpy of hydration $\Delta_{\text{hyd}}H_{6/7}$. The heat of reaction for the dehydration was found to be significantly higher compared to the heat of reaction evolved by the hydration and agrees with the theoretical expected value. In addition the hydration of $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ was investigated by using Raman microscopy. It turns out that the hydration to the thermodynamic stable products $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ or $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ does not take place instead a solution of $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ was formed. Hence the lower heat of reaction evolving during the hydration is caused by the formation of a solution due to a kinetic hindrance of the hydration to the thermodynamically stable products $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ or $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$.

Keywords: zinc sulfate hydrate; thermochemical heat storage, reversible salt hydration

1. Introduction

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was often investigated as promising storage material due to the high theoretical storage density of 2.2 GJ/m³, based on an average enthalpy of hydration ($\Delta_{\text{hyd}}H_0 = -53.9$ kJ/mol $\text{H}_2\text{O}(\text{g})$) for the complete hydration of $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ to $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and the density of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. However, it was found that the use of the theoretical storage potential is limited by incomplete and slow dehydration as well as by incomplete hydration behavior (Posern and Kaps, 2008, Linnow et al. 2014). Although the enthalpy of hydration $\Delta_{\text{hyd}}H_{6/7} = -58.3$ kJ/mol $\text{H}_2\text{O}(\text{g})$ (Chou and Seal, 2005) from $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ to $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ is higher as for the hydration of $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ to $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, this promising candidate has been rarely investigated as heat storage material. Therefore, in the present work, we have studied the drying behavior of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ to clarify, if it can be dehydrated more easily as $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (Posern and Kaps, 2008, Steiger et al., 2011). The dehydration product, that was found to be $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$, was used for the calorimetric investigation of the hydration behavior at 30 °C. For the hydration reaction, a lower limit of 70 % RH was chosen which is slightly below the equilibrium humidity for the hydration from $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ to $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (71.8 % RH at 30 °C, Grevel and Majzlan, 2011). Therefore, $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ was expected as the hydration product. An upper limit of 85 % RH was chosen which is below the deliquescence humidity of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 85.8 % RH at 29.5 °C (Apelblat, 1992), hence the heptahydrate was expected to be the hydration product between 72 % and 85 % RH. Due to the linear trend of the enthalpies of formation $\Delta_f H$ with the number of water molecules x (Jenkins and Glasser, 2010) of several crystal hydrates $\text{MX} \cdot x\text{H}_2\text{O}$ with various hydration states (for

example $x = 1, 4, 6, 7$) an average enthalpy of hydration $\Delta_{\text{hyd}}H_0$, i.e. a nearly constant enthalpy of hydration per mol H_2O (g) independent of the change of the hydration state, can be calculated reasonable. Thus it is also reasonable to assume that $\Delta_{\text{hyd}}H_{1/7}$ or $\Delta_{\text{hyd}}H_{1/6}$ is nearly equal to $\Delta_{\text{hyd}}H_{6/7}$. But it turns out that the heat of reaction measured for the hydration from $\text{ZnSO}_4\cdot\text{H}_2\text{O}$ to $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ was significantly lower than the enthalpy of hydration given for the hydration from $\text{ZnSO}_4\cdot 6\text{H}_2\text{O}$ to $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ from Chou and Seal (2005). Additional attempts were made to clarify this mismatch of the measured heat of hydration and the theoretical heat of hydration, as there are in-situ Raman observation of the hydration and calorimetric measurements of the dehydration from $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ to $\text{ZnSO}_4\cdot 6\text{H}_2\text{O}$.

2. Materials and Methods

Drying experiments

$\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ (Merck 1.08883) was sieved to a grain size less than $125\ \mu\text{m}$ and dried at two different conditions. Dehydration at $130\ \text{°C}$ for 2 h in a drying cabinet were chosen to simulate dehydration conditions of solar heat collectors and in addition $40\ \text{°C}$ and 10 % RH were chosen to prove if the dehydration can also easily be achieved with waste heat at low temperatures. The dehydration products were characterized by X-ray diffractometry (XRD) and thermogravimetry (TG).

Calorimetric experiments

For measuring the heat of hydration of $\text{ZnSO}_4\cdot\text{H}_2\text{O}$ and of dehydration of $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ the calorimeter C 80 (Setaram) connected to the humidity controller Wetsys (Setaram) were used. After placing about 0.2 g of the $\text{ZnSO}_4\cdot\text{H}_2\text{O}$, alternatively 0.3 g of $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$, in the experimental cell a dwell time of 3 h was adjusted at $30\ \text{°C}$ to achieve a constant heat flow signal of 0 mW. To avoid a water uptake or desorption the humidity was kept constant at 30 % RH for the hydration experiments and for the dehydration experiments the humidity was kept constant at 84 % RH during the dwell time. The hydration was then started by increasing the humidity on the desired value whilst the dehydration was activated by decreasing the humidity from 84 % RH to the desired humidity. The heat of reaction was determined by integration of the heat flow curve. The change of the mass was determined by weighing and the water content expressed as mol water per mol ZnSO_4 of the product was calculated.

In-situ Raman microscopy

Raman spectra were recorded on a Senterra Raman dispersive microscope (Bruker Optics GmbH, Germany) with an automated Raman frequency calibration system (SurCal technology). The laser was operated at 532 nm and 20 mW. The Raman microscope was equipped with a humidity chamber made of brass. Humid air at a flow rate of $500\ \text{ml}\cdot\text{min}^{-1}$ is provided by the humidity generator MHG32 (ProUmid GmbH, Germany) and humidity is controlled by a HycroClip C05 probe (Rotronic, Switzerland) placed directly besides the sample holder of glass. The temperature in the 20 mL chamber is controlled by a thermostat (F20, Julabo GmbH, Germany). To observe the hydration reactions in-situ $\text{ZnSO}_4\cdot\text{H}_2\text{O}$ was placed into the chamber and the humidity was kept constant at about 10 % RH until the temperature equilibrium was achieved. Subsequently, the humidity was increased in a single step to the desired value and the phase transition was observed continuously by successively recorded Raman spectra and microphotographs.

3. Results and Discussion

Drying experiments

The TG curves for the dehydration of $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ and $\text{ZnSO}_4\cdot\text{H}_2\text{O}$ up to $400\ \text{°C}$ are shown in Fig. 1. The thermal decomposition of $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ with the loss of 6 mol of water is described in more detail elsewhere (Straszko et al., 1997). As the TG measurement shows, the dehydration of $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ can be easily achieved at about $130\ \text{°C}$ which was proofed by the dehydration in the drying cabinet at $130\ \text{°C}$ for 2 hours. Also the dehydration at $40\ \text{°C}$ for 2 weeks was nearly complete. In both dehydration experiments the exact water content of 1.1 mol H_2O per mol ZnSO_4 was found. XRD confirms the presence of $\text{ZnSO}_4\cdot\text{H}_2\text{O}$ by comparison of the diffractogram with the reference pattern PDF 33-1476 (ICCD, 2001).

Although no other hydrated phase ($\text{ZnSO}_4 \cdot x\text{H}_2\text{O}$, $x = 7, 6$ or 4) was detected, the water content indicates the presence of a higher hydrate. Calculations reveal that contributions of 2.5 % and 3.15 % of the hexahydrate or the tetrahydrate, respectively, yield a total water content of 1.1 mol in a mixture with the monohydrate.

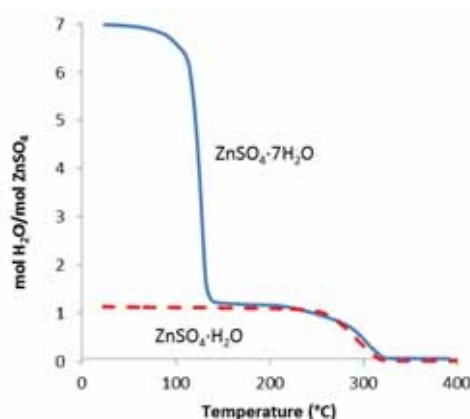


Figure 1: TG curves of thermal decomposition of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (blue) and $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ (red) in dry air

Due to the limited sensitivity of the XRD measurements such small amounts of the higher hydrates might not be found. However, the slightly higher water content of the dehydration product of 0.1 mol H_2O compared to the $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ only restrict the use of the theoretical energy density by 1.7 % which is not a severe disadvantage.

Calorimetric measurements

The results of the calorimetric hydration measurements are listed in Table 1. The water content after hydration expressed as mol H_2O per mol ZnSO_4 (x) shows that neither at 70 % RH nor at 75 % RH the complete hydration to the thermodynamically stable phases hexahydrate or heptahydrate, respectively, is achieved. Besides, in-situ RH-XRD measurement reveal that the hydration to $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ takes place at 75 % RH and 30 °C, whilst the formation of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was not observed within 24 h. Hence the kinetic hindrance of the $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ formation was confirmed. Besides, this kinetic hindrance is similar as found for the $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (Posern, 2008, Steiger et al. 2008) and for the $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ formation (Linnow et al., 2014).

The high water contents (x) at 80 %, 82 %, 84 % and 85 % RH clearly indicate the formation of a solution although the measurements were carried out below the deliquescence humidity of 85.8 % RH at 29.5 °C (Apelblat, 1992). That means that the reaction products of the hydration are not yet in thermodynamic equilibrium. The overall heat of reaction ($Q_{r,m}$) normalized to the mass of $\text{ZnSO}_4 \cdot 1.1\text{H}_2\text{O}$ as given in Table 1 increases with increasing water content of the hydration product. The average enthalpy of reaction $\Delta_r H_m$ is significantly smaller than the enthalpy of hydration $\Delta_{\text{hyd}} H_{6/7}$ (-58.3 kJ/mol H_2O) as given by Chou and Seal (2005). Additional calorimetric measurements were carried out to validate the theoretical enthalpy of hydration $\Delta_{\text{hyd}} H_{6/7}$. Therefore the dehydration of crystalline $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ to $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ was measured at different humidities. The product of the dehydration measurements at humidities between 50 % and 58% RH as given in Table 2 is in every case the stable $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$.

Tab. 1: Water content of the hydration product expressed as mol H_2O per mol ZnSO_4 (x), measured heat of reaction ($Q_{r,m}$) and enthalpy of reaction ($\Delta_r H_m$) measured during hydration of $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ at 30 °C and different relative humidities

RH (%)	x	$Q_{r,m}$ (kJ/g)	$\Delta_r H_m$ (kJ/mol)
70	4.13	-0.83	-50.4
75	5.76	-1.26	-49.6
80	7.06	-1.66	-51.0
82	7.25	-1.69	-50.4
84	7.62	-1.76	-49.3
85	8.20	-1.86	-48.0

Tab. 2: Water content of the dehydration product expressed as mol H₂O per mol ZnSO₄ (x) enthalpy of reaction $\Delta_r H_{m,7/6}$ measured during dehydration of ZnSO₄·7H₂O at 30 °C and different relative humidities

RH (%)	x	$\Delta_r H_{m,7/6}$ (kJ/mol)
50	5.94	56.0
54	5.94	56.2
56	5.97	56.5
58	5.95	56.6

According to Hess law the change of enthalpy is independent from the pathway i.e. the enthalpy of hydration has the same value as the enthalpy of dehydration but the opposed sign. The enthalpy of dehydration $\Delta_r H_{m,7/6}$ is almost in agreement with the value of Chou and Seal (2005), but the measured value is in general smaller and a slight trend to a lower enthalpy of hydrations at rapid dehydration conditions can be seen clearly. However, in general the theoretical enthalpy of hydration is confirmed. Hence, it can be concluded that during the hydration not the expected crystalline phases were formed in the calorimetric measurement cell. Instead the formation of other metastable phases with a lower change of energy takes place.

In-situ Raman measurements

As an example, micrographs taken during the hydration of ZnSO₄·H₂O at 75 % RH and 20 °C are shown in Fig. 2. In general the Raman spectrum of the educt is in total agreement with the reference Raman spectrum of ZnSO₄·H₂O (RRUFFID R070571, Downs, 2006). The most intensive Raman frequency ν_1 was found to be 1022.3 cm⁻¹, which allows the unambiguous identification of ZnSO₄·H₂O besides the most intensive Raman frequency ν_1 of 982.2 cm⁻¹ of an aqueous SO₄²⁻ solution (Linnow et al. 2014). After increasing the humidity from 10 % RH at $t = 0$ the smallest grains of ZnSO₄·H₂O starts to pick up water from the surrounding air and dissolves (Fig.2a). After an exposure time of nearly one hour also bigger crystals dissolve by deliquescence. After two and a half hour changes of the appearance could not be noticed any longer (Fig. 2b). The crystals in the middle of the droplets were clearly identified to be ZnSO₄·H₂O, whilst the most intensive Raman frequency of the ZnSO₄·6H₂O and ZnSO₄·7H₂O at 984.6 cm⁻¹ was not found in the droplets, that means that although the solution is supersaturated with respect to both, ZnSO₄·6H₂O and ZnSO₄·7H₂O, neither the hexahydrate nor the heptahydrate crystallize. The same hydration behavior was also observed at 30 °C and 75 % RH as well as at 32 °C and 78 % RH and 80 % RH. This experiment provides clear evidence of the capability of ZnSO₄·H₂O to dissolve in the calorimetric cell under the conditions applied to hydrate the salt.

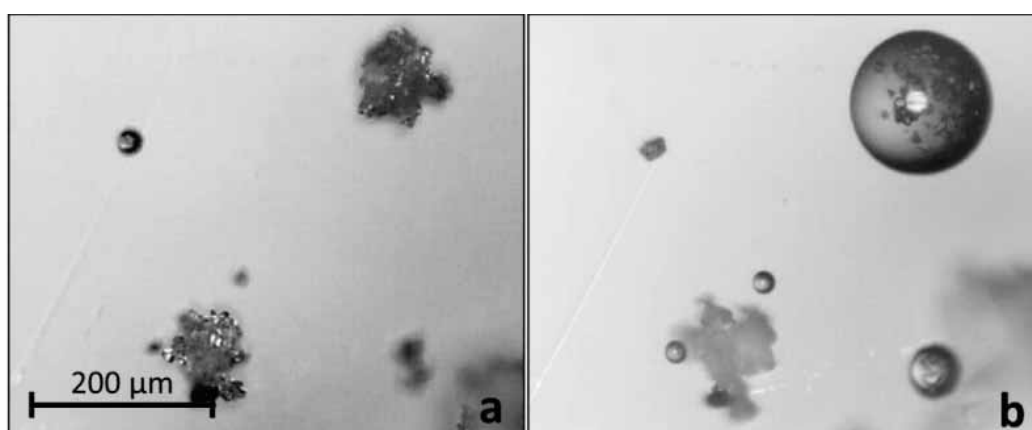


Figure 2: Hydration of ZnSO₄·H₂O at 75 % RH and 20 °C at the beginning (a) and after exposure times of 2.5 h (b)

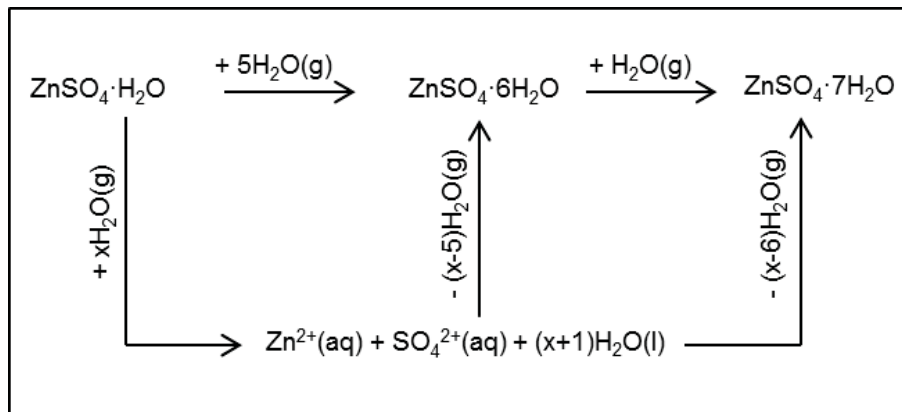


Figure 3: Possible hydration pathways of $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$

All possible hydration pathways of $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ are depicted in Fig. 3. Considering that the hydration/dehydration reaction is a change of state so that the energy released and energy consumed has to be of the same value independent of the pathway, it can be concluded that the hydration in the calorimetric cell also takes place via a dissolution mechanism as depicted in Fig.3. It is reasonable to assume that the hydration is not completed when the release of the heat achieve the constant heat flow value of 0 mW, due to the observed kinetic hindrance of either the $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ crystallization. Taken into account the lower enthalpy of condensation ($\Delta_{\text{con}}H_{303} = -44$ kJ/mol) the intermediate state of the solution yields a lower enthalpy of reaction compared to the enthalpy of hydration.

4. Conclusions

A kinetic hindrance of the formation of the thermodynamically stable product was observed at 70 % and 75 % RH. The thermodynamic stable phases $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ or $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ were not formed under these conditions. At higher humidities (80 %, 82 % and 85 % RH) the water content exceeds the water content of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ clearly indicating the formation of a solution. The heat of reaction increases with increasing water uptake, whilst the average enthalpy of reaction $\Delta_r H_m = -49.8$ kJ/mol was found to be significantly smaller than the theoretical enthalpy of hydration $\Delta_{\text{hyd}}H_{6/7} = -58.3$ kJ/mol ($\text{H}_2\text{O}(\text{g})$) and closer to the enthalpy of condensation ($\Delta_{\text{con}}H_{303} = -44$ kJ/mol). In contrast the enthalpy of hydration $\Delta_r H_{m,7/6} = 56.3$ kJ/mol, measured by dehydrating $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ to $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$, is almost in agreement with the theoretical value. The in-situ Raman measurements prove that at high humidities $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ does not hydrate via a solid-gas reaction, instead it dissolves. The lower heat of reaction during hydration is the result of the formation of a solution, in consequence of a kinetic hindrance of the formation of $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. Although the dehydration to $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ can be easily achieved at low temperatures it is questionable if the high theoretical energy can be released in a solar energy storage application. A severe hindrance of the release of the heat in the calorimetric cell was observed.

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