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HUMIDITY CONTROLLED CALORIMETRIC INVESTIGATION OF THE HYDRATION OF $MgSO_4$ HYDRATES

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The isothermal heat of hydration of $MgSO_4$ hydrates was studied by humidity controlled calorimetry. Two hydrates, starkeyite ($MgSO_4 \cdot 4H_2O$) and a mixture of $MgSO_4$ hydrates with summary 1.3 mol H_2O were investigated. The solid–gas reactions were initiated at 30°C and 85% relative humidity. The heat of hydration was determined in a circulation cell in the calorimeter C80 (Setaram). The crystal phases formed after the hydration process were analyzed by thermogravimetry (TG) and X-ray powder diffraction (XRD).

Starkeyite reacted with the water vapour to the thermodynamic stable epsomite and the $MgSO_4$ hydrate mixture with 1.3 mol water to hexahydrite. The hydration heats of starkeyite and the mixture were determined to be -169 ± 3 and -257 ± 5 kJ mol^{-1}, respectively.

Keywords: *gas phase, heat of hydration, isothermal calorimetry, magnesium sulphate, salt hydration*

Introduction

Searching for alternative energy resources is a main topic of investigations today. Beside of the importance of this sustainable usage of energy is the efficiency of storage a huge problem. A low cost and simple way to storage incidental energy in form of solar heat could be the utilization of salt hydrates. Lot of salt minerals are able to incorporate different amounts of water molecules into the crystal structure. The hydration of salt hydrates with lower water content to a higher one is associated with the release of heat. This heat of hydration can be used for long time or seasonal storage as well as for natural climatisation [1, 2]. The main principle is shown in the following Eq. (1):

$$\mathrm{salt}\cdot x\mathrm{H_2O}(s)+n\mathrm{H_2O}(g)\underset{\longleftarrow\,\text{water discharging}}{\overset{\text{water charging}\,\longrightarrow}{\leftrightarrow}}\mathrm{salt}\cdot[x+n]\mathrm{H_2O}(s)+\mathrm{heat} \quad (1)$$

This release of heat will be generated by the reaction of a salt hydrate containing a low amount of water (max. anhydrous) with gaseous water (water steam or humid air) to a salt hydrate containing higher water content (product of Eq. (1)). There exists an enormous number of salt minerals of different hydrate levels, but the amount of released heat, the decomposition temperature as well as the temperature of dehydration is very different.

Investigations of the hydration of salts in humid air are mostly done in combination with damaging of building materials such as sandstone or porous bricks by changing the volume of the salt during the reversible hydration processes [3, 4]. In these cases the deliquescence relative humidity (DRH) is one of the significant parameters of the salts. In general, the kind of the hydration product at a given temperature depends on the relative humidity (RH) of the environment during the hydration process. There are two types of the formed product: solid salt hydrates or aqueous salt solution. Both cases of reaction product are demonstrated in Eqs (2) and (3) with indicated conditions of hydration.

$$\mathrm{salt}(s)+\mathrm{water}(g)\leftrightarrow\mathrm{salt\ hydrate}(s) \quad \text{for RH<DRH} \quad (2)$$

$$\mathrm{salt}(s)+\mathrm{water}(g)\leftrightarrow\mathrm{salt\ solution}(l) \quad \text{for RH>DRH} \quad (3)$$

For the application as a solar heat storing material the basic conditions require a low dehydration temperature, a high releasing of heat and a fast and reversible separation and sorption of water.

The $MgSO_4$–H_2O system was selected for several reasons:

- Dynamic investigations of dehydration (DSC) [5] let assume a high releasing of heat.
- A dehydration temperature of 130°C is effectual to dehydrate $MgSO_4$ hydrates sufficiently and this temperature is realisable by solar collectors [6].
- $MgSO_4$ hydrates are available in great quantities (waste or by-product).
- Aqueous solutions of alkaline earth sulphates show a neutral pH-range contrary to the solutions of corresponding chlorides (e.g. the often used $CaCl_2$) and they are less corrosive than halides [7].

For increasing the dispersity of the salt hydrates and for preventing an agglomeration of the crystals

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during cyclic charge and discharge processes, the salt hydrate should be inserted in an open porous matrix. Before starting investigations of the salts within the porous matrix and of the interaction between salt and matrix, the data of the pure salt hydration should be known. Although the salt hydration is a long known phenomenon, surprisingly the data about thermodynamics and kinetics of the salt hydrations subjected to temperature and humidity are incomplete.

Magnesium sulphates can exist as temperature dependent precipitates with 12, 7, 6 and 1 mol water hydrates [8]. Epsomite ($MgSO_4{\cdot}7H_2O$), hexahydrite ($MgSO_4{\cdot}6H_2O$) and kieserite ($MgSO_4{\cdot}H_2O$) occur as natural minerals on earth [9]. Hydrates with 3 and 1.25 mole of water had been produced synthetically under several conditions [10]. The hydration states 2, 4 and 5 does not exist in an equilibrium with aqueous solution at no temperature (1 bar) [7], but they were found as efflorescence [9, 10]. Figure 1 shows the phase diagram of the system $MgSO_4$–H_2O in dependency of temperature and relative humidity.

Therefore calorimetric measurements were done in the system $MgSO_4$–H_2O. The aim of the work presented here is to discuss the differences between the kind of hydration products of two different starting $MgSO_4$ hydrates at a humidity below the DRH of $MgSO_4{\cdot}7H_2O$ (epsomite). The temperature of 30°C was chosen for this investigation because of the humidity-dependent coexistence of hexahydrite and epsomite (also Fig. 1) and a practical application at this temperature. The DRH of epsomite ($MgSO_4{\cdot}7H_2O$) at 30°C is approximately 90% RH. For this reason 85% RH was chosen as the condition for the hydration measurements, which is below the DRH.

Starting substances for the hydration were starkeyite also referred to as leonhardtite ($MgSO_4{\cdot}4H_2O$) and a hydrate mixture ($MgSO_4{\cdot}1.3H_2O$). Starkeyite was chosen as a phase with lower water content than epsomite or hexahydrite. Figure 1 is the result of investigations to the salt damage of building materials. For this reason the stability field of starkeyite is not shown. The used second hydrate is a summary composition and should symbolize technically relevant starting substance if dehydrating epsomite at a temperature of 130°C.

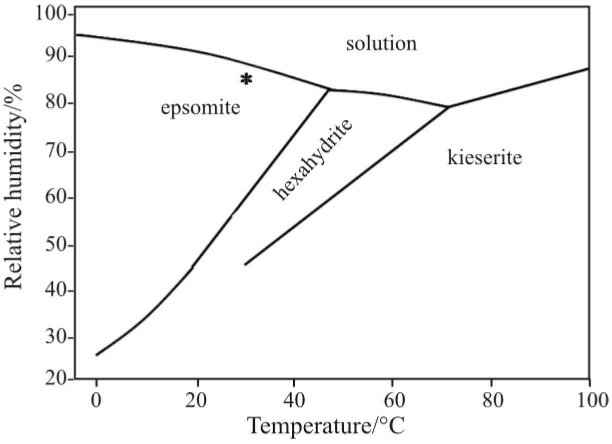

Fig. 1 Phase diagram of $MgSO_4$ hydrates according to [11]

Calculation of the expected heat of hydration

The released heat of hydration can be calculated by using the known standard enthalpies of formation. In the case of a relative humidity of 85% and 30°C the thermodynamic stable final product of the hydration is epsomite. Figure 2 illustrates the way of calculation for the heat of hydration forming epsomite.

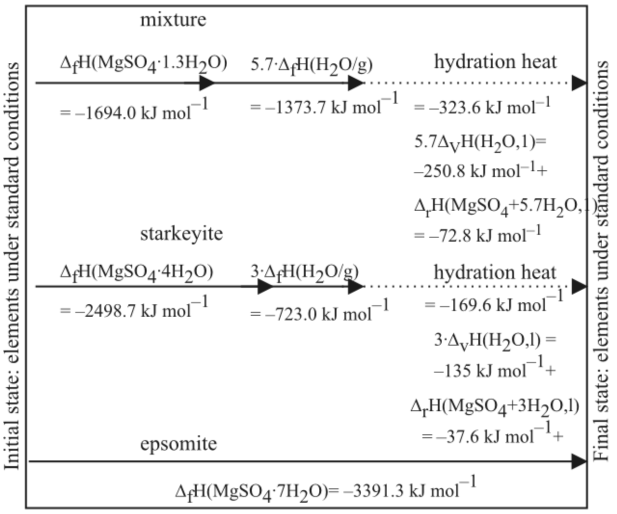

Fig. 2 Heat of hydration calculated for the formation of epsomite [12]

The heat of hydration is a result of the heat of vaporisation (Δ_vH) and the reaction heat (Δ_rH) of the bonding of the water. Basically the hydration heat is the difference of the standard enthalpy of the formation of epsomite (Δ_fH; final hydrate) and the sum of the standard enthalpy of the formation of the initial state (Δ_fH; starting hydrate) with that of the formation of gaseous water (Δ_fH; $H_2O(g)$). The calculated and following measured hydration heats are related to 1 mol of $MgSO_4$. Expected value for the hydration of the hydrate mixture ($MgSO_4{\cdot}1.3H_2O$) to epsomite is -323.6 kJ mol^{-1}. The adequate value if starting with starkeyite ($MgSO_4{\cdot}4H_2O$) is -169.6 kJ mol^{-1}. To bring the calculated thermodynamic data together with the kinetic mechanism of the hydration and the searching for possible interactions is of importance for the application of the storage material.

Experimental

Materials

The starting salt for the preparation of starkeyite and $MgSO_4{\cdot}1.3H_2O$ was $MgSO_4{\cdot}7H_2O$ (Merck; Emprove®; purity 99–100.5%). For equilibrium reason a pre-storage of the sulphate at 75% RH (over a satured NaCl-solution) was required, because the commercial salt consisted of a lower water content than 7 mole. The characterization of the prestored salt hydrate by TG and XRD showed an approximate water content of 7 mole, a crystallite size of 1–2 mm and no other phase than epsomite observed by XRD.

Starkeyite was prepared from this epsomite by using a drying chamber (40°C, 10% RH) according to the conditions described in [9]. A water content of 4 mol H_2O could be verified by TG. 100% $MgSO_4{\cdot}1.3H_2O$ could be quantified by using the XRD-pattern of Bauer [13] in the rietveld refinement. TG curves for the dehydration of epsomite and $MgSO_4{\cdot}1.3H_2O$ up to 400°C are shown in Fig. 3. The typical courses of thermal decomposition of magnesium sulphate hydrates are described by Paulik *et al.* [14] and Emons *et al.* [15].

$MgSO_4{\cdot}1.3H_2O$ is a summary mixture of different states of salt hydrate after drying epsomite at 130°C. The in situ preparation of the hydrate mixture and the measuring of its hydration heat was carried out successively in the C80 calorimeter (Setaram) coupled with the humidity controller Wetsys (Setaram). The program for preparation can be seen in Fig. 4. After placing epsomite in the experimental cell (condition 1) the salt was heated with 2 K min^{-1} up to 130°C with a dwell time of 2 h for a constant heat flow signal. The evaporating hydrate water was removed with dried air (5% RH at 30°C) with a flow rate of 50 mL min^{-1} out of the cell (condition 2). The dehydrated salt was cooled down at the same flow rate and keeping the moisture at 5% RH.

In parallel investigations the dehydrated salt hydrate was taken out of the cell very fast to characterize the starting state for the following measurement without considerable rehydration on air. Immediately the water content by TG and the phase composition (XRD) of this dehydrated epsomite was carried out. Several $MgSO_4$ hydrate phases with 1, 1.25 and 2 mole of water were detected by XRD. The overall water content of 1.3 mole was quantified by TG.

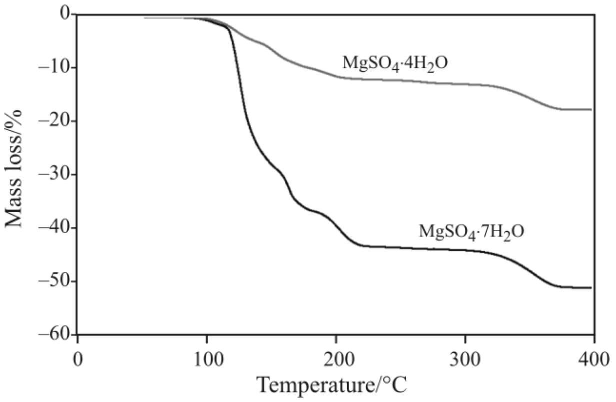

Fig. 3 TG curves for the dehydration of epsomite and $MgSO_4{\cdot}1.3H_2O$ in air

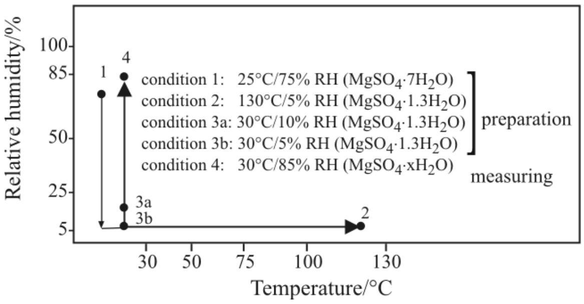

Fig. 4 Conditions for dehydration (preparing) and measuring the hydration heat in the calorimeter

Methods

The heat of hydration was measured in an open system in a circulation cell using the calorimeter C80. The flow rate of the humid air was 50 mL min^{-1} and the humidity during the hydration process was 85% RH. For measuring the heat of hydration of starkeyite the salt was placed in the experimental cell of the calorimeter. At a constant heat flow signal at 30°C and 10% RH (Fig. 4, condition 3a), the humidity was changed to 85% RH (condition 4, Fig. 4). $MgSO_4{\cdot}1.3H_2O$ was prepared in situ in the circulation cell. The measurement started at 30°C and 5% RH (condition 3b, Fig. 4). The total heat of hydration was determined by integration of the heat flow curves.

Powder X-ray diffraction (XRD) was used to characterize the starting and final phases of the hydrates. Data were collected on the Seiffert 3003 TT diffractometer (CuK_α; 4–70° 2θ). For the phase quantification rietveld refinement software Auto Quan® was used. Thermogravimetry (TG) was applied to study the water content of each hydrate phase, using a Setsys 16/18 device from Setaram. The hydrates were dehydrating completely with a heating rate of 10 K min^{-1} in air atmosphere, to calculate the total amount of water.

Results and discussion

The characteristic curves of the time dependence of the heat flow are shown in Fig. 5 for both starting $MgSO_4$ hydrates. The mixture $MgSO_4{\cdot}1.3H_2O$ reached a total heat of –257 kJ mol^{-1} whereas the starkeyite reached –169 kJ mol^{-1}.

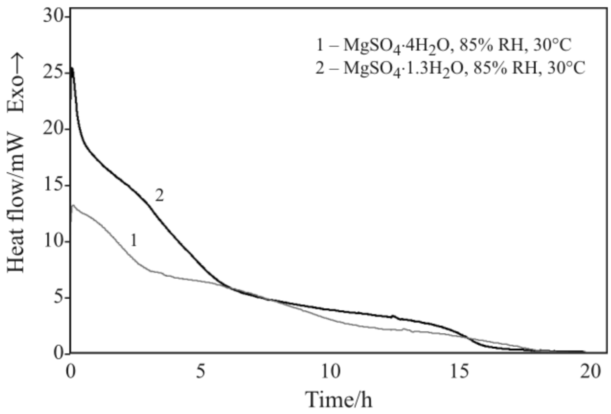

Fig. 5 Heat flow curves during the process of hydration

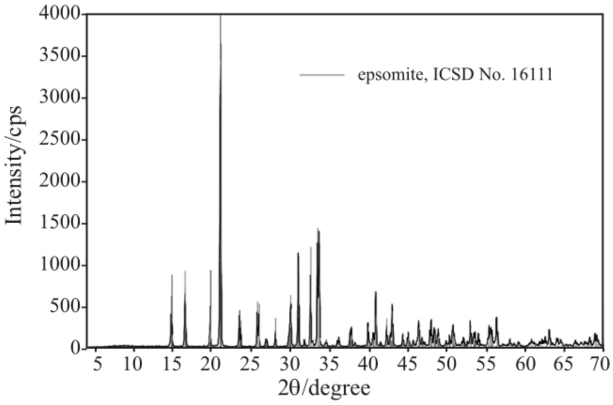

Fig. 6 XRD pattern of the product after the hydration of starkeyite

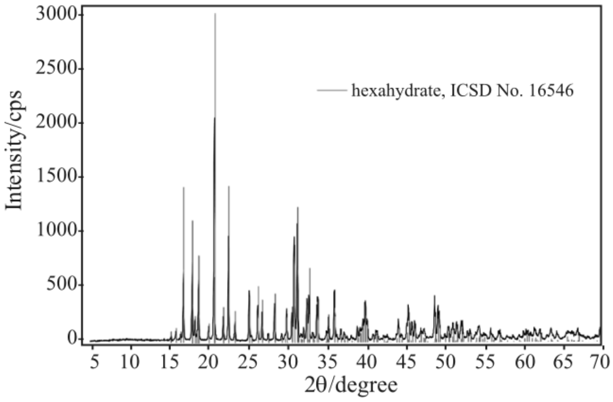

Fig. 7 XRD pattern of the product after the hydration of $MgSO_4 \cdot 1.3H_2O$

At the beginning the peak level of the $MgSO_4 \cdot 1.3H_2O$ is twice as much than that of the level of starkeyite. The reason for this behaviour is that the difference of the water vapour pressure between the humid air and the hydrate with lower content of water ($MgSO_4 \cdot 1.3H_2O$) is significantly higher than that of starkeyite. Consequently, the driving force for reduction of this difference is higher and hence more water vapour can be condensed per time unit. The flattening of the curve after about 5 h could be influenced by the filling level of the measurement cell and the crystallite size. An increasing of the crystallite sizes results in longer diffusion ways of the water molecules. Subsequently, the hydration rate decreases. At this moment detailed investigations of these effects are not the objectives of this work. However, in every case the total heats are about –257 and –169 kJ mol^{-1} (also Table 1).

Finally the measured total heat of the hydrate mixture of –257 kJ mol^{-1} is not in agreement with the calculated value of –323 kJ mol^{-1}. For this reason the products of both reactions were characterized by XRD. The XRD patterns of the final states of the hydration of starkeyite and the hydrate mixture ($MgSO_4 \cdot 1.3H_2O$) are shown in Figs 6 and 7. It can be seen that $MgSO_4 \cdot 1.3H_2O$ not reached the formation of the thermodynamic stable epsomite, as the starkeyite did, but reacted to hexahydrite ($MgSO_4 \cdot 6H_2O$). Also the water content of the hydration products was determined by thermogravimetry. A recalculation of the heat of hydration with the final product hexahydrite was done. A summary of the results of these investigations in comparison with the spread and the calculated values is given in Table 1.

The measured hydration heat of starkeyite at 85% RH (–169 kJ mol^{-1}) is equal to the calculated value for the formation of the thermodynamically stable final state of epsomite. This phase was corroborated by TG and XRD measurements. The final state of hydration of $MgSO_4 \cdot 1.3H_2O$ differ from that of starkeyite. The thermodynamically stable state at the conditions 30°C and 85% RH was not obtained. Hexahydrite was found as final hydration product. The measured hydration heat corresponds to the value of –260 kJ mol^{-1}, calculated from the standard formation enthalpy of –3089.4 kJ mol^{-1} for hexahydrite (also Fig. 2). Obviously kinetic blocking of the lower hydrated phases than starkeyite is the reason for forming an end product, which is not in equilibrium at these

Table 1 Summary and comparison of the measured (5 runs) and calculated results

Starting substance	Measured heat of hydration/kJ mol^{-1}	Calculated value of hydration/kJ mol^{-1}	Content of water of the final state (TG)/mol H_2O	Phase content of the final state (XRD)/mass%
$MgSO_4 \cdot 4H_2O$	–169±3	–170	7.16±0.06	100 (epsomite)
$MgSO_4 \cdot 1.3H_2O$	–257±5	–262	6.22±0.07	100 (hexahydrite)

conditions. Similar observations were described for the hydration of kieserite at analogue conditions [16].

The estimated water content of the hydration products is insignificant higher than the integer amount of the hydrate phases identified by XRD. This additional content of water (0.16 mole for epsomite and 0.22 for hexahydrite) as measured with TG could be caused by adsorptive bounded water in crystal cracks and on the surface of the crystals.

Conclusions

The results of the investigations demonstrate, that the final products of hydration under the condition DRH<RH (30°C) in the system $MgSO_4$–H_2O depend on the starting composition. Starkeyite reacted to the thermodynamic stable epsomite under releasing the calculated heat of -169 kJ mol^{-1}. The hydration product of the mixture $MgSO_4{\cdot}1.3H_2O$ was hexahydrite. This phase is not in the thermodynamic equilibrium at the chosen conditions.

In addition to the hydration heat in general the kinetics of the reactions are of great importance for the application of heat storage materials. The hydration process via solid-gas reaction needs a lot of time (more than 15 h) and the high DRH of epsomite (90% RH) is disadvantageous for the heat storage. If the thermodynamic final state with maximum heat release starting with hydrates with lower water contents than starkeyite should be reached, then it is necessary that the sulphate goes in to solution.

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References

1 E. A. Levitskij, Y. I. Aristov, M. M. Tokarev and V. N. Parmon, Sol. Energy Mat. Sol. Cells, 44 (1996) 219.
2 J. Jänchen, D. Ackermann, H. Stach and W. Brösicke, Sol. Energy, 76 (2004) 339.
3 M. Steiger and W. Dannecker, R. Snethlage, Ed., Jahresberichte Steinzerfall: Steinkonservierung, Ernst & Sohn, Berlin 1993, p. 123.
4 J. Pühringer, Int. Zeitschrift für Bauinstandsetzen und Baudenkmalpflege, 5 (2002) 515.
5 H. Stach, D. Ackermann, W. Brösicke, J. Jänchen and E. Weiler, Schlussbericht, Entwicklung und Charakterisierung von mikroporösen Festkörpern für die adsorptive Langzeitspeicherung von Niedertemperaturwärme, Förderkennzeichen 0329525C, BMWi, 2001, p. 79.
6 H. Stach, J. Mugele, J. Jänchen and E. Weiler, Adsorption, 11 (2005) 393.
7 L. G. Gordeeva, I. S. Glaznev and Y. I. Aristov, Russ. J. Phys. Chem., 77 (2003) 1715.
8 Gmelins Handbuch der Anorganischen Chemie, Syst. No. 27, Magnesium, Weinheim/Bergstraße, 1952, p. 217.
9 S. J. Chipera, D. T. Vaniman, D. L. Bish, J. W. Carey and W. C. Feldman, Lunar Planet. Sci. XXXVI (2005) Abstract #1497.
10 D. T. Vaniman, D. L. Bish, S. J. Chipera, C. I. Fialips, J. W. Carey and W. C. Feldman, Nature, 431 (2004) 663.
11 A. Juling, D. Kirchner, S. Brügerhoff, K. Linnow, M. Steiger, A. E. Jarad and G. Gülker, Proceedings of the 10th International Congress on Deterioration and Conservation of Stone, D. Kwiatkowski and R. Löfvendahl, Eds, ICOMOS, Stockholm 2004, Vol. 1, p. 190.
12 C. W. DeKock, United States Bureau of Mines, Information Circular 9081, 1986, pp. 39–44.
13 W. H. Bauer, Acta Cryst., 15 (1962) 815.
14 J. Paulik, F. Paulik and M. Arnold, Thermochim. Acta, 50 (1981) 105.
15 H.-H. Emons, G. Ziegenbalg, R. Naumann and F. Paulik, J. Therm. Anal. Cal., 36 (1990) 1265.
16 S. J. Chipera and D. T. Vaniman, Geochim. Cosmochim. Acta, 71 (2007) 246.

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