Materials for thermochemical storage: characterization of magnesium sulfate

V.M. van Essen[1*], H. A. Zondag[1], R. Schuitema[1], W.G.J. van Helden[1] and C.C.M. Rindt[2]

[1]Energy research Centre of the Netherlands ECN, P.O. Box 1, 1755 ZG Petten, The Netherlands

[2]Department of Mechanical Engineering, Eindhoven University of Technology (TU/e), 5600 MB Eindhoven, The Netherlands

[*] Corresponding Author, v.vanessen@ecn.nl

Abstract

Magnesium sulfate hepta hydrate ($MgSO_4.7H_2O$) was studied as possible thermochemical material for seasonal storage of solar heat. Both hydration and dehydration were investigated and it was found that the material was able to take up and release almost 10 times more energy than water of the same volume. The amount of water taken up and energy released by the material turned out to be strongly dependent on the water vapor pressure and temperature. Unfortunately, the material was not able to release all the stored heat under practical conditions. Despite this problem, valuable information on the dehydration and hydration behavior of $MgSO_4.7H_2O$ was acquired and the characterization procedure will also be used for future characterization of other salt hydrates for thermochemical materials.

Keywords: compact thermochemical seasonal heat storage, characterization, magnesium sulfate, salt hydrate

Introduction

Households in the Netherlands use about 15% of the total energy consumption for space heating and domestic hot water. The energy consumption in the built environment can be reduced by energy saving measures (improved insulation, heat recovery, etc.). A substantial part of the remaining energy 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: $C + \text{heat} \Leftrightarrow A + B$

During summer, the thermochemical material (TCM) dissociates under influence of solar heat into components A and B, which are stored separately. In the discharging mode, 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.

Interesting TCMs are cheap, non-toxic, non-corrosive, have sufficient energy storage density, and have reaction temperatures in the proper range. These requirements are fulfilled by a number of salt hydrates. A previous theoretical study [1] identified magnesium sulfate hepta hydrate ($MgSO_4.7H_2O$) as a promising material for long-term heat storage, by means of the following reaction:

$MgSO_4.7H_2O(s) + heat \Leftrightarrow MgSO_4(s) + 7H_2O(g)$

In this work, measurements on magnesium sulfate are presented that give information on the suitability of magnesium sulfate as thermochemical material for seasonal heat storage. Additionally, information is given on parameters important for the design of thermochemical seasonal heat storage using magnesium sulfate.

Dehydration of magnesium sulfate

In the literature, several intermediates have been identified during the dehydration of $MgSO_4.7H_2O$. However, the published results are at some points conflicting on which intermediates are formed [2-6]. The dominant natural occurring magnesium sulfates on earth are Epsomite ($MgSO_4.7H_2O$), Hexahydrate ($MgSO_4.6H_2O$) and Kieserite ($MgSO_4.H_2O$). Since it is not clear which other intermediates are formed, it was decided to measure the dehydration of $MgSO_4.7H_2O$ anew. The dehydration of $MgSO_4.7H_2O$ was studied by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA involves the measurement of the mass change as function of time and DSC involves the measurement of heat as function of time, in which both are subjected to a predefined temperature program. The experimental results indicated that dehydration of $MgSO_4.7H_2O$ proceeds in three discrete steps as illustrated in Figure 1:

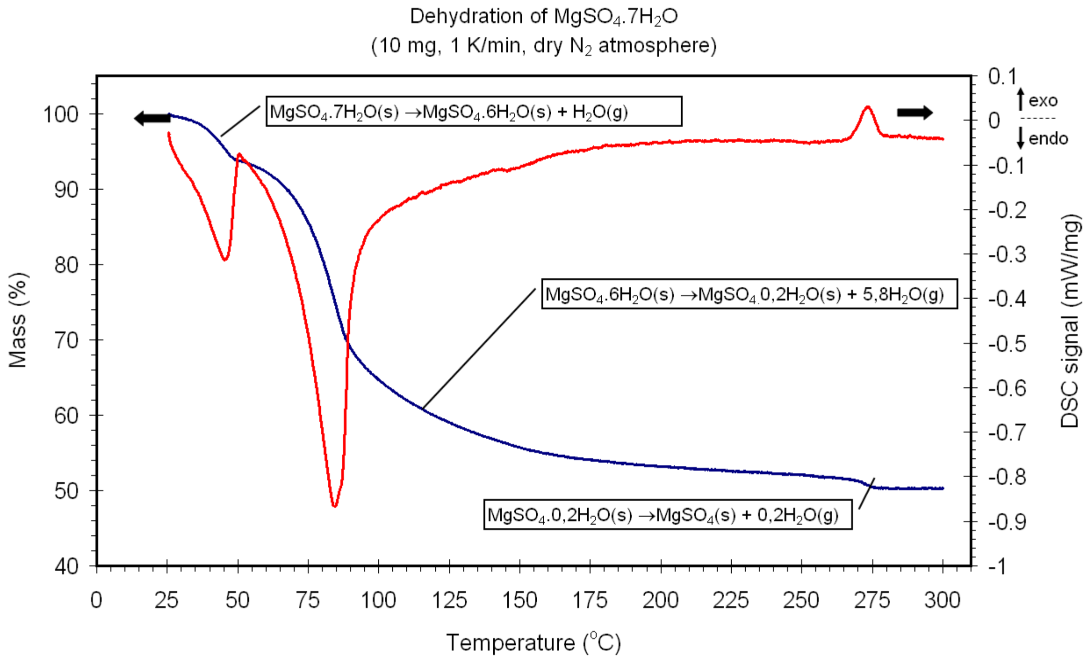

Fig. 1. A typical TGA-DSC curve for dehydration of $MgSO_4.7H_2O$. The blue line denotes TGA curve and the red line denotes the DSC curve.

The above Figure shows that the first dehydration reaction occurs at low temperature (<50°C) and involves the loss of one water molecule. The largest number of water molecules is dehydrated during the second reaction, which also allows storing the largest amount of energy of the three dehydration reactions: almost 10 times more energy compared to water (~2.3 GJ/m^3 compared to 0.25 GJ/m^3 for water in the temperature range 25-85°C). Additionally, the reaction occurs between approximately 60°C and 200°C: a temperature range which can be almost completely covered using a vacuum tube solar collector (T_{max}=150°C). For these two reasons the second dehydration reaction is most interesting for seasonal solar heat storage. Figure 1 also shows that the last water molecules are dehydrated at a high temperature (~275°C). In contrast to the first two dehydration reactions, the third dehydration reaction involves an exothermic process (indicated by the positive DSC signal). Ruiz et al [3] suggests that the final transition to $MgSO_4$ includes an exothermic reaction due to recrystallization of an amorphous precursor. This suggestion was further investigated by performing X-ray diffraction (XRD) experiments as shown in Figure 2:

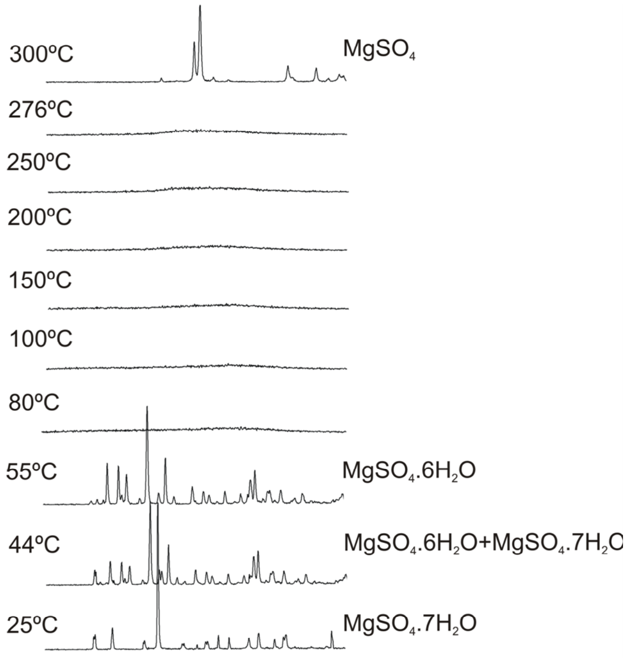

Fig. 2. XRD analysis of the dehydration of $MgSO_4.7H_2O$, where the sample was heated from 25°C to 300°C at 1 K/min.

When the temperature of the sample is increased from 25°C to 55°C, the XRD measurement shows that $MgSO_4.7H_2O$ is converted to $MgSO_4.6H_2O$. This result is in agreement with the results obtained by the TGA-DSC experiments (see also Figure 1). No peaks are observed in Figure 2 between 80°C and 276°C, indicating that an amorphous state is formed when $MgSO_4.6H_2O$ is dehydrated further. This observation is in agreement with the findings of Ruiz et al [3].

The XRD measurements shows that the material only recrystallizes at $T>276°C$. It should be noted that recrystallization only occurs when a small amount of water is present (0.2 water molecules per $MgSO_4$ molecule, see Figure 1) after which an exothermic reaction is observed. This could be explained by the hypothesis that below the critical water content of 0.2 water molecules per $MgSO_4$ molecule, a spontaneous exothermic crystallization occurs that expels the last water that is present in the material. The XRD measurements confirm the observations from TGA-DSC experiments that the material is completely dehydrated at 300°C.

Melting of the material

Several sources indicate that $MgSO_4.7H_2O$ melts at a temperature range of 50-52.5°C during dehydration (see for example Refs [2, 7]). Melting is a problem, since it reduces the bed porosity of the material, and consequently the vapor transport through the bed, which limits the ability of the material to take up water again. The TGA-DSC curve for heating rate at 1 K/min (Figure 1**)** shows that for $MgSO_4.7H_2O$ is completely converted to $MgSO_4.6H_2O$ at 50°C and therefore no melting occurs.

However, if the heating rate is increased, the dehydration peak is shifted to higher temperatures due to kinetics. Figure 3 illustrates the effect of the heating rate on the dehydration peak:

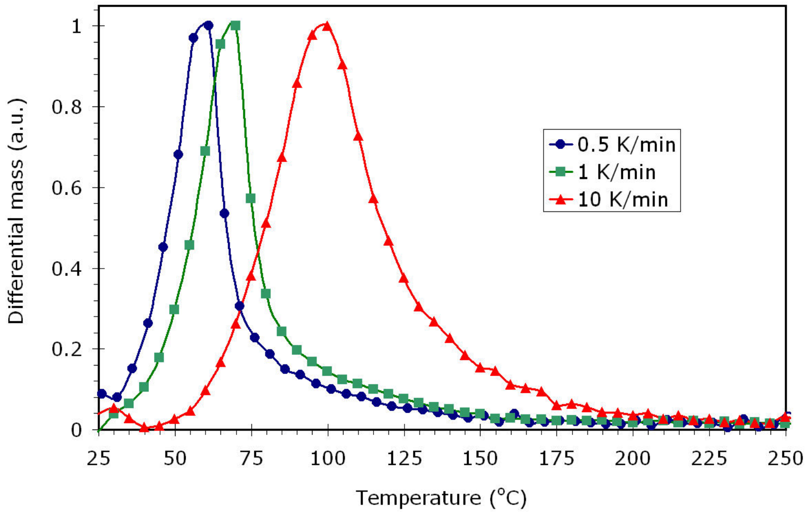

Fig. 3. Influence of heating rate on the dehydration

It means that for higher heating rates (> 1 K/min), $MgSO_4.7H_2O$ may still be present at 50-52.5°C and starts to melt. The melting of $MgSO_4.7H_2O$ was studied by a combined TGA-DSC measurement. This can be distinguished from dehydration since melting causes a heat uptake of the material without a change in mass as illustrated in Figure 4.

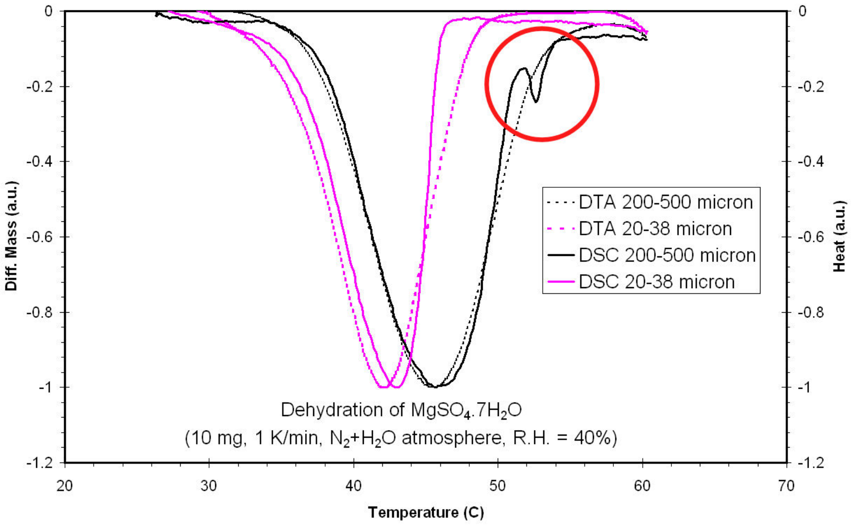

Fig. 4. Melting for large particles. The red circle denotes position of melting temperature of $MgSO_4.7H_2O$

The results of the combined TGA-DSC experiments indicated that melting of $MgSO_4.7H_2O$ typically occurred for high heating rates, large sample masses and/or large particles. The experiments also indicated that only melting of $MgSO_4.7H_2O$ occurs during dehydration of the material.

Hydration of the material

The hydration reaction involves a reaction between water vapor and the dehydrated material. This reaction determines the amount of power that can be delivered to a load in a practical system and the temperature level at which the power can be delivered.

The first hydration experiments [8] at ECN indicated that the material was able to take up water after dehydration. Furthermore it was discovered that the layer thickness is an important factor in hydration: thick layers reduce the hydration rate considerably, indicating that the water vapor transport through the layer is the limiting factor. The experiments also suggested that the water uptake was strongly reduced when the hydration was performed at elevated temperatures and reduced water vapor pressures. To further investigate this observation, it was decided to study the effect of water vapor pressure and temperature on the hydration process for constant layer thickness. The results of these experiments are shown Figure 5:

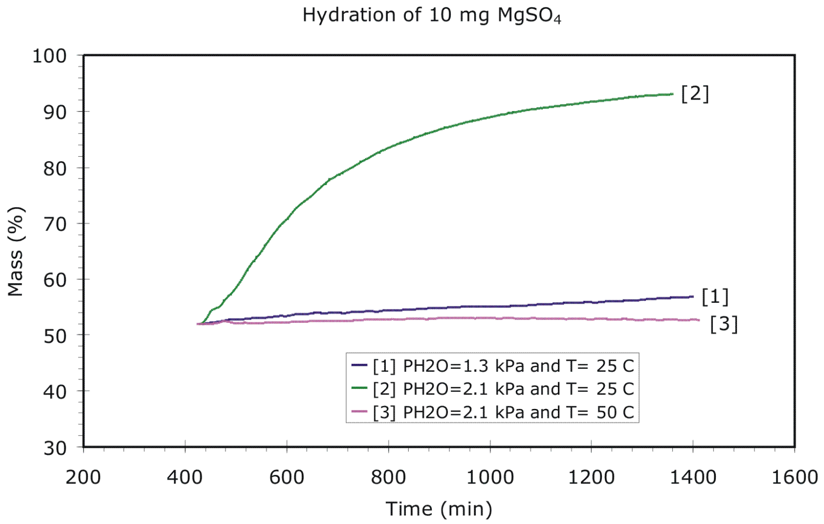

Fig. 5. The effect of water vapor pressure (PH2O) and temperature (T) on hydration

First, the hydration was studied at 25°C and for a water vapor pressure corresponding to the practical conditions (P_{H2O}=1.3 kPa), where a borehole at ground temperature provides the water vapor. In this case, the material slowly takes up a small amount of water (nr.1 in Figure 5). Increasing the water vapor pressure (P_{H2O}=2.1 kPa, nr.2 in Figure 5) at 25°C, results in a larger amount of water taken up by the material, although the hydration rate is still slow. Additional experiments reveal that this large uptake of water results in the release of ~91% of 2.3 GJ/m^3 (or 2.1 GJ/m^3) of the energy stored during dehydration. The results presented in Figure 5 show that the hydration strongly depends on the water vapor pressure and suggest that the water vapor pressure provided by the bore hole at ground temperature may not be sufficient to release all of the energy stored during dehydration.

The effect of temperature on hydration was also investigated. A typical low-temperature domestic heating system requires >40°C for space heating. For this reason it was decided to study the hydration at 50°C at a water vapor pressure of 2.1 kPa. The result (nr.3 in Figure 5) shows that, although the water vapor pressure is almost twice the value used in a practical system (P_{H2O}=1.3 kPa), the material is unable to take up water (and deliver heat) at 50°C. This means that the application of magnesium sulfate as thermochemical storage material is quite problematic.

Conclusions

The characterization of magnesium sulfate revealed that the material can be dehydrated using solar thermal collectors (<150°C). Almost 10 times more energy compared to water of the same volume can be stored using magnesium sulfate. The hydration experiments revealed that the material is also able to take up water while releasing a part of the stored energy. However, the amount of energy released during hydration depends on the temperature and the water vapor pressure. The experimental results indicate that the material cannot release all the stored heat under practical conditions, which severely limits the application of magnesium sulfate as thermochemical storage material.

Nevertheless, the characterization of magnesium sulfate gives us much needed insight in the dehydration and hydration behavior of a salt hydrate. Although the application of magnesium sulfate as TCM turns out to be quite problematic, it gives a blue-print on how to characterize salt hydrates for thermochemical heat storage. It is expected that other salt hydrates can perform better, and the characterization of magnesium sulfate is a reference point for future characterization of other salt hydrates for thermochemical seasonal heat storage.

Acknowledgement

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