CHARACTERISATION OF $MgSO_4$ FOR THERMOCHEMICAL STORAGE

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Advantages of thermochemical storage

Traditional heat storage techniques have a number of disadvantages for long-term heat storage, such as substantial heat loss and relatively low energy density (large volume). As an alternative, it is possible to store energy by means of chemical processes, making use of the reversible chemical reaction $A + B \Leftrightarrow C + heat$. Interesting reactants are low cost, 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. In a previous study (Visscher et al., 2004), magnesium sulfate has been identified as a potentially interesting storage material, by means of the reaction

$$MgSO_4(s) + 7H_2O(g) \Leftrightarrow MgSO_4x7H_2O(s) + 411kJ/mol\_MgSO_4$$

This material could be interesting for seasonal storage. During winter, when heat is needed for e.g. residential heating, the magnesium sulfate is hydrated, producing heat. During summer, the hydrate is dehydrated by heat from a solar collector, which can be regarded as charging of the material. Once the chemical reaction has taken place, the solar heat can be stored in this way for a long time period without losses.

A good characterisation of the magnesium sulfate hydrate is important for an optimal design of a thermochemical storage. In this paper, measurements are presented that give information on the suitability of magnesium sulfate as a material for seasonal heat storage, as well as give information on parameters that are important for the design of a thermochemical storage for solar heat based on magnesium sulfate.

Experimental results

Dehydration

In the literature, different accounts can be found on the dehydration of $MgSO_4x7H_2O$. The NBS database indicates that during the dehydration of $MgSO_4$, the material shows a number of stable states that are characterized by respectively 7, 6, 4, 2, 1 and 0 H_2O, while the Ullmann encyclopedia gives the stepwise dehydration as 7, 6, 4, 3, 2, 5/4, 1 and 0 water. Ruiz (2007) indicates that after a dehydration step from 7 to 6 water, both crystalline states, an amorphous state occurs in which the material is dehydrated until crystalline anhydrous $MgSO_4$ is formed. Because of the different accounts in the literature, it was decided to measure the dehydration of $MgSO_4$ anew. To characterize the dehydration of $MgSO_4x7H_2O$, measurements have been carried out by means of TGA (measurement of the mass change as function of time, subject to a predefined heating program) and DSC (similar as TGA, but, instead of mass, the outgoing power is measured over time). The results are shown in Figure 1.

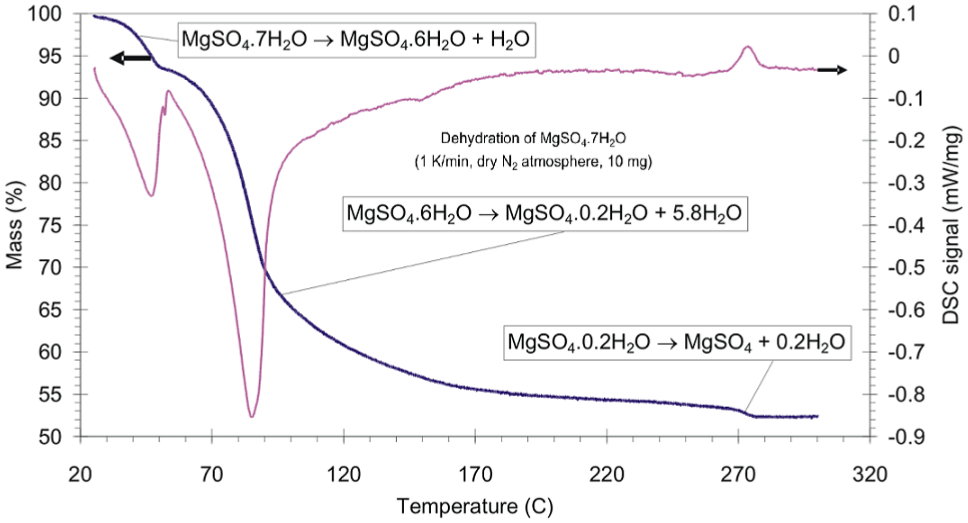

Figure 1: Dehydration of $MgSO_4$x7H2O.

The presented results largely show the same trend as indicated by Ruiz. The figure shows that almost all dehydration occurs at a temperature below 150 °C, which is a temperature that can be delivered by solar collectors. To understand better the changes in the material that occur during dehydration, XRD measurements were carried out, as shown in Figure 2. The fact that no peaks can be observed at temperatures between 80 °C and 276 °C indicate that an amorphous state is formed if the $MgSO_4x6H_2O$ state is dehydrated further, that only recrystallizes at temperatures above 276 °C. It should be indicated, however, that the recrystallization occurs when there is only 0.2 molecules of water per molecule $MgSO_4$ left in the material, after which an exothermic change going from 0.2 to 0 water can be observed (see Figure 1). This could be explained by the hypothesis that below a critical water content in the amorphous $MgSO_4xnH_2O$ (0.2 water), spontaneous exothermic crystallization occurs that drives out the last water in the material.

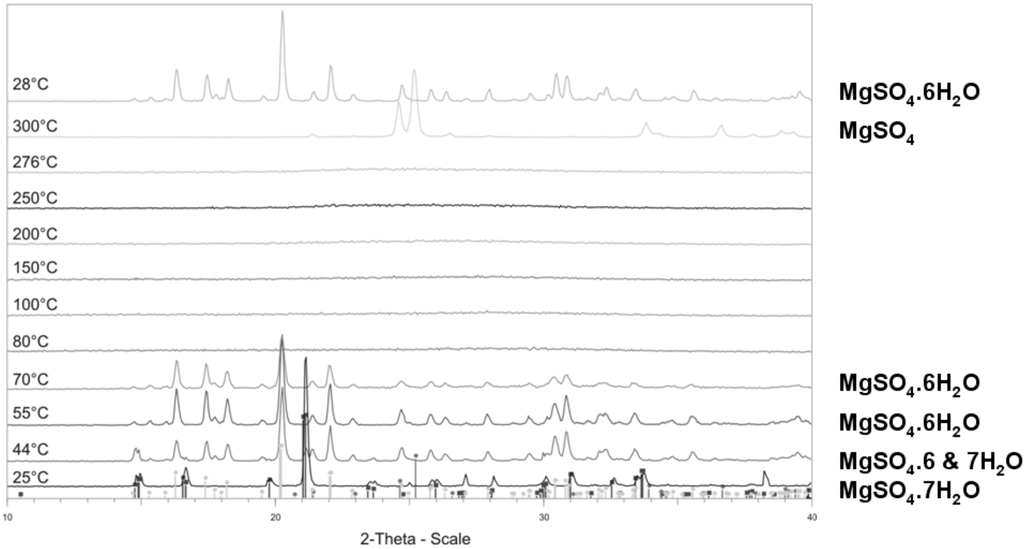

Figure 2: XRD measurements of the dehydration of $MgSO_4$x7H2O

When carrying out such measurements, one has to be aware of the effect of heating rate. Since a thorough dehydration of the sample requires some time, if the heating rate is set to a large value, this will also shift the measured dehydration peaks to higher temperatures, as shown in Figure 3.

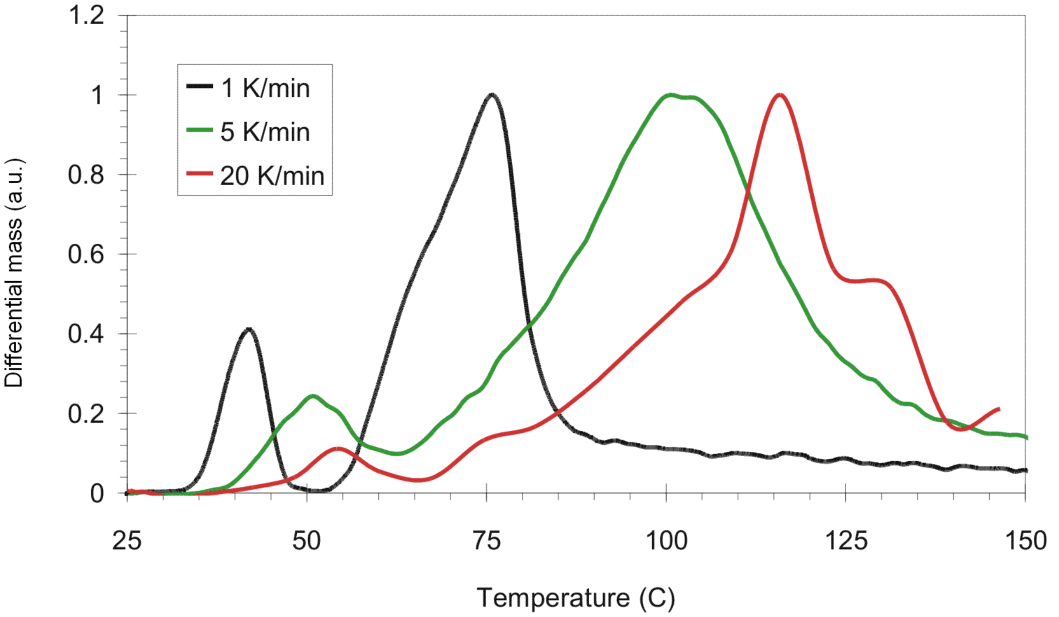

Figure 3: Effect of heating rate on measured dehydration peaks.

Melting

During dehydration, care should be taken that no melting occurs in the material. The melting of the $MgSO_4x7H_2O$ state occurs at a temperature of 48-52 °C. If the dehydration is slow relative to the heating rate, the 7-hydrate form may still be present at this temperature. Therefore, typically melting may occur for large heating rates, large samples and/or large particles. The effect can clearly be observed if the DSC measurements and the TGA measurements are compared, since melting causes a heat uptake of the material at roughly 52 °C, but not a change in mass, as would be the case for dehydration.

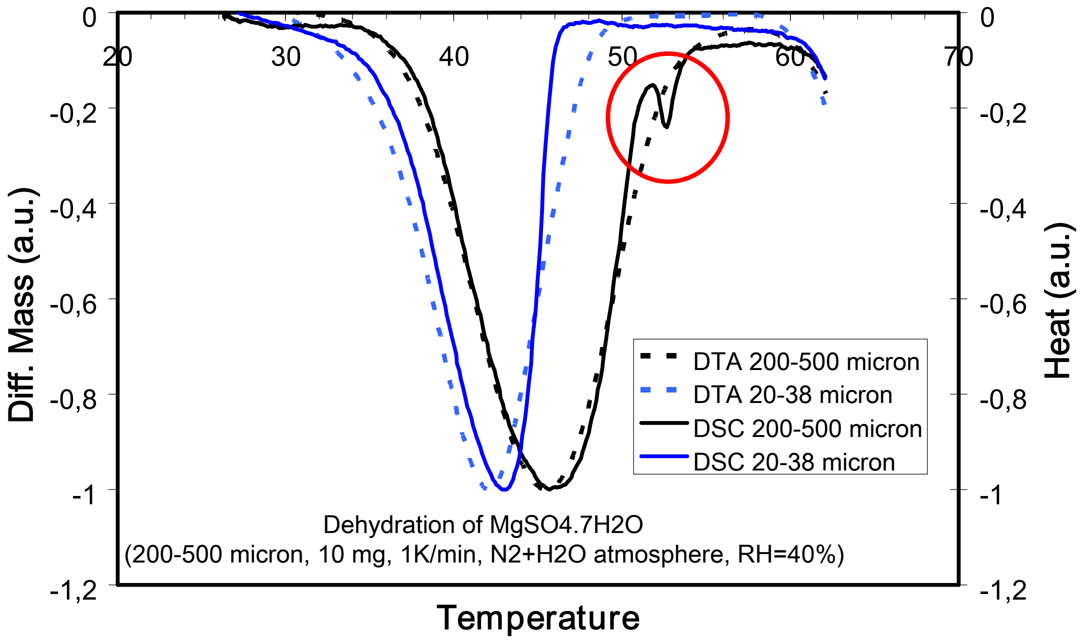

Figure 4: Melting for large particles

Melting is a problem because it reduces the bed porosity of the material, and thereby the vapour transport through the bed, limiting the ability of the material to take up water again.

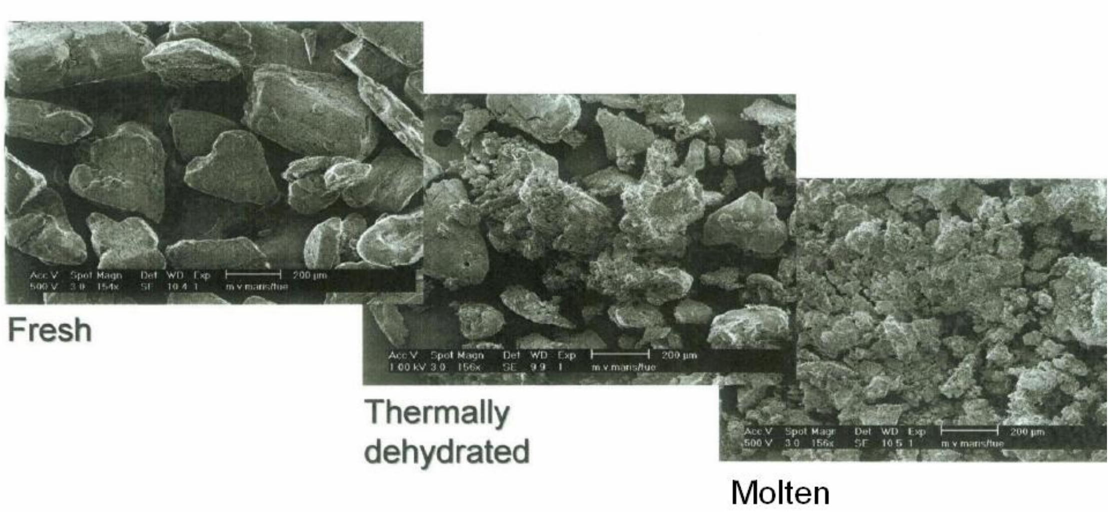

Figure 5: Effect of melting and dehydration on particle structure

Hydration

The hydration reaction is crucial in the performance of a thermochemical storage material, since this determines the specific power that can be delivered to the load and the temperature level at which this power can be delivered.

First of all, it can be observed that the material can be rehydrated at ambient conditions. It appears that the influence of particle size is very limited, but that layer thickness is an important factor in the hydration speed, as can be seen in Figure 6 and Figure 7. This may indicate that the vapour transfer though the layer is a limiting factor in the hydration process.

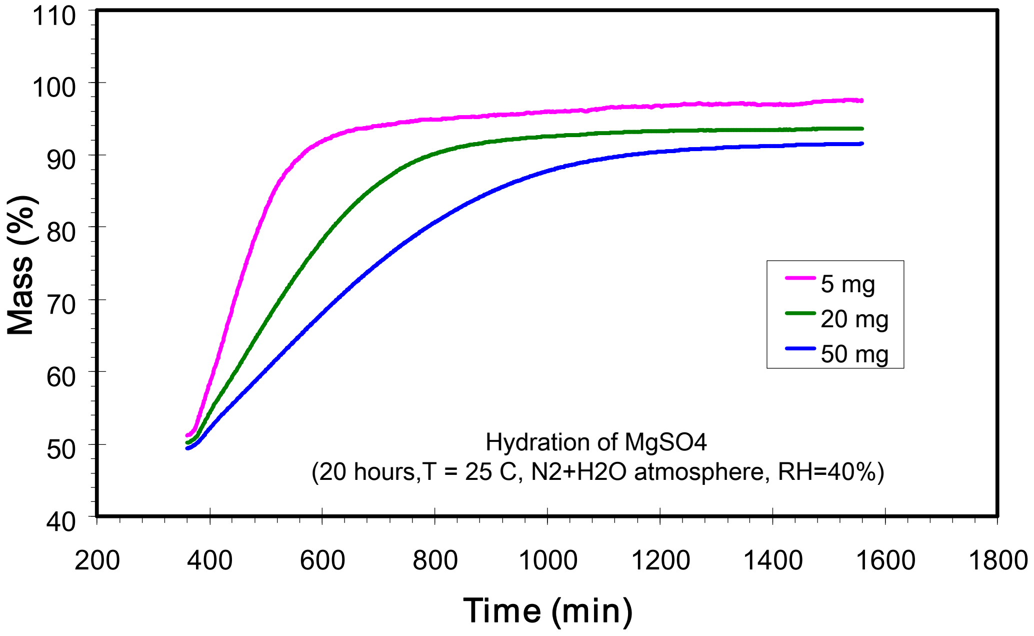

Figure 6: Effect of layer thickness on hydration speed (20 mg corresponds to a layer thickness of roughly 1.5 mm).

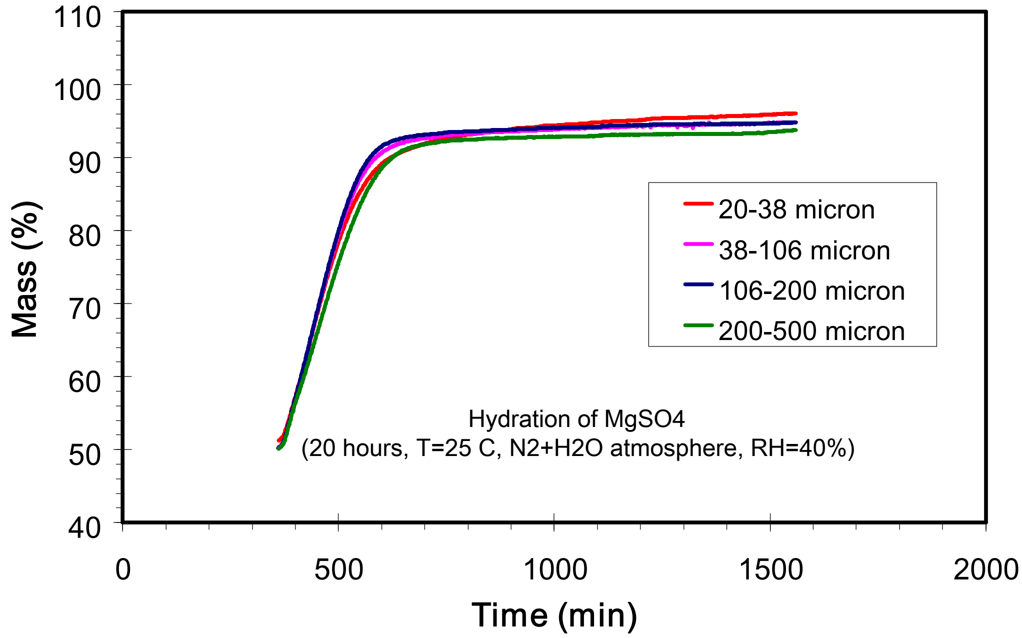

Figure 7: Effect of particle size on hydration.

Cyclability and effect of temperature on hydration

Next, a thick layer of material has been subject to repeated hydration and dehydration in an oven. It was found that the cycling of the material is quite good, as can be seen in Figure 8, but that the reaction rate was rather slow (which corresponds to the slower hydration for thicker layers as shown previously in Figure 6). The low reaction speed indicates the importance of optimizing the vapor transport through the material in the reactor design.

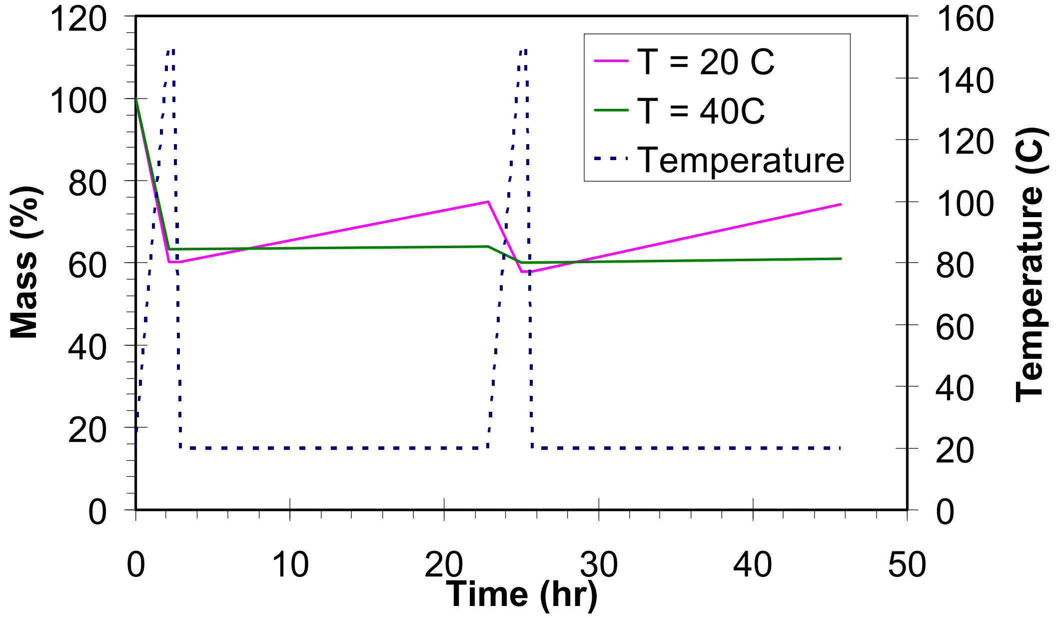

Figure 8: Cycling of $MgSO_4$ at different temperatures.

This figure also shows the effect of temperature on the hydration of $MgSO_4$. This is a very important characteristic because this determines whether the TCM material can deliver heat at the temperature level required for the heating system. It was found that an increase in the temperature level quickly decreased the rehydration speed, as can clearly be seen in Figure 8. The figure shows that at 40 °C, there is hardly any uptake of water anymore. In the interpretation of this figure, one should realise that in ambient air heated to 40 °C, the relative humidity is very low. However, given the fact that the vaporisation heat in a real system will be provided by a borehole heat exchanger at ground temperature, the very low vapour pressure is unfortunately a realistic condition that has to be coped with.

Presently, research is ongoing whether this can be improved. However, if this is not possible, this may be a severe limitation for the application of $MgSO_4$ as a thermochemical storage material, because typical low-temperature domestic heating systems require roughly 40 °C for space heating, and if this temperature cannot be reached, this will be a problem for application of the material.

Conclusions

It was found that $MgSO_4$ can be dehydrated at temperatures at temperatures below 150 °C, that can well be reached by solar thermal collectors. Also, the material shows good cycling behaviour. However, a severe problem may occur if the hydration rate is strongly decreased at higher temperatures, as seems presently to be the case, and it is expected that other TCM materials can be found that will have better characteristics.

References

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