Thermochemical storage - first simulations and experiments

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Introduction

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 at ECN (Visscher et al., 2004), magnesium sulphate has been identified as a particularly suitable storage material, by means of the reaction

$$MgSO_{4(s)} + 7H_2O_{(g)} \Leftrightarrow MgSO_4 \bullet 7H_2O_{(s)} + 411kJ/mol\_MgSO_4$$

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

This paper summarizes the experimental and numerical results found in the MSc graduation work of Ilse van de Voort, second author to this paper. The work on thermo chemical heat storage is part of the long-term work at ECN on compact storage technologies.

Experimental work

Simulations and experimental work have been carried out in order to characterize the dehydration reaction of $MgSO_4 \times 7H_2O$. The experimental work has focused on thermogravimetric (TG) measurements (measurement of mass as a function of temperature, showing the reduction in mass if the sample is dehydrated). In Figure 1, the mass is presented as a function of temperature. The figure clearly shows a decrease in mass of roughly 48%, which almost corresponds to full dehydration of the $MgSO_4 \times 7H_2O$ (corresponding to a 51% decrease in mass). The difference can be explained by the fact that at the start of the measurements, the sample may already have lost some water, so that actually a sample consisting of a mixture of $MgSO_4 \times 7H_2O$ and $MgSO_4 \times 6H_2O$ was dehydrated during the measurement. In addition, figure 1 also shows the differential mass (mass change), which shows more clearly at what temperature the largest loss of mass occurs.

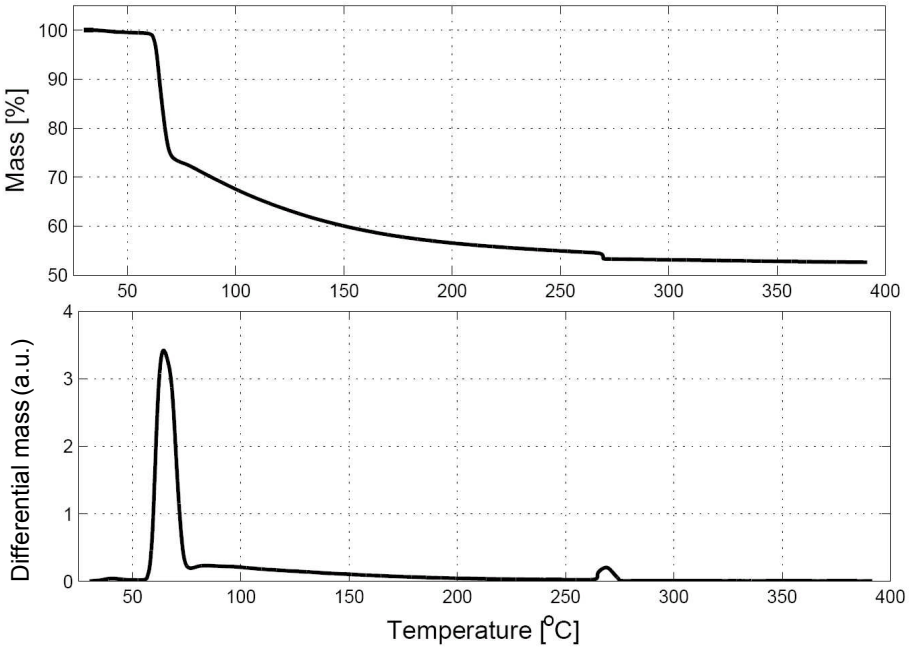


Figure 1: TG measurement results on $MgSO_4x7H_2O$

Now in the measurements, a number of parameters could be varied. The results illustrate the significant effects of heating rate, air moisture, particle size and layer thickness on the dehydration, as can be seen in Figure 2 and Figure 3.

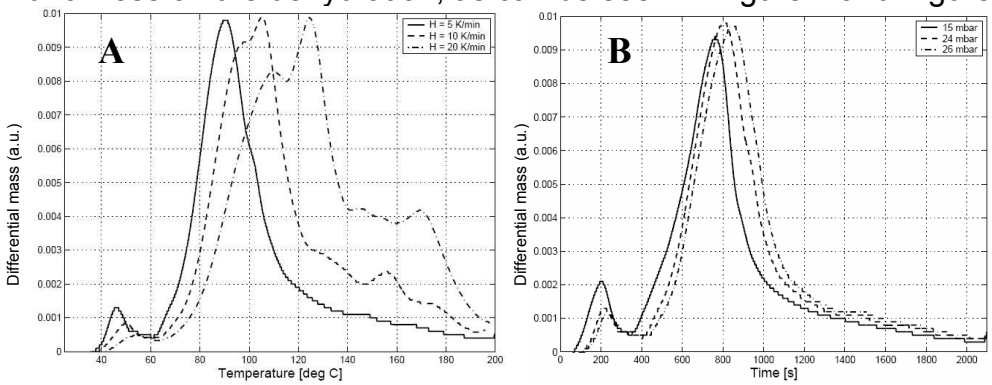


Figure 2: Effect of (a) heating rate and (b) air moisture on TG-measurements

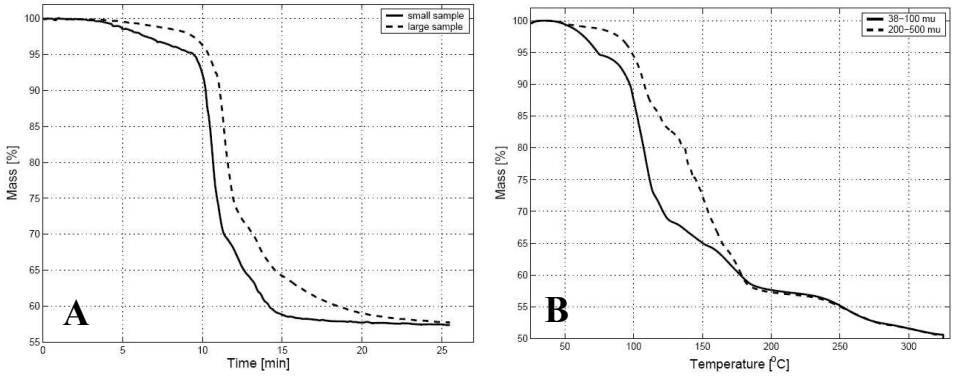


Figure 3: Effect of (a) layer thickness and (b) particle size on TG measurement results.

Figure 2 shows that the reaction shifts to significantly higher temperatures at large heating rates and/or water vapor pressures (the heating rate in figure 2b is 5 K/min, corresponding to a temperature range of 25-200 ºC). In addition, thicker layers and larger particles also shift the reaction temperature to higher values, indicating that heat- or vapor transport is limiting the reaction rate.

Up till now, only the dehydration reaction has been discussed. However, when using the material for heating purposes, it is the hydration reaction that determines the power that can be delivered. Some preliminary measurements on the hydration have been carried out. In Figure 4a, from 0-175 minutes the sample is heated at a constant rate of 1 K/min from 25 to 200 ºC, from 175-350 minutes the sample is cooled at the same rate and finally, during 350-550 minutes, the sample is kept at a constant temperature of 25 ºC. The moisture content of the airflow at ambient temperature and ambient pressure is set to 80%. The hydration reaction is observed to take place at relatively low temperatures and to be rather slow compared to the dehydration reaction, as indicated in Figure 4a. Figure 4b shows the result of thermal cycling at 30 K/min between 45 ºC and 150 ºC. The figure shows that under these conditions the cyclability of the material seems problematic, since the water uptake decreased significantly over a few cycles. Possibly, this may be related to partial melt of the material during the fast heating in the cycling test. Further characterization work on hydration and cycling is ongoing.

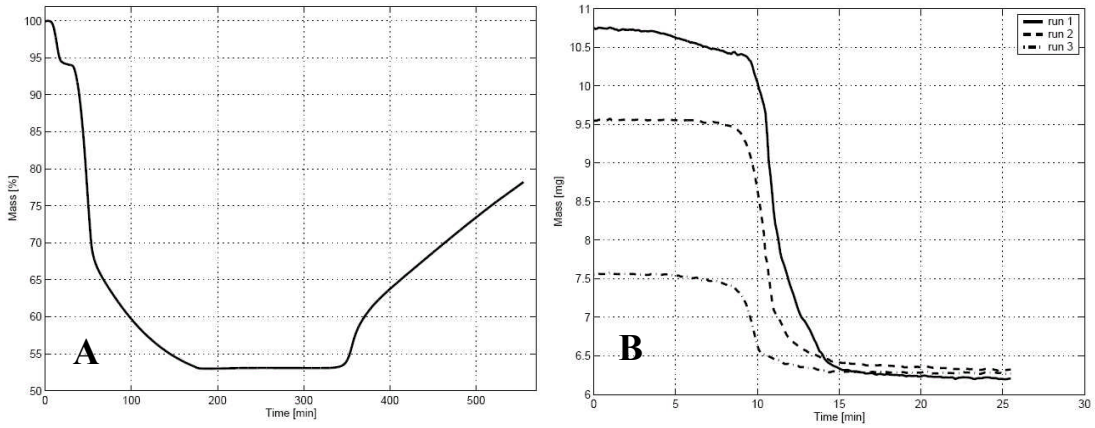
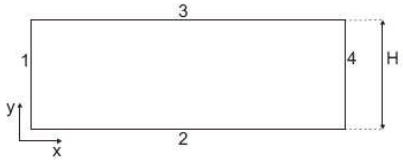


Figure 4: (a) Dehydration-hydration TG measurement (b) Thermal Cycling TG experiment.

Simulation work

A 2D finite element model is built in COMSOL Multiphysics. A porous layer of hydrated magnesium sulfate is considered as a homogeneous continuum and the heat and mass transport through this layer are calculated.



	B1	B2	B3	B4
Heat	$\bar{q} \cdot \bar{n} = 0$	$T_{prescribed}$	$-\lambda \nabla T \cdot \bar{n} = 0$ $\bar{q} \cdot \bar{n} = \rho c_p T \bar{v} \cdot \bar{n}$	$\bar{q} \cdot \bar{n} = 0$
Mass	$N_i \cdot \bar{n} = 0$	$N_i \cdot \bar{n} = 0$	$N_i \cdot \bar{n} = c_i \bar{v} \cdot \bar{n}$	$N_i \cdot \bar{n} = 0$

Figure 5: Model boundary conditions

The chemical reaction rate is described by the Arrhenius relation, the constants of which were determined experimentally. From an analysis of the effect of heating rate on mass change, an activation energy of 55 kJ/mol was found, together with a frequency factor of 1.67×10^5 Hz. Other model input parameters, such as material constants, are obtained either from literature or from experiments. The model has been validated by a comparison between experimental and numerical results for some base case problems, as shown in Figure 6.

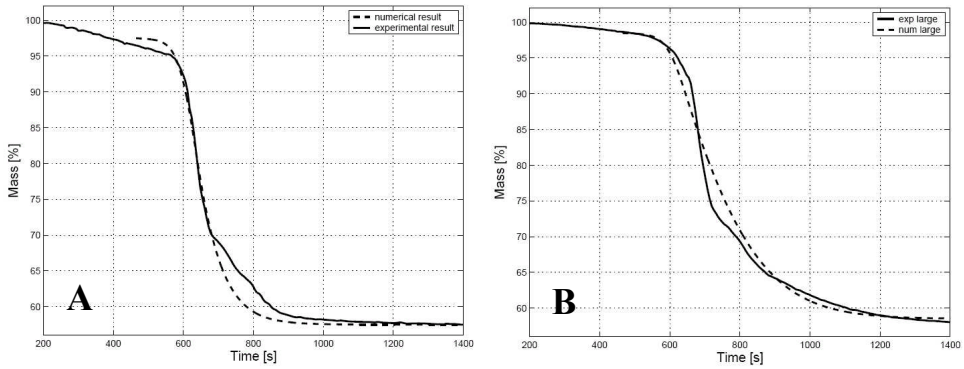


Figure 6: Comparison of experimental and modeling results (a) 11 mg sample (b) 38 mg sample

The simulation results show fairly good correspondence to the measurements. However, it appears than the single value for the Arrhenius activation energy used in the model does not fully capture the dynamics of the process. This is also found in the literature. Ruiz-Agudo (2007) distinguishes in the dehydration the following steps: (1) $MgSO_4 \times 7H_2O$, (2) $MgSO_4 \times 6H_2O$, (3) amorphous hydrate, (4) anhydrous $MgSO_4$. He indicates that the activation energy increases continuously (and not stepwise) at low moisture fractions. The model shows the distribution of the different phases in a layer of material as a function of temperature (Figure 7).

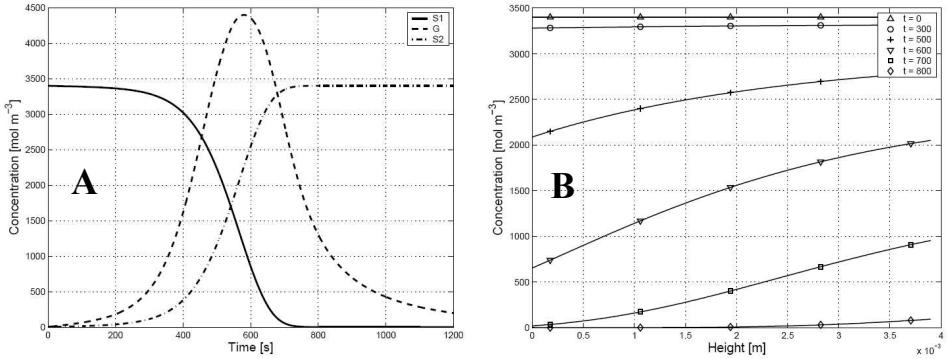


Figure 7: (a) Concentration variation over a reaction step (solid1→solid2, the gas is continuously removed at the upper domain boundary), (b) concentration of solid1 over the domain height as a function of time. T ranges from 20 to 200 ºC, heating rate 10 K/min.

Conclusions

TG measurements on $MgSO_4 \times 7H_2O$ show effective dehydration. The effects of heating rate, particle size and layer thickness are substantial, indicating that heat- or vapor transport are limiting the reaction rate. Hydration measurements indicate that the hydration characteristics and cycling may be problematic and should be examined more closely, which will be part of the next phase of the project. Also the numerical scheme showed good results, but may be improved further by allowing for the activation energy as a function of the moisture content.

References

(1) Voort, I.M. van de (2007), Characterization of a thermochemical storage material, MSc report EUT.

(2) Ruiz-Agudo, E., Martin-Ramos, J.D., Rodriguez-Navarro, C. (2007), Mechanism and kinetics of dehydration of epsomite crystals formed in the presence of organic additives Journal of Physical Chemistry B, Vol.111, pp 41-52.