Materials for thermochemical storage: characterization of salt hydrates

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Introduction

In the Netherlands a large part of the domestic primary energy consumption (~65%) is used for space heating and domestic hot water preparation (Opstelten et al, 2007). 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 during the summer can be completely covered 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 requires a large water tank (>25-50 m^3) that is often too large to be placed inside a building. A more compact way of storing heat is by means of thermochemical materials (TCM). The theoretical energy densities of these TCMs are several times larger than water. The basic reaction process for thermal energy storage using TCMs is:

$$\text{C (solid)} + \text{Q (heat)} \Leftrightarrow \text{A (liquid/gas)} + \text{B (solid)}$$

During the summer, the thermochemical material (solid C) separates into the liquid or gas A and the solid B by adding heat from a solar collector. Materials A and B can be stored separately until a later time. In winter, A and B are mixed to start the reverse reaction to release the stored solar heat. No reactions occur as long as the two components (A and B) are stored separately, which means that thermochemical storage can be used for loss-free storage and transportation of heat. This is particularly advantageous when TCMs are used for long-term heat storage.

Potential candidate materials

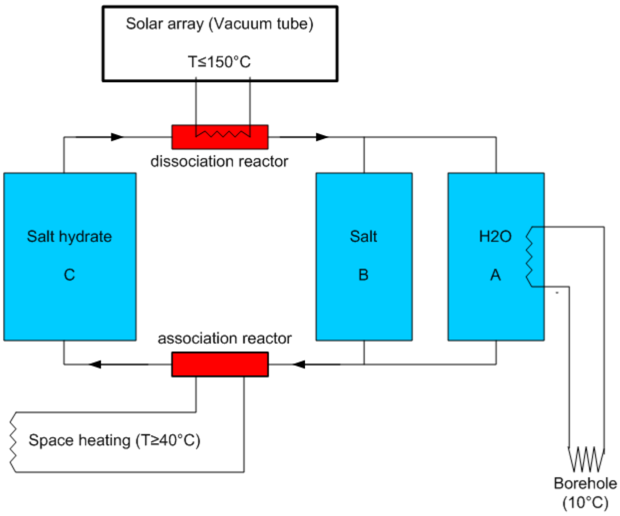
Interesting TCMs are cheap, non-toxic, non-corrosive, have sufficient energy storage density and have reaction temperatures in the proper range. These requirements are fulfilled by a large number of salt hydrates by means of the following reaction:

$$\text{Salt.}nH_2O(s) + \text{heat} \Leftrightarrow \text{Salt}(s) + nH_2O(g)$$

A theoretical study at ECN identified the following four salt hydrates as most promising materials: $MgSO_4.7H_2O$, $Al_2SO_4.18H_2O$, $MgCl_2.6H_2O$ and $CaCl_2.2H_2O$. These four salt hydrates are currently investigated on their potential as TCM for compact seasonal heat storage in the built environment.

TCM heat storage system

A salt hydrate has to be able to store and release solar heat under practical conditions. These conditions are determined by the heat storage system. The TCM heat storage system is shown in Figure 1 (Zondag et al, 2009):



$$\text{Salt(s)} + n\text{H}_2\text{O(g)} \rightleftharpoons \text{Salt.}n\text{H}_2\text{O(s)} + \text{Q(heat)}$$

Figure 1: Schematic overview of TCM heat storage system

The TCM storage consists of 3 vessels: vessel C containing the hydrated salt, vessel B containing the dehydrated salt and vessel A containing the water vapor (in condensed form). On charging the storage, the hydrated salt from container C is fed to a dissociation reactor that is heated by a vacuum collector array (vacuum tube). The hot dehydrated salt is fed to vessel B and the water vapor to vessel A, where it condenses. On discharging the storage, water vapor is produced by evaporating water in vessel A by means of heat from a borehole at 10°C. Both the water vapor and the salt are separately transported to the association reactor. Inside the reactor the dry salt react with water vapor to form the original salt hydrate while releasing the stored solar heat. This heat is used for space heating, for example for under floor heating, which normally operates at temperatures T≥40°C. It means that the material should be able to hydrate and release heat at these temperatures.

Experimental facilities

The potential of salt hydrates to store and release heat in the TCM heat storage system is investigated on a milligram to gram level. The main techniques used for characterization of salt hydrates are discussed in this section.

For example, an important technique that is used is TG-DSC. This technique operates on a milligram level and combines two thermal analysis techniques: differential scanning calorimetry (DSC) and thermo gravimetric analysis (TG). TG involves the measurement of the mass change as function of temperature or time and DSC involves the measurement of heat (enthalpy) changes as function of temperature or time, in which both are subjected to a predefined temperature program. The main application of TG-DSC is to identify steps in dehydration and hydration processes, determination of enthalpy of transition and identification of melting of a material. An typical example of a TG-DSC curve is shown in Figure 2:

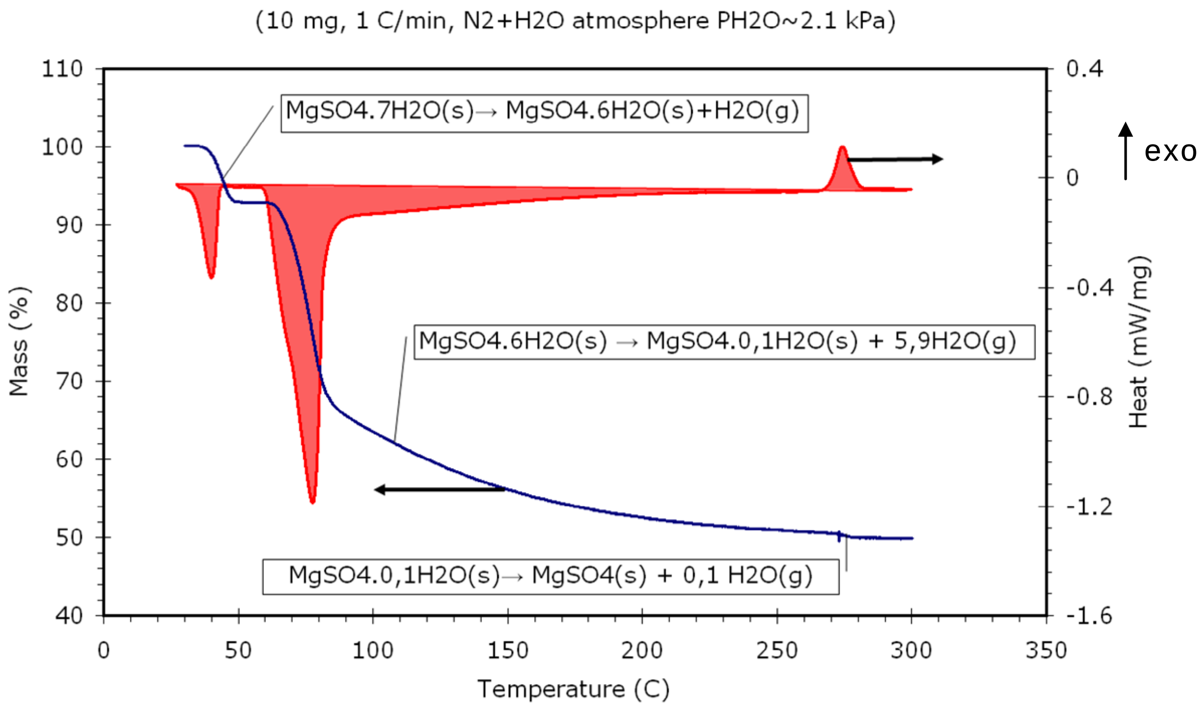


Figure 2: A typical TG-DSC curve for dehydration of $MgSO_4.7H_2O$. A sample of 10 mg is heated up from 25°C to 300°C with 1°C/min. During the experiments a N_2+H_2O gas mixture was used with PH2O~2.1 kPa. The blue line denotes TG curve and the red line denotes the DSC curve.

Water is expelled when a salt hydrate is heated up, which results in a mass change of the sample. The TG curve in Figure 2 shows three distinct mass changes indicating that water is expelled during mass change. Additionally**,** Figure 2 shows that each mass change is associated with a change in DSC signal indicating that heat is stored (endothermic, negative DSC signal) or released (exothermic, positive DSC signal) during each mass change. Based on the TG-DSC curve shown in Figure 2, it was possible to identify the three dehydration reactions and the enthalpy of each reaction that occurs when $MgSO_4.7H_2O$ was heated up (van Essen, 2009).
A scanning electron microscope (SEM) is used to investigate the effect of hydration and dehydration on a grain level. Figure 3 shows SEM images before and after dehydration of $MgSO_4.7H_2O$ particles:

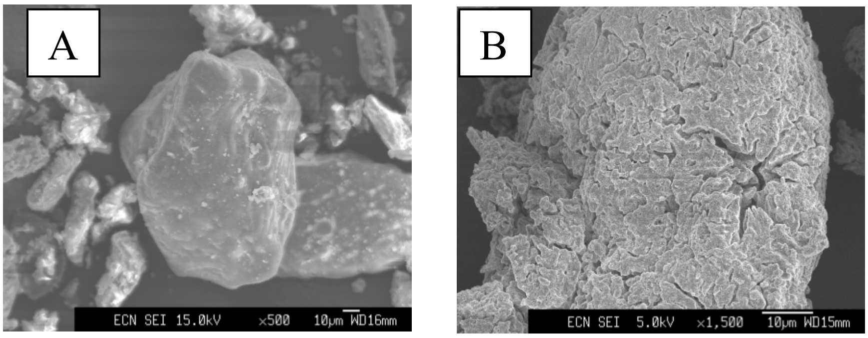


Figure 3: SEM images of magnesium sulfate particles (38-106 μm): A; before dehydration (15 kV, x500 magnification), B; after dehydration (5 kV, x1500 magnification).
As can be seen from the above Figure, the effect of dehydration is that cracks and pores are formed. This could be problematic for a future TCM reactor. For example, when a fluidized

bed is used, the dehydrated particles could easily break forming smaller particles that could flow out of the reactor before being (de)hydrated.

To investigate the dehydration and hydration behavior of salt hydrates on a gram level, a fixed bed reactor is used as shown below.

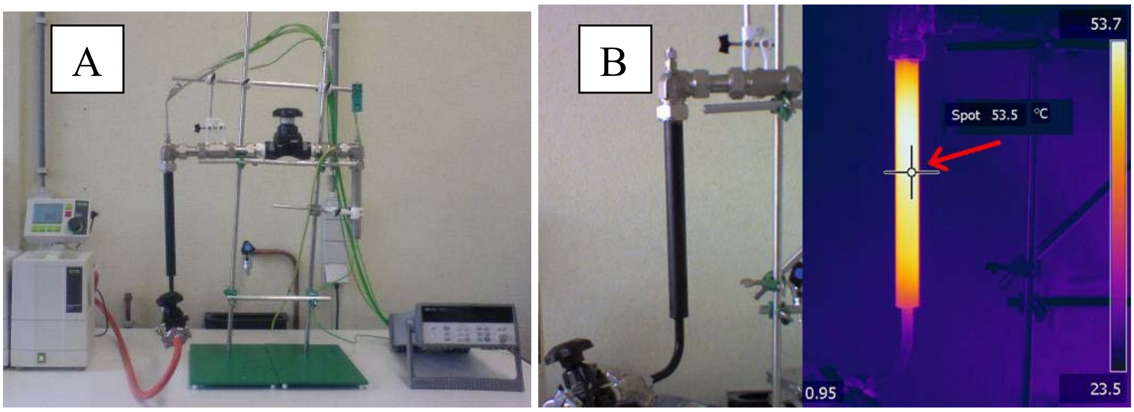


Figure 4: Experimental Set-up (a) set-up, (b) close-up of reactor vessel (normal photograph and infrared photograph showing the reaction temperature for hydration of zeolite)

Through the center of the fixed bed (in the black tube, right side in Figure 4A), a vapor channel consisting of a tubular metal mesh (diameter 1 cm) is placed inside the reactor to facilitate the hydration. In Figure 4B, an infrared photograph is presented showing the effect of hydration on the vessel temperature (in this photograph the temperature effect of the hydration of zeolite is shown). This setup is currently used for investigating the hydration and dehydration behavior of salt hydrates.

Results

The four selected salt hydrates ($MgSO_4.7H_2O$, $Al_2(SO_4)_3.18H_2O$, $CaCl_2.2H_2O$ and $MgCl_2.6H_2O$) are currently investigated on their potential as TCM for compact seasonal heat storage. The results so far indicate that all four salt hydrates can be dehydrated at 150°C, a temperature that can be reached by a medium temperature collector (vacuum tube or other medium temperature collector). Hydration experiments suggest that operating at low-pressure improves water vapor transport in the system. The results indicate that a closed low-pressure TCM heat storage system is required for the successful application of salt hydrates. The hydration experiments also show that the chlorides (magnesium chloride and calcium chloride) show a larger temperature lift than the two sulfates (magnesium sulfate and aluminum sulfate). However, the hygroscopic chlorides tend to form a gel-like material, which is due to the melting of the material during hydration or the formation of a solution.

Concluding remarks / Task 42-Annex 24 activities

The material research at ECN focuses on the application of salt hydrates as TCM for compact seasonal heat storage. The materials of interest can be a single salt hydrate or a composite material consisting of one salt hydrate and another material (e.g. zeolite).

As mentioned above, it is very important to know the heat storage system layout in order to determine the boundary conditions which the material has to meet. Therefore ECN is also focusing on the development of a heat storage system and individual components (e.g. TCM reactor). At the moment a small scale reactor is developed and a field test of a heat storage system is planned for next year.

Another type of material which is gaining more interest are the PCMs for heat storage applications. It is expected that in the next years our material research will also include investigating PCM for heat storage applications in the built environment.

References

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