FIRST SYSTEMS STUDIES AND CHARACTERISATION STUDIES OF $MgSO_4$ AS A TCM FOR COMPACT THERMAL STORAGE

H.A. Zondag, W.G.J. van Helden, R. Schuitema and M. Bakker

Energy research centre of the Netherlands ECN, Westerduinweg 3, 1755 LE Petten, The Netherlands, phone: +31-224-564941 (4500), fax: +31-224-568966, email: zondag@ecn.nl

Introduction

Energy storage is important for the efficient use of solar energy, due to the delay between solar supply and demand. An extreme case is seasonal storage, in which solar heat is stored during the summer for space heating during the heating season. At this moment, storage for solar space heating is realised by means of water storage. However, in order to obtain a large solar space heating fraction, a very large storage volume is required. In addition, the efficiency of this heat storage option is not very high, as a large part of the stored heat is lost to the ambient.

A very interesting alternative is storage by means of TCM (Thermo-Chemical Materials). In this case, one makes use of the chemical reaction A+B→AB + heat. During the summer, one uses solar heat to split AB into A and B. During the winter, A and B are brought together to produce heat. For this application, it is very important that the material will withstand a number of cycles, consisting of the reaction A+B→AB + heat and the reverse reaction. In addition, it is important that the material has a sufficiently high energy storage density, as well as a sufficiently low reaction temperature in order to allow the use of solar energy for the reverse reaction.

TCM selection and characterisation

As the first step in the present research, Visscher et al (2004) have gone through a large number of potentially interesting materials to find suitable candidates for TCM storage. Their search focused on chloride and sulfate salts, based on the formation of the hydrate form, as e.g.:

$MgSO_4 + nH_2O \rightarrow MgSO_4xnH_2O$ + heat

In addition, also oxide salts have been investigated on the basis of the formation of a carbonate, as e.g.:

$ZnO + CO_2 \rightarrow ZnCO_3$ + heat

The emphasis in the selection has been on energy storage density and a good temperature range, that would not be too low for use, neither too high to allow regeneration by solar collectors. For simplicity, the selection was carried out based on an average hydration temperature for the different hydration steps, while it was assumed that all hydration steps could in principle be used. In a further study these aspects will be studied in more detail. In addition, a number of further criteria was applied, such as low toxicity, abundance of the material and sufficiently low corrosivity. From these criteria, a number of materials has been selected as shown in Table 1.

In principle, the materials in this table can be regenerated by means of a solar collector, with the exception of the silicon oxidation reaction. Although the temperature of this reaction is far too high for solar collectors, the energy density is very high, which could make it interesting for periodical recharging in an industrial facility.

A <=>	B +	C	GJ/m^3	T(^{o}C)
$MgSO_4 \cdot 7H_2O$	$MgSO_4$	$7H_2O$	2.8	122
SiO_2	Si	O_2	37.9	4065
$FeCO_3$	FeO (wustite)	CO_2	2.6	180
$Fe(OH)_2$	FeO	H_2O	2.2	150
$CaSO_4 \cdot 2H_2O$	$CaSO_4$	2 H_2O	1.4	89
$MgSO_4 \cdot H_2O$	$MgSO_4$	H_2O	1.3	216
$ZnCO_3$	ZnO	CO_2	2.5	133
$CaCl_2 \cdot 2H_2O$	$CaCl_2 \cdot 1H_2O$	H_2O	0.6	174
$MgSO_4 \cdot 7H_2O$	$MgSO_4 \cdot 1H_2O$	6 H_2O	2.3	105

Table 1: Overview of interesting TCM materials (Visscher et al., 2004)

As a next step in the research, these materials should be tested further, to check whether the actually observed reaction steps correspond to the values as found in the literature, as well as to check for possible additional reaction products that may be formed (e.g. oxide or hydroxide forms of the kation together with acid). In addition, the reaction rate should be checked, to confirm if the conversion takes place sufficiently fast.

First experiments have been carried out for the dehydration of $MgSO_4x7H_2O$, as shown in Figure 1. It can clearly be seen how the water is removed in a number of steps at different temperatures. However, these initial experiments were done with rather high heating rates, which causes the peaks in the dehydration to occur at relatively high temperatures, as well as a very low rate of rehydration. New experiments at lower heating rates are still ongoing to determine the hydration rate as well as the exact equilibrium temperatures. Once this is sufficiently clear for $MgSO_4$, also other materials will be tested, to create a broad base for further R&D on TCM systems.

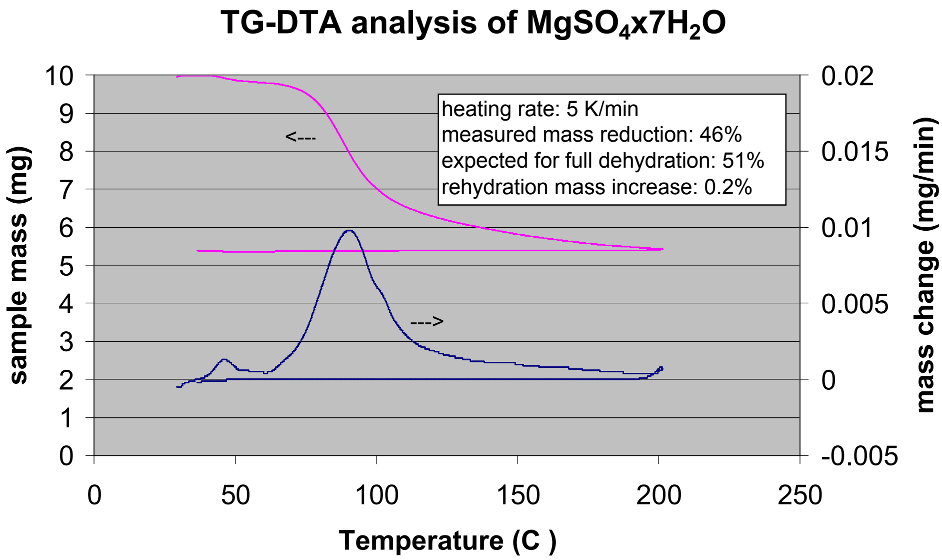

Figure 1:TG-experiments on $MgSO_4x7H_2O$ (high heating rate)

TCM systems studies

Next, systems studies have been carried out for TCM application. First, a typical system was designed as shown in Figure 2. The $MgSO_4x7H_2O$ is dissociated in a reactor by means of solar energy. The hot reaction products (water vapour and hot $MgSO_4$ anhydrate) are stored in two separate storage vessels.

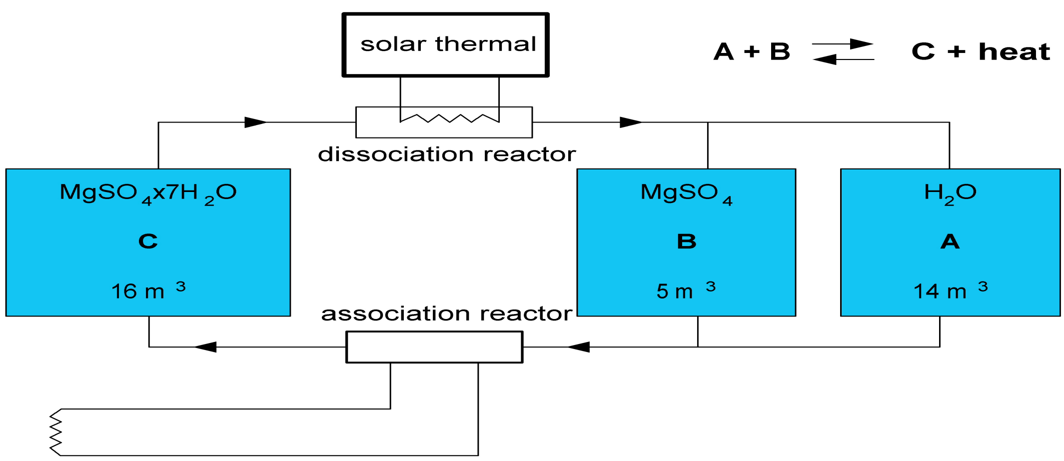

Figure 2: TCM system for seasonal storage for a space heating system (heating demand 44 GJ).

The first system simulations showed very large losses due to the condensation of the water vapour in storage tank A. Typically, the condensation energy for hydrates is of the order of 75%-80% of the hydrate formation energy, which means that one should try to reduce these losses in some way. From other research on TCM (De Boer et al., 2004), it was concluded that the best way of handling these

heat losses is to regain the heat from the ambient again by means of setting up the system in the form of an absorption heat pump.
The pressure-temperature diagram of such a system is shown in Figure 3. The figure shows the equilibrium lines for water (gas to liquid) and for a salt hydration step (e.g. from $MgSO_4$ to $MgSO_4x1H_2O$). From this figure, it is clear that at the same temperature, the dry salt has a much lower water pressure than the water. The functioning of this heat pump system is as follows. A water vapour flow will be generated from the water to the salt due to the difference in water pressure. Thereby the water pressure above the liquid water is reduced, which in turn will lead to further evaporation of the water. Due to this evaporation, the water storage temperature will be reduced, which will allow it to draw heat from the ambient, thereby functioning as an absorption heat pump. At the other hand, by absorption of the water, the salt is heated, which increases the water pressure above the salt again, until a new equilibrium is attained in which the water pressure difference between the liquid water and the salt equals the pressure drop incited by the water transport. The resulting temperature difference determines the maximum temperature step that can be obtained by the heat pump.
One special feature of this type of heat pump is that it has only one cycle per year, and a large amount of TCM is required. For a well-insulated house with 10 GJ space heating demand, about 4 m^3 of hydrate would be required. When dissociated, this would result in about 1 m^3 of anhydrate and about 3 m^3 of water. However, these numbers are based upon crystal densities; in order to have a good reaction rate the salts should be in the form of small particles, which reduces the storage density with about 50%. At the other hand, it may not be necessary to store the water, as fresh water is readily available from the tap. An open system in which the water would not be stored would give the opportunity to reduce the required storage volume with 40-20%. This would also allow new pollutants to come into the system along with the water, but given the low cycling rate of the TCM, this would probably not be a problem.

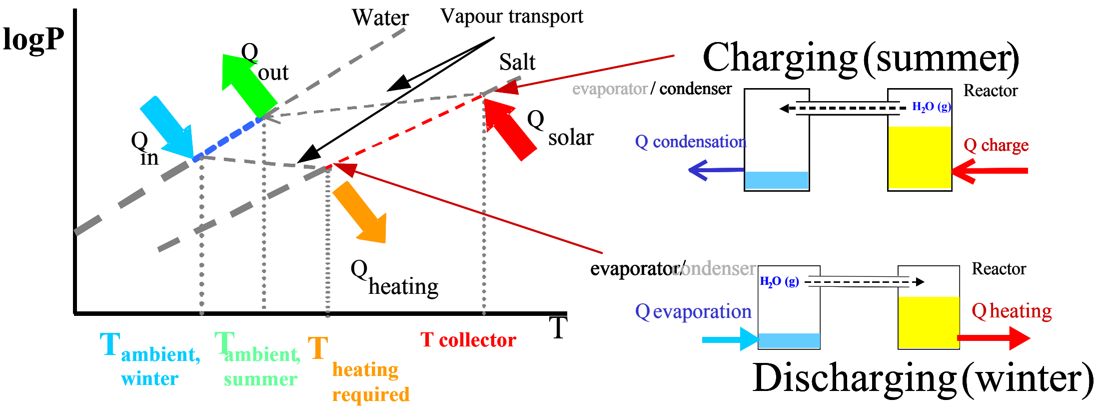

Figure 3: TCM system as an absorption heat pump

Conclusions

TCM is a very interesting storage option. However, condensation loss is very substantial in TCM hydrates. This makes TCM hydrate storage very useful for absorption heat pump application.
A number of promising TCM candidates has been identified, among which $MgSO_4$.
For fully solar heating of the building in the Dutch climate, substantial amounts of TCM are required, over 5m^3 of TCM storage for 10 GJ heating demand.

References

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