

ENGINEERING ASSESSMENT OF REACTOR DESIGNS FOR THERMOCHEMICAL STORAGE OF SOLAR HEAT

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ABSTRACT

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 reversible chemical reactions. For seasonal thermal storage by means of such ThermoChemical Materials (TCM), it would be convenient to have a system containing vessels from which the TCM powder can be fed to a separate reactor where the (de)hydration takes place. An inventory of potentially interesting TCM reactor concepts and a first engineering assessment of these concepts is presented here.

1. 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 reversible chemical reactions of the type $A + B \rightleftharpoons C + \text{heat}$. Interesting reactants are a number of salt hydrates, in which A is the salt, B is water vapour and C is the hydrated form of the salt. During winter, when heat is needed for e.g. residential heating, the salt is hydrated, producing heat. During summer, the hydrated salt is dehydrated again by heat from a solar collector. Once the chemical reaction has taken place, the solar heat can be stored in this way for a long time period without sensible losses.

2. THE THERMOCHEMICAL STORAGE SYSTEM

Two types of ThermoChemical (TC) storage systems can be discerned; either systems in which the reaction occurs within the storage vessel itself, or systems in which the active material is transported to a separate reactor in which the reaction takes place. These two systems are shown in Figure 1. The advantage of a separate reactor is that heat- and vapor transport can be optimized and temperature loss due to heating of inert material is minimized, while the advantage of an integrated system is that transport of the active material is not required, which is complex if the active material is a powder. The focus of the present paper is on the design of a separate (de)hydration reactor for a system as shown in Figure 1a. This system consists of the three storage tanks for the components A, B and C, the hydration and dehydration reactor (that may in a real system be combined) and a borehole to deliver the energy required for the evaporation of the water at borehole temperature. This borehole is required because a large amount of the energy released on hydration is in fact the vaporization energy of the water that is

upgraded by the TC material to the required temperature, causing the TC system to be similar to an absorption heat pump with a large internal storage capacity.

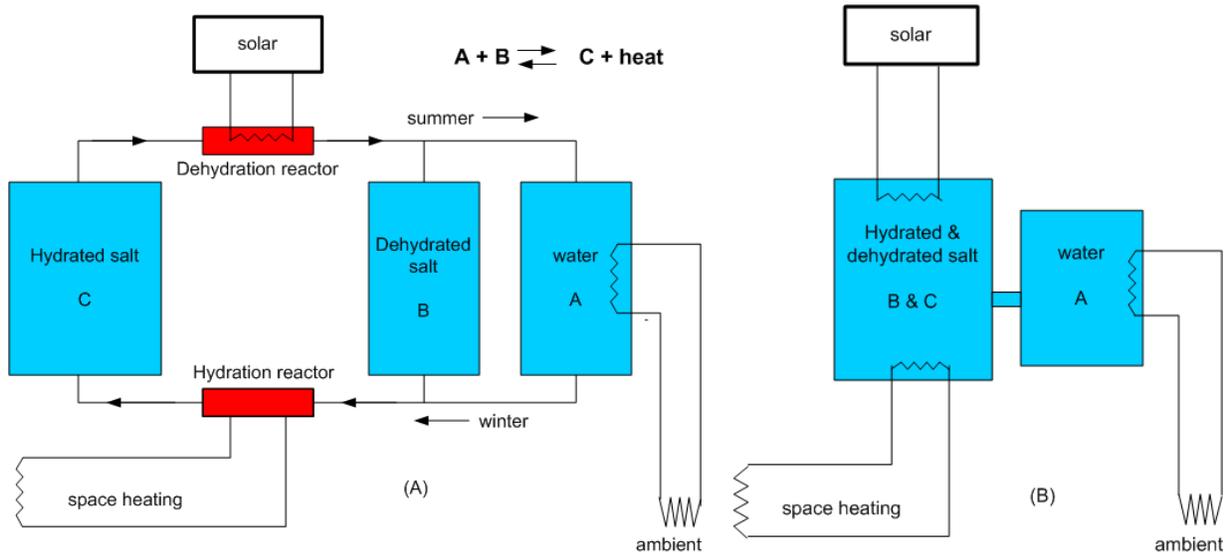


Figure 1: TCM seasonal storage system layout, (a) separate reactor system, (b) integrated reactor system.

3. REACTOR INVENTORY FOR THERMOCHEMICAL STORAGE

At the moment, separate reactors dedicated for TC powder systems do not exist. At ECN, an inventory was carried out on potentially interesting reactor types for a TC storage system, that indicated 3 types of reactors as potentially interesting: an agitated reactor (e.g. screw reactor), a fluidised bed reactor and a gravity assisted bulkflow reactor. These 3 reactor types are indicated in Figure 2. For these three types of reactor, first estimates were made of heat transfer, reactor size and the electrical power required.

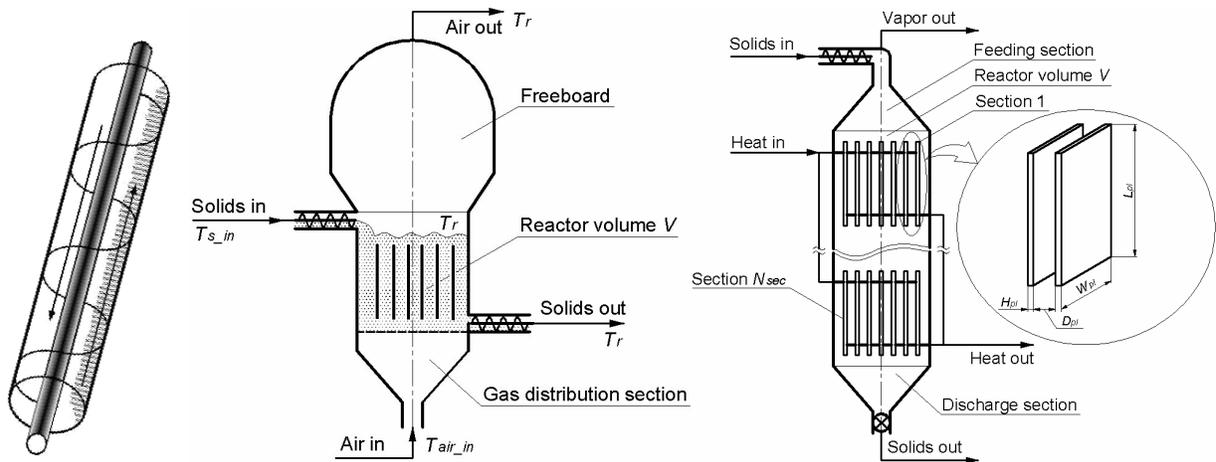


Figure 2: (a) screw reactor, (b) fluidized bed reactor, (c) gravity assisted bulkflow reactor.

4. THERMOCHEMICAL SYSTEM AUXILIARY ENERGY ESTIMATES

A separate reactor system will require additional electrical energy to drive the powder transport, as well as the handling of the powder within the reactor. In addition, other system components will require energy such as the pumps for the borehole and the solar collector system. A first rough estimate was made of the COP that could be obtained under optimized conditions for a 15 m² vacuum tube collector system coupled to a TC storage with a 100 m borehole, for residential heating of a passive house, with the aim of reaching a solar fraction above 90%. It was assumed that the residence time required in the reactor for both hydration and dehydration would be about 2 hours. It was found that with careful optimization, in the case of an screw reactor, very high COP's could potentially be obtained (above 15). For a fluidized bed system, however, the fan energy required for fluidization contributed substantially to the electrical consumption, resulting in a substantially reduced COP. For optimized screw reactor systems, a large part of the electrical energy use is due to the borehole pump and the solar collector pump, as can be seen in Figure 3. For the bulkflow reactor system, it is assumed that the auxiliary energy is similar to the screw reactor system, because also for the bulkflow system a screw is required for the transport of the powder to and from the reactor. However, the powder flow in the screw reactor is seen as more controllable than in the bulkflow reactor, which is especially relevant given the changing flow characteristics and volumetric expansion of the particles during the hydration of the TC powder. For these reasons, the screw reactor is seen as the most promising reactor concept.

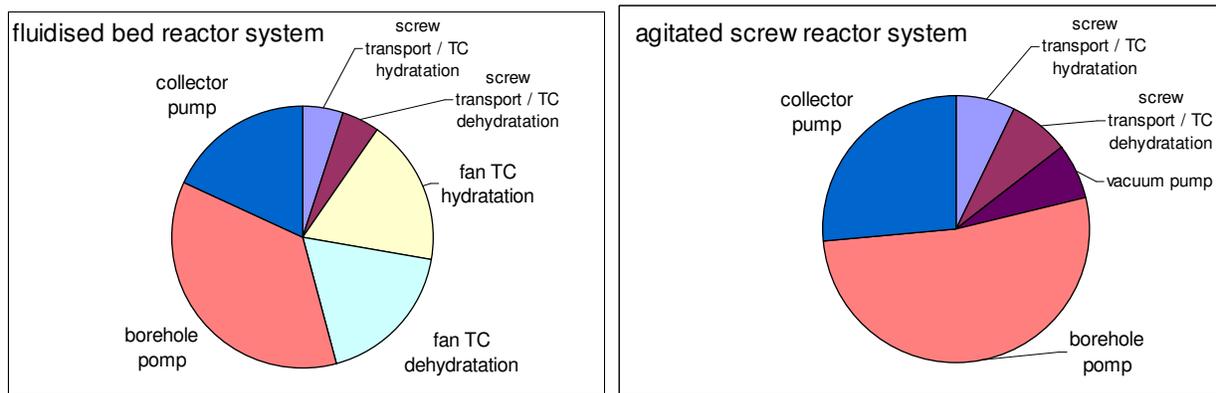


Figure 3: Auxiliary energy requirements for optimized TC storage systems (a) fluidized bed, (b) extruder.

5. THERMOCHEMICAL REACTOR SIZING

In an earlier parameter study, a TC system was examined for domestic hot water and space heating for a passive house of 6 GJ heating demand. It was concluded that the TC reactor power could be limited to 3 kW if the TC storage was combined with a short-term water storage for meeting the peak demand (Zondag et al., 2008). This was used for a first estimate for the reactor sizing. For the practical design of a TC reactor, the following assumptions were made: energy density 0.8 GJ/m³ (due to a voidage of 50%), 5 °C heat exchanger temperature drop for hydration and 30 °C for dehydration, a minimum heat exchanger plate spacing of 1 cm (for bulkflow and fluidized bed only) and an effective heat transfer coefficients of 528 W/m²K for a fluidized bed reactor, 580 W/m²K for a screw reactor and 80 W/m²K for a bulkflow reactor, in accordance with the literature values as shown in Figure 4.

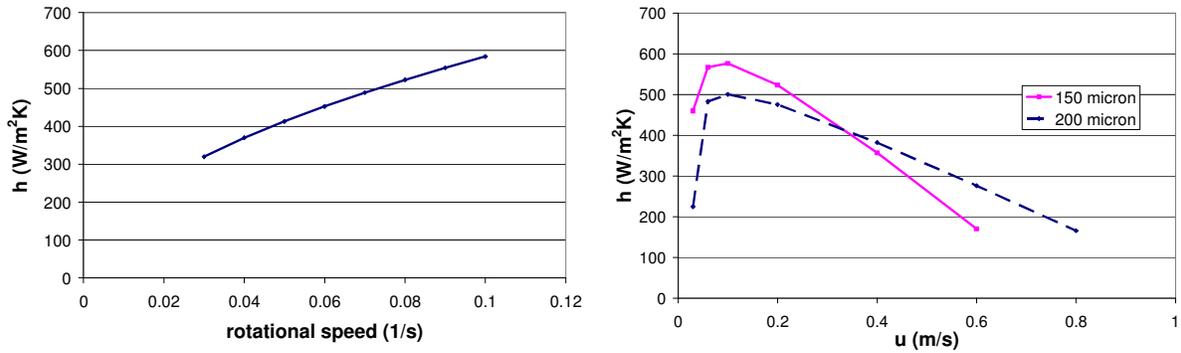


Figure 4: (a) screw reactor according to Jepson model (Kalbasenka, 2008), (b) fluidized bed (VDI Wärmeatlas)

The calculated reactor volumes for the different reactor types are shown in Figure 5. The most important conclusion is that the differences in reactor size are limited and the reactor size itself is modest, provided that the required residence time is not too large.

More in detail, Figure 5a shows that for the dehydration (for which an effective temperature drop of 30 °C was assumed), the reactor size scales almost linearly with the dehydration time, since this time determines how much material the reactor should be able to contain, given a constant power of 3 kW. It appears that the fluidized bed reactor is largest, which is largely due to the assumption that the additional volume required by freeboard and gas distribution section is twice as large as the section containing the active material (see Figure 2b). Next is the screw reactor, due to the significant volume required by the screw and the vapor channel (assumed here to be respectively 20% and 30% of the volume of the active material). The smallest is the bulkflow reactor (containing the same vapor channels but no screw).

Figure 5b for the hydration reactor is based on the assumption of only 5 °C temperature drop, which makes the heat transfer much more critical. For fast reactions, the reactor size is independent of the hydration time, because the reactor size is determined by the volume of the heat exchanger. Only for slow reactions the reactor size scales with the hydration time. For fast reactions the screw reactor is the largest, due to the limited heat exchange area provided by the wall covered with active material. Next is the bulkflow reactor due to the large heat exchange area required because of the relatively low heat exchange coefficient. For very fast reactions the fluidized bed reactor seems the most compact, but since realistic hydration times are in the order of 1-4 hours, this reactor is probably in practice the largest due to the large freeboard and gas distribution sections.

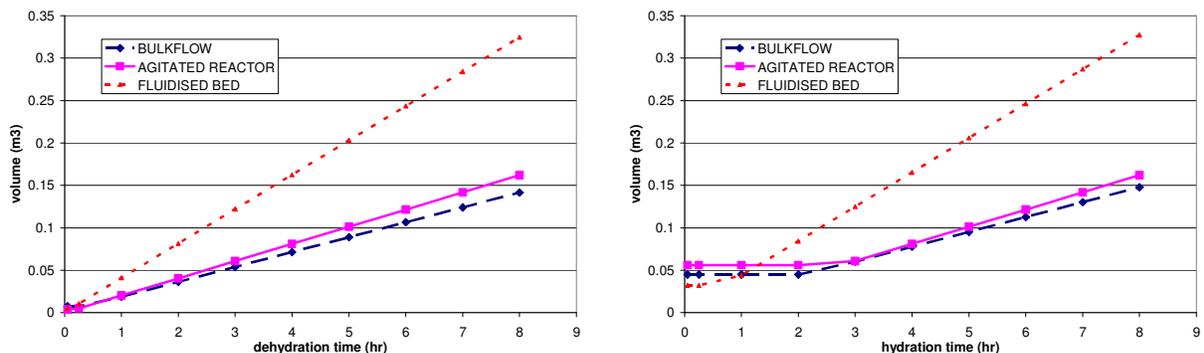


Figure 5: Reactor size as a function of reactor residence time, (a) dehydration reactor, (b) hydration reactor.

Finally, it should be mentioned that in the analysis, a dimensioning problem was found for the fluidized bed TC reactor: to keep the auxiliary energy required for fluidization as low as possible, one would like to have a small particle size to minimize the required fluidization velocity. However, for hydration, a significant volume flow is required to provide all the required moisture to the active material. A compromise can be found by choosing a very shallow bed height (much smaller than the bed diameter), but even then it is difficult to reconcile these issues, especially for particles smaller than 500 micron, and one may have to choose a velocity much higher than the minimal fluidization velocity. In addition, most of the heat of hydration will be carried with the airflow, requiring an air heat exchanger to extract this heat again. A similar problem occurs if one would try to dehydrate the material with hot air, as also in this case the required heat flow, in combination with the small minimal fluidization velocity, would lead to shallow beds. However, this can be avoided by heating through an immersed heat exchanger. Nevertheless, it can be concluded that an optimal sizing for a TC fluidized bed reactor may be problematic in practice.

Because the screw reactor was seen as the most promising candidate, this reactor was investigated in more detail. First, in Figure 6a, the effect of the required power rating on the reactor size is shown. It is found mandatory to find solutions to reduce the required peak power as much as possible, since a larger power, given the reaction time, will strongly increase the reactor volume. In Figure 6b, the effective heat transfer was varied for the screw reactor and it can be seen that if the residence time is in the order of 1-4 hours, as will be the case for realistic materials, increasing the heat transfer is very important to reduce the reactor volume. Because of this, it was found to be of importance to establish the effective heat transfer experimentally.

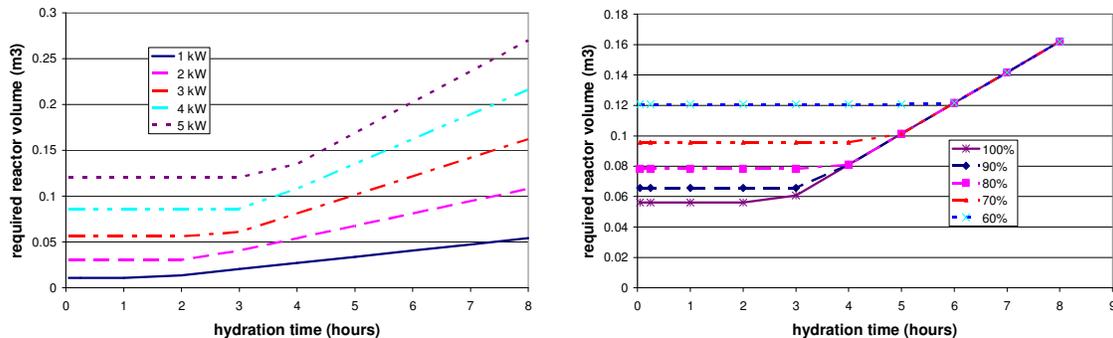


Figure 6: (a) Effect of reactor power on screw reactor volume, (b) Effect of heat transfer on screw reactor volume (100% = 584 W/m²K).

6. HEAT TRANSFER EXPERIMENTS

Essential in a separate reactor system is the active transport of TC powder through the reactor. This transport (using e.g. a screw) will cause stirring in the powder, thereby influencing the heat- and vapor transport. To investigate these effects, a demo reactor setup was built, as shown in Figure 7, consisting of an Erlenmeyer containing a layer of TC material connected by a nitril tube to a second Erlenmeyer containing water (the evaporator), which is immersed in a thermostat bath. It was found essential for sufficient vapor transport to the active material to evacuate the system, thereby increasing the mean free path of the water vapor. Two Buchi V-700 vacuum pumps in series are used to remove all inert gas from the setup before the start of the

measurements. For the TC material, zeolite (Köstrolith NaMSX) was used. The thermostat bath containing the evaporator was set at 19 °C, slightly below the ambient temperature to avoid condensation in the tubing. The TC reactor was at ambient temperature (about 25 °C), and was heated up in the course of the experiment due to the hydration of the TC material.



Figure 7: Experimental setup

Figure 8 shows the effect of stirring the zeolite layer during hydration by a comparison between a stirred and non-stirred (fixed) layer of zeolite, for a bead size of about 1.5 mm and a layer thickness of 2.2 cm. In the case without stirring, a time delay of about 6 minutes is visible between the temperature rise at the side and at the bottom of the Erlenmeyer, which means that the transport of the water vapor through the layer takes a significant time, which is probably due to the relatively slow progress of the reaction front in the zeolite bed. The figure shows that if the bed is stirred, not only the time delay between the hydration at the top and at the bottom of the layer disappears (consistent with a homogeneous layer temperature), but also the maximum temperature is significantly increased.

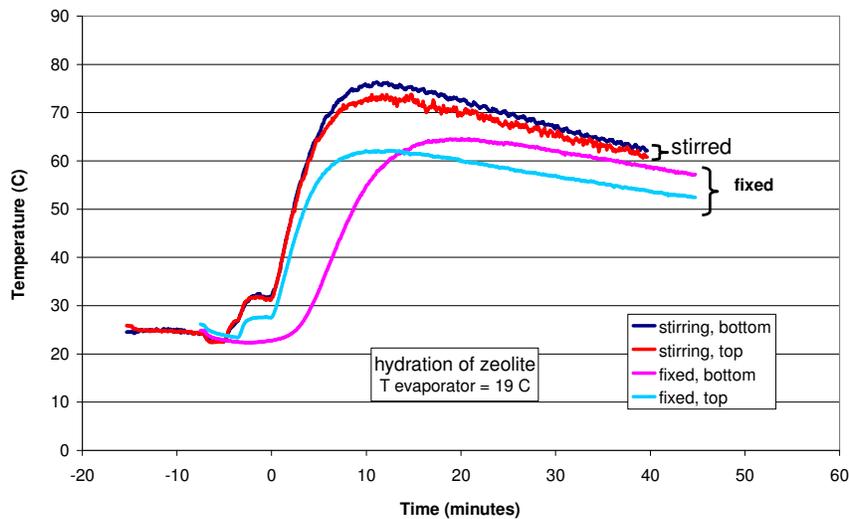


Figure 8: Effect of stirring on hydration of zeolite

The effect of the stirring on the heat transfer was determined in a subsequent hydration experiment, in which the Erlenmeyer with the zeolite was positioned within a small water tub, and the temperature rise in the water tub was measured. During the experiment, the water in the tub was continuously stirred with a magnetic stirrer, both for the case of the stirred and the non-stirred zeolite layer, to optimize the heat transfer and to get a homogeneous water temperature. The results are shown in Figure 9. Clearly, the stirring of the zeolite strongly increases the heating of the water in the tub. From the temperature rise in the tub, the average heat transfer was calculated. A rough estimate indicated that the power transferred to the water increased from about 1.5 kW/m^2 to 3 kW/m^2 due to the stirring effect. Note that this corresponds to the assumptions in the section on TC reactor sizing, since $5 \text{ }^\circ\text{C}$ temperature drop in combination with $580 \text{ W/m}^2\text{K}$ heat transfer leads to 2.9 kW/m^2 .

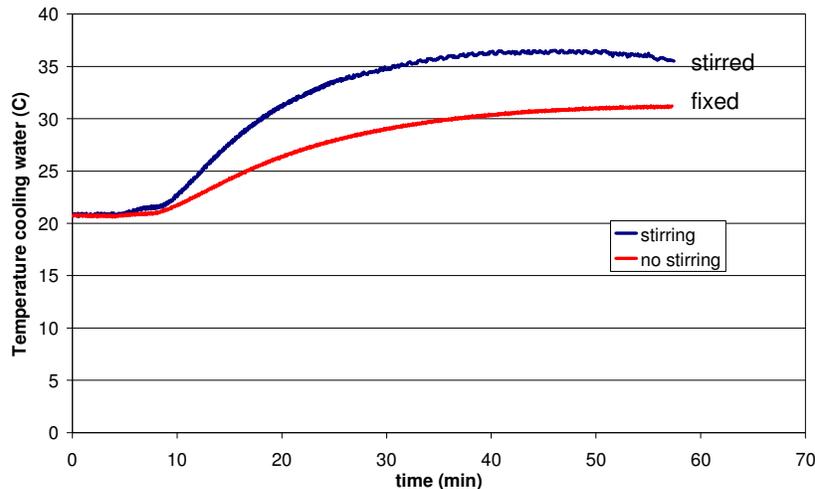


Figure 9: Temperature rise in the water tub due to heat of hydration from the zeolite.

Finally, the hydration time was investigated. A first estimate can already be obtained from the temperature measurements in Figure 9, indicating for the zeolite a typical timescale of about 0.5-1 hour. Next, the mass increase of the zeolite was measured over time, as shown in Figure 10. The measurements were carried out for a fixed bed (no stirring). The zeolite can take up about 30%wt of water, which in this case is 24 grams. A rough indication of the total hydration time can be obtained by extrapolation of the zeolite curve in the figure, indicating that these 24 grams would be taken up in about 3 hours (over which the energy output would gradually decrease). Although the zeolite has a number of very good characteristics, the material is not optimal for seasonal heat storage, due to its price (about 4 euro/kg) and its relatively low energy density. Therefore, also attention was given to some low-cost hygroscopic salts with a potentially higher energy density. As a first trial, the hydration of MgSO_4 was investigated. However, for MgSO_4 , Figure 10 shows a much slower mass increase than for the zeolite. Full hydration will therefore take a much longer time and the specific power of MgSO_4 will be very low. Correspondingly, when trying to heat water with the hydration of MgSO_4 (as done for zeolite in Figure 9), due to the very slow reaction, hardly any increase in the water temperature was measured within the time of the experiment. The slow hydration of the MgSO_4 is very inconvenient, because this requires a very long residence time in the reactor, thereby requiring a large reactor size. The search for better materials is still ongoing (as presented by Van Essen, 2009).

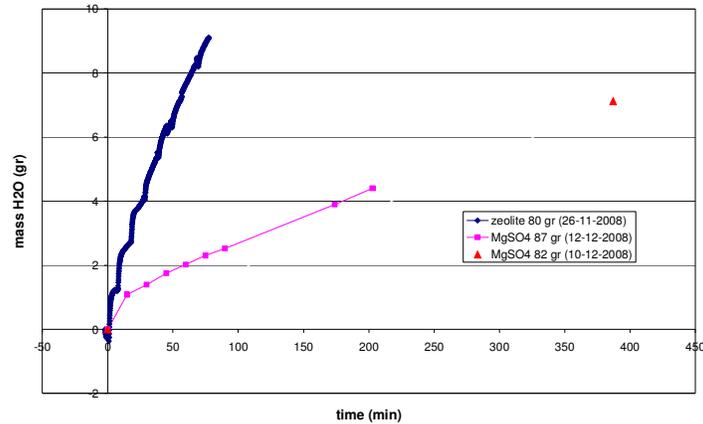


Figure 10: Increase in mass on hydration of zeolite and of MgSO₄.

7. CONCLUSIONS

Thermochemical storage systems with a separate reactor show good technical potential for the seasonal storage of solar heat. Although auxiliary energy use is an important issue, high COP's can potentially be obtained within an optimized system. The auxiliary energy analysis shows the screw reactor as a promising concept, and typical sizes are about 20 liters for a dehydration reactor (assuming a dehydration time of 1 hour) and about 60-80 liters for a hydration reactor (assuming a hydration time less than 4 hours). However, the required reactor size may increase significantly if the heat transfer is low, due to the limited heat exchange area available, which makes it important to optimize the heat transfer. Experiments showed that active stirring of the material is a means of improving the heat transport significantly. Such stirring may conveniently be combined with the transport of the material through a screw reactor. Unfortunately, the two materials examined in this paper (zeolite and MgSO₄) are both not ideal for seasonal storage. The zeolite material hydrates fast, which is as desired, but unfortunately the energy density of zeolite is relatively low and the cost of the material (order of 4 euro/kg) still too high for bulk application. The MgSO₄ hydrates too slow and results in insufficient temperature rise to be used for heating. Therefore, at ECN, the search for better materials is ongoing.

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