

COMPARISON OF REACTOR CONCEPTS FOR THERMOCHEMICAL STORAGE OF SOLAR HEAT

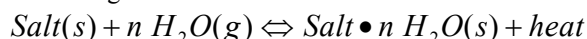
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Introduction

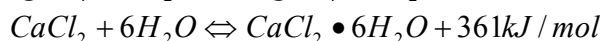
Storing solar heat in the summer for use in the winter is inefficient and requires a large volume, due to significant losses to the ambient and the limited energy storage capacity of water. As an alternative, solar heat could be stored over a long time by means of a reversible chemical reaction within a so called thermochemical material (TCM). This has a number of advantages over traditional sensible storage, such as high energy density and loss free storage. Interesting materials are salts that react with water vapour (salt hydrates), according to the following reaction:



During the summer, solar heat can be used to remove the water from the salt, while during winter, the salt can be hydrated again, producing useful heat.

Powders or suspensions

In the literature, a large number of potentially interesting salt hydrates can be found. Some of these are liquid, such as NaOH, while others are solid, such as MgSO₄. Since the liquids that can be used for thermochemical heat storage are generally highly corrosive and harmful (e.g. H₂SO₄ or NaOH), or expensive (e.g. LiCl), the focus in the present research is on solid salts that are available in bulk at low cost, such as MgSO₄ or CaCl₂. These two salts can be used to store solar heat by means of the following reactions:



These solid salts can be used in two ways: they can be used as powders, or they can be suspended in an inert liquid. Typical cases are shown in Figure 1.

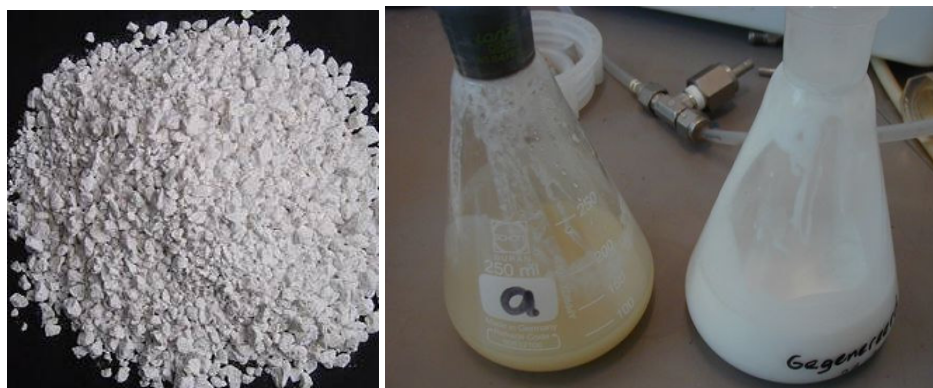


Figure 1: CaCl₂, (a) powder and (b) suspension

Powders have several advantages and disadvantages compared to liquids. In Table 1, CaCl_2 in powder form is compared to CaCl_2 in suspension on various characteristics relevant for seasonal heat storage.

	$\text{CaCl}_2(\text{s})$ as powder	$\text{CaCl}_2(\text{s})$ in suspension
Conductive heat transport	-	+
Transport of active material	-	+
Vapour transport	+/-	-
Thermal capacity	+	+/-
Stability	+/-	-
cost	+	-
safety	+	+
Energy density	+	+

Table 1: Comparison of CaCl_2 in powder form or suspension form

The focus of the present paper is to compare TCM heat storage based on powders and suspensions. The work on powder reactors was carried out at ECN and the work on suspension reactors at TNO.

The chemical reaction

Salt characteristics

A large number of salts is able to take up water. The initial focus at ECN was on MgSO_4 , but also other materials are currently examined such as CaCl_2 and zeolite. In Figure 2, the equilibrium curves for CaCl_2 are shown as found in the literature, as well as a dehydration of CaCl_2 in a TG measurement (in which the reduction in mass due to evaporation of volatile components is recorded as a function of temperature). Figure 2a shows that at a water vapour pressure of 10 mbar, an equilibrium temperature of about 70 °C (according to the data of Brunberg) can be found in the CaCl_2 . Figure 2b shows that full dehydration was found at 110 °C (this temperature is higher than the equilibrium temperature due to non-equilibrium conditions). The hydration temperature is high enough to be used for heating purposes, while the dehydration temperature can easily be reached by vacuum tube solar collectors.

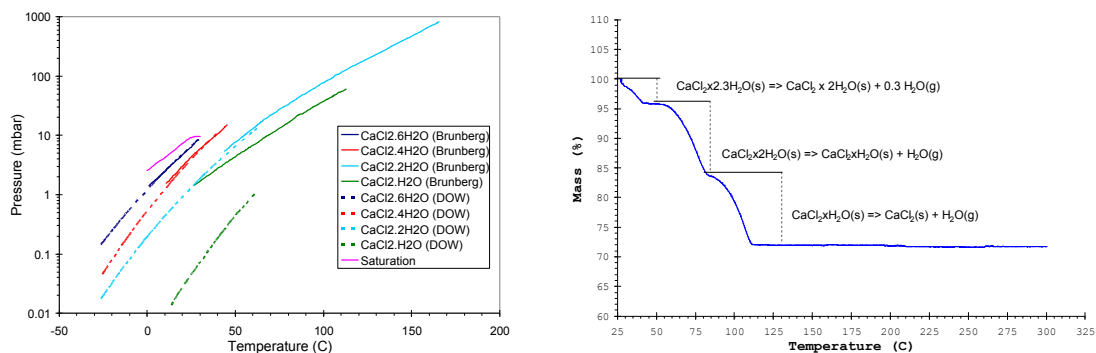


Figure 2: Thermodynamic characteristics of CaCl_2 , (a) literature data on p-T curves (Brunberg, 1980; Dow brochure), (b) measured dehydration of CaCl_2 in a TG.

An important issue in the hydration of the salt using water vapour, is that water vapour is normally only available at very low pressures of about 10 mbar ((roughly corresponding with the evaporation conditions in a borehole). Since the transport of the water vapour to the salt is in most system designs by the difference in water vapour pressure between evaporator and salt, the pressure drop in the system should be minimized, which is mostly done by evacuating the system. If all inert gases can be removed, this very substantially increases the speed of the hydration reaction.

Hydration of powder

A fixed bed hydration-dehydration setup was prepared, as shown in Figure 3. Through the center of the fixed bed (in the black tube), a vapour channel consisting of a tubular metal mesh (diameter 1 cm) is placed inside the reactor to facilitate the hydration. In Figure 3b, 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).

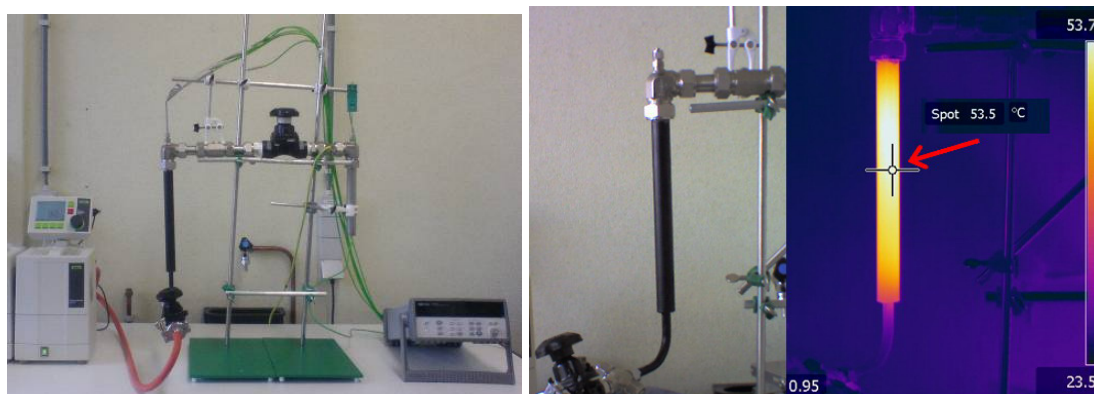


Figure 3: Experimental Set-up (a) set-up, (b) close-up of reactor vessel (normal photograph and infrared photograph showing the reaction temperature for hydration of zeolite)

In the measurements in the setup, first the evaporator and the reactor were both set to a temperature of 25 °C. The temperature inside the salt was monitored using thermocouples. For this case a temperature rise in the CaCl_2 of 60 °C was measured (from 25 °C to 85 °C). However, in a real system the evaporator temperature will be lower and the reactor temperature will be higher, which both have an adverse effect on the temperature rise that can be obtained. This is illustrated in Figure 4, in which the reactor was preheated to 50 °C and saturated water vapour at 10 °C was added, resulting in a temperature rise of about 10 °C (from 50 °C to 60 °C). With respect to these reaction temperatures, it appears that the CaCl_2 powder could be used in a heating system with even a relatively high return temperature.

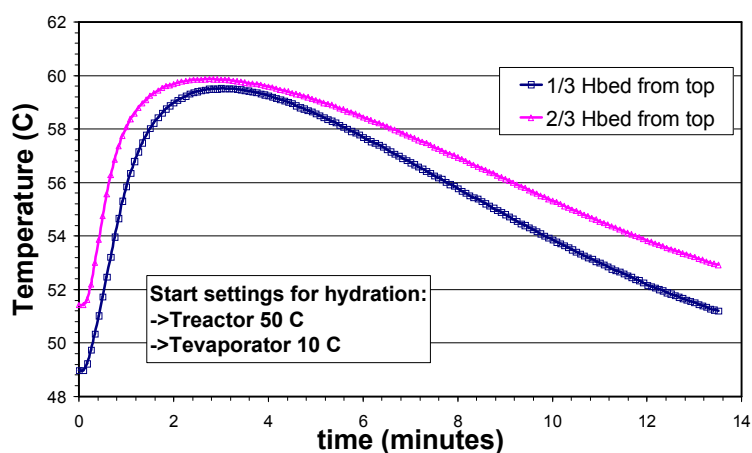


Figure 4: Temperature in fixed bed with CaCl_2 with Tevaporator at 10 °C and Treactor at 50 °C.

Suspensions

At TNO, experiments were carried out with the CaCl_2 suspended in an inert liquid. It was found that if separation in the liquid occurred, with the active particles settling at the bottom, the presence of the liquid seriously reduced the vapour transport towards the active particles, thereby slowing down the reaction. However, with a sufficiently thin layer of fluid, good results were obtained as shown in Figure 5. The

figure shows that at the moment the pressure in the reactor is reduced (enabling a sufficient diffusive vapour flow), the temperature of the suspension starts to rise, while the temperature of the liquid water in the evaporator drops sharply due to the vaporization of part of the water. For an evaporator temperature of 19 °C and a reactor temperature of 21 °C, the salt temperature increased with a step of 13 °C on hydration. This may be improved further by optimizing the vapour transfer.

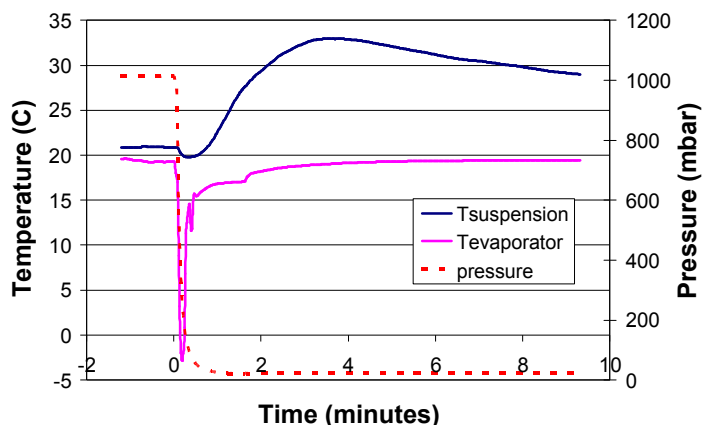


Figure 5: Hydration of a CaCl_2 suspension.

It was found that a high concentration of CaCl_2 could be obtained in the suspension liquid, thereby providing a high energy storage density. A problem was the instability of the suspension, resulting in the settling of the particles into a thick and highly viscous layer at the bottom. Further work is ongoing to stabilize the suspension and to find good methods to get the settled particles back into suspended form.

The reactor design

powders

In a fixed bed, heat transport and vapour transport are critical. Figure 6 shows that a thicker layer of powder may substantially slow down the hydration. This implies that in a good reactor design heat- and vapour transport have to be optimized, e.g. by stirring or by creating a large active interface, as well as removing all inert gases from the system.

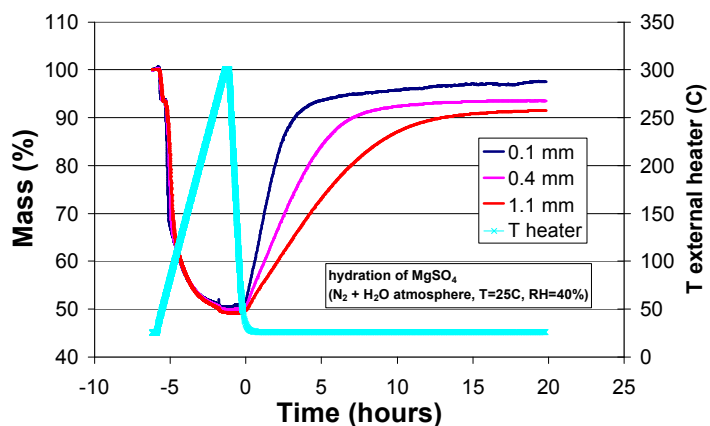


Figure 6: Hydration of MgSO_4 for various layer thicknesses in STA at atmospheric pressure (dehydration before $t=0$ also shown)

The hydration time can be improved by (1) removing all inert gasses to facilitate the diffusion, (2) mixing in the bed to optimize the vapour and heat transport. Various reactor designs are possible that allow the application of these principles. As an example, an agitated heat exchanger is shown in Figure 7.

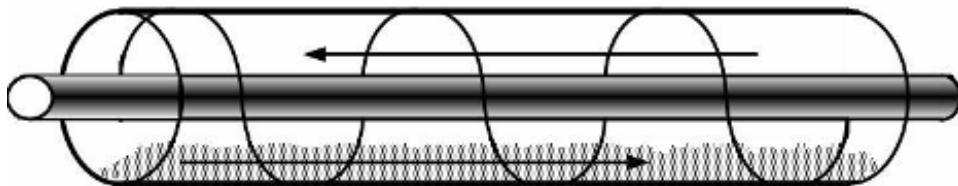


Figure 7: Agitated heat exchanger for hydration and dehydration of the salt.

To examine the effect of mixing experimentally, a container of zeolite (Köstrolith beads) was placed in a setup as shown in Figure 3. The setup was evacuated and the content of the container was either left as a fixed bed or actively stirred. The results are shown in Figure 8. The results show that the stirring strongly increases the heat transport towards the bottom of the tank, the heating of which is shortened from about 8 minutes to 1 minute. Clearly, the results show that stirring significantly improves the heat transfer from the powder to the heating system.

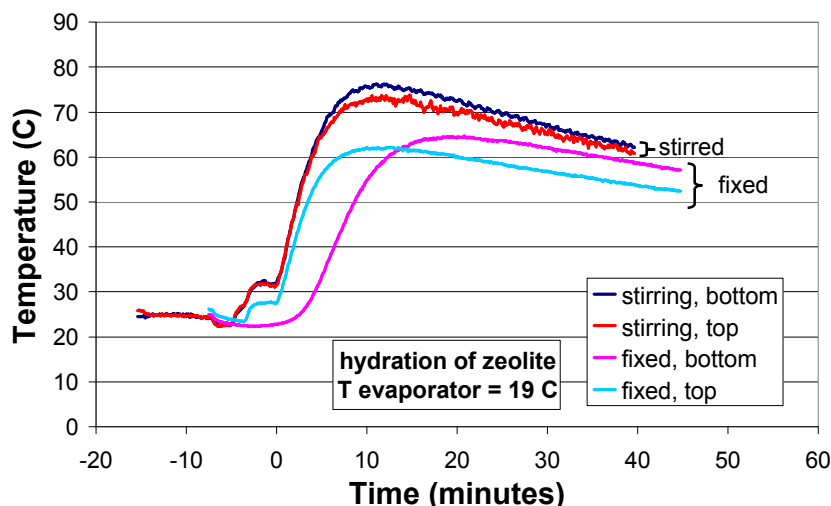


Figure 8: Effect of stirring in an evacuated bed of zeolite.

Suspensions

At TNO, a reactor was built for the hydration of a CaCl_2 suspension as shown in Figure 9. Also here, it was found necessary to evacuate the reactor. In order to optimize the vapour transport, a thin layer of suspension was led over a flat plate, that also functioned as a heat exchanger. However, it was found difficult to obtain sufficient power output, and so far only at high vapour pressures sufficient temperature rise was found, as shown in Figure 9b. Efforts are ongoing to improve the active interface between liquid and gas, thereby enabling a faster vapour transport to speed up the reaction.

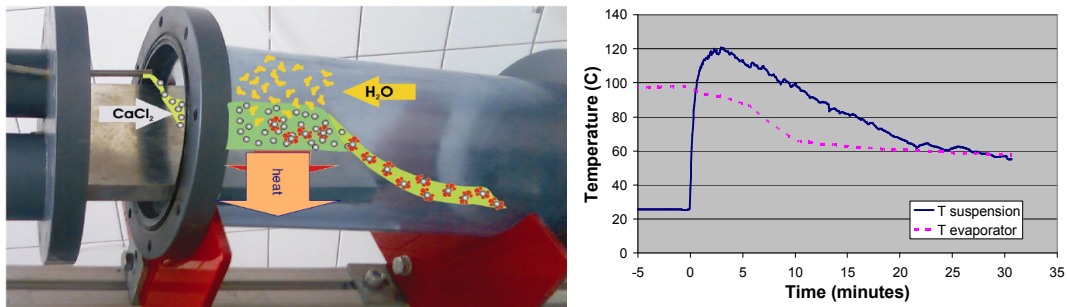


Figure 9: (a) Prototype suspension reactor, (b) temperature rise measured at high vapour pressure.

Conclusion

Thermochemical materials are an interesting means of storing solar heat in a compact and loss-free way. Both TCM powders and TCM suspensions can be used. For TCM powders, optimization of the heat transfer in the reactor is necessary to obtain a sufficiently fast heat transfer, which can be obtained by stirring. This also promoted vapour transfer, leading to a faster hydration and a more compact reactor. For TCM suspensions, the stability of the suspension is an issue and the vapour transfer should be optimized in the reactor by a sufficiently large active interface area.

References

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