

R&D OF THERMOCHEMICAL REACTOR CONCEPTS TO ENABLE SEASONAL HEAT STORAGE OF SOLAR ENERGY IN RESIDENTIAL HOUSES

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1. INTRODUCTION

About 30% of the energy consumption in the Netherlands is taken up by residences and offices. Most of this energy is used for heating purposes. In order to reduce the consumption of fossil fuels, it is necessary to reduce this energy use as much as possible by means of insulation and heat recovery. The remaining demand could be met by solar thermal, provided that an effective way would exist for storing solar heat.

Seasonal heat storage techniques using water have a number of disadvantages, such as substantial heat loss and a low energy density (large volumes are required). A more compact way of storing heat is by using thermochemical materials (TCMs) in which heat is stored by means of a reversible chemical reaction. Salt hydrates are promising TCMs that are cheap, non-toxic, non-corrosive and have sufficient energy storage density. Moreover, on hydration, salt hydrates can provide temperatures that are sufficiently high for heating purposes, while they can be dehydrated at temperatures that can be provided by a solar thermal collector.

In salt hydrates, solar heat is stored and released according the following reaction: $\text{Salt}(s) + n\text{H}_2\text{O}(g) \rightleftharpoons \text{Salt}\cdot n\text{H}_2\text{O}(s) + \text{heat}$. In summer, the salt can be dehydrated using solar heat. In this way the seasonal storage is charged with solar energy. In winter, the dehydrated salt can be hydrated again to release the stored solar energy. This heat can be used to provide space heating and domestic hot water.

2. TC SYSTEM TYPES

The hydration and dehydration processes take place in a ThermoChemical reactor. In general, TC reactors on a household scale, which can provide sufficient power, are a new challenge in reactor design. The processes in this TC reactor are much more complicated than loading a water tank using a heat exchanger. The hydration and dehydration

reactions involve heat transport, water vapor transport and in some cases also the transport of the active TC material.

Two types of TC seasonal storage systems can be discerned; on one hand the integrated reactor system, in which the reaction occurs within the storage vessel, and on the other hand the system with separate reactors, in which a powder flow from the storage vessel to the reactor occurs, in which the active material is (de)hydrated and afterwards transported to another storage vessel. Schematic representations of these two systems are presented in Figure 1 and Figure 2.

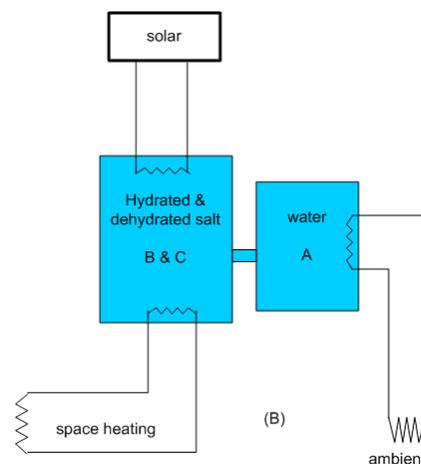


Figure 1: TC storage system with integrated reactor

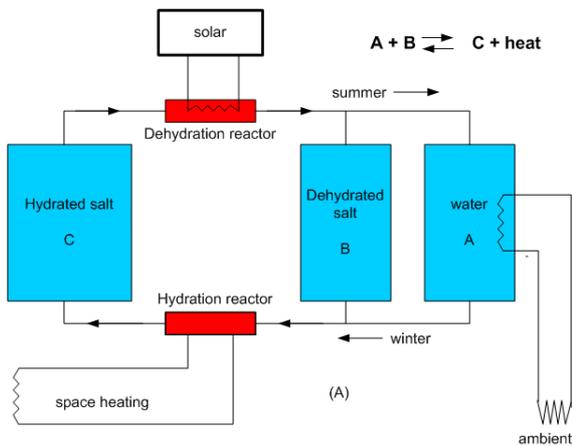


Figure 2: TC storage system with separate reactors

In the present paper, the emphasis will be on a reactor suitable for application in a system similar to the case shown in Figure 2. In particular, the focus will be on an agitated screw reactor, as shown in Figure 3, which is in this stage of the research seen as the most promising reactor type for this application (Zondag, 2009).

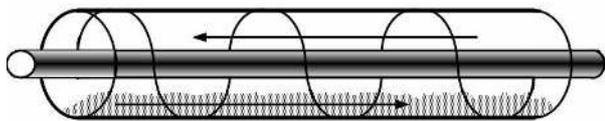


Figure 3: Screw reactor

First of all, in a system simulation study, the power was determined that such a TC system would need for charging and discharging. Next, in an experimental study, the reaction time, the effective heat- and vapor transfer and the flow characteristics of the powder were examined for a setup filled with zeolite in a series of experiments as presented below.

3. TC SYSTEM CALCULATIONS

A numerical simulation of the system was carried out in matlab, to determine the power and the temperature level that the TC system should be able to provide. A passive house was used in the calculations, with a 6 GJ annual heating demand and an additional 9 GJ annual domestic hot water demand. The house had a low temperature heating system (40°C/25°C). A vacuum tube collector array was used to heat up the TC storage. A water vessel of 200 liters was used to reduce the peak power required from the TC storage; peak demand could be drawn from the water vessel, that afterwards could be reheated at a lower rate by the TC storage again. The system control was such that the heat of the collector array was preferentially fed to the water vessel, and the TC storage was heated only after the water vessel had reached its maximum temperature. In this way, the solar heat was used as much as possible directly, and the number of cycles made by the TC

material was reduced. The calculations were carried out for the Dutch climate. The collector system was assumed ideal, in the sense that sensible losses from the piping to and from the collector were not taken into account in the calculations.

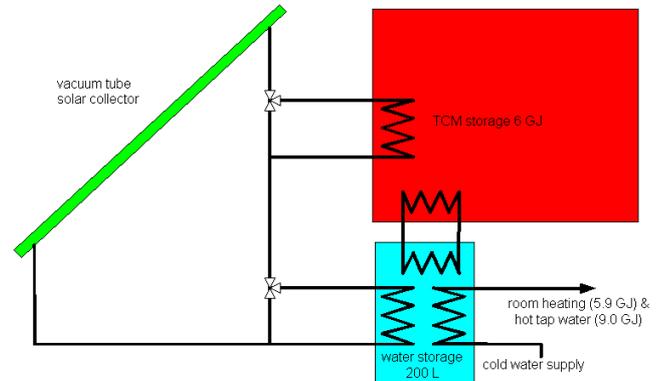


Figure 4: Schematic representation of the simulated system

The results of the calculations are shown in Figure 5 to Figure 7. The figures show the solar fraction that can be obtained for a system with a space heating demand of 6 GJ, a DHW demand of 9 GJ and a 6 GJ TC storage, for various collector aperture areas. The solar fraction is defined here as the heat delivered by the solar system, divided by the total heat demand of the building (space heating + DHW). The results show that for charging, the TC system should be able to take up about 3 kW, while for discharging this may be in the range of 1-3 kW. With respect to the discharge temperature, the figures show that the system should be able to provide at least the space heating temperature of 40°C.

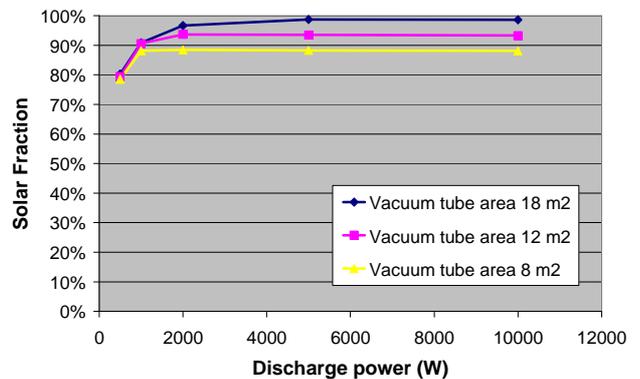


Figure 5: Effect of discharge power on Solar Fraction

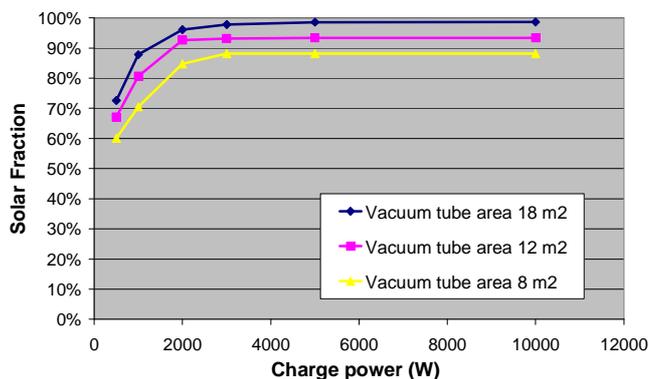


Figure 6: Effect of charge power on Solar Fraction

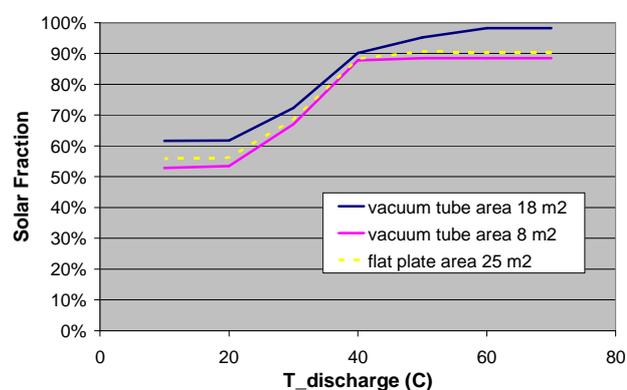


Figure 7: Effect of discharge temperature on Solar Fraction

Also, it was found that the TC system should have a storage capacity of about 6 GJ, which is more or less equal to the annual space heating demand. Assuming an effective energy density of about 1 GJ/m³ for the TC material, this would lead to 6 m³ of salt hydrate that would have to be stored in vessel C in Figure 2, roughly a third of that for the water storage (vessel A) and, depending on the characteristics of the active material, about two thirds of that for the anhydrate (vessel B).

4. TC MATERIALS

A selection of potentially interesting TC material was carried out. The selection was carried out largely based on the materials in the NBS database, taking into account aspects such as enthalpy and entropy of each reaction step, safety of the materials (non-toxic, non-polluting), cost of the materials and stability of the material (avoidance of side reactions). A number of potentially interesting materials was selected, among which CaCl₂, MgCl₂, Al₂(SO₄)₃ and MgSO₄. These materials were subsequently tested to determine the reaction speed of these reactions, as well as the mechanical stability of these materials under hydration and dehydration (see Van Essen, 2009). It was observed that MgSO₄ and Al₂(SO₄)₃ had very slow kinetics, strongly limiting the power that could be withdrawn effectively from the material. On the other hand,

CaCl₂ and MgCl₂ had many promising characteristics, but their mechanical stability could be problematic, since they tended to form a gel-like structure on overhydration.

Apart from the testing of the materials themselves, it was found necessary also to test the heat- and vapor transfer of TC materials within a TC reactor. Due to the problems with the TC salts examined so far, it was decided to carry out these tests with zeolite. Zeolite was used because the characteristics of this material are well known and the hydration is fast. However, zeolite also has a relatively low energy density and a relatively high cost compared to a number of salt hydrates, and would therefore not be very suitable for large scale seasonal storage. Nevertheless, the basic characteristics of vapor uptake and heat release are the same as for TC salts, which made it a suitable material to examine the heat- and vapor transfer within a reactor.

5. EXPERIMENTAL SETUP

An experimental setup was built, as shown in Figure 8, consisting of an Erlenmeyer containing the active material, connected with a nitril tube to an Erlenmeyer containing water, functioning as the evaporator. The Erlenmeyer containing the water was placed in a thermostat bath to control the evaporation temperature. In all measurements, the thermostat bath was set to 19°C, slightly below the lab temperature to avoid condensation in the tubes.

Within the tube, a 3-way splitter was used to connect the system to an evacuation pump (2 Buchi V-700 vacuum pumps in series which were found to reach pressures of about 2.8 mbar). The vapor flow in this system is driven by the vapor pressure difference between the TC material and the evaporator. Evacuation of the system was found essential to obtain sufficient vapor flow. Due to the low evaporation temperature, the vapor pressure is very low and the vapor pressure difference between evaporator and active material is insufficient to drive the vapor flow if also inert gas is present in the system.



Figure 8: Experimental setup.

Finally, the Erlenmeyer with active material was placed on a magnetic stirrer, allowing effective agitation of the material during hydration, thereby resembling the agitation that would occur in practice in a screw reactor. The Erlenmeyer could also be placed in a cooling water tub, to establish the effective heat transfer by measuring the temperature rise of the cooling water. If the tub was placed on top of the magnetic stirrer, stirring of the active material was still possible. In addition, the cooling water in the tub was also stirred (both for the case with and without stirring of the active material), to optimize the heat transfer from the Erlenmeyer to the cooling water and to obtain a homogeneous cooling water temperature within the tub. This resulted in 4 types of hydration experiments:

- Non-cooled, non-stirred, with the temperature of the TC material measured by thermocouples at the side and the bottom of the Erlenmeyer
- Non-cooled, stirred, with thermocouples same as above
- Actively cooled, non-stirred, with thermocouples measuring the cooling water temperature.
- Actively cooled, stirred, with thermocouples measuring the cooling water temperature.

In all cases, two thermocouples were used at the same location for a single temperature measurement, to have a warning if one of the thermocouples needed recalibration.

6. EXPERIMENTAL RESULTS FOR STIRRING

As a first experiment, 2 types of colored sand were used to check the effectiveness of the mixing by the magnetic stirrer. It was found that for a magnet size sufficiently close to the Erlenmeyer diameter, a homogeneous mixture resulted, indicating that no dead areas were present in the Erlenmeyer.

Next, experiments were carried out on the hydration of zeolite. A layer of zeolite (Köstrolith NaMSX, 1.5 mm beads) was hydrated. By visual inspection, it was found that the zeolite could be stirred very well, with the material flowing nicely around the rotating magnet.

Next, the temperature was measured for the cases with and without stirring of the zeolite. The results are shown in Figure 9.

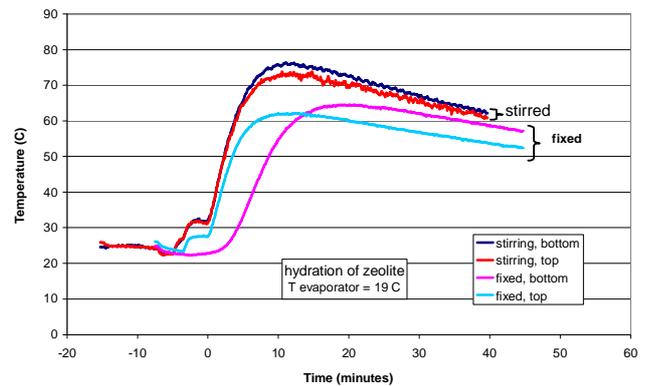


Figure 9: Temperature profile obtained for the hydration of zeolite (comparing stirred and non-stirred zeolite)

First, it can be observed that for the non-stirred case, on hydration a temperature of about 60°C was obtained; corresponding to a temperature rise of almost 40°C. A time delay of almost 6 minutes was found between the temperature rise measured at the side of the Erlenmeyer and the temperature rise measured at the bottom. Given the large particle size of about 1.5 mm and the corresponding high permeability, a fast vapor transport was expected. Probably, the long time delay is caused by the reaction front moving slowly from the top to the bottom of the layer of active material.

Next, a new layer of material was hydrated under active stirring of the material. The figure clearly shows that a much more homogeneous temperature is obtained in the zeolite bed, with the time delay totally disappearing. Also, it was found that a higher temperature was obtained in the bed; the temperature rise now being over 50°C. This will be related to both higher heat transfer to the wall (more homogeneous bed temperature) and better vapor transfer in the bed (the dissipation of energy by the stirring itself was found not to lead to a noticeable rise in temperature, as was tested with inert material).

Before and after the measurement, also the zeolite mass was measured. It was found that the stirring increased not only the temperature rise, but also the rate of water uptake; after 22 minutes the mass increase in the non-stirred case was about 3.4%, while in the stirred case this was 4.6%. Similarly, after 52 minutes, these numbers were respectively 6.4% and 7.6%, showing that the water vapor uptake was increased by the stirring.

Next, an experiment was carried out in which the Erlenmeyer with the zeolite was placed in a tub with cooling water. The temperature of the cooling water was measured for both the stirred and the non-stirred case, as displayed in Figure 10. As expected, the stirring of the zeolite leads to a very significant increase in the heat transfer to the cooling water.

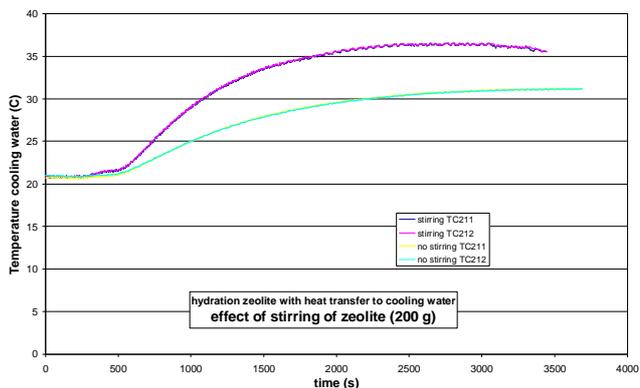


Figure 10: Temperature of the cooling water for hydration of stirred and non-stirred zeolite.

In order to be able to quantify the amount of heat released from the zeolite for the stirred and non-stirred case, in addition to the measurements above, the temperature loss was measured for the same tub, but now filled with hot water and the Erlenmeyer containing inactive zeolite. From these results, combined with the estimated heat capacity of the zeolite and the Erlenmeyer, the heat released by the hydration was found to be as shown in Figure 11. Note that the dotted line representing the heating of the system corresponds to Figure 10.

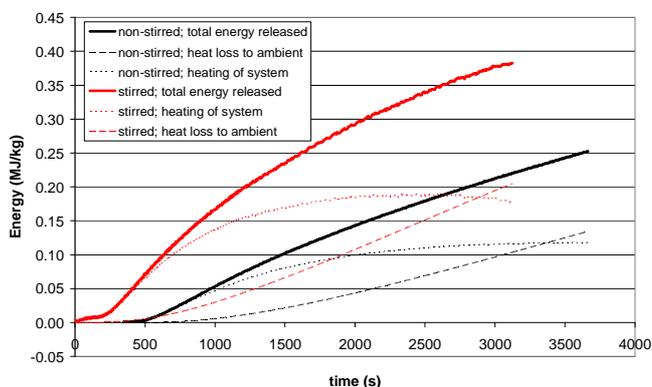


Figure 11: Heat release by zeolite for stirred and non-stirred case.

First of all, the figure shows that after almost 1 hour of hydration, for the stirred case, about 0.38 MJ/kg of heat was released. Although this is a good result, the energy released is substantially lower than the 1 GJ/m³ that one would like to reach with TC storage, which is due to the relatively low energy density of zeolite (as stated before). However, several salts exist that potentially have 4-5 times this energy density. First results from the work at ECN on hydration of TC salts such as MgSO₄, Al₂(SO₄)₃, CaCl₂ and MgCl₂ are also presented in this conference (Van Essen, 2009).

Next, from the figure, also an indication of the power can be obtained from the slope of the curve. Given that the

experiment was carried out with 85 grams of zeolite, and the contact area between zeolite and water tub was 0.006 m² (a layer of 2.2 cm height and 8 cm in diameter), an effective power was found in the experiment of about 1.5 kW/m² for the case without stirring, and 3 kW/m² for the case with stirring.

7. OPTIMISATION OF THE VAPOR TRANSPORT

After obtaining the results for the stirring of the zeolite, it was considered of interest to optimize the setup further, and to find out which changes had the largest effect on the performance, especially since this was expected to give recommendations for the building of a real reactor. In particular, all possible obstacles to the vapor flow were removed successively to find whether these negatively influenced the results.

First, it was tried to optimize the evaporator area. A large bottle was taken as the evaporator and a sponge was added as shown in Figure 12. The results with and without sponge are shown in Figure 13. Clearly, the sponge significantly increases the temperature obtained in the zeolite bed.

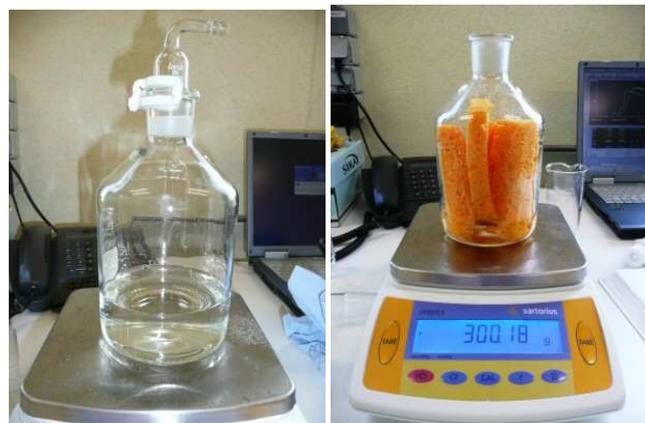


Figure 12: optimization of evaporator surface

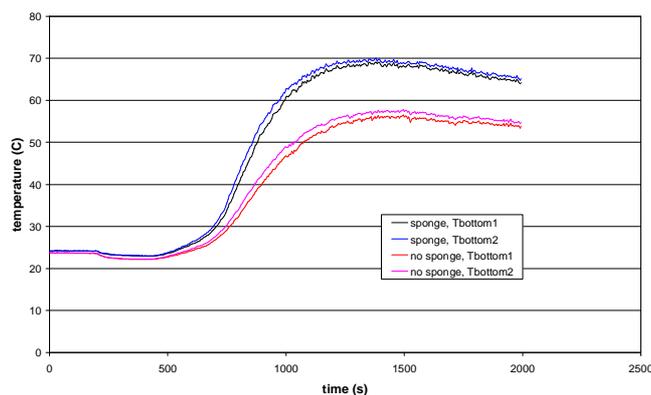


Figure 13: Hydration temperature of zeolite with and without sponge in the evaporator.

Next, it was tried to optimize the removal of all inert gas from the system. It was found that if halfway during the hydration measurement the vacuum pump was switched on again, the temperature in the zeolite bed increased again, even if the setup was evacuated prior to the measurements. An attempt was made to measure the mass increase as a function of time while simultaneously flushing the system for a number of times (by briefly switching on the vacuum pump). The results are shown in Figure 14. Note that for the first number of flushes, the flushing results in a high rate of mass increase that however quickly flattens off, while in later flushes the initial effect of the flushing becomes smaller but also the flattening off seems to become less and less, until after multiple flushes the flushing ceases to have any effect and the rate of mass increase becomes almost continuous. From these results, it was concluded that the initial evacuation of the system was incomplete. A longer evacuation of the zeolite section had no effect, but longer evacuation of the water turned out to influence the results significantly; it turned out that the problem was caused by the inert gas dissolved in the evaporator water. This gas was released from the water during the hydration experiment and blocked the vapor transfer. From this experiment, it was learnt that longer degassing of the water was necessary.

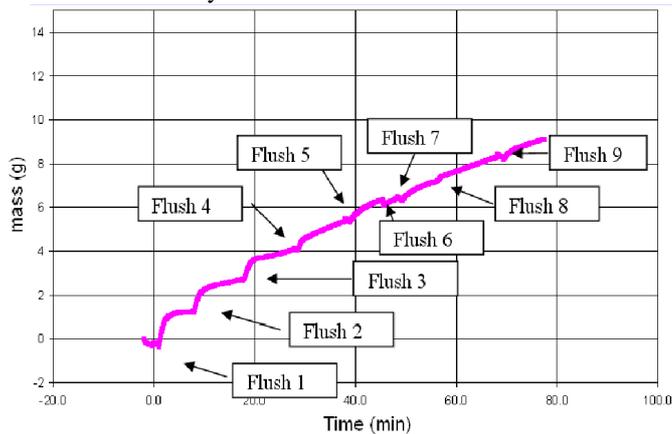


Figure 14: Effect of multiple flushing on mass increase of zeolite

Applying such thoroughly degassed water in the evaporator, significantly higher temperatures were found. For zeolite, the temperature is shown in Figure 15. Zeolite hydration temperatures of up to 120°C were now measured, as compared to temperatures of about 60°C for a single flush (see e.g. Figure 9).

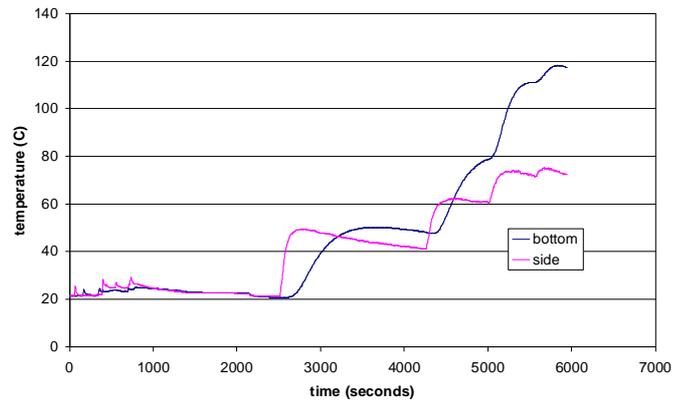


Figure 15: Hydration temperature for zeolite using multiple flushes to degas the water

As an additional check, hydration with fresh water in the evaporator was compared to the case in which water from the previous experiment (partially degassed during this experiment) was reused. The result is shown in Figure 16. Clearly, the partially degassed water leads to higher initial temperatures. After 2700 seconds, an additional flush was applied, which had the largest effect for the fresh water, because for the case with the partially degassed water, a larger amount of the zeolite had already reacted before the flush.

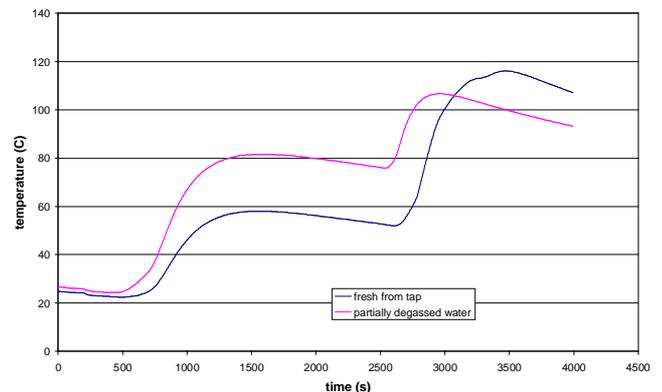


Figure 16: Effect of using partially degassed water.

Finally, the effect of the tube length between the evaporator and the active material was measured. The tube between the active material and the 3-way valve was replaced by various longer tubes and the resulting hydration temperature profiles were recorded, as shown in Figure 17. As shown, a longer tube length can significantly reduce the hydration temperature.

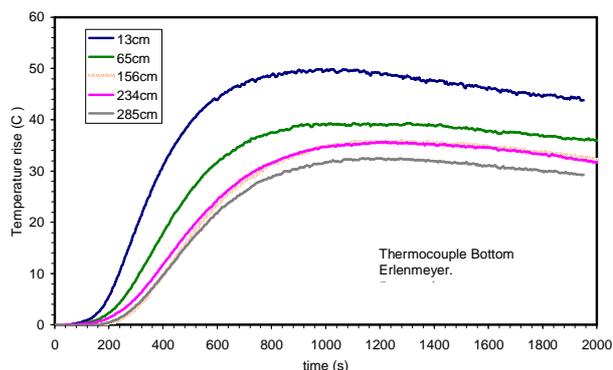


Figure 17: Effect of tube length on hydration temperature of zeolite.

Also the effect of the tube length on the mass increase was measured. Also in this case, a longer tube length was found to reduce the mass increase significantly, as shown in Figure 18.

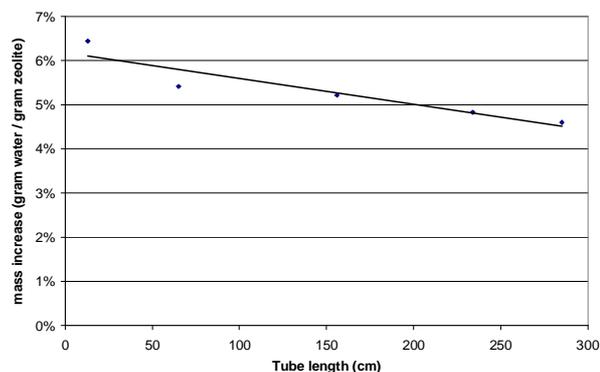


Figure 18: Mass increase on hydration of zeolite as a function of tube length.

8. DISCUSSION AND CONCLUSIONS

From the previous sections, a number of conclusions can be drawn, that have direct consequences for the design of a TC reactor.

- For zeolite, hydration times in the order of 1-2 hours seem possible. Since a power of 3 kW would lead to about 8 kg/hour of TCM flow into the reactor, this leads to a hydration reactor TCM content of about 8-16 kg. However, for salts with a higher energy storage density, hydration times may be longer and the reactor mass will become correspondingly higher.
- For a layer of 2.2 cm thickness, an output power may be obtained of 1.5 kW/m². If the material is stirred, this output power may be doubled to 3 kW/m². Given the required power characteristics of about 3 kW, this would indicate that about 1 m² of heat exchange area could be sufficient in a stirred reactor.

- The zeolite was found to have good flow characteristics; the material could be stirred without problems, both in hydrated and in dehydrated form. This should be examined further, however, for TC salts.
- The evacuation of the setup has a very strong effect on the reactor performance. An important aspect in good reactor evacuation is the degassing of the water in the system. However, also other flow resistances (long tubes, valves etc) will significantly reduce the output power and slow down the hydration.
- The evaporation area should be sufficiently large.

The fact that evacuation was found to be very important for the TC system performance leads to some problems. In particular, in a real TC system, this implies that equipment suitable for vacuum application would need to be applied (e.g. pressure vessels, sealings, special valves etc), considerably adding to the cost of an actual system. First rough estimates indicated almost a doubling of the system cost if such components are necessary.

As an alternative, it could be possible to transport the water vapor by means of a fan. However, if the system is under atmospheric conditions, this implies relatively large airflows to transport the vapor (note that in ambient air, the water vapor mass is about 0.6% of the total air mass). This considerably adds to the electrical energy required to drive the system. An atmospheric system is possible in practice, but care should be taken that air channels are large enough not to cause too much pressure drop. This will make all air channels for vapor transport considerably larger.

At present, at ECN, investigations are ongoing into both atmospheric and evacuated systems. And both systems will require careful optimization before they may be applied in practice.

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