HYDRATION AND DEHYDRATION OF SORPTION MATERIALS: EXPERIMENTS IN A SMALL-SCALE REACTOR

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INTRODUCTION

The present concern about themes like the greenhouse effect, pollution, renewable energy and a durable society has incited researchers to find better ways of using the limited energy resources at our disposal. Solar energy is one of the most promising ways of power generation to limit the greenhouse effect by reducing CO2-emissions. Numerous solar energy systems have been studied and/or are under development like photovoltaic systems, combined photovoltaic and thermal systems, direct solar heating and cooling systems for air conditioning or refrigeration. Whatever the application is, an obvious, yet basic, characteristic of solar systems is the dependence of their performance on the seasonal weather conditions and on the day/night cycle. The fluctuating solar energy availability makes solar energy solutions difficult to control. The energy demand does not always correspond with the solar energy availability. The increasing use of solar energy highly depends on the development of reliable and economically viable storage systems. This work is a contribution to the development of seasonal storage systems of solar heat.

The most often used thermal storage systems are based on hot water storage and phase change materials (PCMs). Their integration in solar systems has been studied, developed and optimized. These systems are relatively simple to realize, with a reasonable cycle yield. However, thermochemical materials (TCM’s) used in sorption systems form a promising alternative. A literature research into candidate materials for use in a thermo-chemical seasonal storage was performed by Visscher [2004]. A number of salt-hydrates was investigated of which magnesium sulfate heptahydrate had the most promising properties. Thermogravimetric experiments on small samples as carried out by Paulik [1981], van de Voort [2007], He et al. [2007] and Essen et al. [2008] show indeed its high potential. The equilibrium reaction of a salt-hydrate can be presented as follows:

\[ \text{salt} \cdot x \text{H}_2\text{O}(s) + \text{Heat} \rightarrow \text{salt} \cdot (x-y) \text{H}_2\text{O}(s) + y\text{H}_2\text{O}(g) \]  \hspace{1cm} (1)

The reaction to the right is called the dehydration reaction which occurs when heat is added to the hydrated salt. The reaction to the left is called the hydration reaction and occurs when water vapour is brought in contact with a dehydrated salt. During this reaction heat is released.

The present study focuses on preliminary experiments to test the suitability of TCM’s as seasonal heat storage material. To that end a reactor is built in which controlled hydration and dehydration experiments are carried out. During the hydration and dehydration cycle temperature profiles are
measured in the reactor to gain insight into the heat and mass transfer processes. Firstly a general description is given of the experimental set-up with special attention to the design of the reactor. Secondly some results are presented of hydration experiments of zeolite 13X and magnesium sulfate heptahydrate. Finally some conclusions are drawn and directions are given for further research.

**EXPERIMENTAL SET-UP**

The main components of the experimental device are the reactor, a heater and an evaporator. Figure 1-left shows a picture of the experimental device. At the left hand side, the pressure at the air inflow (AI) is 7.5 bar. The incoming freeze-dried air flow is filtered by filter (F) and measured and regulated by the gas flow controller (GFC). During a dehydration experiment this air flows at the bottom side of the system through the heater (H) into the reactor (R). during a hydration experiment water is pressed out of the water vessel (WV) by the airflow and measured by the liquid flow controller (LFC). So a controlled water and air stream flows into the controlled evaporator mixer (CEM). By giving set points for the airflow, water flow and temperature, the humidity of the mixture can be controlled. Then the mixture of humid and/or hot air flows into the reactor and then via the condense vessel (CV) to the outflow (O). A humidity data logger (HDL) is used to measure the humidity at the outflow and a thermocouple data logger (TDL) is used to readout the temperature profile of the reactor. The evaporator system is controlled by the computer via the CEM-controller (CC). The heater is controlled by the heat regulator (HR). A more detailed description of the experimental device can be found in Brouwer [2008].

The reactor design consists of a tube with a length of 100 mm and an inner diameter of 60 mm filled with a sorption material. It is made of glass to enable visual inspection of processes like volume changes, layer formation and fluidization. The maximum gauge pressure inside the reactor is 4 bar. The reactor design is shown in figure 1-right. The reactor is placed between two Teflon flanges, which position the filters and seals. The flat seals close the connection between the reactor and the flange as well as the connection between the reactor and the filters. Two clamps are used to close the reactor. The material is fixed between the two filters which can be replaced so that different grain sizes can be tested. The filters have a maximum pore size of 8 micrometer and cause a pressure drop of less than 100 mbar at the maximum flow speed used.
Seven thermocouples are positioned at the central axis of the reactor to estimate the energy flows through the reactor: five (T2-T6) inside the reactor - to determine the temperature profile inside the material, one (T1) at the inlet - to determine the temperature of the gas which enters the reactor and one (T7) at the exit of the reactor - to determine the outlet gas temperature. To determine the heat loss through the glass, 2 thermocouples (T8 and T9) are positioned at the reactor wall.

Figure 2 shows the energy flows during a hydration or dehydration experiment. $Q_{\text{sorption}}$ is the quantity to be calculated representing the sorption energy and is negative during the dehydration reaction and positive during the hydration reaction. This quantity can not be directly measured in the present experiment but needs to be derived from considering an energy balance.

![Figure 2. Heat flows during an experiment](image)

The heat balance over the reactor can be written as:

$$Q_{\text{air in}} + Q_{\text{vapor in}} = Q_{\text{air out}} + Q_{\text{vapor out}} + Q_{\text{conduction}} + Q_{\text{material}} + Q_{\text{sorption}}$$  \hspace{1cm} (2)

with $Q_{\text{air in}}$ the heat content of the incoming air, $Q_{\text{vapor in}}$ the heat content of the incoming vapor, $Q_{\text{air out}}$ the heat content of the outgoing air, $Q_{\text{vapor out}}$ the heat content of the outgoing vapor, $Q_{\text{conduction}}$ the heat loss through the wall and $Q_{\text{material}}$ the heat needed to heat up the material (all in Watts). Details about how to calculate the heat flows can be found in Brouwer [2008]. In the result section below the heat loss through the wall during the hydration experiment of zeolite 13X is calculated as function of time using the temperature measurements.

**RESULTS**

**Zeolite 13X** During the experiment a regulated gas flow of 12 l/min and a liquid flow of 0.33 g/min enter the reactor. The resulting temperature profiles are presented in figure 3-top. The temperature of the inlet mixture has a constant value of about 26 °C. The thermocouples T2, T3, T4 and T5 show successive temperature peaks. This is caused by a moving reaction front. The smaller this front, the more concentrated the energy released and so the higher the temperatures reached. Thermocouple T3 registered the highest temperature of 98 °C. The maximum at that position is caused by two opposing effects. First there is preheating of the material downstream of the reaction front by the hot air-vapor mixture, which would lead to higher temperatures further inside the reactor. However, not all water vapor is consumed within the reaction front so material downstream...
the reaction front will hydrate in steps. So, deeper inside the reactor the salt loses some of its stored energy before the reaction front passes and, as a consequence, less elevated temperatures are reached which last longer.

The above reasoning is supported by figure 3-bottom, in which the mass fluxes of the vapor in- and outflow are shown. The vapor inflow is kept constant by the liquid flow controller and has a value of about 5.5 mg/s during this experiment. The amount of vapor present in the inflowing air has to be added to this value, which gives a total inflow of 5.8 mg/s. The vapor outflow is not constant: at the start of the experiment it decreases to zero, after 80 minutes it starts to rise and it stabilizes after 200 minutes. Figure 3 shows that the moment the vapor outflow increases, the reaction front is positioned around T4 in the middle of the reactor. So, not all vapor is consumed at the moment the reaction front passes. After about 250 minutes the outflow stabilizes. However, this is a distorted representation since a maximum relative humidity of 100 % was measured. According to these measurements 52 g water was adsorbed by the system after 250 minutes.

![Figure 3. Temperature profiles in the reactor (top) and vapor in- and outflow (bottom) as function of time during the hydration reaction of zeolite 13X.](image-url)
The temperature gradient over the reactor wall is presented in figure 4-top. The reactor was insulated during this experiment. Before the temperature peak is reached the inside wall temperature is higher than the outside wall temperature, but a few moments later the tables are turned. This is caused by the cooling effect of the inlet gas mixture after the reaction front has passed. It cools down the reactor wall from the inside, so after about 50 minutes the outside wall temperature exceeds the inside wall temperature.

The thermocouples at the wall, T8 and T9, are at the same height as the axially placed thermocouple T3. However, the maximum temperature at the wall is reached earlier as can be noticed by comparing the sketches in figure 4-left with the sketch of T3 in figure 3-top. Probably this is caused by the higher porosity at the wall.

The temperature data as presented in figure 4-top is used to convert the temperature gradient over the wall into an estimation of the heat loss through the wall by conduction:

Figure 4. Temperature gradient over the reactor wall (top) and estimated conduction heat loss through the reactor wall (bottom) as function of time during the hydration reaction of zeolite 13X.
\[ Q_{\text{conduction}} = -\lambda \frac{\Delta T}{\Delta x} A \]  

with \( \lambda \) the heat conduction coefficient of the glass, \( \Delta T \) the temperature difference over the wall, \( \Delta x \) the thickness of the glass wall and \( A \) the surface area of the glass wall. The result is presented in figure 4-bottom as \( Q_{\text{conduction at position T3}} \). A peak value is present the moment the reaction front passes and the moment the outside wall temperature exceeds the inside wall temperature, its value becomes negative. It is clear that the conduction through the reactor wall cannot be interpreted as homogeneous over the whole reactor wall. However in order to get an impression of the energy flows during the experiment, the mean conduction through the reactor wall as function of time has to be approximated. The largest temperature gradients lead to the highest values for conduction, so the measured conduction at position T3 (the position where the maximal axial temperature was measured) will be about the peak value for conduction, therefore the mean peak value will be smaller than this value. Like the propagation of the axial temperature profile, the following peak values will be lower but the elevated values last longer. The cooling of the glass reactor even leads to negative values for \( Q_{\text{conduction}} \).

![Energy flows as function of time](image)

Figure 5. Heat flows as function of time during the hydration reaction of zeolite 13X

In Brouwer [2008] all other heat flows were also estimated (\( Q_{\text{air in}}, Q_{\text{vapor in}}, Q_{\text{air out}}, Q_{\text{vapor out}} \) and \( Q_{\text{material}} \)) needed to calculate the heat of sorption \( Q_{\text{sorption}} \) according to equation (2). The results are presented in figure 5. The propagation of the sorption energy as presented in figure 5 is not realistic. First a peak value is reached, then it approaches zero. For the period from 50 to 140 minutes it has a negative value, which is not likely since figure 3-top shows that after 100 minutes the reaction front still moves through the reactor and therefore heat is released by adsorption. Besides, it can be seen that the conduction loss through the glass wall is large compared to the heat of sorption over a large time interval. Most probable cause of the unrealistic results for the heat of sorption is the inaccuracy in the calculation of the heat losses. In future experiments these heat losses should be minimized further and should be measured with a higher accuracy.

**Magnesium sulfate** For the hydration reaction with magnesium sulfate the reactor was filled with 150 g of salt, insulated and then dehydrated. Figure 6-top shows the temperature profile during the
hydration reaction in which the highest temperatures were reached. The set point of the heater was 12% and a water flow of 8.6 mg/s water was mixed with a gas flow of 30 ln/min. The gauge pressure at the reactor inlet was 1.0 bar and at the outlet atmospheric pressure is assumed. The maximum temperature of 50 °C, reached after 11 minutes, was measured by thermocouple T5; the last one inside the bed. After the dehydration reaction, the reactor was cooled with freeze dried air that nevertheless contained some vapor, this probably already resulted in the conversion of some salt. This conversion and the higher flow velocity probably caused that this time the vapor transport was less limiting than during the experiment with zeolite. A less clear reaction front formed and from the start of the experiment the salt reacted with the vapor everywhere in the reactor. However, at the start the vapor concentration decreased towards the top side of the reactor by the reaction that took place. Subsequently at the bottom side, the reaction was terminated earlier and preheated the air, so that the highest temperatures were reached at the top side of the reactor.

As can be seen from figure 6-bottom, at the start of the experiment almost all vapor is consumed by the salt, but after 100 minutes the vapor outflow approaches the inflow even though the reaction has not stopped. Possibly this can be clarified with the assumption of a shrinking core model. The reaction at the outer surface of the grains develops fast, but stagnates towards the center due to the low porosity of the solid. If this is the case, higher temperatures can be reached by grinding the salt. Another possible solution is creating a vacuum inside the reactor so that fewer molecules block the transport of vapor inside the grains. Other causes can be the used salt or that the salt is transposed to a form that reacts badly.

A final finding that is worth mentioning in this respect is that during one of the experiments some water vapor condensed inside the reactor. As a result, the magnesium sulfate got lumpy and demonstrated resemblance with limestone. Besides that, the magnesium sulfate was hard to get out of the reactor and the salt did not perform as well as before: the pressure drop over the reactor increased and lower temperatures were reached during following experiments.
CONCLUSION AND PROGRESS

The experimental device has been tested by several experiments with zeolite and magnesium sulfate. During these introductory tests, hydration temperatures of respectively 97 ºC and 50 ºC were reached. Based on the measured temperature profiles insight can be gained into the heat and mass transfer processes in the reactor. Using the experimental device, different TCM’s with different grain sizes can be investigated under varying operating conditions. Further research into the operating conditions and into the reasons why magnesium sulfate reacted in such a limited way is required. This insight can be used for the design of a seasonal heat storage system using sorption materials.
REFERENCES


