

Internship report
Design of a TCM heat store cycle setup
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Abstract

In renewable energy technology the gap between supply and demand of heat is an obstacle in applying durable technologies. Therefore heat storage is an important issue in durable energy technology. One possible option for storing heat is by means of thermo chemical materials, also called TCM. One promising group of possible TCM is the salt hydrate group. In selecting a suitable TCM-salt hydrate the durability is an important factor. With durability is meant the capacity to cycle between a hydrated state and a dehydrated state. This capacity may deteriorate after a number of cycles. Goal of this research is to design a setup for testing the durability of TCM-salt hydrates. A link is made between the process during the cycle and issues facing the setup in practice. The separate functions the setup must perform are listed. From the components required for these functions a setup is devised.

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Preface

This is the internship report of Pim Goedhart, student at the technical university of Eindhoven, department mechanical engineering. The internship is performed at ECN-EGON. In this internship a design for a cycling apparatus for TCM heat storage is designed. The Energy research Center of the Netherlands is a research institute on all areas of renewable energy technology and ECN's main assignment is to form a bridge between fundamental research and application. It is situated near the picturesque village of Petten, in the province Noord-Holland in the Netherlands. The unit Energy in the built environment is specialized in applying durable energy in the built environment. One of its research areas is thermal systems and more specifically heat storage. One of its projects is called WAELS (Woningen Als Energie Leverend Systeem; houses as energy supplying system), the work done in this report is in service of this research. The main goal of WAELS is to make the first steps on the route towards an energy neutral built environment.

Chapter 1

Introduction

This report is a survey to the design an instrument for cycling TCM-salt hydrates, in order to determine the durability of the heat storage capability. A cycle consists of a hydrating and a dehydrating step. TCM are materials potentially used for heat storage or heat pump applications.

The work is done for the project WAELS, which goal is to determine whether TCM's in general and the salt-hydrate magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$ or epsom salt) specifically is potential diurnal heat storage material. The heat storage capacity depends on the capability to hydrate and dehydrate. This may deteriorate after a number of cycles and is therefore an important issue. The hydrating / dehydrating capacity and speed can be affected by contamination, melt and crystal structure reorientation as a result of disperse heat and mass transfer. This is specific per TCM and is a criterion for determining whether the TCM is suitable for the use of thermal heat storage.

At this research stage, the proof of principle is examined. In the master thesis *Characterization of a thermo chemical storage material* [1] magnesium sulfate heptahydrate was characterized by experiments. For background information about energy storage systems and TCM the reader is referred to this report. In [1] samples with a small mass and only dehydration is examined. In bulk materials the temperature will not be uniform through the material due to transient effects in heat and mass transfer, a fact which is assumed in [1]. Therefore there is a need for experiments with larger samples including the hydration step. The aim of this internship is to design a large sample cycling for experimental use setup.

The setup must be able to preform thermal cycles of TCM-salt hydrate, which means going through several hydration and dehydration steps.

Therefore a list of requirements for the measuring setup is made.

The setup must be able to:

- Determine the degree of hydration
- Measure mass between 1-40 g with a sensibility of 0.1 g.
- Heat the sample from 25-300 °C.
- Evacuate the inert gasses.
- Controle vapor pressure at the sample.

- Perform multiple cycles fully automatic
- Have a sample holder which can be externally examined for analysis

The second chapter is about the background of TCM heat storage. Chapter 3 contains the theory of the processes and parameters involved in the cycling operation. Chapter 3 also describes exploratory experiments which are undertaken in order to grasp the behavior of the matter. Finally chapter 4 lists test setups from literature and available off-the-market are examined. A setup complying to our operational demands is designed and described. Conclusions are made in chapter 5.

Chapter 2

Background

2.1 Heat storage

The last decennia the reduction of carbon dioxide emission has become a big topic. This is the a result of two phenomena, namely: global warming and fossil fuel depletion. There is not a single solution, so the complete field of energy needs to change. Generally it is stated that the energy consumption is divided in three areas. Energy needed for transport, electricity and heating.

Heating consumption can be dived into industrial and domestic heating. Solar collectors can produce durable heat in a domestic environment, but only produce heat effectively (in summer) and not when there is a high demand (winter). The need for storage is evident.

How to store heat collected during the summer to use in the winter remains a technical challenge after more than 30 years of research and development [7].

The material of an effective heat storage system must be fully reversible, have a high energy density and good durability. Several options are applied, like using: sensible heat (e.g. heat capacity of water), latent heat or melting enthalpy (e.g. certain paraffins) and chemical heat (e.g. reversible chemical reaction).

Thermochemical storage systems consists of a sorbate - sorbent pair. When the sorbate adsorbs the sorbent, the sorbent is closely bound by v/d Waals forces. This is called physisorption and is the proces behind heat storage materials like porous solids (e.g. silica gel, zeolite). The sorbate can also absorb the sorbent. Then the sorbent is bound by chemical bounds. This is also called chemisorption in literature .

One group of TCMs is the group of salt hydrates. The sorbate or working fluid is water. When the salt is heated, the structural water is driven off. Exposure to water vapor will initiate the reverse reaction and generate heat. A schematic representation is given in figure 2.1 . The reaction looks like:



A very promising TCM sorbent candidate is magnesium sulfaat. The characteristics of this material are examined in the reports [1] to [4]. It is still unclear how to apply the material

so it is suitable as efficient heat storage. Unanswered questions still remaining are about the kinetics of the process, the morphology (crystallinity, porosity, grain size distributions) , the driving forces (T , P_v , activation energy) and heat and mass transfer. One of the unanswered questions is whether the material is durable enough to undergo multiple cycles.

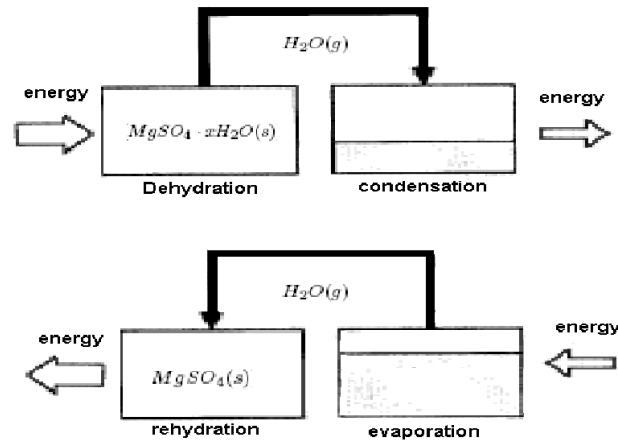


Figure 2.1: TCM heat storage principle based on Magnesium sulfate hydrate

Chapter 3

Theory and experiments

In this chapter the theory of kinetics behind the cycle proces is explored. First is the fundamental process of the material examined, then the processes in the system. Finally some practice experience is acquired by some small experiments.

3.1 Material processes

The heat storage application of TCM is based on a reversible reaction, where dehydration an endotherm process is and hydration exotherm is. During a cycle, water molecules move in and out the crystal lattice. Then they move through a packed bed of particles of the sample into a reactor environment. The TCM morphology changes during a cycle. The material properties, like : volume, mass, enthalpy and entropy are not constant. This has influence on the system properties like mass and heat transport [3].

The state or phase of the material is governed by temperature and vapor pressure and is determined by the number of bound water molecules in the lattice [1]. This is given by the mole fraction is a dimensionless quantity for bound water molecules in the lattice, [9]. Fully hydrated epsomite the number is one, anhydrous magnesium sulfaat has the number zero. The mol fraction x of $MgSO_4$ is given by:

$$x = \frac{\frac{m_{sample}}{m_{epsomite}} - \frac{M_{MgSO_4}}{M_{epsomite}}}{1 - \frac{M_{MgSO_4}}{M_{epsomite}}} \quad (3.1)$$

$$M_{epsomite} = 246.48 \left[\frac{g}{mol} \right]$$

$$M_{MgSO_4} = 120.367 \left[\frac{g}{mol} \right]$$

3.1.1 Crystal structure

As stated before the morphology of the material changes during re/decomposition. Understanding of this phenomena is one of the main goals of the research. Magnesium sulfaat hydrate re/decomposition is very complex. The material will frequently become amorphous [2]. The great reorientation of molecules in the crystal lattice can be seen in the two figures. First the base material, crystalline epsomite ($MgSO_4 \cdot 7H_2O(s)$), see figure 3.1.

Secondly is a crystalline transition between hexahydrate ($MgSO_4 \cdot 6H_2O(s)$) and kieserite ($MgSO_4 \cdot H_2O(s)$), see figure 3.2. This transition is in practice meta stable leads to amorphous structures.

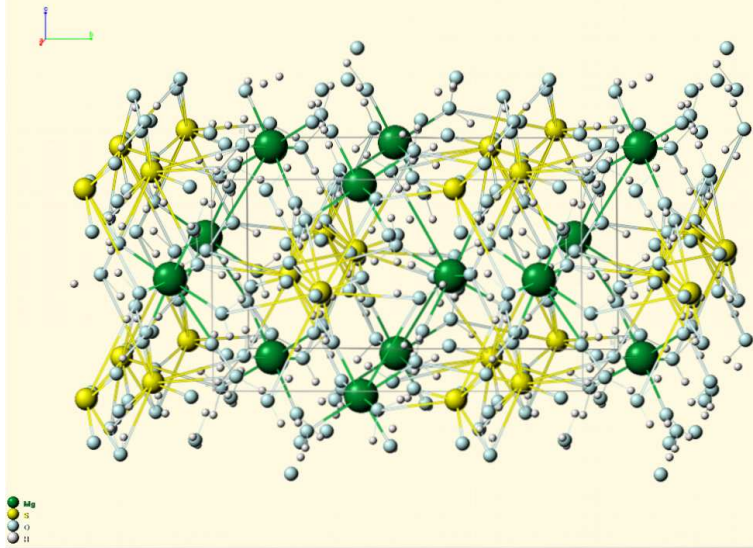


Figure 3.1: *Crystal structure epsomite $MgSO_4 \cdot 7H_2O(s)$*

3.1.2 Phase transitions

The transitions mechanisms between epsomite and anhydrous magnesium sulfate ($MgSO_4$) are stepwise [2]. Above 25 degrees Celsius epsomite, hexahydrate and kieserite are the only stable hydrates [3]. Only at the first and the last transition a single step in mass and temperature is visible, indicating a single water molecule re/deattached per unity cell in the whole sample. These stable phase transitions are the transition between the stable phases epsomite \rightleftharpoons hexahydrate and kieserite \rightleftharpoons magnesium sulfate and therefore are well defined in the literature, but the phases in between depend on the process parameters and frequently are amorphous and heterogenous in composition, see figure 3.3. The only way to obtain accurate vapor-solid equilibrium data is by measurement. This can also be seen from thermo-gravimetric measurements where the previously named stable transitions depict a sharp transition between mass and temperature, while the in-between-transitions form a wide band [1].

3.1.3 Kinetics

During a chemical reaction enthalpy and entropy change. The free Gibbs energy combines these quantities in order to determine whether reaction is spontaneous. Equilibrium occurs when the free Gibbs energy is zero. At equilibrium the forward reaction rate equals the

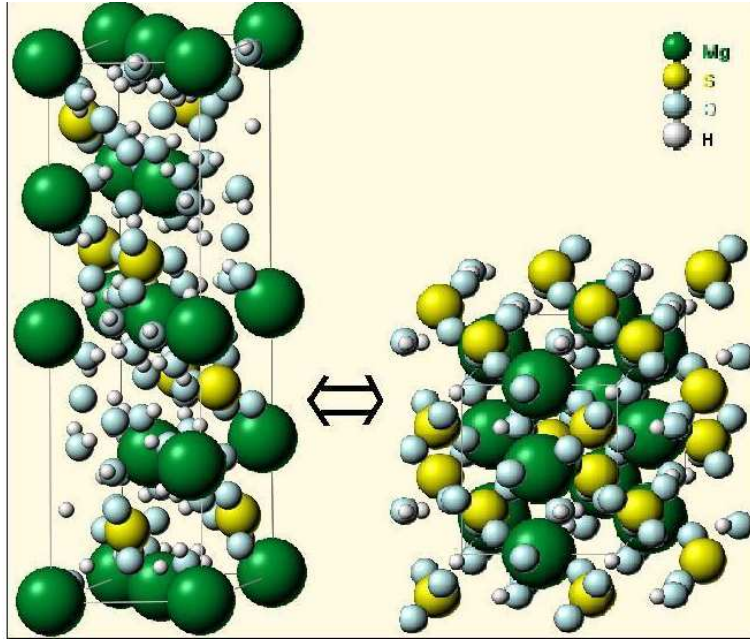


Figure 3.2: *Crystal structure change hexahydrate-kieserite* $MgSO_4 \cdot H_2O(s) - MgSO_4 \cdot 6H_2O(s)$

backward reaction rate. For an magnesium sulfate reaction this relation is , see eq 3.2.

$$k_f[MgSO_4 \cdot xH_2O(s)] = k_b[MgSO_4 \cdot (x - y)H_2O(s)][H_2O(g)]^y \quad (3.2)$$

The equilibrium constant is defined as eq. 3.3:

$$K \equiv \frac{k_f}{k_b} = \exp\left(\frac{\Delta G_0}{RT}\right) = \frac{[MgSO_4 \cdot (x - y)H_2O(s)][H_2O(g)]}{[MgSO_4 \cdot xH_2O(s)]} = \frac{p_{vapor}}{p_{atm}} \quad (3.3)$$

This relation is a first order reaction, typical for a monovariant single step reaction. The forward reaction speed is then determined by the 1st order Arrhenius eq. 3.4. The forward reaction is first order, but the backwards reaction has a higher order.

$$k_f = A \exp \frac{-E_0}{RT} \quad (3.4)$$

The first order thermal dehydration reaction rate is low. Kinetic parameters (E_a and A) depend on mole fraction [2]. Dehydrating with an high heating rate or with a thick layer will result disperse heat / mass flux. The composition can become heterogenous (more phases in the bulk at one temperature) and locally $T > T_{melting}$. The temperature distribution in a dehydrating layer is modeled [1]. The limiting factor in kinetically dehydrating is the melting temperature of the salt.

When the k_f is temperature depended [1] and the K is determined by the p_{vapor} . So at a temperature the k_f is constant and the vapor pressure determines whether the system dehydrates ($k_f < k_b$), is equilibrium ($k_f = k_b$) or hydrates ($k_f > k_b$).

The Thiele modulus determines whether the reaction is controlled by diffusion or kinetics.

$$Th = R_p \sqrt{\frac{k}{D}} \quad (3.5)$$

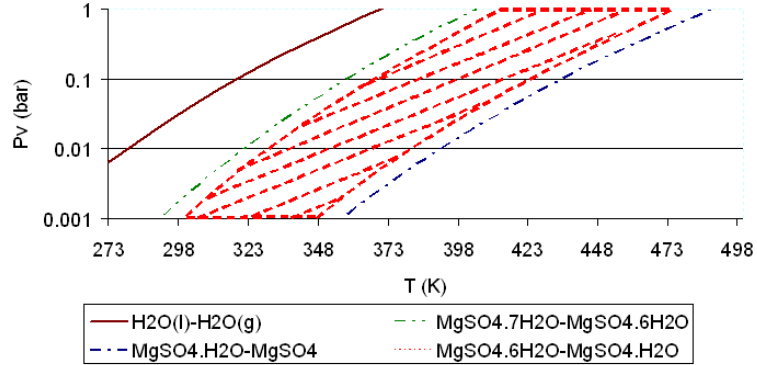


Figure 3.3: Vapor pressure vs temperature according to literature (NBS)

The dehydration experiments in [1] are near the threshold at which diffusion begins to be important. From experiments the hydration step runs slower than dehydration. The reaction is probably not single step. This leads to a higher order reaction rate. The dispersed mass and heat transport effects also have an influence.

3.2 Transport phenomena

The resistances to heat and mass transfer can play important roles in determining the rate of reaction between gas and solid. The sample will operate at set number of conditions, see 1. Pressure, temperature and vapor concentration will influence the transport phenomena near the sample.

3.2.1 Mass transport

During a cycle water vapor is transported from and to the sample. The medium consists of water vapor and inert gases and form a two component system. Due to the reaction kinetics a relative vapor pressure exists around the sample, see figure 3.4. During hydration water vapor is absorbed at the wall, so a mass flux of vapor moves towards the wall. This convective flow will transport both vapor and inert gases ($N_{total} = N_{vapor} + N_{inert}$). The average linear speed is defined as, see eq. 3.6

$$\bar{v} = \frac{N_{total}}{C_{total}} \quad (3.6)$$

As a consequence water will diffuse towards the wall and inert gases will diffuse away from the wall.

Fick's law of diffusion needs to be corrected for this flow. The mass flux will now consist of

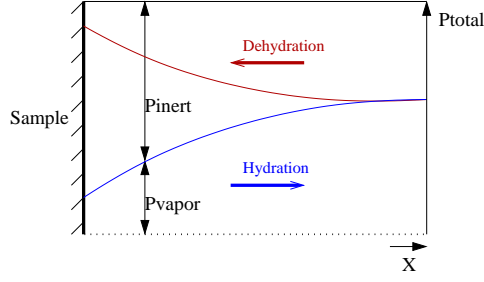


Figure 3.4: Vapor transport mechanism

a convective term and a diffusive term, see eq. 3.7

$$N_{vapor} = C_{vapor}\bar{v} - \mathbb{D}_{air \rightarrow vapor} \frac{dC_{vapor}}{dx} \quad (3.7)$$

If assumed that no inert gasses are absorbed, $N_{inert} = 0$. From this result the *Stefan law* is derived, see eq 3.8. This is a relation for vapor mass flux through air.

$$N_{vapor} = - \frac{P_{total}}{P_{total} - P_{inert}} \frac{\mathbb{D}_{air \rightarrow vapor}}{RT} \frac{dP_{vapor}}{dx} \quad (3.8)$$

When the inert gas are evacuated the water flux increases.

Rehydration is slow at relative pressure $\frac{P_{vapor}}{P_{vapor, equilibrium}}$ and increases linear with higher relative pressure [5].

The diffusion coefficient of water in air [12] is temperature and pressure depend, see eq 3.9.

$$\frac{P\mathbb{D}_{air \rightarrow vapor}}{(P_{crit,air}P_{crit,vapor})^{\frac{1}{3}}(T_{crit,air}T_{crit,vapor})^{\frac{5}{12}}(\frac{1}{M_{air}}\frac{1}{M_{water}})^{\frac{1}{2}}} = 3,64 \cdot 10^{-4} \left(\frac{T}{(T_{crit,air}T_{crit,vapor})^{\frac{1}{2}}} \right)^{2,334} \quad (3.9)$$

The molaire transport coefficient for free convection is determined by the Sherwood correlation, see eq 3.10 .

$$Sh = \frac{k_{mass}D_p}{c_f\mathbb{D}_{air \rightarrow vapor}} \quad (3.10)$$

As stated earlier the reaction speed is dominantly driven by kinetics, and thus temperature. When dehydrating the sample the temperature transport governs the reaction [1]. During hydration the material cools down much faster then the reaction rate of water binding to the sample. So at a low temperature ($T = 25^{\circ}celcius$) there is not equilibrium but an excess of free Gibbs energy. The vapor pressure difference between the atmosphere and the sample is the driving force.

The pressure drop in the sample must be small [14]. The vapor mass transport takes place at the surface and in the porous channels. Granular material consist of many channels running criss-cross though the material. The total volume of these channels per volume unit of the total porous material is the porosity and is around 0.5 for $MgSO_4$ [1]. This effects the diffusivity. The diffusivity in the material is corrected by the porosity ϵ and the tortuosity β , see eq 3.11.

$$\mathbb{D}_{intern} = \frac{\epsilon}{\beta^2} \mathbb{D}_{air \rightarrow vapor} \quad (3.11)$$

3.2.2 Heat transport

The heat effects that occur during a cycle must be transported fast from / to the sample. Otherwise a heterogeneous composition of phases is created ,which can cause melting problems. A high effective heat conduction is needed in the sample and a good heat transport in the air/vapor medium [14].

The only controllable parameter for high effective heat conduction in the sample is higher surface area between the particles. So larger particles of TCM is better for effective heat conduction then smaller particles.

The conduction heat transfer is determined by Fourier law. The heat transfer coefficient of air is very small, so conduction in air is not a significant of heat transport in the medium. The degree convection contributes for heat transport in the medium is mainly depend on the vapor pressure. During hydration the vapor pressure is low. So only radiation, which is independent of the medium pressure is an effective means of heat transport.

3.3 Experiments

Seven exploratory experiments were preformed to find the factors which influence the cycle. The factors that can influence dehydration and hydration are:

- Particle size
- Dehydration heating rate
- Pressure during hydration
- Relative humidity

For the experiments samples of 10 g and were spread in a petri dish of 10 cm diameter. In table 3.1 7 experiments are summarized varying these factors. The hydration rate is plotted in figure 3.5. The hydration was not stepwise like the dehydration, but had a continuous, quadratic course, see figure 3.5. Benefactors for high hydration rate are , low system pressure, high relative humidity and relative large particles . But still hydration under these conditions is a relative slow proces compared to dehydration. The experiments are described more detailed in appendix A.1

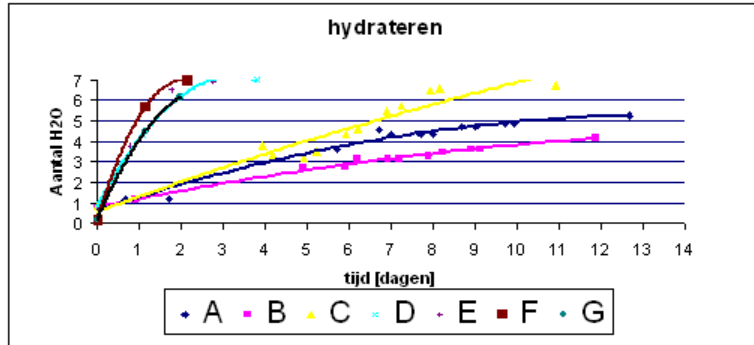


Figure 3.5: *hydrateren*

<i>experiment</i>	<i>dehydration conditions</i>		<i>Hydration conditions</i>		
	<i>particle size</i>	<i>dehydration K/min</i>	<i>Hydration pressure</i>	<i>RH in %</i>	<i># days</i>
A	full range	0.4	atm.	40	13
B	full range	4	atm.	40	12
C	full range	4	closed space atm.	70	7
D	full range	4	0.5 bar	90	2.5
E	100 – 200 μm	1	0.5 bar	80	2.5
F	200 – 500 μm	1	0.5 bar	100	2
G	200 – 500 μm	1	closed space atm.	100	2

Table 3.1: *Hydration experiments*

Chapter 4

Systems design

In this chapter systems for cycling TCM are investigated. First the system requirements are examined. System devices are put in appendix A.2. Secondly the operational procedures are elaborated. Finally existing systems from literature and "off the shelf solutions" are evaluated and a setup that meets our system requirements is made.

4.1 System requirements

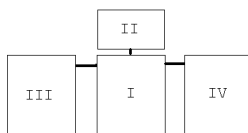


Figure 4.1: *Schematic representation system*

The system will consist of a reactor chamber (I), here a conditioned environment of temperature and vapor pressure surround a sample of TCM-salt hydrate. Secondly a device for measuring mass of the sample (II). A vacuum system (III) for controlling the total pressure and (IV) a system controlling the vapor pressure .

4.1.1 Pressure

The theory and experiments in chapter 3 show that vapor transport is pressure depended. Because the diffusion coefficient is pressure depended, see eq 3.9 and hydration experiments goes faster in a low pressure environment , see figure 3.5. A vacuum pump will reduce the pressure till the low and medium vacuum range (100 to 3 kPa) [10]. The minimum pressure aimed for is the saturation pressure of water at room temperature ($298K \Rightarrow \pm 30mbar$). Water will evaporate when the vapor pressure is higher then the atmosphere pressure. The vapor pressure needs to be measured and recorded for analyzing reasons. The pressure is maintained by a vacuum controller. The controller wil govern when the pump operates and

which automatic vacuum valves is open or closed. The two operation modes (re/dehydrating) have different configurations, see chapter 4.2.

Vacuum pump

The vacuum pump needs to be robust, durable and simple to operate. TCM's can have a volatile and / or corrosive sorbent. A salt hydrate TCM operates in a water vapor environment, so the pump must be water vapor tolerant. In low to medium range vacuum positive displacement pumps are commonly used. There are three types of positive displacement vacuum pumps of interest [15].

Pressure measuring and control

A vacuum controller keeps the pressure at the desired value, see figure A.1. During hydration this is the saturation pressure at the certain temperature. Elastic elements such as diaphragms and capsules are used as sensing elements in combination with different displacement transducers for low/medium vacuum [10].

Vapor transport

Vapor transport is an essential part of a heat storage system based on salt hydrate TCM. The amount of bounded water to salt hydrate is the mechanism for storing energy, see eq 3.3. Vapor is transported from and to the reactor chamber by the vapor system, see figure 2.1. The vapor system consists of thermal controlled vessels, one with water and/or one with desiccant. The flux of the vapor is determined by Fick's law. Diffusion coefficient and the contact surface area determine the speed the vapor pressure reacts to pressure change. The vapor pressure of water and desiccant is a function of temperature and thus can be controlled by temperature. At all times the temperature in the system must be higher than the saturation temperature to avoid condensation. Therefore the temperature of the vapor system is lower than the reactor chamber temperature. The tubes connecting the systems must be temperature controlled by tube jackets.

4.1.2 Temperature

There are three thermal zones. The first zone is the *reactor zone*, where the sample undergoes the cycle. The temperature range will be 298-573 K. The eventual system will operate at lower temperatures. These are limited by the solar collector. The second thermal zone is the *mass measuring zone*. The mass measuring device usually has a maximum temperature of $\pm 80^\circ$ Celsius. Thermal stress can influence the measurement so it is important to keep the mass sensor at a constant temperature, either by purge gassing or external cooling. The third zone is the *vapor control zone*. Here water reservoirs with heaters can control the vapor pressure in the system and thus add or remove vapor from the sample.

Heating

Heating methods are divided heat transport mechanism: conduction, convection and radiation. The sample can be directly heated or separated by a air vapor mixture. In the theory is stated that convection is depended on pressure. Conduction through air is independent of pressure, but very low. So the only effective and fast way to heat a sample in a rough vacuum is by radiation.

Temperature measuring and control

Commonly two kinds of temperature sensors are used: nm. The thermocouple and the electrical resistance sensor.

Temperature control

Temperature control is a process in which the temperature of an object is measured and the passage of heat energy into or out of the object is adjusted to achieve a desired temperature. A controller varies the amount of heat or cooling provided by the heater depending on the difference between the required temperature (the "setpoint") and the actual temperature. This minimizes over/undershoot. This process is called PID (Proportional-Integral-Derivative)is a common feedback loop component in industrial control systems and is implemented using a PID Controller.

4.1.3 Mass

Mass is the primary indicator for determining the dehydration degree, eq 3.1. The purpose of this cycling apparatus is up scaling the sample mass, in order to examine the disperse mass and heat transport. The TGA measurements in [1] till [4] are in the range of 10-40 mg . Scaling up a factor 1000 higher mass 10-40 g would include the disperse heat and mass transfer behavior. As state in paragraph 4.1.2 the area mass is measured needs to be thermally isolated.

Mass measuring

There are two main concepts of measuring mass. The sample decouple from the heating source. The sample is then suspended in the reaction chamber and the mass is measured in a thermal separate area [9] [4]. In an other method described in literature [8] the sample and the furnace are couple and the mass is measured of the complete unit. The later is suitable for large masses ($\pm 50g$). The maximum deviation from the formulated water content amounts to $\pm 0.15 \frac{H_2O}{molMgSO_4}$ in the literature [3].

4.2 Operational procedures

The operational procedures for cycling TCM is dived in three steps. First the experiment is prepared. For comparing results it is important that the base starting material remains

the same. Then the material is cycled, one cycle has a dehydrate step and rehydrate step. Since the phase transitions are mono-variant, one can choose an isothermal or isobaric setup. Dehydration is done quasi-isobaric. The process is not fully isobaric, because vapor pressure is difficult to control. Hydration is done isothermal and quasi-isobaric. Finally, the goal of the experiment is to determine the durability of the cycling property. This is strongly related too the structural change of the lattices.

4.2.1 Preparation

The base material of the experiment is pure epsomite. The purchased material (99 % magnesium sulfate-heptahydrate GR for analysis Merck) is pure epsomite. Preparing pure epsomite from raw material a saturated magnesium sulfaat solution crystalizes into epsomite at room temperature [3]. Repeated washing with different mixtures of ethanol and water removes chloride in the solid phase [3]. Because the transition between epsomite and hexahydrate is at normal room conditions, also the water content must be determined (e.g. *Penfield tube method*) or the material sample is stored at conditions ($T < 25[K]$, $RH > 30\%$) of pure epsomite phase [4]. The material has a heterogeneous grain size composition. The base material must be sieved to one specific grain size. Using X-ray diffraction the structure of the base material can be determined. The X-ray diffraction pattern of pure epsomite crystal is known , see [2]. The porosity and layer thickness determine the degree internal diffusion which is dominant in mass transport, see chapter 3. The differences in particle pore structure can be revealed by mercury intrusion porosimetry data [5].

4.2.2 Measurement

Dehydration

The dehydration is a thermally driven process. In other words when the sample temperature exceeds the equilibrium temperature at a certain vapor pressure, the material expels bounded water molecules. When heat and mass transport resistance is negligible compared reaction kinetics, the process is kinetically driven [1]. So the temperature determines the reaction speed rather than the mass transport. The thermal decomposition the water expulsion occurs under conditions where water is continuously removed from the specimen.

Therefore first the air is evacuated, this promotes mass transfer, see chapter 3. Optional a strong dehydrated absorber (desiccant), like P_2O_5 kept constant at a lower vapor pressure [4] removes the water vapor, then the proces is not thermal driven. Time and mass of the sample is recorded. The reaction chamber is heated according to a preset scheme. From literature the main transition occur at 50, 90-95 and 325 degree Celsius [3]. This scheme will heat fast [$20\frac{K}{min}$] when the mass fraction gain is zero. Around the main transition temperatures the temperature will be coupled to the degree of dehydration, see eq 4.1. To avoid melt the temperature is constant when there is a mass fraction gain is high.

$$\begin{aligned} \frac{d\alpha}{dt} = 0 & \quad , \quad \frac{T}{dt} = 20[\frac{K}{min}]; \\ \frac{d\alpha}{dt} \gg 0 & \quad , \quad \frac{T}{dt} = 0[\frac{K}{min}]. \end{aligned} \tag{4.1}$$

Determining whether the sample is sufficiently dehydrated can be done by setting a fixed value of α . An other criterium can be when there is no mass gain and the sample is heated till a certain value for a certain time.

Hydration

Re-hydration is done quasi-isothermal. The vapor pressure is raised and the sample is cooled. The temperature is decreased slowly. When the temperature is decreased fast till 298 K, re-hydration is isothermal and quasi-isobaric. Inert gasses are evacuated, This increases the relative humidity. The system vapor pressure is controlled by a external water reservoir, filled with distilled water. The temperature of the water reservoir determines the saturation temperature, this will become the vapor pressure in the reactor chamber. The temperature of the water reservoir must be slightly lower then the reactor area, to avoid condensation. The tube connecting the reactor area and the water reservoir is kept at the water reservoir temperature.

4.2.3 Analyse

The structure change is analyzed. The X-ray diffraction pattern is likely amorphous [2], but may show contamination peaks. A SEM measurement will give a visual measure of crystal change, but no quantitative data. The output of the cycle will indicate whether the degree of hydration/dehydration capacity reduces and / or the cycle time increases. Difference in particle pore structure revealed by mercury intrusion porosimetry [5]

4.3 System variants

4.3.1 Isobar controlled

A suspended sample holder approach

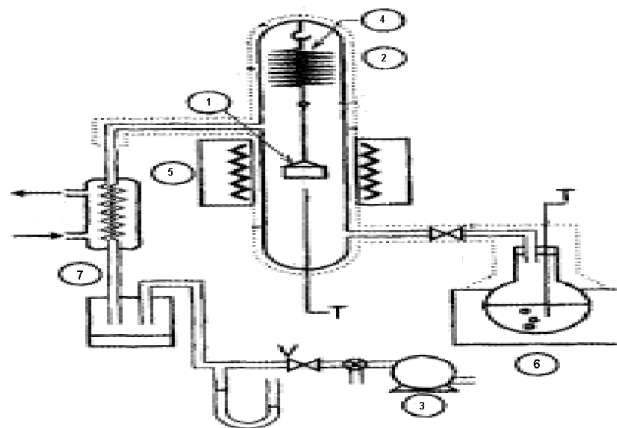


Figure 4.2: A *suspended approach* [9]

1. Sample holder

2. Reactor chamber
3. Vacuum system
4. Quartz spring
5. Electrical furnace
6. Evaporator
7. Condensor

Measuring mass suspended is an approach frequently done in literature , see [9] and [4]. The system consists of a reactor chamber (2), an evaporator (6), an condensor (7) and a vacuum system (3). The sample (1) is suspended in a basket hung under quartz spring (4) near the electric furnace (5). All the reactor parameters are measured, vapor pressure, reactor temperature and sample mass. Reactant vapor is temperature controlled and moves between the reactor and evaporator by pressure difference alone. This setup is not suited for large mass and will not meet all the system requirements. The electric furnace will give problems in vacuum heating a larger sample. The quartz spring is not thermally isolated from the reaction chamber. The measuring devices are manual and there is no system control.

A standing sample holder approach

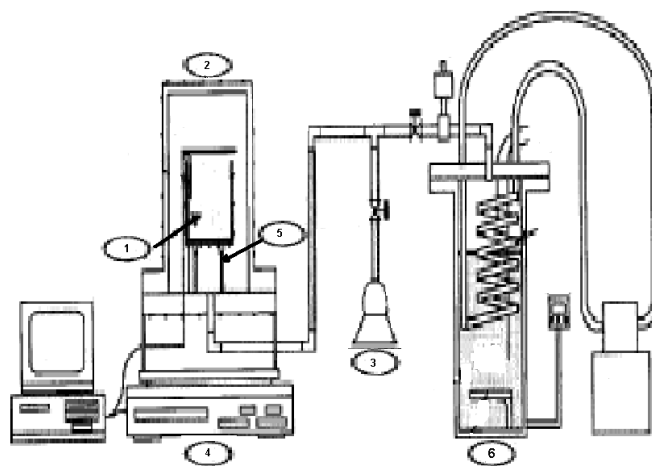


Figure 4.3: A standing sample holder approach [8]

1. Sample holder
2. Reactor chamber
3. Vacuum system
4. Balance

5. Joule heater

6. Condensor

The basic difference between this approach and the previous one is that here the sample holder (1) and the reactor chamber (2) are weighed both on a balance (4). This solves the problem of inefficient heat transport in vacuum, because now a joule heater (5) can directly conduct heat to the sample [8]. The main disadvantage is that the larger mass of the reactor chamber plus the sample still needs a low sensitivity in order to measure sample mass differences. The reactor chamber is connected with a flexible hose to the evaporator. This can influence the mass recording.

TGA with large mass

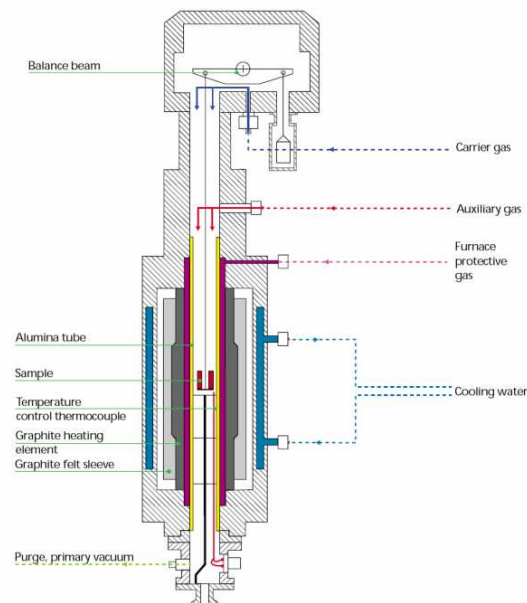


Figure 4.4: An large sample TGA - Setaram TG96

There are TGA's (Thermo gravimetric analyzers) on the market specialized in large mass and volume. Two of these are the *Cahn Thermax TGA* and the *Setaram TG96*, see figure 4.4. These apparatus with the right support equipment, like closed loop control would be more than capable to perform the cycling analyses. The performance in measuring accuracy, vacuum and temperature range far exceed the specified performance demands , see chapter 4.1. The price of such a system is around 60 k euro.

Design of a cycling apparatus meeting the system requirements

1. Sample holder

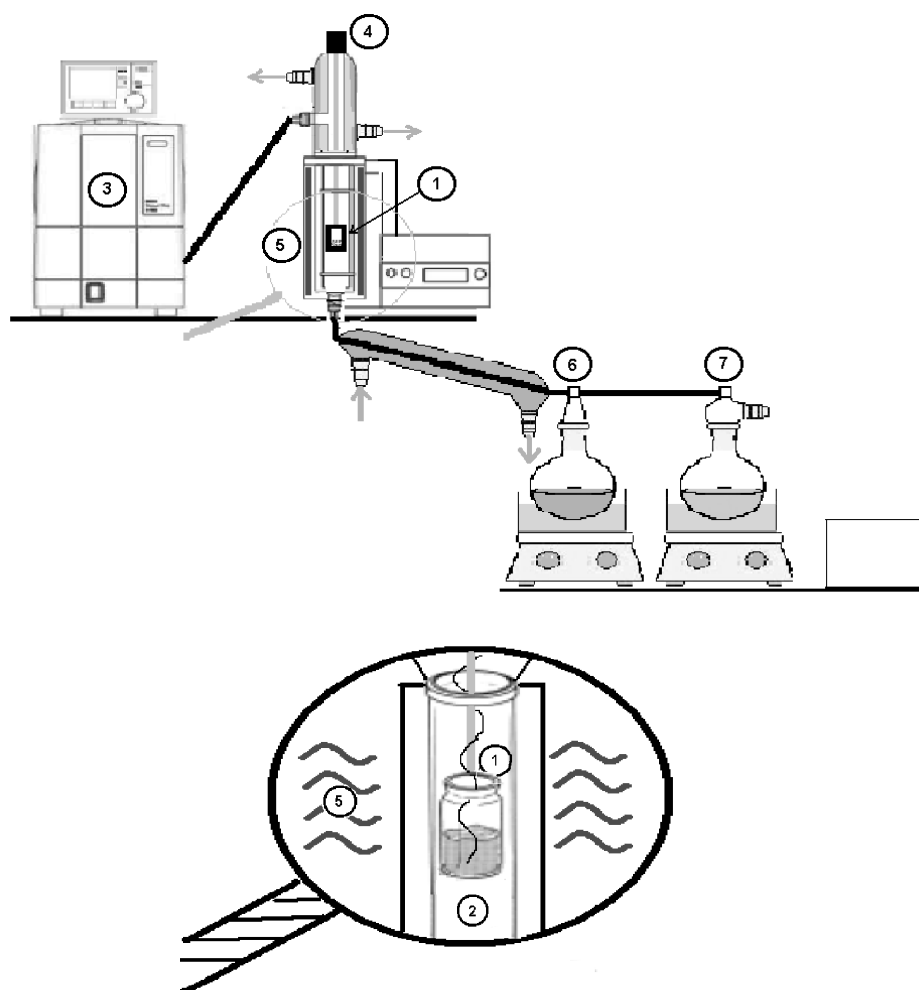


Figure 4.5: *Design of a cycling apparatus*

2. Reactor chamber
3. Vacuum system
4. Load cell
5. Glass furnace
6. Evaporator
7. Desiccant

In behalf of the research an design of a cycling apparatus is made, see figure 4.5. In this design the experience of earlier methods and apparatus are incorporated and combined with the system requirements of chapter 4.1. The system is automated and consists of a vacuum system (3), reactor chamber (2) with the sample suspended (1) and an evaporation/desiccant system. The inert gasses are evacuated by the vacuum pump, this pressure is regulated by

the vacuum controller with a vacuum valve. The reactor is heated by radiation in a glass furnace (5). The evaporation/desiccant system consists of a water reservoir (6), a container of desiccant(7), vacuum valves, heaters with a controller and heating tube jacket. The sample measuring device (load cell s-type) (4) hangs over the reactor chamber and is kept at a constant temperature with heating tube jacket.

Optionally contaminating gasses can be added in order to evaluate the effect on the morphology.

Chapter 5

Conclusions and Recommendations

The technology of TCM heat storage is still in the "proof of principle" fase. The full kinetics, like morphology, non uniform mass and heat transfer occurring during a cycle is still unclear, especially the hydration step. In this light more characterization of TCM materials, like magnesium sulfaat hydrate is necessary. The durability of a TCM depends on in what degree the capability to cycle deteriorates. Therefore a cycling setup and test is necessary.

An cycle deterioration experiment on a small scale TGA will give a initial indication of the cycle behavior. But non uniform mass and heat transport make scaling up the experiment necessary.

An cycle setup like described in chapter 4 can increase the understanding of durability of the material. Such a setup needs to comply to a list of requirements. The temperature, pressure and vapor concentration around the sample must be optimized and controlled. The sample will undergo a complete and fast cycle under these requirements. The setup is built from several components fulfilling these requirements. In principle all components can be selected independently as long as they meet the requirement for that component.

Eventually the cycle deterioration can be a criterium for selecting an TCM material. The choice of material will greatly influence the heat storage system and operational range.

The next step is a "proof of concept". This will demonstrate the feasibility. A bed reactor experiment is necessary in order to evaluate the practical performance of the heat storage, because the reactor bed is a complex system in which chemical reactions, vapor diffusion and thermal conductivity proceed simultaneously. Finally a fully functioning prototype must verify that the concept and theory is capable of operating in the build environment.

Appendix A

Appendices

A.1 Measurements

Measurement report for chapter 3.3.

The experiments are performed to determine the factors that influence the cycling process. These experiments have no quantitative value, but give an indication whether the influence of a parameter is significant. Another reason for these experiments is to gain some "hand-on-experience" with cycling magnesium sulfate as this had not been done before at ECN-EGON.

Dehydration

During dehydration two factors of interest are examined. The heating rate and the particle size.

The heating rate during dehydration is varied between 0.4 till 4 K/min . We are interested whether dehydrating reactively slow or fast influences the hydration. In literature it is stated that crystal structure is influenced by dehydration speed and conditions. This can lead to amorphous lattice structure, which influences the rehydration. Disperse heat transfer can also lead to local exceeding of the melting temperature. Neither of these effects were observed in our experiments. Sample A is relatively slowly dehydrated with 0.4 $\frac{K}{min}$. Samples E, F and G are dehydrated with a speed of 1 $\frac{K}{min}$, while samples B, C and D are heated relatively fast (4 K/min).

The particle size can have an influence on the mass and heat transport. Here a contradiction exists between the benefit of a higher porosity with larger particles against the higher surface area per volume of smaller particles. Samples A to D have a full particle distribution as delivered by the manufacturer. Samples E to G are sieved in the ranges, E (100 – 200 μm), F and G (200 – 500 μm).

Hydration

During the hydration experiment two factors are examined. The total pressure and the relative humidity. The total pressure has an influence on the mass transport resistance. The diffusivity is pressure dependent, see eq 3.9. Samples A, B, C and G are in an atmospheric environment at 1 bar. D till F are in a vacuum environment of 0.5 bar.

The relative humidity is determined by the vapor pressure in the system. The vapor pressure

is a driving force in the reaction. The highest vapor pressure at a temperature is the saturation vapor pressure.

A.2 System devices

A.2.1 Vacuum pumps

Rotary vane pump.

A rotary vane pump is a positive-displacement pump that consists of vanes mounted to a rotor that rotates inside of a cavity. On the intake side of the pump, the vane chambers are increasing in volume. These increasing volume vane chambers are filled with air forced in by the inlet pressure. On the discharge side of the pump, the vane chambers are decreasing in volume, forcing air out of the pump. The action of the vane drives out the same volume of fluid with each rotation. Multistage rotary vane vacuum pumps can attain pressures as low as 1 kPa. Rotary vanes and bearings are lubricated by oil. The water vapor tolerance is the maximum inlet pressure at which you can pump pure water vapor without condensing water inside the pump. If the inlet pressure rises above this level the liquid water will accumulate inside the pump and mix with the oil and harm the pump. Most rotary vane pumps have a water vapor tolerance of 30-60 mbar. The rotary vane pump can create a vacuum of around $10^{-3} - 10^{-2}$ mbar

scroll pump.

A scroll vacuum pump uses two interleaved spiral-like vanes to pump air. Often, one of the scrolls is fixed, while the other orbits eccentrically without rotating, thereby trapping and pumping or compressing pockets of air between the scrolls. These devices are known for operating more smoothly, quietly, and reliably than conventional vacuum pumps. Unlike pistons, the orbiting scrolls mass can be perfectly counterbalanced, with simple masses, to minimize vibration. The scrolls gas processes are more continuous. The more steady flow yields lower gas pulsations, lower sound, lower vibration, and more efficient flow. And the air-conditioning scroll does not have dynamic valves, gaining flow efficiency and reduced sound versus other pumps.

The verticale construction allows condensed vapor to flow out. The scroll pump is oil free. The working pressure range is around 0.1-1 mbar.

diaphragm pump.

A diaphragm pump is a positive displacement pump that uses a combination of the reciprocating action of a rubber or teflon diaphragm and suitable non-return check valves to pump air. When the volume of a chamber of is increased (the diaphragm moving up), the pressure decreases, and fluid is drawn into the chamber. When the chamber pressure later increases from decreased volume (the diaphragm moving down), the fluid previously drawn in is forced out. Finally, the diaphragm moving up once again draws air into the chamber, completing the cycle. This action is similar to that of the cylinder in an internal combustion engine.

The diaphragm pump is water vapor tolerant and can go to a vacuum of 1-10 mbar.

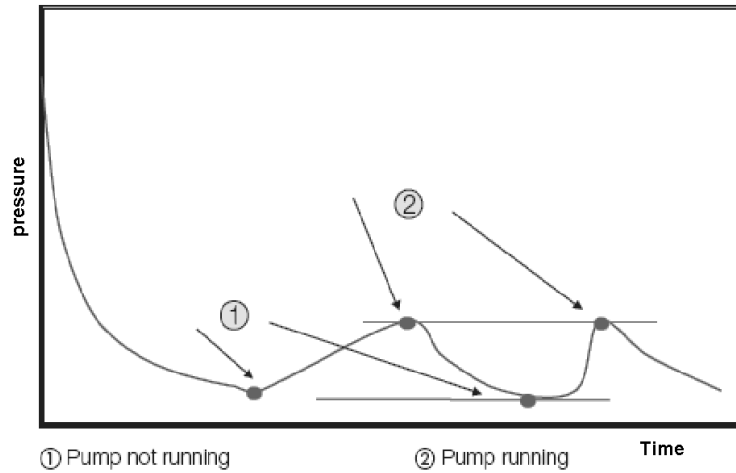


Figure A.1: *vacuum control*

A.2.2 Pressure sensors

Diaphragm sensors The pressure to be measured is separated by a diaphragm from a reference vacuum and compared to the latter. The movement of the diaphragm is registered either by a piezo resistive system or the diaphragm is part of a capacitor. [15].

A.2.3 Temperature sensors

The thermocouple

An thermocouple is an electric circuit consisting of two different materials in the form of wires. When the two junctions are at different temperatures a potential exists at the terminals on a open circuit [10]. One junction, called the hot junction is welded, soldered or pressed together. At the other, cold junction the voltage is measured. There are many types of thermocouples, consisting of material combinations. The K type is frequently used in the temperature range 100-1300 K, because it is stable and very linear. The K-type consists of chromel and alumel and has a tolerance of $\pm 1.5K$.

The electrical resistance detector (RTD)

The electrical resistance of some metals is temperature depended. Together with wheatstone bridge configuration a relation between temperature and the measured current exists [10]. A commonly used RTD is the Pt-100 Ω . The temperature operation range is between 70-870 K with an accuracy of 0.4 K

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