Experimental study on thermochemical heat storage materials

PROEFSCHRIFT

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Cover design: Joey Geerts and Pim Donkers
The cover is a collage of several hydrates of the salts: MgCl₂, NiCl₂, MnSO₄, FeSO₄, MnSO₄, CuSO₄, MgSO₄, CoSO₄ and NiSO₄. The back cover displays the salts before and the front cover displays them after (partially) dehydration at 150 °C.

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Chapter 1

Introduction

Currently society is moving from a carbon-based society to a renewable-based society as to become less dependent on fossil fuels \[1,2\]. A UN report states that cities have to reduce CO$_2$ emissions by 20% in 2020 and 90-100% in 2050 \[3\] compared to 2005. These targets are only reachable if society as a whole is involved. Many reports, e.g. by International Energy Agency (IEA) \[4,5\] and the city of Eindhoven \[6\], stress that a dominant part of the energy consumption is for heating and cooling. In Figure 1.1a, the energy consumption of an average Dutch household is shown \[7\], of which 58% is used for both hot tap water and central heating. Taking the broader picture of the full energy consumption into account, e.g. considering the energy needed for car driving, the boiler still consumes 40% of the total household energy. An average energy bill in an average Dutch household amounts at this moment to 1790 euro per year and can be divided into 26% for electricity, 36% for gas and 38 % for taxes \[7\], see Figure 1.1b. Renewable heat production could replace the gas consumption and save at least 644 euro per year.

![Energy Consumption of an Average Dutch Household](image1.png)

![Energy Bill of an Average Dutch Household](image2.png)

*Figure 1.1: a: The energy consumption of an average Dutch household in 2014. Six groups of energy consumers inside a household are indicated. The total energy consumption is in the order of 81 GJ per household per year. b: The energy bill of an average Dutch household in 2014 divided in taxes, gas and electricity. [7]*
Beside environmental and economical reasons, a third reason to transform the gas-based domestic heat supply into a renewable-based supply is to keep our independence in the energy sector. The heat production in the Netherlands is almost entirely based on gas, primarily due to the gas field found in Slochteren, Groningen, in 1959. This resulted in the realization of a gas distribution network spread across the Netherlands, connecting most of Dutch dwellings. At this moment, the Netherlands is still an exporter of gas, but in the coming years, we will become increasingly dependent on external gas suppliers, i.e. Russia and the Middle East. To keep our independence on the energy market another mindset is necessary and wherein we should consider other sources of heat beside gas. Only recently, the Dutch minister of Economics Affairs recognized these concerns and he placed heat as an equal player on the energy market next to gas and electricity [8]. This step will have its impact on the funding of research, for example in the top sector Energy funded by the government. The Top Sector Energy consists of seven Topconsortia for Knowledge and Innovation (TKIs) in which business, knowledge institutions and government work together to sustainable growth. One of the Topconsortia is TKI-Energo [9]. In this program heat is named as key interest, whereby heat storage is mentioned as a necessary component to become a carbon free society.

1.1 Renewable energy sources

For the transition from a carbon-based society to a renewable-based society, new energy production techniques have to be implemented. Analysis of these techniques should consider the type of produced energy, the controllability of the energy output and the location of the energy production ((de)centralized).

The type of energy production can be divided into electricity and heat. Heat producing techniques can be roughly divided in two main categories based on the heat source; geothermal (high controllability) and solar (low controllability). The possibilities of geothermal heat strongly depend on the geographic location. Countries with volcanic activity, like Iceland, Japan and New Zealand can generate high-temperature heat from geothermal sources. It has a more or less steady output over the whole year. As we do not have volcanic activity in the Netherlands, this type of heat production is not possible. Another option is a heat pump, which provides heat from a source by adding energy. Heat pumps can generate around 5 times the energy from the energy they consume. The disadvantage of this technique is the high electricity consumption, especially when the difference in the temperature of the source and the gained temperature is large. Another disadvantage, is that the heat source will cool down as result of the consumed heat, what limits the usage of these systems. Heat sources based on solar like solar collectors, parabolic solar collectors, solar ponds and solar concentrators are still not fully mature and need further improvement in efficiency and exploitation to produce heat. All discussed techniques for production of heat are mostly used in a decentralized system. Transferring heat over long distances is expensive as a result of the high costs in infrastructure.

Renewable electricity producing techniques will be divided in systems with control of their energy output, like wave power, hydropower or osmotic power, and systems
without control of their output, like wind power or solar energy. At this moment especially the unpredictable systems, i.e. wind power and solar energy, increase their share of the market. The market share of other techniques is smaller, because on the one hand hydro power is bound to specific locations, and on the other hand wave and osmotic power are still in a developmental phase. These three techniques will centrally produce their energy, where wind power and solar energy can be produced both centralized and decentralized.

One of the major drawbacks of most renewable-based energy producing techniques is their uncontrollability in their energy output. Both direct sun and wind energy fluctuate, and consequently overloads and shortages of energy may occur on the market. We will demonstrate the effect of this uncontrollable energy supply in case we have only a heating system, working with solar collectors. As we all know, sunlight fluctuates on a daily basis, day and night, but the amount of sun irradiation is also changing over the year. On the other hand, also a fluctuating demand for heat exists. To indicate the demand for heat, we use the gas consumption, considering that the gas consumption of a household is almost entirely related to the heat demand of a Dutch household. The gas consumption and the sun irradiation in each month [10] are plotted in Figure 1.2. As can be seen, the sun irradiation is out of phase with the gas consumption/heat demand. This means that if our heat supply is only determined by solar collectors, we have different options to match both. We can design our system to the average system and will have shortage of heat in the winter, or we can fit our heating system to our peak demand and have an overshoot in the summer. Introducing a storage system can work as an extra heat consumer in the summer and heat supplier in the winter.

Another consequence of mismatch of demand and supply of energy can be found in the electricity grid. In this case a mismatch can destabilize the entire electricity
1.2 Heat storage options

Different basic principles for heat storage at low temperatures (T<150 °C) are listed in Table 1.1, including the typical energy densities and pros and cons arguments.

Table 1.1: Storage methods with the principle behind this method and an indication of typical storage densities. The pros and cons arguments with respect to the different principles are listed.

<table>
<thead>
<tr>
<th>Sensible Principle: Heat capacity $C_p \Delta T$</th>
<th>Phase change Principle: Phase change $\Delta H_m$</th>
<th>Thermochemical Principle: Heat of reaction $\Delta H_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Storage density: $\sim 0.2$ GJ/m$^3$</td>
<td>Storage density: $\sim 0.4$ GJ/m$^3$</td>
<td>Storage density: $\sim 2$ GJ/m$^3$</td>
</tr>
<tr>
<td>+ Price of raw materials</td>
<td>+ Storage density</td>
<td>++ Storage density</td>
</tr>
<tr>
<td>+ Stage of development</td>
<td>+ Loss of heat during storing time (10-25%)</td>
<td>+ Loss of heat during storing time (0-25%)</td>
</tr>
<tr>
<td>- Variable discharging temperature</td>
<td>+/- Heat storage in small temperature range</td>
<td>+ Wide range application temperatures</td>
</tr>
<tr>
<td>- Loss of heat during storing time (10-50%)</td>
<td>+/- Stage of development</td>
<td>+ Price of raw materials</td>
</tr>
<tr>
<td>- Storage density</td>
<td></td>
<td>- Complex system: two or more components</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Stage of development</td>
</tr>
</tbody>
</table>

Firstly, sensible heat storage is the most commonly used method, using the heat capacity of a storage material. A storage material is heated and stored in an insulated compartment. At the time heat is needed a heat exchanger removes the heat from the storage material. This technique is straight forward and is used for both short term and -less successfully- for long term storage. Considering the daily need for hot tap
water and central heating of an average Dutch house, water storage would require a stratified water tank of 1-2 m$^3$ to cover the diurnal need of 0.2-0.4 GJ. For longer term storage, several projects are installed around the world using this technique [14] and examples are given in Figure 1.3. Main drawbacks are: a) low energy density resulting in large volumes b) heat loss during storage resulting in additional thermal insulation. In this respect, seasonal storage is preferably used on district scale, considering that the storage volumes are larger and the additional isolation is relatively small per stored volume. Note that the overall inefficiency decreases during the duration of heat storage.

A second storage principle concerns latent heat storage, based on the heat exchange during the phase changes of a material. At a phase transition temperature, the system will release or absorb heat depending on the cooling or heating conditions. An known example of ‘short’ term storage refers to a phase change material that is embedded in a wall. The phase change material will melt, when the temperature is high and will solidify when the temperature is low. This additional PCMs will smoothen out temperature fluctuations and the wall will keep a more or less constant temperature during the day [15–17]. Using this method for long(er) term storage requires control of release of heat. This can be realized when the phase change material can be cooled to a lower temperature than its phase transition temperature [18]. An example of a working system is a heat pack, which is filled with sodium acetate trihydrate (see also Figure 1.4). Sodium acetate trihydrate will melt at 54 °C, but by cooling the package till temperatures of 20 °C it remains liquid. This is called super cooling and by destabilizing the system i.e. adding a nucleation site, the package instantaneously solidifies. In these heat packs, this is done by clicking a disk whereby some molecules solidify and work as a nucleation site for the rest of the liquid. During the solidification heat is released. Present research focuses on selecting appropriate phase change materials, with respect to minimizing loss of performance after several cycles [18,19]. At this moment this is one of the key showstoppers for widespread use of latent heat storage. Another factor that needs additional attention is the potential
corrosion effects of PCMs on the metal storage vessel [20].

A third storage option is based on thermochemical principles. Generally, thermochemical storage includes physisorption and chemisorption, both using reversible chemical reactions to store energy in chemical bounds. Energy densities and operation temperatures cover a wide range and highly differ. However, the current state of knowledge is quite low compared to the other proposed techniques. The largest advantages of this method compared to the other methods are that the storage is nearly loss-free and offer a perspective of a substantially higher energy density. The energy production by physisorption is based on the Van der Waals forces, whereby liquid or gas is adsorbed by solids or liquids, respectively. Zeolites are a common material for sorption application, because of its high surface area (>600 m²/gram) for sorption [21].

In case of chemisorption, hydrogen bond energy is responsible for energy production. A promising class of materials are hydrates, producing heat during the hydration and storing heat during dehydration [22, 23] (see Figure 1.5). This class of materials can have energy densities potentially above 2 GJ/m³. A major disadvantage is the physical instability of these materials, i.e. the decrease in rehydration/hydration rates -thus heat absorption/release- with increasing number of cycles, accompanied with grain size variations. An example of an instability of such a system is given in Figure 1.6. This figure shows the rehydration of manganous formate dihydrate of three sequential runs. The measured rehydration is given in percentage of the theoretically expected value against the rehydration time. Obviously, the rehydration is slowed down with the increase of runs of hydration.
Chapter 1. Introduction

**Figure 1.5:** Sodium sulfate decahydrate during dehydration at 25 °C and 0% RH. Sodium sulfate decahydrate is an example of a thermochemical material (TCM).

**Figure 1.6:** The %-rehydration of a single crystal of manganous formate (1.19x1.05x0.66 mm) during three consecutive rehydration experiments (Data from reference [24]). The %-rehydration is the percentage of measured hydration level of the initial hydration level before the first dehydration. As can be seen the rehydration process is slowed down by an increase of runs of hydration of the same sample. The rehydration conditions are: 63% relative humidity and 22.5 °C temperature.
1.3 Thermochemical materials

In this thesis only part of thermochemical materials will be discussed: materials with a gas-solid reaction and more specifically; hydrates, ammoniates and methanol complexes. The raw materials involved in these reactions are relatively cheap and the reaction temperatures of most of these reactions are below 150 °C. In general a gas-solid, i.e. gas-salt equilibrium reaction, can be represented by [25]:

$$MX-nL(s) \rightleftharpoons MX \cdot mL(s)+(n-m)L(g). \quad (1.1)$$

wherein $MX-nL(s)$ is a solid salt complex formed from a salt $MX-mL(s)$ and $(n-m)$ mol of solvent $L$. The amount of solvent $L$ inside salt complex $MX$ is called the loading of the salt. The formation reaction of $MX-nL$ is exothermic, i.e. it produces energy, the enthalpy of reaction $\Delta_r H^{n-m}$, whereas in the endothermic decomposition reaction of $MX-nL$ energy, $-\Delta_r H^{n-m}$, is consumed.

The operational parameters for this equilibrium reaction are the vapor pressure of solvent $L$ and the temperature. By applying a high vapor pressure, complexes with a higher loading of solvent will be formed and heat is generated. On the other hand, upon applying energy to the salt complex by increasing the temperature, the salt complex will decompose. Hence, this system is in principle ideal for storing heat loss-free, while the stored energy is only released in case solvent and salt are exposed to each other. During the storing period no energy will be lost. Energy will be lost only during charging and discharging of the system, which is never 100% efficient.

For a particular heat storage system, the solvent should be selected based on the vapor pressure at the desired working conditions. A trade off should be made between rate of reaction of the solvent with the salt, which is larger in case of a higher vapor pressure of the solvent [26], and the safety precautions as result of higher vapor pressures. Three appropriate solvents [25,27] can be identified as options for heat storage by thermochemical materials: water, ammonia and methanol. These three solvents have the ability to form complexes with inorganic salts with a high energy density and, moreover the discharging temperature are for most complexes in the range between 20 and 150 °C. Each solvent has a specific set of working conditions, as a decomposition temperature and solvent pressure -as working conditions-, in combination with a certain type of salt. Also toxicity and explosive limits have to be taken into account in choosing the most appropriate salt-solvent combination for a certain application. In Table 1.2 the main characteristics of the pure solvents are given.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>NH₃</th>
<th>CH₃OH</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor pressure at 300 K (MPa)</td>
<td>1.2</td>
<td>0.05</td>
<td>0.012</td>
</tr>
<tr>
<td>Boiling temperature (K)</td>
<td>240</td>
<td>337</td>
<td>373</td>
</tr>
<tr>
<td>Melting temperature (K)</td>
<td>196</td>
<td>176</td>
<td>273.2</td>
</tr>
<tr>
<td>Flammability (%)</td>
<td>15-25</td>
<td>6-36</td>
<td>-</td>
</tr>
<tr>
<td>Toxicity (ppm) (US PEL)</td>
<td>50</td>
<td>200</td>
<td>-</td>
</tr>
</tbody>
</table>
About the selection of a solid/gas reaction several reviews exist [22, 23, 31, 32], wherein the selection is mainly based on theoretical energy densities and dehydration temperatures. Presently, only hydrates are commonly considered as useable chemisorption material in building applications, because of safety issues with ammonia and methanol. The chemical structure of the different hydrates has been studied under equilibrium conditions with techniques like XRD (see XRD database [33]), Raman [34,35] and neutron diffraction [36–39]. Other techniques have been used to study the hydrates under dynamic conditions: by changing the temperature: thermal gravimetric analysis (TGA) [40–42], differential scanning calorimetry (DSC) [43–45], XRD [43, 46], Raman [47] and neutron diffraction [48] or by changing the vapor pressure: gravimetric analysis [49, 50] and Raman [51–53]. Repeated hydration/dehydration experiments show that the hydrates may show cyclic instability. This instability has been related to changing rehydration/dehydration rates and/or changing grains sizes [24, 54–56]. The observations are mainly based on mass measurements and no information about the crystal structure of the products nor information about water transport inside a grain is available. The articles [57–60] that describe the release or absorption of water in crystals are mainly based on gravimetrical data or indirect observations of water molecules.

Even when the hydrates and their reactions are well understood and described, the challenge of implementation in practice remains. At this moment, sample weights are generally small, i.e. a few milligrams, which finally should be increased to system amounts that typically are of few hundreds of kilograms. The first experiments are already reposted on larger sample sizes. Such prototype reactors are still small compared to what maybe required in actual use, but contain weights between one and hundred kilogram. On these systems only measurements are reported on the temperature inside the sample and vapor pressure of the in- and outflow of the air, without considering the water transport through the sample [61–64]. Beside studies on the heat storage materials European projects like MERITS, study heat storage system designs [65] and the interaction between the salt hydrates and critical components therein, like the heat exchanger [66,67].

Analysis of gas-solid reactions and solid-container material interactions should consider the boundary conditions of the envisaged application. The frequency of loading/unloading, working temperature and power output will differ between a household and industry. Selection of a different gas-solid combination can tune these parameters in view of the application.

1.4 Aim

Application of thermochemical materials (TCM) in heating/cooling systems requires a profound understanding of the heat output/uptake during solid-gas reactions. Issues like generating a constant heat output during rehydration, a sufficient heat output for applications and a heat output that is constant over several cycles, should be solved. As we know that the solvent uptake of the solid salt is directly related to the heat production of a system, we focus on the interaction of the solvent with the solid salt. A good heat storage system design can only be made, when this interaction is
understood during uptake and release of the solvent. Solvent transport will have its effect on the crystal structure of solid salts. At this moment, no knowledge exists about solvent transport inside salt hydrate grains nor on reactor scale during formation/decomposition of a salt complex. The aim of this thesis is to understand the behavior of a solvent during decomposition and formation reactions of salt complexes to improve the stability of solid-gas reactions for heat storage materials. Ultimately, this should lay the foundation for a heat/cold storage system, which can fulfill the annual heat and cold demand of a house with a service life of at least 30 years. We will study the solid-gas reactions with Nuclear Magnetic Resonance (NMR) next to the accepted techniques like: TGA, DSC, Raman and XRD. This technique gives us the opportunity to non-destructively monitor the solvent molecules within a solid salt during decomposition and formation of a salt complex.

1.5 Outline of the thesis

The thesis starts with a concise overview of thermochemical data of hydrates, ammoniates and methanol solvates in Chapter 2 and an introduction in NMR principles in Chapter 3. The results of the study are given in the Chapters 4-8. Chapter 9 summarizes the main conclusions and outlines follow-up.

The key chapters are outlined as follows. In chapter 4 the main question is: How does water leave a heated hydrated salt? This chapter aims to understand how water is transported on a macroscopic scale during the dehydration of MgSO$_4$·7H$_2$O induced by heating.

Further, in Chapter 5 this study focuses on dehydration experiments with single crystals of Na$_2$SO$_4$·10H$_2$O and extends to dynamics of the water molecules in the crystal structure and to structural changes. Raman spectroscopy, XRD and nuclear magnetic resonance (NMR) are used. Raman spectroscopy and XRD follow the crystal structure in time, while the NMR technique monitors the water distributions in materials, i.e. inside the crystal in situ.

In chapter 6 a selection of hydrates is studied with respect to their dehydration characteristics using TGA, DSC and NMR.

In addition, in Chapter 7 the selected salts of Chapter 6 are studied on their ability of cyclic hydration/dehydration by varying the conditions of the air flow through a small bed of grains. The volumetric variations during hydration and dehydration reactions are particularly considered.

Finally, Chapter 8 describes a study of beds of grains, which are hydrated and dehydrated by varying the relative humidity of the air. Hereby spatial resolved water distributions and temperature profiles are measured during dehydration and rehydration.
Chapter 2

Thermochemical Materials

As explained in the introduction, in this thesis we will focus on the storage of heat on the basis of reversible chemisorption in a gas-solid reaction. Gas-solid reactions have a high heat storage potential as it is (nearly) loss-free and may have a high energy density (2-3 GJ m$^{-3}$). Gas-solid equilibrium reactions of salts with a solvent, like ammonia, water or methanol, are given by the following equations:

$$A\cdot n\text{NH}_3(s) \rightleftharpoons A\cdot (n-x)\text{NH}_3(s) + x\text{NH}_3(g), \quad (2.1)$$
$$A\cdot h\text{H}_2\text{O}(s) \rightleftharpoons A\cdot (h-x)\text{H}_2\text{O}(s) + x\text{H}_2\text{O}(g), \quad (2.2)$$
$$A\cdot m\text{CH}_3\text{OH}(s) \rightleftharpoons A\cdot (m-x)\text{CH}_3\text{OH}(s) + x\text{CH}_3\text{OH}(g). \quad (2.3)$$

wherein A is a salt, n, m and h indicate the amount of solvent in the solvated salt and x is the amount of solvent that is released from the solvated salt. The decomposition reaction of a solid is endothermic, i.e. it consumes energy ($-\Delta rH_{n-m}$), whereas in the exothermic formation reaction of the solvated salt energy ($\Delta rH_{n-m}$) is produced. $\Delta rH_{n-m}$ is the reaction enthalpy and can be calculated for example in case of (de)hydration (Equation 2.2) according to:

$$\Delta rH_{n-m} = \sum_{Products} v\Delta_fH_i - \sum_{Reactants} v\Delta_fH_j$$
$$= \Delta_fH(A\cdot h\text{H}_2\text{O}, s) - \Delta_fH(A\cdot (h-x)\text{H}_2\text{O}, s) - x\Delta_fH(\text{H}_2\text{O}, g). \quad (2.4)$$

where $\Delta_fH_i$ and $\Delta_fH_j$ are the enthalpies of formation of substances i and j and v is the number of moles of products and reactants.

These kind of systems have been discussed in the last centuries [57, 59, 68–71]. In this chapter we will present an overview of the literature of salts, that could be considered suitable for thermochemical heat storage, including hydrates, ammoniates and methanol solvates.

2.1 Hydrates

Hydrates are well studied. Several reviews have been written about hydrates and their high potential as a material for seasonal heat storage [22, 23, 31, 32]. The energy
2.1. Hydrates

Table 2.1: The decomposition reactions of a few salt hydrates are given, where the start loading and final loading are given in the second and third column. $\Delta_r H^\circ$ is the standard reaction enthalpy at 25 °C and 0.1 MPa per mole of a hydrate. $\Delta V$ is the volume difference between reactants and products of the decomposition reaction. The energy density is calculated based on the reaction enthalpy and the volume of the higher hydrate, i.e. the highest volume. This table is composed of data by Wagman et al. (1982) [72] and an XRD database [33].

<table>
<thead>
<tr>
<th>Salt</th>
<th>Start loading (mol)</th>
<th>Final loading (mol)</th>
<th>$\Delta_r H^\circ$ (kJ/mol)</th>
<th>$\Delta V$ (%)</th>
<th>Energy density (GJ/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl$_2$</td>
<td>6</td>
<td>4</td>
<td>-114.7</td>
<td>-21.9</td>
<td>0.89</td>
</tr>
<tr>
<td>-</td>
<td>6</td>
<td>2</td>
<td>-237.7</td>
<td>-38.0</td>
<td>1.86</td>
</tr>
<tr>
<td>-</td>
<td>6</td>
<td>1</td>
<td>-289.6</td>
<td>-55.1</td>
<td>2.26</td>
</tr>
<tr>
<td>CoSO$_4$</td>
<td>7</td>
<td>6</td>
<td>-54.5</td>
<td>-9.7</td>
<td>0.38</td>
</tr>
<tr>
<td>-</td>
<td>7</td>
<td>1</td>
<td>-329.4</td>
<td>-61.0</td>
<td>2.28</td>
</tr>
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<td>-67.1</td>
<td>2.90</td>
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</table>

Densities and volume changes of the different salts discussed in this thesis are given in Table 2.1. The enthalpy data were taken from reference books like the International Critical Tables [73], Gmelin [74] and the NBS tables [72]. The volume changes have been calculated with help of an XRD database. The energy densities were calculated with the enthalpy of reaction divided by the initial volume of a hydrate. As can be seen, theoretical storage densities above 3 GJ m$^{-3}$ can be reached. However
in practice, this will be lower as a result of intergranular porosity in bulk materials. Moreover, as can be seen, the volume changes are large in case of high energy densities.

For a good heat storage system design, information about the energy densities only is not sufficient. Information is also needed about the conditions when hydration/dehydration occurs, which can be found in phase diagrams. For some well studied salts, phase diagrams are available, e.g. MgSO$_4$, Na$_2$SO$_4$ and CaCl$_2$, but for most salts, phase diagrams are missing or incomplete.

The hydration/dehydration conditions determined by the phase diagrams should be linked to the conditions of the air supplied. In case we consider an open system the RH of the airflow in the heat storage system can be linked direct to the external conditions. The average relative humidity (RH) and temperature in the Netherlands over 30 years are shown in Figure 2.1 [10]. The average RH over an entire year is around 80%. As the temperature will change as it is in contact with a thermochemical material, the RH can change significantly.

In Figure 2.1 we have plotted the resulting RH due to a fixed temperate change. As can be seen for temperatures of the reactor well above the external temperature there is not much of influence between summer and winter period, i.e., the RH is almost constant over the entire year. On the other hand for low temperatures, e.g., 10 °C there is a very large influence and at the summer the RH will be 100%, giving rise to condensate in the reactor. As temperatures of 60 °C or higher should be generated in a heat storage system during hydration in the winter, a salt should be able to hydrate at RH of less than 5% or the humidity of the air should be artificially be increased. However, to increase the humidity of an airflow energy is needed to evaporate water, which will decreases the overall efficiency of a heat storage system. During the summer temperatures above 100 °C can be generated to dehydrate. At
these temperatures the humidity of the air will be below 1.6%, i.e., the conditions whereby the salt should dehydrate. After dehydration the temperature will decrease to conditions equal to the environment and the RH can increase to values of 80%. To avoid unwanted rehydration, in such a case the heat storage system should be sealed off.

In the coming section, we will explain how to use a phase diagram, discuss a range of hydrates and summarize their equilibrium data found in literature.

2.1.1 Phase diagrams

In Figure 2.2 a phase diagram of salt A is given, whereby the RH is plotted against temperature. As can be seen, salt A can exist as hydrated salt, A·xH$_2$O(s), anhydrous salt, A(s) and an aqueous solution of salt A, A(aq). Line $\alpha$ indicates the transition conditions between the hydrated and the aqueous solution of material A, i.e., the deliquescence line, line $\beta$ indicates the transition conditions between hydrated and anhydrous phase and finally, line $\gamma$ indicates the transition between anhydrous and the aqueous solution of salt A. The intersect of these three lines is the so-called triple point and under this condition all three phases can coexist.

To understand the complexity of the phase diagram, several examples of transitions will be briefly discussed. As a first example, we consider a hydrated crystal in a box. This crystal will be stable as long as the conditions in the box are enclosed by $\alpha$ and $\beta$, i.e., within the light grey area of Figure 2.2. Now let us assume the conditions within the box are changing. The starting conditions will be at point I. Adding additional water vapor to the box will increase the RH as indicated by arrow a. At the moment the RH reaches line $\alpha$ the RH will not increase any further by adding water vapor to the box. At that moment the crystal will start to dissolve, and until the crystal is totally dissolved the RH will remain constant.

In another example we will fill a box with a 1:1 mole ratio of two phases of salt A, for example a hydrated and anhydrous phase, which are equilibrated at point II. By slowly increasing or decreasing the temperature, the RH in the box will vary in such a way, that point II remains on line $\beta$. This is a so called univariant system. This univariant systems remains, even at ratio's unequal to 1:1, as long as both phases are present in the box. This means, that at the moment the phases in the box are known, one of the variables, the temperature or RH in the box is determined by the respective other one.

In a third example we will consider a hydrated crystal in a box. The box starts at point III and is heated up till the temperature crosses the temperature of the triple point and the hydrated form deliquesces. If the hydrate will not deliquescence but is heated till above the melting temperature, line $\varepsilon$, the hydrate will melt. If the melt is oversaturated for the anhydrous phase, part of the melt will crystallize till the melt is no longer oversaturated. This type of transition is called incongruent melting. In case the melt is not oversaturated for the anhydrous phase, the melt will remain an aqueous solution of A. This transition is called congruent melting.

Up till now, we only considered stable phases and direct transitions from one stable phase into another in such a phase diagram. In reality, this is not always the case and it may happen that the expected transformation from one phase to another
Figure 2.2: A schematic phase diagram of salt A in equilibrium with water. Three stable phases exist in this diagram, the hydrated salt, the anhydrous solid salt and the salt solution. The solid lines $\alpha$, $\beta$ and $\gamma$ are the phase transition or coexistence lines of the phases of material A. The intersection of these three lines is called the triple point. The hydrated phase is stable in the light grey region. The metastable region is colored dark grey and is enclosed by line $\beta$ and $\delta$. The dashed line $\delta$ indicates a phase transition line between the unstable and metastable region of the hydrated phase, but is not an absolute boundary. The dashed line $\epsilon$ indicates the melting temperature of the hydrated salt.

is suspended. This suspended transformation can be a result of the formation of a metastable phase at a certain RH-temperature combination. A metastable phase is a thermodynamically unfavorable phase that persists because the transition is kinetically hindered. A well known example of a metastable phase is supercooled water. A metastable phase can also be observed for phase transitions with hydrates. For example, if we have a hydrated crystal equilibrated at point I and the RH is decreased according to curve b to point IV. We would expect to see a phase transition of the hydrated into anhydrous phase by crossing line $\beta$. But if no anhydrous phase exist, there is a chance to cross this line into the dark grey area of Figure 2.2, below line $\beta$, without observing a transition. This region in the phase diagram is called a metastable region. As long as the system is in it’s metastable state, a small local perturbation in energy can result in a transition. The metastable phase will spontaneously start to transform into the anhydrous phase by further decreasing the RH. This moment is in this graph draw as line $\delta$, but these conditions are not facing absolute boundaries. The RH increases till it is back on line $\beta$, while at that moment two phases exist, the hydrated and anhydrous phase.
As a final example, we will take an equilibrated hydrate sample at point V, which is subjected to a temperature increase and a RH decrease reaching point VI. To reach this point, we consider two possible scenarios. In the first scenario, the crystal is first equilibrated at point VII. The crystal will dehydrate in the anhydrous phase and at the moment the crystal is fully dehydrated, the temperature is changed till it reaches point VI. In this scenario, the conditions of the crystal will follow dehydration curve c, the crystal dehydrates without melting of the crystal, wherein the initial grain structure can still be present after dehydration. In the other scenario, the crystal is first equilibrated at point VIII in a closed container. At the moment the system is in equilibrium, the container is opened and the RH is decreased till it reaches point VI. In that case the condition of the crystal will follow dehydration curve d, i.e. the RH in the closed container will increase during heating. The increase of the RH is a result of the partial dehydration of the crystal. At the moment the temperature reaches the triple point, the crystal will melt. The melt is a supersaturated solution of the anhydrous phase and the sample will partially recrystallize, so the melt was incongruent. When the sample is in equilibrium at point VIII, the container is opened and the RH is decreased. Note, the RH remains constant as long as an aqueous solution of material A is present in the crystal. At the moment the solution has evaporated, the RH of the crystal will be equal to the applied RH. In the second scenario incongruent melting occurs and the initial grain structure is changed. This stresses that the structure is dependent on the transition routes.

2.1.2 Phase diagrams of hydrates

In the phase diagrams discussed in the following sections (Figures 2.3-2.12), the pressure is considered to be $10^5$ Pa and the RH and the temperature are varied. The black lines represent calculated data, whereas the symbols experimental data. Thick grey lines represent the equilibria of the stable phases, while the dotted grey lines represent metastable equilibria. These lines are drawn by ourselves through the experimental data points and the calculated data. The labels inside the figure represent the expected phase of a salt according to the known transition lines. In case the label is a number it represents the hydration levels of the salt and in case the label is 'Solution', it represents a salt in solution with water. A dashed vertical line indicates the temperature of a triple point, but the corresponding RH is unknown. These are labeled with the loadings of the involved hydrates.
2.1.2.1 Na$_2$SO$_4$

The phase diagram of Na$_2$SO$_4$-H$_2$O is well established (see e.g. Steiger [75]) and is shown in Figure 2.3. Indicated are the thermodynamic stable phases, Na$_2$SO$_4$(V) and Na$_2$SO$_4$·10H$_2$O and the metastable phases Na$_2$SO$_4$(III), Na$_2$SO$_4$·7H$_2$O.

![Figure 2.3: Phase diagram of Na$_2$SO$_4$ in equilibrium with water. The metastable phases are drawn with dotted lines (data from ref. [75]).](image-url)
2.1.2.2 MgSO₄

Another well studied system is MgSO₄-H₂O and the phase diagram [76] is given in Figure 2.4. In the phase diagram only data of MgSO₄·11H₂O, MgSO₄·7H₂O, MgSO₄·6H₂O, MgSO₄·5H₂O, MgSO₄·4H₂O and MgSO₄·1H₂O are plotted. This phase diagram for these phases was composed using Steiger et al., 2011. For MgSO₄·5H₂O only solubility data is available over a small temperature range (90-105 °C) and is extrapolated over the entire range. So, the phase transitions with MgSO₄·5H₂O can deviate from the plotted phase transitions. No data are available for the loadings of 1.25, 2, 2.5 and 3 for MgSO₄ [53, 76–78]. Hence additional research is necessary to complete the phase diagram of this system.

![Phase diagram of MgSO₄-H₂O equilibrium with water](image)

*Figure 2.4: The phase diagram of MgSO₄-H₂O equilibrium with water. The metastable phases are drawn with dotted lines (data from ref. [76]).*
2.1.2.3 CuSO₄

The phase diagram of CuSO₄·H₂O is given in Figure 2.5. For CuSO₄ three stable hydrates are known, CuSO₄·5H₂O, CuSO₄·3H₂O and CuSO₄·1H₂O [73, 79–83]. Metastable phases have not been reported in literature. The data are in good agreement with each other [84].

Figure 2.5: Phase diagram of CuSO₄ in equilibrium with water. The data are a combination of experimental and calculated data from the literature, i.e., Kohler [82], Carpenter [79], Chou [80], Collins [81], International critical tables [73] and Partington [83].
2.1.2.4 FeSO₄

The phase diagram of FeSO₄·H₂O is given in Figure 2.6. In the phase diagram only data of FeSO₄·7H₂O, FeSO₄·6H₂O and FeSO₄·4H₂O are plotted [82,85–92]. Data are missing for loadings of 1, 2, 3 for FeSO₄ [85,90,92,93].

The vertical dashed line indicates the temperature at the triple point heptahydrate, tetrahydrate and aqueous solution measured by Cameron [92] and Bullough [94] (56.7-56.8 °C) since the RH at the triple point is not mentioned in their articles. This temperature is in good agreement with the triple point in the phase diagram. Cameron observed 5 transition temperatures between 7-4, 7-x, 7-2, x-2 and 4-2 (x stands for an unknown loading) over the temperature range of 56.7-67.8 °C. This has not been further studied, but indicates that a lot of transitions are present for FeSO₄ hydrates in this temperature range.

The data by Schumb, Bonell and Cohen have probably been misinterpreted as they most likely observed the transition between heptahydrate into tetrahydrate instead of the transition between heptahydrate and hexahydrate. The data is based on equilibrium vapor pressure data during dehydration of heptahydrate. They did not measure the water content of the sample or determined the crystal structure. Based on the current literature, we expect that the described hexahydrate is in reality tetrahydrate. In addition, the data points of Lescoeur [88], which indicate a phase transition between the monohydrate and the anhydrous iron sulfate, are doubtful, while during dehydration experiments the dehydration of the monohydrate is only observed above 200 °C [93].

Beside the mentioned equilibrium data there is also data available of Wiedemann [91] who studied the dehydration of heptahydrate by the vapor pressure under vacuum conditions. The dehydration was performed in an evacuated sample holder at the start of the dehydration experiment. After evacuation, the sample holder was sealed off and no additional evacuation was performed during the experiment. We have used the data of Wiedemann as an indication. Indeed these data points fit well with the phases transition lines.
Figure 2.6: Phase diagram of FeSO$_4$ in equilibrium with water. The data are a combination of experimental and calculated data from the literature, i.e., Chou [85], Kohler [82], Schumb [86], Cohen [87], Lescoeur [88], Reardon [89], Bonnell [90] and Wiedeman [91]. The vertical dashed line indicates the triple point temperature and is taken from Cameron [92] and Bullough [94].
2.1.2.5 ZnSO$_4$

The phase diagram of ZnSO$_4$-H$_2$O is given in Figure 2.7. In the phase diagram only data of ZnSO$_4$·7H$_2$O, ZnSO$_4$·6H$_2$O and ZnSO$_4$·1H$_2$O are plotted [73,90,95–99]. No data are available for the tetrahydrate of ZnSO$_4$ [100].

Copeland and Short [97] and Barieau and Giauque [99] measured three phase transitions for the heptahydrate, hexahydrate and monohydrate at 21 °C, for the heptahydrate, hexahydrate and aqueous solution at 39 °C and for the hexahydrate, monohydrate and aqueous solution at 60 °C. These three temperatures were used as temperatures for the triple points in this constructed phase diagram. These phase transition lines, between hepta- and hexahydrate and of the solution with hexahydrate fit well with the data points from literature. Only equilibrium data points below 35 °C are reported for the transition between hexahydrate and monohydrate. The phase transition line fits well with these data points.

In addition to the equilibrium data, also a dehydration experiment in a closed sample holder of Wiedemann [91] is plotted in this diagram. The dehydration was performed in an evacuated sample holder. These data fit well with the equilibrium data till 60 °C. The discontinuity in the curve of Wiedemann at 70 °C indicates a transition of one phase to another and he indicated that an incongruent melting of the crystals is observed at that temperature.
Figure 2.7: Phase diagram of ZnSO$_4$ in equilibrium with water. The data are a combination of experimental and calculated data from the literature, i.e., Giaque [96], International critical tables [73], Bonell [90], Chou [98] and Wiedemann [95]. The vertical dashed line indicates the triple point temperatures, because no RH data is available from these measurements. They have been taken from Copeland [97] and Barieau [99].
2.1.2.6 CoSO$_4$

The phase diagram for CoSO$_4$-H$_2$O is plotted in Figure 2.8. In the phase diagram only data of CoSO$_4$·7H$_2$O, CoSO$_4$·6H$_2$O and CoSO$_4$·1H$_2$O are plotted [79,82,95,101,102]. No data are available for the loadings of 2, 4, 5 for CoSO$_4$ [79,82,95,101,102].

Data for the transition between hexa- and monohydrate are sparse and were only evaluated by Boers [103]. The data of Kohler and Zaske [82] is doubted by Broers [103], as Kohler reported tetrahydrate instead of hexahydrate. Equilibrium data between monohydrate and anhydrous CoSO$_4$ in this temperature range were only measured by Kohler [82] and can not be verified by other experimental data.

In addition to the equilibrium data, also a dynamic dehydration experiment in a closed sample holder of Wiedemann [91] is plotted in this diagram. The dehydration was performed in an evacuated sample holder. These data points fit well with the the equilibrium data.

![Phase diagram of CoSO$_4$ in equilibrium with water. The data are a combination of experimental and calculated data from the literature, i.e., Kohler [82], Carpenter [79], Broers [101], Chou [102] and Wiedemann [95].](image-url)
2.1.2.7 NaBr

The phase diagram of NaBr-H$_2$O is given in Figure 2.9. For NaBr the dihydrate and the anhydrous state are observed [104–106], but metastable phases of this system have not been reported. As can be seen most data points are close to each other and above 50 °C only the anhydrous salt and the solution exist. The transition lines are drawn based on the experimental data found in the literature. The data of Lescoeur [104] deviate strongly and have not been considered here.

![Phase diagram of NaBr in equilibrium with water](image)

Figure 2.9: Phase diagram of NaBr in equilibrium with water. The data are a combination of experimental and calculated data from the literature, i.e., Bronsted, Schoorl, Pearce, Menzel and Dingemans [105], Lescoeur [104] and Bell [106].
2.1.2.8 CuCl$_2$

The phase diagram for CuCl$_2$-H$_2$O is plotted in Figure 2.10. For CuCl$_2$ three phases are mentioned: the anhydrous CuCl$_2$, the monohydrate and the dihydrate, respectively. The data of the three sources [104, 107, 108] do not match. Consequently, no phase diagram can be drawn. With help of dynamic vapor sorption, at three temperatures the phase transitions between anhydrous-dihydrate and dihydrate-aqueous solution is determined.

![Phase diagram of CuCl$_2$](image)

*Figure 2.10: Phase diagram of CuCl$_2$ in equilibrium with water. The data are a combination of experimental data from the literature, i.e., Derbye [107], Lescoeur [104] and Polyachenok [108]. In addition dynamic vapor sorption (DVS) experiments are performed to determine phase transition conditions at three temperatures.*
2.1.2.9 CaCl$_2$

The phase diagram for CaCl$_2$-H$_2$O, a well studied salt, is plotted in Figure 2.11. In this graph the RH is plotted in logarithmic scale to indicate the transitions at low RH. For CaCl$_2$ four hydrates with loadings of 1, 2, 4 and 6 [81,109], of which monohydrate and tetrahydrate both have two crystal structures ($\alpha$ and $\beta$), respectively.

![Phase diagram of CaCl$_2$ in equilibrium with water. The data are a combination of experimental data from the literature, i.e., Lannung [109] and Collins [81].](image)

*Figure 2.11: Phase diagram of CaCl$_2$ in equilibrium with water. The data are a combination of experimental data from the literature, i.e., Lannung [109] and Collins [81].*
2.1.2.10 MgCl₂

The phase diagram for MgCl₂·H₂O is plotted in Figure 2.12. In this graph the RH is plotted in logarithmic scale to indicate the transitions at lower RH. In the phase diagram data of MgCl₂·6H₂O, MgCl₂·4H₂O, MgCl₂·2H₂O and MgCl₂·1H₂O is plotted [25, 76, 104, 107, 110, 111].

Kipouros and Sadoway [111] reported three triple points, for hexahydrate, tetrahydrate and aqueous solution at 116.7 °C, for tetrahydrate, dihydrate and aqueous solution at 181.5 °C and for dihydrate, monohydrate and aqueous solution at 240 °C, respectively.

The phase transition line of the tetrahydrate and dihydrate has been given by two researchers Kipouros and Sadoway [111] and Carling [25]. The solubility data have been extrapolated to the triple temperature of tetrahydrate, dihydrate and aqueous solution. The same accounts for the transition curve of tetrahydrate and dihydrate of Carling and Kipouros. The intercept of the curve of Carling and the solubility curve is the triple point and the curve of Kipouros crosses the solubility curve already at 150°C. As the curve of Carling fits best with the other data, the transition curve of tetra- and dihydrate of Carling is used in the phase diagram.
Figure 2.12: Phase diagram of MgCl$_2$ in equilibrium with water. The data are a combination of experimental and calculated data from the literature, i.e., Carling [25], Lescoeur [104], Greenspan [110], Kipouros [111], Derby [107] and Steiger [76]. The vertical dashed line indicates the triple point temperatures, because no RH data is available from these measurements. They have been taken from Kipouros [111].
2.1.3 Concluding remarks

For most salt hydrates a complete phase diagram of the stable phases can be composed, except for CuCl$_2$.

From these phase diagrams we see:

- Sulfates hydrates (XSO$_4$, X=Mg$^{2+}$, Zn$^{2+}$, Co$^{2+}$ and Fe$^{2+}$) have similar phase diagrams.
- CuSO$_4$ and MgCl$_2$ have their first triple point at 97 °C and 116.7 °C, respectively, whereas the other salt have already triple points below 60 °C.
- Chloride crystals can deliquesce more easily than sulfates in case they are stored under atmospheric conditions (25 °C, 40-60% RH).

As mentioned in the introduction, salt hydrates can serve as an interesting heat storage system, because of their high energy density. An energy density above 2 GJ m$^{-3}$ is for most salts only reachable if the salt is dehydrated to the monohydrate or the anhydrous form (see Table 2.1). Based on this knowledge, salts like zinc, cobalt and iron sulfate need additional research. As the hexahydrate-monohydrate transition for these salts are not sufficiently analyzed. Also, the iron sulfate transition from tetrahydrate to monohydrate needs to be studied in more detail.

Finally, CuCl$_2$ should be studied, while no information is available about its phase transitions. This salt may be interesting, while it combines a cation with a high deliquescence RH as is seen by CuSO$_4$ and an anion with a low dehydration RH as is seen by all chlorides. We think that a combination of both will results in a hydrate with preferable performance.

For practical application we have to consider the RH of the air during hydration and dehyration in the heat storage system. We can conclude that in general the sulfates will not deliquesce in an open system as most deliquescence RH’s are above 80% at 25 °C. A drawback is that the rehydration process during the winter will not occur without increasing the RH by additional evaporation of the water into the air. For hydration of these sulfates to the highest hydrate at 60 °C, the applied RH should be in the order of 50-90%. Of the sulfates, CuSO$_4$ has the highest potential based on the phase diagram, as it can rehydrate back to its maximum loading at 60 °C by a RH of 52%.

Chlorides rehydrate at lower RH’s and they could (partially) rehydrate with an external airflow. On the other hand, they can easily deliquesce as their deliquescence RH is lower than the external RH during the entire year. According to the phase diagrams especially MgCl$_2$ could be an interesting, because it will almost rehydrate at 60 °C till the hexahydrate, even under extreme winter conditions. In this case only a small increase in humidity (1-2 percentage point) is necessary to complete this reaction.

Only a small part of the available hydrates are studied in this chapter. Probably also other hydrates can be interesting to study as well, which are not mentioned in this chapter. Conclusions and observations are for that reason only based on these hydrates.
2.2 Ammoniates

In the second half of the 19th century, the first articles were published about the dissociation pressures of ammoniates at constant temperature. The first articles published dealt with chloride complexes [112,113]. After the development of the heat theorem of Nernst [114], as first published in 1906, more research was performed on ammoniates. In this research the focus was mainly on the decomposition schemes of the ammoniates by varying the ammonia partial pressure at constant temperature [115–118]. The enthalpies of the complexes were calculated from the pressure-temperature curves with help of the heat theorem of Nernst.

![Figure 2.13: The dissociation pressure curve of MgI₂·6NH₃ at two different temperatures (488 and 503K, respectively). [119]](image)

The most detailed investigations were done by two research groups in the beginning of the 20th century. These two groups studied a large number of salt complexes, using similar procedures as mentioned above. Firstly, they grew highly loaded ammoniates, which were decomposed by changing the ammonia pressure at constant temperature. Examples of the isotherms are given in Figure 2.13, showing the decomposition of MgI₂·6NH₃ at two temperatures, i.e. 488 K and 503 K. As can be seen, in case the system is equilibrated at a higher temperature, the decomposition starts at a higher vapor pressure. After recording these curves, $\Delta_r H^0$ was calculated. This is called the enthalpy of reaction, which is defined by the energy necessary to fully decompose an ammoniakate into a deammoniated salt and ammonia ($MX\cdot n\text{NH}_3(\text{s}) + \Delta_r H^0 \rightleftharpoons MX(\text{s}) + n\text{NH}_3(\text{g})$). The calculations were performed on the basis of the Nernst heat theorem [114,120–122]:

$$\ln (p \cdot 10^{-5}) = -\frac{\Delta_r H^0}{RT} + 1.75 \ln T + \beta + \alpha T,$$

(2.6)

where $p$ is the decomposition vapor pressure in Pa, $\Delta_r H^0$ is the standard enthalpy
of a salt in J/mol, $T$ is the temperature in Kelvin, $\alpha$ is a constant in K$^{-1}$, which depends on the used salt, and $\beta$ is a dimensionless constant, for NH$_3$ $\beta = 5.42$. For MgI$_2$·6NH$_3$ the $\Delta_r H^0 = (43\pm3)\cdot10^1$ kJ/mol $\Delta_r H^0$ at a vapor pressure of 13.3 kPa and a temperature of 475 K and an $\alpha$ of 0.0078 K$^{-1}$ [119].

This equation allows to calculate with a known decomposition temperature and pressure the corresponding enthalpy of reaction $\Delta_r H^0$ of a salt.

### 2.2.1 Literature of ammoniates

We can group the literature about ammoniates:

- **General literature**: [123–132].
- **Alkali metals**: Li [115, 118, 124, 131, 153, 160]; Na [124, 131, 138, 153]; K [124, 138, 153]; Rb [124, 138, 153] and Cs [124, 153].
- **Alkaline earth metals**: Be [124, 134, 154, 155, 165]; Mg [119, 120, 124, 154]; Ca [25, 112, 124, 131, 135, 139, 141, 166]; Sr [124, 137, 154, 166, 167] and Ba [124, 131, 140, 141, 154, 166].
- **Transition metals (3d)**: Cr [117, 142, 143]; Mn [120, 124, 131, 144, 150, 154, 165]; Fe [120, 124, 131, 142, 144, 149, 154, 154, 165]; Co [116, 120, 124, 144, 149, 154, 162, 165]; Ni [120, 124, 131, 144, 145, 152, 154, 158, 162, 165]; Cu [120, 124, 131, 133, 145, 148, 154, 160, 161, 165, 167, 168] and Zn [112, 120, 124, 144, 145, 147, 149, 165, 167].
- **Other metals**: Pt [142]; Ag [112, 113, 124, 156, 159, 165, 167]; Au [151, 163]; Cd [120, 145, 154, 165, 167]; Hg [154, 164, 165]; Al [136, 142, 157]; In [136]; Tl [124, 133, 142]; Sb [164]; Sn [121, 124, 165] and Pb [124].
- **Sulphates** [142, 147, 148, 162, 165, 168];
- **NiXO$_4$ (X=S; Se; Cr; W or Mo)** [169];
- **Double salts** [121, 163, 168, 170].

### 2.2.2 Thermodynamic overview of ammoniates

The literature available gives us the possibility to determine the enthalpy of reaction of various ammoniates, $\Delta_r H^0$, as a function of the decomposition temperature, $T$, which is plotted in Figures 2.14 and 2.15. Here, we made a distinction between ammoniates with cations of charge 2 (Figure 2.14), e.g., MgCl$_2$, ZnBr$_2$ and CaI$_2$, and of charge 1 (Figure 2.15), e.g., NaBr and LiI. As can be seen for various loadings of the ammoniates an approximately linear relationship between enthalpy of reaction and dissociation temperature is found for each specific loading and charge combination. Also, a higher loading corresponds to a higher enthalpy of reaction and a lower dissociation temperature.
Chapter 2. Thermochemical Materials

2.2.2.1 Selection of salts

Selection of the most suitable salt complex for heat storage from the point of view of energy density, is based on the amount of heat that is stored in the system by

Figure 2.14: The dissociation temperatures against the calculated enthalpy of reaction ($\Delta_r H^0$) for different loadings with NH$_3$ equilibrated at an ammonia pressure of 93.1 kPa. The symbols of the data points are ordered by the number of moles of ammonia per mole salt. The lines are first order guides to the eyes. Only ammoniates are used with a cation charge of +2.

Figure 2.15: The measured dissociation temperatures against the calculated enthalpy of reaction ($\Delta_r H^0$) for different loadings with NH$_3$ equilibrated at an ammonia pressure of 13.3 kPa. The symbols of the data points are ordered by the number of moles of ammonia per mole salt. The dotted lines are first order guides to the eyes. Only ammoniates are used with a charge of the cation in the salt complex of +1.
removing one ammonia molecule from the salt crystal. In Figure 2.16, we plotted the enthalpy of reaction stored in a complex divided by the amount of ammonia molecules from a structure \( (\Delta_r H^+ = \Delta_r H^0 / n) \) plotted against the decomposition temperature for the ammonia pressures at 93.1 kPa. The symbols of the datapoints refer to specific loading of the salt complex. As can be seen a linear trend exists at constant pressure. This suggests that \( \alpha \) and the logarithmic term of equation 2.6 are insignificant for this data set. In the inset, the average enthalpy of reaction is plotted for the four groups, indicating that the alkali metals have the lowest energy stored per added mole ammonia and the transition metals (3d) have the highest amount of energy stored per added mole ammonia. As the difference in average enthalpy of reaction between the metals is smaller than the errorbars, no conclusions can be drawn.

In Figure 2.17, we plotted the enthalpy of reaction stored in a complex divided by the number of ammonia molecules against the number of moles ammonia in a complex. The pressure used for this graph is 93.1 kPa. The averaged \( \Delta_r H^+ \) decreases from 69 kJ/mol (mono ammoniate) to 40 kJ/mol (octa ammoniate). It is harder to release the last ammonia molecule of a complex than to release one ammonia molecule at higher loadings. We can understand this by the fact that, relatively, the crystal structure is changing more in case of smaller loadings. At the higher loadings (above six \( \text{NH}_3 \) molecules per mole salt) the enthalpy of reaction falls down to almost the level of the enthalpy of reactions of decomposition of ammonia. In general, from the point of view of heat storage, therefore, it will be of interest to select a complex, which totally decomposes at the applied temperature and pressure, with a maximum loading of six ammonia molecules per complex, based on Figure 2.17.

![Figure 2.16: The dissociation temperature of a complex plotted against the enthalpy of reaction stored in a complex divided by the number of ammonia molecules. The ammonia pressure is 93.1 kPa. In the inset the average enthalpy of reaction of the four different groups are plotted, whereby only complexes with maximum loading of 6 are used in this average. The labels correspond to the number of complexes in the dataset.](image)
Figure 2.17: The enthalpy of reaction stored in a complex divided by the number of ammonia molecules plotted against the number of moles ammonia in a complex. The ammonia pressure is 93.1 kPa. The enthalpy of reaction is the average of all groups and the error bar is the standard deviation. The labels correspond to the number of complexes in the data set. The dashed line indicates the heat of sublimation of an ammonia molecule.

2.2.3 Discussion

The operation conditions are a first criteria for salt selection. For example in the case of a heating system in houses, the turnover temperature should be between 380 K and 420 K [171]. In addition, secondly the amount of ammonia per mol salt refines the selection. With a larger loading number, less salt is needed to store all heat, but as already mentioned, a loading above six is not favorable. The final selection criteria is the amount of ammonia, which is lost at the applied temperature. Moreover, thirdly, the pressure should not be too high, otherwise to much safety precautions should be considered. A vapor pressure of 0.1 MPa has been used commonly to determine the decomposition temperature.

Taking these three criteria into account, on the basis of the considered data appear viable candidates for heat storage: Ca(ClO\textsubscript{4})\textsubscript{2}-6NH\textsubscript{3} [167], NiCl\textsubscript{2}-6NH\textsubscript{3} [152] or CrBr\textsubscript{2}-6NH\textsubscript{3} [143]. These candidates show a drop of ammonia molecules around 410K of 2.5 till 4 ammonia molecules and can decompose even further at higher temperatures. The heat stored in these three systems will be between 120 and 160 KJ/mol with an energy density of 1-2 GJ/m\textsuperscript{3}. The energy densities within reach are comparable with water systems like MgSO\textsubscript{4} and CaSO\textsubscript{4} [171] and obviously sufficient for heat storage applications.

2.2.4 Concluding remarks

We analyzed a large set of thermodynamic data of ammoniates. For various loadings of ammoniates, the dissociation temperature shows an approximate linear relationship
with the enthalpy of reaction for each specific loading-charge combination. Indeed, by dividing the enthalpy of reaction by the loading, all data points fall on one master curve, which can be divided by the periodic groups. Lower loadings have a large heat storage capacity per molecule of complex, implying that complexes with loading of six or lower are more favorable for heat storage application. With the help of this data set, appropriate ammoniates can be selected as heat storage material for a given temperature and ammonia partial pressure.

### 2.3 Methanol solvates

Methanol solvates have been studied in the past [27, 172–176], but comprehensive overviews of data comparable to those for ammoniates have not been found. One of the first describing methanol solvates is Graham [177]. He compared calcium chloride methanol solvates with hydrates and observed that decomposition temperatures are higher in case of methanol solvates. The dissociation pressures of methanol solvates are plotted in Figure 2.18. Like for ammonia and water, most systems studied are bromides and chlorides. However, presently no sufficient data are available to make general conclusions.

![Figure 2.18: Methanol dissociation pressures of methanol solvates at different temperatures. The data is a combination of experimental data from the literature, i.e., Bonell [172], Lloyd [173] and Offenhartz [27].](image-url)
Chapter 3

NMR

3.1 NMR principles

Nuclei of atoms have a net nuclear magnetic moment. In the presence of an external magnetic field $\vec{B}_0$ [T], the magnetic moment $\vec{\mu}$ [N m T$^{-1}$] of a nucleus precesses around the direction of the external field \[178\]:

$$\frac{d\vec{\mu}}{dt} = \gamma (\vec{\mu} \times \vec{B}_0), \quad (3.1)$$

wherein $\gamma$ is the gyromagnetic ratio [rad Hz T$^{-1}$]. The gyromagnetic ratio depends on the nucleus, e.g., $\gamma/(2\pi) = \gamma = 42.58$ MHz T$^{-1}$ for $^1$H. This is schematically represented in Figure 3.1, where the main field $\vec{B}_0$ is directed in the $z$-direction. The precessing rate of a nucleus $\omega$ [Hz] is given by the Larmor frequency:

$$\omega_L = \gamma \cdot |\vec{B}_0|. \quad (3.2)$$

In a sample, an ensemble of all nuclei of a certain type should be considered. The magnetic moments of these nuclei yield a net magnetization $\vec{M}_0 = \sum_i \vec{\mu}_i$. Consider a volume of $^1$H nuclei, which is placed in an external magnetic field. For this spin 1/2 system, the nuclear magnetization is given by Curie’s Law \[179\]:

$$M = \frac{N\gamma^2h^2B_0}{4k_bT}, \quad (3.3)$$

where $N$ is the number of nuclei [mol], $h$ is the Planck constant [J s$^{-1}$], $k_b$ is the Boltzmann constant [J K$^{-1}$] and $T$ is the temperature [K]. This shows that the magnetization is inversely proportional to the absolute temperature. As an example, the measured NMR signal of ZnSO$_4$·H$_2$O is plotted against the reciprocal temperature scale in Figure 3.2. The linear fit of the data shows that the magnetization is inversely proportional to the temperature. Hence, NMR signals at different temperatures can be compared as long as the data is corrected according to the Curie’s Law.

The direction of the net magnetization $\vec{M}$ can be manipulated by applying a Radio Frequency (RF) magnetic field $\vec{B}_1$ at the Larmor frequency perpendicular to $\vec{B}_0$. In
3.1. NMR principles

Figure 3.1: A schematic representation of the interaction of a magnetic moment with a magnetic field. The magnetic moment $\vec{\mu}$ precesses around the main magnetic field $\vec{B}_0$ with frequency $\omega$.

In order to simplify what happens, a coordinate frame is introduced that rotates at an angular frequency $\omega_L$ around the z-axis of the laboratory frame. To distinguish between the rotating frame and the laboratory frame, the rotating frame is denoted by $x'$, $y'$ and $z'$, whereas the laboratory frame is $x$, $y$, $z$. In this rotating frame, the magnetization vector $\vec{M}$ will rotate due to the torque in a plane perpendicular to the direction of $\vec{B}_1$. This field $\vec{B}_1$ is generated by a RF pulse with duration $\tau$ [s], and as a result $\vec{\mu}$ will rotate over a so-called flip angle $\theta$ [rad] (see Figure 3.3), which is given by:

$$\theta = \gamma \vec{B}_1 \tau. \quad (3.4)$$

The pulse, which generates a flip angle $\theta$, is called a $p_\theta$-pulse. After excitation with a $p_{90}$-pulse, the spins will start precessing in the transverse $xy$-plane. If there is a wire loop in a plane parallel to the $xz$-plane, the changing magnetic flux in the loop will induce a current of frequency $\omega_L$, which can be detected. The amplitude of the detected current will change in time with the Larmor frequency. In the remainder, we will only consider the envelope of the detected current amplitude.

After the excitation of the nuclei with a $p_{90}$-pulse, the longitudinal magnetization in the laboratory frame $\vec{M}_z$ will exponentially increase to its equilibrium value $M_0 \vec{e}_z$ due to energy transfer between the spins and the thermal reservoir, i.e., the lattice. The longitudinal magnetization as a function of time is given by:

$$\vec{M}_z(t) = M_0 \cdot (1 - \exp(-t/T_1)) \vec{e}_z, \quad (3.5)$$

wherein $T_1$ is the longitudinal or spin-lattice relaxation time [s].

Similarly, the transverse magnetization $M_{xy}$ will exponentially decay to zero with a typical time constant $T^*_2$, by a process called spin-spin relaxation. This relaxation is a result of loss of coherence of the nuclear magnetic moments. The transverse magnetization as a function of time is given by [179]:

$$\vec{M}_{x,y}(t) = M_0 \cdot \exp(-t/T^*_2) \vec{M}_{x,y}. \quad (3.6)$$
Figure 3.2: The measured NMR signal of ZnSO$_4$·H$_2$O plotted as function of the reciprocal temperature (bottom horizontal axis) and temperature (top horizontal axis). A fit of a straight line to the data confirms that the magnetization varies inversely proportional to the temperature.

This decay is generally referred to as free induction decay (FID). The relaxation time $T_2^*$, consists of a term related to $T_1$, as well as other mechanisms which give rise to a dispersal of the magnetization in the $xy$-plane, like dipolar processes and diffusion effects. The relaxation rate is then given by [180,181]:

$$\frac{1}{T_2} \cong \frac{1}{T_1} + \frac{1}{T_{2,\text{diffusion}}} + \frac{1}{T_{2,\text{dipolar}}},$$

(3.7)

wherein $T_{2,\text{diffusion}}$ is related to the diffusion of the nucleus in field inhomogeneities and $T_{2,\text{dipolar}}$ is related to the dipolar interaction of different nuclei. In general, one of these mechanisms will dominate the relaxation process.

The $T_{2,\text{diffusion}}$ contribution is related to the movement of a magnetic moment due to diffusion in a field inhomogeneity. For free unrestricted diffusion, the relaxation time is given by:

$$T_{2,\text{diffusion}} \sim \frac{12}{G^2 D^2 t_e^3},$$

(3.8)

wherein $G$ is the gradient [Hz m$^{-1}$], $D$ the diffusion coefficient [m$^2$ s$^{-1}$] and $t_e$ is the echo time [s].

$T_{2,\text{dipolar}}$ is determined by the distance between two dipoles, i.e., $T_{2,\text{dipolar}} \sim \frac{r_{12}}{(\gamma_1^2 + \gamma_2^2)}$, wherein $r_{12}$ is the distance between nuclei 1 and 2 and $\gamma_1$ and $\gamma_2$ are the gyromagnetic ratios of respectively nuclei 1 and 2. In static cases, like solid materials where the distances are small, $T_{2,\text{dipolar}}$ can be in the order of 11 µs [182], whereas for liquid, the effects of neighbor nuclei are random and $T_{2,\text{dipolar}}$ is in the
order of seconds. The observed difference in relaxation time between a liquid and a solid material is explained by the Bloembergen-Pound-Purcell-theory [183] theory. This theory gives a relation between rotational motion of a nucleus and its relaxation time, for both the $T_2$ and $T_1$ relaxation time. The rotational motion of a nucleus is given by the rotational correlation time, $\tau_c$, which is the time wherein a the nucleus rotates $2\pi$. For liquid water this is in the order of $10^{-12}$ s and for solids $10^{-5}$ s. In Figure 3.4 the $T_1$ and $T_2$ relaxation times are plotted as a function of rotational correlation time, $\tau_c$.

In principle if $\omega \tau_c \ll 1$, the molecules rotate faster than the Larmor frequency, the $T_1$ and $T_2$ are equal to each other, so the spin-lattice relaxation time dominates equation 3.7. This is the case in homogeneous fields with small molecules such as liquid
water. In case a strong magnetic gradient is working on these kind of molecules, the $T_{2,\text{diffusion}}$ will dominate equation 3.7. In case $\omega \tau_c \gg 1$, the molecules rotates slower than the Larmor frequency, which is the case for large molecules and solid-like structures, in that case the dipolar interactions dominates. For that reason, the ratio $T_1/T_2$ is an indication of the mobility of the water in a sample.

### 3.2 Pulse sequences

When the magnetic field inhomogeneities are large, the FID will be reduced. This so called inhomogeneous broadening effect can reduce the duration of FID to smaller than 1 ms, making it difficult to measure. In case the magnetic field inhomogeneities are static, the Hahn spin-echo pulse sequence [184], $(p_{90})_0^{- t_e} (p_{180})_{90-t_e}^{- t_e}$-echo pulse sequence, can help. A schematic description of this sequence is given in Figure 3.5a. This pulse sequence starts with a $p_{90}$ pulse and a resulting FID. The spins will rotate clockwise with a frequency $\gamma (\vec{B}_0 + \vec{B}_G(x))$ depending on their position. After this pulse, the spins will therefor dephase depending on their position. When the FID has decayed significantly, a $p_{180}$ pulse is applied at time $t_e$. This pulse will flip the phase of all individual spins and the spins will rotate counterclockwise with the frequency $\gamma (\vec{B}_0 + \vec{B}_G(x))$. This will result in a rephasing effect. After this pulse, spin starts to accumulate phase at the same rate as before the $p_{180}$ pulse. Thus, after time $2t_e$, the net phase shift is zero. This holds for every spin in the sample. Therefor, at time $t = 2t_e$, the transverse components of all individual spins are aligned and give a maximum signal intensity in the RF coil. The resulting signal is called a spin echo. With help of a so-called a CPMG (Carr-Purcell-Meiboom-Gill) pulse sequence, the $T_2$-relaxation times [185,186] can be determined. Instead of recording one echo only, a whole pulse echo train is formed by the following sequence: $(p_{90})_0^{- (t_e-(p_{180})_{90-t_e}^{- t_e})}$-echo. A schematic description of this sequence is given in Figure 3.5b. The signal envelope of this sequence will exponentially decay with a decay constant $T_2$ according to:

$$S(t) = S_0 \exp(-t/T_2). \quad (3.9)$$

A spin-echo cancels out the effect of dephasing as result of static field inhomogeneities. Static field inhomogeneities in a NMR experiment are mostly a result of inhomogeneities in the main magnetic field or an applied magnetic field gradient. Another source of field inhomogeneities are the spins themselves. A spin contains a small magnetic moment and if the distance is small enough, it will effect the magnetic field of a neighboring spins. In case of a solid material the distances between spins are small and the spins are static, so a spin will observe a net magnetic field created by its neighbor. Three contributions of magnetic fields have to be considered in this case, i.e. the main magnetic field ($\vec{B}_0$), the field generated by the gradient ($\vec{B}_G$) and the field generated by neighbor nucleus ($\vec{B}_D$).

Let us consider the case, in which the field directions of all three contributions are initially in the same direction. At that moment, the spins will rotate clockwise with a rate of $\gamma (\vec{B}_0 + \vec{B}_G + \vec{B}_D)$. In case of a $p_{90}$-$p_{180}$ sequence, the second RF-pulse is applied at $t = t_e$ and it will flip all nuclei. As a result, the field created by a neighbor
spin is also flipped. The spin will rotate in that case with a rate of $\gamma(B_0 + \vec{B}_G - \vec{B}_D)$. As the spin is flipped itself, it will now rotate counterclockwise instead of clockwise. In a solid $\vec{B}_D \neq 0$ and so the rotation rate will be different before and after the $p_{180}$. As the rotation rate clockwise and counterclockwise are different and the spins can not longer rephase with each other at time $t = 2t_e$.

Nevertheless, a sequence that does result in an echo in solids is the following: $(p_{90})_0 - t_e - (p_{90})_90 - t_e$-echo. The formed echo at time $t = 2t_e$ is the so called solid-echo. This sequence refocuses spins which interact in pairs and cancels out the effect of the neighboring nuclei. Unfortunately, the solid echoes do not have a convenient classical physical explanation like the spin-echo does. The exact theoretical explanation is beyond the scope of this thesis, but can be found in [187–191].

To determine the $T_2$-relaxation times of solid echo’s, an Ostroff-Waugh (OW) pulse sequence is used: $(p_{90})_0 - (t_e - (p_{90})_90 - t_e$-echo)$_{n_{OW}}$. A schematic description of this sequence is given in Figure 3.5c. In general, it is necessary to set $t_e \ll T_2$, since
otherwise the maximum of the echo will be formed earlier than $2t_e$ [181]. The signal envelope of this sequence will again exponentially decay, i.e., [188,192]:

\[ S(t) = S_0 \exp(-t/T_{2,\text{solid}}), \]  

where

\[ T_{2,\text{solid}} = \frac{12}{M_2 M_4^* t_e^2}. \]  

$M_2$ stands for the so called second moment of the NMR line, $M_4^*$ is a modified fourth moment [188,192].

With the OW-pulse sequence, liquids can also form an echo, but the first echo intensities are fluctuating. The calculations of these intensities are beyond the scope of this thesis, but the theoretical background can be found in [182,193].

### 3.3 Measurement procedure

We prefer to measure the signal decay of a hydrate with a CPMG sequence to avoid the echo intensity variations of the first echoes for liquids by the OW sequence. In hydrates, a combination of solid and liquid-like protons can be present, so it is uncertain if we can measure all protons with the CPMG. To study this effect, the signal decay of a hydrate was measured with two sequences i.e. an OW and a CPMG sequence. All settings were kept the same for both sequences, i.e. the $p_{90}$ and $p_{180}$ have the same pulse time, but the magnitude of the pulses are varied. Consequently, the two pulses have the same frequency content. A hydrate MgSO$_4 \cdot 7$H$_2$O was studied at 25 °C, where it is assumed that all water present in the sample is lattice water. The measured signal is plotted against the time after excitation in Figure 3.6 for both

![Figure 3.6: The signal intensity against the time after excitation of a OW-sequence and a CPMG-sequence of MgSO$_4 \cdot 7$H$_2$O. The signal intensities are fitted with help of FLI (see Figure 3.7)](image-url)
sequences. The signal intensity of the OW sequence is almost twice as large as of the CPMG, but it is possible to generate an echo in a hydrate with a CPMG sequence.

Both relaxation curves were analyzed with help of the Fast Laplace Inversion transformation (FLI) \[194–196\], which generates $T_2$ distributions of the decays (the fits are shown in Figure 3.6). In Figure 3.7, the signal intensity of the $T_2$ components is plotted for these two sequences. In this case, these distributions show that less than 2% of the total signal has a relaxation time above 2 ms in both sequences, being a result of the noise. By analyzing the components with a $T_2$-relaxation time below 2 ms, we observe that the CPMG sequence measures a longer relaxation time compared to the OW sequence, but measures a smaller amount of signal, being 0.42 of the signal intensity of the OW sequence. This value has to be determined for each hydrate and should be used as correction factor $\alpha$ of the lattice water component. Here, we assume that -at different loadings- the lattice water is underestimated by the CPMG sequence with a constant factor.

As the CPMG underestimates the lattice water component, the lattice water component is corrected after analyzing the decay curve by dividing the component by the correction factor $\alpha$, e.g. 0.42 in case of MgSO$_4$. An example of a heating experiment is presented in Figure 3.8. A MgSO$_4$·7H$_2$O sample was heated with 3 °C/min from 25-120 °C in a closed sample holder to prevent escape of water. The closed markers show the components of the uncorrected lattice (■) and uncorrected total water (▲) in the sample. The total water component is the summation of the uncorrected lattice water ($T_2 < 500$ μs) and the liquid water ($T_2 > 500$ μs). The uncorrected total amount of water increases with raising temperature. The open markers show the corrected lattice (□) and total water (△) in the sample. The lattice water was corrected with the factor $\alpha$. In that case, the total water component is constant over the entire range.
Chapter 3. NMR

Figure 3.8: The CPMG signal intensity plotted against the temperature of a MgSO$_4$·7H$_2$O sample with a closed sample holder by heating from 25-120 °C at a heating rate of 0 °C/min. The uncorrected total water component is the sum of the uncorrected lattice water and liquid water. The signal intensity of the uncorrected total water component increases with increasing temperature. The corrected total water component is the sum of the corrected lattice water and liquid water. The signal intensity of the corrected total water component is constant with increasing temperature.

This experiment shows that the proposed correction of the CPMG data is adequate. For all hydrates the $\alpha$ is determined.

3.4 NMR setup

The NMR measurements in this thesis were performed on a NMR setup using a 4.7T magnet, i.e., a proton resonance frequency of 200 MHz. A schematic overview is given in Figure 3.9. The magnet has a homogeneity of < 6 ppm over 30 mm Diameter of Spherical Volume (DSV). A magnetic gradient is generated in the z-direction by a set of Helmholtz coils. The strength of the gradient was evaluated by a gradient calibration sample, i.e. a perspex holder with 1 mm slices separated 1 mm of each other and filled with water doped with CuSO$_4$. The resulting measured profile is plotted in Figure 3.10a. From this plot, the frequencies taken at half peak height are plotted against the position in Figure 3.10b. The linear fit through the data points show that a constant gradient up to a strength of 24 kHz m$^{-1}$ can be reached over 12 mm. A gradient in the magnetic field results in a spatial resolution in a NMR experiment and this resolution can be calculated by:

$$\Delta x = \frac{1}{G\tau_{acq}},$$

(3.12)

wherein $G$ is the magnetic gradient [Hz m$^{-1}$] and $\tau_{acq}$ is the acquisition window [s].

Both axial and transverse coils were designed for experiments to follow the dehydration of hydrates/ammoniakates at different sample sizes and conditions. In Table
3.4. NMR setup

3.1 The properties of three coils used are listed. A more detailed description per coil is given in the following paragraphs.

To determine if the coil resonates efficiently, the performance of the coil can be quantified with help of the quality factor. This factor is defined as the ratio of the stored magnetic energy to the energy lost per cycle and given by:

$$Q = \frac{\Delta \omega}{\omega_0} = \frac{L \omega}{R},$$

wherein $\Delta \omega$ is the width of the resonance peak, $\omega_0$ is the resonance frequency, $L$ is the inductance of the coil and $R$ is the resistance.

Apart from the energy stored in the coil, the $Q$-factor is an indication for the sensitivity of the coil at a certain frequency. A large $Q$-factor corresponds with a more sensitive coil. The $Q$-factor also determines the time it takes to accept the maximum delivered power $t=Q/\omega$. Note that in case of a high $Q$-factor, the coil is

![Figure 3.9: A schematic representation and a picture of the NMR setup used.](image)

Table 3.1: The properties of the coils used.

<table>
<thead>
<tr>
<th>Coil name</th>
<th>Solenoid</th>
<th>AGR</th>
<th>Birdcage</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\vec{B}_1$ direction</td>
<td>Axial</td>
<td>Transversal</td>
<td>Transversal</td>
</tr>
<tr>
<td>Sample diameter (mm)</td>
<td>6</td>
<td>6</td>
<td>30</td>
</tr>
<tr>
<td>Sample length (mm)</td>
<td>10</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>Q-factor</td>
<td>30</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>Working temperature (°C)</td>
<td>20-150 °C</td>
<td>20-150 °C</td>
<td>20-30 °C</td>
</tr>
<tr>
<td>$\rho_{90}$-pulse</td>
<td>13</td>
<td>6</td>
<td>30</td>
</tr>
<tr>
<td>Maximal gradient (T/m)</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>
far more sensitive to small shifts in resonance frequency of the coil as result of e.g., temperature or loading. For experiments on hydrates with changing the temperature, we choose a quality factor of 30 to minimize the effects of detuning due to temperature variations.

Figure 3.10: a) The signal intensity measured against frequency for a reference sample and a gradient calibration sample. b) The frequency plotted against the position at half height of the peaks of Figure 3.10a.
3.4.1 Solenoid

The geometry of the solenoid coil is given in Figure 3.11. A Teflon holder with an outer diameter of 10 mm is used as a basis for the coil. Around this holder, a Faraday shield incorporated out of copper wires. These wires are placed parallel to each other and are soldered and grounded on one side, whereby the ring is interrupted at one point. This shield is incorporated in order to reduce the effect of variations in the dielectric permittivity of the sample during moisture variations. [197–199]. A layer of 1 mm Teflon is wrapped over the Faraday shield where on top the actual solenoid is turned consisting of four windings over 20 mm. With a tuning circuit, the coil is connected to the RF-amplifier. The solenoid is placed in a messing box, which is temperature controlled by two heat resistors. The advantages of a solenoid are the simple geometry, its high sensitivity and the homogeneity of the produced $B_1$-field.

On the other hand, to change a sample the coil has to be taken out of the magnet, because of the vertical main magnetic field.

![Figure 3.11: Schematic of the solenoid and a picture of the solenoid used.](image-url)
3.4.2 AGR

An Alderman-Grant resonator (AGR) is a homogeneous resonator [198], based on a "Slotted cylinder". This type of resonator is designed for high field NMR and a schematic representation is given in Figure 3.12. It contains two H shaped copper foils wound about a cylinder. The H shaped copper foils are connected with capacitors and the feed is done by a tuning circuit. Two grounded guard rings consisting of electrically closed rings are placed at both ends, which reduces the effect of variations in the dielectric permittivity of the sample during moisture variations. A length between 1 and 1.5 times the diameter of the resonator is preferred. The advantage of this resonator is the sample accessibility, i.e. the resonator can stay in place to change samples. The disadvantage is that the homogeneity and the sensitivity is lower compared to a solenoid. For our purposes, the homogeneity of the AGR is sufficient. The experiment given in Figure 3.10 is performed with the AGR. It shows that the AGR has an almost constant coil profile over a distance of 12 mm.

![Figure 3.12: Schematic of the AGR and a picture of the AGR used.](image)
3.4.3 Birdcage

The Birdcage resonator was introduced by Hayes [200, 201], which is a homogeneous resonator. It consists of a linear network of identical filter cells connected together in such a way that the last one is identical to the first. Figure 3.13 shows the Low-pass Birdcage resonator that was used. The resonator is designed according to the calculations of Gülker [202] to resonate at 200 MHz. Hereby the legs are connected with the two rings by capacitors of 18 pF. Inside the resonator, two grounded rings minimize detuning by varying the dielectric constant during an experiment. This resonator is fed with inductive coupling by a loop over two legs. In contrast to a solonoid or AGR, the advantage of this resonator is that a large volume can be measured with a Birdcage at high frequencies. The Birdcage resonator produces also a highly homogenous field inside the coil. The disadvantage is the complexity in its design.

![Figure 3.13: Schematic of the birdcage and a picture of the birdcage used.](image)
Chapter 4

Water transport in MgSO$_4$·7H$_2$O during dehydration

The water phases in a MgSO$_4$·7H$_2$O crystal during heating were studied with help of NMR. The TGA data showed that the heating rate has a strong effect on the dehydration process. NMR experiments showed that pore water, i.e. an aqueous solution of MgSO$_4$, was produced during dehydration. Additional NMR measurements indicate a water diffusion coefficient of this pore water that is 10 times lower than that of bulk water. We showed on the basis of a model that pore water is produced as the vapor release is not sufficient at crossing a phase transition temperature.

4.1 Introduction

In literature MgSO$_4$ [77] is seen as a salt with a high potential for heat storage systems [23,31,32]. Different phases of the MgSO$_4$ hydrates can be identified with help of techniques, like XRD, Raman and neutron diffraction under equilibrium conditions [34, 35, 203, 204] and under dynamic conditions, i.e. by changing the temperature [42, 46, 47, 205] or the vapor pressure [49–52].

From the equilibrium data it is known under which conditions (temperature and vapor pressure) which hydrate is stable. How water is dynamically redistributed during a transition of one hydrate into another is not considered. Such knowledge of water transport is, however, needed for a better understanding of the dehydration processes of hydrated salts. The goal of this chapter is to get a better understanding of how water is transported on a macroscopic scale during the dehydration induced by heating. The main question is: How does water leave a hydrated salt during dehydration induced by heating? We will answer this question with help of nuclear magnetic resonance (NMR), which introduces the feature to monitor water molecules within a hydrate during dehydration non-destructively.
4.2 Phase Diagram MgSO\textsubscript{4}-H\textsubscript{2}O

The phase diagram of MgSO\textsubscript{4}-H\textsubscript{2}O is given in Figure 4.1. This diagram shows stability fields and the coexistence curves of the MgSO\textsubscript{4} hydrates as function of temperature and relative humidity (RH). The bold and dotted lines in this graph predict phase transitions at certain RH and temperature and have been composed on the basis of a combination of experimental data and thermodynamic calculations [76]. The label next to lines indicates the transition, e.g. 7-4 stands for the transition between MgSO\textsubscript{4}·7H\textsubscript{2}O and MgSO\textsubscript{4}·4H\textsubscript{2}O, whereas aq indicates an aqueous solution of MgSO\textsubscript{4}. In case of a solid line there is a phase transition between two stable phases, whereas the dotted lines indicate a phase transition with at least one metastable phase. For example, let us assume a MgSO\textsubscript{4} crystal equilibrated at a RH of 80% at 20 °C. In this case MgSO\textsubscript{4}·7H\textsubscript{2}O (heptahydrate) will be formed, as these conditions are within an area enclosed by stable phase transitions lines. As long as the temperature and RH are kept within this area there will be no transformation. Let us now assume that the temperature is kept constant and the RH is slowly decreased to 30%. In this case there will be a phase transition. If during the decrease the crystal is kept in equilibrium with the changing relative humidity there will be a phase transition as indicated by the bold line, i.e., there is a transition from heptahydrate to monohydrate at 47%. Only when all crystals are transformed the relative humidity can be decreased to 30%.

At the moment that the crystal is not kept in equilibrium, i.e. by a sudden change

\begin{figure}
\centering
\includegraphics[width=\textwidth]{phase_diagram.png}
\caption{Relative humidity (RH)- temperature (T) phase diagram of MgSO\textsubscript{4} + H\textsubscript{2}O. The solid lines enclose the areas of the stable phases, the dashed black line is an extrapolation of the phase transition of solution and monohydrate. The dotted lines are the calculated phase transitions of metastable phases.}
\end{figure}
in RH there can also be a transformation in which a metastable crystal is formed. Such transformations are indicated by the dotted lines and in this case the crystal can also transform to the metastable phase MgSO\(_4\)-5H\(_2\)O. If this transition occurs, the pentahydrate can at the same time transform to the monohydrate, as indicated by the dashed line at 48.5% RH. These combined transitions indicate that during such a transformation there is no equilibrium between the crystal and the surrounding RH. Indeed, it is not possible to determine from the phase diagram which crystal will be observed, as this will depend on the transition rate of the various transformations. The transformation can be described by:

\[
\begin{align*}
\text{MgSO}_4\cdot7\text{H}_2\text{O}(s) & \xrightarrow{k_1} \text{MgSO}_4\cdot5\text{H}_2\text{O}(s)+2\text{H}_2\text{O(g)} \xrightarrow{k_2} \text{MgSO}_4\cdot\text{H}_2\text{O}(s)+4\text{H}_2\text{O(g)}, \\
\text{MgSO}_4\cdot7\text{H}_2\text{O}(s) & \xrightarrow{k_3} \text{MgSO}_4\cdot\text{H}_2\text{O}(s)+6\text{H}_2\text{O(g)}. 
\end{align*}
\] (4.1)

Here the \(k_i\) indicate the reaction rate, i.e. metastable transition rate of heptahydrate to pentahydrate \(k_1\), the metastable reaction rate pentahydrate to monohydrate \(k_2\), and finally the direct stable transition rate from heptahydrate to monohydrate \(k_3\). If \(k_1 > k_3\), the dehydration follows the pentahydrate pathway and metastable crystals will be formed. In case that \(k_1 \geq k_2\), pentahydrate will be observed. In case that \(k_1 < k_2\), the formed pentahydrate is immediately transformed into the monohydrate and pentahydrate will not be observed. Hence sudden changes in RH can have strong effects on the interpretation of dehydration or hydration experiments [206,207].

### 4.3 Model

The dehydration process of MgSO\(_4\)-7H\(_2\)O by varying temperature and relative humidity can be modeled with help of the data from the phase diagram of Figure 4.1. In these models it is emphasized that only stable phases and no reaction rates are considered. In this section, three different models will be discussed in order to get a better understanding of the dehydration. Each model has two boxes, box A and box B. In box B only water vapor is present, while in box A MgSO\(_4\) and H\(_2\)O are present.

<table>
<thead>
<tr>
<th>Phase (i)</th>
<th>Molecular formula</th>
<th>(\rho_i) (10(^3) mol/m(^3))</th>
<th>(m_i) (mol/mol)</th>
<th>(h_i) (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hepta</td>
<td>MgSO(_4)-7H(_2)O(s)</td>
<td>6.82</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td>hexa</td>
<td>MgSO(_4)-6H(_2)O(s)</td>
<td>7.71</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>mono</td>
<td>MgSO(_4)-H(_2)O(s)</td>
<td>17.67</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>aqua</td>
<td>MgSO(_4)(aq)</td>
<td>(\frac{S(T)\rho_{\text{solution}}}{S(T)M_{\text{MgSO}_4}+1} \times \exp (29.386-5132/(T+273.15)) \times \frac{R, H, 100}{R,(T+273.15)\times 10^4})</td>
<td>1</td>
<td>(\frac{M_{\text{water}}, S(T)}{R, H, 100})</td>
</tr>
<tr>
<td>vapor</td>
<td>H(_2)O(g)</td>
<td>133.32</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>
4.3. Model

Box A is always in thermal equilibrium according to the phase diagram in Figure 4.1 and the various phases present in box A are homogeneously distributed over its volume. We will not consider density changes as result of temperature in this model for the solid hydrates. For the aqueous solution of MgSO$_4$, the density is taken from literature [208,209], which depends on the MgSO$_4$ concentration and temperature of the solution. The possible phases and corresponding densities are given in Table 4.1. All three models assume that the number of moles of MgSO$_4$ ($m_{\text{MgSO}_4}$) in box A is constant:

$$n_{\text{MgSO}_4} = \sum_i m_i \cdot n_i \equiv \text{constant},$$  \hspace{1cm} (4.3)

wherein $n_i$ is the number of moles of phase $i$ in box A and $m_i$ the number of moles MgSO$_4$ per mole of phase $i$. The possible phases in box A are given in Table 4.1, all the time $n_i \geq 0$.

During an experiment the temperature of boxes A and B are varied according to:

$$T(t) = T_0 + H \cdot t,$$  \hspace{1cm} (4.4)

wherein $T_0$ is the initial temperature in °C and $H$ the heating rate in °C/min, representing a dehydration experiment induced by a temperature change.

4.3.1 Model 1

Figure 4.2a gives a schematic overview of model 1, i.e. the dehydration of box A filled with a single crystal MgSO$_4 \cdot 7$H$_2$O. In this model, we assume that box A ($V_a$) is a single crystal, i.e. the walls of box A are the surfaces of the crystal and no vapor phase is present. The volume of box A is variable and water vapor can pass through the walls. In addition, we assume that the water transport is not a limiting factor inside the box nor through the wall and that all produced vapor during a dehydration reaction is instantaneously released from box A into box B. Box B has an infinite volume with a constant vapor density $\rho_{v,\text{outside}}$. Box A and box B are always in thermal equilibrium. These assumptions are only valid in systems that change extremely slowly in time, as the example discussed in Figure 4.1 on the RH change. Let us now assume we will perform a dehydration experiment by decreasing the RH in box B to RH = 0% and afterwards increase the temperature of both boxes from 18 till 90 °C. In Figure 4.3a the phase diagram used in this model is plotted with the trajectory (thin solid line) of box A in model 1 for this experiment. Initially box A has a volume of $V_0$, which is filled with MgSO$_4 \cdot 7$H$_2$O with a density of $\rho_7$ ($n_7 = V_0 \cdot \rho_7$) and box B has the initial conditions of $T = 18$ °C and RH = 60%. The heating rate in this simulation is irrelevant, because we assume that all reactions and exchanges occur instantaneously. When the RH in box B drops to RH = 0%, box A immediately reacts into monohydrate according to the phase diagram in Figure 4.1. Box B is infinitely large, so the released vapor from box A does not effect the RH in box B. By increasing the temperature to 90 °C, no further reaction occurs, because the monohydrate is stable under the applied conditions.

In this model, the phases in box A are determined by the conditions in box B, no mathematics is necessary to know the phases in box A in this model. This model is ill-defined when the applied conditions in box B cross a phase transition line -which is
Chapter 4. Water transport in MgSO\(_4\)·7H\(_2\)O during dehydration

Figure 4.2: A schematic representation of the three models of dehydration. Model 1: box A is in equilibrium with box B, whereby a fast exchange of vapor is possible. Model 2: box A is isolated from box B, the number of moles water and MgSO\(_4\) are constant in this box. Model 3: box A is in connection with box B, the number of moles water can vary and the number of moles MgSO\(_4\) is constant in this box. Only vapor can escape from box A to box B by an airflow \(v\).

A coexistence line-, because at that moment all possible ratios of the two phases from that phase transition line will fit. The volume of box A in model 1 can be calculated according to:

\[
V_a = \sum_i \rho_i^{-1} \cdot n_i. \tag{4.5}
\]

In this example, the final volume is \(V_a = \rho_{\text{mono}}^{-1} \cdot n_{\text{mono}}\). The amount of water in box A can be calculated by:

\[
n_{\text{water}} = \sum_i h_i \cdot n_i, \tag{4.6}
\]

wherein \(h_i\) is the number of moles of water per mole of material \(i\). In this example \(n_{\text{water}} = h_i \cdot n_{\text{mono}} = n_{\text{mono}}\) at the final conditions. The number of water molecules lost can be calculated by:

\[
n_{\text{water loss}} = n_{\text{water},0} - n_{\text{water}} = \sum_i h_i \cdot (n_{i,0} - n_i). \tag{4.7}
\]

4.3.2 Model 2

A schematic overview of model 2 is given in Figure 4.2b. In this case we assume a closed box A partially filled with a single crystal, with no exchange of water molecules through the walls of box A to box B. This can be seen as an experiment whereby a crystal is placed in a closed sample holder. The volume of box A is determined by the volume of the single crystal inside the box and the free volume around the crystal, which determines the porosity of box A. The water transport inside the box is not a limiting factor. Because we are working with a closed box, the amount of
Figure 4.3: a: The phase diagram of stable phases of MgSO₄·H₂O, whereby the three models are plotted. The curves show the expected RH and temperature during a certain dehydration process. b: The loading of MgSO₄·7H₂O during a dehydration experiment according to model 2. c: The loading of MgSO₄·7H₂O during a dehydration experiment according to model 3 with an air flow v of 1 mm/s with a sample volume of 20 mm³ at a heating rate of 0.35 °C/min. The total amount of water is divided in lattice and pore water.
water \(n_{\text{water}}\) is kept constant during the experiment. Also, in this case the number of moles of MgSO\(_4\) will be constant, i.e. equation 4.3 is valid, as no exchange of material between box A and box B is allowed. As the volume is constant due to the closed sample holder, equation 4.5 can be rewritten as:

\[
V_a = \sum_i \rho_i^{-1} \cdot n_i \equiv \text{constant.} \tag{4.8}
\]

Here it should be noted that we incorporated the gas phase and hence the volume of the gas phase will represent the porosity. Next to a constant volume, the number of moles of water in box A is constant as there is no exchange (\(n_{\text{water loss}} = 0\)):

\[
 n_{\text{water}} = \sum_i h_i \cdot n_i = n_{\text{water, t=0}} = \text{constant.} \tag{4.9}
\]

In the example at 18 °C, water vapor is present in combination with heptahydrate, monohydrate, an aqueous solution of MgSO\(_4\), or a coexistence of two of these three phases. For every case we can calculate the number of moles of phase \(i\) by using three equations 4.3, 4.8 and 4.9. In case of a combination of heptahydrate, water vapor and an aqueous solution of MgSO\(_4\), we have three unknowns \(n_{\text{hepta}}, n_{\text{vapor}}\) and \(n_{\text{aqua}}\) and all three should satisfy \(n_i \geq 0\). These equations can be solved and there will be only one solution. In contrast to model 1, this model is well-defined at phase transition lines. It is only ill-defined at triple points, because in that case four unknowns are present in the system and only three equations exist in the mathematical model.

We consider the same dehydration experiment as in model 1, i.e. decreasing the RH in box B to RH = 0% and a subsequent increase in the temperature of both boxes from 18 till 90 °C. Without exchange between box A and box B the decrease in RH in box B is not relevant. We assume that the crystal in box A occupies 90% of the box. The other 10% defines the porosity in this model. The initial conditions in box A are 60% RH and 18 °C. The heating rate in this simulation is irrelevant, because we assume that all reactions and exchanges occur instantaneously. In Figure 4.3a the results are plotted with the trajectory (dashed line) of box A. Initially in this model the RH slowly decreases, due to the increased water vapor capacity of air with increasing temperature. As the temperature is increasing with a constant number of water vapor molecules in the air the RH will decrease. When the RH reaches the heptahydrate-hexahydrate phase transition line the RH will subsequently follow the phase transition line. By further heating the heptahydrate in the sample will slowly dehydrate to hexahydrate. The released water will appear as water vapor and this will increase the vapor pressure and hence the RH. By crossing the triple point of heptahydrate, hexahydrate and aqueous solution, all heptahydrate present in the sample will dehydrate to the hexahydrate, because according to the phase diagram no heptahydrate can exist at temperatures above the triple point temperature. The released water, i.e. lattice water, is relocated either as vapor or as aqueous solution, which the latter will partially dissolve the hexahydrate. This aqueous solution will be referred to as pore water. In Figure 4.3b the composition of box A is plotted for model 2. As can be seen in Figure 4.3b about 24% of the water is present as pore water at the triple point. That is liquid water (an aqueous solution of MgSO\(_4\)) that
partially fills up the porosity, i.e. the pore space and hence will be referred to as pore water. By further increasing the temperature, the amount of pore water increases as a result of the temperature dependence of the hexahydrate solubility. By crossing the triple point of hexahydrate, monohydrate and solution, again an increase of pore water is observed. In this case, further heating decreases the solubility as well as the pore water contribution. Where initially 90% of the box was a solid hydrate, at 90 °C only 17% is occupied by a solid hydrate, 80% by the aqueous solution and only 3% by the vapor phase.

The dehydration process in this model is strongly affected by the porosity of the system. In the limiting case that the porosity approaches 100%, model 1 and model 2 will be equal to each other.

4.3.3 Model 3

The major drawback of model 2 is that water cannot be released into box B. In reality the situation will be somewhere in between model 1 and model 2. During the decomposition of hydrates, often a pseudomorphic structure appears, i.e. after dehydration of a crystal the outer shape is similar as initially, but the crystal becomes porous. This is incorporated in model 3. The volume of box A is again considered to be constant. The water vapor can escape the box at a limited rate, depending on the exchange rate between box B and box A. Figure 4.2c shows a schematic overview of model 3. Box A has a constant volume and a limited exchange with box B, depending on the surface area of box A and the airflow v over this surface.

The number of moles of water molecules in box A can be calculated from the time integration of the water vapor flux:

\[ n_{\text{water}}(t) = \sum n_i h_i = n_{\text{water}}(t=0) - \int_0^t A \cdot v(\rho_{\text{vapor}}(T(t')) - \rho_{\text{flow}}(T(t'))) \cdot dt' \geq 0, \]

(4.10)

wherein \( A \) is the surface of box A \((A = 6V_a^{2/3})\), \( v \) the airflow in m/s, \( \rho_{\text{flow}} \) is the vapor density of the airflow and \( \rho_{\text{vapor}} \) represents the vapor density in box A.

Let us again assume box A contains initially 90\% \( \text{MgSO}_4 \cdot 7\text{H}_2\text{O} \) and is equilibrated at a RH of 60\% and 18 °C. The initial volume is \( V = 20 \text{ mm}^3 \), and the airflow is \( v = 1 \text{ mm/s} \). The vapor density in box B is equal to 0 \text{ mol/m}^3. The heating rate in this simulation is again 0.35 °C/min and heated up from 18 till 90 °C. In Figure 4.3a the results are plotted with the trajectory (dotted line) of box A. In Figure 4.3c the composition of box A is plotted for model 3 during this experiment. Similar to model 2, equations 4.3 and 4.8 are used, but the water content is calculated by equation 4.10. By solving these three equations, the environmental conditions and phases are calculated. The RH decreases till it touches the phase transition line between the monohydrate and the heptahydrate. It will cross the triple point of monohydrate, hexahydrate, and heptahydrate and the system follows the heptahydrate-hexahydrate line. At crossing the triple point of heptahydrate, hexahydrate and aqueous solution, pore water is produced similar to model 2. This pore water is decreasing with a further increase of the temperature and at a certain moment, all pore water is evaporated and the phases in box A shift from a mixture of an aqueous solution of \( \text{MgSO}_4 \) and hexahydrate to a mixture of hexahydrate and monohydrate. By crossing the triple point of hexahydrate, monohydrate and aqueous solution again some pore water is...
produced, but by increasing the temperature the pore water evaporates and finally inside box A only monohydrate is observed. At that moment the vapor pressure in box A is equal to the vapor pressure in box B and the RH in box A is 0%.

This model emphasizes that vapor transport out of the sample strongly effects the dehydration. Different from the other two models, model 3 strongly depends on the heating rate as related to sample volume and air exchange. In Figure 4.4 the water contents as calculated for 6 different heating rates are plotted ($V = 20 \text{ mm}^3$, $v = 1 \text{ mm/s}$). When the heating rate is equal to infinity, model 3 is equal to model 2. In the limiting case the heating rate is equal to 0, the model will be equal to model 1. As can be seen, the production of pore water strongly depends on the heating rate. It may happen that the lattice water component increases by further heating as result of recrystallization of the pore water. According to this model, it is not possible to totally dissolve the entire crystal in its own crystal water at any heating rate.

4.4 Materials and methods

4.4.1 Sample preparation

Magnesium sulfate heptahydrate crystals were prepared by initially saturating demineralized water at 40 °C with magnesium sulfate heptahydrate (ACS grade, Merck KGaA, Darmstadt). By cooling down the saturated solution to 20 °C, a supersaturated solution was created, which initiated the crystal growth. The solution was stored in a beaker closed with aluminium foil, with a small hole allowing water vapor to escape. The crystals were kept in the saturated solution until a size was reached in the order of 4x4x15 mm$^3$. Afterwards the crystals were crushed to approximately 1x1x1 mm$^3$ and equilibrated with a saturated solution of KCl at 22 °C (RH=85%). Hence, all different experiments are performed starting with the similar material.

4.4.2 Thermogravimetric analysis (TGA)

First we characterized the crushed crystals (1x1x1 mm$^3$) with TGA, i.e. a TG50 of Mettler Toledo. The sample holder was an aluminum cylinder; 12 mm in height and 6.6 mm in diameter, and closed with an aluminum oxide disk of 1 mm thickness and a hole of 1 mm. This hole enables evaporation of water from the sample. Outside the sample holder, a nitrogen atmosphere (~0% RH) was applied.

4.4.3 Nuclear Magnetic Resonance (NMR)

We used NMR to get more information on the state of water molecules inside hydrates during dehydration. NMR measurements were performed on a spectrometer operated at a Proton Resonance Frequency (PRF) of 200 MHz. For detecting nuclei with transversal relaxation times ($T_2$) larger than about 50 μs, we used a home-build RF-coil with a Faraday shield. With this Faraday shield, a quantitative analysis of the NMR signal can be performed. This is possible, as the Faraday shield decreases the effect of varying dielectric constants during dehydration experiments [199]. In
4.4. Materials and methods

Figure 4.4: The water loading of the different components calculated with the help of model 3 for six different heating ratings for an air flow $v$ of 1 mm/s and a sample volume of 20 mm$^3$: a) The total water content, b) The pore water content and c) The lattice water content.
Chapter 4. Water transport in MgSO$_4$·7H$_2$O during dehydration

this setup, the temperature can be controlled with an inaccuracy of 1 °C over a temperature range of 20-150 °C.

The NMR signal $S(t)$ will attenuate according to:

$$S(t) = \sum S_i(t = 0) \cdot \exp \left( -\frac{t}{T_{2,i}} \right),$$

wherein $S_i$ is the proton density from the nuclei, which is related to the water density, and $T_{2,i}$ is the transversal relaxation time of the investigated nuclei.

In the NMR experiments, a cylinder of 1 cm height and 6 mm diameter was filled with crushed crystals (1x1x1 mm$^3$). The porosity in the sample holder is around 30%, which was calculated with help of the mass of the sample and theoretical density of the crystals. The sample holder is open from one side during the dehydration experiment and nitrogen (∼0% RH) is blown over the sample holder.

4.5 Results

4.5.1 TGA

TGA measurements were performed with an initial mass of 300±10 mg and with different heating rates of 0.15-10 °C/min. The loading during this experiments was calculated under the assumption that the initial sample consists of heptahydrate crystals. In Figure 4.5 the measured loading with the TGA is plotted against the temperature. The effect of incomplete dehydration steps can be seen by higher heating rates. Phase transformations are smeared out and shift towards higher temperatures as a result of the limited dehydration time. This fits well with our model 3.

Two main observations can be made from these experiments. First, during dehydration the grains can obviously dehydrate into mixed phases, because the dehydration is incomplete before the temperature crosses a transition line. As a results the average loading of the grains does in general not dehydrate in steps with integer values. These non-integer dehydration steps have previously also been observed in the literature [42,210,211].

Second, the water loading in the sample during dehydration is higher than expected based on the phase diagram. The question is therefore: is additional water still present as crystal water, as result of a slow reaction rate, or is the water present in another phase? With TGA it is only possible to study the amount of water molecules and not possible to clarify the state of water. NMR will be used to study how the water molecules are present in the grain structure.

4.5.2 NMR

In Figure 4.6 the loading is plotted against the temperature of a dehydration experiment with a heating rate of 0.375 °C/min. The corresponding TGA data have been added. The curve of the total water component of the NMR experiments fits reasonable well with the TGA experiments, which indicates that all water is measured during the NMR experiment.
4.5. Results

Figure 4.5: The loading plotted against the temperature during dehydration experiments of MgSO$_4$·7H$_2$O at various heating rates and constant initial sample size. The grains used were about 1x1x1 mm$^3$ and the total sample weight was equal to 300 mg. The legend denotes the used heating rate.

Figure 4.6: The loading of MgSO$_4$·7H$_2$O as measured by NMR and TGA plotted against the temperature during dehydration experiments with 0.375 $^\circ$C. The total water component of the NMR experiment is divided with help of relaxation analysis into lattice water ($T_2 < 10^{-3}$ s) and pore water ($T_2 > 10^{-3}$ s).
Additional information on the state of water can be obtained on the basis of relaxation analysis of the NMR signals. The relaxation curves were analyzed with help of the fast Laplace Inversion Transformation (FLI) [194–196], to calculate $T_2$ distributions of a decay. With help of this relaxation analysis, the decay curves measured during the NMR experiment were analyzed. In Figure 4.7 the $T_2$ relaxation distribution is plotted as a function of the temperature during a dehydration experiment. The relaxation distribution can be divided in two regimes: lattice water with $T_2 < 300 \, \mu s$ and pore water with $T_2 > 300 \, \mu s$. Lattice water is part of the crystal structure. These water molecules are immobile and have strong static interaction with their neighboring water molecules. As a result of this strong static interaction, the relaxation time is small [182]. As can be seen at 25 °C, > 99% signal corresponds to hydrate water with a mean $T_2$ value of 100 $\mu s$. With increasing temperatures the peak around 100 $\mu s$ is always observed, but the peak intensity drops. As can be seen from 52 °C up to 110 °C contributions are observed for $T_2 > 300 \, \mu s$. These components can be attributed to water in pores. Pore water refers to water molecules, which are not part of the crystal structure of the hydrate and, e.g. are located in fluid phases within a pore-like structure. The effective diffusion coefficient of the pore water was measured (see appendix) and found to be approximately 10 times lower compared to bulk water over the entire experiment. This is the result of the combination of two factors, i.e. first, the effective diffusion coefficient decreases with increasing concentration of MgSO$_4$ [212]; second water in porous materials has a smaller effective diffusion coefficient as result of the tortuosity in the system [213].

Based on this additional information, we divided the total amount of water in two contributions, i.e. lattice and pore water, which are also plotted in Figure 4.6. Obviously, part of the lattice water is suddenly transformed to pore water at a temperature of 50 °C. This transition can not be observed in the TGA curve, as the water is still present in the sample in another phase and therefore the total mass will not change. Two hypothesis can be suggested for this sudden change. Firstly, dehydration is a combination of melting and recrystallization. Secondly, dehydration is a combination
of dehydration and deliquescence. Both hypothesis can be summarized as:

$$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}(s) \xrightarrow{k_4} \text{MgSO}_4 \cdot 7\text{H}_2\text{O}(l) \xrightarrow{k_5} \text{MgSO}_4 \cdot 6\text{H}_2\text{O}(s) + \text{MgSO}_4(\text{aq})$$  \hspace{1cm} (4.12)

$$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}(s) \xrightarrow{k_6} \text{MgSO}_4 \cdot 6\text{H}_2\text{O}(s) + \text{H}_2\text{O}(g) \xrightarrow{k_7} \text{MgSO}_4 \cdot 6\text{H}_2\text{O}(s) + \text{MgSO}_4(\text{aq}).$$  \hspace{1cm} (4.13)

The first hypothesis is based on the melting point of the heptahydrate. By analyzing the solubility data [76], the melting temperature was determined at 76.8 °C. In that case the first hypothesis does not hold, because the reaction temperature is 52 °C. The second hypothesis is based on the triple point of heptahydrate, hexahydrate and aqueous MgSO$_4$ at 48.5 °C. The seventh water molecule of the heptahydrate is released by the lattice at the triple point. This molecule initially evaporates inside the crystal, but as the internal vapor transport in the crystal is limited, the evaporated water molecules create an atmosphere, which leads to deliquescence and partial dissolution of the crystal (at 50 °C by an RH > 83.4%) and consequently, there will be an aqueous solution of MgSO$_4$ inside the crystal.

With further increase of the temperature, the pore water evaporates above 100 °C and, simultaneously, most lattice water evaporates as well. At 110 °C almost all pore water has disappeared.

By TGA experiments it was observed that at higher heating rates, the mass decrease shifts to higher temperatures. Repeated dehydration experiments were carried out inside the NMR with different heating rates, to get a better understanding of the influence of the heating rates on the dehydration process. In Figure 4.8 the loadings of the different components, i.e. total water, pore water and lattice water, are plotted as a function of temperature for seven dehydration experiments with different heating rates. In Figure 4.8a the total water component curves show a similar behavior as observed in the TGA experiments: the dehydration curves shift to higher temperatures at higher heating rates. As can be seen in Figure 4.8b, as expected from simulations at 50 °C for each heating rate, pore water is formed. However in contrast at 70 °C we do not observe a similar increase. This could be an effect of the low reaction rate from hexahydrate to monohydrate. We do observe an increase in the pore water for higher heating rates. This might be an effect of a delayed transformation of crystals. As can be seen in Figure 4.8c, as expected from simulations at 50 °C for each heating rate lattice water is decreased. Also in this case no decrease in lattice water is observed at 70 °C. For higher heating rates the dehydration curves shift to higher temperatures.

### 4.6 Discussion and conclusion

The goal of this chapter was to understand how water leaves a hydrated MgSO$_4 \cdot 7\text{H}_2\text{O}$ crystal during dehydration induced by heating. The TGA data showed that the dehydration process of MgSO$_4 \cdot 7\text{H}_2\text{O}$ depends on the heating rate. By studying the dehydration with help of NMR, formation of pore water is observed during dehydration, i.e. an aqueous solution of MgSO$_4$ in the crystal is formed. These measurements indicate that this water is present inside the crystals. We have done an additional experiment wherein we visualized the dehydration of a crystal with a heating rate of 2 °C/min, i.e. see Figure 4.9. As can be seen no water is formed outside of the
Figure 4.8: The loading as measured by NMR plotted against the temperature during dehydration experiments of MgSO$_4$·7H$_2$O with different heating rates varied between 0.0625 and 1 °C/min. In (a) is the total water content plotted, whereas the pore and lattice water in respectively (b) and (c).
4.6. Discussion and conclusion

Figure 4.9: A visualization of the dehydration of a crystal grain of $6 \times 6 \times 10$ mm$^3$ by a heating rate of $2 \, ^\circ C/min$ at 12 different temperatures. The crystal becomes opalescent at a temperature between 55 and 65 $^\circ C$, whereas the grain explodes between 115 and 125 $^\circ C$.

crystal, being in line with the NMR measurements. Eventually, the crystal structure is destroyed during dehydration at high temperatures, i.e. at $T > 115$ $^\circ C$. This water is produced at the triple point of heptahydrate, hexahydrate and solution as consequence of a limited vapor transport through the crystal, as supported by our model. The amount of pore water depends on the amount of heptahydrate at the moment of crossing the triple point.

The observations during the dehydration of MgSO$_4$$\cdot$7H$_2$O are summarized in a schematic representation in Figure 4.10. In Figure 4.10a, the initial crystal is a heptahydrate crystal. During heating, it starts to dehydrate to hexahydrate, which is not completed as long as the temperature is below 48.5 $^\circ C$. While heptahydrate occupies a larger volume, the crystal shrinks over the entire sample and a pseudomorphic structure with secondary porosity is formed (Figure 4.10b). In between the microcrystals voids are formed, these does not have to be connected to the crystal surface. By increasing the temperature above the triple point, the remaining heptahydrate is transformed to hexahydrate and water vapor is produced. The vapor is not immediately and fully released as a result of a limited diffusion out of the crystal or that the pores are not connected to the surface. This leads to a vapor pressure that is above the deliquescence vapor pressure. Upon deliquescence and partial dissolution of the crystal pores filled with MgSO$_4$ solutions are formed (Figure 4.10c). When the solution evaporates, hexahydrate crystals are formed at the evaporation surface as result of recrystallization from the saturated solutions, a crust, and will block the surface. This blocking will happen in case the evaporation is faster than the redistribution of the Mg$^{2+}$ and SO$_4^{2-}$ over the pore volume. This will result in a constant
pore water content at higher heating rates between 55 and 80 °C. By further heating the pores are emptied (Figure 4.10d). This emptying of the pores is a result of three processes: Firstly, more cracks are formed with increasing amounts of crystal forms with lower hydrates, because lower hydrates have higher densities, see table 4.1. Secondly, the hydrates of the crust dehydrate to lower hydrates and the crust breaks open. Thirdly, part of the crust will dissolve, because the solubility product increases with increasing temperature. After breaking of the crust, the dehydration does not occur instantaneously, because of a limited evaporation rate at the surface of the crystal.

Figure 4.10: A schematic representation of the dehydration of a crystal grain. a: The crystal is an ideal heptahydrate crystal without cracks. b: During dehydration the crystal forms cracks, because of volume changes between the heptahydrate and hexahydrate. All formed water vapor can escape. c: The crystal passes the triple point and all heptahydrate transforms into hexahydrate, which results in an overload of water vapor that cannot escape fast enough. The vapor deliquescence and forms pore water inside the crystal. These pores are not emptied, as the evaporation surface is blocked by hexahydrate crystals. d: The crystal continues to dehydrate and more cracks are formed. Additional cracks form pathways to empty the pores that accelerate evaporation.

At the triple points in the MgSO₄-H₂O phase diagram other than at 48.5 °C,
no additional pore water production is observed. So phase transitions do not always occur at each triple point of a phase diagrams. A good explanation is missing for this observation, but can be found in the reaction kinetics or volumetric hinderance. The volume of the MgSO$_4$ containing phases -all solid hydrates and aqueous solution- is varying during dehydration experiments. The density of MgSO$_4$ containing phases is phase dependent according to table 4.1. As we consider the case with maximum heating rate and an initial porosity of 30%, the volume occupied by MgSO$_4$ containing phases increases during a dehydration experiment. The density of the aqueous solution of MgSO$_4$ is determined with help of literature [208, 209]. Just above the triple point of heptahydrate, hexahydrate and aqueous solution the volume increased with 0.61% compared to the initial volume. After crossing the triple point of hexahydrate, monohydrate and aqueous solution this increase is 5.7% and at 90 °C the volume is increase with even 6.8%. So during a dehydration in a closed box, the crystals will expand. If the volume for this expansion is not present, the transition may be mechanically hindered. This might explain that no additional pore water production is observed by crossing the temperature of the triple point of hexahydrate, monohydrate and aqueous solution.

Concluding, pore water may strongly affect the dehydration of MgSO$_4$·7H$_2$O. From application point of view, the amount of pore water in a system during dehydration should be reduced. This water may destroy the crystal structure and affects the internal structure, what can have a negative effect on the reusability of the system. So, a slow dehydration process is preferable with a good ventilation of the system.

4.7 Appendix: Self-Diffusion measurement

The diffusion coefficient of the pore water during dehydration experiments was measured with a home-build NMR spectrometer FEGRIS NT. The NMR spectrometer operated at a proton frequency of 125 MHz, equipped with a Pulsed Field Gradient (PFG) unit providing a maximum magnetic field gradient of 37.9 T m$^{-1}$ [214, 215]. The FEGRIS NT can measure diffusion coefficients of signals with a $T_2$ larger than in the order of 1 ms. The PFG NMR signal intensity is sensitive to the effective self-diffusion coefficient $D$ of diffusing nuclei in the direction of the pulsed field gradient. The NMR signal was generated by using the primary spin echo pulse sequence [216]. In the experiments, the magnetic field gradient width $\Delta$ was fixed to 500 $\mu$s, the observation time $\Delta$ was 10 ms and the magnetic field gradient amplitude $g$ was incremented up to 37.9 T m$^{-1}$. The effective self-diffusion coefficients were determined by measuring the normalized attenuation $S(g)=M(g)/M(g=0)$ of the NMR signal intensity as a function of the magnetic field gradient strength $g$. Thereby the signal attenuation obeys the relation:

$$S(g) = \exp \left( -\gamma^2 \delta^2 g^2 (\Delta - \delta/3) \cdot D \right),$$

wherein $\gamma$ is the gyromagnetic ratio of water. To accurately calibrate the magnetic field gradient of the PFG unit, effective self-diffusion measurements in pure H$_2$O done by Holz et al. [217] were used as reference.

In Figure 4.11 the measured self-diffusion coefficient is plotted against temperature during dehydration of MgSO$_4$·7H$_2$O. This dehydration experiment is performed in
Figure 4.11: The measured effective diffusion coefficient of the pore water component in MgSO$_4$·7H$_2$O by PFD-NMR plotted against the temperature. The same sample is heated three times. First from 22 to 70 °C, subsequently from 22 to 120 °C and finally from 22 to 140 °C. In between the heating curves, the sample is cooled down to 22 °C within 30 minutes. The diffusion coefficient of liquid water is plotted as well.

During the first run of heating the crystal, the measured self-diffusion coefficient drops around the triple point of heptahydrate, hexahydrate and aqueous solution. At the same temperature, the signal intensity increases. During the second time of heating the crystal, above 90 °C, the diffusion coefficient drops as well and the signal intensity increases. The signal intensity drops down above 120 °C and almost no pore water is observed. The measured effective diffusion coefficient is approximately 10 times lower compared to bulk water over the entire temperature range. The dip in the effective diffusion coefficients at 50 and 90 °C can be a result of the released lattice water, which partially dissolves the crystal structure. This can result in a temporary higher MgSO$_4$ concentration and a lower diffusion coefficient [212].
4.7. Appendix: Self-Diffusion measurement
Chapter 5

Na$_2$SO$_4$·10H$_2$O dehydration by RH

The idea of using hydrated salts as working media for thermal energy storage has increased the interest in understanding their phase transitions. During studying the phase transition of mirabilite into thenardite, the crystal structure and water content are monitored by three experimental techniques. With help of NMR, homogenous drying of mirabilite crystals over the entire grain is observed. According to the drying behavior, the mobility of water molecules should be high inside the grain during dehydration. XRD experiments show that during this phase transition no disordered phase or other metastable phases like Na$_2$SO$_4$·7H$_2$O or phase III appear. With Raman spectroscopy, these experiments are repeated at several relative humidities and again no metastable phases are observed.

Adapted from Donkers et al., Chemical Engineering Science 134: 360–366 (2015).

5.1 Introduction

Previous studies performed on salt complexes in combination with heat storage are based on techniques like X-ray diffraction (XRD) [43], thermogravimetric analysis (TGA) [40,41] and differential scanning calorimetry (DSC) [43,44]. In most of these studies the mechanism of penetration of water in and out the hydrate is not fully understood. Different ideas are proposed, but no theory fits all hydrates [57–60]. Each hydrate seems to follow its own dehydration process. Galwey [59] described in his article six different ways of water evolution type (WET). These types are based on the way that water is released, i.e. homogeneously or heterogeneously distributed in the crystal, as well as on the formation of an intermediate phase and product of the dehydration reaction whether or not amorphous, crystalline phase or (partially) melted crystal appear.

The aim of this chapter is to improve the understanding of the dehydration process of mirabilite, Na$_2$SO$_4$·10H$_2$O. This salt is selected on the basis of its high theoretical
energy storage potential (2.37 GJ m$^{-3}$ based on the complete hydration/dehydration and data provided by Marlacity [218]). The second reason is that the dehydration of mirabilite can be easily achieved at comfort temperature and humidity, therefore mirabilite is a promising candidate for cooling applications of residential and office buildings. The experiments described in this chapter focus on dehydration experiments with single crystals and extend to dynamics of the water molecules in the crystal structure and to structural changes. Raman spectroscopy, XRD and nuclear magnetic resonance (NMR) are used. Raman spectroscopy and XRD follow the crystal structure in time, while the NMR technique monitors the water distributions in materials, i.e. inside the crystal in situ.

5.2 The Na$_2$SO$_4$-H$_2$O system

A profound description of the mirabilite structure characteristics as deduced from X-ray diffraction measurements is given by Ruben et al. [219], Levy and Lisensky [220] and Brand et al. [221]. They divided the water molecules in two groups of configuration. The first group consists of 8 of the 10 water molecules and are coordinated to the sodium cation by irregular octahedra. The edges of these octahedra are connected with each other, resulting in a string of water molecules through the crystal structure. The second group consists of the remaining 2 water molecules. These molecules have no coordination classification and have more freedom as the bond strengths of hydrogen are weaker than ion-dipole interactions.

In 1949, Telkes showed that mirabilite, Na$_2$SO$_4$·10H$_2$O, can be used as phase change material for heat storage. The current study uses a different approach, as we focus on the energy storage by a thermochemical reaction [141]. In that case, the system stores heat during dehydration of the salt hydrate and generates heat by hydration of the anhydrous salt, thenardite. The reaction is [72]:

$$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}(s) \rightleftharpoons \text{Na}_2\text{SO}_4(s) + 10 \text{H}_2\text{O}(g), \Delta H = 522 \text{ kJ/mol}. \quad (5.1)$$

The phase diagram of the system Na$_2$SO$_4$-H$_2$O [75] is shown in Figure 5.1, in consideration of the thermodynamic stable phases, Na$_2$SO$_4$(V) and Na$_2$SO$_4$·10H$_2$O and the metastable phases Na$_2$SO$_4$(III), Na$_2$SO$_4$·7H$_2$O. The solid lines represent the equilibria of the stable phases, while the dotted lines represent the metastable equilibria. The dashed line represents the working temperature of our experiments. According to the phase diagram, reaction 5.1 has an equilibrium humidity of 80.7% at 25 °C. This means that dehydration of mirabilite occurs at relative humidities below the 80.7% or that thenardite hydrates above this humidity. The dehydration or hydration rate of a crystal is partially determined by the difference between the applied and equilibrium relative humidity. The larger the difference, the higher the dehydration/hydration rate is expected to be. In case the RH is increased above 93.5%, the mirabilite will dissolve. Therefore, mirabilite samples are stable as long as they are stored at 25 °C between 80.7% and 93.5% RH. During dehydration not only thenardite can be formed, but also two metastable phases can appear: heptahydrate and phase III. Saidov et al. [222] and Hamilton et al. [223] showed that heptahydrate can be formed during evaporation of a solution at low temperatures. The phase diagram shows that formation of the heptahydrate may occur during dehydration of mirabilite below 66% RH.
at 25 °C. The other metastable phase is phase III, an anhydrous phase. This phase can exist in case of dehydration below 76% RH according to the phase diagram. It is known that during the drying of a Na₂SO₄ solution this phase is formed [224].

![Phase diagram of Na₂SO₄ in equilibrium with water. The metastable phases are drawn with dotted lines (data from ref. [75]).](image)

**Figure 5.1: Phase diagram of Na₂SO₄ in equilibrium with water. The metastable phases are drawn with dotted lines (data from ref. [75]).**

### 5.3 Experimental

#### 5.3.1 Sample preparation

Crystals of Na₂SO₄·10H₂O were grown by slow evaporation of an oversaturated solution at 22 °C. The solution was prepared by cooling down a saturated solution from 40 °C to 22 °C, note that the crystal growth was observed when the solution was already cooled down to 22 °C. The used sizes are based on the limitations of the different experimental setups. For the confocal Raman experiments crystals with a size of about 1x1x0.2 mm³ were used. For the NMR experiments crystals with a size of about 30x5x5 mm³ were selected.

The samples for the XRD experiments were also grown from a solution saturated at 40 °C with Na₂SO₄. The difference is that the solution was poured in the sample holder and placed in a desiccator with a relative humidity of 85% and cooled down to 22 °C. Crystals were grown and residual water was absorbed with a tissue afterwards. This was done to achieve a flat top layer as required for the XRD measurements. The sample consisted of several crystals lying parallel to each other. The sample holder had an outer diameter of 2.5 cm and a height of 1.5 mm. The sizes of the crystals used were about 10x3x1.5 mm³. The crystals were all stored in a box with a relative humidity of 85% at 22 °C.
5.3. Experimental

5.3.2 NMR

Nuclear magnetic resonance (NMR) is used for measuring non-destructively and quantitatively hydrogen atoms in a sample. NMR is based on the principle that in a magnetic field, nuclei have a specific resonance frequency and can be excited by a radio frequency field. The signal intensity $S$ is given by [182]:

$$S = kp \left(1 - \exp \left(-\frac{\tau_r}{T_1}\right) \exp \left(-\frac{\tau_{echo}}{T_2}\right)\right),$$  \hspace{1cm} (5.2)

where $k$ is the sensitivity of the nucleus ($k = 1$ for water), $\rho$ the density of the nucleus, $\tau_r$ the repetition time of the pulse sequence, $\tau_{echo}$ the echo time of the sequence and $T_1$ and $T_2$ are the longitudinal relaxation and the transversal relaxation times, respectively. These two relaxation times are properties that depend on the molecular dynamics and structure of the studied nuclei, as well as on the strength and homogeneity of the applied magnetic field [182].

In this study, two types of NMR measurements were performed; multidimensional correlation [225, 226] and moisture content measurements [199]. Moisture content profiles were measured on the basis of a Hahn sequence [184]. In this sequence, the $\tau_r$ is long compared to $T_1$ and $\tau_{echo}$ is short compared to $T_2$ in order to gain as much signal as possible. Spatial resolution is acquired by applying a static magnetic gradient over the sample.

The $T_1 - T_2$ distribution was measured with a combination of a saturation recovery and a Carl-Purcell-Meiboom-Gill (CPMG) sequence. The saturation recovery sequence measures the longitudinal relaxation ($T_1$) of a material [227]. The sequence saturates the signal and after time $\tau_1$ the signal intensity is measured. The echo at time $\tau_1$ is used as the first echo of the CPMG sequence [186]. This sequence measures the transversal relaxation ($T_2$) of a material. The signal intensity of the first echo at different $\tau_1$ times in combination with the $T_2$ relaxation measurement was analyzed by a multidimensional inverse Laplace transformation [194].

The NMR experiments were performed using a home-built NMR setup, which is especially designed for measurements on systems with short relaxation times. A schematic diagram of this setup is shown in Figure 5.2. Two coils in anti-Helmholtz configuration are placed 20 cm apart, generating a static gradient of 300 mT m$^{-1}$ in the direction of the main magnetic field. A RF-coil in birdcage configuration is used for sending and receiving the NMR signal from the sample. The diameter of the coil is 4 cm and inside the coil a Faraday shield is located. The sample is moved through the RF-coil with a step-motor and a load cell measures the mass real-time during an experiment.

The samples for the $T_1 - T_2$ experiments consisted of stacked crystals in a sealed container with crystals diameters ranging between 2-5 mm. The used crystals are the same crystals as in the dehydration experiment, but crushed to get a higher signal to noise ratio in the NMR. The crystals were placed in a sealed container, wherein a relative humidity of 93±2% was measured. This value corresponds to the equilibrium RH of mirabilite and its saturated Na$_2$SO$_4$ solution at 25 °C. This is probably a result of some remaining droplets of saturated solutions in the crystals aggregate.

During the dehydration experiments, another set of crystals was used with sizes of
30x5x5 mm$^3$. Four of them were placed parallel to each other in the sample holder to get more signal during the measurement. The single crystals were sealed with teflon on all sides except the top. In this way the crystal has only one interface in direct contact with its surroundings and water can only escape at that interface. Dry air was blown over the sample with a speed of 1.6 l/min, while the temperature was kept constant at 25°C.

### 5.3.3 Raman microscopy

Depolarized Raman spectra were measured with a Senterra Raman spectrometer (Bruker Optics GmbH, Germany) after sample excitation with a 532.0 nm laser with 20 mW power. The objective used amplifies 20 times, has a NA of 0.4 and a working distance of 10.6 mm. An aperture with a pinhole of 25 μm was used. Spectra between 50-1550 cm$^{-1}$ were recorded with an integration time of 5 seconds and averaged over 4 measurements. The sulfate peak around 990 cm$^{-1}$ is used for analyzing the spectra [228]. The working distance of 10.6 mm was used, because the sample was placed in an environmental chamber, where temperature and relative humidity (RH) were controlled. The temperature was kept constant with a thermostat (DLK and E200, Lauda, Germany) and the relative humidity was generated by an airflow of 500 ml/min produced with a modular humidity generator MGH 32 (ProUmid, Germany). The temperature and RH in the chamber were measured with a RH sensor (Hygroclip SC-05, Rotronic, Germany).

With a Raman experiment, a crystal was placed on a CaCO$_3$ substrate. The laser was focussed 100 μm below the salt-air interface. The initial excitation depth was between 97 and 260 μm below the air-crystal interface according to literature [229,230], implying that in the beginning a small signal of CaCO$_3$ can be observed as the crystal thickness is 200 μm. The CaCO$_3$ spectrum was used to assess the effect of
the dehydration of the crystal on the Raman signal intensity. The measured spectra were analyzed with the help of the reference spectra of the different phases of sodium sulfate measured by Linnow et al. [207]. The Raman shift of the most intensive $v_1$(SO$_4^{2-}$) mode around 980 cm$^{-1}$ was characteristic for the phase of sodium sulfate as can be seen in Figure 5.3. The spectra were analyzed and the contributions of the different phases calculated. Before starting the dehydration experiment, all grains were equilibrated at 85% RH and 25 °C (i.e. mirabilite is stable) in the environmental chamber. When the spectra were stable during at least 10 minutes, the RH was changed to the desired value.

![Figure 5.3: The reference spectra of the different phases of sodium sulfate [228, 231].](image)

### 5.3.4 XRD

XRD parameters were obtained on a Siemens D5000 Bragg-Brentano parafocusing powder diffractometer with a vertical $\theta$:2$\theta$ configuration using Cu Kα-radiation and a position-sensitive detector (PSD). The temperature and RH were controlled by a home-built relative humidity chamber [35].

XRD patterns of the sample were measured from 10-70° 2$\theta$ and compared with X-ray databases; i.e. pdf 11-647 and 24-1132 [33]. The sample conditioning in the XRD setup was similar to the Raman experiment. The crystals were equilibrated at 25 °C and 85% RH. After the equilibration period, the RH was decreased to 78% and every 15 minutes a new XRD pattern is recorded.
5.4 Results and Discussion

5.4.1 NMR

5.4.1.1 Equilibrium experiments

Figure 5.4 shows a $T_1 - T_2$-distribution of the water molecules in $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ at 25 °C and 93±2% RH. In the contour plot two peaks can be distinguished, which are labeled as structural water and non-structural water. The black line corresponds to the $T_1 = T_2$ line, which is characteristic for water molecules in moderately large reservoirs with a similar freedom as bulk water. The non-structural water peak is placed close to this line, so apparently indicating a high mobility. This high mobility is too large to be related to the two weakly bound water molecules in $\text{Na}_2\text{SO}_4$ [219–221]. In addition the peak intensity contributes to only 4% of the total signal intensity, what should be 20% incase it is related to these weakly bound water molecules. In contrast, the other peak is located far from this line, being characteristic of immobile, solid-like or bound water molecules. The difference between the observed structural and non-structural water peak in the NMR experiments is probably caused by imperfections in the crystal structure or adsorbed surface water.

Figure 5.4: The $T_1 = T_2$ distribution of the water molecules in $\text{Na}_2\text{SO}_4$ is shown. The solid line represents $T_1 = T_2$, which corresponds to liquid water molecules in bulk volume.

5.4.1.2 Dehydration experiments

Figure 5.5a shows the moisture content profiles recorded during the dehydration experiment of the four parallel crystals. On the vertical axis the moisture content is plotted against the position on the horizontal axis. The measured moisture content is a combination of structural and non-structural water. The open side of the sample is located on the left side of the graph. Each line corresponds to a moisture content pro-
5.4. Results and Discussion

Figure 5.5: a) water content profiles during the dehydration experiment with four parallel single crystals of Na$_2$SO$_4$. On the vertical axis the average concentration of water molecules pro mol Na$_2$SO$_4$ is plotted versus the position on the horizontal axis. The time between two subsequent profiles is 8 hours. After 70 hours the sample is completely dry. The arrow indicates the progression in time. b) the average concentration of water molecules per mole Na$_2$SO$_4$ plotted against time at position $x=\text{14 mm}$ and the average of the entire crystal.

The dehydration measurement shows that drying of the single crystal occurs almost homogeneously over the entire sample. After the first 8 hours, also at 30 mm from the top of the sample the water level decreased significantly. This implies a very high mobility of the water molecules in the grain. This can be a combination of vapor diffusion and crystal water diffusion. Note that we do not detect water vapor with NMR. We have no clear indication that other phases than mirabilite or thenardite occur during this experiment, see Figure 5.5b. The water content drops continuously from 10 to 0 mol water per mole Na$_2$SO$_4$ both averaged over the entire crystal, and at a specific position. If an intermediate phase should exist, we would expect a discontinuity in the drying rate. Another option is that the intermediate phase exists relatively briefly. Raman and XRD experiments will clarify this. Note that the NMR experiment measures the average water content in a certain area and not the exact amount of water at a specific position. NMR can not distinguish between the coexistence of mirabilite and thenardite domains in a volume or of a continuous loss of water molecules in the observed volume. The first 10 mm in the grain show a minor gradient in its water content profiles, which is a result of a combination of the resolution of the NMR and the grain’s shape, which is a cuboid with two pyramids on the ends. After the dehydration experiment the sample was visually checked. The mirabilite crystal is dehydrated pseudomorphically by small thenardite crystals during dehydra-
tion. This was also observed by Rodriguez-Navarro et al. [224]. Their SEM pictures showed a porous structure after dehydration of mirabilite into thenardite. This porous structure might explain the fast water transport through the grain, resulting in the observed homogeneous drying of mirabilite.

What we can conclude from these homogenous profiles is that no reaction interface is observed in case of dehydration of mirabilite inside the grain. This shows that the evaporation rate at the grain-air interface determines the overall dehydration rate. Dehydration of a mirabilite domain has a similar probability across the grain and is not influenced by other domains or locations in the grain. According to the classification of dehydration reactions of Galwey [59], this system belongs to group WET 4C, homogeneous intracrystalline chemical change.

5.4.2 X-Ray diffraction

In Figure 5.6a XRD patterns collected during the dehydration experiment are plotted. The pattern of the starting material shows only 4 clear peaks instead of the large number reported in the powder diffraction (PDF 11-647 [33]). The observed peaks are in accordance with the reference database and the lack of the other peaks is caused by preferential orientation. During the dehydration, mirabilite reflections disappear and others corresponding to thenardite increasingly appear. The final pattern is in good agreement with the reference database of thenardite (PDF 37-1465 [33]). We observed that during the dehydration, the sample breaks up into smaller grains, as we observed in our NMR experiment.

In the peaks of figure 5.6a two dashed lines are drawn, which belong to characteristic thenardite and mirabilite peaks. By plotting the signal intensities of these two lines against each other, Figure 5.6b is compiled, showing that a one-to-one conversion

![Graph](image)

*Figure 5.6: a) the XRD patterns during the drying process at different times. The mirabilite signal is converted into thenardite in 74 hours. After 36 hours already 80% of the mirabilite is converted. The two dashed lines plotted in the graph are the peaks which are used for figure 5.6b. Here, the signal of mirabilite is plotted versus thenardite. It seems that the thenardite and mirabilite signals are one-to-one interchangeable.*
5.4. Results and Discussion

5.4.3 Raman spectra

Figure 5.7 shows how the Raman spectra change during dehydration at 25°C and RH 70%. The signal contributions of the two observed phases, mirabilite and thenardite, are plotted in the inset. Other phases of sodium sulfate, phase III and heptahydrate, do not give any signal intensities above the detection limit during this experiment. The mirabilite signal drops to approximately 10% of its original intensity within the first ten minutes and afterwards signal growth of thenardite is observed. Similar trends are observed at other depths of focus. This indicates that the dehydration occurs homogenously over the entire sample, with our resolution of 160 μm. By measuring the mass at minimal signal intensity around 993 cm⁻¹ a water content of 8±1 water molecules per Na₂SO₄ molecule was measured in the crystal. So a large amount of crystal water is still present in the crystal at the time that no mirabilite signal is observed. At the time of weighing the sample, the crystal surface was whitish. The intensity of the CaCO₃ signal slowly disappears and halfway through the experiment this signal vanished away completely. While CaCO₃ is not affected by a RH difference, the observed difference is a result of changes in the crystal on top of the tablet. The laser beam does not reach the CaCO₃ anymore, which is probably due to additional air-grain interfaces that increase the path length and the scattering of the beam.

Additional experiments with different RH’s show similar characteristics. In figure 5.8 the time between the start of the experiment and a constant thenardite signal is plotted against the RH. Constant means that the signal does not vary within 10 minutes. It shows that the time needed for complete dehydration strongly depends on the RH. When the difference between the applied RH and the equilibrium RH of mirabilite and thenardite (80% at 25°C) decreases, the time needed to reach its constant thenardite signal increases. During all our experiments we did not find any indication of the formation of heptahydrate or phase III. Even in cases where the applied RH is below the equilibrium RH of respectively mirabilite/heptahydrate and mirabilite/phase III, no signs of a heptahydrate or phase III were observed, which is in agreement with the NMR data. The Raman experiments show that the RH only affects the dehydration rate and not the dehydration process itself.

The exact reason for the observed loss in SO₄²⁻ vibrations during dehydration is unclear. As stated before, the signal intensity can be affected by the additional air-crystal interfaces. Another explanation is that the vibrations are not measured, because they are partially under the noise level. Furthermore, it is known that the peak can be broader in case of smaller grains, which decreases the peak intensity. It is not clear, however, whether such effects may indeed cause such extreme decrease of SO₄²⁻ vibrations. Our observation of the lost sulfate vibrations is similar to the observation of Brotton et al. [47] for two other salt hydrates, i.e. MgSO₄ and ZnSO₄. We think that a similar situation is present in our system, but a satisfying explanation for the observed effect is not found. Some studies [232–235] conclude that a temperature induced transition from an ordered to a disordered phase may cause a signal intensity loss of particular vibrations. However as XRD observations show that a disordered phase is not present during the transition, this explanation is unlikely.
Figure 5.7: Part of the Raman spectrum of the grain plotted during a dehydration experiment at RH=70% at 25 °C. The time between two subsequent lines is 9 minutes. The inset shows the signal contributions of the components in the grain. The signals are calculated with respect to the signal intensities of the reference spectra.

Figure 5.8: The time between the start of the dehydration experiment and the maximum thenardite intensity during dehydration experiments at 25 °C is plotted against the applied relative humidity during dehydration.
5.4.4 Dehydration time

Comparing the dehydration time results of three different experimental techniques is complicated, due to variations in sample size, relative humidity and surface to volume ratio. Comparing the XRD experiment with the Raman experiment at the same RH and temperature (78% at 25 °C) shows that the Raman sample dehydrates in 2.5 hours (see Figure 5.8) while the XRD sample dehydrates in 74 hours. An explanation for this difference can be found in the air-crystal surface to volume ratio (S/V) of the samples. Because we have a homogenous drying of the sample, the evaporation at the air-crystal surface is the limiting step in the dehydration process. The volume behind this surface represents the amount of water that has to escape through the surface. The S/V during the XRD and Raman experiments are respectively roughly 0.7 mm$^{-1}$ and 32 mm$^{-1}$. Correcting the dehydration times proportional to this surface-volume ratio, a difference in the order of 10 hours may reasonably be expected. Considering that only slight deviations in RH may significantly affect the dehydration (see Figure 5.8), the order of magnitude in differences in dehydration time between XRD and Raman may be related to differences in experimental conditions. The NMR experiments give additional information, where we dehydrated the sample at ±0% RH and at 25 °C. The other experiments were all performed above at 30% RH or higher. Repeating these experiments at 0% RH is challenging, because of the time resolution in our experiments. Note that the S/V of the NMR experiment is 0.03 mm$^{-1}$, what is much smaller compared to the others, implying that the long drying time of the NMR even with the low RH is probably caused by the low S/V ratio and not by a different dehydration process.

5.5 Conclusion

In this chapter it is shown that combining NMR to measure water concentrations, with XRD and Raman for phase identification, gives additional information about the dehydration behavior of a crystal.

The phase transformation from mirabilite into thenardite is observed to be a one-to-one process (XRD), and the nucleation is not exclusively at the surface. Besides that, no other crystal phase is observed by XRD and Raman during the phase transformation.

The proposed process is that the dehydration of mirabilite is limited by the air-grain surface. The water molecules are mobile within the grain during dehydration (NMR). The high mobility of water molecules inside the grain compared to the evaporation at the air-grain interface is maybe caused by the white layer on top of the grain (Raman). This results in a homogeneous drying process inside the grain and shows that the phase transition rate is independent on the position in the grain.

From an application point of view, we showed that mirabilite dehydrates into thenardite without formation of metastable phases as intermediate products. This is useful information for thermal heat storage or cooling applications, as the formation of intermediate phases complicates cyclic processes. So the theoretical energy density storage of the salt is reachable in applications. Still, a systematic research on the understanding on heat flows during dehydration and particulary rehydration reactions
are necessary before reactions can be used for heat energy storage.
5.5. Conclusion
Chapter 6

Temperature induced dehydration

A selection of hydrates is studied with respect to their dehydration characteristics using TGA, DSC and NMR. These dynamic experiments are compared with the phase diagrams of Chapter 2. With help of these experiments it was possible to determine which of the salts fits our three selection criteria: the energy density, rehydration RH and not melting during dehydration. From these experiments, we selected four different salts to continue studying as heat storage material: CuCl$_2$, MgSO$_4$, MgCl$_2$ and CuSO$_4$.

6.1 Introduction

For selecting an appropriate heat storage material, ten salt hydrates listed in Table 2.1 were studied. The selection of the salt hydrates was based on three main criteria: First, the energy density, which should be in the order of 2 GJ/m$^3$ in the temperature range of 25-150 °C. Second, the salt should be rehydrated with a difference of at least 20 % RH between the applied RH and the equilibrium RH at 25 °C. Finally, the salt should not melt during dehydration.

The first two selection criteria were already discussed in section 2.1. The final selection criteria will be studied by heating the salt hydrates, till 150 °C with a heating rate of 0.6 °C/min. Here, we used three different experimental techniques: differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and NMR.

6.2 Methods and materials

DSC measurements were performed using a DSC822e of Mettler Toledo. Using a DSC, we can measure the amount of heat required to increase the temperature of a sample as a function of temperature. At phase transitions, e.q. from a solid to a liquid or from one crystal structure to another energy is transformed, which can be detected by a DSC.
TGA experiments were performed on a TGA/SDTA851e of Mettler Toledo. Using a TGA, we can measure the mass of a sample as a function of temperature and dehydration steps can be detected by mass differences.

For the NMR measurements, a home-build setup is used, with a RF-solenoid coil, which resonates at 200 MHz (see Figure 6.1). A Faraday coil has been incorporated in the RF-coil to perform quantitative analysis of the NMR signal. During heating, the temperature can be controlled over a range of 20-150 °C within ±1 °C with help of an electrical heating circuit. With the NMR we can measure the amount of water and the state of the water molecules in a sample. The signal decay of the NMR signal was recorded using the CPMG pulse sequence [186]. During a CPMG pulse sequence, a static magnetic field gradient of 270 mT/m is applied. This gradient adjusts the echoes of the CPMG pulse train in our recording window. The time between two successive echoes within the pulse sequence was 60 μs, whereas the repetition time of the sequence was 24 s, 1024 till 4096 echoes were recorded and an accumulation of 4 scans was performed. A fast Laplace Inversion Transformation (FLI), [194], was used to analyze the $T_2$ decay curves and to calculate the water density by extrapolation the signal to $t = 0$.

The heating rate was kept constant for all three techniques at 0.6 °C/min. For this study, an aluminum pan of 40 μl was used for the TGA and DSC samples. The sample weight was in the order of 5-20 mg, the exact sample sizes can be found in Table 6.1. The samples were layers of grains of the studied hydrate with grain diameters between 0.5-1 mm, with a maximum of two layers of grains. The aluminum pans had a lid with a hole of 1.5 mm diameter on the top. This hole had to prevent pressure building of vapor. The ovens of both the TGA and DSC were both purged with dry nitrogen. For the NMR experiments, sample holders with a height of 10 mm and a diameter of 6 mm were used. The weight of the samples were approximately 300-450 mg, the exact masses can be found in Table 6.1. Layers of grains were stacked on top of each other in this sample holder. Dry air is blown over one side of the bed of grains (see Figure 6.1).
In the following section, we will discuss all experiments and make a comparison with the phase diagrams. General conclusions are given at the end of this section.

Table 6.1: The initial masses of the hydrated salts used in the TGA and DSC experiments. The molar mass of the anhydrous phase ($M_{\text{anhydrous}}$) and the lowest temperature $T_{\text{anhydrous}}$, where the sample become anhydrous according to our TGA experiments, are listed as well.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Initial mass TGA (mg)</th>
<th>Initial mass DSC (mg)</th>
<th>Initial mass NMR (mg)</th>
<th>$M_{\text{anhydrous}}$ (g/mol)</th>
<th>$T_{\text{anhydrous}}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$SO$_4$</td>
<td>12.74</td>
<td>16.31</td>
<td>302</td>
<td>142.04</td>
<td>100</td>
</tr>
<tr>
<td>MgSO$_4$</td>
<td>14.67</td>
<td>11.76</td>
<td>416</td>
<td>120.37</td>
<td>325</td>
</tr>
<tr>
<td>NaBr</td>
<td>4.10</td>
<td>4.08</td>
<td>402</td>
<td>102.89</td>
<td>60</td>
</tr>
<tr>
<td>CuSO$_4$</td>
<td>11.62</td>
<td>13.07</td>
<td>424</td>
<td>159.61</td>
<td>240</td>
</tr>
<tr>
<td>FeSO$_4$</td>
<td>17.27</td>
<td>20.23</td>
<td>368</td>
<td>151.91</td>
<td>270</td>
</tr>
<tr>
<td>ZnSO$_4$</td>
<td>18.35</td>
<td>8.51</td>
<td>416</td>
<td>161.47</td>
<td>275</td>
</tr>
<tr>
<td>CoSO$_4$</td>
<td>16.80</td>
<td>11.02</td>
<td>380</td>
<td>155.00</td>
<td>290</td>
</tr>
<tr>
<td>CuCl$_2$</td>
<td>17.33</td>
<td>18.99</td>
<td>452</td>
<td>134.45</td>
<td>120</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>11.56</td>
<td>11.60</td>
<td>312</td>
<td>110.96</td>
<td>148</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>8.13</td>
<td>7.76</td>
<td>303</td>
<td>95.21</td>
<td>-</td>
</tr>
</tbody>
</table>
6.3 \( \text{Na}_2\text{SO}_4 \)

\( \text{Na}_2\text{SO}_4 \) grains were equilibrated above a saturated solution of KCl at 22 °C (RH = 85%). According to the phase diagram in Figure 2.3, this results in grains of \( \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \). These equilibrated grains were studied using TGA, DSC and NMR. In a TGA experiment, the mass of a sample is measured as a function of temperature. The weight can be recalculated to the loading \( L \) [mol H\(_2\)O per mole salt hydrate] according to:

\[
L(T) = \frac{m(T) - m(T_{\text{anhydrous}})}{M_{\text{water}}} \cdot \frac{M_{\text{anhydrous}}}{m(T_{\text{anhydrous}})},
\]

wherein \( m(T) \) is the mass of the sample at temperature \( T \), \( M_{\text{water}} \) the molar mass of water, i.e. 18.02 g/mol, \( T_{\text{anhydrous}} \) the temperature where the sample become anhydrous in the performed TGA experiment and \( M_{\text{anhydrous}} \) the molar mass of the anhydrous salt hydrate, which are listed in Table 6.1.

In order to determine the heat production per mole salt hydrate from a DSC experiment, the measured heat production is divided by the number of moles of the salt hydrate in the sample. This is calculated by dividing the initial mass of the DSC sample by the molar mass of the salt hydrates in the sample: \( m(T = 25 \degree \text{C}) / M_{\text{hydrate}} \).

With help of the TGA experiment \( M_{\text{hydrate}} \) is calculated. Hereby, the loading of the hydrated grains is multiplied by the molar mass of water and this is added to the molar mass of the anhydrous salt hydrate: \( M_{\text{hydrate}} = L(T = 25 \degree \text{C}) \cdot M_{\text{water}} + M_{\text{anhydrous}} \).

The loading and heat during a dehydration experiment are plotted in Figure 6.2. Note that the initial sample mass of the TGA was smaller than of the DSC, see Table 6.1. The loading of the TGA sample decreases immediately after starting the dehydration experiment and is completed at 72 °C. According to the TGA the sample was initially \( \text{Na}_2\text{SO}_4 \cdot 9.7\text{H}_2\text{O} \) grains. This indicates that the grains were not completely hydrated at the start of the experiment, i.e. the grains were a mixture of 97% \( \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \) and 3% \( \text{Na}_2\text{SO}_4 \) crystals. The measured TGA curve is in agreement with the literature [236]. The DSC curve shows that the dehydration occurs with two endothermic peaks, according to the energy needed to dehydrate. A sharp peak is located at about 35 °C and a broad peak is observed in the range of 25 till 82 °C, with a minimum at 82 °C.

The sharp peak with a minimum at 35 °C indicates a fast transition of one phase to the other, occurring at an almost single temperature. For this salt hydrate, the phase transition may have two processes:

\[
\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}(s) \xrightarrow{T=32.3 \degree \text{C}} \text{Na}_2\text{SO}_4(s) + 10\text{H}_2\text{O}(g) \rightleftharpoons 3\text{Na}_2\text{SO}_4(s) + \text{Na}_2\text{SO}_4(\text{aq}) + 10\text{H}_2\text{O}(l),
\]

\[
\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}(s) \xrightarrow{T=35.0 \degree \text{C}} \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}(l) \rightleftharpoons 3\text{Na}_2\text{SO}_4(s) + \text{Na}_2\text{SO}_4(\text{aq}) + 10\text{H}_2\text{O}(l).
\]

The first process is the dehydration of mirabilite into thenardite by crossing the triple temperature at 32.3 °C. The mirabilite will transform into thenardite and the released water will condensate in the grains, if the ventilation is insufficient. This condensed water will partially dissolve the thenardite. The second process is the incongruent
melting of mirabilite at 35.0 °C [75]. This melt is oversaturated with Na$_2$SO$_4$ and will partially recrystallize to thenardite. Both processes will end up at the same product. As result the energy required for both transitions will be equal. The only difference between both is the transition temperature of the process. As we can see, the DSC curve decreases already by 32.3 °C, being below the incongruent melting temperature of mirabilite. On the other hand, the process peaks at 35 °C, corresponding to the incongruent melting of mirabilite. This peak is probably a combination of both processes in the temperature range between 32.8 and 35.0 °C.

The broad peak over the temperature range of 25-82 °C with a minimum at 82 °C in the DSC curve belongs to the dehydration of the grains, which can be divided in two processes, depending on the temperature:

$$\text{Na}_2\text{SO}_4\cdot10\text{H}_2\text{O}(s) \rightleftharpoons \text{Na}_2\text{SO}_4(s) + 10\text{H}_2\text{O}(g) \quad (T \leq 32.3 \degree \text{C}), \quad (6.4)$$

$$\text{Na}_2\text{SO}_4 \text{ (aq)} + 10\text{H}_2\text{O}(l) \rightleftharpoons \text{Na}_2\text{SO}_4(s) + 10\text{H}_2\text{O}(g) \quad (T \geq 32.3 \degree \text{C}). \quad (6.5)$$

When all water is released from the grains, the salt hydrates reached their stable states and will not transform into other phases in the studied temperature range according to the DSC curve.

The temperatures as indicated by TGA and DSC where the transformation is finished are 72 °C and 82 °C, respectively. As indicated in Table 6.1 the initial mass of the TGA sample is lower than the DSC sample. Consequently, less water should evaporate from the TGA sample compared to the DSC sample. The samples of both techniques have both the same hole in the sample holder. So, the water vapor release from both samples is of the same order. The sample with the largest mass will take more time to dehydrate, and as a result the end of the dehydration will shift to higher temperatures.

Except for the phase diagram we have no direct indication by the TGA and DSC
for incongruent melting. We have, therefore, performed additional NMR measurements, giving direct access to the state of the water molecules in the salt hydrate. The measured $T_2$ relaxation distribution as function of temperature is given as a contour plot in Figure 6.3. Initially, the signal has a relaxation time of 50 μs and at 33 °C the relaxation time shifts to 0.1 s. This transition temperature is in accordance with the DSC. In the NMR sample, water is observed until 100 °C, being a result of the mass of the NMR sample.

Based on the relaxation distributions, the contribution of the total water component measured with NMR is plotted against temperature in Figure 6.4. As can be seen, the total water component of the NMR strongly decreases at 33 °C and that with some fluctuations the water component decreases continuously till 100 °C. In contrast to the TGA, the NMR does not show a continuous decrease of water, which is a result of the melting or dissolution of the salt hydrate grains. As a result, part of the sample flows out of the RF-sensitive area and so part of the sample will not be measured after the phase transition. As can be seen in Figure 6.3, two groups of transversal relaxation times ($T_2$) are present in the relaxation time distribution of Na$_2$SO$_4$·H$_2$O. The first group has $T_2$ values below 500 μs, which will be referred to as lattice water. This type of water is connected to the crystal structure and these water molecules are immobile and have strong static interaction with the neighboring water molecules. The second group has $T_2$ values above 500 μs, which will be referred to as pore water. This water is not connected to the crystal structure and is more mobile. It can be located in voids or pores inside the salt hydrate grains. This water is a saturated solution of Na$_2$SO$_4$. The water component divided up in two groups is plotted in Figure 6.4. Initially, only lattice water is observed and above 40 °C only
pore water is present. Between 33 °C and 40 °C a combination of pore and lattice water is observed. While the melting point and triple point are close to each other, we can not distinguish the effects of incongruent melting of mirabilite and dissolution of the salt hydrate by water vapor.

6.4 MgSO$_4$

MgSO$_4$ grains were equilibrated with a saturated solution of KCl at 22 °C (RH=85%). According to the phase diagram in Figure 2.4, this results in grains of MgSO$_4$·7H$_2$O. These equilibrated grains were again studied with the TGA, DSC and NMR. The loading measured with the TGA and the heat measured with the DSC during dehydration are plotted in Figure 6.5. The TGA experiment shows that the sample was initially MgSO$_4$·6.7H$_2$O, what is a mixture of the heptahydrate and some other lower hydrates, most probably hexahydrate. The measured TGA curve is in agreement with the literature [237–239].

In the DSC curve different peaks are observed, which are indicated with labeled dotted vertical lines. Since energy is needed for dehydration of the sample, a mass decrease will result in a peak in the DSC curve. Here, the differentiate of the mass should overlap with the heat production during the dehydration experiment, which is plotted in Figure 6.6. Again, the different peaks are labeled and listed in Table 6.2. Beside the locations of the different peaks, also the transition temperatures of the triple points and melting points are summarized in Table 6.2. As can be seen, from the eleven peaks, eight temperatures corresponds to dehydration steps in the differentiated TGA curve. These eight temperatures are indicated in the column TGA. The other three peaks are related to transition points or melting points without direct effect on the dehydration. For example, peak 2 belongs to the triple point of
6.4. MgSO₄

Figure 6.5: The loading and heat production for MgSO₄ of a heating experiment with a heating rate of 0.6 °C/min. The initial masses are given in Table 6.1.

Figure 6.6: The differentiate of the TGA curve and the heat production of a heating experiment with MgSO₄ by a heating rate of 0.6 °C/min.

heptahydrate, hexahydrate and their aqueous solution. Peak 9 is in the order of the melting point of tetrahydrate. Only peak 7 can not be explained with the known phase diagram. It is remarkable that no transition is observed from the hexahydrate to monohydrate at 70 °C, while the monohydrate is the stable phase at the applied conditions. Also an exothermic peak is expected at 270 °C according to the literature [238,239]. According to Van Essen et al., this exothermic peak is caused by the release of the last 0.1 water molecule of MgSO₄. This is not observed in our experiments,
which could be a result of the heating rate used, which was almost ten times slower in our experiments than their heating rate of 10 °C/min.

Table 6.2: The labeled DSC peaks in Figures 6.5 and 6.6 are listed, wherein the temperature is indicated, and wherein is marked if the differentiate of the TGA curve shows a peak simultaneous. In this table also the known transition temperatures of the different melting (M) and triple points (T) are given. In the last column the involved hydrates are given. The numbers indicate the hydrates, e.g. 7 stands for MgSO₄·7H₂O, whereas s indicates a solution of MgSO₄.

<table>
<thead>
<tr>
<th>Number</th>
<th>DSC peak</th>
<th>Temperature (°C)</th>
<th>TGA differentiate</th>
<th>Transition</th>
<th>Hydrates</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>46</td>
<td>√</td>
<td>T</td>
<td>7-6-s</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>50</td>
<td></td>
<td>T</td>
<td>4-1-s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>54</td>
<td>T</td>
<td>7-5-s</td>
<td></td>
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<td></td>
<td></td>
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<td>T</td>
<td>7-1-s</td>
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<td>11</td>
<td></td>
<td>277</td>
<td>√</td>
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</tr>
</tbody>
</table>

The dehydration process of the MgSO₄ grains starts with a mixture of different salt hydrates of MgSO₄. Each of these salt hydrates will follow its own dehydration path. The different transitions that the salt hydrates pass during heating will have a different reaction rate and threshold temperature.

Heating a mixture of different hydrates implies that when a transition temperature is passed, some of the salt hydrates are transformed and others not. As a result, grains remain or become mixtures of different salt hydrates and aqueous solutions. The solution will evaporate by further heating, but the recrystallization conditions determine in which state the salt hydrate ends up. This may result in different
recrystallization conditions and consequently in different salt hydrates.

The dehydration experiment was also measured using NMR. The $T_2$ relaxation distribution against temperature is given as a contour plot in Figure 6.7. Initially, all measured signals have a relaxation time of 70 $\mu$s and at 52 $^\circ$C additional relaxation time components of 0.02 and 0.2 s are observed. These two components have a comparable contribution and decrease at the same moment temperature. We will consider these as one component, referring to pore water. Above 130 $^\circ$C, the pore water component disappears and only a short component of 100 $\mu$s in the distribution remains.

The loading measured with NMR is plotted against temperature in Figure 6.8. The signal decreases significantly above 100 $^\circ$C, until that moment only a small decrease of the loading is observed. The total water component decreases slower compared to the TGA experiment, which is due to the larger sample used in the NMR. The relaxation time contribution of pore water ($T_2 > 500 \mu$s) and lattice water ($T_2 < 500 \mu$s) are also plotted in Figure 6.8. The lattice component drops at a temperature that is close to the known triple point temperature of heptahydrate and hexahydrate, as at the same temperature the pore water increases. This indicates dissolution of the material and supports the results of the DSC experiments and the phase diagram. Between 60 and 95 $^\circ$C both components are constant, whereas at 100 $^\circ$C a small increase of pore water is observed. This fits well with peak 5 at 97-10 $^\circ$C in the DSC experiment. At the same moment the lattice water decreases until it reaches a value of 1.5 water molecules per mole MgSO$_4$ at 150 $^\circ$C. This can be again an effect of the larger sample size in case of the NMR. Similar to the dehydration of Na$_2$SO$_4$, we could determine that an aqueous solution is produced in the salt hydrate grains.

![Figure 6.7: A contour plot of the $T_2$ distribution of MgSO$_4$ as function of temperature measured with a NMR experiment with a heating rate of 0.6 $^\circ$C/min. The initial mass is given in Table 6.1.](image)
6.5 CuSO₄

CuSO₄ grains were equilibrated above a saturated solution of KCl (RH=85%) at 22 °C. According to the phase diagram in Figure 2.5, this results in grains of CuSO₄·5H₂O. These equilibrated grains were studied with the TGA, DSC and NMR. The loading measured with the TGA and the heat measured with the DSC during dehydration are plotted in Figure 6.9. The loading of the TGA experiment shows that the sample was initially CuSO₄·5H₂O. Three dehydration steps are visible: from pentahydrate to trihydrate at 78 °C, from trihydrate to monohydrate at 95 °C and from monohydrate to the anhydrous phase at 214 °C, respectively. The measured TGA curve is in agreement with the literature [240]. The three observed dehydration steps in the TGA fit well with the data from the DSC experiment. In the DSC curve, only broad peaks are observed and the dehydration is finished at lower temperatures than the triple temperatures known from the phase diagram in Figure 2.5, so we expect that no dissolution of the structure occurs under these conditions.

The dehydration experiment was repeated using NMR. The $T_2$ relaxation distribution against temperature is given as a contour plot in Figure 6.10. Initially, the measured signals have an average relaxation time of 50 µs and at 98 °C a second relaxation component is observed with a relaxation time of 800 µs. This second component indicates pore water and it appears at a temperature close to the triple point of pentahydrate, trihydrate and aqueous solution. Above 120 °C, this second relaxation time component disappears and one component with an average relaxation time of 200 µs remains.

The two observed relaxation time regimes in the relaxation distribution can be divided in pore water and lattice water. In Figure 6.10 the boundary is indicated with
Figure 6.9: The loading and heat production for CuSO₄ of a heating experiment with a heating rate of 0.6 °C/min. The initial masses are given in Table 6.1.

the dotted line, relaxation times longer than the dotted line belong to pore water, shorter relaxation times belong to lattice water. The relaxation time of the pore water is much shorter compare to previous hydrates, because the Cu²⁺ dissolved in pore water decreases the relaxation time as result of its paramagnetic properties [241]. The relaxation time of the lattice water increases during dehydration from 50 μs to 200 μs, what is probably a result of a combination of increased temperature and a changed interaction between the water molecules in the lattice and their surrounding in case of lower loadings. To distinguish the contributions of pore and lattice water, we varied the boundary between these two contributions.

The total water loading measured with NMR is plotted against temperature during this dehydration experiment in Figure 6.11. As can be seen the loading slowly decreases, till the temperature reaches the 98 °C. At that temperature, the loading decreases to a value just below the monohydrate in accordance to the phase diagram. The sample loses water, but the dehydration process is slower compared to the TGA and DSC. As a result, the two dehydration steps overlapping due to the larger sample.

In Figure 6.11 the pore and lattice water contributions are plotted as well. It shows that close to the triple point of pentahydrate, trihydrate and aqueous solution at 98 °C there is a fast change in the pore and lattice water component. This increase in pore water indicates partial deliquescence of the salt hydrate grains. The pore water component quickly decreases and above 120 °C the pore and lattice water component are constant. As mentioned before, the NMR dehydration process is slower compared to the DSC and TGA. The pore water production in the NMR is not observed in the TGA or DSC, because in these samples the dehydration was already completed by crossing the triple point of pentahydrate, trihydrate and aqueous solution.
Figure 6.10: A contour plot of the $T_2$ distribution of CuSO$_4$ as function of temperature measured with a NMR experiment with a heating rate of 0.6 °C/min. The initial mass is given in Table 6.1.

Figure 6.11: The contribution of the different water components of CuSO$_4$ measured with a NMR experiment with a heating rate of 0.6 °C/min. The initial mass is given in Table 6.1. The dotted line indicates the used boundary between lattice and pore water.
6.6 FeSO$_4$

FeSO$_4$ grains were equilibrated above a saturated solution of KCl (RH=85%) at 22 °C. According to the phase diagram in Figure 2.6, this results in grains of FeSO$_4$·7H$_2$O. These equilibrated grains were studied with the TGA, DSC and NMR. The loading measured with TGA and the heat during dehydration measured with the DSC are plotted in Figure 6.12. The loading of the TGA experiment shows that the sample was initially FeSO$_4$·6.1H$_2$O. According to the phase diagram, this is probably a mixture of heptahydrate and tetrahydrate. Three dehydration steps are visible, at 60 °C, 80 °C and at 250 °C. The measured TGA curve is in agreement with the literature [242]. The DSC experiment shows peaks in the heat consumption at the same temperatures as the dehydration temperatures observed in the TGA. The dehydration step at 60 °C fits reasonably well with the known triple point of heptahydrate, tetrahydrate and its aqueous solution. The transition temperature to the monohydrate is not known, but according to the DSC data this should be close to 80 °C. Zooming in on the DSC data, we observe that both peaks are not continuous, but some fluctuations are present in these peaks. This indicates a combination of different processes at these temperatures and, thus, the dehydration is not a single step process.

The dehydration experiment was repeated using the NMR. The $T_2$ relaxation distribution against temperature is given as a contour plot in Figure 6.13. Initially the measured signal has a relaxation time of 50 μs and at 70 °C a second relaxation component is observed with an relaxation time of 800 μs. Above 100 °C this second relaxation time component disappears and one component with an average relaxation time of 250 μs remains. Similar to Cu$_2$SO$_4$, the relaxation time of the pore water component is shorter than in case of other samples as a result of its paramagnetic properties. The total water loading measured with NMR is plotted against temperature during this dehydration experiment in Figure 6.14. Obviously, the loading decreases above 50 °C, till the temperature reaches the 100 °C. At that temperature, the loading is equal to the monohydrate. The two observed relaxation time regimes are divided into pore water ($T_2 > 300$ μs) and lattice water ($T_2 < 300$ μs) in Figure 6.14. The signal intensity shows at 70 °C a fast change in the pore and lattice water component. This does not correspond to a known triple point in the FeSO$_4$·H$_2$O phase diagram. Probably this is an effect of the reaction kinetics of this transition. This pore water disappeared around above 100 °C and the signal intensity is constant.
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Figure 6.12: The loading and heat production for FeSO$_4$ of a heating experiment with a heating rate of 0.6 °C/min. The initial masses are given in Table 6.1.

Figure 6.13: A contour plot of the $T_2$ distribution of FeSO$_4$ as function of temperature measured with a NMR experiment with a heating rate of 0.6 °C/min. The initial mass is given in Table 6.1.
6.7 ZnSO$_4$

ZnSO$_4$ grains were equilibrated above a saturated solution of NaNO$_2$ (RH=65%) at 22 °C. According to the phase diagram in Figure 2.7, this should result in grains of ZnSO$_4$·7H$_2$O. The loading measured with TGA and the heat during a dehydration measured with DSC are plotted in Figure 6.15. The loading of the TGA experiment shows that the sample was initially ZnSO$_4$·5.7H$_2$O. According to the phase diagram this is probably a mixture of heptahydrate, hexahydrate and monohydrate. Two dehydration steps are visible in the TGA curve, one starting at 30 °C and finished at 80 °C from the initial loading to the monohydrate and the second starting at 250 °C from the monohydrate to the anhydrous phase. The TGA curve is in agreement with the literature [243].

The heating curve of the DSC experiment shows peaks in the heat consumption at temperatures corresponding with the TGA mass decrease, but the peak between 30-80 °C is not smooth. At 65 °C a small sharp peak is observed and between 70 and 80 °C small peaks are observed. A clear explanation is missing for this set of peaks, but indicates several phase transitions. These transitions have no effect on the mass according to the TGA curve. The first sharp peak at 65 °C is delayed compared to the phase diagram, where a transition of hexahydrate to monohydrate is expected at 60 °C.

The dehydration experiment was repeated using the NMR. The $T_2$ relaxation distribution against temperature is given as a contour plot in Figure 6.16. Initially, all measured signals have a relaxation time of 100 μs and at 65 °C a second relaxation component is observed with an relaxation time of 200 ms. Above 100 °C this second relaxation time component disappears and a single component with an average
relaxation time of 200 μs remains.

The total water loading measured with NMR is plotted against temperature during this dehydration experiment in Figure 6.17. As can be seen, the loading decreases above 50 °C, until the temperature reaches 100 °C. At that moment, the loading is equal to the monohydrate. The two observed relaxation time regimes can be divided in pore water (T2 > 1 ms) and lattice water (T2 < 1 ms). The loading against temperature during this dehydration experiment is given in Figure 6.17. It shows at 65 °C, which is close to the triple point of hexahydrate, monohydrate and aqueous solution, a fast change in the pore and lattice water component. This temperature is equal to the observed peak in the DSC. A second increase in pore water is observed at 85 °C, which does not match with the studied phase diagram neither with the DSC experiment. The mismatch with the DSC can be a result of the dehydration rate of both samples. In case of the DSC only monohydrate is present at 85 °C, while in the NMR experiment also higher loadings are present. These higher hydrates present in the NMR experiment can have an (incongruent) melting around 85°C, which results in additional pore water production. The lattice water increases at 90 °C when, simultaneously, the pore water decreases. This indicates a recrystallization of the dissolved ZnSO₄ in the aqueous solution. Above 100 °C, all pore water has disappeared and the total water component is constant.
Figure 6.16: A contour plot of the $T_2$ distribution of ZnSO$_4$ as function of temperature measured with a NMR experiment with a heating rate of 0.6 °C/min. The initial mass is given in Table 6.1.

Figure 6.17: The contribution of the different water components of ZnSO$_4$ measured with a NMR experiment with a heating rate of 0.6 °C/min. The initial mass is given in Table 6.1.
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6.8 CoSO$_4$

CoSO$_4$ grains were equilibrated above a saturated solution of KCl (RH=85%) at 22 °C. According to the phase diagram in Figure 2.8, this should result in grains of CoSO$_4$·7H$_2$O. The loading measured with TGA and the heat measured with DSC during a dehydration are plotted in Figure 6.18. The loading of the TGA experiment shows that the sample was initially CoSO$_4$·7H$_2$O. According to the TGA curve, the sample dehydrates at a much lower temperature as described in literature [244,245], but in that case a higher heating rates of 5 °C/min have been used.

The DSC experiment shows at five temperatures a peak in the heat consumption. The first peak at 45 °C corresponds to the triple point temperature of heptahydrate, hexahydrate and an aqueous solution and no mass decrease is seen. Hence, probably only dissolution of the hydrate occurs at that temperature. At 63 °C, the triple point temperature of hexahydrate, monohydrate and aqueous solution, no clear transition is observed, but some small variations in the DSC curve indicate that transitions may occur in a small part of the grains. At peaks 2 till 5, the DSC peaks at the same temperature where the loading decreases, which indicates dehydration steps. These steps can not be linked to phase transitions as they do not correspond to the known phase diagram.

The dehydration experiment was repeated using the NMR and the $T_2$ relaxation distribution against temperature is given as a contour plot in Figure 6.19. Initially all measured signals have a relaxation time of 200 µs and at 45 °C a second relaxation component is observed with a relaxation time of 2 ms. This transition is in line with the first peak in the DSC. Above 100 °C, the second relaxation time component disappears and a single component with an average relaxation time of 150 µs remains.

The total water loading measured with NMR is plotted against temperature during this dehydration experiment in Figure 6.20. Obviously, the loading decreases above 60 °C, till the temperature reaches 120 °C, where the loading is equal to the monohydrate. The two observed relaxation time regimes can be divided in pore water ($T_2 >$400 µs) and lattice water ($T_2 <$400 µs). Similar to Cu$_2$SO$_4$, the relaxation time of the pore water component is short, as a result of its paramagnetic properties. At the triple point of heptahydrate, hexahydrate and an aqueous solution, the pore water component increases and the lattice water component decrease, with a constant total water loading. This indicates incongruent melting of the material and fits well with the observed peak in the DSC. No additional increase of pore water is observed by further heating and the pore water disappears above 95 °C. At 110 °C the lattice water drops as well. According to this data dissolution occurs at the triple point of heptahydrate, hexahydrate and aqueous solution. This is in accordance with the DSC data. According to the phase diagram at the triple point of hexahydrate, monohydrate and aqueous solution dissolution is also expected at 64 °C, but this is not observed in the NMR data.
6.8. CoSO\textsubscript{4}

Figure 6.18: The loading and heat production for CoSO\textsubscript{4} of a heating experiment with a heating rate of 0.6 °C/min. The initial masses are given in Table 6.1.

Figure 6.19: A contour plot of the $T_2$ distribution of CoSO\textsubscript{4} as function of temperature measured with a NMR experiment with a heating rate of 0.6 °C/min. The initial mass is given in Table 6.1.
6.9 NaBr

NaBr grains were equilibrated above a saturated solution of Mg(NO$_3$)$_2$·6H$_2$O (RH=55%) at 22 °C. According to the phase diagram in Figure 2.9, this results in grains of NaBr·2H$_2$O. These equilibrated grains were studied with the TGA, DSC and NMR. The loading measured with the TGA and the heat measured with the DSC during dehydration are plotted in Figure 6.21. The loading of the TGA experiment shows that the sample was initially NaBr·2H$_2$O. The DSC experiment shows a similar behavior as seen for Na$_2$SO$_4$·10H$_2$O, i.e. a broad peak over the temperature range of 25-60 °C belonging to the dehydration of the sample and a phase transition peak at 50 °C. We could not determine the melting temperature of NaBr·2H$_2$O, but according to the solubility data, it is at least more than 20 °C above 50 °C [246]. So, the peak observed at 50 °C is most probably a result of deliquescence during the phase transition from the dihydrate to the anhydrous form. The dehydration for this hydrate can be summarized by:

\[ \text{NaBr·2H}_2\text{O} \xrightleftharpoons[T = 50 ^\circ \text{C}]{NaBr (aq) + 2\text{H}_2\text{O}(l)} \xrightleftharpoons(T \geq 50 ^\circ \text{C}) \text{NaBr(s)+2H}_2\text{O(g)} \] (6.6)

The dehydration experiment was repeated using NMR. The $T_2$ relaxation distribution against temperature is given as a contour plot in Figure 6.22. Initially, all measured signals have a relaxation time of 100 μs and at 52 °C the relaxation time shifts to 0.2 s. This transition is in accordance with the sharp transition peak in the DSC experiment. The loading of the total water component measured with NMR is plotted against temperature in Figure 6.23. At 50 °C a distinct increase of water signal is observed. This is a result of the melting of the NaBr·2H$_2$O, whereby as a result the

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Figure 6.20: The contribution of the different water components of CoSO$_4$ measured with a NMR experiment with a heating rate of 0.6 °C/min. The initial mass is given in Table 6.1.
Figure 6.21: The loading and heat production for NaBr of a heating experiment with a heating rate of 0.6 °C/min. The initial masses are given in Table 6.1.

Figure 6.22: A contour plot of the $T_2$ distribution of NaBr as function of temperature measured with a NMR experiment with a heating rate of 0.6 °C/min. The initial mass is given in Table 6.1.
Figure 6.23: The contribution of the different water components of NaBr measured with a NMR experiment with a heating rate of 0.6 °C/min. The initial mass is given in Table 6.1.

grain structure of the salt hydrate grains disappeared and part of the amount of sample inside the RF sensitive area fluctuates. Again the dehydration process in the NMR is finished at a higher temperature compare to the DSC and TGA experiment, because of the larger sample. The total water component can be divided in two components: pore water ($T_2 > 500\,\mu s$) and lattice water ($T_2 < 500\,\mu s$). The signal intensity of these components against temperature is given in Figure 6.23. It shows that just above the triple point of 50 °C a fast transformation in the pore and lattice water component takes place. This is a result of dissolution of the material and support the indication given by the DSC experiment.
6.10 CuCl₂

CuCl₂ grains were equilibrated above a saturated solution of NaNO₂ (RH=65%) at 22 °C. The TGA and DSC experiment are plotted in Figure 6.24. The TGA experiment shows that the sample was initially CuCl₂·2H₂O. The TGA curve was in agreement with the literature [108]. The DSC experiment shows a single broad peak, what indicates that the dehydration occurs without any abrupt phase transition, like dissolution of the grains.

The dehydration experiment was repeated using the NMR. The \( T_2 \) relaxation distribution against temperature is given as a contour plot in Figure 6.25. The \( T_2 \) relaxation time was constant over the entire range with a value of 100 μs. No long relaxation time is observed during this experiment.

The signal intensity against temperature during this dehydration experiment is given in Figure 6.26, showing no pore water (\( T_2 >400 \mu s \)) production. This means that during heating of CuCl₂·H₂O, the sample did not cross a triple point nor showed easy deliquescence. In that case also no (incongruent) melting point is crossed during heating.

Figure 6.24: The loading and heat production for CuCl₂ of a heating experiment with a heating rate of 0.6 °C/min. The initial masses are given in Table 6.1.
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Figure 6.25: A contour plot of the $T_2$ distribution of CuCl$_2$ as function of temperature measured with a NMR experiment with a heating rate of 0.6 °C/min. The initial mass is given in Table 6.1.

Figure 6.26: The contribution of the different water components of CuCl$_2$ measured with a NMR experiment with a heating rate of 0.6 °C/min. The initial mass is given in Table 6.1.
6.11 CaCl$_2$

CaCl$_2$ grains were equilibrated above a saturated solution of CH$_3$COOK (RH=25\%) at 22 °C. According to the phase diagram in Figure 2.11, this should result in grains of CaCl$_2$·6H$_2$O. The loading measured with TGA and the heat measured with DSC during a dehydration are plotted in Figure 6.27. The TGA experiment shows that the sample was initially CaCl$_2$·6.2H$_2$O, so the crystals are initially overhydrated. Overhydration means that on average the CaCl$_2$ molecules are surrounded with more water molecules than the loading of the highest hydrated state. This implies that some aqueous solution is also present in or on the surface of the grains.

During the dehydration, two dehydration steps are observed, one immediately after starting and a second one around 88 °C. At 150 °C the sample is completely dehydrated. The TGA curve is in agreement with the literature [247, 248]. Besides two broad evaporation peaks, the DSC shows also two sharp peaks which indicate a fast phase change. The first at 31 °C fits with the transition of hexahydrate to tetrahydrate, but the second at 85 °C can not be matched with the phase diagram.

The dehydration experiment was repeated using the NMR and after removing the sample from the NMR, the grain structure disappeared and only a whitish agglomerate of grains remained. For CaCl$_2$ it was not possible to determine appropriate settings for dehydration experiments in the NMR. At the starting conditions, the lattice water component was not stable, being also visible from the raw data of the NMR experiment. An explanation is lacking at this moment. The $T_2$ relaxation distribution against temperature is given as a contour plot in Figure 6.28. According to the relaxation data, a transition occurs at 60 °C.

The signal intensity against temperature during this dehydration experiment is given in Figure 6.29. It shows an instable measurement and by increasing the tem-
Figure 6.28: A contour plot of the $T_2$ distribution of CaCl$_2$ as function of temperature measured with a NMR experiment with a heating rate of 0.6 °C/min. The initial mass is given in Table 6.1.

Figure 6.29: The contribution of the different water components of CaCl$_2$ measured with a NMR experiment with a heating rate of 0.6 °C/min. The initial mass is given in Table 6.1.
perature the signal even increases at 130 °C. The two observed relaxation time regimes are divided in pore water ($T_2 > 1$ ms) and lattice water ($T_2 < 1$ ms). The signal intensity against temperature during this dehydration experiment is given in Figure 6.29. The graph shows the signal intensity plotted against temperature. In the lower temperature region the lattice water component strongly. At 60 °C a transition to pore water occurs and no lattice water is observed above that temperature. The signal intensities plotted in these graphs are too noisy for a proper interpretation, except for the transition at 60 °C. At this temperature no sudden changes are observed in the DSC and TGA experiment or within the composed phase diagram of CaCl$_2$-H$_2$O.

### 6.12 MgCl$_2$

MgCl$_2$ grains were equilibrated above a saturated solution of CH$_3$COOK (RH=25%) at 22 °C. According to the phase diagram in Figure 2.12, this should result in grains of MgCl$_2$·6H$_2$O. The loading measured with TGA and the heat measured with DSC during a dehydration are plotted in Figure 6.30. The TGA experiment shows that the sample was initially MgCl$_2$·6H$_2$O. During the dehydration, four dehydration steps are observed, from hexahydrate to tetrahydrate, from tetrahydrate to dihydrate, from dihydrate to monohydrate and finally from monohydrate to MgClOH·xH$_2$O, respectively. The latter is a hydrolysis reaction with HCl gas production [43]. The TGA curve is in agreement with the literature [43,247]. The DSC experiment shows similar data, only at 120 °C an additional phase change is observed, which is close to both the melting temperature of MgCl$_2$·6H$_2$O (116.3 °C [249]) and the triple point of the hexahydrate, tetrahydrate and the aqueous solution.

The dehydration experiment was repeated with the NMR and the $T_2$ relaxation

![Graph](image_url)

*Figure 6.30: The loading and heat production for MgCl$_2$ of a heating experiment with a heating rate of 0.6 °C/min. The initial masses are given in Table 6.1.*
distribution against temperature is given as a contour plot in Figure 6.31. Initially, all measured signal has a relaxation time between 100-2000 μs and at 120 °C a second relaxation component is observed with an relaxation time of 0.02-2 s.

The total water loading measured with NMR is plotted against temperature during this dehydration experiment in Figure 6.17. Obviously is that the loading is almost constant till 100 °C, where it starts to decrease, until at 120 °C a fast decrease in the loading occurs, while the experiment finishes with a loading of 3 mol H₂O per mole MgCl₂, but the loading is still decreasing. The two observed relaxation time regimes can be divided in pore water ($T_2 > 2$ ms) and lattice water ($T_2 < 2$ ms). At the triple point of hexahydrate, tetrahydrate and aqueous solution a fast change in the pore and lattice water component is observed and fits well with the observed peak in the DSC. By keeping the sample at 150 °C for 30 minutes longer, the pore water disappears and the lattice water increases. This increase in lattice water component shows that MgCl₂ recrystallized from the evaporating solution.
6.13 Concluding remarks

In this chapter, ten different salt hydrates were studied for selecting a heat storage material, considering the criterion of melting during dehydration in particular. The hydrates of these salts were studied with three different techniques: TGA, DSC and NMR. The three techniques are complimentary to each other, but as result of different sample sizes and air flow over the samples, a one to one comparison is difficult and the three techniques each contribute to the full picture from a different experimental point of view. The TGA and DSC data could be reasonably combined, because their settings are similar to each other and give information about dehydration steps and phase transitions under the same boundary conditions. With help of the NMR data, phase transitions are identified as transitions wherein deliquescence or (incongruent) melting occurs. In generally this was only possible in case of the first phase transitions. In case of transitions at higher temperatures, the NMR and DSC data deviate too much from each other.

If we focus on the application of salt hydrates for heat storage, Na$_2$SO$_4$, CaCl$_2$ and NaBr are not suitable based on this set of experiments. These salt hydrates dissolve their own grains during heating, prohibiting a repeating hydration/dehydration with a constant hydration/dehydration rate. This is based on the idea, that optimal hydration/dehydration rates are partially dependent on the accessibility of the salt to the air. In case the geometry of the grains change during dehydration, the accessibility changes and the hydration/dehydration rates as well. However, NaBr and Na$_2$SO$_4$ can be interesting for cooling, because of their high equilibrium relative humidity between the anhydrous and hydrated phase. The dehydration on the basis of RH will consume energy, which can be used for cooling. In this case, the geometry of the grains will not be affected as a consequence of dissolving.

Figure 6.32: The contribution of the different water components of MgCl$_2$ measured with a NMR experiment with a heating rate of 0.6 °C/min. In the grey area is the sample kept at 150 °C for 30 minutes. The initial mass is given in Table 6.1.
ZnSO$_4$ is a salt hydrate which partially dissolves its own grains in the considered heating rate and, subsequently, changes the grain structure. This makes ZnSO$_4$ unfavorable under the chosen conditions, but with lower heating rates this might be change.

From the other six salts, the grain geometry is still present on macroscopic scale after dehydration. Except for CuCl$_2$, pore water is observed for all hydrates during the dehydration process.

For CoSO$_4$, MgSO$_4$ and FeSO$_4$, the observed first dehydration step is in agreement with the phase diagram. Second transitions are not observed in the phase diagram (FeSO$_4$) or do not occur at the temperatures that are expected on the basis of the phase diagram (CoSO$_4$ and MgSO$_4$). As the phase diagram of CoSO$_4$ and FeSO$_4$ are ill defined, magnesium sulfate was selected for continued studying.

Finally, CuSO$_4$ might be an interesting candidate from the perspective of heat storage material. All phases of CuSO$_4$ hydrates are represented in the phase diagram and the amount of produced pore water is small.

MgCl$_2$ might be a suitable heat storage candidate as well based on the NMR data. The dehydration does not dissolve the grain structure. A disadvantage of this salt is that it easily deliquesces.

The lack of pore water during dehydration makes CuCl$_2$ a good candidate as a heat storage material. Its disadvantage is the relative low energy density of 1.73 GJ/m$^3$, being 10-20% lower than for the other studied salt hydrates.
6.13. Concluding remarks
Chapter 7

Performance of hydrates during cyclic loading

Salt hydrates have a high potential as heat storage material using their hydration/dehydration reaction. These hydration/dehydration reactions are studied in this chapter for CuCl$_2$, CuSO$_4$, MgCl$_2$ and MgSO$_4$. During a hydration/dehydration reaction the salt shrinks and expands as a result of the differences in densities of the phases. As a result, after the first dehydration cycle, the crystal is fractured in a pseudomorphic crystal that releases the water molecules easier. The effect of fracturing is larger in case of hydrates with larger volumetric changes. In this study the performance of hydrates during cyclic loading is related to the pore water production and volume variations. On the basis of such data, it is concluded that CuCl$_2$ is the most promising heat storage material.

7.1 Introduction

Previous studies focussed on a single hydration or dehydration step either induced by temperature changes, i.e. using thermal gravimetric analysis (TGA) [40–42], differential scanning calorimetry (DSC) [43–45], XRD [43,46], Raman [47] and neutron diffraction [48] or by vapor pressure; i.e. using gravimetric analysis [49, 50] and Raman [51–53]. Reviews on the selection of hydrates that are suitable for heat storage [22, 23, 31, 32] are mainly based on single dehydration or hydration steps or are based purely on theoretical energy densities and dehydration temperatures. This selection procedure is insufficient, as it does not take account of multicyclic stability. It has been observed that the salt grains are not stable (physically, mechanically and/or chemically) over several cycles of repeated hydration and dehydration, e.g., considering changes in the rehydration/dehydration rates and/or grain sizes [24, 54–56]. For example, during dehydration a pseudomorphic structure may appear [224, 250] due to volume changes, which facilitates vapor transport through the crystal, thereby influencing the transport in time [55]. Such observations are mainly based on mass measurements and information on the crystal structure or water transport inside the
grains is missing. Furthermore, a drawback of most of the techniques used in these studies, is that during the dehydration or rehydration the air supply is from one side of the sample only, i.e. single-sided induced hydration/dehydration. As a result most experiments are performed on sample mass below 10 mg, because in larger samples diffusion of air through the bed of grains limits the dehydration and (re)hydration processes.

In this chapter, the cyclability of several hydrates is studied, which were selected on the basis of their theoretical volume variation during a hydration/dehydration reaction. Using Nuclear Magnetic Resonance (NMR), the water transport in these hydrates is studied in larger beds of grains where the air is blown through the bed itself. This is in contrast with techniques like TGA or DSC, where air can only be blown along the top of the sample. In such experiments, the number of layers of grains will affect the dehydration process as a result of vapor diffusion through the bed of grains. In the NMR experiments, this effect can be avoided as long as the air flow through the bed is high compared to the vapor production or consumption of the grains in the bed.

### 7.2 Methods

In this study, NMR is used to measure water in the hydrates non-destructively. The signal of water attenuates in a NMR experiment. In the case we can ignore the spin-lattice relaxation time $T_1$, i.e. when the repetition time $T_r > 4T_1$, this reads according to:

$$S(t) = \rho \exp(-t/T_2),$$  \hspace{1cm} (7.1)

wherein $\rho$ is the hydrogen density, $t$ is the time after excitation and $T_2$ is the transversal relaxation time. Hence, it is possible to link the signal intensity of the NMR to the total amount of water present. In general, as to minimize the influence of $T_2$, the time $t$ is chosen as short as possible. The transversal relaxation time $T_2$ can be related to the mobility of the proton [182,183], whereby the $T_2$ increases with increasing mobility.

In a sample, not all water molecules will have the same mobility and equation 7.1 can be rewritten as:

$$S(t) = \sum_i \rho_i \exp(-t/T_{2,i})$$  \hspace{1cm} (7.2)

Here $i$ indicates the types of water in a material, $\rho_i$ is the water density of type water $i$ and $T_{2,i}$ the transversal relaxation time of water $i$. This equation therefore shows that a multi-exponential decay curve is generally observed, which is a result of different types of water with different mobility in a sample.

In this chapter, two groups of transversal relaxation times ($T_2$) in hydrates are considered. The first group has $T_2$ values between 10 to 300-1000 $\mu$s, which will be referred to as lattice water. The upper boundary is variable, depending on the studied hydrate. This type of water is located in the crystal structure and these water molecules are almost immobile and have strong static interaction with their
neighboring water molecules. This component is the only component present in a hydrated crystal. As an example, in Figure 7.1 the relaxation distribution is plotted for MgSO$_4$ at 25 °C and as can be seen only relaxation times below 300 μs are observed. When the sample is heated to 60 °C, the sample crosses the triple point of heptahydrate, hexahydrate and aqueous solution of MgSO$_4$ and the relaxation distribution changes. At this temperature, also $T_2$ values between 0.3-1 and 1000 ms are observed, which will be referred to as pore water. This water is an aqueous solution of the salt in a grain and is mobile compared to the lattice water. It may be located in voids or pores inside a grain. This water component may also appear during dehydration by crossing (incongruent) melting temperatures. In case of a larger sample, the mean relaxation time is plotted and this can be a combination of pore and lattice water.

For studying the dehydration/hydration cycles by NMR, a home-build RF-coil was used which resonates at 200 MHz, which is schematically outlined in Figure 7.2. A Faraday coil has been incorporated in the RF-coil in order to be able to perform quantitative analysis of the NMR signal. During heating, the temperature is controlled in a range of 20-150 °C with ±1 °C in accuracy. The temperature is measured next to the sample. No active cooling is present in this setup. Samples with a size of 10 mm height and 6 mm diameter can be placed in a glass cylinder. The sample is confined by two porous glass filters, through which an airflow of 0.2 l/min takes place (air velocity is 11 cm/s). The airflow temperature before blowing the air into the temperature controlled setup is 25 °C. All experiments were performed at atmospheric pressure. During dehydration, the air flow through the sample is kept at 0-5% RH. As the air flow first passed a glass filter, the airflow temperature which reaches the sample is equal to the temperature measured in the sample. During hydration, the RH of the air flow is set depending on the hydrate studied. The RH

\[ \text{Signal (a.u.)} \]

\[ \text{Pore water} \quad \text{Lattice water} \]

\[ 25 \text{ °C} \quad 60 \text{ °C} \]

\[ T_2 (s) \]

Figure 7.1: The $T_2$ distribution of MgSO$_4 \cdot 7$H$_2$O crystal before dehydration at 25 °C and during a dehydration at 60 °C. The dotted line indicates the boundary between relaxation times belonging to lattice and pore water.
Figure 7.2: A schematic representation of the NMR setup used during dehydration/hydration experiments. The sample can be conditioned by vapor pressure and temperature.

around the sample can be calculated with help of the initial air temperature (25 °C) and sample temperature.

In order to measure the relaxation, the signal decay was recorded using a CPMG pulse sequence [186]. During a CPMG pulse sequence a static magnetic field gradient of 300 mT m$^{-1}$ is applied. This gradient adjusts the echoes of the CPMG pulse train in our recording window. The time between two successive echoes within this pulse sequence was 60 μs, whereas the repetition time of the sequence was 24 s. 1024 up to 4096 echoes were recorded, and an accumulation was performed of 4 scans during dehydration and 16 during hydration. In order to analyse the relaxation, a Fast Laplace Inversion transformation (FLI), [194], was used. The total water density was calculated based on the relaxation analysis by extrapolation of the signal to $t = 0$.

7.3 Materials

In this study, we have selected four hydrates based on two criteria, i.e.; firstly, the energy density calculated with the density of the hydrated salt should be in the order of 2 GJ/m$^3$ in the temperature range of 25-150 °C. Secondly, the crystal can be rehydrated with a difference of at least 20 % RH between the applied RH and the equilibrium RH of the final loading at 25 °C. This means that at 25 °C $\text{RH}_{\text{del}} - \text{RH}_{\text{deh}} \geq 20\%$. $\text{RH}_{\text{del}}$ is the RH where the highest loading dissolves and $\text{RH}_{\text{deh}}$ is the RH whereby the highest loading dehydrates. Based on these criteria, four hydrates were selected: CuCl$_2$, CuSO$_4$, MgCl$_2$ and MgSO$_4$. The main thermochemical characteristics of the selected four hydrates are given in Table 7.1. The volume change and theoretical energy densities of the different reactions were calculated with help of Wagman [72] and XRD data. The table shows that the energy density is generally larger in systems with a larger volume difference. An energy density of about 2 GJ/m$^3$ corresponds with a volume difference in the order of 50%.

In the experiments, grains of 1-2 mm of the chosen hydrates were used. These
Table 7.1: The main thermochemical characteristics of the selected hydrates. The start loading and final loading are given in the second and third column. \( \Delta f H^\circ \) is the standard reaction enthalpy at 25 °C and 0.1 MPa for one mol of a hydrate. \( \Delta \)Volume is the volume difference between the reactors and products of the decomposition reaction. The energy density is calculated based on the reaction enthalpy and the volume of the highest hydrate in the reaction. RH\(_{del}\) is the RH where the highest loading dissolves and RH\(_{deh}\) is the RH whereby the highest loading dehydrates at 25 °C. This table is composed of data by Wagman et al., 1982 [72] and a XRD database [33].

<table>
<thead>
<tr>
<th>Salt</th>
<th>Start loading (mol)</th>
<th>Final loading (mol)</th>
<th>( \Delta f H^\circ ) (kJ/mol)</th>
<th>( \Delta )Volume (%)</th>
<th>Energy Density (GJ/m(^3))</th>
<th>RH(_{del}) (%)</th>
<th>RH(_{deh}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCl(_2)</td>
<td>2</td>
<td>0</td>
<td>-117.6</td>
<td>-43.0</td>
<td>1.73</td>
<td>70</td>
<td>15</td>
</tr>
<tr>
<td>CuSO(_4)</td>
<td>5</td>
<td>3</td>
<td>-111.70</td>
<td>-27.3</td>
<td>1.02</td>
<td>97</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>5</td>
<td>-226.55</td>
<td>-52.0</td>
<td>2.08</td>
<td>97</td>
<td>33</td>
</tr>
<tr>
<td>MgCl(_2)</td>
<td>6</td>
<td>4</td>
<td>-116.39</td>
<td>-59.3</td>
<td>2.75</td>
<td>97</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>6</td>
<td>-252.03</td>
<td>-46.6</td>
<td>1.95</td>
<td>33</td>
<td>3</td>
</tr>
<tr>
<td>MgSO(_4)</td>
<td>7</td>
<td>6</td>
<td>-59.89</td>
<td>-9.5</td>
<td>0.41</td>
<td>90</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>7</td>
<td>-166.66</td>
<td>-34.7</td>
<td>1.14</td>
<td>90</td>
<td>51</td>
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<td>-283.42</td>
<td>-51.8</td>
<td>1.93</td>
<td>90</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>7</td>
<td>-335.70</td>
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<td>2.29</td>
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<td>-411.08</td>
<td>-69.2</td>
<td>2.80</td>
<td>90</td>
<td>51</td>
</tr>
</tbody>
</table>

Grains were equilibrated at 22 °C above a saturated solution of KCl (RH = 85%) for CuSO\(_4\) and MgSO\(_4\) salts, CH\(_3\)COOK (RH = 22%) for MgCl\(_2\) and NaNO\(_2\) (RH = 65%) for CuCl\(_2\). With help of thermogravimetrical analysis (TGA) the initial hydrated state of the salts were determined as CuCl\(_2\)·2H\(_2\)O, CuSO\(_4\)·5H\(_2\)O, MgCl\(_2\)·6H\(_2\)O and MgSO\(_4\)·7H\(_2\)O, which is in agreement with the expected loadings at these conditions from the phase diagrams.

7.4 Results

7.4.1 CuCl\(_2\)

We first studied CuCl\(_2\), as this crystal can only have 2 loadings, i.e., 0 and 2. The CuCl\(_2\) grains were cycled eight times, i.e. eight times heated from 30 °C till 150 °C, with a heating rate of 0.5 °C/min. After reaching 150 °C in the sample, the temperature was kept constant for 0.5 hours and decreased till 30 °C in 2 hours (no active cooling, but cooling by ambient air) in each cycle. The grains were rehydrated with an RH of 60% at a sample temperature of 30 °C. The rehydration times were varied between 5 and 24 hours. The resulting measured loading of the CuCl\(_2\) grains as determined by NMR, as well as the measured sample temperature are plotted as a function of time in Figure 7.3, whereby the time is set to zero at the start of the dehydration of each run. The first dehydration cycle shows that the crystal bed dehydrates between 80 °C and 120 °C. During the second run the bed dehydrates between 75 °C and 110 °C. The other 6 successive cycles overlap with each other and
7.4. Results

The loading of a sample of CuCl$_2$ grains during different runs of dehydration/hydration. Dehydration by a heating rate of 0.5 °C/min over a temperature range of 30–150 °C, after a cooling period of 2 hours (no active cooling), the sample was rehydrated with air of 30 °C and a RH of 66% over a period of 5 till 20 hours. The dashed line indicates the sample temperature.

As can be seen the temperature of dehydration only significantly differs between the first and third dehydration run. The hydration level in all eight cycles is constant, before the dehydration starts and the crystals are entirely dehydrated at the start of the rehydration process. Within 4 hours after the heating period, the sample is in a completely rehydrated phase. Moreover, the timescales for the different rehydration curves are of the same order.

As explained, with the help of NMR it is possible to determine if water is located as lattice water or pore water in a sample. In the case of CuCl$_2$ pore water was not observed on the basis of analyses of the relaxation times, both during the dehydration/hydration cycles. These experiments show that under the conditions used in this study, CuCl$_2$ is a stable material for heat storage application.

7.4.2 CuSO$_4$

For CuSO$_4$ the dehydration was performed with a heating rate of 2 °C/min from 25-150 °C. After reaching 150 °C, the temperature was kept constant for 0.5 hours and decreased till 25 °C in 2 hours (no active cooling present) and an air flow of 25 °C and a RH of 80% was blown through the sample for 20 hours. The measured loading of CuSO$_4$ grains as determined by NMR as well as the temperature are plotted as a function of time in Figure 7.4, whereby the time is set to zero at the start of the dehydration of each run. The loading at the beginning of a dehydration run is decreasing with increasing number of runs, whereas the loading after dehydration was constant 0.8-1 mol water per mole CuSO$_4$ for every run. Although after the first
Chapter 7. Performance of hydrates during cyclic loading

Figure 7.4: The loading of a sample of CuSO$_4$ grains during different runs of dehydration/hydration. Dehydration by a heating rate of 2 °C/min over a temperature range of 25–150 °C, after a cooling period of 2 hours (no active cooling), the sample was rehydrated with air of 25 °C and a RH of 80 % over a period of 22 hours. The dashed line indicates the sample temperature.

cycle the crystal rehydrated completely, an incomplete rehydration is observed in the subsequent runs. With an increasing number of runs, the rehydration rate becomes smaller in the considered time period of 20 hours.

Like for CuCl$_2$, the first run significantly differs from the other runs, i.e. the dehydration in the first run occurs at a temperature which is 20 °C higher than for the subsequent ones. The loading of the crystals for the first cycle starts to decrease strongly at 120 °C, while the other runs are almost dehydrated to an 0.8-1 mol water per mole CuSO$_4$ loading at the same temperature. Note that the loading measured in the NMR is the volume averaged water content over an entire sample, what does not imply that all mole of CuSO$_4$ have the same amount of water, i.e. local differences may occur in loading. As the measured loading of the grains is the averaged loading inside the grains this decrease of loading can be explained in two ways.

First, if we measure a loading of three water molecules per mole CuSO$_4$ in a grain (the last run), it may be interpreted as if in every grain three molecules of water surround each mole CuSO$_4$, like in the trihydrate. As dehydration of the trihydrate occurs at a higher temperature as the pentahydrate, we expect to see a shift of the dehydration process to higher temperatures. Second, the measured lower loading can also be interpreted that only part of a grain is active. To reach a loading of three, in the active part of the grain (50% of the CuSO$_4$ molecules in the grain) the CuSO$_4$ molecules are surrounded by five water molecules, and that in the inactive part (50% of the CuSO$_4$ molecules in the grain) of the CuSO$_4$ molecules are only surrounded by one water molecule. In this case, the start of the dehydration will be the same as for a CuSO$_4$·5H$_2$O crystal. In case a mixture of pentahydrate and trihydrate was
available in these grains, the dehydration curve will start at the same temperature as for a CuSO₄·5H₂O crystal, but the curvature would get two distinguish drops, one for the grains with pentahydrate loading and the second for grains with trihydrate loadings. These two curves can overlap with samples wherein the trihydrate grains have only a small contribution, but especially in case of higher number of runs, we should be able to distinguish the two dehydration processes.

To determine, which of both explanations holds for CuSO₄, we normalized the measured loading between the loading before dehydration and after dehydration for every single run and plotted the normalized loading against temperature in Figure 7.5. With increasing number of runs, the dehydration is only significantly shifted to a lower temperature between the first and second run. In between the other runs, no shift is observed and the curves overlap. This indicates that the second explanation is more probable, so the active part of a grain decreases by increasing number of runs, but that this active part still hydrate to the same loading.

A $T_2$ relaxation analysis was also performed on the relaxation data during rehydration at 25 °C. In the relaxation distributions only single peaks are observed with relaxation times below 0.3 ms, so only lattice water was observed during this experiment. Consequently the mean relaxation time in the sample is the relaxation time of the lattice water component during rehydration.

The mean relaxation time is plotted against time in Figure 7.6. As can be seen, the mean relaxation time increases with increasing number of runs. The $T_2$ relaxation time of lattice water is mainly determined by static dipolar interaction of the surroundings. In case the interactions increase, the relaxation time will decrease. Hence, according to the relaxation measurement, the grains become less ordered with increasing number of runs, decreasing the interactions between the water molecules and their surroundings.

Figure 7.5: The water content normalized between the maximum and minimum loading of a sample of CuSO₄ grains during different runs of dehydration/hydration. Dehydration by a heating rate of 2 °C/min over a temperature range of 25–150 °C (see Figure 7.4). The inset gives the loading of a sample at the start of a dehydration run.
These experiments indicate that structure variations play a role in the hydration/dehydration processes. Previous experiments on sulphate hydrates have shown that the dehydration of a crystal can form a pseudomorphic structure \[224,251\]. The crystal will be fractured after the first dehydration run and the hypothesis we previously postulated (see Chapter 4) is that during a dehydration run the crystals will form a fractured structure. As a result, in every subsequent cycle, more internal surface is available in the grains and water molecules will be adsorbed more efficiently at the outer layer of the grains. At the moment, this outer layer is completely hydrated the water pathways will be sealed off, because the outer layer will expand as result of hydration. As only a limited time is given for rehydration, this mechanism decreases the absorption rate, which will result in an incomplete rehydration. This experiment shows that CuSO\(_4\) is not stable during hydration/dehydration experiments.

**7.4.3 MgCl\(_2\)**

For studying the dehydration and rehydration of MgCl\(_2\)-6H\(_2\)O, we selected two maximum dehydration temperatures, one of 100 °C and the other one of 150 °C, resulting in a loading of respectively 4 and 2. With these two dehydration temperatures, we vary the volume change (approximately with a factor of 2) during the hydration and dehydration process and the number of phase transitions during a hydration/dehydration process.

The temperature increase to a temperature of 150 °C was performed to dehydrate the hexahydrate to dihydrate. The cycle consisted of heating of 105 minutes from 25 to 150 °C (i.e. 1.2 °C/min), followed by 30 minutes constant temperature at 150 °C. The sample was cooled down till 25 °C in 2 hours (no active cooling present) and the conditions kept constant afterwards for 18 hours at a RH of 25% at 25 °C. This cycle was repeated 7 times. The measured loading by NMR and the temperature are
Figure 7.7: The loading of a sample of MgCl$_2$ grains during different runs of dehydration/hydration. Dehydration by a heating rate of 1.2 °C/min over a temperature range of 25–150 °C. After a cooling period of 2 hours (no active cooling), the sample was rehydrated with air of 25 °C and a RH of 25% over a period of 22 hours. The dashed line indicates the sample temperature. The inset gives the dehydration rate at 150 °C for the different runs.

plotted as function of time in Figure 7.7, whereby the time is set to zero at the start of the dehydration of each run. Initially, on average the crystals dehydrate below the dihydrate phase of MgCl$_2$, but after four cycles the sample is on average dehydrated till the dihydrate. The rehydration level decreases by additional runs as result of a decreasing rehydration rate. No significant difference is observed in dehydration temperature between the first and other runs, in contrast to what we observed for CuCl$_2$ and CuSO$_4$. Moreover, dehydration still continues during the period of a constant temperature of 150 °C.

In the inset, the dehydration rate at 150 °C is plotted against the number of the run. The dehydration rate is calculated by taking the derivative in time of the loading at 150 °C, because the temperature is constant over 30 minutes and the grains can only dehydrate considering that no phase transition line is crossed. In addition, during dehydration to 150 °C, the measured loading at the beginning of the 150 °C dehydration period is constant over the different runs (maximum variation of 0.25 mol H$_2$O per mole MgCl$_2$). The dehydration rate is smaller in case of a higher number of run. The difference may be a result of the change in grain structure, because the other conditions (temperature and air flow) are the same. Obviously, such change in grain structure decreases the releasing rate of vapor from the grain. This change in grain structure will not only affect the dehydration, but also the rehydration process.

The grain structure may be affected due to production of pore water during dehydration. Therefore, $T_2$ relaxation time analysis is performed on this dehydration experiment (in Figure 7.8), the mean $T_2$ relaxation time of the sample is plotted against time after starting the dehydration process. In this case, the relaxation time
is a combination of pore and lattice water. The initial mean relaxation time is around 400 μs at 25 °C. At the beginning of the heating of the sample, the relaxation time increases to 1 ms at 60 °C, where it remains constant till 135 °C. Until this temperature is reached, a single peak is observed in the relaxation time distribution and, consequently, water in the sample is still identified as lattice water. At 135 °C, the mean $T_2$ relaxation time strongly increases. The measured mean relaxation time is between 10 and 100 ms. This implies that a large part of water in the crystals is pore water, i.e. mobile water in the grains. This may be explained on the basis of incongruent melting of the part of the grains at 135 °C. The transition temperature is above the triple point of heptahydrate, tetrahydrate and the solution of MgCl$_2$ [111]. So, it may happen that part of the crystal was not dehydrated till tetrahydrate and during this transition, part of the crystal is melted in its own crystal water.

The dehydration to 100 °C was performed to dehydrate the hexahydrate to tetrahydrate. The cycle is a heating of 40 minutes from 25 to 100 °C (i.e. 2 °C/min), 50 minutes constant at 100 °C. The sample is cooled down till 25 °C in 2 hours (no active cooling present) and the conditions are kept constant afterwards for 19.5 hours at a RH of 25% at 25 °C. This cycle was repeated 11 times. The loading and the temperature are plotted against time in Figure 7.9, wherein the time is set to zero at the start of the dehydration of each run. Initially crystals dehydrate below the tetrahydrate, but after four cycles the sample is, on average, dehydrated till the tetrahydrate form. The rehydration level decreases slowly by additional runs. No significant difference is observed in dehydration temperature between the first and other runs. The rehydration rate is going down with increasing number of runs, but the effect is small compared to the cycle experiment at 150 °C.

Obviously, the first four runs are different from the subsequent ones, which is also

Figure 7.8: The mean $T_2$ relaxation time of a sample of MgCl$_2$ grains plotted against time after the start of each dehydration run. The dehydration was performed with a heating rate of 1.2 °C/min. The dashed line indicates the sample temperature.
Figure 7.9: The loading of a sample of MgCl$_2$ grains during different runs of dehydration/hydration. Dehydration by a heating rate of 2 °C/min over a temperature range of 25–100 °C. After a cooling period of 2 hours (no active cooling), the sample was rehydrated with air of 25 °C and a RH of 25% over a period of 22 hours. The dashed line indicates the sample temperature.

Figure 7.10: The mean $T_2$ relaxation time of a sample of MgCl$_2$ grains plotted against time after the start of each dehydration run. The dehydration was performed with a heating rate of 2 °C/min between 25 and 100 °C. The dashed line indicates the sample temperature.
underlined in the relaxation analysis given in Figure 7.10. In this case, the observed relaxation times are all short, indicating lattice water. In the first cycle, the mean relaxation time of the water in the sample increases during the dehydration process, and after reaching 100 °C the relaxation time decreases. In subsequent cycles, the relaxation time at temperatures below 100 °C overlap. This indicates that the water molecules in the grains experience a similar environment and have the same mobility. A difference between the runs is only visible above 100 °C, where in the runs 5-11, the relaxation time stay constant.

These two set of experiments show that MgCl$_2$ produces easily mobile water during dehydration by heating above 135 °C. This affects the grain structure, resulting in a change in the dehydration and hydration rates. A smaller dehydration step, will help to stabilize the system, but decreases at the same moment the energy storage dramatically.

### 7.4.4 MgSO$_4$

The dehydration of MgSO$_4$ was performed with a heating rate of 0.5 °C/min from 25-150 °C. With the rehydration the temperature was cooled from 150-25 °C in 2 hours and an air flow of 25 °C with 85% inflow. The loading as measured by NMR and temperature of the cyclic dehydration/hydration of MgSO$_4$·7H$_2$O is plotted as a function of time in Figure 7.11, wherein the time is set to zero at the start of each dehydration run.

Obviously the maximum loading before dehydration is varying with each run (10% variations), but no clear trend downwards is observed. After dehydration, the loading is 1.2 mol H$_2$O per mole MgSO$_4$ for all seven runs. The first time the sample is dehydrated, the water is released at a higher temperature than in subsequent cycles. The difference in this temperature (between the first and second dehydration cycle) is about 24 °C. For the other cycles the temperature where dehydration starts slightly decreases. The rehydration rates of the first two runs are slightly lower than the other 5 runs.

The mean relaxation time and temperature are plotted as a function of time in Figure 7.12. In the first run, the relaxation time is a combination of pore and lattice water. In the other runs only lattice water components are observed. We observe that the initial grains have a short relaxation time of 70 μs (1), which increases around 50 °C to 70 ms (2). This strong increase of relaxation time during the first run indicates pore water is formed inside the grains. Such pore water formation appears after passing the triple point of heptahydrate, hexahydrate and aqueous solution of MgSO$_4$ at 48 °C. The pore water disappears at 95 °C and the relaxation time decreases to 120 μs. After three hours of dehydration, the relaxation time increases to 250 μs (3). This is probably a result of the formation of lower hydrates, what changes the surrounding of the remaining water molecules in the crystal structure. Such production of pore water is however, not observed in the subsequent runs. During the rehydration, the mean relaxation time decreases to 120 μs, but does not drop to reach its initial value of 70 μs. The subsequent cycles overlap.

This experiment showed that during cyclic experiments with MgSO$_4$ the dehydration/hydration process is changing. The rehydration level slowly drops with increas-
Figure 7.11: The loading of a sample of MgSO$_4$ grains during different runs of dehydration/hydration. Dehydration by a heating rate of 0.5 °C/min over a temperature range of 25–150 °C, after a cooling period of 2 hours (no active cooling), the sample was rehydrated with air of 25 °C and a RH of 85% over a period of 22 hours. The dashed line indicates the sample temperature.

Figure 7.12: The mean $T_2$ relaxation time of a sample of MgSO$_4$ grains plotted against time after the start of each dehydration run. The dehydration was performed with a heating rate of 0.5 °C/min between 25 and 150 °C, after a cooling period of 2 hours (no active cooling), the rehydration was performed with an air flow of 25 °C with a RH of 85%. The dashed line indicates the sample temperature.
ing number of runs. With our NMR experiments we could not determine the crystal structure of MgSO$_4$, so we could not conclude anything about the influence of the known metastable phases on the cyclic dehydration/hydration process [76].

7.5 Discussion and conclusion

A relative hydration level of the considered salts was defined on the basis of the ratio of the loading at the start of each dehydration run and the initial loading of the sample. This relative hydration level is plotted against increasing number of runs in Figure 7.13 for all salts studied. Obviously, the level of relative hydration level is constant for CuCl$_2$ and MgCl$_2$ (100 °C) grains rehydrate up to 90% for the first 11 runs. The decrease in relative hydration level is larger for the other three dehydration/hydration reactions. The hydration level of MgSO$_4$ strongly fluctuates over the measured runs between 95 and 85% and shows a decreasing hydration level with increasing number of cycles. Both CuSO$_4$ and MgCl$_2$ (150 °C) show a decreasing trend in dehydration after the first three runs.

The production of pore water may probably be considered as a good indicator with respect to the potential to return to the initial loading. This is exemplified in the dehydration/hydration reaction of MgCl$_2$ at 100 °C and 150 °C. In case no pore water is produced, i.e. at 100 °C, the performance in terms of recuperation of the original loading only slightly changes with increasing number of runs. In case pore water is produced, the hydration level decreases steeply (i.e. consider the 150 °C run).

![Figure 7.13: The relative hydration level at the beginning of each hydration/dehydration run is plotted against the number of the run.](image)

Considering the four reactions without pore water production, the theoretical volume variations in CuCl$_2$ and MgCl$_2$ (100 °C) are smallest, i.e. 43.0% and 21.6%, respectively. The other two reactions have larger theoretical variations of 52.0% and
61.3\% for CuSO\textsubscript{4} and MgSO\textsubscript{4}, respectively. This set of experiments indicates that volume variations between a hydrate and dehydrate may be related to the stability of a dehydration/hydration reaction. As we did not measure the volume variations or the crystal structures during hydration/dehydration runs we cannot draw solid conclusions about the stability of the loading with respect to the volume variations. Besides the crystal structure variations inside a grain, also the structure of the granular bed can change during hydrations as the grains agglomerate if the applied RH is above the RH\textsubscript{del}, what can have its affects on the hydration or dehydration rate. In further research attention should be drawn to these kind of variations, with help of X-ray computed tomography (CT-scan) for variations in a granular bed and XRD for crystal structure changes.

Grains that are dehydrated for the first time (original grains) obviously dehydrate at higher temperatures than grains that dehydrate in subsequent runs. This may be a result of the vapor mobility in a grain. In an original grain the mobility is low, as the evaporation of the vapor only takes place at the walls of the grains. In case the grain is dehydrated, the grain is fractured in a pseudomorphic structure [224, 251]. This pseudomorphic structure adsorbs and desorbs water faster than the original crystal, because more surface is available and paths reach the outer surface. A difference is observed of 10 °C for CuCl\textsubscript{2}, 20 °C for CuSO\textsubscript{4} and 24 °C for MgSO\textsubscript{4}.

These experiments show CuCl\textsubscript{2} to be the most promising heat storage material to store heat from the point of view of stability, and considering the experimental conditions applied, with this limited number of runs. It has a constant rehydration level and reaches a heat storage capacity of 1.2 GJ/m\textsuperscript{3} with a porosity of 30\%. MgCl\textsubscript{2}, MgSO\textsubscript{4} and CuSO\textsubscript{4} have higher theoretical storage potentials (about ±20\% higher), but this energy storage density appears not fully available in cyclic hydration/dehydration as result of incomplete rehydration.
Chapter 8

Dehydration/hydration of granular beds for heat and cold storage applications

For heat/cold storage systems a granular bed of salt hydrates is studied during dehydration/hydration. The water density in these beds are measured with help of NMR. Diffusion based dehydration of a granular bed of Na\textsubscript{2}SO\textsubscript{4}·10H\textsubscript{2}O is shown to be internally limited as larger grains dehydrate faster than smaller grains as result of cooling of the grains. In case of air flow dominated dehydration of Na\textsubscript{2}SO\textsubscript{4}·10H\textsubscript{2}O the supply of dry air was the limiting factor. On the other hand, for hydration of CuCl\textsubscript{2} with air flow through a granular bed, the absorption rate of water of the grains in the grain was the limiting factor and not the airflow. The observed limitations are no general observations for salts during dehydration and hydration, but may be different for other salts.

8.1 Introduction

In any heat/cold storage reaction, the solid-gas reaction should be studied. Permeability of salt-beds, particle sizes and gas flows will affect the hydration/dehydration processes. In reported studies on such reactions in salt-beds, only measurements on the temperature inside a gas-solid reactor and vapor pressure of the in and outflow of the air are performed, and no data are available on water transport through the gas-solid reactor [61–64, 252–254].

In this chapter, we will study the water density profiles during rehydration (CuCl\textsubscript{2}) or dehydration (Na\textsubscript{2}SO\textsubscript{4}·10H\textsubscript{2}O) of a gas-solid reactor. The salts are selected based on their low hydration RH and their high dehydration RH, respectively. The water density profiles are measured with help of Nuclear Magnetic Resonance (NMR), a technique that introduces the feature to monitor the water during dehydration/hydration of a salt complex non-destructively. The temperature at different positions inside the granular bed was monitored during hydration/dehydration experiments. We have
looked at two situations: diffusion dominated dehydration and convection dominated dehydration/hydration through a sample.

8.2 Methods

Nuclear Magnetic Resonance (NMR) was used for measuring proton densities in a sample non-destructively and quantitatively. The signal of water attenuates in a NMR experiment, if we can ignore the spin-lattice relaxation time $T_1$, i.e. when the repetition time $T_r > 4T_1$, according to:

$$S(t_e) = \rho \exp(-t_e/T_2).$$

Wherein $\rho$ is the hydrogen density, $t_e$ the echo time and $T_2$ the transversal relaxation time. Hence, it is possible to link the signal intensity of the NMR to the water density as the hydrogen density in directly related to the water density. In order to minimize the influence of $T_2$, the time $t_e$ is chosen as short as possible. The transversal relaxation time $T_2$ can be related to the mobility of the proton [182,183], whereby $T_2$ increases with increasing mobility. To measure the maximum signal, $t_e$ should be chosen as short as possible, i.e. in this set of experiments $t_e = 70 \mu s$.

The NMR experiments were performed using a home-built NMR setup, with a dedicated design for systems with short relaxation times. Figure 8.1 shows a schematic diagram of this setup. Two coils in anti-Helmholtz configuration are used for generating a maximum static gradient $G_z$ of 0.6 T m$^{-1}$ in the direction of the main magnetic field $B_0$ of 200 MHz. This gradient results in a spatial resolution of 5 mm. A RF-coil in birdcage configuration is used for sending and receiving the NMR signal from the sample. The resonator is designed according to the calculations of Gürler [202] to resonate at 200 MHz. The diameter of the coil is 4 cm and inside the coil a Faraday shield is located to perform quantitative measurements. The sample is moved through the RF-coil with a step-motor and water density profiles were measured on the basis of the Hahn sequence [184].
Figure 8.1: A schematic representation of the used setup: on the left, the NMR setup used during dehydration and hydration experiments; in the middle the used sample holder during dehydration by diffusion and on the right the used sample holder during dehydration and hydration by air flow through the sample.
8.3 Dehydration of Na$_2$SO$_4$·10H$_2$O by diffusion

The effect of the grain size on the dehydration characteristics was studied by dehydration of a bed of grains from one side. A schematic overview of the used sample holder is given in Figure 8.1. The reactor has an internal cylinder volume of 60 mm height and 20 mm diameter. Dry air (RH=0%, T=25 °C) is blown over a sample. The air and vapor can only escape at the top of the sample, i.e. by diffusion through the sample. Four experiments were performed to study the effect of grain diameters on the dehydration process, i.e. using grains with average sizes of 0.5-1 mm, 1-2 mm, 2-5 mm and 5-10 mm, respectively. The experiments were performed with Na$_2$SO$_4$·10H$_2$O. This hydrate has a low melting temperature of 35 °C, what making it unfavorable for heat storage. However as it has only a single dehydration step and a high storage density of 2.37 GJ/m$^3$, it has potential application perspective for cooling applications.

The water density profiles of two of these experiments are plotted in Figure 8.2. In Figure 8.2a grains have a diameter of 0.5-1 mm, whereas in Figure 8.2b the sizes are in the 2-5 mm range. The time between the different profiles is 1.6 hours, only every fifth profile is plotted. The water density profile at a specific moment in time is deduced from the experimental data through interpolation of the local water density as a function of time using least-squares fits with cubic splines. As can be seen the dehydration starts from the top of the sample and a sharp dehydration front can be seen, indicating the dehydration of the sample is internally limited.

In order to compare the dehydration experiments of four different grain diameters, the total water loss is plotted as function of time in Figure 8.3. Obviously, the rate of water loss increases with increasing the grain size. At a certain temperature dehydration of a grain is induced by the local relative humidity at the grain. The release of water vapor from the granular bed is driven by diffusion in this setup. The pore size of the interspaces between grains are in the order of 0.1 mm. Consequentially, its

![Image](image-url)

*Figure 8.2: Water density profiles during dehydration of Na$_2$SO$_4$·10H$_2$O induced by an air flow at the top of a sample consisting of a granular bed of grains with an average diameter of a) 0.5-1 mm; b) 2-5 mm. The time between two successively profiles is 8 hours.*
effect on the diffusion coefficient is negligible [255]. The effective diffusion coefficient ($D_{eff}$) of water vapor through a granular bed of grains is determined by [213]:

$$D_{eff}(T) = D(T) \cdot T^* \cdot \phi, \quad (8.2)$$

wherein $D(T)$ is the diffusion coefficient of water vapor in air, $T^*$ the tortuosity of the system and $\phi$ the porosity of the system. The porosity of the different beds were measured with help of weighing the sample and height and are all in the order of 30%. The tortuosity is considered to be equal for the different grains, because only the size of the grains was varied, not the geometry. Hence, the only variation in the diffusion coefficient may originate from temperature variations, but initially, the temperatures in the samples are uniform and the same for all geometries considered. Thus, on the basis of diffusion of water in the considered granular bed, the observed differences in the water density profiles for the different grain sizes can not be explained.

Water release of a single grain of Na$_2$SO$_4$ by RH variations is limited by the evaporation rate at the surface [256]. When applying a certain RH, the grains produce an amount of water depending on the surface area of the grain $A$ and the difference between the applied RH and the equilibrium RH (RH$_{eq}$). When we assume a cylinder with volume $V_{cylinder}$, radius $r_c$, porosity $\phi$ and length $l$ filled with grains with radius $r_s$, the volume of the cylinder should be multiplied by $(1-\phi)$ to calculate the volume of all the grains. Assuming a sphere geometry for identical grains, the total surface of the grains per unit length in a cylinder is given by:

$$\frac{A_{total}}{l} = \frac{n_{grains} A_{sphere}}{l} = \frac{V_{cylinder}(1-\phi)}{V_{grains} l} A_{grains} = \frac{2\pi r_c^2 (1-\phi)}{\frac{4}{3} \pi r_s^3} 4\pi r_s^2 = \frac{6\pi r_c^2 (1-\phi)}{r_s}. \quad (8.3)$$

\[Figure 8.3: \text{The total water loss in the sample during dehydration experiments of Na}_2\text{SO}_4\cdot10\text{H}_2\text{O as a function of time for four different grain sizes. In the legend the range of the grain diameter are given.}\]
wherein \( n_{\text{grains}} \) is the number of grains in the cylinder, \( A_{\text{grains}} \) the surface of a single grain, \( V_{\text{grains}} \) the volume of a grain and \( \phi \) the porosity of the system. Consequently a bed with small grains will have a larger surface area per length unit. Therefore it is expected on the basis of this first order straight forward approach that smaller grains correspond with a higher water loss at the dehydration front. However, as the grain dehydrates, energy is consumed, i.e., 52.2 kJ/mol, in case of \( \text{Na}_2\text{SO}_4\cdot10\text{H}_2\text{O} \). Therefore, a bed of smaller grains cools much faster at the front. As can be seen from the phase diagram of \( \text{Na}_2\text{SO}_4 \) [75], for 25 °C the equilibrium RH between the hydrate and anhydrous phase is 80%, whereas if we cool down the equilibrium RH between the hydrate and anhydrous phase for \( \text{Na}_2\text{SO}_4\cdot10\text{H}_2\text{O} \) will drop, e.g., to 65% for 15 °C. As a result, the RH difference between applied and equilibrium RH will decrease, i.e. the driving force become smaller and is seen, finally large grains dehydrate faster than small grains.

The contradiction in this explanation is that the amount of water desorbed per time unit is higher in case of the larger grains, so more energy is consumed for the larger grains per time unit. Following our own explanation, this should result in a slower dehydration rate, but we have neglected in our explanation two things. Firstly, the dehydration volume is larger in case of larger grains according to equation 8.3. This results in a reaction area which has a higher heat capacity than the smaller grains, which means that the energy consumption in larger grain systems have a smaller effect on the temperature than in case of the smaller grains. Secondly, our sample holder is poorly isolated and is located in a surrounding of 25 °C. In case the temperature will decrease, energy will be added to the system. The amount of energy added to the system depends on the temperature difference between both systems and the surface area between the cold and warm area. As the dehydration length is linearly dependent on the grain size (equation 8.3) the heat lack into the sample holder will result in a higher temperature in the granular beds with the larger grains. In case the isolation is ideal or in case the temperatures of the grains are ideal controlled during dehydration, the effect of grain sizes on dehydration by diffusion should not be observed.

### 8.4 Dehydration of \( \text{Na}_2\text{SO}_4\cdot10\text{H}_2\text{O} \) by convection

In the next step, the convection induced dehydration of \( \text{Na}_2\text{SO}_4\cdot10\text{H}_2\text{O} \), i.e. using a dry air flow through the reactor was measured. A schematic overview of the sample holder used is given in Figure 8.1. The reactor has an internal cylinder volume of 37 mm height and 26 mm diameter, wherein at distances of 5 mm a thermocouple is placed, starting at the bottom of the holder. The air inflow takes place at the top of the reactor and passes through a bed of grains with grain size of 0.5-1 mm. The air was initially dry (RH<2%, \( T = 19 \) °C) and blown through the reactor at 3 l/min, i.e. an average air velocity of 0.6 m/min. At the bottom of the reactor a sieve is placed and the outflow temperature is registered with a thermocouple. The measured water density inside the granular bed is plotted against the position in Figure 8.4. Obviously, the sample starts dehydration at the inflow side. Every profile took 31 minutes to measure and within 17 hours the entire reactor was dehydrated. During
Chapter 8. Dehydration/hydration of granular beds

The dehydration, a front is entering from the inflow side of the granular bed. At the same time a small decrease of water density is observed at the outflow side of the sample, which is in contrast to diffusion induced dehydration.

The water density and the corresponding temperatures at the thermocouple positions are plotted against time in Figure 8.5. As can be seen the dehydration time increases with increasing distance from the inflow surface. The temperature is lower compared to the inflow temperature as long as the dehydration at the corresponding position is ongoing. The outflow temperature is in the range of 12 to 14 °C for almost 15 hours.

This experiment was repeated for different airflow rates (1 and 6 l/min) and a different grain size of 2-5 mm. As to compare the experiments, the results were scaled using the air flow $t' = t \cdot v_{air}$. We expect that the airflow velocity will determine the flux of water, that can be removed from a granular bed. In Figure 8.6, the water density at position 30 mm below the inflow of the air is plotted against the scaled time for these experiments. As can be seen the different experiments overlap after scaling, indicating that the dehydration process is determined by the supply of dry air and, therefore, the capacity to dehydrate the grains. The dehydration process of a bed of grains of $\text{Na}_2\text{SO}_4\cdot10\text{H}_2\text{O}$ by convection with the used grain sizes and air flows is limited by the supply of dry air.
8.4. Dehydration of Na$_2$SO$_4$·10H$_2$O by convection

Figure 8.5: Temperature and water density against time during dehydration of Na$_2$SO$_4$·10H$_2$O by blowing dry air through the sample (3 l/min, inflow: $T = 19^\circ$C and RH = 0%).

Figure 8.6: Water density at 30 mm below the inflow surface during convection induced dehydration of Na$_2$SO$_4$·10H$_2$O at different air flow rates (inflow: $T = 19^\circ$C and RH = 0%) and grain sizes as a function of scaled time.
8.5 Rehydration of CuCl₂ by convection

Finally, rehydration of anhydrous CuCl₂ grains was studied in the NMR. CuCl₂ was selected on the basis of its theoretical heat density of 1.73 GJ/m³, its single rehydration step and its obvious multi-cyclic stability (see Chapter 7). To prepare anhydrous CuCl₂ grains with a grain size of 1-2 mm, CuCl₂·2H₂O grains were dehydrated in a oven at 150 °C. The dehydrated CuCl₂ grains were placed in sample holder and rehydrated by an airflow of 4.5 liter per minute at 19 °C and a RH of 60%. The reactor is similar to that used for the dehydration of Na₂SO₄·10H₂O. The water density of CuCl₂ during rehydration is plotted in Figure 8.7. Every profile took 25 minutes to measure and within 11 hours the entire reactor was hydrated. It shows that the rehydration is initially occurring (is fastest) at the inflow inside and that all grains start to rehydrate directly after starting the experiments in the reactor with the chosen dimensions.

The water density at the thermocouple positions and the corresponding temperatures are plotted against time in Figure 8.8. As can be seen, the water density increases over the entire sample immediately after starting the experiment. This indicates that the amount of water applied to the sample is larger than the grains can process in the granular bed under consideration of the applied conditions. In this case the rehydration process is limited by the hydration reaction and not the wet air supply. As at the bottom of the sample the reactor still hydrates, the RH of the air should there be above 15%. The local temperature in the granular bed has a maximum temperature lift of 16 °C to 35 °C.

![Figure 8.7: Water density profiles during convection based rehydration of a reactor filled with CuCl₂ grains(4.5 l/min, inflow: T= 19 °C and RH=60%). The time between two subsequent profiles is 25 minutes.](image-url)
8.6 Conclusion

In this chapter, we have shown the possibilities of the NMR equipment to follow the water density during hydration or dehydration of a salt hydrate in a reactor. In combination with the temperature profiles, this can provide us all data to understand the water transport in granular beds for heat or cold storage. These experiments are exploring experiments on reactor scale. The experiments are performed on small reactors, without sufficient isolation around the reactor and whereby the produced heat or cold was not removed by an heat exchanger.

From these exploring experiments, we can conclude:

- In case of dehydration induced by diffusion a bed of grains of Na$_2$SO$_4$·10H$_2$O, the dehydration process is grain size dependent (faster dehydration by larger grains) and internally limited under the applied conditions.

- In case of convection induced dehydration of a bed of grains of Na$_2$SO$_4$·10H$_2$O, the dehydration process could be scaled with help of the air flow, indicating that the dehydration is limited by the supply of dry air under the applied conditions. In addition no significant effect is observed of the grain sizes in our set of experiments.

- In case of convection induced rehydration of a bed of grains of CuCl$_2$, it was observed that not all supplied water by the airflow could be adsorbed and that the adsorbing rate of water of the CuCl$_2$ grains was the limiting factor during rehydration. For a constant heat supply, we advise to use smaller grains to increase the surface area in the bed of grains or increasing the length of the reactor.

Figure 8.8: Temperature and water density against time during convection based rehydration of CuCl$_2$ (4.5 l/min, inflow: T = 19 °C and RH=60%) through the sample. The position of the measured water density and thermocouple given in the legend is calculated from the top of the sample.
Chapter 9

Conclusion and Outlook

9.1 Conclusions

The aim of this thesis was to understand the behavior of a solvent during decomposition and formation reactions of salt complexes to improve the stability of solid-gas reactions for heat storage materials. In this study, we focussed on the absorption and desorption rate of a limited number of hydrates, wherein we used a maximum desorption temperature of 150 °C. We observed that the hydration and dehydration characteristics are strongly dependent on the studied hydrate.

The overall conclusion with respect to the ten hydrates that we studied: a cyclic loading/unloading without variations in geometry that result in varying absorption rate or desorption rate is a utopia.

The general observations in this work are summarized in Figure 9.1. The dehydration process as the transition from one phase to another can follow several pathways according to the phase diagram. Depending on the (de)hydration, induced by RH or temperature variations, the geometry of the structure is affected.

To predict the performance of the system, the geometry of the salt grains should be stable or have predictable variations with increasing number of hydration/dehydration cycles. The geometry of the salt grains strongly affects the rate of absorption (Chapter 7) and desorption (Chapter 8).

This work sketches that there are at least two main causes for geometry changes in case of dehydration of the considered salt hydrates. Firstly, an aqueous solution can be produced inside hydrated grains when crossing a triple point temperature during heating in case of limited water transport as result of deliquescence. This aqueous solution is a saturated solution, which is in equilibrium with the enclosing hydrate (Chapters 4 and 6).

Secondly, dehydrating grains produce internal pathways of water vapor as result of cracking of the grains. This is a result of the different densities of hydrated and anhydrous salt (Chapters 2 and 7).

A solid-gas reaction is controlled by the relative vapor pressure of the gas phase of the solvent and the temperature of the solid. The conditions of these decomposition and formation reactions can be found in phase diagrams. In this thesis, only a limited
Figure 9.1: A schematic overview of the hydration/dehydration process in grains during cyclic loading. The transition from one phase to another can follow several pathways according to the phase diagram. Depending on the dehydration process, induced by RH or temperature, the grain structure can be affected by volume variations and pore water formation. In case of cyclic hydration/dehydration experiments, the crystals in the grains are growing/shrinking, which decreases the absorption or desorption rate of the grains.
amount of ten salt hydrates was studied (Chapter 2). These salts were initially selected based on their high energy density and from these hydrates, most are sulphates or chlorides. The observed general trend is that most chlorides hydrate at low RH, but also deliquescence at relative low RH. The sulphates, on the other hand, have a high deliquescence RH, but the (re)hydration RH is high too.

According to our study the hydrate with the most stable performance as heat storage material is CuCl$_2$·2H$_2$O. This hydrate showed stable characteristics during dehydration/rehydration by experiments over 8 runs. The hydrate does not melt at a temperature below 150 °C. The anhydrous phase (re)hydrates at 25 °C with a RH above 15-20% and has a deliquescence RH of 65%. The stored energy density is 1.1 GJ/m$^3$ with a porosity of 30%.

In this research on dehydration and hydration processes, it is shown that NMR is a technique that is complementary to accepted techniques like TGA, DSC, Raman and XRD. NMR can give additional information compared to these techniques about water inside a crystal/reactor during a hydration/dehydration process, because location and mobility of the water molecules are determined. By studying the dehydration of a mirabilite grain, NMR observations showed that a homogeneous dehydration process occurs inside the grain (Chapter 5).

9.2 Outlook

As related to the main aim of this thesis, a number of remaining questions which need to be answered before reactors can be designed based on thermochemical heat storage materials. The next follow-up issues are suggested for research:

9.2.1 Selection criteria

In current literature, a database of phase diagrams of dehydration and hydration conditions of hydrates is missing. In Chapter 2 a first attempt is made to generate an overview of the available data from ten hydrates. As phase diagrams are essential points of reference, more research is needed on salts from this list to get the full picture in the temperature range that is desired from the point of view of thermal storage applications. As it is impossible to study all hydrates, a selection should be made of the salts. The study of N’Tsoenkpo et al. [23] made a short-list of hydrates, which can be used as heat storage materials. Based on a combination of his list with phase diagrams, suitable candidates may be chosen that show a promising potential to fit the demands of a heat storage system. The demands to hydrates based on the results of this thesis are listed for heat and cold storage systems in Table 9.1. The most important differences between both systems are the working temperatures.

For heat storage, it is necessary to have an output temperature of at least 55 °C, so the salt should hydrate above this temperature. To have a sufficient hydration rate, the difference between RH$_{del}$ and RH$_{deh-hyd}$ should be at least 40%. As to produce wet air may cost energy, RH$_{deh-hyd}$ should be smaller than 20% and RH$_{del}$ above 60%
Table 9.1: The preferred properties of a hydrate in heat and cold storage systems.

<table>
<thead>
<tr>
<th>Heat storage system</th>
<th>Cold storage system</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Output temperature</strong></td>
<td>&gt;55 °C</td>
</tr>
<tr>
<td><strong>Hydration by RH variation</strong></td>
<td></td>
</tr>
<tr>
<td>Heating</td>
<td></td>
</tr>
<tr>
<td>At 55 °C</td>
<td></td>
</tr>
<tr>
<td>• RH_{deh-hyd}&lt;20%</td>
<td>• RH_{del}-RH_{deh-hyd}&gt;10%</td>
</tr>
<tr>
<td>• RH_{deh-hyd}&gt;60%</td>
<td></td>
</tr>
<tr>
<td><strong>Dehydration by temperature</strong></td>
<td></td>
</tr>
<tr>
<td>Regeneration</td>
<td></td>
</tr>
<tr>
<td>At 55-150 °C</td>
<td>At 15-35 °C</td>
</tr>
<tr>
<td>• RH_{deh-hyd}&gt;60%</td>
<td>• RH_{deh-hyd}&gt;60%</td>
</tr>
<tr>
<td>Melting temperature&gt; 150 °C</td>
<td>Melting temperature&gt; 35 °C</td>
</tr>
</tbody>
</table>

for a salt. For regeneration a heat storage salt need to be heated till 60-150 °C and the RH_{deh-hyd} should be at least 60%.

For cold storage a salt should dehydrate at temperatures of 15-35 °C. The salt should be able to dehydrate even by applying warm humid air. Therefore RH_{deh-hyd} should be as high as possible with a minimum of 60%. During regeneration of the cold storage salt, the rate of the process is not crucial, so the difference between RH_{deh-hyd} and RH_{del} may be quite small with a minimum difference of 10%.

For both systems, the melting temperature of the salt should be higher than the maximum dehydration temperature to avoid grain structure changes and therefore preserve the performance of the system.

### 9.2.2 Phase ‘transition rate’ diagrams

In this study, we compared our dynamic experiments with phase diagrams of the studied solid-gas systems, whereby we observed deviations between the experiments and the phase diagrams. These deviations are expected, as the reactions rates are not considered in a phase diagram. A limitation of phase diagrams is that only information is included about equilibrium data. To avoid, for example, pore water formation during dehydration it is important to have knowledge of the transition rates from the involved hydrates and water release rates from a grain.

**Phase transition rates of suitable solid-gas combinations for heat storage materials should be studied to generate a phase ‘transition rate’ diagram.** In such a phase ‘transition rate’ diagram information on phase transitions rates is incorporated. Transitions rates should be determined depending on the difference between the applied and equilibrium conditions from the studied hydrate phase. As these transitions rates are probably depending on the grain size, sample size and air flow, this information should be incorporated as well.

These transition rates have not only their affect on hydration or dehydration experiments, but also on the preparation of samples before an experiment start. In chapter 6 all salts are hydrated with help of RH. Even after equilibrium periods of
months, some salts were not completely hydrated. By slow evaporation of a saturated solution, the grown hydrates were loading in line with the expected loading (chapters 4 and 5).

### 9.2.3 Tuning a system based on a salt

Based on the studied hydrates, CuCl₂ is an apparent suitable candidate for a heat storage system. According to 2015 prices of this salt (Sigma Aldrich, 1-5-2015 on 500 gram, purity >99%), the system costs 0.23 Euro/kJ and will be way more expensive than other salts studied such as MgSO₄ (0.04 Euro/kJ) or CaCl₂ (0.06 Euro/kJ). If the decomposition conditions of a specific salt can be tuned in a new and broader perspective in viable heat storage, applications may be introduced for inexpensive salts like CaCl₂ and MgSO₄. The main research question is: **can we tune a salt into our desired decomposition/formation conditions?** In this section, we suggest four possible ways to tune a salt.

One of the options is to switch the solvent. In this thesis, we mainly focussed on water as solvent, but other solvents like ammonia and methanol can be used as well. To show the effect of these two solvents, we preliminary explored CuSO₄·nNH₃ and CaCl₂·cCH₃OH in the DSC and TGA. CuSO₄ grains were equilibrated at a vapor pressure of 1 bar ammonia at 22 °C. CaCl₂ grains were grown via slow evaporation of a saturated CaCl₂ in methanol. These equilibrated grains were studied with the TGA and DSC by a heating rate of 0.6 °C/min.

Both the mass (measured with TGA) and the heat during a decomposition (measured with DSC) of CuSO₄·nNH₃ are plotted in Figure 9.2. As can be seen the decomposition is not finished at 500 °C. Whereas three dehydration steps for CuSO₄·5H₂O are observed, the ammoniate shows at least five decomposition steps. The DSC and TGA fit well with each other. In case of CuSO₄, with the switch from hydrate to ammoniate, the decomposition occurs at higher temperatures, however with more intermediate phases (fitting with the observations of Ephraim, [165]) than in case of the hydrate.

The mass (measured with TGA) and the heat during a decomposition (measured with DSC) of CaCl₂·cCH₃OH are plotted in Figure 9.3. For CaCl₂·cCH₃OH the decomposition was finished at 150 °C and the DSC and TGA data match. The maximum loading is lower and as a result the energy density will be lower in case of the methanol complex compare to the hydrate. In the decomposition temperature of both the hydrate and methanol complex only a minor shift is observed.

Another option to change the working conditions of a salt is to use a combination of different pure salts. Mixtures of salts have a different phase diagram as pure salts [76]. The phase diagram can be changed or tuned with added impurities to the salt. Next to tuning the systems into the desired hydration-dehydration characteristics, it may also have an economic advantage. Pure salts are in general more expensive than salts with impurities, so if the effect of the impurities is known, a heat storage system could be designed with the less expensive impure salts.

Two other options to change the phase diagram are the applied pressure on a crystal or the grain size of a crystals. By increasing the pressure [257] or decreasing the grain sizes [258], the phase diagrams will shift to lower RH’s. The consequence of
Figure 9.2: The mass and heat production for an ammoniate of CuSO₄ equilibrated at a pressure of 1 bar NH₃ at 22 °C, in a heating experiment with a heating rate of 0.6 °C/min.

Figure 9.3: The mass and heat production for a methanol complex of CaCl₂ grown from a saturated methanol solution of CaCl₂ at 22 °C, in a heating experiment with a heating rate of 0.6 °C/min.
increasing the pressure is that the system has to be transformed to a closed system. In case the grain sizes are decreased, the permeability of the bed of grains increases, which will increase the pressure necessary to obtain an airflow through the granular bed.

9.2.4 Gas-release in grains and granular beds

In case of a solid-gas combination knowledge is required on how does the solvent release or enter the grain/granular bed? In this thesis the dehydration of a mirabilite crystal was studied with decreasing the RH, showing that the dehydration occurs homogeneously over the crystal. It is unknown how the dehydration process takes place for other salts. For hydrating, we even did not determine the process yet. Knowledge on both absorption and desorption processes is required, because the absorbing-desorbing process of crystals will limit the rates of absorbing-desorbing.

9.2.5 Grain structure variations

We have observed during cyclic experiments, the uptake rate of water decreases during hydration with increasing number of runs of loading and unloading of the grains (Chapter 7). Our hypothesis is that the grain structure is changing during these runs, resulting in a decrease of water uptake rate. In a follow-up study this hypothesis should be checked. As the present set of experiments is too small to draw final conclusions, additional hydration/dehydration conditions should be studied. Cyclic experiments in the NMR are needed to measure the loading in the grains, but other techniques for complementary information are suggested. Firstly, XRD, which gives information about the crystal structure on the top layer of the grains. Secondly, (micro) CT to study the grain structure, which might also show the cracking of the grains during cyclic loading/unloading.
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Summary

Experimental study on thermochemical heat storage materials

Currently society is moving from a carbon-based society to a renewable-based society as to become less dependent on fossil fuels. Renewable heat production could replace gas consumption. This will reduce CO$_2$ emissions, has economical benefits and will keep the Netherlands more independent from foreign energy suppliers. In order to realize such this transition, new renewable energy production techniques have to be implemented. In general, a major drawback of renewable-based energy techniques is the unpredictability of the production. As a result, the main challenge in the transition from carbon- to renewable-based society is to balance consumer demands with renewable energy supply. In order to balance the fluctuation in demand and supply, both short (daily) and long (seasonal) term energy storage is required. Energy can be stored in two forms primarily, electricity and/or heat. In this thesis, we focus on heat storage, considering that most energy in the Netherlands is consumed as heat.

Heat storage techniques can be divided into three main groups: sensible, latent and thermochemical heat storage. Of these three groups thermochemical heat storage has the highest energy storage density. This thesis is focused on thermochemical materials and in particular on gas-solid reactions: hydrates, ammoniates and methanol complexes. The solids involved in these gas-solid reactions are salts, which are relatively cheap, and thus heat can basically be stored at low costs.

Most of the published papers on heat storage with gas-solid reactions are devoted to a single dehydration or hydration run. Experiments on cyclic hydration/dehydration experiments have shown that the hydrates may show instabilities. These instabilities have been related to changing rehydration/dehydration rates and/or changing grains sizes. Observations are mainly based on mass measurements and no information is available on the crystal structure of the products or on water transport inside a grain.

This thesis aims to understand the behavior of a solvent during decomposition and formation reactions of salt complexes lay a foundation for improvement of stability of solid-gas reactions for heat storage materials. We studied the solid-gas reactions using Nuclear Magnetic Resonance (NMR), in addition to well accepted techniques like: TGA, DSC, Raman and XRD. NMR gives the opportunity to non-destructively monitor the solvent molecules within a solid salt during decomposition and formation of a salt complex.

An overview of thermochemical data of a selection of hydrates, ammoniates and methanol solvates is given in Chapter 2. With help of this set of data, the decompo-
sition and formation conditions of different complexes can be determined.

Chapter 3 gives a brief introduction of general NMR principles. In addition, dedicated NMR setups are discussed.

The key results of the study are presented in chapters 4-8.

Chapter 4 discusses how water leaves a heated hydrated salt. NMR experiments on MgSO$_4$ showed that pore water is produced during dehydration, i.e. an aqueous solution of MgSO$_4$. This pore water is a result of insufficient vapor release from the crystal when crossing a triple point temperature. We verified this with a model based on the phase diagram of MgSO$_4$. Additional NMR measurements indicate that the diffusion coefficient of this pore water is ten times lower than that of bulk water.

Chapter 5 focuses on dehydration experiments with single crystals of Na$_2$SO$_4$·10H$_2$O wherein we focused on the water molecules in the crystal structure and structural changes during dehydration. The phase transformation from mirabilite to thenardite is observed to be a one-to-one process (XRD), and the nucleation is not exclusively at the surface. Besides mirabilite and thenardite, no other crystal phase is observed by XRD and Raman during the phase transformation. According to this set of experiments the dehydration of mirabilite is limited by the air-grain surface.

A selection of hydrates is studied in chapter 6 with respect to their dehydration characteristics using dynamic experimental techniques: TGA, DSC and NMR. We have compared the measured dehydration process of the different hydrates with the composed phase diagrams in Chapter 2. On the basis of these experiments it is possible to determine which of the selected salts do not melt during dehydration. Four hydrates were selected: CuCl$_2$, MgSO$_4$, MgCl$_2$ and CuSO$_4$.

In Chapter 7 the selected salts are studied on water uptake performance during cyclic hydration and dehydration in the NMR. The humidity and temperature applied were varied during these experiments. With NMR, the amount of water inside the sample and the mobility of the water is measured. The water uptake performance appears affected by the volume variations during hydration reactions and the pore water production during dehydration. From the four hydrates considered, CuCl$_2$ is the most promising heat storage material from the point of view of cyclic stability, with the most constant water uptake rate and loading over several cycles.

Finally, chapter 8 addresses beds of grains, which are hydrated or dehydrated by varying the relative humidity. Spatially resolved water distribution and temperature profiles were measured during dehydration and rehydration. Two types of dehydration experiments were performed: dehydration of a granular bed of Na$_2$SO$_4$·10H$_2$O by diffusion and by convection (i.e. air flow) through a bed of grains. It is shown that dehydration by diffusion is internally limited. In this case larger grains dehydrate faster than smaller ones as result of cooling of the grains. In case of dehydration of the same hydrate with air flow through the bed, dehydration was not longer internal limited and the supply of dry air was the limiting factor. For hydration of CuCl$_2$ with air flow through the bed, however, the adsorption rate of water of the grains was the limiting factor and not the airflow.
Samenvatting

Een experimentele studie naar materialen voor thermochemische warmte opslag

Onze productie van energie transformeert van een energie productie gebaseerd op het verbranden van fossiele brandstoffen naar een duurzame energie productie. Het gasverbruik zal hierdoor verminderen in Nederland en wellicht uiteindelijk zelfs volledig vervangen. Dit biedt niet alleen economische voordelen, maar zal ook het CO\textsubscript{2} verbruik verminderen. Bovendien zal Nederland onafhankelijker worden van buitenlandse energie leveranciers. Voor deze transitie moeten nieuwe technieken voor het produceren van duurzame energie worden geïmplementeerd. Een belangrijk nadeel van deze technieken vormt de onvoorspelbaarheid van de energie productie. Een van de belangrijkste uitdagingen is als gevolg daarvan het in evenwicht brengen van de productie en het verbruik. Om de fluctuatie tussen vraag en aanbod, zowel op korte (dagelijks) en lange (meerdaags tot seizoensgebonden) termijn op te vangen, is energieopslag vereist. Energie kan typisch worden opgeslagen in twee vormen; elektriciteit en warmte. In dit proefschrift richten we ons op warmteopslag, omdat warmte de grootste bijdrage levert in het energie verbruik in Nederland.


Het grootste deel van de gepubliceerde artikelen over warmteopslag met vast stof-gas reacties zijn gewijd aan de eenmalige dehydratatie of hydratatie van een zout. Experimenten met meerdere opeenvolgende hydratatie / dehydratatie experimenten hebben aangetoond dat het hydratatie en dehydratatie proces instabiel is. Deze instabiliteit is gerelateerd aan de verandering in de opname en afgifte snelheden van gas en / of veranderingen in de zoutkorrel(geometrie). Waarnemingen in de literatuur zijn voornamelijk gebaseerd op gewichtsmetingen. Informatie over de kristalstructuur van de zouten of het transport water in van een zoutkorrel is nauwelijks beschikbaar.

Het doel van dit onderzoek is de rol van het gas (in dit geval van water, ammonia of methanol) in de vaste stof-gas reactie tijdens de vorming en decompositie van
zoutcomplexen te begrijpen om de stabiliteit van vaste stof-gas reacties voor warmteopslag materialen te verbeteren. Naast bekende technieken als TGA, DSC, Raman spectroscopie en röntgen diffractie hebben we vaste stof-gas reacties met behulp van kernspinresonantie (NMR) bestudeerd. Met NMR is het mogelijk om niet-destructief te meten tijdens de vorming en decompositie van een zout complex, waarbij de locatie en hoeveelheid watermoleculen in een zout bepaald kunnen worden.

Een overzicht van thermochemische gegevens van een selectie van hydraten, ammonia en methanol complexen wordt gegeven in hoofdstuk 2. Met behulp van deze set van gegevens, kunnen van de verschillende complexen de vorming en decompositie omstandigheden worden bepaald.

Vervolgens wacht een korte introductie van NMR principes gegeven in hoofdstuk 3 en worden de gebruikte NMR opstellingen besproken.

De belangrijkste resultaten van dit onderzoek worden beschreven in hoofdstuk 4 tot en met 8.

Hoofdstuk 4 bespreekt hoe water tijdens het opwarmen een hydraat verlaat. Met NMR is aangetoond dat tijdens dehydrateren porie water wordt geproduceerd. Dit porie water is een oplossing van MgSO$_4$ en is een gevolg van de gelimiteerde afname van waterdamp uit het kristal nadat de zogeheten triepelpunt temperatuur bereikt is. Met een model is dit geverifieerd op basis van het fasediagram van MgSO$_4$. Met extra NMR-metingen is aangetoond dat de diffusie coëfficiënt van het poriewater tien keer lager is dan die van normaal water.

Hoofdstuk 5 richt zich op de dehydratie van een enkel Na$_2$SO$_4$·10H$_2$O kristal waarbij de focus ligt op watermoleculen in de kristalstructuur en structurele veranderingen tijdens dehydratatie. Hierbij is waargenomen (röntgen diffractie) dat de faseovergang van mirabiliet in thenardiet een één-op-één proces is. Tevens blijkt de nucleatie niet uitsluitend plaats te vinden aan het oppervlak. Met röntgen diffractie en Raman spectroscopie zijn tijdens het dehydratatie proces geen andere kristalfases naast mirabiliet en thenardiet waargenomen in de experimenten. Deze experimenten laten zien dat dehydratatie beperkt wordt door het contact oppervlak tussen de korrels en de lucht.

Een selectie van hydraten is bestudeerd in hoofdstuk 6 met behulp van TGA, DSC en NMR. We hebben de gemeten hydraten vergeleken met de samengestelde fasediagrammen uit Hoofdstuk 2. Met behulp van deze experimenten is het mogelijk te bepalen welke van de zouten niet smelten tijdens dehydratatie. Op basis van deze experimenten zijn vier hydraten geselecteerd: CuCl$_2$, MgSO$_4$, MgCl$_2$ en CuSO$_4$.

In hoofdstuk 7 wordt de wateropname en afgifte beschreven voor de geselecteerde hydraten tijdens cyclisch hydrateren en dehydrateren van een zout in de NMR opstelling. Zowel de opgelegde lucht vochtigheid als temperatuur zijn gevarieerd tijdens deze experimenten. Met behulp van NMR is de hoeveelheid water in het preparaat gemeten. De wateropname lijkt te worden beïnvloed door een veranderde geometrie als gevolg van volume variaties tijdens (de)hydratatie reacties en de vorming van porie water tijdens opwarming van het hydraat. Van de vier hydraten is CuCl$_2$ het meest veelbelovende warmteopslag materiaal, met de meest constante wateropname snelheid over meerdere cycli.

Tot slot zijn kleine reactoren exploratief bestudeerd in hoofdstuk 8. Deze reactoren bestaan uit een cilinder gevuld met korrels van hydraten. Deze worden gehydrateerd of gedehydrateerd door het variëren van de relatieve vochtigheid van de lucht. De water
en de temperatuur profielen werden gemeten tijdens dehydratatie en (re)hydratatie. Er zijn twee types van dehydratatie experimenten uitgevoerd: dehydratatie van een reactor van Na$_2$SO$_4$·10H$_2$O door diffusie en dehydratatie door middel van een luchtstroom door de reactor. Aangetoond is dat dehydratatie intern door diffusie beperkt wordt. Grotere korrels dehydrateren sneller in dit geval dan kleinere korrels, doordat de korrels intern afkoelen. Dehydratatie van hetzelfde hydraat met behulp van luchtstroom door het bed is niet langer intern beperkt, maar de toevoer van droge lucht is de beperkende factor. Voor hydratering van CuCl$_2$ bij een luchtstroom door het bed is de mate van adsorptie van water bij de korrels de beperkende factor en niet de snelheid van de luchtstroom.
List of publications

Journal publications


Conference proceedings


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