Sodium sulfate crystallisation in fired-clay brick during drying. Pore size evolution during the hydration of cement

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Part A:
Sodium sulfate crystallisation in fired-clay brick during drying

Part B:
Pore size evolution during the hydration of cement

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This master’s thesis consists of two parts. Part A: The crystallisation of sodium sulfate in fired-clay brick studied by NMR. As the drying of fired-clay brick saturated with salt solutions usually took up to four weeks, additional NMR measurements were done on the hydration of cement paste. This work is described in part B.
Part A
Abstract

When salts crystallise inside porous materials they can generate pressures large enough to cause damage. The precise mechanisms behind the crystallisation pressure are still not fully understood, although the first observations of salt damage date back thousands of years ago.

Sodium sulfate is one of the most damaging salts. It has two stable crystal phases mirabilite and thenardite. In previous experiments by Rijniers et al. it was shown that in case of crystallisation induced by temperature change, sodium sulfate crystallises in a meta-stable phase, i.e., the heptahydrate. It was also shown that this crystal has a low surface tension and hence does not generate pressure.

In this study crystallisation was initiated by drying. Drying experiments were performed at different temperatures on fired-clay bricks saturated with sodium sulfate solutions. The moisture and sodium profiles inside the fired-clay bricks were measured with NMR. The resulting concentration profiles reveal information about the crystallisation processes inside the brick.

In the experiments at temperatures where the heptahydrate can exist, a significant increase in concentration above the maximum solubility of mirabilite was observed during drying. In temperature regions where only one stable phase exists, i.e., mirabilite and thenardite, no increase of concentration above the maximum solubility was observed during drying. In the drying experiments besides mirabilite and thenardite also the heptahydrate plays an important role. Therefore it should be taken into account in future studies on sodium sulfate crystallisation.
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Chapter 1

Introduction

Building materials, e.g., stone, concrete, bricks, mortar, etc., are examples of porous materials. In the Netherlands masonry is a well known example of a combined porous material. As a consequence of the porous nature of these materials water and dissolved salts can be absorbed. These salts can be present before construction, originating from the clay of which the brick are made or the water used for making the mortar. However, after construction water sources such as groundwater, rain, floods also play a role. Deicing salts used in the winter or the presence of the sea can also act as sources of salt. Churches were frequently used for housing livestock (manure) and food storage (preservation with salt), resulting in large amounts of salts.

Due to environmental conditions, e.g., temperature, wind, and relative humidity, the dissolved salts can crystallize inside the pores and exert a pressure on the material. Old statues and even newly build houses are affected by salt crystallisation (see figure 1.1). At temperatures below zero the water itself can also freeze. The growing ice expands and exerts a pressure.

If the crystallisation pressure overcomes the tensile strength of the porous material it will crack. The salts can crystallize just under the surface, resulting in defacing, surface chipping, or disintegration. The salts can also crystallise on the surface, i.e., efflorescence (esthetic damage). Crystallisation of salts is one of the main hazards for buildings and monuments. All over the world research is done on the mechanism of salt crystallisation in porous materials.

Figure 1.1: Examples of damage due to salt crystallisation. On the left a statue in La Rochelle (France) with mechanical damage. On the right a new building with salt efflorescence on walls (esthetic damage).
1.1 Scope of this research

One of the most damaging salts is sodium sulfate (Na₂SO₄). In previous measurements by Rijniers et al. [Rij04] where crystallisation was initiated by temperature changes yielded a metastable phase, heptahydrate (Na₂SO₄·7H₂O), instead of the expected stable phase mirabilite (Na₂SO₄·10H₂O). The metastable phase is not considered in present literature on damage generated by sodium sulfate. In the present research crystallisation of sodium sulfate is studied during drying of fired-clay brick.

1.2 Layout of thesis

In Chapter 2 the principles behind salt crystallisation and the pressures generated will be explained. Chapter 3 provides the theory behind moisture and salt transport in a porous medium. The theory behind NMR and the setup are treated in Chapter 4. The results of the drying experiments will be presented in Chapter 5. Finally the conclusions and recommendations will be given in Chapter 6.
Chapter 2

Salt crystallisation

The damage to porous building materials is often caused by the crystallisation of salts inside the pores. Before the mechanisms behind the pressure generation are discussed first crystallisation of salts from a solution will be described.

2.1 Bulk crystallisation

The concentration $C$ of a salt solution is indicated in moles of dissolved salt per kg of solvent (1 mol kg$^{-1}$ = 1 molal (m)). A salt can be dissolved in water up to a maximum concentration. The maximum solubility of a salt depends on the temperature, and can be shown in a so-called phase diagram. A typical salt phase diagram is shown in Fig. 2.1. From a certain starting concentration two ways can be distinguished in order to reach the maximum solubility. First, water can be evaporated from a bulk salt solution which is in contact with air. The concentration of the solution will increase until the maximum solubility is reached. If the evaporation continues, a further increase in concentration will result in salt precipitation from the solution. Secondly, by cooling the solution to a temperature at which the maximum solubility is lower.

In both situations a so-called supersaturation can develop. Supersaturation indicates that at a certain temperature more than the maximum amount of salt is dissolved in the solution. Supersaturation is a result of a (temporary) inability of the system to nucleate. In order to initialise crystallisation a certain size of crystal is needed. The supersaturation defined here is unstable.

![Figure 2.1: A phase diagram, i.e., the solubility of a salt as a function of temperature. The two processes that cause crystallisation, cooling and evaporation are indicated. A supersaturation, i.e., a concentration above the maximum solubility, can be created by rapid cooling or rapid evaporation.](image-url)
Table 2.1: List of most damaging salts and their common sources.

<table>
<thead>
<tr>
<th>Type of salt</th>
<th>Chemical formula</th>
<th>Common sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Sulfate</td>
<td>Na₂SO₄</td>
<td>Clothes washing powders, soil; by action of polluted air on sodium carbonate</td>
</tr>
<tr>
<td>Sodium Carbonate</td>
<td>Na₂CO₃</td>
<td>Clothes washing powders, cleaning aids; fresh concrete and mortars</td>
</tr>
<tr>
<td>Magnesium Sulfate</td>
<td>MgSO₄</td>
<td>Some fired-clay bricks, rain washings from dolomite limestone affected by polluted air</td>
</tr>
<tr>
<td>Potassium carbonate</td>
<td>K₂CO₃</td>
<td>Fresh concrete and mortars; fuel ashes and ash mortars</td>
</tr>
<tr>
<td>Potassium sulfate</td>
<td>K₂SO₄</td>
<td>Some types of fired-clay bricks; by action of polluted air on potassium carbonate</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>NaCl</td>
<td>Seawater, road and pavement deicing salts</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>KCl</td>
<td>Soil</td>
</tr>
<tr>
<td>Calcium sulfate</td>
<td>CaSO₄</td>
<td>Some types of fired-clay bricks; gypsum based wall plasters</td>
</tr>
<tr>
<td>Sodium nitrate</td>
<td>NaNO₃</td>
<td>Soil, fertilisers</td>
</tr>
<tr>
<td>Potassium nitrate</td>
<td>KNO₃</td>
<td>Soil, fertilisers</td>
</tr>
</tbody>
</table>

A number of salts cause damage to building materials. Table 2.1 contains a list of the most damaging salts and their origin.

**Sodium chloride (NaCl)**

In Fig. 2.2a the phase diagram of sodium chloride is shown. The maximum solubility only varies slightly with the temperature. Crystallisation due to evaporation will take place at a concentration of 6 m.
Sodium carbonate (Na₂CO₃)

Some salts are capable of forming hydrated crystals. A hydrated crystal contains, besides salt molecules, also water molecules. The number of water molecules in the crystal can vary. Sodium carbonate, or 'soda' can crystallise in a number of different hydrates. The phase diagram of soda is shown in Fig. 2.2b. In the temperature region of 0-32°C soda will crystallise in Na₂CO₃·10H₂O. At a temperature above 35°C it will crystallise to Na₂CO₃·1H₂O, and between 32°C and 35°C crystals of Na₂CO₃·7H₂O will be formed. At high concentrations various regions are present in which combinations of hydrates are stable. Below 35°C a combination of 7H₂O and 10H₂O are in equilibrium with a solution of concentration ~6-8 m. Although the solubility line of 7H₂O phase is shown in Fig. 2.2b, in practice it is never found.

The solubility of the 10H₂O phase depends strongly on the temperature, which makes it possible to induce crystallisation by cooling down a solution of, e.g., 3 m (molal) at 40°C to 20°C. The resulting solution in contact with the 10H₂O crystals will have a concentration of 2.2 m.

![Figure 2.3: Phase diagram of sodium sulfate. In the temperature range 0-24°C two different hydrates, the 7H₂O and 10H₂O phase, can crystallise. Above 32°C only one the anhydrous crystal phase can crystallise.](image)

2.2 Sodium sulfate

The salt of interest in this thesis is sodium sulfate (Na₂SO₄). The phase diagram (see Fig. 2.3) of the sodium sulfate-water system was measured during the 19th century by various researchers. Sodium sulfate can crystallise in three different phases: thenardite (anhydrous), mirabilite (decahydrate), and heptahydrate. Thenardite crystallises from solution above 32.4°C. Below 32.4°C the only stable crystal phase is mirabilite. The heptahydrate phase can also exist below 23.6°C. The solution in contact with the heptahydrate crystals is supersaturated with respect to mirabilite. Therefore it is a metastable phase. However, crystals of the heptahydrate, once formed, are 'stable'. Sodium sulfate solutions can easily become supersaturated (Gay Lussac, 1813), which indicates the difficult nucleation of mirabilite. If a solution, which is saturated at 40°C, is cooled down to 6°C crystal of the heptahydrate will form. However, the solution must be sealed from the outside environment and the glasswork needs to be free of any mirabilite crystals [Gme26].

In several articles dating to the early 20th century the presence of the heptahydrate is indicated [HHH08, Wui14, WC38]. In more recent literature on salt damage caused by sodium sulfate the heptahydrate phase is neglected in the damaging mechanisms [CRNS00]. In the ESEM studies on crystallisation of sodium sulfate both thenardite and mirabilite are identified. In the crystal identifica-
tion the heptahydrate phase is not considered. In general, only the mirabilite and thenardite solubility lines are considered in the phase diagram. Previous NMR experiments on sodium sulfate solutions in porous media by Rijniers et al. [Rij04] indicated the presence of heptahydrate crystals. The concentrations measured inside the pores followed the solubility curve of the heptahydrate. These experiments were performed on sealed containers and crystallisation was induced by temperature changes.

Intermezzo: Supersaturation

In various literature the term supersaturation is used to indicate both unstable as stable situations. In this thesis the term supersaturation is used to indicate a solubility above the equilibrium solubility of a crystal. Indicating an unstable situation. The term increased solubility will be used to indicate a situation in which a crystal is in equilibrium with a solution of higher concentration than the maximum solubility. Situations of increased solubility will be introduced in Section 2.3

2.3 Theory on crystallisation pressure

Damage to the pyramids due to salt was already observed by Herodotus (485 B.C.). He stated: "I observed that salt exuded from the soil to such an extent as even to injure the pyramids.". The concept that crystals are able to exert a pressure was first introduced by Lavalle in 1853. He observed that growing crystals were able to lift a certain amount of weight. The principle that a crystal under pressure has a higher solubility than an unstressed crystal was first introduced by Thomson in 1862. The first measurements on the pressure generated by a crystal in a supersaturated solution were done by Correns. He provided an actual theory in 1939 [Cor49]. He stated that the pressure \( \Delta p \) exerted by a crystal in contact with a solution with concentration \( C \) is given by:

\[
\Delta p = \frac{RT}{V_m} \ln \frac{C}{C_s}
\]  

where \( V_m \) is the molar volume of the crystal, and \( C_s \) the saturated concentration. According to Eq. 2.1 growing crystals in contact with a solution with \( C > C_s \) can exert a pressure. However, if an unstressed crystal (with lower solubility) is also in contact with the same solution it will grow in favour of the stressed crystal. No pressure in generated, and the stressed crystal will eventually dissolve.

2.3.1 Crystal in a pore

Now consider a salt solution inside a pore. When the concentration is above the maximum solubility crystals can nucleate and grow inside the pore. The crystal is unlimited in its growth until it reaches the pore wall (see Fig. 2.4). Two possible situations can occur. The interfacial tension of the crystal-pore interface is larger than the liquid-pore interface. In this case the crystal will grow on the pore surface, i.e., a negative pressure drop is present across the crystal-liquid interface. However, if the interfacial tension of the crystal-solid interface is smaller than the liquid-solid interface, the crystal avoids contact with the pore wall. A small gap filled with solution will remain in between the crystal and the pore wall (see Fig. 2.4). The pressure in the crystal phase will be higher due to the crystal surface tension. This excess pressure is exerted on the pore wall. Consider a small spherical crystal with radius \( r \) (shown in Fig. 2.4a). The crystal grows and the radius increases to \( r + dr \). The amount of work required for the growth in volume \( dV \) is equal to \( (p_c - p_s) dV \) with \( p_c \) the pressure in the crystal and \( p_s \) the pressure in the solution. The surface increases with \( dA \) resulting in an increase in surface energy equal to \( \gamma_{cl} dA \). For a spherical crystal the pressure \( p_c \) caused by the surface tension is given by:

\[
\Delta p = p_c - p_s = \gamma_{cl} \frac{dA}{dV} = \frac{2\gamma_{cl}}{r}
\]  

As a consequence a small crystal has a higher solubility (see Eq. 2.1).
2.3 Theory on crystallisation pressure

The pressure \( \Delta p \) exerted by a crystal in a pore can be calculated in the same way using the crystal-liquid interfacial energy \( \gamma_{ci} \). The pressure is the same as in Eq. 2.2. The pressure calculated appears to be in conflict with Eq. 2.1. According to Correns’ equation the concentration is a limiting factor for the pressure, while in Eq. 2.2 it is the interfacial pressure. Furthermore, according to Eq. 2.2 only very small crystals can exert a pressure.

A thermodynamical review [Ste05a, Ste05b] of the crystallisation pressure provides an answer. Consider a large crystal (interfacial tension is neglected for the moment) which is confined in a pore (Fig. 2.4). The crystal faces in contact the solution are under ambient pressure \( p_s \), and the crystal faces in contact with the pore wall are under an increased pressure \( p_c > p_s \). It is assumed that the porous medium is saturated, otherwise \( p_s \) would be lower than the ambient pressure due to the liquid-air interface. The chemical potential \( \mu_p \) of a solid, e.g., a crystal, under pressure \( p \) is given by:

\[
\mu_p = \mu_0 + pV_m + w, \tag{2.3}
\]

with \( \mu_0 \) and \( V_m \) the chemical potential and molar volume of the unstressed crystal, and \( w \) the molar strain energy. The stressed (\( p=p_c \)) and unstressed (\( p=p_s \)) crystal faces each have a different chemical potential. If the solution and the crystal are in equilibrium the chemical potential of the salt in solution must equal the chemical potential of each of the crystal faces. The chemical potential of the salt in solution is given by:

\[
\mu_s = \mu_s^0 + RT \ln a, \tag{2.4}
\]

where \( \mu_s^0 \) is the chemical potential in the standard state, \( T \) the temperature, \( R \) the gas constant, and \( a \) the activity of the salt in solution. Equating Eqs. 2.3 and 2.4 yields:

\[
\mu_0 + pV_m + w = \mu_s^0 + RT \ln a \tag{2.5}
\]

According to Eq. 2.5 the stressed surface is in equilibrium with a solution of a higher concentration, i.e., a higher activity.

Figure 2.4: a) A schematic diagram of a small spherical crystal with radius \( r \) in a solution. The crystal grows, and the radius increases to \( r+dr \). b) Crystal inside a pore. The porous medium is saturated. The pore solution is under ambient pressure \( p_s \). The narrow gap between the crystal face and the pore wall allows crystal to keep growing, and at the same time exert a pressure \( p_c \).
The increased solubility of the stressed crystal surface is calculated with respect to a reference state. The reference state is defined as a crystal under isotropic ambient pressure ($p_s$) in equilibrium with a solution of activity $a_0$. By comparing these two situations the increased solubility of the stressed surface is given by:

$$\ln \frac{a}{a_0} = \frac{(\Delta p)V_m}{RT},$$  \hspace{1cm} (2.6)

it is assumed that both the difference in molar volume and molar strain energy between the stressed and unstressed crystals can be neglected for pressures smaller than 100 MPa. By rewriting Eq. 2.6 it follows that:

$$\Delta p = \frac{RT}{V_m} \ln \frac{a}{a_0},$$  \hspace{1cm} (2.7)

with $\Delta p = p_c - p_s$. A crystal surface can only grow and exert a pressure if it is in contact with a solution with a higher activity than the activity $a_0$ at maximum solubility. If the activity $a$ is below the equilibrium activity of the surface it will dissolve. If Eq. 2.7 is to be compared with Correns' equation the activity of a solution must be replaced with the concentration. Consider a salt dissolved in water. The following dissolution reaction is used:

$$M_{\nu_M}X_{\nu_X}V_0H_2O \leftrightarrow \nu_M M^{2+} + \nu_X X^{2-} + \nu_0 H_2O$$

The activity of the solution on the right hand side of the reaction is then given by:

$$a = (\nu_M^{\nu_M} \nu_X^{\nu_X})(C\gamma_{\pm})\alpha_{w0}^{\nu_0},$$  \hspace{1cm} (2.8)

in which $C$ is the concentration of the solution, $\nu = \nu_M + \nu_X$ the total amount of ions released, $\alpha_w$ the water activity, and $\gamma_{\pm}$ is the mean activity coefficient for the two dissolved salts $M$ and $X$. If Eq. 2.8 is inserted in Eq. 2.7 the following equation for the crystallisation pressure is obtained:

$$\Delta p = \frac{RT}{V_m} \left( \ln \frac{C}{C_0} + \ln \frac{\gamma_{\pm}}{\gamma_{\pm0}} + \frac{\nu_0}{\nu} \ln \frac{\alpha_w}{\alpha_{w0}} \right)$$  \hspace{1cm} (2.9)

The first term in between the brackets is the concentration ratio, which is the same as in Correns' equation. The other two terms account for the non ideal behaviour of the salt ions and water in the solution. For an ideal solution the second term with the ratio of the mean activity coefficients can be neglected. With increasing salt concentrations the water activity always decreases. Therefore, the third term will always be negative, resulting in a smaller pressure. For a non-hydrous salt with $\nu_0 = 0$ the third term is zero. For the hydrated salts the increase in pressure as a result of increased ion activity, is compensated by the decrease in water activity. Furthermore an extra factor $\nu$ is present which represents the number of ions that are released when a salt is dissolved. For sodium sulfate $\nu=3$, and for NaCl $\nu=2$. This means that the Correns Equation underestimates the crystallisation pressure by a factor 2 or 3. In Fig. 2.5a the pressures calculated with Eq. 2.9 are plotted as a function of the supersaturation for different salts. Hydrated salts with an increasing number of water molecules can generate less pressure. This can be seen for both Na$_2$SO$_4$ and MgSO$_4$. The salt which generates the most pressure is NaCl. However, from experiments it is known that NaCl does not create large supersaturations. It should be noted that the tensile strength of a fired clay brick is in the order of a 5-10 MPa. The supersaturation needed to exceed this pressure is in the order of a few percent for both NaCl and Na$_2$SO$_4$. Sandstones have a lower tensile strength of 2-3 MPa.
2.3 Theory on crystallisation pressure

The crystal-liquid interfacial tension will also have an influence on the crystallisation pressure (see Fig. 2.5b). According to Eq. 2.2 a small crystal has an increased solubility caused by the interfacial tension. For the same concentration the ratio \( \frac{\rho}{\rho_0} \) will be smaller. If the crystal becomes increasingly smaller it will eventually dissolve and is not capable of generating any pressure at all. This is shown in Fig. 2.5. If the interfacial tension is taken into account the pressure generated by a crystal of size \( r \) is given by:

\[
\Delta p = \frac{RT}{V_m} \ln \frac{a}{a_0} - \gamma_c \frac{dA}{dV}
\]  

(2.10)

In fired-clay brick the pores are in general larger than 0.1 \( \mu m \), and hence the influence of the interfacial tension on the crystallisation pressure can therefore be neglected in this thesis.

2.3.2 Equilibrium pressure

A solution in equilibrium with a stressed crystal surface will be supersaturated with respect to the unstressed surface. The unstressed surface will keep on growing until the supersaturation is consumed. As a consequence the pressure calculated with Eq. 2.9 is a transient pressure. No equilibrium is achieved. In some special cases, it is possible to get an equilibrium crystallisation pressure. In Fig. 2.6 a possible situation is sketched. In this situation a pressure is generated by a large crystal in a spherical pore with small cylindrical 'access' pores. A large spherical crystal will grow inside the pore leaving only a small solution film between the crystal and the pore wall. A further growth of the large crystal will result in a pressure. The large crystal will have no increased solubility and will be in equilibrium with the maximum solubility of the salt. The large crystal does not exert pressure. However, if the crystal continues growing in the small pores, the small satellite crystals will have an increased solubility due to the curved surfaces. The solution in the small pores is under ambient pressure and will be in equilibrium with the small crystals. However, the large spherical crystal will be in contact with a supersaturated solution and will be under increased pressure. In order to reach equilibrium the large crystal will be under increased pressure. The increased solubility for the curved surface of the satellite crystal in the small entrance pore is calculated by combining Eq. 2.2 and Eq. 2.6. This yields:
The large crystal will be in contact with this increased concentration. If it is assumed that the interfacial tension has no effect on the large crystal the pressure $\Delta p$ exerted by the large crystal can be calculated using Eq. 2.7 combined with Eq. 2.11:

$$\ln \frac{a_E}{a_0} = \frac{\Delta p V_m}{RT} = \frac{2\gamma_{cl} V_m}{r_E RT}$$

(2.11)

As can be seen, the pressure calculated using the interfacial tension is the same as derived with the thermodynamical derivation above.

Figure 2.6: Equilibrium pressures generated by a large crystal in a spherical pore with radius $r_p$ and cylindrical entrance pores with radius $r_e$. 
Chapter 3

Transport of moisture and ions in porous materials

Fired-clay brick and mortar are examples of porous materials. A porous material consists of a solid matrix with void spaces, called pores, which can be isolated or interconnected. The pores can be empty or filled with fluids. When all the pores are completely filled the medium is called saturated. In a non-saturated medium the pores are either filled with water or air/vapour. In Fig. 3.1 a schematic representation of a non-saturated porous material is shown. In this research the fluids are limited to water, aqueous salt solutions, and vapour. Processes such as absorption and evaporation cause the fluids to be transported through the porous medium. Dissolved ions are transported by a combination of fluid advection and diffusion. In this chapter the transport of moisture and ions in porous materials is introduced. For more information the reader is referred to [Pel95, Hal02, Pet05].

Figure 3.1: A schematic representation of a non-saturated porous medium with different pore sizes. The pores are filled with water, air, and vapour.
3.1 Moisture transport

The transport of moisture in porous media can be studied at a microscopic level. The moisture flow inside the individual pores can be described, and the macroscopic properties can be derived from that. However, porous media are so complicated that a microscopic approach is not practically. Therefore a macroscopic approach is more useful to describe moisture transport. When describing drying of a porous material both saturated and non-saturated moisture transport are important at different drying stages. The moisture flux \( q \) through a saturated porous material as a result of an external pressure gradient \( \frac{\partial p}{\partial z} \) can be described by Darcy’s law:

\[
q = -\frac{k}{\mu} \frac{\partial p}{\partial x},
\]

where \( k \left[ m^2 \right] \) is the permeability of the material and \( \mu \left[ kg \cdot m^{-1} \cdot s^{-1} \right] \) is the viscosity of the liquid. In a non-saturated porous medium the total moisture flux is a combination of liquid and vapour transport. The moisture flux in a non-saturated porous material can be described by the extended Darcy’s law:

\[
q = -\frac{k(\theta)}{\mu} \frac{\partial P(\theta, C, T)}{\partial x}.
\]

where the pressure is now also a function of the moisture content \( \theta \), and the temperature \( T \). In case of a salt solution the concentration \( C \) is also of influence on the pressure. The pressure in the liquid phase is given by:

\[
p(\theta, C, T) = p_a - p_c(\theta, C, T),
\]

where \( p_a \) is the atmospheric pressure, and \( p_c \) is the capillary pressure. Due to the liquid-air interfacial tension \( \gamma_{la} \) the liquid-air surface in a pore is curved. This causes a pressure difference across the air-water interface called capillary pressure. For a cylindrical pore with radius \( r \) the capillary pressure is given by:

\[
p_c = -\frac{2\gamma_{la}}{r} \cos \phi,
\]

with \( \gamma_{la} \) the interfacial energy of the liquid air interface, and \( \phi \) the angle between the liquid air and liquid solid interfaces. The angle \( \phi \) is assumed to be zero in case of a wetting liquid. The capillary pressure as a function of the moisture content is characteristic for each porous medium and is called the capillary pressure curve. In Fig. 3.2 a schematic representation of the capillary pressure curve is shown. The capillary pressure at a certain moisture content depends on whether it was reached by drying or wetting. Hysteresis occurs between the wetting and drying of the medium. The maximum moisture content which can be reached by absorption under atmospheric pressure is the capillary moisture content \( \theta_{cap} \).

Combining conservation of mass with Eq. 3.2 yields the following equation for the moisture content as a function of time:

\[
\frac{\partial \theta}{\partial t} = -\frac{\partial q}{\partial x} = \frac{\partial}{\partial x} \left( D_{\theta, l} \frac{\partial \theta}{\partial x} \right) + \frac{\partial}{\partial x} \left( D_{c, l} \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial x} \left( D_{T, l} \frac{\partial T}{\partial x} \right),
\]

where \( D_{\theta, l}, D_{c, l}, \) and \( D_{T, l} \) are the diffusivity coefficients for the transport as a result of gradients in the moisture content, concentration, and temperature respectively. In our experiments only isothermal situations occur, so moisture transport due to temperature gradients can be neglected. If water is in contact with a solution of high concentration, besides diffusion of the solute also water transport will cause the concentration gradient to level (osmotic pressure). However, the influence can be neglected with respect to the water transport due to a gradient in moisture content.
3.2 Salt transport

Besides liquid transport, moisture is also transported by vapour. When both contributions are combined the following equation follows for the moisture transport in a non-saturated medium:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left( D_{\theta,v+1} \frac{\partial \theta}{\partial x} \right), \quad (3.6)$$

where $D_{\theta,v+1}$ is the isothermal moisture diffusivity coefficient.

### 3.2 Salt transport

Ions are transported both by diffusion and advection, which are two competing processes. Advection transports the ions in the direction of the moisture flow, and diffusion levels off the gradient in salt concentration. The molar ion flux $J$ is given by:

$$J = \chi \theta (CU - D \frac{\partial C}{\partial x}), \quad (3.7)$$

where $D \, [m^2 s^{-1}]$ is the ion diffusion coefficient, $U$ is the water velocity, and $\chi=10^3 \, l \, m^{-3}$ corrects for the dimensions of the concentration (mol $l^{-1}$ instead of mol $m^{-3}$). The ion diffusion coefficient $D$ in a porous medium is lower than the bulk ion diffusion coefficient. It depends on the porosity, and moisture content of the medium, and is also a function of the concentration. The salt content as a function of time can be found by applying the law of mass conservation on Eq. 3.7:

$$\frac{\partial C \theta}{\partial t} = \frac{1}{\chi} \frac{\partial J}{\partial x} = \frac{\partial}{\partial x} \left[ \theta (D \frac{\partial C}{\partial x} - CU) - R(C) \right], \quad (3.8)$$

where $R(C)$ is the crystallisation rate. The onset of crystallisation is not a smooth process but step-wise, hence $R(C)$ is a step-function. When the maximum solubility is reached crystallisation will consume the dissolved ions.
Whether advection or diffusion plays a dominant role can be determined by the dimensionless Péclet number:

\[ P_e = \frac{U L}{D}, \quad (3.9) \]

where \( L \) is the characteristic length scale on which the transport takes place. For \( P_e \gg 1 \), advection is dominant and for \( P_e \ll 1 \), diffusion is dominant. In case of dominant advection the salt will be transported to the evaporating surface and a concentration peak will result at or just below the surface. If diffusion is dominant the salt will remain distributed equally over the sample. No peak will result in the concentration.

\[ \text{Figure 3.3: a) Schematic diagram of a drying sample isolated at all sides except for the drying surface on the left. Water evaporates from the drying surface. The two competing transport processes for ions are advection and diffusion. b) Moisture content profiles of a drying fired-clay brick. The top of the sample where evaporation takes place is positioned at -12.5 mm and the bottom at 12.5 mm. At high moisture contents the moisture is homogeneously distributed indicating that the drying process is limited by external factors. Below the critical moisture content a drying front appears. Indicating that the drying process is limited by internal factors.} \]

3.3 Drying

A saturated porous material will dry due to evaporation of water from the pores. In Fig. 3.3a a schematic diagram of a drying fired-clay brick sample is shown. The moisture from the brick sample will evaporate if the vapour pressure of the drying air is lower than the local vapour pressure in the sample. The vapour pressure is the partial pressure of water vapour in air. Due to the curved liquid-air interface in a pore the vapour pressure \( P_v \) depends on the pore size \( r \):

\[ P_v = p_0 \exp\left(-\frac{2\gamma_{lv}}{rRT}\right), \quad (3.10) \]

with \( p_0 \) the saturated vapour pressure above a flat surface, and \( v_l \) the molar volume of the liquid. The relative humidity (RH) is defined as \( \frac{P_v}{p_0} \times 100\% \).

The moisture content of a porous material with a range of pore sizes is a function of the environmental RH. The moisture content as a function of the RH is called a sorption isotherm or hygroscopic curve. In Fig. 3.4 the hygroscopic curves for fired-clay brick and a sand-lime brick are shown. A hysteresis due absorption and desorption is also present in the hygroscopic curves. A fired clay brick has only a small fraction of pores below 0.1 \( \mu \)m, which is reflected in the hygroscopic curve. A calcium-silicate
brick on the other hand has a fraction of pores smaller than 0.1 μm, resulting in a higher moisture content at low RH.

![Graph](image)

Figure 3.4: Hygroscopic curves, i.e., the moisture content as a function of the relative humidity for fired-clay brick (●), and calcium-silicate brick (□).

At the material air interface water can evaporate. The moisture flux $q$ perpendicular at the material air interface is given by:

$$ q = \frac{\beta}{\rho_l} (RH_{env} - RH_r) $$  \hspace{1cm} (3.11)

where $\beta$ [mol m$^{-2}$s$^{-1}$] is the molar mass transfer coefficient, and $RH_{env}$ and $RH_r$ are the equilibrium relative humidities of the environment and material respectively. The transfer coefficient $\beta$ depends on many factors such as the air velocity, the roughness of the surface, and the porosity. Due to water evaporation the moisture content decreases. The minimum moisture content which is reached is limited by the $RH_{env}$ and hygroscopic curve. The opposite of evaporation, condensation, can also occur if the environmental RH is higher than the equilibrium RH for a certain pore size. This is called capillary condensation.

At high moisture content the drying is limited by the external conditions such as air speed and relative humidity. The moisture can be transported via the large pores to the surface where it evaporates. This regime is indicated by the flat moisture profiles in Fig. 3.3b. However, when a certain moisture content is reached, the so-called critical moisture content ($\theta_c$), internal limitations become dominant. The liquid moisture transport is broken up, and liquid islands develop. The moisture is transported dominantly by vapour. As a consequence a receding drying front develops (see Fig. 3.3b, $\theta_c \sim 0.05$).

### 3.3.1 Salt influence on drying

Besides the pore size also the salt concentration has an influence on the vapour pressure. Hence, the drying properties will also be different. The concentration of the solution influences the water activity and hence the vapour pressure above the solution surface. In general, the water activity and hence the vapour pressure decreases with increasing concentration. As a result the RH gradient in Eq. 3.11 will decrease, and slower drying is observed.

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The water activities as a function of concentration for both NaCl and Na₂SO₄ are shown in Fig. 3.5. Both these influences can be summed in one single equation [Rij04] for the equilibrium RH above a salt solution with concentration $C$ confined in a cylindrical pore with radius $r$:

$$\ln(RH(r,C)) = -\chi nRT \nu_1(C + X) - \nu_1(1 - \chi C \nu_1)\sigma \ln \frac{2}{r},$$

(3.12)

where $n$ is the number of ions per unit of salt ($n=3$ for sodium sulfate), and $\nu_1$ is the partial molar volume of the salt in solution. The first term on the right handside is the osmotic pressure and the factor $X$ is a correction factor for the non-ideal behaviour of a salt solution. The second term accounts for the pore size dependence of the vapour pressure (see also Eq. 3.10. In Fig. 3.6a) the correction $X$ as a function of the salt concentration is shown for Na₂SO₄, NaCl, and Na₂CO₃.

In Fig. 3.6b the influence of both the pore size as the concentration is shown. As can be seen, the pore size only has an influence for pore size smaller than 1 $\mu$m. Consider a solution with a certain water activity, e.g., $a_w=0.898$ in Fig. 3.6b. The environmental RH is 80%. Evaporation of water will take place in all pores larger than 0.01 $\mu$m. However, capillary condensation will occur in all pores smaller than 0.01 $\mu$m. As mentioned before fired-clay brick has no pores smaller than 0.1 $\mu$m. Therefore the
only contributing effect on the vapour pressure inside the pores is the concentration of the salt solution. During drying the concentration of the salt solution increases and therefore the equilibrium RH decreases. The gradient in the RH in Equation 3.11 becomes smaller and the evaporation decreases.


Chapter 4

NMR

Nuclear Magnetic Resonance (NMR) is a non destructive measurement technique which makes use of the nuclear magnetic moment of atoms. With NMR measurements can be done on a variety of hydrogen containing materials, e.g., biological tissues, soil, and thin paint layers. In this thesis NMR is used to measure amounts of $^1$H (water) and $^{23}$Na (sodium sulfate solution) inside technological porous materials such as fired-clay brick and mortar.

In this chapter the theory behind NMR is explained. Only information which is useful for this thesis is described, for more information the reader is referred to [Vla99].

4.1 NMR Theory

Most atoms have a netto nuclear magnetic moment $\mu$. This magnetic moment is a result of the combined spins of the individual particles that make up the nucleus. In Table 4.1 the properties of the two nuclei of interest $^1$H and $^{23}$Na are given.

When placed in an external static magnetic field $B_0$ the individual moments will align with the magnetic field. Due to the magnetic field the magnetic moment will experience a torque, causing it to precess around the main magnetic field with a frequency given by:

$$\omega_l = \gamma B_0,$$

(4.1)

with $\gamma$ [MHz T$^{-1}$] is the gyromagnetic ratio, and $\omega_l$ is the resonance frequency or Larmor frequency. The gyromagnetic ratio is different for each nucleus, making it possible to identify a nucleus by its resonance frequency.

In an macroscopic object, an ensemble of magnetic moments will align with the main magnetic field, resulting in a netto magnetisation ($M$). The netto magnetisation can be measured. The individual spins precess each with a different phase angle. The transverse component of $M$ will therefore cancel out. $M$ is aligned with the main magnetic field (see Fig. 4.1a). The direction of $B_0$ is defined as the $z$-direction.

Table 4.1: NMR properties of $^1$H and $^{23}$Na.

<table>
<thead>
<tr>
<th>nucleus</th>
<th>spin</th>
<th>gyromagnetic ratio (MHz T$^{-1}$)</th>
<th>sensitivity</th>
<th>$\omega_l/2\pi$ @ 0.79 T (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>1/2</td>
<td>42.58</td>
<td>1.00</td>
<td>33.8</td>
</tr>
<tr>
<td>$^{23}$Na</td>
<td>3/2</td>
<td>11.26</td>
<td>9.25 $10^{-2}$</td>
<td>8.95</td>
</tr>
</tbody>
</table>

The netto magnetisation can be manipulated by applying a magnetic field $B_1$ with the Larmor frequency in the $x$-direction (see Fig. 4.1). The $B_1$ field is created by an RF pulse. The magnetisation is rotated in a plane perpendicular to the $x$-axis. The angle $\alpha$ over which the magnetisation is rotated depends on the time $\tau$ the RF pulse is applied:

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A pulse that will rotate $M$ in the xy plane is called a 90 degree pulse. If the magnetisation is placed in the xy plane it will rotate with $\omega_l$. Therefore it is convenient to adopt a rotating frame of reference $x'y'z$ instead of the reference frame $xyz$ used in Fig. 4.1a. The $x'y'z$ frame rotates with $\omega_l$. The component of the magnetisation in the z-direction is called the longitudinal magnetisation, the component in the x'y' plane is called transverse magnetisation. The transverse magnetisation induces a signal which can be measured in the NMR setup.

\[ \alpha = \gamma B_1 \tau \]  

(4.2)

Figure 4.1: On the left the netto magnetisation $M$ is positioned along the z-axis. A 90° RF-pulse ($B_1$) rotates $M$ in the $x'y'$ plane (on the right).

### 4.2 Relaxation

In equilibrium the magnetisation is positioned along the z-axis with a magnitude $M_0$. After a 90° RF pulse is applied the magnetisation is positioned in the xy-plane. It will relax back to the equilibrium position along the z-axis. The transverse magnetisation will decrease to zero, and the longitudinal magnetisation will relax back to $M_0$. Both these processes take place with a characteristic exponential time constant. The relaxation of the longitudinal magnetisation is caused by interactions of the spins with the surroundings and has a characteristic time constant $T_1$. The relaxation of the transverse magnetisation is caused by spin-spin interactions and by dephasing of individual spins due to field inhomogeneities. The characteristic relaxation time is $T_2$.

In an NMR experiment RF pulses are used to manipulate the magnetisation. The first pulsed NMR sequence was done in 1950 and was called a spin echo. Today this sequence is called a Hahn spin echo after its inventor E.L. Hahn. The principles behind the Hahn spin echo are not further explained in this thesis, the reader is referred to other literature [Hah50, Vla99]. The Hahn spin echo sequence is used to measure the amount of atoms ($^1$H and $^{23}$Na) which are present in a slice. The slice is selected by applying a magnetic field gradient. Only the spins that satisfy the resonance criterium (Eq. 4.1) are measured. The intensity $S$ of the spin echo signal, which is proportional to the transverse magnetisation, is given by:

\[ S \approx k \rho \left( 1 - e^{-T_R/T_1} \right) e^{-T_E/T_2} \]  

(4.3)

with $k$ the NMR sensitivity of the nuclei relative to $^1$H, $\rho$ the density of spins, $T_E$ is the so-called echo time, and $T_R$ is the repetition time between two successive spin echo measurements.

After a spin echo the magnetisation has to relax back to the equilibrium $M_0$ (along the z-axis) before another spin echo can be measured, e.g., for averaging. The repetition time is typically chosen $T_R \approx 4T_1$. Measuring in a material with a long $T_1$ requires more time. The spin echo signal decays with $T_2$. After a time $T_E$ the spin echo signal is measured. The spin echo needs to be measured before the transverse magnetisation has relaxed completely.

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Pure bulk water has relative long relaxation times, and \( T_1 = T_2 \). Water which is confined in a porous material such as fired-clay brick has shorter relaxation times due to magnetic impurities and interactions of the water molecules with the pore wall. In general the \( T_2 \) is more affected than the \( T_1 \).

In Table 4.2 the relaxation times for water in a number of different porous materials and sodium are given.

The problem with fired-clay brick is that due to the high iron content (~4%) the \( T_2 \) of water is very short (210 \( \mu \)s). This requires a dedicated NMR setup capable of measuring with \( T_E \approx 200 \mu s \) in order to get a signal. The \( T_1 \) of water in fired-clay brick is relative long (0.23 s) so \( T_R \approx 1 s \).

For sodium the sensitivity for sodium is very low (\( k \approx 0.09 \)), hence more averages are needed (1024). The \( T_2 \) for sodium is longer than for water (40 ms). Because \( T_1 \) is in the order of 40 ms the repetition time can be reduced a factor 10 compared to hydrogen. Making the total measuring time for sodium comparable to hydrogen.

The spin echo intensities are calibrated for both hydrogen and sodium, making it possible to do quantitative measurements of the concentration. The sodium atoms inside a crystal are not measured because \( T_2 \sim 10 \mu s \). Therefore, crystallisation can be observed due to a decrease in sodium signal.

### Table 4.2: \( T_1 \) and \( T_2 \) relaxation times for pure bulk water, and water in confined in a variety of porous materials. The relaxation times for a aqueous copper sulfate solution and sodium (\( Na^+ \)) are also included for comparison.

<table>
<thead>
<tr>
<th>material</th>
<th>( T_1 ) (ms)</th>
<th>( T_2 ) (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk water</td>
<td>3000</td>
<td>3000</td>
</tr>
<tr>
<td>fired-clay brick</td>
<td>230</td>
<td>0.21</td>
</tr>
<tr>
<td>calcium-silicate brick</td>
<td>45</td>
<td>0.85</td>
</tr>
<tr>
<td>mortar</td>
<td>35</td>
<td>0.1</td>
</tr>
<tr>
<td>0.1 m CuSO4</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>( Na^+ )</td>
<td>40</td>
<td>40</td>
</tr>
</tbody>
</table>

### 4.3 NMR setup

The NMR setup for the drying experiments consists of an electromagnet and a PhyDas data acquisition unit (see Fig. 4.2 on the next page). A thermostated sample holder is used to keep the samples at a constant temperature.

A schematic diagram of the RF coil circuit is shown in Fig. 4.3. The RF coil is used to transmit the RF pulses and to receive the magnetisation signal. The coil has a diameter of 35 mm and consists of 7 turns of 1 mm copper wire. A Faraday shield is used so that changes in the dielectric permittivity of the sample have a negligible influence on the tuning of the electric circuit, making it possible to do quantitative measurements on a variety of materials.

In the drying setup both hydrogen and sodium signals are measured. Therefore it is possible to switch the tuning frequency of the coil from hydrogen (~31.8 MHz) to sodium (~8.94 MHz). A gradient in the z-direction is used to make slice selective measurements.

### 4.4 Experimental methods

The setup used in the drying experiments is shown in Fig. 4.2. The cylindrical samples are 40 mm long and 20 mm in diameter. The samples are dried in an oven at 60 °C. After capillary saturation with the desired solution, the sample is coated with teflon tape, thus creating a one dimensional drying experiment. The sample is placed in a PVC thermostated holder in the NMR setup (see Fig. 4.4). The holder is kept at a constant temperature with an accuracy of 0.1 °C by a Lauda thermostat (RE207). Galden HT70 is used as a heat transfer liquid, as it contains no hydrogen atoms so signal is obtained...
Figure 4.2: NMR setup for sodium sulfate drying experiments, with electro magnet, phydas acquisition system, and Lauda cooler with pump.

Figure 4.3: Schematic diagram of the RF coil circuit. The resonance frequency of the circuit can be switched between hydrogen (31.8 MHz) or sodium (8.94 MHz). To obtain quantitative results, a Faraday shield is used. The circuit is used for both sending of RF pulses and receiving spin echo signals.

from the liquid. The Galden remains liquid down to -110°C and has a boiling point of 70°C. The liquid is pumped round by a peristaltic pump. The teflon tape and PVC holder also have a very low signal contribution. For the sample positioning a stepper motor is used.

The drying of the brick is achieved by blowing air with an adjustable RH over the top surface of the sample. The RH of the air was adjusted by mixing dry air (0% RH) with wet air (100% RH). The drying conditions were 2% RH with an air flow of 5 l/min, unless indicated otherwise.

Slice selective measurements in the sample (40 mm) were done every mm for the first 10 mm and from 10-40 mm every 2 mm. The parameters which were used for both hydrogen and sodium measurements are shown in Table 4.3. The z-gradient for hydrogen is 14 kHz/mm and for sodium it is 7 kHz/mm resulting in a spacial resolution of 0.25 mm for hydrogen and 0.5 mm for sodium. The gradient for sodium is chosen smaller because of the lower sodium signal. A smaller gradient will result in a larger measuring volume and hence a larger signal. The effect of the difference in measuring volumes on measuring the concentration is compensated by using reference sample (3 m NaCl). The reference sample is also used to compensate for daily fluctuations (due to temperature changes) in the resonance frequency.
4.4 Experimental methods

Figure 4.4: A schematic diagram of the drying setup. The fired-clay brick sample is fitted in a teflon holder which can be held at a constant temperature by a thermostat (Lauda RE207). Galden is used as a heat transfer liquid, and is pumped round by a peristaltic pump. The airflow can be set at a relative humidity (2-100%).

The number of averages are 32 for hydrogen and 1024 for sodium. One slice takes $32 \times 1.5$ s for hydrogen and $1024 \times 0.1$ s for sodium. A total profile (34 points) takes about 100 minutes to measure, and is repeated every 120 minutes. The time to measure one profile is justified compared to the total time of a typical drying experiment (several weeks).

Table 4.3: Parameters for hydrogen and sodium NMR measurements.

<table>
<thead>
<tr>
<th></th>
<th>$^1$H</th>
<th>$^{23}$Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>90° pulse (μs)</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>180° pulse (μs)</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>$t_E$ (μs)</td>
<td>205</td>
<td>800</td>
</tr>
<tr>
<td>long delay (s)</td>
<td>1.5</td>
<td>0.1</td>
</tr>
<tr>
<td>averages</td>
<td>32</td>
<td>1024</td>
</tr>
<tr>
<td>z-gradient (Hz/mm)</td>
<td>14000</td>
<td>7000</td>
</tr>
<tr>
<td>spatial resolution (mm)</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>
Chapter 5

Results

In this chapter the results for the sodium sulfate drying experiments will be presented. First, the results from Rijniers et al. [Rij04] are verified in fired-clay brick. Next, the crystallisation behaviour of sodium sulfate during drying will be compared with sodium chloride and sodium carbonate. Finally, seven drying experiments with sodium sulfate at different temperatures and environmental conditions will be discussed.

![Graph showing concentration and temperature over time](image)

Figure 5.1: (Top graph) The mean concentration in the sealed sample as a function of time. (Bottom graph) The corresponding temperature at the top of the sample as a function of time.

Sodium sulfate

Before the drying experiments will be discussed, first only temperature changes will be considered. As a starting point for this experiment a fired-clay brick sample is saturated with a solution of 2.5 molal (m) at 40°C. The sample is sealed on all sides. The temperature is decreased from 40°C to 20°C.

In the top graph of Fig. 5.1 the concentration as a function of time is shown. In the bottom graph the corresponding sample temperature is shown. At 20°C no crystallisation is observed, although the concentration is above the maximum solubility of mirabilite.

At t=50 h the temperature was again decreased to 12°C. After 5 hours at this temperature a drop of saturated sodium tetraborate solution (Na₂B₄O₇) was put on the top of the sample. From literature it is known that this solution is supersaturated with respect to mirabilite. At t=190 h the temperature was again decreased to 12°C. After 5 hours at this temperature a drop of saturated sodium tetraborate solution (Na₂B₄O₇) was put on the top of the sample.

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is known that the crystal of sodium tetraborate decahydrate (Na₂B₄O₇·10H₂O or Borax) has the same crystal structure as mirabilite. It is used in solar energy storage to initiated mirabilite crystallisation [LL78]. Immediately after application the entire sample crystallised instantaneously to mirabilite. After the mirabilite crystallised the temperature was increased step by step and the concentration was measured for each temperature. The concentration as a function of temperature corresponding to this experiment, see Fig. 5.1, is shown in Fig. 5.2.

![Graph showing concentration as a function of temperature](image)

**Figure 5.2:** The concentration in the fired-clay brick as a function of temperature. The arrows indicate the time evolution. The * indicates the application of a drop of Borax solution on top of the sample.

### 5.1 Drying

**Sodium Chloride**

Before further measurements on sodium sulfate will be presented first the behaviour of sodium chloride is shown. Sodium chloride can only crystallise in one crystal phase (see Fig. 2.2a). A fired-clay brick sample was saturated with a 3 m NaCl solution. The temperature is kept constant at 20°C. An airflow of 5 l/min with an RH of 2% is used. In Fig. 5.3 the concentration profiles of the solution in the fired-clay brick are shown every 10 hours for a total of 90 hours. The top of the sample is positioned at 4 mm and the bottom at 38 mm.

Water is transported to the surface due to evaporation (Pe>1). The salt is advected to the surface, which results in an increase of the concentration at the surface (Pe>1). When the concentration at the surface reaches 6 m no further increase of the concentration is measured, indicating crystallisation; i.e., no supersaturation is seen. After crystallisation the drying rate decreases and diffusion becomes dominant (Pe<1). The concentration increases to 6 m in the entire sample.

**Sodium Carbonate**

The phase diagram of sodium carbonate is similar to sodium sulfate. Depending on the temperature three possible crystal morphologies can crystallise (see Fig. 2.2b). At 20°C it also has two hydrates with different solubilities, 10H₂O and 7H₂O with solubilities of 2 m and 3.5 m respectively. A fired-clay brick sample was saturated with a 1 m Na₂CO₃ solution at 20°C.

In Fig. 5.4 both the moisture and concentration profiles are shown every 10 hours for a total of 300 hours. The sample is positioned from 3-40 mm. Due to evaporation water is transported to the top
5.1 Drying

The salt is advected to the surface, and the concentration in the top 10 mm of the sample increases (Pe>1). The concentration increases until the maximum solubility of the 10H₂O phase is reached, and crystallisation is observed. No significant increase of the concentration above the maximum solubility is observed.

At high moisture content, the moisture remains homogeneously distributed in the sample, i.e., the drying is limited by external factors. A distinct drying front can be observed once the critical moisture content (S~0.3) is reached. The critical moisture content is indicated by a dashed line in Fig. 5.4a. Below the critical moisture content the drying is limited internally.

Figure 5.3: Drying of a fired-clay brick sample saturated with a 3 m NaCl solution. All sides are sealed except for the top surface (4 mm). The concentration profiles are shown every 10 hours for a total of 90 hours.

Figure 5.4: Drying of a fired-clay brick sample saturated with a 1 m Na₂CO₃ solution. All sides are sealed except for the top surface. The moisture profiles a) and concentration profiles b) are shown every 10 hours for a total of 300 hours. The critical moisture content is indicated by a dashed line. A distinct drying front can be observed.
5.2 Behaviour of thenardite

Above 32.4°C the only stable phase in the phase diagram of sodium sulfate is thenardite. Therefore the first experiment was started at 40°C. A fired-clay brick sample was saturated with a 2.0 molal solution at 40°C. The temperature was kept constant during the drying (see Fig. 5.5).

In Fig. 5.6a) the moisture profiles and b) the salt concentration profiles are shown. The top of the sample (evaporation surface) corresponds to 4 mm, and the bottom of the sample corresponds with 40 mm. At t=0, the moisture is homogeneously distributed across the sample. During the drying the moisture profiles remain flat, indicating that the moisture transport is limited only by external factors. No drying front is yet observed for low moisture content. The moisture is transported to the surface were it evaporates. Along with the moisture the salt is advected to the surface. The concentration near the top surface increases until the maximum solubility corresponding to thenardite (3.5 m) is reached. Eventually the entire sample reaches a concentration of 3.5 m.

NB. Near the end of the experiment the moisture content reaches zero. As a result the concentration cannot be calculated. The concentration profiles near the end are therefore not shown due to an increased noise.

In Fig. 5.7 the sodium profiles are shown for a) the first 30 hours and b) from 30 to 100 hours. The sodium which is measured is still in solution. A decrease in sodium is a result of crystallisation. In the first 30 hours the transport of sodium ions due to advection is observed. An increase of sodium at the surface and a decrease at the back of the sample can be seen (Pe>1). After 20 hours the maximum solubility of 3.5 m is reached at the front of the sample and crystallisation is initiated. In Fig. 5.7b can be seen that the amount sodium in solution is decreasing at the front. The drying of the sample continues and thus sodium is still transported to the surface resulting in a further decrease of sodium in the back of the sample. Eventually the transport of water to the surface will decrease and diffusion will dominate (Pe<1), resulting in an increase of the concentration in the entire sample.

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Figure 5.6: a) Moisture profiles are shown every 10 hours for a total of 140 hours. At low moisture content no distinct drying front is observed. b) Concentration profiles are shown every 10 hours for a total of 120 hours. The start concentration (2 m) and the maximum solubility (3.5 m) at 40° are shown by the dashed lines.

Figure 5.7: a) Sodium profiles are shown every 10 hours for the first 30 hours and b) from 30 to 140 hours. The first and last sodium profiles are indicated by the dashed lines.
4.5 Results

Figure 5.8: Schematic representation of the experiment. A fired-clay brick sample saturated with a 2.5 m solution at 40°C is cooled down to 20°C. The drying is started at 20°C. The maximum solubility for mirabilite (10 H₂O) is 1.35 m and for the heptahydrate is 3.15 m. Drying air flow of 5 l/min and 2% RH.

5.3 Heptahydrate or Mirabilite?

Below 23.6°C two phases are present in the phase diagram, mirabilite and the heptahydrate. As shown by Rijniers et al. that with crystallisation induced by temperature change in general the heptahydrate is being formed. In this experiment a fired-clay brick sample was saturated at 40°C with a 2.5 m solution. After measuring 1 profile at 40°C, the temperature was decreased to 20°C, which forced the solution to supersaturate with respect to mirabilite, but still not at the concentration of the heptahydrate. After 1 profile at 20°C the air flow was started. The temperature was kept constant at 20°C throughout the drying (see Fig. 5.8).

In Fig. 5.9a the moisture profiles are shown every 20 hours for a total of 600 hours. The sample is positioned from 3-40 mm. The moisture remains homogeneously distributed until the moisture reaches the critical moisture content. However, no distinct drying front develops and in the top half of the sample (3-15 mm) the moisture remains homogeneous. A drying front is observed from 15-40 mm. Without salt the drying front will start at the top of the sample (see Fig. 3.3b). The high concentration of 2.5 m results in a decrease of the critical moisture content.

In Fig. 5.9b the concentration profiles are shown every 20 hours for a total of 600 hours. Due to advection salt is transported to the top of the sample (Pe>1). However, due to crystallisation no significant increase of salt in the top 10 mm of the sample is observed (see Fig. 5.10). The concentration in the top 10 mm of the sample increases to ~3 m. The maximum solubility of the heptahydrate is 3.15 m (see Fig. 5.9). The bottom half of the sample (20-40 mm) the concentration remains at 2.5 m.

In the first experiment at the beginning of the chapter it was seen that mirabilite crystallisation at one point in the sample caused a decrease in concentration to the maximum solubility of mirabilite (1.35 m) in the entire sample. No decrease in concentration due to mirabilite crystallisation is observed. This is an indication that no mirabilite has crystallised.
5.3 Heptahydrate or Mirabilite?

Figure 5.9: a) Moisture and b) concentration profiles are shown every 20 hours for a total of 600 hours. The maximum solubility lines are shown for the heptahydrate (3.15 m) and mirabilite (1.35 m) phases at 20 °C.

Figure 5.10: Salt content profiles are shown every 20 hours for a total of 600 hours.
5.4 Drying from equilibrium starting point

In the previous experiment the starting point for drying was a supersaturated solution with respect to mirabilite. For the next experiment, the sample was saturated with a 1 m solution at 20°C. The temperature was kept constant at 20°C (see Fig. 5.11).

In Figures 5.12a and 5.12b the moisture and concentration profiles are shown. The sample is positioned from 3-40 mm. The moisture remains homogeneously distributed during almost the entire drying process. No distinct drying front is observed. In the front half of the sample (3-20 mm) the moisture remains homogeneously distributed while it decreases to zero. From 20-40 mm a drying front develops. The critical moisture content is \( \approx 0.2 \).

A peak in the concentration develops at the top of the sample (\( Pe > 1 \)). The concentration increases to about 2.5 m, which is above the maximum solubility for mirabilite (1.35 m) but below the maximum solubility of the heptahydrate (3.15 m). Two possible explanations can account for the increase of the concentration. First, it is known that the sodium sulfate solution can sustain an amount of supersaturation. However, if the supersaturation increases above a certain maximum concentration (threshold) the supersaturation cannot be sustained. Crystallisation to mirabilite is initiated. Secondly, the maximum concentration of the heptahydrate is reached. This means that the concentration is underestimated. In the discussion at the end of this chapter possible explanations are given on why the concentration can be underestimated.

In Fig. 5.13a the sodium content profiles are shown every 10 hours for the first 30 hours, and in Fig. 5.13b for the remaining 314 hours. In the first 30 hours sodium is transported to the surface and a peak builds up near the surface (\( Pe > 1 \)). After 30 hours the increase of sodium at the surface stops due to crystallisation. In Fig. 5.13b a further decrease in sodium is observed in the top of the sample. In the bottom half of the sample (20-40 mm) the sodium content remains constant indicating that no crystallisation is taking place.
5.4 Drying from equilibrium starting point

Figure 5.12: a) Moisture and b) concentration profiles are shown every 10 hours for a total of 140 hours. No distinct drying front is observed. The critical moisture content is low. The maximum concentration which is reached is 2.5 m, in between mirabilite (1.35 m) and the heptahydrate (3.15 m).

Figure 5.13: Sodium content profiles are shown every 10 hours for a) the first 30 hours and b) for 30-140 hours. a) Initial increase of sodium near the top surface and a decrease at the bottom, indicating salt transport due to advection. b) Crystallisation taking place in the top half of the sample.
5.5 High relative humidity drying

The influence of the relative humidity on the drying process was studied by increasing the RH to 70%. An RH of 70% was chosen because it is closer to the equilibrium RH of mirabilite (~80%). The sample was saturated with a 1 m solution at 20°C (see Fig. 5.17). In Fig. 5.15 the moisture profiles a) and concentration profiles are shown every 10 hours. The sample is positioned from 3-40 mm. In the first 24 hours the same drying rate is observed as with an RH of 2%. After 24 hours the drying rate decreases. At a moisture content of 0.4 the drying stopped. Examining the sample after the experiment revealed a salt crust (1-2 mm) on the top surface, preventing further drying. The salt on top of the sample was thenardite. Advection of water and salt to the surface results in an increase of concentration at the top surface (Pe>1). The maximum concentration reached is ~3 m. After the drying stopped the concentration increased also at 10-30 mm due to diffusion of sodium (Pe<1). In Fig. 5.12 the sodium content profiles are shown every 10 hours for a) the first 90 hours and b) the remaining 570 hours. Initially fast evaporation is observed (Fig. 5.15a). The salt content increases in the top 10 mm of the sample. After 60 hours crystallisation is observed. The remaining 480 hours the evaporation decreased and eventually stopped at a moisture content of 0.4. No significant change can be observed in the corresponding sodium content profiles. All the salt has been transported to the surface where it crystallised on top of the sample.
5.5 High relative humidity drying

Figure 5.15: a) Moisture profiles and b) concentration profiles are shown every 10 hours. Evaporation stopped at a moisture content of 0.4 due to salt which accumulated at the top surface. The concentration increases at the top surface to 2.7 m, which is higher than the maximum solubility of 1.35 m for mirabilite. At the bottom of the sample the concentration decreased slightly.

Figure 5.16: Sodium content profiles are shown every 10 hours for a) 0-90 hours, and b) for 90-570 hours. Initially sodium transport to the surface is observed. After 60 hours crystallisation is initiated, and a decrease in sodium is observed. No change is observed in the salt content after the evaporation stopped.
Figure 5.17: Schematic representation of the experiment. Drying of a fired-clay brick sample saturated with a 1 m solution at 20°C. The maximum solubility for mirabilite is 1.35 m, and for the heptahydrate is 3.15 m. Drying air flow of 1.7 l/min and 2% RH.

5.6 Slow drying

The influence of the air flow was also studied by decreasing the air flow from 5 l/min to 1.7 l/min. A fired-clay brick sample was saturated with a 1.0 m solution at 20°C (same as with the previous two experiments). The air flow had an RH of 2%.

In Fig. 5.18 the moisture profiles a) and concentration profiles b) are shown every 10 hours for a total of 314 hours. In the first 24 hours the same evaporation rate as with the previous two experiments was observed. The concentration increases at the top surface to ~2.5 m (Pe>1) and crystallisation takes place in the top 5 mm of the sample. After 24 hours the evaporation rate decreased the same as for drying with 70%. The concentration front moves further in the sample due to diffusion (Pe<1). The salt which crystallised just below the surface could be acting as a source.

In Fig. 5.19 the sodium profiles are shown every 10 hours for a) the first 160 hours and b) the remaining 154 hours. Initially Pe>1 and a sodium peak builds up. Due to a decrease in evaporation, diffusion becomes dominant (Pe<1).

Figure 5.18: a) Moisture and b) concentration profiles are shown every 10 hours for 314 hours. After the first 24 hours the evaporation decreases significantly. The maximum concentration which is reached is about 2.6 m.
5.6 Slow drying

Figure 5.19: Sodium profiles for a) 0-70 hours and b) 70-314 hours. The profiles are shown every 10 hours. During the first 24 hours salt is transported by advection to the surface. A decrease in the overall sodium signal indicates some crystallisation close to the surface. Due to very low evaporation rate diffusion is the dominant transport mechanism. The crystallised salt at the surface is acting as a buffer.

If diffusion is the dominant transport mechanism the salt content in Fig. 5.19 profiles will move further in the sample with $\sqrt{t}$. In case of no advection and a homogeneous moisture distribution the salt transport equation (Eq. 3.8) simplifies to:

$$\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2}$$

(5.1)

The sodium density $\rho$ is defined as $\rho = C \theta$. The solution of this equation is the error-function:

$$\rho(x, t) = \rho_b + (\rho_s - \rho_b) \text{erfc} \left( \frac{x}{\sqrt{4Dt}} \right),$$

(5.2)

where $\rho_s$ and $\rho_b$ are the sodium densities at the evaporation surface and the bottom of the sample respectively. The salt content profiles in Fig. 5.19 are scaled with the $\sqrt{t}$ and are shown in Fig. 5.20. The salt content profiles can be fitted with Eq. 5.2 in Fig. 5.20. From the fit a diffusion coefficient of $D=0.5 \times 10^{-10} \text{m}^2 \text{s}^{-1}$ is found. The diffusion coefficient is lower than the bulk diffusion for sodium ($D=1.3 \times 10^{-9} \text{m}^2 \text{s}^{-1}$) which is realistic.

Figure 5.20: The salt profiles of Fig. 5.19 are scaled with the $\sqrt{t}$. An error function (Eq. 5.2) is fitted through the scaled sodium profiles a diffusion coefficient of $0.5 \times 10^{-10} \text{m}^2 \text{s}^{-1}$ is found.
5.7 Low temperature drying

To study the influence of the temperature on the maximum concentration reached before crystallisation, two additional experiments were done. A fired-clay brick sample was saturated with a 0.5 m solution at 10°C (see Fig. 5.21). The maximum solubility of mirabilite is 0.65 m and for the heptahydrate 2.15 m.

In Fig. 5.22a) the moisture profiles are shown every 10 hours for a total of 120 hours. The sample is positioned from 3-42 mm. The evaporation rate is fast compared to the previous experiments due to the low salt concentration (as explained in Section 3.3.1). At a critical moisture content of 0.3 a distinct drying front can be observed, starting at the top of the sample.

Ions are transported to the surface by advection \((\text{Pe}>1)\) (see Fig. 5.23). As a result the concentration increases close to the surface. The maximum concentration which is reached is \(\sim 2\) m (see Fig. 5.22). Crystallisation started at 1.3 m which is below the maximum solubility of the heptahydrate. From 20-40 mm the concentration slightly decreases.

The starting concentration of 0.5 m is a factor 2 lower than for the previous measurements. The amount of sodium is on the limit of what is possible to measure with this setup. The noise in the salt profiles and corresponding concentration profiles is therefore high.
Figure 5.22: a) Moisture and b) concentration profiles are shown every 10 hours for 0-120 hours. Due to the low concentration of 0.5 m the evaporation rate is fast compared with other experiments. A drying front develops at the top of the sample. The maximum concentration which is reached is ~ 1.5 m.

Figure 5.23: Sodium content profiles are shown every 10 hours for a) 0-30 hours, and b) for 30-120 hours. Initially sodium transport to the surface is observed. After 30 hours crystallisation is initiated, and a decrease in sodium is observed.
### 5.8 Absence of heptahydrate

![Figure 5.24: Schematic representation of the experiment. Drying of a fired-clay brick sample saturated with a 1 m solution at 28°C. Drying air flow of 5 l/min and 2% RH.](image)

The heptahydrate phase can only exist below 23.46°C. To study the crystallisation behaviour of sodium sulfate in absence of the heptahydrate phase the next experiment was started at 28°C with a solution of 1 m. This temperature is below the mirabilite-thenardite transition point of 32.4°C (see Fig. 5.24).

In Fig. 5.25a the moisture profiles are shown every 10 hours for a total of 210 hours. Above the critical moisture content the moisture remains homogeneously distributed. At a critical moisture content of 0.15 a drying front develops at the top surface.

In Fig. 5.25b the concentration profiles are shown every 10 hours. At the top 10 mm of the sample the concentration increases (Pe>1) to a maximum concentration of ~2.7 m before crystallisation started. The maximum solubility for mirabilite at 28°C is 2.5 m, indicating that mirabilite is crystallising. At 28°C the solubility line for mirabilite strongly depends on the temperature. Within the accuracy of the temperature control (≈0.3°C) the maximum concentration can change ±0.2 m. Therefore the interpretation of the maximum solubility is difficult. The concentration in the top 15 mm further increases to ~3 m.

In Fig. 5.26 the salt content profiles are shown every 10 hours for a) the first 40 hours and b) for the remaining 170 hours. The sodium content increases at the top surface until crystallisation starts (Pe>1). In Fig. 5.26b it can be seen that almost all the salt is transported to the top surface where it crystallises.
Figure 5.25: a) Moisture profiles and b) concentration profiles are shown every 10 hours for 0-210 hours. The maximum solubility of the mirabilite phase is at 2.5 m. The moisture profiles show a very low critical moisture content compared to previous experiments.

Figure 5.26: Sodium profiles for a) 0-40 hours and b) 40-210 hours. The profiles are shown every 10 hours. During the first 40 hours salt is transported by advection to the surface. A decrease in the overall sodium signal indicates some crystallisation close to the surface. b) Almost all the salt is transported to the top 10 mm of the sample.
The salt distribution after drying in the fired-clay brick sample was measured with an ion chromatograph (IC). The sample was cut in 8 pieces of each 5 mm long. Each piece was ground to fine dust. To each sample 15 ml ultrapure water was added to dissolve the salt. The salt content for each of the 8 pieces is shown in Fig. 5.27. As can be seen almost all salt is transported to the top of the sample. The salt contents in Fig. 5.27 correspond with the salt concentration profiles in Fig. 5.25b and the salt content in Fig. 5.26.

Figure 5.27: Salt content in the fired-clay brick sample measured with an ion chromatograph, with 1 corresponding to the top surface and 8 to the bottom of the sample. All samples were 5 mm thick. Almost all the salt is transported to the top of the sample, where it has crystallised.
5.9 Discussion

5.9.1 Comparison of the experiments

In the previous experiments three were started with a solution of 1 m at 20°C. The drying conditions (air speed and RH) were varied for each experiment, changing the drying rate. An RH of 2% and 70% and an air flow of 1.7 and 5 l/min were used.

The drying rates for these three experiments are shown in Fig. 5.28. Drying with 5 l/min yields a significantly higher drying rate as for 1.7 l/min. Furthermore, drying with 70% RH (5 l/min) yielded the same drying rate as with an air flow of 0% (1.7 l/min).

For all three experiments the initial drying rate for the first 24 hours is independent of the environmental conditions. A possible explanation is that no crystallisation was observed in the first 24 hours.

![Figure 5.28: a) The total moisture content for the previous 3 experiments which all started with 1 m concentration at 20°C. Only the environmental conditions are varied. The three different experiments were with an air flow of 5 l/min and an RH was 2%, an air flow of 5 l/min with an RH of 70%, and an air flow of 1.7 l/min with an RH of 2%. b) The mean concentration in the top 5 mm of the sample as a function of time for the same three experiments.](image)

The maximum concentration which is reached is the same for all three experiments. The different environmental parameters influence the rate at which the maximum concentration is reached. The mean concentration in the top 5 mm of the sample for the three experiments are shown in Fig. 5.28b. The maximum concentration is first reached with an RH of 2%, and 5 l/min air flow. The increase in concentration for the other two experiments is the same with RH 70% - 5 l/min, and RH=2% - 1.7 l/min respectively.

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5.9.2 Maximum concentration

The maximum concentration which is reached depends on the temperature. The relative humidity and air speed only influence the rate at which the concentration is reached. In order to compare the maximum concentrations at different temperatures three experiments were done at 10°C, 20°C, and 28°C. The air flow was the same in all three experiments (2% RH, 5 l/min).

In Fig. 5.29 the maximum concentrations as a function of temperature are shown in the solubility diagram of sodium sulfate. The maximum concentration depends strongly on the temperature and has the same trend as the solubility of the heptahydrate. However, the concentrations are too low. Two possible explanations for an underestimation of the concentration can be given. First, due to evaporation the top part of the sample can cool down significantly (~2-3°C) [Pel95]. The maximum solubility of both the heptahydrate and mirabilite phases depend strongly on the temperature.

Secondly, the relaxation time $T_2$ for hydrogen and sodium depends on the pore size. Faster relaxation is observed for water and sodium confined in increasingly smaller pores. In a drying porous material the water or salt solution will recede in smaller pores, and thus decreasing the relaxation times for hydrogen and sodium. Hydrogen is measured with a shorter $T_E$ as sodium, $T_E$ is 205 μs and 800 μs respectively. It is possible that the decrease in sodium signal due to fast relaxation is higher than the decrease in hydrogen signal. As a result the concentration will be underestimated. If these arguments are taken into account the maximum concentration line corresponds more to the maximum solubility of the heptahydrate.

At a temperature of 28°C the concentration corresponds to the maximum solubility of thenardite. Although 28°C is below the mirabilite-thenardite transition temperature of 32.4°C, thenardite precipitation from a bulk solution below 32.4°C has been observed before [?].

![Figure 5.29: The maximum supersaturation reached during drying as a function of temperature in the solubility diagram of sodium sulfate. The air flow and RH of the drying air were the same for all three experiments (2% RH, 5 l/min).](image-url)
5.9.3 XRD experiments

With the NMR experiments only the concentration of the solution inside the porous material can be measured. The concentration is used as an indirect way to identify the crystal phase which is crystallising. X-ray diffraction (XRD) can be used to identify crystalline materials. XRD experiments were performed on stones saturated with a sodium sulfate solution. The experiments were done at the Synchrotron Radiation Source (SRS) in Daresbury England. At the SRS it is possible to identify salt crystals inside the stone.

Three different stone types (fired-clay brick, Savonière, and Monks Park Limestone) were saturated with a 2.5 m sodium sulfate solution at 40°C. Crystallisation was initiated by cooling the samples down to 5°C. Two XRD diffraction patterns are shown in Fig. 5.30. On the horizontal axis the reciprocal d-spacing, with \(d\) the distance between the crystal planes, and on the vertical axis the intensity. The diffraction peaks for mirabilite are shown with a vertical black line, the heptahydrate with a vertical dashed line, and calcite with a vertical dash-dotted line. A close up of Fig. 5.30a can be seen in Fig. 5.30b. Three heptahydrate peaks and two mirabilite peaks can be seen close to one another. However, the peaks observed in the close up are not from the mirabilite alone. Most likely the diffraction pattern is generated by a combination of both heptahydrate and mirabilite.

![XRD diffraction patterns](image)

**Figure 5.30:** XRD diffraction pattern of the salt inside a fired-clay brick sample. On the horizontal axis the reciprocal d-spacing with \(d\) the distance between the crystal planes. The sample was saturated with a 2.5 m sodium sulfate solution. The XRD pattern is measured at 5°C. The black lines represent peaks from mirabilite and the dotted lines are from the heptahydrate. The dashed line in b) represent peak from the fired-clay brick.
Chapter 6

Conclusions and recommendations

A total of eight drying experiments were performed on fired-clay brick samples saturated with sodium sulfate solutions. In these eight experiments the concentration, temperature, air speed, and relative humidity were varied. The conclusions from these experiments will be presented in this chapter. Also some recommendations will be given on future investigation of salt crystallisation in porous building materials.

6.1 Conclusions

The phase diagram of sodium sulfate can be divided in three temperature regions. Above 32.4°C thenardite is the only stable phase. Crystallisation of thenardite was observed during drying of a fired-clay brick at 40°C.

In the temperature region 0-23.6°C both the heptahydrate and mirabilite phases are present. During drying of a fired-clay brick in this temperature region a significant increase of the concentration above the maximum solubility of the mirabilite phase was observed. The maximum concentrations reached in these experiments were close the maximum solubility of the heptahydrate.

The heptahydrate phase plays an important role in the crystallisation behaviour of sodium sulfate during temperature changes as well as drying. Therefore the metastable phase should be taken into account in future studies on sodium sulfate crystallisation.

6.2 Recommendations

A number of recommendations will be given for future studies on sodium sulfate crystallisation. First of all additional measurements alongside NMR are important. With NMR only the concentration can be used as an indication for which phase is crystallising.

Furthermore, the pressure which is generated during the drying can be monitored by measuring the expansion of the sample or with piezo-electric sensors. The nature of the pressure, e.g. a transient pressure during the actual crystallisation or a pressure which is present for a prolonged period time, is important for future damage models.

With the current NMR setup water and sodium can only be measured in the liquid phase. With continuous wave NMR water and sodium in both solution and crystal can be measured. Hence, a distinction can be made between water lost by evaporation and crystallisation. By weighing the sample a quantitative indication can be given on which hydrated phase is crystallising.

In practical crystallisation experiments repeated cycling of RH and temperature are commonly used. In these experiments (so-called accelerated crystallisation tests) the damage to stones is visible within days. These accelerated tests can also be monitored using NMR.
Part B
Abstract

Concrete is one of the most commonly used building materials. The main components of concrete are cement and water. Mixed together cement and water react in a so-called hydration reaction. The most important phase in the development of cement are the first 3 days. In these first days the changes in the cement are most pronounced. The weak cement paste is converted into a strong material with a high compressive strength ($\sim 10^6$ N/m$^2$).

During the hydration the pore size distribution of a cement changes. Also, the total water content decreases because water is used in the reactions. Both these processes can be monitored with NMR. The pore size evolution during the initial 72 hours of hydration is followed with NMR relaxometry. To obtain a quantitative indication for the pore size distribution additional cryoporometry measurements were done after 72 hours. A total of seven different cements were studied.

No significant differences were measured in the hydration rates of the cements. In the evolution of the pore sizes distinct differences were found. Furthermore, with cryoporometry it was possible to obtain a quantitative measure for the capillary pore size.

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B.1 Hydration of cement

In the construction/building sector concrete is one of the most commonly used building materials. It is often used because it is easy to shape, primary products are easily available all over the world, it has a high compressive strength, and most importantly it is a very cheap building material. Concrete is a mixture of cement, water, and coarse aggregates (gravel, or crushed stone). The cement and water react in a so-called hydration reaction. The first 72 hours of cement hydration are most important for the development of cement. After 72 hours the changes in a cement due to hydration are minimal. With NMR it is possible to measure the water content, and the pore size distribution of a cement paste (basic component of concrete) during hydration. This was done for a number of different cements during the initial 72 hours of hydration.

1.1 Cement

Cement is defined as a fine, anorganic powder which forms a paste that hardens when mixed with water. This reaction is called hydration. The reaction products keep their strength and stability after hydration, even underwater [Kri03]. There are different types of cement which all consist of a main ingredient, 'Portland cement klinker'. However, based on secondary ingredients the cement types can be divided in five main groups: CEM I to V. These main categories are divided in a number of cements each with slightly different constituents and properties. In Table 1.1 the six ENCI cements which were investigated are given. The begin binding time, the specific surface, and the 2-day strength are also given. The begin binding time gives an indication how long the cement is workable, and a larger specific surface means a faster reaction. The 2-day strength is the strength of the cement after two days.

Table 1.1: The six cements which are produced by ENCI. These six cements were investigated with NMR. The data is from ENCI [Kri03].

<table>
<thead>
<tr>
<th>Cement type</th>
<th>Common name</th>
<th>Begin binding (min.)</th>
<th>Specific surface ($m^2/kg^{-1}$)</th>
<th>2-day strength (N mm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM I 32.5 R</td>
<td>Portland cement</td>
<td>150</td>
<td>290</td>
<td>19</td>
</tr>
<tr>
<td>CEM I 42.5 N 'white'</td>
<td></td>
<td>180</td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>CEM II/B-M (V-L) 32.5</td>
<td>Portland composite</td>
<td>190</td>
<td>420</td>
<td>23</td>
</tr>
<tr>
<td>CEM II/B-V 32.5 R</td>
<td></td>
<td>180</td>
<td>430</td>
<td>22</td>
</tr>
<tr>
<td>CEM III/B 42.5 N LH HS</td>
<td>Blastfurnace</td>
<td>240</td>
<td>520</td>
<td>12</td>
</tr>
<tr>
<td>CEM V/A (S-V) 42.5 N</td>
<td>Puzzolane</td>
<td>190</td>
<td>500</td>
<td>19</td>
</tr>
</tbody>
</table>
1.2 Hydration

The hydration of cement can be divided in 4 different phases:

1. Pre-induction phase (first minutes)
2. Dormant period
3. Acceleration phase (after 5-12 hours)
4. Post acceleration phase

In the first phase, called the pre-induction phase, the cement is just mixed with the water. An initial fast exothermal reaction takes place in the first few minutes after the mixing, which forms a protective layer around the cement grain. Due to this layer the initial reaction slows down or even stops completely. This is the beginning of the dormant period, which takes about 3-5 hours. In this period the crystals which are formed due to hydration are too small to connect between the cement grains. After the dormant period the acceleration phase begins. In this phase the hydration speeds up again due to hydration of tri-calcium silicate (C₃S). The hydration products of this hydraulic compound (tobemorite) gives the concrete its initial strength. The crystals which are formed are needle like and will interconnect. This reaction is also exothermal. The hydration speed gradually decreases and the post acceleration phase begins. In this phase the bi-calcium silicate (C₂S) is the main reaction component. The reaction is less exotherm. The same hydration products are formed as with the hydration of C₃S. However, these will have a smaller crystal form and will occupy the space in between the tobermorite needles (see Fig. 1.1). The water which is consumed by the hydration reaction leaves pores with a typical radius ~30nm. The pores created in between the tobermorite crystals are smaller (~ 5-10nm). These two pore types are called the capillary and gel-pores respectively.

Figure 1.1: a) Hydrated cement crystals. Picture is made with a scanning electron microscope. b) Heat produced by a cement paste during hydration. The 4 different hydration phases are indicated.
Figure 1.2: a) The NMR signal as a function of time for bulk water and water present in cement. For bulk water mono-exponential decay is observed, and for the water in cement bi-exponential decay. b) A schematic diagram of a pore with volume V and surface area S. A water molecule moves through the pore due to diffusion.

1.3 Theory

1.3.1 NMR relaxometry

In Chapter 4 of part A, the magnetisation relaxation mechanisms were described. The transverse and longitudinal relaxation of bulk water can be described with a mono-exponential decay ($T_1 \sim T_2 \sim 2-3$ s). However, when water is confined in a porous material the relaxation is much faster and in case of cement it is no longer mono-exponential (see Fig. 1.2a). Consider a pore with a diameter $d$, surface area $S$ and volume $V$ (see Fig. 1.2b). During an NMR experiment a water molecule moves through the pore space due to diffusion. According to the Brownstein-Tarr model the relaxation time of a liquid inside a pore ($T_{2,\text{pore}}$) is given by:

$$\frac{1}{T_{2,\text{pore}}} = \frac{1}{T_{2,\text{bulk}}} + \rho_2 \frac{S}{V}$$  \hspace{1cm} (1.1)

where $T_{2,\text{bulk}}$ is the $T_2$ of the bulk solution, $\rho_2$ is the surface relaxivity, and $\frac{S}{V}$ is the ratio between the surface and volume of the pore. The basic assumption in this model is that a water molecule near the surface has a higher relaxivity than a water molecule in the middle of the pore. The model also holds for the longitudinal relaxation time ($T_1$). For a cylindrical pore $\frac{S}{V} = \frac{\pi d}{4}$ and for a spherical pore $\frac{S}{V} = \frac{4}{3}$. Often the bulk relaxation $T_{2,\text{bulk}}$ is much larger than $T_{2,\text{pore}}$. Therefore the transverse relaxation time of a liquid confined in a porous material (assuming spherical pores) simplifies to:

$$T_{2,\text{pore}} = \frac{d}{6\rho_2}$$  \hspace{1cm} (1.2)

The $T_2$ or $T_1$ distribution of water confined in a porous material will give an indication for the pore-size distribution. If the surface relaxivity ($\rho$) is known it is possible to calculate a quantitative pore-size distribution.
Table 1.2: Typical NMR parameters which are used for the CPMG sequence during the hydration of cement.

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
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<td>inter echo spacing (μs)</td>
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<tr>
<td>number of echoes</td>
<td>2048</td>
</tr>
<tr>
<td>number of averages</td>
<td>512</td>
</tr>
<tr>
<td>long delay (s)</td>
<td>0.5</td>
</tr>
<tr>
<td>90° pulse (μs)</td>
<td>15</td>
</tr>
<tr>
<td>180° pulse (μs)</td>
<td>30</td>
</tr>
<tr>
<td>z-gradient (mT/m)</td>
<td>96</td>
</tr>
</tbody>
</table>

The $T_2$ distribution is measured using a CPMG (Carl Purcell Meiboom and Gill) sequence [Vla99]. A CPMG sequence is basically a series of Hahn spin echoes (see Chapter 4). If a short inter echo spacing ($\approx 200\mu s$) and a small gradient (0.1 T/m) are used the influence of diffusion on the signal decay can be neglected. The spin echo intensities will decay with $\exp(-t/T_2)$. The typical NMR parameters which are used for the CPMG sequence are shown in Table 1.2.

In a porous material a variety of pore sizes are present. The total magnetisation is a sum of the individual pores with their own relaxation time $T_2,i$ and a weight factor $P_i$, which corresponds to the volume of the pore, i.e., $\sum P_i \exp(-t/T_2,i)$ [RVK02]. For a continuous distribution of pore sizes the sum is converted to the integral:

$$M(t) = M_0 \int_0^\infty P(T_2) \exp \left( -\frac{t}{T_2} \right) dT_2$$  \hspace{1cm} (1.3)

where $P(T_2)$ gives the volume fraction of pores with a relaxation time $T_2$. In fact, $M(t)$ is the Laplace transform of $P(T_2)$. The $T_2$ distribution is obtained by calculating the inverse laplace transform of the CPMG decay signal with the program Contin.

An example of a typical $T_2$ distribution of a cement is shown in Fig. 1.3. Two pore types can be distinguished, the gel-pores with a typical diameter in the order of 10 nm, and the capillary pores (30 nm).

![Figure 1.3: Typical $T_2$ distribution of a cement sample during hydration. Two pore types can be distinguished: gel pores and capillary pores.](image-url)
1.3.2 Cryoporometry

A method to get a quantitative pores size distribution is Cryoporometry, which is based on the melting point depression of a liquid confined in a pore. The growth of a small ice crystal will be impeded by the crystal liquid interfacial tension $\gamma_{cl}$, the same as with small salt crystals (see Section 2.3). As a consequence a small ice crystal can only maintain itself at a temperature below the bulk melting point of the liquid. This is completely analogous to the increased solubility of a small salt crystal. This phenomenon is called the melting point depression and is described by the Gibbs-Thomson equation:

$$\Delta T_m = T_m - T_m(d) = \frac{4\gamma_{cl} T_m}{d\Delta H_f \rho_c}$$

Where $T_m$ is the melting point of the free liquid, $T_m(d)$ the melting point of a crystal with diameter $d$, $\gamma_{cl}$ is the crystal liquid interfacial tension, $\Delta H_f$ the bulk enthalpy of fusion, and $\rho_c$ the density of the frozen liquid. The Gibbs Thomson equation applies to spherical crystals in a solution, but can also be applied to crystals in cylindrical pores because of the spherical sides of the crystal. According to Eq. 1.4 ice which is present in small pores ($d<1\mu m$) will have a lower melting point than the ice crystals in larger pores. In Equation 1.4 only the liquid-crystal interface is taken into account, and the solid-liquid and solid-crystal interfaces are neglected. When these surfaces also play a significant role a $\cos(\phi)$ correction factor has to be taken into account. The angle $\phi$ is the contact angle of the crystal, which is usually assumed to be 180°.

Equation 1.4 can be simplified to:

$$\Delta T_m = \frac{k}{d}$$

in which $k$ depends only on parameters of the liquid itself and interactions between the liquid and its solid ($\gamma_{cl}$). For water $k = 58 \text{nm}K^{-1}$, cyclohexane $k = 179 \text{nm}K^{-1}$, and benzene $k = 44 \text{nm}K^{-1}$.

In porous materials the pore geometry is often far from cylindrical, and deviations are to be expected. The value $k$ in Equation 1.5 is therefore not only a property of the liquid/crystal but depends also on the porous material and the pore geometry.

The melting of ice inside a porous material can be monitored with NMR [RVK02, Web01]. When a cement is cooled down to -50°C the water in the pores is frozen. No NMR signal is measured because of the very small $T_2$ of ice ($6 \mu s$). It must be noted that in small pores often cubic instead of hexagonal ice crystals are formed. Cubic ice has a longer $T_2$ ranging from 100 $\mu$s at -60°C to 200$\mu$s at -20°C.

During slow heating of the sample the NMR signal is measured continuously. At a certain temperature depending on the radius of the pore the ice begins to melt and the signal increases. At a certain temperature $T_m$ all pores with a diameter $d<k/T_m$ (see Eq. 1.5) contribute to the signal (S). Therefore the signal increase as a function of temperature is related to the pore size distribution in the following way:

$$\frac{\partial V}{\partial d} = \frac{\partial V}{\partial \Delta T_m} \frac{\partial \Delta T_m}{\partial d} = \frac{k}{d^2} \frac{\partial S}{\partial \Delta T_m}$$

In which $\frac{\partial V}{\partial d}$ represents the volume $V$ of all pores with diameter $d$, the so called pore size distribution. A review on cryoporometry is given by Webber et al. [WD04].

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1.4 Experimental setup

The cement hydration experiments were done on the 0.8 T NMR setup shown in Fig. 1.4a. The data acquisition is the same as for the setup described in part A (see Section 4.3).

Figure 1.4: a) NMR setup for mortar hydration experiments, with electro magnet, phydas acquisition system, and Lauda cooler with pump. b) A schematic diagram of the cryoporometry setup. Mortar sample is fitted in a teflon holder which can be cooled down to -70°C. A reference sample is used for compensating daily fluctuations.

1.5 Experimental methods

For the hydration experiments a small amount of cement paste (~100 ml, w/c=0.5) is prepared. A cylindrical perspex sample holder with a diameter of 17.8 mm and a height of 16.2 mm is used. To prevent evaporation of water the sample holder is sealed. A thermocouple is used to monitor the temperature during the hydration and the cryoporometry experiment. The perspex holder is placed in a pvc thermostated holder (see Fig. 1.4b). The holder is kept at a constant temperature by a Lauda thermostat (RL6CP). This Lauda is capable of cooling down to -70°C. The Galden HT70 liquid is used as the heat transfer liquid.

The amount of water lost due to the different hydration reactions is monitored during 72 hours. Every 30 minutes the total intensity, \( T_2 \) distribution, and temperature are measured. A reference sample is used to compensate for daily fluctuations in the resonance frequency.

After 72 hours of hydration the sample is cooled down to -50°C for a cryoporometry measurement. The sample is slowly heated (0.04 °C/min) up to a temperature of 5 °C. During the heating of the sample the \( T_2 \) distribution is measured continuously, making it possible to measure the gel and capillary pores independently.
1.6 Results

In this section the results of the hydration experiments for seven different cements and the cryoporometry measurements on two cements will be presented.

1.6.1 Hydration

In Figure 1.5a the total water content as a function of time of a cement sample during hydration is shown. Water is used in the hydration reaction, and hence the total water content decreases. The different hydration phases can be identified. The pre-induction period is missed because it takes some time to place the sample in the NMR setup. However, the dormant period (II) and the two acceleration periods (III and IV) can be identified.

In Figure 1.5b the evolution of the two pore sizes (gel and capillary pores) is shown. The short relaxation times correspond to the gel pores and the longer relaxation times correspond to the capillary pores. During the hydration a shift towards shorter relaxation times can be observed for both gel and capillary pores. The intensity of the capillary pores decreases because water is used in the hydration reactions. The intensity of the gel pores increases, indicating that more gel pores are being formed and water is transported to the smallest pores.

**Figure 1.5:** a) NMR measurements of the total water content in a CEM II sample during the initial 72 hours of hydration. The three different hydration phases can be identified. After the cement and water are mixed it takes a few minutes to place the sample inside the NMR sampleholder. Therefore the pre-induction period is missed. b) Time evolution of the signal intensities and $T_2$ of the two pore systems (capillary (\(\times\)) and gel pores (\(\cdot\)) during the initial 72 hours of hydration. The arrows indicate the direction of increasing time.

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The total moisture content for the seven different cements during 72 hours of hydration are shown in Fig. 1.6. All cements show the same hydration behaviour. Small differences in the hydration speed can be seen, e.g., the two CEM I cements hydrate faster than the other cements. The 'gamma' cement hydrates the slowest.

![Figure 1.6: Total amount of water in cement samples during the 72 hours after mixing.](image)

In Fig. 1.7 the $T_2$ relaxation times for a) the capillary pores and b) the gel pores during the first 72 hours are shown. The two pore systems develop almost identical in time. The CEM I 'white' cement has less iron impurities. Therefore it has longer relaxation times. After hydration the relaxation times for both pores are however in the same range as for the other cements with iron.

The fast decrease in relaxation times for both CEM I cements can be a result of the high content of C$_3$S. C$_3$S is the first hydraulic component that reacts. The other cements have a lower content C$_3$S.

The evolution of the capillary pores of CEM I cements have a short delay from 10-30 hours, which is more distinct as for the CEM II, III or 'gamma' cements.

![Figure 1.7: $T_2$ relaxation times for a) the capillary pores and b) the gel pores during the 72 hours after mixing.](image)
Water cement ratio

The water cement ratio (w/c) influences the speed of the hydration reaction and also the strength of the cement. A lower w/c ratio results in a shorter distance between non-hydrated cement particles. The growing tobermorite crystals will bind the cement paste faster. Furthermore, the pores left behind by the water which is used during hydration will be smaller. A high water cement ratio will result in a more porous and hence brittle cement. The influence of the w/c ratio on the hydration reaction is shown in Fig. 1.8a for two cements: CEM I 42.5 N 'white' and CEM I 32.5 R. A w/c ratio of 0.3 will result in a faster hydration reaction.

Temperature

The temperature will also influence the hydration reaction. The diffusion will increase with temperature. In Fig. 1.8 the influence of the temperature is shown for one cement (CEM I 32.5 R) at 20°C and 30°C. Due to the increased diffusion the hydration reaction is accelerated.

Figure 1.8: The influence of the a) water/cement ratio and b) the temperature on the hydration reaction. The influence of the w/c ratio was measured for CEM I 42.5 N 'white' and CEM I 32.5 R. The influence of the temperature was measured only on the CEM I 32.5 R cement.
1.6.2 Cryoporometry combined with relaxometry

The cryoporometry results will be limited to the CEM II/B-V 32.5 R and CEM I 42.5 N white cements. In Figure 1.9 an intensity plot of the two combined cryoporometry and relaxometry measurements are shown. On the horizontal axis the temperature is given, and on the vertical axis the relaxation time ($T_2$) is shown. The color represents the intensity of the relaxation time distribution.

![Figure 1.9: Intensity plot of the combined cryoporometry and relaxometry measurement on the a) CEM II/B-V 32.5 R cement and b) CEM I 42.5 N 'white'. Blue indicates low intensity and red is a high intensity.](image)

Bulk ice has a $T_2 \approx 6\mu s$. In theory no signal should be measured at $-40^\circ C$. The signal which is observed at low temperatures and very short relaxation times in Fig. 1.9 is a result of cubic ice crystals.

As the temperature increases the intensity at very short relaxation times begins to shift towards longer relaxation times. The temperature at which the signal begins to shift is different for each cement type. The shifting of the signal to longer relaxation times can be contributed to melting of ice. During melting the ice crystal will decrease in size and the layer of water between the ice crystal and the pore wall will increase. The water molecules which are present in this layer will contribute to the signal with increasing relaxation time. In Fig. 1.9 it can be seen that the for CEM II the signal shifts at $-6^\circ C$, and for CEM I at $-15^\circ C$.

The signal from the capillary pores with a longer $T_2$ comes up around $-1^\circ C$ for all cements. No shift in relaxation time is observed.

As mentioned before the problem with the cryo experiments is the unknown surface relaxation. The signal of the gel pores for the CEM I cement comes up at a lower temperature than the signal of the CEM II cement. This indicates that the gel pores of CEM I are smaller. However, the relaxation time for the gel pores of CEM I at temperatures above $0^\circ C$ is longer than for the CEM II. Hence, the CEM I type cement must have a lower surface relaxivity due to a lower iron content.
In Fig. 1.10a the increase in the total signal intensity is shown as a function of the temperature. The signal increases as the temperature increases due to melting of ice confined in the pores. The derivative of the total signal as a function of the temperature is shown in Fig. 1.10b. From this curve the pore size distribution can be calculated using Eq. 1.6. However, only the capillary pores contribute significantly to the signal increase. A temperature of ~-1.5°C (see Fig. 1.10b) corresponds to a pore size of 39 nm according to Eq. 1.5. The contribution of the gel pores should be at a temperature of -6°C (corresponding to a pore size of 10 nm. A small increase in Fig. 1.10b can be seen in Fig. 1.10b at -6°C.

1.7 Conclusions

The hydration reaction of cement can be followed with NMR. The total amount of water, which gives an indication for the rate of hydration, can be measured as a function of time. Also, the evolution of the gel and capillary pore sizes can be measured with NMR relaxometry. Cryoporometry in combination with NMR relaxometry gives a quantitative indication for the capillary pore sizes. For the gel pores the gel pores the setup has to be improved to get a better result.
Dankwoord

bedankt! (wordt t.z.t. aangepast)
Bibliography


