Moisture and ion transport in layered porous building materials: a Nuclear Magnetic Resonance study

PROEFSCHRIFT

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1. Introduction

Plasters and renders may be applied as a finishing layer on masonry, for decorative, protective, and sometimes insulation reasons. They are used in new buildings, but also for restoration purposes in old buildings and monuments. The word ‘plaster’ is generally used for indoor, the word ‘render’ for outdoor applications. For simplicity, in this thesis only the word ‘plaster’ will be used. Plasters are applied on masonry, which here is generally referred to as substrate.

Once a plaster is applied it should be durable and its maintenance costs should be low. Among the most recurrent causes of damage of plasters and substrates are moisture and salt decay processes. Although salt damage has been intensively investigated for several decades [Püh83, Gou97], the mechanisms and factors that control the formation of salt crystals in porous media and the development of damage by crystal growth are poorly understood. Salt crystallization may occur at the surface of a plaster, causing efflorescence, or just below the surface, i.e., as sub-florescence or crypto-florescence. Here it may cause more severe damage like sanding and crumbling of the surface or exfoliation and delamination. Salt crystallization and subsequent salt weathering of porous building materials are important consequences of the drying process.

Special (‘better’) salt resistant plasters have been developed for application on salt loaded substrates. Based on their transport properties, two main categories of ‘better’ salt resistant plasters have been developed by industry: transporting and accumulating plasters [Wij97]. These are schematically shown in figure 1.1. In salt transporting plasters, salt is transported and is supposed to crystallize on the surface, where efflorescence may appear. Application of a paint layer may influence the moisture and salt transport in these plasters because of reduction of the drying speed. One of the problems in case of a paint application is that salt may crystallize just below the paint, which may cause damage to the paint, like blistering or peeling.

In salt accumulating plasters salt crystallizes in the base layer of the plaster, near the substrate. In general salt accumulating plasters contain additives, such as a water repellent in the finishing plaster layer, which prevents water and salt penetration into the top layer. Application of a completely water repellent layer has a big disadvantage, e.g., the risk of spalling of such a layer due to salt crystallization just below it.

In case of application of traditional plasters on salt loaded substrates, failures of traditional (lime based) plaster materials are reported, while prefabricated restoration plasters have shown a better performance [Hil95, Hil98, Kün96]. However, in several cases the durability and performance of these salt resistant plasters appears to be not quite satisfactory [Wij97, Lub05]. The prefabricated special plasters may fail because of their incompatibility with plasters that are already present and because of incompatibility with the substrate. A compatible plaster must allow the moisture and salt transport from...
1. Introduction

Fig. 1.1: Transport and accumulation in salt resistant plasters: a) transporting type, b) accumulating type (note that the actual system contains two layers). Salt crystallizes mainly in the dashed area.

the underlying material (substrate) to the plaster layer. Furthermore, the plaster should have a high durability and prevent damage to the substrate as much as possible [vH03b]. The compatibility between plasters and underlying materials is an important durability issue. However, in the guidelines of the Wissenschaftlich-Technische Arbeitsgemeinschaft (WTA) for restoration plasters [WTA92] the influence of the substrates on the plaster performance is not considered. Plasters are tested solely, without taking into account the properties of the substrate [Wij00].

To achieve a better plaster performance, more knowledge about transport and salt crystallization in the plasters and the substrates is needed. This thesis focuses on the moisture and salt transport in plaster/substrate systems during drying. Our aim is to investigate which material properties determine the transport behavior of the plaster, in particular, whether plasters are behaving as a transporting or an accumulating system. To study the influence of the substrate on the transport in the plasters, we have applied the same plaster on substrate materials with significantly different pore-size distributions. We also want to investigate the possibility to develop salt accumulating plasters without the use of a water repellent additive. To this end we have applied combinations of two layers of plasters with different pore sizes on the substrate.

In chapter 2 the theory of moisture and ion transport is introduced. The basic principles of the NMR technique, used for the experimental verification of the transport properties of porous materials, are given in chapter 3. The NMR equipment is reviewed together with the additional setup for controlling the environmental conditions of the samples that are investigated. The transport of moisture and salt in two-layer plaster/substrate systems is treated in chapter 4. In chapter 5 studies on the transport and salt accumulation in some three-layer systems are presented. Chapter 6 is devoted to the measurement of the water diffusion in building materials by NMR, which is complicated by the presence of high internal magnetic field gradients in these materials. Finally, in chapter 7 the main conclusions and suggestions for future research are given.
2. Transport of moisture and ions in porous media

The moisture and ion transport in saturated and unsaturated porous media is reviewed briefly. The drying behavior of a material is determined by capillary pressure, and therefore by pore-size distribution. As a consequence the largest pores are emptied first. In layered systems of different materials the material with larger pores should dry first. Ions are transported via diffusion and advection with the flow of the water. These processes are described by a diffusion-advection equation. The competition between advection and diffusion can be characterized by a Péclet number $Pe$. For high drying rates ($Pe \gg 1$) advection dominates the ion transport, whereas for low drying rates ($Pe \ll 1$) diffusion dominates the ion transport.

2.1 Introduction

The transport of moisture and salts can be considered at both a microscopic and macroscopic level. However, the detailed pore network and the transport over microscopic interfaces can hardly be assessed experimentally and are too complex to describe mathematically. Therefore, for practical relevance a description of the transport on a macroscopic level is needed. In this chapter some aspects of the theory of moisture and ion transport in porous media will be discussed. First, moisture transport in saturated and unsaturated porous materials is treated on a macroscopic level. Next, transport in multi-layer systems, including transport across the interfaces between the various layers, is connected to the macroscopic capillary pressure and the pore sizes of the layers. Finally, diffusive and convective transport of ions are considered.

2.2 Moisture transport

2.2.1 Saturated materials

Generally, moisture is transported by liquid and vapor. Liquid transport in a saturated porous medium can be described with Darcy’s law. The volume flux of water $q$ [$m^3m^{-2}s^{-1}$] through a water saturated porous medium is a function of the gradient of the pressure $p$ [Pa]. In the one-dimensional case this law reads:

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

(2.1)

where $k$ [$m^2$] and $\mu$ [kg m$^{-1}$s$^{-1}$] are the permeability of the material and the viscosity of the liquid, respectively.
2. Non-saturated materials

In non-saturated materials the volume flux \( q \) is the sum of the liquid flux \( q_l \) and the vapor flux \( q_v \). The liquid flux \( q_l \) can also be described with Darcy’s law [Dul91, Hal02]. However, now both the permeability \( k \) and the pressure \( p \) are functions of the liquid content \( \theta \):

\[
q_l = -\frac{k(\theta)}{\mu} \frac{\partial p(\theta)}{\partial x} .
\]  

The pressure in the liquid phase \( p \) [Pa] is given by the following expression:

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

where \( p_a \) and \( p_c \) [Pa] are the external air pressure and the capillary pressure, respectively.

At a macroscopic level the capillary pressure can be regarded as a function of the liquid moisture content \( \theta \). This dependence is described by capillary pressure curves [Dul91], which show that \( p_c \) increases with decreasing \( \theta \) in the case that water wets the solid. This can be understood as follows. At a certain water content \( \theta \), a pore radius \( r_m \) can be defined [Plu03, Kop00], that discriminates between pores filled with water \( (r < r_m) \) and empty pores \( (r > r_m) \). Assuming cylindrical pores, the capillary pressure at a certain value of \( \theta \) is given by the following expression [Dul91, Bea90]:

\[
p_c = \frac{2\gamma}{r_m} \cos \phi ,
\]

where \( \gamma \) [N m\(^{-1}\)] is the surface tension of the liquid/vapor interface and \( \phi \) is contact angle between liquid/air and liquid/solid interface. With increasing \( \theta \) the radius of the widest pore just filled with water, \( r_m \), increases and therefore \( p_c \) decreases.

The transport in the vapor phase is a diffusive process. When the vapor behaves as an ideal gas and the temperature over the sample is constant, the vapor flux \( q_v \) [m\(^3\) m\(^{-2}\) s\(^{-1}\)] obeys the following expression for the one-dimensional case [Dul91]:

\[
q_v = -vD_v \frac{\partial \rho_v}{\partial x} ,
\]

where \( D_v \) [m\(^2\) s\(^{-1}\)] and \( \rho_v \) [mol m\(^{-3}\)] are the diffusion constant and the molar density of the vapor, respectively. The quantity \( v \) [m\(^3\)] is the molar volume of water in the liquid phase. Both \( D_v \) and \( \rho_v \) are functions of the water content \( \theta \).

The rate at which the local moisture content varies can be found with the help of the law of mass conservation:

\[
\frac{\partial \theta}{\partial t} = -\frac{\partial q}{\partial x} = -\frac{\partial}{\partial x} (\theta U) ,
\]

where \( U \) [m s\(^{-1}\)] is the water velocity. When liquid transport dominates the water movement, \( U \) is in fact the velocity of the water in the liquid phase.

The velocity profiles can be calculated from the moisture profiles using the following equation, which can be derived directly from Eq. 2.6:
2.2. Moisture transport

\[ U(x) = \frac{1}{\theta(x)} \frac{\partial}{\partial t} \int_x^l \theta(x') \, dx'. \]  

(2.7)

In this equation \( l \) [m] is length of the sample and \( \int_x^l \theta(x') \, dx' \) is the integral of the moisture content over the sample from position \( x \) to \( l \). Here it is assumed that at \( x = l \) there is no flux, for instance, because the sample is sealed at that side.

Masonry is a composite material, consisting of brick units and mortar, which are materials with different transport properties. Additional mortar layers (plasters) are often applied on the masonry for decorative and protective reasons. In such multi-layer materials two types of interfaces can be identified: air/material and material/material [Pel95]. The air/material boundary conditions are treated in [Pel95, Hal02]. The drying rate is proportional to the vapor flux \( \vec{q}_v \) [m\(^3\)m\(^{-2}\)s\(^{-1}\)] at this boundary, which is given by:

\[ \vec{q}_v \cdot \vec{n} = \beta \rho_l (h_a - h_l), \]  

(2.8)

where \( \vec{n} \) is the unit vector perpendicular to the air/material interface, \( \beta \) [mol m\(^{-2}\)s\(^{-1}\)] the molar mass transfer coefficient, and \( \rho_l \) [mol m\(^{-3}\)] the molar density of liquid water. \( h_a \) is the relative humidity of the air and \( h_l \) the relative humidity at the air/fluid interface. The transfer coefficient \( \beta \) depends on many parameters, such as the air velocity, the thickness of the boundary layer above the drying surface, and the porosity of the material.

If two materials are in perfect hydraulic contact, at their interface a local equilibrium is assumed. Therefore, the pressure drop is negligible in comparison to the pressure drop in the whole system. The flux \( q \) and total pressure \( p \) at the interface are assumed to be continuous [Hal02, Bro97]:

\[ q_1 = q_2 \quad \text{and} \quad p_1 = p_2, \]  

(2.9)

where the indices 1,2 indicate both sides of an interface between two materials. Since at the interface local equilibrium is assumed, the composition of the fluid is the same at both sides of the interface and, hence, the salt concentration \( c \) is continuous at the interface. For partially saturated materials, the continuity of the total pressure results in a continuity of the capillary pressure, see Eq. 2.3. Therefore, \( r_m(\theta_1) = r_m(\theta_2) \), where \( \theta_1 \) and \( \theta_2 \) are the moisture contents in material 1 and material 2, respectively. In figure 2.1, pore-size distributions of some materials are shown. At a certain moisture content, water is present in pores with a radius smaller than \( r_m \) (shaded areas in Fig. 2.1). Since, generally, \( \theta_1 \) and \( \theta_2 \) are different functions of the pore-size distribution, the moisture contents in both materials will differ \((\theta_1 \neq \theta_2)\) and \( \theta \) will be discontinuous at the interface.

In the case of an imperfect contact the pressure drop cannot be neglected and an interfacial resistance should be incorporated for a correct description of the experimental results [Bro98b]. The equations for the moisture flux for perfect and imperfect hydraulic contact are given [Bro97]. One should note that the study described in this thesis is confined to drying experiments, which generally involve much longer time scales and much slower processes than wetting experiments. Indeed, numerical simulations of the transport over a brick-mortar joint [Bro98a] were in much better agreement with the experimental data for drying than for water absorption. Moreover, the impact of an interface permeability seemed to decrease as the drying of the sample proceeded.
2. Transport of moisture and ions in porous media

Fig. 2.1: Cumulative and differential pore volumes versus pore radius for two arbitrary materials. At a certain drying stage water is present in pores with pore radii \( r < r_m \). In general \( \theta_1 \neq \theta_2 \), since \( \theta_1 \) and \( \theta_2 \) are functions of the pore-size distribution, which is different for different materials.

2.3 Salt transport

For ion transport, the molar flux \( J \) [mol m\(^{-2}\)s\(^{-1}\)] obeys the following expression [Bea90]:

\[
J = 10^3 \theta \left( cU - D \frac{\partial c}{\partial x} \right).
\]

(2.10)

In this equation \( D \) [m\(^2\) s\(^{-1}\)] and \( U \) [m s\(^{-1}\)] are the ion diffusivity and the water velocity, respectively. The correction factor \( 10^3 \) is present since the concentration is given in mol l\(^{-1}\) instead of mol m\(^{-3}\). Because diffusion in porous media is restricted by pore walls, the diffusivity \( D \) [m\(^2\) s\(^{-1}\)] will always be smaller than the bulk diffusivity \( (D_0) \). The decrease of \( D \) in porous media can be quantified with a tortuosity factor \( \alpha \) [Bea90, Won99]:

\[
\alpha \equiv D_0/D.
\]

(2.11)

Tortuosity is a measure of the effective length of the transport paths in a porous material. Using a simple model of nonintersecting pores, the tortuosity is given by [Won99]:

\[
\alpha = \left( \frac{l_e}{l} \right)^2,
\]

(2.12)

where \( l_e \) is the effective length of the flow path through the system and \( l \) is the system size. Generally, the tortuosity increases with decreasing porosity \( n \) and with decreasing
moisture content $\theta$. The bulk diffusivity of the ions ($D_0$) and the ion diffusivity in a porous material ($D$) depend on the ion concentration $c$ \cite{Mil89}.

Changes in salt content can be calculated with the following law of mass conservation:

$$\frac{\partial c \theta}{\partial t} = -10^{-3} \frac{\partial J}{\partial x}. \quad (2.13)$$

where $10^{-3}$ is again the correction factor accounting for the fact that the concentration is given in mol l$^{-1}$ instead of mol m$^{-3}$.

By combining equations 2.10 and 2.13, the ion transport can be described with a diffusion-advection equation \cite{Wil88}:

$$\frac{\partial c \theta}{\partial t} = \frac{\partial}{\partial x} \left[ \theta \left( D \frac{\partial c}{\partial x} - cU \right) \right]. \quad (2.14)$$

This equation yields the variation of solute density $c \theta$ [mol l$^{-1}$] with time $t$ and position $x$. The first term at the right hand side accounts for diffusion and the second term for advection. The dissolved ions are transported by advection in the same direction as the water flows. Diffusion tends to level off the concentration differences in the sample.

The competition between advection and diffusion is characterized by a dimensionless Péclet number $Pe$ \cite{Bea90, Dul91}, which is defined as follows:

$$Pe = \frac{|U| L}{D}, \quad (2.15)$$

where $L$ [m] is the length scale of interest. For $Pe \gg 1$, the product of the water velocity and the length scale $|U| L$ exceeds the diffusion constant $D$. This reflects the situation where advection dominates the ion transport. For $Pe \ll 1$, the diffusion constant exceeds the $|U| L$ product, and diffusion dominates the ion transport.
2. Transport of moisture and ions in porous media
3. NMR

Nuclear Magnetic Resonance (NMR) is a non-destructive technique, suitable for probing the molecular motions on both microscopic and macroscopic scales, such as the transport of water and dissolved ions in porous materials. In this chapter we introduce the NMR methods and the NMR setup used for the experimental investigations described in this thesis. The time evolution of the moisture profiles and the profiles of dissolved sodium can be measured quasi-simultaneously, which enables us to monitor the transport of moisture and salt during drying of (layered) porous media on a macroscopic level. Using a Hahn spin-echo pulse sequence and a static magnetic field gradient of 0.3 T/m, measurements can be performed with a spatial resolution of 0.9 ± 0.1 mm for H and 3.5 ± 0.5 mm for Na, which is very accurate compared to conventional destructive techniques (hygroscopic moisture content analysis, chemical methods). It is outlined that using a stimulated echo pulse sequence the self-diffusion of water in porous materials can be measured up to diffusion times exceeding 1 s.

3.1 Introduction

Diffusion on both macroscopic and microscopic scales (self-diffusion) plays an important role in moisture and ion transport in porous media. For the experimental assessment of such molecular motions in bulk or in porous media, Nuclear Magnetic Resonance (NMR) has proven to be a non-destructive and sensitive technique [Woe61, Tan68, Kim97, Blü00]. NMR has been used to determine microscopic (self)diffusion constants of water and ions in a broad concentration range [Mil89]. In the present chapter the basics of the NMR technique are introduced first, followed by the Magnetic Resonance Imaging (MRI) method, which we use for monitoring macroscopic transport in porous media. Next, the methods and the NMR sequences for the determination of diffusion coefficients are given. Finally, the NMR measurement equipment used for the experiments presented in this thesis is described.

3.2 Principles of NMR

The principles of Nuclear Magnetic Resonance are treated in numerous papers and textbooks [Far71, Cal91, Lev01]. The method is based on the fact that most nuclei posses a nuclear magnetic moment (for $^1$H, this moment is about 2000 times smaller than that of an electron [Atk02]). When a sample is placed in an external magnetic field $\vec{B}_0$, the Hamiltonian ($H$) describing the interaction between the nuclear magnetic moment $\vec{\mu}$ and
the field $\vec{B}_0$ is:

$$H = -\vec{\mu} \cdot \vec{B}_0,$$

(3.1)

where

$$\vec{\mu} = \gamma \hbar \vec{I}.$$

(3.2)

Here $\gamma$ is the gyromagnetic ratio of the nucleus, $\hbar$ is Plank’s constant ($\hbar = 6.626 \times 10^{-34}$ Js) divided by $2\pi$, and $\vec{I}$ is the spin angular momentum (also called nuclear spin). The $\gamma$ and $I$ values of the nuclei that are of interest for the research presented in this thesis are given in the table 1, together with their natural abundances and relative NMR sensitivities.

Table 3.1: The gyromagnetic ratios ($\gamma$) and magnitudes of the nuclear spin ($I$) of some NMR sensitive nuclei.

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>$^1$H</th>
<th>$^7$Li</th>
<th>$^{19}$F</th>
<th>$^{23}$Na</th>
<th>$^{35}$Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin ($I$)</td>
<td>1/2</td>
<td>3/2</td>
<td>1/2</td>
<td>3/2</td>
<td>3/2</td>
</tr>
<tr>
<td>$\gamma/2\pi$ (MHz/T)</td>
<td>42.58</td>
<td>16.55</td>
<td>40.06</td>
<td>11.26</td>
<td>4.17</td>
</tr>
<tr>
<td>Natural abundance (%)</td>
<td>99.98</td>
<td>92.58</td>
<td>100</td>
<td>100</td>
<td>75.53</td>
</tr>
<tr>
<td>Relative sensitivity</td>
<td>1.00</td>
<td>0.29</td>
<td>0.83</td>
<td>0.093</td>
<td>0.0047</td>
</tr>
</tbody>
</table>

The nuclear energy levels are given by:

$$E = -\gamma \hbar m_I B_0,$$

(3.3)

where $\hbar m_I$ is the component of the spin angular momentum in the direction of $B_0$ ($z$ axis). $m_I$ has $2I + 1$ possible values: $I, I - 1, \ldots, -I$. The separation between two energy levels of a nucleus $\Delta E = \gamma \hbar B_0 \Delta m_I$. Resonance is achieved by absorption of energy which matches the separation between two nuclear levels. For $\Delta m_I = \pm 1$, the corresponding frequency is equal to $\gamma B_0 / 2\pi$.

A quantum mechanical approach is necessary to describe some features of NMR spectroscopy, but in most cases is easier to explain the NMR technique in terms of a semiclassical model, which will be given below.

At non-zero temperatures, the nuclear magnetic moments are generally inclined at some angle from the direction of $\vec{B}_0$. Because the nuclear magnetic moment is coupled to the spin, the magnetic moments will precess about the direction of the field with the Larmor frequency $\nu_L$:

$$\nu_L = \frac{\gamma B_0}{2\pi}.$$

(3.4)

Since the Boltzmann distribution slightly favors a lower energy state (orientation parallel to $\vec{B}_0$), at equilibrium a net magnetization ($\vec{M} = \sum_i \vec{\mu}_i$) is present in the same direction as $\vec{B}_0$ (longitudinal magnetization), whereas no net magnetization is present in the $xy$ plane (transverse magnetization). This net magnetization can be manipulated by applying an alternating radio frequency (RF) field $\vec{B}_1$ perpendicular to $\vec{B}_0$. The rate of
change of $\vec{M}$ depends upon the torque, $\vec{M} \times \vec{B}$, exerted on the magnetization by the magnetic field:

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{B}. \quad (3.5)$$

Here $\vec{B}$ is the total magnetic field, which now consists of the static field $\vec{B}_0$ and the RF field $\vec{B}_1$, rotating in the $xy$ plane at an angular frequency $\omega$:

$$\vec{B}(t) = \begin{pmatrix} B_1 \cos \omega t \\ B_1 \sin \omega t \\ B_0 \end{pmatrix}. \quad (3.6)$$

The resulting motion of the magnetization is given by the Bloch equations [Blo46]:

$$\begin{align*}
\frac{dM_x}{dt} &= \gamma (M_y B_0 + M_z B_1 \sin \omega t) - M_x / T_2 \\
\frac{dM_y}{dt} &= \gamma (M_z B_1 \cos \omega t - M_x B_0) - M_y / T_2 \\
\frac{dM_z}{dt} &= -\gamma (M_x B_1 \sin \omega t + M_y B_1 \cos \omega t) - (M_z - M_0) / T_2.
\end{align*} \quad (3.7)$$

These equations contain two relaxation times, $T_1$ and $T_2$, describing the restoration of the longitudinal magnetization to its equilibrium value and the decay of transverse magnetization, respectively.

When, at equilibrium, the RF field $\vec{B}_1$ is applied at the Larmor frequency, it can be shown that the net nuclear magnetization starts to rotate from the $z$ axis towards the $xy$ plane. By applying the RF field during a ‘pulse’), the net magnetization is rotated by an angle $\theta$:

$$\theta = \gamma B_1 \Delta t. \quad (3.8)$$

The duration of the RF pulse is chosen such to rotate the net magnetization $M$ by a so-called flip angle, specific for a particular experiment (and pulse sequence). After a commonly used $90^\circ$ pulse, the magnetization is in the $xy$ plane. This so-called transverse magnetization now rotates around $\vec{B}_0$ at the Larmor frequency, thereby inducing a signal in a pick up coil. The decay of this transverse magnetization by relaxation processes and by diffusion of nuclei will be considered in the next section in more detail.

### 3.3 Determination of water and salt profiles by MRI

Magnetic resonance imaging (MRI) is based on the principles of Nuclear Magnetic Resonance. It is described extensively in the literature [Haa99, Vla99]. MRI is a non-destructive method for obtaining images from the NMR signal of thin slices through the human body or another medium. It can be used for quantitative and selective mapping of several chemical elements in materials, because the resonance condition of a certain type of nucleus depends on the gyromagnetic ratio (table 3.1). Since the degradation of building materials is closely connected to the moisture and salt transport, we will focus on $^1H$ and $^{23}Na$ density profiles.

When the applied magnetic field is homogeneous, all nuclei of a certain type in the sample are at resonance at the same frequency, and a signal from the whole sample
is obtained. To achieve spatial resolution, the resonance frequency is made position dependent by superimposing a magnetic field gradient \( G_\alpha \) (\( \alpha = x, y, z \)) on the main magnetic field \( B_0 \):

\[
\nu(\alpha) = \gamma (B_0 + G_\alpha \alpha),
\]

where \( \alpha \) is a position in the sample along the direction of the magnetic field gradient \( G_\alpha \). For 3D imaging magnetic field gradients are applied in three orthogonal directions. Selection of an imaging plane (slice) through the sample is done by a slice selection gradient, applied during the RF pulse. The selected slice is perpendicular to the field gradient. The RF pulse will rotate only the spins within the selected slice. The rest of the spins in the sample will be unaffected by the RF pulse.

![Figure 3.1: Timing diagram of a Hahn spin-echo imaging sequence in the presence of a constant magnetic field gradient (G). \( \tau \) is the period between the 90° and 180° RF pulses, \( t_E \) is echo time, \( t_R \) is the repetition time of the pulse sequence and \( t_{acq} \) is the acquisition time.](image)

To observe one-dimensional profiles of \(^1\text{H}\) and \(^{23}\text{Na}\) in building materials we use a Hahn spin-echo sequence [Hah50] in the presence of a constant magnetic field gradient (figure 3.1). This sequence consists of two RF pulses, with \( \theta = 90^\circ \) and \( \theta = 180^\circ \), respectively. It yields a so-called spin-echo signal at a time \( 2\tau \), where \( \tau \) is the distance between the two RF pulses. Fourier transforming the spin-echo signal yields the density profile along \( G_\alpha \) of the excited nuclei within the slice.

The spatial resolution of the profiles is limited by \( T_2 \) relaxation of the NMR signal, field inhomogeneities, and diffusion [Far71, Cal91]. The best achievable resolution \( R \) depends on the gyromagnetic ratio of the nucleus (\( \gamma \)) and gradient magnitude (\( G_\alpha \)) according to [Vla99]:

\[
R = \frac{1}{\Delta \alpha} = \frac{\gamma G_\alpha t_{acq}}{2\pi}.
\]

In this equation \( \Delta \alpha \) is the minimum distance that can be resolved and \( t_{acq} \) is the acquisition time, i.e., the width of the data acquisition window (figure 3.1).
3.4 Determination of the diffusion coefficient

For moisture and ions within a porous material $T_2 \ll T_1$. In this case the intensity of the received signal is given by [Cal91]:

$$S = k \rho \left[1 - \exp(-t_R/T_1)\right] \exp \left(-t_E/T_2\right), \quad (3.11)$$

where $k$ is the sensitivity of the nuclei relative to that of hydrogen, $\rho$ is the density of the nuclei, $t_R$ is the repetition time of the pulse sequence and $t_E$ is the echo time (figure 3.1). To obtain absolute values for the density profile within the selected slice, the signal attenuation due to $T_1$ and $T_2$ has to be taken into account. By changing the Larmor frequency, the position of the selected slice can be changed, see Eq. 3.9. Alternatively, the position of the selected slice can be changed by moving the sample by means of step-motor along the direction of the field gradient (see chapter 4). From the density profiles of all individual slices, H or Na density profiles in the complete sample are obtained.

3.4 Determination of the diffusion coefficient

The diffusion coefficient is the important parameter which describes the transport properties of the moisture and ions. Diffusion leads to dephasing of the transverse components of the individual magnetic moments in a gradient $G$ and, consequently, to attenuation of the NMR signal. Therefore, NMR gives the possibility to measure a diffusion coefficient. The classical NMR methods for determination of diffusion coefficients are the constant gradient Hahn spin-echo sequence [Hah50] and pulsed field gradient (PFG) sequences [Ste65].

![Timing diagram of a CPMG sequence in the presence of a constant magnetic field gradient (G). $\tau$ is the time interval between the 90° and 180° RF pulse and $t_E = 2\tau$ is the echo time.](image)

For free (unrestricted) diffusion, the magnetization ($M_{\text{Hahn}}$) decay is governed by diffusion and transverse relaxation [Hah50, Val01b]:

$$M_{\text{Hahn}} = M_0 \exp(-t_E/T_2) \exp \left(- \frac{D_0(G)^2(t_E)^3}{12}\right), \quad (3.12)$$

where $M_0$ is the equilibrium (longitudinal) magnetization, $D_0$ is the diffusion coefficient in the bulk, $G_\alpha$ the applied magnetic field gradient and $t_E$ the echo time. From a series of
measurements at different values of $t_E$ it is possible to determine the diffusion coefficient if the $T_2$ relaxation term is known. The latter can be obtained from a Carr-Purcell-Meiboom-Gill (CPMG) measurement \cite{Car54}. The CPMG sequence consists of a train of RF pulses (Fig. 3.2), of which the first one (a 90$^\circ$ pulse) rotates the net magnetization in the transverse ($xy$) plane. After that the magnetization is manipulated in the $xy$ plane by a series of 180$^\circ$ pulses resulting in a series of echoes. If the time interval between the successive 180$^\circ$ pulses is sufficiently short \cite{Val01b}, the signal decay of this echo series is governed by $T_2$ relaxation, because the dephasing due to diffusion is largely compensated. In that case, the decay of the magnetization ($M_{CPMG}$) is given by:

$$M_{CPMG} = M_0 \exp(-t/T_2).$$

(3.13)

The Hahn spin-echo pulse sequence is mainly used to determine the diffusivity in bulk liquids. The transverse relaxation of the spins in a liquid confined in a porous medium is often very fast ($T_2 < 20$ ms \cite{Val01a, Val02}) and depends on the pore size \cite{Bro79, Val01a}. This hampers an accurate determination of the diffusivity, especially at longer time scales (up to a few seconds). In that case the stimulated echo method is used.

### 3.4.1 Stimulated echo pulse sequence

To preserve the excited nuclear magnetization at longer time scales a stimulated echo sequence was used \cite{TAN70}. By applying three 90$^\circ$ pulses (Fig. 3.3) a part of the magnetization is stored in the longitudinal direction for the most of the time (period $d_s$ in the figure 3.3). Because in porous media the longitudinal relaxation of water is much slower than the transverse relaxation and dephasing effects do not occur for the longitudinal component, the signal is preserved for several seconds. The stimulated echo signal occurs after the third 90$^\circ$ pulse. The signal after the second 90$^\circ$ pulse is the ‘primary echo’ or ‘eight-ball echo’ signal. Its formation, as well as that of the stimulated echo signal, is explained illustratively in \cite{Vla99}.

In an unrestricted medium the stimulated echo signal decays according to \cite{Tan70}:

$$\ln(M_{st}) = \ln\left(\frac{M_0}{2}\right) - \frac{(\tau_2 - \tau)}{T_1} - 2\tau/T_2 - (\gamma G)^2 D\tau^2(\tau_2 - \frac{1}{3}\tau),$$

(3.14)

where $T_1$ and $T_2$ are the longitudinal and transverse relaxation times, respectively, $\gamma$ is the gyromagnetic ratio of the nucleus, $G$ is the magnetic field gradient, $D$ is the diffusion coefficient, $\tau$ is the period between the first two RF pulses and $\tau_2$ the period between the first and third pulse. Note that $\tau$ is also the time by which the echoes succeed the pulses (Fig. 3.3). Therefore the stimulated echo time $t_E = \tau_2 + \tau$. Rearranging the terms in equation 3.14 yields:

$$\ln(M_{st}) = \ln\left(\frac{M_0}{2}\right) - \frac{d_s}{T_1} - 2\tau/T_2 - (\gamma G)^2 D\tau^2d_s - \frac{2}{3}(\gamma G)^2 D\tau^3,$$

(3.15)

where $d_s = \tau_2 - \tau$ is time between second and third 90$^\circ$ pulse (see figure 3.3). The equation describing the decay of the primary echo signal is:

$$\ln(M_{pr}) = \ln\left(\frac{M_0}{2}\right) - 2\tau/T_2 - \frac{2}{3}(\gamma G)^2 D\tau^3.$$

(3.16)
3.4. Determination of the diffusion coefficient

Fig. 3.3: Timing diagram of the stimulated echo pulse sequence with a constant field gradient. The signal decay can be measured as a function of echo time ($\tau_E$) by changing the time between the second and third RF pulse ($d_s$), for different $\tau$ and $G$ values.

By dividing Eq. 3.15 by Eq. 3.16, $T_2$ relaxation effects and attenuation due to diffusion during the time interval $\tau$ are eliminated:

$$\ln \left( \frac{M_{st}}{M_{pr}} \right) = -\left[ \frac{1}{T_1} + (\gamma G)^2 D \tau^2 \right] d_s. \quad (3.17)$$

For measurements of the diffusivity at long time scales $\tau \ll \tau_2$ in equation 3.17, $d_s = \tau_2 - \tau \approx t_E$, where $t_E$ is the stimulated echo time. Dividing the two echo intensities also eliminates the effect of variations of the sensitivity of the equipment, if measurements are performed during extended periods of time. Another advantage of this approach is that measurements on different materials can be compared directly without any signal normalization.

Fig. 3.4: Diffusion in porous media. At short times the diffusivity ($D$) is equal to bulk diffusion constant ($D_0$). At long times the particles feel the pore wall restrictions and the diffusivity is lower.
The stimulated echo decay in Eq. 3.17 is governed by longitudinal relaxation and diffusion. Therefore both $D$ and $T_1$ can be determined from the time dependence of $\ln(M_{st}/M_{pr})$ for different $\tau$ and $G$ values. For the determination of the diffusion coefficient in porous media following two aspects should be considered. First, the diffusivity measured in a porous material depends on the observation time, since the excited particles need some time to feel the pore wall restrictions (figure 3.4). At very short times the diffusivity is equal to the bulk diffusion constant $D_0$ (figure 3.5 [Kle99]). After sufficiently long times the diffusivity is constant and determined by the tortuosity ($\alpha$), see chapter 2. The second aspect is that large magnetic field gradients are present in many porous materials. These gradients give rise to an enhanced dephasing of the individual magnetic moments. This results in measured diffusivities that may largely exceed the bulk diffusivity [Sna97], which is of course not realistic. In chapter 6, a method will be presented to determine the diffusivity in such materials at long time scales.

![Graph](image)

**Fig. 3.5:** Diffusion coefficient in open and closed cell systems as a function of the observation time [Kle99]. $D_0$ is the diffusion coefficient of the bulk fluid.

### 3.5 Measurement setup

The measurement setup consists of a home built NMR scanner and an air flow unit, see figure 3.6. Due to the fast $T_2$ relaxation in building materials, the NMR scanner is specially developed [Kop94, Pel95] for sampling the NMR signal at short echo times ($t_E < 0.5$ ms). It is designed to measure quantitatively both $^1$H and $^{23}$Na contents at different positions within the sample. Besides, the NMR setup allows controlling the temperature and relative humidity of the environment and the positioning of the sample.

A teflon sample holder is placed in a copper RF coil (diameter 35 mm) of a resonant LC circuit. To reduce the effect of variations of the dielectric permittivity of the sample...
3.5. Measurement setup

due to changes of the moisture content, a cylindrical Faraday shield has been placed between the coil and the sample. For quasi-simultaneous measurement of H and Na, the RF frequency is toggled by a computer-controlled switch between $\nu_H = 31$ MHz and $\nu_{Na} = 8.2$ MHz. A schematic of this circuit is given in [Pel00]. The duration of the 90° pulse was 12 µs for H and 22 µs for Na, whereas the echo times were as short as possible (200 µs for H and 450 µs for Na). Because the transverse relaxation time of Na in NaCl crystals is of the order of 10 µs [Pel03], only dissolved Na ions are detected. The resonator is placed in an iron cored electromagnet ($B_0 = 0.73$ T), cooled with water.

A magnetic field gradient ($G$) is generated in the vertical ($x$) direction by a set of Anderson coils. Gradients up to 0.33 T/m are used. The one-dimensional spatial resolution of the equipment was evaluated by measurements on two cylindrical samples with a flat top or bottom. The first sample was a fired-clay brick, saturated with NaCl solution ($c = 4$ mol/l). The second was a standard sample, containing an NaCl solution ($c = 3$ mol/l) with addition of CuCl$_2$ ($c = 0.03$ mol/l) for decrease of $T_1$ relaxation time and repetition time $t_R$. From these measurements the resolution was found as $0.9 \pm 0.1$ mm for H and $3.5 \pm 0.5$ mm for Na (figure 3.7).

During the drying experiments the air flow and the relative humidity of the air $h_a$ were controlled with an home built air flow unit (the right side of figure 3.6). After oil filtering air is dried in cylinders filled with silica gel until $h_a < 0.01$. Next, this dry air is split in two fractions of which the flow is controlled by flow controllers (Bronkhorst Hi-Tec, model F-201C-FBC-22-V). One fraction is saturated with water until $h_a \simeq 0.95$ by flowing through bottles filled with water. The wet and dry air fractions are mixed.

![Fig. 3.6: Picture of the NMR setup consisting of the main magnet with the gradient coils, resonator and sample holder (middle), electronics (left) and air flow unit (right).]
Fig. 3.7: Normalized NMR signal intensity versus position for $^1$H (square symbols) and $^{23}$Na (dots). The samples were fired-clay brick saturated with a 4 mol/l NaCl solution (full symbols) and a standard containing a 3 mol/l NaCl solution and 0.03 mol/l CuCl$_2$ (open symbols). The edges of the samples were positioned in the middle of the RF coil ($x=0$). The resolution was evaluated from the positions at which the signal drops from 95 % to 5 % of its maximum value. The noise floor of the measurements on Na is about 10 % of the signal intensity.

again and the relative humidity $h_a$ is calculated according to:

$$h_a = \frac{Q_w}{Q_{tot}}, \quad (3.18)$$

where $Q_w$ is the flow of wet air, and $Q_{tot}$ is the total flow of wet and dry air. The accuracy of $h_a$ was checked by the wet-bulb method with a Psychrometer (Wilhelm Lambrecht KG, Göttingen, type 761b), and it appeared to be better than 1 %.

For diffusion measurements at constant temperature, a ‘Lauda’ model RL6CP temperature control unit is used. The temperature of the water reservoir of this unit can be controlled between 0 °C to 100 °C. For temperature control of the sample, a closed circuit was used. The circuit contains a perfluorinated fluid ‘Galden HT 70’ (Solvay Solex, Milan) which is circulated by a peristaltic pump through a copper spiral in the temperature controlled reservoir and the wall of the PVC sample holder of the NMR equipment.
4. Moisture and salt transport in plaster/substrate layers

Moisture and salt decay processes are amongst the most recurrent causes of damage of buildings and monuments. Plasters are often present as a finishing layer. The performance of specially developed restoration plasters is not always as good as expected. In some cases salt is transported to the surface of the plaster, where efflorescence occurs. In other cases salt crystallizes in the masonry, giving rise to degradation. Apart from this, salt may crystallize between the masonry and the plaster, causing the plaster layer to detach. To understand these processes in more detail, we have investigated how transport and accumulation of salt in a plaster depends on the underlying masonry material.

Moisture and sodium profiles have been measured non-destructively with a Nuclear Magnetic Resonance technique during drying of plaster/substrate systems. The same plaster is applied on two substrates of which the pores are either an order of magnitude larger or an order of magnitude smaller than those of the plaster. The moisture and salt transport and the salt accumulation differed significantly for these two systems. In a plaster/Bentheimer sandstone system (the pores of the plaster are smaller than those of the substrate) all salt is removed from the substrate and accumulates in the plaster, because this layer remains wet for a longer time than the substrate. In a plaster/calcium-silicate brick system (the substrate has a considerable amount of pores that are smaller than those of the plaster) some salt crystallizes in the plaster layer, but a significant amount of salt crystallizes within the substrate itself.

The salt transport from substrate to plaster is quantified in terms of an efficiency number $\epsilon$, which can be estimated from the pore-size distributions measured by mercury intrusion porosimetry. Based on the results of this study, we discuss the salt transport for various combinations of plasters and substrates, of which the pore-size distributions have been reported in the literature.

4.1 Introduction

The choice of restoration plasters, suitable for long-time protection and performance, is a delicate conservation problem. The performance of specially developed plasters is not always satisfactory [Wij97, Lub05]. The durability of a plaster and its ability to protect the underlying masonry strongly depend on its transport properties with respect to salt and moisture. Although salt damage has been investigated intensively for several decades [Gou97], the mechanisms that control salt crystallization in porous media are poorly understood. A better understanding of the transport of water and dissolved ions during
drying and salt crystallization in plasters and the underlying masonry (the substrate) is necessary for understanding salt damage and for developing plasters that meet the requirements with respect to durability and protection.

The fluid transport in a single medium depends on its pore structure [Dul91]. In principle, knowledge about the pore-size distribution, the geometry of the pore network, the connectivity of the pores, and the properties of the pore walls is necessary for understanding the transport behavior, because these properties determine the permeability [Rei90, Nua81, Meh80, Die94], diffusivity [Gar90, Que98], and capillary pressure [Bea90, Dul91]. The pore-size distribution is one of the parameters which determine the material durability. Generally, bricks with large pores seem to be more resistant to damage than bricks with small pores [Rob84, Lub04, RM91].

In the existing recommendations for the application of plasters on salt-loaded substrates [WTA92] the influence of the substrate materials is not taken into account. The aim of the work described in this chapter is to investigate the influence of a difference in pore-size distribution between the plaster and substrate layer on the water and salt transport and the salt accumulation during drying. Until now, the details of the drying process of two-layer materials has not been investigated very extensively [Bro97, Bro98a]. Using a Nuclear Magnetic Resonance (NMR) technique we are able to measure non-destructively the time evolution of water and dissolved ions in these layered materials during drying.

In section 4.2 we will discuss some theoretical aspects of the relation between the pore structure and the water and salt transport during drying. The salt transport from the substrate to the plaster will be quantified in terms of an efficiency number. In section 4.3 the Nuclear Magnetic Resonance (NMR) technique will be explained and the main characteristics of the materials will be given. In section 4.4 the time evolution of the water and salt distribution during drying will be presented. From these measurements, the efficiency number is calculated. In section 4.5 we will discuss the salt transport in systems of which the substrate is salt loaded but the plaster layer is saturated with pure water. In this section we will also discuss the salt transport in plaster/substrate combinations of which the pore-size distributions are known from literature. The conclusions are presented in section 4.6.

### 4.2 Theory

The general description of moisture and salt transport in porous materials has been presented in chapter 2. Here we focus on moisture and salt transport during drying of 2-layer materials consisting of a plaster and a substrate. A typical experiment is shown schematically in figure 4.1. The plaster/substrate system is isolated on all sides except at the air/plaster interface, where single-sided drying occurs.

Drying of a homogeneous, uniformly wet, non salt-loaded material occurs in two stages: a uniform drying period and a receding drying front period [vB80, Bra99]. During the first period, moisture transport is fast and occurs through the water network. During the period characterized by the receding drying front, water near this drying front is present in the form of isolated clusters, and transport occurs through the vapor phase. The water
clusters evaporate because of the large difference in relative humidity between the vapor near the clusters and the air at the drying surface of the material.

During drying air will invade the largest pores, where the capillary pressure is lowest, as can be seen from the following equation [Dul91, Bea90]:

\[ p_c = \frac{2\gamma \cos \phi}{r_m}. \]  

(4.1)

In this equation \( r_m \) is a pore radius that discriminates between the pores filled with water \((r < r_m)\) and the empty pores \((r > r_m)\). \( \gamma \) [Nm\(^{-1}\)] is the surface tension of the liquid/vapor interface and \( \phi \) is the contact angle between the liquid/air and liquid/solid interface.

In two-layer systems the drying is determined by the pore-size distributions of the two materials, as long as the following assumptions are valid:

- the two materials are in perfect hydraulic contact
- the water network is a percolating network
- external pressure gradients are negligible, i.e., drying is completely determined by \( p_c \), which is continuous at the interface between the two materials

At a given moisture content, water is present in the pores with diameters smaller than \( r_m \) in each material. Therefore, the material with the largest pores is emptied first, as explained in chapter 2. In the case of plaster/substrate systems, the plaster will dry first if it has larger pores than the substrate. On the other hand, if the plaster has smaller pores than the substrate, the substrate will dry first.

Ions are transported both by advection and diffusion, as has been discussed in chapter 2. Advection drives the salt in the same direction as the water. During drying, advection will lead to salt accumulation and crystallization at the drying surface. Diffusion is a competitive process which tends to level off concentration differences within the liquid in the sample. The competition between advection and diffusion can be characterized by the Péclet number \( Pe \), given by:

\[ Pe = \frac{|U| L}{D}, \]  

(4.2)
where \(|U|, L\) and \(D\) are the water velocity, the length scale of interest, and the ion diffusivity, respectively. For \(Pe \gg 1\) advection dominates the ion transport, which happens at sufficiently high drying rates, whereas for \(Pe \ll 1\) diffusion dominates the ion transport, which happens at low drying rates.

In plaster/substrate systems, a plaster, applied on a substrate with larger pores, stays wet during a longer time than the substrate. If the condition \(Pe \gg 1\) is valid everywhere in the system, advection dominates and salt will be transported and accumulated at the air/plaster interface. If \(Pe \ll 1\), diffusion dominates and salt will precipitate everywhere in the plaster. If the plaster has larger pores than the substrate, the plaster will dry first. For \(Pe \gg 1\), salt will be transported to the drying interface, which in this case is not necessarily the air/plaster interface, but rather the plaster/substrate interface, since the plaster dries first. For \(Pe \ll 1\), salt will precipitate everywhere in the substrate.

The ion transport from the substrate to the plaster can be characterized by means of a dimensionless efficiency \(\epsilon\):

\[
\epsilon = \frac{|\Delta m|}{m_0}.
\]  

In this equation \(m_0\) is the initial mass of the sodium in the substrate and \(|\Delta m|\) is the mass of the sodium which is transported from the substrate to the plaster layer at a time \(t'\) when the top plaster layer has dried out. The efficiency number is easy to estimate, since \(m_0\) and \(|\Delta m|\) are experimentally accessible parameters.

Since salt is transported with water, the efficiency number \(\epsilon\) can be estimated from the water quantities, even without knowing the salt quantities. When \(Pe \gg 1\), the salt concentration in the sample during drying equals the initial concentration, except in a narrow region just below the drying surface [Pel02]. Therefore, it follows from Eq. 4.3 that:

\[
\epsilon \simeq \epsilon_w = \frac{|\Delta V|}{V_0} = \frac{|\Delta \theta|}{\theta_0},
\]  

where \(\epsilon_w\) is efficiency number calculated from the water quantity. \(\theta_0\) and \(V_0\) are the initial moisture content and the initial volume of water in the substrate, respectively. \(|\Delta \theta|\) and \(|\Delta V|\) are the moisture content and the volume of water that disappeared from the substrate at the time \(t'\) when the plaster has dried out, respectively.

Since the water transport in a two-layer system is characterized by the pore size differences between the two materials, the efficiency number \(\epsilon\) for the case \(Pe \gg 1\) can also be estimated from the capillary pressure law (Eq. 4.1). The volume of water that disappears from the substrate while the plaster completely dries out equals the volume of the pores in the substrate with a radius larger than that of the smallest pores in plaster. Hence \(\epsilon_p\) can be calculated from the total pore volume \(V_p\) of the substrate and the volume of the pores \(V'_p\) in the substrate with a radius larger than that of the smallest pores in the plaster:

\[
\epsilon_p = \frac{V'_p}{V_p}.
\]  

By measuring the cumulative pore volume of both materials as function of pore size with mercury intrusion porosimetry, \(\epsilon_p\) can be calculated and the salt accumulation can
be estimated even without investigating the actual transport at all. In section 4.6.2 we will use mercury intrusion data reported in the literature for an analysis of the salt accumulation of various plaster/substrate combinations.

\( \epsilon_w \) and \( \epsilon_p \) are defined as ideal numbers which are estimated assuming \( Pe \gg 1 \). The situation is less clear when this assumption is not satisfied. In the case of very slow drying (\( Pe \ll 1 \)), diffusion dominates and there is no salt accumulation at the drying surface. During drying the salt concentration will increase uniformly in both materials of the sample from the initial concentration \( c_0 \) to the saturation concentration. If the substrate dries first, the salt concentration will increase faster in the substrate than in the plaster, and dissolved ions will diffuse into the plaster. If the drying process is sufficiently slow, the efficiency number may tend to 1 for low initial salt quantities or if the thickness of the substrate is much smaller than the thickness of the plaster. If, on the other hand, the plaster dries first, dissolved ions may diffuse back to the substrate, which may even reduce the efficiency number to negative values.

### 4.3 Experimental

Nuclear Magnetic Resonance (NMR) imaging is a non-destructive technique for quantitative mapping of certain chemical elements in materials. Using a home-built NMR scanner, designed for the imaging of the building materials [Kop94, Pel95], it is possible to follow the distribution of water and dissolved sodium ions in time during wetting [Pel00] or drying [Pel02].

As already mentioned in chapter 3, the resonance frequency of a certain type of nucleus, called the Larmor frequency, is determined by the magnitude of the applied magnetic field \( B \):

\[
\nu_i = \frac{1}{2\pi} \gamma_i B ,
\]

where the index \( i \) refers to the type of nucleus (H or Na), \( \nu_i \) [Hz] is the Larmor frequency, \( \gamma_i \) is the gyromagnetic ratio of the nucleus (\( \gamma_H/2\pi = 42.58 \text{ MHz/T}; \gamma_Na/2\pi = 11.27 \text{ MHz/T} \)) and \( B \) [T] is the strength of the magnetic field.

When the applied magnetic field is homogeneous, the nuclei in the whole sample are at resonance at the same frequency, and a signal from whole sample is obtained. To achieve spatial resolution it is necessary to excite the nuclei in the limited volume of the sample. This is done by making the resonance frequency position dependent by superimposing a constant magnetic field gradient \( G \) on the main magnetic field \( B_0 \):

\[
B = B_0 + G(x - x_0) ,
\]

where \( x \) [m] is a position in the sample along the direction of the magnetic field gradient \( G \) [T m\(^{-1}\)] and \( x_0 \) is the position where \( B = B_0 \).

The NMR signal \( S \) is proportional to the density of the nuclei \( \rho \) [Cal91]:

\[
S = Ck\rho[1 - \exp(-t_R/T_1)]\exp(-t_E/T_2) .
\]

In this equation \( C \) is a calibration factor, \( k \) is the sensitivity of nuclei relative to that of hydrogen, \( T_1 \) [s] is the spin-lattice (longitudinal) relaxation time, \( t_R \) [s] is the repetition
time of the spin-echo experiment, $T_2$ [s] is spin-spin (transverse) relaxation time, and $t_E$ [s] is the spin-echo time. The relaxation times $T_1$ and $T_2$ are proportional to the pore size [Bro79, Val01b], which enables us to distinguish water present in different pores. To measure the water in the entire pore system, which may include a certain fraction of nuclei with a small $T_2$, $t_E$ has to be as short as possible. In our experiments we have used $t_{E,H} = 0.2$ ms and $t_{E,Na} = 0.45$ ms. Nevertheless, we observed some Na signal loss in materials with small pores, due to fast $T_2$ relaxation. If quantitative measurements are required, this loss has to be corrected for. Since the NMR sensitivity for Na is low, the Na signals from 256 successive spin-echo measurements were averaged to obtain a sufficient signal to noise ratio.

![Fig. 4.2: Set-up for the drying experiments. The teflon holder with the sample and the standard is moved in the vertical direction (x) by means of the step motor. The signal from the H or Na nuclei at resonance is received by the RF coil. The air that is blown over the sample has a relative humidity $h_a < 0.01$.](image)

In our experiments the main magnetic field $B_0$ and the gradient $G$ were 0.7 T and 0.33 Tm$^{-1}$, respectively. The resulting one-dimensional resolution was 0.9 mm for H and 3.5 mm for Na. The sample holder is schematically depicted in figure 4.2. Since the transverse relaxation time of Na in NaCl crystals is of the order of 10 µs [Pel03], in our equipment
are only able to measure dissolved Na ions. During the acquisition of the profiles the RF frequency is switched in such a way that the H and Na signals can be recorded quasi-simultaneously [Pel00]. H and Na signal intensities are related to the corresponding volume of water [cm$^3$] and quantity of Na [mol] using a standard (see Fig. 4.2). This consisted of an NaCl solution ($c = 3$ mol l$^{-1}$) to which a small amount of CuCl$_2$ ($c = 0.03$ mol l$^{-1}$) was added to decrease the $T_1$ relaxation time and, correspondingly, the repetition time $t_R$. To determine the H and Na profiles over the whole sample and the standard, the sample holder was moved in the vertical ($x$) direction by means of a step motor. The time to measure both a water and Na profile within the sample and the standard was about 2 hours. Before the actual drying was started, i.e., before the air flow was switched on, a water and a Na profile were measured that served as $t = 0$ reference. The moisture and Na profiles for $t > 0$ were obtained by interpolating the successive experimental profiles measured at different times.

![Diagram](image)

**Fig. 4.3:** a) Moisture content and b) amount of Na per volume of material of the sample and the standard plotted as a function of position for every 2 hours of a drying process. The moisture contents are only given for the first 100 h.
Cylindrical samples were cut with a diameter of 19 mm and a total length of 50 mm. Initially the samples were uniformly capillary saturated by immersing them in water or a NaCl solution, \( c = 4 \text{ mol l}^{-1} \), for about 20 hours. Because of the low NMR sensitivity for Na, a rather high concentration has been chosen. The corresponding salt quantity amounts to roughly 0.02 gram per gram of sample. To be able to model the observed drying and salt transport as 1D processes, the samples were sealed with teflon tape at all sides except at the top (the plaster/air interface), over which the dry air is blown. The relative humidity of the air was less than 1 % and the air flow was kept at 0.7 l min\(^{-1}\). This corresponds to an air speed over the drying surface in the range of 0.03 – 0.15 m/s, estimated from the geometry of the NMR set-up.

Fig. 4.4: Pore sizes of a) plaster and Bentheimer sandstone and b) plaster and calcium-silicate brick measured by mercury intrusion porosimetry. The efficiency of the salt transport from the substrate to the plaster \( \epsilon_p \) can be estimated from the total pore volume of the substrate \( V_p \) and the volume of pores in the substrate \( V'_p \) with a size larger than the smallest pores in the plaster. The size corresponding to \( V'_p \) is taken as the pore size at which the cumulative volume of the smaller pores in the plaster equals 5 % of the total pore volume.
An example of the H and Na profiles in the sample and the standard for every 2 hours of a drying process are given in figure 4.3a and figure 4.3b, respectively. In the next section only profiles in the sample will be plotted.

Experiments were done on two different plaster-substrate systems. Bentheimer sandstone and calcium-silicate brick were used as substrates. The plaster had the same composition in both systems: lime:cement:sand = 4:1:10 (v/v). The two substrates were selected because of the significant differences in their pore-size distributions. The systems were dried during seven days in a plastic box and during 21 days at 40°C and 65% relative humidity. After that the systems were carbonated during a few weeks, until full carbonation was reached, in a box with 3% CO2 (v/v) at 50% relative humidity.

The pore sizes and open porosities of the materials have been measured by means of mercury intrusion porosimetry. The cumulative and differential pore volumes vs. pore diameter are presented for both systems in figure 4.4. This figure shows that the pores of the plaster are an order of magnitude smaller than those of Bentheimer sandstone and an order of magnitude larger than the nanometer pores of the calcium-silicate brick. We like to add that the fraction of large pores (10−100 µm) in, e.g., the calcium-silicate brick may have been underestimated, due to ink-bottle effects. Mercury intrusion porosimetry actually probes the distribution of the pores as a function of the size of the pore entrance, which causes the results to depend on the geometry of the pore system.

4.4 Results

4.4.1 Plaster/Bentheimer sandstone

Pure water

First, the drying behavior of plaster/substrate systems saturated with pure water has been studied. In figure 4.5a the water profiles in the plaster/Bentheimer sandstone system are plotted for several times during the drying process. In all systems we have studied, the water evaporates from the sample through the air/plaster interface (x = 4). The total amounts of water in the plaster and the Bentheimer sandstone as a function of drying time are presented in figure 4.5b. Two drying stages can be observed. During stage 1 (t < 2 h) the Bentheimer sandstone dries, whereas the plaster remains saturated. The plaster starts to dry during the second drying stage (t > 2 h). After about 6 hours the water network in the plaster breaks down and a receding drying front enters the plaster. This drying behavior can be understood as follows. During drying water tends to remain in the pores where the capillary pressures (p_c) is highest, which are the smallest pores according to equation 4.1. The Bentheimer sandstone dries first, because its pores are generally an order of magnitude larger than the pores in the plaster (figure 4.4a).

Salt solution

To study the salt transport in the plaster/Bentheimer sandstone system, the sample was initially saturated with a NaCl solution, c = 4 mol l−1. In figure 4.6a we have plotted water profiles for several times during the drying process. The total amounts of water
4. Moisture and salt transport in plaster/substrate layers

Fig. 4.5: a) Moisture profiles in the plaster/Bentheimer sandstone system during drying. The sample was initially saturated with water. Dry air is blown over the top of the sample ($x = 4 \text{ mm}$) with a flow of $0.7 \text{ l min}^{-1}$. b) Total volumes of the water present in the plaster and Bentheimer sandstone as a function of the drying time.

in the plaster and the Bentheimer sandstone as a function of drying time are shown in figure 4.6b. Similar to the case of pure water discussed above, two drying stages are observed. However, the drying of the salt loaded sample is much slower, which can be partly explained by the dependence of the drying rate on the relative humidity, as can be seen from Eq. 2.8. The presence of salt decreases the relative humidity $h_l$ near the liquid-air interface and, consequently, decreases the drying rate [Hal02, Dai02]. It should be noted, however, that the decrease of the relative humidity near the liquid-air interface is smaller than a factor of 2, and therefore cannot account for the observed decrease of the drying rate by a factor of 5 to 10. This suggests that the transfer coefficient $\beta$ in Eq. 2.8 has also decreased. This is probably caused by blocking of the pores near the the drying surface by salt crystals, which reduces the effective surface area that is available for evaporation.
Apart from this, in the presence of salt no receding drying front is observed (Fig. 4.6a). This might be caused by a change in the wetting properties in the presence of NaCl [Pel03]. This change may be related to the decrease of the contact angle $\phi$ between the liquid-air and the solid-liquid interface in the presence of salt [Nij04]. In such a case, liquid films may be present and the liquid network will be complete until very low saturations.

![Figure 4.6](image-url)

Fig. 4.6: a) Moisture profiles in the plaster/Bentheimer sandstone system during drying. The sample was initially saturated with a NaCl solution ($c = 4 \text{ mol l}^{-1}$). Dry air is blown over the top of the sample ($x = 4 \text{ mm}$) with a flow of $0.7 \text{ l min}^{-1}$. b) Total volumes of the water present in the plaster and Bentheimer sandstone as a function of the drying time.

In figure 4.7a the Na profiles are presented for several times during the drying process. The total amounts of dissolved Na in the plaster and the Bentheimer sandstone as a function of the drying time are shown in figure 4.7b. In the Bentheimer sandstone there appears to be no Na signal loss, and the amount of dissolved Na is measured quantitatively. The Na concentration can be calculated from the Na and water quantities. In the plaster not all Na can be measured, due to the fast transverse ($T_2$) relaxation of Na in the small
30

4. Moisture and salt transport in plaster/substrate layers

Fig. 4.7: a) Profiles of dissolved Na in the plaster/Bentheimer sandstone system. The data were recorded during the same drying experiment as that presented in figure 4.6. b) Total amounts of dissolved Na ions in the plaster and Bentheimer sandstone as a function of the drying time.

pores [Rij04]. This signal loss in the plaster can be roughly corrected for by multiplying the measured signal with a correction factor $f$:

$$f = \frac{c_0}{c_{0,NMR}}.$$  \hspace{1cm} (4.9)

In this equation $c_0$ and $c_{0,NMR}$ are the initial Na concentrations that are actually present and measured by NMR, respectively. It is assumed that the transverse relaxation rate of Na does not change with moisture content. Of course this is a rather crude approximation, that obviously does not hold when the moisture content in the plaster has decreased to less than about 20% of the saturation value. At lower moisture contents, only the smallest pores are filled with NaCl solution (see Fig. 4.4a), which leads to a
4.4. Results

A drastic decrease of $T_2$ and hence the NMR signal intensity.

Inspection of figure 4.7 shows that during the first drying stage ($t < 25$ h) the Na in the Bentheimer sandstone remains uniformly distributed, while the total amount of dissolved Na in the system decreases. The calculated Na concentration in the Bentheimer sandstone does not exceed the initial concentration of 4 mol l$^{-1}$. The amount of dissolved Na in the plaster increases during the first 25 hours of drying. The resulting salt distribution in the plaster is not uniform, but a Na peak develops at the drying surface, see figure 4.7a. Correcting for the signal loss of the Na in the plaster, the estimated Na concentration at the top of the plaster after 25 hours of drying is 6 mol l$^{-1}$, which is around the solubility limit of NaCl. At this stage, crystallization at the air/plaster interface is visually observed.

These results indicate that diffusion plays a minor role in this stage of the drying process. This is confirmed by the velocity profiles that are calculated from the experimentally observed moisture profiles. In figure 4.8 the absolute value of the water velocity multiplied by the thickness of the plaster layer $|U|L$ is shown as a function of the position for several drying times. The horizontal line indicates the situation where $|U|L$ equals a diffusion constant of $10^{-9}$ m$^2$ s$^{-1}$, i.e., $Pe = 1$.

![Fig. 4.8: Water velocity multiplied by the thickness of the plaster layer, $|U|L$, as a function of the position in the sample for several times during the drying process of a plaster/Bentheimer sandstone system. The horizontal line indicates the situation where $|U|L$ equals a diffusion constant of $10^{-9}$ m$^2$ s$^{-1}$, i.e., $Pe = 1$.](image)

During the first drying stage ($t < 25$ h) $|U|L$ in the plaster decreases but does not vary much with $x$, since the water is distributed rather uniformly and $\theta$ is constant in time. During this stage the plaster acts only as a transport medium for moisture and ions from the Bentheimer sandstone to the drying surface. This is supported by the fact
that the drying rate in the present system is almost the same as the drying rate of a Bentheimer sandstone substrate without plaster at the same experimental conditions. In the Bentheimer sandstone $|U|L$ decreases with position, since the integral $\int_x^L \theta(x') \, dx'$ in equation 2.7 decreases with $x$. During this stage, $|U|L$ always exceeds $D$, which indicates that advection dominates. Ions that are present in or transported to the plaster layer will never be able to diffuse back to the Bentheimer sandstone. Therefore all salt will crystallize within the plaster. During the second drying stage ($t > 25$ h) the Bentheimer sandstone is rather dry and the plaster starts to dry. The salt that is present in the plaster will crystallize and, therefore, the amount of dissolved Na decreases.

![Graph showing Na content in plaster and substrate](image)

**Fig. 4.9:** Amount of Na in 8 slices of a plaster/Bentheimer sandstone sample and a plaster/calcium-silicate brick sample determined by ion chromatography. The data are normalized to the total amount of Na in the respective samples.

Our NMR results suggest that salt mainly accumulates and crystallizes in the plaster layer. To validate this, a sample was cut in 8 slices after the drying process and the total amounts of Na and Cl of these slices were measured quantitatively by ion chromatography. Figure 4.9 shows the amount of Na in each slice. These Na contents have been divided by the total amount of Na ions in the sample, i.e., the summed contents of all slices. The vertical line indicates the interface between the plaster and Bentheimer sandstone. The Cl distribution, which is not shown in the figure, was found to match the Na distribution within experimental inaccuracy, indicating that both types of ions are transported together. The ion chromatography results confirm the conclusions derived from the NMR measurements, in the sense that after drying almost all salt is present in the plaster layer.

The efficiency numbers for the salt transport from the Bentheimer sandstone to the plaster layer have been calculated from the ion chromatography and NMR data and were estimated from the pore-size distributions (Fig. 4.4a) and the moisture contents (Eq. 4.4). The results are presented in table 4.1. The actual efficiency $\epsilon$ is obtained from the amounts of Na measured by ion chromatography, presented in Fig. 4.9. The amount of Na in the
Table 4.1: Efficiency numbers for salt transport from substrates to plasters calculated in different ways. \( \epsilon \) is the efficiency number calculated from the total Na quantity measured by ion chromatography. \( \epsilon' \) is estimated from the amount of dissolved Na measured by NMR. \( \epsilon_w \) and \( \epsilon'_w \) are estimated from the water quantities in the samples saturated with pure water and a NaCl solution, respectively (Eq. 4.4). \( \epsilon_p \) is the efficiency numbers estimated from the pore-size distributions.

<table>
<thead>
<tr>
<th></th>
<th>plaster/Bentheimer sandstone</th>
<th>plaster/calcium-silicate brick</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \epsilon )</td>
<td>0.9</td>
<td>0.2</td>
</tr>
<tr>
<td>( \epsilon' )</td>
<td>1</td>
<td>–</td>
</tr>
<tr>
<td>( \epsilon_w )</td>
<td>1</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>( \epsilon'_w )</td>
<td>1</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>( \epsilon_p )</td>
<td>1</td>
<td>0.7 ± 0.1</td>
</tr>
</tbody>
</table>

slice between 21 and 27.3 mm is attributed to the interface and is therefore not taken into account in the calculation of the amount of Na in the Bentheimer sandstone.

The efficiency number \( \epsilon' \) calculated using the amounts of dissolved Na, measured by NMR, equals 1. This efficiency number is in good agreement with the actual efficiency number \( \epsilon \). The efficiency number \( \epsilon_w \), defined in equation 4.4, is a good approximation of the actual value for \( Pe > 1 \), which holds for our experiments on the plaster/Bentheimer sandstone system. Indeed the efficiency numbers \( \epsilon_w \) and \( \epsilon'_w \) agree nicely with \( \epsilon \).

In practice it is very difficult or even impossible to identify the smallest pore in a certain material. Therefore, in the calculation of \( \epsilon_p \), the radius of the smallest pores in the plaster is defined as the radius where the cumulative pore volume of the plaster has reached 95% of the total pore volume (Fig. 4.4). This corresponds to the situation where the moisture content in the plaster has decreased to 5% of its saturation value. This value may seem somewhat arbitrary, but at such a moisture content no percolating water network is present anymore, and no salt transport is possible.

The results presented in the left column of table 4.1 all show that at the conditions used in our experiments, the efficiency of salt transport from the Bentheimer sandstone to the plaster is very good, which is clearly related to the characteristic differences in the pore-size distributions of these two materials (figure 4.4a).

4.4.2 Plaster/calcium-silicate brick

Pure water

The plaster/calcium-silicate brick sample is initially saturated with pure water. The water profiles in this system for several times during the drying process are plotted in figure 4.10a. The total amounts of water in the two layers of this system as a function of drying time are presented in figure 4.10b. In this system three drying stages are observed. During the first drying stage \( (t < 4 \text{ h}) \), both the calcium-silicate brick and the plaster dry rapidly (Fig. 4.10b). During the second drying stage \( (4 - 40 \text{ h}) \) the plaster continues to dry rapidly, whereas the drying of the calcium-silicate brick is much slower than during
the first stage. During the third drying stage ($t > 40\ h$) the plaster is almost dry, and the calcium-silicate brick still contains a significant amount of water.

![Fig. 4.10: a) Moisture profiles in the plaster/calcium-silicate brick system during drying. The sample was initially saturated with water. The drying conditions were the same as in Fig. 4.6. b) Total volumes of water present in the plaster and calcium-silicate brick as a function of the drying time. The time $t'$ indicates the time at which the moisture content in the plaster has decreased to 5% of its saturation value.](image)

The drying behavior of the plaster/calcium-silicate brick system differs significantly from the drying of the plaster/Bentheimer sandstone system. This is a consequence of the different pore-size distributions of both systems (see Fig. 4.4b). The drying again can be explained by the capillary pressure (Eq. 4.1). Air first invades the pores with the lowest capillary pressure, i.e., the widest pores. In the calcium-silicate brick two dominant pore sizes ($\sim 20\ \text{nm}$ and $20\ \mu\text{m}$) are present. The first pore size is at least an order of magnitude smaller than the dominant pore size of the plaster ($\sim 1\ \mu\text{m}$), the second at least an order of magnitude larger. The volume of the nanometer pores of the calcium-silicate brick is
4.4. Results

significant and the presence of these pores has a large effect on the drying behavior of the plaster/calcium-silicate brick system. During the first drying stage, water evaporates from the largest pores in the brick and the plaster. During the second drying stage the largest pores in the calcium-silicate brick are empty, and now mainly the pores in the plaster are drying. During the third drying stage only the smallest pores of the calcium-silicate brick still contain water.

Fig. 4.11: a) Moisture profiles in the plaster/calcium-silicate brick system during drying. The sample was initially saturated with a NaCl solution \((c = 4 \text{ mol l}^{-1})\). The drying conditions are the same as in Fig. 4.10. b) Volume of water in the plaster and the calcium-silicate brick as a function of the drying time. The meaning of the time \(t'\) is explained in the text.
Salt solution

The sample was initially saturated with a NaCl solution, \( c = 4 \text{ mol l}^{-1} \). The water profiles are presented in figure 4.11a for several times during the drying process. The total amounts of water in the plaster and the calcium-silicate brick during drying are shown in figure 4.11b. Again, three drying stages can be distinguished, similar to the case of the pure water. The main influence of the salt is that the drying is much slower than in the case of pure water (figure 4.10) and that no receding drying front is present. Possible causes of these characteristics have already been discussed in section 4.4.1.

![Fig. 4.12: a) Profiles of dissolved Na in the plaster/calcium-silicate brick system. The data were recorded during the same drying experiment as that presented in figure 4.11. b) Total amounts of dissolved sodium ions in the plaster and the calcium-silicate brick as a function of the drying time. The meaning of the time \( t' \) is explained in the text.](image-url)

In figure 4.12a, the Na profiles are plotted for several times during the drying process. The total amounts of dissolved Na in the plaster and the calcium-silicate brick during drying are shown in figure 4.12b. In this case the Na signal loss in both the plas-
ter and calcium-silicate brick was corrected for according to the procedure outlined in section 4.4.1.

During the first drying stage \((t < 12 \text{ h})\) the amount of Na in the plaster stays constant within experimental accuracy, whereas the amount of Na in the calcium-silicate brick decreases. The velocity profiles calculated from the experimental moisture profiles are plotted in figure 4.13. This figure shows that, advection dominates during the first drying stage; in both materials \(|U|L\) is larger than \(D\) \((Pe > 1)\), with the obvious exception of a small region near the sealed end of the substrate, where \(U = 0\). As a result, salt is transported from the calcium-silicate brick to plaster, where it accumulates near the drying surface.

![Fig. 4.13: Water velocity multiplied by the length of the plaster layer, \(|U|L\), as a function of the position in the sample for several times during the drying process of a plaster/calcium-silicate brick system. The horizontal line indicates the situation where \(|U|L\) equals a diffusion constant of \(10^{-9} \text{ m}^2 \text{ s}^{-1}\), i.e., \(Pe = 1\).](image)

During the second drying stage \((12 - 100 \text{ h})\), the amount of dissolved Na in the plaster decreases. If we estimate the NaCl concentration in the plaster from the amounts of water and dissolved Na, corrected for the signal loss, it has reached the solubility limit \((c = 6 \text{ mol l}^{-1})\), which implies that crystallization will occur in the plaster. At the same time the amount of dissolved Na in the calcium-silicate brick increases.

Because of the slower drying of the calcium-silicate brick the diffusive transport becomes more important [Pel04]. This is confirmed by the velocity profiles, plotted in figure 4.13. During this stage, \(|U|L\) in calcium-silicate brick is lower than \(D\) \((Pe < 1)\) and diffusion dominates advection. Back diffusion and redistribution of the salt occurs and salt accumulates in the calcium-silicate brick. The amount of dissolved Na continues to increase until the moment that the solubility limit is reached and crystallization occurs. During the third drying stage \((t > 100 \text{ h})\) no dissolved Na is present in the plaster, because the plaster is essentially dry. The quantity of dissolved Na in calcium-silicate brick decreases due to crystallization.
The NMR results on the calcium-silicate brick system suggest that salt crystallizes everywhere in the sample. After the drying process the sample was cut in 8 slices and the Na and Cl contents of these slices were measured quantitatively by ion chromatography. The amount of Na in each slice, divided by the total amount of Na in the sample, is shown in figure 4.9. The measured Cl distribution was found to follow the Na distribution within experimental inaccuracy, which indicates that both ions are transported together. The salt has crystallized in the whole plaster/calcium-silicate brick sample, which confirms the conclusion drawn from the NMR experiment. Part of the salt has accumulated near the drying surface. Some salt seems to have accumulated at the end of the calcium-silicate brick substrate, which suggest that drying also occurred at the back surface of the sample. In this respect one should note that in the present experiment the drying of the substrate was very slow, in which case the unavoidable imperfections of the sealing of the back surface by the teflon tape may have a noticeable effect.

The efficiency numbers for the salt transport from the calcium-silicate brick to the plaster layer have been calculated from the ion chromatography and NMR data and were estimated from the pore-size distributions (Fig. 4.4) and the moisture contents (Eq. 4.4). The results are included in table 4.1. The efficiency numbers are determined from the sodium or water amounts in the substrate at the time \( t' \) when the moisture content in the plaster has decreased to 5 % of its saturation value. As mentioned in section 4.4.1, it is assumed that below this moisture content no further transport of salt is possible. These times are indicated by the vertical dashed lines in the figures 4.10b, 4.11b, and 4.12b. The error margins in the right column of table 4.1 reflect the uncertainty in the determination of the time \( t' \). In this respect one should note that at the start of our experiments not the entire pore volume is filled with fluid, since we start from capillary situation. Consequently, the time \( t' \) corresponds to a situation where the moisture most likely occupies less than 5 % of the total pore volume measured by mercury intrusion porosimetry. Hence the present estimates of the efficiency number using Eq. 4.4 should be considered as upper limits.

The actual efficiency number \( \epsilon \), obtained from the total Na amount measured by ion chromatography, amounts to 0.2. From the Na amounts measured by NMR no reliable value of the efficiency number \( \epsilon' \) can be calculated, since as the drying in this system proceeds, not only dissolved Na is present in the calcium-silicate brick, but also Na has crystallized. Only dissolved Na is measured by NMR, and therefore the total amount of Na that remains in the substrate will be underestimated. Since in the plaster/calcium-silicate brick system the condition \( Pe > 1 \) does not hold during a large part of the drying process, the efficiency numbers estimated from the water quantities in both layers or from the pore-size distributions, such as \( \epsilon_w \) and \( \epsilon_p \), should only be regarded as crude estimates of the efficiency of salt transport.

Generally, the efficiency of salt transport from the calcium-silicate brick to the plaster is poor, in contrast to that of the plaster/Bentheimer sandstone system. This difference is a direct consequence of the nanometer pores that are present in the calcium-silicate brick. During the last part of the drying process, when the large pores of the calcium-silicate brick and the plaster layer are dry, water and salt are still present in these nanometer pores.
4.5 Discussion

4.5.1 Non-uniformly salt loaded systems

Fig. 4.14: a) Moisture profiles in the non-uniformly salt loaded plaster/Bentheimer sandstone system for different times during the drying process. The plaster was initially saturated with pure water and the Bentheimer sandstone was saturated with a NaCl solution (c = 4 mol l\(^{-1}\)). The drying conditions are the same as in figure 4.6. b) Total volumes of water present in the plaster and the Bentheimer sandstone as a function of the drying time.

Until now we have investigated the salt and moisture transport in plaster/substrate systems which are uniformly salt loaded. In reality, the initial salt distribution might be inhomogeneous, depending on the salt and water sources in the system. In order to investigate the effect of a non-uniform initial salt distribution, we have studied the transport in a plaster/Bentheimer sandstone sample of which the plaster layer is immersed...
in pure water for several seconds and the Bentheimer sandstone is immersed in a NaCl solution \((c = 4 \text{ mol l}^{-1})\).

![Fig. 4.15: a) Profiles of dissolved Na in the non-uniformly salt loaded plaster/Bentheimer sandstone system. The data were recorded during the same drying experiment as that presented in figure 4.14. b) Total amounts of dissolved sodium in the plaster and the Bentheimer sandstone as a function of the drying time.](image)

Water profiles of this sample for several times during the drying process are plotted in figure 4.14a. The total amounts of water in the plaster and the Bentheimer sandstone as a function of drying time are shown in figure 4.14b. In figure 4.15a the Na profiles are presented for several times during the drying process. The total amounts of dissolved Na in the plaster and the Bentheimer sandstone as a function of the drying time are shown in figure 4.15b.

Since the plaster layer is now saturated with pure water, the drying of this sample is much faster than that of the uniformly salt loaded sample, described in section 4.4.1. The salt transport is completely different, since in this case the initial salt content of the
4.5. Discussion

plaster layer is zero. Fig. 4.15 shows that salt is transported to the drying surface, and the total amount of salt in the plaster layers increases.

![Diagram](image)

**Fig. 4.16:** The water velocity multiplied by the thickness of the plaster layer (|U| L) versus the position in the sample for several times during the drying process of a non-uniformly salt loaded plaster/Bentheimer sandstone system. The horizontal line indicates the situation where |U| L equals a diffusion constant of $10^{-9}$ m$^2$ s$^{-1}$, i.e., $Pe = 1$.

The velocity profiles plotted in figure 4.16 indicate that the salt is transported by advection, since $|U| L \gg D$. Most of the salt is already transported to the plaster within the first 10 hours of the drying process. After 50 h the Bentheimer sandstone is dry. The NMR results suggest that all salt is transported to the plaster. This indicates that the efficiency of the salt transport from the Bentheimer sandstone to the plaster equals 1, similar to the uniformly salt loaded sample (section 4.4.1).

To validate this, the sample was cut in 9 slices after the drying experiment and the total amount of Na in these slices was measured quantitatively by ion chromatography. Figure 4.17 shows the amount of Na in each slice. These Na contents have been divided by the total amount of Na ions in the sample, i.e., the summed contents of all slices. This figure shows that the almost all salt is present in the plaster layer and in the interface layer, which confirms the results obtained by NMR. The overall salt distribution resembles the salt distribution obtained by ion chromatography for the uniformly salt loaded plaster/Bentheimer sandstone system, which is plotted in figure 4.9.

### 4.5.2 Other plaster/substrate combinations

In our experiments we have demonstrated how moisture and salt are transported in two rather extreme systems, where the same plaster is applied on a very coarse (Bentheimer sandstone) or a fine substrate (calcium-silicate brick). Based on the results of this study, we will now discuss the salt transport for various combinations of plasters and substrates, of which the pore-size distributions have been reported in the literature.
In order to achieve the desired salt transport properties, a plaster should be selected on the basis of the pore sizes of both plaster and substrate. The pore-size distributions of various mortars and substrates which have been reported in the literature are given in tables 4.2 and 4.3, respectively. The materials have been classified according to their pore diameters: S refers to small pores (nanometer size), M to medium size pores (0.1 μm – several μm), and L to large pores (> 10 μm). Table 4.2 shows that two groups of mortars can be distinguished: mortars which have only small pores (S) [Mos02] and mortars with both medium size and large pores (M+L) [Mag04]. The mortar denoted by L-C [Mag04] which, similar to our mortar, has medium size pores (M) is classified in the second group.

If the mortars with small pores [Mos02] are applied on substrates with medium size and large pores, we expect moisture and salt to be transported quickly into the mortar layer, similar to the plaster/Bentheimer sandstone system that was discussed in section 4.4.1. Table 4.3 shows that some substrates with medium size pores are orange [Lub04] and clinker bricks, Baumberger [Que98] and Cyprus sandstones [The04], and various tuff stones [vH03a]. The substrates with large pores are Elm-limestone [Gri90], Rhodes [The04], and Tunisian [Zog04] sandstones, bricks of high durability [Rob84, Lub04], and also tuff and Sebastopol stone [Bec04].

If mortars with medium size and large pores [Mag04] are applied on substrates with smaller pores, we expect salt to accumulate in the substrate, similarly to the plaster/calcium-silicate brick system discussed in section 4.4.2. Table 4.3 shows that some substrates with small pores are Felsberg diorite, marble, and dolomite [Gri90]. Small and medium size pores are present in granite, Ettringer tuff, and quartz [Gri90]. Similar to calcium silicate brick, small and large pores are present in basalt-lava [Gri90].
Table 4.2: Compositions, pore-size distributions, and porosity of some mortars measured by mercury intrusion porosimetry. For an easier classification of these materials according to their pore diameters three letters are used, S denotes small pores (nanometer size), M medium size (0.1 – several µm), and L large pores (>10 µm).

<table>
<thead>
<tr>
<th>Ref.</th>
<th>mortar</th>
<th>pores</th>
<th>composition</th>
<th>small pores (nm)</th>
<th>medium pores (µm)</th>
<th>large pores (µm)</th>
<th>porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mos02]</td>
<td>1</td>
<td>S</td>
<td>sand / cement (3:1)</td>
<td>3 - 40</td>
<td>16.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>S</td>
<td>sand / cement (6:1)</td>
<td>4 - 40</td>
<td>18.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>S</td>
<td>sand / cement (9:1)</td>
<td>3 - 30</td>
<td>24.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>S</td>
<td>sand / lime / cement (6:1:1)</td>
<td>2 - 60</td>
<td>0.1 - 0.4</td>
<td>24.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>S</td>
<td>sand / pozolan / cement (6:1:1)</td>
<td>10 - 70</td>
<td>22.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>S</td>
<td>Euromix (sand / cement) (6:1)</td>
<td>3 - 50</td>
<td>32.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Mag04]</td>
<td>L-AH</td>
<td>M+L</td>
<td>air lime / artificial hydraulic lime / mixed sand (1:1:6)</td>
<td>0.2 - 1</td>
<td>7 - 40</td>
<td>50.7</td>
<td></td>
</tr>
<tr>
<td>AH</td>
<td>M+L</td>
<td>artificial hydraulic lime / mixed sand (1:3)</td>
<td>0.1 - 1.5</td>
<td>2 - 10</td>
<td>29.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L-C</td>
<td>M</td>
<td>air lime / white cement / sand (1:3:12)</td>
<td>0.2 - 1</td>
<td>21.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>M+L</td>
<td>air lime / sand (1:3)</td>
<td>0.3 - 0.8</td>
<td>4 - 15</td>
<td>25.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is important to notice that the same mortars [Mag04] applied on substrates with larger pores, will behave differently. Salt will be transported and accumulated in the mortar. The large pores are present again in, for instance, Bentheimer [Gri90], Rhodes [The04], and Tunisian [Zog04] sandstones, as well as in tuff and Sebastopol stone [Bec04].

4.6 Conclusions

Our drying experiments demonstrate that systems with the same plaster applied on a different substrate have a different drying behavior. This can be explained by differences in the pore sizes between the plaster and the substrate. The layer with the largest pores dries first. Therefore, the drying behavior of a plaster/substrate system depends on the pore-size distributions of both the plaster and the substrate.

Measurements on salt loaded systems indicate that the salt transport and accumulation is determined by drying behavior of the plaster/substrate system and, therefore, by the pore sizes of both the plaster and the substrate. When the plaster has small pores
Table 4.3: pore-size distributions and porosity of some substrates measured by mercury intrusion porosimetry. The letters S, M and L have the same meaning as in table 4.2.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Stone</th>
<th>Pores</th>
<th>fraction of pores &lt; 0.1 µm (%)</th>
<th>medium pores (µm)</th>
<th>large pores (µm)</th>
<th>porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Gri90]</td>
<td>Granite</td>
<td>S+M</td>
<td>40 - 95</td>
<td>0.2 - 1.2</td>
<td>0.5 - 2.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Felsberg diorite</td>
<td>S</td>
<td>90</td>
<td></td>
<td></td>
<td>0.2 - 0.3</td>
</tr>
<tr>
<td></td>
<td>Basalt</td>
<td>S+L</td>
<td>30 - 65</td>
<td>10 - 100</td>
<td>15 - 30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ettringer tuff</td>
<td>S+M</td>
<td>30</td>
<td>0.25 - 10</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Quartz</td>
<td>S+M</td>
<td>60</td>
<td>0.2 - 30</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Shale</td>
<td>S</td>
<td>90</td>
<td></td>
<td></td>
<td>0.4 - 1.2</td>
</tr>
<tr>
<td></td>
<td>Carbonate stones: Marble</td>
<td>S</td>
<td>55</td>
<td></td>
<td></td>
<td>0.3 - 0.6</td>
</tr>
<tr>
<td></td>
<td>Carbonate stones (limestone)</td>
<td>S</td>
<td>60 - 100</td>
<td></td>
<td></td>
<td>0.2 - 8</td>
</tr>
<tr>
<td></td>
<td>Carbonate stones (limestone)</td>
<td>S+M</td>
<td>10 - 45</td>
<td>0.25 - 15</td>
<td>12 - 22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Carbonate stones (limestone)</td>
<td>L</td>
<td>2</td>
<td></td>
<td></td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>Dolomite</td>
<td>S</td>
<td>20 - 70</td>
<td>0.1 - 0.8</td>
<td>4 - 6</td>
<td></td>
</tr>
<tr>
<td>[Rob84]</td>
<td>durable 100 year old brick</td>
<td>L</td>
<td></td>
<td></td>
<td>1 - 10</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>Granville, Ohio</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Lub04]</td>
<td>orange brick (damaged)</td>
<td>M</td>
<td>0.5 - 2</td>
<td></td>
<td></td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>purple brick (undamaged)</td>
<td>L</td>
<td></td>
<td></td>
<td>10 - 30</td>
<td>30</td>
</tr>
<tr>
<td>[Que98]</td>
<td>Clinker brick</td>
<td>M</td>
<td>0.1 - 1</td>
<td></td>
<td></td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Baumberger sandstone</td>
<td>M</td>
<td>0.05 - 1</td>
<td></td>
<td></td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>Lime silica brick</td>
<td>S+L</td>
<td>60</td>
<td></td>
<td>8 - 12</td>
<td>30</td>
</tr>
<tr>
<td>[The04]</td>
<td>Cyprus sandstone</td>
<td>M</td>
<td>5</td>
<td>0.5 - 10</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Rhodes sandstone</td>
<td>L</td>
<td></td>
<td></td>
<td>10 - 100</td>
<td>39</td>
</tr>
<tr>
<td>[Zog04]</td>
<td>Sandstone (monumental patrimony of Tunisia)</td>
<td>L</td>
<td>10 - 40</td>
<td>17 - 25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Bec04]</td>
<td>Tuff</td>
<td>L</td>
<td>20</td>
<td></td>
<td>1 - 10</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>Sebastopol stone</td>
<td>L</td>
<td>8</td>
<td>10 - 40</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>[vH03a]</td>
<td>Tuff</td>
<td>M</td>
<td>8</td>
<td>0.1 - 6</td>
<td>30 - 45</td>
<td></td>
</tr>
</tbody>
</table>

Compared to the substrate (plaster/Bentheimer sandstone system), the salt accumulates in the plaster for all drying rates. On the other hand, when the plaster has larger pores than the substrate, like the plaster/calcium-silicate brick system, a significant amount of salt will crystallize within the substrate itself. When the drying rate is low, we expect that hardly any salt will crystallize in the plaster. At high drying rates, advection dominates the ion transport and salt will crystallize in both the plaster and the substrate.
4.6. Conclusions

The drying of the plaster/Bentheimer system of which the substrate was saturated with a salt solution and the plaster was saturated with pure water is very fast compared to the system that was uniformly saturated with a salt solution. At the drying conditions used in the present study (air speed over the drying surface of the order of 0.1 m/s and a very low relative humidity) advection dominates. The salt is transported to the plaster and accumulates there.

We have seen that the salt transport is determined by the Péclet number $Pe$, which can be calculated from the drying rate. In practice a lot of factors are influencing the drying rate and, correspondingly, the salt transport and accumulation. With increasing external temperature or air speed or with decreasing relative humidity of the environment, the drying rate increases, which results in increase of $Pe$.

We have introduced an efficiency number $\epsilon$, which is a measure of the efficiency of salt transport from the substrate to the plaster. It is a simple, practical number, which can be estimated without performing actual measurements of moisture or salt transport. The efficiency number, estimated in various ways, shows that the efficiency of salt transport from the Bentheimer sandstone to the plaster is very good, whereas the efficiency of salt transport from calcium-silicate brick to the same plaster is poor. Even without knowing the salt or water quantities in the plaster and the substrate, it is possible to obtain an estimate of $\epsilon_p$ using the cumulative pore-size distributions of the two materials. Therefore, it is possible to estimate the efficiency number $\epsilon_p$ before the materials are in physical contact. Finally, on basis of our results, we have discussed the salt transport properties of various combinations of plasters and substrates, of which the pore-size distributions have been reported in the literature.

Concluding we like to note that all estimates for the efficiency number $\epsilon_p$ are based on various assumptions, such as that the materials are in the perfect hydraulic contact and that the drying is sufficiently fast, i.e., $Pe \gg 1$. In the case of slow drying $\epsilon_p$ can only be regarded as crude approximation of the efficiency of salt transport. In composite materials which consist of more than 2 layers, the simple model that we used to estimate the efficiency number $\epsilon_p$ may not be correct, and a non-invasive technique like NMR is necessary to investigate the moisture and salt transport in these materials during the drying process.
4. Moisture and salt transport in plaster/substrate layers
5. Moisture and salt transport in three-layer plaster/substrate systems

For the application on salt loaded substrates, special salt resistant plasters have been developed. Based on their transport properties, two main categories of these salt resistant plasters exist: transporting and accumulating plasters. In accumulating plasters salt crystallizes in the plaster and not in the substrate or at the external surface. On the other hand, in salt transporting plasters, salt is transported to and crystallizes at the external surface of the plaster. We have investigated whether a plaster/substrate system which has two plaster layers with different pore sizes, can act as an accumulating system. In this study we used two substrates; fired-clay brick and Bentheimer sandstone. On the substrate we applied two plaster layers, of which the first (base) plaster layer has pores that are significantly smaller than the pores of the second (external) plaster layer. These systems were either saturated with pure water or a NaCl solution. We also studied non-uniformly salt loaded systems, in which the two plaster layers were saturated with pure water, and the substrate with a NaCl solution. The moisture and salt transport during drying are investigated with a Nuclear Magnetic Resonance technique. Among the investigated systems, it is found that only a system consisting of a gypsum and lime-cement plaster layers on a Bentheimer sandstone substrate behaves as a salt accumulating system when only the substrate is salt loaded. We conclude that it is difficult to make an accumulating system only based on differences in the pore-size distributions of the individual layers, because in practice it is difficult to prepare plasters with exactly specified pore-size distributions, in particular, plasters with pores which are larger than the pores of the substrate. Apart from this, the wetting properties of a salt solution differ from those of pure water; and, consequently, the drying behavior changes significantly.

5.1 Introduction

Plasters are often applied on masonry for decorative or protective reasons. For the application on salt loaded substrates, special (better) salt resistant plasters have been developed. Based on their transport properties, two main categories of these salt resistant plasters exist: transporting and accumulating plasters [Wij97, vH03b]. The aim of salt transporting plasters is that salt is transported to the surface of the plaster and crystallizes at this surface. The aim of accumulating plasters is that salt is not transported to the surface, but crystallizes in the base layer of the plaster, near to the substrate. In practice, an accumulating system is often achieved by applying a water repellent agent in the finishing
plaster layer, which prevents water and salt migration into the surface layer. However, application of a completely water repellent layer has a big disadvantage, e.g., the risk of spalling of such a layer due to salt crystallization just below it.

We have investigated whether a plaster system which contains no water repellent additive, but which consists of two layers with different pore sizes, can act as an accumulating plaster. In chapter 4 we have shown that in a layered system moisture and salt largely remain in the material with the smallest pores. Therefore, to achieve an accumulating system, the base plaster layer should have pores that are an order of magnitude smaller than the pores of the substrate and the external plaster layer. On the other hand, to minimize the salt accumulation in the external plaster layer, it should dry first. Therefore, the pores in this plaster layer should be the largest. The ideal pore-size distribution of such a three-layer system is sketched in figure 5.1.

First, in section 5.2 the theoretical concept behind a three-layer system with accumulating properties is outlined. Next, the experimental procedure and the NMR technique used to measure the moisture and salt profiles is briefly reviewed in section 5.3. The measurements of water and salt profiles during drying are discussed in section 5.4. Two three-layer systems were investigated: a fired clay brick substrate with a combination of lime-cement plasters and a Bentheimer sandstone substrate with a lime-cement plaster on which as a finishing a gypsum layer was applied. Finally, in section 5.5 the main conclusions are given.

5.2 Theory

In this section we briefly discuss the moisture and salt transport during drying of three-layer systems consisting of two plaster layers and a substrate, in order to clarify the idea behind an accumulating plaster based on pore size differences. Drying of a multi-layer system is determined by the capillary pressure, i.e.,

$$p_c = \frac{2\gamma \cos \phi}{r_m}.$$  \hspace{1cm} (5.1)

Here $r_m$ is the pore size that discriminates between the pores filled with water ($r < r_m$) and the empty pores ($r > r_m$). $\gamma$ [N m$^{-1}$] is the surface tension of the liquid/vapor interface and $\phi$ is the contact angle between air/liquid and air/solid interfaces. More details can be found in chapters 2 and 4.

At some time during the drying process and at a certain moisture content, water is present in the pores with diameters smaller than $r_m$ in all materials. Therefore, the material with the largest pores is ‘emptied’ first [Bra99]. According to the same principle, the layer with the smallest pores will dry last. In accumulating systems we would like the external layer to dry first, and therefore it should have larger pores than the base layer and the substrate, as is shown in figure 5.1. In that case the drying behavior resembles the drying of a plaster where a water repellent is applied in the outer layer.
As already outlined in chapter 2 and chapter 4, the drying behavior of the different layers influences the salt transport. The competition between ion advection and diffusion is characterized by a Péclet number $Pe$, which can be estimated from the water velocity $|U|$: 

$$Pe = \frac{|U| L}{D},$$  \hspace{1cm} (5.2)

where $L$ and $D$ are the length scale of interest and the ion diffusivity, respectively. For $Pe \gg 1$ advection dominates the ion transport, which happens at sufficiently high drying rates, whereas for $Pe \ll 1$ diffusion dominates the ion transport, which happens at low drying rates.

If the external layer has the largest pores, it dries first and the transport of liquid water and salt through this layer stops. During a later stage of the drying process, the rest of the salt that is present in the system will remain in the the base layer, the substrate or both. If the smallest pores are present in the base layer, as sketched in figure 5.1, we expect that salt accumulates preferably in that layer.

5.3 Experimental

The samples used in our study are cylindrical rods of about 19 mm diameter and 50 mm height. They were uniformly capillary saturated by immersing them in water or a NaCl solution, $c = 4$ mol l$^{-1}$, for about 20 hours. The corresponding salt quantity amounts to roughly 0.02 gram per gram of sample. The samples were sealed with teflon tape from all sides except the top surface. The drying of the samples is enhanced by dry air (0.7 l min$^{-1}$) flowing over the exposed surface.
The H and Na profiles have been measured with NMR using the setup described in chapter 3. The echo times for measuring hydrogen and sodium were 0.2 and 0.45 ms, respectively. Some Na signal loss occurred in the plaster layers, due to fast $T_2$ relaxation.

Since the NMR sensitivity for Na is low, a high NaCl concentration ($c = 4 \text{ mol l}^{-1}$) was used. Moreover, the Na signals from 256 successive spin-echo measurements were averaged to obtain a sufficient signal to noise ratio. The main magnetic field $B_0$ and the gradient $G$ were 0.7 T and 0.33 T m$^{-1}$, respectively. The one-dimensional resolution was $0.9 \pm 0.1 \text{ mm}$ for H and $3.5 \pm 0.5 \text{ mm}$ for Na. To determine the H and Na profiles the sample was moved in the vertical ($x$) direction by means of a step-motor [Pel95]. Due to the short transverse relaxation time of Na in the solid phase [Pel03], in our equipment only dissolved Na ions are measured. During the acquisition of the profiles the RF frequency is switched in such a way that the H and Na signals can be recorded quasi-simultaneously [Pel95, Pel00].

Using an external standard, the H and Na signal intensities can be related to the volume of water [cm$^3$] and the quantity of Na [mol]. This standard contained a NaCl solution ($c = 3 \text{ mol l}^{-1}$), to which a small amount of CuCl$_2$ ($c = 0.03 \text{ mol l}^{-1}$) was added to decrease the longitudinal relaxation time of hydrogen and, consequently, the repetition time of the spin-echo sequences (see chapter 3).

### 5.4 Results

#### 5.4.1 Plaster layers on a fired-clay brick substrate: an LS system

First a system was measured consisting of a fired-clay brick (FCB) substrate on which two plaster layers (S and L) where applied. These plaster layers were prepared using different sand particle distributions in such a way that plaster S should have small pores and plaster L large pores.

<table>
<thead>
<tr>
<th></th>
<th>Blast furnace slag cement</th>
<th>Ca(OH)$_2$</th>
<th>sand 0.5–1 mm</th>
<th>fine particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>L plaster</td>
<td>1</td>
<td>4</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>S plaster</td>
<td>1</td>
<td>4</td>
<td>8.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

The ingredients used for the plaster preparation are shown in table 5.1. The system was dried during seven days in a plastic box and during 21 days at 40 °C and 65 % relative humidity. After that the system was carbonated during a few weeks, until full carbonation was reached, in a box with 3 % CO$_2$ (v/v) at 50 % relative humidity. This system will further be referred to as the LS system.

The pore sizes of the various materials have been measure by means of mercury intrusion porosimetry (MIP). The differential intrusion and the cumulative pore volume versus pore diameter are presented in figure 5.2. Both the S and L plasters appear to have bimodal pore-size distributions. The pore sizes, however, are rather similar, indicating that the initial goal was not reached.
Fig. 5.2: Pore-size distributions of the S plaster, the L plaster, and fired-clay brick (FCB) measured by mercury intrusion porosimetry.

Pure water

First, the drying behavior of an LS system saturated with pure water has been studied. The moisture profiles are presented in figure 5.3a. The time between two successive profiles is 2 hours. The water evaporates from the sample through the air/L-plaster interface at $x = 4\text{ mm}$.

In figure 5.3b the time dependence of the average saturation, $S \equiv \theta/\theta_0$, in the two plaster layers and the substrate is plotted. $\theta_0$ is the initial saturation of the respective materials at the start of the drying process. In our experiments, $\theta_0$ usually corresponds to the capillary saturation. Inspection of this figure shows that three drying stages can be distinguished. During stage 1 ($t < 1\text{ h}$), the external plaster layer (L) and the FCB substrate dry simultaneously. The base plaster layer (S) dries only slightly. During the second drying stage ($t = 1 - 4\text{ h}$) the water content in both plaster layers remains constant and the substrate continues to dry.

This behavior can be explained by the dependence of the capillary pressure on the pore size, see equation 5.1. Water evaporates first from the pores with the lowest capillary pressure, i.e., the largest pores. In this sample the largest pores ($\sim 100\text{ mm}$) are present in the two plaster layers and to some extent in the FCB substrate (see Fig. 5.2). During the second drying stage these pores are empty and now only the pores in the range $1 - 10\text{ µm}$ present in the FCB substrate dry. During the third drying stage ($t > 4\text{ h}$) the L and S plaster layers start to dry, whereas the drying rate of the FCB substrate is lower than during the previous stage. A significant decrease of the total drying rates observed at $t \approx 7\text{ h}$. At this time the water network breaks down and a receding drying front enters the external (L) plaster layer. From this moment on the drying is slower, since the moisture transport is limited by water vapor diffusion. After about 20 hours the external plaster layer is dry.
Next, the combined transport of water and salt in the LS system was studied. The sample was initially saturated with a NaCl solution, \( c = 4 \text{ mol l}^{-1} \). The moisture profiles are plotted in figure 5.4a for every 5 hours of the drying process. The time dependence of the average saturations in the two plaster layers and the substrate is shown in figure 5.4b.

Again three drying stages can be observed, similar to the case of pure water. However, the drying of the salt loaded system is much slower. By the presence of salt the relative humidity at the air-liquid interface is decreased and, consequently, the drying rate decreases [Hal02]. Moreover, the transfer coefficient in the expression for the evaporation rate at the surface (\( \beta \) in Eq. 2.8) is very likely decreased. As discussed in section 4.4.1,
5.4. Results

Fig. 5.4: a) Moisture profiles in the LS system for every 5 hours of the drying process. The samples were initially saturated with a NaCl solution (\( c = 4 \text{ mol l}^{-1} \)). The drying conditions are the same as in figure 5.3. b) Water saturation vs. drying time in the L and S layer, the FCB substrate, and the whole sample.

This may be caused by salt crystals blocking the pores near the drying surface, which reduces the effective surface area that is available for evaporation.

Apart from this, the total drying rate is almost constant during all drying stages. This can be explained by the absence of a receding drying front in the salt loaded systems. This might be due to a change of the wetting properties in the presence of NaCl [Pel03]. In such a case, liquid films may be present and the liquid network will be complete until very low saturations.

Initially, the external plaster layer (L) dries very fast, similar to the case of pure water. After about 5 hours the moisture content in this layer is almost constant. During this second drying stage only the FCB substrate is drying. After about 60 hours, all pores in the range 1 – 10 \( \mu \text{m} \) in the FCB are empty, and the L and S plaster layers start to dry.
5. Moisture and salt transport in three-layer plaster/substrate systems

Fig. 5.5: a) Profiles of dissolved Na in the LS system for every 5 hours of the drying process. The samples were initially saturated with a NaCl solution \( c = 4 \text{ mol l}^{-1} \). The drying conditions are the same as in figure 5.3. b) Amount of dissolved Na vs. drying time in the L layer, the S layer, and the FCB substrate.

In figure 5.5a the Na profiles are presented for every 5 hours of the drying process. The time dependence of the total amounts of dissolved Na in the plaster layers and the substrate is shown in figure 5.5b. We have to remark that in the plaster layers the Na content is underestimated, since not all dissolved ions could be measured due to the fast transverse \( T_2 \) relaxation of Na in the small pores. In fired-clay brick there is no Na signal loss, and the amount of dissolved ions can be measured quantitatively.

Inspection of figure 5.5b reveals that during the second stage of the drying process the Na content in the FCB substrate decreases. This is supported by the value of the Péclet number \( (Pe) \). This number can be calculated from the velocity profiles, similar to the
procedure outlined in chapter 4, but it can also be estimated from the drying rate of the fired-clay brick [Pel02, Hui02, Pel04]. During this drying stage $Pe \approx 3$, indicating that advective transport of ions dominates over ion diffusion and the Na ions are transported from the FCB substrate to the plaster layers. As both plaster layers stay wet, the salt will mainly crystallize in the external layer near the air/plaster interface. Indeed, salt crystallization at the drying surface has been observed by visual inspection.

During the third drying stage ($t > 60$ h) $Pe \approx 0.35$ and therefore diffusion is dominant. Hence no Na ions will be transported by advection from the FCB substrate to the plaster layers.

![Fig. 5.6: Normalized Na and Cl contents in the uniformly salt loaded LS system as a function of position.](image)

In order to determine the final Na distribution, the sample has been cut in 8 slices after the end of the drying process and the amounts of Na and Cl in these slices have been measured quantitatively by ion chromatography. In figure 5.6 we have plotted the measured ion contents of these slices. These ion contents have been divided by the total amount of the corresponding ions in the sample, i.e., the summed contents of all slices. The vertical lines indicate the positions of the interfaces between the various materials. The Cl profiles match the Na profiles within experimental inaccuracy, indicating that both ions are transported together. The ion chromatography results show that about 60 % of the salt is present in the external plaster layer, while the rest is distributed over the base layer and the substrate. This indicates that the present system does not behave as a salt accumulating system.
Non-uniformly salt loaded system

In practice, the initial salt distribution in the plaster layers and the substrate might be inhomogeneous, as restoration plasters can be applied on salt loaded substrates. Therefore, we have investigated the transport in an LS sample where the plaster layers were immersed in pure water and the FCB substrate was immersed in a NaCl solution, \( c = 4 \text{ mol l}^{-1} \). The moisture profiles at every five hours of the drying process are presented in figure 5.7a. The time dependence of the average water saturations in the two plaster layers and the substrate is plotted in figure 5.7b, together with the average saturation of the whole sample.

![Figure 5.7](image)

**Fig. 5.7:** a) Moisture profiles in the LS system presented for every 5 hours of the drying process. The plaster layers were initially saturated with pure water and the FCB substrate was saturated with an NaCl solution (\( c = 4 \text{ mol l}^{-1} \)). The drying conditions are the same as in figure 5.3. b) Water saturation vs. drying time in the L and S layer, the FCB substrate, and the whole sample.
Fig. 5.8: a) Profiles of the dissolved Na in the LS system for several moments during the drying process. The plaster layers were initially saturated with pure water and the FCB substrate was saturated with an NaCl solution \((c = 4 \text{ mol l}^{-1})\). The drying conditions are the same as in figure 5.3. b) Amount of dissolved Na vs. drying time in the L layer, the S layer, and the FCB substrate.

Inspection of figure 5.7a and 5.7b shows that two drying stages can be distinguished. During the first drying stage \((t < 8 \text{ h})\) the FCB substrate dries fast and the moisture content in both plaster layers is high. During the second drying stage \((t > 8 \text{ h})\) the plaster layers start to dry. Since the plaster layers were saturated with pure water, the drying rate of the sample is much higher than for the sample that was uniformly saturated with a NaCl solution.

In figure 5.8a the Na profiles are plotted for several moments during the drying process. In figure 5.8b the amounts of dissolved Na in the two plaster layers and the substrate are presented. It is obvious that the salt transport differs significantly from that in the
uniformly saturated sample, since in this case the initial salt content in the two plaster layers is zero.

During the first drying stage \((t < 8 \text{ h})\) the Na content in the FCB substrate decreases significantly (i.e. about 50 %), while the Na concentration, calculated from the observed Na and water contents, stays at the initial concentration of 4 mol l\(^{-1}\). The Péclet number calculated from the drying rate of the FCB substrate is about 23. Hence the salt is transported by advection from the FCB substrate to the plaster layers, and the total amount of salt in the plaster layers increases, as can be seen from figure 5.8b. Visual inspection revealed salt efflorescence at the air/plaster surface.

During the second drying stage \((t > 8 \text{ h})\) the observed Na content in the two plaster layers and the substrate decreases. The drying rate of the substrate decreases significantly and the plaster layers start to dry. During this stage \(Pe \approx 0.65\), which indicates that diffusion dominates and salt will accumulate in the substrate as well. After about 45 h the top plaster layer is dry and no further salt transport is possible in this layer.

\[
\text{Fig. 5.9: Normalized Na and Cl contents as a function of position in the non-uniformly salt loaded LS system.}
\]

After the end of the drying process the final Na distribution in the sample was determined again by ion chromatography. The sample was cut in 9 slices and the total amounts of Na and Cl in these slices were measured. In figure 5.9 measured ion contents are plotted. These ion contents have been divided by the total amount of the corresponding ions in the sample, i.e., the summed contents of all slices. The Cl profiles match the Na profiles within experimental inaccuracy, indicating that both ions are transported together. The figure shows that the most of the salt is present in the external layer and at the S plaster/FCB interface. The rest of the salt is distributed in the base (S) plaster layer and the FCB substrate.
5.4. Results

5.4.2 Plaster layers on Bentheimer sandstone substrate: a GPB system

Fig. 5.10: Pore-size distributions of gypsum, plaster, and Bentheimer sandstone, measured by mercury intrusion porosimetry.

The second system which was tested consisted of a Bentheimer sandstone substrate on which a plaster layer was applied. This system was essentially the same as the system that was used for the measurements presented in chapter 4. The plaster layer had the following composition: lime:cement:sand = 4:1:10 (v/v). On top of this lime-cement plaster layer a layer of a coarse porous gypsum plaster (Knauff; MP75SL) was applied. The system was dried during four days in a plastic box and three days at 40 °C. After that the system was carbonated during a few weeks, until full carbonation was reached, in a box with 3 % CO₂ (v/v) at 60 % relative humidity. This system will further be referred to as GPB system.

The pore-size distributions of the gypsum, the plaster, and the Bentheimer sandstone measured by mercury intrusion porosimetry are shown in figure 5.10. This figure reveals that the Bentheimer sandstone and the base lime-cement plaster layer have ideal pore-size distributions, as mentioned in section 5.2. To achieve an ideal accumulating plaster, the external layer should have pore sizes that are an order of magnitude larger than those of both the substrate and the base plaster layer. However, the pores of the gypsum, as measured by mercury intrusion porosimetry, were smaller than the pores of the Bentheimer sandstone.

Pure water

First, the drying behavior of the GPB system saturated with pure water has been studied. In figure 5.11a the moisture profiles are plotted for every 2 hours of the drying process. The time dependence of the average water saturation in the gypsum and plaster layer and in the substrate is plotted in figure 5.11b. Inspection of this figure shows that two drying
Fig. 5.11: a) Moisture profiles in the GPB system for every 2 hours of the drying process. Dry air is blown over the top of the sample \((x = 4 \text{ mm})\) with a flow of \(0.7 \text{ l min}^{-1}\). The sample was initially saturated with pure water. b) Water saturation vs. drying time in the gypsum and plaster layer, the Bentheimer sandstone substrate, and the whole sample.

Stages can be distinguished. During stage 1 \((t < 5 \text{ h})\) the Bentheimer sandstone and the external gypsum layer are drying simultaneously, whereas the base plaster layer remains almost saturated. In the gypsum layer a receding drying front is observed. According to the pore-size distributions presented in figure 5.10, Bentheimer sandstone should dry faster than gypsum. The simultaneous drying of the gypsum layer and the Bentheimer sandstone might be explained by a higher contact angle \(\phi\) of water in the gypsum layer in comparison with the contact angle of water in the Bentheimer sandstone. In such a case, the value of \(r_m\) for gypsum may be of the same order as that for Bentheimer sandstone (see Eq. 5.1) in the relevant range of the capillary pressure \(p_c\).
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Around \( t \approx 5 \text{ h} \) the total drying rate decreases because the gypsum layer is nearly dry and the moisture in this layer is transported by vapor diffusion. During the second drying stage \((t > 5 \text{ h})\), the base plaster layer dries relatively slow, since it has the smallest pores.

Salt solution

![Graphs showing moisture profiles and water saturation vs. drying time](image)

Fig. 5.12: a) Moisture profiles in the GPB system for every 10 hours of the drying process. The samples were initially saturated with NaCl solution \((c = 4 \text{ mol l}^{-1})\). The drying conditions are the same as in figure 5.11. b) Water saturation vs. drying time in the gypsum and plaster layer, the Bentheimer sandstone substrate, and the whole sample.

In this case, the GPB system was initially saturated with a NaCl solution with a concentration \(c = 4 \text{ mol l}^{-1}\). In figure 5.12a we have plotted the moisture profiles for every 10 hours of the drying process. The time dependence of the average saturations in the gypsum and plaster layers and in the substrate is plotted in figure 5.12b. This figure shows that the drying of this salt saturated system is very different from the drying of the system saturated with pure water.
Fig. 5.13: a) Profiles of the dissolved Na in the GPB system for several moments during the drying process. The samples were initially saturated with NaCl solution (c = 4 mol l\(^{-1}\)). The drying conditions are the same as in figure 5.11. b) Amount of dissolved Na versus drying time in the gypsum layer, the plaster layer, and the Bentheimer sandstone substrate.

During the first drying stage (t < 30 h) the Bentheimer sandstone substrate dries, but the gypsum layer remains almost wet. Because of the presence of salt the wetting properties of the gypsum obviously have changed. The contact angle \(\phi\) has decreased [Nij04], resulting in an increase of the pore size \(r_m\), below which the pores are filled at a certain capillary pressure (see equation 5.1). During the second drying stage (t > 30 h) the Bentheimer sandstone is rather dry, and the gypsum layer starts to dry rapidly. After about 50 hours of drying the plaster layer starts to dry and drying speed of the gypsum layer decreases.

The Na profiles for several moments during the drying process are plotted in figure 5.13a. The time dependence of the amounts of dissolved Na in the gypsum and plaster
layer and in the substrate is shown in figure 5.13b. In the gypsum and plaster layer not all sodium could be measured due to the fast transverse ($T_2$) relaxation of Na in the small pores. In the Bentheimer sandstone no Na signal loss occurs, and hence the amount of dissolved sodium can be measured quantitatively.

During the first drying stage ($t < 30$ h) the Na in the Bentheimer sandstone remains uniformly distributed, while the total amount of dissolved Na decreases. Using the drying rate of the Bentheimer sandstone, the calculated Péclet number is about 4, which indicates that advective transport of ions dominates over ion diffusion. During this stage about 70% of the Na ions are transported from the Bentheimer sandstone to the plaster layer and the gypsum layer. Simultaneously, the amount of dissolved Na in the gypsum layer and the plaster layer increases which indicates that salt accumulates in these two layers. The salt distribution in the gypsum layer and plaster layer is not uniform, but a Na peak develops near the external surface of the gypsum layer, see figure 5.13a. From this we can conclude that salt precipitates at the external surface of the sample, which was confirmed by visual inspection. During the second drying stage, $Pe \simeq 0.1$ in the Bentheimer sandstone, and diffusion dominates the ion transport. Salt which is present at this stage in the Bentheimer sandstone substrate will accumulate there.

To determine the final salt distribution, the sample was cut in 9 slices after the end of the drying process and the Na and Cl amounts in each slice were measured quantitatively by ion chromatography. The amount of Na in the individual slices divided by the total amount of Na in the sample is plotted in figure 5.14. The vertical line indicates the position of the interfaces between the successive layers. The Cl profiles, which are not shown in the figure, again matched the Na profiles within experimental inaccuracy, indicating that both ions are transported together. The ion chromatography results confirm the conclusions with respect to the salt accumulation derived from the NMR measurements.

![Normalized Na content in the GPB system as a function of position](image)
Non-uniformly salt loaded system

In order to investigate the effect of a non-uniform initial salt distribution, we have monitored the transport in the GPB system where the external (gypsum) layer and the base (plaster) layer were initially saturated with pure water and the Bentheimer sandstone was saturated with a NaCl solution ($c = 4 \text{ mol l}^{-1}$). The moisture profiles are plotted in figure 5.15a for every 2 hours of the drying process. The time dependence of the average water saturation in the gypsum and plaster layer and in the substrate is plotted in figure 5.15b, together with the average saturation of the whole sample.

Because the gypsum layer and the plaster layer are saturated with pure water, the

![Fig. 5.15: a) Moisture profiles in the GPB system for every 2 hours of the drying process. The gypsum and plaster were initially saturated with pure water and the Bentheimer sandstone was saturated with an NaCl solution ($c = 4 \text{ mol l}^{-1}$). The drying conditions are the same as in figure 5.11. b) Water saturation vs. drying time in the gypsum and plaster layers, the Bentheimer sandstone substrate, and the whole sample.](image-url)
5.4. Results

drying rate is much higher than for the uniformly salt loaded sample. This was also found in the LS system discussed in section 5.4.1. In the GPB system the gypsum layer is dry already after about 6 hours, which is even faster than for the GPB sample saturated with pure water. During the same time the water saturation in the plaster layer increases. This results from water transport from the gypsum layer to the plaster layer. The calculated water velocity profiles are presented in figure 5.16. The calculated water velocity in the gypsum layer is not very accurate, since the drying speed of the gypsum layer is very fast. Negative velocities in this figure indicate that water moves towards the external surface (negative $x$ axis direction). Inspection of this figure shows that at the start of the drying process the water velocity at both sides of the gypsum/plaster interface is positive, which implies that water is transported from this region to the region more close to the substrate.

![Water velocity in a GPB sample versus position for several drying times.](image)

Fig. 5.16: Water velocity in a GPB sample versus position for several drying times.

The most likely cause of this phenomenon is the preparation of the sample. In order to prevent diffusion of ions from the salt solution in the substrate to the pure water in the gypsum and plaster layer before the start of the drying process, these layers were immersed in water for only about 10 seconds. Immediately after this procedure the actual experiment was started. As a result the plaster layer may not have reached capillary saturation, which may cause water to move from the gypsum layer into the plaster layer. This explanation is supported by comparing the initial saturations of the plaster layers in Fig. 5.11a (0.27) and Fig. 5.15a (0.23).

During the first drying stage ($t < 8 \text{ h}$) the drying rate of the Bentheimer sandstone substrate is high. It starts to decrease during the second drying stage ($t > 8 \text{ h}$), where the plaster layer starts to dry.
Fig. 5.17: a) Profiles of the dissolved Na in the GPB system for several moments of the drying process. The gypsum and plaster were initially saturated with pure water and the Bentheimer sandstone was saturated with an NaCl solution ($c = 4 \text{ mol l}^{-1}$). The drying conditions are the same as in figure 5.11. b) Amount of dissolved sodium vs. drying time in the gypsum layer, the plaster layer, and the Bentheimer sandstone substrate.

In figure 5.17a the Na profiles are presented for several moments of the drying process. The time dependence of the amounts of dissolved Na in the gypsum and plaster layer and in the substrate is plotted in figure 5.17b. Initially, all salt is present in the Bentheimer sandstone substrate. During the first drying stage ($t < 8 \text{ h}$) the amount of salt in the Bentheimer sandstone substrate decreases by about 60 %, while it increases in the plaster layer. Obviously salt is transported from the Bentheimer sandstone to the plaster layer. This is confirmed by the high value of the Péclet number calculated for the Bentheimer sandstone ($Pe \simeq 18$), which indicates that advection dominates during this drying stage. Since the gypsum layer is already dry, further transport of salt to the drying surface
is disabled. Therefore, we expect that salt mainly accumulates in the plaster layer, as required for an accumulating system. During the second drying stage \((t > 8 \text{ h})\), the Péclet number calculated for the Bentheimer sandstone is about 0.2, indicating that diffusion dominates the ion transport and salt accumulates in the Bentheimer sandstone as well.

After the end of the drying process the sample was cut in 9 slices and the Na and Cl contents of these slices were measured quantitatively by ion chromatography. The amount of Na for each slice divided by the Na content of the whole sample is plotted in figure 5.14. The measured Cl distribution, which is not shown in the figure, again matches the Na distribution, which indicates that both ions are transported together. The salt is accumulated mainly in the plaster layer. Also inside the gypsum layer some salt has crystallized. One should note that the salt that is present in the first slice \((0 - 7.2 \text{ mm})\) reflects the total amount in the gypsum layer. Since the NMR results indicate that the surface of the gypsum layer has dried very fast, we expect that the salt in the gypsum is mainly present near the gypsum/plaster interface and that the salt content decreases near the external surface. This is confirmed by visual inspection of the external surface, where no salt was observed. From these results we conclude that in case of a non-uniformly salt loaded GPB system a salt accumulating system is achieved.

5.5 Conclusions

From our experiments on three-layer systems it was found that only in case of a non-salt loaded plaster and gypsum layer and a salt loaded Bentheimer sandstone substrate a salt accumulating system is formed. Our results indicate that it may be difficult to make an accumulating system that is based only on differences between the pore sizes of the individual layers. In practice it may be difficult to prepare plasters with exactly specified pore-size distributions. Apart from this, the selection of appropriate materials is complicated by the fact that the wetting properties of a salt solution differ from those of pure water, and, consequently, the drying behavior changes significantly. Even if the pore-size distributions suggest that a particular system will be salt accumulating, actual measurements of the drying behavior and the ion transport in a salt loaded system are necessary to verify this point.
5. Moisture and salt transport in three-layer plaster/substrate systems
6. Diffusion in porous building materials with high internal magnetic field gradients

Measuring the water diffusivity in porous building materials with NMR is hindered by the presence of large internal magnetic field gradients originating from magnetic impurities (Fe). To investigate the diffusion of water in these materials, a stimulated echo NMR technique is applied. A new analytical equation for the long-time signal decay in the presence of spatially varying internal field gradients is derived. This equation is experimentally confirmed by measurements on representative materials with large internal gradients (fired-clay brick and sintered crushed glass) and a material with very small internal gradients (glass filter). The diffusivity is determined in the long time limit, where it is constant and limited by the tortuosity of the pore structure. Tortuosities of different samples derived from the NMR data show an excellent agreement with the macroscopic tortuosities measured by electrochemical impedance spectroscopy. The developed technique can also be applied in unsaturated media, during e.g., drying, water absorption, and concentration changes. The characteristic length scales of the internal field fluctuations estimated from the model are compared with the structural length scales, whereas the magnitude of these fluctuations is compared with results of macroscopic magnetization measurements.¹

6.1 Introduction

In porous building materials, moisture and (dissolved) ions can give rise to several kinds of damage, e.g., frost damage, salt crystallization, corrosion of the reinforcement and mould growth. Moisture and salt are naturally present in the materials, and their quantity is increased by atmospheric influence (rain), neighborhood of salt water, etc. Knowledge of the transport properties of moisture and salt is necessary to obtain information about the durability of building materials. In this paper we will study the diffusivity of the fluid in some representative building materials and relate it to structural parameters like the tortuosity [Bea90].

NMR is a nondestructive technique that can be used for measuring the effective diffusivities of water, hydrocarbons and ion species in porous materials [Kim97, Hol01, Vog02]. The diffusivities obtained from these measurements are found to depend on the measurement time. With increasing times diffusing molecules start to feel the pore walls and the diffusion become restricted. From the measured time dependence of the diffusivity it is possible to obtain important structural information on the material [Vog02, Lat93]. From

¹ This chapter has been published in [Pet04]
the results for short times, it is possible to obtain the surface-to-volume ratio and pore diameter, whereas for long times (order of seconds) the diffusivity is constant and limited by the tortuosity of the pore structure. Therefore NMR offers the possibility to determine the tortuosity of the pore system [Lat95]. An alternative method to determine the tortuosity is electrochemical impedance spectroscopy, which is based on the measurement of the conductivity of ions dissolved in the pore fluid [Kle99]. NMR is preferred when chemical reactions or adsorption of ions at the pore walls occur, when the pore fluid already contains ions (cement and concrete) [Sny02] and during monitoring of time-dependent processes, like drying or absorption. Especially in the unsaturated state of a material, the diffusivity of the dissolved ions, which is measured electrochemically, can no longer be related to the diffusivity, since the latter may contain an important contribution from transport by vapor diffusion.

Generally, NMR diffusion measurements are performed using Pulsed Field Gradient (PFG) techniques [Ste65]. By analyzing the NMR signal decay induced by PFG’s, accurate results can be obtained when the internal field gradients are small. However, in many building materials a large amount of magnetic impurities (Mn, Fe, Co) can be present, which may give rise to internal gradients that are at least an order of magnitude larger than the gradients that can be applied externally [Val00, Val01b]. These gradients are often several orders of magnitude larger than the gradients induced by susceptibility differences between, e.g., water and a clean (diamagnetic) porous material. In fired-clay brick, for instance, the internal field gradients induced by the presence of about 4 % Fe cause such a rapid dephasing of the transverse nuclear magnetization, that even down to echo spacings of 100 µs, CPMG measurements show very pronounced diffusion effects. Using Hahn spin-echo pulse sequences with varying echo time, we observed a decay of the spin-echo signal in this material by more than a factor of 100 within 10 ms. Within experimental inaccuracy, this decay was independent of the magnitude and direction of the applied field gradient (0.2 – 1 T/m).

Since our aim is to determine the diffusivity at times of the order of seconds, we have to use a pulse sequence in which the part of the nuclear magnetization that generates the relevant NMR signal is in the longitudinal direction during most of the measurement time, such as the stimulated-echo sequence [Tan70]. This sequence has proven to be appropriate for diffusivity measurements in heterogeneous systems, but often very specialized pulse sequences like the ‘13-interval’ sequence [Cot89] have to be used, to suppress the effect of the cross terms between the internal and applied gradients [Vog02, Lat93, Lat95, For94], even if these gradients are small compared to the applied PFG’s. It has been shown that at long observation times this approach may fail, since it is based on the assumption that the diffusing molecules experience a constant internal field gradient during the experiment [Sel00]. In principle, the genuine diffusivities in heterogeneous media can be obtained by extrapolation of the data obtained from simple PFG stimulated-echo measurements [Vas01]. This technique, however, has only been applied to systems with single-exponential signal decays, and may therefore not be suitable for our materials, which show pronounced multi-exponential decays [Val01b].

In principle, the cross terms between the internal magnetic field fluctuations and the applied field gradients may be suppressed by using RF field gradients instead of $B_0$ gradi-
ents [Can97]. This may be an interesting alternative if the $B_1$ gradient can be made large enough to overcome the very large resonance offset fields present in magnetically ‘dirty’ materials. In this paper, however, we will focus on the question whether it is possible to apply a simple, constant field gradient NMR method to determine the diffusivity in such materials.

We will first define the characteristic length scales of pore structure and the internal magnetic fields. In this respect one should note that the distribution of the Fe impurities in our materials is not precisely known, and hence we will not a priori assume that both length scales are equal [Son00]. Next, we will introduce a new equation for the long-time stimulated-echo decay in materials with large internal gradients and confirm it experimentally for two materials with and one material without magnetic impurities. We will determine the diffusivity and quantitatively characterize the fluctuations of the internal magnetic fields. Finally, we will compare these results with data obtained by other methods.

6.2 NMR method

As already mentioned in the introduction, in porous media containing large amounts of magnetic impurities the transverse magnetization decays very fast, so it will have vanished at time scales at which the effect of the pore geometry on the diffusion of the water molecules can be observed. The stimulated-echo magnetization decay is governed by the longitudinal relaxation time ($T_1$) for a substantial part of the measurement time, during which it is in the longitudinal direction. Therefore $T_2$ and dephasing effects are minimized.

Fig. 6.1: Porous media characterized by a structural length scale $\xi_S$ and a length scale $\xi_B$, associated with the fluctuations of the internal field. During the measurements a constant external gradient is applied. The internal field gradients are superimposed on these external gradients.
In figure 6.1 we have schematically plotted the pore structure of the material and the magnetic field fluctuations, together with their characteristic length scales. At long time scales molecules diffuse over distances longer than the correlation length of the medium $\xi_S$. The typical time scale related to $\xi_S$ is $t_S \equiv \xi_S^2/6D$, where $D$ is the diffusivity of the water molecules within the pore system. At length scales much larger than $\xi_S$ the porous medium can be considered as homogeneous; the diffusivity $D$ is constant and determined by the geometry of the pore system. This is often called the tortuosity limit [Kle99]. The tortuosity of a medium is defined by the following relation.

$$\alpha = D_0/D,$$  \hspace{1cm} (6.1)

where $D_0$ is the bulk (self) diffusion constant of the pore fluid.

The stimulated echo pulse sequence [Tan70] is plotted schematically in figure 6.2. The signal attenuation for free diffusion is well known and can be described analytically. When the stimulated echo intensity $M_{st}$ is divided by primary echo intensity $M_{pr}$, the following equation is obtained:

$$\ln(M_{st}/M_{pr}) = -\left[1/T_1 + (\gamma G)^2 D \tau^2 \right] t.$$  \hspace{1cm} (6.2)

In this equation $T_1$ is longitudinal relaxation time, $\gamma$ is the gyromagnetic ratio (for a $^1$H nucleus $\gamma = 2.67 \times 10^8$ rad s$^{-1}$T$^{-1}$), $G$ is the applied external gradient, $\tau$ the time between the first two 90° pulses and $t$ is stimulated-echo time. By dividing the two echo intensities the $T_2$ relaxation term is eliminated automatically.

![Fig. 6.2: Stimulated echo pulse sequence with a constant field gradient. The magnetization decay is measured by changing the time between the second and third RF pulse (period 2). Measurements are performed for different values of $\tau$ and the applied field gradient $G$.](image)

Equation (6.2) holds for diffusion in bulk liquids and for diffusion in a macroscopically isotropic porous medium on length scales larger than $\xi_S$, where the medium can be considered as homogenous (the tortuosity limit). When internal gradients are present, the initial signal decay is generally very fast, and cannot be described by equation 6.2. The internal fields can be characterized by a characteristic length scale $\xi_B$ (Fig. 6.1).
typical time scale related to $\xi_B$ is $t_B \equiv \xi_B^2/6D$. At time scales shorter than $t_B$, the internal fields experienced by a spin during the periods 1 and 3 of the stimulated-echo sequence (Fig. 6.2), when the magnetization is in transverse plane, are still correlated. For time scales much larger than $t_B$ these internal fields become uncorrelated [Nes02] and the spins experience a purely random internal field.

For these time scales ($t \gg t_B$) the magnetization decay can be described by the equation

$$\ln \frac{M(t)}{M_0} = -\gamma^2 \tau^2 \left< (\bar{B}_r)^2 \right> - \left( T_1^{-1} + \gamma^2 G^2 \tau^2 D \right) t.$$ (6.3)

In this equation $\left< (\bar{B}_r)^2 \right>$ is the ensemble average of $\bar{B}_r$, which is the temporal average of the internal field experienced by a spin during an interval $\tau$ (periods 1 and 3, Fig. 6.2). For very small $\tau$, $\left< (\bar{B}_r)^2 \right>$ becomes equal $\sigma_B^2$, the squared standard deviation of the internal field $\bar{B}$. For details of the derivation we refer to the appendix. In this derivation it was assumed that $\tau \ll T_2$, the transverse relaxation time.

Equation 6.3 shows that the magnetization decay at long time scales can be described by a single exponent. This equation consists of three parts. The first term gives the total signal attenuation due to diffusion in the internal gradients. The second term is the contribution of the longitudinal relaxation. The third term describes the signal attenuation due to diffusion in the externally applied gradient. The important feature of the first term is that it does not depend on $t$, because the internal fields have become uncorrelated (spatially random) on the length scales much larger than $\xi_B$. With increasing echo times $t$, the second and third term of equation 6.3 become more important. At these times, decay due to diffusion is governed only by externally applied gradients and as such can be quantified.

From the right hand side of Eq. (6.3) we are able to define a crossover time $t^*$

$$t^* \equiv \frac{\gamma^2 \tau^2 \left< (\bar{B}_r)^2 \right>}{1/T_1 + (\gamma G)^2 D \tau^2}.$$ (6.4)

At time scales shorter than $t^*$ the internal fields dominate the signal decay. At longer time scales ($t > t^*$) the longitudinal relaxation and dephasing due to the applied gradients start to play significant role. Therefore, the diffusivity $D$ can only be measured when the signal is still above the noise level for $t > t^*$.

In a stimulated-echo experiment, the signal intensities of both the primary and the stimulated echo can be measured. In equation 6.2 the ratio of these two intensities is directly related to, amongst others, the diffusion coefficient $D$. On the other hand, equation 6.3 contains the ratio $M(t)/M_0$. In our experiments, this ratio is not necessarily equal to $M_{st}/M_{pr}$. The reasons for this are twofold. First, a significant dephasing of the transverse components of the magnetization forming the primary echo may occur during the time interval between the first and second $90^\circ$ pulse, which is not completely refocused at the time of the primary echo, due to the diffusive motion of the spins in the large local field inhomogeneities. Second, even if complete refocusing would occur, $M_{st}/M_{pr}$ would only be equal to $M(t)/M_0$ for perfect $90^\circ$ pulses. Since our samples are often much larger than thickness of the slices selected by our RF pulses (see section 6.3), this condition is generally not satisfied in our experiments. However, we measure the decay of the stimulated
echo for a constant value of $\tau$, and hence for a constant intensity of the primary echo. Since, on the other hand, only one coherent pathway contributes to the stimulated echo, the only effect of using $M_{st}/M_{pr}$ instead of $M(t)/M_0$ in equation 6.3 is the introduction of a constant scaling factor. This was checked experimentally by comparing stimulated-echo decay curves of our samples measured with RF flip angles optimized to 90° with decay curves measured with RF flip angles set to about 64° (reducing the RF power by 3 dB). The two sets of decay curves were found to coincide within experimental accuracy when a constant scaling factor was applied. These observations were corroborated by numerical simulations of the time evolution of the magnetization of a system of up to $10^6$ spins. In these simulations the Bloch equations were solved in the presence of both longitudinal and transverse relaxation, pulsed RF fields, as well as diffusion in a uniform magnetic field gradient.

Before detailed measurements on a sample were started, both the primary and stimulated echoes was measured for a set of echo times below 10 ms. The RF power was adjusted such that the observed echo-time dependence of $M_{st}/M_{pr}$ extrapolated to 1 for echo times going to zero. This adjustment was performed for each value of $\tau$. Although this procedure is not required for the analysis of the echo decay, it has the advantage that no scaling factors have to be applied afterwards. An experimental advantage of using $M_{st}/M_{pr}$ instead of $M_{st}$ alone is that variations in the sensitivity of the receiver chain during these very time-consuming measurements are automatically compensated.

### 6.3 Experimental setup and materials

A home-built nuclear magnetic resonance apparatus was used. The operating frequency was 30.9 MHz ($B_0 = 0.7$ T). A constant magnetic field gradient was generated with a set of Anderson coils. The maximum gradient strength used in the experiments was 425 mT/m. A detailed description of the apparatus is given elsewhere [Kop94].

The ratio of the amplitudes of the stimulated echo and the primary echo was measured as a function of the echo time, by changing the time interval between the second and third RF pulse (cf. Fig. 6.2) from 1 ms to 3 s. The complete set of data was obtained by varying the interpulse time $\tau$ and the applied external gradient $G$. The time $\tau$ was varied between 70 and 500 $\mu$s, and the magnitude of $G$ between 94 mT/m and 425 mT/m. The width of the RF pulses was 12 $\mu$s.

NMR diffusivity measurements were performed on porous samples of glass filter (Durran, borosilicate glass), fired-clay brick, and sintered crushed glass. The porosity of fired-clay brick is 23 %. The pore sizes have been measured previously [Pel95] and are in the range of $1 - 10$ $\mu$m. The porosity of sintered crushed glass is 53 % and the pore size measured by mercury intrusion amounts to $14 \pm 3$ $\mu$m. Glass filter is made from borosilicate glass. According to the supplier the pore sizes are in the range $10 - 16$ $\mu$m. The measured porosity is 33 %. Glass filter is used as a standard, magnetically ‘clean’, material with pore sizes comparable to that of fired-clay brick and sintered crushed glass.

The samples have a cylindrical shape with a diameter of 2 cm and a length of 5 cm in the case of fired-clay brick and sintered crushed glass. The length of the glass filter sample was 6 mm. The samples were vacuum saturated with deionized water.
6.4 Results

6.4.1 Glass filter

As already mentioned above, this material contains a negligible amount of magnetic impurities. In figure 6.3a the measured ratio between the amplitudes of the stimulated echo and the primary echo is plotted semi-logarithmically against the spin-echo time \( t \) for various interpulse times \( \tau \) at a constant gradient strength \( G \). In figure 6.3b this ratio is plotted for various gradient strengths \( G \) at a constant \( \tau \). In all cases a mono-exponential decay is observed. The dashed lines represent fits of such decays to the experimental data. For all sets of data, the intercept of these fits with the vertical axis is given by \( M/M_0 = 1 \) within experimental inaccuracy, from which it can be concluded (Eq. 6.3) that internal gradients are negligible. This suggests that the diamagnetic susceptibility of the solid pore matrix of this material is almost equal to that of water, which is present in the pore space. Within experimental accuracy, this is corroborated by the results of magnetization measurements presented in table 6.2.

In order to determine the diffusivity we have plotted the slope \( R = [1/T_1 + (\gamma G)^2 D\tau^2] \) of the fitted exponential decay as a function of \((\gamma G)^2 \tau^2\) (see figure 6.6). Within experimental inaccuracy, a linear relation is found, indicating a constant diffusivity. This suggests that the water molecules are probing the complete pore space in the range of echo times \( t \) from 0.1 to about 5 s. The longitudinal relaxation time \( T_1 \) was measured independently by a saturation recovery sequence. The corresponding decay is reflected by the solid line in figure 6.3. The value of \( T_1 \) determined this way is in perfect agreement with the value...
determined from the intercept of $R$ with the vertical axis in Fig. 6.6. The $T_1$ values and the diffusivity are given in table 6.1.

![Graph showing the ratio between the stimulated echo and primary echo in sintered crushed glass plotted against the spin-echo time.](image)

**Fig. 6.4:** Ratio between the stimulated echo and primary echo in sintered crushed glass plotted against the spin-echo time. a) $\tau$ is varied at $G = 330$ mT/m. For clarity only the data for $t < 1.5$ s are plotted. b) $G$ is varied at $\tau = 410$ $\mu$s. The solid line reflects the decay due to longitudinal relaxation only. Dashed lines are fits of a mono-exponential decay to the data for $t > t^*$. The vertical dotted lines reflect the range of $t^*$ for these experiments (see text).

### 6.4.2 Fired-clay brick and sintered crushed glass

Both fired-clay brick and sintered crushed glass contain a rather large amount of magnetic impurities [Val00, Val01b]. In figures 6.4 and 6.5 the measured ratio between the amplitudes of the stimulated echo and the primary echo is plotted semi-logarithmically.
against the spin-echo time \( t \) for various \( \tau \) (a) and gradient strengths \( G \) (b). Inspection of these figures shows that for both materials the decay is not mono-exponential. Only in the long time limit the magnetization decay can be described by a single exponent. Also for these materials, the value of \( T_1 \) has been determined independently by saturation recovery sequences.

Fig. 6.5: Ratio between the stimulated echo and primary echo in fired-clay brick plotted against the spin-echo time. a) \( \tau \) is varied at \( G = 188 \) mT/m. b) \( G \) is varied at \( \tau = 410 \) \( \mu \)s. See the caption of figure 6.4 for further explanation.

There are two possible mechanisms which may explain the initial decay: diffusion in the internal gradients and diffusion in the external gradients. As the initial decay appears to be insensitive to the magnitude of the applied field gradient, at least in the range of \( G \) used in our experiments (see Fig. 6.4b, 6.5b), this decay is mainly caused by diffusion in the internal gradient fields, i.e., the water molecules feel a fluctuating magnetic field (Fig. 6.1). At longer time scales the external gradient strength has a significant effect on the signal decay, as can be seen from figures 6.4b and 6.5b.
In order to improve the signal to noise ratio, a large number of signal averages was used (up to 300 in the case of fired-clay brick and 100 in the case of sintered crushed glass). It is obvious, however, that the noise cannot be neglected and has to be taken into account when fitting theoretical model predictions to the data. The magnitude of the noise was measured in a separate experiment and incorporated as a constant term in the fitting procedure.

By fitting the linear part of the decay curves with straight lines we observed that in the case of varying $G$ (constant $\tau$) the intersection $f(\tau) = -\gamma^2 \tau^2 \langle \langle \vec{B}_G \rangle \rangle$ of these lines with the vertical axis is constant within experimental inaccuracy (Fig. 6.4b, 6.5b), whereas it changes significantly with varying $\tau$ (Fig. 6.4a, 6.5a). This agrees with the behavior predicted by our model (Eq. 6.3).

The time at which the effects resulting from diffusion in external gradients become significant, $t^*$, is given by Eq. 6.4. It can be estimated from plots of $M_{st}/M_{pr}$ versus $t$ from the time at which $R \times t^* = f(\tau)$. The range of $t^*$ obtained this way is denoted by the dotted vertical lines in figures 6.4b and 6.5b. The diffusion coefficient can only be measured if the signal is still above the noise level for $t > t^*$. As already mentioned above, we had to use many signal averages to meet this condition.

In figure 6.6 the slope $R = [1/T_1 + (\gamma G)^2 D \tau^2]$ obtained from fits of straight lines to the data for $t > t^*$ is plotted against $(\gamma G)^2 \tau^2$. Within experimental inaccuracy, a linear relation is found for both sintered crushed glass and fired-clay brick, indicating that the diffusivity does not depend on the observation time and the internal fields experienced by the spins have become uncorrelated. The fitted values of $R$ for variations of both $G$ and $\tau$ are located on a single line. The diffusivities and longitudinal relaxation times $T_1$ for both materials are given in table 6.1. This table reveals that the values of $T_1$ obtained from figure 6.6 agree nicely with the values obtained from saturation recovery experiments.

The tortuosity of the pore space is estimated from the long time behavior of the diffusivity (Eq. 6.1). We measured the self-diffusion coefficient $D_0$ of bulk water by stimulated echo experiments. At 25 °C the measured value of $D_0$ is $(2.34 \pm 0.02) \times 10^{-9}$ m$^2$/s, which is in good agreement with the literature value $(2.30 \times 10^{-9}$ m$^2$/s) [Mil89]. Tortuosities for the three samples are given in the table 6.1.

<table>
<thead>
<tr>
<th></th>
<th>glass filter</th>
<th>sintered crushed glass</th>
<th>fired-clay brick</th>
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<tbody>
<tr>
<td>$T_1$ (s) (SE)</td>
<td>1.50 ± 0.02</td>
<td>0.36 ± 0.02</td>
<td>1.04 ± 0.02</td>
</tr>
<tr>
<td>$T_1$ (s) (SR)</td>
<td>1.49 ± 0.01</td>
<td>0.37 ± 0.01</td>
<td>1.10 ± 0.02</td>
</tr>
<tr>
<td>$D$ (10$^{-9}$m$^2$/s)</td>
<td>1.20 ± 0.05</td>
<td>1.55 ± 0.05</td>
<td>0.41 ± 0.02</td>
</tr>
<tr>
<td>$\alpha$ (SE)</td>
<td>1.8 ± 0.1</td>
<td>1.5 ± 0.1</td>
<td>5.6 ± 0.5</td>
</tr>
<tr>
<td>$\alpha$ (EL)</td>
<td>--</td>
<td>1.4 ± 0.1</td>
<td>5.9 ± 0.2</td>
</tr>
</tbody>
</table>

Table 6.1: Comparison of the stimulated echo (SE) results with the values of $T_1$ obtained by the saturation recovery method (SR) and the electrolytically (EL) determined tortuosity $\alpha$. The thickness of the glass filter sample was insufficient to perform electrochemical tortuosity measurements.
6.5 Discussion and conclusions

We have demonstrated that in porous materials with a large amount of magnetic impurities the diffusivity of the pore fluid at long observation times (the tortuosity limit) can be measured from stimulated-echo experiments in static external gradient fields. The measured signal decay is interpreted in terms of a model (Eq. 6.3) that describes the decay at times \( t \gg t_B \), where the internal magnetic field fluctuations experienced by the diffusing spins at the start and the end of the observation time are uncorrelated.

As mentioned above, in the limit \( \tau \to 0 \) the term \( \langle (\vec{B}_r)^2 \rangle \) is equal to the squared standard deviation \( \sigma_B^2 \) of the internal field fluctuations. To estimate the magnitude of these fluctuations, we have plotted the intercept \( f(\tau) \) of the lines fitted to the data for \( t > t^* \) in figures 6.4b and 6.5b against \( \tau^2 \). The results for both sintered crushed glass and fired-clay brick are presented in figure 6.7. One should note that, in principle, the location of the intercepts \( f(\tau) \) may be affected by the procedure described in section 6.2 to relate \( M_{st}/M_{pr} \) to \( M(t)/M_0 \). However, the possible error rapidly decreases for smaller values of \( \tau \), since in the limit \( \tau \to 0 \) no dephasing occurs. For this reason, a point \( f(0) = 1 \) has been added to the experimental data. The initial slope \( -\gamma^2 \sigma_B^2 \) has been estimated from smooth curves through the data. The standard deviations \( \sigma_B \) obtained from this procedure are presented in table 6.2.

6.5 Discussion and conclusions

The method presented in this paper may be useful for diffusivity measurements in many classes of materials in which internal magnetic fields interfere with the applied gradients (i.e. susceptibility induced fields in natural stones, inorganic and biologic mater-
Diffusion in porous building materials with high internal magnetic field gradients

Fig. 6.7: Intercepts $f(\tau)$ of the fits presented in Fig. 6.4b and 6.5b plotted against $\tau^2$. Dashed curves represent fits of a smooth function through the experimental values of $f(\tau)$. Solid lines reflect the estimated initial slope $-\gamma^2 \langle (\bar{B}_r)^2 \rangle$.

In contrast to electrochemical measurements, the present method is also applicable to investigations of transport processes in unsaturated media, during drying, absorption, or crystallization.

One should note that the method can only be used in situations where the internal field fluctuations have become uncorrelated before the signal has dropped below the noise level, for instance, due to fast longitudinal relaxation. Attempts to determine the diffusivity of $^{23}$Na ions in a fired-clay brick sample saturated with a NaCl solution did not succeed, because $T_1 \approx 60$ ms for $^{23}$Na in a bulk solution [Eis66] and decreases even more in a porous material.

The standard deviation $\sigma_B$ of the internal field fluctuations determined from the first term of Eq. 6.3 in the limit $\tau \to 0$ (Fig. 6.7) for sintered crushed glass and fired-clay brick is of the same order of magnitude as the amplitude of the internal field fluctuations ($\Delta B_{int}$) determined from bulk magnetization measurements (table 6.2). One should note that these magnetization data, which were obtained using a SQUID magnetometer, were

Table 6.2: Standard deviation of the internal field fluctuations $\sigma_B$ determined by NMR, together with the amplitudes of internal magnetic fields $\Delta B_{int}$ obtained from bulk magnetization measurements. All values of $\Delta B_{int}$ are the difference of the values obtained from the magnetization measurements on a completely dry sample and the value corresponding to a water-air interface at 0.8 T.

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<th>glass filter</th>
<th>sintered crushed glass</th>
<th>fired-clay brick</th>
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<tbody>
<tr>
<td>$\sigma_B$ ($\mu$T)</td>
<td>0</td>
<td>25 ± 5</td>
<td>35 ± 5</td>
</tr>
<tr>
<td>$\Delta B_{int}$ ($\mu$T)</td>
<td>1 ± 1</td>
<td>25 ± 3</td>
<td>59 ± 6</td>
</tr>
</tbody>
</table>
analyzed assuming that the magnetic impurities are distributed homogeneously within the material. In that case the internal field fluctuations can be related directly to the maximum variation of the demagnetizing field at the pore to liquid interfaces [Val01b]. Both magnetization and EPMA measurements [Val00], however, indicate that, especially in fired-clay brick, a fraction of these impurities is present in the form of small clusters, which act as localized magnetic dipoles. The internal fields in the direct vicinity of these dipoles may be much larger than the field variations arising from homogeneously distributed impurities, and hence the value of $\Delta B_{\text{int}}$ presented in table 6.2 should be considered as a lower limit. Because of the presence of these clusters, the length scale of the internal field fluctuations $\xi_B$ may also differ from the typical pore dimension $d$.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig6_8.png}
\caption{Echo-time dependence of $\lambda(t)$, which represents the ratio between the stimulated echo and primary echo in sintered crushed glass minus the fitted long-time part of the signal decay. The inset shows a semi-logarithmic plot of $\lambda(t)$. The solid line in this inset reflects a fit of a mono-exponential decay to the data between 0.01 and 0.3 s.}
\end{figure}

To investigate this point in more detail we focus on the behavior of the decay curves for $t < t^\ast$. We subtract the part of the decay that is dominated by the applied gradients (Eq. 6.3) from the experimental data. As an example, the behavior of the remaining part $\lambda(t)$ for sintered crushed glass, $G = 188$ mT/m and $\tau = 400$ $\mu$s is plotted in figure 6.8. This figure shows that the part of the signal decay that can be attributed to the internal field fluctuations has vanished at $t \simeq 0.3$ s. This value would correspond to some characteristic time constant between 0.05 and 0.1 s.

To analyze the decay process more precisely, we plotted $\lambda(t)$ on a semi-logarithmic scale (inset of the figure). This plot suggests a mono-exponential decay, except for very short echo times. If we assume that, for constant $G$ and $\tau$, the decay $M_{st}/M_{pr}$ can be factorized as $g(t) \exp(-t/T_1)$, the observed decay rate $1/T_d$ might be associated with a
6. Diffusion in porous building materials with high internal magnetic field gradients

typical correlation time \( t_B \) according to

\[
\frac{1}{T_d} = \frac{1}{t_B} + \frac{1}{T_1}.
\] (6.5)

This yields a correlation time \( t_B = 80 \text{ ms} \). This correlation time can be related to a typical length scale of the internal gradient fields using the expression \( \xi_B = \sqrt{6D t_B} \). The values of \( \xi_B \) for sintered crushed glass and fired-clay brick obtained this way are presented in table 6.3.

For fired-clay brick, \( \xi_B \) seems to be significantly larger than the average pore size, which is in agreement with the presence a small amount of clusters of magnetic impurities. Because \( \xi_B \) is estimated assuming three-dimensional diffusion and the pore size \( r \) is obtained from a model-dependent interpretation of, e.g., mercury intrusion experiments, such a conclusion is not justified for sintered crushed glass.

It is obvious that our model does not give a complete description of the signal decay for \( t < t^* \). One should note, however, that, except for \( t_B \) and \( \xi_B \), all parameter values presented in this paper are obtained from the long time behavior of the signal decay, where details of the initial dephasing process of the spins are unimportant. The constant field gradient stimulated-echo NMR method, in conjunction with the model presented in this paper, provides a reliable method for the quantitative characterization of water transport in magnetically ‘dirty’ porous media (diffusivity), including the pore geometry of the media (tortuosity). We therefore intend to apply this method to investigations of macroscopic transport properties in building materials at different degrees of water saturation.

6.6 Appendix: Magnetization Decay

Our aim is to measure the macroscopic diffusion coefficient \( D \) in ‘dirty’ porous media with the help of a stimulated-echo experiment. The long-time behavior of the echo decay in such an experiment contains information about this coefficient. In this appendix, we derive an expression for the echo decay on time scales \( t > t_B \), when the pore space that

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<th>fired-clay brick</th>
</tr>
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<tbody>
<tr>
<td>( t^* ) (s)</td>
<td>0</td>
<td>0.37 ± 0.07</td>
<td>1.3 ± 0.1</td>
</tr>
<tr>
<td>( t_B ) (s)</td>
<td>0</td>
<td>0.08 ± 0.01</td>
<td>0.20 ± 0.02</td>
</tr>
<tr>
<td>( \xi_B ) (µm)</td>
<td>0</td>
<td>27 ± 4</td>
<td>22 ± 3</td>
</tr>
<tr>
<td>( r ) (µm)</td>
<td>10 – 16</td>
<td>14 ± 3</td>
<td>1 – 10</td>
</tr>
</tbody>
</table>

Table 6.3: Typical time scales and correlation length scales \( (\xi = \sqrt{6D t}) \) characterizing the three porous materials used in our experiments. \( t^* \) is the time above which the effect of external gradients on the diffusion can be observed, \( t_B \) is the time related to the correlation length \( \xi_B \) of the internal field fluctuations, and \( d \) is the dominant pore size. In the glass filter sample no detectable internal field gradients are present (section 4.1) and hence \( t^* \) and \( t_B \) have a value of zero.
is probed by the spins can be considered as homogeneous. The magnetization decay in a stimulated-echo experiment occurs via three different mechanisms: longitudinal relaxation ($T_1$), transverse relaxation ($T_2$), and dephasing. CPMG measurements on a glass filter sample revealed a perfect mono-exponential decay described by $T_2 = 0.65 \pm 0.02$ s. In similar measurements on sintered crushed glass and fired-clay brick always significant diffusion effects were present, even at the smallest attainable spacing between adjacent 180° pulses (150 µs). Nevertheless, these measurements clearly indicate that the value of $T_2$ in the latter two materials exceeds 10 ms. Because in our stimulated-echo experiments the echo decay is measured for fixed time intervals $\tau \leq 500$ µs between the first and second 90° pulse, the effect of $T_2$ can be neglected. The mechanisms underlying longitudinal relaxation and dephasing are independent, and hence the magnetization $M(t)$ yielding the stimulated echo can be described by the following equation:

$$M(t) = M_0 \left\langle \exp (i\phi) \exp \left( -\frac{\zeta}{T_{1,S}} \right) \exp \left( -\frac{t - \zeta}{T_{1,B}} \right) \right\rangle. \quad (A1)$$

In this equation $t$, $M_0$, $T_{1,S}$, and $T_{1,B}$ are the echo time, the initial magnetization, the longitudinal relaxation time of the spins in a boundary layer close to the pore wall, and the longitudinal relaxation time of the spins in the ‘bulk’ pore fluid, respectively. The quantities $\phi$ and $\zeta$ are properties of a group of spins that follow exactly the same path in space and time; $\phi$ and $\zeta$ are their phase angle and their total residence time near pore walls, respectively. Equation A1 represents an ensemble average over all spins.

At the time scale of interest ($t > t_B$) the pore space probed by spins can be considered as homogeneous and all spins have the same residence time near the pore wall, $\zeta = t\lambda S/V$, where $\lambda$, $S$, and $V$ are the thickness of the boundary layer, the pore surface, and the pore volume in the system, respectively [Bro79]. For these time scales equation A1 can be rewritten as

$$M = M_0 \left\langle \exp (i\phi) \right\rangle \exp \left[ -t \left( \frac{1 - \lambda S/V}{T_{1,B}} + \frac{\lambda S/V}{T_{1,S}} \right) \right] \equiv \left\langle \exp (i\phi) \right\rangle \exp \left( -\frac{t}{T_1} \right). \quad (A2)$$

The phase angle of a spin $k$, $\phi_k$, can be calculated from:

$$\phi_k = \gamma \left[ \int_{t-\tau}^{t} B (\vec{r}_k) \, dt - \int_{0}^{\tau} B (\vec{r}_k) \, dt \right]. \quad (A3)$$

In this equation $\gamma$, $B$, $\tau$, and $\vec{r}_k$ are the gyromagnetic ratio, the magnitude of the magnetic field, the time between the first two 90° pulses, and the position of spin $k$, respectively. The magnetic field experienced by a spin $k$ consists of various contributions:

$$B (\vec{r}_k) = B_0 + x_k G_x + \tilde{B} (\vec{r}_k), \quad (A4)$$

where $B_0$, $G_x$, and $\tilde{B}$ are the main magnetic field, the applied gradient (along $x$), and a fluctuating field, $\langle \tilde{B} \rangle = 0$, respectively. We only consider the component of the fluctuating field along $B_0$, which is allowed as long as $\tilde{B} \ll B_0$. Apart from this, we assume that any background gradients caused by, e.g., inhomogeneities of the main magnetic field or
macroscopic demagnetization effects due to the non-spherical geometry of the sample, are very small compared to $G_x$. By combining equations A3 and A4 we arrive at:

$$
\phi_k = \gamma G_x \left[ \int_{t-\tau}^{t} x_k dt - \int_0^{\tau} x_k dt \right] + \gamma \left[ \int_{t-\tau}^{t} \tilde{B}(\vec{r}_k) dt - \int_0^{\tau} \tilde{B}(\vec{r}_k) dt \right] \equiv \phi_{k,G} + \phi_{k,B}. \tag{A5}
$$

In this equation $\phi_{k,G}$ and $\phi_{k,B}$ are respectively used for the contributions of the applied gradient and the fluctuating field to the dephasing.

As already mentioned in section 6.2, at time scales $t > t_B$ the spins experience a purely random field $\tilde{B}(\vec{r}_k)$, for which $\langle \tilde{B}(\vec{r}_k) \rangle = 0$. Hence $\langle x_k \tilde{B}(\vec{r}_k) \rangle$ will also be zero, which implies that $\phi_{k,G}$ and $\phi_{k,B}$ will be uncorrelated at time scales $t > t_B$. If we use this fact and substitute equation A5 in equation A2, we obtain

$$
M \propto \exp \left( -t/T_1 \right) \langle \exp (i\phi_G) \rangle \langle \exp (i\phi_B) \rangle. \tag{A6}
$$

The second term at the right hand side of this equation is well known:

$$
\langle \exp (i\phi_G) \rangle = \exp (-\gamma^2 G^2 \tau^2 D t). \tag{A7}
$$

The last term at the right hand side of equation A6 can be written as

$$
\langle \exp (i\phi_B) \rangle = 1 - \frac{1}{2!} \langle \phi_B^2 \rangle + \frac{1}{4!} \langle \phi_B^4 \rangle + O(6). \tag{A8}
$$

Here $O(6)$ represents terms of sixth and higher order in $\phi_B$. It is important to note that $\langle \exp (i\phi_B) \rangle$ does not vary with time and only depends on the interpulse time $\tau$. By using equation A5 we can obtain expressions for the terms at the right hand side of this equation. For example, $\langle \phi_B^2 \rangle$ is given by:

$$
\langle \phi_B^2 \rangle = 2\gamma^2 \tau^2 \langle (\tilde{B}_r)^2 \rangle, \quad \tilde{B}_r \equiv \frac{1}{\tau} \int_{u}^{u+\tau} \tilde{B} dt, \tag{A9}
$$

where the quantity $\tilde{B}_r$ is the value of $\tilde{B}$ averaged over a time interval $\tau$. Note that the ensemble average of this quantity is a function of $\tau$ when a significant dephasing occurs during the interval $\tau$. In the limit $\tau \to 0$ this equation reduces to

$$
\langle \phi_B^2 \rangle = 2\gamma^2 \tau^2 \langle \tilde{B}^2 \rangle = 2\gamma^2 \tau^2 \sigma_B^2, \tag{A10}
$$

where $\langle \tilde{B}^2 \rangle$ can also be thought of as the spatial average of $\tilde{B}^2$ and $\sigma_B \equiv \langle \tilde{B}^2 \rangle^{1/2}$ is the standard deviation of the field $\tilde{B}$. By combining the equations A6, A7, and A9 we arrive at the following expression for the magnetization,

$$
M = M_0 \left( 1 - \gamma^2 \tau^2 \langle (\tilde{B}_r)^2 \rangle + O(4) \right) \exp \left[ - \left( T_1^{-1} + \gamma^2 G^2 \tau^2 D \right) t \right]. \tag{A11}
$$

For small values of $\tau$ this expression can be written as:

$$
M = M_0 \exp \left[ -\gamma^2 \tau^2 \langle (\tilde{B}_r)^2 \rangle - \left( T_1^{-1} + \gamma^2 G^2 \tau^2 D \right) t \right]. \tag{A12}
$$

This equation shows that by varying $t$, $\tau$ and $G$ systematically we are able to obtain the diffusion coefficient $D$ and the magnitude of the internal fields $\sigma_B$. We wish to note again that equation A11 is valid as long as $t > t_B$ and $\tau \ll T_2$, whereas equation A12 additionally assumes that $\tau$ is so small that no significant dephasing due to diffusion occurs during this time interval.
7. Conclusions and outlook

In this chapter, the main conclusions based on the research described in this thesis are presented. Next, recommendations are given for future research on salt transport in layered systems, which is important for improving the performance of plasters.

7.1 Conclusions

NMR is a non-destructive technique, very suitable for probing the transport of water and dissolved ions in porous materials. We have measured the time evolution of the hydrogen and sodium profiles quasi-simultaneously, which enabled us to monitor the moisture and salt transport during drying of layered porous media. Measurements have been performed with a spatial resolution of the order of one millimeter, which is very accurate compared to conventional destructive techniques (hygroscopic moisture content analysis, chemical methods). We have to remark that in gypsum, plaster, and calcium-silicate brick not all dissolved Na could be measured by NMR, due to the fast transverse ($T_2$) relaxation of Na in the small pores. Although this signal loss has been corrected for in first order, this correction may be less reliable at very low moisture contents. In Bentheimer sandstone and fired clay-brick no Na signal loss occurs, and hence the amount of dissolved Na can be measured quantitatively.

The drying behavior of salt contaminated layered porous systems has been studied. Two key factors could be identified: the pore-size distributions of the individual layers and the presence of the salt. First of all, drying is determined by the pore sizes in the various layers. During drying air first invades the pores with the lowest capillary pressure. According to equation 2.4 these are generally the largest pores. Therefore, during drying of layered materials the layer with the smallest pores remains wet while the other layers dry. Secondly, the presence of salt strongly influences the drying process by suppressing the formation of a receding drying front and by reducing the drying rate. The suppression of the formation of a receding drying front most likely results from a change of the wetting properties in the presence of salt [Pel03]. This may be related to the decrease of the contact angle $\phi$ between the liquid-air and the solid-liquid interface in the presence of salt [Nij04]. In such a case, liquid films may be present and the liquid network will be complete until very low saturations.

The slower drying of the salt loaded sample can partly be attributed to the dependence of the drying rate on the relative humidity [Hal02]. The presence of salt decreases the relative humidity near the liquid-air interface and, consequently, decreases the drying rate [Daï02]. Apart from this, the drying rate may have been decreased by blocking of the pores near the drying surface by salt crystals, which reduces the effective surface area.
that is available for evaporation. This explanation is supported by our measurements on non-uniformly salt loaded systems in which the layer adjacent to the drying surface was saturated with pure water. These systems have drying rates that are significantly higher than those of the corresponding uniformly salt-loaded systems.

For two-layer systems it was shown that the moisture transport in the plaster layer was largely influenced by the pore-size distribution of the underlying substrate. The layer with the largest pores dried first. This has important implications for the transport and accumulation of salt in plaster/substrate systems. When the plaster was applied on a substrate with larger pores, salt tended to accumulate in the plaster layer, because this layer remained wet for a longer time than the substrate. When the plaster was applied on a substrate with smaller pores, some salt crystallized in the plaster layer, but a significant amount of salt crystallized within the substrate itself. In the latter case, the salt accumulation is also influenced by the drying rate.

The effect of the drying rate on the salt transport can be described by a Péclet number ($Pe$), which characterizes the competition between advective and diffusive ion transport. At high drying rates, $Pe \gg 1$, advection dominates the ion transport and salt accumulates at the drying surface. Therefore salt will primarily crystallize in the plaster. During a later stage of the drying process, salt will crystallize in the region that stays wet for the longest time, which is the system with the smaller pores. On the other hand, at very low drying rates, $Pe \ll 1$, diffusion dominates the ion transport and the salt concentration tends to be uniform everywhere in the sample. For a system in which the pores of the plaster are larger than those of the substrate, we expect hardly any salt to crystallize in the plaster, since it will diffuse to the relatively slow drying substrate.

For the two-layer systems an efficiency number was introduced, as a measure for the efficiency of salt transport from the substrate to the plaster. It is a simple, practical number, useful for the choice of a compatible plaster for a particular substrate. The efficiency number can be calculated or estimated in different ways: from the moisture content of the layers, from the amount of salt present in the layers, or from the pore-size distributions of the materials.

Using a three-layer system, with two different plaster layers applied on a substrate, we tried to achieve an accumulating system in which salt would crystallize in the base layer of the plaster, near the substrate, and not in the cover layer, near the surface. Our experiments suggest that it is rather difficult to make a salt accumulating system which is purely based on differences between the pore-size distributions of the individual layers. In practice it is difficult to prepare a plaster with an exactly specified pore-size distribution. On the other hand, the wetting properties of a porous medium may change significantly in the presence of salt, which has a large effect on the drying behavior and, consequently, the salt transport.

One of our experiments on a non-uniformly salt loaded three-layer gypsum/plaster/Bentheimer sandstone sample revealed that, at the beginning of the drying process, water was transported from the cover layer to the base layer of the plaster. This has been attributed to the preparation of the sample. In order to prevent diffusion of ions from the salt solution in the substrate to the pure water in the gypsum and plaster layer before the start of the drying process, these layers were immersed in water for only about 10
seconds. Immediately after this procedure the actual experiment was started. As a result
the plaster layer may not have reached capillary saturation, which may cause water to
move from the gypsum layer into the plaster layer. Because in this system the cover
layer also dried very fast, no salt was transported to the external surface, and a salt
accumulating system has been formed.

NMR also offers the possibility to measure the microscopic moisture diffusion constants
in porous materials. In many building materials, these measurements are hindered by the
presence of internal magnetic field gradients originating from magnetic impurities, like
Fe. A new analytical equation was derived for the long-time stimulated echo decay in
the presence of spatially varying internal field gradients. This equation was used to
interpret our NMR diffusion measurements on three materials with different amounts of
magnetic impurities. It was found that the moisture diffusivity in these materials could be
determined correctly. The tortuosity coefficients of these materials have been calculated,
and were found to be in good agreement with the values obtained by electrochemical
impedance spectroscopy. Compared to this technique, NMR has the advantage that it
can be used for investigations of the diffusion in the presence of chemical reactions or
in unsaturated media, i.e., during drying, absorption, or crystallization. Our approach
may be useful for diffusivity measurements in many classes of materials in which internal
magnetic fields strongly interfere with the applied magnetic field gradients. Due to the
fast longitudinal relaxation of Na, even in the bulk, it was not possible to determine the
microscopic diffusivity of Na in building materials.

7.2 Outlook

Although the study on moisture and salt transport in layered systems presented in this
thesis has provided a lot of information that may be useful for practical applications,
there are still many open questions, which will be addressed below.

First, our experiments on three-layer systems show that is rather difficult to make
a salt accumulating system which is purely based on differences between the pore-size
distributions of the individual layers. In an accumulating system the cover layer should
dry first. It follows from the capillary pressure law that the drying process is not only
determined by the pore size but also by the contact angle $\phi$ between the liquid-air and the
solid-liquid interface. Therefore a relatively fast drying top layer could also be realized
by making the pore walls more hydrophobic, i.e., by increasing the contact angle $\phi$.
This can be achieved by applying a water repellent agent on the outer layer. To relate
the performance of such systems to possible damage, for instance, spalling of the water
repellent layer, research should be done on moisture and salt transport and crystallization
in the presence of water repellent agents.

Second, in our study we have only investigated the transport and accumulation of
NaCl. It is obvious that also research should be done on the transport and accumulation
of other salts like $\text{Na}_2\text{SO}_4$ and $\text{Na}_2\text{CO}_3$, which cause serious damages to building materials.
In the case of NaCl the crystals can easily nucleate and hence a NaCl solution does not
show supersaturation. NaCl crystals are deposited at all positions in the sample where
the concentration reaches the saturation concentration. When ions are transported by
advection to the drying surface, NaCl crystals will be deposited mainly at the drying surface. Na$_2$SO$_4$ and Na$_2$CO$_3$ are salts which nucleate more difficult, and therefore their solutions may show supersaturation. If ions are transported to the drying surface, their concentration may exceed the saturation concentration in a wider region of the sample, where they can eventually crystallize causing damage. Since the NMR technique offers the possibility to determine Na concentrations, it is possible to investigate the supersaturation of Na$_2$SO$_4$ and Na$_2$CO$_3$ solutions in porous materials.

In contrast to NaCl, which has only an anhydrous crystal structure, Na$_2$SO$_4$ and Na$_2$CO$_3$ can have hydrous crystal phases as well (Na$_2$SO$_4$·7H$_2$O; Na$_2$SO$_4$·10H$_2$O and Na$_2$CO$_3$·10H$_2$O), depending on the temperature and relative humidity. During drying of porous materials containing Na$_2$SO$_4$ or Na$_2$CO$_3$ solutions liquid water can be removed by two processes: evaporation and hydration. By using a balance it might be possible to measure the mass of the evaporated water. The mass of the hydrated water could then be determined from the initial mass of the water and the mass of the evaporated water. Such a study might answer the question which crystal phase is present in the porous material.

Third, we have studied the salt accumulation in materials only during a single drying process. In practice, frequent wetting-drying cycles occur because of the weather, day-night, and season cycles. Therefore it is important to study the transport of moisture and salt for several cycles, since damages of building materials generally only occur after a number of cycles [Gou97]. We expect that repeated wetting-drying cycles will change the initial salt distribution in the system and, therefore, influence the drying and salt accumulation behavior. In order to investigate this point, successive wetting-drying experiments should be done under controlled laboratory conditions.

Fourth, in our experiments the drying process started at (almost) capillary saturation of the various materials. To investigate the effect of other initial conditions and other boundary conditions (air speed relative humidity), it might be useful to model the water and salt transport in these systems following an approach as outlined in [Bro98b, Bro98a]. One should note that such modeling requires additional information about the macroscopic (equilibrium) properties of the various materials. This information might be obtained from measurements of the capillary pressure curves (wetting curve, drying curve) and the hygroscopic curves. This type of simulation might, for instance, also provide information on the consequences of a non-perfect hydraulic contact between the plaster layer and the substrate.

Finally, in some porous media like gypsum, plaster, and calcium-silicate brick we were not able to measure the amount of Na quantitatively by NMR. We corrected for the NMR signal loss by calibrating the Na signal in the completely saturated sample and assumed that the transverse relaxation time ($T_2$) of Na and, therefore, the signal loss does not change with moisture content. Of course this is a rather crude assumption, since at low moisture contents only the smallest pores are filled with NaCl solution, which leads to a drastic decrease of $T_2$ and hence the Na signal intensity. To solve this problem, calibrations of the Na signal should be performed at different saturations.
Bibliography


Summary

Moisture and salt decay processes are amongst the most recurrent causes of damage of built objects and monuments. Although salt damage has been intensively investigated for several decades, the mechanisms and factors that control salt transport, accumulation, and crystallization in porous media and the development of damage are poorly understood. Knowledge about the transport of water and ions and salt crystallization in masonry (in the thesis referred to as substrate) and plasters is needed to explain salt damage and to develop durable materials.

In chapter 2 the moisture and ion transport in porous media is reviewed briefly. The drying behavior of a material is determined by the capillary pressure, and therefore by pore-size distribution. As a consequence the largest pores are emptied first. In layered systems of different materials the material with larger pores should dry first. Ions are transported via diffusion and advection with the flow of the water. These processes are described by a diffusion-advection equation. For high drying rates advection dominates the ion transport, whereas for low drying rates diffusion dominates the ion transport.

Chapter 3 reviews the Nuclear Magnetic Resonance (NMR) technique and the experimental set-up, that is used for the investigations described in this thesis. NMR is a non-destructive technique, suitable for probing the transport of water and dissolved ions in porous materials. The time evolution of the hydrogen profiles and the profiles of dissolved sodium can be measured quasi-simultaneously, which enables monitoring the moisture and salt transport during drying of (layered) porous media. The spatial resolution of the NMR measurements is of the order of one millimeter, which is very accurate compared to conventional destructive techniques (hygroscopic moisture content analysis, chemical methods). It is outlined that using a stimulated echo NMR pulse sequence the self-diffusion of water in porous materials can be measured up to diffusion times exceeding 1 s.

In chapter 4 the moisture and salt transport in a two-layer plaster/substrate system is discussed. It is shown experimentally that moisture and salt transport in the plaster layer is influenced by the pore-size distribution of the underlying substrate. The same plaster was applied on a Bentheimer sandstone substrate and a calcium-silicate brick substrate. In case of the plaster/Bentheimer sandstone system the plaster has pores that are an order of magnitude smaller than those of the substrate. On the other hand, in case of the the plaster/calcium-silicate brick system the plaster has pores that are an order of magnitude larger than the smallest pores of the substrate. The moisture and salt transport and the salt accumulation differs significantly for these two systems. During the drying process, air invades first the layer with the largest pores. Therefore, in the plaster/Bentheimer sandstone system the substrate dries before the plaster, while in
the plaster/calcium-silicate brick system the substrate stays wet longer than the plaster. This has important implications for the transport and accumulation of salt. In the plaster/Bentheimer sandstone system (the pores of the plaster are smaller than those of the substrate) all salt is removed from the substrate and accumulates in the plaster, because this layer remains wet for a longer time than the substrate. In the plaster/calcium-silicate brick system (the substrate has smaller pores than the plaster) some salt crystallizes in the plaster layer, but a significant amount of salt crystallizes within the substrate itself. The efficiency of the salt transport from substrate to plaster is quantified in terms of an efficiency number $\epsilon$, which can be estimated in different ways. It is a simple, practical number, useful for the choice of a compatible plaster for a particular substrate. Based on the results of this study, we have discussed the salt transport for various combinations of plasters and substrates, of which the pore-size distributions have been reported in the literature.

In chapter 5 the question is addressed whether a plaster/substrate system which has two plaster layers with different pore sizes, can act as an accumulating system, i.e., a system in which salt crystallizes in the plaster layer and not in the substrate or at the external surface. To this end we have studied the drying behavior of such plasters applied on two different substrates: fired-clay brick and Bentheimer sandstone. On the substrate we applied two plaster layers, of which the first (base) plaster layer has pores that are significantly smaller than the pores of the second (external) plaster layer. These systems were either saturated with pure water or a NaCl solution. We also studied non-uniformly salt loaded systems, in which the two plaster layers were saturated with pure water, and the substrate with a NaCl solution. The moisture and salt transport during drying were investigated. Among the investigated systems, it is found that only a system consisting of an external gypsum layer and a base lime-cement plaster layer on a Bentheimer sandstone substrate behaves as a salt accumulating system when it is non-uniformly salt loaded. We conclude that it is difficult to make an accumulating system only based on differences in the pore-size distributions of the individual layers, because in practice it is difficult to prepare plasters with exactly specified pore-size distributions, in particular, plasters with pores which are larger than the pores of the substrate.

Chapter 6 describes NMR measurements of the self-diffusion of water in porous materials containing a large amount of magnetic impurities. These impurities (Fe), which are often present in building materials, hinder the diffusivity measurements by NMR. To investigate the self-diffusion of water in these materials, a stimulated echo NMR technique is applied. A new analytical equation for the long-time stimulated-echo decay in the presence of spatially varying internal field gradients is derived and experimentally confirmed. This equation is used to interpret our NMR diffusion measurements on three materials with different amounts of magnetic impurities. It is shown that, using this method, the self-diffusion constant of water in these materials can be determined correctly. The method presented in this chapter may be useful for diffusivity measurements in many classes of materials in which internal magnetic fields interfere with the applied gradients (i.e. susceptibility induced fields in natural stones, inorganic and biologic materials).
Samenvatting

Verwering ten gevolge van vocht en zout is een van de meest voorkomende oorzaken van schade aan bouwconstructies en monumenten. Hoewel al tientallen jaren lang veel onderzoek is verricht naar zoutschade, zijn de mechanismen en factoren die van invloed zijn op zouttransport, ophoping van zout en kristallisatie nog steeds slecht begrepen. Inzicht in het transport van water en ionen en zoutkristallisatie in metselwerk (in dit proefschrift ondergrond genoemd) en pleisters is nodig om zoutschade te kunnen verklaren en om duurzame materialen te ontwikkelen.


In hoofdstuk 3 wordt een overzicht gegeven van de kernspinresonantie (NMR) techniek en van de experimentele opstelling, die is gebruikt voor het onderzoek dat in dit proefschrift is beschreven. NMR is een niet-destructieve techniek, waarmee het transport van water en daarin opgeloste ionen in poreuze materialen kan worden onderzocht. De tijdsafhankelijkheid van de profielen van waterstof en opgeloste natrium-ionen kunnen quasi-simultaan worden gemeten, wat het mogelijk maakt het vocht- en zouttransport tijdens het drogen van (gelaagde) poreuze media waar te nemen. Het ruimtelijk oplossend vermogen van de NMR metingen in ruwweg 1 mm, hetgeen veel nauwkeuriger is dan meer conventionele destructieve technieken (hygroskopische analyse van het vochtgehalte, chemische analyses). Beschreven wordt dat met behulp van een stimulated echo NMR pulserie de zelfdiffusie van water in poreuze materialen kan worden gemeten tot diffusietijden langer dan 1 s.

pleister/Bentheimer zandsteen systeem droogt de ondergrond eerder dan de pleisterlaag, terwijl in het pleister/kalkzandsteen systeem de ondergrond langer nat blijft dan de pleisterlaag. Dit heeft belangrijke gevolgen voor het zouttransport. In het pleister/Bentheimer zandsteen systeem (de poriën van de pleister zijn kleiner dan die van de ondergrond) verdwijnt alle zout uit de ondergrond en hoopt zich op in de pleisterlaag, omdat deze langer nat blijft. In het pleister/kalkzandsteen systeem (de poriën van de ondergrond zijn kleiner dan die van de pleister) kristalliseert een deel van het zout in de pleisterlaag, maar het merendeel in de ondergrond zelf. De efficiëntie van het zouttransport van de ondergrond naar de pleister kan worden uitgedrukt in een efficiëntie-getal $\epsilon$, dat op verschillende manieren afgeschat kan worden. Dit is een eenvoudig, praktisch getal, dat nuttig is bij de keuze van een compatibele pleister voor een bepaalde ondergrond. Uitgaande van deze resultaten wordt het zouttransport besproken voor verschillende combinaties van pleister en ondergrond, waarvan de porie-verdelingen in de literatuur zijn gerapporteerd.

Hoofdstuk 5 gaat in op de vraag of een systeem waarin zich op de ondergrond twee pleisterlagen met verschillende porieverdelingen bevinden, zich kan gedragen als een accumulerend systeem. Dit is en systeem waarbij het zout kristalliseert binnen in de pleisterlaag, dus niet in de ondergrond of aan het uitwendige oppervlak. Hiertoe is het drooggedrag van een degelijk type pleister bestudeerd op een ondergrond van rode baksteen en op een ondergrond van Bentheimer zandsteen. Op de ondergrond werden twee pleisterlagen aangebracht. De eerste (basis)laag heeft poriën die beduidend kleiner zijn dan die van tweede (buiten)laag. Deze systemen werden verzadigd met water of met een NaCl zoutoplossing. Verder zijn niet-uniform zoutbelaste systemen bestudeerd, waarin de pleisterlagen verzadigd werden met puur water en de ondergrond met een zoutoplossing. Onderzocht werd het vocht- en ionentransport van deze systemen tijdens het drogen. Van alle systemen die zijn bestudeerd, gedraagt alleen het systeem dat bestaat uit een buitenlaag van gipspleister, een basislaag van cement-pleister en een ondergrond van Bentheimer zandsteen zich als een accumulerend systeem, wanneer het niet-uniform zoutbelast is. Hieruit kan geconcludeerd worden dat het lastig is een accumulerend systeem te maken dat gebaseerd is op verschillen in de porieverdelingen van de individuele lagen, omdat het in de praktijk moeilijk is om pleisters te vervaardigen met exact gespecificeerde porieverdelingen, in het bijzonder poriën die groter zijn dan die in de ondergrond.

In hoofdstuk 6 worden NMR metingen beschreven van de zelfdiffusie van water in poreuze materialen die veel magnetische verontreinigingen bevatten. Deze verontreinigingen (Fe), die veel voorkomen in bouwmaterialen, bemoeilijken de metingen van de diffusie met behulp van NMR. Om de zelfdiffusie van water in dit soort materialen te onderzoeken, is een stimulated echo NMR techniek gebruikt. We hebben een nieuwe analytische uitdrukking afgeleid voor het signaalverval van de stimulated echo wanneer in het systeem plaatsafhankelijke magneetveld-gradiënten aanwezig zijn. Met behulp van deze uitdrukking, die geldig is voor lange diffusie-tijden, zijn NMR diffusie-metingen geïnterpreteerd die verricht zijn aan drie materialen met een verschillende hoeveelheid magnetische verontreinigingen. We hebben aangetoond dat met behulp van deze methode de zelfdiffusie van water in dit soort materialen correct kan worden bepaald. De methode kan nuttig zijn voor diffusiemetingen in tal van materialen waarin de interne magneetvelden de aangelegde magneetveldgradiënten verstoren (bijvoorbeeld susceptibiliteits-geïnduceerde velden in natuursteen, inorganische en biologische materialen).
List of Publications


• J. Petković, L. Pel, H.P. Huinink, K. Kopinga, and R.P.J. van Hees, Salt transport and crystallization in plaster layers: a nuclear magnetic resonance study, accepted for publication in *Int. J. for Restoration*.


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