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Pressure measurements during one-sided heating of concrete

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Abstract

The explosive spalling of heated concrete is a complex process that is not yet completely understood. The spalling may be caused by increasing vapor pressures in the pores of the concrete. The experiments discussed in this report are the first to combine temperature and pressure measurements with 1D-moisture profiles, during the heating of concrete.

For this, cylindrical concrete (W/C=0.54) samples with a diameter of 75 mm and a length of 100 mm are heated at one flat face. Pressures are measured with a CSTB-type pressure gauge, located at the central axis of the cylinder, at a depth of 20-40 mm from the heated face. Maximum pressures ranged from 0.27 MPa to 0.85 MPa.

The spatial moisture distribution is obtained by placing the sample in an NMR scanner during heating. Temperatures are measured with thermocouples in the pressure gauge and at several depths at the side of the samples.

The combination of temperature, pressure and moisture measurements shows that the highest pressures are reached when the drying front passes. Furthermore, near the drying front the pressure follows the saturated vapor pressure.

The results of the combined measurements of moisture, pressure and temperature are promising for future verifications of numerical simulations.
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Chapter 1

Introduction

The use of concrete as a building material has been known for millennia. The Pantheon (126 AD) in Rome is one of the oldest still surviving well-known concrete buildings [1]. Due to its great compressive strength, concrete is still often used for new buildings and infrastructure. However, over the last decades the fire resistance of concrete has been subject of research. Figure 1.1 shows some recent examples of concrete structures exposed to fire.

![Figure 1.1: Pictures of the reinforced concrete affected by fire in (a) the Channel Tunnel (1996) and (b) the Gotthard Road Tunnel (2001). In both pictures the reinforcement is clearly exposed. Pictures taken from [2].](image)

Figure 1.1a shows the results of a train fire in the Channel Tunnel between England and France in 1996, whereas Figure 1.1b shows a similar picture for the Gotthard Road Tunnel in Switzerland after a truck fire in 2001. The temperature in both tunnels reached 800°C during the fires [2]. In some places the concrete was destroyed over 100% of its depth and the reinforcement bars became visible. This violent destruction of concrete under influence of fire is referred to as spalling.

Next to the fires in the Channel Tunnel and the Gotthard Road Tunnel there have been many other tunnel fires in for example the Great Belt Railway Tunnel (Denmark, 1994) and the Mont Blanc Tunnel (France, 1999). In the case of the fire in the Channel Tunnel, the tunnel train services were severely disturbed for weeks and could only be fully restored after 6 months. The direct financial losses were estimated to be €340 million [3]. Many tunnel safety guidelines have arisen focusing on for example the evacuation criteria for a tunnel. In order to improve the guidelines and create buildings that are more fire-resistant, there is also a great interest in understanding the underlying physical processes dominating the spalling of concrete under fire [4].
1.1 Causes of spalling

The fire spalling of concrete is generally attributed to two causes: (i) thermal stresses due to temperature gradients in the concrete itself and (ii) high pressures due to water vapor inside the concrete [5].

1.1.1 Thermal stresses

The thermal stresses can be generated in different ways. When a concrete wall is heated locally, the concrete will tend to expand. The expansion is limited by the cooler regions surrounding the heated site. This results in a buildup of energy in the concrete, which can be released violently by explosive spalling [6]. Furthermore, temperature gradients will exist between the heated surface and the inner material. These temperature gradients cause tensile stresses in the concrete. Spalling can occur when these tensile stresses exceed the tensile strength of the concrete [7, 8].

Furthermore, thermal stresses may also be caused by the variations in deformation (strain) of different aggregates and the cement paste, caused by the increasing temperature and dehydration of the cement paste [8].

1.1.2 High pressures

When water is heated inside a closed environment, such as a kettle, water will reach an equilibrium with its vapor. The pressure of this vapor increases with increasing temperature. This saturated vapor pressure is shown in Figure 1.2 as a function of the temperature. If, for example, the water in the closed kettle would reach a temperature of 200°C, the pressure would be 1.5 MPa.

![Figure 1.2: Saturated water vapor pressure p as a function of temperature T. At T = 100°C p is equal to atmospheric pressure (normal boiling point).](image)

Wet concrete which is exposed to high temperatures during a fire, can be compared with this closed kettle. The high temperatures cause the water in the pores of the concrete to evaporate. Due to the relatively low permeability of concrete, the evaporating water is unable to escape. Meanwhile the temperature, and therefore the pressure, keeps increasing. If the pressure exceeds the tensile strength of concrete, the concrete may spall. For a typical tensile strength of concrete of 4 MPa, this corresponds to the saturated vapor pressure at a temperature of 250°C [1, 9, 10].
1.1.3 Dominating mechanism

The relative importance of the high pressures on one side and thermal stresses on the other side has been subject of discussion for decades and the issue is still unresolved [11,12]. This is due to the great complexity of concrete as a material in combination with the many factors influencing the processes leading to spalling. There are many degrees of freedom when simulating the heating of concrete.

At first there are many different kinds of concrete, each having a different porosity and/or water permeability. When concrete is made from cement, the water to cement ratio (w/c) can be varied. A lower water to cement ratio generally results in a higher compressive strength but a poorer workability and a lower water permeability [1]. Concretes with a water to cement ratio below 0.35 (kg/kg) are classified as High Strength Concrete (HSC). The HSC has the ability to better withstand high compressive stresses. The lower water permeability of HSC on the other hand will cause a faster increase of vapor pressure when exposed to high temperatures [13].

![Figure 1.3: Typical fire curves that are used for testing building materials for fire exposure. Temperatures (as function of the time) are based on fires of building materials (ISO-834) and fuel tanks (HC/RWS) in confined spaces. The dashed magenta line shows a heating rate of 10°C per minute, starting at 20°C.](image)

A second important factor during the heating of concrete is the heating rate or fire curve. An overview of typical fire curves used to simulate a fire in spalling experiments is shown in Figure 1.3. The fire curves are all based on estimates of the increase of temperature in confined spaces (for example tunnels) due to burning building materials (ISO-834) or fuel tanks (HC/RWS). These temperatures however do not indicate the temperature of the concrete itself. A passive fire protection system such as a protective coating or insulating layer may be placed between the concrete and the fire [14]. Therefore many different heating rates have been used in experiments modeling spalling, leading to conflicting conclusions. On one hand, a high heating rate causes a big temperature gradient and therefore great tensile stresses. On the other hand, this rapid heating might also induce microcracks that can function as channels to reduce the pressure build-up. The microcracks however might also reduce the strength of the concrete altogether [8].

The moisture saturation is a third factor influencing the spalling behavior. On one hand, a high moisture saturation of concrete creates a moderator for heat. On the other hand, in the case of spalling due to vapor pressure, a higher degree of saturation leaves less space for the water to expand. This may lead to higher pressures [15,16].
The compressive strength of concrete is known to depend on the rate of loading and on the temperature of the concrete [1]. Furthermore, concrete subject to static loading shows different resistance to high temperatures than unloaded concrete. Loaded concrete may reduce the forming of cracks and thereby cause a bigger build-up of energy, leading to a higher probability of spalling [6,13,17].

Next to the four forementioned experimental degrees of freedom, many other factors can be varied. For example, the addition of polypropylene fibers to reduce risk of spalling, is currently being actively investigated. Next to that, the position of reinforcement in the concrete and the shape of the concrete (for example an I-beam or a flat wall) have influence on the spalling behavior. Recently, also the effect of the size of the aggregates in the cement paste has been subject of research [6,9,13,16].

1.2 This thesis

As explained in the previous section, many factors influence the different types of spalling. Although the process of spalling due to increasing pressures due to the vaporization of water has been predicted many times before, the process has never been verified. In earlier experiments on concrete, spatial distributions of the temperature, moisture and pressure have been obtained separately. However, the pressure has never been measured simultaneously with the moisture profiles. Therefore, the research described in this thesis focuses on combining the pressure, temperature and the spatial moisture distribution in one experiment. The results of the research will show whether the pressure indeed follows the vapor pressure curve of Figure 1.2. Furthermore, the research aims to link the measured pressures to a decreasing moisture content. The data obtained may also help in verifying earlier computer models of concrete spalling.

For these purposes small cylindrical concrete samples will be equipped with a pressure gauge and thermocouples, after which the samples will be heated inside of an NMR scanner. The NMR scanner will be used to obtain the spatial moisture profiles. Combined with the pressure data, this may add proof to the theory of concrete spalling due to high vapor pressure build-up.

1.3 Outline

At first the introduction is concluded with a short literature overview in section 1.4. The literature overview contains an overview of vapor pressures measured in concrete by different authors and different methods.

A conceptual model of the increasing pressures in heated concrete is given in Chapter 2. In Chapter 3 an introduction to NMR in general is given, followed by an overview of the specific difficulties of using NMR in the current experiments. The concrete samples and the experimental setup are described in Chapter 4. This includes the selection of a suitable pressure sensor, characterization of the concrete samples, a description of the NMR setup and an overview of the experiments. Chapter 5 explains the processes influencing temperature and energy during the experiments. Finally, the measured pressures and moisture profiles can be found in Chapter 6.
1.4 Literature overview

In the last decade many attempts have been made to obtain the maximum vapor pressures reached during the heating of concrete. In subsection 1.4.1 an overview is given of the pressures measured experimentally, while in subsection 1.4.2 different numerical models are discussed.

1.4.1 Pressure measurements

Table 1.1 gives a (far from exhaustive) overview of some of the pressures obtained in earlier research. Studies on the topic of pressure measurements in concrete are hard to compare directly, due to the many experimental degrees of freedom that were discussed in subsection 1.1.3.

Table 1.1: Overview of several pressure measurement experiments in concrete exposed to high temperatures. The type of pressure sensor (see Figure 1.4) can be found in the first column. The materials used are Normal-Strength Concrete (NSC), High-Strength Concrete (HSC) and cement. The fire curves are shown in Figure 1.3. The maximum (absolute) pressure \( p_{\text{max}} \) measured, was measured at a distance \( \delta \) from the heated surface. \( T_{p_{\text{max}}} \) is the temperature at the pressure sensor at the moment of maximum pressure. Samples were saturated in a chamber at the relative humidity given in column “RH”. “Wet” means samples were kept underwater.

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Material</th>
<th>Fire curve</th>
<th>( T_{p_{\text{max}}} ) (°C)</th>
<th>( p_{\text{max}} ) (MPa)</th>
<th>( \delta ) (mm)</th>
<th>RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>C - oil [18]</td>
<td>NSC</td>
<td>ISO</td>
<td>211</td>
<td>0.8</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>B/C - ? [19]</td>
<td>HSC</td>
<td>ISO</td>
<td>-</td>
<td>1.15</td>
<td>20</td>
<td>65%</td>
</tr>
<tr>
<td>NSC</td>
<td>ISO</td>
<td>200</td>
<td>1.28</td>
<td>30</td>
<td>65%</td>
<td></td>
</tr>
<tr>
<td>D [20]</td>
<td>Cement</td>
<td>925°C constant</td>
<td>-150</td>
<td>3.1</td>
<td>19</td>
<td>Wet</td>
</tr>
<tr>
<td>B - air [21]</td>
<td>HSC</td>
<td>10°C/imin</td>
<td>-</td>
<td>2.9 - 3.5</td>
<td>30</td>
<td>Wet</td>
</tr>
<tr>
<td>B - oil [21]</td>
<td>HSC</td>
<td>10°C/imin</td>
<td>-</td>
<td>3.5 - 4.0</td>
<td>30</td>
<td>Wet</td>
</tr>
<tr>
<td>C - air [21]</td>
<td>HSC</td>
<td>10°C/imin</td>
<td>-</td>
<td>3.7 - 3.8</td>
<td>30</td>
<td>Wet</td>
</tr>
<tr>
<td>C - oil [21]</td>
<td>HSC</td>
<td>10°C/imin</td>
<td>-</td>
<td>3.9 - 4.5</td>
<td>30</td>
<td>Wet</td>
</tr>
<tr>
<td>E - oil [7]</td>
<td>HSC</td>
<td>20°C/imin</td>
<td>-210</td>
<td>3.2</td>
<td>8</td>
<td>Wet</td>
</tr>
<tr>
<td>-270</td>
<td>3.4</td>
<td>8</td>
<td>40%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C - oil [22]</td>
<td>NSC</td>
<td>600°C constant</td>
<td>205</td>
<td>0.16</td>
<td>40</td>
<td>Dry</td>
</tr>
<tr>
<td>207</td>
<td>1.6</td>
<td>50</td>
<td>50%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>212</td>
<td>0.9</td>
<td>10</td>
<td>Wet</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A - oil [5]</td>
<td>NSC</td>
<td>HC</td>
<td>-</td>
<td>0.15</td>
<td>20</td>
<td>Room</td>
</tr>
</tbody>
</table>

Figure 1.4: Overview of types of pressure sensors used in literature. The concrete is heated from below. A. Hollow tube, either filled by oil or water. B. Tube with internal rod. Cavity around the tip to span a bigger area. C. Tube connected to a sintered metal plate. Tube can be filled with a thermocouple. D. Internal pressure sensor. E. Tube leaving the sample sideways. Figure adapted from [23].
There are many different types of pressure sensors, some of which are displayed in Figure 1.4. The letters in the first column of Table 1.1 correspond to the types of pressure sensors displayed in Figure 1.4. Many of these sensors can be filled with either water, air or oil, again introducing an extra problem in comparing pressures obtained in different experiments. The type of concrete used is displayed in the second column of Table 1.1 and the used fire curve (see Figure 1.3) can be found in the third column. $p_{\text{max}}$ indicates the highest value of the pressure obtained during each experiment and $T_{p_{\text{max}}}$ the temperature at the pressure gauge at the time of maximum pressure. $\delta$ indicates the depth of the pressure sensor, relative to the heated surface of the concrete. The samples are preconditioned in a room with a relative humidity as shown in the column “RH”.

It is clear from Table 1.1 that there are big differences between the measured pressures, possibly due to a combination of the factors discussed before (for example different porosities, heating rates and saturation). When, for example, a normal-strength concrete is mentioned, it can still be made of different cement compositions. For this reason focus should be laid on the underlying processes of spalling due to increasing vapor pressures.

### 1.4.2 Pressure simulations

Next to the many different fire spalling experiments described in the previous subsection, concrete spalling has been subject of many numerical simulations. Since multiple processes take place during the spalling of concrete, these computer models show great variations. Some models, for example, do not include vapor pressure or thermal stresses, while others try to combine both [24,25]. A big difference in complexity exists even for the the simulations which do include vapor pressures.

- One model, for example, considers the diffusion of heat and vapor in high-strength concrete. However, only the temperature effects in the water vapor are considered, assuming no vapor sources or sinks exist in the concrete [26].

- A more complex one-dimensional hydrothermal model includes a mass balance which does include the evaporation of water and combines it with a heat transfer analysis. On the other hand, dehydration of concrete and mechanical changes of concrete, such as cracking, are partially ignored, as are the energies required for evaporation and dehydration [27].

- In a third model dry air is included in the mass balance, next to the liquid water and water vapor. Furthermore, the energy of vaporization is included, but the porosity is assumed constant during the heating [28].

All these models have in common that even though a lot of simplifications are applied, they still result in a set of differential equations. Furthermore, most of the computer simulations lack experimental verification.
Chapter 2

Conceptual model

In order to sketch a conceptual model of the increasing pressures during the heating of concrete, first the one-sided drying of porous materials is discussed in section 2.1. In section 2.2 a model is given for the heating of concrete.

2.1 One-sided drying of porous media

Consider a one-dimensional sample of a water-saturated porous medium starting at $x = 0$ and stretching to $x = L$ (see Figure 2.1a, with $L = 25$ mm). When the sample is dried by blowing dry air on the front surface, moisture will evaporate at the front surface. As long as the moisture content $\theta$ of the sample stays above the critical moisture content $\theta_c$, capillary forces in the porous medium will resupply the evaporated water, in order to keep the moisture content and the capillary pressure in equilibrium throughout the sample (see Figure 2.1). This first stage of the drying process is referred to as the externally limited drying stage [10, 29, 30].

![Figure 2.1: a. Schematic drawing of a 1D-drying experiment. Air is blown over a saturated sample. The sample is placed in a PTFE cup (dashed) to ensure a 1D experiment. b. Moisture profiles resulting from a 1D-drying experiment on gypsum by Pel et al. [31]. The red arrow indicates progress in time. The externally limited and internally limited drying stages are indicated by I and II respectively.](image)

In the second drying stage the moisture content will decrease below $\theta_c$ and the moisture will not be a continuous phase in the sample anymore. This stage is referred to as the internally limited...
drying stage. At this point the moisture transport is dominated by vapor pressure gradients. In the moisture profiles of Figure 2.1b this can be seen by a front moving to the right. This front is referred to as drying front, since it starts when the moisture content becomes lower than the critical moisture content ($\theta < \theta_c$).

Whether the drying of a sample is internally limited, externally limited or a combination of both depends on parameters such as the initial moisture content $\theta_0$, the permeability $k$ and the drying rate. The flow of fluids through permeable media is described by Darcy’s law in equation (2.1):

$$q = -\frac{k}{\mu} \frac{\partial p}{\partial x}. \quad (2.1)$$

In this equation $q$ (m/s) indicates the volume flux per unit area caused by a pressure gradient $\partial p/\partial x$ in a porous medium. $k$ indicates the permeability (m$^2$) of the porous medium and $\mu$ (Pa·s) the viscosity of the fluid. According to Darcy’s law, moisture can more easily flow, and therefore redistribute, in media with a higher permeability, given the same pressure gradients [32]. The faster the drying rate at the front surface, the more water evaporates and the more water that needs to be resupplied.

Concrete has a low permeability in the order of $10^{-17}$ m$^2$, compared to for example $10^{-14}$ m$^2$ for gypsum (see Figure 2.1b). It is therefore expected that the experiments described in this thesis are dominated by internally limited drying [10]. A drying front is expected to be visible throughout the experiments.

### 2.2 One-sided heating of concrete

The one-sided drying of porous media discussed in section 2.1 can be extended to the one-sided heating of concrete.

#### 2.2.1 First approximation

Consider the case where a water saturated semi-infinite concrete sample is dried by heating its front surface. Evaporation of moisture will take place at the drying front. If the drying front is located at a distance $u(t)$ from the heated surface (as shown in Figure 2.2), the speed at which the drying front progresses into the concrete equals $du/dt$. Assuming all moisture exits the concrete through the heated front surface as water vapor, the vapor mass flux per unit area (kg·m$^{-2}$·s$^{-1}$) is given by $J_m$ in equation (2.2):

$$J_m = -n \frac{du}{dt} \rho_{L,0}. \quad (2.2)$$

In this equation $n$ is the porosity of the medium, so that $ndu$ is the volume (per unit area) of liquid water that evaporates from the pores in a time $dt$. $\rho_{L,0}$ is the density (kg/m$^3$) of liquid water at $T = T_0$, with $T_0$ the initial temperature.

Combining equation (2.2) for the mass flux with Darcy’s law for water vapor (equation (2.1)) gives:

$$J_m = q_v \rho_v = -\frac{k}{\mu} \frac{\partial p_v}{\partial x} \rho_v = -n \frac{du}{dt} \rho_{L,0}, \quad (2.3)$$

where the index $v$ denotes the vapor state. For small distances $u$, the vapor is assumed to behave as an ideal gas so that $\rho_v$ can be replaced by $p_v M/RT_w$, with $M = 18.02$ g/mol the molar mass,

---

[14]
Figure 2.2: Schematic drawing of the one-sided heating of a semi-infinite concrete medium. Heat enters the medium at \( x = 0 \). The drying front is moving away from the heated side at a speed \( \frac{du}{dt} \) and is located at \( x = u \).

\[ R = 8.31 \text{ J/mol/K} \] the universal gas constant and \( T_u \) the temperature at the front. When a quasi-stationary situation is assumed, \( p(x,t) \) becomes \( p(x) \) so that equation (2.3) becomes:

\[
\frac{k}{2\mu} \frac{d}{dx} \frac{M}{RT_u} = n \frac{du}{dt} \rho L_0. \tag{2.4}
\]

As a first approximation \( \frac{dp_v^2}{dx} \) can be replaced by \( \Delta p_v^2/\Delta x \). Since \( \Delta x = u \) (see Figure 2.2) this results in a differential equation for \( u \):

\[
\frac{k}{2\mu} \frac{\Delta p_v^2}{u} \frac{M}{RT_u} = n \frac{du}{dt} \rho L_0. \tag{2.5}
\]

In order to solve equation (2.5), an estimate of the temperature \( T_u(t) \) at the drying front has to be made. For this equation (2.6) is used at a position \( x = u \):

\[
T(x,t) = T_0 + \frac{2F}{K} \left( \sqrt{\frac{\kappa t}{\pi}} \exp \left( -\frac{x^2}{4\kappa t} \right) - \frac{x}{2} \text{erfc} \left( \frac{x}{2\sqrt{\kappa t}} \right) \right). \tag{2.6}
\]

Equation (2.6) gives the temperature \( T(x,t) \) in a semi-infinite medium which is heated at \( x = 0 \) starting at \( t = 0 \) with a constant heat flux \( F \) per unit time per unit area [33]. \( T_0 \) indicates the initial temperature of the medium and \( K \) and \( \kappa \) represent the thermal conductivity and thermal diffusivity of the medium, respectively.

The temperature \( T_u \) is used to calculate the pressure at the position of the drying front. The relation between temperature and the pressure of evaporating water is given by saturated vapor pressure curve which was discussed in subsection 1.1.2. This curve is described mathematically by the empirical Antoine equation, given by equation (2.7):

\[
\log_{10}(p_v) = A - \frac{B}{T + C}, \tag{2.7}
\]

with \( p_v \) the saturated vapor pressure (Pa) at a temperature \( T \) (K) and \( A \), \( B \) and \( C \) empirical constants given in Table 2.1.

The results of numerically solving the differential equation for \( u \) (equation (2.5)) are shown in Figure 2.3 for a typical concrete permeability of \( k = 1 \cdot 10^{-17} \text{ m}^2 \). The porosity is chosen to be 10\%, the initial temperature 20\(^\circ\)C and the viscosity \( 1.2 \cdot 10^{-5} \text{ Pa-s} \). The thermal conductivity and thermal diffusivity are 1 W/m/K and \( 4.2 \cdot 10^{-7} \text{ m}^2/\text{s}, \) respectively. The initial pressure is assumed to be 0.1 MPa.
Table 2.1: Constants used to calculate the vapor pressure using the Antoine equation (equation (2.7)) for two different temperature ranges (K). The maximum error in the pressure calculated using the Antoine equation is 1.4% over the used temperature range, compared to the pressure found in steam tables [34].

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.15 ≤ T &lt; 373.15</td>
<td>10.196</td>
<td>1730.6</td>
<td>-39.724</td>
</tr>
<tr>
<td>373.15 ≤ T ≤ 647</td>
<td>10.265</td>
<td>1810.9</td>
<td>-28.665</td>
</tr>
</tbody>
</table>

The differential equation for the position of the drying front is based upon many simplifications. However, it already provides a model that is able to predict an increasing pressure due to the evaporation of water inside the concrete pores. According to the results displayed in Figure 2.3c, the pressure reaches the typical tensile strength of concrete of 4 MPa already after half an hour at a heating rate of 20 kW/m².

![Figure 2.3](image)

**Figure 2.3**: Numerical solutions of equation (2.5) with heating rates of 5 kW/m² and 20 kW/m², indicated by the blue solid and red dashed lines, respectively. The position of the drying front and the temperature and pressure at the drying front are shown in Figures a, b and c, respectively.

### 2.2.2 Moisture clog

The model described in the previous subsection is a first approximation for the case of saturated concrete. In practice, the high pressures at the drying front cause the water to move away from the front in any direction. Since a one-dimensional sample is considered, the water can move either to the open front surface of the sample or further into the sample. In the latter case the water vapor will move into regions of lower temperature (since these are further away from the
heating source) and is able to recondense. In earlier experiments it has been observed that this condensation indeed takes place [10,35]. When the initial moisture content $\theta_0$ is high enough, a region of liquid water saturation can be formed. This so-called moisture clog limits further vapor transport into the sample.
Chapter 3

Nuclear Magnetic Resonance

Nuclear Magnetic Resonance (NMR) is the driving principle behind (medical) MRI (Magnetic Resonance Imaging) scanners. NMR is non-destructive, making it a suitable measurement technique to observe moisture in concrete without disturbing an experiment.

The basic principles of NMR are explained in sections 3.1 and 3.2. In the following sections, some commonly used NMR pulse sequences are discussed. The effects of temperature differences on NMR measurements, are discussed in section 3.5. Finally, section 3.7 explains an implementation of a multi slice pulse sequence, required to perform measurements in concrete.

3.1 Fundamentals

When a nucleus with a nonzero net magnetic moment is placed in an external magnetic field $B_0$, the magnetic moment tends to align with the field. Due to the angular momentum the nucleus starts to precess around this magnetic field, with a frequency that is proportional to the magnitude of the applied magnetic field \[36\]. The angular frequency of the precession is the Larmor frequency $\omega_0$, which is defined in equation (3.1):

$$\omega_0 = \gamma |B_0|.$$  

(3.1)

In equation (3.1) $\gamma$ is the gyromagnetic ratio, which is different for each type of nucleus. For $^1H$ $\frac{\gamma}{\pi}$ is 42.58 MHz/T \[37\]. All the precessing nuclei in a certain volume add up to give a net magnetization $M$ in the direction of the external magnetic field $B_0$, as depicted in Figure 3.1a.

By applying another external magnetic field $B_1$, which is oscillating at the Larmor frequency $\omega_0$ in a plane perpendicular to $B_0$, it is possible to flip some of the magnetic moments. This means that these magnetic moments now do not align with the $B_0$ field anymore. When the magnitude $|B_1|$ and duration $\tau$ of the $B_1$ field are chosen correctly, it is possible to flip $M$ into the plane perpendicular to $B_0$ \[36,38\]. Mathematically this can be stated as in equation (3.2) and graphically this is displayed in Figure 3.1b:

$$\alpha = \tau \omega_1 = \tau \gamma |B_1|,$$

(3.2)

where $\alpha$ is the so-called flip angle and equation 3.1 is used.

Figure 3.1b makes use of the rotating frame that is rotating around the z-axis at a frequency of $\omega_0$. This frame is chosen so that the $B_1$ field (or RF-field) is always directed along the $x'$-axis. This implies that $M$ moves in the $y'z$-plane during the RF-pulse. The magnitude
$M_z$ of the magnetization that is pointing in the direction of $B_0$, is called the \textit{longitudinal magnetization}, while the magnitude $M_{xy}$ of the magnetization perpendicular to $B_0$ is called \textit{transversal magnetization}. After a 90°-RF-pulse all magnetization is transversal and, since $M$ is processing in the xy-plane, it can induce a signal in a \textit{pick-up coil}.

### 3.1.1 Gradient

In addition to the main magnetic field $B_0$ often another magnetic field is applied in the $z$-direction. This \textit{gradient field} causes a controlled magnetic field gradient in the $z$-direction and therefore, according to equation (3.1), a gradient in the frequency. If a sample is placed along the $z$-axis, the gradient field can be used to excite different \textit{slices} of the sample, by varying the frequency of the $B_1$ field. This \textit{1D-imaging} is depicted in Figure 3.2.

![Figure 3.2](image)

\textbf{Figure 3.2:} Schematic drawing of 1D-imaging. The sample is placed along the $z$-axis parallel to a magnetic field gradient. Since each position in the sample now is located at a different field strength, the frequency is also position dependent (solid red line). By exciting the sample and measuring the signal at 5 different frequencies, and therefore at 5 different positions or slices, a 1D image is created.

### 3.1.2 Fourier

As explained in the first part of this section, the $B_1$ field needs to be oscillating at the Larmor frequency $\omega_0$ in order to flip $M$ into the xy-plane. If the $B_1$ field is caused by a coil along the x-axis in the non-rotating \textit{laboratory frame}, the magnitude $B_{1x}$ of this field along the x-axis is given by equation (3.3):

$$B_{1x}(t) = |B_1| \cos(\omega_0 t).$$

(3.3)
Since the $B_1$ field should only be present for a limited time according to equation (3.2), $B_{1x}(t)$ is multiplied by a block pulse of amplitude 1 and width $\tau$.

Taking the Fourier transform of an ideal sine function yields the Dirac delta function at the frequency $\omega_0$ of the original sine function. The Fourier transform of a block wave is a sinc function in the frequency domain [38]. This means that the multiplication of the $B_{1x}$ with the block pulse, results in a sinc-like distribution of frequencies, centered around $\omega_0$. Taking into account a magnetic field gradient, the result is that a finite length sine pulse will excite a sinc-like slice of the sample. Furthermore, the longer the sine is allowed to run (or: the wider the block pulse), the sharper the peak (or: the narrower the slice) in the frequency domain [39].

3.2 Relaxation of the magnetization

After applying the 90° RF-pulse all spins point in the $y'$-direction and therefore have the same phase. However, each spin will experience the magnetic field caused by neighboring molecules and therefore will, according to equation (3.1), precess at a slightly different frequency [36]. This results in dephasing of the spins and will decrease the transversal magnetization in a process called spin-spin relaxation or $T_2$-decay. The $T_2$-decay is described by equation (3.4) [36]:

$$M_{xy} = M_0 \exp \left( -\frac{t}{T_2} \right),$$  \hspace{1cm} (3.4)

where $M_0$ is the equilibrium magnetization, $t$ the time since the end of the RF-pulse and $T_2$ the time constant of the $T_2$-decay. $T_2$ depends on for example the type of nuclei and the environment of the measured substance.

If there are macroscopic gradients in the magnetic field, the dephasing of the spins will go even faster. The macroscopic field gradients can be caused either on purpose or by field inhomogeneities. The combined spin-spin relaxation and relaxation due to macroscopic field gradients is indicated by a time constant $T_2^*$ and is therefore called $T_2^*$-decay. The $T_2^*$ time constant is generally denoted as:

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \gamma \Delta B,$$  \hspace{1cm} (3.5)

where $\Delta B$ indicates the magnitude of the magnetic field inhomogeneities.

Another type of relaxation is the spin-lattice relaxation. This is the recovery of the longitudinal relaxation $M_z$ and is given by equation (3.6) [36]:

$$M_z = M_0 \left( 1 - \exp \left( -\frac{t}{T_1} \right) \right),$$  \hspace{1cm} (3.6)

where $M_0$ is the equilibrium magnetization, $t$ the time since the end of the RF-pulse and $T_1$ the time constant of the recovery. Equation (3.6) states that if, for example, a waiting time of $4T_1$ is chosen between two measurements (or: “scans”), ~98% of the nuclei will realign with $B_0$ in-between.

3.3 Single echo pulse sequences

3.3.1 Hahn spin echo

A Hahn spin echo sequence consists of a combination of two RF-pulses and one NMR measurement. First a 90° RF-pulse is given, so that the magnetization $M$ flips into the $x'y'$-plane,
as described in section 3.1. The transversal magnetization will start to decrease due to the $T_2^*$-decay. After some time a 180°-pulse is given, so that $M$ will flip to the other side of the $x'z$-plane, as is shown in Figure 3.3. The 180°-pulse will help rephasing of the spins, since all spins that have a phase lag or phase lead before the pulse, will have a phase lead or lag respectively after the pulse. This cancels out the macroscopic field gradients and therefore a signal (or: “echo”) can be measured in the pick-up coil at the moment the spins refocus. The time from the start of the 90°-pulse until the center of the echo is referred to as the echo time $t_E$. The 180°-pulse is centered around $t_E/2$. As can be seen in equation (3.2), a 180°-pulse is obtained by either doubling the amplitude or the duration of the 90°-pulse.

![Figure 3.3: a. Dephasing of the spins in the rotating frame, due to frequency differences. b. When the 180°-pulse is applied along the $x'$-axis, the dephasing spins are mirrored in the $x'z$-plane. This will allow the spins to rephase and form an echo when they refocus at the -$y'$-axis. Figures adapted from [39].](image)

### 3.3.2 Solid echo

An alternative pulse sequence replaces the 180°-pulse of the Hahn spin echo sequence by another 90°-pulse. This sequence is known as a solid echo sequence. The second 90°-pulse now flips $M_0$ into the $x'z$-plane instead of mirroring $M_0$ in this plane (as in subsection 3.3.1). A disadvantage of this second 90°-pulse is that at the point of refocusing of the spins, only 50% of the signal is obtained, compared to a Hahn spin echo with an equal 90°-pulse [36,38]. On the other hand, an advantage of the solid echo sequence is that both 90°-pulses are equal. This means that both pulses act on the same frequency range and therefore on the same slice (see subsection 3.1.2). Furthermore, less power is needed for a 90°-pulse than for a 180°-pulse.

### 3.4 NMR signal

The signal $S$ obtained by a Hahn spin echo or solid echo sequence is given by equation (3.7), as long as $T_2 \ll T_1$ and $t_E \ll t_R$ [10,38]:

$$S(t_E) = kM_0 \left(1 - \exp \left(-\frac{t_R}{T_1}\right) \exp \left(-\frac{t_E}{T_2}\right)\right),$$

(3.7)

where $t_R$ is the repetition time, $t_E$ the echo time and $k$ is a proportionality constant which equals 1 for a Hahn spin echo and 0.5 for a solid echo [38]. The repetition time is the time between the start of two subsequent measurements. If for example eight averages of one point are necessary, this would take $8t_R$. If $t_R$ is chosen large enough, $\exp(-t_R/T_1)$ becomes ~0 and the signal is solely dependent on $t_E$. 

22
3.5 Temperature effects

During the fire spalling experiments described in this thesis, the temperature in the concrete samples will vary between room temperature and ~500°C. Due to this broad temperature range, some corrections need to be applied to the obtained NMR signal. An overview of these corrections is given in this section.

3.5.1 Magnetization

During an NMR experiment the measured signal is proportional to the magnetization (see equation (3.7)). The magnetization, however, is proportional to the inverse temperature according to Curie’s law [40]:

\[ M = \frac{CB}{T}, \]  

(3.8)
as long as equation (3.9) is satisfied (Curie regime):

\[ \frac{\mu B}{kT} \ll 1. \]  

(3.9)

In these equations \( C \) is the Curie constant, \( B \) the magnetic induction, \( T \) the temperature, \( \mu \) the magnetic moment and \( k \) Boltzmann’s constant. The magnetic induction in the current experiments is ~1.5 T, the magnetic moment of a hydrogen nucleus \( 1.4 \cdot 10^{-26} \text{ J/T} \) and Boltzmann’s constant \( 1.4 \cdot 10^{-23} \text{ J/K} \) [37]. For a temperature of 293 K, equation (3.9) becomes \( 5 \cdot 10^{-6} \ll 1 \), so that equation (3.8) can be used.

Equation (3.8) implies that at higher temperatures, less signal is recorded from the same sample. By multiplying the intensity of the recorded signal at each point in the sample by the absolute temperature at that point, the signal is corrected for the temperature dependent magnetization.

3.5.2 Relaxation

Next to the magnetization, also the T\(_2\)-relaxation time is temperature dependent. As can be seen in equation (3.7), a changing T\(_2\) time constant results in a changing signal intensity.

The temperature dependence of the T\(_2\) time constant can be attributed to three processes. At first there is the bulk relaxation caused by interactions between neighboring molecules. This interaction decreases with increasing temperature and therefore increases the T\(_2\)-relaxation time constant [10].

Secondly, there is the relaxation due to diffusion in a magnetic field gradient. When excited spins move through a gradient field they will precess at varying frequencies and therefore dephase. The temperature dependence in this case comes from the diffusion coefficient of water which has a linear relation with the temperature. This process causes the T\(_2\) time constant to decrease with temperature [10].

The last component of T\(_2\) temperature dependence can be found in the relaxation of molecules at the surface of the pore walls of a solid. Interaction between excited spins and for example paramagnetic ions at the surface can cause a fast relaxation of the magnetization. This relaxation is given by equation (3.10):  

\[ \frac{1}{T_{2s}} \sim \rho_2 \frac{S}{V}, \]  

(3.10)
with $T_{2s}$ the relaxation time in a solid in the absence of magnetic field gradients and ignoring the bulk relaxation, $\rho_2$ the surface relaxivity, and $S$ and $V$ the typical surface area and volume of a pore respectively [41]. If spherical pores are assumed, $S/V$ can be replaced by $3/r$, with $r$ the typical pore radius. The surface relaxivity depends on both the liquid and the solid and can be described by equation (3.11):

$$\rho_2 \sim \exp\left(\frac{\Delta E}{RT}\right),$$

in which $R$ is the gas constant, $T$ the temperature and $\Delta E$ is the effective surface interaction energy, which is generally positive [10,41]. This implies that $T_{2s}$ increases with increasing temperature.

Due to the small pore radius of concrete, the surface relaxation is the process dominating the temperature dependence of the $T_2$ time constant of water in concrete [10]. This implies a positive temperature dependence of the $T_2$ time constant. At higher temperatures more signal will be recorded from the same sample (not taking into account the decreasing magnetization). In section 3.6 a pulse sequence is given that can be used to correct for the increasing signal.

### 3.6 Multiple echo pulse sequences

As explained in subsection 3.3.1 the $180^\circ$-pulse in a Hahn spin echo sequence is used to cancel out the macroscopic field gradients. Therefore the signal intensity is governed by $T_2$-decay instead of $T_2^*$-decay. If several subsequent Hahn spin echo measurements were performed, each with a different echo time $t_E$, the signal intensity would be different each time (see equation (3.7)). This way the $T_2$ time constant can be determined, which helps in identifying, for example, different materials. However, a disadvantage of this method of finding the $T_2$ time constant, is that one has to wait a repetition time $t_R$ between each two measurements. Furthermore, the relaxation due to diffusion of water molecules will be significant [42].

An alternative that is faster and less diffusion-dependent, is to adapt the Hahn spin echo by applying a train of $180^\circ$-pulses after the first $90^\circ$-pulse, each spaced $t_E$ apart, as is shown in Figure 3.4. This way the spins keep dephasing and rephasing between each pulse, each time generating an echo in the pick-up coil. The signal intensity of the echoes in this Carr-Purcell-Meiboom-Gill-sequence (or: CPMG-sequence) decays with the time constant $T_2$ [43].

![Figure 3.4: Timing scheme of the CPMG- and OW-pulse sequences. The RF-pulses are represented by $\alpha$ and $\beta$. For CPMG $\alpha=90^\circ$ and $\beta=180^\circ$. For OW both equal $90^\circ$. Figure adapted from [39].](image)

Similar to replacing the $180^\circ$-pulse by a $90^\circ$-pulse when going from Hahn spin echo to solid echo in section 3.3, the train of $180^\circ$-pulses can be replaced by a train of $90^\circ$-pulses. This sequence is called the Ostroff-Waugh-sequence (or OW-sequence). The signal between two $90^\circ$-pulses again decays with a time constant referred to as $T_2$. However, it must be noted that this time constant is somewhat greater (longer) than the $T_2$ obtained by the CPMG-sequence. This is due to some of the longitudinal magnetization $M_z$ being transfered to transversal magnetization $M_{xy}$ during the $90^\circ$-pulses [10,39]. The $T_2$ obtained with an OW-sequence can still be used to distinguish different tissues.
3.7 Multi slice sequence

As explained in section 3.1.1 a gradient can be applied to divide a sample into slices. These slices each have a different central frequency. Consider $N$ slices of interest numbered as $i = 0, 1, \ldots, N - 1$, each centered around $\omega_i = \omega_0 + i\Delta\omega$, where $\Delta\omega$ is the frequency difference between two slices. One way of obtaining the signal of these $N$ slices is by first performing a spin echo sequence on slice 0, followed by a spin echo sequence on slice 1 and so on, as depicted in Figure 3.5. Creating a 1D-image this way would take $N t_R$, with $t_R$ the repetition time between two measurements.

![Figure 3.5](image)

**Figure 3.5:** Timing scheme for scanning $N = 20$ frequencies with a single slice sequence (top) and a multi slice sequence (bottom) with $n_{\text{sweeps}} = 5$. With the single slice sequence $t_R$ is waited between each two frequencies so that it takes $20t_R$ to scan all frequencies. In the case of the multi slice sequence $\omega_0$, $\omega_5$, $\omega_{10}$ and $\omega_{15}$ are scanned in $t_R$ so that it takes only $5t_R$ to scan all frequencies.

The process can be speeded up by not waiting $t_R$ before going to the next slice, but going to the next slice right after the echo of the first slice. A disadvantage is that the magnetization left from the first slice may influence the second slice. Therefore, often the slices are divided into $n_{\text{sweeps}}$ sweeps, so that first slices 0, $n_{\text{sweeps}}$, $2n_{\text{sweeps}}$, ... are measured followed $t_R$ later by slice 1, $n_{\text{sweeps}} + 1$, $2n_{\text{sweeps}} + 1$, ... A schematic drawing of this timing is shown in Figure 3.5 for the case $N = 20$ and $n_{\text{sweeps}} = 5$. By using multiple sweeps, the time between two neighboring slices (e.g. $\omega_0$ and $\omega_1$) is still $t_R$. By using this multi slice sequence the 1D-imaging takes only $n_{\text{sweeps}}t_R$ instead of $N t_R$ and the time between two slices is $t_Rn_{\text{sweeps}}/N$. Since multiple slices are measured in one $t_R$, this sequence is called a multi slice sequence.
Chapter 4

Experimental setup

In order to investigate concrete which is exposed to fire, experiments are performed on small concrete samples. During such an experiment a concrete sample is heated from one side, while the pressure and temperature inside the sample and the moisture content of the sample are monitored. First, in section 4.1, suitable pressure sensors are selected. The concrete samples themselves are discussed in section 4.2 while a complete overview of the setup can be found in section 4.3. In section 4.4 the NMR setup is discussed in more detail. Finally, in section 4.5, an overview of the experiments is given.

4.1 Pressure Sensors

As explained in the introduction in Chapter 1 pressure measurements may be required to obtain a full physical understanding of the processes playing a role at the fire spalling of concrete. However, from an experimental point of view there are many constraints on the suitability of different pressure sensors. An overview of these constraints is given in subsection 4.1.1. The selected sensors are discussed in subsection 4.1.2, while some other types of pressure sensors are discussed in subsection 4.1.3.

4.1.1 Constraints

First, experiments will take place in an NMR scanner. This limits the use of metals and polymers. Ferromagnetic materials such as iron and nickel would be attracted by the main magnetic field of the NMR scanner. Furthermore most metals can distort the NMR imaging and may cause image artifacts due to Eddy currents [44]. Since the NMR scanner is used to monitor water in concrete, the use of hydrogen should be avoided as much as possible, so that less background noise is introduced in the system. This excludes many polymers, such as PVC, PMMA and polypropylene.

A second constraint is found in the high temperatures that are to be expected during the experiments. Similar experiments with a lower input power than the current experiments, showed that temperatures in the concrete can reach up to ~400°C [10]. It is therefore essential that the materials used for a pressure sensor inside the concrete are able to last long enough to register the relevant pressures. Due to their relatively low melting point this again excludes most polymers [37].

A third constraint can be found in the size and the implementation of the pressure sensor. The sensor should disturb its environment as little as possible. It should not introduce a big volume
of voids in the sample, since this could function as a pressure moderator. Furthermore, the sensor should not allow an open pressure gateway from the measurement site to the laboratory. It might therefore be necessary for the sensor to be present at the time of casting the concrete.

Since the sensor will be used in an aqueous environment exposed to high temperatures, the sensor should be able to measure gas, water and water vapor pressures. According to Table 1.1 in subsection 1.4.1 the range of pressures is expected to be from 0 to 5 MPa (0 to 50 bar). The selected pressure sensor should therefore cover at least this range.

4.1.2 Selected sensors

Two pressure sensors are selected to be used in the concrete spalling experiments, obeying the constraints posed in the last subsection as good as possible.

The first is a Honeywell 24PCGFM6G miniature piezoresistive pressure sensor that is capable of measuring pressures up to 1.7 MPa over a temperature range up to 100 °C. Although this temperature range is a lot smaller than the constraint given in subsection 4.1.1, the low price (~€20) of the sensor allows it to be destroyed during the experiments. If the sensor is shielded from the heat it may be able to measure the initial stages of the expected pressure increase. Furthermore, it can be located close to the sample due to its small size (~1 cm³), as is explained in more detail in subsection 4.2.1 below.

The second selected sensor is a custom made sensor, developed by the Centre Scientifique et Technique du Bâtiment (CSTB) [2, 35]. The sensor is based on a water-filled pipe and silicon-filled tube which transfer the pressure from inside the concrete samples to an external pressure sensor at room temperature. More details of this setup are given in in the overview of the samples in subsection 4.2.1.

The CSTB pressure gauge is selected for its good temperature resistance and its ability to measure the full expected pressure range. Furthermore, the gauge is also equipped with a thermocouple so that the temperature at the position of the pressure measurement is known. A disadvantage is that the gauge is made of stainless steel and may therefore produce imaging artifacts in the NMR images. The gauge is embedded in the concrete and therefore has to be present at the time of casting.

4.1.3 Other sensors

Next to the selected pressure sensors discussed in subsection 4.1.2, other sensor types have been considered. Two types are discussed in this subsection.

Piezoelectric pressure sensors are based on the accumulation of charge that occurs when stress is applied on some solid materials. Piezoelectric sensors can be designed for high temperatures, but often contain metal. The typical costs (~€1500 [45]) of a high-temperature piezoelectric sensor require the sensor to be recycled after each use. Furthermore, piezoelectric sensors are optimized for high frequency pressure changes and may be inaccurate for slowly changing pressures [46]. For this reason the piezoelectric sensors are not used for the current research.

Another option to measure pressures is by using fiber optics [47]. Fiber optic sensors are based on an environmental variable (for example pressure) changing a property of light (for example intensity, polarization or frequency) in a glass fiber. In the case of fiber Bragg gratings a periodic change in refractive index of the fiber (the grating) is present. This grating reflects one wavelength of light while transmitting all other wavelengths. When the environment of the grating changes by for example compression of the fiber, this will have an effect on the grating
and therefore on the reflected wavelength of the light. By measuring the wavelength shift of the light, the pressure could be measured.

The fiber Bragg gratings also respond to temperature changes. The advantage is that the fibers can be used for both temperature and pressure measurements. The disadvantage is that the pressure effects and temperature effects should be distinguishable.

Another advantage is the size of the fiber optic sensors. Sensors exist with a diameter below 1 mm, so that these sensors are suitable for pressure measurements inside the concrete. A disadvantage is the costs of the sensors. A typical fiber optic pressure sensor that is small and is able to withstand the desired temperatures costs ~€2000, not including the hardware required to measure the wavelength shift [48]. For this reason these fiber optic sensors are not used in the current experiments, but may be used in similar experiments in the future.

4.2 Concrete Samples

4.2.1 Sample Overview

The concrete samples used for the spalling experiments are cylindrical with a diameter of 75 mm and a length of 100 mm, drilled out of a bigger block. The samples are wrapped tightly in PTFE (“Teflon”) tape, leaving one flat face open. The samples with the PTFE tape are squeezed into a 1-2 mm thick PTFE cup, again leaving the face open. For each sample a PTFE cup is made to fit tightly. A schematic cross-section of the samples is shown in Figure 4.1. Each sample is equipped with 7 K-type thermocouples placed at approximately 5, 15, 25, 35, 45, 60 and 80 mm from the open front face. The thermocouples are placed in 1 mm diameter holes 8 mm deep into the concrete. The thermocouple wires are guided to the back of the sample at the outside of the PTFE cup.

Figure 4.1: A schematic drawing of a concrete sample. The concrete cylinder is wrapped in PTFE tape and put in a tight-fitting PTFE beaker (orange). Both types of pressure sensors are drawn. The Honeywell piezoelectric pressure sensor (diagonal lines) is connected to the sample with a MACOR plug (dark blue). The CSTB pressure gauge is located along the main axis, exiting the sample at the back (right). The tube of the pressure gauge is almost completely filled by a thermocouple (red). Thermocouple wires are displayed in purple. The tube filled with silicone oil (green) conducts the pressure to a pressure transducer (not shown).
As discussed in subsection 4.1.2, each sample is equipped with either a pressure gauge that has been developed by the Centre Scientifique et Technique du Bâtiment (CSTB) or a Honeywell piezoresistive pressure sensor. Both are drawn in Figure 4.1.

The piezoresistive sensor (diagonal lines in Figure 4.1) is twisted into a plug (dark blue). The plug reaches 35 mm into the concrete and has an outer diameter of 4 mm. A 1.5 mm diameter channel inside the plug transfers the pressure from the center of the sample to the pressure sensor. The free volume of the channel is ~62 mm$^3$ and is filled by water from the sample. The sensor is placed at a fixed position 35 mm from the heated side of the sample (not shown). The plug is made of MACOR glass ceramic and is bound to the concrete using high temperature (1450°C) mortar glue in order to make a leak-tight connection [49, 50]. The pressure sensor is connected to a computer outside of the scanner, using 4 thin wires leaving the sample at the back (not shown).

The CSTB pressure gauge consists of a 1 mm thick sintered metal disk (light blue in Figure 4.1) which is squeezed into a metal cup. The disk has a diameter of 12 mm, while the pores in the disk have a maximum diameter of 30 µm [2]. A straight stainless steel tube with an outer diameter of 2 mm and inner diameter of 1.6 mm exits the metal cup at the back. This tube gets almost completely filled by a K-type thermocouple with a diameter of 1.5 mm. This thermocouple is shoved in from the back until it touches the sintered disk. The rest of the space in the stainless steel tube is filled by the water that passes through the sintered disk.

The stainless steel tube with the thermocouple enters a watertight connector in which the pressure is passed on to a 4 m long PTFE tube filled with silicon oil. The tube with silicon oil ends in a custom made CSTB pressure transducer which is able to measure pressures from 0 to 60 bar (0 to 6 MPa). The pressure is sampled at 0.5 Hz along with the temperature in the pressure gauge.

The total free volume of the stainless steel tube and the connector is approximately 130 mm$^3$ and is filled with water from the sample [2]. As a comparison: the volume of pores in a cylinder with a diameter of 12 mm and a length of 10 mm equals 130 mm$^3$, assuming 11.5% porosity (see subsection 4.2.2). The pressure gauges are located at different depths in different samples. In two samples the gauge can be found 20 mm from the front end of the sample, in two others at 40 mm from the front end and in one sample at 30 mm.

### 4.2.2 Sample Characterization

The samples equipped with the Honeywell piezoresistive sensors are made of unknown concrete and used for testing only. The samples with the CSTB pressure gauges are made of normal B40 concrete which has a water to cement ratio (W/C ratio) of 0.54. The constituents of this concrete are shown in Table 4.1.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Amount (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>350</td>
</tr>
<tr>
<td>Sand (0-2 mm)</td>
<td>845</td>
</tr>
<tr>
<td>Gravel (8-12.5 mm)</td>
<td>330</td>
</tr>
<tr>
<td>Gravel (12.5-20 mm)</td>
<td>720</td>
</tr>
<tr>
<td>Water</td>
<td>188</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>1%*</td>
</tr>
<tr>
<td>W/C ratio (-)</td>
<td>0.54</td>
</tr>
</tbody>
</table>

* Mass percent of cement.
The cement used is classified as CEM II/A-LL 42.5 R, which indicates a Portland cement with a minimal compressive strength of 42.5 MPa 28 days after casting [1]. The main constituents of type II Portland cement are alite (C₃S, ~46%), belite (C₂S, ~29%), celite (C₃A, ~6%) and tetracalcium aluminoferrite (C₄AF, ~12%) [1]. In this cement chemist notation C stands for CaO, S for SiO₂, A for Al₂O₃ and F for Fe₂O₃.

When water (abbreviated as H) is added to the cement, the framework of the cement is formed. This framework, the calcium silicate hydrate (CSH), is formed due to the following exothermic hydration reactions [1,10]:

\[ 2\text{C}_3\text{S} + 6\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 + 3\text{CH} \]  
\[ 2\text{C}_2\text{S} + 4\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 + \text{CH} \cdot \]

The celite and tetracalcium aluminoferrite also hydrate exothermically, as shown in equation (4.2) with ¯S symbolizing SO₄ [1,10,51]:

\[ \text{C}_3\text{A} + 3\text{C}_3\text{H}_2 + 26\text{H} \rightarrow \text{C}_6\text{A}_3\text{SH}_{32} \]  
\[ \text{C}_4\text{AF} + 2\text{CH} + 10\text{H} \rightarrow \text{C}_3\text{AH}_6 + \text{C}_3\text{FH}_6. \]

The hydration equations (4.1) and (4.2) are ideal equations. Other reaction products may be formed due to for example an insufficient amount of water (H) or sulfate (¯S) being present during the actual hardening of the cement paste.

Typically two types of pores are formed during the hydration process: capillary pores and gel pores. The capillary pores consist of the space between the cement aggregates. This space is created during the hydration due to the difference between the volume of hydrated cement and the combined volume of water and dry cement. The size of the capillary pores is typically in the order of 10 nm to 10 µm. The gel pores are located within the CSH-gel itself and their size ranges approximately from 1 Å to 10 nm [2,10,51]. A schematic drawing of the gel pores and capillary pores is shown in Figure 4.2.

![Figure 4.2: Schematic drawing showing cement grains in black. The gel pores are located between the layers of the CSH-gel while the capillary pores can be found between the cement grains. Figure taken from [10].](image)

Any bigger pores present in the concrete can be due to entrapped air bubbles or due to cracking.

In order to further classify the concrete samples, the pore size distribution of the samples is determined using mercury intrusion porosimetry (MIP). MIP is based on applying pressure to liquid mercury so that it enters the concrete samples. The smaller the pores the higher the pressure required to fill them. Therefore if the volume of mercury entering the sample is monitored as function of the applied pressure, a pore size distribution can be obtained. These
distributions are shown in Figure 4.3. It must be noted that MIP sometimes underestimates the volume of bigger pores, due to the *ink-bottle effect*. Some bigger pores can only be reached by first filling smaller pores (just like an ink bottle) [30]. Furthermore, the MIP data does not include pores <7 nm.

**Table 4.2:** The porosity and bulk density of the two types of concrete, as obtained with mercury intrusion porosimetry (MIP). The last column contains the bulk density and porosity as measured in reference [2]. The bulk density includes the voids. Each measurements is performed on two samples.

<table>
<thead>
<tr>
<th></th>
<th>Honeywell</th>
<th>CSTB</th>
<th>CSTB [2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density (kg/m$^3$)</td>
<td>(2.2 ± 0.1) · 10$^3$</td>
<td>(2.3 ± 0.1) · 10$^3$</td>
<td>(2.28 ± 0.01) · 10$^3$</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>11.1 ± 0.2</td>
<td>11.9 ± 0.2</td>
<td>13.9 ± 0.1</td>
</tr>
</tbody>
</table>

The measured porosity and bulk density of both types of concrete are shown in Table 4.2, along with the porosity and bulk density of the same concrete as measured gravimetrically at the CSTB in reference [2]. The bulk density (the density including the volume of voids) is the same in both measurements, but the porosity is higher in the samples measured in reference [2]. This difference in porosity may be explained by again noticing that pores <7 nm are not included in the MIP results. This will yield a lower porosity.

### 4.3 Overview

In order to be able to measure the position-dependent moisture content of the concrete samples, all spalling experiments take place in an NMR scanner. A Philips Gyroscan 1.5 T full-body scanner is used to generate the main magnetic field (referred to as $B_0$ in section 3.1). A custom made “spalling insert” is put into the bore of the full-body scanner. A picture of the spalling insert and the 1.5 T scanner is shown in Figure 4.4. A schematic cross-section of the insert is displayed in Figure 4.5.

---

$^1$Both concretes are made with the same cement. However, the source of the cement described in this thesis is the Ranville plant, while the cement tested at the CSTB is from the Airvault plant.
The base of the spalling insert is an \( \text{Al}_2\text{O}_3 \) cylinder with a diameter of 140 mm. \( \text{Al}_2\text{O}_3 \) is used since high temperatures are expected during the spalling experiments and the melting point of \( \text{Al}_2\text{O}_3 \) is at 2054°C [53]. Furthermore, since \( \text{Al}_2\text{O}_3 \) does not contain hydrogen, it does not give a background signal during the NMR measurements. The long axis of the \( \text{Al}_2\text{O}_3 \) cylinder is pointing along the z-direction in Figure 4.5. The main magnetic field \( B_0 \) is also directed axially, while a birdcage coil is able to generate an RF-field (referred to as \( B_1 \) in section 3.1) in radial direction, along the r-axis. This birdcage coil is positioned at the outside of the \( \text{Al}_2\text{O}_3 \) cylinder. Within the birdcage coil, at the inside of the cylinder, the sample is placed. The open face of the sample is heated by 7 reflector lamps. Glass wool is used to fill the space between the sample and the \( \text{Al}_2\text{O}_3 \) cylinder. The glass wools insulates the sample and also protects the Faraday shield at the inside of the birdcage coil. This Faraday shield is required to perform quantitative measurements on samples with changing dielectric permittivity due to changing moisture content [54].

The thermocouple wires and the connections for the pressure gauge/sensor leave the birdcage through the glass wool at the backside of the sample. A cylindrical Faraday cage with open ends encloses the \( \text{Al}_2\text{O}_3 \) cylinder. The big Faraday cage, the Faraday shield and the stainless steel tube of the CSTB pressure gauge are all grounded. Two gradient coils with a diameter of 35 cm supply a magnetic field gradient in the direction of \( B_0 \).

The lamp array consists of 7 halogen lamps, each equipped with a reflector. The reflectors are covered with a thin layer of gold. Gold is used since it is a good reflector for infrared radiation, which is needed to heat the sample [55]. The lamps are connected in series and can operate at a maximum of approximately 11 V and 9 A each, leading to a maximum total power of 700 W. The heating efficiency of the lamps has been determined calorimetrically in reference [10] to be 40% and behaves linearly with the power applied to the lamps. However, computer simulations on dry concrete in the same reference [10] show that in practice only ~15% of the input energy is transferred to the concrete. The lamp array is cooled with coolant at the back (not shown). Compressed air is blown in the space between the sample and the lamps, to prevent evaporated water from condensing on the coils.
4.4 NMR electronics setup

In this section a description of the NMR electronics setup is given. The base of the NMR setup is a RadioProcessor board designed by SpinCore Technologies, Inc. [56]. This RadioProcessor board is connected to a computer via USB and is capable of sending out shaped pulses with a duration and timing set by a user-defined pulse program. Furthermore, the board also contains a connection with an ADC for data acquisition [57]. The board is controlled with custom made “Digital NMR” software written in MATLAB. A more detailed description of this software is given in section A.1 in Appendix A. Averaging of data is done on the board itself, while any other further data processing is performed in MATLAB.

A schematic drawing of the NMR electronics setup is given in Figure 4.6. The shaped pulses sent out by the RadioProcessor get amplified by an external 600 W pulsed amplifier (Type Tomco BT00500alphaSA-100mS) [58]. The amplifier is switched off between two subsequent pulses to make sure only the pulses are amplified, not the noise between the pulses. This switching is done by the “gate” output of the RadioProcessor. The amount of amplification (the gain) is set in advance by a TUEDACS PicoGiant [59]. The PicoGiant also controls the current through the gradient coils. The duplexer makes sure that the amplified RF-pulses enter the birdcage, while the returning RF-signals get amplified and sent back to the “Receiver” of the RadioProcessor.

The pulses sent out by the RadioProcessor are square shaped RF pulses, i.e. a block wave multiplied by a sin with a frequency $\omega$. As explained in subsection 3.1.2, a finite-length sinusoidal pulse in the time domain results in a sinc function in the frequency domain, centered around $\omega$. This means that the “slice” of the sample that gets excited by the square shaped RF pulse, ideally, has a sinc shape.
Figure 4.6: A schematic drawing of the NMR electronics setup. Orange blocks represent components of the NMR insert, while blue blocks indicate components outside of the main magnetic field. The RadioProcessor sends out shaped pulses to an amplifier, which forwards the amplified pulses to the sample in the birdcage coil. The PicoGiant controls the amplifier gain and the gradient coils. The RF-signals returning from the birdcage get averaged by the RadioProcessor, before being sent back to the computer for further processing.

4.4.1 Gradient calibration

Since the gradient coils of the insert are not actively cooled, they can only dissipate their heat to the surrounding air. The typical duration of a spalling experiment is ~2 hours. The maximum current through the gradient coils that can run for 2 hours is found to be ~8.7 A. Figure 4.7 shows the calibration of the gradient with a current of 8.7 A.

![Gradient calibration graph](image)

Figure 4.7: Intensity (blue solid line) of the NMR signal as a function of the frequency during the calibration of the gradients. A cylindrical sample consisting of 5 mm wide water-filled compartments spaced 5 mm apart is placed parallel to the magnetic field gradient after which a solid-echo sequence is used. The red crosses indicate the points used for the calibration, while the green vertical dashed lines are 5 mm apart. The gradient strength is found to be 3.8 kHz/mm.

For the gradient calibration a cylindrical sample is placed parallel to the magnetic field gradient (in the z-direction in Figure 4.5). This sample consists of five 5 mm wide compartments filled...
with water, spaced 5 mm apart. A solid-echo sequence (see section 3.3.2) with a pulse length of 100 µs and echo time of 400 µs is used. The scanning frequency \( \omega \) is varied in steps of 3 kHz, so that after a total of 67 frequencies Figure 4.7 is obtained. In this Figure, the 5 peaks indicate the positions of the 5 water-filled compartments, while the 4 dips show the spaces in-between. Taking the frequencies at the middle of the outermost flanks (indicated by the red stars) of the graph and dividing by \( 9 \times 5 \text{ mm} \), a gradient strength of 3.8 kHz/mm (or 89 mT/m according to equation (3.1)) is found. For clarity green dashed lines are drawn to indicate 5 mm blocks. Ideally the signal intensity would change as a unit step function when crossing the boundary from water filled cavity to a dry space in-between. Figure 4.7 however shows that, on average, a slope with width of approximately 15 kHz is visible between each peak and dip. Therefore the resolution at a gradient strength of 3.8 kHz/mm is in the order of 4 mm.

### 4.5 Experiments

As explained in subsections 4.2.2 and 4.1.2 respectively, two types of concrete and two types of pressure sensors are used. An overview of the experiments with the *Honeywell* pressure sensors is given in Table 4.3. The experiments with the *CSTB* sensors are presented in Table 4.4.

**Table 4.3:** Overview of the experiments performed with the Honeywell pressure sensors. The distance between the open front surface and center of the pressure sensor is given in the second column, while the sample ID of each sample is given in the first column.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>( L_p ) (mm)</th>
<th>( P_{\text{Lamps}} ) (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Honeywell 35A</td>
<td>35</td>
<td>((3.9 \pm 0.1) \times 10^2)</td>
</tr>
<tr>
<td>Honeywell 35B</td>
<td>35</td>
<td>((3.9 \pm 0.1) \times 10^2)</td>
</tr>
</tbody>
</table>

**Table 4.4:** Overview of the experiments performed with the pressure gauges of the Centre Scientifique et Technique du Bâtiment. The distance between the open front surface and the pressure gauge is given in the second column, while the sample ID of each sample is given in the first column. * The PTFE back is removed for sample CSTB 30.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>( L_p ) (mm)</th>
<th>( P_{\text{Lamps}} ) (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSTB 20A</td>
<td>20</td>
<td>((4.5 \pm 0.1) \times 10^2)</td>
</tr>
<tr>
<td>CSTB 20B</td>
<td>20</td>
<td>((5.1 \pm 0.1) \times 10^2)</td>
</tr>
<tr>
<td>CSTB 30 *</td>
<td>30</td>
<td>((4.8 \pm 0.1) \times 10^2)</td>
</tr>
<tr>
<td>CSTB 40A</td>
<td>40</td>
<td>((4.5 \pm 0.1) \times 10^2)</td>
</tr>
<tr>
<td>CSTB 40B</td>
<td>40</td>
<td>((4.8 \pm 0.1) \times 10^2)</td>
</tr>
</tbody>
</table>

The first column in Tables 4.3 and 4.4 shows the sample ID that is used to identify the experiments in the rest of this thesis. The distance \( L_p \) from the pressure sensor/gauge to the heated front surface of the samples is given in the second column. Two experiments are performed with the Honeywell sensors, both at 35 mm from the front surface. The CSTB pressure gauges are used in five experiments. Twice the pressure gauge is at 20 mm, twice at 40 mm and one time at 30 mm. For the experiment with the gauge at 30 mm, the PTFE at the back of the sample is removed due to practical reasons. This experiment therefore deviates from all other experiments.

As described in section 4.3 the concrete samples are heated by 7 halogen lamps with a maximum total power of 700 W. The actual power used for the experiments is lower, since parts of the setup started to melt in earlier experiments at 700 W. The power \( P_{\text{Lamps}} \) supplied for each
experiment is found in the third column of Tables 4.3 and 4.4. The uncertainty in $P_{Lamps}$ is due to the changing resistance of the lamps while heating up.

All samples are vacuum saturated in tap water for at least one week.

The gradient coils supply a magnetic field gradient of 89 mT/m. A solid echo sequence is used with a pulse time of 60 µs and an echo time of 180 µs. The recording window has a width of 75 µs. A repetition time of 1 s is used and each point is averaged 32 times. Within one repetition time 6 slices are measured, yielding a total of 24 slices after 4 sweeps (see section 3.7). Slices are spaced 5 mm apart. The first NMR moisture profile is obtained before the heating lamp array is switched on.
Chapter 5

Temperature increase of concrete

When wet concrete is heated from one side, water in the concrete will evaporate and the cement will dehydrate. These processes are described in more detail in section 5.1. Furthermore, a temperature gradient will develop in the concrete. The temperature profiles are discussed in section 5.2.

5.1 Heating of concrete

Several processes occur when concrete is heated, leading to a mass loss due to, for example, evaporation of water. These processes occur at different temperatures.

- At first, any free water present in the concrete pores evaporates and gets expelled. Under atmospheric pressure, this process takes place up to ~100°C. When a high heating rate is chosen, free water may still be present for higher temperatures \[10,60\].

- For temperatures >100°C the calcium silica hydrate (CSH) starts to dehydrate and the reactions (4.1) and (4.2) given in subsection 4.2.2 are partially reversed. Chemically bound water is converted into free water.

- At temperatures between 450°C and 550°C the Ca(OH)\(_2\) (Portlandite) decomposes and more water is released. For even higher temperatures (exceeding 600°C) calcium carbonate gets decarbonated \[61\].

The amount of free water in the concrete is determined by the porosity and the saturation level. If 100% saturation is assumed for a concrete with a porosity of 11.5% (see Table 4.2), 115 kg of free water per cubic meter of concrete can be expelled in the first process described above. The mass loss of the cement paste (cement and water) during the last two processes, will be in the order of 10% if the paste is heated up to 400°C and 15% when heated to 950°C \[28,62\]. For the case of the concrete described in Table 4.1, this would mean a mass loss of the concrete of 54 kg and 81 kg per cubic meter of concrete, respectively. Compared to the mass loss due to evaporation of free water, this dehydration is significant.

From an energy point of view, the heat of dehydration of the CSH during the heating up to 200°C, is found to be in the order of 250-350 kJ per kilogram unhydrated cement \[1,28\]. For concrete with a cement content of 350 kg/m\(^3\), this corresponds to a required energy input of ~105 MJ per m\(^3\) of concrete. As a comparison, the evaporation of the free water in concrete with a porosity of 11.5%, requires 260 MJ/m\(^3\) \[28\]. For temperatures up to 200°C the energy consumption is therefore dominated by the evaporation of water \[10\].
The decomposition of Portlandite between 450 and 550°C consumes ~165 kJ per kg cement paste [10]. This corresponds to 89 MJ per m³ of concrete.

Table 5.1: Overview of the energies involved when heating a concrete sample with a bulk density of \((2.3 \pm 0.1) \cdot 10^3\) kg/m³ and a porosity of 11.5%. The sample has a diameter of 75 mm and a length of 100 mm. All values are based on the whole sample. Heating input power is 75 W.

<table>
<thead>
<tr>
<th>Process</th>
<th>Energy (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating influx (3600 s)</td>
<td>270</td>
</tr>
<tr>
<td>Evaporation of pore water</td>
<td>115</td>
</tr>
<tr>
<td>Dehydration of CSH</td>
<td>46</td>
</tr>
<tr>
<td>Decomposition of Portlandite</td>
<td>39</td>
</tr>
<tr>
<td>100°C concrete temperature increase</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 5.1 gives a comparison of these energies with the input energy provided by the lamp array. A cylindrical sample with a diameter of 75 mm and length of 100 mm is assumed. Furthermore, an input power of 500 W and a heating efficiency of 15% are assumed, as explained in sections 4.5 and 4.3, respectively. A specific heat of concrete of 1 kJ K⁻¹ kg⁻¹ is used [4, 63].

5.2 Temperature profiles

When a semi-infinite solid is heated at \(x = 0\) starting at \(t = 0\), the temperature \(T\) at position \(x\) and time \(t\) is given by equation (5.1) [33]:

\[
T(x, t) = T_0 + \frac{2F}{K} \left( \sqrt{\frac{Kt}{\pi}} \exp\left(\frac{-x^2}{4Kt}\right) - \frac{x}{2} \text{erfc}\left(\frac{x}{2\sqrt{Kt}}\right) \right)
\]

(5.1)

with \(T_0\) the initial temperature of the solid, \(F\) the constant heat flux per unit time per unit area, \(K\) the thermal conductivity and \(\kappa\) the thermal diffusivity. This equation was already used in the conceptual model in subsection 2.2.1.

In Table 5.2 typical values of the thermal conductivity \(K\) and the thermal diffusivity \(\kappa\) are given for concrete, water and air at different temperatures. The values for concrete should be used as an indication only, since the thermal properties of concrete depend on the exact composition of the concrete [64]. The porosity of the samples used for the experiments described in this thesis is around 11.5% (see Table 4.2). Therefore it is assumed that the thermal conductivity and thermal diffusivity of the complete samples are comparable to the thermal conductivity and thermal diffusivity of the concrete matrix. For this reason equation (5.1) can be used as a first approximation to the temperature profiles in the concrete samples discussed in this thesis. The thermal conductivity and thermal diffusivity of the sample are assumed to be independent of position and other sources/sinks of heat (e.g. latent heat) are ignored in this approximation.

As explained in section 4.2 all concrete samples are equipped with 7 thermocouples at one side. Equation (5.1) is used to fit temperature profiles through the temperature data. As an example the fitted temperature profiles for sample CSTB 20A are shown with the measured temperatures in Figure 5.1. The time between two subsequent profiles is generally ~70 seconds, but, for clarity, only one profile for each 15 minutes is shown in Figure 5.1. The fitted temperature profiles are used to correct the NMR profiles for the temperature dependent magnetization, as described in subsection 3.5.1. To get an estimate of the validity of using the fitted profiles for this temperature correction, the difference between the fitted temperature and the measured temperature is calculated. Equation (5.2) gives the maximum relative difference \((\delta T)_{\text{max}}\) as a
Table 5.2: Overview of typical values of the thermal conductivity $K$ and the thermal diffusivity $\kappa$ for concrete and the fluids present in a one-sided heating experiment. Values of concrete depend on many parameters such as the water-cement ratio and size of aggregates and should be used as a first estimation only.

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>$K$ (W m$^{-1}$ K$^{-1}$)</th>
<th>$\kappa$ (m$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O (L) [37,65]</td>
<td>0.6062</td>
<td>1.45 $\cdot$ 10$^{-7}$</td>
</tr>
<tr>
<td>H$_2$O (g) [37,66]</td>
<td>1.86 $\cdot$ 10$^{-2}$</td>
<td>4.62 $\cdot$ 10$^{-2}$</td>
</tr>
<tr>
<td>Concrete [33,64]</td>
<td>1.1 - 2.3</td>
<td>4.2 $\cdot$ 10$^{-1}$</td>
</tr>
<tr>
<td>Air [37,66]</td>
<td>2.64 $\cdot$ 10$^{-2}$</td>
<td>2.25 $\cdot$ 10$^{-5}$</td>
</tr>
</tbody>
</table>

function of the distance $x$ from the sample front face:

$$ (\delta T)_{\text{max}}(x) = \left| \frac{T_{\text{fit}}(x) - T_{\text{TC}}(x)}{T_{\text{TC}}(x)} \right|_{\text{max}} $$ (5.2)

In equation (5.2) $T_{\text{fit}}$ is the absolute temperature according to the fitted curves and $T_{\text{TC}}$ the absolute temperature measured with the thermocouples. Since there are generally 7 thermocouples for each experiment, $x$ can only be one of these 7 discrete values. The subscript $\text{max}$ indicates that for each experiment (and each value of $x$) only the maximum value of the relative difference obtained at any time during the experiment is used. The maximum relative difference for each CSTB experiment is displayed in Figure 5.2.

As can be seen in Figure 5.2, the maximum relative difference tends to get larger further away from the front face of the sample. The temperature at the back of the sample is higher than predicted by equation (5.1). There are multiple explanations for this. First, equation (5.1) describes a semi-infinite medium, so that heat can always move further down the medium. The samples have a finite length of 100 mm so that heat may stack up at the back of the sample.

A second explanation for the increasing temperature at the back may be found in the hot vapor that is released at the drying front. Since this vapor can move deeper into the sample, it can cause a temperature increase at the back.
The maximum relative difference stays below 10% for all experiments and all positions. It is therefore acceptable to use the fitted temperature curves to correct for the temperature dependence of the magnetization.

5.2.1 Temperature of the front surface

In order to get an idea of the heating rate of the samples, the fire curves of Figure 1.3 are plotted again in Figure 5.3.

![Figure 5.3: The fire curves discussed in Chapter 1 (dashed lines) and the temperatures of the front surface of the CSTB samples during the experiments. The temperatures at the front surfaces are obtained by calculating the fitted temperatures at a position of 0 mm.](image)

The dashed lines in Figure 5.3 represent the fire curves discussed in section 1.1 of the Introduction. The solid lines represent the temperature at the front surface of the CSTB samples during the different experiments. The fitted extrapolated temperatures at a position of 0 mm are used as the temperatures of the front surfaces.

On first inspection of the temperatures in Figure 5.3 the heating rate of the front surface seems to be much lower than for example the ISO-834 and RWS heating curves. However, it must be noted again that these fire curves do not give the maximum allowed temperature of the concrete itself. Instead they give the temperature expected in a confined space due to a specific fire (e.g. a burning fuel tank in a tunnel). The RWS curve, for example, assumes a layer of isolation between the fire and the concrete and states that the temperature at the interface of the isolation and the concrete should not exceed 380°C [14].

According to Table 4.4 the power applied to the lamp heating array is in the range of 450–510 W for all experiments. However, according to Figure 5.3 the temperature of the front surface of sample CSTB 40A is much lower than the front surface temperature of the other samples. CSTB 40A was the only sample in which the thermocouples were located at the bottom of the sample during the experiment, instead of at the top. Although cylindrical symmetry is assumed for the experiments, the temperature difference between the CSTB 40A experiment and the other experiments, suggests that this assumption might be incorrect. A possible explanation is that the thermocouple holes in the PTFE could allow for a water, vapor or gas flux, even though the holes themselves are covered with PTFE tape. This way hot air coming from the front can enter the thermocouple wholes when they are on top, while (condensed) water will block this influx of hot air when the holes are at the bottom. If this is the case, the latter situation gives the more accurate temperature as function of position. However, more research is required to verify this hypothesis.
Chapter 6

Moisture content and pressure

This chapter focuses on the pressure measurements and the measured moisture content of the samples. First the results of the experiments with the Honeywell sensors are discussed in section 6.1. The results of the CSTB experiments can be found in sections 6.2-6.6. The weight loss of the samples during heating can be found in section 6.2. An example of the signal corrections that need to be applied to the raw NMR profiles is given in section 6.3, followed by the NMR results in section 6.4. The measurements of pressure and temperature in the pressure gauge are discussed in section 6.5. Finally, an energy balance for the experiments is given in section 6.6.

6.1 Experiments with Honeywell pressure sensor

As discussed in subsections 4.1.2 and 4.2.2 the experiments with concrete samples equipped with a Honeywell pressure sensor are primarily used for testing, since it was unknown if the pressure sensors would last long enough due to the expected high temperatures. Furthermore, the used concrete is not well defined.

During experiment Honeywell 35A the pressure sensor survived for half an hour, before short-circuiting in the sensor was observed. The short-circuiting can be caused by melting of the sensor. During the first half hour however, no pressure increase occurred. This may indicate that the connection of the plug to the concrete was not airtight (see subsection 4.2.1) and environmental pressure was measured.

In the case of the Honeywell 35B experiment, the short-circuiting was observed almost right from the start of the experiment and no pressure data was recorded.

Furthermore, the moisture profiles obtained by NMR for experiment Honeywell 35A are extremely noisy and do not provide quantitative information about the moisture content. The moisture measurements for experiment Honeywell 35B show much less noise, indicating that the noise is not caused by the pressure sensor itself. The noise may be caused by a bad connection in the coil circuitry.

The combination of noisy moisture content measurements and the lack of pressure increase, make the Honeywell experiments not suitable for a better understanding of the spalling process in concrete. Therefore, the remainder of this thesis will be focused on the experiments with the CSTB pressure gauges.
6.2 Weight loss

To get an indication of the amount of water in the samples, the samples are weighed. In Table 6.1 the mass of the CSTB samples is given after the samples have been vacuum saturated under water for at least one week \((m_{\text{Sat}})\), after the respective spalling experiment \((m_{\text{Spalling}})\) and after being vacuum-dried at 40°C for two weeks \((m_{\text{Dry}})\). The latter is measured after the spalling experiment. The mass includes the PTFE cup, PTFE tape and pressure gauges.

Table 6.1: Mass of the CSTB samples in various conditions. \(m_{\text{Sat}}\) indicates the mass after vacuum saturation, \(m_{\text{Dry}}\) the mass after vacuum drying and \(m_{\text{Spalling}}\) the mass after the spalling experiment. \((\Delta m)_{\text{Rel}}\) represents the percentage of mass lost during the experiment.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>(m_{\text{Sat}} ) (kg)</th>
<th>(m_{\text{Spalling}} ) (kg)</th>
<th>(m_{\text{Dry}} ) (kg)</th>
<th>((\Delta m)_{\text{Rel}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSTB 20A</td>
<td>1.206</td>
<td>1.137</td>
<td>1.149</td>
<td>6.7%</td>
</tr>
<tr>
<td>CSTB 20B</td>
<td>1.215</td>
<td>1.141</td>
<td>1.144</td>
<td>7.1%</td>
</tr>
<tr>
<td>CSTB 30</td>
<td>1.158</td>
<td>1.091</td>
<td>1.095</td>
<td>6.8%</td>
</tr>
<tr>
<td>CSTB 40A</td>
<td>1.274</td>
<td>1.196</td>
<td>1.199</td>
<td>7.1%</td>
</tr>
<tr>
<td>CSTB 40B</td>
<td>1.260</td>
<td>1.192</td>
<td>1.195</td>
<td>6.3%</td>
</tr>
</tbody>
</table>

The relative mass loss \((\Delta m)_{\text{Rel}}\) during the spalling experiments is given in the last column of Table 6.1 and is defined in equation (6.1): \[
(\Delta m)_{\text{Rel}} = \frac{m_{\text{Sat}} - m_{\text{Spalling}}}{m_{\text{Sat}} - m_{\text{PTFE}}}.
\] (6.1)

where \(m_{\text{PTFE}}\) is the mass of the PTFE cup and tape, which is found to be \((170 \pm 20)\) g. This yields a relative mass loss of \((6.8 \pm 0.5)\%\). The maximum relative mass loss \(|(\Delta m)_{\text{Rel}}|_{\text{Max}}\) that can be expected due to evaporation of free water based on 100% water saturation of the sample, is given by equation (6.2):

\[
|(\Delta m)_{\text{Rel}}|_{\text{Max}} = \frac{m_w}{m_w + m_c} = \frac{n \rho_w}{n \rho_w + \rho_c},
\] (6.2)

where \(m_w\) is the mass of water present in the concrete pores, \(m_c\) the mass of the concrete sample, \(n\) the porosity of the concrete, \(\rho_w\) the density of water and \(\rho_c\) the bulk density of the concrete. When the porosity and the bulk density of the concrete are taken from Table 4.2 to be 11.9% and \(2.3 \cdot 10^3\) kg/m\(^3\) respectively and the density of water is \(1.0 \cdot 10^3\) kg/m\(^3\), the maximum relative mass loss will be 4.9% [53]. This value is lower than the actual measured relative mass loss of 6.8%. An explanation for this difference is that due to the high temperatures during the experiments, the concrete dehydrated chemically and therefore lost more water than just the free water present in the pores. This dehydration is explained in section 5.1. Working with a typical mass loss of 54 kg/m\(^3\) (see section 5.1) and a volume of \(4.42 \cdot 10^{-4}\) m\(^3\), an extra mass loss of 2.3% is expected when the whole sample would reach 400°C. As can be seen in Figure 2.1b only part of the sample reaches this temperature. Therefore the real mass loss will be lower.

Furthermore, as explained in subsection 4.2.2, the porosity obtained by mercury intrusion porosimetry may be underestimating the porosity, since MIP does not includes pores <7 nm.

As can be seen in Table 6.1, the value of \(m_{\text{Dry}}\) is higher than the value of \(m_{\text{Spalling}}\). This can be caused by the rehydration of the concrete after the experiments [67].
6.3 NMR signal corrections

6.3.1 Applied corrections

As explained in section 3.4, the signal obtained by the NMR scanner ideally would quantify the amount of water at different positions in the sample. In practice however, corrections need to be applied to the NMR data in order to give a good indication of the moisture content. An overview of the applied corrections is given in this section.

At first inspection of the NMR profiles of all CSTB experiments, 2 out of the total of 24 frequencies (or points) in each profile show unexpected behavior. The signal at one point (63.815 MHz) is consequently at a higher intensity, while the neighboring point (63.795 MHz) is consequently at a lower intensity than expected. Furthermore the signal at these points varies much less during the experiments, than the signal at other neighboring points. Samples cannot be positioned in the exact same way for different experiments. Therefore, a frequency that corresponds to a certain position in the first sample, may correspond to a different position in the second sample. Since the unexpected behavior is observed at the same two frequencies for each sample (and therefore not at the same position) it is possible that there is, for example, some uncontrolled resonance in the circuit or an external RF-field which interferes with the measurements. The two points are therefore omitted out of the results.

Figure 6.1: Overview of the corrections applied to the raw NMR profiles. The sample extends from the heated side at 0 mm to the back side at 100 mm. a. “Raw” NMR profiles with two questionable points omitted. b. Profiles corrected for the temperature dependence of the magnetization. c. Profiles normalized by dividing by the first profile. d. Normalized profiles smoothed by averaging each point with its two direct neighboring points. Arrows indicate direction of progression in time.
Figure 6.1 shows the further signal correction steps. As an example sample CSTB 40A is used. For clarity only half of the NMR moisture profiles is shown in alternating fashion. Figure 6.1a shows the raw data as obtained (after averaging) from the SpinCore RadioProcessor (see section 4.4). The frequencies are already converted to positions, with 0 mm (red dashed line) the heated front surface of the sample. The blue dashed line represents the back of the sample. Positions <0 mm or >100 mm represent points outside of the sample. The signal that is still present at these positions can be due to several reasons. At first noise will be present (e.g. noise picked-up by the coil or noise in the electronics). Secondly, the measured slices of the samples have a certain width (see subsection 3.1.2) and signal from the sample may still be picked up for points outside of the sample.

The different colored profiles represent different times in the experiment (see legend on the right) relative to \( t = 0 \), the time at which the heating started. The first profile, at \( t = -548 \) s, is obtained before the heating was turned on.

As explained in section 3.5.1 the signal needs to be corrected for the temperature dependence of the magnetization. The “raw” NMR data of Figure 6.1a is multiplied by the interpolated absolute temperature profiles obtained in section 5.2. The resulting NMR profiles are displayed in Figure 6.1b. The signal intensities in Figures 6.1a-b have arbitrary units which can only be used to compare the profiles in the same graph.

The circuit and coil used to pick-up the signal in an NMR scanner is tuned to the frequency of the main magnetic field. When a gradient in the magnetic field is present only the center of the sample will be at the frequency of the main magnetic field (see section 3.1.1). Therefore the coil will be less sensitive for the signal from the sides of the sample and generally a lower intensity is measured at the sides [10]. To account for this coil profile all profiles are divided by the first profile. The normalized profiles are shown in Figure 6.1c. The first profile (before the heating was switched on) is represented by the horizontal blue line. Note that in Figure 6.1c only the positions inside the sample are shown, since the normalized intensities outside of the sample show great fluctuations.

In the last step the results are smoothened to make the general trend of the evolution of the profiles better visible. Each point is therefore averaged with its two directly neighboring points. The leftmost and rightmost points of the sample are not averaged. The smoothened profiles are shown in Figure 6.1d. Two arrows are drawn to indicate the direction of the progression of the profiles.

6.3.2 Relaxation correction

Ideally a \( T_2 \) temperature correction should be applied to correct for the temperature dependence of the \( T_2 \) decay constant (see subsection 3.5.2). Therefore, an Ostroff-Waugh pulse sequence is performed after each moisture profile. As explained in section 3.6, the results of these OW-sequences can be used to find the \( T_2 \) time constant at the current temperature of the sample. Unfortunately the combination of a small \( T_2 \) and low signal to noise ratio do not allow for a \( T_2 \)-fit through the obtained data. Therefore, this \( T_2 \) temperature correction is omitted from the results. This may lead to an overestimation of the signal at higher temperatures [10].
6.4 NMR results

The temperature-corrected normalized smoothened NMR profiles of sample CSTB 40A can be found in Figure 6.1d in the previous section. The profiles of the other four CSTB samples are shown in Figure 6.2.

![Figure 6.2](image)

**Figure 6.2:** Normalized temperature-corrected smoothened moisture profiles for four CSTB experiments. Note that for sample CSTB 20A the profiles are normalized with the third profile instead of the first profile. The black arrows indicate direction of progression in time.

On first visual inspection, the moisture profiles of the four samples shown in Figure 6.2 appear less smooth than the same moisture profiles of sample CSTB 40A used as an example in Figure 6.1d. In order to produce a clear graph, the moisture profiles of sample CSTB 20A are actually smoothened by dividing by the third profile (second profile shown) instead of the first profile. The disadvantage is that there is already a temperature gradient present in this third profile. Therefore the normalization for the coil profile and the sample inhomogeneities is influenced by temperature effects, in the case of sample CSTB 20A.

A physical explanation for the difference in noise of the profiles of the different experiments is not straightforward. The samples are drilled out of the same batch of concrete, contain an identical pressure gauge (albeit at different depths) and are equally saturated with water. The samples each contain 7 thermocouples. There is no relation between the chronology of the experiments and the amount of noise. The same NMR setup and scripts are used. An explanation could be sought in the electronic circuits of the insert. It is for example possible that there is a bad
connection somewhere in the system. However, such a bad connection is not found upon first inspection of the setup.

In general the same trend is visible in all experiments. Water starts to evaporate at the heated side of the sample \( (x = 0) \). The moisture content at the heated side starts to decrease and a drying front develops. As explained in section 2.1 this indicates that the moisture content at the front side of the sample is below the critical moisture content \( \theta_c \). The moisture transport is now governed by vapor transport. As indicated by the horizontal black arrow in Figure 6.2b, the moisture front progresses further into the sample. In the end also the moisture content at the back of the sample decreases below the critical moisture content. This eventually results in the sample losing all its moisture (vertical arrow).

As explained in section 2.1 it has been observed in earlier experiments, that a moisture clog is formed due to water vapor that moves into the sample and recondenses. This moisture clog would be visible in the profiles of Figure 6.2, due to a locally increased normalized moisture content (normalized signal intensity >1). However, many profiles already show an overall normalized signal intensity greater than unity, so that the moisture clog could not be observed in these profiles. Since the samples were vacuum saturated at the beginning of the experiments, it is very unlikely that the moisture content actually increased by \( 30 - 70\% \) after the start of the experiment. The increased signal intensities might be caused by for example a temperature increase of the coil.

### 6.4.1 Systematic errors

Next to the possible errors due to unknown (temperature) effects in the coil and electronics discussed above, some systematic errors are present in the measurements.

At first it must be noted that measurements with the same setup in reference [10] show that the NMR signal behaves linear with the amount of free moisture present in concrete. However, when no free moisture was present in the sample, still some NMR signal was visible. Since this signal was visible for temperatures up to ~800°C, this indicates signal coming from chemically bound water. No linear relation was found between the signal and the amount of chemically bound water.

The second systematic error comes from the temperature correction of the magnetization. Although the temperatures returned by the thermocouples have an accuracy in the order of 0.1 K, the fitted temperature curves may have an error of up to 10% (see Figure 5.2). Furthermore, as will be shown in the next section, a difference is present between the fitted temperatures and the temperatures measured in the pressure gauge. In the worst case this difference reaches 19% during experiment CSTB 20B, but on average (including all experiments) this difference is 7%.

The last systematic error comes from the omission of a \( T_2 \)-temperature correction, as discussed in subsection 6.3.2. The signal at a temperature of 200°C was found to be overestimated by up to 20% in earlier experiments, compared to the signal at room temperature [10].

### 6.5 Pressure measurements

The results of the pressure measurements are shown in Figure 6.3 for experiment CSTB 20A. The results of the other four CSTB experiments are shown in Figures B.1-B.4 in Appendix B.

In the top left graph of Figure 6.3, the temperatures at the position of the pressure gauge \( (x = 20 \text{ mm}) \) are given. The temperature measured with the thermocouple in the gauge itself
Figure 6.3: Pressure gauge measurements for sample CSTB 20A. Top left: Temperatures at the position of the pressure gauge (20 mm) as measured by the thermocouple in the pressure gauge (blue) and linearly interpolated for the thermocouples at the side of the sample (green). Right: Pressure as measured with the gauge (magenta). Saturated vapor pressures calculated from the temperatures shown in the top left figure (blue and green). Bottom left: NMR signal intensity decay at the position of the pressure gauge, found by linear interpolation of the two nearest points. Vertical dashed line corresponds to time of maximum measured pressure.

is displayed in blue. The temperatures of the thermocouples at the side of the sample are linearly interpolated to obtain the interpolated temperature at \( x = 20 \) mm. This interpolated temperature is displayed in green. In experiments CSTB 20A, CSTB 20B and CSTB 40B the temperature in the pressure gauge is significantly lower than the interpolated temperature. This suggests that the temperature at the central axis of the sample is lower than the temperature at the sides. The interpolated temperature of CSTB 40A however does agree with the gauge temperature. As explained in subsection 5.2.1, CSTB 40A is the only sample where the thermocouples are located at the bottom of the sample during the experiment. The combination of the results of the two types of temperature measurements, seems to confirm again that the temperature measured on top of the samples CSTB 20A, CSTB 20B, CSTB 30 and CSTB 40B overestimates the real temperature in the sample.

The bottom left graph of Figure 6.3 shows the normalized NMR signal intensity at the position of the pressure gauge. Since no NMR measurement is done exactly at \( x = 20 \) mm, again linear interpolation is applied to obtain the signal.

The right graph of Figure 6.3 shows the pressure as measured with the pressure gauge (magenta). The time at which the measured pressure is at its maximum, is indicated by the vertical dashed line in all three graphs. The blue and green lines in the right graph show the saturated vapor pressures corresponding to the gauge temperature and interpolated temperature, respectively.

A summary of the maximum pressures for the five experiments is given in Table 6.2.

A goal of the research described in this thesis is to combine the pressures, temperatures and moisture profiles in order to link the decreasing moisture content to the pressure. One feature that is visible in all gauge temperatures (in the top left graphs) except for sample CSTB 30, is the plateau of approximately constant temperature near the time of maximum pressure. In earlier work this plateau has been attributed to energy consumption due to the vaporization of water [12, 22, 68]. In a comparison between drying of dry concrete samples and partially
Table 6.2: Summary of the maximum pressures $p_{\text{max}}$ for the five CSTB experiments. $t_{\text{pmax}}$ indicates the time of the pressure peak relative to the start of the heating, while $T_{\text{pmax}}$ gives the temperature in the gauge at the time of maximum pressure. Uncertainties only relate to reading data from the graphs.

* For sample CSTB 30 the interpolated temperature is displayed. Note that for sample CSTB 30 also the PTFE back was removed.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$p_{\text{max}}$ (MPa)</th>
<th>$t_{\text{pmax}}$ (s)</th>
<th>$T_{\text{pmax}}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSTB 20A</td>
<td>0.852 ± 0.002</td>
<td>2124 ± 5</td>
<td>168 ± 1</td>
</tr>
<tr>
<td>CSTB 20B</td>
<td>0.58 ± 0.01</td>
<td>1680 ± 60</td>
<td>158 ± 1</td>
</tr>
<tr>
<td>CSTB 30</td>
<td>0.843 ± 0.003</td>
<td>3190 ± 20</td>
<td>227 ± 1*</td>
</tr>
<tr>
<td>CSTB 40A</td>
<td>0.266 ± 0.001</td>
<td>2601 ± 2</td>
<td>124 ± 1</td>
</tr>
<tr>
<td>CSTB 40B</td>
<td>0.498 ± 0.001</td>
<td>3910 ± 40</td>
<td>154 ± 1</td>
</tr>
</tbody>
</table>

wet concrete samples, the plateau was indeed only observed in the partially wet concrete [22]. This indicates that the maximum pressure coincides with the passing by of the drying front. In experiments CSTB 20A, CSTB 20B, CSTB 40A and CSTB 40B this is confirmed by the decreasing moisture content at the time of maximum pressure (see bottom left graphs).

Another goal of this research was to observe whether the pressure would follow the saturated vapor pressure curve. As can be seen in experiments CSTB 20A, CSTB 20B, CSTB 40A and CSTB 40B the pressure indeed follows the calculated saturated vapor pressures closely, especially for pressures approaching the maximum pressure. A bigger deviation is visible for lower pressures, partly due to the presence of air. In future experiments it might be sufficient to measure the moisture profiles and the temperature near the time of maximum pressure (the time the drying front passes by), depending on parameters such as the initial saturation and permeability.

6.6 Energy balance

In order to get an overview of the energies involved in the experiments, an energy balance can be made. Table 6.3 shows the time $t_{\text{End}}$ of the last moisture profile for each experiment (shown in Figure 6.2). Since this time corresponds to the duration of the heating, it can be used to calculate the total energy $E_{\text{in}}$ supplied to the samples. For this, the time $t_{\text{End}}$ is multiplied by the power supplied by the lamp array (see Table 4.4) and the expected heating efficiency of $(15 \pm 2)\%$.

Table 6.3: Overview of the energies involved in the experiments. $E_{\text{in}}$ and $E_{\text{cons}}$ indicate the supplied and consumed energies, respectively. The time of the last moisture profile is given in column $t_{\text{End}}$. $T_{\text{End}}$ is the average temperature of the sample at $t_{\text{End}}$.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$t_{\text{End}}$ (s)</th>
<th>$T_{\text{End}}$ (°C)</th>
<th>$E_{\text{in}}$ (kJ)</th>
<th>$E_{\text{cons}}$ (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSTB 20A</td>
<td>6564</td>
<td>238</td>
<td>$(4.4 \pm 0.7) \cdot 10^4$</td>
<td>379</td>
</tr>
<tr>
<td>CSTB 20B</td>
<td>5583</td>
<td>245</td>
<td>$(4.3 \pm 0.7) \cdot 10^4$</td>
<td>354</td>
</tr>
<tr>
<td>CSTB 30</td>
<td>7274</td>
<td>265</td>
<td>$(5.2 \pm 0.8) \cdot 10^2$</td>
<td>406</td>
</tr>
<tr>
<td>CSTB 40A</td>
<td>7405</td>
<td>217</td>
<td>$(5.0 \pm 0.8) \cdot 10^2$</td>
<td>358</td>
</tr>
<tr>
<td>CSTB 40B</td>
<td>6423</td>
<td>253</td>
<td>$(4.6 \pm 0.7) \cdot 10^2$</td>
<td>394</td>
</tr>
</tbody>
</table>

An estimate for the consumed energy $E_{\text{cons}}$ is made using the values from Table 5.1 in section 5.1:

- 100 kJ is needed to heat a complete concrete sample by 100°C. The average temperature $T_{\text{End}}$ of the sample during the last moisture profile is shown in Table 6.3. The energy
required for the increase in temperature from 20°C ranges from 197 kJ to 245 kJ for samples CSTB 40A and CSTB 30, respectively.

- All samples except for sample CSTB 20B have dried out almost completely at the time of the last profile (see Figure 6.2). Therefore 115 kJ is used for the evaporation of all the water from the other samples. For sample CSTB 20B 80% of this 115 kJ is used as a first estimate.

- A further 46 kJ is required for the dehydration of the CSH gel. Again 80% is used for sample CSTB 20B.

Adding these three energies gives $E_{cons}$ in Table 6.3. The estimated consumed energy is lower than the supplied energy $E_{in}$. Partly this may be caused by energy escaping from the sides and back of the sample. Furthermore, the water that is released during the dehydration of the CSH-gel, also consumes energy when evaporating. Finally, the heating of water from 20°C to >100°C removes some more energy (~20 kJ) from the sample.
Chapter 7

Conclusions and outlook

7.1 Conclusions

Experiments have been performed in order to investigate fire spalling due to the build-up of a high vapor pressure. For the first time, these experiments were successful in combining temperature and pressure measurements with a spatial moisture distribution, during the heating of concrete.

A multi slice echo sequence has been implemented successfully to allow for capturing the progress of the drying front.

Two types of pressure sensors were used. The Honeywell piezoresistive sensors turned out to be unable to record any pressure increase. The sensors started to melt, or short-circuiting occurred within 30 minutes after the start of the experiment.

A more suitable pressure sensor was found in a sensor based on a water filled pipe, which transfers the pressure from inside the concrete samples to an external pressure sensor. This sensor, which was developed by the Centre Scientifique et Technique du Bâtiment (CSTB), was selected for its ability to operate in the expected pressure and temperature ranges.

The fitted temperature at the front surface of the samples after one hour of heating, reached 250°C during experiment CSTB 40A, while it reached ~450°C during the other CSTB experiments. The thermocouples were located at the bottom of the sample for experiment CSTB 40A, instead of at the top for all other experiments. Experiment CSTB 40A is the only experiment in which the fitted temperature at the position of the pressure gauge agrees with the temperature measured inside the gauge. This suggests that thermocouples may need to be placed at the bottom of the sample for more accurate temperature readings. Possibly, the samples do not show the assumed cylindrical symmetry.

The moisture profiles obtained by NMR show varying noise levels. After temperature correction and normalization, a drying front was observed in all experiments. Although an increased moisture intensity was observed in front of the drying front, it is unclear if this indicates the predicted moisture clog. Possibly the increase in signal was caused by heating of the coils.

The pressure measurements showed a clear pressure peak in all experiments. The maximum pressures ranged from 0.27-0.50 MPa at a depth of 40 mm, to 0.58-0.85 MPa at a depth of 20 mm. This suggests that the highest pressures can be found in the front of the sample, although the number of experiments may be too low to draw definite conclusions. The pressures found are in the same range as the pressures found for normal strength concrete in Table 1.1 in the Introduction.
In experiments CSTB 20A, CSTB 20B, CSTB 40A and CSTB 40B the maximum pressures were observed during the “plateau” in the temperature measured in the pressure gauge. Since in earlier works this plateau has been linked to the energy consumption due to the evaporation of water, the highest pressures are expected to be found during the passing of the drying front, when the moisture content is decreasing. This decreasing moisture content at the time of maximum pressure is indeed confirmed by the NMR signal in all four experiments. There is however a difference between for example experiment CSTB 40A and CSTB 40B. In the case of sample CSTB 40A the maximum pressure is found right after the moisture content starts to decrease, while in sample CSTB 40B the highest pressure is found near the end of the decrease.

The saturated vapor pressures of water are calculated at the temperatures measured in the pressure gauge. The measured pressure in samples CSTB 20A, CSTB 20B, CSTB 40A and CSTB 40B follow the saturated vapor pressure near the maximum pressure. For lower pressures, the pressure in samples CSTB 20A, CSTB 40A and CSTB 40B is somewhat higher than the saturated vapor pressures. In earlier experiments this has been attributed to either entrapped air or the temperature increase of liquid water [35]. Since the liquid water cannot expand in the saturated pores, the pressure will increase with increasing temperatures [63].

7.2 Outlook

The experiments in this thesis have shown, that it is possible to measure moisture distributions in combination with vapor pressures and temperatures, while heating concrete. They have shown qualitatively that the highest pressures coincide with the drying front. However, some improvements are required for a more quantitative analysis in future experiments.

7.2.1 Improvements

At first the moisture profiles obtained by NMR contained a lot of noise. Solutions can be:

- A different pressure sensor can be used. The CSTB sensors did contain metal which is not desired during NMR measurements. A possible pressure sensor for future experiments could be based on fiber optics. Miniature fiber optic sensors for the desired temperature and pressure ranges do exist, but are expensive.

- Less thermocouples may be used to correct for the temperature dependence of the magnetization, since each thermocouple again adds metal to the setup.

- The heating needs to be improved, since the birdcage coil and Faraday shield got too hot with the current heating. The current heating efficiency was only 15%. If the energy could enter the concrete more efficiently, the setup would likely stay cooler.

7.2.2 New experiments

If all improvements discussed above are implemented, there are still many interesting degrees of freedom for future experiments:

- In practice high-strength concrete seems to be much more prone to spalling than normal strength concrete, due to its lower permeability. This lower permeability will lead to higher pressures.

- Different geometries can be tried. In a tunnel fire, the concrete will generally have a layer of rock at the back of the concrete. In a building fire, the concrete walls will have air at
the back face. This difference will affect the vapor and moisture flux to the back of the sample. Therefore different behavior is expected in these two cases.

- Different initial moisture saturation levels can be used to model concrete in wet or dry environments.

In all of these experiments it can be checked whether the maximum pressure can still be linked to the passing by of the drying front and whether the pressure follows the saturated vapor pressure.

### 7.2.3 Verifying simulations

Finally, the data obtained in the experiments can be used to verify numerical simulations. The simulations in, for example, reference [63] also show that the maximum pressure is to be found when the drying front passes. However, the simulations in reference [28] show that the maximum pressure is to be expected when the sample is almost completely dry. In order to make a fair comparison with these numerical simulations, the parameters (e.g. permeability, heating rate and porosity) of the simulations should be chosen to match the concrete used for the experiments.
References


J. Blumm and A. Lindemann. Thermophysical properties characterization of molten polymers and liquids using the flash technique. 2005.


Appendix A

Implementation of multi slice sequence

The multi slice sequence that is described in section 3.7, had to be implemented in the already existing “Digital NMR” software. A general introduction to this software is given in section A.1. The multi slice script is explained in section A.2.

*All files described in this Appendix are altered for readability and differ from real filenames and real file structure.*

A.1 Digital NMR software

The Digital NMR software is based on a combination of MATLAB and the SpinCore API which is necessary to communicate with the RadioProcessor that is introduced in section 4.4. The block diagram drawn in Figure A.1 shows the basic working of the Digital NMR software. In Figure A.1 blue blocks represent MATLAB scripts, while orange blocks represent compiled C-files which call the SpinCore API functions.

In *Start.m* all NMR parameters (e.g. scan frequency or number of averages) are defined and parsed to the compiled file *PulseProgram.mex32*. The latter file initializes the communication with the Digital NMR apparatus. The board gets reset and the pulse program is programmed and started, after which the communication is closed and MATLAB takes over again.

MATLAB now enters a loop (referred to as *Wait.m*) in which the compiled file *CheckStatus.mex32* is called to check the status of the measurements. This is repeated until all measurements are finished and averaged. Before and after each status check the communication with the board has to be opened and closed, respectively.

In the next step MATLAB calls *GetData.mex32* to retrieve the data from the board. Again communication has to be initialized and closed. MATLAB processes the data (i.e. applies Fourier transform etc.) and saves the data. If another frequency needs to be scanned, the whole process starts again in *Start.m*. This process repeats until all frequencies are measured and a complete (1D) image is obtained.
Figure A.1: Schematic drawing of the software controlling the NMR scanner. Blue blocks represent MATLAB code, while orange blocks indicate compiled C-files calling the SpinCore API.

A.2 Multi slice software

As described in section 3.7 a multi slice sequence requires multiple slices to be measured in one repetition time. The sequence described in section A.1 needs to be adapted for this purpose. The adapted sequence is shown in the block diagram in Figure A.2.

In order to be able to do more averages in the same amount of time, some improvements have to be made. The first improvement seen in Figure A.2 is the separate InitCom.mex32 and CloseCom.mex32. These files initialize and close the communication line between MATLAB and the RadioProcessor. In the multi slice sequence this communication line is kept open during the whole experiment, while in all earlier developed pulse sequences the communication line was opened and closed for each mex32 function call. The first column of Table A.1 shows the time $t_{\text{Closed}}$ required by Checkstatus.mex32 and Overflow.mex32 when the communication line needs to be opened by the functions themselves. The second column shows the time $t_{\text{Open}}$ required when the communication line is already opened. These numbers show for example that by leaving the communication open throughout the whole pulse sequence, the time Wait.m has

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1 Overflow.mex32 has been omitted from the schematic drawings in Figures A.1-A.2 for clarity. However, it is used in every pulse sequence to check for memory overflow errors of the RadioProcessor.
Figure A.2: Schematic drawing of the working of the multi slice software. Blue blocks represent MATLAB code, while orange blocks indicate compiled C-files calling the SpinCore API.

to wait for the status of the board is reduced from 1.44 to 0.019 s. This reduction is significant when comparing it to a typical repetition time ($t_R$, see section 3.4) in the order of 1 s.

The second big time reduction can be found in `GetData.mex32`. In earlier pulse sequences it was only possible to let the `RadioProcessor` return either 1000 or 16000 or 256000 data points. This means that when for example only 32000 points are required, 256000 points need to be fetched. For the multi slice sequence a function was developed that allows a variable amount of data...
Table A.1: Time $t_{\text{Closed}}$ and $t_{\text{Open}}$ required to run mex32-functions when the communication line still needs to be opened (as in older sequences) or is already opened (as in the new multi slice sequence), respectively. All timing values in this section are averaged over 32 function calls. Timing is performed on a laptop running Windows 7, MATLAB 2009bSP1, SpinAPI library version 20100714 and board firmware version 12-15.

<table>
<thead>
<tr>
<th>Function</th>
<th>$t_{\text{Closed}}(s)$</th>
<th>$t_{\text{Open}}(s)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>InitCom.mex32</td>
<td>1.42</td>
<td>-</td>
</tr>
<tr>
<td>CloseCom.mex32</td>
<td>-</td>
<td>$8.7 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>Checkstatus.mex32</td>
<td>1.44</td>
<td>0.019</td>
</tr>
<tr>
<td>Overflow.mex32</td>
<td>1.48</td>
<td>0.023</td>
</tr>
</tbody>
</table>

points. Limitations of the RadioProcessor however always require a multiple of 8192 points to be fetched [56].

Figure A.3: Comparison between the time $t$ needed with the old and new data fetching function GetData.mex32. Thirty-two averages are performed for $2^i$ data points, with $i = 7..17$. It must be noted that the new function does not have to initialize and close the communication line, which already reduces the time required by 1.4 s.

The third and final significant time reduction is achieved by removing the starting of the pulse sequence from the PulseProgram.mex32 to a separate function. This way the scanning frequency can be updated without having to reprogram the complete pulse program. Figure A.4 shows the time required to program the pulse program of the multi slice sequence as a function of the number of frequencies to be programmed.

Figure A.4: Time $t$ required to program the pulse program as a function of the number of frequencies to be programmed. The apparent decrease in time after 8 frequencies is caused by the division of frequencies into batches. This requires updating of the frequencies during the pulse sequence itself.
Figure A.4 shows that the time required to program the multi slice pulse program for only 1 frequency takes ~3.5 s and increases linearly to ~14 s for 8 frequencies. The RadioProcessor allows only 8 frequencies to be programmed at once. Therefore, for a higher number of frequencies the frequencies need to be divided into batches of equal length. For 9 frequencies this would result in 3 batches of 3 frequencies, for 10 frequencies in 2 batches of 5 frequencies and for 11 frequencies in 11 batches of 1 frequency. Although on first inspection Figure A.4 shows that the time $t$ required to program the pulse program decreases when going from 8 to 9 frequencies, it must be noted that the 9 frequencies require the frequencies to be updated during the pulse sequence itself. This updating requires interaction between MATLAB and the RadioProcessor and, depending on the desired long delay, might take too long.

Finally, as can be seen in the block diagram of Figure A.2 it must be noted that after each sweep (see section 3.7) the data is fetched by MATLAB and saved, instead of waiting for all sweeps of one 1D-image to finish. This is the result of limitations of the RadioProcessor in combination with the choice to first perform all averages of one sweep, before continuing to the next sweep.
Appendix B

Pressure measurements

The results of the pressure measurements of samples CSTB 20B, CSTB 30, CSTB 40A and CSTB 40B are presented in Figures B.1-B.4 below.

**Figure B.1:** Pressure gauge measurements for sample CSTB 20B. **Top left:** Temperatures at the position of the pressure gauge (20 mm) as measured by the thermocouple in the pressure gauge (blue) and linearly interpolated for the thermocouples at the side of the sample (green). **Right:** Pressure as measured with the gauge (magenta). Saturated vapor pressures calculated from the temperatures shown in the top left figure (blue and green). **Bottom left:** NMR signal intensity decay at the position of the pressure gauge, found by linear interpolation of the two nearest points. Vertical dashed line corresponds to time of maximum measured pressure.
Figure B.2: Pressure gauge measurements for sample CSTB 30. **Top left:** Temperatures at the position of the pressure gauge (30 mm) linearly interpolated for the thermocouples at the side of the sample (green). **Right:** Pressure as measured with the gauge (magenta). Saturated vapor pressures calculated from the temperatures shown in the top left figure (blue and green). **Bottom left:** NMR signal intensity decay at the position of the pressure gauge, found by linear interpolation of the two nearest points. Vertical dashed line corresponds to time of maximum measured pressure.

Figure B.3: Pressure gauge measurements for sample CSTB 40A. **Top left:** Temperatures at the position of the pressure gauge (40 mm) as measured by the thermocouple in the pressure gauge (blue) and linearly interpolated for the thermocouples at the side of the sample (green). **Right:** Pressure as measured with the gauge (magenta). Saturated vapor pressures calculated from the temperatures shown in the top left figure (blue and green). **Bottom left:** NMR signal intensity decay at the position of the pressure gauge, found by linear interpolation of the two nearest points. Vertical dashed line corresponds to time of maximum measured pressure.
Figure B.4: Pressure gauge measurements for sample CSTB 40B. **Top left:** Temperatures at the position of the pressure gauge (40 mm) as measured by the thermocouple in the pressure gauge (blue) and linearly interpolated for the thermocouples at the side of the sample (green). **Right:** Pressure as measured with the gauge (magenta). Saturated vapor pressures calculated from the temperatures shown in the top left figure (blue and green). **Bottom left:** NMR signal intensity decay at the position of the pressure gauge, found by linear interpolation of the two nearest points. Vertical dashed line corresponds to time of maximum measured pressure.