MASTER

Solute transport in porous building materials
an NMR study

Borgharts, J.J.A.M.

Award date:
2014

Link to publication
Solute transport in porous building materials, an NMR study

J.J.A.M. Borgharts

August 2012

Eindhoven University of Technology
Department of Applied Physics
Transport in Permeable Media

Professor:
Prof. dr. ir. K. Kopinga

Supervisor:
Dr. ir. L. Pel
Abstract

The major degradation mechanism in concrete structures is corrosion of steel reinforcement bars. Active corrosion is initiated when the chloride content in the pore solution has reached a critical threshold value. Recently, transport of chloride in cracked concrete has gained much attention as cracks form fast transport routes.

Various models are available to describe chloride transport in (un)cracked concrete, but there is lack of reliable experimental data to verify them. To our knowledge, no reports have been made of employing a non-destructive technique to quantitatively investigate basic chloride transport phenomena in porous building materials in a spatially and temporally resolved way.

Nuclear Magnetic Resonance (NMR) is a technique that allows such measurements and is unique as it provides the ability to measure moisture and ion transport simultaneously. In this study diffusion-based transport problems concerning porous building materials are investigated by means of $^1$H, $^7$Li, $^{23}$Na and $^{35}$Cl NMR, using two home-built NMR setups.

Diffusion of Na$^+$ and Cl$^-$ ions from 4.6 M NaCl solution into two types of water-saturated bricks (i.e. fired-clay brick and calcium-silicate brick) is studied. The salt diffusion coefficient of NaCl is equal to $1.611 \cdot 10^{-9}$ m$^2$s$^{-1}$.

For fired-clay brick diffusion coefficients of $(0.68 \pm 0.04) \cdot 10^{-9}$ m$^2$s$^{-1}$ and $(0.66 \pm 0.04) \cdot 10^{-9}$ m$^2$s$^{-1}$ are obtained from the sodium and chloride diffusion profiles, respectively. The agreement of these values shows that diffusion is coupled. The reduction in the diffusion coefficient is caused by the porosity of fired-clay brick, which restricts the cross-sectional area available for transport.

For calcium-silicate brick salt diffusion coefficients of $(0.24 \pm 0.04) \cdot 10^{-9}$ m$^2$s$^{-1}$ (sodium) and $(0.27 \pm 0.06) \cdot 10^{-9}$ m$^2$s$^{-1}$ (chloride) are found. Again diffusion is coupled. The decrease in the diffusion coefficient is attributed to the porosity of calcium-silicate brick as well as tortuous effects, as ion binding to the solid matrix is of negligible extent. A tortuosity of $\sim 1.9$ is found.

A second study is performed to gain knowledge about the pore size dependency of the self-diffusion coefficients of hydrogen and lithium in 5M LiCl solution. The self-diffusion coefficients of both species are determined for three saturated aluminum oxide samples with distinct pore sizes in the 170-250 nm range. Due to limited experimental accuracy no clear pore size dependency is found. However, the obtained self-diffusion coefficients are significantly reduced compared to the bulk self-diffusion coefficients: a factor $\sim 4.5$ for hydrogen and $\sim 3.5$ for lithium. This reduction is attributed to the restricted geometry introduced by the pore space of aluminum oxide.
B  Differential weighing porosimetry  60

C  Monolayer adsorption  61
Chapter 1

Introduction

Steel bars are used as reinforcements in concrete. They are exposed to a highly alkaline pore solution during hydration of cement (i.e. pH $\gtrsim 13$). In this environment the thermodynamically stable compounds of iron are iron oxides and oxyhydroxides. Therefore the steel, embedded in the structure, develops a thin protective oxide film. This passive film is only a few nanometers thick and is composed of hydrated iron oxides with a varying degree of $Fe^{2+}$ and $Fe^{3+}$ [1]. The stability of this layer is jeopardized when it is exposed to solutions with too low alkalinity or too high chloride ion content [2]. If the passive film is broken down, active corrosion is initiated and consequently the strength, utility and esthetic quality of the concrete structure is reduced. Typical forms of damage associated are spalling, chipping and cracking, as shown in Figure 1.1.

Figure 1.1: Typical forms of corrosion-induced damage regarding concrete structures: spalling (A), chipping (B) and cracking (C).

It is widely acknowledged that chloride-induced corrosion is one of the main degradation mechanisms in civil structures based on reinforced concrete. As seawater contains predominantly sodium (Na$^+$) and chloride (Cl$^-$) as dissolved ions [3], concrete structures in maritime zones suffer from chloride-enhanced corrosion. Typical situations are, amongst others, bridge decks that are supported by concrete pillars that are partly submerged in seawater. An example of such a structure is shown in Figure 1.2A, depicting the Øresund bridge that connects Copenhagen (Denmark) to Malmö (Sweden). As these columns are partly under sea level, breaking of the waves and periodic tides can give rise to cyclic wetting and drying. In the latter case, chloride concentration levels are expected to rise well above seawater concentration and even the solubility limit may be reached. This leads to salt crystallization and associated damage mechanisms [4, 5].

Another typical situation where concrete is exposed to an aggressive environment (i.e. a chloride-laden environment) is in regions where chloride-bearing deicing salts are used for road safety. Deicing of concrete roads is traditionally done by dump trucks spreading deicing salt (mainly NaCl) over slabs designated for treatment. Immediately after deicing, the melted water and deicing salt form a chloride-based solution that can penetrate the concrete. An example of this type of chloride exposure is shown in Figure 1.2B, depicting a typical deicing scenario in the Alps (Switzerland).
Figure 1.2: Examples of concrete structures in aggressive environments commonly encountered in practice. A. Numerous concrete pillars support the deck of the Øresund bridge between Copenhagen (Denmark) and Malmö (Sweden). These columns are partly submerged in seawater, which contains significant amounts of chloride ions. B. Chloride-bearing deicing salts are often used to remove ice formations on roads to ensure safe transport in the Alps, Switzerland.

The aforementioned cases are common examples of external sources of chloride that can penetrate into concrete. A less common case is the internal presence of chloride in concrete. This occurs when chloride-containing mixtures are added to concrete from the moment of mixing (e.g. CaCl$_2$ may be added to accelerate the setting and hardening process) or if beach aggregates are used.

The situations outlined above illustrate the importance of chloride transport in concrete. The presence of chlorides in the pore solution of concrete structures forms a real threat in civil structures. Gaining insight in these transport phenomena can not only improve the assessment of durability aspects of existing structures, but might lead to improved design for new reinforced concrete structures that are to be used in aggressive environments.

Furthermore, there is lack of experimental data on this topic that can be used to validate or discredit the wide range of models available in literature. While such models might be correct, erroneous input is bound to lead to false predictions (i.e. the garbage in, garbage out principle). Modeling with faulty input parameters might have catastrophic consequences. This is witnessed by the 1985 Val di Stava Dam collapse for instance [6], where the actual margin of safe operation was much smaller than predicted.

Recently transport of chloride in cracked concrete has gained much attention in the scientific community, as cracks form fast transport routes for chlorides [7, 8, 9, 10]. Measures taken to suppress chloride transport in cracked concrete are crack blocking and self-healing. Crack blocking refers to filling the cracks of the concrete structure with a fill material like mortar. Self-healing is less unambiguous as this term refers to all kinds of cement-based materials that repair themselves after the material or structure gets damaged due to some sort of deterioration mechanism. Various approaches are taken in this perspective, e.g. the application of bacteria as self-healing agent for concrete [11]. Nevertheless, there is lack of fundamental experimental knowledge about the effect of these measures on the chloride transport. The physics underlying these poorly understood prevention measures can be obtained with the right experimental data. Eventually, this can be used to optimize these mechanisms or even explore novel techniques aimed to prevent chloride ingress in concrete.
1.1 Monitoring chloride transport in porous materials

Since our focus is on chloride transport in concrete, it is important to determine its principle transport mechanisms. Transport of fluids in concrete happens predominantly via diffusion, capillary suction and permeation [1, 12, 13]. Diffusion is driven by concentration gradients, capillary suction by capillary action in the concrete pores and permeation is induced by pressure gradients. In absence of electric fields, the ions are transported along with the pore fluid via advection or due to concentration differences by diffusion. The kinetics that describe the transport depend upon the transport mechanism, concrete material properties, binding processes and environmental conditions existing at the concrete surface.

Since concentrations in these transport processes are a function of position and time, a detection method is necessary that can both spatially and temporally resolve species contents. For chloride transport, one wants to measure chloride concentrations in the porous material as function of position and see how these levels evolve over time.

There are various methods available to measure ionic chloride content in porous building materials. The most common method is to drill a specimen out of a concrete structure and analyze it chemically in the laboratory (see e.g. [14]). Traditionally this is done by pulverizing the sample and extracting the soluble chloride content using nitric acid solution. The solution is then analyzed for chloride ion concentration using wet chemistry. The most obvious drawback of this method is its destructiveness, but there are more shortcomings such as its poor resolution and irreproducibility.

The aforementioned example nicely illustrates the demand for non-destructive techniques to determine chloride concentrations in porous materials. Various non-destructive methods based on electrochemical, optical or radiographic principles have been proposed in literature.

Figure 1.3: Schematic overview of the Prompt Gamma Neutron Activation (PGNA) spectroscopy system, designed and evaluated by Saleh and Livingston. This image is adapted from [15].
Most common non-destructive methods are of electrochemical nature: electrokinetic-based techniques and Electrical Impedance Spectroscopy (EIS). For instance, Polder and Peelen [16] studied chloride penetration in concrete by measuring electrical resistivity of concrete, the potential of the steel reinforcing bars and corrosion rates. Similar approaches using electrokinetic methods can be found in e.g. [12] and [17]. Electrical Impedance Spectroscopy can be used to measure dielectric properties of the porous medium as function of the frequency. This can in turn be related to transport quantities, see e.g. [18, 19, 20, 21]. Despite these efforts, there are important hindrances associated with these techniques as electrochemical methods suffer from drawbacks related to interpretation of results and electromagnetic interferences. Moreover, these methods generally produce information related to corrosion rates without quantifying chloride concentrations. Hence, no quantitative chloride concentration profiles are measured.

A somewhat unconventional approach is taken by Laferrière et. al. [22] by studying the feasibility of an optical fiber system to detect chloride in concrete. The system is based on fluorescence of an indicator dye that is sensitive to chloride. Through spectroscopy, fluorescence intensity fluctuations are related to variations in the free chloride concentration. Despite its good stability and reproducibility, the system is found to be operable in a limited range only (i.e. 30-350 mM). Also, the measurements show poor signal-to-noise ratio (SNR).

A twofold of radiographic methods are suggested regarding chloride detection in concrete: neutron radiography and autoradiography. Saleh and Livingston [15] experimentally evaluated a Prompt Gamma Neutron Activation (PGNA) spectroscopy system for detecting chloride in reinforced concrete. This system is schematically depicted in Figure 1.3. The system utilizes a $^{252}$Cf neutron source to irradiate saturated mortar slabs in which the neutrons are absorbed by the chlorides: $^{35}Cl + n \rightarrow ^{36}Cl + \gamma$ [23]. The emitted gamma rays are detected by a High Purity Germanium (HPGe) detector. The system is able to determine chloride concentrations in the mortar slabs within 10% accuracy in approximately 6 minutes, but there are a few drawbacks. Spectroscopic analysis is hampered by interfering peaks that are likely to appear in spectra obtained in contaminated systems due to the presence of additional elements [15]. Also, these systems increase the Compton scattering background observed in the spectra. Manera et. al. studied diffusion of NaCl in Portland cement samples via autoradiography [24]. Hereto a negligible quantity of $^{36}Cl$ was added to the solution as a radioactive tracer. $^{36}Cl$ is a long-lived radioisotope (half-life $\approx 3 \cdot 10^5$ year), decaying by emitting $\beta^-$ radiation with a maximal energy of 0.7 MeV. The nuclear radiation is detected by a photographic film, and the grayscale intensities are related to actual dose via external calibration. Although this technique provides high spatial resolution (<1 mm), there is difficulty in interpreting the qualitative results. In general, the use of a radiographic method is not very convenient due to the hazards associated with the radiation. Moreover, the systems discussed here are relatively expensive.

While the methods described above are able to detect chloride content non-destructively, none of them is able to measure moisture and ion transport simultaneously. Furthermore, a method that can measure such profiles with high accuracy and high temporal and spatial resolution is desired. A technique that might offer these requirements, but is not discussed yet, is Nuclear Magnetic Resonance (NMR). This method relies on absorption and emission of electromagnetic radiation and can be made sensitive to various nuclei. Therefore, NMR allows to measure different nuclei simultaneously. NMR has proven to be a versatile technique and is used in various fields (e.g. medicine and chemistry). However, standard NMR scanners are not suitable for the kind of research in mind since quantitative information is desired. This requires the development of a Faraday shield. Furthermore, building materials contain magnetic impurities that reduce relaxation times significantly and therefore the magnetic gradient fields are required to switch fast (<200 $\mu$s). Attempts to realize these conditions with home-built setups are reported, but $^{35}$Cl NMR studies are rather limited since $^{35}$Cl has a low sensitivity. However, NMR is able to provide superior resolution compared to other discussed techniques and the desired accuracy can be obtained (to a certain extent) by signal averaging. Therefore, NMR is a suitable candidate to monitor chloride transport mechanisms in porous media. Moreover, NMR can potentially be used in situ as single sided NMR is possible [25], but a parametric study is required to study the feasibility of this concept (see e.g. [26]).
1.2 NMR imaging of chloride transport in porous media

Various $^{23}\text{Na}$ and $^{35}\text{Cl}$ NMR studies have been undertaken regarding solute transport in porous media. For traditional echo-imaging purposes, the most relevant quantities are the relaxation times (i.e. $T_1$, $T_2$ and $T_2^*$) of the nuclei under investigation. Observations of these characteristic times are summarized in Table 1.1.

Table 1.1: Relaxation time observations regarding $^{23}\text{Na}$ and $^{35}\text{Cl}$ NMR imaging in porous media. References are put in chronological order.

<table>
<thead>
<tr>
<th>Author</th>
<th>Material</th>
<th>Element</th>
<th>$T_1$ (ms)</th>
<th>$T_2$ (ms)</th>
<th>$T_2^*$ ($\mu$s)</th>
<th>Main field (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pel [27]</td>
<td>calcium-silicate brick</td>
<td>$^{23}\text{Na}$</td>
<td>20</td>
<td>6</td>
<td>-</td>
<td>0.78</td>
</tr>
<tr>
<td>Porion [28]</td>
<td>Laponite clay</td>
<td>$^{23}\text{Na}$</td>
<td>5-50</td>
<td>-</td>
<td>-</td>
<td>2.4-8.5</td>
</tr>
<tr>
<td>Cano [29]</td>
<td>Mortar</td>
<td>$^{23}\text{Na}$</td>
<td>1.7 and 3.5</td>
<td>147, 291 and 755</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>Yu [31]</td>
<td>Cement hydrate suspensions</td>
<td>$^{35}\text{Cl}$</td>
<td>10-45</td>
<td>-</td>
<td>-</td>
<td>11.7</td>
</tr>
<tr>
<td>Cano [29]</td>
<td>Mortar</td>
<td>$^{35}\text{Cl}$</td>
<td>1.5 and 2.2</td>
<td>184, 390 and 917</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>Yun [26]</td>
<td>Portland cement</td>
<td>$^{35}\text{Cl}$</td>
<td>&lt;20</td>
<td>-</td>
<td>$\leq$55</td>
<td>2.35</td>
</tr>
</tbody>
</table>

Pel et. al. [27] investigated absorption of 4M (i.e. mol/L) NaCl solution in calcium-silicate brick using conventional spin-echo techniques [32]. Hardly any sodium ions were present near the wetting front due to binding of the ions to the pore surface. Porion and coworkers [28] studied relaxation phenomena of sodium in Laponite clay solutions using the same spin-echo techniques. They found that the counter ions of the negatively charged clay are in the solution between the clay plates. Therefore, the system is in the so-called slow modulation regime and bi-exponential relaxation of $^{23}\text{Na}$ is observed. Both $^{23}\text{Na}$ and $^{35}\text{Cl}$ NMR are used by Cano et. al. [29] to study absorption of 3.4 M NaCl in concrete using the so-called SPRITE technique [33]. Although it is a successful demonstration of monitoring free chloride in concrete, the analysis of the observed profiles remained rather limited (e.g. the relation between the ion profiles was not addressed). Barberon and colleagues [30] directly mixed NaCl solution in their cement paste samples. They used NMR relaxometry to investigate the effect of NaCl on the structural chemistry of the cement pastes. Yu and Kirkpatrick [31] investigated chloride sorption mechanisms in Portland cement systems using conventional spin-echo techniques. They found that chloride is in rapid exchange (i.e. exchange frequency $> 1.6$ kHz) between surface and bulk solution sites for all phases under investigation and is predominantly in a hydrated, solution-like chemical environment. Yun et. al. [26] used solely the Free Induction Decay (FID) sequence to investigate the feasibility of NMR to be used in practice as detection method for chloride in both white and gray Portland cement. The experiments demonstrated that the signal-to-noise ratio (SNR) for a centimeter-scale cement sample volume is so small, even after averaging, that sample volumes much lower than that are unlikely to produce measurable signals at magnetic fields of 1T or below.

These studies show that it is possible to quantitatively study chloride transport in porous materials using NMR imaging techniques. However, studies investigating even basic transport mechanisms by measuring chloride concentration profiles in porous media and their evolution over time are not found in literature, to our knowledge.
1.3 Outline of this thesis

In this thesis an NMR approach is taken to investigate its feasibility regarding quantitative chloride content measurements in porous media with high spatial and temporal resolution. An overview of the basic principles underlying NMR is given in Chapter 2 including the relevant properties of the spin echo technique used in the experiments. Next, theoretical treatment of solute diffusion in porous media is given in Chapter 3. Hereafter two home-built setups dedicated to study solute transport in porous media are presented and characterized in Chapter 4. Before any experiments concerning NaCl solution in porous media are performed, a pilot study on bulk solution is undertaken of which details are given in Chapter 5. Calibration and relaxation measurements on NaCl and LiCl in porous media are described in Chapter 6. Three types of porous media are used: fired-clay brick, calcium-silicate brick and aluminum oxide. These materials are chosen due to their structural and chemical properties. Thereafter, one-dimensional diffusion of sodium chloride solution in the two types of bricks (i.e. fired-clay brick and calcium-silicate brick) is studied in Chapter 7. In order to gain more information about NMR of quadrupolar nuclei, experiments on $^7\text{Li}$ are performed and described in Chapter 8. Here the pore size dependency of the self-diffusion coefficients of hydrogen and lithium is studied. The main conclusions that can be drawn from these experiments are given in Chapter 9 which concludes with recommendations for further research.
Chapter 2

Nuclear Magnetic Resonance (NMR)

This chapter describes the fundamentals Nuclear Magnetic Resonance (NMR) is based on. First, the general principles are discussed in Section 2.1. Here Larmor precession, the Zeeman effect, equilibrium magnetization and manipulation thereof are discussed. Next, NMR of nuclei with non-zero quadrupole moment is discussed in Section 2.2. The quadrupole interaction is discussed here as this is required for adequate description of NMR of such nuclei. The Hahn spin echo technique, often used as NMR imaging method, is discussed in Section 2.3. The use of a magnetic field gradient to obtain spatial resolution using this technique is also addressed. The decay of the echo signal in the Hahn spin echo sequence is discussed in Section 2.4 including three mechanisms that govern its behavior: free diffusion, local magnetic field averaging and dephasing due to a uniform magnetic field gradient.

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Nuclear spin</th>
<th>Natural abundance (%)</th>
<th>$\gamma/2\pi$ (MHz/T)</th>
<th>Relative sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>1/2</td>
<td>99.9850</td>
<td>42.5775</td>
<td>1.00000</td>
</tr>
<tr>
<td>$^7$Li</td>
<td>3/2</td>
<td>92.41</td>
<td>16.5483</td>
<td>0.29356</td>
</tr>
<tr>
<td>$^{23}$Na</td>
<td>3/2</td>
<td>100</td>
<td>11.2688</td>
<td>0.09270</td>
</tr>
<tr>
<td>$^{35}$Cl</td>
<td>3/2</td>
<td>75.78</td>
<td>4.1765</td>
<td>0.00472</td>
</tr>
</tbody>
</table>

2.1 Basic principles

Almost all nuclei possess a magnetic moment $\vec{\mu}$, resulting from their spin-angular momentum. This magnetic moment is called spin and will experience a torque if placed in a static magnetic field $\vec{B}_0$. Consequently, the magnetic moment will precess along the direction of $\vec{B}_0$ with the so-called Larmor frequency $f_0$:

$$f_0 = \frac{\gamma}{2\pi} |\vec{B}_0|,$$

(2.1)

where $\gamma$ is the gyromagnetic ratio. This is the ratio of the magnetic moment of the nucleus and its angular momentum. The gyromagnetic ratios of nuclei relevant to this study are given in Table 2.1. The precession principle is illustrated in Figure 2.1A. In order to find the macroscopic equilibrium magnetization, an ensemble of spins is considered as typically a large number of nuclei are probed simultaneously in NMR experiments. For instance, a typical volume of 1 mm$^3$ pure water contains approximately $3 \cdot 10^{19}$ H$_2$O molecules. The magnetization $\vec{M}$ is given by the individual magnetic moments in the volume $V$:

$$\vec{M} = \frac{1}{V} \sum \vec{\mu}_i.$$

(2.2)
Figure 2.1: A. Larmor precession of a single spin in a stationary frame of reference. B. Flipping the magnetization vector $90^0$ in a rotating frame of reference, which rotates about the z-axis at the Larmor frequency.

The individual spins gyrate at the same frequency but with different phases. Therefore the net magnetization is directed parallel to $B_0$, as the perpendicular component cancels out. From quantum mechanics it is known that the spins can align either along with or opposite to the magnetic field (i.e. spin-up and spin-down) for a spin-1/2 system. The energy levels associated with these states are different due to the presence of the magnetic field. This is known as the Zeeman effect and the difference between these energy levels is given by \[ (2.3) \]:

$$
\Delta E = hf = \frac{\gamma h |\vec{B}_0|}{2\pi}.
$$

Using statistical mechanics it can be shown that the population of these states ($N_\uparrow$ for spin-up, $N_\downarrow$ for spin-down) is Boltzmann distributed \[ (2.4) \]:

$$
\frac{N_\downarrow}{N_\uparrow} = \exp \left( \frac{-\gamma h |\vec{B}_0|}{2\pi k_b T} \right),
$$

where $k_b$ is the Boltzmann constant and $T$ is the temperature. Filling out these numbers for $^1\text{H}$ at $B_0=1.5$ T and room temperature (reflecting the experiments in this thesis), yields $N_\downarrow/N_\uparrow \approx 0.9999896$. This shows the small polarizing effect of the magnetic field opposed to the random distribution favored by temperature: only a fraction of $1 \cdot 10^{-5}$ of the saturation magnetization is reached.

The equilibrium magnetization can be manipulated by suitably chosen radio frequent (RF) fields. The appropriate frequency follows from the resonance condition given by Equation \[ (2.1) \]. Typically a RF magnetic field $B_1$ is applied perpendicular to the main magnetic field to reorient the spins. The net effect is a spiralling movement of the magnetization along a spherical surface. This can be imagined by considering a co-rotating frame where the x’y’-plane rotates about the z-axis at the Larmor frequency. This is illustrated in Figure \[ 2.1B \] for a so-called $90^0$ pulse. The net effect in this frame of reference is thus a rotation of the magnetization vector. The so-called flip angle $\alpha$ denotes the angle of rotation and depends on the pulse time, which represents the duration of the pulse in which the $B_1$ field is applied \[ (2.5) \]:

$$
\alpha = 2\pi f_0 t_{\text{pulse}}.
$$

\[ 11 \]
After bringing the magnetization into an excited state via the RF field, it will relax back to equilibrium. There are two relaxation phenomena involved in this process: longitudinal and transversal relaxation. The first refers to relaxation of the magnetization vector in longitudinal direction and is due to interactions of the magnetic moments with their environment (i.e. the so-called lattice). This relaxation mechanism is governed by the spin-lattice relaxation time $T_1$. Transversal relaxation refers to relaxation of the magnetization in the transversal plane to its zero equilibrium value due to mutual interactions of the different spins (i.e. loss of phase coherence between the individual spins). This relaxation mechanism is governed by the spin-spin relaxation time $T_2$. The equations of motion for these relaxation processes, after a $90^\circ$ pulse, are given by (see e.g. \[34\]):

\[
M_x = M_0 \exp\left(-\frac{t}{T_2}\right) \cos(2\pi f_0 t) \tag{2.6}
\]

\[
M_y = M_0 \exp\left(-\frac{t}{T_2}\right) \sin(2\pi f_0 t) \tag{2.7}
\]

\[
M_z = M_0 \left[1 - \exp\left(-\frac{t}{T_1}\right)\right], \tag{2.8}
\]

where a stationary frame of reference is considered using x, y and z-components for decomposition of the magnetization. These are the well-known Bloch equations and show the time evolution of the magnetization due to precession, spin-lattice and spin-spin relaxation.

### 2.2 NMR of quadrupolar nuclei

The model considered so far suffices for spin-1/2 systems. However, the non-hydrogen nuclei studied in this thesis are spin-3/2 systems (see Table 2.1). The energy level degeneration due to the Zeeman effect is now fourfold and schematically depicted in Figure 2.2. These different energy levels are characterized by the magnetic quantum number $m$, which can take values $\{-I, I+1, \ldots, I-1, I\}$, with $I$ the spin of the nucleus. The transition frequencies, obeying $\Delta m = \pm 1$ as follows from quantum mechanical selection rules, are then given by the expression in Equation 2.1 \[34\].

Since spin-3/2 nuclei have a non-zero quadrupole moment, an additional interaction must be considered to adequately describe these systems: the quadrupole interaction. This refers to the interaction between the electric quadrupole moment of the nucleus and the electric field gradient (i.e. $\nabla \cdot \vec{E}$), originating in the non-spherical charge distribution in the nucleus. An extensive quantum mechanical description of this interaction is beyond the scope of this thesis, but can be found elsewhere \[34\].

The net effect is splitting of the energy levels, which increase with an equal amount for the $m = \pm 3/2$ states and decrease with an equal amount for the $m = \pm 1/2$ states. For the experiments described in this report, the quadrupole interaction can be considered as a small perturbation to the Zeeman interaction \[5, 34\]. A graphical depiction of this situation is shown in Figure 2.2. Since the energy level shifts induced by the quadrupole interaction depend upon the local electric field, the corresponding energy levels may be different for the various nuclei.

So far the spins are considered to be static, but relaxation might be influenced by movement of the ions in solution. This movement is due to Brownian motion and in general there are two regimes that can be distinguished for quadrupolar nuclei: the slow and fast modulation regime \[28\]. In the slow modulation regime ions experience a net electric field gradient and consequently the energy levels shift as described before (see Figure 2.2). In this case 40% of the magnetization decays with a time constant $T_{\text{central}}$ which corresponds to the central transition (i.e. $m = -1/2 \leftrightarrow m = +1/2$), and 60% decays with a time constant $T_{\text{satellite}} > T_{\text{central}}$ which corresponds to the satellite transitions (i.e. $m = -3/2 \leftrightarrow m = -1/2$ and $m = 1/2 \leftrightarrow m = 3/2$) \[5, 39\].

This bi-exponential decay applies to transversal as well as longitudinal relaxation. In the fast modulation regime the movement and tumbling of ions is fast compared to the timescale of the NMR experiment and therefore no net electric field gradient is experienced by the ions. In this case the magnetization decays mono-exponentially.
2.3 Spin echo technique

The ability to manipulate the magnetization through pulsed RF fields has led to a wide range of pulse sequence designs. Here only the Free Induction Decay (FID), Hahn spin echo [32] and Carr-Purcell-Meiboom-Gill (CPMG) [37, 38] sequences are discussed. The timing diagram and spin echo intensities of these sequences are schematically shown in Figure 2.3.

Free Induction Decay consists of a single 90° pulse, and the time evolution of the signal $S$ induced in the pick-up coil is given by:

$$S(t) \propto \rho \exp(-\frac{t}{T_2^*}), \quad (2.9)$$

where $\rho$ is the number density of the nucleus of interest. The enhanced transversal relaxation time $T_2^*$ is related to the spin-spin relaxation time $T_2$:

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{\gamma}{2\pi} \Delta B, \quad (2.10)$$

where $\Delta B$ represents macroscopic magnetic field inhomogeneities that cause additional dephasing. The Hahn spin echo technique consists of a 90° and subsequent 180° pulse (see Figure 2.3). The 180° pulse effectively flips the phase of the spins. If translational motion of the excited nuclei can be neglected, the intensity of the spin echo is only influenced by the transverse relaxation mechanism and is not affected by magnetic field inhomogeneities. The spin echo intensity (SEI) at echo time $t_e$ is given by [33]:

$$SEI(t_e) \propto k\rho \left[ 1 - \exp\left( -\frac{t_e}{T_1} \right) \right] \exp\left( -\frac{t_e}{T_2} \right). \quad (2.11)$$

Here $k$ is the sensitivity of the nucleus of interest and $t_r$ is the repetition time of the spin-echo experiments. It is assumed that both the transversal and longitudinal decays are mono-exponential. Signal loss due to $T_1$ effects can be minimized by choosing a suitable repetition time. A commonly used rule of thumb is that it should be chosen at least $4T_1$. The second exponent shows that the echo time should be chosen much smaller than $T_2$ in order to prevent signal loss due to transversal relaxation.
An extension of the Hahn spin echo sequence is the Carr-Purcell-Meiboom-Gill (CPMG) sequence. Instead of a single 180° pulse, multiple 180° pulses are applied. The spin echo decay is governed by $T_2$ relaxation:

$$SEI(nt_e) \propto \exp \left( -\frac{nt_e}{T_2} \right), \quad (2.12)$$

where $n$ the denotes echo number. An arbitrary number of 180° pulses can be chosen, but for clarity only three 180° pulses are shown in Figure 2.3.

The Hahn spin echo technique can made selective to position by applying a magnetic gradient field $G$ superimposed on the main field. In the one-dimensional case, using $x$ as spatial coordinate, this can be expressed as:

$$f = f(x) = \gamma B(x) = \gamma (B_0 + Gx). \quad (2.13)$$

Hence, the frequency is a linear function of the spatial coordinate in case of a uniform magnetic field gradient. It follows that the slice thickness $\Delta x$ is related to the excitation bandwidth $\Delta f$ according to:

$$\Delta x = \frac{\Delta f}{\gamma G}. \quad (2.14)$$

Figure 2.3: A few NMR pulse sequences relevant to this study: the Free Induction Decay (FID), Hahn spin echo and CPMG sequences.
2.4 Spin echo decay

For the spin echo decay of the Hahn spin echo sequence in presence of uniform magnetic field gradient, three length scales are important [35, 39]:

- The diffusion length $L_d = \sqrt{6D_0 t}$, where $D_0$ is the molecular self-diffusion coefficient of the species under investigation.
- The structural length $L_s = V/S$, where $V$ is the volume and $S$ is the surface area of the pore.
- The dephasing length $L_g = \frac{\sqrt{D_0 \gamma G}}{2\pi}$.

The shortest of these length scales determines the dominant mechanism governing the spin echo decay. The diffusion length is the distance over which a particle can travel and increases with time. Diffusion is a consequence of Brownian motion and characterized by the self-diffusion coefficient. If the diffusion length is the shortest, the particles can diffuse freely and are considered to be in the free diffusion regime.

The structural length scale indicates the distance over which a particle can travel due to restricted geometry, such as in a porous medium. Assuming cylindrical or spherical pores, this structural length is proportional to the pore radius. If the structural length scale is shortest, the particles probe all parts of the pore. They average their local magnetic field by their diffusive motion and are in the so-called local averaging regime.

The dephasing length scale represents the typical length over which a particle needs to travel to dephase by $2\pi$. Only particles with less dephasing contribute significantly to the spin-echo decay. If the dephasing length is shortest, particles are in the localization regime. This happens if the magnetic field gradient is large enough so that the particle has already dephased significantly before reaching the pore wall.

Particles diffusing in a restricted geometry can be subject to surface relaxation [5, 35]. In this case Brownian motion causes the spins to spend time in the vicinity of the pore wall where fast relaxation occurs. This can be due to susceptibility mismatches [40] or magnetic impurities [41] that effectively induce magnetic field variations. Brownstein and Tarr [42] developed a model to describe the influence of surface relaxation behavior on the longitudinal and transversal relaxation times:

$$\frac{1}{T_{1,2}} = \frac{1}{T_{\text{bulk}}} + \rho_{1,2} \frac{S}{V}. \quad (2.15)$$

Here $T_{\text{bulk}}$ is the bulk relaxation time and $\rho$ is the surface relaxivity. This expression is valid when the spins are in fast exchange between the pore center and pore wall during the timescale of the experiment. This is the so-called fast diffusion regime, as defined by Brownstein and Tarr, and can be quantified by the condition $r << L_d = \sqrt{6D_0 t}$. Because the surface-to-volume ratio depends on the pore geometry, this model can be used to determine the pore size distribution of the porous material (see e.g. [43]). While often applied with $^1\text{H}$ NMR, the Brownstein-Tarr model can also be applied to $^{23}\text{Na}$ under specific conditions [44]. Three requirements are met in this case: ions are in the fast modulation and fast diffusion regimes, and surface relaxation is fast enough to influence the relaxation behavior. The latter requires the second term on the right hand side to be comparable to the bulk relaxation rate, which is determined by relatively fast quadrupole relaxation for $^{23}\text{Na}$.

Magnetic impurities in the porous material may lead to internal field gradients that are substantially larger than the magnetic gradient field applied externally (see e.g. [45, 46]). These impurities may be present in the pore liquid or solid matrix and induce magnetic field gradients that cause rapid dephasing of the NMR signal. Consequently, the transversal decay of the magnetization can show pronounced diffusional dephasing effects.
Chapter 3

Solute diffusion in porous media

As stated in Section 1.1, transport of ions happens predominantly via diffusion and advection. In this chapter theoretical analysis of diffusion is given, which is driven by concentration gradients. In particular diffusion of Na\(^+\) and Cl\(^-\) ions from aqueous sodium chloride solution into a water-saturated porous medium is of interest. This type of experiment is schematically shown in Figure 3.1 for the case of one-dimensional transport. In this chapter a solution is found for the concentration profiles as function of position and time.

![Figure 3.1: Schematic representation of the one-dimensional diffusion experiment. Na\(^+\) and Cl\(^-\) ions diffuse from the bulk NaCl solution into the water-saturated porous material.](image)

3.1 Governing equation

Diffusion of solutes is driven by Brownian motion, which is a stochastic process. This random motion is a consequence of finite kinetic energy that the particles possess at nonzero temperature. It can be shown via volume averaging techniques that one-dimensional pure solute diffusion in saturated porous media is macroscopically expressed as [47]:

\[
\frac{\partial C_{\text{free}}}{\partial t} = \frac{\partial}{\partial x} \left( D_{\text{eff}} \frac{\partial C_{\text{free}}}{\partial x} \right) - \frac{1}{\phi} \frac{\partial C_{\text{bound}}}{\partial t} .
\] (3.1)

Here \( t \) denotes the time, \( x \) the position, \( D_{\text{eff}} \) is the effective diffusion coefficient and \( C_{\text{free}} \) and \( C_{\text{bound}} \) represent the free and bound concentrations, respectively. This equation can be applied individually to the sodium and chloride ions. Before attempting to find a solution to this equation, the effective diffusion coefficient is discussed more extensively.

This experiment focuses on diffusion of sodium and chloride ions from aqueous solution into pure water. The diffusion coefficient associated with this process is the so-called ambipolar diffusion coefficient \( D_{\text{ambipolar}} \). The term \textit{ambipolar} comes from the polarity of the charged ions and reflects coupled diffusion as macroscopic charge neutrality must prevail. It can be shown that the ambipolar diffusion coefficient in this case is given by [48]:

\[
D_{\text{ambipolar}} = \frac{2D_Na D_{Cl}}{D_{Na} + D_{Cl}} .
\] (3.2)
Here $D_{Na}$ and $D_{Cl}$ represent the self-diffusion coefficients of sodium and chloride, respectively. These are equal to $1.334 \cdot 10^{-9} \text{ m}^2\text{s}^{-1}$ for $\text{Na}^+$ and $2.032 \cdot 10^{-9} \text{ m}^2\text{s}^{-1}$ for $\text{Cl}^-$ at 25 °C [3]. Plugging in these values gives an ambipolar diffusion coefficient of $1.611 \cdot 10^{-9} \text{ m}^2\text{s}^{-1}$, illustrating that the fast $\text{Cl}^-$ ions are retarded by the slower $\text{Na}^+$ ions.

\[ D = D_0 \]

Figure 3.2: Diffusion in a porous medium. For sufficiently short times the diffusion length is smaller than the structural length. In this case the particle does not feel restrictions imposed by the porous medium and the diffusion coefficient is equal to the bulk diffusion coefficient (i.e. $D = D_0$). For longer times the diffusion length becomes larger than the structural length of the porous medium and the particle is restricted in its movement due to the geometry of the porous medium. The diffusion coefficient is now smaller than the bulk diffusion coefficient (i.e. $D < D_0$).

The influence of the porous medium on the effective diffusion coefficient is twofold in absence of binding. The porosity $\phi$ restricts the cross-sectional area available for transport. Note that the macroscopic surface porosity is equal to the volumetric porosity [47]. Secondly, transport might be hindered due to tortuous effects. The so-called tortuosity $T$ is a measure for the effective length of the transport paths in a porous material and is determined by the structural properties of the medium. Its effect is schematically depicted in Figure 3.2. For sufficiently small times, the diffusion length is smaller than the characteristic length scale of the porous medium (i.e. $\sqrt{6D_0 t} < V/S$). In this case the diffusion coefficient is equal to the bulk diffusion coefficient (i.e. $D=D_0$) and the porous medium has no effect on diffusion. When the diffusion length is much larger than the pore size of the medium, the diffusion coefficient is reduced due to the restricted geometry introduced by the porous material. This regime is referred to as the tortuosity limit [49]. A qualitative representation of the behavior of the self-diffusion coefficient is given in Figure 3.3 (see e.g. [50]). Since tortuous paths are longer than straight flow paths by definition, it follows that the tortuosity is bounded by unity (i.e. $T \geq 1$). Taking these two effects into account and with the help of Equation 3.2, the effective diffusion coefficient can be written as [51]:

\[ D_{effective} = \frac{\phi}{T} D_{ambipolar} = 2\frac{\phi}{T} \frac{D_{Na}D_{Cl}}{D_{Na} + D_{Cl}}. \]  

(3.3)
Figure 3.3: The behavior of the diffusion coefficient of a species in a porous medium. Initially, the diffusion length is small enough for the particles not to experience an effect of the restricted geometry introduced by the porous medium. In this case the diffusion coefficient is equal to the bulk diffusion coefficient (i.e. $D=D_0$). As time progresses, the diffusion length becomes larger. Eventually the diffusion length will be much larger than the pore size and the tortuosity limit is reached. In this case the diffusion coefficient is significantly reduced due to the restricted geometry introduced by the porous medium (i.e. $D<D_0$).

So far the binding term on the right hand side of Equation 3.1 has not been considered yet. The accumulation of chemical species (present in the liquid) on the solid matrix at the solid-liquid interface is known as adsorption. The binding term accounts for both adsorption and its inverse process referred to as desorption. These processes can be of physical (e.g. attraction of ions to the solid matrix due to a surface potential) or chemical (i.e. reactive interaction between solute and solid) nature and various models are proposed to adequately describe these processes. Amongst these are models that assume equilibrium conditions so that the amount of absorbed species $C_{\text{bound}}$ is solely a function of the concentration of species in the liquid $C_{\text{free}}$ [i.e. $C_{\text{bound}} = C_{\text{bound}}(C_{\text{free}})$]. In practice, these so-called binding isotherms are determined experimentally and details of their behavior are governed by characteristics of the porous medium and adsorbate. Well-known examples of equilibrium isotherms describing transport in porous media are linear, Freundlich [52] and Langmuir isotherms [53]:

\[
C_{\text{bound}} = K_{\text{linear}}C_{\text{free}}, \quad \text{Linear} \tag{3.4}
\]

\[
C_{\text{bound}} = K_{\text{Freundlich}}C_{\text{free}}^N, \quad \text{Freundlich} \tag{3.5}
\]

\[
C_{\text{bound}} = \frac{K_{\text{Langmuir}}C_{\text{free}}}{1 + K_{\text{Langmuir}}C_{\text{free}}}C_{\text{bound,max}}, \quad \text{Langmuir} \tag{3.6}
\]

Here $K$ and $N$ denote binding parameters to be determined empirically, and $C_{\text{bound,max}}$ represents the bound chloride concentration at saturated monolayer adsorption. While these isotherms are widely used in literature (see e.g. [54, 55, 56]), the assumption of equilibrium conditions is not straightforward and it is observed that equilibrium isotherms fail to describe binding processes adequately in dynamical systems (an example can be found in the work of Pel et. al. [27]).
3.2 Solution to the diffusion equation

A solution for the spatial and temporal evolution of the free concentration based on Equation 3.1 is desired \[ C_{\text{free}}(x,t) \]. Here initial and boundary conditions are required. Initially, the porous medium contains no Na\(^+\) or Cl\(^-\) ions. The concentration at the interface of the reservoir and the porous material remains constant at \( C_0 \). Three additional assumptions are made to simplify matters: the binding isotherm is linear (i.e. as in Equation 3.4), the porosity does not vary with time and the effective diffusion coefficient is taken constant. For this specific case the solution is given by (see Appendix A):

\[
\frac{C(x,t)}{C_0} = 1 - \text{erf} \left( \frac{x}{2\sqrt{D_{\text{eff}}t}} \right),
\]

\[
\text{erf}(p) \equiv \frac{2}{\sqrt{\pi}} \int_0^p e^{-q^2} dq.
\]

Here the so-called error function \( \text{erf}(p) \) is introduced using the dummy variables \( p \) and \( q \). Note that the subscript of the free concentration is dropped for clarity. The effective diffusion coefficient is given by:

\[
D_{\text{eff}} = \frac{2\phi^2}{(\phi + K)T} \frac{D_{\text{Na}}D_{\text{Cl}}}{D_{\text{Na}} + D_{\text{Cl}}},
\]

In case of linear binding the net effect is a mere reduction of the effective diffusion coefficient by a factor \( \phi/(\phi + K) \). For non-linear binding, such as described by the Freundlich and Langmuir isotherms, the net effect on the solution to the diffusion equation is not so straightforward. Nevertheless, numerical simulations can provide insight in such transport processes. It is stressed that this solution is valid for the semi-infinite medium approach only. If the diffusion length becomes comparable to the sample length (which is just a matter of time), a second boundary condition has to be introduced. For this experiment this would be a no-flux boundary condition at the end of the sample.
Chapter 4

NMR scanners

In this chapter two home-built NMR scanners dedicated to image solute transport in porous media are addressed. They are hereafter denoted by NMR02 (Section 4.1.1) and NMR06 (Section 4.1.2), according to local laboratory convention. The design of these scanners is described in Section 4.1, followed by the imaging approach (Section 4.2) and the typical performance of the scanners (Section 4.3).

4.1 NMR scanner design

The basic design of the scanners is schematically depicted in Figure 4.1. The experiments are managed from the host PC which controls the digital NMR (RadioProcessor™, SpinCore Technologies Inc.), which is a commercially available timing and data acquisition system. Its board contains three main components: a timing, excitation and acquisition core. The excitation core produces the RF output signal and is connected to a digital-to-analog converter (DAC), allowing to directly couple its output to an external amplifier. The acquisition core captures incoming RF signals. A tunable amplifier is installed prior to its input to amplify the received analog signal before it is converted to a digital signal by an analog-to-digital converter (ADC). Next, the signal is demodulated using quadrature detection after which the real and imaginary signals are filtered and decimated before they are stored in the internal Random-Access Memory (RAM). Signal averaging happens in this core before data is transferred to the host PC.

![Diagram of NMR scanner design](image)

Figure 4.1: Schematic representation of the design of the NMR scanners.

The RF output is connected to an external amplifier that amplifies the signal if the pulse line is high. The gating, by means of the pulse line, is controlled via the digital NMR. The high power pulse is then transferred to the electronic duplexer, which allows bidirectional communication over the single inductance/capacitance (LC) circuit feed. The duplexer therefore has two modes of operation: transmit and receive. If transmitting, the incoming high power signal is fed to the resonant coil to excite the nuclei in the specimen of interest. The RF signal from the sample that is detected in the same coil is led to the duplexer, which then operates in receive mode. The signal is then filtered and amplified before it is send to the RF input of the digital NMR.
4.1.1 NMR02 scanner

The main magnetic field of 0.96 T and the magnetic gradient field are produced by conventional electromagnets and two pairs of Anderson coils \[57\], respectively. These gradient coils are air-cooled and able to provide a magnetic gradient field of 0.3 T m\(^{-1}\). To maintain the temperature to an ambient level, gradient strengths up to 0.20 T m\(^{-1}\) can be used. Pulses are amplified by a custom built amplifier (\(~1\) kW), which is suitable for the frequency range desired in the experiments (see Table 4.1). The sample is placed in the so-called insert which is schematically depicted in Figure 4.2. The internal cylindrical bore of the insert allows to measure specimens with a diameter up to 30.0 mm.

![Figure 4.2: Top view of the insert that is positioned in between the gradient coils. The main magnetic field is provided by electromagnets and the magnetic gradient field is generated by Anderson coils. The sample is surrounded by a Faraday shield and coil that is shared by the RF circuits optimized for \(^1\)H and \(^7\)Li NMR.](image)

The sample is surrounded by a coil that is shared by two LC-circuits. These circuits are optimized for respectively \(^1\)H and \(^7\)Li, and toggling between these circuits is possible by a mechanical switch controlled by a stepper motor. The transmittance of the RF circuits as function of frequency is shown in Figure 4.3A and can be quantified by its quality factor (a.k.a. Q-factor). This factor is defined as the ratio of the resonant frequency over the 3 dB bandwidth: \(Q \equiv f_0/\Delta f_{3\,\text{dB}}\). The calculated Q-factors are tabulated in Table 4.1. A high Q-factor is desired as this is a measure for the power that is transferred to the sample, but this will consequently increase the ringing time of the RF coil. Hence, tuning the LC circuit is a trade-off between the shortest time at which one can measure in an NMR experiment and the power that is transferred to the sample. The coil that is shared by the circuits contains an internal Faraday shield to reduce the effect of variations of the dielectric permittivity of the sample.

<table>
<thead>
<tr>
<th>Scanner</th>
<th>Element</th>
<th>Resonant frequency (f_0) (MHz)</th>
<th>Q-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMR02</td>
<td>H</td>
<td>40.9</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>Li</td>
<td>15.9</td>
<td>14</td>
</tr>
<tr>
<td>NMR06</td>
<td>H</td>
<td>63.9</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>Na</td>
<td>16.9</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>6.3</td>
<td>32</td>
</tr>
</tbody>
</table>

Table 4.1: Approximate resonant frequencies of the elements detectable with the NMR02 and NMR06 setups. Also, the Q factors of the optimized (inductance/capacitance) LC circuits are given.
4.1.2 NMR06 scanner

The main magnetic field of 1.5 T is provided by a whole-body medical scanner (Philips Gyroscan S15/ACS). The remaining NMR hardware is contained in a home-built setup, which is schematically depicted in Figure 4.4. This setup is placed inside the bore of the medical scanner and contains three pairs of gradient coils in Anderson configuration [57]. Only two pairs are used when scanning a certain species: the upper set is used for $^{23}$Na and $^{35}$Cl, and the lower set is used for $^1$H. These gradient coils are liquid cooled and capable of providing a magnetic gradient field up to $0.25 \, \text{Tm}^{-1}$. However, the maximum gradient while keeping the temperature to an ambient level is only $0.10 \, \text{Tm}^{-1}$. The internal cylindrical bore of the home-built setup allows to measure specimens with a diameter up to 30.0 mm. The upper RF coil belongs to two LC circuits optimized for $^{23}$Na and $^{35}$Cl, respectively. A stepper motor allows to mechanically switch between the two circuits. The lower RF coil is tuned for $^1$H. Both coils contain internal Faraday shields. The optimization of the circuits is shown in Figure 4.3B and the calculated Q-factors are listed in Table 4.1. The setup contains two custom built amplifiers: one is used for $^1$H ($\sim 3.6 \, \text{kW}$) and the other for $^{23}$Na and $^{35}$Cl ($\sim 4.2 \, \text{kW}$).
4.2 NMR imaging approach

Block pulses in time domain are used in the NMR measurements, resulting in so-called sinc functions in frequency domain. Therefore a sinc-like excitation profile is generated, which is illustrated in Figure 4.5. Here the excitation profile is approximated by the main sinc-lobe. Truncated sinc-pulses in time domain would result in a better slice definition, but the power required to excite a considerable amount of spins in this way is too high for the current amplifiers in use (i.e. $\alpha_{\text{max}} < 90^\circ$). Modulation of the 90° block pulses to produce 180° pulses is done by amplitude modulation rather than time modulation, because the latter excites another volume by definition (see Equation 2.1 and recall that the excitation bandwidth is related to the pulse time). Note that time modulation is shown in Figure 2.3 for the sake of clarity. To conclude this section, an overview of typical experimental NMR parameters used in this thesis are given in Table 4.2.
Figure 4.5: *The main sinc-lobe as an approximation to the excitation profile. This profile is related to the slice thickness via the magnetic gradient field (see Equation 2.14).*

Table 4.2: *Typical NMR settings used in the experiments described in this thesis.*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$^1$H</th>
<th>$^7$Li</th>
<th>$^{23}$Na</th>
<th>$^{35}$Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse time ($\mu$s)</td>
<td>20</td>
<td>30</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>Echo time ($\mu$s)</td>
<td>250</td>
<td>300</td>
<td>350</td>
<td>600</td>
</tr>
<tr>
<td>Acquisition window ($\mu$s)</td>
<td>150</td>
<td>200</td>
<td>250</td>
<td>420</td>
</tr>
<tr>
<td>Long delay (ms)</td>
<td>4000</td>
<td>4000</td>
<td>250</td>
<td>250</td>
</tr>
</tbody>
</table>

4.3 Typical performance

To inspect the performance of the setups, noise levels are measured using the Hahn spin echo sequence. This is done by measuring the spin echo intensity without placing a sample in the sensitive area of the NMR scanner. This is repeated 50 times for each number of averages. The results for $^1$H and $^7$Li for the NMR02 scanner are shown in Figure 4.6. The results for $^1$H, $^{23}$Na and $^{35}$Cl for the NMR06 scanner are shown in Figure 4.7. The maximum number of averages chosen (i.e. 1024) has nothing to do with the internal memory size of the digital NMR, but rather with the measurement time (as this obviously increases when more averages are taken). The Hahn spin echo intensities of 1M LiCl and 1M NaCl aqueous solution are also measured and shown in the noise graphs for the NMR02 and NMR06 scanners, respectively. For the latter, it shows that NaCl concentrations in the order of seawater concentration (i.e. \( \sim 0.6 \text{ M} \)) are easily detectable. The fitted exponents through the noise data are all equal to -0.5 within experimental accuracy. This is expected as the signal-to-noise ratio (SNR) is proportional to the square root of averages. The thermal noise floor is not reached yet for 1024 averages.
Figure 4.6: Noise maps of $^1$H (A) and $^7$Li (B) as measured with the NMR02 scanner. The signal intensity of 1M LiCl aqueous solution is also shown to estimate the signal-to-noise ratio. The exponents of the fits through the noise data equal -0.5 within experimental accuracy. The thermal noise floor is not reached yet for 1024 averages for both elements.

For the NMR06 scanner, the nominal spatial resolutions for $^{23}$Na and $^{35}$Cl are determined by varying the sample position with the stepper motor and measuring the signal of 4 M NaCl solution subsequently. Hereto a cylindrical PolyVinylChloride (PVC) tube is used (inner ø: 20.0 mm, outer ø: 28.1 mm, length: 91.7 mm) of which is verified that it did not give a background signal. A similar procedure is done to determine the nominal resolution of $^1$H. Now a 0.1 M CuSO$_4$ solution is used because it significantly decreases the T$_1$ relaxation time of $^1$H. Hence the measurement time is reduced accordingly. Results obtained with a magnetic gradient field of 0.10 and 0.20 Tm$^{-1}$ are shown in Figure 4.8. For the latter gradient strength, resolutions in the order of 3, 6 and 8 mm for respectively $^1$H, $^{23}$Na and $^{35}$Cl are found. Decreasing the gradient by a factor 2 (i.e. from 0.20 to 0.10 Tm$^{-1}$) should double the resolution (see Equation 2.14), which is observed for all elements.
Figure 4.7: Noise maps of $^1$H (A), $^{23}$Na (B) and $^{35}$Cl (C) as measured with the NMR06 scanner. The signal intensity of 1M NaCl aqueous solution is also shown to estimate the signal-to-noise ratio. The exponents of the fits through the noise data equal -0.5 within experimental accuracy. The thermal noise floor is not reached yet for 1024 averages for all the elements.
Figure 4.8: Nominal resolution of $^1$H (A), $^{23}$Na (B) and $^{35}$Cl (C) as measured by varying the sample position and performing Hahn spin echo measurements. The nominal resolutions for a gradient field of 0.20 Tm$^{-1}$ are in the order of 3, 6 and 8 mm for $^1$H, $^{23}$Na and $^{35}$Cl, respectively. The resolutions for the different gradients differ by a factor of $\sim$2 for all the elements as expected (see Equation 2.1).
Chapter 5

NMR on bulk sodium chloride solution

An NMR calibration and relaxation study on bulk sodium chloride (NaCl) aqueous solution is performed to investigate quadrupolar effects. Quantitative measurements are only possible if the signal intensity varies linearly with concentration. Furthermore, such a relation verifies that the ions are in the fast modulation regime [5, 28, 36]. Longitudinal and transversal relaxation times are important for NMR imaging using the Hahn spin echo sequence, as they affect the signal via Equation 2.11.

5.1 Materials and methods

Reference solution concentrations of 1, 2, 3, 4 and 5 M are prepared by weighing a specific amount of NaCl salt and dissolving it in demineralized water (conductivity lower than 10 µSm$^{-1}$) in an Erlenmeyer flask to achieve the desired concentrations. For the NMR measurements, cylindrical tubes (length: 98.5 mm, inner φ: 27.8 mm, outer φ: 30.0 mm) filled with the reference solutions are used. Measurements are performed with the NMR06 scanner (see Section 4.1.2). Intensities are measured using the Hahn spin echo sequence and relaxation times are obtained via the Saturation Recovery and CPMG sequences.

![Graph A: Hahn spin echo intensities for 23Na and 35Cl](image)

**Figure 5.1:** The Hahn spin echo intensities as function of concentration for $^{23}$Na (A) and $^{35}$Cl (B). The error bars are an indication of the signal-to-noise ratio. The intensities show linear variation for both species.
5.2 NMR calibration and relaxation

The intensities as function of concentration are measured for $^{23}\text{Na}$ and $^{35}\text{Cl}$ and shown in Figure 5.1. The error bars are an indication of the signal-to-noise ratio (SNR), which is predominantly determined by the concentration ($\sim$ signal) and number of averages ($\sim$ noise) used in the experiments. The spin-echo intensities vary linearly with concentration for both species. This proves that the ions are in the fast modulation regime and that quantitative measurements are possible, at least for bulk solution.

The relaxation rates as function of concentration are shown in Figure 5.2A. The transversal relaxation rates are free from diffusion as checked by varying gradients and echo times. In all cases mono-exponential behavior is observed, verifying that the ions are indeed in the fast modulation regime. It is known that the relaxation rates are related to the dynamic viscosity $\eta$ and temperature according to [39, 40]:

$$\frac{1}{T_{1,2}} \propto \frac{\eta}{T}$$

(5.1)

The relaxation rates found in Figure 5.2A can be corrected for viscosity to reveal a potential concentration dependency. The relative viscosity of NaCl to that of H$_2$O ($\eta_{\text{H}_2\text{O}} = 1.002$ mPa s) is shown in Figure 5.3. A second order polynomial fit is also shown. The relaxation rates obtained after viscosity correction are shown in Figure 5.2B and are independent of concentration within experimental accuracy. This is in agreement with the theory and experiments of Woessner [36]. For bulk solution $T_1 \approx T_2$, which is observed for $^{23}\text{Na}$. For $^{35}\text{Cl}$ however, there is a clear distinction between transversal and longitudinal relaxation rates. It is beyond the scope of this study to exactly determine the origin of this observation, but it has likely to do with quadrupolar effects. For completeness, the average values of the longitudinal and transversal relaxation times are extracted for both $^{23}\text{Na}$ and $^{35}\text{Cl}$ and listed in Table 5.1.

![Figure 5.2: A. The relaxation rates for $^{23}\text{Na}$ and $^{35}\text{Cl}$ as obtained from Saturation Recovery and CPMG measurements. B. The relaxation rates after viscosity correction, revealing to be independent of concentration within experimental accuracy for both ions.](image)

<table>
<thead>
<tr>
<th>Species</th>
<th>$T_1$ (ms)</th>
<th>$T_2$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{23}\text{Na}$</td>
<td>63 ± 2</td>
<td>57 ± 2</td>
</tr>
<tr>
<td>$^{35}\text{Cl}$</td>
<td>41 ± 3</td>
<td>34 ± 3</td>
</tr>
</tbody>
</table>
Figure 5.3: The dynamic viscosity of NaCl relative to that of H$_2$O correlates positively with NaCl concentration. The red curve is a second order polynomial fit, which is in accordance with Woessner [36]. The data correspond to a temperature of 20°C and atmospheric pressure conditions [3].
Chapter 6

NMR calibration and relaxation in porous building materials

In practice it is not known a priori whether the ions in the pore solution of a porous medium are in the slow or fast modulation regime. Therefore, a calibration has to be performed where the signal intensity is measured as function of known ion content. If the signal intensity varies linearly with concentration, the fast modulation regime is dominant [5, 28, 36]. Only in this case quantitative measurements are possible. Besides these calibration measurements, relaxation measurements are performed on NaCl in fired-clay brick and calcium-silicate brick. These relaxation measurements are also performed on LiCl in saturated aluminum oxide samples with distinct pore sizes. These materials are characterized in Section 6.1, addressing relevant structural and chemical properties. For the NaCl experiments reference solutions of 1, 2, 3, 4 and 5 M are used and prepared as described in Section 5.1. For the LiCl experiments a reference solution of 5 M is prepared according to the same method.

Figure 6.1: A. Pore size distribution of the fired-clay (A) and calcium-silicate (B) bricks used in the experiments, as measured by Mercury Intrusion Porosimetry. The dominant pore sizes of fired-clay brick are in the range of 1-10 µm. The pore sizes of calcium-silicate brick extend over a range of 0.001-100 µm. This distribution can be approximated by a bimodal pore size distribution, characterized by two pore sizes: 10 nm and 5 µm. These pore sizes are indicated by the dashed lines.
6.1 Material characterization

Three different porous building materials are studied: fired-clay brick, calcium-silicate brick and aluminum oxide. The choice for these materials is based on their chemical and structural properties.

When clay is sintered at a temperature that is high enough for a sufficiently long period of time (a.k.a. firing, hence the nomenclature), fired-clay brick is formed. The fired-clay brick used in this study has a porosity of \( \sim 34\% \) and is chemically inert to \( \text{Na}^+ \) and \( \text{Cl}^- \) ions. By means of Mercury Intrusion Porosimetry (MIP) the pore size distribution that characterizes the pore space can be estimated. The result is reported in Figure 6.1A, showing that the dominant pore sizes are in the range of 1-10 \( \mu \text{m} \). Fired-clay brick is known to contain significant amounts of ferromagnetic impurities, of the order of 5 weight-% iron-oxide \([35, 46]\).

Calcium-silicate bricks are manufactured by mixing lime and quartz sand with the admixture of a minor amount of water. The brick used in the experiments has a porosity of \( \sim 31\% \). Calcium-silicate brick is not necessarily chemically inert to \( \text{Na}^+ \) and \( \text{Cl}^- \) ions (see e.g. \([27]\)). Mercury Intrusion Porosimetry measurements are performed and the resulting pore size distribution is shown in Figure 6.1B. The pore sizes of calcium-silicate brick extend over a range of approximately 0.001-100 \( \mu \text{m} \). This pore size distribution can be approximated by a bimodal pore size distribution, characterized by two pore sizes: 10 nm and 5 \( \mu \text{m} \).

Aluminum oxide (\( \text{Al}_2\text{O}_3 \)) is a ceramic material of which three different samples are used that have distinct pore sizes. The porosities and pore sizes of these samples are listed in Table 6.1. The porosities are determined by means of the differential weighing method (see Appendix B). The pore sizes are determined from Mercury Intrusion Porosimetry measurements \([58]\).

<table>
<thead>
<tr>
<th>Name</th>
<th>Porosity (%)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample I</td>
<td>25</td>
<td>180( \pm 4 )</td>
</tr>
<tr>
<td>Sample II</td>
<td>24</td>
<td>207( \pm 6 )</td>
</tr>
<tr>
<td>Sample III</td>
<td>11</td>
<td>244( \pm 2 )</td>
</tr>
</tbody>
</table>

6.2 Calibration of NaCl in fired-clay brick and calcium-silicate brick

Spin echo intensities for fired-clay brick and calcium-silicate brick are measured as function of concentration, using the NMR06 scanner. Cylindrical samples (length: 80.0 mm, \( \phi \): 19.8 mm) are used and the results for \( ^{23}\text{Na} \) and \( ^{35}\text{Cl} \) are shown in Figure 6.2. The error bars are an indication of the signal-to-noise ratio, which is predominantly determined by the concentration (\( \sim \) signal) and number of averages (\( \sim \) noise) used in the experiments. The intensities vary linearly with concentration, so both ions are in the fast modulation regime. Furthermore, quantitative sodium and chloride measurements for these bricks is possible. For reference, the measured intensities of 1M NaCl solution are also shown in Figure 4.7.
Figure 6.2: The measured spin echo intensities of $^{23}\text{Na}$ (A) and $^{35}\text{Cl}$ (B) in fired-clay and calcium-silicate brick samples, saturated with different concentrations of NaCl solution. The error bars are an indication of the signal-to-noise ratio. The spin echo intensities show linear variation with concentration in all cases. The lines are linear fits through the data.

6.3 Relaxation in porous building materials

Three length scales are important for the spin-echo decay, as described and defined in Section 2.4. For the materials discussed in this chapter, these length scales are estimated and listed in Table 6.2. For the diffusion length, the echo time is used as typical time scale for the NMR experiment. For fired-clay brick and calcium-silicate brick, the self-diffusion coefficient of sodium is used (i.e. $1.334 \times 10^{-9}$ m$^2$s$^{-1}$). For aluminum oxide the self-diffusion coefficient of lithium is used (i.e. $1.029 \times 10^{-9}$ m$^2$s$^{-1}$). For the structural length of calcium-silicate brick two length scales are calculated based on the bimodal pore size distribution found in Section 6.1.

Table 6.2: Length scale estimates for the different building materials used in this study.

<table>
<thead>
<tr>
<th>Property</th>
<th>Fired-clay brick</th>
<th>Calcium-silicate brick</th>
<th>aluminum oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion length</td>
<td>$L_d$ ($\mu$m)</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Structural length</td>
<td>$L_s$ ($\mu$m)</td>
<td>1.5</td>
<td>0.003 &amp; 1.5</td>
</tr>
<tr>
<td>Dephasing length</td>
<td>$L_g$ ($\mu$m)</td>
<td>0.17</td>
<td>5.5</td>
</tr>
</tbody>
</table>

The shortest length scale determines the dominant relaxation mechanism in the spin echo decay. For fired-clay brick this the dephasing length, which is due to the presence of a relatively large amount of magnetic impurities in the material [35, 46]. These impurities are known to induce internal field gradients ($\sim 7 \times 10^3$ Tm$^{-1}$) much larger than the externally applied gradient ($\sim 0.20$ Tm$^{-1}$), thereby causing significant dephasing. For calcium-silicate brick, pore relaxation is dominant in the small pores (i.e. the 10 nm pores). For the large pores (i.e. the 5 $\mu$m pores) the diffusion length becomes comparable to the dephasing length. For aluminum oxide the structural length is clearly the smallest length scale. Therefore, pore relaxation is dominant in this building material.
6.3.1 Relaxation of NaCl in fired-clay brick and calcium-silicate brick

The CPMG sequence is used to investigate transversal relaxation phenomena of $^{23}$Na and $^{35}$Cl in fired-clay brick and calcium-silicate brick. For $^{23}$Na transversal relaxation reveals multi-exponential decay for both fired-clay brick and calcium-silicate brick, as shown in Figures 6.3A and 6.4A. To quantitatively interpret these results, use can be made of the CONTIN routine [59, 60]. In essence, the magnetization $M$ is composed of different components $M_i$ that decay with characteristic decay times $T_{2,i}$:

$$M(t) = \sum_{i} M_i \exp \left( -\frac{t}{T_{2,i}} \right).$$  \hfill (6.1)$$

The magnetization can thus be written as a sum of distinct magnetization components, each with their own relaxation time and weight factor which is equal to the partial volume of contributing spins to the total magnetization. This sum can be converted to an integral if no distinct relaxation times are considered, but rather a relaxation time distribution:

$$M(t) = M_0 \int_{0}^{\infty} P(T_2) \exp \left( -\frac{t}{T_2} \right) d(T_2).$$  \hfill (6.2)$$

Here $M_0$ is the equilibrium magnetization and $P(T_2)$ is the distribution function of the transversal relaxation times. This function can be obtained numerically using the CONTIN inversion routine. This routine uses the so-called Inverse Laplace transformation. A drawback of this method is that its results are sensitive to noise in the measurement. For instance, it is known that the peaks in the distribution become wider for lower SNR [5].

![Figure 6.3: A. Decay of the sodium signal in the CPMG sequence of 5M NaCl in fired-clay brick, measured with $^{23}$Na NMR. The red curve represents a tri-exponential fit. B. Distribution of the transversal relaxation times obtained with the CONTIN routine. The dashed lines indicate the fitted relaxation times of the red curve in the left panel.](image)

Results of the CONTIN analyses for the $^{23}$Na decay curves of fired-clay brick and calcium-silicate brick are shown in Figures 6.3B and 6.4B, respectively. For fired-clay brick, clearly three dominant relaxation times characterize the decay curve. The red lines show the actual fitted relaxation times of the red fitted curve in Figure 6.3A. Analysis of the CPMG decays for the other concentrations show similar results. The obtained relaxation times are in the order of $\sim 1.5$ ms, $\sim 6.5$ ms and $\sim 25$ ms. The latter is a result of bulk relaxation, while the other two are diffusion effects due to large internal magnetic field gradients (i.e. the localization regime). This difference is indicated by the dashed line in Figure 6.3B. The effect of the large internal magnetic field gradients on the decay behavior is expected from the length scale analysis in Table 6.2. Such effects have also been observed in literature for fired-clay brick at time scales down to 100 µs in the CPMG sequence [40].
Figure 6.5: A. Transversal relaxation of $^{35}\text{Cl}$ in calcium-silicate brick, as measured by the CPMG sequence for 1, 3 and 5 M. The white curves are fitted bi-exponential decay curves. B. Transversal relaxation time distributions of the decay curves shown in the left panel. These distribution functions are obtained with the CONTIN inversion routine.
For $^{35}$Cl mono-exponential relaxation is observed for fired-clay brick. Furthermore, the relaxation time is found to be independent of concentration and in the order of $\sim 9$ ms. The signal-to-noise ratios are too low even for the CONTIN routine to indicate multi-exponential relaxation. For $^{35}$Cl in calcium-silicate brick bi-exponential relaxation behavior is found in the CPMG decay for all concentrations. The relaxation times are found to be in the order of $\sim 4$ ms and $\sim 20$ ms. The peaks tend to become smaller when the SNR is increased, which is a characteristic of the CONTIN inversion routine as discussed earlier. The large $T_2$ component is attributed to bulk relaxation, while the small component is due to pore relaxation. Due to the finite SNR, the CONTIN routine cannot identify three relaxation times which are expected from the bimodal pore size distribution (and corresponding length scale analysis) and the relaxation results for $^{23}$Na in calcium-silicate brick.

If the intensities found in the calibration of bulk solution (Figure 5.1) and the bricks are corrected for sample volume and relaxation loss, the ratio should be equal to the porosity of fired-clay brick. The porosity determined via this way is found to be $32\%$ for fired-clay brick and $29\%$ for calcium-silicate brick. These values are in agreement with the porosity values obtained by MIP and differential weighing (see Appendix B) within experimental accuracy.

Table 6.3: Volumetric porosities of fired-clay brick and calcium-silicate brick, as measured by three different techniques: Mercury Intrusion Porosimetry (MIP), differential weighing and NMR.

<table>
<thead>
<tr>
<th>Method</th>
<th>fired-clay brick</th>
<th>calcium-silicate brick</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury intrusion porosimetry (MIP)</td>
<td>33</td>
<td>31</td>
</tr>
<tr>
<td>Differential weighing</td>
<td>34</td>
<td>32</td>
</tr>
<tr>
<td>NMR</td>
<td>36</td>
<td>29</td>
</tr>
</tbody>
</table>
6.3.2 Relaxation of LiCl in aluminum oxide

First the bulk 5M LiCl solution relaxation times for $^1$H and $^7$Li are measured with the Saturation Recovery and CPMG sequences, and listed in Table 6.4. Relaxation was mono-exponential in all cases, so the Li$^+$ ions are in the fast modulation regime. The relaxation times of $^7$Li are at least an order of magnitude larger than the relaxation times of the other quadrupolar nuclei studied in this thesis (see Figure 5.2 and Table 5.1).

Table 6.4: Longitudinal and transversal relaxation times of $^1$H and $^7$Li for 5M LiCl solution.

<table>
<thead>
<tr>
<th>Element</th>
<th>$T_1$ (s)</th>
<th>$T_2$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>1.87±0.04</td>
<td>0.409±0.002</td>
</tr>
<tr>
<td>$^7$Li</td>
<td>7.8±0.3</td>
<td>2.86±0.04</td>
</tr>
</tbody>
</table>

Figure 6.6: Longitudinal (top) and transversal (bottom) relaxation rates of $^1$H (left) and $^7$Li (right) as function of the reciprocal pore size, as measured with the Saturation Recovery and CPMG sequences. The data corresponds to LiCl-saturated aluminum oxide samples with distinct pore radii. The red horizontal lines indicate the bulk relaxation rates and the red diagonal lines are fits through the data. Relaxation is dominated by bulk relaxation or pore relaxation and transition between these regimes is associated with a crossover pore size.
The longitudinal and transversal relaxation times are measured for both $^1$H and $^7$Li for the different aluminum oxide samples saturated with 5M LiCl solution. The results are given in Table 6.5 showing that the relaxation times for both species are significantly reduced. From the length scale analysis (see Table 6.2), it is expected that pore relaxation governs this decay. In this case the Brownstein-Tarr model can be applied and Equation 2.15 is valid. Bulk relaxation occurs relatively slow compared to relaxation in aluminum oxide for both $^1$H and $^7$Li. Assuming cylindrical or spherical geometry, it follows that the surface-to-volume ratio is proportional to the reciprocal pore size. Based on these findings, Equation 2.15 can be approximated by: $T_{\text{eff}}^{-1} \propto r^{-1}$. Relaxation rates are shown as function of the inverse pore size in Figure 6.6 verifying the expected dependency based on the Brownstein-Tarr model. The red diagonal lines represent linear fits through the data and the red horizontal lines denote the bulk relaxation rates. A crossover pore size can be identified at which the regime changes from bulk relaxation dominated to pore relaxation dominated. Assuming spherical pores, the surface relaxivity can be determined from the slopes of the linear fits. The results are listed in Table 6.6. The surface relaxivities for both species agree for both transversal and longitudinal surface relaxivity. The transversal surface relaxivity is $\sim 4.5$ times higher than the transversal relaxation for both hydrogen and lithium.

Table 6.5: Longitudinal and transversal relaxation times of $^1$H and $^7$Li in aluminum oxide samples saturated with 5M LiCl solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{1,\text{H}}$ (ms)</th>
<th>$T_{2,\text{H}}$ (ms)</th>
<th>$T_{1,\text{Li}}$ (ms)</th>
<th>$T_{1,\text{Li}}$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>189.8±0.8</td>
<td>31.1±0.1</td>
<td>192±4</td>
<td>27.6±0.1</td>
</tr>
<tr>
<td>II</td>
<td>289±6</td>
<td>36.5±0.1</td>
<td>(30±1)·10$^1$</td>
<td>32.0±0.3</td>
</tr>
<tr>
<td>III</td>
<td>507±4</td>
<td>55.4±0.2</td>
<td>(52±5)·10$^1$</td>
<td>52±2</td>
</tr>
</tbody>
</table>

Table 6.6: Longitudinal and transversal surface relaxivities ($\rho_1$ and $\rho_2$, respectively), as determined from the linear fits of the measured relaxation rates as function of the reciprocal pore size. Spherical pores are assumed to determine these surface relaxivities.

<table>
<thead>
<tr>
<th>Surface relaxivity</th>
<th>$^1$H</th>
<th>$^7$Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_1$ (µms$^{-1}$)</td>
<td>0.75±0.02</td>
<td>0.77±0.07</td>
</tr>
<tr>
<td>$\rho_2$ (µms$^{-1}$)</td>
<td>3.3±0.3</td>
<td>3.5±0.3</td>
</tr>
</tbody>
</table>
Chapter 7

Diffusion of sodium chloride in fired-clay brick and calcium-silicate brick

This chapter covers diffusion of Na\(^+\) and Cl\(^-\) ions from 4.6 M aqueous NaCl solution into water-saturated bricks, as studied by \(^{23}\)Na and \(^{35}\)Cl NMR. In these experiments fired-clay and calcium-silicate bricks are used. Theoretical treatment of problem is given in Chapter 3 including a schematic representation of the experiment (see Figure 3.1).

In this one-dimensional diffusion experiment a custom built sample holder is used which is schematically depicted in Figure 7.1. The sample holder is made of a hollow cylindrical PolyVinylchloride (PVC) tube that contains a PolyTetraFluoroEthylene (PTFE) screw in the bottom to hold the sample in place at a height of 15 mm. There are two polypropylene tubes (inner ø: 2 mm, outer ø: 3 mm) entering the PVC tube from the bottom. These ∼5 m long tubes are connected to a reservoir (∼1 L in volume) and two flow pumps (2× GE Healthcare High Precision Pump P-500) of which the flow rate can be controlled. The pumps are used continuously throughout the experiment to refresh the concentration in the bath below the sample with 4.6 M NaCl solution stored in the reservoir. The inflow (100 ml/h) is set to a lower flow rate than the outflow (150 ml/h) to maintain a constant level of solution in the bath (∼8 mL in volume). The brick samples (length: 80.0 mm, ø: 19.8 mm) themselves are saturated with H\(_2\)O (conductivity lower than 10 \(\mu\)S/m). The brick is wrapped in PTFE tape on the curved sides to prevent drying in radial direction. At the top face a PolyMethylMethAcrylate (PMMA) disc is glued using conventional two-component adhesive, to prevent drying in axial direction. Moreover, a heat-shrink tubing is applied to seal off all sides except the brick-bath interface. The sample holder is connected to a stepper motor to control its position (note: the sample holder is depicted as sample in Figure 4.4).

7.1 Diffusion in fired-clay brick and calcium-silicate brick

Profiles are measured by moving the sample to the desired position and measuring the spin echo intensity using the Hahn spin echo sequence subsequently. This process is repeated until the full grid is scanned before switching to another element. Only sodium and chloride profiles are measured, since the hydrogen content is not expected to change significantly. Potential loss of moisture in the sample due to drying is checked by weighing the sample before and after the NMR measurement. For \(^{23}\)Na and \(^{35}\)Cl 64 and 256 averages are taken and measurements are done every 1 and 4 mm, respectively. This results in a nominal scan time of 35 (\(^{23}\)Na) and 85 (\(^{35}\)Cl) seconds per point. For other NMR settings see Table 4.2. During the experiment a gradient field of 0.10 T/m is used, resulting in a nominal resolution of approximately 8 and 10 mm for \(^{23}\)Na and \(^{35}\)Cl, respectively (see Figure 4.8). The measured intensities of the bath are used as reference to correct for small intensity fluctuations that might occur when measuring over extensive periods of time.
Figure 7.1: The sample holder used in the experiments. The brick sample is held in place on top of a bath of which the solution is refreshed to keep the concentration constant. The position of the sample holder is varied by means of a stepper motor.

Cylindrical brick samples (length: 80.0 mm, ø: 19.8 mm) are used in the experiments. For fired-clay brick the profiles are measured every ∼130 minutes over a period of ∼5 days. The results are shown in Figure 7.2. For calcium-silicate brick profiles are also measured each ∼130 minutes, but now for a period of ∼3.5 days. The diffusion profiles are shown in Figure 7.3. The reference concentration remained constant throughout the experiment, as was verified by a density measurement of the reservoir solution after the NMR experiment. Also, by weighing the sample after the NMR measurements, it is found that drying is negligible during the experiments (i.e. moisture content loss <1 %).

Ions are increasingly penetrating the bricks. For calcium-silicate brick some of the $^{35}$Cl profiles are quite noisy compared to the noise levels of other profiles. At the brick-bath interface reference ions are contributing to the signal, giving rise to distortions for positions <5 mm. The noise levels are in agreement with the expected noise levels shown in Figure 4.7. The signal-to-noise-ratio is lower for calcium-silicate brick compared to fired-clay brick, as expected. The diffusion profiles can be scaled according to the similarity variable $xt^{-0.5}$. The results are shown in Figure 7.4 and 7.5 for fired-clay brick and calcium-silicate brick, respectively. The individual profiles collapse onto one master curve, which is a fingerprint of the $x \propto \sqrt{t}$ relation. This verifies that transport in this experiment is a diffusion controlled process. The effect of the noisy $^{35}$Cl profiles is clearly visible in the Boltzmann plot of calcium-silicate brick, as significant scatter is observed. The diffusion lengths are <50 mm and <30 mm for fired-clay brick and calcium-silicate brick, respectively. This justifies the semi-infinite medium approach taken in Section 3.1. Therefore, the error function solution from Equation 3.7 is fitted to the data, from which the concentration at the brick-bath interface $C_0$ and the effective diffusion coefficient $D_{eff}$ are determined. The results are tabulated in Table 7.1.
Figure 7.2: Evolution of sodium and chloride ion profiles for diffusion into water-saturated fired-clay brick, as measured by $^{23}\text{Na}$ and $^{35}\text{Cl}$ NMR. Profiles are measured every $\sim 130$ minutes over a period of $\sim 5$ days.

Figure 7.3: Evolution of sodium and chloride ion profiles for diffusion into water-saturated calcium-silicate brick, as measured by $^{23}\text{Na}$ and $^{35}\text{Cl}$ NMR. Profiles are measured every $\sim 130$ minutes over a period of $\sim 3.5$ days.

The experimentally determined concentration at the interface is in agreement with the concentration of the solution in the reservoir for both ions. The effective diffusion coefficients of both ions agree for both bricks within experimental accuracy, indicating that diffusion is coupled (i.e. the ambipolar diffusion concept holds).

The salt diffusion coefficient of sodium chloride is equal to $1.611 \cdot 10^{-9} \text{ m}^2\text{s}^{-1}$ (see Section 3.1). The effective diffusion coefficients found for fired-clay brick are lower by a factor $\sim 0.41$. Since binding is not relevant to fired-clay brick, Equation (3.9) shows two possible mechanisms for this reduction: porosity and tortuosity. The porosity of fired-clay brick is given in Table 6.3 and approximates the ratio of the diffusion coefficients. Temperature effects are the main source for the discrepancy, as the diffusion coefficients vary 2 to 3% per $^0\text{C}$ [3]. Therefore, it is concluded that porosity is the only mechanism responsible for the reduction in the diffusion coefficient.
Figure 7.4: Boltzmann transformation of the diffusion profiles given in Figure 7.2. The profiles collapse onto one master curve for both ions. The red curves are the fitted error function solutions from Equation 3.7.

Figure 7.5: Boltzmann transformation of the diffusion profiles given in Figure 7.3. The profiles collapse onto one master curve for both ions. The red curves are the fitted error function solutions from Equation 3.7.

The effective diffusion coefficients for calcium-silicate brick are a factor $\sim 0.16$ smaller than the bulk salt diffusion coefficient. The porosity of calcium-silicate brick is equal to $\sim 31\%$ (see Table 6.3) and can therefore not be solely held accountable for this reduction. As evident from Equation 3.8 two other mechanisms can be responsible: binding and tortuosity effects.
Figure 7.6: The concept of binding in pores. The grey area represents the volume of the ions bounded to the pore wall and has a thickness $\delta$. The white area represents the volume of ions in bulk solution, and has a radius of $r - \delta$.

First the effect of binding is estimated. This concept is illustrated in Figure 7.6. It is assumed that there is at most monolayer coverage in the pores. The monolayer has a thickness of $\delta = 2r_{\text{atom}}$. Here $r_{\text{atom}}$ is the atomic radius and taken $2A = 0.2$ nm, which is a rather crude approximation [3]. The pores are assumed to be spherical and can be shown that for this geometry the ratio of the volume of bound ions to the volume of ions in bulk solution is given by $\left[\frac{r}{r - \delta}\right]^3 - 1$, where $r$ is the pore radius (see Appendix C). The smallest pores are considered (i.e. 10 nm, see Figure 6.1B), to calculate the largest binding effect. This is found to be $\sim 6\%$ and is less in larger pores. Therefore binding cannot be held accountable for the significant decrease in the diffusion coefficient. Note that pores are commonly assumed to be cylindrical rather than spherical [39, 61], but this yields an even smaller binding effect (see Appendix C).

Tortuosity effects are known to reduce the diffusion coefficient significantly (see e.g. [46]). These effects are concluded to be responsible for the significant reduction in the diffusion coefficient and a tortuosity of $T \approx \phi/0.16 \approx 0.31/0.16 \approx 1.9$ is found.

Table 7.1: The diffusion coefficients and reference concentrations for fired-clay brick and calcium-silicate brick. These data are obtained by fitting the Boltzmann profiles with the error function curve given in Equation 3.7.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>$D$ (10$^{-9}$ m$^2$/s)</th>
<th>$C_0$ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fired-clay brick</td>
<td>$^{23}\text{Na}$</td>
<td>0.68±0.04</td>
<td>4.5±0.2</td>
</tr>
<tr>
<td></td>
<td>$^{35}\text{Cl}$</td>
<td>0.66±0.04</td>
<td>4.5±0.2</td>
</tr>
<tr>
<td>Calcium-silicate brick</td>
<td>$^{23}\text{Na}$</td>
<td>0.24±0.04</td>
<td>4.6±0.2</td>
</tr>
<tr>
<td></td>
<td>$^{35}\text{Cl}$</td>
<td>0.27±0.06</td>
<td>4.4±0.4</td>
</tr>
</tbody>
</table>
Chapter 8

Pore size dependent self-diffusion of LiCl

Self-diffusion plays an important role in transport processes in porous media. NMR allows to directly measure the self-diffusion coefficient. In this chapter the Stimulated Echo (SE) and Hahn-T\textsubscript{2} sequences are introduced (Section 8.1) and used for self-diffusion coefficient measurements of hydrogen and lithium in 5M LiCl aqueous solution (Section 8.2). This chapter concludes with an investigation of the pore size dependency of these self-diffusion coefficients (Section 8.3). Hereto aluminum oxide samples with distinct pore sizes are used. In all the NMR experiments described in the subsequent sections of this chapter, a magnetic gradient field of 0.20 Tm\textsuperscript{-1} is used.

8.1 Measuring the self-diffusion coefficient with NMR

There are various pulse sequences that allow to directly measure the self-diffusion coefficient. Two of such sequences are the Stimulated Echo (SE) and Hahn-T\textsubscript{2} sequences.

The SE sequence consists of three 90\degree pulses, and is schematically depicted in Figure 8.1. The echoes obtained after the second and third pulses are referred to as solid and stimulated echo, respectively. It can be shown that the ratio of these echo intensities (i.e. \(S_{\text{stimulated}}\) and \(S_{\text{solid}}\)) is related to the self-diffusion coefficient \[46, 62\]:

\[
\frac{S_{\text{stimulated}}}{S_{\text{solid}}} = \exp \left[ - \left( \frac{1}{T_1} + (\gamma G T_1)^2 D_0 \right) (\tau_2 - \tau_1) \right],
\]

(8.1)

where \(\tau_1\) and \(\tau_2\) are the times between first and last two 90\degree pulses, respectively. For diffusional attenuation to become evident, the diffusion term is required to be comparable to longitudinal relaxation (i.e. \((\gamma G \tau_1)^2 D_0 \approx T_1^{-1}\)). Two experimental parameters determine the effect of diffusion in the decay: the gradient strength and the time between the first two 90\degree pulses (assuming the gradient field can be applied externally).

The Hahn-T\textsubscript{2} sequence consists of the conventional Hahn spin echo technique where the echo time is varied. If translational motion of the particles is taken into account, the signal is attenuated due to diffusional dephasing. The spin-echo decay in such a measurement is given by \[35, 62\]:

\[
SEI(t_e) = S(0) \exp \left( - \frac{t_e}{T_2} \right) \exp \left( - \frac{D_0 \gamma^2 G^2 t_e^3}{12} \right).
\]

(8.2)

For diffusional effects to become evident in the decay, it is necessary the relaxation and dephasing terms in Equation 8.2 are comparable (i.e. \(D_0 \gamma^2 G^2 \approx 12T_2^{-3}\)). Note that the diffusional attenuation is governed by the magnetic gradient field and echo time, which are again two experimental parameters that can generally be controlled externally.
Figure 8.1: Schematic representation of the Stimulated Echo (SE) sequence. This sequence consists of three 90° pulses. The time between the first two pulses is given by $\tau_1$, whereas time between the last two pulses is given by $\tau_2$.

8.2 Self-diffusion measurements on H$_2$O and 5M LiCl solution

In order to check the feasibility of these sequences to determine the self-diffusion coefficient, a preliminary study is performed on H$_2$O (conductivity lower than 10 $\mu$S/m). First, the characteristic decay rates associated with diffusion for the SE and Hahn-T$_2$ sequences are calculated and listed in Table 8.1. The characteristic relaxation rates due to longitudinal and transversal relaxation are listed in Table 8.2. These decay rates show that diffusion effects should govern the decay in both the SE and Hahn-T$_2$ experiments.

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Decay rate (s$^{-1}$)</th>
<th>$^1$H</th>
<th>$^7$Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stimulated Echo (SE)</td>
<td>$(\gamma G \tau_1)^2 D_0$</td>
<td>9.4</td>
<td>0.61</td>
</tr>
<tr>
<td>Hahn-T$_2$</td>
<td>$\sqrt{\gamma^2 G^2 D_0}$</td>
<td>55</td>
<td>22</td>
</tr>
</tbody>
</table>

Table 8.2: Characteristic decay rates involved in the Stimulated Echo (SE) and Hahn-T$_2$ experiments. Estimates are made for hydrogen as well as lithium for respectively H$_2$O, 5M LiCl solution and the three aluminum oxide samples saturated with 5M LiCl.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Decay rate (s$^{-1}$)</th>
<th>$^1$H</th>
<th>$^7$Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>$1/T_1$</td>
<td>0.36</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\sqrt{T_2/T_2}$</td>
<td>6.0</td>
<td>-</td>
</tr>
<tr>
<td>5M LiCl</td>
<td>$1/T_1$</td>
<td>0.53</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>$\sqrt{T_2/T_2}$</td>
<td>5.6</td>
<td>0.80</td>
</tr>
<tr>
<td>Aluminum oxide</td>
<td>$1/T_1$</td>
<td>5.3</td>
<td>5.2</td>
</tr>
<tr>
<td>Sample I</td>
<td>$\sqrt{T_2/T_2}$</td>
<td>74</td>
<td>83</td>
</tr>
<tr>
<td>Aluminum oxide</td>
<td>$1/T_1$</td>
<td>3.5</td>
<td>3.3</td>
</tr>
<tr>
<td>Sample II</td>
<td>$\sqrt{T_2/T_2}$</td>
<td>63</td>
<td>72</td>
</tr>
<tr>
<td>Aluminum oxide</td>
<td>$1/T_1$</td>
<td>2.0</td>
<td>1.9</td>
</tr>
<tr>
<td>Sample III</td>
<td>$\sqrt{T_2/T_2}$</td>
<td>41</td>
<td>44</td>
</tr>
</tbody>
</table>
The decay curve of the Stimulated Echo sequence is shown in Figure 8.2A. The decay line for pure $T_1$ relaxation is also shown to highlight diffusion effects. The data are fitted with Equation 8.1 to obtain the self-diffusion coefficient, which is found to be $(2.21\pm0.09)\times10^{-9}\ \text{m}^2\text{s}^{-1}$. The decay curve of the Hahn-$T_2$ sequence is shown in Figure 8.2B. The decay for pure $T_2$ relaxation is also shown to make diffusion effects obvious. The data are fitted with Equation 8.2 to obtain the self-diffusion coefficient, which is found to be $(2.15\pm0.06)\times10^{-9}\ \text{m}^2\text{s}^{-1}$. The values found for the self-diffusion coefficients are in agreement within experimental accuracy. For $\text{H}_2\text{O}$ the self-diffusion coefficient is equal to $2.3\times10^{-9}\ \text{m}^2\text{s}^{-1}$ at 25°C [3]. The discrepancy between this reference value and the experimentally determined values is likely to be caused by temperature effects, as the self-diffusion coefficient varies 2 to 3% per °C [3].

A similar study is performed on 5M LiCl aqueous solution to determine the self-diffusion coefficients of hydrogen and lithium. The decay rates from Tables 8.1 and 8.2 show that again diffusion effects should dominate the decay over relaxation phenomena. The SE and Hahn-$T_2$ decay curves for hydrogen are given in the top panels of Figure 8.3. Self-diffusion coefficients of $(1.3\pm0.1)\times10^{-9}\ \text{m}^2\text{s}^{-1}$ and $(1.25\pm0.09)\times10^{-9}\ \text{m}^2\text{s}^{-1}$ are obtained from the SE and Hahn-$T_2$ data, respectively. For lithium, the decay curves of the SE and Hahn-$T_2$ sequences are shown in the lower panels of Figure 8.3. Diffusion coefficients of $(1.0\pm0.1)\times10^{-9}\ \text{m}^2\text{s}^{-1}$ (SE sequence) and $(1.1\pm0.1)\times10^{-9}\ \text{m}^2\text{s}^{-1}$ (Hahn-$T_2$ sequence) are obtained. For hydrogen as well as lithium, the self-diffusion coefficients measured by both sequences agree within experimental accuracy.

No reference data regarding the self-diffusion coefficients for this particular reference solution (i.e. 5M LiCl) is found. However the results seem plausible as the self-diffusion coefficient for lithium at infinite dilution is equal to $1.029\times10^{-9}\ \text{m}^2\text{s}^{-1}$ [3]. Moreover, the obtained self-diffusion coefficients are in the order of self-diffusion coefficients for LiCl solutions with other concentrations, as reported in literature [63, 64, 65]. The self-diffusion coefficient of hydrogen is significantly reduced in 5M LiCl compared to water. This is expected as 5M LiCl solution is $\sim$2 times more viscous than water [3]. For completeness, an overview of the self-diffusion coefficients obtained so far is given in Table 8.3.

Table 8.3: The self-diffusion coefficients of hydrogen and lithium, as obtained from the Stimulated Echo and Hahn-$T_2$ measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stimulated Echo $D_H(10^{-9}\ \text{m}^2\text{s}^{-1})$</th>
<th>Hahn-$T_2$ $D_H(10^{-9}\ \text{m}^2\text{s}^{-1})$</th>
<th>Stimulated Echo $D_{Li}(10^{-9}\ \text{m}^2\text{s}^{-1})$</th>
<th>Hahn-$T_2$ $D_{Li}(10^{-9}\ \text{m}^2\text{s}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>2.21±0.09</td>
<td>2.15±0.06</td>
<td>1.0±0.1</td>
<td>1.1±0.1</td>
</tr>
<tr>
<td>5M LiCl</td>
<td>1.3±0.1</td>
<td>1.25±0.09</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 8.2: Self-diffusion coefficient measurements performed on $\text{H}_2\text{O}$ using $^1\text{H}$ NMR. A. The decay curves of the Stimulated Echo sequence and pure $T_1$ relaxation. B. The decay curves of the Hahn-$T_2$ sequence and pure $T_2$ relaxation. The pure relaxation decays are shown to make self-diffusion effects obvious.
Figure 8.3: Decay curves of the Stimulated Echo (left) and Hahn-\(T_2\) (right) sequences for \(^1\)H (top) and \(^7\)Li (bottom), performed on 5M LiCl solution. The \(T_1\) and \(T_2\) decays are also plotted where relevant to highlight diffusion effects.

### 8.3 Self-diffusion of LiCl in aluminum oxide

The same approach is taken as in the measurements on H\(_2\)O and 5M LiCl bulk solution discussed in the previous section. First Stimulated Echo measurements are performed on \(^1\)H and \(^7\)Li of which the results are shown in Figure 8.4. Diffusion effects are pronounced for hydrogen, but not for lithium. This is in line with the decay rate estimates given in Tables 8.1 and 8.2. Due to limited SNR, the self-diffusion coefficients cannot be determined accurately for lithium. Nevertheless, the self-diffusion coefficients for hydrogen are obtained and shown in Figure 8.6 as function of pore size. No clear dependency of the self-diffusion coefficient on pore size is observed within experimental accuracy. However, the diffusion coefficients are reduced by a factor \(~4.5\) compared to bulk self-diffusion coefficient (see Table 6.4). This might be an effect of the porous medium. Using \(0.5\cdot10^{-9} \text{ m}^2\text{s}^{-1}\) for the diffusion coefficient and 200 ms as typical time scale, the diffusion length is found to be \(L_d \approx 25 \mu\text{m}\). This is much larger than the typical pore size of the aluminum oxide samples, which is approximately 200 nm (i.e. \(L_d/r \approx 125 >> 1\)). This suggests that the decrease of the self-diffusion coefficient is due to tortuous effects.
Figure 8.4: Stimulated echo decays of $^1H$ (A) and $^7Li$ (B) and the respective longitudinal decays (dashed lines) for the different aluminum oxide samples. The solid lines represent exponential fits through the data. For hydrogen the effect of diffusion is clearly visible, opposed to lithium where the Stimulated Echo data is too inaccurate to observe diffusion effects.

The results of the Hahn-$T_2$ experiments on the aluminum oxide samples are shown in Figure 8.5. The $T_2$ decays are also shown for clarity. Diffusion effects are clearly apparent for both hydrogen and lithium. This is in agreement with the decay rate estimates of Tables 8.1 and 8.2. The data are fitted with Equation 8.2 to obtain the self-diffusion coefficient. The results are shown in Figure 8.6. Again the self-diffusion coefficients are a factor $\sim 4.5$ lower than the bulk self-diffusion coefficients. The diffusion length for hydrogen for these experiments is equal to $L_d \approx 10 \, \mu m$, using 30 ms as typical time scale. The ratio of the diffusion length and the structural length is now $\sim 50$, so again this suggests tortuous effects being responsible for the reduction in the self-diffusion coefficient.

The self-diffusion coefficients found for lithium are shown in Figure 8.6. The self-diffusion coefficient is reduced by a factor $\sim 3.5$ compared to the bulk self-diffusion coefficient. The diffusion length is found to be $L_d \approx 10 \, \mu m$, using a diffusion coefficient of $0.3 \cdot 10^{-9} \, m^2 s^{-1}$ and a typical time scale of 50 ms. This is again much larger than the structural length scale (i.e. by a factor $\sim 50$). This suggests that tortuous effects are responsible for the significant reduction in the self-diffusion coefficient.
Figure 8.5: Hahn-$T_2$ decay for $^1H$ (left panel) and $^7Li$ (right panel) in the different aluminum oxide samples saturated with 5M LiCl. The $T_2$ decays are given for reference to highlight diffusion effects, which are obvious for both hydrogen and lithium. The red lines represent fits through the data from which the self-diffusion coefficients are determined.
Figure 8.6: Self-diffusion coefficients of hydrogen and lithium as function of pore size, as measured by the Stimulated Echo ($^1$H) and Hahn-$T_2$ ($^1$H and $^7$Li) sequences. For both species the self-diffusion coefficient is significantly reduced with respect to the self-diffusion coefficients found for bulk 5M LiCl solution. No pore size dependency is found for hydrogen as well as lithium within experimental accuracy.
Chapter 9

Conclusions and recommendations

Nuclear Magnetic Resonance (NMR) is used to investigate solute transport phenomena in porous materials. To this end two home-built setups are introduced that are capable of measuring different elements quasi-simultaneously. The NMR02 scanner allows to measure $^1$H and $^7$Li, while the NMR06 scanner is able to detect $^1$H, $^{23}$Na and $^{35}$Cl.

Diffusion of Na$^+$ and Cl$^-$ ions from 4.6 M NaCl solution into water-saturated brick is studied. The salt diffusion coefficient of NaCl is equal to $1.611 \times 10^{-9}$ m$^2$s$^{-1}$. Measurements using the NMR06 scanner are performed by measuring sodium and chloride concentrations as function of position via $^{23}$Na and $^{35}$Cl NMR, respectively. These measurements are repeated every $\sim 130$ minutes to see how these profiles evolve over time. The measurements are performed with a spatial resolution of 8 mm (sodium) and 10 mm (chloride).

Profiles are obtained over a period of $\sim 5$ and $\sim 3.5$ days for fired-clay brick and calcium-silicate brick, respectively. After scaling the diffusion profiles according to the Boltzmann-Matano transformation [66], the individual profiles collapse onto one master curve. This supports modeling with the diffusion equation. The Boltzmann profiles are fitted with an analytical error function solution to obtain the brick-bath interface concentration as well as the effective diffusion coefficient. The brick-bath interface concentrations are all in agreement with the reservoir concentration. The effective diffusion coefficients obtained from the fits are given in Table 9.1.

<table>
<thead>
<tr>
<th></th>
<th>$^{23}$Na</th>
<th>$^{35}$Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>fired-clay brick</td>
<td>0.68±0.04</td>
<td>0.66±0.04</td>
</tr>
<tr>
<td>calcium-silicate brick</td>
<td>0.24±0.04</td>
<td>0.27±0.06</td>
</tr>
</tbody>
</table>

The diffusion coefficients for the different species agree with each other for both bricks. This indicates coupled diffusion, which is expected as macroscopic charge neutrality must prevail. The reduction in the diffusion coefficient for fired-clay brick is due the porosity, which restricts the cross-sectional area available for transport. For calcium-silicate brick the diffusion coefficient is even further reduced, which cannot be explained solely by porosity. Two other mechanisms can be held accountable for this reduction: tortuous and binding effects. A back-of-the-envelope calculation of monolayer absorption and experimental data show that binding is of negligible extent. Therefore, the decrease of the diffusion coefficient is attributed to tortuous effects and a tortuosity of $\sim 1.9$ is found.
A second study is performed on lithium to gain knowledge about NMR of quadrupolar nuclei. The pore size dependency of the self-diffusion coefficients of hydrogen and lithium in 5M LiCl solution is investigated. The Stimulated Echo (SE) and Hahn-$T_2$ sequences are used for these measurements. Bulk self-diffusion coefficients are measured and listed in Table 9.2. Results obtained for both sequences agree within experimental accuracy and are in line with theory. The self-diffusion coefficient of hydrogen is significantly reduced in 5M LiCl compared to $\text{H}_2\text{O}$. This is due to viscous effects, as 5M LiCl solution is $\sim 2$ times more viscous than $\text{H}_2\text{O}$.

Table 9.2: The self-diffusion coefficients of hydrogen and lithium as obtained with the Stimulated Echo and Hahn-$T_2$ sequences.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stimulated Echo</th>
<th></th>
<th>Hahn-$T_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_H (10^{-9} \text{m}^2/\text{s})$</td>
<td>$D_H (10^{-9} \text{m}^2/\text{s})$</td>
<td>$D_Li (10^{-9} \text{m}^2/\text{s})$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>2.21±0.09</td>
<td>2.15±0.06</td>
<td>1.0±0.1</td>
</tr>
<tr>
<td>5M LiCl</td>
<td>1.3±0.1</td>
<td>1.25±0.09</td>
<td>1.0±0.1</td>
</tr>
</tbody>
</table>

To investigate the influence of porous media on self-diffusion, three aluminum oxide samples with distinct pore sizes in the 170-250 nm range are used. These samples are saturated with 5M LiCl solution and the self-diffusion coefficients are obtained using the same pulse sequences. Self-diffusion coefficients of $\sim 0.5 \cdot 10^{-9} \text{m}^2\text{s}^{-1}$ and $\sim 0.3 \cdot 10^{-9} \text{m}^2\text{s}^{-1}$ are found for hydrogen and lithium, respectively. No pore size dependency is found within experimental accuracy. The self-diffusion coefficients are significantly reduced compared to the bulk self-diffusion coefficients: a factor $\sim 3.5$ and $\sim 4.5$ for lithium and hydrogen, respectively. This decrease is attributed to tortuous effects introduced by the pore space of aluminum oxide.

9.1 Outlook

Although it is demonstrated that the NMR06 setup can successfully be used for measurements concerning NaCl transport in porous media, the spatial resolution is rather limited. According to Equation 2.14 the spatial resolution can be increased by using a higher magnetic field gradient. In the experiments described in this thesis a gradient strength of 0.10 Tm$^{-1}$ is used to keep the temperature to an ambient level. The maximum gradient that can be applied with the current setup is 0.25 Tm$^{-1}$. Using such a gradient would theoretically lead to an increase of spatial resolution with a factor 2.5. To keep the temperature to a moderate level, the cooling system should be improved as cooling is currently not sufficient. An alternative, yet more rigorous, solution to this challenge would be to design new gradient coils. The resistance of these coils should be minimized to reduce heating as power is dissipated in the coils when the gradient field is applied.

Other components of the setup that should be checked are the amplifiers of the NMR06 scanner. It is witnessed that for large pulse times (i.e. $t_{\text{pulse}} > 50 \mu\text{s}$) the amplifiers cannot always sustain full power throughout the whole period of the pulse. This issue should be resolved in order to be able to apply high power pulses in combination with relatively large pulse times.

The next step for the NaCl diffusion experiments described in this thesis is to do a similar experiment, but use a concrete sample instead of a brick sample. Diffusion of chloride into concrete has gained much attention, and literature reports indicate that the associated diffusion coefficient is in the order of $10^{-12} \text{m}^2\text{s}^{-1}$ [67, 68]. Using this value and a characteristic length scale of 1 cm, a diffusion time of $t = l^2/D = 10^8 \text{s} \approx 38$ months is obtained. This time scale is much larger than for the brick samples, which is in the order of days. Therefore, measuring chloride in concrete allows to measure on a denser spatial grid and with a larger number of averages. However, fast relaxation (see e.g. Table 1.1) of the ions in concrete and the relatively low porosity of concrete ($\sim 10 \%$ [39, 67]) increase the difficulty to detect sodium and chloride via $^{23}\text{Na}$ and $^{35}\text{Cl}$ NMR.
If such an experiment can be successfully performed, more difficult transport problems can be investigated with this setup. Possible suggestions are to investigate the time dependent diffusion coefficient in concrete, which is often referred to in literature (see e.g. [11, 69, 70, 71]). Absorption measurements can be performed. This requires to measure hydrogen profiles as well, which is readily possible with the current setup. Also, American Society for Testing and Materials (ASTM) standards regarding chloride transport in concrete can be explored (e.g. the ASTM C1152, C1218, C1543 and C1582 standards). Last but certainly not least, experiments on cracked concrete can be performed to investigate the influence of cracks on chloride transport.

For the Lithium experiments, the NMR02 setup can be modified by manufacturing a custom sample holder able to provide isothermal measurements. This allows to compare experimental data more easily with theory. To investigate the pore size dependency of the self-diffusion coefficient, a higher SNR is required compared to the experiments described in this thesis. To do this, a sample with a larger radius and higher porosity could be used. The radius of the aluminum oxide samples is 19.8 mm and the radius of the cylindrical bore of the NMR02 scanner is 30.0 mm. The ratio of volumes is proportional to the square of the ratio of radii (due to the cylindrical geometry). Therefore, an optimal increase in signal of a factor \((30.0/19.8)^2 \approx 2.3\) can be achieved with the current setup.
Bibliography


Appendix A

Analytical solution to the diffusion equation

The solute diffusion equation is given by Equation 3.1:

\[
\frac{\partial C_{\text{free}}}{\partial t} = \frac{\partial}{\partial x} \left( D_{\text{eff}} \frac{\partial C_{\text{free}}}{\partial x} \right) - \frac{1}{\phi} \frac{\partial C_{\text{bound}}}{\partial t}. \tag{A.1}
\]

Next, two assumptions are made: the diffusion coefficient is constant and the porosity does not change in time. This allows to rewrite Equation A.1 as:

\[
\frac{\partial}{\partial t} \left( C_{\text{free}} + \frac{C_{\text{bound}}}{\phi} \right) = D_{\text{eff}} \frac{\partial^2 C_{\text{free}}}{\partial x^2}. \tag{A.2}
\]

To proceed it is assumed that the binding isotherm is linear, as given by Equation 3.4. The left hand side of Equation A.2 can then be written in terms of the free concentration only:

\[
\left( 1 + \frac{K}{\phi} \right) \frac{\partial C_{\text{free}}}{\partial t} = D_{\text{eff}} \frac{\partial^2 C_{\text{free}}}{\partial x^2}. \tag{A.3}
\]

Defining a new effective diffusion coefficient \( D_{\text{eff}}^* \equiv D_{\text{eff}} \phi / (\phi + K) \) yields:

\[
\frac{\partial C_{\text{free}}}{\partial t} = D_{\text{eff}}^* \frac{\partial^2 C_{\text{free}}}{\partial x^2}. \tag{A.4}
\]

This is a well-known general form of the diffusion equation. To solve this equation the so-called Boltzmann-Matano transformation can be performed [66]. Hereto a similarity variable \( \lambda \) is introduced:

\[
\lambda \equiv \frac{x}{\sqrt{t}}, \tag{A.5}
\]

The spatial and time derivatives are found accordingly:

\[
\frac{\partial \lambda}{\partial x} = \frac{1}{\sqrt{t}}, \tag{A.6}
\]
\[
\frac{\partial \lambda}{\partial t} = -\frac{\lambda}{2t}. \tag{A.7}
\]
Now Equation [A.4] can be reduced to an ordinary differential equation in terms of $\lambda$:

$$\frac{\partial \lambda}{\partial t} \frac{\partial C}{\partial \lambda} = D_{\text{eff}}^* \left( \frac{\partial \lambda}{\partial x} \right)^2 \frac{\partial^2 C}{\partial \lambda^2}, \quad (A.8)$$

$$-\frac{\lambda}{2t} \frac{\partial C}{\partial \lambda} = D_{\text{eff}}^* \frac{1}{t} \frac{\partial^2 C}{\partial \lambda^2}, \quad (A.9)$$

$$-\frac{\lambda}{2} \frac{\partial C}{\partial \lambda} = D_{\text{eff}}^* \frac{\partial^2 C}{\partial \lambda^2}. \quad (A.10)$$

Next, a boundary and initial condition are required to solve this equation for a semi-infinite medium. These conditions are applied in accordance with Section 3.1: the brick contains no Na$^+$ or Cl$^-$ ions initially and at the brick-reservoir interface the concentration remains constant at $C_0$. Mathematically, these conditions are expressed as:

$$x > 0, t = 0 : C = 0 \iff \lambda \to \infty : C = 0, \quad (A.11)$$

$$x = 0, t > 0 : C = C_0 \iff \lambda = 0 : C = C_0. \quad (A.12)$$

The solution to the diffusion equation under these conditions is found by using the Laplace transform, which yields (see e.g. [72]):

$$\frac{C(x, t)}{C_0} = 1 - \text{erf} \left( \frac{x}{2\sqrt{D_{\text{eff}} t}} \right). \quad (A.13)$$

Here $\text{erf}$ represents the error function (see Section 3.1). Note that the superscript of the effective diffusion coefficient and the subscript of the free concentration is dropped for the sake of clarity.
Appendix B

Differential weighing porosimetry

The porosity of a porous material can be estimated by differential weighing of dry and saturated specimens. The sample is considered *dry* when the mass loss is negligible. The mass is then measured and given by $m_{\text{dry}}$. Next, the sample is fully saturated with a liquid with density $\rho_{\text{liquid}}$ (i.e. the voids are now completely filled with liquid). The mass is again measured and equal to $m_{\text{wet}}$. The total volume of the sample is also measured (i.e. $V_{\text{total}}$). The volumetric porosity $\phi$ can then be calculated as follows:

$$\phi = \frac{V_{\text{voids}}}{V_{\text{total}}} = \frac{1}{V_{\text{total}} \rho_{\text{liquid}}} \frac{m_{\text{wet}} - m_{\text{dry}}}{\rho_{\text{liquid}} V_{\text{total}}} = \frac{m_{\text{wet}} - m_{\text{dry}}}{\rho_{\text{liquid}} V_{\text{total}}}$$  \hspace{1cm} (B.1)
Appendix C

Monolayer adsorption

To find the relative amount of adsorbed species in a pore, spherical geometry is considered first. The pore has a radius \( r \) and the outer shell of thickness \( \delta \) represents the volume in which bound ions reside. The volume of the bulk solution in the pore and the volume of the outer shell are given by:

\[
V_{\text{pore}} = \frac{4}{3} \pi (r - \delta)^3 \\
V_{\text{monolayer}} = \frac{4}{3} \pi r^3 - \frac{4}{3} \pi (r - \delta)^3.
\]

In case of cylindrical geometry the volume per unit length is given by:

\[
V_{\text{pore}} = \pi (r - \delta)^2 \\
V_{\text{monolayer}} = \pi r^2 - \pi (r - \delta)^2.
\]

The relative amount of adsorbed species is then given by the respective ratios of these volumes:

\[
\frac{V_{\text{monolayer}}}{V_{\text{pore}}} = \frac{\frac{4}{3} \pi r^3 - \frac{4}{3} \pi (r - \delta)^3}{\frac{4}{3} \pi (r - \delta)^3} = \left( \frac{r}{r - \delta} \right)^3 - 1, \ Spherical \ geometry,
\]
\[
\frac{V_{\text{monolayer}}}{V_{\text{pore}}} = \frac{\pi r^2 - \pi (r - \delta)^2}{\pi (r - \delta)^2} = \left( \frac{r}{r - \delta} \right)^2 - 1, \ Cylindrical \ geometry.
\]