Preliminary research of the use of NMR for mortar

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Preliminary research
on the use of NMR for mortar
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Summary

The applicability of Nuclear Magnetic Resonance (NMR) for mortar was studied. It has been shown that with NMR the moisture profile can be determined non destructively. Using NMR both the absorption and drying of mortar samples can be studied. It is shown that in addition to the moisture content additional information can be obtained from the relaxation of the NMR signal. This relaxation can be used to determine the distribution of both Na and moisture in the pore structure of mortar. Finally it has been shown NMR can be used for cryoporometry since no signal is obtained from ice.
0. INTRODUCTION

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0. INTRODUCTION

The durability of concrete is known to depend on its pore structure. Degradation mechanisms such as for instance carbonation- or chloride-initiated corrosion depend among other on the water content, permeability and diffusion rate of chloride-ions or $\mathrm{CO}_2$. The water content of concrete will be (or will become) in equilibrium with the relative humidity of the environment. Because condensation or vaporisation is dependent on the pore size, so is the water content. Also most of the transport processes in the concrete depend on the pore structure. Large, interconnected pores will easily allow transport of fluids, while transport will be much slower in small interconnected pores and impossible when only isolated pores are present.

In a literature survey of degradation mechanisms due to frost and thawing in combination with de-icing salts [1] it was found that the pore structure of concrete is also of importance in degradation due to frost or thawing. In addition to the above mentioned relation between water content and pore size, also the freezing temperature of pore water is related to the pore size. At freezing, the water in the largest pores will freeze first. Since ice has a higher specific volume than water, a pressure is build up in the concrete. When the freezing rate is high in relation to the permeability, the not yet frozen pore water cannot escape leading possibly to damage if the pressures are high enough. No damage will however arise when no or low pore pressures are build up as a result of the phase transformation. This may be the case if the pores are not completely saturated with water or when the yet unfrozen pore water has ample time to move. In addition, when the water in the large pores is frozen, water from the smaller pores may be transported to the large, already frozen pores, due to mechanisms such as vapour transport or osmoses in case dissolved salts are present.

In frost- and thawing, damage will thus also be strongly correlated to the pore structure of the concrete, but exactly how remains unclear. In the literature many possible mechanisms have been proposed but evidence on their occurrence is lacking. It is felt that this is partly because detailed knowledge of the structure of concrete is lacking so that discrimination of damage mechanisms on the basis of the material properties can not be made. Knowledge of the pore structure itself (porosity, pore size distribution and permeability), the water content and the
water distribution, the distribution of dissolved salts in the pore water as well as freezing and thawing temperature of the pore water will be a great help in understanding the degradation mechanisms at freezing and thawing.

To determine the pore structure of concrete, its related pore water distribution, dissolved salt distribution as well as freezing and thawing temperatures, Nuclear Magnetic Resonance (NMR) may be an excellent technique. In order to investigate the applicability of the NMR technique to concrete under freezing and thawing, a preliminary investigation was set-up at the Technical University of Eindhoven, in co-operation with TNO Building and Construction Research. The preliminary investigation was set-up to determine the following characteristics of the concrete:
- porosity and pore size distribution
- water distribution
- Cl and Na distribution
- freezing and thawing temperatures

In this report, the results of the preliminary experiments will be reported.

The experiments of the preliminary research has been performed on mortar specimens with an age of more than eight years. A mortar was chosen to have a homogeneous specimen (diameter 20 mm x length 50 mm). A high age was mandatory to maintain a constant pore structure during the testing. All specimens were made with portlandcement, with a cement-sand ratio of 1:3 and a water cement factor of 0.5. Two different portlandcement mortars have been used in the preliminary research, namely a regular portlandcement mortar (TNO-2) and a polymer modified portlandcement mortar (TNO-1).

Experiments will be discussed on mortars of TNO, (TNO-1 and TNO-2), and a mortar used in the Ph.D. research of K. Hazrati [2] (HAZ, water to cement ratio 0.40).
1. NMR TECHNIQUE

1.1 Nuclear magnetic resonance technique

Nuclear Magnetic Resonance (NMR) makes use of the fact that most nuclei posses a spin and therefore a magnetic moment. NMR is a magnetic resonance technique, where the resonance condition for the nuclei is given by [3, 4]:

$$f = \gamma B_0$$  \tag{1}$$

In this equation $\gamma$ is the so-called gyromagnetic ratio and $B_0$ is the externally applied static magnetic field. The gyromagnetic ratio is dependent on the type of nucleus (see table 1). Since NMR is a resonance technique it can be made sensible to hydrogen and therefore to water. Indeed also other liquids containing hydrogen can be measured, like petrol or oil.

<table>
<thead>
<tr>
<th>nucleus</th>
<th>$\gamma$ (MHz/T)</th>
<th>$G$ (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>42.6</td>
<td>1.0</td>
</tr>
<tr>
<td>$^7$Li</td>
<td>16.5</td>
<td>0.29</td>
</tr>
<tr>
<td>$^{19}$F</td>
<td>40.0</td>
<td>0.83</td>
</tr>
<tr>
<td>$^{23}$Na</td>
<td>11.3</td>
<td>0.093</td>
</tr>
<tr>
<td>$^{35}$Cl</td>
<td>4.2</td>
<td>0.0047</td>
</tr>
</tbody>
</table>

Table 1: The values of NMR parameters for various nuclei

Often a so-called spin-echo technique is used with NMR. Assuming a single exponential decay, the magnitude of a NMR spin-echo signal is given by ($T_1>>T_2$):

$$S \sim G \rho [1-\exp(-TR/T_1)]\exp(-TE/T_2)$$  \tag{2}$$

where $G$ is the relative sensitivity of the nuclei in comparison to hydrogen (see table 1), $\rho$ the density, $T_1$ the so-called spin-lattice (longitudinal) relaxation time, $TR$ the repetition time of
the spin-echo experiment, $T_2$ the so-called spin-spin (transverse) relaxation time, and TE the spin-echo time. As can be seen from Eq. 2, small $T_2$ values lead to a decrease of the spin-echo signal whereas, on the other hand, small $T_1$ values are preferred, as this parameter limits the repetition time (usually $TR \approx 4T_1$).

For most solids containing hydrogen, like e.g. plastics, the $T_2$ is extremely short (< 10 µs) in comparison to TE (factor 10) and hence these materials can not be imaged. For most building materials due to their iron content $T_2$ is also small (in the order of 400 µs) in comparison to TE and hence no standard equipment can be used (i.e., a medical scanner which have a TE in general of >5 ms). Therefore specialized scanners were developed at Eindhoven University which can image materials with a short $T_2$.

1.2 Experimental set up

For the experiments described in this report, a NMR apparatus built at the TU-Eindhoven was used which operates at a frequency of 34 MHz ($B_0 = 0.8$ T). This instrument was especially designed for quantitative measurements of moisture in porous materials with short transverse relaxation ($T_2$) times [5, 6].

An example of a NMR probe head for the water absorption experiments is presented in figure 1. A coil, which forms part of a tuned LC circuit, is placed around the sample for creating and receiving the radio frequency fields during the NMR experiments. A specially designed Faraday shield is placed between the coil and the sample to suppress the effects of changes of the dielectric permittivity by variations of the moisture content, thereby making the NMR experiments quantitative (unlike standard Magnetic Resonance Imaging (MRI), which is generally used in a qualitative way).

A well defined magnetic field gradient is applied and hence the resonance frequency will be a function of the position. Therefore at a certain frequency one can only image one position and the NMR signal will be proportional to the total amount of hydrogen atoms at that position. An entire profile is measured by moving the sample with the help of a step motor. In general the one-dimensional resolution is in the order of 1.0 mm. Typically it takes 30 seconds to measure the moisture content at one position. During the measurements a time stamp is added to each measurement point.
2. PROFILE MEASUREMENT

2.1 Water absorption

In figure 2 the measured moisture profiles are given during water absorption for a mortar. As can be seen a sharp wetting front is observed. These moisture profiles were measured during absorption for both oven dried and propanol dried mortar (HAZ) samples. During absorption the moisture profiles can be scaled by $\sqrt{t}$, which is also known as the Boltzmann transformation: $\lambda = x t^{1/2}$ (see, e.g., [6, 7]). The observed moisture profiles for one type of mortar after the Boltzmann transformation are plotted in figure 3. In both cases this transformation yields a distinct curve on which the data from the various profiles for a sample coincide. For both materials a sharp wetting front is observed. The intersection of these curves with the x-axis gives the position of wetting front as a function of time which is the waterpenetration coefficient $B$. As can be seen the water penetration factor for the oven dried sample is about a factor 4 higher than for the propanol dried sample. The area under these curves gives the total mass of water which is absorbed as function of time which is the waterabsorption coefficient $A$.

2.2 Drying

In figure 4 the resulting moisture profiles are given for a drying experiment of mortar sample TNO-2. The drying experiment was performed for a period of 48 hours. Inspection of the profiles show variations, which are substantially larger than the experimental noise, and reproduce from profile to profile, e.g., at a position of 5 mm. These variations reflect the inhomogeneities of the sample. As can be seen during the first 7 hours the drying is proceeding faster which is probably due to water transport in liquid form. As soon as the drying front enters the materials the transport has to go in vapour form which slows down the drying process. For this mortar no clear drying front is observed. As can be seen a residual moisture content is observed as the drying front enters the material. This is due to water still present in the gel pores.
3. NMR and MICROSTRUCTURE

The relaxation of the NMR signal can provide additional information on the water distribution in the microstructure. During an NMR experiment the water molecules will move randomly due to Brownian motion (see also figure 5). In bulk water there are no relaxation centres and hence the relaxation will be long. However if the water molecules are confined to a restricted volume, the molecules will collide with the wall. During these collisions there will be fast a relaxation of the hydrogen atoms and hence these will no longer take part in the NMR experiment. Hence as the pores become smaller the decay of nuclei taking part in a NMR experiment will go faster. Therefore the NMR signal will be dependent on the pore size.

In case of a material built up of interconnected spherical pores, the relaxation of the water in one pore is given by a single exponential decay with a relaxation time $T_2 [8, 9]$:

$$T_2 = \frac{T_{2s} a}{\lambda \frac{a}{3}}$$

Here $T_{2s}$ is the surface relaxation time, $\lambda$ the thickness of the surface layer, which will be taken equal to 3 Å [9, 10] and $V$ the volume of water in the pore with total surface area $S$ where $a$ is the pore radius. For other pore geometries, the proportionality constant $a/3$ may be slightly different (e.g., $a/2$ for cylinders). From measurements the surface relaxation time for mortars $T_{2s} = 85 \pm 15 \mu s [10, 11]$ was found, hence:

$$T_2 = a \times 9.4 \times 10^4 \ (\mu s \ \mu m^{-1})$$

(In this report sometimes the pore size will be given in $\mu s$ since this is directly related to the measurement. However using eq. 4. one can directly convert this to a pore size)

In figure 6 the NMR signal is given as a function of time for a mortar (TNO-1). As can be seen a clear two-exponential decay is found, which can be understood from the structure of mortar. The gel pores which are of the order of 5-100 Å will give a fast relaxation which is the first steep decay. The capillary pores have dimensions of the order of 0.01-10 µm will give a slower relaxation which is the second slower decay. The pronounced bimodal pore distribution of mortar is reflected in the relaxation as a two exponential decay.

Using the relaxation curve one can calculate the pore water distribution using the Laplace transformation. This has been performed using a the program CONTIN. The resulting
distributions for two types of mortar are given in figure 7. As can be seen both types of mortar have a bimodal pore distribution. In both cases it is found that the gel pores are in the order of $2 \times 10^3$ μm (20 Å).

In figure 8 a comparison is made for mortar (HAZ) between the pore distribution determined by NMR, mercury intrusion and water vapour sorption (BET). As can be seen the results correlate well. For BET more small pores are measured which can be contributed to the fact that also the surface layer will be measured of the larger pores. Of these methods NMR has the advantage that it is really measuring the water present within the pore structure. In addition both the gel and capillary pores can be measured simultaneously and in a non-destructive way.

In addition one can determine the pore water distribution as a function of the height by measuring the relaxation at each position. In figure 9 an example is given. Here the pore water distribution was determined each mm for the first 18 mm of a mortar sample. One can clearly see the pore water distribution changing near the top of the sample.

Since the NMR method is non-destructive one can also determine the pore water distribution as a function of time. In figure 10 an example is given of the development of the pore structure of a fresh mortar as function of time over the first 60 days [11]. One can clearly see the development of the pores, i.e., the growing of the gel pores and the decrease in size of the capillary pores.

4. Na PROFILE MEASUREMENT

Besides with hydrogen nuclei, NMR can also be done with other types of nuclei. In general other atoms have a lower sensitivity which in general will result in a longer measurement time (see table 1). At present only the Na nuclei can be measured in addition to hydrogen. Analog to the pore water distribution using the relaxation of the Na one can also determine the pore Na-ion distribution within the pore structure using the measured relaxation of the Na-ions. In figure 11 an example is given of the measured relaxation and the calculated distribution for a mortar sample saturated with a 4 M NaCl solution. One can see that the Na-ions are present in both the capillary and the gel pores.

In a second experiment the diffusion of Na into a water saturated sample (TNO-2) was
measured. The sample was brought into contact with a 4 M NaCl solution during 2 months allowing the Na-ions to enter by means of diffusion. In figure 12 the results are given of the measured moisture and Na-ion profile after 2 months. As can be seen both the moisture and Na-ions are in first order homogeneously distributed over the sample. On the sample also chemical analysis was done and the Cl profile was determined. This data is also plotted in figure 12. For comparison the Na and Cl profiles are given in arbitrary units. As can be seen a good correlation is found between these profiles. At present only measurements can be performed on the Na. The sensitive of NMR for Cl is about a factor 20 less then Na, and hence Cl can not be measured with the present low field NMR. However a NMR instrument has been built which uses a 4.7 T superconducting magnet with which it will be possible to measure the chloride concentration (S/N for NMR is proportional to the field squared). In addition this instrument will have the possibility of measuring simultaneously both the Na and Cl concentration.

5. CRYOPOROMETRY

Additional information about the pore size distribution can be obtained from cryoporometry. This technique is based on the fact that the melting temperature of the fluid in the pore increases with decreasing pore size. This can be seen from the Gibbs-Thomson relation:

$$\Delta T = T(a) - T(\infty) = \frac{k}{a}$$

In this equation $T(\infty)$ is the bulk melting temperature, $T(a)$ the melting temperature of water in a pore with pore size $a$ and $k$ a constant which is dependent on the liquid used. For water $k$ is in the order of 6.2 $10^{-4}$ Km.

Since the transverse relaxation time of the frozen fraction of the pore fluid is usually very short (6 $\mu$s), only the liquid fraction will be observed in NMR experiments with echo times larger than 100 $\mu$s. This makes NMR an ideal tool for cryoporometry but also for investigating the freezing and thawing phenomena.

The experimental set-up for the cryoporometry measurements is schematically depicted in figure 13. The sample is placed in a teflon sample holder, which is inserted in a double
walled glass cryostat. The sample is cooled using a controlled flow of cooled (77 K) nitrogen gas. For the cryoporometry measurement to avoid supercooling of the water in the pores, the measurements were performed at increasing temperatures. The actual sample temperature is determined from the resistance of two miniature Pt100 thermometers, located just above and just below the sample. Generally, the temperature difference over the sample is below 2 K, allowing the actual sample temperature to be determined with an accuracy better than 1 K.

As a test measurements were performed on a series of Polygosil samples with well-defined pore size distributions. The measured temperature dependence of the NMR signal intensity of these samples is plotted in figure 14. For each sample two melting trajectories were observed: one at 0 °C, corresponding to melting of the bulk fluid between the powder grains, and one at lower temperatures, associated with melting of the fluid in the pores. It is obvious that the freezing point of the pore fluid monotonically decreases with pore size.

Measurements were also performed on an oven dried (105 °C) mortar sample (HAZ). The sample was first cooled down to −120 °C, and then warmed up at an initial rate of about 4 K per hour, gradually decreasing to about 1 K per hour at 0 °C. The spin-echo intensity in the temperature region between −90 °C and +0 °C is plotted in figure 15. The spin-echo intensity shows a gradual increase with temperature, indicating a very broad pore size distribution. A distinct additional feature shows up at −45 °C, which we associate with the melting process of the water in the gel pores in the mortar. Using the Gibbs-Thomson relation the diameter of these pores is of the order of 1 nm (10 Å). The very broad distribution of the remaining pores is somewhat surprising, since in general the pore-size distribution in mortar is believed to be bimodal in character as also indicated by the relaxation measurements. Further studies on a series of different mortars will be performed to clarify this point.

The temperature dependence of the transverse relaxation process of this sample has also been measured between −90 °C and +10 °C. In figure 16 the pore water distribution is plotted for three temperatures. At low temperature only a water in very small gel pores can be seen, i.e., a very short relaxation can be seen. In the temperature region between −5 °C and 0 °C the relaxation time distribution starts to develop more structure. At −3 °C the gel pores transforms into a broadened peak. Next, at about −2 °C, a second peak in the distribution develops which is attributed to the capillary pores. This indicates that at −2 °C the water smaller capillary pores starts to melt, which was not separately visible in the cryoporometry measurements. Apart from these two peaks, a relatively small peak appears at 8 ms, which
probably reflects the melting of the water in the larger pores. This peak is better visible in the inset of figure 16.

6. CONCLUSIONS

- With NMR one can determine the moisture and sodium content non destructively
- With NMR one can determine the various transport processes, i.e., absorption and drying, in mortar.
- The relaxation of the NMR signal can provide information on the pore water/sodium distribution within the pore system.
- Since with NMR no ice signal is measured it can be used for cryoporometry

7. REFERENCES


Figure 1: An experimental NMR probe for measuring the moisture profiles during water absorption. The sample is moved with the help of a step motor.
Figure 2: The measured moisture profiles for mortar during water absorption
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Figure 15: Temperature dependence of the spin-echo intensity for an oven-dried mortar sample (HAZ).
Figure 16: The pore water distribution as determined from the relaxation as a function of the temperature for an oven dried mortar (HAZ). In the inset the pore water distribution is given for -2 °C.