DETECTION OF TRANSPORT PROCESSES DURING FREEZE-THAW DEICING SALT ATTACK USING SINGLE-SIDED NMR

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Abstract

Damage of concrete structures exposed to a combined freeze-thaw deicing salt attack (FTDSA) is one of the major deterioration mechanisms in cold climates. Before damage occurs, concrete structures subjected to freeze-thaw cycles (FTC) in the presence of water or deicing salt solution exhibit fast moisture uptake known as frost suction. There is still need for research in describing and modelling the mechanisms that lead to freeze-thaw induced surface scaling of concrete. Therefore, the moisture transport under FTDSA was investigated using single-sided \(^1\)H NMR.

The technique enables the observation of dynamic transport processes of water inside the sample non-destructively. Furthermore, porosity and pore size distribution of water saturated samples can be determined. The method also provides information on the mobility of water, i.e. water in capillaries or in gel pores.

Water redistribution in pores as well as changes in the pore structure inside the near surface concrete sample under FTDSA were observed with single-sided \(^1\)H NMR. The measurements confirmed the additional saturation of gel pores during thawing previously described by the micro ice lens model. The results are discussed within the context of the mechanisms of freeze-thaw deicing salt attack of concrete and contribute to a deeper understanding of the mechanisms that lead to freeze-thaw deterioration of concrete.

1. INTRODUCTION

FTDSA may result in inner or outer deterioration (salt scaling). However, up to now many different mechanisms leading to salt scaling are discussed in literature. For example, the glue-spall mechanism [1 - 3] describes salt scaling as a consequence of the different thermal expansion of the ice layer and the concrete surface which is mechanically bound to the surface ice. Besides, Fagerlund [4] explained damage by the hydraulic pressure caused by the expansion of water when a critical degree of saturation is reached. In addition, the model of “layerwise freezing” [5 - 6] assumes that the temperature in the near-surface layer as well as in deeper layers is lower than the freezing point depression. As a consequence, pore solution starts to freeze in the surface concrete layer as well as in deeper layers. Further cooling leads
to freezing of the intermediate layers. If the stresses which arise cannot be released, surface scaling occurs.

It is well-known that water redistribution occurs during freeze-thaw cycles in concrete in contact with outer moisture [7 - 9]. Since ice contains only water, the ion concentration inside the gel pore water increases which leads to a significant increase in disjoining pressure [10]. This enhances salt scaling.

Despite the different causes, salt scaling occurs owing to processes in the near surface concrete (few mm). ¹H NMR enables the analysis of transport processes in the near surface concrete with a resolution up to 0.1 mm non-destructively. This measurement technique is used here to increase the knowledge of mechanisms leading to salt scaling.

2. SINGLE-SIDED NMR: METHOD AND MATERIALS

2.1 Single-sided ¹H NMR

NMR is based on the interaction of the magnetic dipole moment of a nuclei spin with an outer magnetic field. The orientation of the magnetic moments is manipulated by electromagnetic radio pulses. When the outer magnetic field is turned off, the magnetic dipole moments return to their thermodynamic equilibrium state and two different time constants can be measured [11 - 13]. The longitudinal or spin-lattice relaxation time T₁ refers to longitudinal magnetization recovery and the transverse relaxation time T₂ (or T₂,eff for measurements in inhomogeneous magnetic fields) corresponds to the loss of magnetization in the transverse plane (xy plane) [11]. In this contribution measurements of the T₂,eff relaxation are performed.

The initial intensity of the measured T₂,eff decay (hydrogen density) is directly proportional to the overall water content within the detected object volume. Therefore, normalization of the initial intensity of the sample with the initial intensity of a water sample provides information on the total water content within the screened volume. While pure liquid water at room temperature shows values for T₂,eff in the range of seconds the relaxation time is severely reduced if a water molecule is chemically combined or adsorbed by a surface. As a consequence, T₂,eff of chemically bound ¹H nuclei becomes so short that it cannot be observed within low-field NMR [14]. Hydrogen of water in concrete covers a range of T₂,eff values from approx. 10 ms for capillary pores up to about 0.1 ms for gel pores [15].

To provide information about the distribution of water inside the specimen data processing was carried out using bi-exponential fit and inverse Laplace transformation. Both techniques enable to distinguish between gel pore water and capillary pore water, figure 1.

Figure 1: a) T₂,eff decay of a saturated concrete sample. b) Biexponential fit. c) Inverse Laplace transformation
In contrast to conventional NMR spectroscopy, single-sided NMR uses quite small devices and is therefore referred to as mobile NMR. The biggest advantage of this method is that there are no limitations on the sample size.

2.2 Materials and measurements

To remain the volume of the near-surface concrete constant concrete with high freeze-thaw deicing salt resistance were cast, table 1. CEM I 32.5 R as well as frost resistant aggregates (grading curve AB 16) were used for all concrete compositions.

Table 1: Concrete composition, air content and compressive strength

<table>
<thead>
<tr>
<th>Name</th>
<th>w/b ratio</th>
<th>Cement content [kg/m³]</th>
<th>Aggregate content [kg/m³]</th>
<th>Entrained air</th>
<th>Air content [% by vol.]</th>
<th>28 d fₚ [N/mm²]</th>
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</thead>
<tbody>
<tr>
<td>0.40/nAE</td>
<td>0.40</td>
<td>320</td>
<td>2064</td>
<td>No</td>
<td>1.0</td>
<td>60.5</td>
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<tr>
<td>0.40/AE</td>
<td>0.40</td>
<td>320</td>
<td>1982</td>
<td>Yes</td>
<td>5.3</td>
<td>42.7</td>
</tr>
<tr>
<td>0.50/AE</td>
<td>0.50</td>
<td>320</td>
<td>1892</td>
<td>Yes</td>
<td>5.0</td>
<td>36.1</td>
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<tr>
<td>0.60/AE</td>
<td>0.60</td>
<td>320</td>
<td>1806</td>
<td>Yes</td>
<td>4.9</td>
<td>29.6</td>
</tr>
</tbody>
</table>

After casting, the concrete specimens were stored in 20°C / >98% R.H. and demoulded after one day. Afterwards, they were stored in water at 20 ± 2°C. They were sawn to the required size at an age of 35 days (70 x 70 x 10 mm³ for calibration measurements and 110 x 150 x 70 mm³ for freeze-thaw experiments).

In order to investigate the potential of single-sided NMR in the context of transport processes of concrete under FTDSA, four different measurements were carried out. First calibration measurements were performed to analyse the performance of single-sided NMR. For this purpose, three specimens from each series were stored at 20°C under water for a period of at least 180 days to reduce the effect of early hydration. The specimens were weighed and packed in foil. The $T_{2,eff}$ decay was measured with different settings. To evaluate the scatter, each measurement was conducted three times. This process was repeated at different moisture states. Therefore, the specimens were stored at 20°C /85% R.H., 20°C /65% R.H., 23°C /50% R.H. and oven-dried at 40°C and approx. 20% R.H. respectively until the mass loss of two consecutive measurements was below 1% by mass. Afterwards, the water content resulting from single-sided NMR measurements was compared with the gravimetric determined water content.

In addition, measurements during one FTC and after consecutive FTC were conducted. While it is a well-known fact that initial drying and pre-saturation has a significant effect on scaling [16 - 20], little is known about the effect of intermediate dry periods. Therefore, concrete samples from the same batch of each series were exposed to FTDSA with and without intermediate dry periods. For the freeze-thaw investigations, the specimens were stored for 35 d under water and additional 21 days in a climatic chamber (20°C / 65% R.H.). Afterwards, they were exposed to capillary suction and freeze-thaw exposure according to the CDF-method [21].

The NMR measurements were carried out with the NMR MOUSE PM 25 [12]. To reduce the measurement time copper sulphate solution with a $T_1$ time of 100 ms was used for
normalization. All measurements were performed using the CPMG pulse sequence. For calibration and measurements after FTC 128 echoes and 256 scans were used. The measurements were conducted to a total depth of 4.2 mm. For measurements during FTC 512 echoes and 128 scans were applied. The total depth was 9.2 mm.

3. RESULTS AND DISCUSSION

3.1 Calibration Measurements

The settings like the maximum depth, the resolution, the number of scans and echoes as well as the repetition time are responsible for the total acquisition time and the signal quality of a measurement. In order to observe transport processes or ice formation in the near surface concrete, short acquisition times need to be realized. However, a reduction of acquisition time can lead to a loss in signal quality and increased noise. To evaluate the performance of the measurements with different settings calibration measurements were carried out. The functional dependence between the water content determined with single-sided NMR and the water content from gravimetric experiments with the lowest settings used (acquisition time 10 to 30 min depending on the number of incremental depths) is summarized in Fig. 2.

![Figure 2: Calibration of water content measurements with mobile NMR (repetition time = 200 ms, 256 scans, 128 echoes) to gravimetric determined moisture content related to samples dried at 105°C.](image)

The correlation is almost proportional. The inaccuracy of determined water content is between 0.3 and 1 % by vol. The scatter in between the NMR measurements increases with decreasing moisture content (variation coefficient VC ≤ 0.3 % for completely saturated...
samples, VC ≤ 8.2% for oven-dried samples at 105°C). The results confirm the good reproducibility and efficiency of the NMR MOUSE.

3.1 Measurements during freeze-thaw cycles

As ice is far more structured than liquid water, the NMR signal is reduced. Hence, phase transition is observed by a sudden decrease of the $T_{2,eff}$ decay. This is exemplarily illustrated for the outer surface layer (0.75 to 1.05 mm) of concrete 0.4/0/AE in figure 3. This depth was chosen to eliminate effects of surface scaling.

During cooling from +20°C to about 0°C a slight increase in the total water uptake is observed which corresponds to an increase of the water predominately in capillary pores (fig. 3a and b). From 0°C to -5°C ice formation occurs and proceeds. This can be measured by a sudden decrease in the total water content (fig. 3a) and the capillary pore water content (fig. 3b). Further cooling results in a slight increase of the total and physically bound water content. Moreover, thawing appears to start between -10°C and -5°C. However, this might be due to the fact that the measurements were carried at room temperature. Each measurement is conducted from top to bottom. As a consequence, the near-surface concrete exhibits changes in temperature explaining the early thawing. To eliminate this effect for further studies the influence of low temperatures on NMR measurements is currently investigated.

During thawing gel pores are expected to take up water from external surfaces due to depression generated by water redistribution [8]. This is confirmed by our measurements where a clear increase in the physically bound water is observed (fig. 3b). The uptake of meso and capillary pore water is retarded due to the fact that water inside coarser pores (capillary pores) melts later than in smaller ones (fig. 3b). After one FTC the water content in the meso and capillary pore system is significant higher than before freeze-thaw exposure. This shows that measurements of the $T_{2,eff}$ decay enable the observation of thermodynamic processes non-destructively. Taking this knowledge into account, measurements after FTC at a temperature of 20°C have been performed to observe transport processes in the near-surface concrete.

3.2 Measurements after freeze-thaw cycles: Continuous exposure

It is well known that freeze-thaw attack leads to additional saturation of the pore system [9]. However, in the near surface zone (0.75 to 1.05 mm) this effect is not as distinct as
expected (fig. 4a). The biggest uptake of water appeared during the first day of capillary suction and the first FTC. During the subsequent 27 FTC only minor water uptake can be observed. While a continuous increase in the gravimetrically determined water uptake is measured (fig. 4b), minor increase in the near-surface concrete occurred (fig. 4a). This allows the conclusion that further FTC basically lead to a transport of water into deeper layers of the specimen.

No significant differences in moisture uptake of concrete composition with and without air entrainment could be detected. However, differences concerning the degree of deterioration were measured. This can be derived from the shift in the inverse Laplace transformation of the $T_{2,\text{eff}}$ decay. An increasing shift to greater times corresponds to an increase in pore size distribution. Therefore, the entrained air free concrete is more damaged than the concrete with entrained air (fig. 4c and d). This is confirmed by the measured scaling (0.40/AE showed a total scaling of 399 g/m² while for 0.40/nAE a total scaling of 999 g/m² was determined). The results indicate that entrained air voids have a positive effect on the evolution of salt scaling that is not completely related to transport processes inside the sample.

![Figure 4](image)

Figure 4: a) Water content $w_{\text{NMR}}$ during freeze-thaw deicing salt exposure in the near surface concrete (0.75 to 1.05 mm). b) Gravimetric determined solution uptake $w_{\text{grav}}$. c) Inverse Laplace (IL) transformation of the $T_{2,\text{eff}}$ decay measured in the outer zone (0.75 to 1.05 mm) of 0.40/nAE. d) IL transformation of the $T_{2,\text{eff}}$ decay measured in the outer zone (0.75 to 1.05 mm) of 0.40/AE.

3.2 Measurements after freeze-thaw cycles: Alternating exposure

In the light of field conditions where drying periods usually occur between freeze-thaw cycles, exposed concrete samples from the same batch were dried at 20°C/65% R.H. and re-exposed. For all investigated concretes intermediate dry periods after 8 FTC for a period of seven days led to a decreased moisture uptake rate as well as to decreased scaling (not shown...
here) of up to 51%. Analysis of the structure type of water confirmed that drying led to a reduction primarily in capillary pore water while the content of physically bound water increased. This is exemplarily illustrated for concrete 0.50/AE in Fig. 5b. The results lead to the assumption that either drying in moderate climatic conditions causes a change in the pore structure or irreversible salt crystallization occurs.

**Figure 5:** a) Moisture uptake from 0.70 to 1.05 mm of the near surface zone during freeze-thaw deicing salt exposure with and without intermediate dry periods. b) Relative moisture uptake of gel pore (lower lines) and capillary pore water (upper lines) in a depth of 0.70 to 1.05 mm of the near surface concrete during freeze-thaw experiments with intermediate drying (0.50/AE/-20/7d dry period) and without (0.50/AE/-20/no drying). The results yield from IL transformation of the measured T2,eff decay (Fig. 1a).

### 4. CONCLUSIONS

When considering the destruction mechanisms of freeze-thaw deicing salt induced scaling, transport processes in the very outer zone (few mm) play an important role. Therefore, single-sided NMR was used to investigate the transport processes during FTDSA. The method was chosen because it enables the determination of depth-resolved moisture profiles and is quite easy to perform. In addition, there are no limitations concerning the sample size and the acquisition time is acceptable (less than 30 min per sample). Calibration experiments showed that the correlation of the water content measured with single-sided NMR is almost the same to the gravimetrically determined moisture content (R² > 0.99). Nevertheless, there are some limitations to the technique. It is not possible to detect heavily structured ¹H nuclei like ice or chemically bound ¹H nuclei. However, these facts can be advantageously used as well. The amount of frozen water can indirectly be determined by a sudden decrease in the measured water content. Measurements during freeze-thaw cycles with 3% NaCl solution confirmed transport processes previously explained by the micro ice lens model. In addition, intermediate dry periods led to reduced moisture uptake of the near surface concrete on re-exposure. This observation is in accordance with the measured scaling. As drying periods are a relevant factor in field conditions, the positive effect should be considered when designing concrete structure in freeze-thaw deicing salt exposure. Based on the presented results single-sided NMR in combination with other techniques will be used to develop a model that enables service life prediction under FTDSA. In addition, further investigations to deepen the understanding of the mechanisms of salt scaling will be carried out.

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REFERENCES