

# Freeze–thaw damage gradients in concrete: Insights into water uptake and microstructural evolution by single-sided $^1\text{H}$ NMR

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## ABSTRACT

Reliable prediction of the service life of concrete structures requires models capable of describing not only the temporal evolution but also the spatial distribution of damage. Freeze–thaw deterioration typically initiates at the exposed surface and propagates into the concrete, leading to pronounced depth-dependent damage gradients. However, commonly applied test methods predominantly rely on global damage indicators and do not resolve the internal damage distribution. In this study, freeze–thaw damage in concretes with different cement types and water-to-cement ratios was investigated using the CIF test in combination with single-sided proton nuclear magnetic resonance ( $^1\text{H}$  NMR) relaxometry. Freeze–thaw-induced water uptake and microstructural alterations were monitored non-destructively as a function of depth. Signal intensity profiles were used to quantify the rate and penetration depth of moisture ingress caused by freeze–thaw pumping and compare it to pure capillary suction. Furthermore, analysis of the transverse relaxation times enabled the identification of the range of microstructure most affected by frost attack. While the combination of CIF test and single-sided  $^1\text{H}$  NMR enables a spatially and temporally resolved characterization of freeze–thaw damage propagation, the study identifies clear methodological challenges. These arise from scatter due to the inhomogeneous magnetic field, the heterogeneous concrete microstructure, and cement-specific paramagnetic effects, highlighting the need for further methodological refinement. Nevertheless, the approach provides a promising experimental basis for the development of depth-dependent damage models relevant for practical service life prediction of freeze–thaw exposed concrete.

## 1. Introduction

Concrete infrastructure elements are commonly exposed to a range of degradation mechanisms. In Central European climates, frost i.e. freeze–thaw attack, with or without the presence of de-icing salts, represents one of the dominant deterioration processes. The frost resistance of concrete is typically ensured through a descriptive approach, which defines limit values for the concrete composition and the use of air-entraining agents. However, this approach is increasingly reaching its limitations. On the one hand, the growing application of innovative binder systems extends beyond the empirical foundation on which the descriptive concept was originally based. On the other hand, it does not allow for the assessment of the remaining service life once the initially specified design life has been exceeded.

For a reliable service-life prediction of frost-exposed concrete structures, which enables precisely such an assessment, a detailed understanding of the temporal evolution of frost-induced damage is required. However, none of the models developed over the past decades to describe frost attack have yet become established in engineering practice. One reason for this is the lack of practical limit criteria that would allow a threshold-based evaluation. In this context, the wide range of possible forms of damage must be considered (e.g. internal cracking, scaling, pop-outs of the aggregates, loss of steel–concrete bond strength). Moreover, many of the commonly used laboratory test criteria reflect changes occurring only at a specific depth. For instance, the relative dynamic modulus of elasticity (RDME) is typically measured at the center of the specimen, whereas surface scaling inherently represents damage confined to the near-surface region. In addition, both

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methods, as well as measurements of length change, require reference to an initial state, which is rarely known under practical conditions. Furthermore, moisture content—one of the key indicators of frost-induced damage—is typically determined gravimetrically and therefore only on a global scale.

For a practical and meaningful limit-state assessment, however, not only the type and degree of damage are of importance, but also its depth distribution, i.e., the distance from the exposed surface at which the damage occurs. As both temperature and moisture exposure act unilaterally on most concrete structures, the frost-induced damage is highest on the surface, gradually decreasing into the structure. Analogous to the critical corrosion-inducing chloride content, different threshold values for frost damage could be defined for different depth levels.

Microstructural investigations, which in principle allow for a higher spatial resolution than the damage criteria applied in standard laboratory tests, generally focus on mercury intrusion porosimetry (MIP) [1–5] or microscopic observations using scanning electron microscopy (SEM) [3,6–10]. However, these methods require destructive specimen preparation, which may introduce additional damage [11]. Analyses with x-ray computed tomography [5,12,13] that allow for a detailed investigation of the pore structure are mostly time-consuming and therefore not suitable for in-situ damage evaluation.

An analysis of the depth-dependent damage gradient is rarely conducted and, if so, is typically limited to a comparison of the state before and after freezing exposure [10,14,15]. For a realistic service-life prediction, however, it is essential to predict the evolution of damage both spatially and temporally, as done in [16,17].

As part of a joint research project, the combined temporal and spatial progression of frost-induced damage in concrete was investigated on a microscopic and macroscopic scale to establish a basis for service-life prediction of frost-exposed concretes. The investigations comprise two parallel studies conducted on identical concrete compositions. In one study, the reduction in RDME is analyzed at several depth levels and combined with AI-assisted evaluation of the distribution of cracks. Due to the scope of this work, these results are presented in a separate publication.

In the present study, frost-induced water uptake and microstructural alterations are investigated using proton nuclear magnetic resonance ( $^1\text{H}$  NMR). This method enables a spatially and depth-resolved assessment of the aforementioned parameters which allows the validation of numerical models as for example presented in [18]. Moreover, it is non-destructive, allowing measurements to be performed on the same specimen at different damage stages.

In the past, most studies on freeze-thaw behavior using  $^1\text{H}$  NMR have focused on closed NMR systems and/or specimens consisting of hardened cement paste or mortar [15,19–22], in which both the microstructure and, in particular, the damage mechanisms can differ significantly from those in concrete. A distinctive feature of the present study is therefore the use of a single-sided  $^1\text{H}$  NMR system, which enables the investigation of real macroscopic specimens from the “capillary suction, internal damage and freeze-thaw” (CIF) test [23]. However, the combination of a single-sided measurement setup with an inhomogeneous magnetic field, the inherently heterogeneous nature of concrete, and the use of gray cements with high paramagnetic components is challenging [24–28].

Previous studies using single-sided  $^1\text{H}$  NMR devices have already investigated moisture distributions in concretes made with ordinary Portland cement [29] or other building materials [30,31]. However, the combined analysis of frost-induced moisture distributions and microstructural alterations in macroscopic specimens by means of single-sided  $^1\text{H}$  NMR has, to the authors' knowledge, been addressed only in [32] to date. A key novelty of the present work lies in the determination of the depth-dependent progression of frost-induced damage in concrete. At the same time, the study identifies parameters of the method that require further optimization to improve its reliability and significance.

## 2. Materials and methods

### 2.1. Sample preparation

Within this study, six concrete compositions were investigated covering a broad range of pore structures and freeze-thaw resistance. The concretes whose exact compositions are summarized in Table 1, differed in terms of cement type, water-to-cement ratio (w/c ratio), and cement content, with a comparable paste content.

Three cements, complying with the requirements of DIN EN 197-1 [33], were used: an ordinary Portland cement (CEM I), a Portland-composite cement (CEM II/B), and a blast-furnace slag cement (CEM III/A). Before mixing, the aggregates were dried at 105 °C for at least 24 h, and the water demand of the aggregates was added to the mixing water. Superplasticizers and workability-enhancing admixtures, both PCE-based, were used to achieve comparable consistency of the concrete mixes. To achieve a sufficiently high degree of damage at which actual alterations of the microstructure and differences in water uptake can be detected, no air-entraining agent was used. The water content of the admixtures was considered in the total water calculation for the w/c ratio when the admixture dosage exceeded 2.0 kg/m<sup>3</sup>. The concrete made of CEM III/A with a w/c ratio of 0.40 had a slightly lower actual w/c ratio than calculated. Therefore, this concrete composition is marked in the following with an additional \*.

The specimens were cast according to CEN/TR 15177 [23] in steel molds with PTFE inserts, demolded after 1 day, and stored in tap water for 6 days. At the age of 7 days, the geometry of the exposed surface was reduced from 150 mm × 140 mm to 150 mm × 110 mm by saw cutting. Subsequently, the specimens were stored at 20 °C and 65% relative humidity until the start of the freeze–thaw testing at an age of 28 days. Table 2 presents the flow diameter determined according to DIN EN 12350-5 [34] and the air content according to DIN EN 12350-7 [35]. The compressive strength, determined in accordance with DIN EN 12390-3 [36], was measured on three cubes per composition at 28 days in dry state and converted into  $f_{c,cube}$ .

### 2.2. CIF-Test

Freeze-thaw testing of the specimens was carried out with demineralized water using the CIF test following CEN/TR 15177 [23] and CEN/TS 12390-9 [37]. At an age of 25 days, the specimens were sealed on the lateral surfaces using primer and aluminum–butyl rubber tape. At 28 days, pre-saturation was initiated by capillary suction at 20 °C. At 35 days, the freeze–thaw testing commenced, comprising a total of 56 freeze-thaw cycles (FTC) between 20 °C and –20 °C. At regular intervals, the relative dynamic modulus of elasticity (RDME), surface scaling, and water uptake were determined. The RDME was measured using ultrasonic pulse velocity in water, with the measurement performed only along the long side due to the specimen geometry. Seven specimens per composition were tested for CEM I and CEM II/B, and six specimens for CEM III/A. At each measurement interval, one specimen per composition was removed from the CIF-chamber for subsequent  $^1\text{H}$  NMR measurements. Table 3 presents the measurement intervals and the corresponding number of specimens used for the determination of RDME, surface scaling, and water uptake. Concretes with the same cement type were tested simultaneously.

### 2.3. $^1\text{H}$ NMR measurements

#### 2.3.1. Measuring principle

The measuring principle of proton nuclear magnetic resonance ( $^1\text{H}$  NMR) is based on the alignment and subsequent relaxation of atomic spins under the influence of an external magnetic field. After the magnetic field is removed, the proton spins relax, emitting a voltage that is detectable as a signal. The signal intensity (SI) decreases over time until equilibrium is re-established. The initial nuclear magnetization, i.e., the

**Table 1**Mix design of the tested concrete compositions, components in kg/m<sup>3</sup>.

| composition     | cement type             | w/c ratio | cement content | 0–2 mm | 2–8 mm | 8–16 mm | SP <sup>1)</sup> | WEA <sup>2)</sup> |
|-----------------|-------------------------|-----------|----------------|--------|--------|---------|------------------|-------------------|
| CEM I-0.40      | CEM I 42.5R             | 0.40      | 350            | 688    | 465    | 751     | 2.98             | -                 |
| CEM I-0.50      | CEM I 42.5R             | 0.50      | 320            | 679    | 459    | 740     | 2.34             | -                 |
| CEM II/B-0.40   | CEM II/B-M (S-LL) 42.5R | 0.40      | 350            | 686    | 464    | 748     | 2.49             | 1.75              |
| CEM II/B-0.50   | CEM II/B-M (S-LL) 42.5R | 0.50      | 320            | 677    | 458    | 738     | 2.60             | -                 |
| CEM III/A-0.40* | CEM III/A 42.5N         | 0.40      | 350            | 684    | 463    | 746     | 1.62             | 1.75              |
| CEM III/A-0.50  | CEM III/A 42.5N         | 0.50      | 320            | 675    | 456    | 736     | 1.16             | -                 |

\* w/c ratio of CEM III/A-0.40 was actually slightly smaller <sup>1)</sup> SP = superplasticizer; <sup>2)</sup> WEA = workability enhancing admixture**Table 2**

Properties of fresh and hardened concrete.

| composition       | flow diameter | air content | $f_{c,cube, 28d}$ |
|-------------------|---------------|-------------|-------------------|
|                   | mm            | Vol.-%      | N/mm <sup>2</sup> |
| CEM I – 0.40      | 410           | 2.2         | 69.6 ± 0.3        |
| CEM I – 0.50      | 420           | 2.2         | 51.7 ± 0.4        |
| CEM II/B – 0.40   | 390           | 3.2         | 62.4 ± 1.1        |
| CEM II/B – 0.50   | 440           | 2.2         | 48.3 ± 0.5        |
| CEM III/A – 0.40* | 370           | 2.9         | 67.3 ± 0.6        |
| CEM III/A – 0.50  | 400           | 2.6         | 47.0 ± 0.1        |

SI at the beginning of the decay, is proportional to the hydrogen proton content within the measured volume, thereby providing information about the moisture content. The decay rate of the signal depends on the interaction of the protons with the pore walls. Smaller pores lead to faster relaxation due to higher surface interaction. Assuming fully saturated pores, the transverse relaxation time  $T_2$  therefore provides information on the pore size distribution.

### 2.3.2. Sample preparation and measurement procedure

At the measurement times shown in Table 3, the SI was analyzed for moisture content determination with a measurement duration of approximately 1.5 h per specimen. On the following day, the specimens were vacuum-saturated and subsequently stored in demineralized water for 6–8 days. This was followed by the determination of the relaxation behavior for pore size distribution with a measurement duration of approximately 24 h. To prevent drying during the measurements, the specimens were placed in an LD-PE bag (thickness approximately 50  $\mu$ m).

In parallel with the SI determination on the frost-exposed specimens, reference measurements were performed for the CEM I and CEM II/B compositions on specimens of the same concrete, which were only subjected to capillary water uptake without freezing. Measurements on the reference specimens were consistently performed on the same specimens, whereas measurements on the freeze–thaw–exposed specimens were carried out on different specimens at each measurement interval. In addition, for referencing the SI of the specimen to a moisture content, a saturated  $\text{CuSO}_4$  solution was measured with the same measurement parameters. The measurements of the relaxation behavior for the undamaged state for CEM I and CEM II/B were determined on the sawn surface of the cut-off residues.

A measurement of the dry specimen at 28 days was not performed, as no reliable results were expected due to the high scatter of specimens with low moisture. Therefore, the first  $^1\text{H}$  NMR measurements for CEM II/B and CEM III/A were carried out after 7 days of pre-saturation. For

the CEM I specimens, the first  $^1\text{H}$  NMR measurement took place after 4 additional days of capillary suction.

### 2.3.3. Measurement device and parameters

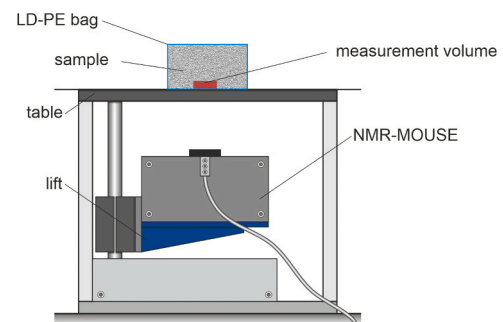
The measurements were performed using an NMR MOUSE<sup>®</sup> PM 25 by Magritek with a 25–10 spacer configuration, which allows a maximum measurement depth of 15 mm. Fig. 1 shows the measurement device and the test setup schematically.

For all measurements, CPMG sequences [38,39] were used, applying the measurement parameters listed in Table 4. The spatial resolution was 0.1 mm for all tests. The obtained signal decay curves represent the mean values of the number of scans specified in Table 4.

For the determination of moisture content based on the SI, only a small number of echoes is required. The number of echoes was therefore selected based on the required repetition time. For the  $T_2$  relaxation time measurements aimed at determining the pore size distribution, the entire signal had to be recorded. Hence, the number of echoes was chosen such that the signal had decayed to the order of the noise level.

In single-sided  $^1\text{H}$  NMR devices, the first echoes of decay curves often exhibit either underestimated or overestimated SI due to imperfect flip-angle distributions of the radio-frequency pulses [40]. Therefore, in such systems, the first one or two echoes are commonly excluded from interpretation [41,42]. For the measurements performed on  $\text{CuSO}_4$  solution, the first two echoes were discarded. The signal decay curves obtained from the concrete specimens showed a continuous decrease starting from the second echo. Consequently, for the determination of the initial SI and the  $T_2$  relaxation times of the concrete samples, only the first echo was omitted.

For CEM I and CEM III/A, the SI measurements were performed at ten graduated depths (see Table 5), while the  $T_2$  relaxation measurements were conducted at depths of 10 mm, 5 mm, and 1.5 mm. Based on

**Fig. 1.** Schematic test setup of  $^1\text{H}$  NMR measurements, not to scale.**Table 3**

Number of specimens at the respective number of freeze-thaw cycles (FTC) for the determination of RDME, surface scaling, and water uptake.

| Cement type | 4 | 8 | 10 | 14 | 28 | 34 | 38 | 42 | 48 | 52 | 56 |
|-------------|---|---|----|----|----|----|----|----|----|----|----|
| CEM I       | 7 | 7 | -  | 6  | 6  | 5  | -  | 4  | 3  | -  | 2  |
| CEM II/B    | 7 | - | 7  | 6  | 5  | -  | 4  | 3  | -  | 2  | 1  |
| CEM III/A   | 6 | - | 6  | 5  | 4  | -  | 3  | 3  | -  | 2  | 1  |

**Table 4**Parameters of the  $^1\text{H}$  NMR setup of the two measurements.

| Determination of                                                     | Repetition time (ms) | No. of Echoes | Nr. of Scans (CEM I and CEM III/A) | Nr. of Scans (CEM II/B) |
|----------------------------------------------------------------------|----------------------|---------------|------------------------------------|-------------------------|
| Initial signal intensity (after extraction from freeze-thaw chamber) | 550                  | 50            | 720                                | 1024                    |
| $T_2$ relaxation behavior (after vacuum saturation)                  | 40.000               | 3700          | 720                                | 1024                    |

**Table 5**

Depths of the initial signal intensity measurements for the determination of moisture content.

| Cement type         | Measurement depths (mm)                  |
|---------------------|------------------------------------------|
| CEM I and CEM III/A | 15 – 13 – 11 – 9 – 7 – 5 – 4 – 3 – 2 – 1 |
| CEM II/B            | 15 – 12 – 9 – 7 – 5 – 4 – 3 – 2 – 1      |

the results of these measurements, the number of measurement depths for CEM II/B series was reduced to nine depths for the SI (see Table 5) and two depths for the  $T_2$  relaxation times (10 mm and 1.5 mm), to increase the possible number of scans (see Table 4). All measurements were conducted from the interior toward the exterior, i.e., from the greatest to the smallest depth. In addition, measurements were performed at depths of 0.2 mm or 0.1 mm; however, these exhibited such a high variability that no meaningful information could be obtained, and they are therefore omitted here.

#### 2.3.4. Data evaluation

The pore size distribution derived from relaxation curves is commonly determined using an Inverse Laplace Transformation (ILT) [43,44]. However, this method is highly sensitive to noise and requires the selection of an appropriate smoothing parameter.

The present data show considerable scattering due to material heterogeneity and measurement noise. The signal-to-noise ratio (SNR) was determined as the ratio of the amplitude of the second echo to the imaginary part of the total signal and ranged between approximately 10 and 50 (exception: CEM II/B-0.40 at 1 mm with lower SNR). For the reference measurement using the  $\text{CuSO}_4$  solution (calculated as the ratio of the third echo to the imaginary part of the total signal), the SNR was between 40 and 75.

Since ILT analysis with such high scatter would require a specific smoothing parameter for each measurement to gain reliable results, a tri-exponential fitting approach was adopted instead (Eq. 1). This approach is more robust to data scattering and provides sufficient accuracy for the present dataset while improving comparability between samples. The total signal over time  $t$  is modeled as the sum of three exponential decays characterized by their respective  $T_2$  times  $T_{2,i}$  and amplitudes  $A_i$ . The selection of three components was based on literature [15,28,45] and supplementary ILT analyses.

$$SI(t) = \sum_{i=1}^3 A_i e^{-\left(\frac{t}{T_{2,i}}\right)} \quad (1)$$

Higher  $T_2$  values correspond to larger pores, while higher amplitudes indicate a greater hydrogen content and thus higher moisture content within these pores. The conversion of  $T_2$  times into a pore radius  $r$ , i.e., the ratio of volume  $V$  to surface area  $S$ , can be performed according to Eq. 2, depending on the surface relaxivity  $\rho_2$ . This parameter depends, among others, on the pore geometry (represented by the factor  $n$  in Eq. 2), the cement type, including its para- and ferromagnetic constituents, and the general test setup [24,46,47].

$$\frac{1}{T_2} = \rho_2 \frac{S}{V} = \rho_2 \frac{n}{r} \quad (2)$$

Values of  $\rho_2$  reported in the literature typically range between 1 and 10 nm/ms, although these values are usually derived from measurements on white cement and/or closed low-field  $^1\text{H}$  NMR systems [46, 48–50]. Since only a few studies have determined  $\rho_2$  in concretes made from gray cement using single-sided  $^1\text{H}$  NMR setups [24,51], a quantitative pore size determination remains subject to considerable uncertainty. Therefore, no absolute pore sizes are provided in this study. Instead, the data are classified into small, medium, and large pores. Depending on the approach, these categories approximately correspond to the ranges of gel pores, smaller capillaries or interhydrate pores, e.g. spaces between the C-S-H needles, and larger capillaries [24,52].

Freeze–thaw–induced alterations of the microstructure are primarily caused by microcracking [15,53]. However, since most methods for analyzing the concrete microstructure focus on pore size distribution, freeze–thaw damage is often described as an increase of porosity or a coarsening of the pore structure [15,22,32,54,55]. Furthermore, differentiating  $T_2$  relaxation times between pores and microcracks would require additional information on their geometry and distinct relaxation behavior. For convenience, in the present study, microstructural alterations resulting from microcracking are therefore classified according to pore size ranges.

### 3. Results and discussion

#### 3.1. Relative dynamic modulus of elasticity, scaling, and water uptake

To contextualize the  $^1\text{H}$  NMR results on water uptake and alterations in microstructure, the macroscopic results of the CIF test are presented. Fig. 2 shows the decrease in the RDME and the surface-related scaling mass during the freeze-thaw test. Fig. 3 illustrates the water uptake of the CIF specimens (left) and of the reference specimens made from CEM I and CEM II/B (right), which were exposed exclusively to capillary suction throughout the entire test duration.

The curves of the CIF specimens (Fig. 2 and Fig. 3, left) represent the mean values of the number of specimens listed in Table 3. Because the number of specimens varies between measurement times, the standard deviations differ considerably in their statistical reliability and are therefore not reported here. The curves in Fig. 3, right each correspond to repeated measurements of the same specimen.

As intended in the experimental design, the investigated concretes are of very different frost resistance. After 56 FTC, the RDME varies between approximately 20% and 84%, while the scaling mass ranges between 0.13 kg/m<sup>2</sup> and 0.65 kg/m<sup>2</sup>. Within each cement type, concretes with higher w/c ratios consistently show lower frost resistance. As is well known, the different damage parameters RDEM and scaling generally do not correlate [53]. Therefore, no clear ranking of frost resistance can be established among the three cement types when considering both damage parameters. For example, concretes made with CEM II/B show a pronounced decrease in RDME while exhibiting the lowest surface scaling compared to CEM I and CEM III/A.

Regarding water uptake, the largest differences between the compositions were observed during the initial days of capillary pre-saturation, after which the curves converged toward a similar asymptotic behavior. During freeze–thaw exposure, the curves exhibited a concave trend, further amplifying the differences between the compositions. As expected, specimens subjected exclusively to capillary suction showed a significantly lower water uptake throughout the test period and maintained an asymptotic progression over the entire duration.

#### 3.2. Signal intensity and moisture content by $^1\text{H}$ NMR

The SI of the tested concretes are presented in Fig. 4 and Fig. 5. The SI values are normalized with respect to the SI of a  $\text{CuSO}_4$  solution

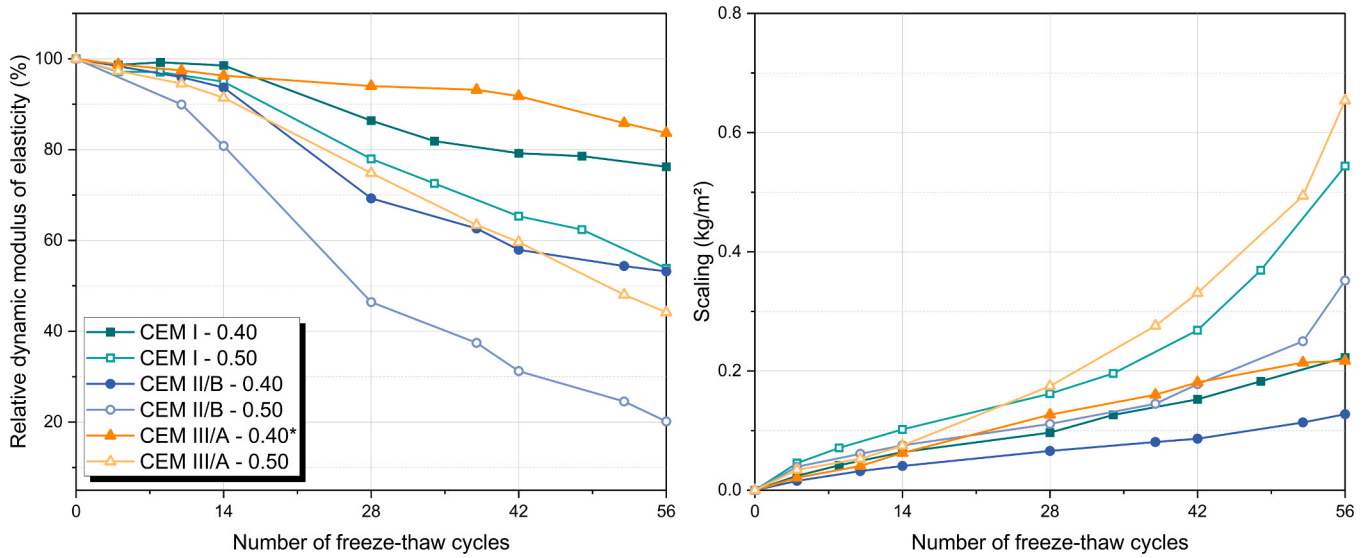


Fig. 2. RDME (left) and scaling (right) during CIF-test.

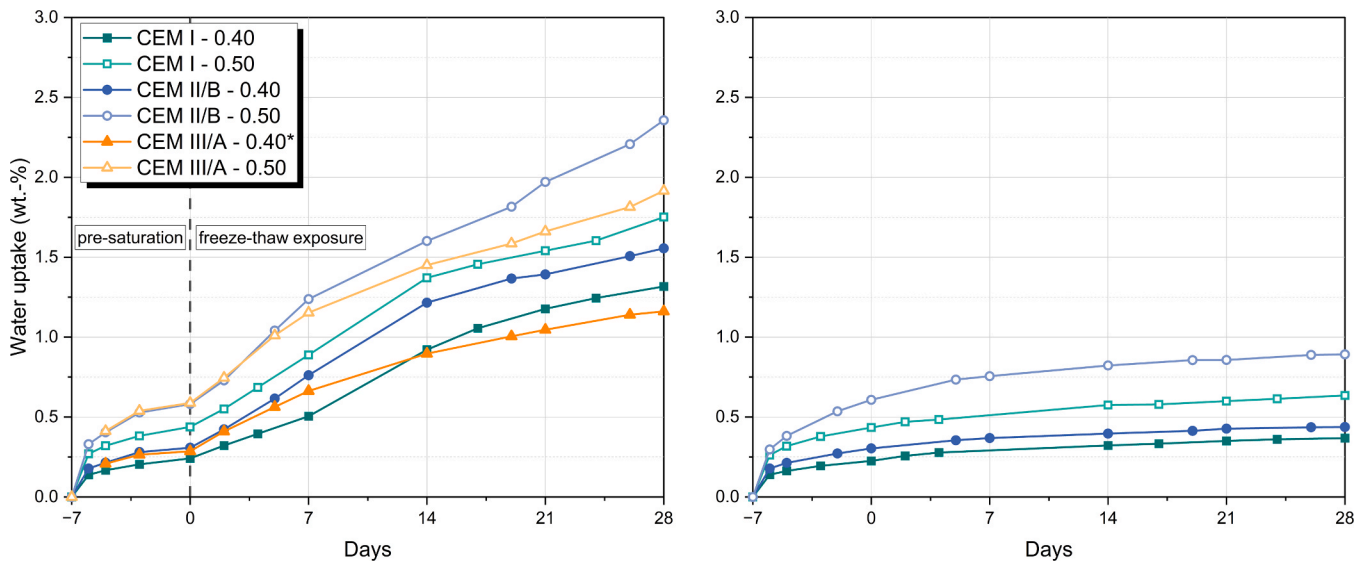


Fig. 3. Left: Water uptake of the specimens exposed to freeze-thaw cycles; Right: water uptake of specimens only exposed to capillary suction.

reference sample, in which the entire measurement volume consists of saturated liquid. The resulting ratios  $SI/SI_{CuSO_4}$ , therefore, represent the total water content within the investigated measurement volume.

Assuming that the examined volumes of  $40 \times 40 \times 0.1 \text{ mm}^3$  contain a comparable paste content, differences in the relative SI values can be interpreted as differences in relative moisture content. However, it must be noted that for the frost-exposed specimens (see Fig. 5), different samples were measured, and thus local variations in the paste and aggregate content may occur that can lead to different total moisture content.

Fig. 4 shows the SI of the CEM I- and CEM II/B-specimens that remained exposed to capillary suction without freezing for the same time span as the CIF test duration.

The SI values of the four investigated concretes are comparable in magnitude and vary, depending on the composition, between 0 and 0.15, with maxima ranging from 0.07 to 0.15. A clear influence of the composition is observable. Higher SI values are observed in compositions with higher w/c ratios. This can be attributed to the larger total pore volume and the greater proportion of capillary pores. Concretes made with CEM II/B tend to exhibit slightly higher SI than those made

with CEM I, which can be partly explained by the lower degree of hydration and the higher amount of inert components, both resulting in a higher porosity.

The SI of the specimens exposed to capillary suction change only slightly over time. For CEM I in particular, the curves are very closely clustered, indicating only minor variations in moisture content. For CEM I-0.40, no clear trend with increasing exposure duration can be identified, as the SI values at different measurement times are very similar. Consequently, both increases and decreases in SI over time are observed.

Concretes made with CEM II/B show slightly different trends compared to those made with CEM I. For CEM II/B-0.40, SI decreases within the investigated depth range as exposure duration increases. In CEM II/B-0.50, a more pronounced decrease is observed near the surface, extending to approximately 6 mm, whereas higher SI values are measured in deeper regions at later measurement times. However, these developments do not display a consistently uniform trend, which is also attributable to the very similar SI values over the entire measurement period.

In general, higher SI values are observed near the specimen edges, reflecting the direction of capillary water transport. An exception is the

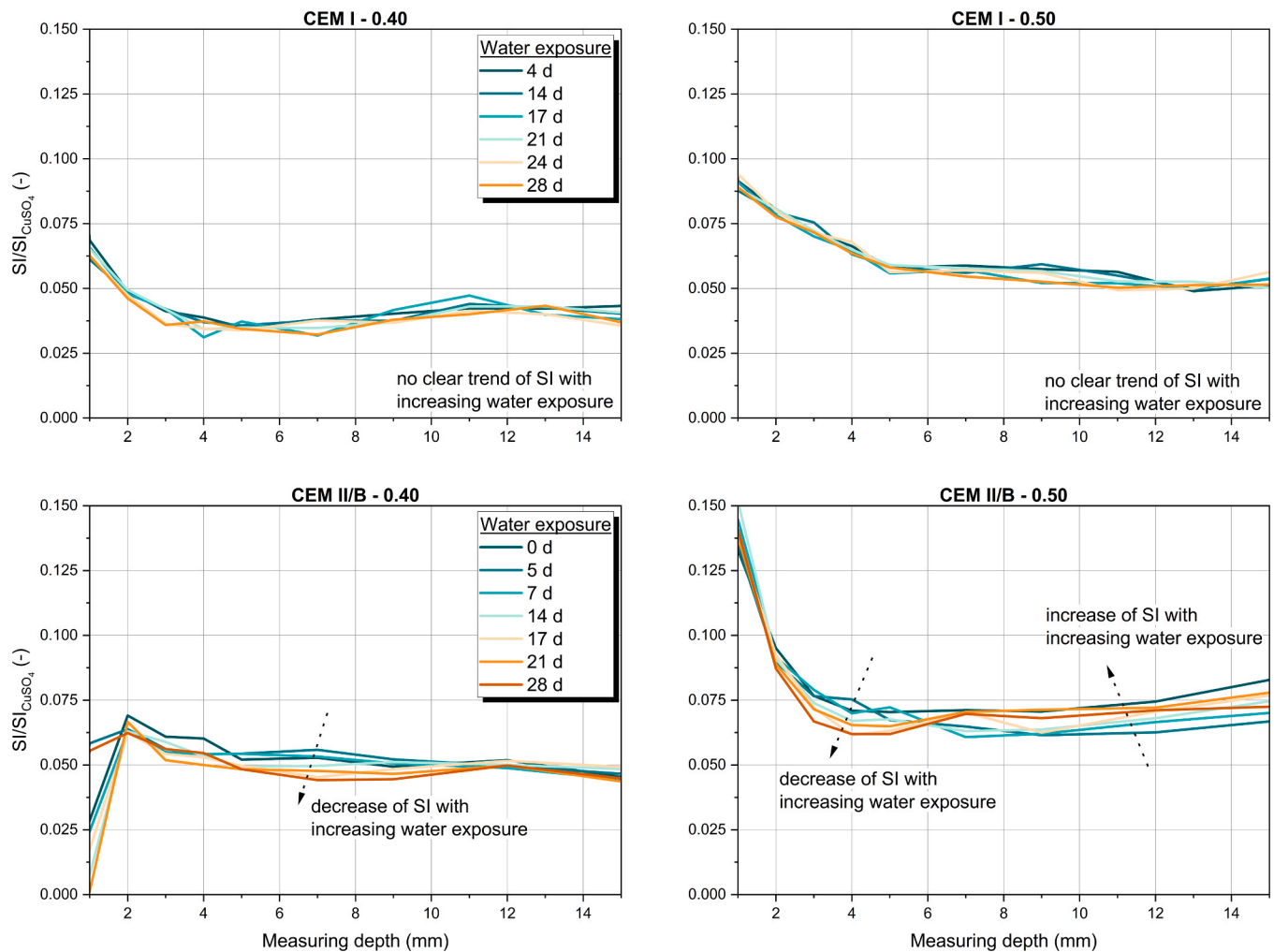


**Fig. 4.** Signal intensity of the specimens only subjected to water exposure without freezing; duration of water uptake is calculated beginning after the initial capillary suction of 7 days.

specimen of CEM II/B-0.40, which shows lower SI within the first 2 mm, likely due to slight surface unevenness. Overall, SI decreases with increasing measurement depth. However, for CEM I-0.40 and CEM II/B-0.50, SI partially increases again at greater depths.

Overall, specimens that were exclusively exposed to capillary suction exhibit only minor temporal changes in SI and, thus, in moisture distribution. These observations correlate with the small overall increase in moisture determined for the entire specimen after the initial 7-day pre-exposure (Fig. 3, right).

Fig. 5 shows the SI of the frost-exposed specimens. As a reference for the undamaged state (0 FTC), the measurements of the unfrozen specimens at an age of 39 days for CEM I and at 35 days for CEM II/B and CEM III/A are included.

The SI of the freeze-thaw exposed specimens vary between 0.04 and 0.36, with maxima ranging from 0.11 and 0.36 (maximum not shown in Fig. 5). As already observed for the specimen only exposed to capillary suction, the SI differ between the individual compositions depending on the cement type and w/c ratio.

The 0.50-compositions consistently exhibit higher SI than the 0.40-compositions. This behavior can be attributed to three main factors. The first factor concerns the general pore structure, which has already been discussed previously. Second, the micro ice-lens pump, as a main reason for water uptake during freeze-thaw exposure, is more pronounced in compositions with higher w/c ratios and therefore leads to a higher moisture content [56]. And third, the 0.50-compositions show more pronounced frost damage than the 0.40-compositions (see Fig. 2).

The higher SI may therefore also result from the presence of cracks and additional pore connections, which provide more space for water accumulation. The latter two factors also explain why the differences between the 0.50 compositions and 0.40 compositions are more pronounced in the frost-exposed specimens than in those exposed solely to capillary suction.

The frost-exposed specimens show an increase in SI with a higher number of FTC. This increase occurs primarily near the surface but is also observable at greater depths. However, due to variations resulting from measurements on different specimens, a fully consistent trend is not apparent. Nevertheless, almost all compositions exhibit higher SI values after 56 FTC compared to the state before freezing. An exception is CEM III/A-0.40\*, which shows lower SI values after freezing, particularly in the depth range between 4 and 12 mm. However, this concrete also shows the lowest decrease in RDME (see Fig. 2, left) and the smallest increase in global water uptake (see Fig. 3, left), leading to very similar SI.

CEM II/B-0.50 exhibits a disproportionately strong increase in SI near the surface with increasing numbers of FTC. This pronounced water uptake is also reflected in the CIF results of water absorption (see Fig. 3, left). However, this composition already shows significantly higher water absorption in the unfrozen state compared to the other compositions (see Fig. 3, right). Furthermore, it is evident that all specimens of this concrete, regardless of the duration of freezing or capillary suction, consistently show much higher SI near the surface than the specimens of the other compositions.

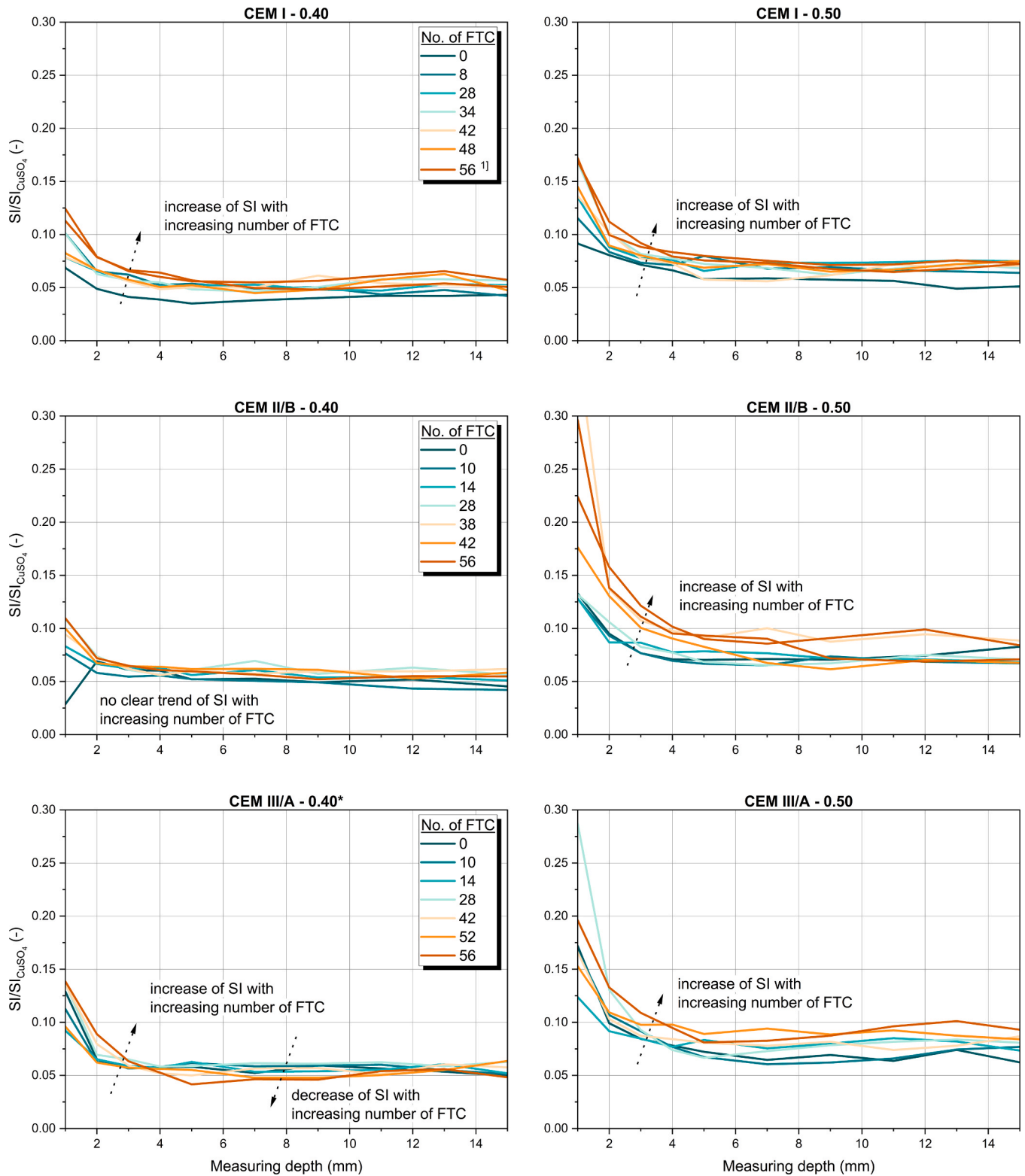


Fig. 5. Signal intensity of freeze-thaw exposed specimen; <sup>1)</sup> for CEM I, two specimens were tested at an age of 56 days.

In general, the increase in SI detected by <sup>1</sup>H NMR correlates well with the global water uptake determined from the CIF test. Compositions with higher water absorption also show a greater increase in SI.

For all compositions, frost-induced water uptake was detected down to the maximum measurement depth of 15 mm. This effect is more pronounced for concretes with low frost resistance, as seen for example in CEM II/B-0.50 and CEM III/A-0.50 in Fig. 5. In [57], a shift of the

maximum SI towards greater depths was observed by the authors for heavily damaged specimens. A comparable observation could not be made in the present study. This difference is mainly attributed to the amount of material scaling. In [57], concretes with a w/c ratio of 0.60 were used, exhibiting scaling up to approximately 2.0 kg/m<sup>2</sup>, whereas the maximum scaling observed in this study was about 0.65 kg/m<sup>2</sup>. Nevertheless, with increasing freeze-thaw exposure, a progressive

saturation of the near-surface concrete becomes evident, gradually extending into deeper regions.

### 3.3. $T_2$ relaxation times and pore size distribution by $^1\text{H}$ NMR

In figures Fig. 6, Fig. 7, and Fig. 8, the signal decay curves obtained from the  $T_2$  relaxation measurements on the saturated specimens, decomposed using a tri-exponential fit, are presented. The determined  $T_2$  relaxation times and the corresponding amplitudes are shown for measurement depths of 1.5 mm (left) and 10 mm (right).

The  $T_2$  values of the smallest pore class range from 0.19 to 0.7 ms, those of the medium pore class from 1 to 15 ms, and those of the largest pore class from 65 to 135 ms. Differences can be observed between w/c ratios, cement types, measurement depths, pore classes, and exposure durations, with variations present in both the  $T_2$  values and the corresponding amplitudes.

In general, for each cement type, the composition with a w/c ratio of 0.50 exhibit higher amplitudes than the 0.40-composition. As already discussed in Section 3.2 with regard to the SI results, this can primarily be attributed to the larger overall pore volume as well as a higher proportion and larger sizes of capillary pores. However, a few exceptions caused by outliers deviate from this overall trend. For example, Fig. 6 (left) shows a comparably high amplitude for the small pore class for the 0.40 composition at 34 FTC, whereas a rather low amplitude is observed for the 0.50 composition at 0 FTC.

With respect to the cement types, the most pronounced differences are observed in the  $T_2$  values. In addition to variations in the microstructure, these differences are likely related to the distinct surface relaxivities of the individual cements, which, however, were not investigated in detail within the scope of the present study.

The amplitudes at a measurement depth of 10 mm are, on average, lower than those measured at 1.5 mm. Smaller amplitudes generally correspond to a lower amount of water within the pores. Provided that the entire measurement range up to 10 mm was saturated during the vacuum saturation process, these differences are primarily attributed to variations in the microstructure. The near-surface region usually contains a higher proportion of hardened cement paste than deeper zones and therefore more capillary pores. Moreover, air storage of the samples prior to capillary suction may have resulted in a lower degree of hydration in the near-surface region and, additionally, in more micro-cracks that became filled with water during saturation.

Differences between the measurement depths increase with freeze-thaw exposure. For the undamaged samples (0 FTC) of the CEM I and CEM II/B compositions (see Fig. 6 and Fig. 7), only minor variations between depths are observed. Measurements conducted after distinct frost exposure show increasing differences between the depths. This indicates that, at later stages, a more pronounced damage gradient has developed compared to the beginning of the freezing period. These observations therefore enable the temporal evolution of the damage gradient, as discussed in the following Section 3.4.

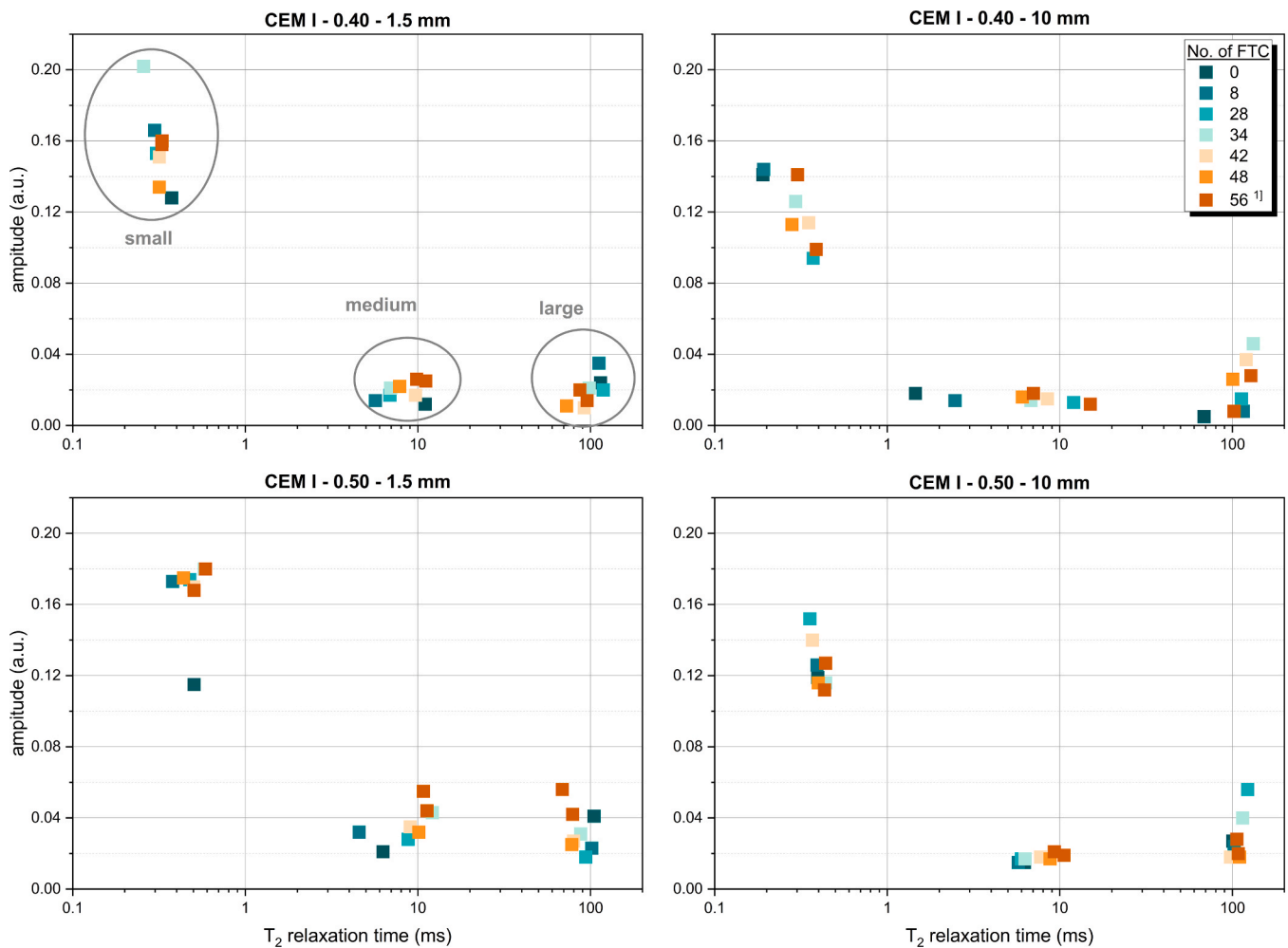


Fig. 6.  $T_2$  relaxation times and corresponding amplitudes of CEM I determined on saturated samples,  $^1$ ) two specimens were tested at an age of 56 days.

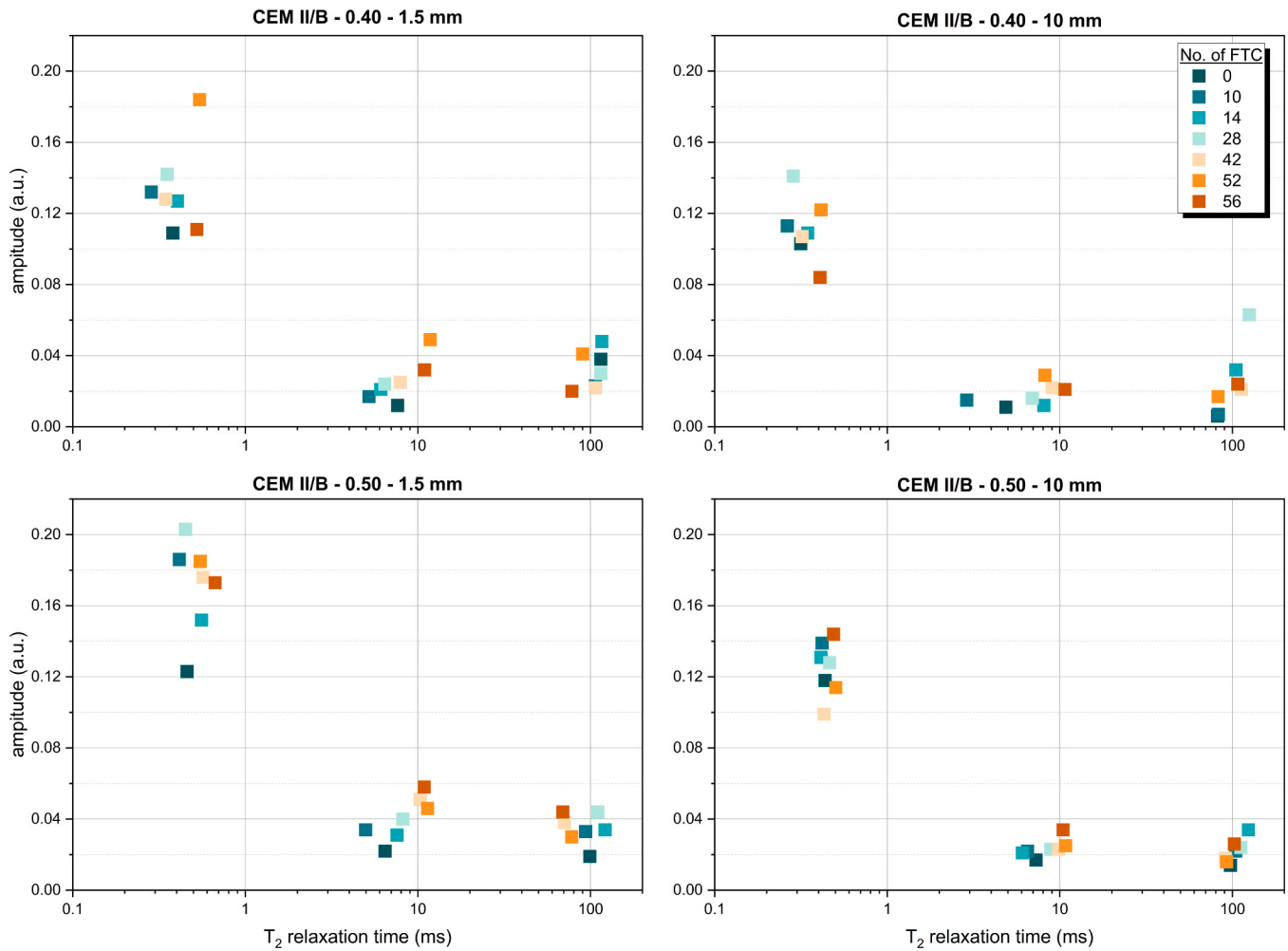


Fig. 7.  $T_2$  relaxation times and corresponding amplitudes of CEM II/B determined on saturated samples.

With regard to the influence of freezing duration on the microstructure within the same measurement depth, a distinction must be made between the three **pore classes**.

For the smallest pore class, no clear trends can be identified. The measurement results appear highly scattered and show neither a continuous change nor a general tendency with increasing freezing duration. Both increases and decreases in  $T_2$  times and amplitudes are observed. Some concretes, such as CEM I-0.50 in a depth of 1.5 mm (see Fig. 6, bottom left), exhibit very similar amplitudes over the number of FTC. In contrast, measurements such as CEM III/A-0.40\*10 mm (Fig. 8, top right) and CEM III/A-0.50–10 mm (Fig. 8, bottom right), show a high degree of variability.

The medium pore class exhibits the clearest trends with respect to frost-induced alterations in the microstructure compared to the other pore classes. With increasing exposure to freezing, both an increase in  $T_2$  times, indicating a coarsening of the microstructure, and an increase in amplitude, indicating an increase in pore volume, are observed. However, occasional outliers interrupt the continuity of the increase of  $T_2$  times and amplitudes with increasing freezing. The increases are more pronounced for compositions that show a higher decrease in RDME (see Fig. 2, left), for example CEM II/B compared to CEM I and CEM III/A as well as the 0.50-compositions compared to the 0.40-compositions. Thus, the frost-induced alteration of this pore class detected by  $^1\text{H}$  NMR correlates well with the established damage criterion based on RDME.

For the largest pore class, slightly reduced  $T_2$  times are observed with increasing number of FTC. This effect is particularly pronounced at the measurement depth of 1.5 mm. Regarding the amplitudes, both increases and decreases are detected without any discernible correlation to the number of FTC. As this largest pore class is assumed to represent larger capillaries and even cracks, it is expected that the biggest alterations in microstructure occur in this pore class. Such results were obtained by the authors in [58]. The deviation between these findings may be attributed to differences in the experimental setup. In [58], the damaged specimens were immersed in water throughout the entire measurement, allowing the damaged area to become saturated with water, which resulted in higher signal amplitudes. In contrast, in the present study, the specimens were placed in LD-PE bags during the  $^1\text{H}$  NMR measurements, so no additional water ingress occurred.

The results show both consistencies and discrepancies compared to previous studies in which microstructural alterations induced by freeze–thaw exposure were investigated using  $^1\text{H}$  NMR. In general, freeze–thaw attack causes microcracking, described by an increase in porosity, which is reflected by higher signal amplitudes and longer  $T_2$  relaxation times [15, 22,32,54]. However, the contribution of the respective pore classes varies among the studies. In [15], the most pronounced alterations, namely an increase in  $T_2$  relaxation times, were observed for the smallest pore class, with  $T_2$  times of approximately 0.06–0.6 ms. In contrast, no distinct trends were identified for the pore class of these  $T_2$  relaxation times in the present

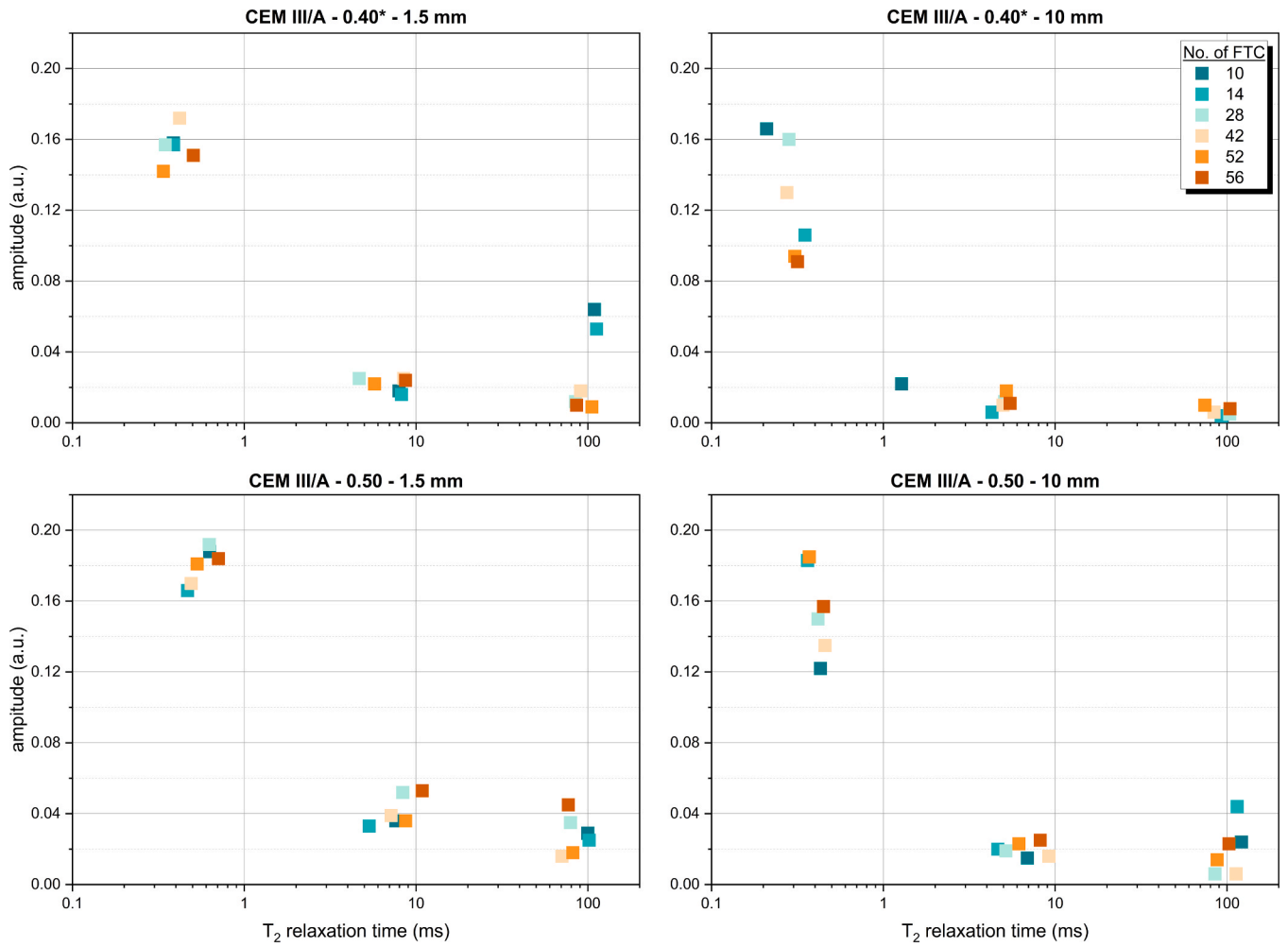


Fig. 8.  $T_2$  relaxation times and corresponding amplitudes of CEM III/A determined on saturated samples.

study. However, as in [15] a closed NMR setup was used, different correlations between  $T_2$  times and pore sizes are assumed. In [32] a comparable test setup to the present study was used to determine changes of microstructure due to combined freeze-thaw de-icing salt attack. There, the smaller pore class exhibited increases in both  $T_2$  relaxation time and signal

amplitude. Pores with  $T_2$  relaxation times of approximately 1 ms, which in the present study showed increases in both  $T_2$  relaxation time and amplitude, exhibited in [32] a reduction in amplitude accompanied by an increase in  $T_2$  relaxation time which may result from different saturation degrees of these samples.

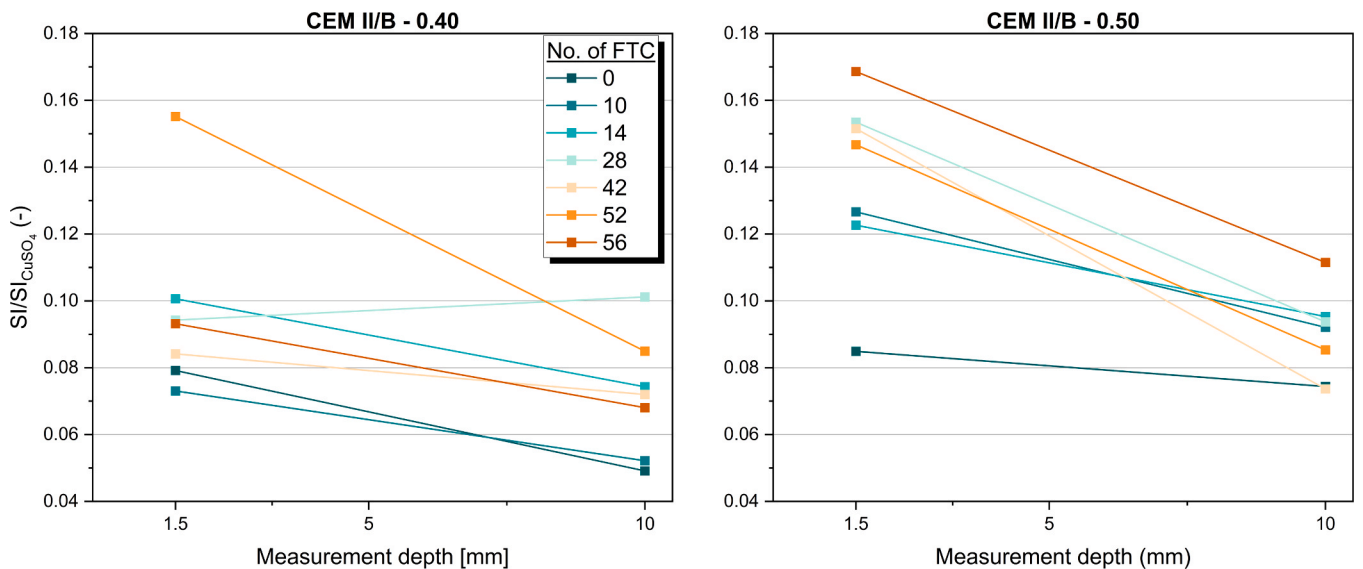


Fig. 9. Damage gradient as difference in signal intensity of the saturated freeze-thaw exposed specimens of CEM II/B.

### 3.4. Damage gradients

The initial SI of the saturated samples, which is identical to the sum of the amplitudes of all three pore classes (see Eq. 1), provides information about the total pore volume (including microcracks). The measurements at different depths therefore allow for the analysis of a depth-dependent damage gradient resulting from the freeze-thaw exposure. To clearly resolve such a gradient, a larger number of measurement depths would be required. However, in the present study, the term “damage gradient” refers to the different damage levels observed within the two to three depths investigated. Fig. 9 presents the SI of the saturated CEM II/B samples, referenced to the SI of a saturated  $\text{CuSO}_4$  sample, in the depths of 1.5 mm and 10 mm. Additionally, Fig. 10 shows the results for CEM I and CEM III/A, for which measurements were also conducted at a depth of 5 mm.

For all six concretes, the SI in the near-surface region are generally higher than those measured at greater depths. Even the undamaged specimens (0 FTC) exhibit this gradient. Since the measurements on the undamaged specimens (CEM I and CEM II/B) were conducted on the sawn surface, the general difference in pore structure between the surface and the inner concrete is not sufficient to explain the observed

gradient. For the compositions containing CEM II/B and CEM III/A, surface carbonation that may have occurred during drying before the freeze–thaw exposure could have contributed to this effect, as it can promote coarsening of the pore structure in these cement types [59–61].

With increasing freezing duration, the SI rise both in the near-surface region and in greater depth. This indicates that pore connections increase and microcracks are formed during the freezing process, which become filled during vacuum saturation. At the same time, the increase in SI near the surface (1.5 mm) is more pronounced than at depths of 5 mm and 10 mm, resulting in a steeper gradient. This effect is particularly evident in specimens exhibiting a greater reduction in RDME (see Fig. 2, left). The time-dependent depth gradient reflects the progression of freeze-thaw damage from the exposed surface into the interior of the concrete.

However, as outlined in the previous sections, the time-dependent changes do not follow a perfectly continuous trend; some specimens even exhibit lower SI after frost exposure than the unfrozen reference specimens. Additionally, when considering the measurement depth of 5 mm in Fig. 10, the damage gradient shows an inflection point that does not correspond to the expected behavior. Some measurements show higher SI at 5 mm compared to the surface region (see e.g. CEM I-0.50 at

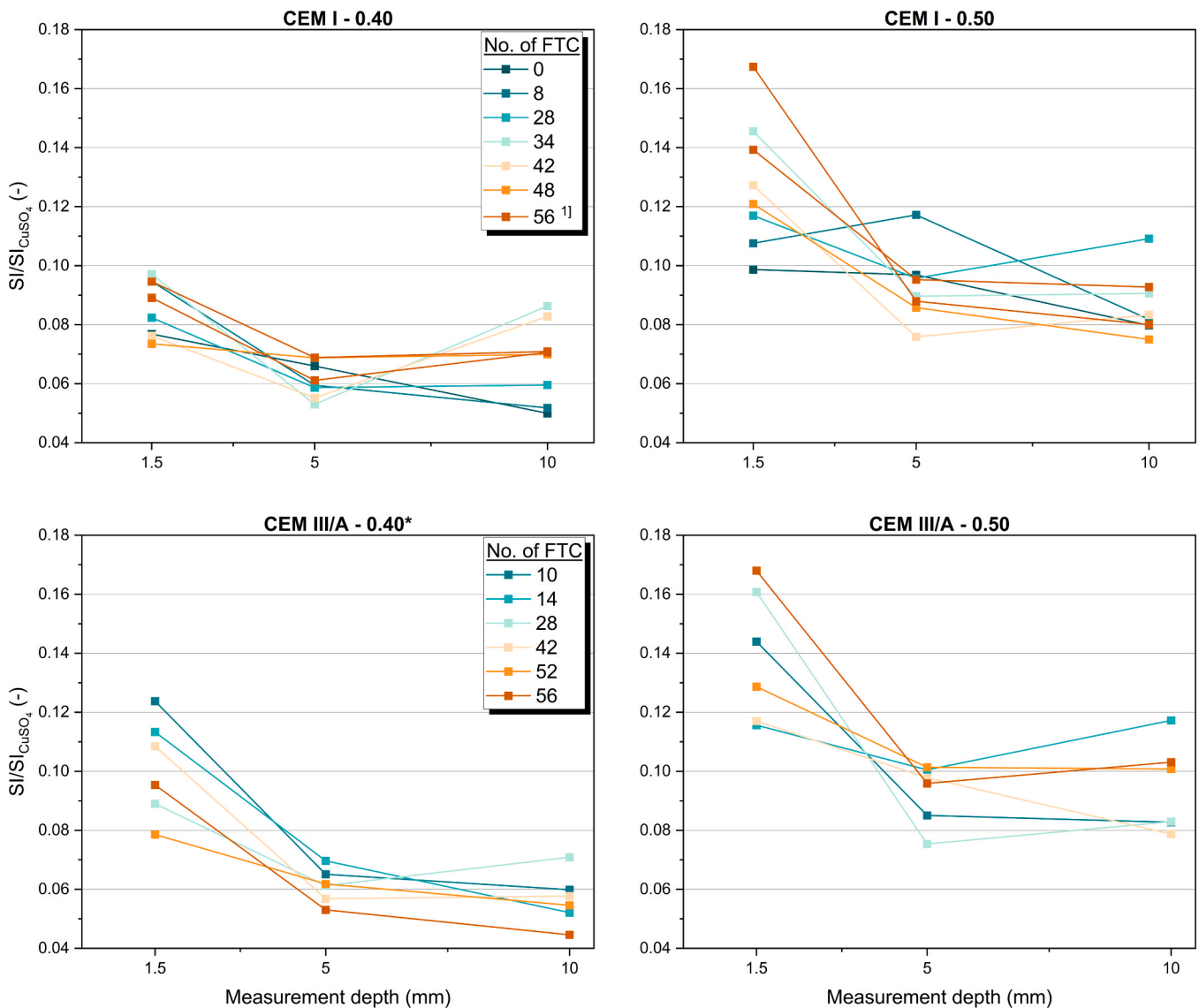


**Fig. 10.** Damage gradient as difference in signal intensity of the saturated freeze-thaw exposed specimens of CEM I and CEM III/A; <sup>1)</sup> for CEM I, two specimens were tested at an age of 56 days.

8 FTC), likely reflecting the inherent scatter in the data. Conversely, in other cases, SI at 5 mm is lower than at 10 mm (see e.g. CEM I-0.40 at 34 and 42 FTC), again deviating from the anticipated gradient. Since SI values at this depth are generally low, variations between individual samples have a proportionally greater impact than at the surface, which can result in apparent outliers. These observations highlight the need for further studies with an increased number of measurement depths to better resolve the gradient.

Despite these limitations, the applied procedure reveals discernable trends for concretes with low frost resistance, demonstrating its potential for quantifying time- and depth-dependent damage gradients. Further optimization will improve the reliability of the method, particularly for concretes with higher frost resistance.

#### 4. Conclusions

In this study, concretes of various compositions were subjected to freeze-thaw exposure in the CIF test, while  $^1\text{H}$  NMR measurements were simultaneously performed to analyze signal intensities and  $T_2$  relaxation times. This combined approach enabled the assessment of depth- and time-dependent frost-induced water uptake and the derivation of corresponding damage gradients.

Investigating macroscopic CIF specimens made from concretes containing cements with varying paramagnetic contents presents certain challenges for  $^1\text{H}$  NMR analysis. Despite these limitations, the method successfully captured frost-induced water uptake in comparison with purely capillary absorption. The water uptake detected by  $^1\text{H}$  NMR correlated well with the global water uptake determined in the CIF test and with the damage levels derived from the reduction of the RDME. Moreover, the  $^1\text{H}$  NMR measurements provided both temporal and spatial resolution of the moisture distribution.

The analysis of  $T_2$  relaxation time distributions and their corresponding amplitudes enabled the identification of the range of microstructure most affected by frost. The largest changes were found in pores with  $T_2$  times of approximately 1–15 ms, which can be associated with smaller capillary pores. Further investigations are, however, required to confirm this assignment.

Based on the signal intensities of saturated specimens, a depth-dependent damage gradient was determined as a function of freeze-thaw cycles. With increasing freeze-thaw exposure, the microstructural differences between the near-surface region and the inner zones became more pronounced, while results at an intermediate depth of 5 mm deviated from the expected trend. Steeper damage gradients correlated well with the global damage detected by RDME.

A secondary objective of the study was to identify potential improvements to the test setup to enhance result reliability. The following aspects were identified:

- The number of scans needs to be further increased to reduce data scatter, though the total measurement time must remain short enough to minimize moisture redistribution during scanning.
- The referencing procedure for determining the degree of saturation should be refined to account for variations in aggregate–paste ratios within the measurement volume and to remain independent of frost-induced alterations in the pore structure.
- To further reduce variability, the signal intensity should ideally be measured on the same specimen. This requires deviating from the standard CIF regime, which allows only a 1–2 h interval between freezing cycles, too short for extended  $^1\text{H}$  NMR scans.
- The number of measuring depths should be increased to allow a more detailed analysis of the damage gradient progression and, at the same time, to reduce the influence of the aggregates within the respective measuring depths.
- Within this study, freeze-thaw induced damage of non-air entrained concretes with a broad range of frost resistance was investigated. Further analyses of air-entrained concretes and combined freeze-

thaw de-icing salt attack may increase the applicability to practical conditions.

Considering these proposed improvements, the  $^1\text{H}$  NMR method proves to be a promising tool for determining depth- and time-dependent damage gradients resulting from frost exposure. This provides a sound basis for predicting the time- and spatial-dependent progression of frost-induced deterioration in concrete, which is essential for a practical service life assessment of concrete infrastructures.

#### CRedit authorship contribution statement

**Vanessa Mercedes Kind:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Sophie Unbehau:** Writing – review & editing, Conceptualization. **Matthias Müller:** Writing – review & editing, Supervision, Conceptualization. **Franka Pfirrmann:** Investigation. **Horst-Michael Ludwig:** Supervision, Funding acquisition. **Frank Dehn:** Writing – review & editing, Supervision, Funding acquisition.

#### Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work, the authors used ChatGPT-4 in order to improve the linguistic quality and readability of the English text. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Data availability

Data will be made available on request.

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