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NMR diffusion and relaxation studies during cement hydration—A non-destructive approach for clarification of the mechanism of internal post curing of cementitious materials

Karen Friedemann, Frank Stallmach *, Jörg Kärger

Abteilung Grenzflächenphysik, Fakultät für Physik und Geowissenschaften, Universität Leipzig, Linnèstasse 5, 04103 Leipzig, Germany

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Abstract

Internal post-curing of hardening cement pastes by addition of alginate spheres, which contain 98% of water, is studied by non-destructive ^{1}H NMR measurements of transverse relaxation time and self-diffusion. The onset and amount of water transition from the alginate gel used as additive with temporary delayed release of water to cement pastes was observed continuously during the dormant and accelerated period of cement hydration. During hydration, the water transition from the alginate into the cement matrix as well as the development of pore size is monitored quantitatively by studying the time dependence of characteristic peaks in the transverse relaxation time distribution. Comparison between samples without and with internal post curing shows that the addition of alginate gel does not influence the pore size in the micropore region. NMR diffusion studies demonstrate that the physically bound pore water has sufficient mobility to ensure homogeneous distribution of water from the alginate source into the surrounding cement matrix during the dormant and accelerated period.

Keywords: Cement; Hydration; NMR spectroscopy; Curing; Polymers

1. Introduction

Internal post-curing of cements and concretes represents a relatively new idea. It was first mentioned by Philleo [1] in 1991 and again suggested by Reinhardt and Weber [2,3] in the mid-1990s, who introduced a new method for curing of high performance concretes (HPC) by replacing 25% of volume of normal weight aggregates by water-saturated lightweight aggregates. As a result of the very dense structure of HPC, externally supplied curing water cannot reach regions of hydration inside the concretes [4]. Thus, the traditional external curing is ineffective for post-curing of HPC. Only water evaporation from the outer surfaces can be prevented. Furthermore, external curing methods on vertical structural elements are always problematic. Thus, besides HPC, internal post-curing (IPC) could be an excellent alternative also in such application.

The main idea of IPC is that additives with temporary delayed release of water are mixed with fresh cements or concretes prior to their concreting. These additives deliver water to the hardening cement matrix during times where the hydration process consumes water. Generally, water curing has to start before the end of the dormant period, as soon as hydration of cement begins [5]. If IPC-materials meet these demands, IPC is more advantageous than external post-curing. It would allow a homogeneous curing, a continuous cement hydration and, thus, prevent self-desiccation and reduce the tendency of forming of microcracks in HPC.

During the last 5 years much work was done in the field of IPC. Different types of lightweight (fine) aggregates (LW(F)A) [2–4,6–14] and superabsorbent materials [14–16], their content in a concrete mixture [3,10,11], the grain size [4,8] and the influence of IPC on the properties of HPC [3,4,9,11] were investigated. Some researchers developed models to describe and to calculate the process of IPC [25]. Up to now, mainly lightweight (fine) aggregates are used for IPC. On systems optimised with respect to the type, grain size and content of

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* Corresponding author. Tel.: +49 341 973 2518; fax: +49 341 973 2549.
E-mail address: stallmac@physik.uni-leipzig.de (F. Stallmach).

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saturated LW(F)A [11,13], a reduced autogenous shrinkage was observed [2–4,7,13,14,17,18]. In some cases a positive influence of IPC with LW(F)A on compressive strength and durability were discussed [9,13,17].

However, the lightweight aggregates often have a small water retention, which makes it necessary to determine the moisture of the aggregates and the consistence of fresh concrete during concreting [19,20]. Easier to handle is the IPC with polymers and superabsorbent polymers [14,16] with temporary delayed release of water. They produce a highly controlled microstructure with a controlled self-desiccation and an improved autogenous shrinkage [14,16]. Nevertheless, reversible water uptake of these materials might reduce the durability of concretes.

Excellent results with respect to compressive strength and to its frost de-icing salt resistance on HPC were obtained using the biological polymer alginate for IPC [26]. Alginate is a hydrophilic gelling material, containing 98 wt.% of water [21]. Application of biological gels (gelatine, alginate, carrageen, pectin and starch, respectively) was mentioned for the immobilisation of asbestos fibres, where the fibres are bound [22] by hydration of the cement using the water in the gels. Furthermore, alginate is utilised in calcium phosphate cements for implanting of prostheses (bones, tooth), where they improve the setting behaviour, the consistency and the mechanical properties of these biocements ([23,24] e.g.).

In this contribution, nuclear magnetic resonance (NMR) methods are used to study the water balance during hydration with IPC. Investigation of transverse relaxation and self-diffusion of physically bound water by NMR relaxometry and diffusometry, respectively, allow important non-destructive insights in the water dynamics of hydrating cement. As already described in [27], the transverse (spin–spin, T_2) relaxation times of the water in the pores of the hydrating cement matrix decrease during the first hours of hydration. The averaged relaxation time $\langle T_2 \rangle$ of water in a pore decreases with decreasing pore size [28,30,31]. This relation yields information on the pore size of these materials which is qualitatively equivalent to the (destructively operating) mercury intrusion porosimetry [29,31] as long as the concentrations of paramagnetic ions in solution do not change significantly during hydration. By monitoring the hydration time-dependence of the transverse relaxation time, hydration kinetics in the dormant and acceleration period can be followed [32–34]. With the NMR diffusion studies, a decrease of the self-diffusion coefficients of the physically bound water within the first 24 h of hydration was observed in earlier studies [35,36]. Both, decreasing relaxation times and self-diffusion coefficients reflect increasing surface-to-volume ratios of the pores (main influence on relaxation times) and increasing tortuosity (main influence on diffusion) during the hydration [35].

The first NMR investigations on internal post-curing of cement with alginate are reported in [26,36]. In our study, we use these NMR approaches to monitor water transition from the alginate added as internal water source for post-curing into the hardening cement matrix. Relaxation time studies are performed with the so-called Carr–Purcell–Meiboom–Gill (CPMG) NMR sequence [37,38], which is quick and allows the hydration progress and water transition to be followed non-destructively on one sample with a time-resolution of a few minutes. NMR diffusion studies are performed with the pulsed field gradient (PFG) NMR [39] yielding information on the diffusion of physically bound water, which is still available for hydration in the pore system. The influence of IPC on the development of $\langle T_2 \rangle$ and, thus, on development of pore size and on self-diffusion coefficient are discussed. Conclusions on water retention of the alginate additive for IPC and on temporal moisture requirement of the cement during hydration reaction are drawn.

2. Materials and methods

2.1. Cement paste preparation

Non-destructive NMR relaxation and diffusion measurements of water in hardening cement pastes were performed on samples of white cement (CEM I 42.5 R) with water-to-cement ratios (w/c) between 0.3 and 0.5. About 10 g of cement powder were mixed with tap water according to the target w/c-ratio and stirred in a beaker for about 1 min. Samples I to IV (Table 1) are prepared without additional alginate. They are used as reference for studying the hydration without internal post-curing.

For the studies of hydration with internal post-curing (samples Ia, Ib and Ic), a cement paste with initial w/c-ratio of 0.30 was prepared as described above. After stirring, water containing spheres of alginate [21] were added. The contents of alginate were chosen in such a way that the total w/c-ratios of the samples increase from 0.30 to 0.32 (sample Ia), to 0.35 (sample Ib) and to 0.40 (sample Ic), respectively (Table 1). The samples were carefully mixed to achieve a homogeneous distribution of the alginate spheres.

The prepared cement pastes and cement paste/alginate mixtures, respectively, were introduced into NMR sample tubes made of glass. The tubes were sealed by a cap to prevent the evaporation of water. The mass of the samples was registered and monitored throughout the hydration.

Alginate, which is a natural polysaccharide, was obtained as sodium alginate (Manugel DJX) from Kelco, Germany. Prior to mixing with the cement paste of w/c-ratio 0.30, it was transformed into calcium alginate by ion exchange reaction as described in Ref. [21]. This procedure yields spheres of alginate

Table 1
List of samples and w/c-ratios for investigations of internal post-curing (IPC) of cements by addition of alginate spheres (sample Ia, Ib and Ic) and composition of reference materials (samples I–IV)

Sample	Initial w/c-ratio	Additional content of water from alginate/% relating to cement	w/c-ratio after IPC
I	0.30	–	–
II	0.32	–	–
III	0.40	–	–
IV	0.50	–	–
Ia	0.30	2	0.30 + 0.02
Ib	0.30	5	0.30 + 0.05
Ic	0.30	10	0.30 + 0.10

gel containing 98% (by weight) of water. The spheres have a diameter of 2–3 mm and are stable over long periods of time (at least months).

2.2. NMR relaxometry

Investigations of water balance and transverse nuclear relaxation time T_2 were performed, using a PC controlled NMR console MARAN DRX (Resonance Instruments, GB). The magnet and the rf probe for these low-field NMR studies are home-built. The magnet consists of two opposing FeNbB permanent magnet plates with a gap of 4.1 cm between the pole faces. It yields a magnetic flux density of $B_0 = 0.2$ T, which corresponds to a hydrogen (proton: ^{1}H) resonance frequency of 9.1 MHz (Lamor condition: $f = \gamma \cdot B_0/(2\pi)$). The NMR signal is excited and detected by a tunable solenoid rf coil placed in the centre between the magnet pole faces. The design allows the use of cylindrical sample tubes of 20 mm outer diameter and arbitrary length. The sensitive region in the centre of the rf coil has a length of 20 mm. Thus, this technique probes a sample volume of roughly 6 cm^3 of the total NMR sample.

The transverse magnetization decay $M(t)$ of the water in the cement paste samples was monitored with this low-field NMR spectrometer using the CPMG pulse sequence [35,36]. It generates a series of spin echoes by application of π rf pulses in the distance of $2\tau = T_E$ after an initial exiting $\pi/2$ rf pulse. The length of the $\pi/2$ and π rf pulses was 7 and 14 μs, respectively. The inter echo time T_E can be varied and was usually set to 100 μs. This allows only the ^{1}H NMR signal of water in gel pores and in capillary pores to be detected. Hydrogen, which is chemically bound, for instance, to solid calcium silicate hydrate phases has T_2 relaxation times much shorter than 100 μs. Thus, it cannot contribute to the observed NMR signal.

In order to increase the signal-to-noise ratio of these CPMG relaxation time measurements, 128 successive scans were added together. With a repetition delay time of $R_D = 5$ s, which was sufficient to allow the nuclear spins to relax to equilibrium after each individual scan, such a measurement takes roughly 11 min. The hydration of the cement paste samples was monitored by automatically repeating the CPMG measurements after preselected waiting times via a Visual Basic script on the spectrometer host PC. All CPMG NMR measurements were performed at 20 °C.

The recorded transverse magnetization decays $M(t)$ were analysed with a regularized inverse Laplace transformation using WINDXP software (Resonance Instruments, GB), which yields the discrete distributions $m_i(T_{2i})$ of transverse relaxation times T_{2i}, Here, m_i denotes the contribution of water molecules (^{1}H spins) relaxing with relaxation time T_{2i} to the total magnetization. This approach assumes that the total magnetization decay $M(t)$ is given by a superposition of exponential decays of the form $m_i \exp(-t/T_{2i})$. From the discrete distribution of relaxation times, the initial magnetization $M_0 = \Sigma m_i$, which corresponds to the area under the relaxation time distribution, and a logarithmic mean relaxation time $\langle T_2 \rangle$ are derived. Both values are robust parameters, which, generally, are independent on regularization parameters in the inverse Laplace transformation. The area under the relaxation time distribution (= the initial magnetization M_0) is proportional to the total amount of physically bound water and is used to calculate the water balance during hydration. This method is equivalent with the well-established procedure to determine porosities of water-saturated rocks by low-field NMR relaxometry [31] and was previously and successfully applied to characterise dolomite rocks and fired-clay bricks in our lab [40]. The logarithmic mean relaxation time $\langle T_2 \rangle$ is a measure of the averaged size of the pores filled with water. In the cement paste samples, it is used to monitor the development of pore size during hydration and qualitatively assess differences with respect to pore size in the samples after complete hydration.

2.3. NMR diffusometry and 1d profiling

PFG NMR diffusion studies were performed on the home-built spectrometer FEGRIS 400 FT operating at a ^{1}H resonance frequency of 400 MHz [39]. The cement paste sample in the NMR sample tube has a diameter of 6 mm and a length of about 12 mm (volume 0.34 cm^3). For all measurements the stimulated spin echo 13-interval pulse sequence with alternating pulsed gradients [39] was used. This sequence suppresses distortions of the PFG NMR result by internal magnetic field inhomogeneities induced by magnetic susceptibility differences between pore and matrix space in the hydrating cement paste samples. The total time of transverse relaxation in these experiments was 1.4 ms, which is split into 4 equally spaced τ intervals between the $\pi/2$ and π rf pulses. Thus, as in the above described CPMG experiment, only the physically bound water (capillary-bound water and gel pore water) contributes to the observed NMR signal and only the diffusion of this water fraction was studied.

To obtain the self-diffusion coefficient D, the attenuation of the NMR spin echo signal was measured as a function of the amplitude of the applied pulsed field gradients. Changes in self-diffusion coefficients were recorded on samples with and without internal post-curing during the first 25 h of hydration. Pulsed field gradients of a duration of 200 μs and amplitudes between 0 to 6 T/m (unit: Tesla per meter) were sufficient for these measurements. After 56 days of hydration, the samples were completely saturated with water and measured again, which required pulsed field gradient amplitudes of up to 12 T/m. Details of the procedure of these PFG NMR diffusion measurements and of the data analysis are described in ref. [39].

Due to the small sample volume, only a few alginate spheres are contained in the samples for studying the diffusion during hydration with internal post curing. Their location inside the sample and the development of their water content during hydration was monitored simultaneously to the PFG NMR studies using a 1-dimensional spin echo imaging technique with an additional constant (read) magnetic field gradient of 0.3 T/m. By successive Fourier transformation of the spin echo signal one obtains a 1-dimensional profile along the gradient direction, which coincided with the direction of the axis of the cylindrical sample. It represents the relaxation time weighted axial distribution of water. All measurements of diffusion and spatial water distribution were performed at 27 °C.

3. Results and discussion

3.1. Water balance and pore size during cement hydration with and without IPC

Water balance and changes of transverse relaxation time T_2 in the hardening cements without IPC and with IPC were investigated by low-field NMR relaxometry during the first 25 h of hydration. As an example, Fig. 1 shows the relaxation time distributions of sample I ($w/c=0.3$) and sample Ia ($w/c=0.3+0.02$) observed about 1 and 12 h after sample preparation. With successive hydration, the relaxation time distributions are found to shift to smaller relaxation times indicating a decrease in pore size due to the growth of the hydrate crystals. Simultaneously, the area under the distribution decreases slightly, which corresponds to the fact that water is consumed by formation of hydrate crystals and thus, does not contribute anymore to the observed NMR signal. The relative decrease in the content of physically bound water ($c_{\mathrm{p,H_2O}}$), which is measured by the area under the relaxation time distribution and referred to the initially detected amount of water (=100%), and the decrease in logarithmic mean relaxation time, characterizing the decrease in pore size, are plotted in Fig. 2a and b, respectively.

The content of the physically bound water (Fig. 2a) is constant during the first 2 h, which coincides with the so-called dormant period [34]. With the onset of the accelerated period between 2 and 5 h, which depends on the initial w/c-ratio [41], the observed water content starts to decrease. During the following 10 to 12 h about 15% of the water is consumed. Since the total masses of the samples remain constant, this water fraction is bound by chemical reaction to hydrate crystals, such as calcium silicate hydrate phases, portlandite and ettringite, respectively [34].

During the accelerated period, the pore size is expected to decrease as a result of forming and growth of these hydrate crystals. In fact, such an effect is observed by NMR relaxometry by a successive shift to the left of the relaxation time distribution, which is quantified by the decreasing mean relaxation time (see Fig. 2b). After 25 h of hydration there is a clear trend between the 3 samples of different initial w/c-ratio. The higher the w/c-ratio, the larger the $\langle T_2\rangle$-value and thus, the larger the pore size. This observation corresponds to the well known fact that cements with smaller initial w/c-ratios have better mechanical properties and an improved durability than cements with higher w/c. However, the hydration after 25 h is not complete. Therefore, the same samples were investigated after 56 days of hydration again. After this time, the samples were dried at 105 °C and re-saturated completely with water (15 mm Hg). Table 2 shows that the amount of uptake of capillary-bound water and its mean transverse relaxation time depends on the initial w/c-ratios. These results confirm that the total volume of capillary pores and their size increase with increasing w/c-ratio.

Fig. 2a includes also the amount of physically bound water as function of hydration time for the samples with IPC. For these samples, the amount of physically bound water is obtained from the area under the left peak in Figs. 3–5, which is characteristic for water in the hardening cement paste. The relative amounts show the same tendency like the plot for sample I without IPC. Since water disappears from the alginate phase, as observed by the decreasing area under the right peak at the higher relaxation times (Figs. 3–5) and since the total sample masses remain constant during the whole time of hydration, it must be concluded that (i) the relative amount of physically bound water in the cement phase is the same with and without IPC by alginate and that (ii) water from the alginate phase is consumed by the cement paste. Clearly, the hydrating cement particles can only uptake physically bound water from their direct vicinity. However, this water is replaced by water from the alginate phase. We assume that the resulting capillary pressure is the driving force for the water transition from the alginate to the cement paste.

In Fig. 2b, the development of mean transverse relaxation time of the samples with IPC is also shown. The mean relaxation time for physically bound water in the samples with

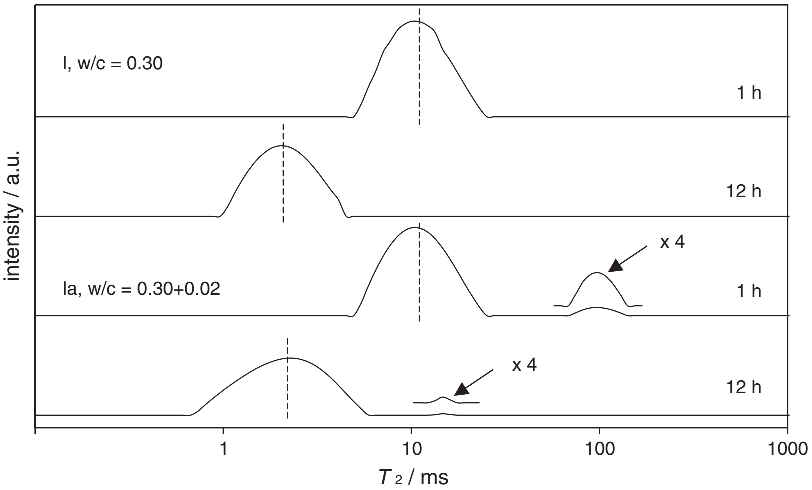

Fig. 1. Distribution of the transverse relaxation time during hydration with (sample Ia, bottom two curves) and without (sample I, top two curves) IPC. Doted lines indicate logarithmic mean relaxation time $\langle T_2\rangle$ used to qualitatively assess decrease of pore size with increasing hydration time.

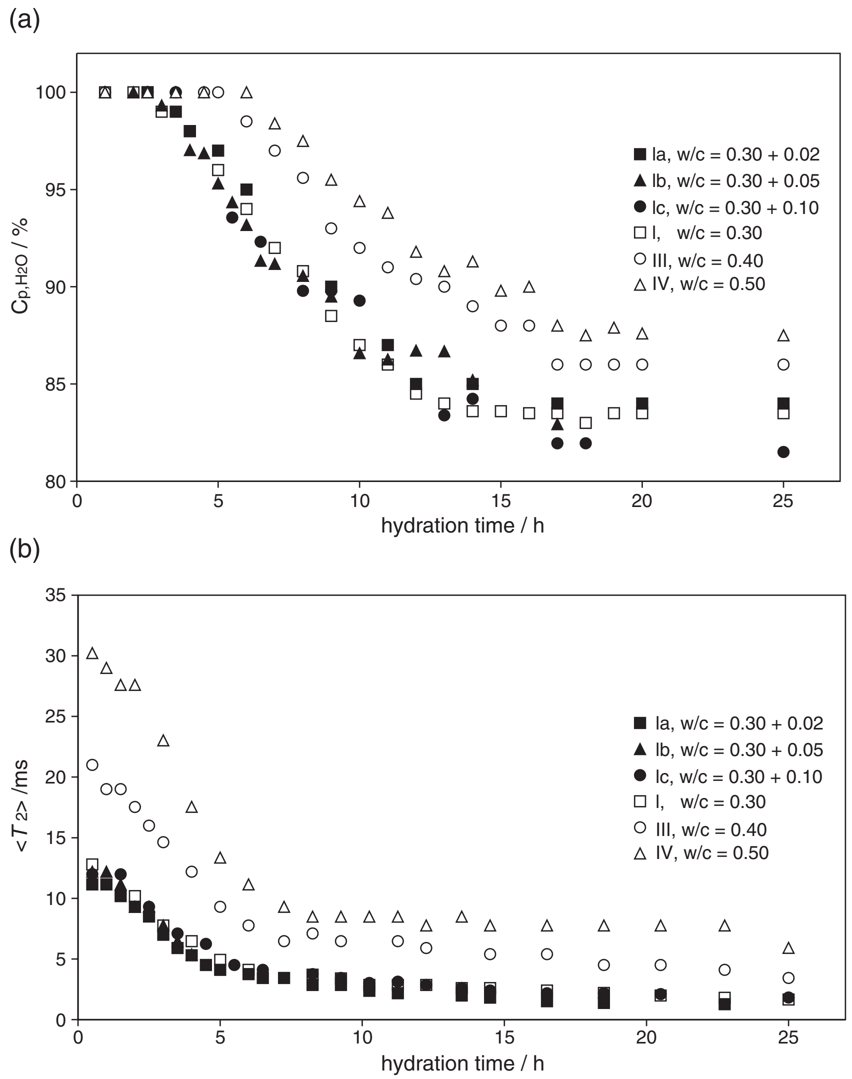

Fig. 2. Content of physically bound water of cement ($c_{\mathrm{p,\,H_2O}}$, Fig. 2a) and its logarithmic mean transverse relaxation time ($\langle T_2 \rangle$, Fig. 2b) for reference samples (empty symbols) and samples with IPC (full symbols) during the first 25 h of hydration.

IPC, which is obtained by the averaged position of the characteristic peak in the relaxation time distribution (Figs. 3–5), shows the same course like the sample I of w/c-ratio 0.30 without IPC and does not depend significantly on the amount of water added by alginate for the IPC. Consequently, the IPC doesn't influence the development of pore size in the cement phase during the first 25 h. These NMR relaxation time studies suggest that all cement pastes prepared with an initial w/c of 0.3 have the same pore size in the cement phase and that, thus, internal post curing by alginate might have no negative effect on mechanical properties. Nevertheless, transition of water from alginate into the cement matrix is detected and confirmed by additional experiments.

Table 2
Characterisation of reference samples (I, II, IV) after 56 days of hydration with respect to capillary-bound water uptake (u_c), mean logarithmic relaxation time $\langle T_2 \rangle$ and self-diffusion coefficient D

		Sample I (w/c=0.30)	Sample III (w/c= 0.40)	Sample IV (w/c=0.50)
u_c	mg/g	12.01	16.08	20.08
$\langle T_2 \rangle$	ms	0.47	0.67	0.74
D	m^2/s	5.81×10^{-11}	6.61×10^{-11}	8.92×10^{-11}

3.2. Characteristics of water transition from the alginate to the cement paste phase

Figs. 3–5 show the transverse relaxation time distributions of all three samples with IPC. At the beginning of the hydration reaction, the transverse relaxation time T_2 of the water in the alginate sphere is about 100 ms (sample Ia, Fig. 3), which agrees very well with the T_2 of pure water-saturated alginate spheres (98 ms). During the hydration of the cement paste, ions from the cement matrix diffuse into the water of alginate sphere, which decreases the characteristic T_2 due to increasing ionic concentrations. This is observed for all three samples with IPC (Figs. 3–5) by the shift to the left of the characteristic peak for alginate.

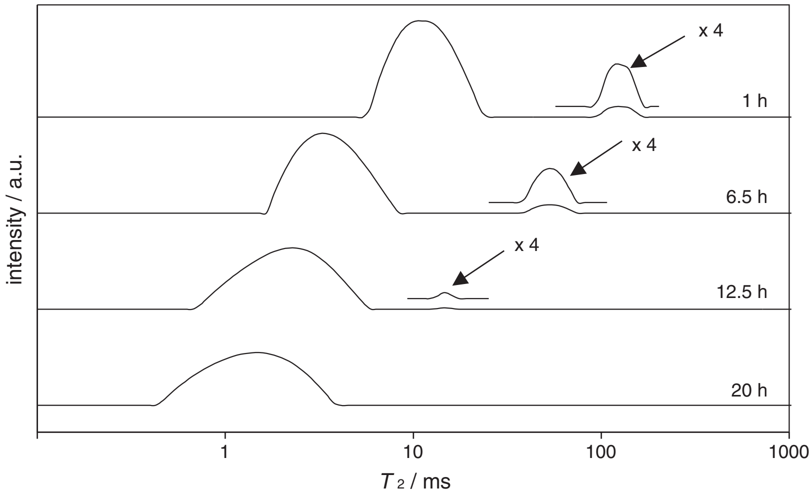

Fig. 3. Distribution of the transverse relaxation time T_2 of sample Ia during the first 20 h of hydration reaction.

The transition of water from the alginate spheres into the cement matrix is also evidenced in these relaxation time distributions. E.g., the alginate peak of sample Ia (w/c-ratio of 0.30+0.02) flattens. After 20 h no water in alginate is detected anymore (Fig. 3), which means, that all the additional water from the alginate spheres is consumed by the hydration reaction. Similar trends are observed for sample Ib (w/c-ratio of 0.30+0.05, Fig. 4) and Ic (w/c-ratio of 0.30+0.10, Fig. 5). However, residual water remains in the alginate phase of these samples even after 7 and 14 days of hydration, respectively.

Fig. 6 summarizes the time-dependence of this residual water in the alginate phase for all three samples with IPC. The data are obtained from the area under the relaxation time distribution, which is characteristic for the water in alginate. For sample Ia, this additional water is consumed already after about 12 h. This means that the 20 g of water per kilogram of dry cement, which correspond to the increase of w/c ratio by 0.02 due to addition of alginate spheres, are totally used by the hydration reaction during IPC. In sample Ic (increase of w/c-ratio by 0.10), only 25% of the water from the alginate phase is consumed by IPC hydration, which corresponds to 25 g water per kilogram dry cement (Fig. 6). The residual water, which amounts to 75 g per kilogram dry cement, remains in the alginate phase and is detectable by NMR relaxometry even over a period of a few weeks (data are not plotted in Fig. 6). From these experimental results on cement pastes with initial w/c-ratio of 0.3, one can conclude that an increase in w/c-ratio by 0.025 by addition of alginate spheres would be the optimum to supply sufficient water for IPC.

Corresponding investigation on sample Ib (increase of w/c-ratio by 0.05) suggest that even up to 45 g water per kilogram dry cement might be consumed by IPC, since in this sample only 10% water remain in the alginate peak in the relaxation time distribution (see Figs. 4 and 6). However, it could also be that in a part of the alginate spheres of this sample (e.g. the outer shell) hydration of the ions which diffused from the cement paste into the alginate sphere takes place. The corresponding solid cement matrix would have most likely larger pore diameters. This is in fact visible in the shoulder of the relaxation time distribution of this sample appearing at 8 ms for hydration time exceeding 15 h, which is not observed in all other samples. Nevertheless, also in this sample not all of the water added by

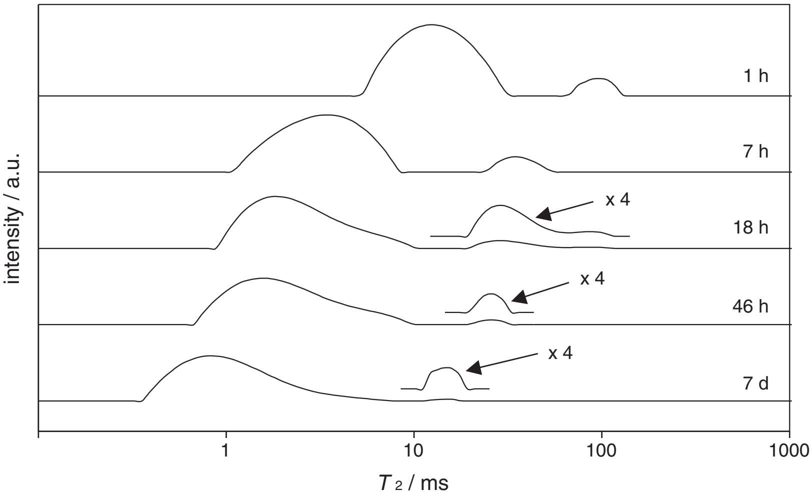

Fig. 4. Distribution of the transverse relaxation time T_2 of sample Ib during the first 7 d of hydration reaction.

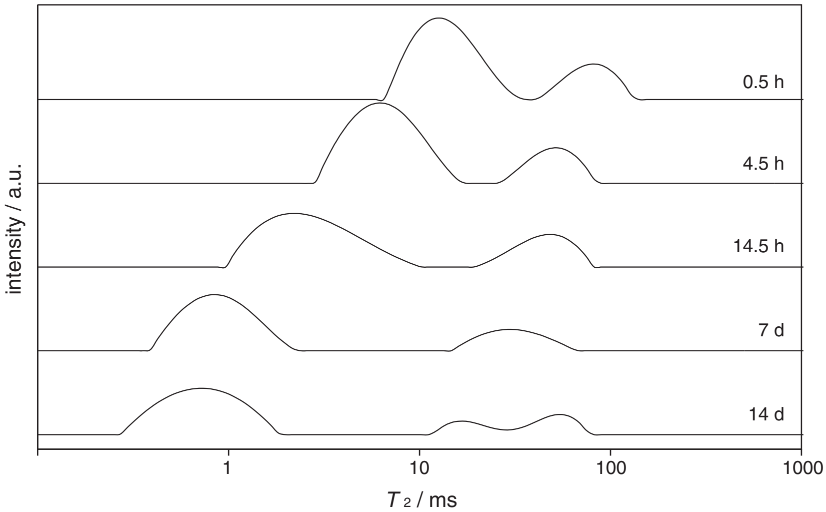

Fig. 5. Distribution of the transverse relaxation time T_2 of sample Ic during the first 14 d of hydration reaction.

alginate is consumed by the IPC hydration reaction. Thus the 45 g water per kilogram dry cement may be considered as the upper limit of water consumption by IPC in the investigated cement/alginate system.

3.3. Water diffusion during cement paste hydration

The water transition from the alginate spheres to the cement paste during hydration, which is evidenced in the experiments described above, raises the question of how the water diffuses in the different regions of the sample and whether the supply of water from the alginate to the cement is limited by the diffusion through the pore space of the hydrating cement. To address these questions the spatially resolved distribution and the self-diffusion of water were measured by combining 1-dimensional NMR imaging (profiling) with PFG NMR diffusometry. Fig. 7 shows the time-dependence of the axial profile of relaxation time weighted water distribution across sample Ia (w/c ratio $0.30+0.02$). Due to the small sample size required for these studies, the sample contains only a single alginate sphere. At the beginning of hydration reaction, the alginate sphere is water-saturated. It is visible by the large intensities at position coordinates from -2 to -5 mm in Fig. 7. The cement paste region extends from $+5$ and -2 mm.

Fig. 7 shows that the relaxation time weighted NMR signal intensity decreases across the whole profile during hydration. The short relaxation times of the physically bound water in the cement paste region and its strong decrease with hydration time (compare Figs. 2b and 3) lead to a time-dependent relaxation time weighting of the observed NMR signal and do not allow a straightforward calculation of physically bound water content from this measurements. This would require separate time and spatially resolved studies of transverse relaxation time in this sample, which where not performed. However, the transverse relaxation time of alginate with a minimum of about 12 ms prior to total water consumption (compare Fig. 3) is always long compared to the total period of transverse relaxation in the 13-interval pulse sequence ($4\tau=1.4$ ms) used for this study. Thus, the observed intensities in this region are proportional to the water content in the alginate sphere.

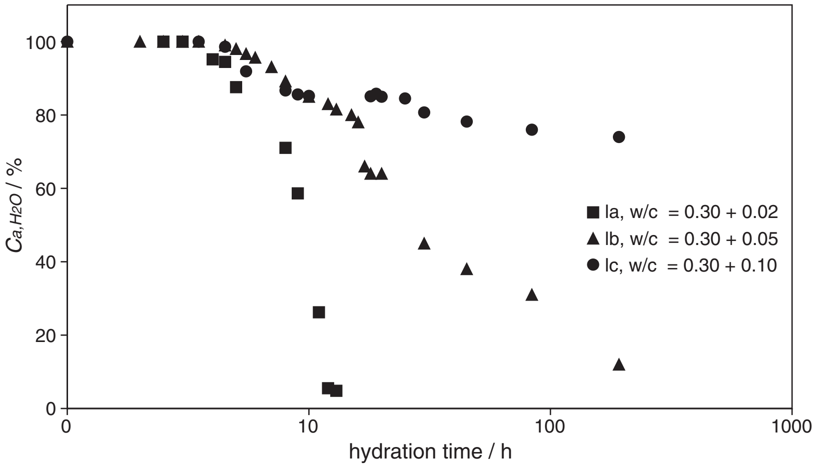

Fig. 6. Content of water in the alginate spheres c_{a,H_2O} during the hydration reaction with IPC, samples Ia, Ib and Ic.

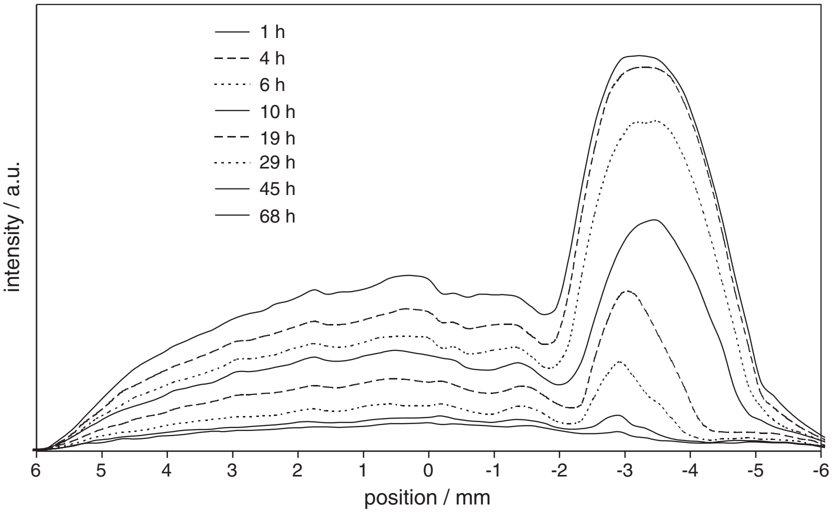

Fig. 7. Time dependence of water distribution (axial profiles, weighted by relaxation times) across sample Ia during the first 68 h of hydration.

After the onset of the accelerated period in cement hydration, a decreasing intensity and width of the alginate region in Fig. 7 is observed. Since the sample is sealed, this loss of signal intensity can only be interpreted as transition of water from the alginate to the cement region. The loss of water from the alginate leads to a successive shrinking of the sphere (region between −5 and −4 mm). The contact of the alginate sphere with the cement paste at −2 mm is not affected by this shrinking, which is important to maintain continuous water transport from alginate into the cement paste.

The self-diffusion coefficient of the physically-bound water in the cement paste was measured by PFG NMR during the first 25 h of hydration. It is plotted as function of hydration time in Fig. 8. As in the low-field studies on water balance and relaxation time of samples I to IV, there is no change in this parameter during the dormant period. Initially, the self-diffusion coefficient is between 1.2×10^{-9} and 1.5×10^{-9} m^2/s, which is only about a factor of 2 smaller than the diffusion coefficient of pure water at the same temperature. The higher value reflects the smaller concentration of dissolved ions and dispersed solid fine materials in the fresh cement paste of the largest w/c-ratio of 0.5. The diffusion coefficients start to decrease with the beginning of the hydration reaction in the accelerated period. This reflects the increasing sterical hindrances by growing hydrate crystals, which the water molecules have to overcome on their diffusion path through the pore space.

After a hydration time of 25 h the following sequence in self-diffusion coefficients is observed: $D(w/c=0.30)<D(w/c=0.32)<D(w/c=0.40)<D(w/c=0.50)$. This is in agreement with the expected trend in pore sizes that increase with increasing w/c-ratio. The corresponding self-diffusion coefficients after 56 days of hydration and re-saturation of the samples with water are given in Table 2. They show the same trend in dependence on the w/c-ratio but are about an order of magnitude smaller than the values measured after 25 h of hydration. These observations demonstrate the influence of the pore size on diffusion of the physically bound water,

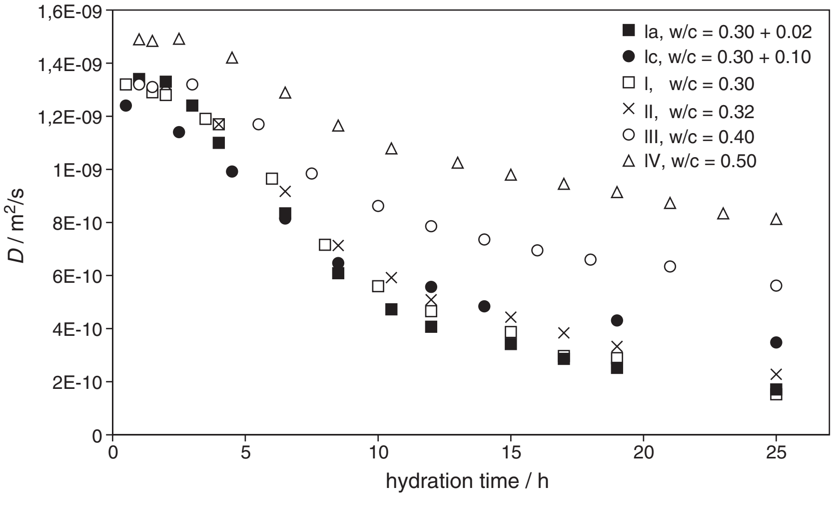

Fig. 8. Time dependence of the self-diffusion coefficients of the physically bound water in hydrating cements with (full symbols, samples Ia, Ic) and without IPC (empty symbols, samples I, II, III, IV).

which is decreased during successive hydration but still depends on the initial *w*/*c*-ratio.

The internal post-curing, for which the water from the alginate spheres was shown to be consumed by the hydration reaction, might have also an influence on diffusion. However, within the experimental accuracy of these diffusion studies, we found that there is no significant difference in the time-dependence of the diffusion coefficients of the physically bound water between the samples with and without IPC (see Fig. 8). This might be due to the fact that diffusion studies of the physically bound water are a much more indirect method to investigate cement hydration than observing the water consumption from the alginate phase directly by the above described NMR methods.

Nevertheless, the diffusion studies show that during the first 25 h of hydration the physically bound water has a sufficiently high mobility to be transported from the alginate sphere, as the internal water source for IPC, to those sites in the cement matrix where the hydration reaction proceeds. Using a value of 5×10^{-10} m^2s^{-1} for the self-diffusion coefficients observed in our experiments for the samples with initial *w*/*c*-ratios of 0.30 after 10 h (see Fig. 8), the water molecules from the alginate sphere cover an averaged diffusion length of roughly 1 cm through the hydrating cement matrix around the sphere during 10 h. Therefore, an averaged distance of 2 cm between neighbouring alginate spheres and a volume fraction of about 10^{-3} of alginate spheres in the cement paste, respectively, would be sufficient to achieve homogenous supply of water for IPC by addition of alginate spheres to the cement paste. The actual volume fraction of alginate spheres for realistic increases in *w*/*c*-ratio is more than one order of magnitude higher and the averaged distance between the spheres is less than 1 cm. Thus, on a time scale important for internal post-curing, the self-diffusion of water in the capillary pores of the hydrating cement ensures homogenous water distribution from the internal source of water throughout the whole hydrating cement paste region.

4. Conclusions

We observed water transition from gel-like water-saturated alginate spheres added as internal water source for internal post-curing of cement pastes of a low initial *w*/*c*-ratio of 0.3 by non-destructive NMR methods. The relaxation time distributions measured by low-field NMR relaxometry and calculated via regularized inverse Laplace transformation allow to distinguish between physically bound water in the cement paste region, which appears at short transverse relaxation times, and the gel water in the alginate at much longer relaxation times. Following the changes in the relaxation time distribution with hydration time allows changes in the pore size of the hydrating cement to be assessed and the water transition from the alginate to the cement paste to be quantitatively monitored.

By analysing these relaxation time distributions, we found that the cement paste starts to uptake water from the alginate spheres with the onset of the accelerated period in the cement hydration. Simultaneously, ions from the cement paste diffuse into the alginate spheres. Small additional amounts of water added via the alginate spheres (20 g per kilogram dry cement and less) are completely transferred to the cement paste and consumed in the hydration reaction. If too much water-saturated alginate is added, only a fraction of the water is used by the cement paste. From our experiments we estimate a water requirement of about 25 g per kilogram dry cement for internal post curing of the investigated cement pastes of initial *w*/*c*-ratio of 0.3.

Evidence of water transition from alginate to the cement paste is also provided by a 1-dimensional spin echo NMR imaging technique. These experiments allowed the time dependence of the water content in a single alginate sphere in contact with cement paste and its shrinking due to the loss of water to be observed.

Diffusion studies by PFG NMR showed that the diffusion coefficient of the physically bound water in the cement paste during the accelerated period of cement hydration is high enough to ensure homogenous water distribution from the alginate spheres throughout the cement paste during the period where water release from the alginate spheres and formation of silicate hydrates are observed.

These studies are a contribution to the investigation of the mechanism of IPC. The NMR methodology developed is new in this field, non-destructive and applicable to other IPC-systems. The only pre-conditions are that an ^{1}H NMR signal from the water inside the internal source is detectable and that it differs in its transverse relaxation time from the signal of the physically bound water in the cement paste matrix. Possible candidates for such studies are e.g. further water-saturated biological gelling materials, several superabsorbent materials and inorganic porous materials in hydrating white as well as in ordinary Portland cement pastes. They are currently investigated in our lab.

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