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Liquid-phase self-diffusion in hydrating cement pastes — results from NMR studies and perspectives for further research

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Abstract

The changes in the pore structure of hydrating cement are accompanied by changes in the dynamics of liquid phases contained in the pore system of the hydrating matrix. Dynamic NMR methods (relaxometry, diffusometry) allow the non-destructive observation of these changes. Relaxometry can be performed using quite simple equipment and has been widely used in studies of the kinetics of cement hydration. Diffusion studies, by contrast, require much more sophisticated equipment. On the other hand, the diffusion coefficient has a direct relevance for the transport of moisture or contaminants in the cement matrix while relaxation time measurements provide more indirect information. The purpose of the present paper is to review the possibilities of field gradient NMR in diffusion studies on hydrating cement and to provide an outlook on how this information can be used for improving our understanding of the properties and microstructure of hydrating cement. As an example, new results on the relationship between the diffusive exchange length in the sample and non-exponential relaxation in cement are discussed at the end of the contribution.

Keywords: Hydration; Diffusion; Physical properties; Portland cement

Contents

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1. Introduction

Despite the long and wide-spread use of cementitious materials in construction, many aspects of the hydration process, the microstructure formed during this process and their relationship to the macroscopic properties of cement and concrete materials are still poorly understood. In the last 50 years, many new experimental tools to investigate the structure and the chemical composition of nanostructured materials have become available. A special challenge in applying these techniques to hydrating cement is the presence of volatile water which is not only reactant but at the same also reaction medium and essential part of the newly formed hydration products. Furthermore, hydrating cement is intrinsically a bulk material with an irregular 3D pore network.

While many standard tools from materials science do not allow the presence of liquid water in the sample and/or also are only sensitive to a thin layer of the material, NMR methods are fully compatible with a water-wet sample and furthermore offer a more or less unlimited intrusion depth into the sample material. Dynamic NMR methods (i.e. proton spin relaxometry and diffusometry) have first been applied to cementitious materials in the late 1970s by the Blinc group [1,2]; a few years later, solid-state NMR spectroscopy was introduced into cement research, too [3]. Within recent years, much progress has been made in the field of solid state NMR spectroscopy (which provides information on the chemical nature of cement hydration products). In the field of dynamic (or "low resolution") NMR, many groups have been working with NMR relaxometry (which provides information on the hydration kinetics and pore structure development in the cement). Despite the strong interest in diffusion and moisture transport in hydrating cement, only few NMR diffusometry studies have been realized in the same time. The comparatively low number of studies on water self-diffusion in hydrating cement is probably due to the fact that non-standard NMR equipment is needed for such measurements and that there are also some specific complications in NMR diffusometry on hydrating cement pastes.

The purpose of this contribution is to review different approaches to NMR diffusometry and the specific requirements and pitfalls in application to cementitious materials. After that, some results of recent field gradient diffusometry studies on cement shall be presented and their relevance to various fields of cement and concrete research and to a better understanding of NMR relaxometry results is discussed. At the end, an outlook to open questions and perspectives for the further development of NMR diffusometry in cement science will be given.

2. NMR diffusometry on hydrating cement

While NMR diffusometry can in principle be conducted with any NMR-sensitive nucleus, there are several reasons why most NMR diffusometry experiments are carried out on protons. The main reason is the high NMR sensitivity of protons (which is orders of magnitude higher than for most other nuclei): water and also most organic solvents contain plenty of hydrogen, and the gyromagnetic ratio of protons (i.e. the ratio between the NMR resonance frequency and the magnetic field) is the highest of all stable nuclei. The high gyromagnetic ratio of the protons furthermore leads to an especially high sensitivity of the proton NMR signal to magnetic field gradients in diffusion studies (see Eq. (2)) which is again favourable for NMR diffusometry.

As the applicability of NMR diffusometry to a given sample depends critically on the proton NMR relaxation behaviour of the sample, we will shortly discuss the proton NMR properties of hydrating cement before describing the main NMR diffusometry methods.

2.1. Proton NMR properties of hydrating cement

2.1.1. Short overview of relaxation times

The response of a nuclear spin magnetization to a resonant excitation is usually described by means of a set of time constants — the longitudinal relaxation time T_1, the transverse relaxation time T_2 and T_2^*, the time constant of the free induction decay (FID). The meaning of these relaxation times shall be explained only roughly here. More basic information on NMR and relaxation times can be found in textbooks such as [4,5].

In any case, the length of the relaxation times obeys the following relationship:$T_1 \geq T_2 \geq T_2^*$.

The longitudinal relaxation time T_1 describes the time constant which it takes for an excited nuclear spin magnetization to revert to thermal equilibrium. It therefore limits the time window available for encoding any type of information in an NMR experiment (if the excited magnetization is gone, the information encoded into it is gone, too). Longitudinal relaxation needs energy transfer from the nuclear spin system to the outside world (which is called the lattice in condensed matter physics). This energy transfer needs to occur in a resonant way so that longitudinal relaxation is most effective when there are molecular correlation times that roughly match the inverse of NMR frequency.

The transverse relaxation time T_2 describes the irreversible decay of precession phase relationships between individual spins. It therefore limits the time window available for manipulating the precession phases of nuclear spins (e.g. by the presence of magnetic field gradients). The processes responsible for transverse relaxation need no resonant energy transfer and are most effective for long molecular correlation times. The qualitative dependence of longitudinal and transverse relaxation time on the molecular correlation time is given in Fig. 1.

T_2^* finally describes the length of a detectable NMR precession signal taking into account both the irreversible losses of phase information due to transverse relaxation and the reversible losses due to the range $\Delta\omega$ of resonance frequency offsets between different nuclear spins:

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \Delta\omega. \qquad (1)$$

The reversible dephasing of the magnetization due to frequency offsets can be refocused by means of a so-called spin echo [6]. Roughly speaking, the spin echo is a detectable NMR signal observable at the echo time $t_e = 2\tau_1$ after the initial RF pulse which is produced by irradiating a second RF pulse at a time τ_1 after the first RF pulse (see also Fig. 2A). The amplitude of the spin echo decreases exponentially with $2\tau_1/T_2$. The signal transient of the echo itself decays like the FID with T_2^*.

In proton NMR of freshly prepared cement pastes, one observes typically a T_2^* much smaller T_2 which is mainly due to the effect of magnetic field inhomogeneities in the sample. These inhomogeneities are due to susceptibility variations between the cement grains and the water. Even in white cement, these susceptibility variations are still considerable. Their impact on NMR diffusometry experiments shall be discussed in the next section. In ordinary Portland cement and even more in cements rich in fly ash and/or slag, the magnetic field variations inside the sample are stronger due to the high content in paramagnetic or even ferromagnetic materials.

Typical values for the proton NMR relaxation times are given in Table 1 (compiled from data in [7–9]). The dominating mechanism for the spin relaxation of the pore water in most hydrating cement materials is the interaction of surface-adsorbed water with paramagnetic ions on the surface (even for white cements) [10,11]. This information was obtained from Nuclear Magnetic Relaxation Dispersion (NMRD) (i.e. measurements of T_1 as a function of the NMR frequency). At very low proton NMR frequencies (<1 MHz), T_1 is about a factor of 3 to 10 shorter than that at frequencies in the range of several 100 MHz.

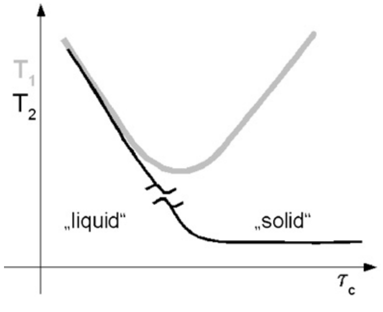

Fig. 1. Qualitative dependence of the longitudinal and transverse relaxation times on the correlation time of molecular motions.

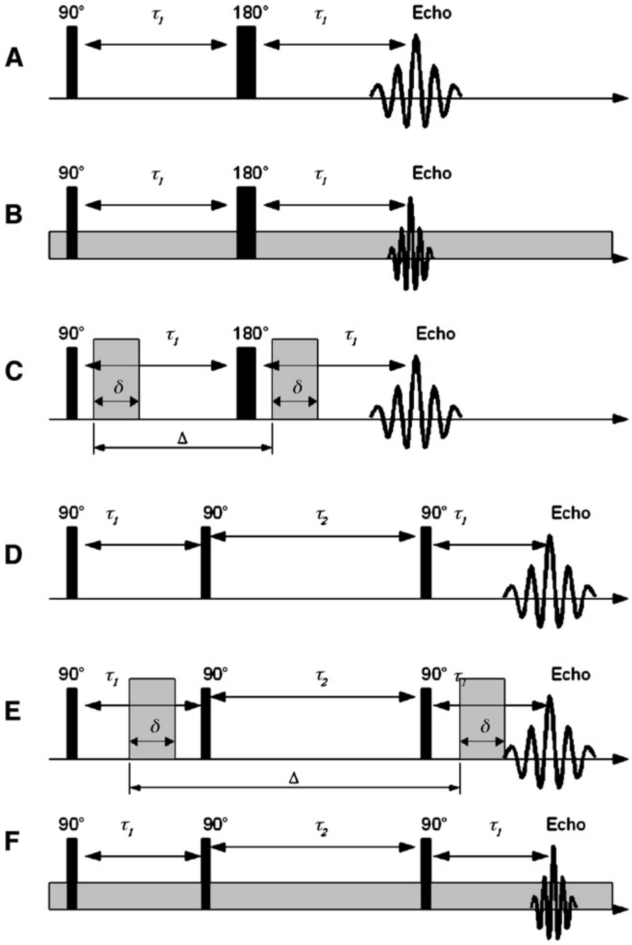

Fig. 2. NMR sequences for spin echo and stimulated echo diffusometry. (A) Spin echo in absence of a gradient. (B) Spin echo with a constant field gradient. Note the shorter echo duration compared to the echo in absence of a gradient. (C) Spin echo with pulsed gradients. (D) Stimulated echo in absence of a gradient. (E) Stimulated echo with a pulsed field gradient. (F) Stimulated echo with a static field gradient.

As we will see later, the measured transverse relaxation rates in materials with strong internal magnetic field gradients may be

Table 1
Typical proton NMR relaxation times (at a proton resonance frequency of 22 MHz) in freshly mixed cement pastes and pastes after 1 day of hydration

Cement sample (w/c=0.33)	Typical T_1 [ms]	Typical T_2 [ms]	Typical T_2^* [ms]
White cement, freshly mixed	100	5	0.25
White cement, one day of hydration	<10	<1	0.1
Ordinary Portland cement, fresh paste	20	<1	0.1
Ordinary Portland cement, 1 day	<10	0.1	0.05

further enhanced due to diffusion effects. This is most pronounced in slag cements where the initial transverse relaxation times may be a short as 200 μs and even increase apparently with the hydration process [12]. At late hydration stages, diffusion in internal gradients plays only a minor role, and the ratio of the transverse and the longitudinal relaxation time takes a constant value which is only dependent on the magnetic field and the surface dynamics of the adsorbed water molecules [11]. At high magnetic field corresponding to proton resonance frequencies of several 100 MHz, the ratio $T_1 : T_2$ is about 8 : 1.

2.2. NMR diffusometry

When trying to measure transverse relaxation times in the presence of a magnetic field gradient, one observes that the amplitude of the spin echo does not only decay exponentially with the echo time but there is an additional signal loss with an exponential term proportional to the 3rd power of the echo time and the second power of the gradient strength. This effect has already been reported by Erwin Hahn in his first paper on the spin echo [6]. The reason for this additional echo attenuation is the fact that the frequency offset of a nuclear spin moving relative to a magnetic field gradient will not be refocused in a spin echo any more. Since the 1960s, this echo attenuation due to diffusion is used as a non-invasive experimental technique for measuring self-diffusion coefficients known as field gradient NMR. This technique shall be discussed in the next subsection. A different NMR approach for observing diffusion phenomena is the non-destructive imaging of tracer concentration profiles which will be discussed in Section 2.2.3.

2.2.1. Field gradient NMR diffusometry

The basic effect of a constant magnetic field gradient G on the NMR signal in a spin echo (see Fig. 2B) was already mentioned in the introduction of this section. The equation for the echo attenuation can be written as:

$$M(t_e) = M_o A_R(t_e) A_D(t_e) = M_o \exp\left(-\frac{2\tau_1}{T_2} - \frac{2}{3}\gamma^2 G^2 D \tau_1^3\right) \quad (2)$$

With $A_R(t_e) = \exp\left(-\frac{2\tau_1}{T_2}\right)$ and $A_D(t_e) = \exp\left(-\frac{2}{3}\gamma^2 G^2 D \tau_1^3\right)$ describing the echo attenuation due to relaxation and diffusion at the echo time t_e, respectively. D denotes the self-diffusion coefficient, $M(t)$ the magnetization at the time t, M_o the magnetization immediately after the NMR excitation and γ the gyromagnetic ratio.

The static field gradient (SFG) spin echo technique has been used for measuring diffusion coefficients for over 40 years [13]. While this experiment looks quite straightforward and easy to do, this method has several drawbacks in actually measuring diffusion coefficients: As the excitation and the detection of the NMR occur in the presence of a magnetic field gradient, both T_2^* and the RF bandwidth needed for exciting a sample slice of given thickness depend on the gradient strength G. This makes a quantitative comparison of signal amplitudes recorded for different values of G quite difficult. It is therefore not advisable to vary G in this type of diffusion experiment. In order to determine the self-diffusion coefficient of a given sample, one therefore has to measure the echo attenuation at different values of τ_1 while leaving the magnetic field gradient static and unchanged. However, according to Eq. (2) this leads inevitably also to a change in the signal decay due to transverse relaxation. Separating these two effects is quite straightforward when the effect of transverse relaxation is small compared to the effect of diffusion. While this is typically the case for free liquids with transverse relaxation times on the order of several seconds, the situation in cement with smaller self-diffusion coefficients and transverse relaxation times on the order of a millisecond or less, the relaxation effect may actually dominate over the diffusion effect.

Both the bandwidth problems with changing values of the gradient and the coupling between the time delays for diffusion and for relaxation can be overcome when working with pulsed field gradients (PFG) instead of constant field gradients (SFG) (see Fig. 2C). In this experiment, the NMR excitation and detection always take place in the absence of a gradient so that one can work with a narrow receiver bandwidth and excite the whole volume of the sample. This leads to a much better signal/noise ratio than in the SFG experiment. In the PFG experiment, the signal attenuation due to diffusion is given as

$$A_D = \exp\left(-\gamma^2 G^2 D \delta^2 \left(\Delta - \frac{1}{3}\delta\right)\right) \approx \exp(-4\pi^2 q^2 D \Delta) \quad (3)$$

with $q = \frac{1}{2\pi}\gamma G \delta$ denoting a so-called generalized scattering coordinate.

As we can see from Eq. (3), the parameters responsible for the diffusive attenuation of the signal are independent from the relaxation term which is only dependent on τ_1. However, the echo time of the spin echo is still a limiting parameter as the maximal diffusion time Δ is limited by τ_1 which must be chosen sufficiently short in order to keep the signal losses due to transverse relaxation at an acceptable level. This so-called pulsed field gradient spin echo (PGSE) technique was introduced into NMR in 1965 [14]. In a PGSE experiment where the duration of the gradient pulses δ is short compared to the overall diffusion time Δ, there is a well-defined diffusion time. This allows studying the time-dependence of the diffusion coefficient [15] or even reciprocal space encoding of diffusion length scales analogous to scattering techniques [16–19]. When the scattering analogy is used, one often finds the name q-space imaging in the literature (in reference to the generalized scattering coordinate introduced in Eq. (3)). A review of PFG NMR diffusometry with special emphasis on porous media can be found in [20]. Scattering-like patterns and time-dependent diffusion coefficients in porous materials are the result of restricted diffusion due to the pore walls: the diffusing liquid phase is confined to the pore system. Whenever the diffusive trajectory of a molecule reaches the pore walls, it is deflected back into the pore. With increasing observation time, more and more liquid molecules experience a slowdown in their diffusive displacement compared to unrestricted diffusion in a bulk liquid phase. This leads to a decrease of the measured diffusion coefficient with the observation time. In case there are regular structures in the pore system, there will be certain preferred values of the diffusive shift which are related to the geometry of the pore system. Such shift values then will give rise to scattering-like structures as a function of the strength of the applied gradient pulse.

For materials in which T_1 is much longer than T_2 the time-window available for a diffusion experiment can be increased by using a stimulated echo instead of a spin echo. The stimulated echo is observed after the application of three RF pulses as shown in Fig. 2D. The amplitude of this echo (which is observed at an echo time $t_e=2\tau_1+\tau_2$) is

$$M(t_\mathrm{e}) = M(\tau_1, \tau_2) = \frac{1}{2} M_\mathrm{o} A_R(\tau_1, \tau_2) A_D \text{ with } A_R(\tau_1, \tau_2) = e^{-\frac{\tau_2}{T_1}} e^{-\frac{2\tau_1}{T_2}} \tag{4}$$

In the case of a PFG experiment (see Fig. 2E), the echo attenuation due to diffusion is given by the same term as in the case of the spin echo (see Eq. (3)).

The stimulated echo is favourable over a spin echo if the T_2 relaxation attenuation of the NMR signal necessary to reach a given diffusion time is considerably smaller for the stimulated echo than for the spin echo. This is typically the case in hydrating cement (see Section 2.1). Stimulated echo PFG NMR experiments (PGSTE) have been suggested for the first time by [21]. A major problem in the application of PFG methods to cement and other materials with internal magnetic field gradients is the presence of a cross-term between the internal gradient G_o and the pulsed field gradient G. For the stimulated echo, the echo attenuation due to diffusion in the presence of a background gradient G_o is given as:

$$\begin{aligned} A_D(G) = \exp(-\gamma^2 D(G^2\delta^2(\Delta-\delta/3) + G_o^2\tau_1^2(\tau_2 + 2/3\tau_1)) \\ + GG_\mathrm{o}\delta(2\tau_1(\tau_2+\tau_1)-(t_1^2+t_2^2)-\delta(t_1+t_2)-2/3\delta^2)) \end{aligned} \tag{5}$$

With the time t_1 denoting the time between the first RF pulse and the beginning of the first gradient pulse and t_2 the time between the end of the second gradient pulse and the center of the echo (see also Fig. 4A). The existence of this cross-term GG_o is especially relevant in the PGSTE case due to the longer possible observation times allowed in a stimulated echo. A similar cross-term also exists in PGSE experiment [14]. For very long diffusion times, the influence of internal field-gradients may become even relevant in magnetically “clean” materials such as cellulose or plant tissue [22]. Ways to compensate the distortion of PFG NMR results in the presence of internal magnetic field gradients will be discussed in Section 2.2.3. Like for the spin echo, for the stimulated echo there is also the possibility to conduct an SFG experiment instead of a PFG experiment. The diffusive contribution to the echo attenuation in a SFG stimulated echo experiment is given as

$$A_D = \exp\left(-\gamma^2 G^2 D \tau_1^3 \left(\frac{2}{3} + \frac{\tau_2}{\tau_1}\right)\right) \tag{6}$$

The stimulated echo SFG experiment combines advantages and disadvantages of the SFG spin echo experiment and a PFG experiment: like in the SFG spin echo experiment, the excitation and detection of the NMR signal must again be performed using broad RF bandwidth. This leads to similar losses in the signal intensity as already described for the spin echo SFG experiments. However, the diffusion time in this kind of experiment is much better defined than in a spin echo SFG spin echo experiment as the gradient generates resonance offsets only during the first two RF pulses and after the third RF pulse. As long as a possible internal gradient inside the sample is not in the same order of magnitude than the external gradient applied in the NMR experiment, the detrimental influence of internal magnetic field gradients on the overall diffusive echo attenuation can be neglected. In typical stimulated echo SFG diffusometry, very strong static magnetic field gradients are used which can be found in the fringe field of ordinary superconducting magnets for NMR spectroscopy [23]. Some groups have even realized stronger magnetic field gradients by the use of dedicated gradient magnets [24]. Changing the gradient strength in such magnets is quite difficult as they use superconducting coils. Furthermore, a change in the gradient intensity during the diffusometry experiment would lead to similar problems with changing RF bandwidth as described already for the spin echo SFG technique. Therefore, the experiment is again performed by varying τ_1. The variation of τ_1 in a SFG stimulated echo experiment on a sample with a short T_2 can lead to magnetization decay curves with both contributions from A_R and A_D in an equal order of magnitude. In addition to transverse and longitudinal relaxation, also dipolar correlation effects (DCE) [25] or quadrupolar couplings [26] may disturb the diffusometry experiment. For water diffusion in cement, the DCE and quadrupolar effects are of minor importance so that only A_R and A_D in the SFG stimulated echo experiment need to be separated. Two approaches to achieve this are sketched in Fig. 3. The first approach involves the acquisition of both the echo produced by the second 90° pulse (which is attenuated by T_2 in the same way as the stimulated echo) and the evaluation of the diffusion effect from the ratio of both echoes. This double echo acquisition approach requires a spectrometer capable of acquiring two echoes within one experiment. While this might be a problem with older NMR spectrometer hardware, such

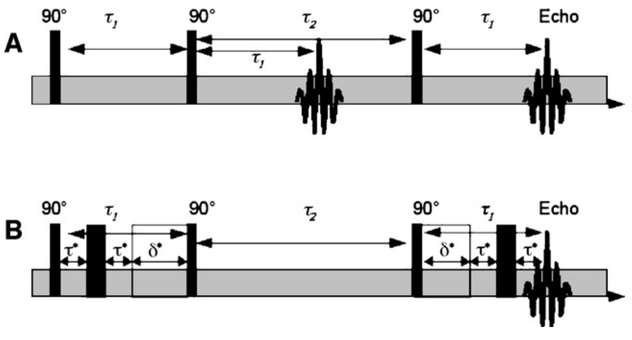

Fig. 3. Approaches to separate the influence of relaxation and diffusion on the echo attenuation in a SFG stimulated echo experiment according to [26]. (A) double-echo acquisition; (B) five-pulse sequence.

multitriggering capabilities are nowadays a standard feature of most NMR systems. The five-pulse sequence does not need the acquisition of a second echo. Instead, it introduces two additional 180° pulses into the stimulated echo sequence. By generating a spin echo with a short echo time $2\tau^*$, these pulses reduce the gradient time relevant for the diffusion effect in the stimulated echo to a time $\delta^* = \tau_1 - 2\tau^*$. There are two problems with this approach: Switching additional RF pulses during the τ_1 interval requires additional time. Furthermore, there are no well-defined pulse angles in a strong magnetic field gradient [17]. Therefore, parasitic echoes are formed which can contribute to the echo signal in an unexpected way. In a spectrometer with multitriggering capabilities, the double-echo technique is therefore superior to the five-pulse sequence.

While relaxation-time weighting problems can be partially overcome like this, the low signal/noise ratio is more fundamental to the SFG experiment: The combination of a high bandwidth needed for signal detection means acquiring a lot of noise and the small amount of excited sample volume that actually contributes to the NMR signal leads to a low actual signal intensity. This creates a need for long signal accumulation and correspondingly long measuring times in stimulated echo SFG experiments. Possible applications of this method to cement are therefore limited to late hydration stages where the diffusion coefficient undergoes only minor changes any more.

While PFG experiments offer the advantage of much higher NMR signal intensity over the SFG experiments, the price to pay for this is the need for more sophisticated experimental equipment. This is especially the case for experiments on samples with short transverse relaxation rates: Here one has to be able to switch very strong electrical current (to generate the magnetic field gradients) up to over 100 A within less than 300 µs to a well-defined value and back to zero again. The reproducibility achieved in this switching process must be better than 10^{-5} both for the current values and the pulse durations [28].

Table 2 gives an overview over the four basic sequences used for NMR diffusometry and their specific advantages and problems.

2.2.2. Special challenges in hydrating cement

None of the basic techniques for NMR diffusometry described in the last subsection seems to be well-fitted for diffusion studies in a hydrating cement paste: SFG approaches with their intrinsically low signal/noise ratio are just too slow for measuring a fast-changing diffusion coefficient during the first days of hydration (although they actually may prove very well-fitted for diffusion studies in aged samples where the diffusion coefficient is not changing fast any more).

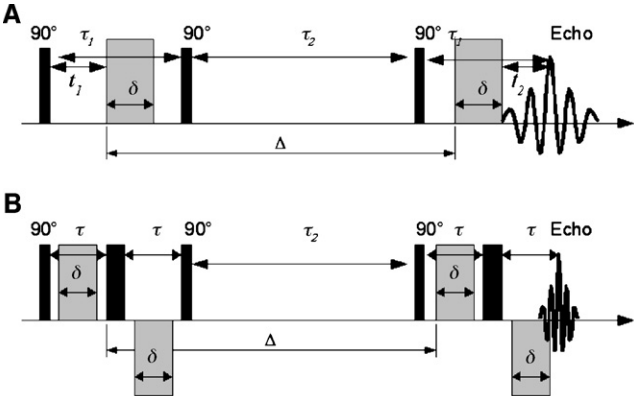

Fig. 4. (A) Ordinary stimulated echo PFG sequence and (B) 13-interval modified stimulated echo sequence for PFG diffusometry in samples with internal magnetic field gradients. The dephasing in the internal magnetic field gradient is reset at the time of the 2nd $\pi/2$ pulse due to the action of the π pulse. As the gradient pulse is applied as a bipolar pulse pair symmetrically to the gradient, its position encoding is not reset by the π pulse.

Due to the relatively short transverse relaxation times in cement, the spin echo technique seems to be generally less well-fitted for measurements on hydrating cement than the stimulated echo. However, also the stimulated echo PFG technique is hampered in its applicability due to its sensitivity to internal magnetic field gradients. A possible approach to reduce the effect of internal magnetic field gradients in stimulated PFG was already suggested in 1989 [27]. The corresponding sequence (known as 13-interval sequence or 5-pulse sequence) and an ordinary stimulated PFG experiment are sketched together in Fig. 4. As can be seen from the figure, the gradient pulse applied during the τ_1 period in the stimulated echo is split into two gradient lobes with opposite polarity which are separated by a 180° pulse. The spin echo generated by the 180° pulse resets the effect of the internal gradient which changes its sign from the viewpoint of the spins when they are exposed to a 180° pulse. The effects of the two bipolar pulsed gradient lobes, by contrast are additive under these conditions. The diffusive attenuation of the echo produced at $t_e = \tau_2 + 4\tau$ after all five RF pulses is given as:

$$A_D(t_e) = A_D(\tau_2, \tau) = \exp\left(-\gamma^2\delta^2G^2D\left(4\tau_2 + 6\tau - \frac{2}{3}\delta\right)\right) = \exp\left(-\gamma^2\delta^2G^2D\left(4\Delta - 2\tau - \frac{2}{3}\delta\right)\right) \quad (7)$$

Using this sequence for materials with short transverse relaxation time and strong internal gradients requires even faster

Table 2
Basic properties and advantages and disadvantages of the basic field gradient NMR diffusometry sequences

Sequence	A_R	A_D	Accessible diffusion time window	S/N	Sensitivity to background gradients	Well-defined diffusion time	Best fitted for
SFG spin echo	$e^{-\frac{2\tau_1}{T_2}}$	$e^{-\frac{2}{3}\gamma^2G^2D\tau_1^3}$	Short (limited by T_2)	Low	Low	No	$D > 10^{-10}$ m²/s
PFG spin echo	$e^{-\frac{2\tau_1}{T_2}}$	$e^{-\gamma^2G^2D\delta^3\left(\frac{4}{\delta}-\frac{1}{3}\right)}$	Short (limited by T_2)	High	High	Yes	$D > 10^{-10}$ m²/s
PFG stimulated echo	$e^{-\frac{2\tau_1}{T_2}-\frac{\tau_2}{T_1}}$	$e^{-\gamma^2G^2D\delta^3\left(\frac{4}{\delta}-\frac{1}{3}\right)}$	Medium (limited mainly by T_1)	High	High	Yes	$D > 10^{-13}$ m²/s
SFG stimulated echo	$e^{-\frac{2\tau_1}{T_2}-\frac{\tau_2}{T_1}}$	$e^{-\gamma^2G^2D\tau_1^3\left(\frac{2}{3}+\frac{\tau_2}{\tau_1}\right)}$	Medium (limited mainly by T_1)	Low	Low	Yes	$D > 10^{-11}$ m²/s

gradient switching capabilities than those needed in an ordinary PFG experiment. Furthermore, matching the gradient lobes with different signs to the required precision is far from simple. Appropriate spectrometer equipment has only recently become available [28]. While reducing the effect of internal gradients, the 5-pulse sequence may also lead to artifacts in itself as it is more sensitive to incorrectly set RF pulses than the stimulated echo sequence [22].

A second problem in NMR diffusometry on hydrating cement is the heterogeneity of the material: in the discussion up to now, we always have assumed one transverse and one longitudinal relaxation time for the whole sample. While this is more or less the case in a freshly prepared cement paste [29,7], this is not any more given after a few hours of hydration (see also Section 4.2). After this time, non-exponential magnetization decay curves are observed in the hydrating cement paste. The non-exponential relaxation behaviour of the whole sample is mainly due to a superposition of exponentially decaying NMR signals from compartments of the sample which are at least partially isolated from each other. The observed NMR signal is therefore a superposition of contributions from several components i which all are weighed by different relaxation times:

$$M(\tau_1, \tau_2, G) = \sum M_{o,i} e^{-4\tau/T_{2i} - \tau_2/T_{1i}} A_D(D_i(\varDelta), G, \varDelta, \tau) \qquad (8)$$

The diffusion coefficient measured in a PFG NMR experiment is therefore a Relaxation time Weighted Mean Diffusion coefficient (RWMD) [30].

Disentangling the relaxation time weighting and the diffusion effect is a very tough challenge as both the echo attenuation due to diffusion and to relaxation lead to monotonous signal decay. Only recently reliable 2D Laplace inversion techniques have become available to evaluate such data sets [31,32]. Even with such evaluation tools available, the required experiments nevertheless remain very difficult to perform due to the high requirements with respect to signal/noise ratio needed for a numerically stable 2D Laplace inversion.

For the presently available data, we have tried to minimize possible relaxation time filtering by keeping the gradient duration δ and the time intervals τ_2 and τ_s as short as possible. Working with short δ and $\varDelta$ (essentially given by τ_2) limits of course the achievable echo attenuation A_D for the maximally available gradient strengths. This in turn makes diffusion measurements with small diffusion coefficients more and more difficult to realize.

As the longitudinal relaxation time increases with the magnetic field (see Section 2.1, [10,11]), the impact of relaxation-time filtering should be less problematic in diffusion studies at higher magnetic fields than at low fields. However, the increase in the available time window by a factor of 2 or 3 is not really dramatic. In the recently published diffusometry work on cement, useful results could be achieved both at 23.5 MHz [33] and at 400 MHz [30] proton resonance frequency.

While paramagnetic ions dominate relaxation even in “clean” materials such as white cement (see Section 2.1, [11]), the shorter absolute relaxation time values in cement materials with a higher content in paramagnetic materials make relaxation-time filtering an increasingly severe problem in these materials. In order to keep these difficulties as small as possible, most of the presently available field gradient diffusometry work in cements was done on white cements.

2.2.3. *Other approaches to NMR diffusometry in cementitous materials*

Under favourable conditions, the PFG NMR experiment is sensitive to molecular displacements in the micrometer range during a time interval of about 1 ms to several seconds. Within the experimental limits set by spin relaxation, the observation times can be varied. The field gradient NMR experiment is truly non-invasive as the RF and gradient pulses can penetrate the whole sample and there is no long-term memory effect for the applied NMR pulses in the material. The lack of a long-term memory for the diffusion-marking is at the same time also a limitation as diffusion lengths of more than a few 10 μm (corresponding to diffusion times in the range of 1 s) are not accessible like that.

However, for many technical questions, it is exactly this long-range diffusion which is relevant for the technical performance, durability and barrier action of a cement sample. In order to be able to measure diffusion coefficients under these conditions, one has to resort to tracer diffusion techniques or to interdiffusion processes along a concentration gradient. The resulting diffusion coefficient is an interdiffusion coefficient (which describes a diffusion process which is driven from a spatially non-uniform concentration profile and which goes along with changes in the local concentration of the diffusant). By contrast, the diffusion coefficient measured in field gradient NMR is a self-diffusion coefficient. Self-diffusion describes the average distance travelled by the diffusing molecules due to thermal motion in a chemically uniform environment.

The tracer approach is quite common. Both stable isotope tracers such as deuterium or ^{18}O and radioactive tracers such as tritium can be used for such studies. Similarly, also dissolved salts are often used as tracers in interdiffusion studies. In tracer diffusion studies, the tracer distribution profile is mapped as a function of the time after tracer administration, and the diffusion coefficient is determined by analyzing the profiles. The time and length scales accessible in such a diffusion experiment are only limited by the patience of the experimentator and (in the case of radioactive tracers) by the half-life time of the tracer isotope. Tracer profiles can either be obtained by destructive sampling techniques or non-destructively by appropriate imaging techniques such as neutron radiography [34], X-ray tomography [35] or Magnetic Resonance Imaging (MRI). Both 1D MRI profiling and 2D imaging techniques have been applied to a range of different mineral sample materials such as clays and sediments [36,37] and also cement, mortar and other construction materials [33]. In construction materials, interdiffusion processes of moisture into dry materials [38,39] and transport of ionic substances [40] have received the greatest attention. Compared to PFG NMR, the profiling technique is not fully non-invasive as a tracer or a concentration change must be administered to the sample. However, when coupled with NMR profiling, at least the recording of the profiles themselves is non-destructive in nature. This is not the case for most other tracer diffusion techniques such as those described in the next subsection. The minimal length scales for NMR-profiling diffusion studies are limited by the resolution achievable in the MRI observation. For several MRI techniques, resolutions down to about 5 μm have been reported in materials similar to cement. Resolutions on the order of several 100 μm are easily feasible. This allows the observation of long-time diffusion processes over time scales ranging from several minutes to days and years. It should be noted that the concentration front observed in a tracer diffusion experiment is the integral resulting from the diffusion process over all the observation time. In case the diffusion coefficient is not constant during the observation time, this greatly complicates the analysis of the diffusion process.

Like in PFG experiments, relaxation-time weighting is also an issue in MRI of tracer distribution profiles; as one example, tracer signals in sample regions with transverse relaxation times on the order of the echo time or shorter may be “lost” in the imaging experiment. To minimize these effects one has to work very carefully to establish a pure spin density contrast for the tracer.

Even from NMR measurements without full profiling, some rough information on diffusion coefficients can be obtained from magnetization decay curves if there is a pronounced difference in the relaxation time between the free tracer in solution and the tracer inside sample bodies of well-defined geometry. Such approaches and the corresponding evaluation methods have been suggested for ion exchange studies [41].

2.2.4. Destructive and long-range transport diffusion studies in hydrating cement

PFG NMR, MRI and other tomographic techniques for diffusion studies have become available only quite recently. Other approaches have been around for longer time. These include destructive sampling of tracer profiles along exposed sample sections (e.g. by electron microprobe analysis [42]) and diffusion cell tests. For studies of moisture diffusion in unsaturated concrete samples, moisture sensors integrated into the sample can be used for monitoring the local relative humidity as a function of time [43].

In diffusion cell tests, the sample (typically a thin slice of the material of interest) is used as a barrier between a solution with the tracer and a solution originally without tracer. In the experiment, the increase in the tracer concentration in the second reservoir is studied [44,45].

In contrast to PFG NMR experiments, long-range diffusion experiments and imaging/profiling studies cannot be performed continuously on a given sample. Rather, they allow a measurement of the long-range diffusion behaviour in a sample which is sufficiently mature that changes in the internal structure due to the long-range diffusion experiment during the diffusion experiment are negligible. Furthermore, in long-range diffusion studies, no information on the time-dependence of the diffusion coefficient (and thus on the internal micron-scale structure of the sample) can be obtained.

3. Results

In this section, some results of our own diffusion studies on water and on organic solvents in hydrating cement pastes shall be presented and discussed also in relation to new work by other groups in the field. Substantial parts of the data shown here have already been published during the last years [46,47].

3.1. Diffusion of water in hydrating cement

3.1.1. Materials and methods

In order to keep relaxation-time-weighting problems as small as possible, we worked with commercial white cement in most of our experiments. Two different brands of white cement were used in the studies: a (A) CEM I 32.5 R called Aquila Bianca from Cemen-Koll, Forlí, Italy and (B) Dyckerhoff white CEM I 42.5 R from Dyckerhoff, Wiesbaden, Germany.

While the material (A) exhibited especially favourable long relaxation times, (B) is closer to the ordinary Portland cements used for the production of high-quality concretes in construction. Some other experiments were done on Portland cement and on ground blast furnace slag (obtained from Alsen-Zement, Sehnde-Höver, Germany) which was either activated by means of 1 M NaOH or by means of white cement.

All diffusion data shown in this article were obtained in the FEGRIS NT PFG NMR facility of the university of Leipzig

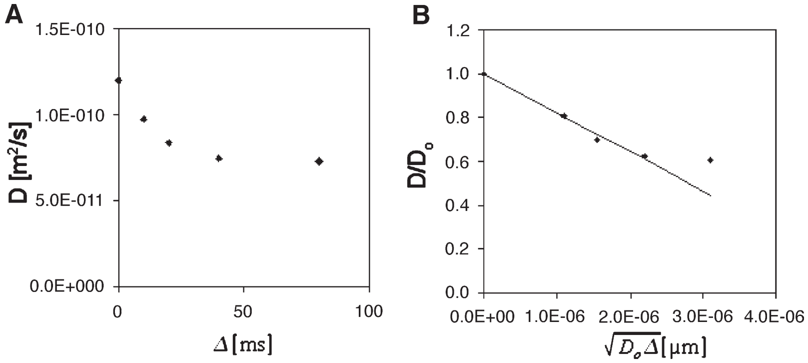

Fig. 5. (A) The self-diffusion coefficient of *n*-octanol in a paste prepared from ground blast furnace slag (about 4000 cm^2/g) and *n*-octanol measured for different diffusion times. (B) The same data set shown as a function of the mean diffusive shift of the *n*-octanol molecules.

using the 13-interval PFG sequence [28,30] at a proton resonance frequency of 400 MHz. Relaxation experiments were carried out at 22 MHz in an MRS 6 spectrometer (JSI, Ljubljana, Slovenia) [7].

3.1.2. Liquid phase self-diffusion in freshly prepared cement pastes

A freshly prepared cement paste is essentially a thick suspension of mineral grains with sizes on the range of a few microns in water. As already mentioned above, the diffusive shift mapped in a PFG NMR experiment is on the order of a few microns, too. The presence of the cement grains corresponds to a geometrical restriction of the space available for water self-diffusion. The long-range diffusion coefficient of water in the paste will therefore be reduced by a so-called tortuosity factor compared to the one in bulk water. For very small diffusive displacements, the influence of the pore walls should become less and less important and a diffusion coefficient close to the one in the bulk liquid should be expected.

Studying the tortuosity of a liquid phase in a fresh cement paste in water is complicated by the ongoing reactions in the paste and by the fact that the water molecules already diffuse over a typical grain size range of several microns even for a diffusion time as short as 1 ms. When suspending the cement grains in a solvent such as *n*-octanol, no hydration reactions take place and the diffusion process is slow enough to see the effect of tortuosity. Fig. 5 A shows the self-diffusion coefficient of *n*-octanol in saturated ground blast-furnace slag measured for different diffusion times. In Fig. 5 B the same data are shown again as a function of $\sqrt{D_o \Delta}$ (which is proportional to the mean free diffusive path of the molecules). The linear fit given along with the data was performed using the model discussed in [48,49] according to which

$$\frac{D(\Delta)}{D_o} = 1 - \frac{4}{9\sqrt{\pi}} \frac{S}{V_p} \sqrt{D_o \Delta} + R(\sqrt{D_o \Delta}) \qquad (9)$$

When analyzing the slope of the curve, the resulting surface/volume ratio is about a factor of 2 smaller than it should be according to the manufacturer's data (based on gas adsorption measurements). This deviation suggests that there is some flocculation so that not all the intergrain space is actually available to the *n*-octanol.

As one can see from Fig. 5, the diffusion coefficient decreases from its bulk value down to about 0.6 times the bulk value while the molecules sample a diffusive path of a few microns. This corresponds to a tortuosity factor *T* of 1.67. For water, the diffusion occurs much faster and only the tortuosity limit can be observed directly from our data. The self-diffusion coefficient measured in a white cement paste with a water/cement ratio of about 0.5 corresponds to a similar tortuosity factor than that observed for *n*-octanol in the ground slag. For lower water/cement ratios, the tortuosity factor of the freshly prepared pastes tends to increase to about a value of 2 (see Table 3). No dependence of the measured diffusion coefficient on the diffusion time was observed for diffusion times between 5 and 20 ms.

Table 3
Water self-diffusion coefficients at 31 °C and a diffusion time of 10 ms in freshly prepared pastes of white cement (A) at different water/cement ratios

w/c	*D* [m²/s]	*T*
0.25	$1.30 \cdot 10^{-9} \pm 1.4 \cdot 10^{-11}$	2.05 ± 0.022
0.33	$1.35 \cdot 10^{-9} \pm 2.3 \cdot 10^{-11}$	1.97 ± 0.037
0.5	$1.60 \cdot 10^{-9} \pm 1.6 \cdot 10^{-11}$	1.63 ± 0.016

The tortuosity factors were computed using a value of $D = 2.66 \cdot 10^{-9}$ m²/s (according to [50]). The length scale sampled by the diffusing spins is about 7 μm. Water self-diffusion in cement data taken from [30].

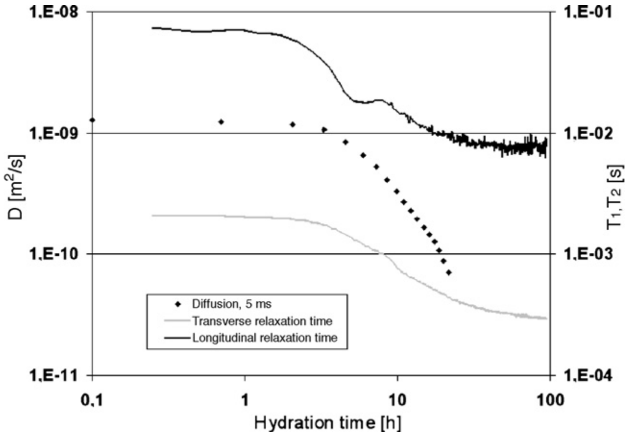

Fig. 6. Diffusion coefficient (measured with a diffusion time of 5 ms) and relaxation times in a hydrating white cement sample (type B, w/c 0.33). The decrease of the relaxation times (especially in T_1) sets in before a decrease in the diffusion coefficient is observed.

3.1.3. Decrease of the diffusion coefficient during hydration

In Fig. 6, the change of the measured self-diffusion coefficient and of the longitudinal and transverse relaxation time of the water with the hydration time are depicted for white cement type (B) at a water/cement ratio of 0.33. As can be seen from the figure, the decrease of the relaxation times already sets in before there is a notable change in the diffusion coefficient. These early changes are especially obvious in the longitudinal relaxation rate. The earlier onset of changes in the relaxation time than in the diffusion coefficient can be qualitatively explained by the fact that relaxation-time changes during the early stages of hydrating are brought about by any increase in the surface/volume ratio (which can also be due to acicular crystallites which contribute only minimally to an increase in tortuosity) while changes in the diffusion coefficient actually needs the formation of continuous extended structures that act as barriers for diffusion.

In Fig. 7, the development of the diffusion coefficient relative to the bulk diffusion coefficient of free water is plotted as a function of the hydration time for several white cement pastes (material A) prepared with different water/cement ratios. Experimental details are described in [30]. While there is no notable dependence of the diffusion coefficient on the diffusion time in the dormant paste, we can observe that the overall decrease of the diffusion coefficient at later hydration stages is accompanied by the formation of a small but significant decrease of the diffusion coefficient with the diffusion time, too.

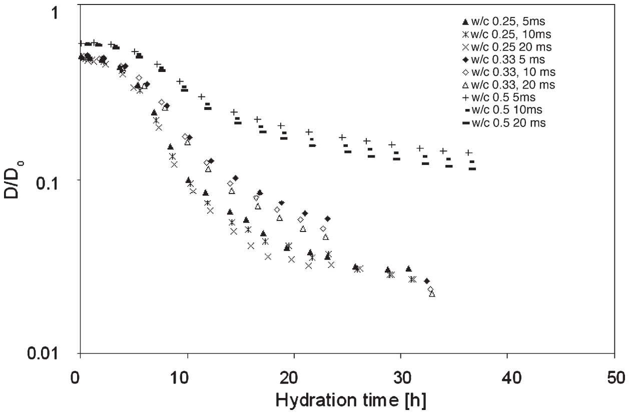

Fig. 7. Water self-diffusion coefficients (relative to the diffusion coefficient of free water) measured in hydrating pastes of material A prepared at different water/cement ratios. Hydration temperature: 31 °C.

For the paste with w/c 0.25 the observation-time-dependence seems to be levelling off after about 20 h of hydration. The most likely reason for this is the unwanted relaxation-time weighting of the NMR signal already described in Eq. (8): the contribution of slower-diffusing components with a shorter T_1 is reduced for the longer diffusion times. At the latest hydration times in the study, the relaxation time weighting most probably affects also the diffusion coefficient measured at 5 ms as the diffusion coefficients measured for the w/c 0.33 sample are all lower than the last diffusion coefficients measured for the w/c 0.25 sample.

As already described in [30,33], relaxation-time weighting most probably leads to an increasing bias towards highly mobile water fractions with increasing diffusion time which might mask or even reverse a decrease in the mean diffusion coefficient in the overall liquid water content of the sample. Due to shorter τ values used in our experiments, this effect is probably less pronounced for the data in Fig. 7 than for those by Hansen et al. [33]. The observation time dependence of the diffusion coefficient in a one-day-old paste of Danish Super White Portland BSI class 62.5 N cement with w/c 0.4 presented by Hansen et al. covers a wider range of diffusion times (from 2.2 to 100 ms), and the decrease of the diffusion coefficient over this range of observation times is about a factor of 5. In the range from 5 to 20 ms diffusion time covered by our experiments, the Hansen data suggest a decrease of the diffusion coefficient by a factor of about 2 while our data both for the w/c 0.5 and for the w/c 0.33 sample only exhibit a decrease of about 20%. This is quite surprising as the stronger relaxation-time weighting in Hansen's data should rather obscure a possible observation-time dependence of the diffusion coefficient than enhance it. However, the absolute values of the diffusion coefficients measured by Hansen in the w/c 0.4 paste are quite similar to those measured by us in the w/c 0.5 paste.

In Fig. 8, the results of diffusion measurements on material B at a water/cement ratio of 0.33 are given. In this case, the time-dependence of the diffusion was measured over a wider interval up to 40 ms. Over that whole range of diffusion times, the diffusion coefficient decreases by nearly a factor of two. Also in the time range between 5 and 20 ms, the time-dependence of the diffusion coefficient is stronger (about 30% decrease) than for the material A. Combining these findings with the results obtained by Hansen et al., there seems to be a tendency for a more pronounced time-dependence of the diffusion coefficient in cements with higher strength certification. In order to see whether this is really the case, further experiments will be necessary in the future.

One reason for the change in the diffusion coefficient from diffusion-time-independent (i.e. having reached the tortuosity limit) to diffusion-time-dependent (i.e. not yet in the tortuosity limit) is the decrease in the length scale sampled by the diffusion water molecules during a given diffusion time (see Fig. 8). However, at the later hydration times there is already a notable diffusion-time-dependence for length scales (see grey line) still longer than the initial mean diffusive shift of the water molecules at the shortest diffusion time (see black line). This suggests that the representative length scale inside the hydrating paste increases during the acceleration phase. In other words, the partially hydrated cement paste is spatially heterogeneous over a greater length scale than the freshly mixed paste (see also Section 4.2).

3.1.4. Diffusion at later hydration times

The measurements presented in the last subsection show a strong decrease in the self-diffusion coefficient of the water in hydrating cement paste over the first days of hydration. The combination of smaller self-diffusion coefficients, shorter relaxation times and the increasingly heterogeneous microstructure of the cement paste complicate NMR diffusion studies at later hydration stages. Even if a diffusion measurement is feasible, it might be distorted due to relaxation-time weighting [30,33]. A clear indication for relaxation-time weighting is a diffusion coefficient increasing with the observation time. Even if no such increase is observed, it might just be masked by a much stronger decrease in the diffusion coefficient with diffusion time in the long-hydrated sample which dominates over the relaxation-time weighting.

Comparisons with results from long-range diffusion measurements on similar materials are also difficult to do as studies of water-self diffusion in moist-cured cement are scarce in the literature. [43] report a moisture diffusion coefficient (including a contribution due to vapour-phase diffusion) of about

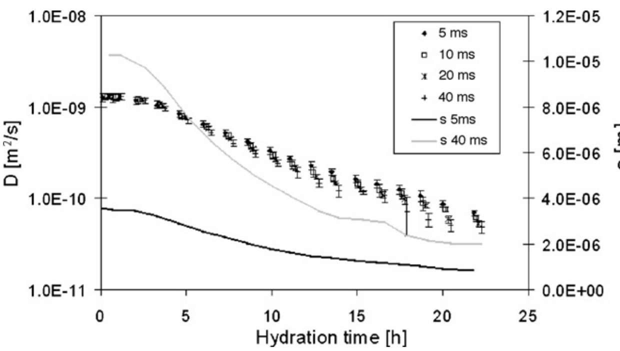

Fig. 8. Water self-diffusion coefficient in a paste of white cement B (w/c 0.33) hydrating at 31 °C. In addition to the diffusion coefficients measured in the range between 5 and 40 ms, also the mean diffusive shifts for the shortest and the longest diffusion time are given in the diagram (solid lines).

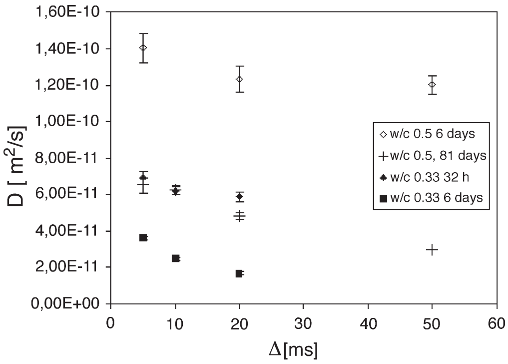

Fig. 9. Time-dependent diffusion coefficients measured on the type A samples with w/c 0.33 and w/c 0.5 at long hydration times.

$4 \cdot 10^{-10}$ m^2/s after 3 days of moist-curing in Portland cement at w/c 0.4, and of about $3 \cdot 10^{-10}$ m^2/s after 28 days of moist curing. Due to the contribution of fast vapour-phase diffusion, these values are nearly one order of magnitude higher than the diffusion coefficients measured in our experiments. Bejaoui et al. [51] performed tritium tracer diffusion studies on Portland cement samples moist-cured for one year. In these experiments, a water self-diffusion coefficient of $8 \cdot 10^{-12}$ m^2/s was found for a sample prepared at a water/cement ratio of 0.5. This value lies about a factor of 3 lower than the value for the longest diffusion time measured for the 81-day old sample in Fig. 9.

The comparison with the diffusion coefficients reported in the literature indicates that despite all caveats, the NMR diffusometry results for the long-cured samples are at least in a reasonable order of magnitude. However, it must also be noted that at lower water/cement ratios, no PFG studies are feasible for comparably long diffusion times so that a direct comparison with long-term studies such as those in [51] becomes more and more difficult.

3.2. Diffusion of non-watery solvents in hydrating cement

While the dynamics of water in hydrating cement has been studied for a long time, experimental data on the fate of organic solvents in hydrating cement have only recently become available [52,53,54]. Information on the behaviour of solvents in cement is on one hand of interest in the context of solidification of wastes containing organic solvents as co-contaminants. On the other hand, the influence of organic solvents on the hydration process and the changes in the pore structure available to the solvents may also provide new insights into the cement hydration itself.

In the studies of solvent dynamics in hydrating cement, it was found that even small quantities of polar solvents such as cyclohexanone and *n*-hexanol lead to an extreme delay of the cement hydration. In contrast to the delay produced in the presence of superplasticizers, the polar solvents do not just lead to a prolonged dormant period but continue to slow down also the hydration after the dormant period. Added non-polar solvents, by contrast, do not lead to considerable changes in the hydration behaviour of the cement paste. At a water–cement ratio of 0.33, no indications for macroscopic phase separation between the water and the solvent could be observed for any of the solvents under study. The NMR relaxometry [53] data obtained for all the solvents studied suggest that for all added solvents, the organic droplets undergo some change in geometry inside the hydrating cement matrix. However, the nature of this change seems to be very different for different types of solvents. Both the NMR and the synchrotron data [52,53] indicate that there are especially strong changes in the distribution of aromatic solvents in the hydrating cement stone matrix: at solvent contents up to about 0.03 ml/g cement, all the solvent seems to be distributed from micron-sized droplets into a fine pore network with nanometer-sized pores. As a result of this process, the transverse relaxation time of the toluene is reduced to values similar to those of water in a hydrating cement paste. In the case of the other solvents, only minor relaxation time changes were observed for the solvent phase. In a cement paste prepared with ordinary water and added solvents, it is problematic to unambiguously discern the signals originating from the water and from the solvent phase. Due to the small NMR chemical shift range of protons and the magnetic field variations inside the cement stone matrix, spectroscopic separation of the solvent signal and the water signal is also problematic even for residual water leaching out from the cement in the preparation of deuterated pastes [54]. The most straightforward approach to separate the solvent from the water signal is to deuterate one of the liquid phases. When studying a solvent phase in a cement paste prepared with heavy water, one has to be aware of the considerable delay of the cement hydration process in heavy water compared to ordinary water. This delay has been observed by several groups since a long time [1,54,55] but is still not fully understood. Nevertheless, there seems to be no major change in the morphology of the hydration products so that the dynamics of solvent phases in a deuterated paste should be sufficiently representative for that in a paste prepared from ordinary water. Studying a deuterated solvent added to a paste prepared with ordinary water would also be an option. However, the NMR signal intensity would be much smaller in this case. Furthermore, the sensitivity of the NMR signal to diffusion effects would also be dramatically reduced (the diffusive attenuation of the NMR signal depends on the square of the gyromagnetic ratio) so that experiments using ordinary solvents and heavy water seem to be the easier path.

In [54], data on relaxation times and liquid-phase self-diffusion coefficients for various solvents have been reported. For all solvents studied, a decrease in the diffusion coefficient during the first few days of hydration could be observed. There were however big differences between the different solvents:

- For cyclooctane, a decrease in the diffusion coefficient by about a factor of 5 with respect to the initially recorded value could be observed during the first 100 h of hydration. After that, no further significant change in the diffusion coefficient took place.
- For *n*-hexanol, the diffusion coefficient was found to decrease by a factor of about 10 during the first 100 h. This decrease was followed by a slower decrease during several months.

- For toluene, the decrease in the diffusion coefficient was found to be nearly as pronounced as for water.

Relaxation time weighting – as expectable on the basis of the relaxometry data [47,53] – proved to be a problem only for toluene where the low overall signal intensity and the short relaxation times made it impossible to conduct meaningful PFG NMR experiments after about 100 h of hydration.

The diffusion data obtained for the three solvents confirm that none of the solvents is just present in form of inert droplets of constant geometry in the hydrating paste. Rather, for all of the solvents, we see the formation of a more tortuous, mazelet-like pore structure incorporating the majority of the solvent. This means that some ingrowth of hydration products into volume originally occupied by the non-aqueous solvent takes place for all materials. The nature of the pore-system filled by non-aqueous solvent is however very different for the three solvents: in the case of the cyclooctane, the tortuosity of the pore system does not change any more after the first few days of hydration. In the case of the *n*-hexanol, we see very slow processes leading to further reductions in the diffusion coefficient even at very long hydration times of several months. An analysis of the diffusion-time dependence of the *n*-hexanol in such an aged paste indicates a pronounced increase in tortuosity at short length scales (in the micron range) and an additional decrease of the diffusion coefficient for longer diffusion times. Whether this decrease is due to confinement into separate mazelets or into a connected network with very high tortuosity cannot be unambiguously determined from the experimental data as the observation time window for the diffusion is too short. As long-range diffusion of solvents in cement is of interest in the context of solidification and of anti-solvent-barriers, further experiments with NMR profiling or non-NMR techniques should be done in the future.

The diffusion behaviour of the toluene is again fully in accordance with the findings from NMR relaxometry [53] and synchrotron X-ray tomography [52]: The toluene is dispersed into a very narrow pore network with very high tortuosity. Unfortunately, the short relaxation times of the dispersed toluene molecules again does not allow a determination of a long-range diffusion coefficient in the NMR experiment.

4. Discussion

A lot of technical aspects to the diffusion measurements have already been discussed in the last section. Here, some further aspects and open questions shall be discussed at slightly more detail.

4.1. Diffusion and internal post-curing

Water-transport in hydrating cement is most relevant for construction applications in the context of post-curing of high-performance concrete, especially internal post-curing [56,57]. The basic idea behind internal post-curing is the incorporation of moisture-storing aggregates into a concrete mixture prepared at very low water/cement ratio. At water/cement ratios below 0.25, the water in the paste is not sufficient for stoichiometric hydration of the cement. In order to prevent increased shrinkage and also damage due to late hydration upon later access of water, additional moisture is administered to the hydrating cement during the first few days of hydration. In the case of internal post-curing, this moisture comes out of the moisture-storing aggregates and travels diffusively through the cement stone matrix. The length scale $s(t)$ for diffusive water transport inside the cement matrix could be estimated as $s(t) = \sqrt{6Dt}$ if the diffusion coefficient was constant during the hydration time. However, as the diffusion coefficient decreases by more than one order of magnitude during the first few days of hydration, one must take into account this decrease when calculating $s(t)$:

$$s(t) = \sqrt{6 \int_0^t D(t')dt'} \qquad (10)$$

Doing so indicates that the efficiency of diffusive moisture transport through the hydrating cement stone matrix is extremely low after the first few days [30]. This finding could be verified from observations made on a phenolphtaleine colour tracer for diffusion.

These findings from diffusion studies suggest that in internal post-curing no homogeneous increase in the degree of hydration of the cement stone matrix is achieved. Nevertheless, the macroscopic behaviour of concrete with internal post-curing is favourable compared to conventionally post-cured high-performance concrete samples. This raises the question whether a spatial modulation in the degree of hydration of the cement stone matrix is the actual reason for the superior properties of concretes with internal post-curing.

4.2. Diffusion and non-exponential relaxation behaviour in cement

As already described in [7], the longitudinal relaxation of water in freshly prepared cement pastes can be fitted quite well by a single-exponential relaxation time. At later hydration stages, the magnetization decay curves in hydrating cement samples are obviously non-exponential. This change from exponential to non-exponential – the separation of an initially uniform pore water pool into separate components – is relevant for the interpretation of NMR diffusometry data as non-exponential relaxation suggests possible relaxation-time filtering. Furthermore, an explanation of the onset of non-exponential relaxation might also provide new insights into the formation of the cement pore structure itself. The availability of diffusion data along with relaxation data has prompted us into exploring a possible relationship between both. First results of this shall be presented here along with a short discussion of different approaches to quantitatively describing non-exponential relaxation.

4.2.1. Evaluation of non-exponential relaxation

In order to track down the change from exponential to non-exponential relaxation, one has to find a way of quantifying the non-exponentiality in a series of magnetization decay curves.

This could be done by the use of the inverse Laplace transform. However, the use of the inverse Laplace transform is limited to data sets with a sufficiently good signal/noise ratio. The numerical stability of inverse Laplace transforms was only recently improved quite a lot [32]. An alternative is fitting the data with simple analytical functions. Widely used examples are bi- or multiexponential decay curves or the stretched exponential (KWW function) [58].

$$M(t) = A\exp\left(-(t/T)^{\beta}\right) \tag{11}$$

While fitting multiexponential decay curves to near-exponential data sets is numerically not very stable, the KWW function is also stable when fitting near-exponential data. However, a major problem of the KWW function in analysis of magnetization decay curves is its diverging slope at $t=0$ for $\beta<1$ which prevents a meaningful extrapolation of the magnetization decay curve to $t=0$. Furthermore, the value of β obtained when fitting the KWW function to a magnetization decay curve is sensitive to the time window used for fitting. This is especially problematic in data with low signal/noise ratio. A modified KWW function which allows a meaningful extrapolation to $t=0$ was suggested by [59].

$$M(t) = M_{\mathrm{o}}\exp\left(-\frac{t}{T_M}(1+t/T_B)^{\beta-1}\right) \tag{12}$$

which behaves for $t \ll T_B$ like a single exponential with a time constant T_M and for $t \gg T_B$ like a KWW function with a stretching exponent β and a time constant $T = T_M^{1/\beta} T_B^{\frac{\beta-1}{\beta}}$. However, this model is again numerically not very stable for near-exponential decay curves and thus cannot be used for identifying the onset of non-exponential relaxation in a series of magnetization decay curves measured on a hydrating cement sample.

A function that provides excellent numerical stability also in fitting near-exponential curves was suggested by [29]. It is a parabolic exponential model

$$M(t) = M_{\mathrm{o}}(1-\rho\exp(-at+bt^2)) \tag{13}$$

with M_{o} denoting the overall NMR magnetization, ρ the degree of inversion, a the average relaxation rate and b half of the variance of the relaxation time distribution. Again, this model is obviously only valid over a limited time window as an extrapolation to long t leads to a diverging value of the magnetization. However, this problem is not really relevant from a practical point of view when using the model for identifying the onset of non-exponential relaxation as the magnetization decay curves are measured over a limited time window anyway. Furthermore, it is possible to overcome this problem for $b<a^2$ by a modified parabolic function:

$$M(t) = M_{\mathrm{o}}\left(1-\rho\exp\left(-at+b\frac{t^2}{1+at}\right)\right) \tag{14}$$

This function approximates a single exponential with a reduced relaxation rate $(a-b/a)$ for long t and for $t \ll 1/a$ it corresponds to the Kudryavtsev parabolic exponential Eq. (13).

When fitting Eq. (13) or Eq. (14) to longitudinal magnetization decay curves obtained using the sequence described in [7], one observes very small values for b on the fresh paste. After a few hours, the b values then start to increase significantly. As can be seen from Fig. 10, the time at which the increase in b sets in is independent from the window of relaxation delays used for the fitting procedures. (See the different fitting masks shown on the right side of the figure. In the fitting masks, the relaxation delay is shown in x-direction, the hydration time in y-direction. Data points marked white in the masks are used for the fitting, data points marked in black are discarded.) This makes the parabolic exponential model the ideal model for identifying the cross-over from exponential to non-exponential relaxation behaviour.

4.2.2. Non-exponentiality and diffusive averaging

Plotting the b values along with the water self-diffusion data obtained for a given sample, one finds that the onset of non-exponential behaviour is preceded by a major decrease in the water self-diffusion coefficient (see Fig. 11A). Both non-exponential relaxation and time-dependent diffusion coefficients indicate heterogeneity in the sample on the time and length scale of the NMR experiment. The time scale of longitudinal relaxation is given by the average longitudinal

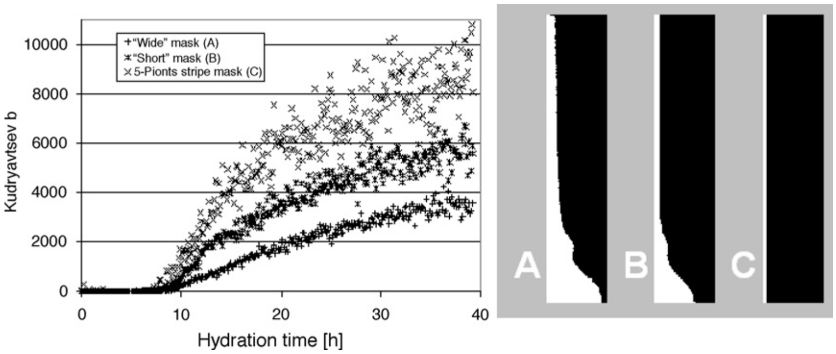

Fig. 10. Time-development for the b parameter in Eq. (13) when evaluating a time series of relaxation measurements using three different noise-suppression masks (according to the evaluation procedure described in [12]): (A) noise suppression, (B) noise suppression and variable limitation of time window, (C) short, constant time window.

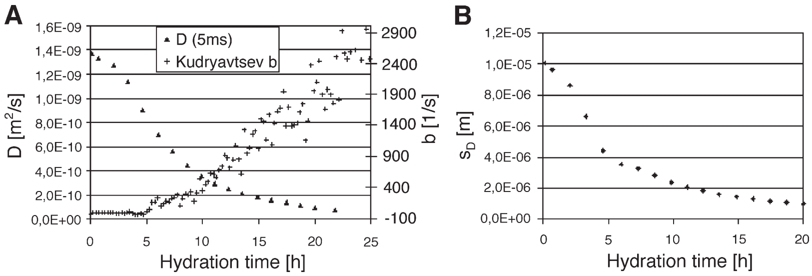

Fig. 11. (A) Self-diffusion coefficient and *b* parameter of a hydrating white cement sample (w/c=0.33) as a function of the hydration time. (B) Hydration time dependence of the characteristic length scale s_D computed from diffusion and relaxation data for the same sample. The change in the slope of s_D coincides with the onset of non-exponential longitudinal relaxation.

relaxation rate determined in Eq. (13). By combining this with the diffusion coefficient, one can compute a spin-averaging length scale (see Fig. 11B) over which the NMR properties of the sample are averaged due to diffusion:

$$s_D = \sqrt{2DT_1} = \sqrt{2D/a} \tag{15}$$

As we can see from the figure, the onset of non-exponential relaxation coincides with a very strong decrease of s_D. Non-exponential relaxation therefore sets in when the length scale s_D becomes shorter than the representative length scale of the hydrating cement paste. In this case, the exchange between pores of different radius and thus different relaxation rates becomes incomplete. For later hydration times, the decrease in s_D seems to level off while non-exponentiality becomes more and more pronounced.

With the availability of more reliable Laplace inversion techniques, it seems interesting to compare relaxation time distributions computed from Laplace inversion with the results from the parabolic exponential model. In Fig. 12, the results from such an analysis are given for some selected magnetization decay curves from the data set of Fig. 11. The inversion calculations were done using the 1D module of the software described in [31]. For the measurements after 1 and 4 h of hydration, a single relaxation time peak is found. For the later measurements, two or more relaxation time peaks are found which are increasingly further apart from each other. These findings are in good accordance with the onset of non-exponential relaxation after about 5 h which was identified by the increase of the *b* parameter in the parabolic exponential model of Eq. (13). Furthermore, the broadening of the relaxation time range with the hydration time agrees quite well with the interpretation of *b* as the variance of the relaxation time distribution.

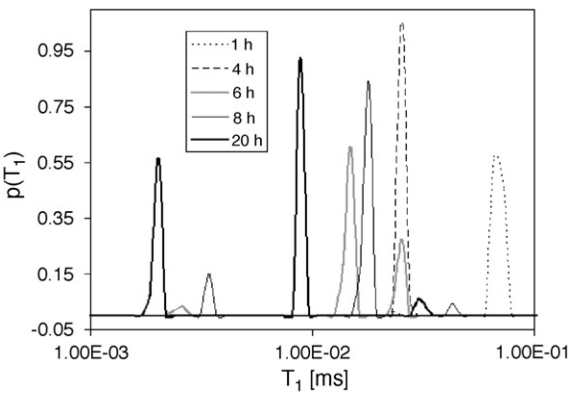

Fig. 12. Selected T_1 distributions in the hydrating cement sample determined using the Laplace inversion software described in [31].

The onset on non-exponential relaxation in longitudinal relaxation is a parameter which can be observed even on the basis of very simple NMR experiments, e.g. also from data obtained with a single-sided NMR device [60]. Given the relationship between non-exponential relaxation and strongly reduced diffusive averaging as presented here, non-exponentiality may be used to obtain at least a crude indication on the onset of the decrease in the diffusion coefficient in the hydrating paste. As single-sided NMR has a potential for use directly at the construction site, such measurements could be used for monitoring of post-curing processes in concrete.

5. Outlook

As can be seen from the data presented in this article, NMR diffusometry provides some unique possibilities in the study of self-diffusion properties of liquid phases in hydrating cement samples.

Due to their non-destructive and non-invasive nature, field gradient NMR techniques are especially attractive as they allow following the change in the diffusion properties in one sample during the hydration process. Furthermore, the possibility of diffusion studies at variable diffusion times allows the identification of characteristic time and length scales in the pore system of the hydrating paste. However, especially for late hydrating stages and long diffusion times, there remain open questions with respect to relaxation-time weighting. Overcoming these problems will require the combination of several approaches in the future:

- Systematic comparisons between FG NMR diffusion and data from tracer diffusion studies (both by imaging/profiling and by conventional transport techniques),
- Careful 2D Laplace inversion studies on the distributions of relaxation times and diffusion coefficients in cement pastes at different hydration stages. First data of this kind have become recently available [10].

- FG NMR studies using even stronger gradients. In PFG, the development of strong (and fast-switched) gradients is the major experimental challenge and it remains to be seen how much potential for further improvement there is. In SFG, the low signal / noise ratio (which is prohibitive during the first days of hydration with fast changes in the diffusion coefficients) can be overcome by longer signal accumulation for samples at late hydration stages. Such experiments are presently under way.
- Correlating diffusion data with transport models taking into account the microstructure of the cement. The major question in this field will be how much of the reduced diffusion coefficient is attributable to increased tortuosity of the pore system and how much to diffusion through C–S–H phases.

While diffusometry is a very powerful tool in the lab, bringing diffusometry to the construction site seems to be quite difficult (see [61] for a proof of principle of unilateral NMR diffusometry). A much more simple way to obtain at least some information on diffusion properties is offered by the relationship between non-exponential relaxation and the diffusive exchange length presented in this contribution.

From the application point of view, diffusion studies are especially relevant in the contexts of post-curing of concrete and in waste-treatment applications.

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References

[1] R. Blinc, M. Burgar, G. Lahajnar, M. Rozmarin, V. Rutar, I. Kocuvan, J. Ursic, NMR relaxation study of adsorbed water in cement and C3S pastes, Journal of the American Ceramic Society 61 (1978) 35–37.

[2] G. Lahajnar, R. Blinc, V. Rutar, V. Smolej, I. Zupancic, I. Kocuvan, J. Ursic, On the use of pulse NMR techniques for the study of cement hydration, Cement and Concrete Research 7 (1977) 385–394.

[3] E. Lippmaa, M. Mägi, M. Tarmak, W. Wieker, A.R. Grimmer, A high resolution ^{29}Si NMR study of the hydration of tricalciumsilicate, Cement and Concrete Research 12 (1982) 597–602.

[4] D. Canet, Nuclear Magnetic Resonance: Concepts and Methods, John Wiley and Sons, New York, 1996.

[5] B. Blümich, NMR Imaging of Materials, Clarendon, Oxford, 2000.

[6] E. Hahn, Spin echoes, Physical Review 80 (1950) 580–594.

[7] N. Nestle, C. Zimmermann, M. Dakkouri, J. Kärger, Transient high concentrations of chain anions in hydrating cement — indications from proton spin relaxation measurements, Journal of Physics. D, Applied Physics 35 (2002) 166–171.

[8] N. Nestle, A simple semi-empiric model for NMR relaxometry data of hydrating cement pastes, Cement and Concrete Research 34 (2004) 447–454.

[9] N. Nestle, NMR relaxometry study of cement hydration in the presence of different oxidic fine fraction materials, Solid State Nuclear Magnetic Resonance 25 (2004) 80–83.

[10] F. Barberon, J.P. Korb, D. Petit, V. Morin, E. Bermejo, Probing the surface area of a cement-based material by nuclear magnetic relaxation dispersion, Physical Review Letters 90 (2003), doi:10.1103/PhysRevLett.90.116103.

[11] P.J. McDonald, J.P. Korb, J. Mitchell, L. Montheilhet, Surface relaxation and chemical exchange in hydrating cement pastes: a two-dimensional NMR relaxation study, Physical Review E 72 (2005), doi:10.1103/PhysRevE.72.011409.

[12] N. Nestle, M. Dakkouri, O. Geier, D. Freude, J. Kärger, Blast furnace slag cements — a construction material with very unusual nuclear spin relaxation behavior during hardening, Journal of Applied Physics 88 (2000) 4269–4273.

[13] J.H. Simpson, H.Y. Carr, Diffusion and nuclear spin relaxation in water, Physical Review 111 (1958) 1201–1202.

[14] E.O. Stejskal, J.E. Tanner, Spin diffusion measurements: spin echoes in the presence of a time-dependent field-gradient, Journal of Chemical Physics 42 (1965) 288–292.

[15] J.E. Tanner, E.O. Stejskal EO, Restricted self-diffusion of protons in colloidal systems by the pulsed-gradient, spin-echo-method, Journal of Chemical Physics 49 (1968) 1768–1777.

[16] P.T. Callaghan, Principles of Magnetic Resonance Microscopy, Clarendon Press, Oxford, 1990.

[17] B. Geil, Measurement of translational molecular diffusion using ultrahigh magnetic field gradient NMR, Concepts in Magnetic Resonance 10 (1998) 299–321.

[18] W.S. Price, Pulse-field gradient nuclear magnetic resonance as a tool for studying translational diffusion: Part I. Basic theory, Concepts in Magnetic Resonance 9 (1997) 299–336.

[19] W.S. Price, Pulse-field gradient nuclear magnetic resonance as a tool for studying translational diffusion: Part II. Experimental aspects, Concepts in Magnetic Resonance 10 (1997) 197–237.

[20] F. Stallmach, J. Kärger, The potentials of pulsed field gradient NMR for investigation of porous media, Adsorption 5 (1999) 117–133.

[21] J.E. Tanner, Use of stimulated echo in NMR diffusion studies, Journal of Chemical Physics 52 (1970) 2523–2526.

[22] N. Nestle, A. Qadan, P. Galvosas, W. Süss, J. Kärger, PFG NMR and internal magnetic field gradients in plant-based materials, Magnetic Resonance Imaging 20 (2002) 567–573.

[23] R. Kimmich, E. Fischer, One- and two-dimensional pulse sequences for diffusion experiments in the fringe field of superconducting magnets, Journal of Magnetic Resonance A 106 (1994) 229–235.

[24] Fujara F. Chang, B. Geil, G. Hinze, H. Sillescu, A. Tölle, New perspectives of NMR in ultrahigh static magnetic field gradients: I. Journal of Non-Crystalline Solids 172–174 (1994) 674.

[25] F. Grinberg, R. Kimmich, Characterization of order fluctuations in liquid crystals by the dipolar correlation effect of the stimulated echo, Journal of Chemical Physics 103 (1995) 365–370.

[26] R. Kimmich, NMR-Tomography, Diffusometry, Relaxometry, Springer, Heidelberg, 1997.

[27] R.M. Cotts, M.J.R. Hoch, T. Sun, J.T. Markert, Pulsed field gradient stimulated echo methods for improved NMR diffusion measurements in heterogenous systems, Journal of Magnetic Resonance 83 (1989) 252–266.

[28] P. Galvosas, F. Stallmach, G. Seiffert, J. Kärger, U. Kaess, G. Majer, Generation and application of ultra-high-intensity magnetic field gradient pulses for NMR spectroscopy, Journal of Magnetic Resonance 151 (2001) 260–268.

[29] A.B. Kudryavtsev, T.V. Kouznetsova, W. Linert, G. Hunter, A study of the hydration of aluminate minerals based on the measurements of the mean and the variance of the proton magnetic resonance relaxation rate, Chemical Physics 215 (1997) 419–427.

[30] N. Nestle, P. Galvosas, O. Geier, C. Zimmermann, M. Dakkouri, J. Kärger, Nuclear magnetic resonance study of diffusion and relaxation in hydrating white cement pastes of different water content, Journal of Applied Physics 89 (2001) 8061–8065.

[31] S. Godefroy, P.T. Callaghan, 2D relaxation/diffusion correlations in porous media, Magnetic Resonance Imaging 21 (2003) 381–383.

[32] Y.Q. Song, L. Venkataramanan, M.D. Hürlimann, M. Flaum, P. Frulla, C. Straley, T_1–T_2 correlation spectra obtained using a fast two-dimensional Laplace inversion, Journal of Magnetic Resonance 151 (2002) 260–268.

[33] E.W. Hansen, H.C. Gran, E. Johannessen, Diffusion of water in cement paste probed by isotopic exchange experiments and PFG NMR, Microporous and Mesoporous Materials 78 (2005) 43–52.

[34] L. Pel, A.A.J. Ketelaars, O.C.G. Adan, A.A. van Well, Determination of moisture diffusivity in porous media using scanning neutron radiography, International Journal of Heat and Mass Transfer 36 (1993) 1261–1267.

[35] Y. Nakashima, Diffusivity measurement of heavy ions in Wyoming montmorillonite gels by X-ray computed tomography, Journal of Contaminant Hydrology 61 (2003) 147–156.

[36] Y. Nakashima, S. Nakashima, D. Gross, K. Weiss, K. Yamauchi, NMR imaging of 1H in hydrous minerals, Geothermics 27 (1998) 43–53.

[37] A.J. Fagan, N. Nestle, D.J. Lurie, Continuous wave MRI diffusion study of water in bentonite clay, Magnetic Resonance Imaging 23 (2005) 317–319.

[38] L. Pel, K. Kopinga, G. Bertram, G. Lang, Water absorption in fired-clay brick observed by NMR scanning, Journal of Physics. D, Applied Physics 28 (1995) 675–680.

[39] H.J.P. Brocken, O.C.G. Adan, L. Pel, Moisture transport properties of mortar and mortar joints: a NMR study, HERON 42 (1997) 55–69.

[40] L. Pel, H. Huinink, K. Kopinga, L.A. Rijniers, E.F. Kaasschieter, Ion transport in porous media studied by NMR, Magnetic Resonance Imaging 19 (2001) 549–550.

[41] N. Nestle, NMR studies on heavy metal immobilization in biosorbents and mineral matrices, Reviews in Environmental Biotechnology 1 (2002) 215–225.

[42] D.P. Bentz, O.M. Jensen, A.M. Coats, F.P. Glasser, Influence of silica fume on diffusivity in cement-based materials: 1. Experimental and computer modelling studies on cement pastes, Cement and Concrete Research 30 (2000) 953–962.

[43] J.K. Kim, C.S. Lee, Moisture-diffusion of concrete considering self-desiccation at early ages, Cement and Concrete Research 29 (1999) 1921–1927.

[44] J. Tits, A. Jakob, E. Wieland, P. Spieler, Diffusion of tritiated water and 22Na+ trough non-degraded hardened cement pastes, Journal of Contaminant Hydrology 61 (2003) 45–62.

[45] P. Pivonka, C. Hellmich, D. Smith, Microscopic Effects on chloride diffusivity of cement pastes — a scale-transition analysis, Cement and Concrete Research 34 (2004) 2251–2260.

[46] N. Nestle, P. Galvosas, J. Kärger, Direct measurement of water self-diffusion in hardening blast furnace slag cement pastes by means of nuclear magnetic resonance techniques, Journal of Applied Physics 90 (2001) 518–520.

[47] N. Nestle, P. Galvosas, C. Zimmermann, F. Stallmach, J. Kärger, Direct investigation of the fate of NAPL contaminations in a hydrating cement matrix by means of magnetic resonance techniques, Environmental Science Technology 38 (2004) 880–885.

[48] P.P. Mitra, P.N. Sen, L.M. Schwartz, Short-time behaviour of the diffusion coefficient as a geometrical probe of porous media, Physical Review B 47 (1993) 8565–8574.

[49] F. Stallmach, C. Vogt, J. Kärger, K. Helbig, F. Jacobs, Fractal geometry of surface areas of sand grains probed by pulsed field gradient NMR, Physical Review Letters 88 (2002), doi:10.1103/PhysRevLett.88.105505.

[50] M. Holz, S.R. Heil, A. Sacco, Temperature-dependent self-diffusion coefficients of water and six selected molecular liquids for calibration in accurate 1H NMR PFG measurements, Physical Chemistry Chemical Physics 2 (2000) 4740–4742.

[51] S. Bejaoui, B. Bary, Modeling of the link between microstructure and effective diffusivity of cement pastes using a simplified homogenization method, Cement and Concrete Research, submitted.

[52] L.G. Butler, J.W. Owens, F.K. Cartledge, R.L. Kurtz, G.R. Byerly, A.J. Wales, P.L. Bryant, E.F. Emery, B. Dowd, X. Xie, Synchrotron X-ray microtomography, electron probe microanalysis, and NMR of toluene waste in cement, Environmental Science Technology 34 (2000) 3269–3275.

[53] N. Nestle, C. Zimmermann, M. Dakkouri, R. Niessner, Action and distribution of organic solvent contaminations in hydrating cement: time-resolved insights into solidification of organic waste, Environmental Science Technology 35 (2001) 4953–4956.

[54] N. Nestle, P. Galvosas, C. Zimmermann, F. Stallmach, J. Kärger, Direct investigation of the fate of NAPL contaminations in a hydrating cement matrix by means of magnetic resonance techniques, Environmental Science Technology 38 (2004) 880–885.

[55] J.J. Thomas, H.M. Jennings, A.J. Allen, The surface area of cement paste as measured by neutron scattering: evidence for two C–S–H-morphologies, Cement and Concrete Research 28 (1998) 897–905.

[56] S. Weber, H.W. Reinhardt, A new generation of high-performance concrete: concrete with autogenous curing, Advanced Cement Based Materials 6 (1997) 59–68.

[57] O.M. Jensen, P.F. Hansen, Water-entrained cement-based materials: I. Principles and theoretical background, Cement and Concrete Research 31 (2001) 647–654.

[58] G. Williams, D.C. Watts, Non-symmetrical dielectric relaxation behaviour arising from a simple empirical decay function, Transactions of the Faraday Society 66 (1970) 80–85.

[59] M. Peyron, G. Pierens, A.J. Lucas, L.D. Hall, R.C. Steward, The modified stretched-exponential model for characterization of NMR relaxation in porous media, Journal of Magnetic Resonance 118 (1996) 214–220.

[60] S. Sharma, F. Casanova, W. Wache, A. Segre, B. Blümich, Analysis of historical porous building materials by the NMR-MOUSE, Magnetic Resonance Imaging 21 (2003) 249–255.

[61] M. Klein, R. Fechete, D.E. Demco, B. Blümich, Self-diffusion measurements by a constant-relaxation method in strongly inhomogeneous magnetic fields, Journal of Magnetic Resonance 164 (2003) 310–320.