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# Usage of internal magnetic fields to study the early hydration process of cement paste by MGSE method

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ABSTRACT

Internal magnetic field gradients, arising within the porous media due to susceptibility differences at the interfaces of solid and liquid as well as due to the contained magnetic impurities, can be employed by the method of modulated gradient spin echo to get insight into the velocity autocorrelation spectrum of liquid confined in the porous structure. New theoretical treatment of spin interaction with the radio-frequency field and the simultaneously applied static non-uniform magnetic field provides the formula that match well with the measurement of restricted diffusion of water in pores of cement paste. Its fitting to the experimental data gives the changes in the mean size of capillary pores, the spin relaxation and the magnitude of mean internal magnetic field gradients during the induction period and early acceleration stage of hydration processes at different temperatures.



## 1. Introduction

The cement paste is a material with a complex porous structure containing pores ranging from nanometers to micrometers and represents the main constituent of all cement based materials (concrete, mortars) [1,2]. The cement paste is obtained by the hydration of Portland cement grains in the presence of water [1]. The material resulting from the hydration reaction is a rigid and complex mixture of various minerals, both highly crystalline, such as ettringite and Portlandite, as well as minerals with a weak crystalline structure, namely C—S—H (here we use the cement chemistry abbreviations) [1]. The C—S—H is a heterogeneous nano-porous material containing sheets of calcium, oxygen atoms and silicate tetrahedra separated by sheets of water [3,4]. Along with the remaining non hydrated cement grains and the admixtures, the growth of these minerals creates inside the cement based materials a porous network in which three pore types can be distinguished: intra-C—S—H sheet pores, inter-C—S—H gel pores and capillary pores [3].

The hydration reaction is influenced by a variety of internal and external factors such as the presence of different admixtures (silica fume, fly ash) [1,5] or additives (superplasticizers, silanes) [6–8] as well as by the curing temperature [9]. These factors influence both the pore size and their connectivity, with important consequences on the final strength and durability of cement based materials (concrete, mortars). It is already known that capillary pores allow the penetration of carbon dioxide and of sulfate in various forms, leading to carbonation, as well as cracking, spalling and general loss of durability due to external sulfate attack [10]. That is why, decreasing the permeability of the cement based materials used in general applications allows for an increase in long-term durability, protection of steel reinforcements and reduction of deterioration, by preventing the ingress of highly reactive chemicals from the environment. To control the permeability, reliable methods for pore size determination are mandatory. These methods should allow monitoring of the pore size evolution even during the hydration process.

The NMR relaxometry techniques allow in principle the pore size determination even during sample evolution provided that the relaxivity constant is known [2,11]. One option would be to calculate the relaxivity constant by taking into account the magnetic impurity content of the cement sample [2]. This approach is

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however cumbersome and relies on the assumption that the only relaxation mechanism in cement based materials is determined by the interaction of the proton spins with the paramagnetic centers located on the pore surface [12]. The other option for the relaxivity calibration would be to compare the relaxation data with the pore sizes provided by different techniques. Note however that this task is difficult to be accomplished in the case of cement paste due to the fact that the pore surface continuously changes during the hydration process [9]. Moreover, it has been already shown that even for the hardened cement-based materials the mercury porosimetry technique is an inappropriate method for the measurement of pore size distributions [13]. Furthermore, different techniques may lead to pore dimensions differing by orders of magnitude [14]. Consequently, an alternative approach which does not require the knowledge of the relaxivity constant should be implemented in systems with pore evolution.

A widely used NMR approach for determining the pore sizes of porous media without the need for previous calibrations of the relaxivity constant relies on time dependent diffusion measurements [15]. The most implemented technique for diffusion measurements in porous media uses the pulsed magnetic field gradient (MFG) stimulated echo sequence [15]. The main drawback of this sequence is however that it is restricted to the porous samples with low internal gradients [16]. The internal MFG are generated inside pores due to the susceptibility differences between the porous matrix and the confined liquid [17]. They are proportional with the external magnetic field and are enhanced by the presence of magnetic impurities in the cement grains or in other components of the cement mixture. These MFG which overlap the external gradient used for diffusion measurements make the diffusion measurements unreliable. A solution to overcome this problem is to use compensating pulse sequences [16]. Note however that implementing of compensating pulse sequences requires the rapid switching of MFG pulses and this is problematic for investigation of water inside cement samples, due to the short transverse relaxation time.

Previous investigations have shown that the internal MFG may have not only a negative role in NMR diffusion measurements but they can be also exploited as an instrument for the pore size characterization [18–20]. One such approach takes into consideration the influence of internal MFG of the echo train arising in a Carr-Purcell-Meiboom-Gill (CPMG) experiment [18,20,21]. On this basis, it was possible to extract information about the pore size evolution of cement paste without the need of previous calibration for the relaxivity constant [21]. Note however that the interpretation of the CPMG echo decays in the frame of the theory derived in Ref. [18] by adapting the scattering theory from quantum mechanics is strictly valid for short diffusion times when diffusion length is much smaller both than the structural length of the sample and the dephasing length defined by the distance a tagged molecule must diffuse in order to dephase by radians. This limiting condition could introduce errors in the evaluation of the data and make the technique more appropriate for bigger pores.

To overcome the above mentioned limitation, in the present work the modulated gradient spin echo (MGSE) approach [22] will be used to get insight into the velocity autocorrelation spectrum of liquid molecules confined inside the porous structure. For that purpose, a new theoretical formalism of spin interactions with the radio-frequency field and the simultaneously applied internal magnetic field was developed. The formula for the relaxation attenuation of the CPMG echo train will be compared with the experimental data on cement paste during early hydration. This will allow estimation of the changes taking place in the mean size of capillary pores and the magnitude of the mean internal MFG during the hydration process at two different curing temperatures.

## 2. Internally induced magnetic field gradient and the MGSE method

Using the conventional NMR technique, the externally applied MFG is superimposed to the internally generated fields, which makes the diffusion measurements very cumbersome [17]. Moreover, the measurements with PGSE method are limited in the ability to measure short diffusion times and thus limited with the size of pores, which can be probed in the porous medium. Here, we are concern with the NMR method, termed the modulated gradient spin echo (MGSE) [23], which allows a direct insight into the molecular velocity autocorrelation spectrum. In fact, it is the CPMG sequence of $\pi$-radiofrequency (RF) pulses [24,25] combined with MFG [26,27]. The CPMG sequence was initially introduced to provide reliable measurements of $T_2$, because a large number of RF pulses applied in short enough intervals, $\tau$, suppresses the attenuation created by the molecular self-diffusion attenuation in the non-uniform magnetic fields [24,25]. Much later, another property of the CPMG sequence was discovered: When applied simultaneously with MFG, it does not remove unwanted effect of diffusion but on the contrary, it reveals the details of diffusion processes, which are hidden in the velocity autocorrelation spectrum (VAS) of the diffusion motion. The velocity autocorrelation function is the key quantity of the dynamic molecular system that contains details about the underlying nature of molecular interactions. In the case of restricted diffusion the VAS holds also information about the structure of porous media.

When using the version of MGSE, which combines the CPMG train with the pulses of MFG [27], the upper limit to the sampling frequency is determined by the rate of MFG pulses, which is limited by the gradient coil induction. The method allowed the studies of flow through porous media [27], the restricted diffusion in porous media [22,28–30] and the diffusion in emulsions [29], Because the maximal achievable frequency was below 1 kHz, this method prevents the study of restricted diffusion in pores smaller than a few μm. No such upper limit applies to the method combining CPMG with the fixed MFG. This version of MGSE was proposed for the first time in reference [23], but with a concern about the side effects introduced by the application of RF pulses in the presence of a background inhomogeneous magnetic field [23,31,32]. Therefore, in the first part of the article we are revealing some new understanding of spin dynamics in the case of simultaneous application of RF-pulses and inhomogeneous magnetic field. The rest of article is dedicated to the use of this method for the study of restricted water dynamics in the matrix of hydrating cement.

### 2.1. Spin dynamics

In the quantum mechanical notation, the interaction of the spin system with RF field and the magnetic fields, which consist of the uniform static external magnetic field applied along longitudinal $z$-axis, $B_{oz}$, and the additional non-uniform magnetic field $\vec{B}(\vec{r})$ internally induced by the susceptibility differences or/and magnetic impurities, is described by the Hamiltonian

$$\mathcal{H} = -\hbar\sum_i [\omega_o \mathcal{I}_{zi} + \vec{\omega}(\vec{r}_i)\vec{\mathcal{I}}_i] + \mathcal{H}_{rf}(t) + \mathcal{H}_{sL}, \quad (1)$$

in which the sum is taken over all individual spins and where $\vec{\omega}(\vec{r}_i) = \gamma\vec{B}(\vec{r}_i)$ denotes the resonance off-set frequency of the $i$-th spin at location $\vec{r}_i$. The CPMG sequence, which begins with $\pi/2$-RF pulse to turn magnetization from the longitudinal into the transverse direction along $y$-axis, is followed by the train of $\pi$ pulses with the RF magnetic field applied along $y$-axis. It is described by $\mathcal{H}_{rf}(t) = \mathcal{H}^x_{\pi/2}(t) + \mathcal{H}^y_{cpmg}(t)$ in which the spin manipulation with the train of $\pi$-RF pulses is included in $\mathcal{H}_{cpmg}(t) = -2\hbar\omega_\pi(t)$