Cement and Concrete Research 77 (2015) 76–81

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Monitoring the size evolution of capillary pores in cement paste during the early hydration via diffusion in internal gradients

Alexandra Pop, Ioan Ardelean *

Technical University of Cluj-Napoca, Department of Physics and Chemistry, 400114 Cluj-Napoca, Romania

ARTICLE INFO

Article history:
Received 18 April 2015
Accepted 14 July 2015
Available online 31 July 2015

Keywords:
Hydration
Pore size distribution
Diffusion
Portland cement NMR

ABSTRACT

The internal gradients arise inside porous media due to the susceptibility contrast between the porous matrix and the confined liquid. They produce in the presence of diffusion phenomena an extra attenuation of the echo train signal in the Carr–Purcell–Meiboom–Gill (CPMG) experiment. In the present work we exploit this extra attenuation of the echo train to determine the pore size evolution of capillary pores in cement paste during the early age hydration. Thus, both the effects of the temperature and of a superplasticizer on the pore size evolution are investigated. It is observed a slight reduction in the size of capillary pores of cement paste by decreasing the temperature. However, no reduction of the pore size could be detected as result of introducing a superplasticizer and this can be due to the preparation approach of the sample.

1. Introduction

The cement paste acts as a glue for the components forming the cement based composite materials. It is obtained by the hydration of cement grains in the presence of water, a complex and irreversible chemical reaction which is influenced by a variety of internal and external factors [1,2]. Among these factors, the temperature [3,4] and the presence of superplasticizers [5–7] significantly influence the hydration reaction and the characteristic times in which it takes place. They also influence the pore size and the porosity of the produced cement based materials with important consequences on their final strength and durability [3,8]. That is why monitoring the pore size of cement paste, eventually during its hydration, is an important issue.

The most widely used techniques for pore size determination of porous materials rely on gas adsorption or mercury intrusion [9,10]. Note however that both techniques can be applied only to a solid porous matrix and consequently cannot be used in monitoring the pore size evolution during the early age hydration of cement based materials. An alternative approach that allows the characterization of the pore size during their evolution is provided by nuclear magnetic resonance (NMR) relaxometry techniques [11–14]. These techniques rely on the proportionality between the relaxation rate and the surface to volume ratio of the investigated pores. The proportionality constant also called the relaxivity is determined both by the adsorption properties of the surface [15] and the magnetic impurity content [16].

The main difficulty in implementing the NMR relaxometry techniques for the pore size characterization is the need for a previous calibration of the relaxivity constant. This could be done in principle by comparing the relaxation data with the pore sizes provided by a different technique. However 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 and the fact that different techniques may lead to pore dimensions differing by orders of magnitude [10]. Another option would be to calculate the relaxivity constant by taking into account the magnetic impurity content of the cement sample [12,13]. This approach is 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 [12,13]. Consequently, an alternative approach which does not require the knowledge of the relaxivity constant should be implemented in systems with pore evolution.

One well established NMR technique for determining the pore sizes of porous media without the need for previous calibration of the relaxivity constant relies on time dependent diffusion measurements [17]. These measurements are generally performed using the pulse field gradient stimulated echo technique and are restricted to the porous samples with low internal gradients as for instance white cement [18,19]. The internal gradients are generated inside pores due to the susceptibility differences between the porous matrix and the confined liquid [20]. 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 gradients which overlap the external gradient used for diffusion measurements make the diffusion measurements by conventional gradient technique cumbersome [17]. A solution to overcome the difficulties associated

* Corresponding author.
E-mail address: ioan.ardelean@phys.utcluj.ro (I. Ardelean).

http://dx.doi.org/10.1016/j.cemconres.2015.07.004
0008-8846/

with diffusion measurements in the presence of internal gradients relies on applying of compensating pulse sequences [21]. Note however that implementing of compensating pulse sequences requires the rapid switching of gradient pulses and this could be problematic for investigation of water inside cement samples due to the short transverse relaxation time. An alternative approach would be applying radiofrequency gradients pulses for encoding and decoding the position of tagged spins, as described in Ref. [17].

It was already shown that the internal gradients may have not only a negative role by affecting the accuracy of NMR diffusion measurements but they can be used as a tool for the pore size characterization [22–24]. One way of doing that is by exploiting the dependence of Carr–Purcell–Meiboom–Gill (CPMG) echo train on diffusion in the presence of internal gradients [25–28]. Thus, it was possible to extract information about the pore size and their distribution without the need of previous calibration or calculation of the relaxivity constant [23]. In the present work the same technique will be implemented to determine the size evolution of capillary pores in cement paste during the early hydration. Both the effects of the temperature and of a superplasticizer on the pore size evolution will be monitored in a completely noninvasive manner.

2. The CPMG technique in the presence of internal gradients

The transverse relaxation time T_2 of fluids confined inside porous media is often measured using the well-known Carr–Purcell–Meiboom–Gill (CPMG) technique [25]. In the CPMG pulse sequence an initial 90° radiofrequency pulse around y-axis is followed by a train of 180° pulses around x-axis at time instants τ, 3τ, 5τ, …. The train of echoes recorded at time instants 2τ, 4τ, 6τ, …, $2n\tau$ allows extraction of a unique relaxation time in the case of homogeneous samples or a relaxation time distribution in samples with heterogeneous structure. The main advantage of such a multiple echo technique as compared with other spin echo techniques is that it allows fast multiple accumulations of the echo train signal—an important issue in increasing the detection sensitivity. Furthermore it reduces the effects of diffusion on transverse relaxation measurements if τ is adequately short.

If the transverse magnetization evolution during the time interval τ is influenced by diffusion in internal gradients, then the attenuation of the n-th echo in the echo train can be described by an effective relaxation rate given as [26]:

$$\frac{1}{T_2{}^{eff}} = \frac{1}{T_2} + \frac{1}{3} D_0 \gamma^2 g^2 \tau^2 \left[1 + \frac{C(n)}{2n} \frac{g_\nu^2}{g^2} \frac{S}{V} \sqrt{D_0 \tau} \right]. \quad (1)$$

Here the first term describes the relaxation contribution while second term accounts for diffusion effects on echo attenuation and is a function of surface to volume ratio S/V. Other parameters in the above formula are: g^2 the average gradient square over the entire pore volume and g_ν^2 the average gradient square over the internal surface. γ is the gyromagnetic ratio and $C(n)$ are negative numerical constants tabulated in Ref. [26]. Analyzing the values of the $C(n)$ coefficients in Ref. [26] one can observe that the ratio $C(n)/2n$ reaches an asymptotic limit $C(n)/2n \to -0.57$ already after several echoes ($n > 5$). Note that the above Eq. (1) was derived in Ref. [26] by adapting the scattering theory from quantum mechanics. An alternative approach could be provided by the spectral characterization of diffusion in a modulated gradient spin echo experiment [29].

The evaluation of the g_ν^2/g^2 ratio is only possible for well-defined geometries providing known gradient distributions. This ratio was already calculated for a slit pore model and two possible space variations of the internal field inside the sample [28]. Thus, in the case of a constant gradient (linear variation of the internal field) the ratio is $g_\nu^2/g^2 = 1$ whereas, in the case of a linearly increasing gradient (parabolic variation of the internal field) the ratio is $g_\nu^2/g^2 = 1.5$. For an arbitrary pore geometry (porous ceramics) it was experimentally established in Ref. [23] that a good approximation is given by the ratio $g_\nu^2/g^2 = 2.5$. In that case the effective relaxation rate describing the attenuation of the CPMG echo train starting from the echo with $n > 5$ can be approximated (asymptotic regime) as:

$$\frac{1}{T_2{}^{eff}} \cong \frac{1}{T_2} + \frac{1}{3} D_0 \gamma^2 g^2 \tau^2 \left(1 - 1.42 \frac{S}{V} \sqrt{D_0 \tau} \right). \quad (2)$$

The above formula suggests that it can be used for the determination of the surface to volume ratio of the porous media if the effective relaxation rate is recorded as a function of time interval τ.

The above Eq. (2) is strictly valid only in the so called short time limit when diffusion length during τ intervals 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 π radians [26,30–32]. Depending on the pore size, the strength of the internal gradients and the length of τ intervals, the interpretation of relaxation data can be done in the so called motional averaging regime or in the localization regime. A comprehensive discussion about the effects of diffusion through internal gradients on relaxation measurements in different diffusion regimes can be found in Refs. [31,32]. Note that in the short time limit condition the term $1.42(S/V)\sqrt{D_0\tau} << 1$ and therefore the effects of the surface are too small to be detected. Consequently, for experimental reasons, this condition should be exceeded. Recent computer simulations on model porous media of the spin echo attenuation in the presence of a steady gradient and restricted diffusion have proved that it is possible to exceed the short time limit [33]. Thus, it was demonstrated that the evaluation of the pore size remains in an accuracy range of approximately 15% even if the term describing the surface contribution reaches a value of 0.75. In the present work we will also exploit this allowance to evaluate the size of capillary pores during the early hydration.

In porous media with a distribution of pore sizes the effective relaxation times $T_2{}^{eff}$ exhibit a spread of values which reflects that distribution. That is why, the recorded CPMG envelope can be expressed as

$$A_n(2n\tau) = A_0 \int_0^\infty P\left(T_2{}^{eff}\right) \exp\left(-2n\tau / T_2{}^{eff}\right) dT_2{}^{eff} \quad (3)$$

Here A_n is the amplitude of the n-th echo appearing at in instant $t = 2n\tau$ in the echo train and A_0 is a constant depending on the sample magnetization, filling factor and other experimental parameters. $P(T_2{}^{eff})$ represents the relaxation time probability density. The above equation suggests that the analysis of the experimental data using a Laplace inversion algorithm provides the relaxation time distribution. A valuable algorithm for such an analysis has been proven to be CONTIN [34] which was also implemented in our previous studies [7].

Due to the fact that the results of the numerical Laplace inversion may be affected by the presence of noise, it is better to evaluate the characteristic times of the relaxation process by an alternative approach. Thus, in systems where a continuous variation of the effective relaxation time exists, Eq. (3) suggests that in the limit of short evolution times an average relaxation rate

$$\left\langle \frac{1}{T_2{}^{eff}} \right\rangle = \int_0^\infty \frac{1}{T_2{}^{eff}} P\left(T_2{}^{eff}\right) dT_2{}^{eff} = -\left.\frac{\partial [A_n(t)/A_0]}{\partial t}\right|_{t\to 0} \quad (4)$$

can be extracted from the initial slope of the echo train. This definition is similar with that previously used in Ref. [35] for diffusion measurements in heterogeneous samples and will be considered in the following for evaluating the average relaxation time of capillary water in cement paste. An alternative approach of describing the mean relaxation rate would be to calculate the first moment of the relaxation rate