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Original contribution

Diffusion of water in industrial cement and concrete

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ABSTRACT

We propose a deuterium diffusion tracer approach to measure diffusion coefficient in the case of very short NMR relaxation times, too short for NMR pulsed field gradient sequences (T_1 or T_2 below 1 ms). We also treat the case of porous media containing metallic fibers (such as reinforced concrete) strongly disturbing the magnetic field, and the case of inhomogeneous porous media containing large non porous granulates. For the latter, we propose a hollow geometry maximizing the investigated volume and minimizing the experimental time. The method is a 3D diffusion technique in which samples are immersed in deuterium and the water content inside the sample is monitored as a function of time. Water diffusing outside the sample with very long relaxation times can be subtracted either from T_2 relaxation time distribution or not polarizing these components using a short repeat delay. Using analytical formulations describing the concentration of a tracer diffusing out of a cylinder or a hollow cylinder, we can calculate the corresponding pore diffusion coefficient.

1. Introduction

Cement based material are difficult porous media to characterize and there is no exception concerning the NMR technique. In the past ten years, most of the attention has been paid to the hydrating mechanisms during curing and the evolution of the state of water, with various NMR relaxation techniques employed [1–3]. However, the determination of diffusion properties once the cement material is aged and ready to be used for industrial application remains a challenge [4]. Especially for the application of low activity radioactive waste in which cement or concrete is used as a barrier, diffusion measurement are mostly based on through diffusion techniques using tritiated water (HTO) as a tracer. In these methods, one measures a flux of tracer diffusing from one side of a disk-shaped sample to the other side. However, because the tested materials are specifically chosen or designed to have the lowest possible effective diffusivity of the order of 10^{-12} m^2/s, an experiment can take several months or even years before observing a stable flux. Efforts have been made to speed up such experiment [5] but the study of various cement composition remains a tedious task from the experimental point of view. For the case of cement pastes in which the disk thickness can be made small because the material has a very fine structure, optimized typical experimental duration are of the order of 100 days and more [6,7]. Unfortunately, NMR-PFG techniques that could provide answers within hours are not applicable because relaxation are so short (< 1 ms) that diffusion sequences cannot be implemented [4] and even if they could, it would be extremely difficult to observe a signal attenuation with such low diffusion coefficient at very short diffusion time. Using tracers, 1D NMR profiling is another possibility of measurement [4] but quantitative issues are present due to relaxation time weighing. Furthermore, the presence of metallic fibers for mechanical reinforcement as considered in this study would generate strong difficulties. We propose in this study a 3D variant of NMR deuterium tracer techniques that requires only basic NMR sequences and are applicable in the worst situation. It can be very fast for cement pastes and small samples, and reasonably slow for larger samples required in the case of heterogeneous structures.

2. Methodology

The methodology described here has been partially developed earlier in the framework of the measurement of water diffusion in tight natural porous media (in particular caprocks [8]) for which relaxation times are too short for applying NMR-PFG techniques. The method is further developed here for cement, mortar and concrete and a hollow geometry is proposed to take into account the potential heterogeneous nature of cement based materials while maintaining reasonable experimental duration.

The principle is to use a tracer technique in which deuterium oxide (D_2O) is diffusing into the sample and water outside in the bulk. The method that can be labeled “inside out diffusion technique” consists of immersing a water saturated sample into D_2O (Fig. 1) and recording an appropriate NMR signal detailed later as a function of time using an

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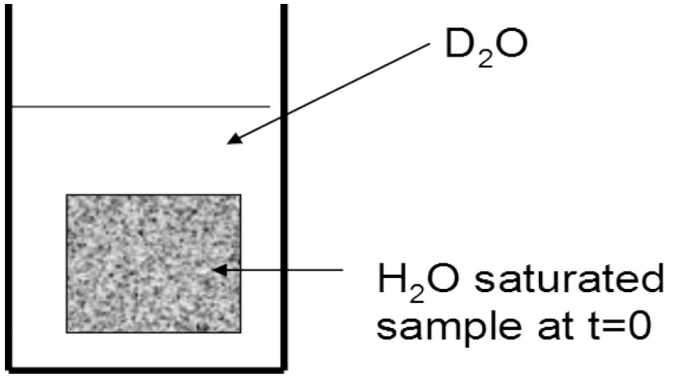

Fig. 1. Schematic indicating the deuterium tracer method for measuring diffusion coefficient.

apparatus tuned on protons (hence not sensitive to deuteron) to measure the hydrogen content. To get the hydrogen content inside the sample, we take advantage of the very large contrast of relaxation time between protons inside the sample and outside in the bulk. Indeed, T_1 or T_2 relaxation times of protons inside the sample dominated by surface interaction are in the range 0.1 to 1 ms, whereas they are in the range of 3 to 8 s for hydrogen-deuterium mixture. During diffusion, HDO molecules will be present either inside or outside the sample depending on concentration; however hydrogen content will still be properly measured inside the sample because proton relaxation time of a HDO molecule will still be short inside the sample due to surface relaxation. Moreover, the diffusion of bulk D_2O being slightly smaller than bulk H_2O [9], the diffusion coefficient measured when following a proton density in D_2O-H_2O mixtures will be slightly concentration dependent; this variable bulk diffusion coefficient is not taken into account in the analysis presented below. Note also that the exchange of hydrogen or deuterium to form HDO molecules does not influence the diffusion coefficient [9].

The recorded NMR signal can either be a CPMG decay, a free induction decay (FID) or a single Hahn echo, both repeated such as not to polarize the long components (i.e. apply a repeat delay between scans of about 100 ms without recording the first scan). When CPMG decays are recorded, a Laplace transform is performed and long component amplitudes subtracted to calculate the total magnetization M; when a FID or Hahn echo is recorded, the signal maximum amplitude M is simply used directly without specific processing. This is the preferred mode of acquisition because it is fast and a high signal to noise ratio can be obtained when a large number of scans is used (e.g. 500). As will be detailed later, a Hahn echo must be used when metallic fibers are present because the FID decay in these cases is faster than the probe dead time and thus not exploitable.

To analyze the un-calibrated NMR magnetization signal M(t) function of diffusion time representative of the hydrogen content in the sample using the acquisition mode explained above, we build a normalized time dependent water concentration C^* defined as:

$$C^* = \frac{M(t) - M(t=\infty)}{M(t=0) - M(t=\infty)} = C_{ps} C_{cyl} \tag{1}$$

The magnetization at infinite time $M(t = \infty)$ may not be zero if non-exchangeable hydrogen exists in the sample (e.g. solid-like protons part of the CSH structure in cements). Following the analytical expressions and methodology detailed in Crank [10], the resolution of a diffusion equation in a cylinder of length $L = 2\,l$ and radius $r = d/2$ is the product of two terms, C_{ps} and C_{cyl}, respectively representing the diffusion in a plane sheet ("ps") and in an infinite cylinder ("cyl"), and are given by:

$$C_{ps} = \sum_{n-0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left(-D_p (2n+1)^2 \pi^2 \frac{t}{4l^2}\right) \tag{2}$$

$$C_{cyl} = \sum_{n-1}^{\infty} \frac{4}{r^2 q_n^2} \exp(-D_p q_n^2 t) \tag{3}$$

where q_n are the positive roots of the equation $J_0(rq_n) = 0$ for the C_{cyl} term, J_i is the Bessel function of the first type of order i. These equations are valid when the deuterium/water volume ratio is large, i.e. when the boundary condition of 100% deuterium concentration is verified during the experiment. If this is not the case, another set of solution exist taking into account this variable boundary condition:

$$C_{ps} = \sum_{n-0}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 p_n^2} \exp\left(-D_p p_n^2 \frac{t}{l^2}\right) \tag{4}$$

$$C_{cyl} = \sum_{n-0}^{\infty} \frac{4\alpha(1+\alpha)}{4+4\alpha+\alpha^2 p_n^2} \exp\left(-D_p p_n^2 \frac{t}{r^2}\right) \tag{5}$$

where p_n are the positive roots of the equation $\tan p_n = -\alpha p_n$ for the C_{ps} term, and of the equation $\alpha p_n J_0(p_n) + 2J_1(p_n) = 0$ for the C_{cyl} term, α is the volumetric D_2O/H_2O ratio. However, in practice, there is little influence of α when $\alpha > 10$, which can be realized experimentally.

Another geometry of interest as detailed later is the hollow cylinder. While keeping unchanged the term C_{ps} in Eq. (1), the term C_{cyl} must be replaced by C_{holcyl} defined as:

$$C_{holcyl} = \frac{4}{b^2 - a^2} \sum_{n=0}^{\infty} \frac{J_0(ak_n) - J_0(bk_n)}{k_n^2 (J_0(ak_n) + J_0(bk_n))} \exp(-D_p k_n^2 t) \tag{6}$$

where b and a are respectively the outer and inner diameter of the hollow cylinder, k_n are the positive roots of the equation $J_0(ak_n) Y_0(bk_n) - J_0(bk_n) Y_0(ak_n) = 0$, Y_0 is the Bessel function of the second type and of order zero.

In all equations, we use the notation D_p as the pore diffusion coefficient which is an intrinsic property of the porous medium under investigation. When tracer fluxes are measured instead of tracer concentration inside the porous media, the measured coefficient is often called effective diffusion coefficient D_e such as [8]:

$$D_p = D_e/\phi \tag{7}$$

where Φ is the porosity of the medium. More details about this relationship derived from Fick's law and the terminology are given elsewhere [8]. From these measurements as well as NMR-PFG experiments, one determines directly a pore diffusion coefficient diffusion whereas an effective diffusion coefficient is directly determined in through diffusion techniques. Hence, to compare NMR based methods with radioactive tracer methods, one needs to know the porosity, and there can be some ambiguity about its determination with traditional drying and weighing methods in cement based material. Nevertheless, it is the pore diffusivity that characterizes a porous medium directly determined by NMR, and the effective diffusivity is determined directly when measuring tracer fluxes [8] typically using tritium, a common non interactive tracer suitable in cement or concrete. Indeed, when comparing cement paste, mortar and concrete, D_p should not vary whereas De will according to the relation $D_e = D_{paste}$ $(1\text{-}V_{solid})$ where V_{solid} is the volume of non-porous material added to the paste (sand, granulates). This is however approximate because the interfacial transition zone (ITZ) between the paste and non-porous elements play a role [6,11], but this is outside the scope of this study. Hence, the experimental time will increase as porosity is decreasing in through diffusion experiments, whereas it may not for NMR based methods. The drawback is however the potential decrease of SNR but this can be compensated by using a high sensitivity instrument or increasing the number of acquisitions.

The experimental durations can be investigated using Eqs. (2) and (3) assuming that the experiment is finished when C^* reaches 1%, an arbitrary criteria. Taking $D_p = 1.0 \times 10^{-11}\,m^2/s$ as a typical value in cement, the experimental time will be about 14 days for a cylinder with D = L = 10 mm, and 56 days when $D = L = 20$ mm. The sample dimensions influence the experimental duration with a square

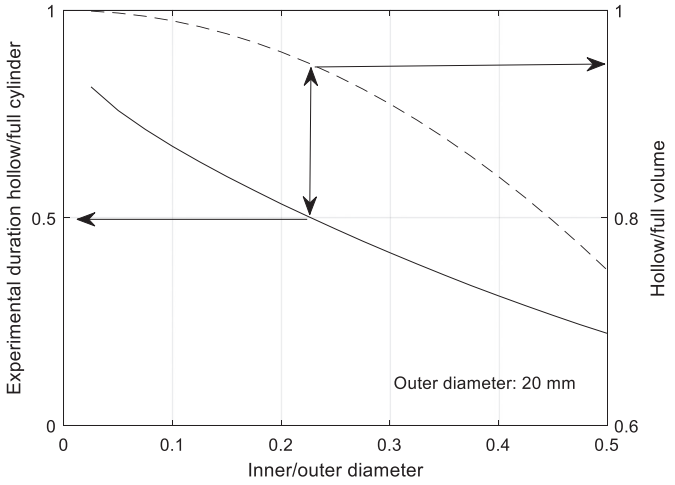

Fig. 2. Comparison of the experimental duration of the hollow cylinder and full cylinder as a function of the size of the inner diameter in the hollow geometry (left scale, full line). The decrease of volume relative to the full cylinder geometry is also shown (right scale, dashed line).

dependence. However, in some situation, the dimensions cannot be reduced too much because the sample may not be representative anymore, or the homogeneity assumptions in the diffusion model may not be valid anymore; this is the case for concrete in which granulates with typical sizes of 5 mm and more are incorporated into the paste. The solution then is to use the hollow cylinder geometry; indeed, experimental duration can decrease significantly even with large external diameter (Fig. 2). For example, for a cylinder with $D = L = 20$ mm, drilling a hole of about 5 mm will decrease the experimental duration by a factor of two, keep a representative volume whereas the decrease of the investigated volume compared to the full cylinder will only be about 5%.

In practice, any NMR apparatus can be used for monitoring the water content in porous media using the above method. However, the probe size must be adapted to the sample's size and the sensitivity of the NMR device adapted to the porous volume encountered. We found that a good compromise is to use low field permanent magnet devices with proton frequency around 20 MHz. In our case, the instruments are from Oxford Instruments Ltd., with probe size varying from 10 up to 30 mm. With such devices, we could follow deuterium diffusion curves on sample with porosity as low as 1% in natural tight porous media (unpublished).

3. Results

We present here a few results demonstrating the method. First, we show a deuterium diffusion experiment on a standard Portland cement paste (CEM I, Fig. 3). A small cylinder of diameter 5.6 mm and length 9.1 mm was drilled out of a standard larger sample that was aged 3 months underwater of pH 11.5. The deuterium used in the experiment was also equilibrated at a similar pH to avoid any potential chemical reaction. In practice, the small cylinder is placed in the NMR tube and in the NMR apparatus, then deuterium is placed around the sample and the recording is started (deuterium purity of 0.995%). Beforehand, all the fluids and sample are equilibrated at 30 °C, the equilibrium temperature of the NMR device. In this case, we used a 10 mm probe at a proton frequency of 23.7 MHz. Without polarizing the long components (repeat delay between scans of 100 ms), the FID amplitude vs. time was recorded continuously during 120 h (5 days). Using Eqs. (2) and (3) we obtained a diffusion coefficient $D_p = 1.0\ 10^{-11}\ m^2/s$ with a standard deviation of 1.5%. The data fitting was performed by minimizing an error function both for D and the asymptotic final concentration yielding $C_f = 0.028$. In this case, the NMR tube was nearly full of

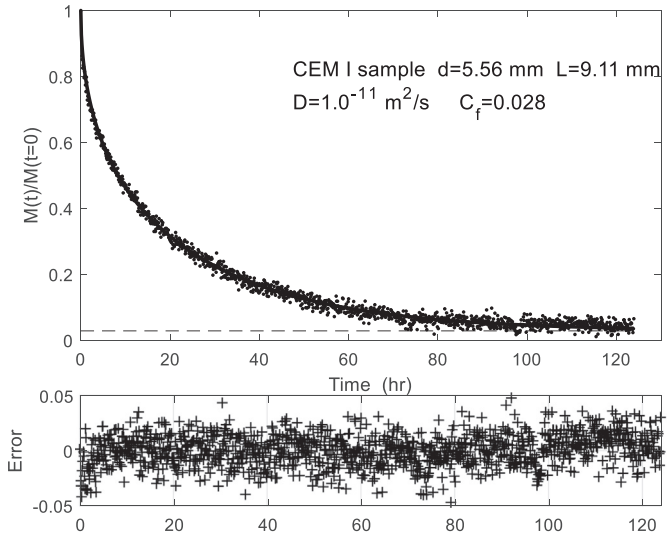

Fig. 3. Diffusion curve on a Portland cement paste (CEM I type). The magnetization amplitude is obtained from FID recordings with a short repeat delay between scans to not polarize long components. The dashed line indicates the fitted asymptotic value M(t = ∞)/M(t = 0). The lower panel shows the error between the model and the data. The T_2 relaxation time distribution of this sample is centered around 0.1 ms.

deuterium and therefore, the volume ratio D_2O/H_2O is large (~100). Thus we deduce that a small fraction of protons are not exchangeable (~1.8%). Since the T_2 distribution of this sample is centered around 0.1 ms (not shown), the use of NMR pulsed field gradient techniques is clearly not feasible.

The purpose of the second example is to validate the hollow cylinder approach although there is no specific theoretical issue. This was performed on a tight carbonate sample to speed up the experiments. From a large block originating from an outcrop situated in the village of Tavel (France), a sample of diameter 25.2 mm and length 26.7 mm was first drilled. Then a smaller cylindrical sample of diameter 10.8 mm and length 18.6 mm was drilled out of the first larger cylinder. Using a similar protocol as above (pH equilibration is however not necessary), we measured diffusion curves of the resulting hollow and full cylinders (Fig. 4). We see a very close agreement between data and model for both cases. The experimental duration for the hollow cylinder is faster (~12 h) compared to the full cylinder geometry (~18 h) although the volume is 5.7 times larger, clearly highlighting the benefit of the hollow geometry when large volumes are needed. The diffusion coefficients are however not strictly the same (4.7 vs. 3.6 $10^{-10}\ m^2/s$ respectively for the hollow and full cylinder geometry). This is partially due to a difference of porosity between these two samples (respectively 13.3% vs. 11.8%), a larger porosity yielding a slightly different pore structure and thus a different pore diffusion coefficient.

The third example is a diffusion curve obtained on a cement paste containing metallic fibers. They are used to increase mechanical strength in concrete and are typically 10 mm in length, 3 mm in width and 0.1 mm thickness. They can be made of stainless steel or not, implying magnetic or non-magnetic disturbances in the NMR device beside severe signal to noise issue on the antenna. In such conditions, no FID can be detected in our apparatus but only a Hahn echo recorded at the minimum inter-echo time TE = 0.14 ms (Fig. 5). As predicted by theory in strongly inhomogeneous magnetic field [12], the Hahn echo is narrow and its maximum shifted at longer times. There is however no specific difficulties of recording such signal and to obtain a reasonable signal to noise ratio; 1024 scans were used with a repeat delay of 40 ms (hence a total acquisition time of about 41 s). For a concrete with much less porosity (~10%), the signal to noise ratio is reduced but can still be used for diffusion measurements (Fig. 5).

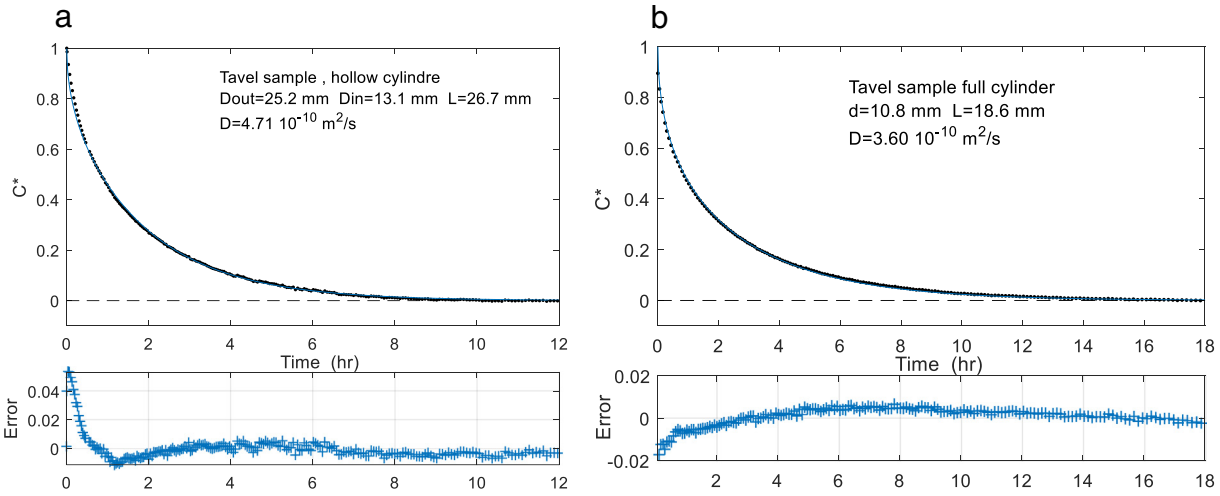

Fig. 4. Diffusion curves obtained from a hollow (left) and full (right) cylinder of the same porous material.

A diffusion curve measured on a cement paste in which fibers were incorporated together with a hollow geometry (d_{out} = 25.1 mm, d_{in} = 11.4 mm, L = 26.6 mm) is shown in Fig. 6. Since the diffusion coefficient is low (9.8 10^{-12} m^2/s), the experiment lasted about 600 h (25 days). For practical reasons, the recording was not performed continuously. During the unrecorded periods the sealed NMR tube was placed in an oven at the same temperature (30 °C).

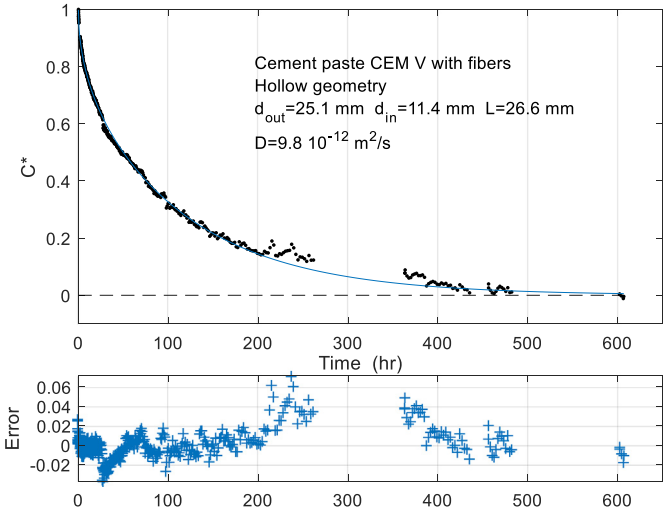

Fig. 6. Diffusion curve on a cement paste CEM V containing metallic fibers.

4. Conclusion

We describe in this paper a 3D deuterium diffusion method that uses NMR relaxation to measure the hydrogen content inside the sample as a function of time. It is useful when water saturated porous media have short relaxation times (< 1 ms) preventing the use of NMR pulsed field gradient techniques. In practice, the method is simple to implement and requires only a FID or Hahn echo to be recorded. The diffusion coefficient is then calculated with well-known analytical formulas taking into account the sample geometry. Two geometries are proposed: a cylinder and a hollow cylinder. The latter has the advantage of considering a much larger volume without excessive experimental duration. The method is the fastest when small samples are used with the appropriate NMR probe; for typical pore diffusion coefficient of 1.0 10^{-11} m^2/s valid for cement based material, the measurement time is about 5 days

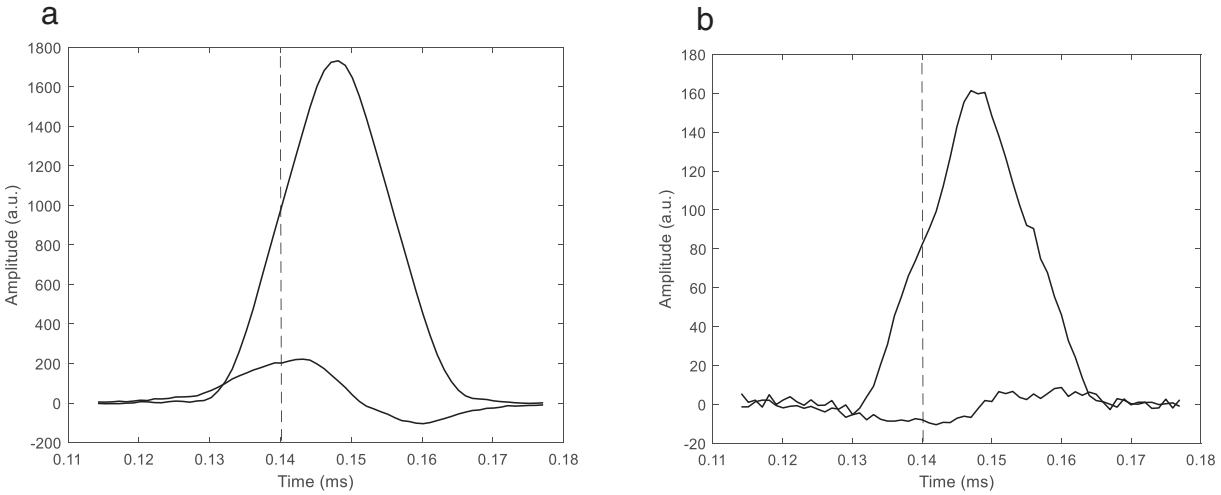

Fig. 5. Hahn echo at TE = 0.14 ms on a cement paste (left) and a concrete (right) containing metallic fibers. Number of scans: 1024 with a repeat delay of 40 ms. The magnetization M corresponds to the echo maximum. Note that the amplitude scale is 10 times smaller for the concrete.

for a cylinder of diameter 5.5 mm, and 25 days for a hollow cylinder of outer and inner diameter of 25.1 mm and 11.4 mm respectively. We show also that NMR diffusion measurements are still possible in the presence of metallic fibers.

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