NUCLEAR MAGNETIC RESONANCE PROFILING OF HIGH-STRENGTH CONCRETE SAMPLES

Marius Simina[1], Ioan Ardelean[1]

[1]Technical University of Cluj-Napoca, Physics Department, 400114, Cluj-Napoca, Romania

Email adress: Marius.Simina@phys.utcluj.ro

Abstract: The present work proposes an indirect way of identifying and monitoring the evolution of inter C-S-H and capillary pores from the surface layer of some high-strength concrete samples with different water to cement ratios as a function of depth. The method is based on measuring the nuclear magnetic resonance spin-spin relaxation of the water confined inside the porous matrix of the cementitious material. The concrete samples were prepared using a mixture of cement (CEM I 52.5 R), quartz sand, sillica fume (Elkem Microsillica), water and superplasticizer (Glenium ACE 30 - BASF). All experiments were performed in low fields using a single-sided NMR-MOUSE (**MO**bile **U**niversal **S**urface **E**xplorer) operating at the protons resonance frequency of 11.7 MHz. The NMR profiles were acquired for each sample with a maximum depth of 2.4 mm, and the evolution of the moisture content versus depth was extracted. The relaxation time distributions were obtained from the echo decays using a regularized numerical Laplace inversion algorithm. The results show a decrease of the relaxation time with the increase of the measuring depth, proving that the moisture content decays along with the measuring depth. The method can easily be applied for nondestructive in situ monitoring of the curing, setting and hardening processes of concrete structures.

Key words: NMR relaxometry, high-strength concrete, single sided NMR

1.   INTRODUCTION

Owing to its completely non-destructive character, nuclear magnetic resonance (NMR) is a powerful tool for investigating high-strength concrete both with respect to its structure and the dynamics of molecules (especially water) under confinement conditions. NMR measurements of diffusion coefficients [1] and relaxation times [2] render quantitative data on the dynamics of confined molecules and the restrictions of the confinement imposes on their translational and rotational mobility. NMR relaxation experiments are suitable in studying liquids (water) in porous media mainly due to an observed enhanced relaxation rate under confinement conditions [3, 4]. This behavior is generated by the interactions of the probed molecule with the surface depending on the porous sample composition, morphology, the nature of the filling fluid and its distribution inside pores [3, 4]. Consequently, relaxation time measurements may provide information about molecules location inside porous media and were comprehensively discussed in the NMR logging applications [5].

Due to its porous structure and the relative high water content, concrete makes an excellent candidate for low-field NMR spin-spin relaxometry investigations. Many NMR studies have been performed on concrete samples including diffusion and relaxation during hydration [6], microstructure determination [7] or micro-pore size analysis [8, 9] of the hydrated cement paste.

High-strength concrete has usually a very compact structure and low porosity and permeability due to the lack of coarse aggregates, the addition of silica fume or fly ash for enhancing the structural density and due to the low water-to-cement ratio generally obtained with the use of a super-plasticizer (water reducing agent). Although the structure gains high-compressive strength values after following all these steps, the composite material becomes less ductile and more prone to shrinkage. Often the defective curing treatment and exposure conditions may lead to the appearance of micro-cracks in the internal structure interconnecting the pores and leaving the material exposed to many moisture related deleterious processes.

Concrete structures are generally expected to display a high durability and resistance to chemical, physical and mechanical deleterious phenomena. One of the governing factors of concrete durability is permeability which also finds itself controlled by the pore structure and connectivity [10]. The pore types of concrete can be identified by NMR methods using the water reservoirs present in the structure of the material [11]. Once one has a pertinent image of the pore structure of a concrete material it will be easier to predict and to avoid the damage induced by the moisture transport. That is why this study investigates the pore-size distribution of some high-strength

concrete samples in order to understand and characterize this type of composite cementitious materials.

2.   METHODS

Three high-strength concrete samples with different water-to-cement ratios (0.2, 0.3 and 0.4) were prepared using a mixture of cement CEM I 52.5 R (Carpatcement – Heidelberg Cement Group), quartz sand (particle diameter < 0.31 mm), silica fume (Elkem Microsilica), water and super-plasticizer (Glenium ACE 30 – BASF) following the exact mass-ratios presented in Table 1. The concrete mixture was produced following the structural model of non-fibered RPC 200 [12], but using materials available on the local market.

Table 1. Typical high-strength concrete composition (by weight)

Materials	W/C 0.2	W/C 03	W/C 0.4
Cement CEM I 52.5 R	1	1	1
Silica fume	0.25	0.25	0.25
Quartz sand	1.1	1.1	1.1
Superplasticizer	0.026	0.026	0.026
Water	0.2	0.3	0.4

The samples were poured-in-place in polystyrene Petri dishes of 65 mm diameter and kept at a relative temperature of 25^0 C. After one day the shrinkage of the concrete allowed the easily striking of the samples from the Petri dishes and they were immersed in distilled water until they were investigated with the NMR profiler after 28 days of hydration. After 28 days the surface of the concrete samples was dried-up and the individual samples were placed back into the Petri dish in order to diminish the water evaporation and laid-down on a single-sided NMR scanner (NMR Mouse [13]) with the sensitive sensor underneath the centre of the Petri dish. The device has an accessible vertical range of 2.5 mm and is operated at 11.7 MHz proton resonance frequency.

The Carr – Purcell – Meiboom – Gill (CPMG) [14] pulse sequence was applied to acquire the depth profiles and the echo decay trains for each sample. The placement of the sensitive volume along the surface of the sample in order to measure the profiles is done owing to a powered high-precision elevation/dropping system. For all the samples the position of the

sensor was moved from the surface of the concrete sample to a maximum depth of 2.4 mm in twelve steps of 200 μm with a slice thickness of 200 μm.
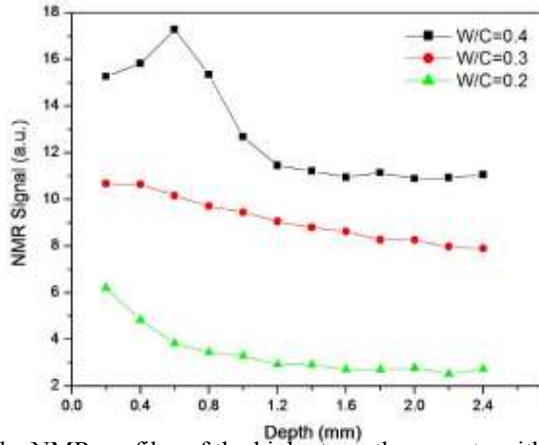
Figure 1. The NMR profiles of the high-strength concrete with different water-to-cement ratios versus the depth inside the sample

Sixty-four echoes were accumulated for each CPMG echo-train, with an echo-time of 56.5 μs and a repetition time of 50 ms, 4096 scans were used to obtain a better signal-to-noise ratio. Each point of the profile (*Figure 1*) represents the sum of the area of the second to fifth echoes in the CPMG train in order to reduce the influence of the transversal magnetization decay constant T_2 in the determination of the NMR signal intensity [15]. For the sample with a water-to-cement (w/c) ratio of 0.4, we observed an enhancement of the signal. Consequently, the CPMG echo decays were measured using a longer echo-time of 87.5 μs and a smaller number of echoes (only 42). The contribution of the diffusion in the overall signal intensity was estimated as being negligible.

One can observe multi-exponential decays of the CPMG echo train envelopes for each sample indicating the heterogeneity of the sample under study. In order to extract the relaxation time distributions, the experimental data in *Figure 2* have been analyzed numerically using the inverse Laplace transform based on the regularized CONTIN algorithm [16]. The results are depicted in *Figure 3* for all three water-to-cement ratios. Note however that the numerical Laplace inversion is ill-conditioned. That is, for a given CPMG decay envelope, there are a multitude of possible combinations of characteristic times which fit well the solution. This problem appears especially in the case of measurements which contain noise in the measured data and may lead to large perturbations in the resulting relaxation time distributions. Therefore the numerical inverse Laplace transforms must be used with precaution when interpreting the experimental results.
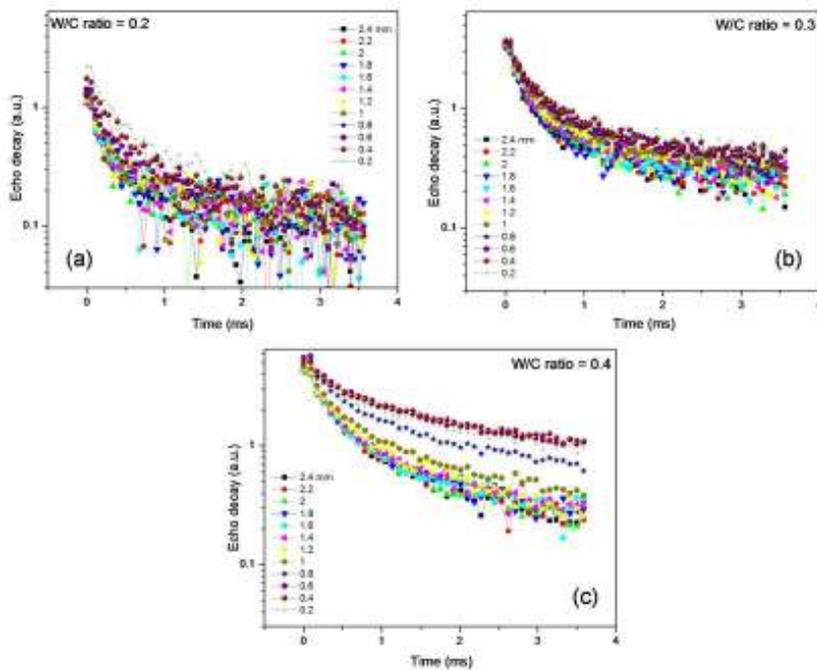
Figure 2. The echo amplitude versus echo time in a CPMG relaxation experiment on high-strength concrete samples with different water-to-cement ratios: w/c=0.2 (a), w/c=0.3 (b), w/c=0.4 (c)

3. RESULTS AND DISCUSSION

The NMR moisture profiles (*Figure 1*) reveal a decrease in the signal amplitude with the penetration depth. For the samples with a w/c ratio of 0.2 or 0.3 respectively, the decrease is more severe until the depth of 1mm. After this range the slope is diminishing until 2 mm depth wherefrom the amplitude of the signal is almost constant. The sample with a w/c ratio of 0.4 follows the same behavior as the other two for depths bigger than 1 mm, but in the range of 0.2 – 1 mm the NMR signal amplitude profile exhibits a peak indicating a higher moisture content at a depth of 0.6 mm.
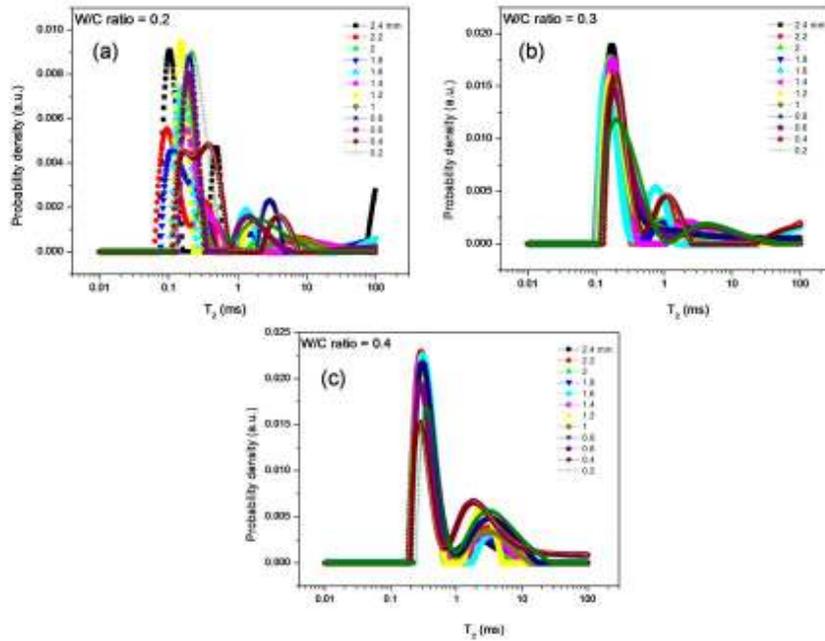
Figure 3. The relaxation time distributions of water molecules confined inside the high-strength concrete samples with different water-to-cement ratios: w/c=0.2 (a), w/c=0.3 (b), w/c=0.4 (c)

The CPMG echo decays depicted in *Figure 2* show an enhancement of the signal-to-noise ratio of the samples with the increase of the water-to-cement ratio. This enhancement starts from the more scattered data in *Fig. 2*a (w/c=0.2) where the structure of the material is more dense and the porosity is lower and evolves to the much more accurate echo trains corresponding to the w/c=0.4 in *Fig. 2c* for whom the porosity and implicitly the NMR signal intensities are higher. Also analyzing the CPMG echo decays one can notice that all three w/c ratios exhibit a double exponential behavior indicating the contribution of two different relaxation components. This behavior is obvious when the data are analyzed using the regularized Laplace inversion algorithm CONTIN [16]. Hence on the relaxation time distributions in *Figure 3* the presence of two peaks is noticed, each corresponding to a distinct water configuration inside the sample. The shorter component, with T_2 values ranging between $0.1 - 0.35$ ms is assigned to the gel pore water [11], the longer component with values ranging between $0.3 - 3$ ms is attributed to the capillary pore region [11]. Any longer components can derive from water in cracks or adsorbed on the surface of the sample or, it can be an artifact induced by the inverse Laplace transform. Therefore in this study the analysis has focused only on the evolution and the behavior of the shortest components, corresponding to the gel and capillary pores and the

long relaxation times representing the surface adsorbed water contributions were neglected.

By exploring the relaxation time distributions in *Figure 3* one can observe that the position of the first peak has a more dynamic evolution for the sample with a 0.2 w/c ratio than for the other two. For this sample (w/c=0.2) the peak position (*Fig.* 3a) is not just decreasing in amplitude but it has a slight and clear shift to the right. This indicates that the pore dimension decreases with the penetration depth. For the other two samples the evolution is similar but less obvious.

Figure 4 shows the evolution of the transverse relaxation times (T_2) of the two components capillary (*Fig.4a*) and gel (*Fig.4b*) versus the measuring depth. The values were extracted from the relaxation time distributions in *Figure 3*. As can be observed the behavior of the gel T_2 values (*Fig. 4b*) are similar to that of the NMR profiles indicated in *Figure 1* offering a clear distinction between the different water to cement ratios. The slowly decrease of the T_2 value with the depth indicates that the gel porosity decays with the penetration depth. On the other hand, the capillary water evolution presented in (*Fig. 4*a) has a much unpredictable behavior and one can easily notice that a clear separation between samples is hard to be done. The scattered evolution of the capillary water can be explained by the appearance of micro-cracks in the structure of the concrete sample which will perturb the pore system and give rise to the peaks with values larger than 3 ms one can notice in (*Fig. 3 a*). Those cracks may appear as a result of defective curing or can be induced by the endogenous shrinkage and the self-desiccation which are common phenomena in the high-strength concrete [17].
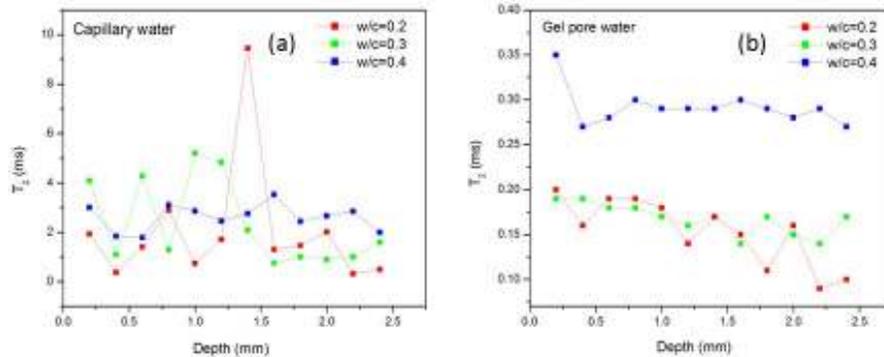
Figure 4. The evolution of the capillary (a) and gel (b) pores transverse relaxation time versus depth as extracted from the Laplace inversions in *Fig.3*.

4.   CONCLUSIONS

In the present work it is proved that the low-field NMR relaxometry profiling technique can be successfully used as a tool in diagnostic of high-strength concrete samples or other cement based materials. Using a numerical Laplace inversion it was possible to extract information on liquid distribution inside partially saturated high-strength concrete samples at different depths. Two peaks were found in the relaxation time distribution at each depth independently of the water-to-cement ratio. These two peaks could be attributed to different locations of the water molecules: the gel pore water and the capillary water. The monitoring of the transverse relaxation time versus penetration depth for three water-to-cement ratios (0.2, 0.3 and 0.4) indicates a decrease of the gel pores with the penetration depth for the samples with 0.2 and 0.3 W/C ratio. The results presented here may contribute to a better understanding of the deleterious processes taking place in concrete under the influence of the water transport inside the porous structure of the composite cementitious materials.

It is also important to note that the NMR – MOUSE profiling technique presented here can be used as a completely nondestructive tool for investigating the cement based materials in situ. Thus it can provide a quick and precise moisture content monitoring or even the crack formation analysis at different depths inside concrete walls.

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