Scientific Report

on the implementation of the project **PN-II-IDEI 305/2011** *during the inteval*

January – September 2016

Theme of the project:

The surface effect on the dynamics of molecules confined inside porous media with magnetic impurities

The objective of the stage 2016:

Application of the previous knowledge to the investigation of rotational dynamics of water molecules confined inside cement paste

Associated activities:

A1. Measurement of the relaxation rate in cement paste as a function of temperature and frequency of the external magnetic field at different hydration times;

A2. Comparison of the results obtained on cement paste with those on porous ceramics with similar amount of magnetic impurities and pore dimensions.

The objective of the 2016 stage was to use the knowledge gained in the previous stages on materials with controlled magnetic impurities in the study of rotational dynamics of water molecules confined inside cement paste. Two types of cement pastes were considered: the pure cement paste and the cement paste containing SiO_2 nanoparticles introduced in order to increase the mechanical strength of cementitious products. To accomplish this goal two main activities were considered: A1) Extraction of nuclear relaxation rates versus temperature and the frequency of the externally applied field at different times of hydration; A2) Comparison of the experimental results with those previously obtained on ceramic samples containing the same amount of magnetic impurities and pore sizes. In the following we will briefly describe the activities associated with the achievement of the objective corresponding to the stage 2016 of the project and the main results.

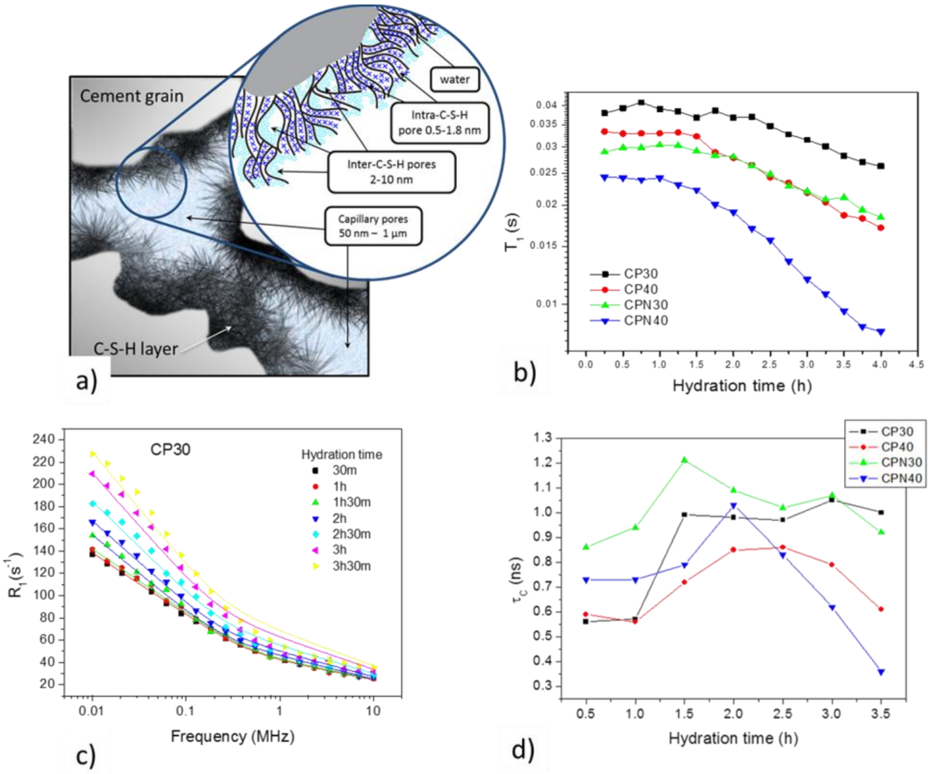

Fig.1. a) The porous structure of a cement paste after hydration (see Ref. [1]). Evolution of the longitudinal relaxation time corresponding to the capillary pores of cement paste at two temperatures (CP30, CP40) and in the presence of silica nanoparticles (CPN30, CPN40). c) Tipical relaxation dispersion curves obtained with FFC at different hydration times. d) Tipical correlation times extracted from FFC data.

A1. Measurement of the relaxation rate in cement paste as a function of temperature and frequency of the external magnetic field at different hydration times

Cement paste is a porous material with a complex structure containing pores with sizes ranging from nanometers to micrometers and is the main constituent of all cement-based materials (concrete, mortar). Cement paste is obtained by the hydration of Portland cement grains in the presence of water. The material resulting from the hydration reaction is a rigid and complex mixture of different minerals both crystalline, such as ettringite and portlandite and low crystalline, namely C-S-H (here we use the cement chemistry abbreviations) [2]. The main constituent of the cement paste is the C-S-H gel which is a nano-porous heterogeneous material which contains calcium layers, oxygen atoms and silica tetrahedra separated by layers of water. Together with the non-hydrated cement grains or other admixtures introduced inside cement materials they create a complex porous system with pores ranging from nanometeres to tens of micrometers. It is generally accepted in the cement literature that one can distinguish three types of pores: intra-CSH pores, inter-CSH pores and capillary pores respectively (see Fig. 1a) [1].

For the investigations performed during the 2016 stage of the project the cement pastes (CP) were prepared using white cement CEM I 52.5 N (Holcim, Romania). White cement was chosen on purpose because it contains a relatively small amount of Fe_2O_3 (0.5%), as provided by the manufacturer. The samples were prepared at room temperature, with a water-to-cement (w / c) ratio of 0.6 using distilled water produced in our laboratory. The mixture was stirred for 6 minutes using an electric mixer with a rotation frequency of 500 rpm. Immediately after mixing the obtained samples were poured into the NMR tube with an outer diameter of 10 mm, which fits inside the RF coils of the NMR instruments used in our measurements (MinispecMQ20, Bruker, Germany and Stellar

SMARTracer, Italy). The hydration process of all samples took place inside the NMR tube remaining open inside the RF coil at a controlled temperature of 30 °C or 40 °C respectively. These temperatures were chosen because they are close to the temperatures at which the hydration takes place in summer. On the other hand higher hydration temperatures (>40 ^{o}C) determine faster chemical reactions which affect the porous structure inside the formed cement paste. Moreover due to a the accelerated hydration process introduced by the higher temperatures, the FFC technique, which requires longer acquisition intervals, does not provide reliable results due to the sample change during the experiment. That is why, only the CPMG technique can be used at higher temperatures but this technique provides incomplete information, at a single frequency and is affected by the internal gradients [3-8].

The study of nuclear relaxation rates can provide us information on the dynamics of molecules confined inside the cement paste pores even during the hydration process. However, this is not easy to achieve with the CPMG technique due to the presence of impurities that introduce errors in measurements due to diffusion effects in the presence of internal gradients [3-8]. Furthermore, the CPMG pulse technique operates at a single resonance frequency and the extracted information is incomplete [9]. This issue was already discussed in detail in the previous stages of the project and several papers were published in this regard [3-7]. That is why in the stage 2016 the longitudinal relaxation component was mainly investigated using the Fast Field Cycling equipment acquired during the 2012 stage of the project. The first NMR measurements were always performed after 15 minutes counting from the initiation of mixing process and the last after 5 hours of hydration.

The experimental results (see Fig. 1b as an example) show that the presence of nanoparticles has a significant influence in reducing the dormancy period, in a similar way with rising the temperature. In addition, it produces a significant reduction in the pore size even at earlier hydration times. It is also observed a clear dependence of shortening the dormancy period by the increase in the content of nanopartilcles (not shown here) in accordance with the studies carried out by alternative methods [2]. The same effect of reducing the dormancy period it is provided by the increase in the hydration temperature but in this case the pores become larger [2] as can be seen from the corresponding relaxation time. Let us note, however, that these conclusions are not trivial when one considers the complexity of surface pores and that the same effect as introduced by the presence of nanoparticles can be determined by a partial saturation of the sample [1]. Therefore, for the above conclusions the experimental data (see Fig.1c as an example) were compared with a theoretical model of relaxation developed in earlier stages of the project [7]. They were also compared with the data obtained on ceramic samples with a low content of Fe_2O_3 (average pore size of about 13 μm) prepared by the method described in earlier stages of the project.

A2. Comparison of the results obtained on cement paste with those on porous ceramics with similar amount of magnetic impurities and pore dimensions.

In the fast exchange limit the longitudinal relaxation rate of molecules confined inside porous media under partially saturated conditions satisfy an equation of the form [1]

$$\frac{1}{T_1} = \frac{1}{T_1^{bulk}} + \rho_1 \frac{S}{V_0} \frac{1}{f^k} . \tag{1}$$

In the above equation $1/T_i^{bulk}$ is the longitudinal relaxation rate of molecules under bulk conditions (temperature dependent), S/V_0 -surface to volume ratio of the pores, f -the saturation degree of the pores and k an empiric constant characterizing the molecular distribution on the pore surface. The physical quantity ρ_1 represents the surface relaxivity and is a function of the surface nature the polar character of the confined molecules, the magnetic impurity content at the surface of the pores, the temperature and the magnetic field strength of the experiment (Larmor frequency of the nuclear spins). For materials containing magnetic impurities, as is the case of cement paste, the relaxivity is given by an equation of the form: [7,9]

$$\rho_1 = C_{dip} \tau_m \left[3 \ln \left(1 + \frac{1}{\omega_I^2 \tau_m^2} \right) + 7 \ln \left(1 + \frac{1}{\omega_S^2 \tau_m^2} \right) \right] \tag{2}$$

Where C_{dip} is a constant describing the strength of dipolar interaction between the nuclear spin and the electronic spin of the magnetic impurities on the surface, τ_m the correlation time of molecules on the surface [7,9].

To understand how the temperature influences the interaction of molecules with the surface of capillary pores in cement paste during the hydration process the data were compared with those on porous ceramics with similar pore sizes and magnetic impurity content. The results have shown that in the investigated temperature range the temperature effects can be neglected and only the surface effects on molecules dynamics need to be considered. By comparing the experimental data (Fig.1c is a typical example) with the theoretical relaxation rate described by equation (1), the correlation time can be extracted and its relationship with the hydration time of cement paste hydrating under different conditions (See Fig. 1d as an example). Let us note, that the fitting of experimental data can be performed only during the dormancy stage and the early stage of acceleration (<3h) when the capillary pores are still quite large and relaxation time is long enough to allow FFC measurements. Also during this time the porous structure is not yet fully formed and the dominant NMR signal comes from the capillary pores. After the dormancy stage relaxation time is very short and the FFC technique cannot be applied. Our research also showed that for later hydration period (after 28 days) is preferable to use ethanol (as a representative of polar molecules) or cyclohexane (as a representative of apolar molecules). These two molecules have relaxation times longer than water and, in addition, are better absorbed inside the capillary pores.

Typical correlation times characterizing the movement of water molecules on the pore surface are represented in Fig.1d for the 4 samples indicated on the figure. Comparing the pure cement paste (CP30 and CP40) during the dormancy period, it is observed that the correlation time is not influenced by the heat of hydration (30 ^{o}C or 40 ^{o}C). In the case of samples containing nanoparticles (CPN30 and CPN40) the temperature dependence is manifested already in the early stage of hydration and accelerates the formation of certain compounds in the presence of higher temperatures. The correlation time values in our measurements are somewhat lower than those obtained in the case of porous ceramics as observed in the previous stages of the project. This indicates a lower affinity of water molecules on the surface of capillary pores of the cement paste.

Conclusions

During the reporting period we have studied molecule-surface interaction effects on the dynamics of rotation of molecules confined inside cement paste prepared with different amounts of silica nanoparticles and hydrating at different temperatures. The purpose of these investigations was to understand the molecular dynamics within the complex porous structure of cement paste. Our studies were based both on the conventional NMR relaxometry technique (CPMG) and the Fast Field Cycling technique allowing the observation of nuclear spins at different frequencies. The FFC technique has the advantage that it is sensitive to a broader spectrum of molecular motions and that it is not influenced by diffusion in internal gradients. The disadvantage of FFC technique as compared with CPMG technique at a certain frequency is that the signal/noise is smaller and requires longer duration experiments.

The experimental data on cement paste were compared with those on model samples and the applicability of the theoretical relaxation model taking into account relaxation via paramagnetic centers was verified. It was found that this model applies only during dormancy stage and the early stage of acceleration when the C-S-H gel phase is not yet dominant. After that time the molecular exchange process between inter-C-S-H and capillary pores should be considered as a possible mechanism of relaxation. Our investigations have shown an increased relaxation rate by rising the temperature despite the drop in the rotational correlation time. This behavior may be attributed to the partial desaturation of the pores at high temperatures, and thus increasing the role of the exchange process.

Our findings were disseminated through the publication of 3 ISI papers and one book chapter. Another article is in preparation. They have been also presented at international conferences as shown in the list below. The results were also included in a doctoral report of Mrs. Andrea Bede, a member of the project team.

References

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Publications during the year 2016

Articles in ISI journals

- Pop, A. Bede, M.C. Dudescu, F. Popa, I. Ardelean, Monitoring the Influence of Aminosilane on Cement Hydration Via Low-field NMR Relaxometry, Appl. Magn. Reson. 47, 191-199 (2016).
- Bede, A. Scurtu, I. Ardelean, NMR relaxation of molecules confined inside the cement paste pores under partially saturated conditions, Cem. Conc. Res. 89, 56-62 (2016) (5 Year IF=4.07);
- J. Stepisnik, I. Ardelean, Usage of internal magnetic fields to study the early hydration process of cement paste by MGSE method, J. Magn. Reson. 2016 (accepted, in press)
- A. Bede, C. Badea, I. Ardelean, Monitoring the effect of water-to-cement ratio on pore size distribution of hydrated cement paste via NMR relaxation of cyclohexane molecules, Cement and Concrete Research 2016 (in preparation)

Book chapters

- Ardelean and R. Kimmich, Beyond the Limits of Conventional Pulsed Gradient Spin Echo (PGSE) Diffusometry: Generalization of the Magnetization-grating Principle, in „Diffusion NMR of Confined Systems: Fluid Transport in Porous Solids and Heterogeneous Materials”, (Ed. R. Valiullin), Publisher: Royal Society of Chemistry (in press, corrected proof, 35 pages.)

Conference presentations

- I. Ardelean, A. Bede, A. Scurtu, Probing into the porous structure of hydrated cement paste with the NMR relaxometry of cyclohexane and ethanol molecules under partially saturated conditions, 13th International Bologna Conference on Magnetic Resonance in Porous Media (MRPM13), Bologna, September 3-8, 2016 (oral presentation).
- A. Bede, C. Badea, I. Ardelean,Revealing the porous structure of cement materials via the NMR relaxometry and diffusometry of cyclohexane molecules, 13th International Bologna Conference on Magnetic Resonance in Porous Media (MRPM13), Bologna, September 3-8, 2016 (poster)
- I. Ardelean, A. Bede and C. Badea, NMR relaxation under partially saturated conditions: applications to cement paste, Alpine NMR Workshop, Cluj-Napoca, Sep 23-25, 2016 (oral presentation).
- A. Bede, I. Ardelean and C. Badea, The effect of silanized nanoparticles on the hydration and the properties of cement materials, Alpine NMR Workshop, Cluj-Napoca, Sep 23-25, 2016 (oral presentation).

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