Scientific Report

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

during the stage January-December 2012

The theme of the project:

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

The objective of the stage 2012:

The influence of the internal gradients on diffusion and relaxation measurements

Specific activities:

A1. Extracting the internal gradients of the produced samples;

A2. Evaluating the influence of internal gradients on diffusion measurements;

A3. Evaluating the influence of internal gradients on relaxation measurements;

A4. Evaluating the influence of internal gradients on the thickness of the surface layer used in the interpretation of relaxation data;

A5. Testing the efficiency and the limits of compensating gradient techniques for diffusion measurements;

A6. Acquisition and testing of a Fast Field Cycling NMR instrument

Results

In the **second stage (2012)** of the present project the model samples developed in the first stage and containing a controlled amount of magnetic impurities were used as model samples to investigate the influence of internal gradients on molecular self-diffusion and nuclear relaxation measurements [1-3]. The results obtained on these model samples were compared with those obtained on samples of cement paste, mortar and concrete which naturally contain magnetic impurities. New theoretical models were developed in order to explain the experimental results and based on these models the correlation times characterizing the molecular motion at the solid-liquid interface were extracted. Furthermore, new NMR techniques for the determination of the pores size were developed and their application and limitations were discussed. In the following a short presentation of the investigations during the second stage will be given. The above mentioned activities are **implicitly** included.

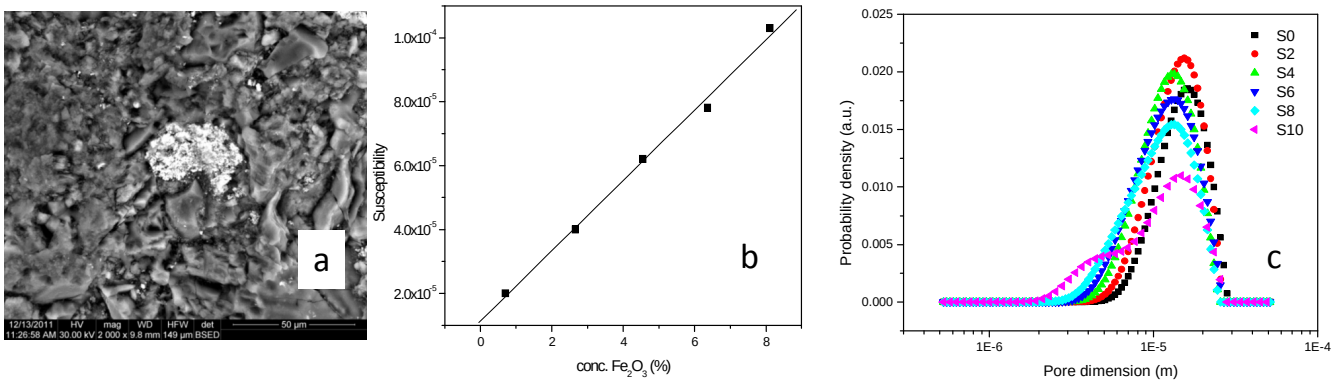

Fig.1 (a) The SEM image of a ceramic sample S2; (b) The dependence of the susceptibility constant on the amount of magnetic impurities; (c) The pore size distribution of the produced ceramics obtained with the DDIF technique.

1. Preparation of porous ceramics with a controlled amount of magnetic impurities

In the first stage of the project (2011) were investigated two different possibilities for the preparation of porous ceramics with a controlled amount of magnetic impurities (the polymeric matrix and the powder pressing method) [4] and was evaluated how the produced samples fit our NMR studies. It was concluded that the method based on powder compression followed by sintering is more reliable and is better suited for the use the iron oxide (III) as magnetic impurity. This method was then implemented in the preparation of all samples for the NMR investigations in the stage 2012. The mix used in the preparation of traditional ceramic [4] consists of 60% kaolin (1% Fe_2O_3), with grain size between 63-80 micrometers 30% feldspar (0.33% Fe_2O_3) and 10% quartz sand with grain size between 80-120 µm. There were prepared 6 cylindrical samples (H ≈ D ≈ 7 mm) by adding to 100 g of the mixture a quantity of 0, 2, 4, 6, 8 or 10 g of Fe_2O_3. The iron oxide (III) was purchased from Merck, Germany, with an average grain size of 1 µm and consists of α- Fe_2O_3. The produced samples were compressed at a pressure of $1.2 \cdot 10^4\,\mathrm{N/cm^2}$ and then sintered at 1150 °C for 3 hours after which they were left in the oven for slow cooling for 24 hours. These samples will be denoted in the following by S0, S2, S4, S6, S8 and S10, respectively.

All samples were then investigated using a SEM microscope (FEI Quanta Inspect F) and Fig.1 shows an example of a SEM image obtained on the sample S2. The SEM images showed a consistent increase in the amount of impurity in the sample with the increase in the content of magnetic iron oxide in the mixture. The magnetic susceptibility was also measured for all samples and a linear increase in susceptibility value with the quantity of Fe_2O_3 was observed (Fig.1b). From the SEM images could be also observed an average pore size of 10-20 µm which was confirmed by the method exploiting diffusion in internal gradients described below (Fig.1c).

2. Study of the internal gradient effects on molecular diffusion measurements

The difference between the magnetic susceptibility of a porous matrix and the confined fluid induces inside the pores internal magnetic fields proportional to the difference in susceptibility and the external magnetic field [1,3,5]. The estimates preformed in the present project have shown that our spectrometer operating at an external field of 0.47T produces internal field gradients of the order of 5-15 T/m in ceramic samples (S0-S10) and 9-12 T/m in the case of cement samples. These values of the internal gradients are much larger than produced by the gradient coils (in our case 2T / m). Therefore any attempt to measure the molecular diffusion of liquid confined inside porous media with magnetic impurities are unrealistic with the classical pulsed field gradient approaches [1]. Therefore in the following we present two unconventional uses of the diffusion effects in the presence of internal gradients for investigating the fluids confined inside porous samples.

The DDIF technique

This technique was recently introduced in the literature as a non-invasive technique for determining the pore size of porous media having high content of magnetic impurities (rocks, soils) [3]. The DDIF technique (diffusion decay in internal fields) consists mainly in comparing the NMR signal appearing in two RF pulse sequences: i) the stimulated echo sequence $\pi/2-t_e-\pi/2-t_d-\pi/2-t_e-\text{Echo}$- generating an echo (E) and ii) a reference sequence (R) $\pi/2-t_e-\pi-t_e-\pi/2-t_d-\pi/2-\text{Ref}$ -which generates a signal sensitive only to the longitudinal relaxation. The first period of evolution in the stimulated echo sequence induces a modulated longitudinal magnetization depending of the spins position inside the pores. This modulation is generated by internal gradients and therefore contains information about pore geometry. The modulated component of the longitudinal magnetization will be attenuated in the second evolution interval both as a result of diffusion effects and relaxation effects. The amplitude of the stimulated echo generated at an instant t_e after the third pulse can be written as [3]:

$$E(t_d)=a_0e^{-t_d/\tau_0}e^{-t_d/T_{1b}}+\sum_{n=1}^{\infty}a_ne^{-t_d/\tau_n}e^{-t_d/T_{1b}}\ . \qquad (1)$$

In the above expression the first term describes the contribution of the pure relaxation to the signal attenuation and the second term describes both relaxation and diffusion in the internal gradients effects. A numerical Laplace inversion of the recorded signal would provide the characteristic relaxation time spectrum τ_n $(n=0,1,2,...)$ of the investigated system. Note that the bulk relaxation time, T_{1b}, is known and the first term in Eq. (1) can be eliminated by comparing the echo signal arising in the stimulated echo experiment with the signal recorded in the reference sequence (R) and thus only the diffusion modes are contributing to the characteristic spectrum.

It can be demonstrated theoretically [3] that the characteristic times of the diffusion process in internal gradients can be restricted to the first order $n=1$ if the condition $\gamma\Delta B_z^i t_e<<1$ is satisfied. Here γ is the gyromagnetic ratio and ΔB_z^i is the variation of the longitudinal component of the internal magnetic field inside the pores. In this case the amplitude of the NMR signal is proportional with $a_1\propto\gamma\Delta B_z^i t_e\propto\gamma\Delta\chi B_0 t_e$ and the only characteristic diffusion mode contributing to the signal attenuation in Ec. (1) is that for $n=1$, i.e. [3]

$$\tau_1\approx d^2/D\pi^2\ . \qquad (2)$$

This characteristic time provides us the dimension distribution of our samples containing magnetic impurities. An essential condition is for a correct application of the technique however that $\gamma\Delta B_z^i t_e<<1$. Our investigations on porous samples containing a controlled amount of magnetic impurities have allowed us for the first time the verification of this condition [6]. Figure 1c shows the pore size distributions of our samples. It can be observed a shoulder of the S10 distribution curve that can be associated with the no-fulfillment of the condition $\gamma\Delta B_z^i t_e<<1$ for the experimental parameters. In this case the second order diffusion modes become significant.

The CPMG technique in the presence of diffusion effects

The most used technique for relaxation measurements is the so called CPMG (Carr–Purcell–Meiboom–Gill) technique. The RF pulse sequence generating the CPMG echo train is formed of an initial $(90^0)_Y$ pulse followed by a series of $(180^0)_X$ pulses applied at the time intervals $\tau,\ 3\tau,\ 5\tau,\ldots$. An echo train is then recorded at the time intervals $2\tau,\ 4\tau,\ 6\tau,\ldots,2n\tau$ (n-is the echo order) [7]. It is assumed, most often a priori, that the attenuation of the CPMG series occurs only under the action of transverse relaxation phenomena and thus this technique is often used in NMR transverse relaxation time measurements being recognized as a robust and fast technique. However, neglecting diffusion effects on the CPMG echo series can be made only in samples with moderate field gradients (<1T / m) and short intervals of evolution between pulses ($\tau<0.2$ ms) but not for some natural porous samples (rocks, soils,

concrete) where diffusion in the internal gradients is an important mechanism for attenuation. Therefore, in the 2nd stage

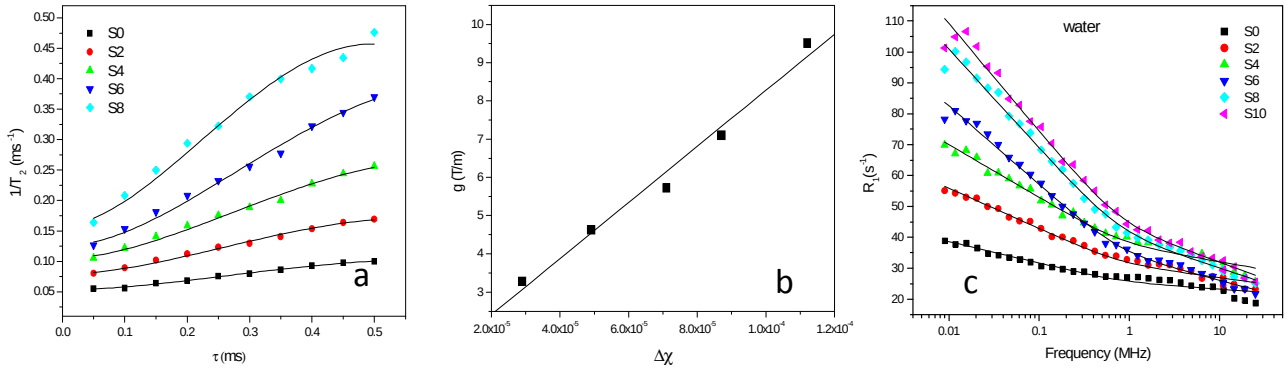

Fig.2 (a) The dependence of transverse relaxation rates on the evolution interval τ; (b) The effective internal gradient versus the difference in the susceptibility; (c) The relaxation dispersion curves in the case of 6 ceramic samples saturated with water. The theoretical curves are described by Eq. (4).

of the present project we analyzed the effect of diffusion in internal gradients on the echoes attenuation in a CPMG experiment.

In our project was shown [8] that, if the influence of internal gradients can be neglected, the transverse relaxation time is not a constant but depends on the gradient strength, the molecular diffusion coefficient, the pore size S / V and the time evolution between two successive radiofrequency pulses 2τ. Thus it was shown that the effective transverse relaxation time of the echoes of an order n>5 in the CPMG train can be described by a relation of the form [8]:

$$\frac{1}{T_2} \cong \frac{1}{T_{2r}} + \frac{1}{3} D\gamma^2 g^2 \tau^2 \left[1 - 0.57 \frac{g_v^2}{g^2} \frac{S}{V} \sqrt{D\tau} \right]. \qquad (3)$$

In the above equation the first term quantifies the pure relaxation and the second term the effects of diffusion (D) in the internal gradients on relaxation measurements. In our studies on model samples (S0-S8) we proved the dependence of relaxation rate on the echo time interval and magnetic impurity content (Figure 2a). It was also possible to estimate the average effective internal gradient (see Fig.2b) and the ratio between the surface and volume averaged gradient $g_v^2 / g^2 = 2.5$. This allowed us the development of a new approach for the determination of the pore size of porous media containing magnetic impurities. The results of the new CPMG technique provide similar values with those extracted from the DDIF technique (13μm). These values are consistent with the direct SEM observations. This new technique has been applied successfully in porous media as cementitious materials to monitor the pore size evolution during the hydration process. Let us note that our proposed CPMG technique is the only technique that can monitor the progress of pores size in the cement based materials during their early hydration.

3. Study of the internal gradient effects on longitudinal relaxation

The dispersion curves of longitudinal nuclear relaxation are useful tools in extracting information on the dynamics of molecules confined in porous media [2]. From the comparison of the longitudinal relaxation rate of the dispersion curve with a theoretical model it is possible to extract the correlation time of the molecular motion or the diffusion coefficient at the pores surface [5]. These correlation times can be linked with the polar or nonpolar character of molecules or with the physical properties of the pores surface. In general, there are two mechanisms contributing to the nuclear relaxation of molecules confined inside porous media: i) the reduction of the mobility of the molecules on the surface of pores [2], and ii) the fluctuating magnetic field produced by the magnetic

impurities from the surface [2]. Depending on the density and pore size of magnetic impurities one or the other of these mechanisms can become dominant.

In the case of porous media without magnetic impurities with micrometer or nanometer-sized pores (Vycor, Vitrapor # 5) it was experimentally demonstrated that the dominant mechanism producing the longitudinal relaxation is the reduction of the mobility of molecules at the surface [2]. Therefore in the current stage of the project we investigated if it is the dominant mechanism of relaxation also in porous media containing magnetic impurities. Thus, it was proposed to describe the nuclear relaxation using a two-phase fast exchange model considering the rapid change in the position of molecules located inside two regions: one surface layer of thickness λ (of the order of molecular dimensions) and the region within the pore volume. In the region λ the nuclear spins relax by interaction with the paramagnetic ions (Fe^{3+}) on the surface generating a specific surface relaxation rate ($1/T_{1surf}$) [5]. Inside the bulk-like region the relaxation is characterized by the bulk relaxation rate ($1/T_{1b}$). A rapid exchange between these two regions leads to a dependence of the nuclear relaxation rate of the applied magnetic field of the form [9]:

$$\frac{1}{T_1} = P_1 + P_2 \cdot \left\{ 7\ln\left[1+\left(658.21\,\omega_I\right)^{-2}\tau_\perp^{-2}\right] + 3\ln\left(1+\omega_I^{-2}\tau_\perp^{-2}\right)\right\}. \qquad (4)$$

In the above equation ω_I represents the Larmor frequency of the nuclear spins and $\tau_\perp = \delta^2 / 4D_\perp$ is the transverse correlation time of molecules on the surface of porous media. The time $\tau_\perp$ is defined as the average time of molecules for a jump on the surface of a molecular size δ. Comparing the experimental relaxation dispersion curves obtained with the FFC technique it was thus possible to extract the correlation time of molecules at the surface and from here the surface diffusion coefficient.

In our experimental studies on samples with magnetic impurities S0-S10 we have demonstrated the validity of equation (4), we identified the limits in which it can be applied and we have shown that the dominant relaxation mechanism is the interaction with the paramagnetic centers on the surface [5]. The comparison of experimental data (Fig.2c) with eq. (4) allowed us extraction the correlation time of water ($\tau_\perp^{apa} = 0.32\,\text{ns}$) and cyclohexane ($\tau_\perp^{ciclo} = 0.24\,\text{ns}$) molecules at the surface. The different values observed indicate a different behavior of polar molecules (water) at the pores surface as compared with the nonpolar molecules (cyclohexane). It is also observed that the presence of paramagnetic centers on the surface does not influence the dynamics of confined molecules. These studies on model samples (S0-S10) allowed us to test the technique which can be then applied to other samples of practical interest, namely the study of the effects of temperature on the hydration of cement paste and high strength concrete in the presence of plasticizers.

Conclusions

In the present stage of our studies were produced ceramic porous media of micrometer pore size containing iron oxide III as magnetic impurities in different concentrations (0-10%). These samples were then used in NMR diffusion and relaxation experiments in order to understand the role of internal gradients and of the magnetic impurity on the surface. To explain the experimental data were developed new theoretical models which have allowed the extraction of important parameters characterizing the molecular dynamics of solid-liquid interface such as the correlation time and the diffusion coefficient. These parameters could be related to the nature of the polar or nonpolar molecules confined. In our investigations were also developed new approaches for determining the pore size which could be applied to study the hydration of cement paste, mortar and concrete [9] (material with natural magnetic impurities). Our findings were used by the publication of two ISI articles in ISI [6,7] or sending other two papers for publication in ISI journals [8,9]. They were also communicated in international conferences (MRPM11 Surrey, NT2F12 Brasov, Alpine NMR Workshop). The results of the project were also introduced in two theses (Simina M., Muncaciu S.) developed in the laboratory. Another activity carried out was related to the purchase and installation of an Fast Field Cycling NMR relaxometer (STELAR SmarTracer) allowing us nuclear relaxation dispersion studies. Let us note that there are only 12 such instruments in

the world and so far the measurements of this type of were done in collaboration with the colleagues from TU Ilmenau, Germany.

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