

# Scientific Report

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

during the stage January-December 2013

## **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 2013:**

Study of the molecule-surface interaction effects on macroscopic translational dynamics and the distribution mode of polar and nonpolar molecules on the pores surface

## **Specific activities:**

- A1. Study of molecule-surface interactions on the translational dynamics of molecules confined in porous media without magnetic impurities;
- A2. Study of molecule-surface interactions on the translational dynamics of molecules confined in porous media with a controlled amount of magnetic impurities;
- A3. Applications of earlier studies to the case of cement-based materials.

## **Results**

It is well known that the translational motion of molecules confined inside porous media is strongly influenced by their interaction with the surface. Up to now, most NMR studies of molecular dynamics in porous media have been carried out on samples saturated with liquid. In this case, however, the contribution of the surface to diffusion phenomena is less effective and the information extracted from the effective diffusion coefficient is incomplete because the molecular exchange with the bulk phase plays a dominant role. Therefore, during the stage 2013 of the present project we extended the investigations to the partially saturated samples where the surface has a more important contribution. In our investigations we have done comparative studies on two types of porous samples: with magnetic impurities and without magnetic impurities. To interpret the experimental results and in order to propose a new theoretical model able to explain the nuclear relaxation in partially saturated porous media we used Monte Carlo simulations of molecular diffusion.

### **A1. Study of molecule-surface interactions on the translational dynamics of molecules confined in porous media without magnetic impurities**

To quantify the contribution of vapor phase diffusion phenomenon, and thereby determine the influence the vapor phase to the interpretation of the experimental data we performed first experiments on model samples without magnetic impurities. As representatives of samples without

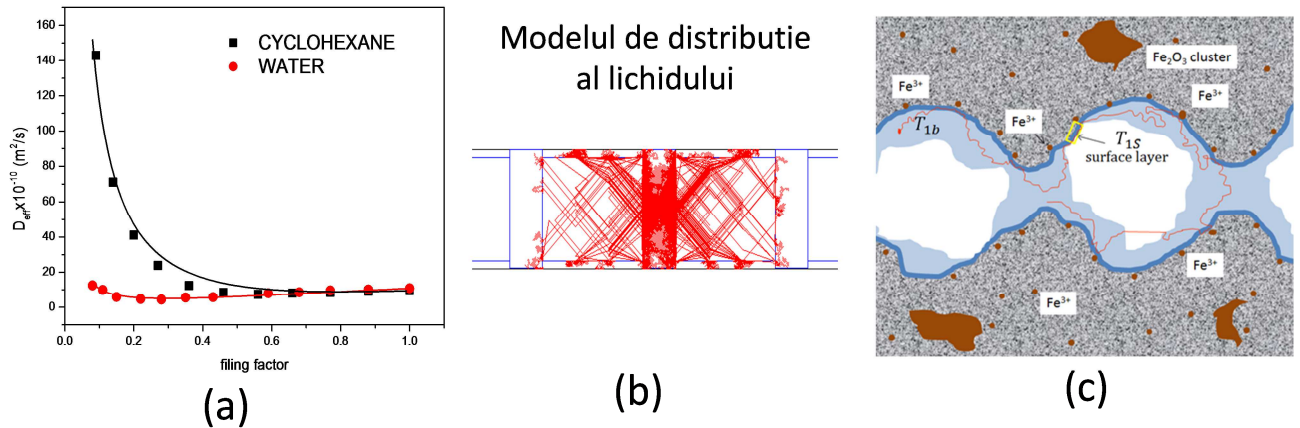


Fig.1. (a) The dependence on the filling of the effective diffusion coefficient of water and cyclohexane molecules confined inside Vitrapor#5 sample. (b) The model of distribution used in the simulations. (c) The distribution model developed in order to explain the relaxation rates under partially saturated conditions.

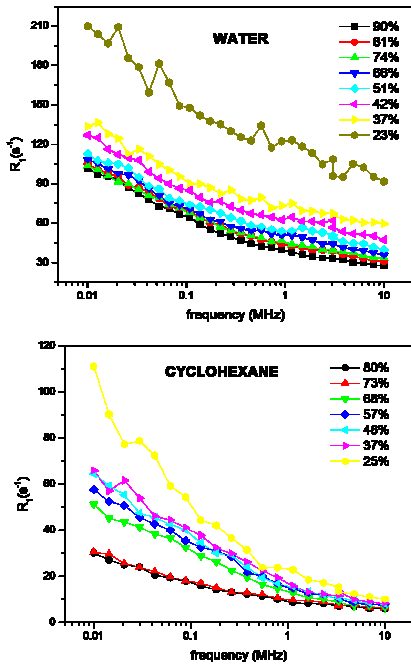
magnetic impurities we have chosen the porous glasses VitraPor # 4 (10  $\mu\text{m}$  pores) and VitraPor # 5 (1  $\mu\text{m}$  pores) purchased from the ROBU Glasfilter-Geraete, Germany. These samples were chosen because they have pore sizes on the same order of magnitude as the porous ceramic (S0-S8) with an increased content of magnetic impurities and the cement samples during the early stage of hydration.

In the case of model samples the effective diffusion coefficient of water and cyclohexane molecules was measured using the PFG (pulse field gradient) technique for a different saturation degree. As can be observed in Fig.1a, there was an increase of the diffusion coefficient in the case of cyclohexane in VitraPor # 5 (1  $\mu\text{m}$  pores) by reducing the filling factor. This increase is attributed to the contribution of the vapor phase to the effective diffusion coefficient and is present only in the case of cyclohexane. On the other hand, if VitraPor # 4 (10  $\mu\text{m}$  pores) is used one can observe no contribution from the vapor phase. That means, in our porous ceramics (approx. 13  $\mu\text{m}$  pores) the contribution of the vapor phase to the effective diffusion coefficient can be neglected.

To establish a correlation between the pore size distribution of the liquid phase and the polar character of the confined molecules we performed Monte - Carlo simulations using two different liquid distributions inside pores: an uniform distribution model and the surface plugs model(Fig.1b). The liquid phase and the vapor phase were simulated by setting the random step in the vapor phase 100 times bigger than in the liquid phase. It is known that in the vapor phase diffusion coefficient is 10000 times larger than in the liquid phase. The simulations were performed on  $10^6$  molecules randomly distributed inside the pores. By comparing the measured diffusion coefficient with the simulated one we could conclude that the vapor phase makes its effects detectable only for sub micrometer pore sizes. This means that the contribution of the vapor phase to the effective diffusion coefficient of molecules confined in our porous ceramics with magnetic impurities can be neglected. This is an important result because it allows us a simpler interpretation of the relaxation data.

## A2. Study of molecule-surface interactions on the translational dynamics of molecules confined in porous media with a controlled amount of magnetic impurities

The second set of samples which were investigated in our project, are the porous ceramics with controlled amount of magnetic impurities (produced in the previous stage of the project and denoted S0-S8). In this case, diffusion measurements with the conventional pulsed field gradient techniques are not reliable because the internal gradients can exceed the external ones by an order of magnitude or even more. Let us note that if the measurements would be performed in a high field instrument at a proton resonance frequency of 500MHz (NMR spectrometers used for chemical analysis) the internal gradients would reach values of the order of 400-500 T/ m for which diffusion measurements are impossible. However, in our project we have shown that information about the diffusion of



**Fig.2.** The relaxation dispersion curves of water and cyclohexane molecules confined in sample S6 at different saturation degrees.

the liquid is uniformly distributed within the pores and there is no region which does not participate in the exchange process (the case of water) we have for  $k=1$ . If there are molecules on the pores surface which do not participate in the exchange (cyclohexane) the empiric coefficient  $k < 1$ . In the above relation  $1/T_1^{surf}$  describes the nuclear relaxation rate of molecules in the surface layer of thickness  $\lambda$  (1-2 molecule diameters). A different behavior of the filling factor was observed on water and cyclohexane molecules confined inside all S0 to S6 samples indicated a different distribution of water (polar) molecules as compared with the cyclohexane (nonpolar) ones.

### A3. Applications of earlier studies to the case of cement-based materials

Cement is one of the most used materials on Earth and that is why there is an increased interest in producing new types of materials based on cement. One of the most important processes that determine the final strength and properties of materials based on cement is the hydration process of cement grains. These granules of cement immediately after mixing with water form a complex porous structure in which one can initially identify two components of water (Figure 3a) which evolve over time: flocculated water and capillary water. The porous structure of cement is saturated with water in the early hydration stages and therefore can be studied by NMR techniques [3-5]. Because the cement paste (cement and water mixed at different ratios: 0.3, 0.4) contains magnetic impurities in the structure, only low field NMR techniques can be implemented to monitor water reservoirs evolution.

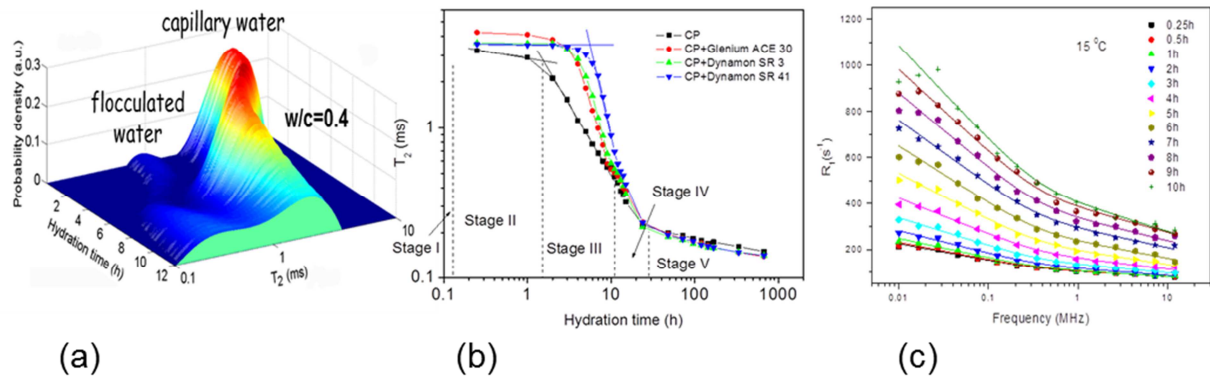
In our investigations the cement paste was prepared using CEM I 52.5R gray cement (Holcim Romania) for a water to cement ratio  $w/c = 0.3$  and cured 28 days. This sample has shown a magnetic susceptibility close to the value measured for the ceramic sample S4 (see stage 2012 of the present project). Also, in the early hours of hydration of the cement paste we evaluated gradients of the order 9 T/m in an external magnetic field of 0.47T (the field of our spectrometer) close to the values determined for the porous ceramics. This makes the study of confined water in cement paste difficult by conventional NMR techniques and instruments and therefore a previous

molecules at the surface of the pores can be extracted using an unconventional approach with the aid of Fast Field Cycling NMR relaxometry [1].

Thus, during the 2013 stage we have extracted from the frequency dependent relaxation measurements the correlation times of the movement of molecules on the surface of porous ceramics S0 and S6 for different filling factors. This allowed us to obtain the effective diffusion coefficients of water and cyclohexane molecules at the pores surface  $D_{\perp}^{water} = 0.7 \cdot 10^{-10} \text{ m}^2 / \text{s}$  and  $D_{\perp}^{cyclo} = 3.7 \cdot 10^{-10} \text{ m}^2 / \text{s}$ . These values are independent of the filling factor (saturation degree of the investigated samples). The different dependence of the relaxation curves on filling factor in the case of water and cyclohexane (Figure 2) can be attributed to different distributions of water as compared with cyclohexane. To explain the experimental results, we considered the model of fluid distribution depicted in Figure 1c. Such a distribution determines the longitudinal relaxation time to satisfy the relationship [2]:

$$\frac{1}{T_1} = \frac{1}{T_1^{bulk}} + \frac{\lambda S}{V} \frac{1}{T_1^{surf}} \frac{1}{f^k}$$

where  $f$  is the filling factor and  $k$  is a coefficient that describes the distribution of the pore fluid. For the case that



**Fig.10.** (a) The macroscopic porous structure immediately obtained after mixing water and cement. (b) The superplasticizers effect on relaxation time evolution of capillary water. (c) The relaxation dispersion curves during the hydration of cement paste in the presence of a superplasticizer.

analysis of well-known samples with well-defined pores and unchanged in time was necessary for calibration of the technique (earlier stages of the project).

Superplasticizers are additives that alter the surface of the cement particles. They are introduced in cement paste in order to create a more homogeneous structure with smaller pores and to prolong the dormant phase (when concrete can be transported) of the hydration process. Superplasticizers are also used to produce ultra-high strength concrete. Therefore in this stage the superplasticizers effect on cement paste hydration was studied using NMR relaxometry [4]. By using CPMG measurements have been identified two water components in the structure of cement paste immediately after mixing. Their evolution could be monitored during the hydration time and the effect of superplasticizers could be observed. By monitoring the position of the capillary peak the retarding of the dormancy stage was clearly demonstrated (Figure 3b) and the presence of the second ettringite formation was demonstrated [4]. Other important information about the investigated cement paste can be extracted from the dispersion curves of the longitudinal relaxation (Figure 3c) recorded as a function of the hydration time. Based on the formalism developed by us and tested on ceramic materials [6] it was possible to extract water diffusion coefficient at the surface of cement grains:  $D_{\perp} = 3.3 \cdot 10^{-11} m^2 / s$ . This value which is smaller than that measured in the case of ceramic samples (S0-S8) indicates greater affinity of water molecules to cement granules as compared to ceramic materials. Our results also indicate that there is a change in the diffusion coefficient of the hydration during the dormancy stage and a dependence of curing temperature.

## Conclusions

During the stage 2013 of our project the effect of molecule-surface interaction on the translational dynamics and distribution of polar and nonpolar molecules under partially saturated conditions was studied. The investigated porous media were porous glasses (VitraPor), porous ceramics (S0-S6) and the cement paste prepared with gray cement. To explain the experimental data new theoretical models have been developed which allowed us extraction of important parameters characterizing the molecular dynamics at the solid-liquid interface such as: the correlation time and the diffusion coefficient at the surface. These parameters could be related to the polar or nonpolar character of the confined molecules. In our research we have also developed new techniques for determining the pore size which could be applied to study the hydration of cement paste, mortar and concrete (materials with natural magnetic impurities). Our findings were disseminated through publication of **one book** (partially containing results of the project) **4 ISI papers** and **2 ISI Proceedings**. The results of the project were also disseminated and in several international conferences one as **invited speaker** (see the list of publications). Some of the results obtained in the stage 2013 of the project are included in the PhD thesis of S. Muncaci and A. Pop which will be completed in 2013 and 2014 respectively.

### **Selected references**

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Project director  
Prof.dr. Ioan Ardelean