Translational diffusion at the surface of porous media with magnetic impurities via Fast Field Cycling NMR relaxometry

I. Ardelean[1], S. Muncaci[1], C. Badea[1], A. Pop[1], C. Mattea[2], S. Stapf[2]

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

[2] Ilmenau University of Technology, Department of Technical Physics II/Polymer Physics, 98684 Ilmenau, Germany

(e-mail: ioan.ardelean@phys.utcluj.ro)

Abstract

Many natural or manufactured porous media intrinsically contain paramagnetic impurities inside their solid matrix which generate internal gradients when introduced in a magnetic field [1]. These internal gradients may lead to significant errors in the measurements of the diffusion coefficient if the classical pulse field gradient techniques are used [2]. The implementation of compensating pulse sequences based on bipolar gradients is also less effective due to the short relaxation times experienced in such samples [2]. In the present contribution exactly the shortening of the longitudinal relaxation time of protons due to their interaction with the paramagnetic centers (Fe^{3+}) located on the surface is exploited to extract information about the translational displacement of molecules on the surface. The porous samples under investigation are both porous ceramics containing increased amount of magnetic impurities and gray cement under different hydration conditions. The diffusion coefficient of water (polar) and cyclohexane (nonpolar) molecules at the interface is extracted using the Fast Field Cycling NMR relaxometry [3]. The technique relies on comparison of the experimental relaxation dispersion curves with a two phase exchange model taking into account the protons relaxation by the interaction with paramagnetic centers located on the surface of porous media [3, 4]. It is observed a stronger reduction of the diffusion coefficient by the interaction with the surface in the case of water (polar) molecules as compared with cyclohexane (nonpolar) ones. The porous ceramics under study were fabricated with a controlled amount of magnetic impurities using the conventional method of preparation from powders which are first dry pressed and then subject to thermal treatment [4]. Six samples (S0-S10) with increasing concentration of Fe_2O_3 were prepared by adding 0, 2, 4, 6, 8 or 10g of Fe_2O_3 to 100g of mixed powder. To extract the pore size distribution of the produced samples they were examined by scanning electron microscopy, the DDIF (Decay due to Diffusion in the Internal Fields) technique [1] and a new proposed technique [5] which relies on the attenuation of the echo train in the well-known CPMG technique due to diffusion in internal gradients. The magnetic characterization of the produced samples was done using a vibrating sample magnetometer indicating a linear dependence of the susceptibility constant with the Fe_2O_3 content. The cement samples under study were prepared using gray cement CEM I 52.5 R and different water to cement ratios. The diffusion coefficient on the surface of cement grains was evaluated at different hydration temperatures (5, 15, 25 and 35 ^oC) revealing a constant value in the investigated temperature range.

References

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[2] I. Ardelean, R. Kimmich, Annu. Rep. NMR Spectr. 49, 43(2003)

[3] J. P. Korb, New J. Phys. 13, 035016 (2011).

[4] S. Muncaci, C. Mattea, S. Stapf, I. Ardelean, Magn. Reson. Chem. 51, 123(2013)

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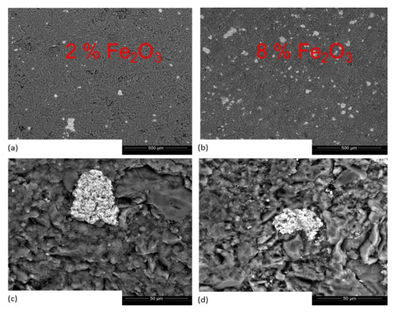
The porous ceramics with magnetic impurities

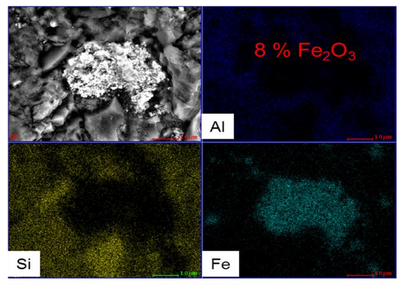
The porous ceramics

Six samples of porous ceramics with increased concentration of Fe_2O_3 were prepared by adding 0, 2, 4, 6, 8 or 10g of Fe_2O_3 to 100g of mixed powder. The samples are denoted S0, S2, S4, S6 S8 and S10 respectively. They reveal a linear increase of the susceptibility constant with the iron oxide content. The white spots on SEM images represent the Fe_2O_3 clusters. One can notice the higher concentration of magnetic impurities (white spots) in the case of sample S8 as compared with sample S2. The investigations done with DDIF technique revealed pore sizes in the range of 13µm.

The SEM image of sample S2 (a,c) and S8 (b,d)

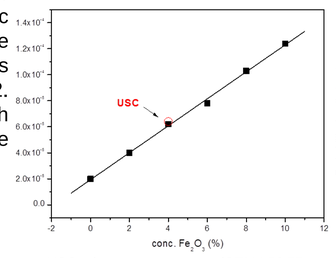


The distribution of elements



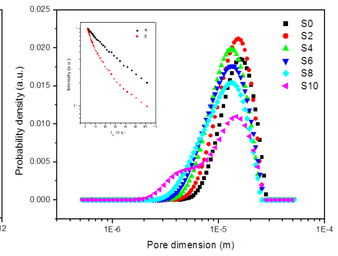
Images recorded with a FEI Quanta Inspect SEM

The magnetic susceptibility

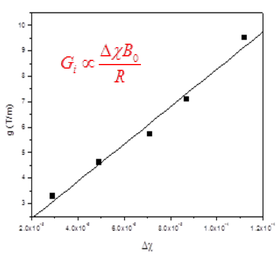


USC=ultra strong concrete (CEM I 52.5R, w/c=0.25, 1% superplasticizer)

The pore size using DDIF



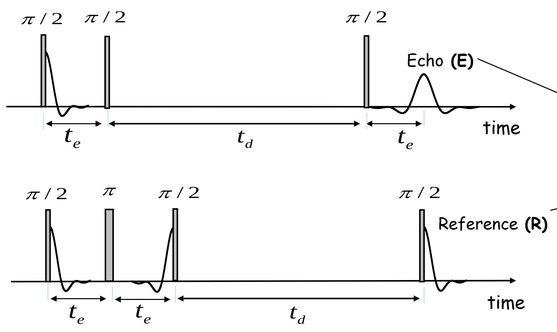
The internal gradient



The linear dependence indicates constant radius

The NMR techniques

•The DDIF technique



The stimulated echo (E) intensity in a homogeneous sample

$$E(t_d) = \underbrace{a_0 e^{-t_d/\tau_0} e^{-t_d/T_{1b}}}_{relaxation\ mode} + \underbrace{\sum_{n=1}^{\infty} a_n e^{-t_d/\tau_n} e^{-t_d/T_{1b}}}_{diffusion\ modes}$$

$\tau_0 = \frac{d}{\rho}$ -for the slit pore model; T_{1b} = the bulk relaxtion time;

$\tau_n \approx \frac{d^2}{D\pi^2 n^2}$, $n = 1,2,3,\ldots$

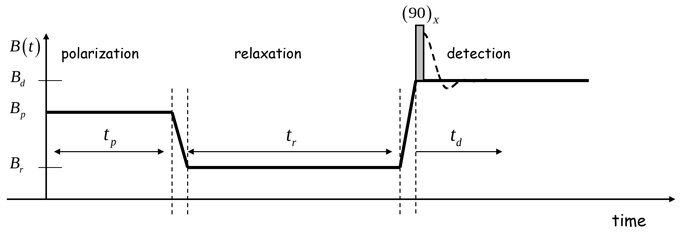
d = the pore size; ρ = the relaxivity; D = the diffusion coefficient;

$\gamma \Delta B_z^i t_e << 1$ -the limit of weak phase encoding

$$\Rightarrow \boxed{E(t_d) \approx \underbrace{a_0 e^{-t_d/\tau_0} e^{-t_d/T_{1b}}}_{relaxation\ mode} + \underbrace{a_1 e^{-\frac{t_d}{\tau_1}} e^{-t_d/T_{1b}}}_{diffusion\ mode}} \Rightarrow$$

The pore size distribution can be obtained from the DDIF spectra = Inverse Laplace transform of $E(t_d)$ $\Rightarrow \boxed{d = \pi\sqrt{D\tau_1}}$

• The Fast Field Cycling (FFC) technique



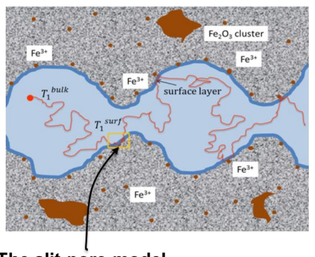
Signal attenuation versus relaxation interval

$A(t) = C_0 + A_0 e^{-t/T_1}$ - low relaxation fields

$A(t) = C_0 - A_0 e^{-t/T_1}$ - high relaxation fields

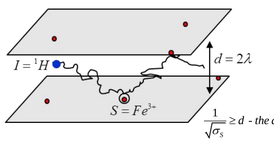
The relaxation model

The two-phase fast exchange model



The slit pore model

[J.P. Korb, M.W. Hodges, R.G. Bryant, Phys.Rev.E56, 1934, (1997)]



$$\frac{1}{T_1} = \frac{1}{T_{1b}} + \frac{\lambda S}{V}\frac{1}{T_1^{surf}} = \frac{1}{T_{1b}} + \frac{S}{V}\rho_{1S}$$

$\rho_{1S} = \lambda / T_1^{surf}$ - surface relaxivity

$$\frac{1}{T_1^{surf}} = \frac{\pi}{15}\sigma_S(\gamma_I\gamma_S\hbar)^2 S(S+1)\frac{\tau_\perp}{(2\lambda)^2\delta'^2}\left\{10\ln\left(\frac{2\lambda}{\delta'}+1\right) - 30.8 + \frac{1}{4}\left[7\ln\left(1+\omega_S^{-2}\tau_\perp^{-2}\right) + 3\ln\left(1+\omega_I^{-2}\tau_\perp^{-2}\right)\right]\right\}.$$

The effective relaxation rate

$$\boxed{\frac{1}{T_1} = P_1 + P_2 \cdot \left[7\ln\left(1+\omega_S^{-2}\tau_\perp^{-2}\right) + 3\ln\left(1+\omega_I^{-2}\tau_\perp^{-2}\right)\right]}$$

$$P_1 = \frac{1}{T_1^{bulk}} + \frac{\pi}{60}\sigma_S\frac{S}{V}(\gamma_I\gamma_S\hbar)^2 s(s+1)\frac{\tau_\perp}{\lambda\delta'^2}\left[10\ln\left(\frac{2\lambda}{\delta'}+1\right) - 30.8\right],$$

$$P_2 = \frac{\pi}{240}\sigma_S\frac{S}{V}(\gamma_I\gamma_S\hbar)^2 s(s+1)\frac{\tau_\perp}{\lambda\delta'^2}$$

σ_S - surface density of paramagnetic centers

$\tau_\perp = \delta^2/4D_\perp$ - transverse diffusional correlation time

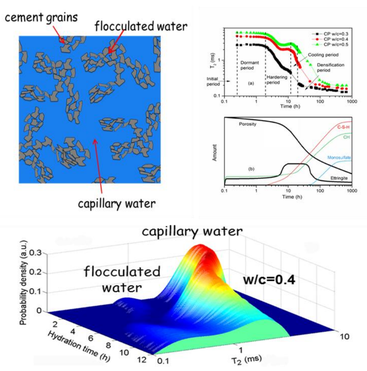
$D_\perp$ - transverse diffusion coefficient; δ - the molecules size;

δ' - the distance of minimum approach between I and S spins;

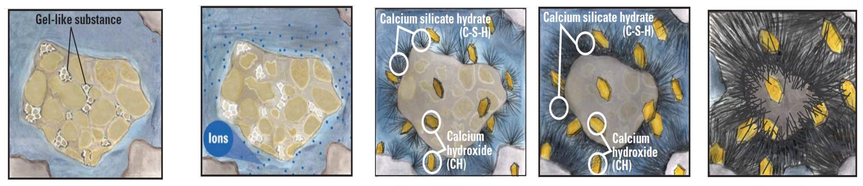
$\omega_S = 658.21\,\omega_I$

The cement paste hydration

T_2 - evolution during hydration



The hydration products



Stage 1: Mixing (<15min)
The ettringite formation takes place creating an isolating coating on cement grains which limits water access to aluminate (C_3A). Such a layer creates a gap between C_4AF and surrounding water

Stage 2: Dormancy (15min<t<4h)
The silicates (C_3S and C_2S) slowly dissolve releasing calcium ions (Ca^{2+}) and hydroxyl ions (OH^-).

Stage 3: Hardening (4h>t<8h)
The solution becomes saturated with calcium and hydroxyl ions causing the formation of new compounds (C-S-H –fiber like particles and CH-crystals)

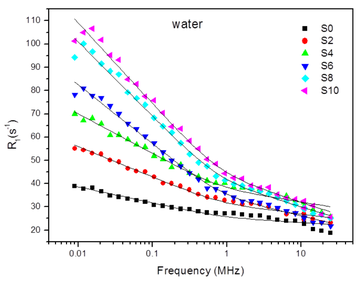
Stage 4: Cooling (8h>t<1day)
C-S-H and CH limits water access to grains and the process slows down

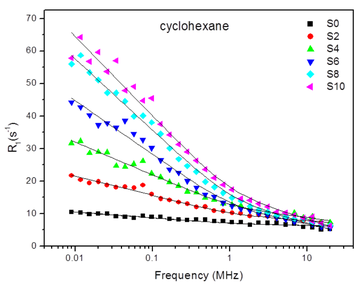
Stage 5: Densification (t>1day)
Belite (C2S) starts to react also producing C-S-H and CH

(P. C. Taylor, et al., Integrated Materials and Construction Practices for Concrete Pavement, Iowa State University, October, 2007)

The relaxation dispersion curves and the surface diffusion coefficient

FFC on porous ceramics





Observations:

- In the fitting approach the transverse diffusional correlation times were kept constant;
- The effective internal gradients between 2 T/m and 10 T/m at 20 MHz

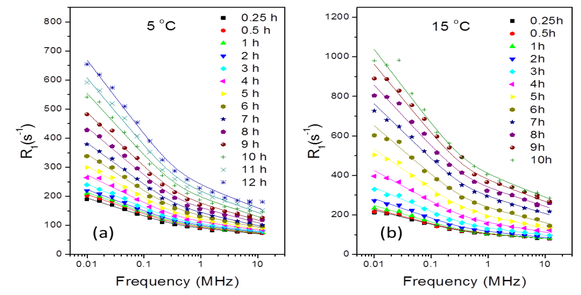
$\tau_\perp^{water} = 0.32\,ns$; $\tau_\perp^{cyclo} = 0.24\,ns$

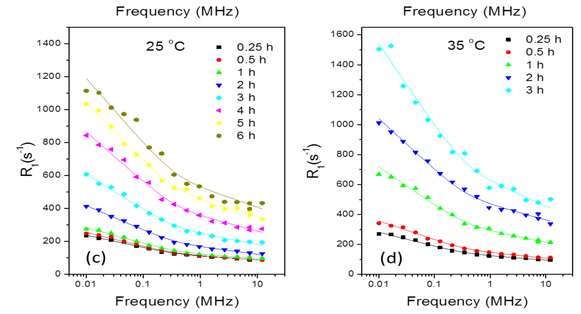
$\Rightarrow$

$\boxed{D_\perp^{water} = 0.7\cdot10^{-10}\ m^2/s;\quad D_\perp^{cyclo} = 3.7\cdot10^{-10}\ m^2/s}$

The transverse diffusion coefficients on the surface from FFC data

FFC during the cement paste hydration





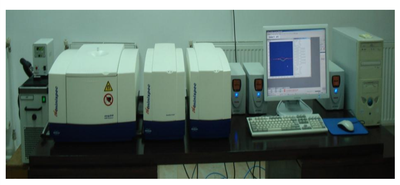
Observations:

- One unique parameter $\tau_\perp$= 0.68ns was used for all the curves = NO temperature dependence in the investigated range
- The effective internal gradients estimated between 14-18T/m at 20MHz

$\Rightarrow$

$\boxed{D_\perp = 3.3\cdot10^{-11} m^2/s}$

The NMR instruments



Bruker MINISPEC MQ20

-^{1}H frequency: 20MHz

-max. gradient strength: 2T/m

-temp. range: -10+100 ^oC

STELAR-Fast Field Cycling Relaxometer

-^{1}H frequency: 40- 0,01 MHz

-temp. range: -140+140^oC

Conclusions

- The relaxation dispersion curves can be fitted well with a two phase exchange model taking into account relaxation by interaction with paramagnetic centers on the surface;
- A similar behavior in relaxation dispersion curves of water (polar) and cyclohexane (nonpolar) filled samples was observed;
- Fe_2O_3 clusters inside the porous matrix do not contribute to the relaxation in the frequency range of our experiments;
- The presence of paramagnetic centers does not influence the transverse diffusional correlation times;
- An unique surface diffusion coefficient could be extracted in the case of cement samples independent of temperature

Acknowledgements

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