Monitoring the Pore Size Distribution of Ultra Strong Concrete Samples During the Early Stages of Hydration via the Internal Gradients

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Abstract

One of the most important parameters characterizing the concrete samples is their pore size distribution. This feature can be easily linked with other properties of the porous material such as mechanical strength or molecular transport (flow and diffusion). Most of the techniques involving pore size distribution measurements of porous media are destructive or induce sample changes and must be used with caution. That is why developing of nondestructive techniques for pore size characterization is an important issue.

One recent approach in determining the pore size distribution of porous media via NMR is the so called DDIF technique (DDIF = decay due to diffusion in the internal fields) [1]. The technique relies on internal fields occurring in many natural or fabricated porous media as a result of susceptibility contrast between the porous matrix and the confined liquid or as an effect of magnetic impurities contained inside these materials. Another NMR technique exploits the diffusion dependence of the CPMG echo train in the presence of a static gradient [2]. Both techniques can be applied without special preparation or previous calibration of the sample.

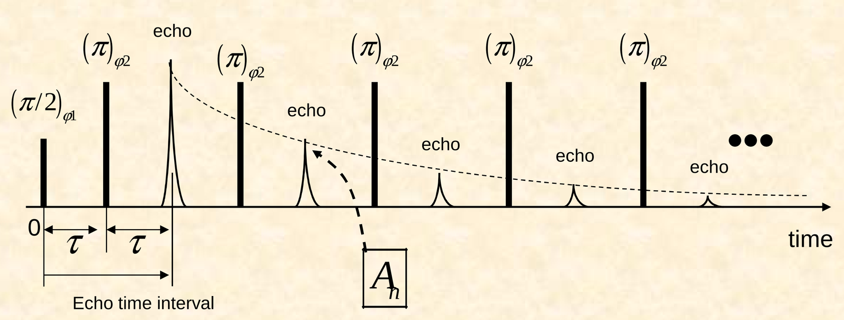
In our work we will explore the possibility of implementing the two techniques to monitor the size evolution of capillary pores arising in fabricated high-strength concrete and cement paste during the early stages of the hydration process (0-6h) [3]. In our CPMG approach we will consider the recent results in Ref. [4] where the echo attenuation in the presence of inhomogeneous gradients is discussed. The ultra strong concrete samples (P>200N/mm^2) were prepared using a mixture of cement (CEM I 52.5 R), quartz sand, silica fume (Elkem Microsillica), water and super plasticizer (Glenium ACE 30 - BASF). The water-to-cement ratio in all the samples was kept constant (W/C=0.4). All experiments were performed in low fields using a Bruker MINISPEC MQ20 time domain analyzer. The pore size distribution was extracted from the two techniques using a regularized numerical Laplace inversion algorithm (CONTIN) [5] and could be related to different experimental parameters. Before applying the two techniques (CPMG and DDIF) for monitoring the pore size evolution of cement and concrete samples they were first validated on porous ceramics of known pore sizes. The two NMR techniques could in principle be applied for nondestructive in situ characterization of the curing, setting and hardening process of concrete structures. They can also be applied in soil science or other porous materials with magnetic impurities.

References

1. Y. Q. Song, Concept. Magn. Reson. 18A (2003), 97-110.
2. L. J. Zielinski, M.D. Hurlimann, J. Magn. Reson 172 (2005), 161-167.
3. P.F. Faure, S. Rodts, Magn. Reson. Imag. 26 (2008) 1183-1196.
4. L. J. Zielinski, J. Chem. Phys. 121 (2004), 352-361.
5. S. W. Provencher, Comp. Phys. Comm. 27 (1982), 229-242.

The NMR techniques

•The CPMG technique in the presence of internal gradients



The echo train attenuation in heterogeneous samples

$$A_n = A_0 \int_0^{\infty} P(T_2^*) e^{-2n\tau \frac{1}{T_2^*}} dT_2^*$$

$P(T_2^*)$ = distribution function of the transverse relaxation time

The effective relaxation rate

$$\frac{1}{T_2^*} \approx \frac{1}{T_2} + \frac{1}{3} D_0 \gamma^2 G_{eff}^2 \tau^2 \left(1 - 0.57 \frac{g_v^2}{G_{eff}^2} \frac{S}{V} \sqrt{D_0 \tau}\right) \Rightarrow$$

$1/T_2$ = relaxation rate

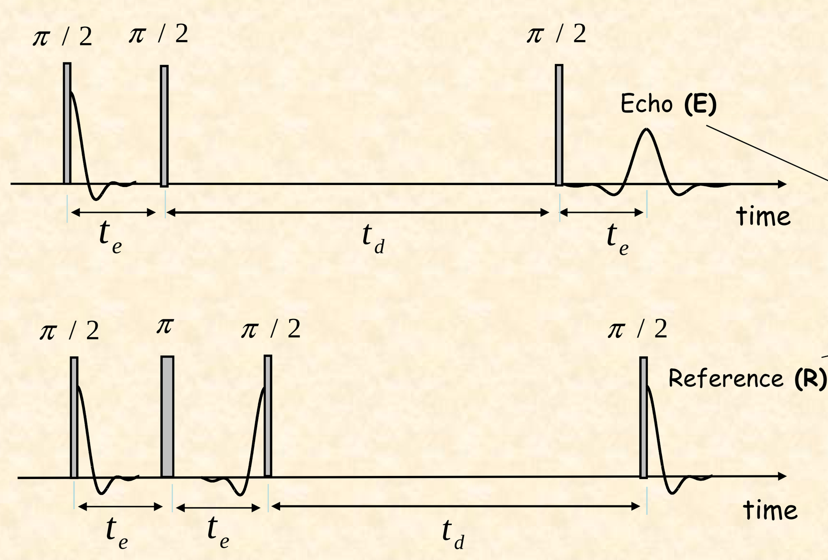
D_0 = bulk diffusion coefficient

S/V = surface to volume ratio

$$\begin{cases} \text{no gradient} \Rightarrow \frac{1}{T_2^*} \approx \frac{1}{T_2} \\ \text{constant gradient} \Rightarrow \frac{g_v^2}{G_{eff}^2} = 1 \Rightarrow \frac{1}{T_2^*} \approx \frac{1}{T_2} + \frac{1}{3} D_0 \gamma^2 G_{eff}^2 \tau^2 \left(1 - 0.57 \frac{S}{V} \sqrt{D_0 \tau}\right) \\ \text{parabolic gradient} \Rightarrow \frac{g_v^2}{G_{eff}^2} = 1.5 \Rightarrow \frac{1}{T_2^*} \approx \frac{1}{T_2} + \frac{1}{3} D_0 \gamma^2 G_{eff}^2 \tau^2 \left(1 - 0.57 \cdot 1.5 \cdot \frac{S}{V} \sqrt{D_0 \tau}\right) \\ \text{internal gradient} \Rightarrow \frac{g_v^2}{G_{eff}^2} = ? \Rightarrow \frac{1}{T_2^*} \approx \frac{1}{T_2} + \frac{1}{3} D_0 \gamma^2 G_{eff}^2 \tau^2 \left(1 - 0.57 \cdot ? \cdot \frac{S}{V} \sqrt{D_0 \tau}\right) \end{cases}$$

$\frac{g_v^2}{G_{eff}^2} \cong 3$ - from investigations on porous ceramics

•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

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

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

The NMR instrument

Bruker MINISPEC MQ20

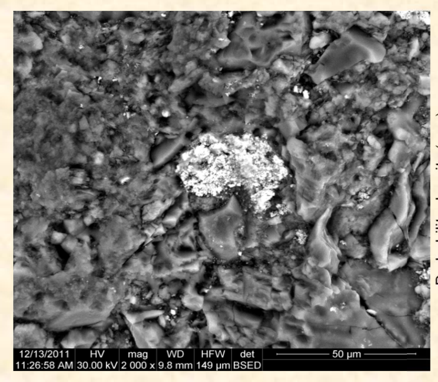
- ^{1}H frequency 20MHz
- max. gradient strength 2T/m
- temp. range: -10+100 ^{o}C

The pore size distribution of porous ceramics with magnetic impurities

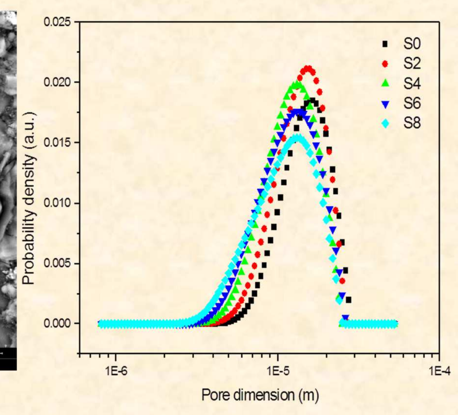
The test samples

Porous ceramics were fabricated as standard samples in order to calibrate the two techniques. They were manufactured from powders which are first dry pressed and then subject to thermal treatment. Five samples with increased concentration of Fe_2O_3 were prepared by adding 0, 2, 4, 6, or 8g of Fe_2O_3 to 100g of mixed powder. The samples are denoted S0, S2, S4, S6 and S8 respectively. They reveal a linear increase of the susceptibility constant with the iron oxide content. The samples were examined by scanning electron microscopy. The results were compared with those extracted from DDIF and CPMG technique in the presence of diffusion effects.

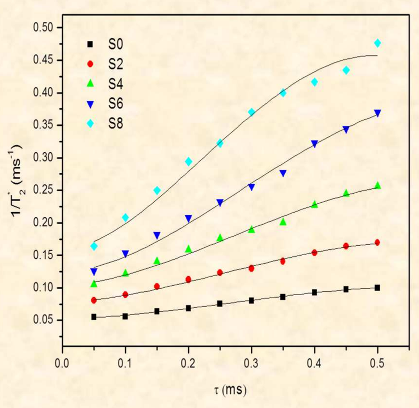
The SEM image of sample S4



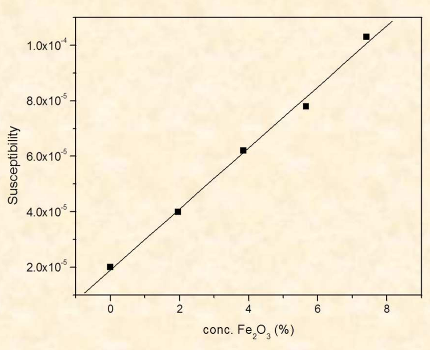
The DDIF results



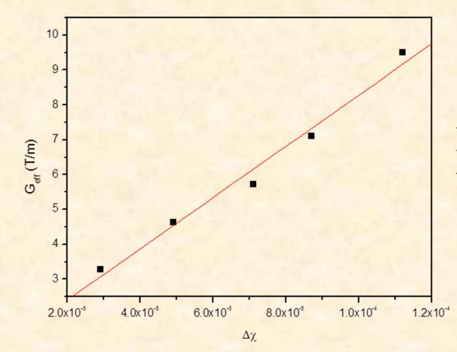
The CPMG results



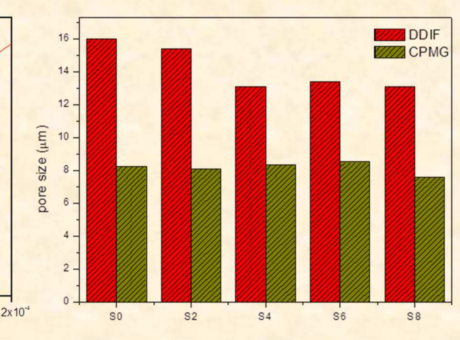
The magnetic susceptibility



The effective gradient

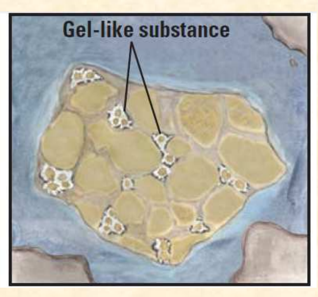


The pore size

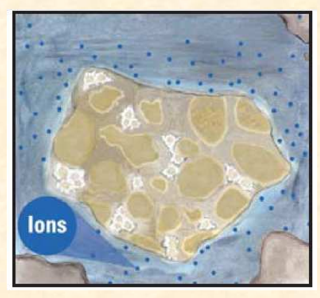


The pore size evolution of cement paste and concrete sample

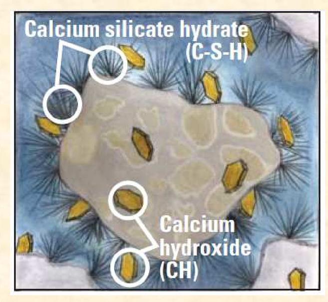
The hydration stages of a cement paste



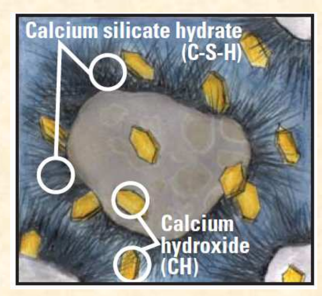
Stage 1: Mixing (<15min)



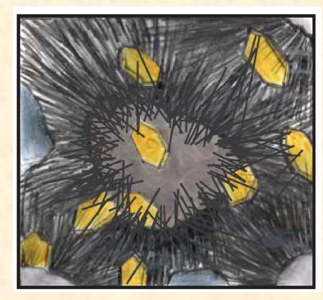
Stage 2: Dormancy (15min<t<4h)



Stage 3: Hardening (4h>t<8h)



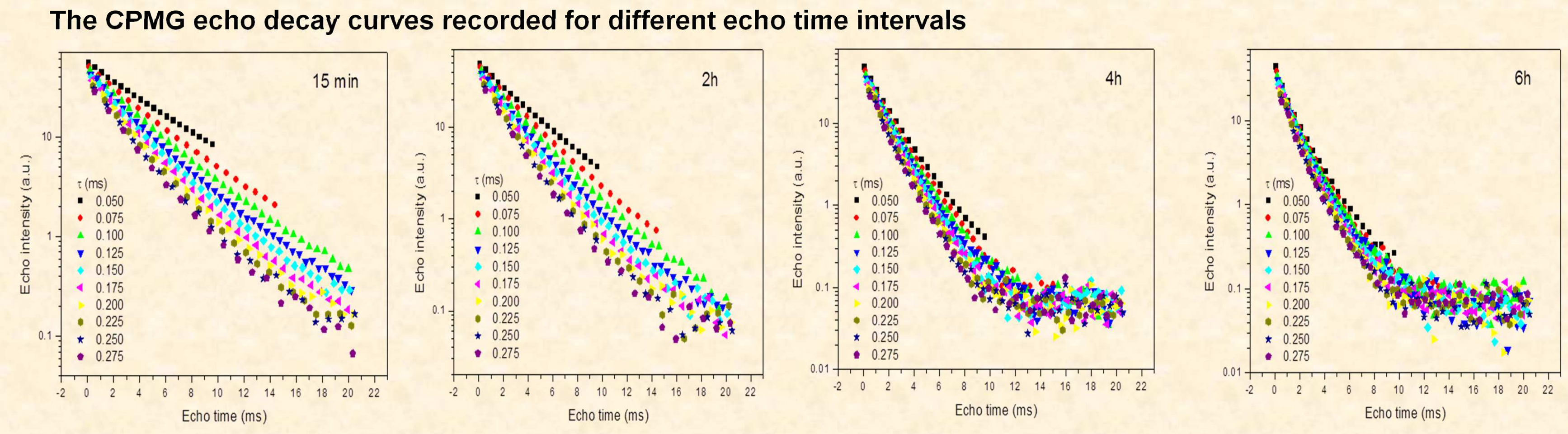
Stage 4: Cooling (8h>t<1day)



Stage 5: Densification (t>1day)

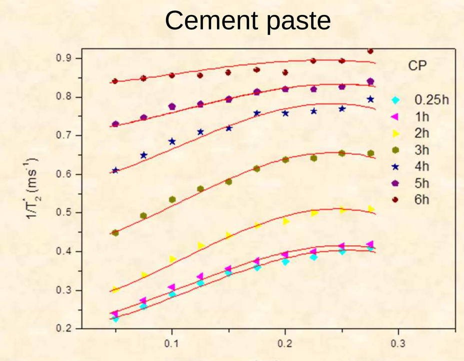
(Captured from: "Integrated Materials and Construction Practices for Concrete Pavement", Iowa State University, October, 2007 http://www.cptechcenter.org/publications/imcp/)

The CPMG echo decay curves recorded for different echo time intervals

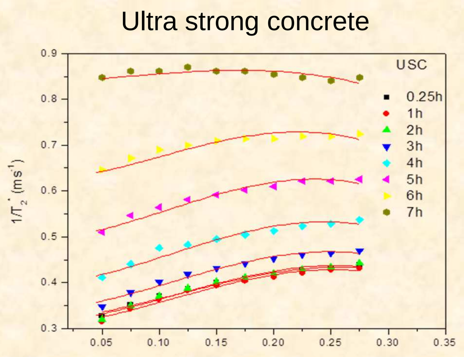


The effective relaxation rate of the CPMG decay curves as a function of echo time interval for different hydration times

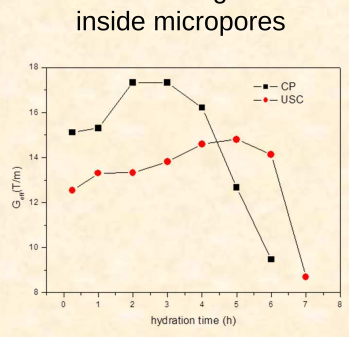
Cement paste



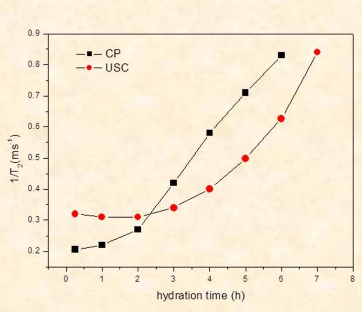
Ultra strong concrete



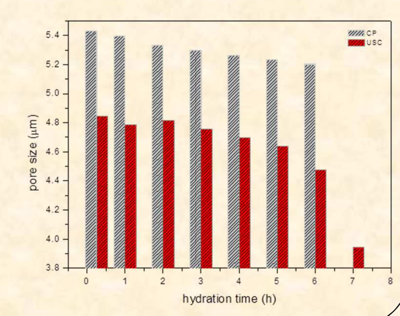
The effective gradient inside micropores



The relaxation rate

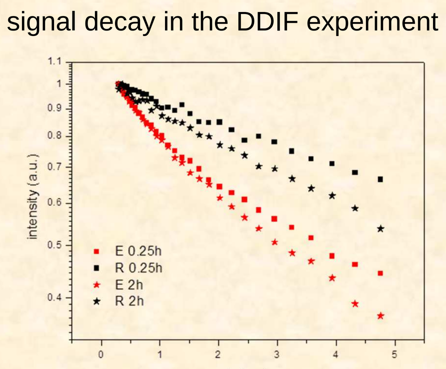


The pore size extracted from CPMG data

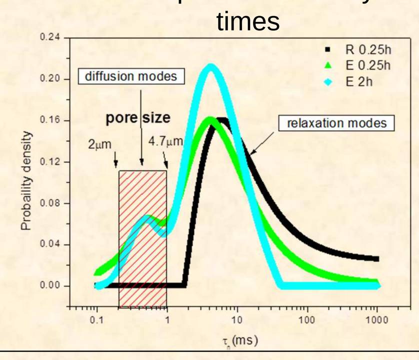


The pore size distribution of concrete sample via DDIF

The signal decay in the DDIF experiment



The DDIF spectra for two hydration times



Conclusions

- Both CPMG and DDIF can be used as instruments for monitoring the pore size evolution of concrete samples during the early stage hydration
- The CPMG technique allows extracting of the effective gradient inside porous samples
- The two techniques do not require previous calibrations on known porous samples
- The CPMG technique is faster compared to DDIF and can be implemented for longer hydration times
- The pore sizes extracted via the two techniques are similar but not equal.

Acknowledgements

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