Comparison between NMR Non Destructive Method and Common Invasive Methods used for Concrete Structuration Evolution

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ABSTRACT

A better understanding of the cement hydration evolution and of the development of cementitious materials microstructure at early age is very important for improving concrete durability. The microstructure, which depends on various factors (water-cement ratio, curing conditions …), is characterized by water content and pore-size distribution.
The originality of this study is to compare relaxation and MRI along with common destructive methods (capacitive method, mass loss by heating or freeze drying …) to characterize cement porosity and free water content. With this approach, common techniques are used to identify phenomena observed by NMR and also provide validation of NMR as a tool to investigate cement hydration. The NMR technique is unique and allows to follow a same sample through time at a very early age and in a non-destructive way.
Results obtained by these different techniques show a good correlation. Furthermore, this novel approach shows that NMR gives complementary information, and thus provides a complete study of cement hydration.

Keywords: hydration, cement paste, T_1 relaxation, Magnetic Resonance Imaging (MRI), microstructure

1. INTRODUCTION

Cementitious materials are mainly characterized by their free and bound water contents and by their porous network. The free water is defined by the original blending water which has not reacted with the cement particles. Two kinds of porosity are conventionally defined: capillary porosity and gel pores. The capillary porosity (pore radii between 10 and 1000 nm) is formed from residual spaces occupied by the original blending water and the gel porosity (pores <10 nm) is contained within the calcium silicate hydrates. During hydration, porosity and free water content evolve with time.
The microstructure characterization of cement-based materials is important in order to evaluate the durability of concrete structure. For example, durability of cementitious materials is primarily related to their

porosity (penetration of chloride ions or carbon dioxide) and to the presence of water within porosity (deleterious internal chemical reaction or electrochemical corrosion of reinforcements).
The need for measuring these durability indicators led the experimenters to develop and to use several techniques (mercury intrusion porosimetry, thermoporometry, and gas adsorption to characterize pore size distribution and mass loss by heating or gammadensimetry to determine water content).
A new way to investigate concrete microstructure opens with Magnetic Resonance Imaging (MRI) and the associated techniques (relaxation, spectrocopy). These techniques are not destructive for the material and thus have the advantage of following the same sample during process such as cement hydration or moisture exchanges.
MRI techniques allow a better comprehension of mechanisms of hydration process but still require research to improve some of the experimental conditions (especially definition of MRI sequences).
This paper presents a study on cement hydration evolution by using MRI supplemented by other microstructural determination methods. The final objective of this study aims both:
- to improve MRI technique
- to determinate the limits of common techniques,

2. MATERIALS AND METHODS

2.1. Samples

An ordinary Portland cement (CEM I 52,5 B) with low iron amount was used to limit magnetic perturbations during MRI experiments. Its chemical analysis is given in Table 1. Cement paste specimens were cast with a water/cement ratio (W/C) of 0.40 in cylindrical moulds (50 mm diameter and 100 mm long). The samples were stored at a temperature of 20°C in closed moulds to avoid any moisture exchange for MRI tests. After being cured for 24 h, the hardened paste cylinders were removed from the plastics moulds and stored in lime-saturated water for common techniques.

Oxides	% by mass
SiO_2	21.88
Al_2O_3	4.09
TiO_2	0.18
Fe_2O	0.29
CaO	66.40
MgO	0.57
Na_2O	0.03
K_2O	0.10
MnO	0.00
SO_3	2.72
insoluble	0.76
loss on ignition	2.80
TOTAL	99.82

Table 1. Chemical analysis of the cement

The experiments are carried out on cement pastes after 1, 7, 14, 21, 28, and 90 days of hydration. For the MRI experiments, samples with a diameter 4.5 mm and 100 mm length are used.

2.2. MRI/NMR

Nuclear Magnetic Resonance is a non destructive method to study cement hydration. Following the water content in the material, NMR allows to understand the hydration phenomena at very early age with a same sample. This approach associates NMR with common methods to analyze results. Two different techniques were used: spectroscopy by NMR with T_1 relaxation and MRI with Single Point Imaging (SPI) sequence for the water content. All tests were realized with a vertical imaging spectrometer DBX 34/80 Bruker operating at 0.5 T. A proton birdcage coil is used which has 20 cm inner diameter.

T_1 relaxation

Nuclear Magnetic Resonance is employed to study cement chemistry and cement pore structure. The NMR relaxation times are sensitive to pore structure and are well known to decrease as pore size is reduced [1]. Longitudinal proton magnetization decays is obtained through inversion recovery method. Laplace inversion of relaxation measurements is used in order to get relaxation spectra of the sample in T_1 space [2,3,4].
Indeed, the signal obtained with inversion recovery method is given by:

$$S = M_0\left(1 - 2\exp\left(\frac{t_i}{T_1}\right)\right) \quad \text{(eq. 1)}$$

The solve of the equation is easy with a mono-exponential expression. But, with several values of T_1, the Laplace inversion method is the best solution [5].

SPI profiles [6,9,10,20]

The relaxation times of water in concrete are several orders of magnitude shorter than relaxation times typically observed in human tissue. The SPI method is ideal for water imaging in concrete samples. This technique was proposed by Emid and Creython [11] and thereafter was developed by Balcom and al. [7,8,12,13].
In this study, cylindrical samples were studied for which the experimental problem is reduced to one dimension.
The SPI signal intensity is proportional to $\rho(z)$ (eq. 2) which is the local water content along z direction:

$$S(z) \propto \mathrm{r}(z)\exp\left(-\frac{t_p}{T_2^*}\right) \quad \text{(eq. 2)}$$

where t_p is the encoding time and T_2^* is the effective spin-spin relaxation time.

2.3. Other Methods

Water content and drying procedure:

Different methods present interest to evaluate the variation of density or the free water in various sample. For example, gammadensimetry determination is commonly used to control the density of civil engineering materials. It is based on the gamma ray absorption by matter, and allows to measure the variation of water content (free water) after drying [14]. This method is interesting in case of water exchanges with atmosphere or in case of bleeding.

In absence of bleeding or exchanges with atmosphere, more simple methods are based on water content determination by measuring the loss of mass after sample drying. This method needs water removal from the specimen. Several techniques can be applied to reach full desaturation: oven-drying at temperatures usually between 50°C and 105°C, vacuum-drying, freeze-drying, solvent replacement drying [15].

In this study, water content is determined by several techniques: vacuum-drying, freeze-drying and oven-drying at 80 and 105°C. At the end of each curing period, 20 mm thickness slices were cut from a cylinder and dried until constant mass loss was reached.

Porosity:

Different methods can be used for the determination of pore size distribution: in particular Mercury Intrusion Porosity (MIP) for capillary porosity and capacitive method for gel porosity. Table 2 shows the different treatments and characteristics of sample corresponding to the different used techniques.

	NMR	MIP	Capacitive method
sample	10x4.5 cm²	1 cm^3	2x4.5 cm²
drying	No drying	Vacuum drying	Vacuum- and freeze-drying
Time of experiment	30 mn	½ day	24 h saturated+ 8 h dried

Table 2. Characteristics of techniques used for porosity determination

MIP is a method that consists of injecting mercury into desaturated porous material [15]. The pore size distribution is obtained by the Washburn-Laplace equation for which the size of the intruded pore accesses, assimilated to cylindrical capillaries, is inversely proportional to the applied pressure. The measurements were made with a MIP apparatus for which Pmax = 400 MPa so that pore radii between 1.8 nm and 60 μm are reachable. In this study, at the end of each curing period, 10 mm thickness slices were cut from a cylinder and dried by vacuum-drying method until constant mass loss was reached. For MIP tests, the specimens were sampled in the slice's center and about 1 cm^3 of cement paste was tested.

The capacitive method (freezing-thawing method), developed in author's laboratory [16,17], consists in measuring the electric capacitance of a sample in the radio-frequency range. The sample is inserted between two planes and circular stainless steel electrodes. These are connected in parallel to a 30~MHz-50~MHz oscillator circuit, which forms an oscillating circuit. The experimental apparatus delivers a reduced resonant frequency that depends on the sample capacitance. A plane capacitance is proportionate to its real dielectric constant. In cementitious material, the dielectric constant of cement paste samples is measured as a function of water saturation degree and temperature. In this study, at the end of each curing period, 20 mm thickness slices 20 mm were cut from a cylinder and are then wrapped by a Parafilm foil and tested. Tests consisted in 24 hours freezing-thawing cycles from 0°C to -40°C. The cooling (and heating) rate was 4°C/h. Samples were dried (until constant mass loss) during several days and tested a second time (8 hours cycles) in order to evaluate the dielectric curve. The pore size distribution was given by the freezing or the thawing test by using the improved Gibbs-Thomson equation.

All these methods are destructive because they require to dry the material to have access to porous network.

3. RESULTS AND DISCUSSION

3.1. Porosity

The used methods allow to characterize the evolution of the cement paste porosity during hydration process at different ages.

MIP results from [18] show that pore size distribution curves for paste at 1 day of curing time exhibits a defined peak around 175 nm. At 7 days of curing, the peak is observed around 15 nm. After 14 days, the porosity does not evolve and stays at 15 nm. The experimental results confirm these values.

The accuracy of MIP is limited by several assumptions and different effects may also be a source of error and may damage the microstructure:

- the drying procedure
- the high pressure of mercury
- the "ink bottle" effect [19] (a large volume has intruded into narrow pore)

Capacitive method gives different peaks for 1 day and 7 days of curing (fig.1 for the freezing tests). Two peaks are obtained at 2 nm (gel pore) and 100 nm (capillary pore) after 1 day, and three peaks are determined at 2.5, 8 and 150 nm after 7 days (the precision of this last pore radius is not significant so only the first two peaks are considered at 7 days). After 14 days, only one peak is observed at approximately 2 nm. It is not possible to determine an evolution after 14 days.

The principal limitations of capacitive method are:

- drying procedure for the second test

- the precision of temperature, measurements near 0°C (the results are only valid for small pores i.e. the gel porosity)

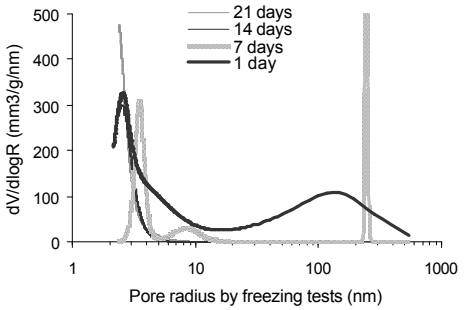


Fig.1. Capacitive method: freezing tests of cement paste at different ages

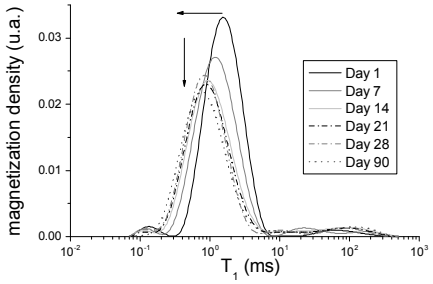


Fig.2. Magnetization density vs. T_1 after Laplace inversion of the curve, at different ages for a same saturated sample

Fig.2 shows T_1 evolution after setting phase. NMR relaxation gives global information of free water in the cement paste porosity. As it can be observed on the graphs, T_1 curves evolve with time. Indeed, surface area of peak, decreases, so free water amount contained in pore decreases with hydration. In the same way, the peak move towards the left i.e. towards the small pores. The principal peak may correspond to free water which decreases with time. After 14 days the evolution is less important.
The comparison of the common methods and MRI is not immediate; for example after 7 days, the three peaks defined by T_1, at 0.128, 1.30 and 26.5 ms, are not related easily to pore radius determined by capacitive method or MIP. Indeed, the peak area of different methods is not comparable because the explored domains are different. In spite of the fact that it is difficult to make a direct conversion of pore size distribution, the range of pore obtained confirms the estimations (fig. 3).

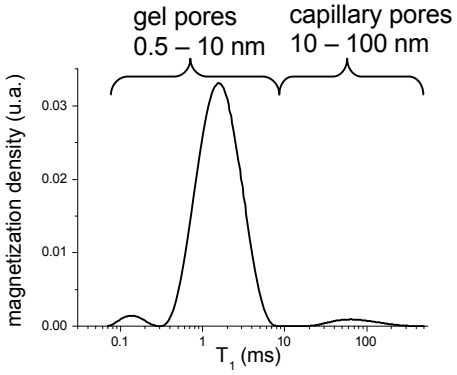


Fig.3. Estimation of range pores for NMR relaxation

Nevertheless, the advantages of NMR are multiple:

- the experiments lasts only 30 mn
- the sample does not suffer drying, the microstructure is not affected
- NMR has a better sensibility, a bigger range of pore are found
- pore size distribution can be followed during hydration on a same sample.

3.2. Water content

The use of SPI 1D (profiles) or 3D (images) allows to follow free water content evolution. Three cases are studied:

- case I: study of a sealed sample (hydration without external exchanges),
- case II: study of a saturated sample (specimen stored in lime-saturated water after being cured for 24h),
- case III: study of a dried sample (specimen dried by vacuum-drying technique after being cured for 24h).

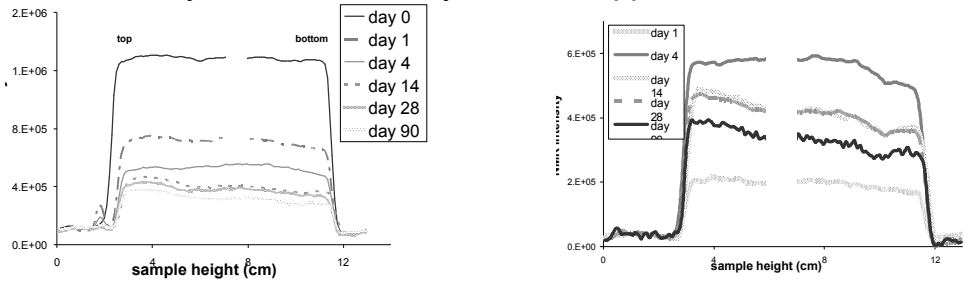
Profiles:

The profiles give information on free water content evolution in the hardened cement paste. Fig. 4 shows the profiles' evolution for the cases I and II. It can be seen on the graph A the decrease of NMR intensity with time, for the sealed sample (case I), due to the decrease of free water which is consumed by hydration.

For the saturated sample (case II) an increase of the signal is noticed after 1 day of immersion because of sample resaturation. This increase of the signal may be attributed to water which fills empty porosity created by self-desiccation effects. It is possible to determine the free water content percentage with the ratio $\rho(t)/\rho(0)$.

The profiles allow to emphasize:

- free water content evolution in all the sample types,
- cement hydration kinetics by water disappearance.



A **B**

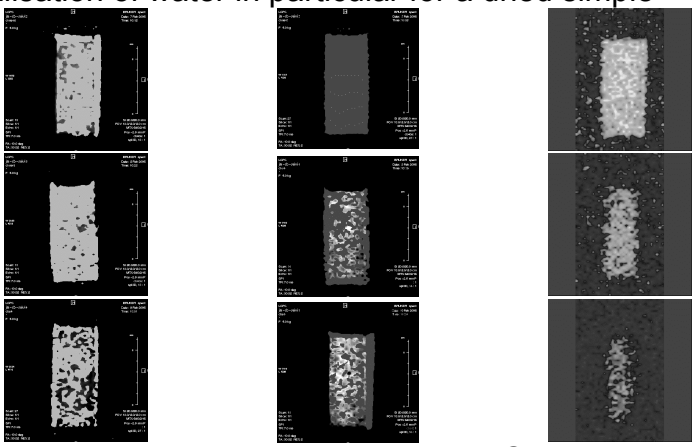
Fig.4. Profiles SPI 1D, **A**- sealed sample (case I) and **B**- saturated sample (case II).

Images:

Images give qualitative information on water localisation.

What is interesting to remark is the decrease of water content for a sealed sample (case I, fig.5-A) and the increase of signal for a saturated sample (case II, fig.5-B). For a dried sample (case III), the drying is first on the edges of the sample, and fig.5 shows that after two days of drying, water stay inside the sample,: the sample is not totally dried.
SPI 3D allows to follow:

- different phenomena: hydration, saturation, or drying
- the localisation of water in particular for a dried simple



A **B** **C**

Fig.5. Images SPI 3D at 1, 2, 3 days after setting **A**- in clearly grey, the decrease of the water content during time for the sealed sample (case I) by hydration, **B**- in dark grey, the increase of the water content by saturation (case II) , **C**- the decline of the water content by vacuum drying (case III).

Water content:

Hydration process is usually characterized by determining the hydration degree which is calculated from the mass loss of the cement pastes on heating from 105 to 1100°C. In this study, water content is given by $\frac{(w_i - w)}{w_{water}}$ where w_i and w are the weights of the specimen before and after drying, and $w_{water} = \frac{w_i}{1 + \frac{1}{0.4}}$ (see Table 3).

This ratio characterizes the decrease of water content during hydration process.

days	freeze-drying	vacuum-drying	oven-drying at 80°C	oven-drying at 105°C
1	38%	62%	63%	66%
7	33%	42%	56%	60%
28	29%	36%	50%	53%
90	37%	34%	47%	51%

Table 3: Comparison between different drying method for free water evolution for a saturated sample (case II),

days	1	7	28	90
RMN	73%	66%	61%	55%

Table 4: NMR results for a sealed sample (case I).

Table 3 gives the free water content evolution obtained by the different drying techniques; results were calculated with added water(case II). Results show that freeze and vacuum drying methods are less effective to dry the sample than oven-drying at 80°C and 105°C. Indeed, free water is not totally evaporated, and the various dryings do not remove all free water. Material continues to evolve and the results at early age with drying method do not really reflect free water content.
Table 4 shows the free water evolution contained in a sealed sample. After 1 day, water content is very high and decrease with time.
The calculated water content can not be directly compared with the measurements given by drying methods, MRI profiles give “instantaneous” information of water content whereas drying techniques; especially at early age need time to remove free water.

4. CONCLUSION

Comparison between NMR and different common techniques results is not obvious. The differences of protocol, the size of sample, the different drying, intervene in the comparison which becomes quite difficult. Nevertheless, NMR determination shows the limits of the common techniques:

- limits of the different dryings studied: SPI images and profiles show that a sample is not totally dried, free water still remains in the sample
- MIP and capacitive method do not allow to identify all the different pore radii and are not noticeable to the hydration evolution after 14 days, NMR relaxation give more information.

An interesting result is the evolution of peaks with T_1 relaxation, NMR gives discrete results whereas MIP and capacitive method give continuous pore size distribution. But if a range of pore is well identified, the next step will be to correlate each peak with a pore radius.
Obviously, MRI brings complementary information. Comparison with other techniques is however necessary to identify and understand results given by NMR.
In conclusion, NMR has so many advantages:

- non destructive way, study on a same sample
- time of experiments
- size of samples
- no drying effects
- follow-up at very early age, just after mixing

Moreover, MRI/NMR has a double interest, the possibility to follow the sample microstructure with relaxation and with the same apparatus to study the water content with SPI method during time.

MRI/NMR is unique and thus provides a complete study of concrete hydration process.

5. BIBLIOGRAPHY

[1] E. Laganas, G. Papavassiliou, M. Fardis, A. Leventis, and F. Milia, E. Chaniotakis and C. Meletiou , Analysis of complex ^{1}H nuclear magnetic resonance relaxation measurements in developing porous structures: A study in hydrating cement, J. Appl. Phy., 77 (7) (1995) 3343-3348

[2] K.S. Mendelson, W.P. Halperin, J-Y. Jehng, Y-Q. Song, Application of spin-spin relaxation to measurement of surface area and pore size distributions in a hydrating cement paste, Magn. Reson. Imag.., 12 (2) (1994)

[3]] S. Philippot, J.P. Korb, D. Petit, H. Zanni, Analysis of microporosity and setting of reactive powder concrete by proton nuclear relaxation, Magn. Res. Im 16 (5-6) (1998) 515-519

[4] J.-Y. Jehng, D.T. Sprague,W.P. Halperin, Pore structure of hydrating cement paste by magnetic resonance relaxation analysis and freezing, Magn. Reson. Imag 14 (1996) 785.

[5] K.P. Whitall, A.L. MacKay, Quantitative interpretation of NMR relaxation data, J. Magn. Reson. 84 (1989) 134–152.

[6] S.D. Beyea, B.J. Balcom, T.W. Bremner, P.J. Prado, D.P. Green, R.L. Armstrong, and P.E. Grattan-Bellew, Magnetic resonance imagning and moisture content profils of drying concrete, Cem Concr Res 28 (3) (1998) 453-463

[7] P.J. Prado, B.J. Balcom, S.D. Beyea, R.L. Armstrong, T.W. Bremner, P.E. Grattan-Bellew, Concrete/mortar water phase transition studied by single-point MRI methods, Magn. Reson. Imag.., 16 (5-6) (1998) 521-523

[8] M. Bogdan, B.J. Balcom, R.L. Armstrong, T.W. Bremner, Single-point imaging of partially dried, hydrated White Portland Cement, J. Magn. Reson, A116 (1995) 266-269

[9] P. Faure, S.Caré, Suivi par IRM et par T_1 de l'effet du couplage hydratation–séchage sur la microstructure de pâte de ciment, Comptes Rendus Chimie 9 (3-4) (2006) 548-555

[10] P. Faure, S.Caré, C. Po, S. Rodts, an MRI-SPI and NMR relaxation study of drying–hydration coupling effect on microstructure of cement-based materials at early age, Magn. Res; Im. 23 (2) (2005) 311-314

[11] S. Emid, J.H.N. Creyghton, High resolution NMR imaging in solids, Physica B 128 (1985) 51

[12] B.J. Balcom, R.P. MacGregor, S.D. Beya, D.P. Green, R.L. Armstrong, T.W. Bremmer, Single-Point Ramped Imaging with T_1Enhancement (SPRITE) , J.Mag.Res. A 123 (1996) 131

[13] J. Tritt-Goc, N. Pislewski, S. Koscielski, F. Milia, The influence of the superplasticizer on the hydration and freezing processes in white cement studied by ^{1}H spin-lattice relaxation time and single point imaging ,Cem.Conc.Res. 30 (2000) 931-936

[14] G. Villain , M. Thiery, Gammadensimetry: a method to determine drying and carbonation profiles in concrete, NDT & E International, 39 (4) (2006) 328-337
[15] C. Gallé, Effect of drying on cement-based materials pore structure as identified by mercury intrusion porosimetry: a comparative study between oven-, vacuum-, and freeze-drying, Cem Concr Res, (31) (2001) 1467-1477
[16] A. Fabbri, T. Fen-Chong, O. Coussy, Dielectric capacity, liquid water content, and pore structure of thawing–freezing materials**,** Cold Regions Science and Technology 44 (2006) 44-66.
[17] T. Fen-Chong, A. Fabbri, A. Azouni.Cold, , Regions Science and Technology, Accepted in 2006.
[18] R.A. Cook, K.C. Hover, Mercury porosimetry of hardened cement pastes, Cem Concr Res, 29 (1999) 933-943.
[19] F Moro, H. Bohni, Ink-bottle effect in mercury intrusion porosimetry of cement-based materials, J Colloid Interface Sci., 246 (1) (2002) 135-49
[20] S.J. Jaffer, C. Lemaire, C.M. Hansson and H. Peemoeller. MRI: A Complementary Tool for Imaging Cement Pastes. Cem. Conc. Res., in press (2007).