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Cementitious nanostructures: Nanoporosity

Philippe Boch*, Arnaud Plassais, Marie-Pierre Pomies, Jean-Pierre Korb^a and Nicolas Lequeux

ESPCI, 75005 Paris (France) ^aÉcole Polytechnique, 91128 Palaiseau, France

Relaxation ¹H-NMR was used to characterize the nanostructure of cementitious pastes, together with measurements of hydration and mechanical properties. The influence of cure parameters (hydration time and temperature) and composition parameters (water-to-cement ratio and silica and superplasticizer addition) was studied. In silica-free materials, the relaxation-time curve shows five characteristic times, $T_{1,i}$, each of them being related to a given class of porosity, ranging from very small pores, at the inside of C-S-H nanocrystallites, to large, capillary pores. In silica-containing materials, there is an appearance of a supplementary signal, which is due to a pozzolanic reaction.

Key words: Cement, nanostructure, nanoporosity, relaxation ¹H-NMR.

Introduction

Nanostructure features, in particular nanoporosity, play a prominent role in cement paste characteristics, for instance mechanical properties or fluid permeability [1, 2]. Pore sizes in cement pastes range from nanopores to macropores. Macroporosity can be investigated by intrusive techniques such as mercury porosimetry. By contrast, the study of nanoporosity requires non-intrusive techniques, such as nuclear magnetic resonance (NMR).

The present work was mainly devoted to the study of C_3S pastes. Tricalcium silicate (C_3S in cement notation where C is for CaO, S for SiO₂, and H for H₂O) is the main component in anhydrous Portland cement, and hydration of C_3S is the main source for hydrated calcium silicates ("C-S-H"). Silica fume is a common additive in cementitious materials, which explains why we have studied its influence by investigating pastes with silica fume additions. The technique used for investigating nanoporosity (\leq 50 nm) was time-resolved, proton nuclear magnetic resonance (¹H-NMR). Special emphasis was put on measurement of longitudinal relaxation time (T₁). The technique offers two advantages:

• Since the protons are components of water and hydrated phases, it is not necessary to use complex preparation procedures, such as drying, which can change the nanostructure, for instance through pore collapse [1].

• There is no fluid (liquid or gas) intrusion, which

allows us to probe the smallest pores -a key requirement when the goal is the study of nanostructure.

Materials and techniques

We used a synthetic C_3S doped with about 0.7 wt% of iron oxide. Iron oxide brings paramagnetic ions (Fe³⁺). Unless otherwise stated, the pastes were made by mixing distilled water and C₃S at 20°C with a water-to-cement ratio (w/c) of 0.4. Cure was conducted in lime water. The silica fume particle diameter was around 0.15 µm. Silica fume incorporation was facilitated by addition of 1 wt% of PNS (sodium salts of naphthalene formaldehyde condensates) superplasticizer.

¹H-NMR spectra were obtained using a 500 MHz spectrometer. The relaxation curve is characteristic of the return toward equilibrium of the ¹H nuclear magnetization after a perturbation. In the simplest case, the relaxation curve has an exponential profile. Thus, fitting the curve leads to the determination of the time constant, noted as " T_1 ". T_1 can be evaluated by using an inversion-recovery method. The value of T_1 depends on time-changing interaction between protons and surrounding spins, in particular spins of paramagnetic species, hence the role of the ferric ions. The prominent relaxation mechanisms involve interaction between protons and solid surfaces [3]. In a spherical pore of radius R there is a fast exchange between bulk-related protons and surface-related protons, which is characterized by a single value of T₁. This value is proportional to the volume-to-surface ratio, that is $\overline{R}^{3/2}$ $\overline{R}^2 = \overline{R}$ [4, 5]. In a porous material, therefore, the distribution of equivalent pore radii can be derived from the distribution of T_1 times $(T_{1,i})$.

The NMR experimental relaxation curve can be decomposed into a sum of exponentials, each of them

^{*}Corresponding author: Tel : 01-40-79-44-42 Fax: 01-40-79-47-50

E-mail: philippe.boch@espci.fr

being characterized by its time value:

$$\sum A_i \cdot \exp(-\tau/T_{1,i})$$

We operate as follows. First, the experimental curve (called C₁) is plotted by putting the logarithm of magnetization (LnM) versus decay time (τ). Secondly, the long-time side of C₁ is fitted to extract the longest T_{1,i} time, labeled as T_{1,maxi}. Thirdly, the single-value curve (A_{maxi}exp($-\tau/T_{1,maxi}$)) is subtracted from C₁ to give C₂, and the same treatment is repeated again to find the secondary time, labeled T_{1,2}, etc. At the end, the result is that of five discrete values: T_{1,maxi} > T_{1,2} > T_{1,3} > T_{1,4} > T_{1,5}. The validity of this time extraction was confirmed by a Laplace inversion treatment carried out using *CONTIN* software [6].

Besides NMR experiments, the materials were characterized by quantitative X-ray diffraction (QXRD), differential thermal analysis (DTA) and thermogravimetric analysis (TGA), to measure the degree of hydration and the portlandite content. Moreover, non-destructive ultrasonic (US) measurement of longitudinal and shear wave velocities were carried out to evaluate elastic moduli. Those US experiments were not conducted on C_3S pastes but on ordinary Portland cement (OPC) [7, 8].

All characterization experiments, except US experiments, were carried out at room temperature.

Results and Discussion

T_{1,i} attribution

The inversion of relaxation curves of mature C_3S pastes leads to times $T_{1,i}$ which distribute along five characteristic values. To explain this distribution, we used both spectroscopy/relaxation coupling and relaxometry (that is: a study of the frequency dependence of the relaxation rates) [9]. The spectroscopy/relaxation coupling shows that the distribution of $T_{1,i}$ does not give a direct image of the distribution of protonated chemical species. This result was confirmed by relaxometry, using a relaxation model based on the presence of protons close to the surface of C-S-H particles. By combining all NMR methods, we suggest the following interpretation of the $T_{1,i}$ distribution:

• The shortest T_1 time ($T_{1,5}$, of less than 1 ms) is attributed to a large SiOH and CaOH-like spectroscopic signal. Its frequency behavior corresponds to protons located in the inside of C-S-H nanocrystallites ("intracrystallite protons"). This scale corresponds to the lower limit of the relaxation model.

• The three following T_1 times ($T_{1,2}$, $T_{1,3}$, and $T_{1,4}$, 1, 10 and 100 ms, respectively) correspond to three classes of porosities where the protons are located at the outside of C-S-H nanocrystallites ("inter-crystallite protons"). Spectroscopy and relaxometry experiments are coherent with an explanation that, at the surface of



Fig. 1. C_3S paste: Model of nanostructure compatible with the distribution of T_1 times. "Elementary bricks" are proton-rich C-S-H nanocrystallites. Each porosity class corresponds to a class of packing faults.

a pore, the relaxation is induced by interaction between paramagnetic ions (ferric ions in the present case) and mobile protons, subjected to fast exchange with the bulk. On the surface, there is a coexistence of HOH, SiOH, and CaOH species. Each value of $T_{1,i}$ is related to a given class of porosity, characterized by its surface-to-volume (S/V) ratio, i.e. by its mean radius \overline{R} .

• The longest T_1 time ($T_{1,maxi}$, at about 1000 ms) is related to protons located in the inside of portlandite and/or to protons in the water that fills capillary macropores.

Model for the T_{1,i} distribution

Fitting the three dispersion curves (T_{1,2}, T_{1,3}, and T_{1,4}) that are related to inter-crystallite porosity leads to three values for the mean pore radius, namely $\overline{R} = 5$, 40, and 500 nm.

Various studies, especially those by atomic force microscopy [10], have indicated that the "C-S-H nanobricks" have a platelet shape with typical dimensions of $5\times50\times50$ nm. Those dimensions are in the range of the first two classes of porosity we find. This allows us to propose a model of C-S-H nanostructure where the paste is organized by packing C-S-H nanocrystallites and where each porosity class corresponds to a class of packing faults (see Fig. 1).

Influence of cure time

Cure time is a major parameter to be considered when studying cement nanostructure. Figure 2 shows the continuous change in T_1 as hydration proceeds, which can be understood from literature data [11, 12]. The paste nanostructure development follows three stages. For the first stage (induction period), there is a unique value of T_1 . For the second stage (development of C-S-H nanocrystallites, with correlative increase in surface area), there is still a unique value of T_1 , which decreases continuously as time increases. Finally, for the third stage, T_1 splits into five separate values which means, as previously explained, that the porosity architecture comprises five classes of pores, ranging from



Fig. 2. Changes in $T_{1,i}$ times versus cure time, at early ages. C_3S paste hydrated at 20°C, w/c = 0.4. The size of dots reflects the relative weight of each $T_{1,i}$. The advancement of hydration is also shown. NMR: 500 MHz spectrometer.

very small intra-crystallite pores to large capillary pores, through three classes of intermediate inter-crystallite pores. An interesting point is that, although hydration is close to completion after 100 hours, the system continues to evolve after this time.

The quantitative distribution of $T_{1,i}$ in C_3S pastes was measured for cure times ranging from seven days to six months. Figure 3 shows the change in relative proportions of $T_{1,2}$, $T_{1,3}$, and $T_{1,4}$ versus cure time. One sees that i) all the $T_{1,i}$ values decrease as time increases and ii) the relative weight of $T_{1,3}$ decreases while the proportion of $T_{1,4}$ increases, which means the size of porosity decreases as time increases. This confirms that there is a progressive rearrangement of C-S-H nanocrystallites. After three months of cure, the $T_{1,i}$ distribution reaches a steady-state plateau, where the three times $T_{1,2}$, $T_{1,3}$, and $T_{1,4}$ are related together by a power law whose power exponent, p, is related to surface fractal dimension (D_f , with $p = 2-D_f$). We found that D_f $\approx 2.5-2.6$, which is in good agreement with literature



Fig. 3. Relative proportion of the three inter-crystallite, porerelated $T_{1,i}$ times for various cure times, as indicated. C₃S paste hydrated at 20°C, w/c=0.4. Hydration degree close to 100%. NMR: 500 MHz spectrometer.



Fig. 4. Shear modulus versus cure time for OPC pastes cured at three different temperatures, as indicated.

data [13-15].

Influence of cure temperature

Figure 4 shows changes in shear modulus for ordinary Portland cement (not plain C_3S) pastes cured at 20, 30, and 60°C. As is known, an increase in cure temperature accelerates the setting rate and hydration rate, with particular effect on the first stage (dissolution) of the process, which is thermally activated [16]. This kinetic effect shortens the induction period and increases the initial rate of hydration of C_3S . For long times of cure, the hydration rate becomes much lower [17]. For the highest temperature of cure we studied (60°C), the increase in the hydration kinetics is accompanied by a decrease in the final value of modulus. This result supports the assumption that there is a threshold temperature, at about 50°C, beyond which stiffness drops [18, 19].

Figure 5 shows the $T_{1,i}$ distribution, hence the pore radius distribution, of C₃S pastes cured for three months at various temperatures (6, 20, 45, and 80°C). For temperatures up to 45°C, the pore size distribution does not change very much and the scaling law keeps a constant profile. For a cure at 80°C, however, the change is more pronounced, \overline{R} increases, and D_f decreases.

It was established [20-23] that an increase in cure temperature results in changes in nanostructure. Heating makes the C-S-H denser, which is due to a decrease in the water content inside the C-S-H and an increase in



Fig. 5. Relative proportion of the pore-related $T_{1,i}$ times after various cures, as indicated. C₃S paste, w/c = 0.4. NMR: 500 MHz spectrometer.

the degree of polymerization of silicon based tetrahedra. Moreover, the C-S-H nanocrystallites that are formed at an early stage are densely packed, which decreases the proportion of pores of intermediate size but increases the size of capillary pores [18]. At a macroscopic scale, however, the C-S-H packing is less dense, which can explain the decrease in elastic modulus. It must be noticed, however, that an increase in temperature also influences the paste macrostructure, for example by inducing cracking flaws [24].

Influence of water-to-cement (w/c) ratio

The general trend is that mechanical properties of cement pastes decrease as w/c increases [7, 25]. The higher the w/c ratio, the wider the gap between cement particles and the larger the final porosity. The "ideal" value of w/c is a compromise between ease of placement (in the green state) and final characteristics (in the long term, hardened state). Figure 6 shows the $T_{1,i}$ distribution of C_3S pastes cured at various w/c ratios.

After a cure of 10 days, one can notice that:

• when w/c = 0.4, the $T_{1,i}$ distribution is similar to what has been previously seen,

• when w/c = 0.3, the $T_{1,i}$ distribution exhibits a power law profile,

• when w/c = 0.7, there is a majority of protons with a high value of $T_{1,i}$.

After a cure of three months:

• when $w/c \le 0.4$, the $T_{1,i}$ distribution exhibits a power law profile,

• when w/c = 0.7, the $T_{1,i}$ distribution is similar to the short-time distribution in pastes made with a lower w/c.

The results on relaxation times show that a decrease in the w/c ratio reduces the time that is required to reach a "stable" arrangement of nanocrystallites, and that a better packing favors a power-law $T_{1,i}$ distribution. An elevated w/c ratio has the opposite effect. The fact that the w/c ratio influences the fine-pore size distribution confirms that the decrease in mechanical properties



Fig. 6. Relative proportion of the inter-crystallite, pore-related $T_{1,i}$ times for C₃S hydrated pastes with w/c \leq 0.4 and = 0.7. Time cure > 6 months. NMR: 500 MHz spectrometer.

associated with a high value of w/c is not solely due to macroscopic defects, but also comes from nanostructure changes.

Influence of silica fume and plasticizer addition

Figure 7 shows the change in shear modulus versus cure time for OPC cement pastes with and without "additives" (silica fume plus plasticizer). The presence of additives increases the induction period and increases the elastic modulus in the hardened state. Actually, it was shown [26-28] that the increase in the induction period is mainly due to the superplasticizer, whose molecules are adsorbed onto the cement particle surface, which slows down the dissolution kinetics.

Figure 8 shows the $T_{1,i}$ distributions for C_3S pastes with various additive contents. The results are as follows:

• The inter-crystallite parameters $(T_{1,4}, T_{1,3}, and T_{1,2})$ are not very much affected by the presence of additives.

• Once the pozzolanic reaction has begun, there is a decrease in the relative weight of $T_{1,maxi}$, which is the



Fig. 7. Shear modulus versus cure time for OPC pastes with 0 or 20% silica fume addition. w/c = 0.4.



Fig. 8. Relative proportion of $T_{1,i}$ times for C₃S hydrated pastes, versus additive content. $T = 20^{\circ}$ C, w/c = 0.4. Time cure = 4 months. NMR: 500 MHz spectrometer. The time related to intracrystallites protons, $T_{1,5}$, is not plotted.

longest $T_{1,i}$, at about 1000 ms, and there is the appearance of a sixth time, $T_{1,6}$, at about 300 ms. There are two possible explanations, which are not mutually exclusive, for these results:

• If $T_{1,maxi}$ corresponds to portlandite, the pozzolanic reaction would have two effects. Firstly, the consumption of portlandite decreases the relative weight of $T_{1,maxi}$. Secondly, since the content of paramagnetic iron in pozzolanic C-S-H nanocrystallites is lower than that in non-pozzolanic C-S-H nanocrystallites, the relaxation time associated with pozzolanic C-S-H shifts towards a value ($T_{1,6}$) that is much higher than that ($T_{1,5}$) for non-pozzolanic C-S-H.

• If $T_{1,maxi}$ corresponds to capillary water, the decrease in the relative weight of $T_{1,maxi}$ can be explained by partial filling of macropores by pozzolanic C-S-H. In this case, $T_{1,6}$ corresponds to the relaxation time in capillary pores of reduced size.

To discriminate between the two explanations, we need more information, in particular on the iron content in portlandite. Experiments are currently under way to check this point.

The present data show that silica fume addition decreases gross porosity ($\approx 1 \mu m$) and increases elastic modulus. Another point is that an increase in cure temperature accelerates hydration, but may degrade the nanostructure and decrease the elastic moduli of hardened material. Figure 8 shows the T_{1,i} distribution for a C₃S paste with silica fume addition, cured at 80°C. The distribution is similar to that in a paste cured at 20°C. Moreover, hydration data show fast hydration, with a very short induction period. Taken together, these data confirm the beneficial influence of the additives and cure temperature on the mechanical properties of the paste.

It is worth noting that similar NMR characterization

can be used to study the nanostructure of various cementitious materials. For instance, Porteneuve et al. [29] used $T_{1,i}$ measurements to investigate high-performance, reactive-powder concrete (RPC). In RPC, the size of particles (silica fume and cement) are chosen to built up an Appolonian-like packing. In this case, the $T_{1,i}$ distribution obeys a power law over five decades.

Conclusion

A longitudinal relaxation ¹H-NMR technique was used for characterizing nanoporosity in cementitious pastes. Using the T_1 frequency dependence and the coupling with NMR spectroscopy signal, relaxation curve decomposition shows the existence of five typical times ($T_{1,i}$). The shortest time ($T_{1,5}$) is associated with intra-C-S-H porosity, the three intermediate times ($T_{1,4}$, $T_{1,3}$, $T_{1,2}$) are associated with three scales of inter-C-S-H porosity, and the longest time ($T_{1,maxi}$) is associated with portlandite and/or capillary macropores.

There is evidence of a long-term effect, nanoporosity still continuing to evolve as hydration is close to completion. In this matured state, the three medium porosity classes lead to a distribution curve that obeys a power-law.

Changes in cure and composition parameters essentially influence the gross porosity. This explains why the shear modulus is greatly affected by high temperature of cure (> 50°C) and high water content (w/c > 0.4). The presence of additives (silica fume plus superplasticizer) or an increase in cure temperature accelerate the kinetics but do not change the nanostructure very much. Silica fume, however, has a noticeable influence in reducing gross porosity.

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