Pergamon

Cement and Concrete Research 31 (2001) 263–269

CEMENT AND CONCRETE RESEARCH

Proton spin–lattice relaxation study of the hydration of self-stressed expansive cement

T. Apih[a,*], G. Lahajnar[a], A. Sepe[a], R. Blinc[a], F. Milia[b], R. Cvelbar[c], I. Emri[c], B.V. Gusev[d], L.A. Titova[d]

[a]*J. Stefan Institute, SI-1000 Ljubljana, Slovenia*
[b]*NCSR Demokritos, 153 10 Ag. Paraskevi, Attiki, Greece*
[c]*Center for Experimental Mechanics, University of Ljubljana, Cesta na Brdo 49, SI-1125 Ljubljana, Slovenia*
[d]*International Academy of Engineering, RU-103905 Moscow, Russia*

Received 17 April 2000; accepted 24 October 2000

Abstract

Proton spin–lattice relaxation, compressive strength, and water tightness measurements have been undertaken in order to study the hydration process and the mechanical properties of Portland cement modified with a calcium sulfoaluminate-based expansive additive (EXPAD). The compression strength of the modified cement was more than 70% higher while water permeability was about 60% smaller than in the unmodified cement. Magnetization–recovery curves analysis allowed for a time-resolved monitoring of both the increase of the internal surface as well as the formation of solid products during the hydration. A significant difference between the hydration kinetics of modified and unmodified cement was observed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Hydration; NMR; $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$; High performance concrete

1. Introduction

Though the use of hydraulic cement [1] as a waterproof binder of mortar or concrete goes back to the Roman Empire, the hydration and hardening process are still not very well understood and more work has to be done for the clarification of the mechanism of solidification. Even though the application properties of Portland cement have been improved with respect to its compressive strength, there are still intrinsic disadvantages connected with stiffness, tensile strength, fracture toughness, and creep properties, which have not yet been completely overcome.

It is of prime importance for the construction industry in general to further improve and develop strong ordinary Portland cement-based binder materials with the addition of various additives that may improve the final performance. It has been proved [2] that several additives like clays, organic solutions, kiln-dust, etc., when added (co-ground) with the clinker, increase the compressive strength and/or decrease the permeability of the material. Admixtures frequently used in the cement industry also include calcium chloride, air entraining agents, set retarders, water reducers, corrosion inhibitors, color pigments, etc. Among various admixtures, expansive additives are especially interesting. They are used to achieve either nonshrinkage cements, where the degree of expansion is just enough to offset shrinkage, or expansive cements, where expansion of a few percent can used for chemical prestressed concrete, when properly restricted.

The expansive additive EXPAD (produced by the NIIZhB Institute, Moscow, Russia) has been reported [3,4] to successfully increase water tightness, tensile strength, crack resistance and durability of concrete and reinforced concrete structures. It is widely used for monolithic concrete constructions, for manufacture of prefabricated concrete constructions, and for repair work. The sulfoaluminate-based EXPAD ensures the expansion due to chemical interaction of aluminate and sulfate phases of the binder components. As a result ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$) is formed. The needle-

---

* Corresponding author. Tel.: +386-1-4773620; fax: +386-1-4263269.
E-mail address: tomaz.apih@ijs.sl (T. Apih).

PII: S0008-8846(00)00460-9

shaped crystals of ettringite penetrate the body of the cement stone, fill its pores and increase the density of the hydrated material. Hardening and compactness of the structure of hydro-silica component increase the strength of the cement stone. The special feature of the expansive additive EXPAD is that they can be obtained both by calcination technology and without calcination. Natural materials and industrial byproducts (waste materials) can be used as the raw material for their production.

When using a new admixture with a given cement, it is always important to ensure the compatibility of the selected cement and the admixture. For example, a recent nuclear magnetic resonance (NMR) study of hydration kinetics of three different high-range water-reducing admixtures with five different Portland cements showed that selected mixtures had a very different effect on a particular cement [5]. In order to add some additional information on the quality and properties of EXPAD modified cement and to compare its hydration kinetics to that of nonmodified Portland cement, we decided to undergo a series of NMR, mechanical strength, and permeability measurements.

2. Theory of NMR relaxation in a hydrating cement paste

The use of NMR as a tool for the study of porous systems like sandstones, zeolites, clays, and various cementitious materials is now a well-established experimental technique. Here we apply this technique to study the details of the hydration process in the self-stressing cement based on the EXPAD additive and to compare the results with those of classical Portland cement.

It is known that measurements of the NMR spin–lattice relaxation time T_1 of protons of exchangeable water in hydrating cement pastes offer a convenient tool for following the development of hydration process of cement [2,5–15]. There are of course several methods to measure the specific internal surface of cement (Blain, Hg, etc.), but besides small angle scattering (SANS and SAXS) [12], NMR T_1 is the only method that allows for a continuous and nondestructive determination of the internal surface of the CSH gel, which is directly related to the strength of the hydrating cement paste [8].

During the hydration process, part of the water enters the structure of the newly formed minerals, while the exchangeable water (i.e. interlayer, micropore, and gel adsorbed) remains in a liquid-like phase in close contact with the gel surface.

Due to the fast (on the T_1 time-scale) exchange of "free" water and of water bonded to the gel surface, the spin–lattice relaxation rate $1/T_1$ of the exchangeable water can be written as Eq. (1) [7]

$$T_1^{-1} = (T_1^{-1})_{\text{bonded}}\ \eta + (T_1^{-1})_{\text{free}}\ (1-\eta). \tag{1}$$

Here η is the fraction of bonded molecules $\eta = \eta_{\text{bonded}}/(\eta_{\text{bonded}} + \eta_{\text{free}})$.

Assuming spherical pores of radius R as well as that bonded water molecules form a layer of thickness k, one finds that η for a given pore may be written [7] as

$$\eta = kS/V = 3k/R. \tag{2}$$

Here S/V is the pore surface to volume ratio.

Since $(T_1{}^{-1})_{\text{bonded}} \gg (T_1{}^{-1})_{\text{free}}$ the relaxation rate can be approximated as

$$T_1^{-1} \cong (3k/R)(T_1^{-1})_{\text{bonded}}. \tag{3}$$

It should be noted that $(T_1)_{\text{bonded}}$ is Larmor frequency dependent and generally increases with increasing Larmor frequency [7]. In the special case of relaxation via fast diffusion in internal magnetic field gradients due to the water–cement interface [7] one finds, on the other hand, that T_1 decreases with increasing Larmor frequency ω_L in the fast motion regime $\omega_L\tau \ll 1$, whereas it is Larmor frequency independent in the slow motion regime $\omega_L\tau \gg 1$.

Eqs. (2) and (3) show that the fraction of bonded molecules η that is proportional to the pore surface to volume ratio S/V, together with $(T_1{}^{-1})_{\text{bonded}}$ determines the experimentally observed T_1 in hydrating cement paste. The thickness of the surface layer k occurring in Eq. (2) is generally assumed to be of the order 2–3 Å.

The time evolution of T_1 thus reflects the increase in the active gel–pore water interface and the change in the geometry of the surface of the newly formed hydration products Eq. (4) [7],

$$T_1^{-1} = (T_1^{-1})_{\text{bonded}}\ \eta \propto kS/V. \tag{4}$$

By measuring the proton spin–lattice relaxation rate one can thus monitor the increase in the internal surface of cement paste, S, which in turn determines its mechanical properties.

Another important information, which can be obtained by NMR spin–lattice relaxation measurements, is the form of the magnetization recovery function $M(t)$. In cement we generally deal with a distribution of pore sizes with different surface to volume ratios. This leads to Eq. (5)

$$M(t) - M_0 \propto \int W(T_1)\exp(-t/T_1)\mathrm{d}T_1, \tag{5}$$

resulting in a nonexponential form of the magnetization recovery function $M(t)$. The magnetization recovery function $M(t)$ is thus the Laplace transform of the spin–lattice relaxation time distribution function $W(T_1)$, which is related to the pore size distribution $P(R)$ by Eq. (6)

$$W(T_1)\mathrm{d}T_1 = P(R)\mathrm{d}R. \tag{6}$$

With the help of expression (3) we find $P(R)$ as [Eq. (7)]

$$\begin{aligned} P(R) &= (T_1)_{\text{bonded}}/3k \cdot W(T_1) \\ &= \frac{(T_1)_{\text{bonded}}}{3k} W(R/(3k)(T_1)_{\text{bonded}}). \end{aligned} \tag{7}$$

Pore size distribution is thus proportional to scaled T_1 distribution. By determining precisely the thickness of the surface layer k and the surface-induced spin–lattice relaxation time $(T_1)_{\text{bonded}}$, one can in principle obtain $P(R)$ from the measured magnetization recovery function $M(t)$. Unfortunately the inverse Laplace transform is numerically unstable and some models for $M(t)$ or $W(T_1)$ usually have to be applied, e.g. by supposing that $W(T_1)$ can be represented as a sum of log-Gaussian distributions. The spin-grouping [15] method, on the other hand, relies on a simultaneous discrete multicomponent analysis of both longitudinal and transverse magnetization decays to obtain the fraction of protons in different phases, but neglects that the liquid component itself contains a distribution of relaxation times, which is related to the pore size distribution $P(R)$. Both approaches require prolonged measurements in order to acquire reliable results and usually cannot be used for kinetic studies of fast setting cements. Another approach is to determine the mean and the variance of T_1 only [13]. In present study we find, in agreement with Ref. [7], that the nonexponential form of exchangeable water part of $M(t)$ is well approximated by stretched exponential function [Eq. (8)] [7]

$$M(t) - M_0 \propto \exp(-(t/T_1^*)^{\alpha}) \tag{8}$$

in the whole hydration time range (see Fig. 1). One should note that T_1^* and α have a related, but not equivalent meaning as mean and variance of T_1 in Ref. [13]. The stretched exponent α is related to the distribution width of $W(T_1)$. It is equal to 1 in the initial stages of hydration when the relaxation is of a mono exponential type and approaches 0.5 as the $W(T_1)$ distribution broadens in later stages of hydration. In addition to this so-called "liquid" part of the magnetization $M_{(\text{liquid})}$, a part of the NMR signals comes from some of the chemically bounded water protons as a consequence of water reacting into solid products at a later stage of hydration. This so-called "solid component" $M_{(\text{solid})}$ is characterized by a rather long spin–lattice relaxation time [14] of the order of 1 s and a very short spin–spin relaxation time T_2 of the order of 20 μs. The T_1 and T_2 difference between the solid and liquid component enables one to separately observe the two components by measuring either T_1 or T_2 weighted spectra [14]. In the case of a nonweighted pulse sequence, both exchangeable-water and solid components of the signal are observed simultaneously and the complete magnetization–recovery function $M(t)$ is written as

$$M(t) = M_0 - M_{0(\text{liquid})}\exp(-(t/T_1^*)^{\alpha}) - M_{0(\text{solid})}\exp(-t/T_{1(\text{solid})}). \tag{9}$$

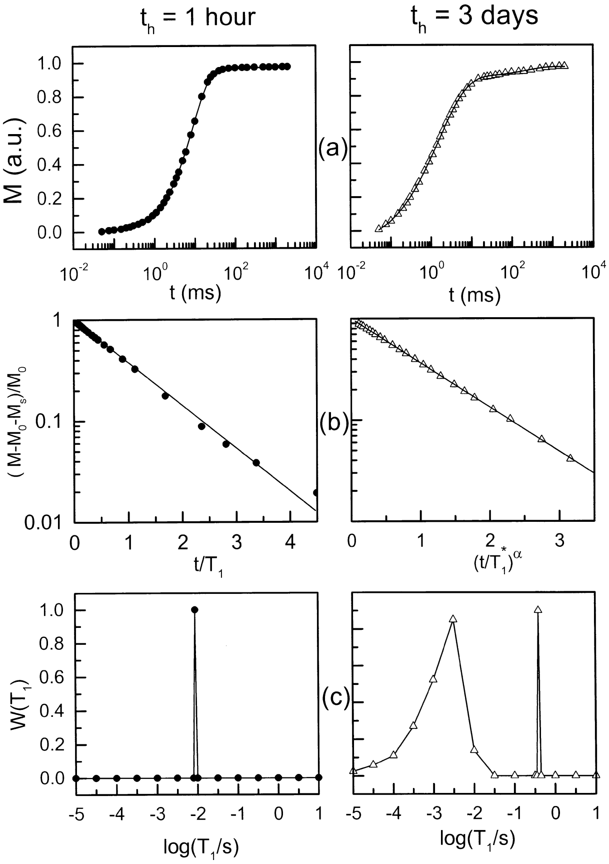

Fig. 1. Spin–lattice relaxation measurements of the hydration of EXPAD modified Portland cement at $t_h = 1$ h (left column) and at $t_h = 3$ days (right column). (a) Magnetization–recovery curves $M(t)$. The solid lines are fits to Eq. (9). (b) $\log(M_{(\text{liquid})})$ vs. $(t/T_1^*)^{\alpha}$ plot for the normalized "liquid-part" of the magnetization $M_{(\text{liquid})} = (M - M_0 - M_{(\text{solid})})/M_0$. Here $\alpha = 1$ for $t_h = 1$ h and $\alpha = 0.6$ for $t_h = 3$ days. (c) The spin–lattice relaxation time distribution $W(T_1)$ vs. T_1. For $t_h = 1$ h (dormant period) the relaxation is monoexponential and $W(T_1)$ consists of a single δ-function. For $t_h = 3$ days the there is a broad "liquid" component reflecting a broad distribution of pore sizes, and a δ-function for the "solid" component. Numerical inversion of $M(t)$ was obtained using a procedure described in Ref. [16].

3. Experimental work

3.1. Mechanical measurements

For 10 dm^3 of concrete we have mixed 7.5 kg of sand, 11 kg of crushed gravel (with granulation up to 8 mm), 2 l of water, 3.4 kg cement (standard PC45z15), and 0.4 kg of additive. For the reference a sample with 3.8 kg of cement and no additive was also tested. During the casting samples were vibrated with an actuator.

Molds were disassembled 24 h after the casting. Specimens were then immersed into water for 14 days, and afterwards stored at room conditions ($T = 23$°C, and RH = 60%) until testing. Mechanical measurements were performed 28 days after the casting.

3.2. Water-tightness measurements

Water-tightness tests were performed according to standard GOST 12730.5-84. The GOST 12730.5-84 stan-

Table 1
Basic data on samples for water-tightness measurements

Type of test	Standard sample	Concrete with additive
Consistency–slump test (cm)	2.0	2.0
Air content in fresh concrete (%)	1.6	1.4
Density of fresh concrete (kg/m^3)	2400	2405
Water/cement ratio	0.45	0.45

dard samples were exposed to hydrostatic pressure of 8 bars for 3 days, then they were split and water penetration was measured.

Similarly as for mechanical measurements we have prepared two types of specimens, one with additive and one without additive. Aggregation was consistent with the Slovenian Regulations for Concrete and Reinforced Concrete No. 11/97. The reference sample was made of sand (0–2 mm), gravel (0–4 mm), gravel (4–8 mm), cement PC15z45b from Anhovo (DC = 400 kg/m^3), and water (w/c ratio 0.45). Two samples with the additive contained 1 kg additive/8 kg cement, so that the additive replaced an equivalent amount of cement. Basic data on both types of specimens are listed in Table 1.

3.3. NMR measurements

The NMR experiments were performed on a 100 MHz high power NMR spectrometer on a standard Oxford superconducting magnet.

In each experiment 10 g of cement powder with or without 15 wt.% of the additive was hydrated with water to cement ratio w/c = 0.27. The paste was mixed by hand for 2 min in order to ensure homogeneity of mixing and then was left to hydrate in hermetically closed glass tubes in order to eliminate the evaporation of water.

The spin–lattice relaxation time has been here measured with the “inversion-recovery” pulse sequence [180°–τ–90°–*signal*], so that both the signals with long T_2 (protons of exchangeable water) and short T_2 (protons of chemically bonded water) were observed. The contributions of both types of protons were separated by a two component fitting procedure (see Eq. (9)).

To confirm that the long T_1 component ($T_{1(\mathrm{solid})}$) originates from chemically bounded protons, the same set of measurements was repeated on a 20-MHz portable industrial NMR spectrometer with a 20-MHz permanent magnet. The pulse sequence used here was [90°–τ–90°–τ_{ec}–180°–τ_{ec}–*echo*]. The fixed echo time τ_{ec} was chosen to be 100 μs for the performed experiments while the 90° pulse separation time τ was varied in the T_1 experiment. The value of τ_{ec} assures that the signal with a short T_2 (protons of chemically bonded water) was filtered out and only the signal from the exchangeable water was observed.

4. Results

4.1. Mechanical measurements

Compressive stress measurements gave $\sigma_{\mathrm{comp}} = 23 \pm 2$ MPa for the samples without the additive and $\sigma_{\mathrm{comp}} = 40 \pm 3$ 3 MPa for the samples with the additive.

4.2. Water-tightness measurements

Depths of water penetration for the reference sample, and two samples with the additive are given in Table 2. Similarly as in the case of mechanical measurement samples with the additive are significantly better than the reference samples made of Portland cement only. The difference, relative to the reference sample, is approximately 60%.

4.3. NMR measurements

The form of the proton magnetization recovery function $M(t)$ is shown in Fig. 1(a) for two different hydration times $t_{\mathrm{h}} = 1$ h and $t_{\mathrm{h}} = 3$ days. It can be easily seen then at $t_{\mathrm{h}} = 1$ h when we are in the dormant period the magnetization recovery is purely monoexponential while it becomes strongly nonexponential in the advanced stages of the hydration process. If one subtracts the long-T_1 component contribution [Eq. (10)]

$$M_{(\mathrm{solid})}(t) = M_{0(\mathrm{solid})}\exp(-t/T_{1(\mathrm{solid})}), \tag{10}$$

which is due to the water that enters the crystal structure, we are left with the contribution of the exchangeable water that can be very well described with a stretched exponential function [Eq. (11)]

$$M_{(\mathrm{liquid})}(t) = M_{0(\mathrm{liquid})}\exp(-(t/T_1^*)^{\alpha}) \tag{11}$$

[Fig. 1(b)]. $T_{1(\mathrm{solid})}$ amounts to about 0.5–1 s and only weakly depends on the hydration time t_{h}.

In the following we shall therefore describe the results of the relaxation time measurements by three parameters, the stretched exponent α, the spin–lattice relaxation time parameter T_1^*, and the solid component ratio $M_{(\mathrm{solid})}/(M_{(\mathrm{liquid})} + M_{(\mathrm{solid})})$.

Fig. 2(a) shows the NMR spin–lattice relaxation time T_1 as a function of the hydration time on an Anhovo Portland cement sample with and without the EXPAD additive. In both cases T_1^* is nearly constant in the “dormant period,”

Table 2
Results on water-tightness measurements

	Reference sample	Samples with the additive
Depth of water penetration	23 mm	Sample 1: 15 mm Sample 2: 14 mm

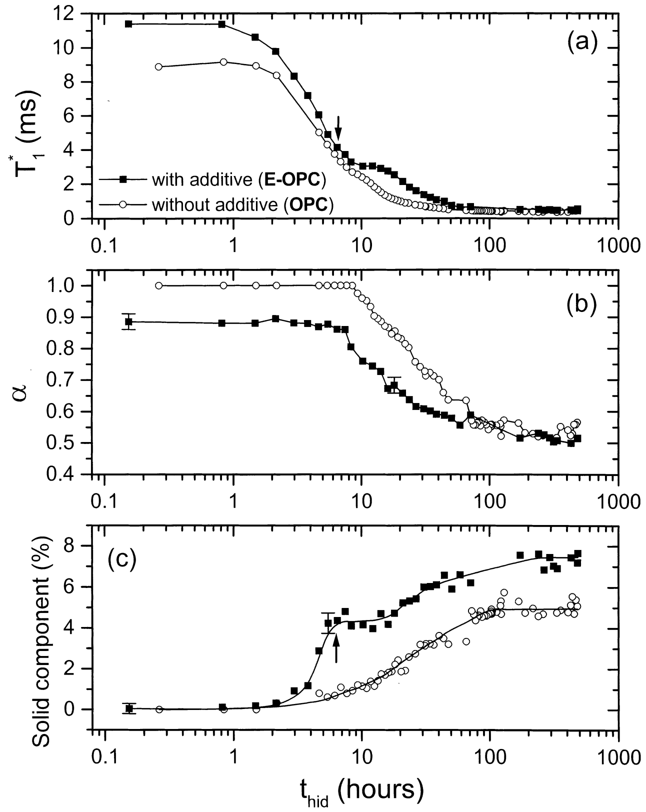

Fig. 2. (a) Dependence of the proton spin–lattice relaxation time parameter T_1^* for EXPAD modified (E-OPC) and nonmodified (OPC) Portland cement on the hydration time t_h. (b) The stretched exponent α versus the hydration time for cement with (full circles) and without (empty circles) the additive. (c) Hydration time evolution of the solid (long T_1) magnetization component fraction $M_{0(\mathrm{solid})}/(M_{0(\mathrm{solid})}+M_{0(\mathrm{liquid})})$.

rapidly decreases in a period when the compressive and bending elastic strength of cement starts to increase and then slowly decreases with increasing hydration time. In the sample with the new additive we find, however, a "shoulder" in the T_1 versus hydration time plot that is absent in the normal Portland cement.

Fig. 2(b) shows the hydration time dependence of the stretched exponent α for the samples with and without the additive. Fig. 2(b) thus reflects the time dependence of the pore size distribution, which becomes broader and broader with increasing hydration time. It should be noted that the T_1 and pore size distributions can be quantitatively determined from the nonexponentially of the proton magnetization time recovery function $M(t)$. The hydration time evolution of α is similar in both cases, with and without the additive. However, in the presence of additive α has somewhat lower value than in the sample without the additive, suggesting that that the pore size distribution is wider in the sample with the additive than in the sample without it.

The hydration time dependence of the solid component fraction of the magnetization, $M_{0(\mathrm{solid})}/(M_{0(\mathrm{solid})}+M_{0(\mathrm{liquid})})$, is shown in Fig. 2(c). The coefficients $M_{0(\mathrm{solid})}+M_{0(\mathrm{liquid})}$ were obtained by fitting Eq. (9) to the measured magnetization recovery functions $M(t)$. The solid component $T_{1(\mathrm{solid})}$ was 0.5–1 s and was found to be hydration time independent. To additionally verify that the $M_{0(\mathrm{solid})}$ part originates from the crystalline water protons we repeated T_1 measurement with a three-pulse sequence where the magnetization is measured with the spin-echo signal. The spin-echo delay was set to $\tau_{ec}=100$ µs. The measured magnetization–recovery curves were again fitted with Eq. (9). The resulting T_1^* and α were identical to the original measurements (Fig. 2), while the solid component of the signal was negligible ($M_{0(\mathrm{solid})}\approx 0$) indicating that spin–spin relaxation time T_2 of the solid (long T_1) component is much shorter than that of liquid (short T_1) component. This is in agreement with previous results [14,15].

5. Discussion

Mechanical and water-tightness measurements confirm that the EXPAD additive significantly improves the concrete performance. NMR spin–lattice relaxation time study has revealed a substantial difference in the hydration kinetics of cement with and without the additive. An important feature of the calcium sulfoaluminate-based expansive additives like EXPAD is that they induce expansion in concrete within the period where the structure of concrete begins already to be formed, but still can be deformed plastically. Expansion and self-stress of shrinkage compensating concrete are known to reach their maximum at around 10 days of hydration time. While self-stress measurements are not directly applicable for the very early stages of hydration when the cement paste is not yet rigid, NMR technique can continuously and nondestructively probe the internal surface development in the cement paste immediately after mixing. By simultaneous determination of both the "liquid" (short T_1, long T_2) and the "solid" (long T_1, short T_2) part of the signal, we were able to follow both internal surface and solid products growth during the hydration process. The following conclusions have been obtained:

- The time evolution of the exchangeable water proton T_1 in the ordinary Portland cement samples without additive (OPC) behaves normally as it was already shown by us and other groups [6–15]. The dormant period is approximately 2 h and T_1 decreases from 18 ms to the 50% of its value after 5 h. In contrast, the time evolution of the exchangeable water proton T_1 in the sample with the EXPAD additive (E-OPC) has a faster initial decay. The dormant period is shorter (approximately 1 h) and the 50% of the initial value of T_1 is reached in 3 h. This means that E-OPC has a faster initial hydration and hardening process.

- While T_1 as a function of the hydration time continuously decreases for the OPC sample, there is a clearly visible shoulder resembling a plateau (hydration pause) in E-OPC sample between 8 and 16 h. After about $t_h = 16$ h T_1 starts to decrease for E-OPC again demonstrating a faster internal surface growth. In comparison, the surface growth of the OPC sample is almost complete at this stage. This shows then that the hydration of the sample with the additive is a two-stage process.
- The hydration time evolution of the magnetization recovery stretched exponent α (Fig. 2b) behaves in a similar way as the time evolution of T_1. In the dormant period both OPC and E-OPC have $\alpha \approx 1$ showing monodispersion in the spin–lattice relaxation. After the end of the dormant period, when the active surface of the cement paste starts to increase rapidly, α begins to deviate from 1, demonstrating the onset of polydispersivity in the pore size distribution as it was already predicted and measured [9]. At the end of the hydration process α approaches the final value of $\alpha \approx 0.5-0.6$. α is smaller for E-OPC than for OPC, demonstrating that the width of the pore distribution is larger in the sample with the additive than in the sample without it.
- A multicomponent analysis of the magnetization recovery curves $M = M(t)$ allows for the determination of the hydration time development of solid component contribution to the NMR signal, i.e. of the water entering the crystal structure of the cement. This component is characterized by a short T_2 and a long T_1 of about 800 ms. The development of this "solid" component is very gradual for the pure OPC sample. On the other hand, there is a steep increase of the solid component in the sample with the additive at $t_h = 5$ h, followed by a plateau where the fraction $M_{0(\text{solid})}/(M_{0(\text{solid})} + M_{0(\text{liquid})})$ does not increase appreciably. This plateau, or hydration pause, coincides with the plateau in $T_1(t_h)$, and is followed by another, more gradual growth after $t_h = 15-20$ h.
- At $t_h = 21$ days there is about 7.5% of "solid" NMR signal for E-OPC sample and about 5% for the OPC sample. This is compatible with the higher density of the E-OPC sample.
- During the "hydration pause" of E-OPC both the internal surface and the solid component of the NMR signal do not change appreciably. The stretched exponent α, however, shows a pronounced decrease during the same period. Therefore, although the *average* internal specific surface does not change much, it is obvious that the pore geometry significantly changes during the same period.

To summarize, ordinary Portland cement modified with the EXPAD expansion additive shows superior mechanical and water permeability properties. The NMR comparison of the hydration kinetics of ordinary and modified Portland cement shows significant differences both in the growth of the internal surface as well as the growth of the solid products. A combination of NMR with microstructural and kinetic scattering studies on normal and modified cements would help gain further insight into the relation between the microstructural effects and the expansion. To the best of our knowledge, no such study has so far been undertaken.

Acknowledgments

One of the authors (F.M.) would like to acknowledge the financial support from the NATO linkage grant HTEC LG 971363.

References

[1] H.F.W. Taylor, The Chemistry of Cements, Academic, London, 1964.

[2] F. Milia, G. Papavassiliou, M. Fardis, E. Laganas, E. Chionitakis, D. Fragoulis, C. Meletiou, NMR and MRI studies of cementitious materials, Mol. Phys. Rep. 6 (1994) 97.

[3] L. Titova, M.Yu. Titov, Increased concrete durability with the use of expansion agents, Proceedings of the International Conference "Durability and Protection Against Corrosion of Constructions", Moscow, Russia, 1999, p. 260.

[4] A. Zvezdov, L. Titova, Expansion of concrete — the real way of rise of the effective reinforced concrete construction, Concr. Reinf. Concr. 5 (1997) 23.

[5] J. Strupi Šuput, D. Dimic, T. Apih, Study on the influence of HRWR admixtures on the hydration processes of different types of Portland cements by means of NMR spectroscopy, in: J.G. Cabrera, R. Rivera-Villarreal (Eds.), Proceedings of the International Symposium "The Role of Admixtures in High Performance Concrete", RILEM, Monterrey, Mexico, 1999, p. 57.

[6] G. Lahajnar, R. Blinc, V. Rutar, V. Smole, I. Zupančič, I. Kocuvan, J. Uršič, On the use of pulse NMR techniques for the study of cement hydration, Cem. Concr. Res. 7 (1977) 385.

[7] R. Blinc, J. Dolinšek, G. Lahajnar, A. Sepe, I. Zupančič, S. Žumer, Spin–lattice relaxation of water in cement gels, Z. Naturforsch. 43a (1988) 1026.

[8] L. Barbic, I. Kocuvan, J. Uršič, G. Lahajnar, R. Blinc, I. Upančič, M. Rožmarin, Recherces de l'hydratation et des resistances des ciments par la resonance magnetique nucleaire, Ciment, Betons, Platers, Chaux 718 (1979) 172.

[9] G. Papavassiliou, M. Fardis, E. Laganas, A. Leventis, A. Hassanien, F. Milia, A. Papageorgiou, E. Chaniotakis, Role of the surface morphology in cement gel growth dynamics: A combined nuclear magnetic resonance and atomic force microscopy study, J. Appl. Phys. 82 (1998) 449.

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

[11] W.P. Halperin, J.-Y. Yehng, Y.-Q. Song, Application of spin–spin relaxation to measurement of surface area and pore size distributions in a hydrating cement paste, Magn. Reson. Imaging 12 (1994) 169.

[12] J.J. Thomas, H.M. Jennings, A.J. Allen, The surface area of hardened cement paste as measured by various techniques, Concr. Sci. Eng. 1 (1999) 45.

[13] A.B. Kudryavtsev, T.V. Kouznetsova, W. Linert, G. Hunter, A study of the hydration of aluminate minerals based on the measurements of the mean and the variance of the proton magnetic resonance relaxation time, Chem. Phys. 215 (1997) 419.

[14] J. Dolinšek, T. Apih, G. Lahajnar, R. Blinc, G. Papavassiliou, M.M. Pintar, Two-dimensional nuclear magnetic resonance study of a hydrated porous medium: An application to white cement, J. Appl. Phys. 83 (1998) 3535.

[15] J.C. MacTavish, L. Miljkovič, M.M. Pintar, R. Blinc, G. Lahajnar, Hydration of white cement by spin grouping NMR, Cem. Concr. Res. 15 (1985) 367–377.

[16] I. Emri, N.W. Tschoegl, Determination of mechanical spectra from experimental responses, Int. J. Solids Struct. 32 (1995) 817.