

J. Am. Ceram. Soc., 90 [12] 3973–3976 (2007)
DOI: 10.1111/j.1551-2916.2007.02034.x

Effect of nanosilica additions on Belite cement pastes held in sulfate solutions

J. S. Dolado^{a,c*}, I. Campillo^{a,c}, E. Erkizia^{a,c}, J. A. Ibáñez^{a,c}, A. Porro^{a,c},
A. Guerrero^{b,c}, S. Goñi^{b,c}

^a- Centre for Nanomaterials Application in Construction (NANOC), LABEIN-Tecnalia, Bilbao, Spain

^b- Institute of Construction Science “Eduardo Torroja, CSIC, Madrid, Spain

^c- Nanostructured and Eco-efficient Materials for Construction Unit, Associated Unit LABEIN-Tecnalia/CSIC, Spain

*- corresponding author: jsanchez@labein.es

Abstract

Fly Ash Belite cement (FABC) pastes with and without nanosilica additions have been prepared and maintained in sulfate solutions (Na_2SO_4 0.5 M) for 180 days. The mechanical performance and the changes in microstructure have been monitored at 28, 90 and 180 days by compressive strength, X-ray diffraction (XRD) and ^{29}Si MAS NMR measurements. We have found that, unexpectedly, and contrary to what happens in Ordinary Portland Cements (OPC), the addition of nanosilica particles induces an initial fall in the compressive strength of the samples. Only in samples maintained for long time (180 days), do the nanosilica addition improve the mechanical properties. Our XRD and ^{29}Si NMR experiments have revealed that although the nanosilica additions trigger the consumption of Belite phases, this is not always accompanied by formation of longer Calcium-Silicate-Hydrate (C-S-H) gel structures. Only at long time (180 days), and due to a mechanism that seems to be controlled by the pH of the samples, do the nanosilica additions lead to high polymerized C-S-H gels.

Keywords: cement-based materials, nanomaterials, mechanical properties, microstructure

(1) Introduction

Belite cements (BC) are nowadays receiving a great deal of attention by the scientific community due to the low CO₂ emissions produced during their fabrication.¹⁻⁴ Among them, those obtained from wastes such as fly ash from coal combustion as raw materials are called Fly Ash Belite Cements (FABC) and are especially appealing, since the CO₂ emissions could be totally avoided.^{3,4} Nevertheless, and although long-term hydrated BCs and FABCs display comparable mechanical properties to OPCs, their low reactivity and their low mechanical strength gain at early ages have limited their applicability.

Most of the attempts to circumvent these drawbacks have centered their attention into the synthesis procedure. High reactive β - C₂S structures have been sought by either quick cooling of clinkers or by incorporation of additive ions, such as alkalis or sulphates.⁵ Recently a new pathway based on the additions of nanoalumina has been explored to achieve faster strength gains.⁶ Although in Ordinary Portland Cements (OPC) the beneficial effect of adding nanoparticles has been studied for some time,⁷⁻¹⁰ in the case of Belite cements, to the best of our knowledge, no other work that previously mentioned Ref. [6] has been presented. In OPCs, the nano-SiO₂ and nano Al₂O₃ particles serve as surplus source of Si and Al atoms so that C-S-H gels can grow further and yield improved mechanical properties.⁷ Whether something akin occurs in Belite cements is unclear. On the one hand, Belite cements develop pore-solution with lower pHs (about 11-12) than that of OPCs (about 13-14) during the hydration process, fact clearly connected to their lower calcium content (C₂S versus C₃S) and low (or lack of) portlandite (Ca(OH)₂) formation, among other things. This difference is of extreme importance if one is aware that the pH governs most of the aggregation/disaggregation mechanisms involved in nanoparticle solutions. On the other hand, the microstructure of FABC cement pastes is noticeably different to the one found in

OPC pastes. Differently to the case of OPCs, where the C-S-H gel is the only hydrated product which contains Si atoms, the microstructure of FABC cement pastes also contain alumino-silicates and zeolite-like products which incorporate Si atoms into their structure.¹¹

This work aims precisely to investigate the effect of nanosilica additions on the mechanical properties and the microstructure changes of FABC pastes held in sulfate solutions. The employment of sulfate solutions as curing media was motivated by the need of simplifying as much as possible this study. As it will be shown later (Section II, Results and Discussion), when the hydration of FABC pastes is carried out in sulfate solutions no zeolite-like structures appear, being the C-S-H gel the only hydrated product with Si content. This considerably facilitates the discussion, since the effect of nanosilica additions can be solely looked for at the C-S-H gel level, and a closer parallelism with OPCs can be established.

II. Experimental Procedure

(1) Synthesis of FABC

Spanish coal fly ash of high Ca content (ASTM Class C) called FA-2, was used as raw material. The chemical composition of the FA-2, determined according to the Spanish standard UNE-EN 196-2, is given in Table 1. The FA-2 is in accordance with the requirements of ASTM Class C and the EN-UNE 450 specifications: $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ contents lower than 70% and high CaO content; its CaO/SiO₂ molar ratio is 1.

The fabrication process of the fly ash belite cement, called FABC-2-W, has two steps. A mixture of FA-2 and commercial CaO at a Ca/Si molar ratio of 2 was firstly hydrothermally treated in demineralised water at a solution-to-solid ratio of 3:1, with continuous stirring, at the temperature of 200°C, 1.24 Mpa pressure for 4 h. In a further step, the dried solid (80°C

over night) was heated at a rate of 10°C/min up to 600°C and 5°C/min from 600°C to 800°C.

The chemical composition of the product cements is presented in Table 1.

(2) Preparation of FABC pastes

Different kinds of samples have been prepared. As well as plain FABC-2-W cement pastes that have served as references (from now on denoted by R-samples), others with 7.5 % (by weight of cement) of colloidal nanosilica additions have been produced (hereafter N-samples). The nanosilica additions consisted of commercial aqueous dispersions of 15 nm-sized silica sols (Levasil, Bayer AG) which are ammonia stabilized and 30 mass % SiO₂.

Pastes were prepared at a demineralised water-to-cement ratio (w/c) of 0.75, with a commercial water reducer additive (Sika Viscocrete 20 HE) in a proportion of 1% (by weight of cement). It is worth mentioning that the colloidal silica samples were directly added to the mixing water and their water content was always accounted for when fixing the w/c ratio.

After mixing, the cement pastes were cast into prism-shaped moulds (1x1x6 cm) and compacted by vibration. The specimens were demoulded after 2 days at 90% relative humidity. Afterwards, and to raise further the pH of the pore-solutions, the samples were directly stored in sodium sulfate solution of 0.5 M (several sets of 40 samples per 1.7 L of the sodium sulfate solution) at 20 °C and held there for 180 days.

The mechanical properties of produced samples were assessed by compressive strength measurements, at 28, 90 and 180 days, and they were carried out under a Tester Ibertest Press. At the same ages, and due to the small amount of sample, an estimation of the pH of the pore-solutions was made by dissolving 1.25 g of powdered sample in 2.5 mL of de-ionized water. The mixture was maintained during 1 day at ambient temperature, after which

the solid was filtered and the liquid analyzed. The pH was measured with a combined electrode for the pH range 0-14. Belite consumption and the appearing crystalline phases were monitored by XRD experiments using a Phillips X'Pert Diffractometer. Finally, the effect at the C-S-H level of the nanosilica addition was analyzed by ^{29}Si MAS NMR measurements (Bruker Avance DSX300 spectrometer).

III. Results and Discussion

(1) Mechanical properties

In Figure 1 the obtained compressive strengths of R- and N-samples are compared for different curing times (28, 90 and 180 days). In view of this figure, it is fair to say that, in contrast to what happens in OPCs, nanosilica additions do not lead to an almost immediate mechanical gain. Interestingly the effect of nanosilica particles on the compressive strengths evolves through time. At 28 and 90 days, N-samples show a relative reduction in their compressive strength, about 20% and 15% of the R-samples respectively. However, at 180 days this behavior is completely reversed. In fact, at these long times, the usage of nanosilica additions entails mechanical gains of the order of 12%.

(2) XRD Analysis

The above discussed effects of the nanosilica additions on the mechanical properties must be somehow correlated to changes in the microstructure. To this end, the crystal structure of our samples was studied by XRD. On the one hand our study has shown (see Figure 2) that appearing crystalline structure consists of non-expansive ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$), Calcite (CaCO_3), unreacted Belite (Ca_2SiO_4), hydrated Belite ($\text{C}_2\text{SH}_{0.35}$), C-S-H gel ($\text{Ca}_{1.5}\text{SH}_x$), and negligible amounts of stratlingite ($\text{Ca}_2\text{Al}_2\text{SiO}_7 \cdot 8\text{H}_2\text{O}$). It should be

mentioned that some samples cured in water were also analyzed by XRD for comparison purposes. Although no presented, they confirmed the importance of stratlingite and zeolite-like forms in the microstructure of FABC pastes, as previously found elsewhere.¹¹ On the other hand, our XRD analysis has also revealed that, in general, the crystalline structure seems to be quite insensitive to the nanosilica additions. This finding seems to be consistent with some results reported on the effects of nanosilica additions on OPC pastes.⁷ The only perceptible difference might be at the main peaks of hydrated Belite and the C-S-H gel ($2\theta \sim 29-30^\circ$), where N-samples might present best defined peaks at cost of larger consumption of Belite ($2\theta \sim 32-33^\circ$)

(3) ²⁹Si MAS NMR Analysis

The most probable impact of nanosilica additions on cementitious matrices should be looked for at the level of the C-S-H gel. To this end several ²⁹Si MAS NMR experiments have been carried out, since this technique has proved to be a good tool to follow the polymerization of the (alumino)silicate chains that make up the cementitious C-S-H gel. In the case of C-S-H, and in general in silicates, a Qⁿ(mAl) nomenclature is used for the peaks, where Q is silicate tetrahedron connected via oxygen bridges to m Al and n-m Si atoms. In Figure 3 the obtained ²⁹Si MAS NMR spectra at 28, 90 and 180 days are plotted for the samples without (a) and with nanosilica additions (b). To aid the discussion the ²⁹Si NMR patterns obtained for the starting FABC-2-W cement and those of dried nanosilica particles are also plotted. As expected, they correspond to Q⁰ and Q⁴ peaks respectively. From these experimentally derived Qⁿ peaks, interesting information such as the degree of polymerization of the silicate chains (%P) (eq. 1), and the mean chain length (MCL) (eq. 2) can be extracted.¹²

$$\%P = 100 - Q^0 \quad (1)$$

$$MCL = 2(Q^1 + Q^2(0Al) + 3/2Q^2(1Al)) / Q^1 \quad (2)$$

The results obtained by employing the above formulas are listed in Table II. For reasons that will become clear in the discussion, the percentage of Q^4 sites and the pHs are also represented in Table II. In view of these data several conclusions can be extracted.

The first thing that it is worth noting is that, supporting the results found by XRD, the polymerization of the C-S-H gels of the samples with nanosilica additions seems to be faster than those without additions. This is especially noticeable at 28 days, where samples without additions have %P = 48%, whereas samples with nanosilica additions develop C-S-H polymerizations of about 62%. Only at long times (180 days) the polymerization of both kinds of samples reaches almost similar values (76-77 %).

Secondly we would like to draw the attention to the clear correlation between the MCLs and the mechanical properties. Similarly to the compressive strengths, the MCLs of the R-samples are clearly longer than those of N-samples at 28 and 90 days. However, as it happens for the compressive strengths, the situation is completely reversed at 180 days, and the N-samples exhibit longer chains.

It could seem contradictory at first sight the quick polymerization of N-samples and their short initial MCLs. However this point can be easily explained in terms of the appearance of non-linear forms (basically Q^4 sites). Note that at 28 days and 90 days, N-samples (see Table 2 and Figure 3 (b)) exhibit a noticeable presence of Q^4 -sites. In fact, the larger content of Q^4 sites at 90 days than at 28 days suggests that for some unclear reasons (see below for further discussion) the polymerization of N-samples is initially serving not only to produce C-S-H gels, but also to form bigger silica particles by some kind of Ostwald ripening mechanism.

Interestingly, and as it can be seen from Fig 3 (b) and Table 2, the content of Q^4 sites in N-samples is negligible at 180 days. This explains the large rise of their MCLs, since the whole silica content could participate in the formation of longer C-S-H structures. Why the previously formed tri-dimensional structures disappear at long times is a question that remains not completely clear to us. Since the pH of silica dissolutions governs the aggregation and dissolution mechanisms^{13,14} we have analyzed the pH of our samples at 28, 90 and 180 days. The values for the R-samples were 12.7, 12.3 and 12.4 respectively, whereas for the N-samples were 12.8, 12.2 and 13.1 respectively. It is noteworthy the large raise in the pH that occurs in the N-samples at 180 days. This high pH, as occurs in OPCs, seems to favor the dissolution of nanosilica particles, and consequently the formation of longer C-S-H structures. However, no definitive answer is given, and further research is needed.

IV. Conclusions

The effect of nanosilica additions on the compressive strengths of Belite pastes maintained in sulfate solutions (Na_2SO_4 0.5M) has been assessed at 28, 90 and 180 days. Basically we have found that, although at 28 and 90 days the compressive strength of the samples without nanosilica additions exceed the values found in samples with nanosilica additions, at 180 days the behavior is reversed.

Aiming at explaining these results in terms of microstructural changes, both XRD and ^{29}Si MAS NMR studies have been carried out, finding a clear correlation between the mechanical properties (compressive strengths) and the MCLs. Basically we have observed that although the nanosilica additions entail quick polymerizations, they haven't lead to the expected increase of the MCLs. The MCL of the samples with nanosilica additions only exceed those

of the reference samples at very long times (180 days). Moreover we have shown that, dissimilarly to the case of cement pastes without nanosilica additions, those with nanosilica additions present Q^4 sites. Although the fraction of % Q^4 sites is almost negligible at 180 days (below the 5%), noticeable amounts of Q^4 sites are observed both at 28 and 90 days.

The existence of such sites evidences that apart from C-S-H gel formation, in these samples there is a new growth mechanism (formation of silica clusters) that competes with the C-S-H gel for Si supply. This finding explains why quick polymerizations can be consistent with short silicate chains. Finally we have suggested that the pH of the cement paste seems to be ultimately responsible for the appearance/disappearance of such tri-dimensional structures, and therefore, a pivotal variable that regulates the mechanical performance.

References

- ¹ A. Guerrero, S. Goñi, A. Macías and M.P. Luxán, “Hydraulic Activity and Microstructural Characterization of New Fly Ash-Belite Cement Synthesized at Different Temperatures”, *J. Mater. Res.*, vol. **14**, pp. 2680-2687 (1999).
- ² S. Goñi, A. Guerrero, M.A. Macías, R. Peña and E. Escalante, “Secondary Raw Materials for Synthesising New Kind of Cements”, *Mater. Construcc.*, vol. **51**, pp. 263-264 (2001).
- ³ S. Goñi, A. Guerrero, A. Moragues, M.F. Tallafigo, I. Campillo, J.S. Dolado and A. Porro, “New Belite Cement Clinkers from Fly ash of Coal Combustion of High Ca Content”. *Spanish Patent Publication Number ES 2223275A1*.
- ⁴ A. Guerrero, S. Goñi, I. Campillo and A. Moragues, “Belite Cement Clinker from Coal Fly Ash of High Ca content. Optimization of Synthesis Parameters”. *Environ. Sci. Technol.*, vol. **38**, pp. 3209-3213 (2004).
- ⁵ P.C. Hewlett (Ed.) *Lea’s Chemistry of Cement and Concrete*, 4th Edition; Butterworth-Heinemann, 2004.
- ⁶ I. Campillo, A. Guerrero, J.S. Dolado, A. Porro, J.A. Ibáñez, S. Goñi. “Improve of initial mechanical strength by nano-alumina in Belite cements”. *Materials Letters* **61** (8-9) 1889-1892 (2007).
- ⁷ A. Porro, J.S. Dolado, I. Campillo, E. Erkizia, Y. R. de Miguel, Y. Sáez de Ibarra, A. Ayuela in *Applications of Nanotechnology in Concrete Design*, edited by R. K. Dhir, M. D. Newlands and L. J. Csetenyi, pp. 87-98 (Thomas Telford, London, 2005).

⁸ J. J. Gaitero, Y. Sáez de Ibarra, E. Erkizia, and Campillo, I. “Silicate Nanoparticle Addition to Control the Calcium Leaching in Cement-Based Materials” *Phys. Status Solidi A* **203**(6) 1313-1318 (2006).

⁹ G. Li. “Properties of High-volume Fly Ash Concrete incorporating nano-SiO₂”. *Cement and Concrete Research* **34** 1043-1049 (2004).

¹⁰ Z. Li, H. Wang, S. He, Y. Lu and M. Wang. “Investigations on the Preparation and Mechanical Properties of the Nano-Alumina Reinforced Cement Composite”. *Materials Letters* **60** 356-359 (2006).

¹¹ A. Guerrero, S. Goni, A. Moragues and J.S. Dolado. “Microstructure and mechanical performance of belite cements from high calcium coal fly ash”. *Journal of the American Ceramic Society* **88** (7) 1845-1853 (2005).

¹² I. G. Richardson. “The nature of C-S-H in hardened cements”. *Cement and Concrete Research* **29** 1131-1147 (1999).

¹³ Iller R. K ; *The Chemistry of Silica* (Wiley-Interscience, 1979)

¹⁴ C.J. Brinker and G.W. Scherer, *Sol-Gel science: the physics and chemistry of sol-gel processing* (Academic Press, San Diego, 1990).

FIGURE CAPTIONS

Figure 1. Compressive strengths for the reference samples (R-Samples) and for the ones obtained by adding colloidal nanosilica particles (N-samples) at 28, 90 and 180 days. The bars show the standard deviation of the data.

Figure 2. X-ray diffraction patterns for R-samples (upper panel) and N-samples (lower panel b) at 24, 90 and 180 days (**E** ettringite; **C** calcite; **a** α' -C₂S; **1** C₂SH_{0.35}; **2** C_{1.5}SH_x; **ST** stratlingite).

Figure 3. ²⁹Si MAS NMR spectra for C-S-H gels of the R-samples (a) and N-samples (b) after being 24, 90 and 180 days in a sulfate solution (0.5 M NaSO₄). To aid the discussion, the ²⁹Si NMR patterns of the starting cement (FABC-2-W) and those of the nanosilica additions (once dried) are also shown.

TABLE CAPTIONS

Table I Chemical Composition of the Starting Fly Ash (FA-2) and Belite cement (FABC-2-W) (% by weight).

Table II. Results obtained from the ²⁹Si MAS NMR: percentage of polymerisation of C-S-H gels (%P), Mean Chain Lengths (MCL) and percentage of Q₄ peaks. To aid the discussion the pH is also indicated.

Figure1

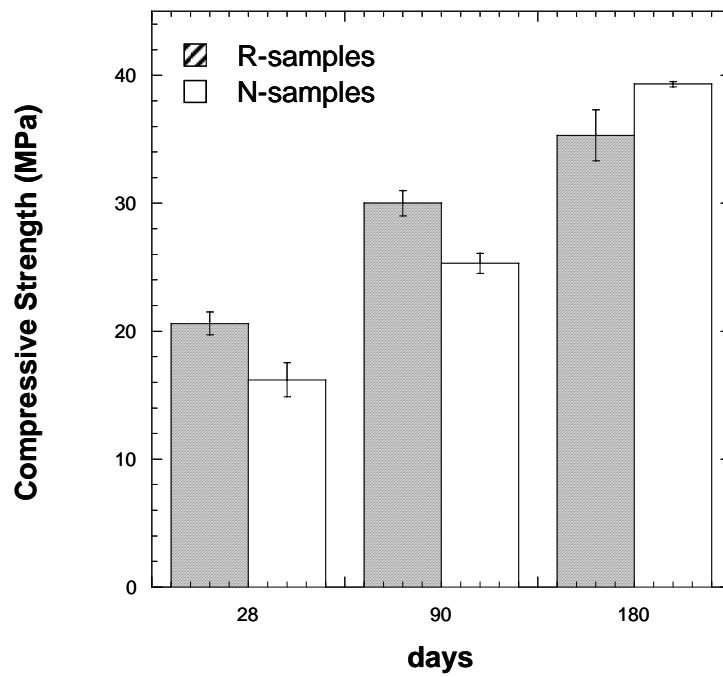


Figure 1. Compressive strengths for the reference samples (R-Samples) and for the ones obtained by adding colloidal nanosilica particles (N-samples) at 28, 90 and 180 days. The bars show the standard deviation of the data.

Figure 2

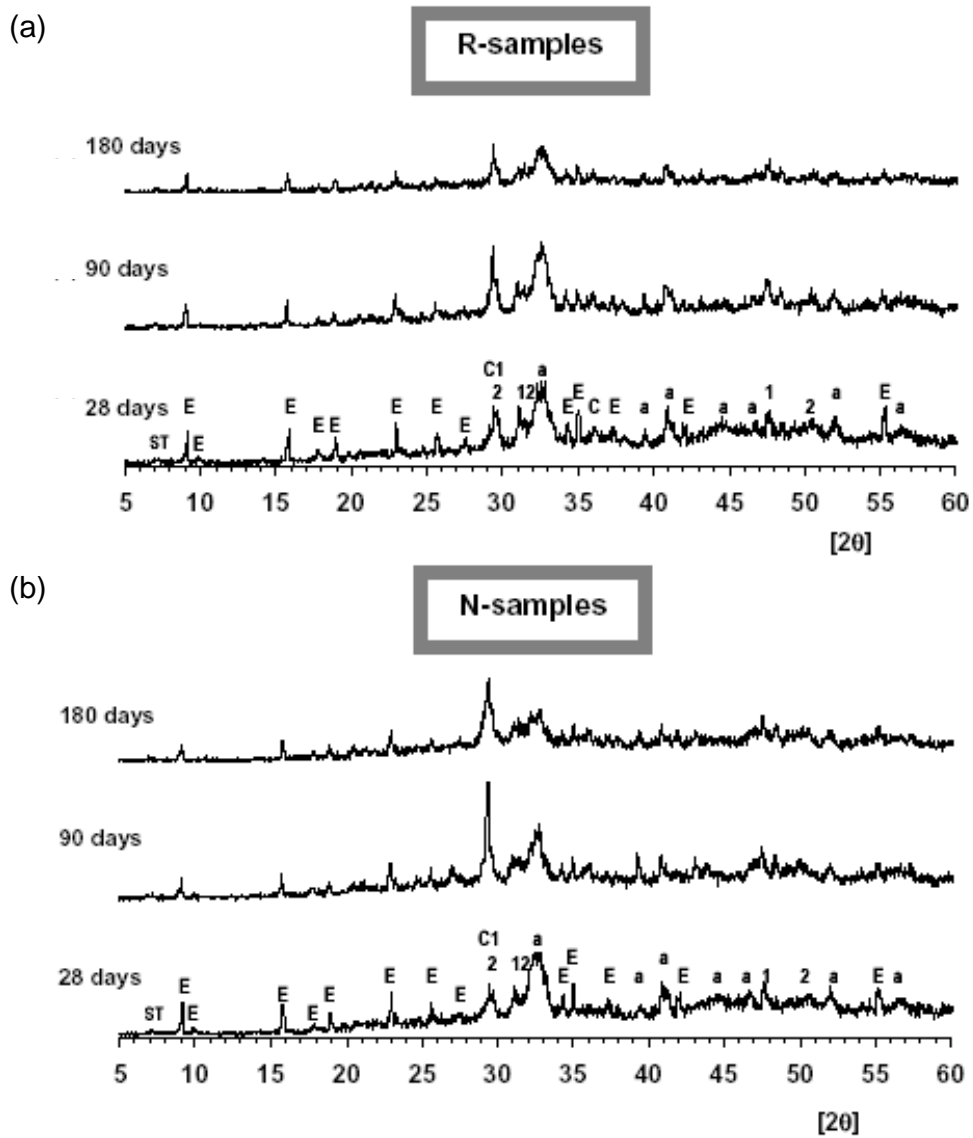


Figure 2. X-ray diffraction patterns for R-samples (upper panel) and N-samples (lower panel) at 28, 90 and 180 days (E ettringite; C calcite; a α' -L-C₂S; 1 C₂SH_{0.35}; 2 C_{1.5}SH_x; ST stratlingite).

Figure 3

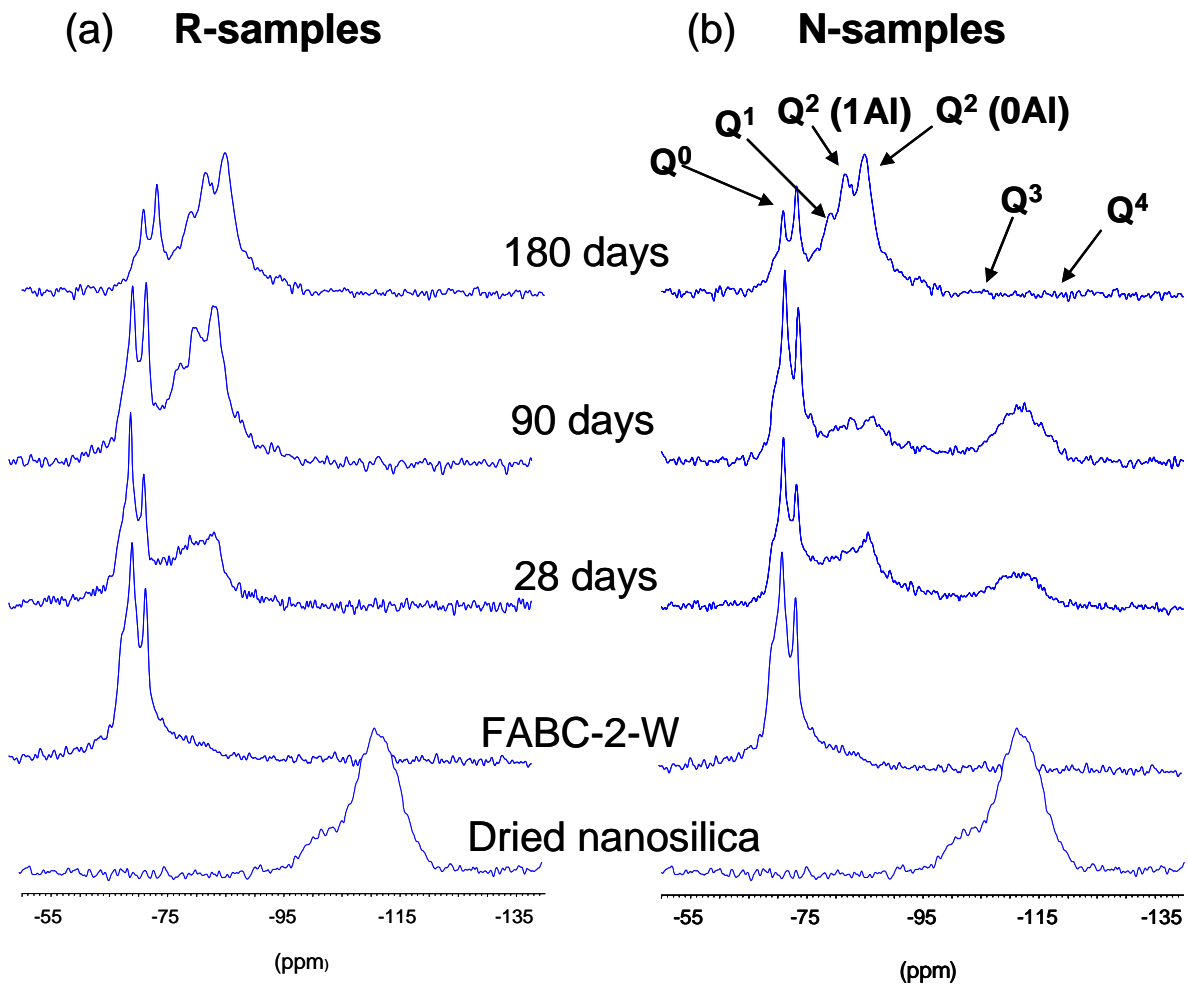


Figure 3. ^{29}Si MAS NMR spectra for the R-samples (a) and N-samples (b) after being 28, 90 and 180 days in a sulphate solution (0.5 M Na_2SO_4). To aid the discussion, the ^{29}Si NMR patterns of the starting cement (FABC-2-W) and those of the nanosilica additions (once dried) are also shown.

Tables

Table I Chemical Composition of the Starting Fly Ash (FA-2) and Belite cement (FABC-2-W) (% by weight).

	LOI	CaO	SiO ₂ (total)	Fe ₂ O ₃	Al ₂ O ₃	MgO	SO ₃	Na ₂ O	K ₂ O	SiO ₂ (reactive)	BET (m ² /gr)
<i>FA-2</i>	4.0	32.0	32.8	4.2	19.3	2.2	2.8	0.44	1.6	25.2	3
<i>FABC-2 W</i>	1.4	48.3	28.7	2.3	15.2	1.4	1.7	0.25	0.5	28.6	6.4

*LOI = loss on ignition; &Silica reactive according to Spanish standard UNE-80-224

Table II. Results obtained from the ²⁹Si MAS NMR: percentage of polymerisation of C-S-H gels (%P), Mean Chain Lengths (MCL) and percentage of Q₄ peaks. To aid the discussion the pH is also indicated.

	R-SAMPLES			N-SAMPLES		
	28 days	90 days	180 days	28 days	90 days	180 days
%P	48	58	76	62	67	77
MCL	15.6	15	14	10.8	12.5	16.95
%Q⁴	0	0	0	23	34	4
pH	12.7	12.3	12.4	12.8	12.2	13.1