Pergamon

Cement and Concrete Research, Vol. 26, No. 1, pp. 93-100, 1996

0008-8846/96 $15.00 + .00

0008-8846(95)00197-2

INVESTIGATION OF HYDRATION AND POZZOLANIC REACTION IN REACTIVE POWDER CONCRETE (RPC) USING ^{29}Si NMR

Hélène Zanni*, Marcel Cheyrezy, Vincent Maret**,**
Samuel Philippot, and Pedro Nieto***
*Laboratoire de Physique et Mécanique des Milieux hétérogènes, URA CNRS 857,
Ecole Supérieure de Physique et Chimie Industrielles de Paris
et Université Pierre et Marie Curie, Paris, France
**Direction Scientifique BOUYGUES, 78061 St Quentin en Yvelines, France

(Refereed)
(Received May 8; in final form November 6, 1995)

ABSTRACT

Hydration of RPC (Reactive Powder Concrete) and pozzolanic reaction were studied by ^{29}Si NMR using SPE/MAS technique. Industrial cement and materials (silica fume, crushed quartz) constitutive of RPC imposed a careful study of spectra acquisition (relaxation times, spinning velocity). . . . Two RPC formulations were tested. Samples having undergone heat treatment at temperatures between 20°C and 250°C were investigated in order to gain a better understanding of the influence of temperature on hydration and pozzolanic activity. It was shown that silica fume consumption was highly dependent on heat treatment temperature and duration. Crushed quartz reactivity was also clearly demonstrated. It was proved to be dependent on heat treatment temperature and duration. Q^3 peaks attributed to the presence of a crystal hydrate, xonotlite were identified at 250°C. Microstructural changes in hydrates structure were also observed. Average C-S-H chain length was shown to increase with increasing heat treatment temperature.

Introduction

Reactive Powder Concretes (RPCs) are chararacterized by high silica fume content and very low water to cement ratio; they also contain crushed quartz (1). They exhibit very high mechanical and durability properties (2). RPCs are a class of concretes with compressive strength between 200MPa and 800MPa, depending on the temperature of the heat treatment applied to concrete before and during its setting period. It was shown that mechanical and microstructural properties of RPCs were highly dependent on heat treatment (3).

^{29}Si NMR technique using single pulse excitation with magic angle spinning (SPE/MAS) was used to investigate hydration and pozzolanic reaction of two formulations of RPC with selected heat treatments temperatures and duration. The evolution of C-S-H oligomers average statistical size with temperature as well as the consumption of silica fume and crushed quartz are particularly important for the properties of RPC both on a mechanical and microstructural level.

Materials

Two RPC formulation were studied:

Formulation 1: OPC cement, silica fume, superplasticizer, water to cement ratio w/c = 0.115

For formulation 1, heat treatment was applied directly after demolding. Samples were placed in water at 20°C for 3days (C1/20°C/3d), 7days (C1/20°C/7d) or 28 days (C1/20°C/28d). A dry mix of OPC cement and silica fume in the same proportion as in composition 1 was also studied (C1/ref). This mix was not heat treated, it is a reference for composition 1.

Formulation 2: OPC cement, silica fume, crushed quartz, superplasticizer, w/c = 0.15.

For formulation 2 also, heat treatment was applied directly after demolding. Samples were submitted to various heat treatment conditions.

Some samples were heat treated with a final step in dry air at 90°C, the duration of which was 8 hours (C2/90°C/8h) or 24 hours (C2/90°C/24h) or 48 hours (C2/90°C/48h).

Some samples were heat treated with a final step in dry air at 200°C, the duration of which was 8 hours (C2/200°C/8h).

Some samples were heat treated with a final step in dry air at 250°C, the duration of which was 8 hours (C2/250°C/8h).

A dry mix of OPC cement, silica fume and crushed quartz in the same proportion as in composition 2 was also studied (C2/ref). This mix was not heat treated, it is a reference for composition 2.

Experimental

^{29}Si NMR experiments were carried out on two NMR BRUKER spectrometers, ASX 300 and ASX 500, combined with two superconducting magnets operating at 7.04 T and 11.7 T. In these fields, ^{29}Si nuclei resonance frequencies are respectively 59.62 and 99.35 MHz.

It is well known (4) that in the case of spin 1/2 nuclei, like ^{29}Si, single pulse excitation (SPE) allows to make a quantitative analysis of the different silicon species coexisting in the sample, the peaks area being proportional to the amounts of ^{29}Si entities.

Hence, those peaks follow, during hydration, the evolution of the different chemical species present in the sample—i.e.: anhydrous cement, silica fume, quartz, C-S-H. SPE was used associated with sample magic angle spinning (MAS). The MAS effect is to eliminate in the spectra the peaks broadening due to magnetic dipolar interaction and chemical shift anisotropy. Therefore only chemical shift isotropic contribution remains, leading to well-resolved peaks in the spectra, the positions of which are characteristic of the different ^{29}Si sites types. The analysis is based on the Q^n entities classification (5) where Q represents a SiO_4^{4-} unit and the degree of connectivity, n, is related to the oxygen bonds number between the SiO_4^{4-} units.

Chemical shift values were calibrated before the experiments using Q_8M_8 Si $[(CH_3)_3]_8Si_8O_{20}$ as a secondary standard, the major peak being at 11.6 ppm relatively to TMS, the tetramethylsilane $[Si(CH_3)_4]$.

In order to maximize the signal, ninety degree pulses were used, the duration of which was 5μs.

For a quantitative analysis three conditions were required:

- long enough recycle times to insure the spins relaxation of all the species present in the sample;
- fast rotation of the sample to eliminate sidebands in MAS experiments; a spinning speed

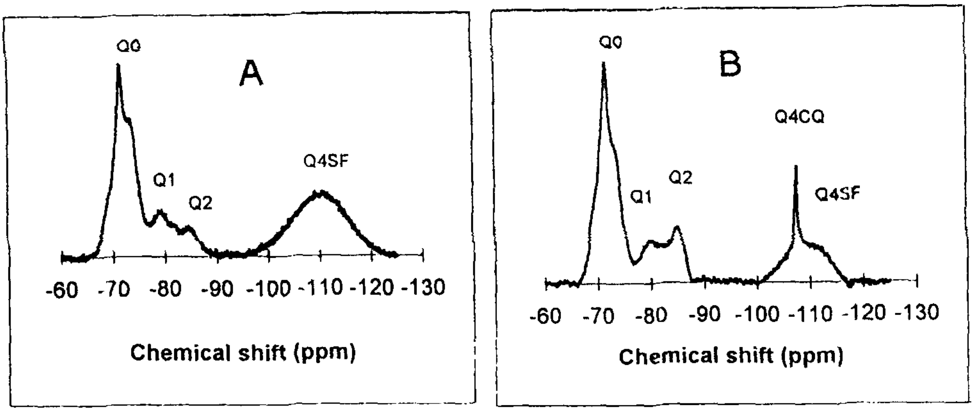

FIG. 1.
^{29}Si SPE/MAS Spectra of A: C1/20°C/28d sample and B: C2/90° C/8h sample.

equal to 7.5 KHz was used;

- sufficient acquisitions numbers due to the low material abundance of ^{29}Si nuclei (4,7%).

The recycle time between two acquisitions must be long enough (at least 3 times as much) compared to the time necessary for the relaxation of the species having the longest spin-lattice relaxation time T_1. In the case of formulation 1, the longest relaxation time is that of silica fume and a recycle delay of 30s was enough. In the case of formulation 2, quartz has the longest T_1 equal to 300s. Therefore two types of experiments were achieved for this formulation, one with a recycle time of 900s, in order to determine the proportion of Q^4 entities (Q^4_{FS} for silica fume and Q^4_{CQ} for crushed quartz) versus the other entities as a whole (cement and hydrated species). Another spectrum with a shorter recycle time (20s) to make a more precise analysis of Q^0, Q^1, Q^2 and Q^3 entities was acquired. In the first experiment the acquisition number was equal to 40, giving a total experiment duration of 10 hours. In the second experiment, the acquisition number might be equal to 3000 giving a maximum experiment duration of 17 hours.

The WINFIT BRUKER NMR program was used to simulate the spectra and determine by integration the respective proportions of each Q^4 unit.

Results

Commercial cement was used and it was possible to clearly identify Q^0 peaks attributed to anhydrous cementitious compounds. Nevertheless, it is obvious that the resolution of this peak was not sufficient to obtain separation between C_3S and C_2S. In the same way and as we discussed it before, Q^1 to Q^4 peaks could be integrated.

Heat treatment at 20°C was investigated with duration of 3 days, 7 days and 28 days. A dry mix of formulation 1 was also tested, as a reference. For each spectrum (Figs. 1A and B) the repartition of Q^0 to Q^4 species (Q^4 is separated into Q^4_{CQ} relative to crushed quartz and Q^4_{SF} relative to silica fume when crushed quartz is present in formulation) as a percentage of the total

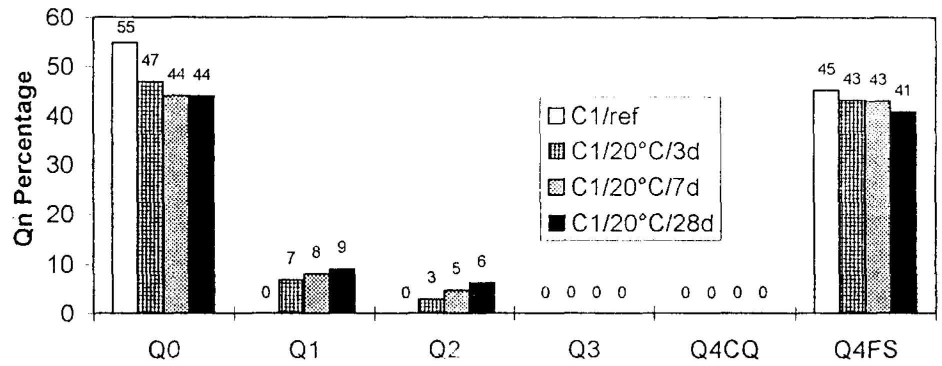

FIG. 2.
Q^0 to Q^4 percentages for formulation 1 samples with heat treatment at 20°C.

signal is computed (Fig. 2). The accuracy is approximately 5%.

Results are presented in Table 1. In this table, three parameters were computed:

Hydrates formation ratio, $H = (Q^1 + Q^2 + Q^3)$. H describes the proportion of cementitious compounds that were hydrated.

Connectivity ratio, $C = (Q^1 + 2Q^2 + 3Q^3)/(Q^1 + Q^2 + Q^3)$. C is related to the statistical average chain length of hydrate species.

Pozzolanic activity, relative to silica fume, $PFS = (Q^4_{FS}-Q^4_{FS0})/Q^4_{FS0}$. PFS is the percentage of silica fume that was consumed in comparison with the silica fume content of C1/ref dry mix reference composition for which consumption is assumed to be nil.

H and PFS values are given with a precision of 5%.

It is clear from Table 1 that hydration is progressing between zero day and 28 days at 20°C. Hydrates formation ratio is increased to 15% at 28 days. It is also important to notice that hydrates present at 20°C exhibit a majority of Q^1 peaks. This shows that hydration yields to the formation of relatively short C-S-H hydrate chains. Typically, the average statistical chain length corresponds to dimers or trimers. Hydrates remain linear since no Q^3 species are detected (Fig. 2). This behavior is typical of OPC hydration at room temperature [6,7].

TABLE 1

Hydrates Formation Ratio H, Connectivity Ratio C and Pozzolanic Activity of Silica Fume PSF of Formulation 1 Samples with Heat Treatment at 20°C

Sample	H	PSF	C	Statistical Length
C1/ref	0%	0%	—	—
C1/20°C/3d	10%	5%	1.31	dimer or trimer
C1/20°C/7d	15%	5%	1.38	trimer or quadrimer
C1/20°C/28d	15%	10%	1.41	trimer or quadrimer

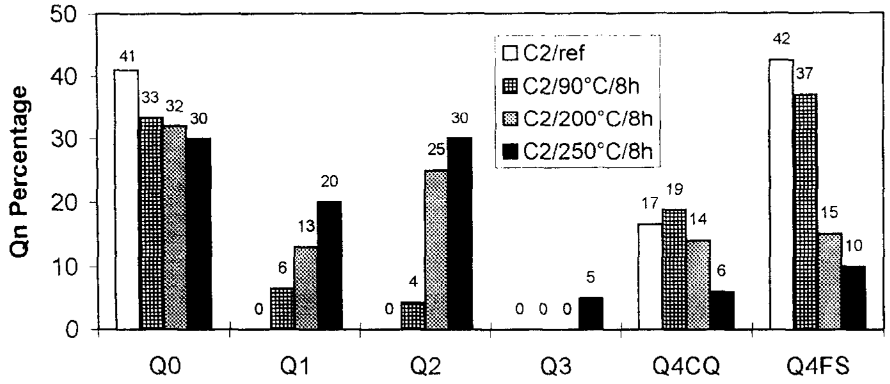

FIG. 3.

Q^0 to Q^4 percentages for formulation 2 samples with heat treatment at 90°C, 200°C, 250°C for 8 hours.

Pozzolanic activity is relatively low with a pozzolanic ratio of 5% to 10% between 3 days and 28 days. Nevertheless, it is confirmed that pozzolanic activity of silica fume exists at 20°C and that it progresses with time, leading to an increase of the C value (1.31 at 3 days, 1.41 at 28 days (8,9,10,11).

For temperatures between 90°C and 250°C, formulation 2 with the presence of crushed quartz was analyzed. Pozzolanic activity, relative to crushed quartz, $PCQ = (Q^4_{CQ} - Q^4_{CQ0})/Q^4_{CQ0}$. PCQ is the percentage of crushed quartz that was consumed in comparison with the crushed quartz content of C2/ref dry mix reference formulation for which consumption is assumed to be nil.

Samples with formulation 2 followed a heat treatment of constant duration (8 hours) in dry air at 90°C (C2/90°C/8h), 200°C (C2/200°C/8h) and 250°C (C2/250°C/8h). The percentages of Q^0 to Q^4 species at each temperature are gathered in Fig. 3. The results are presented in Table 2.

It is clear from Table 2 that there is an important effect of temperature on hydration of RPC. Hydrates formation ratio is increased from 10% to 55% between 90°C and 250°C. It is also

TABLE 2

Hydrates Formation Ratio H, Connectivity Ratio C, Average Statistical Chain Length, Pozzolanic Activity of Silica Fume PSF and Crushed Quartz PCQ of Formulation 2 Samples with Heat Treatment at 90°C, 200°C, 250°C

Sample	H	PSF	PCQ	C	Statistical Length
C2/ref	0%	0%	0%	—	—
C2/90°C/8h	10%	10%	0%	1.40	trimer or quadrimer
C2/200°C/8h	40%	65%	20%	1.65	pentamer or hexamer
C2/250°C/8h	55%	75%	65%	1.73	hexamer or heptamer

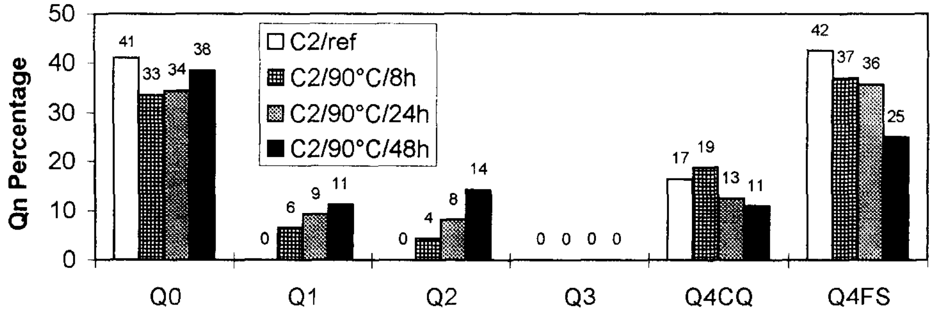

FIG. 4.
Q^0 to Q^4 percentages for formulation 2 samples with heat treatment at 90°C for 8 h, 24 h, or 48 h.

significant to notice that Q^2 increases faster with temperature than Q^1 (Fig. 3). This shows that C-S-H average statistical chain length is increasing with temperature. This point is also clearly demonstrated by statistical average chain length that corresponds to pentamer at 200°C when it was trimer at 90°C or 20°C. We can then conclude that microstructure of RPC is changed at high temperatures (200°C or more as compared to low temperatures 20°C to 90°C).

Between 200°C and 250°C another microstructural change was observed with the appearence of a Q^3 peak at 250°C (Fig. 3).

This peak was attributed to the presence of a crystal hydrate, xonotlite, whose structure implies the presence of silicon-oxygen tetrahedra connected to three neighbor tetrahedra (Q^3 species). This assumption was confirmed by XRD and water loss measurements (3).

The pozzolanic activity of silica fume is also greatly enhanced by temperature. PSF rises from 10% to 75% between 90°C and 250°C. It was also possible to demonstrate the engagement of crushed quartz in pozzolanic reaction at 200°C and 250°C (PCQ increases from 20% to 65%); it was not clearly observed at 90°C. We can conclude that pozzolanic activity of both silica fume and crushed quartz are greatly increased by temperature, silica fume being more active. This is not surprising since average grain size of silica fume (1µm) is much lower than that of crushed quartz (10µm). On NMR spectra (Fig. 1b) it is also clear that silica fume line is broader than the one of crushed quartz. This indicates a higher reactivity of silica fume due to a distortion of tridimensional SiO_4 lattice of silica fume (amorphous) compared to quartz (crystalline).

Finally, we investigated the influence of heat treatment duration with constant, 90°C, temperature. Results are presented on Fig. 4 and Table 3.

From the results of Table 3, we see that heat treatment duration is also very important between 8 h and 48 h, H increases from 10% to 25% which is much more than between 3 days and 28 days at 20°C. We must say that heat treatment duration is all the more important since temperature is increased. Statistical average chain length of C-S-H hydrates is also increased from trimer to quadrimer between 8 h and 48 h at 90°C.

Pozzolanic activity of both silica fume and crushed quartz were increased by heat treatment duration. Crushed quartz that was not clearly shown to be chemically involved after 8 h [PCQ = 0%] was shown to be very active after 48 h [PCQ = 40%].

We can conclude from this analysis that heat treatment duration is also very important for hydration and pozzolanic activity. It should also be mentioned that in Fig. 4, Q^0 peak at 48 h

TABLE 3

Hydrates Formation Ratio H, Pozzolanic Activity of Silica Fume PSF and Crushed Quartz PCQ of Formulation 2 Samples Cured at 90°C for 8 h, 24 h, 48 h

Sample	H	PSF	PCQ	C	Statistical Length
C2/ref	0%	0%	0%	—	
C2/90°C/8	10%	10%	0%	1.40	trimer or quadrimer
C2/90°C/24	15%	10%	30%	1.47	trimer or quadrimer
C2/90°C/48	25%	40%	40%	1.56	quadrimer or pentamer

[Q^0 = 38%] is extremely surprising since it is higher than at 8 h and 24 h. The explanation has not yet been clearly understood.

Conclusion

In conclusion, 2 RPC formulations with or without crushed quartz were analysed by SPE-MAS ^{29}Si NMR. Hydration reaction, statistical average chain length of C-S-H hydrates, pozzolanic reaction with both silica fume and crushed quartz were investigated. RPCs have followed heat treatments between 20°C and 250°C with various durations.

It was shown that at 20°C even after 28 days C-S-H chains were very small. Pozzolanic reaction was weak and slow.

At 90°C, it was shown that duration of heat treatment was very important and that long durations could lead to longer chains. Pozzolanic activity of both crushed quartz and silica fume were proved to increase with duration. Results similarly showed that increased heat treatment temperature led to longer C-S-H chains. This phenomenon can be attributed to the progression of cement hydration (12, 13, 14) as well as pozzolanic activity of both silica fume (15, 16) and crushed quartz. At 250°C, a microstructural change with the occurrence of Q^3 peak, attributed to the formation of xonotlite, was observed.

References

1. P. Richard, M. Cheyrezy, "Composition of Reactive Powder Concretes, Cement and Concrete Research", 25, 1501 (1995).
2. J. Dugat, N. Roux, G. Bernier, "Mechanical properties of Reactive Powder Concretes (RPC)", Materials and Structures, submitted.
3. M. Cheyrezy, V. Maret, L. Frouin, "Microstructural analysis of RPC (Reactive Powder Concrete)", Cement and Concrete Research, 25, 1491 (1995).
4. P. Granger, "Nuclear Magnetic Resonance Basic Principles", in Application of NMR Spectroscopy", p. 5–28, edited by P. Colombet and A. Grimmer, Gordon and Breach (1994).
5. G. Engelhardt, D. Michel, "High resolution ^{29}Si NMR of silicates and zeolites", John Wiley, Chichester (1987).
6. S.A. Rodger, G.W. Groves, N.J. Clayden, C.M. Dobson, "Hydration of tricalcium silicate followed by ^{29}Si high-resolution NMR with cross-polarization", J. Am. Ceram. Soc., 71, 91–96 (1988).
7. R. Rassem, H. Zanni-Théveneau, I. Schneid, M. Regourd, "^{29}Si high-resolution NMR study of tricalcium silicate hydration", "J. Chim. Phys., 86, 1253–64 (1989).

8. S.S. Beedle, G.W. Groves and S.A. Rodger, "The effect of fine pozzolanic and other particles on the hydration of C_3S", Adv. Cem. Res., 2, 5, 3-8 (1989).
9. G.W. Groves and S.A. Rodger, "The hydration of C_3S and ordinary Portland cement with relatively large additions of microsilica", Adv. Cem. Res., 2, 8, 135–140 (1989).
10. J. Hjorth, J. Skibstedand, H.J. Jakobsen, "^{29}Si MAS NMR studies of Portland Cement and effects of microsilica on the hydration reaction", Cem. Concr. Res., 18, 789–798 (1988).
11. H. Justnes, I. Meland, J.O. Bjoergum, J. Krane, "A ^{29}Si MAS NMR study of the pozzolanic activity of condensed silica fume and the hydration of di- and tricalcium silicates", Adv. Cem. Res., 3, 11, 111-116 (1990).
12. G.M.M. Bell, J. Bensted, F.P. Glasser, E.E. Lachowski, D.R. Roberts, M.J. Taylor, "Study of calcium silicate hydrates by solid state high resolution ^{29}Si nuclear magnetic resonance", Adv. Cem. Res., 3, 9, 23-27 (1990).
13. S. Masse, "Synthèse hydrothermale d'hydrates de silicate tricalcique. Analyse structurale en phase solide. Etude comparative avec les ciments utilisés pour chemiser les puits de pétrole", Thèse (Paris-1993).
14. S. Masse, H. Zanni, J. Lecourtier, J.C. Roussel, A. Rivereau, "^{29}Si solid state NMR study of tricalcium silicate and cement hydration at high temperature", Cement and Concrete Research, 23, 1169-1177 (1993).
15. A.R. Brough, M. Dobson, I.G. Richardson, W. Groves, "Application of selective ^{29}Si isotopic enrichment to studies of the structure of calcium silicate hydrate (C-S-II) Gels", J. American Ceramic Society 77 (2) 593-96 (1994).
16. G. Sun, J. Young, "Quantitative determination of residual silica fume in DSP cement pastes by ^{29}Si NMR", Cement and Concrete Research, Vol. 23, pp. 480–483 (1993).