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Structural characterization of magnesium silicate hydrate: towards the design of eco-sustainable cements

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1. pH measurements

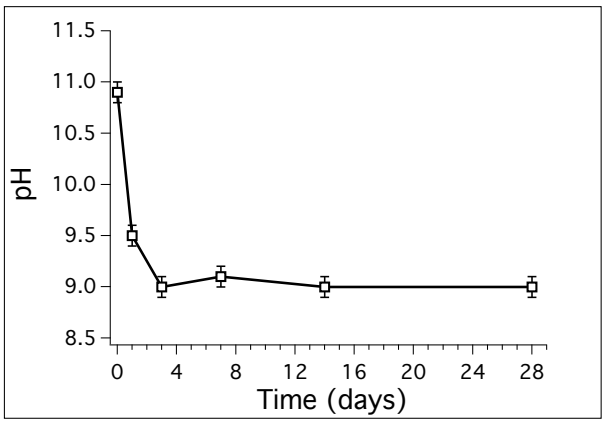

Figure S1. pH values of MS paste during the first 28 days of hydration.

2. Mass losses from TG measurements

Table S1. Mass losses from TG measurements during hydration.

	Mass loss from TG% curves (±0.5%)		
	RT-200 °C	310-400 °C	400-800 °C
MS_1d	13.4	6.8	4.6
MS_ 7d	19.4	4.0	5.4
MS_28d	15.3	3.2	6.5

3. ^{1}H-^{29}Si CP-MAS spectra at variable contact time

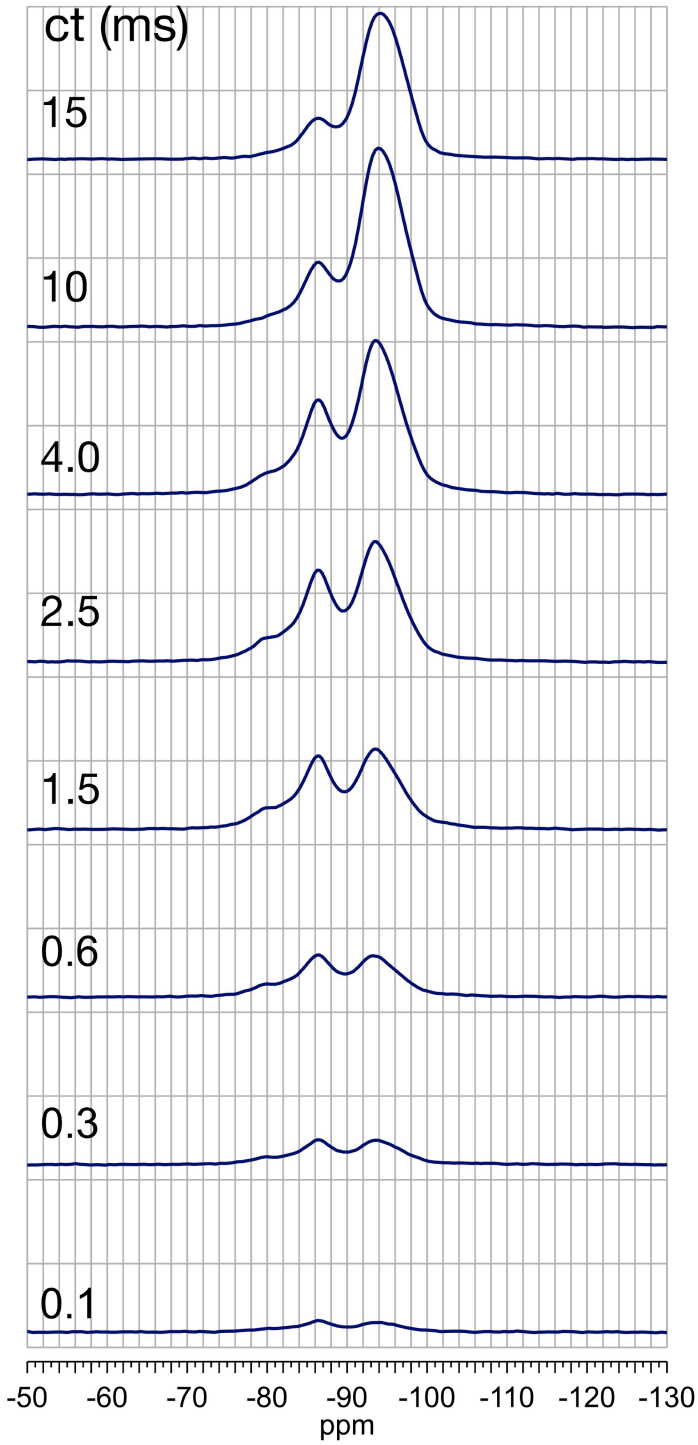

Figure S2. ^{1}H-^{29}Si CP-MAS spectra of MS_28d sample, recorded with the contact time (ct) values reported in the figure.

The ^{1}H-^{29}Si CP-MAS spectra recorded at different contact times (ct) have been successfully deconvoluted using the same peaks found from the fitting of ^{29}Si DE-MAS spectra.
The trends of the CP peak intensity vs. ct are typically fitted using the following equation [1]:

$$I(ct) = I_0 \frac{1}{(1 - T_{SiH} / T_{1\rho}^{H})} \left[\exp\left(-\frac{ct}{T_{1\rho}^{H}} \right) - \exp\left(-\frac{ct}{T_{SiH}} \right) \right]$$

where T_{SiH} is the so called cross-polarization time constant, $T_{1\rho}^{H}$ is the proton spin-lattice relaxation time in the rotating frame, and I_0 is the maximum intensity which could be theoretically obtained in a CP experiment, proportional to the intensity obtainable from a quantitative DE-MAS spectrum.
It is usually assumed that $T_{SiH} < T_{1\rho}^{H}$ (fast CP regime). In such case T_{SiH} is the time constant that determines the growth of the curve at short ct values, while $T_{1\rho}^{H}$ regulates the decrease at long ct values. However, one potential misinterpretation of the data might arise from the fast CP regime not being satisfied. Indeed, rarely, when Si and H nuclei are weakly dipolar coupled, their internuclear distance being quite large, the opposite situation $T_{SiH} > T_{1\rho}^{H}$ (slow CP regime) may occur. In this case the above equation still reproduces the experimental data, but the role of T_{SiH} and $T_{1\rho}^{H}$ is reversed with respect to the fast CP regime. A correct interpretation of the data therefore requires the knowledge of the CP regime. Although the same curve shape is obtained by exchanging T_{SiH} and $T_{1\rho}^{H}$ values, a striking difference between the two regimes is that the maximum value of I(ct) in the fast regime is quite close to I_0, while in the slow CP regime it is much lower, depending on T_{SiH} and $T_{1\rho}^{H}$ relative values [2]. In other words, fitting the same data with the assumption of fast CP regime gives a best-fitting I_0 value much lower than that obtained assuming a slow CP regime.
The CP intensity vs. ct curves were fitted for all silicon nuclei assuming a fast CP regime, and the best-fitting parameters (I_0, T_{SiH} and $T_{1\rho}^{H}$) so obtained are reported in Table S2. From the quantitative intensity values obtained from ^{29}Si DE-MAS spectrum (A%), reported in Table 3 of the manuscript, we found the ratios I_0/A%, which must be the same for all types of ^{29}Si nuclei, if I_0 is obtained assuming the correct CP regime. Considering the presence of close silanol protons, the fast CP regime can be safely assumed valid at least for Q^{1A}, Q^{1B} and Q^{2} silicons, for which I_0/A% values of 1.8, 2.2, and 2.0 were found. It can be seen that for Q^{3} silicons, for which the a priori assumption of one of the two CP regimes is more uncertain, I_0/A% values of the same order of magnitude (2.3 and 2.8) were obtained assuming the fast CP regime, while unacceptably larger values (16 and 9) were obtained assuming the slow CP regime. This is a clear indication that the fast CP regime is satisfied by all the silicons considered in this analysis.
Although the values of T_{SiH} reported in Table S2 are affected by quite large errors, the order T_{SiH} (Q^{1A})≈ T_{SiH} (Q^{1B})≈ T_{SiH} (Q^{2}) < T_{SiH} (Q^{3A}) < T_{SiH} (Q^{3B}) can be considered reliable, as also clearly observable from the slopes at short ct of the curves reported in Figure S3. This is in agreement with the fact that silanol protons contribute to the shorter T_{SiH} of Q^{1} and Q^{2} and suggests that Q^{3A} silicons have a larger number of close protons (Mg-OH) than Q^{3B} silicons.

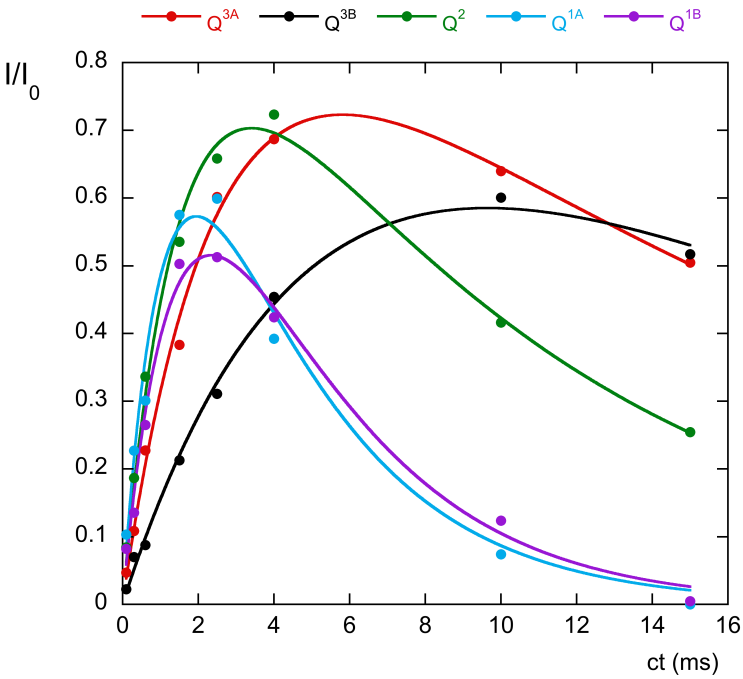

Figure S3. Experimental (points) and calculated (lines) values of I/I_0 vs contact time (ct) for the different peaks present in ^{1}H-^{29}Si CP-MAS spectra of MS_28d sample.

Table S2. Parameters obtained from the fitting of trends of the intensity vs the contact time for the different peaks present in the ^{1}H-^{29}Si CP-MAS spectra of the MS_28d sample, using the equation reported in the text.

	Q^{1A}	Q^{1B}	Q^{2}	Q^{3A}	Q^{3B}
I_0 (a.u.)	7 ± 1	11 ± 2	57 ± 4	67 ± 8	94 ± 8
T_{SiH} (ms)	1.2 ± 0.5	1.6 ± 0.4	1.6 ± 0.2	2.5 ± 0.4	6 ± 1
$T_{1\rho}^{H}$(ms)	4 ± 1	3.5 ± 0.9	10 ± 1	18 ± 4	18 ± 8

[1] W. Kolodziejski, J. Klinowski, Chem. Rev., 2002, 102, 613.
[2] C.A. Fyfe, D.H. Brouwer, P. Tekely, J. Phys. Chem. A, 2005, 109, 6187.

4. FTIR spectra deconvolution

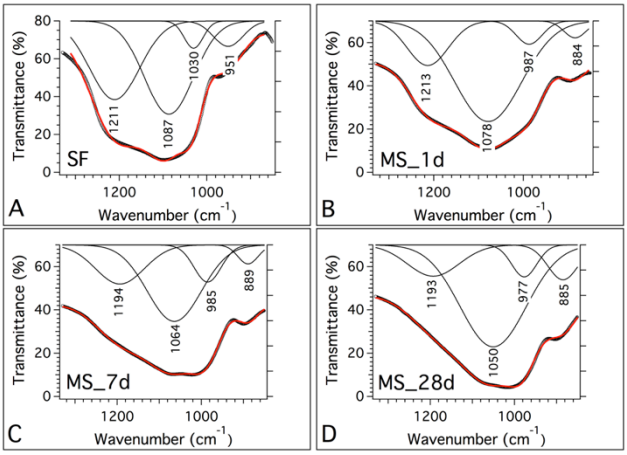

Figure S4. Deconvolution of FTIR spectra of Silica, MS_1d, MS_7d and MS_28d in the 1350-850 cm^{-1} range. Black markers and red lines represent experimental and calculated spectra, respectively. The Gaussian peaks obtained by means of the fitting procedure are shown as black lines.

Table S3. FTIR spectra deconvolution parameters for silica and MS_1d, MS_7d, MS_28d. Wavenumber of the maximum, Wn_{max} (cm^{-1}), and area (%) of the peaks are reported.

	silica	MS_1d	MS_7d	MS_28d
Wn_{max}	1211	1213	1194	1193
area	40.1	19.1	25.6	15.8
Wn_{max}	1087	1078	1064	1050
area	46.9	70.6	55.4	66.0
Wn_{max}	1030	987	985	977
area	5.3	6.3	13.9	7.8
Wn_{max}	951	884	889	885
area	7.7	3.9	5.1	10.3

Four Gaussian peaks were necessary to describe the vibrations of the Q^n silicon sites. According to the literature, the contribution at higher wavenumber is associated to the vibration of more condensed Si-O bonds. In particular the strong absorption at 1211 cm^{-1} in the silica spectrum is attributed to the vibration of Q^3 and Q^4 silicon sites [3]. Roughly at the same wavenumber the stretching of Q^3 silicon sites in M-S-H gel is also reported to occur [4]. The peak at higher wavenumber is observed to increase in the first week of hydration while it decreases afterwards. This fact can be explained considering that the disappearance of silica and the growth of M-S-H occur simultaneously. The same behaviour was already observed in the literature for M-S-H

samples synthesized from solution [4]. It is worth noting that after 28 days silica is completely consumed (see SSNMR data), so the 1193 cm^{-1} peak can be entirely ascribed to the presence of Q^3 silicon sites in the M-S-H binder phase. The three other peaks in deconvoluted spectra are related to stretching and bending vibrations of Q^2 silicon sites [4]. Also in this case the trend of the areas vs hydration time is not monotonic.

[3] P. Yu, R. J. Kirkpatrick, B. Poe, P. F. McMillan, X. Cong, J. Am. Ceram. Soc., 1999, 82, 742.
[4] D.R.M. Brew, F.P. Glasser, Cem. Concr. Res., 2005, 35, 85.