

COMPARISON OF MORPHOLOGY AND CHEMICAL STRUCTURE OF C-S-H SYNTHESIZED BY SILICA-LIME REACTION AND BY THE CONTROLLED HYDRATION OF C₃S

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1. Introduction

C-S-H is the main product of Portland cement hydration. In a CEM I system, the C-S-H has a Ca/Si ratio of ~1.7 and exhibits a fibrillar morphology. In other blends with SCMs (Supplementary Cementitious Materials) C-S-H composition and morphology vary. For example, the Ca/Si ratio exhibits a wide range, ranging from 0.66 to 2.2 [1]. For some systems, the morphology changes from foil-like to fibrillar as the Ca/Si ratio increases. However, very little is known about the origin of this change. It is still a subject of debate if this change in morphology depends exclusively on the chemical composition or if it is kinetically driven [2].

To investigate the relationship between the chemical composition, chemical structure and morphology of C-S-H phases, two synthesis routes have been explored. The mechanochemical route was used for silica-lime reactions; obtaining products with bulk Ca/Si ratios from 0.75 to 1.5. The second route was the hydration of C₃S under controlled lime concentration, which yields products with Ca/Si from ~1.2 to ~1.65. The chemical structure of the samples has been studied with ²⁹Si MAS NMR and the morphology with TEM.

2. Experimental procedure

2.1. Synthesis details

The mechanochemical synthesis, which was first used by Saito [3] to synthesize both C-S-H and tobermorite, was performed following the process described by Garbev et al. [4]. Mixtures of CaO and SiO₂ (Aerosil 200) were mixed in a roller mill with w/s=8. The amount of silica used to prepare each sample was 5 g, and the amount of CaO was adjusted to get bulk Ca/Si of 0.75, 0.83, 1, 1.25, 1.33 and 1.5. The water was deionized and freshly boiled to prevent carbonation. The materials were poured into a ball mill pot placed inside a glovebox under an N₂ atmosphere. Samples were milled for 20 min intervals, pausing for 10 min between milling. The total residence time was 36 hours (24 hours of milling). The slurries were rinsed with ethanol, filtered inside the glovebox and dried inside a reaction vessel for 3 days at 60°C, with an N₂ flow of 20 cm³/min. After drying, the samples were stored in sealed containers before analysis.

The hydration of C₃S was performed at 25°C in a reaction vessel where the lime concentration was controlled via the conductivity of the solution, according to a method described by Nonat [5, 6]. The solution was prepared at a fixed lime concentration, using CaO for undersaturated conditions, or by hydrating C₃S for supersaturated conditions. Samples were hydrated at fixed lime concentrations of 12, 15, 20 and 27 mmol/l for 10, 19, 23 and 14 hours respectively, which in turn corresponded to Ca/Si ratios of 1.25, 1.3, 1.5 and 1.65. The w/s was 50. While C₃S was hydrating, the controlled addition of deionized water was used to keep the lime concentration constant. The w/s ratio was maintained by pumping the same volume of added water from the solution. Hydration was stopped by filtering the solution and rinsing with a mixture of 50%-50% ethanol-water and afterwards pure ethanol. The samples were subsequently dried in vacuum for a day.

2.2. ²⁹Si MAS NMR

All the samples were studied using a Varian Direct-Drive VNMRS-600 spectrometer (14.09 T), using a homebuilt CP/MAS probe for 7 mm o.d. zirconia rotors. The spectra were acquired at 119.137 MHz, employing a spinning speed of 6.0 kHz, a 90 s relaxation, and were referenced to TMS using belite as an external reference. The spectra were deconvolved and iteratively fitted using the vnmrj software.

2.3. TEM

Bright field images were taken in a Tecnai TF20 FEGTEM at magnifications of 10-19K operating at 200 kV and spotsize 3.

3. Results and discussion

The ^{29}Si MAS NMR spectra of the mechanochemical samples are shown in Fig.1. The silicate structure of the C-S-H samples was dominated by middle chain groups (Q^2) for samples with $\text{Ca/Si} \leq 1$ and by dimers of SiO_4 tetrahedra (Q^1) for samples with $\text{Ca/Si} > 1$. For $\text{Ca/Si} < 1.25$, distinct resonances from the bridging and paired Q^2 ^{29}Si sites of the dreierketten silicate chain structure are observed at -83.2 and -85.5 ppm, respectively.

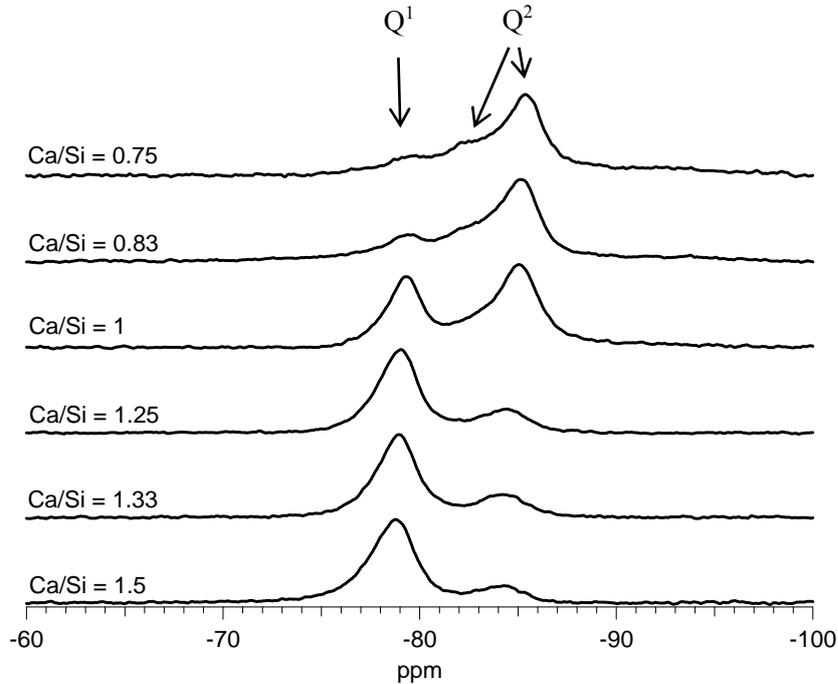


Fig. 1: ^{29}Si MAS NMR spectra of the mechanochemically synthesized C-S-H samples.

The results from the deconvolution of the spectra in Fig. 1 are summarized in Table 1. The silicate mean chain length (MCL) was calculated using the expression:

$$MCL = 2 \frac{\%Q^1 + \%Q^2}{\%Q^1} \quad (1)$$

Table 1. Summary of the silicate chemical species for the series of mechanochemical samples and the mean chain lengths (MCL).

Bulk Ca/Si	Q^1	Q^2	Q^3	MCL
0.75	9.5 %	79.8 %	10.7 %	18.8
0.83	19.1 %	77.1 %	3.8 %	10.1
1	35.7 %	62.0 %	2.3 %	5.5
1.25	74.0 %	26.0 %	0%	2.7
1.33	79.9 %	20.1 %	0%	2.5
1.5	87.7 %	12.3 %	0%	2.3

The MCL varied from 18.8 to 2.3 with increasing Ca/Si ratio; however, not in a linear manner. The MCL decreased dramatically when the Ca/Si ratio increased from 0.75 to 1.0. For $\text{Ca/Si} > 1$ the silicate structure

was similar in all samples, being dominated by dimeric units; hence the MCL was also similar. The morphology of the samples, shown in Fig.2, was foil-like irrespective of the Ca/Si ratio.

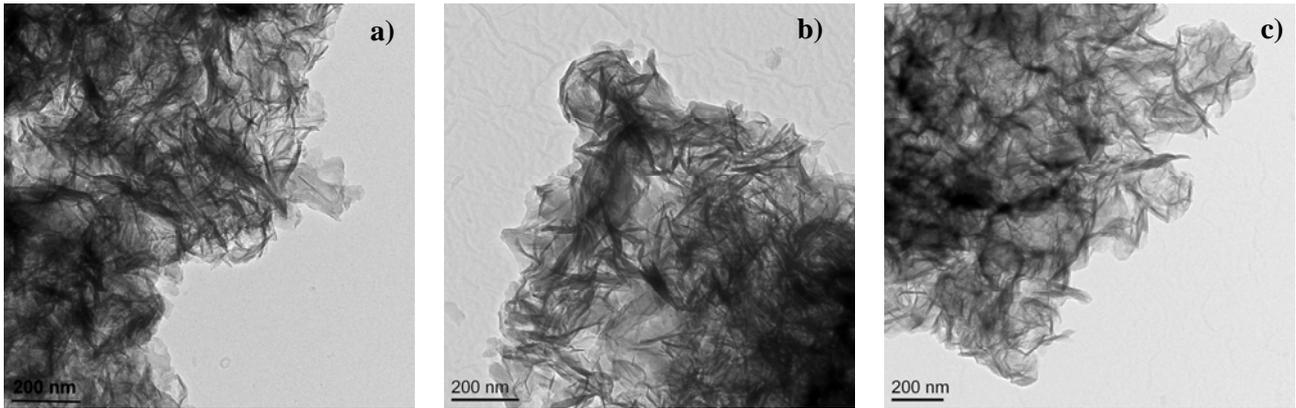


Fig. 2: TEM micrographs showing the crumpled foil-like morphology of the mechanochemically synthesized samples with bulk Ca/Si ratios of (a) 1.5, 1.25 (b) and (c) 1.0.

The ^{29}Si MAS NMR spectra of the samples fabricated at lime concentrations of 12, 15, 20 and 27 mmol/l are shown in Fig.3. The spectra show that most of the intensity originated from unreacted C_3S (Q^0), however, distinct peaks from the Q^1 and Q^2 sites of the C-S-H are also clearly observed. The silicate structure of the C-S-H in samples hydrated at $[\text{CaO}] > 12$ mmol/l was dominated by dimers, as is the case for the C-S-H that forms during the early hydration of C_3S without controlled lime conditions [7]; however, it is clear that the ratio Q^1/Q^2 is lower for the sample hydrated at a lime concentration of 15 mmol/l. The spectrum of the sample hydrated at $[\text{CaO}] = 12$ mmol/l shows similar intensities for both Q^1 and Q^2 sites.

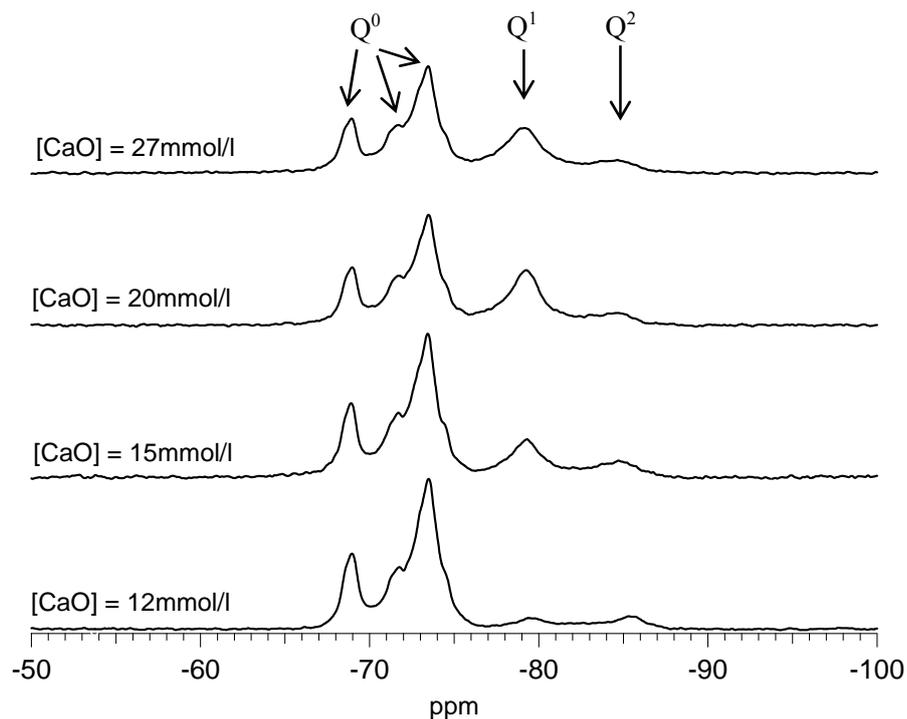


Fig. 3: ^{29}Si MAS NMR spectra of C_3S samples that were hydrated at fixed lime concentrations of 12, 15, 20 and 27 mmol/l.

The two micrographs (Fig.4) obtained from the samples that were hydrated with the lowest and the highest lime concentrations, 12 mmol/l and 27 mmol/l respectively, show very different morphologies. The sample that was hydrated at lower lime concentration is foil-like, while the sample that was hydrated at higher lime concentration, and hence has a higher Ca/Si ratio, is fibrillar.

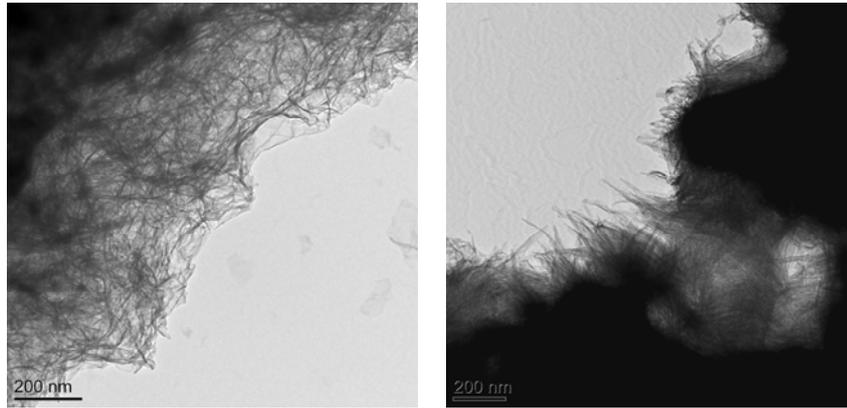


Fig. 4: TEM micrographs showing the foil-like morphology of a C_3S sample hydrated at $[CaO]=12\text{mmol/l}$ (left), and the fibrillar morphology of a C_3S sample hydrated at $[CaO]=27\text{mmol/l}$ (right). The dark areas correspond to unreacted C_3S .

4. Conclusions

Whatever the synthesis route (mechanochemical or controlled hydration of C_3S), C-S-H shows the same characteristics (morphology and silicate structure) for the same composition (Ca/Si ratio). In addition, the mechanochemical route yields samples of a similar morphology, being foil-like for all samples over a large range in composition and silicate structure. The controlled hydration of C_3S meanwhile yields systems that exhibit a change in morphology with a small change in silicate structure, being foil-like when prepared in low lime solutions (12mmol/l) and fibrillar when prepared in high lime solutions (27mmol/l). A similar change in morphology has been reported for water activated blends of Portland cement with slag [2]. The morphology changes from foils to fibers while the Ca/Si increases or the content of slag decreases. The results presented in this paper suggest that the calcium concentration in solution is the key parameter that drives this morphological change.

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