

Chemical structure and morphology of C-S-H synthesized by silica-lime reaction and by the controlled hydration of C₃S

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ABSTRACT

The main product of Portland cement hydration is C-S-H. Despite being more than half of the volume in hydrated pastes and having an important role in the strength development, very little is known about the factors that determine its morphology. To investigate the relationship between the chemical composition, chemical structure and morphology of C-S-H, several samples have been synthesized via silica-lime reactions (Ca/Si ratios from 0.75 to 1.5) and by the hydration of C₃S under controlled lime concentration [1] (Ca/Si ratios from ~1.3 to ~1.8) with and without accelerators. To investigate the role of hydration kinetics in the development of C-S-H morphology, the hydration was stopped at the acceleration period and the deceleration period for a given lime concentration without the use of accelerators. The chemical structure of the samples was studied with ²⁹Si MAS NMR and the morphology and chemical composition with TEM and SEM.

1. INTRODUCTION

C-S-H is the main product of cement hydration. It is known as the glue of cement, since it is the strength developing phase. However, very little is known about the relationship between its morphology with its chemical structure and composition. In a CEM-I system C-S-H has an accepted Ca/Si~1.7 and a fibrillar morphology. In water activated OPC-slag blends, C-S-H morphology changes from foils to fibers with increasing Ca/Si, or decreasing content of slag. However, in similar alkali activated pastes, the morphology is foil-like regardless the Ca/Si. The question whether C-S-H morphology depends only on the chemical composition or on growth kinetics remains open [2]. The simplest way to answer this question is to find synthetic analogues of C-S-H grown at controlled conditions, to determine the parameters that affect the morphology development. However, this has not been done in a systematic way yet. Kalousek and Prebus reported a similar morphological change from foils to fibers in synthetic C-S-H, nonetheless samples with Ca/Si up to 1.5 were synthesized via different routes and different reactants to samples with higher Ca/Si [3]. Moreover, some of their high Ca/Si products were not homogeneous, and

were possibly a mixture of a fibrous lime rich phase and a lower Ca/Si phase. It is accepted that the limiting Ca/Si of synthesis routes such as the silica-lime reaction and the double decomposition is ~1.5. To obtain C-S-H with higher Ca/Si ratios the use of C₃S is normally involved. Chen reported a method of decalcification and recalcification of hydrated C₃S pastes to fabricate C-S-H with a range of Ca/Si ratios from 0.62 to 1.87 [4], but never reported the morphology of these samples. Nonat implemented the hydration of C₃S at controlled lime concentration via the conductivity of the solution [1], obtaining C-S-H with Ca/Si ratios from 1.2 to 2. The influence of the acceleration (fast growth) and deceleration (slow growth) periods on C-S-H morphology was never studied.

2. EXPERIMENTAL DETAILS SYNTHESIS

Five different sets of samples were fabricated: 2 batches via silica-lime reactions and 3 batches via the controlled hydration of C₃S. Samples with Ca/Si=0.75, 0.83, 1, 1.25, 1.33 and 1.5 were fabricated via the mechanochemical route. Mixtures of lime and aerosil 200 were milled with w/s=8 for 36h, with on-off cycles of 20-

10min. The slurries were rinsed with ethanol and filtered in a buckner funnel and dried for 3 days over a hot plate at 60°C with a N₂ flow of 20cm³/min. Another set of similar samples called the CaO-SiO₂-Dijon series was fabricated with Ca/Si=0.75,0.8,1,1.27,1.35 and 1.42 continuously stirring at 20°C with w/s=50 for 4 days. The slurries were then filtered and rinsed with a mix of 50%-50% ethanol-water and pure ethanol afterwards. The samples were dried in vacuum for a day. The controlled hydration of C₃S was used to fabricate a set of samples at fixed lime concentrations of 12, 15, 17, 20, 22, 25 and 27mmol/l (Concentration controlled via the conductivity of the solution by the addition and removal of water) with Ca/Si from ~1.3 to ~1.8. The hydration was stopped at the acceleration period and at the deceleration period obtaining thus 2 different samples per concentration. The w/s was 50 and the temperature was 25°C. The samples were filtered and dried as the previous batch. Another set of 3 samples was synthesized via the controlled hydration of C₃S at controlled lime concentrations of 27, 28 and 29mmol/l with Ca/Si~1.6 using an ultrasound gun to accelerate the reaction. The w/s was 50 and the temperature 25°C. The samples were dried as the previous batch. A final batch of 3 samples was synthesized hydrating C₃S at lime concentrations of 27, 28 and 29mmol/l with Ca/Si~ 1.55 adding 1ml of Xseed solution. The initial w/s was 100 and it was not controlled (Continuous addition of water to maintain the conductivity). The temperature was 20°C. The samples were dried as the previous batch.

²⁹Si MAS NMR

All the samples were studied using a Varian Direct-Drive VNMRs-600 spectrometer (14.09 T), equipped with 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. The percentages of the silicate species that resulted from the deconvolutions were used to calculate the mean silicate chain lengths (MCL) and the degree of hydration (DR) using eq.1 and 2:

$$MCL = 2 \frac{\%Q^1 + \%Q^2}{\%Q^1} \quad \text{eq.1}$$

$$DR = 100 \cdot \frac{\%Q^1 + \%Q^2}{\%Q^0 + \%Q^1 + \%Q^2} \quad \text{eq.2}$$

TEM AND SEM

The morphology and chemical composition were studied with transmission electron microscopy and scanning electron microscopy. For TEM the samples were dispersed in ethanol and stirred in an ultrasonic bath for 1.5 min. A drop of the dispersed samples was deposited with a pipette over a 200 Cu mesh with a carbon film (Agar). Bright field images were taken in a Tecnai TF20 FEGTEM at magnifications of 10-19K operating at 200 kV and spotsize 3. For SEM the samples were dispersed on carbon sticks and then coated with a carbon layer of about 15 nm with a 208 Carbon Cressington carbon coater. An XL-30 SFEG FEI HR-SEM, equipped with an Oxford Si(Li) EDX detector, was used for imaging. UHR mode (ultra high resolution mode), with an accelerating voltage of 2.5 kV, spot 3, working distance of ~2.5 mm and magnification of 15000x were used.

3. RESULTS AND DISCUSSION

The morphology of the samples synthesized via the mechanochemical route and the CaO-SiO₂-Dijon is foil like, as can be seen in Fig.1. However samples of the latter set appear to have thinner and more defined features. Since the mechanochemical method is harsher, it is sensible that the surface of the samples appears rougher in this case. The evolution of the silicate species and the mean silicate chain length varies as expected with the Ca/Si (Fig.2 and Table 1). Low Ca/Si samples are dominated by middle chain groups (Q²), while high Ca/Si samples are dominated by dimers (Q¹). The mean silicate chain length decreases with the Ca/Si. For the samples fabricated via the controlled hydration of C₃S at constant lime concentration, the morphology varies from foils ([CaO]=12mmol/l) to fibers ([CaO]=27mmol/l) (Fig.3). However, for a given lime concentration, the morphology is the same stopping the reaction at the acceleration and deceleration period. The ²⁹Si NMR spectra show that very little C-S-H has grown during the acceleration period, since most of the intensity comes from unreacted C₃S (Q⁰) (Fig.4). For the deceleration period, C-S-H silicate structure starts showing a higher percentage of Q¹ species, as it is expected for high Ca/Si (>1.2). The MCL for the samples stopped at the deceleration period is practically the same (dimeric), except for the sample fabricated at [CaO]=12mmol/l, that shows a longer silicate chain (Table 4). The morphology of the samples synthesized with the aid of an ultrasound gun and Xseed at [CaO]=27mmol/l is mainly fibrillar (Fig.5), but the sample fabricated with the ultrasound gun has a flatten and more featureless surface.

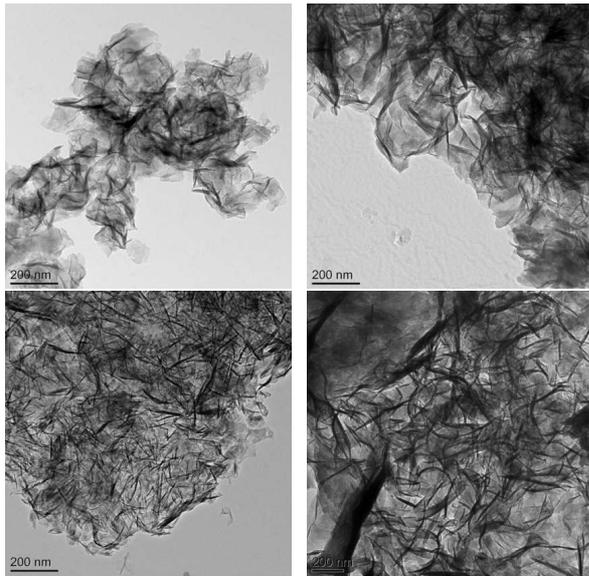


Figure 1. TEM micrographs of the mechanochemical C-S-H samples with Ca/Si= 0.75 and 1.25 (top left and right respectively) and the CaO-SiO₂-Dijon samples with Ca/Si=0.75 and 1.27 (bottom left and right respectively), showing foil-like morphology.

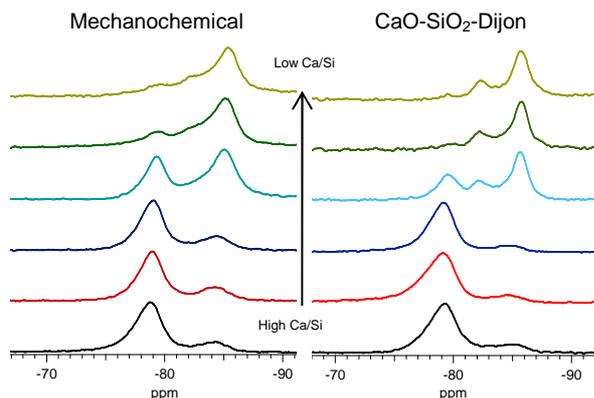


Figure 2. ²⁹Si MAS NMR spectra of the set of samples fabricated via the mechanochemical route and the CaO-SiO₂-Dijon set showing the progression of Q¹ (-79ppm) and Q² (-85 ppm) silicate species with the Ca/Si.

Table 1. Percentages of the silicate species and the mean silicate chain lengths of the mechanochemical (top) and the Dijon series of C-S-H samples (bottom) from NMR deconvolutions.

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
1.00	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
1.50	87.7%	12.3%	0%	2.3
0.75	1.5%	83.5%	15%	116.8
0.80	4.0%	90.8%	5.2%	47.1
1.00	34.3%	65.7%	0%	5.8
1.27	90.6%	9.4%	0%	2.2
1.35	92.5%	7.5%	0%	2.2
1.42	88.0%	12.0%	0%	2.3

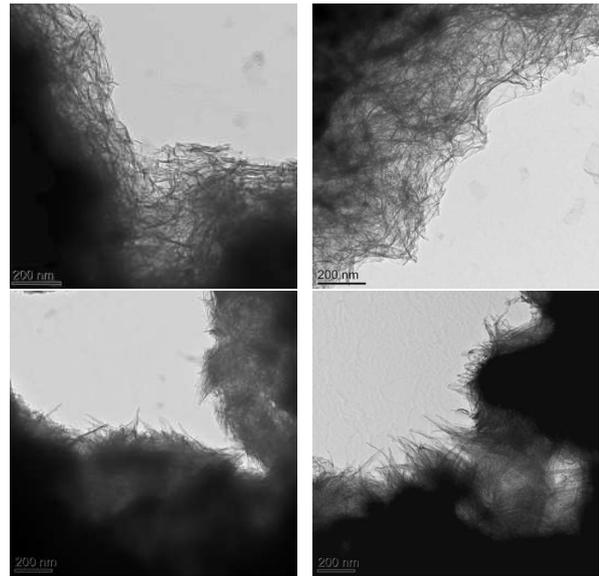


Figure 3. TEM micrographs of the C-S-H samples fabricated by hydrating C₃S at [CaO]=12mmol/l stopping the hydration at the acceleration period (top left) and deceleration period (top right) (Ca/Si~1.34) showing foil-like morphology, and equally for [CaO]=27mmol/l (bottom left and right), showing fibrillar morphology (Ca/Si~1.86).

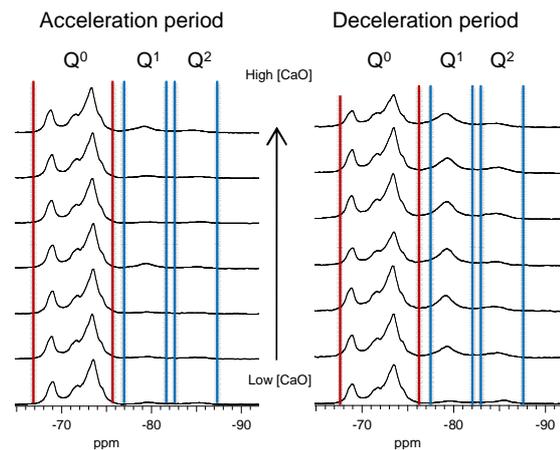


Figure 4. ²⁹Si MAS NMR spectra of the C-S-H samples fabricated by the controlled hydration of C₃S at lime concentrations from 12 to 27mmol/l, stopping the hydration at the acceleration period (left) and the deceleration period (right). The spectra show intensity coming from unreacted C₃S (Q⁰) and C-S-H (Q¹ and Q²).

The ²⁹Si NMR spectra show that the samples with ultrasound have longer silicate chains than the ones fabricated with Xseed, since they present higher percentage of Q² (Fig. 6). For similar degrees of reaction, the samples fabricated with the ultrasound show a higher ‘apparent’ degree of reaction, since they are more polymerized (Fig.7). The MCL is clearly related to the degree of reaction in both ultrasound and Xseed samples, since it increases for higher degrees of reaction (Table 2).

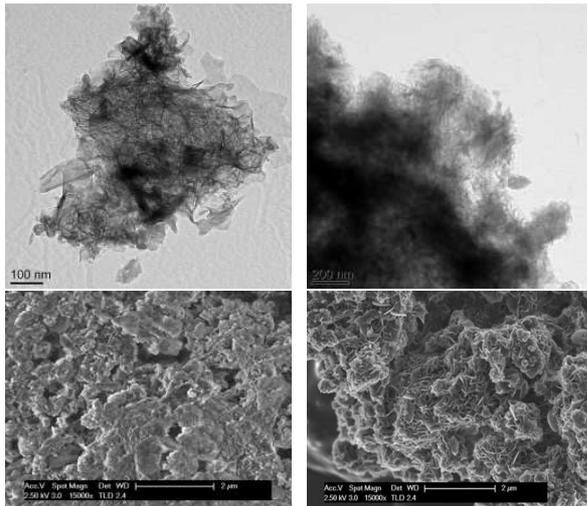


Figure 5. TEM and SEM micrographs of the C-S-H samples fabricated via the controlled hydration of C_3S at $[CaO]=27\text{mmol/l}$ with an ultrasound with $Ca/Si\sim 1.6$ (left) and Xseed with $Ca/Si\sim 1.56$ (right), showing fibrillar morphology.

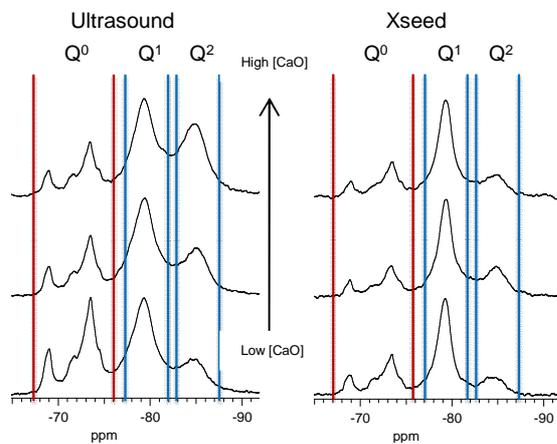


Figure 6. ^{29}Si MAS NMR spectra of the C-S-H samples fabricated by the controlled hydration of C_3S at high lime concentrations of 27, 28 and 29 mmol/l with the use of an ultrasound (left) and Xseed (right).

Table 2. Percentage of the silicate species, mean silicate chain length and degree of reaction of the C-S-H samples fabricated via the controlled hydration of C_3S stopped at the deceleration period (top), with the use of an ultrasound gun (marked with *) and the use of Xseed (marked with **) ($[CaO]$ is in mmol/l).

[CaO]	Q ⁰	Q ¹	Q ²	MCL	DR
12	87.0%	5.8%	7.2%	4.5	13%
15	74.3%	18.2%	7.4%	2.8	25.7%
17	71.7%	20.1%	8.2%	2.8	28.3%
20	67.6%	27.2%	5.2%	2.4	32.4%
22	67.8%	24.7%	7.5%	2.6	32.2%
25	68.2%	24.7%	7.5%	2.6	31.8%
27	63.0%	22.5%	9.3%	2.8	37.0%
27*	34.7%	49.9%	15.4%	2.6	65.3%
28*	23.8%	46.9%	29.3%	3.3	76.2%
29*	17.3%	44.7%	38.0%	3.7	82.7%
27**	29.0%	58.8%	12.2%	2.4	71.0%
28**	19.4%	58.8%	21.8%	2.7	80.6%
29**	22.6%	61.6%	15.8%	2.5	77.4%

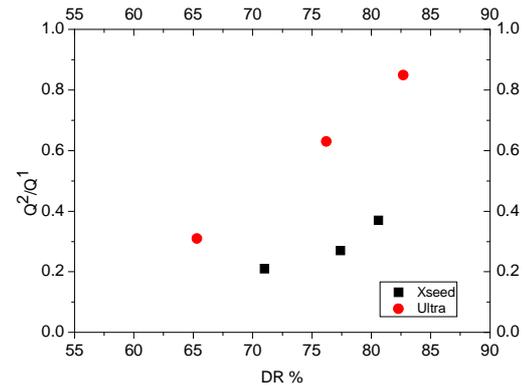


Figure 7. Graph showing the ratio Q^2/Q^1 over the degree of reaction for the C-S-H samples fabricated via the controlled hydration of C_3S with the use of an ultrasound and Xseed.

4. CONCLUSIONS

The results shown in this paper point out that the parameter which drives the morphological change in C-S-H is the lime concentration in solution, rather than the hydration kinetics. Samples which have grown at low lime concentrations in solution are foil like (mechanochemical, $CaO-SiO_2$ -Dijon and controlled hydration of C_3S with $[CaO]<22\text{mmol/l}$), while samples that have grown at high lime concentrations are fibrillar. However, the morphology is related to the silicate chemical structure of the sample, since samples with higher percentage of Q^2 (ultrasound) are shown to have more flatten surfaces than samples with lower percentages of Q^2 (Xseed). This agrees with the fact that flatten surfaces could accommodate longer silicate chains, while surfaces with edges and features would have more Q^1 groups.

REFERENCES

- [1] Nonat A. and Lecoq X. The structure, stoichiometry and properties of C-S-H prepared by C_3S hydration under controlled conditions. In: *NMR Spectroscopy of Cement Based Materials*, Springer-Verlag, 1998. p.197-207.
- [2] Richardson, I.G. Tobermorite/jennite-and tobermorite/calcium hydroxide-based models for the structure of C-S-H: applicability to hardened pastes of tricalcium silicate, beta-dicalcium silicate, Portland cement, and blends of Portland cement with blast-furnace slag, metakaolin, or silica fume. *Cem. Concr. Res.*, 2004, 34(9):p.1733-1777.
- [3] Kalousek, G. L. and Prebus, A.F., Crystal chemistry of hydrous calcium silicates: III Morphology and other properties of tobermorite and related phases, *J. Am. Cer. Soc.* 1958. 41(4):p.124-132.
- [4] Chen J.J., *PhD Thesis*, 2003, Northwestern University.

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