

P8: Relationship between composition, structure and morphology in C-S-H

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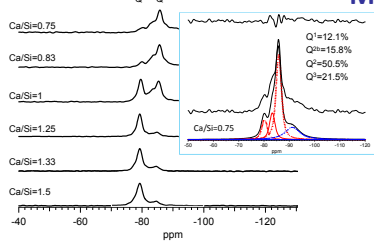
A native of Spain, Elena Tajuelo got her MS in Materials Physics and Nanotechnology at the University of Linköping in Sweden in 2010. She started to work at the University of Leeds in December 2010.

Project description

- Problem** → Outer product C-S-H exhibits different morphologies, from fibrillar to sheet-like foils in different cementitious systems. For some systems there is a change from foil-like to fibrillar morphology when the Ca/Si increases. It is not clear whether the change in morphology is determined by the structure and chemical composition (Ca/Si ratios) or it is kinetically driven. In general foil-like morphology is associated with tobermorite structural units while fibrillar morphology may be associated to the presence of jennite-like units [1].
- Relevance** → The capillary porosity is defined by the outer product C-S-H. Thus, the morphology of C-S-H partially determines transport properties and the durability of cementitious materials. This underlines the importance of understanding it to model the degradation and predict the service life of such materials.
- Methodology** → To investigate the relationship between the chemical composition, structure and morphology in C-S-H, synthetic C-S-H, with Ca/Si ratios covering the range of values that all commercial cements exhibit, between 0.66 and 1.5 and even >1.5, will be fabricated and compared with C-S-H in real systems. Synthetic systems are chosen because the conditions that affect the growth can be modified to study the influence of all of them individually, while in a cement paste, the influence of individual factors in the growth of C-S-H cannot be controlled. The main techniques to analyze the samples will be TEM and NMR.

Project results

MECHANOCHEMICAL SAMPLES



Synthesis details:
 • Stoichiometric mixtures of aerosil 200 and CaO were ball milled with w/s=8. The slurries were rinsed with ethanol and filtered. They were dried at 60°C for 3 days in an N₂ atmosphere.

The results show that;
 • The samples are single phase up to bulk Ca/Si of 1.33. XRD and FTIR/TG shows presence of portlandite in the sample with bulk Ca/Si= 1.5.

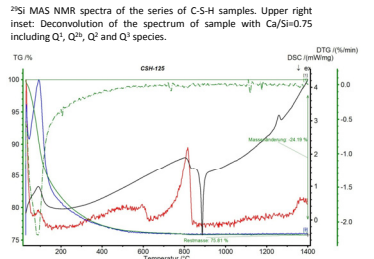
• The Ca/Si of the C-S-H is lower than the bulk ratio due to the formation of traces of carbonates and portlandite.

• Higher Ca/Si ratios in C-S-H than previously reported have been achieved for the samples with bulk Ca/Si=1.33 and 1.5, which for similar samples were reported as 1.24 and 1.28 [3]. In addition, the sample with Ca/Si=1.33 was portlandite free.

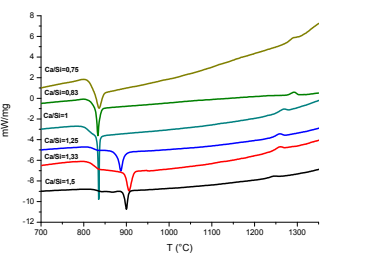
• The silicate structure in the samples is dominated by middle-chain groups (Q²) for the samples with Ca/Si up to 1 and dominated by dimers (Q¹) for the samples with Ca/Si between 1.25 and 1.5. The silicate MCL (mean chain length) varies over a wide range, from 13 to 2.4, with increasing Ca/Si.

• The morphology is crumpled foil-like regardless of the Ca/Si.

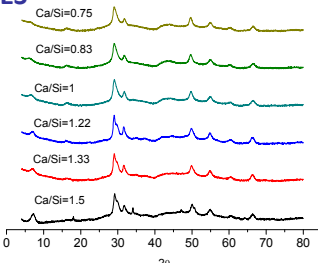
• The temperature for the transformation of C-S-H into wollastonite (800° C-900° C) depends on the Ca/Si, being lower for lower Ca/Si. The temperature for the transformation of β-wollastonite into α-wollastonite (~1250° C) is higher for lower Ca/Si, which implies that excess SiO₂ stabilizes the β polymorph, while an excess of CaO stabilizes the α polymorph.



FTIR/TG results for the sample with Ca/Si=1.25. TG in green, DTG in green, DSC in black, water FTIR trace in blue, CO₂ FTIR trace in red.



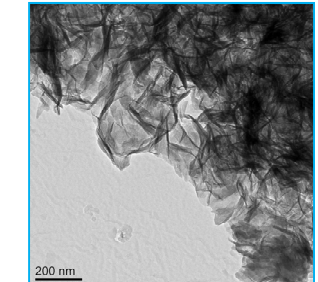
DSC of the samples showing the transformation of C-S-H into wollastonite (800-900° C), and the transformation from β-wollastonite into α-wollastonite (~1250° C).



XRD patterns of the series of C-S-H samples showing the resemblance to C-S-H (J). Portlandite is seen in the sample with higher Ca/Si (Peaks at 2θ=18°, 34° and 47°).

Bulk Ca/Si	Actual Ca/Si	Q ¹	Q ²	Q ³	MCL
0.75	0.71	12.1%	66.3%	21.5%	13.0
0.83	0.79	14.2%	70.9%	15%	12.0
1	0.96	41.7%	50%	8.3%	4.4
1.25	1.22	81.4%	18.5%	0%	2.5
1.33	1.29	82.6%	17.4%	0%	2.4
1.5	1.34	82.7%	17.3%	0%	2.4

Table showing the corrected Ca/Si calculated from TG results taking into account carbonates and portlandite content and mean chain lengths MCL=2*(Q²+Q³)/Q¹, where %Q are given by NMR deconvolution.

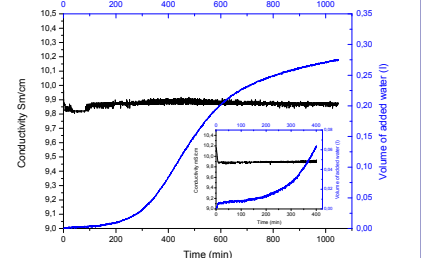


TEM micrograph showing the crumpled foil-like morphology of C-S-H with bulk Ca/Si=1.25.

HYDRATED C₃S AT CONSTANT [CaO]

Synthesis details:
 • The Ca/Si of C-S-H formed by the hydration of C₃S can be controlled by the lime concentration in solution (higher Ca/Si if higher [CaO]). C₃S was hydrated at 25° C and w/s=50. The [CaO], which is proportional to the conductivity in the solution, was kept constant by the controlled addition of deionized water, whilst water was simultaneously removed from the solution to keep the w/s constant. The hydration was stopped at two different times, when the growth rate was high and when the growth rate slowed down, to explore if growth kinetics affect the morphology of C-S-H. At these conditions the degree of hydration can be calculated as:

$$\alpha = \text{Volume added water} [\text{CaO}] / \{ [3-\text{Ca/Si}] \text{ moles of } \text{C}_3\text{S} \}$$



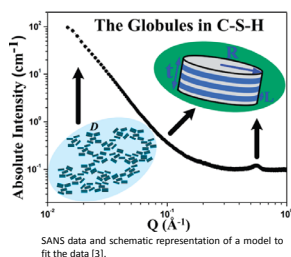
Graph showing the controlled hydration of C₃S at [CaO]=22mmol/l (~9.9 mS/cm at 25° C). The controlled conductivity is shown in black. It can be noticed that from a mean conductivity value, the variations were not higher than ± 0.1 mS/cm. The hydration curve expressed as the addition of water vs time is shown in blue. The hydration was stopped after 1000 min, when the growth rate was low. The inset figure shows the hydration of a sample at the same conditions but stopped when the growth rate was high (before the inflexion point in the hydration curve).

[CaO] mmol/l	Approx. Ca/Si	α(low)	α(high)
15	1.3	11%	30%
17	1.4	8%	29%
20	1.5	18%	37%
22	1.6	8%	33%
25	1.7	13%	41%
27	1.8	24%	49%

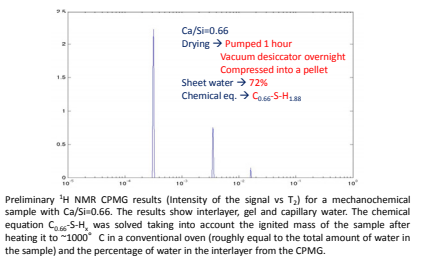
Table showing a list of samples fabricated by this method. For each time concentration two different samples were fabricated stopping the hydration at high and low growth rate. The approximate Ca/Si and the degree of hydration are shown.

What I am planning to do for the remaining time

- Assess if the growth kinetics and/or the Ca/Si affect the morphology of C-S-H fabricated by controlled hydration of C₃S.
- Solubility measurements (Holcim) to be compared with Chen's data [2] and to elucidate if the interlayer Ca may have some influence on morphology.
- Perform SANS to characterize a variety of samples to get information about how the growth kinetics, the Ca/Si, the dilution and the drying method affect the morphology and the globule assembly in C-S-H. A model developed by E. Fratini will be applied to fit SANS data.



- Try out other synthesis routes, such as the double decomposition and the decalcification of fully hydrated C₃S pastes.
- Collaboration with other projects:
- Define a method to measure the interlayer water using ¹H NMR to improve preliminary results in collaboration with project 7. Synthetic tobermorite shall be tested for validation of results and to provide T₁ and T₂ relaxation times for project 1.
- Gain information about the microstructure from TEM image analysis in collaboration with project 2.



Preliminary ¹H NMR CPMG results (Intensity of the signal vs T₂) for a mechanochemical sample with Ca/Si=0.66. The results show interlayer, gel and capillary water. The chemical equation C₃S + 5H₂O → C₃S₂H_{1.28} was solved taking into account the ignited mass of the sample after heating it to "1000° C in a conventional oven (roughly equal to the total amount of water in the sample) and the percentage of water in the interlayer from the CPMG.

Outstanding questions

- Is the change in morphology of C-S-H dependent on chemical composition? or Do growth kinetics play a role?
- Is the morphology of C-S-H affected by different drying methods such as heating or pumping?
- Does the amount of interlayer water in C-S-H depend on the Ca/Si?
- Are differences in solubility in C-S-H not only related to interlayer Ca and MCL but to morphology changes?
- How are the C-S-H globule assembly and globule geometrical parameters affected by changes in dilution, Ca/Si, growth rate and drying method?

References

[1] Richardson, I.G, Cement and Concrete Research, 2004. 34(9): p. 1733-1777.
 [2] Chen J. J. et al., Cement and Concrete Research, 2004.34(9): p. 1499,1519
 [3] Chiang, W.-S., et al., Journal of Physical Chemistry C, 2012. 116(8): p. 5055-5061.