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

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OVERVIEW

❖ **Problem→**The 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 and C-A-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, such as temperature and the addition of other elements (Al or alkalis) 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.

SYNTHESIS ROUTES

❖ **Mechanochemical:** Stoichiometric mixtures of CaO and SiO_2 are mixed with boiled deionized water (w/s=8) in a roller mill to obtain samples with Ca/Si from 0.66 to ~1.5. The slurries are then filtered in a buckner funnel and dried at 60˚C.until their water content is ~20-25%. The process is very similar to the one used by Garbev et al. [2], but introducing the filtering step to minimize the drying time. The products are expected to resemble C-S-H (I) and have foil like morphology. Al substituted samples can be fabricated by adding either $Al(OH)_3$, hydrogarnets or C_3A in the raw mixture.

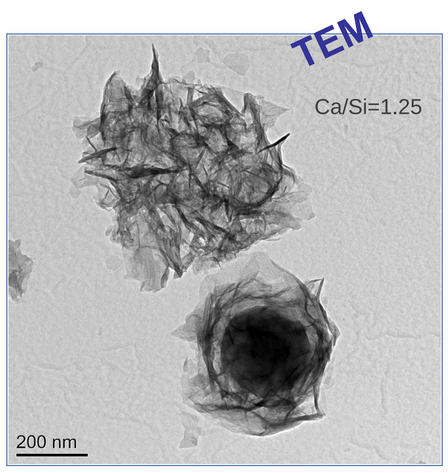
❖**Stirred suspensions of CaO and SiO_2 with enrichment of ^{29}Si:** Similar products than the ones fabricated by the previous method can be fabricated by this route. The silicon enrichment is necessary to examine the structure in terms of correlations of the silicate species [3].

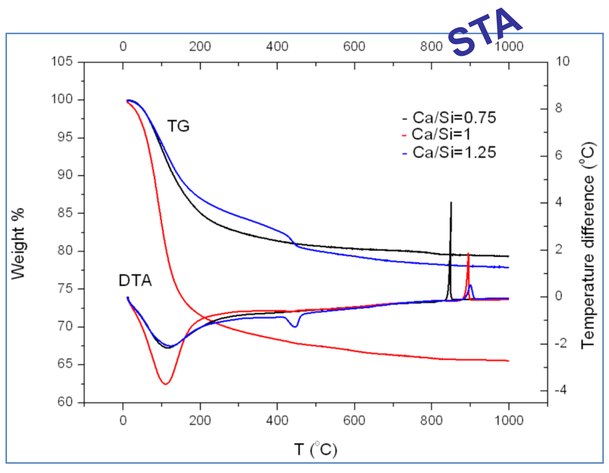
❖**Hydration of C_3S under controlled conditions:** The hydration of C_3S under ultrasonication and maintaining the lime concentration constant from 6 to 30 mmol/l ,can yield C-S-H products with Ca/Si ratios from 1.2 to 2 [4]. It will be used in this project with the aim of obtaining samples with Ca/Si>1.5, since it is not clear if their morphology will be foil-like or fibrillar.

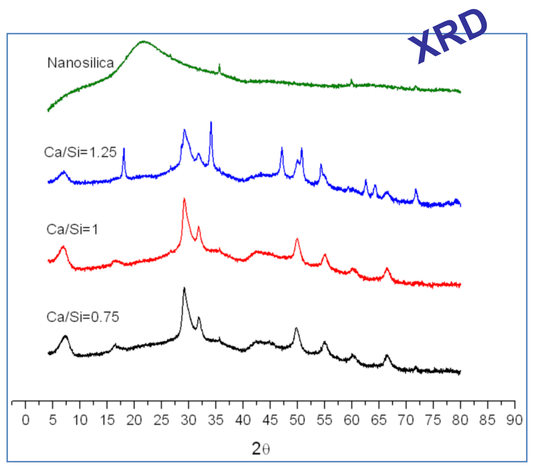
❖**Decalcification and recalcification of hydrated C_3S paste:** Leaching a fully reacted C_3S paste with NH_4NO_3 can serve to eliminate all the portlandite in the paste. The recalcification of the leached products in saturated lime solutions has been reported to yield C-S-H with a Ca/Si ratio of 1.08 to 1.87 [5].

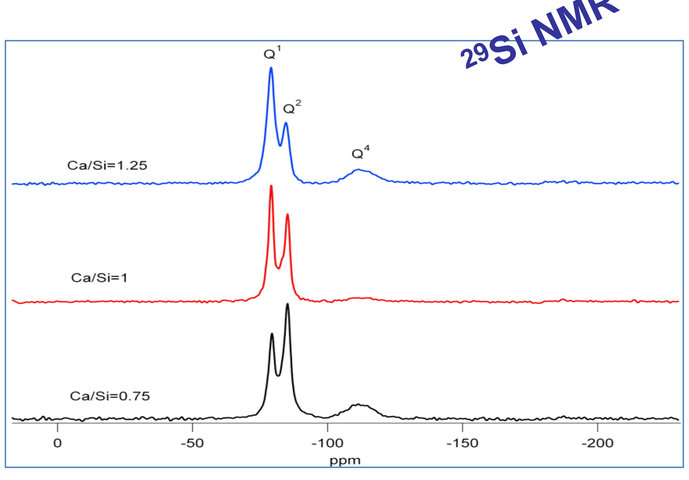
❖**Adding already synthesized C-S-H into a calcium aluminate solution:** C_3A is hydrated in a diluted suspension and already synthesized C-S-H is added to the solution so that Al is incorporated in the C-S-H [6].

RESULST FROM MECHANOCHEMICALLY SYNTHESIZED SAMPLES









DISCUSSION OF THE RESULTS

❖ **TEM:**The morphology of the samples is foil-like, as it is expected, since they resemble C-S-H (I), which has some structural features related to tobermorite. The samples are inhomogeneous presenting unreacted silica particles of ~200 nm diameter.

❖ **STA:** The samples with Ca/Si ≤ 1 present a weight loss characteristic of C-S-H, while the sample with Ca/si=1.25 also contains portlandite. The exothermic peak at ~900˚C corresponds to the transformation of C-S-H into wollastonite. The weight loss of the samples, hence the amount of water, varies due to different hours of drying. The sample with Ca/Si=1 was heated for 1 day while the other samples were heated for 3 days.

❖ **XRD:** The XRD patterns resemble C-S-H (I). The peaks that appear in the sample with Ca/Si=1.25, that are not present in the other two samples belong to portlandite. The comparison of the pattern of the nanosilica used for the synthesis with the patterns of the samples confirms the existence of crystalline impurities that remain unreacted (peaks at 2θ~ 27˚C and 36˚C).

❖**NRM:** The evolution of the silicate structure is consistent with the variation of the Ca/Si ratios. The sample with Ca/Si=0.75 is dominated by middle chain groups (Q^2), while the rest of the samples are dominated by dimers (Q^1). The intensity associated with three dimensional networks (Q^4) corroborates the presence of unreacted silica.

FUTURE WORK

❖ Replace the nanosilica by aerosil, which is more pure and more reactive, to avoid the inhomogeneity of the samples evidenced by the presence of unreacted silica particles.

❖ Perform SANS and fit the data to the model developed by Chiang et al. [7] to investigate the structure of the globules of C-S-H in terms of a stack of water and calcium silicate layers.

❖Synthesize C-S-H by the other routes described above.

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ACKNOWLEDGMENTS: The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7 / 2007-2013) under *grant agreement* 264448.