Supplementary Information:

The Nano-branched structure Of Cementitious Calcium-Silicate-Hydrate Gel

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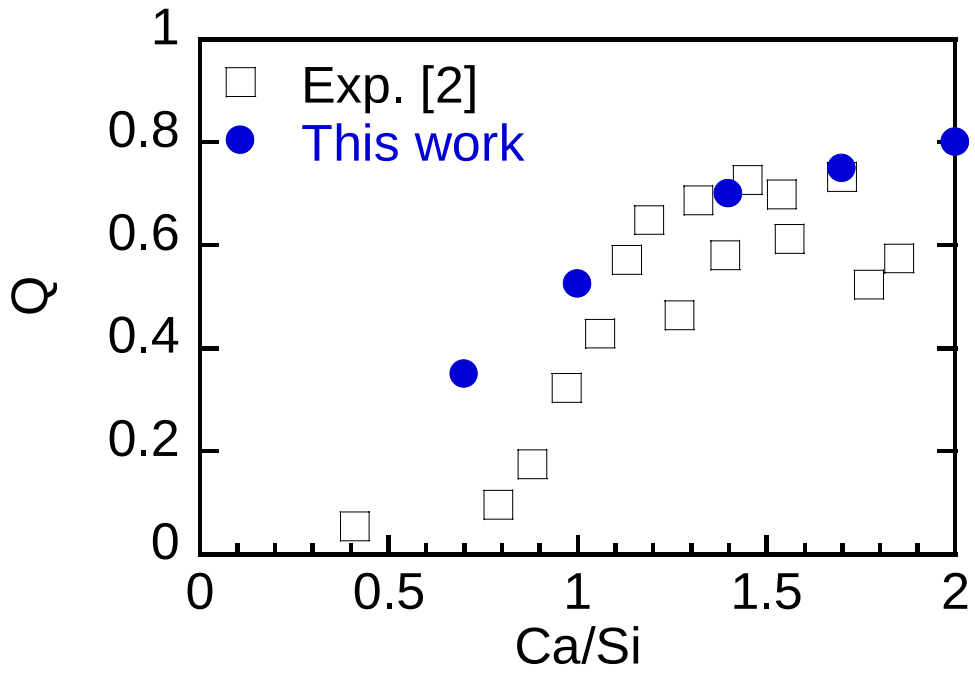
References refer to those in main text except SR1.

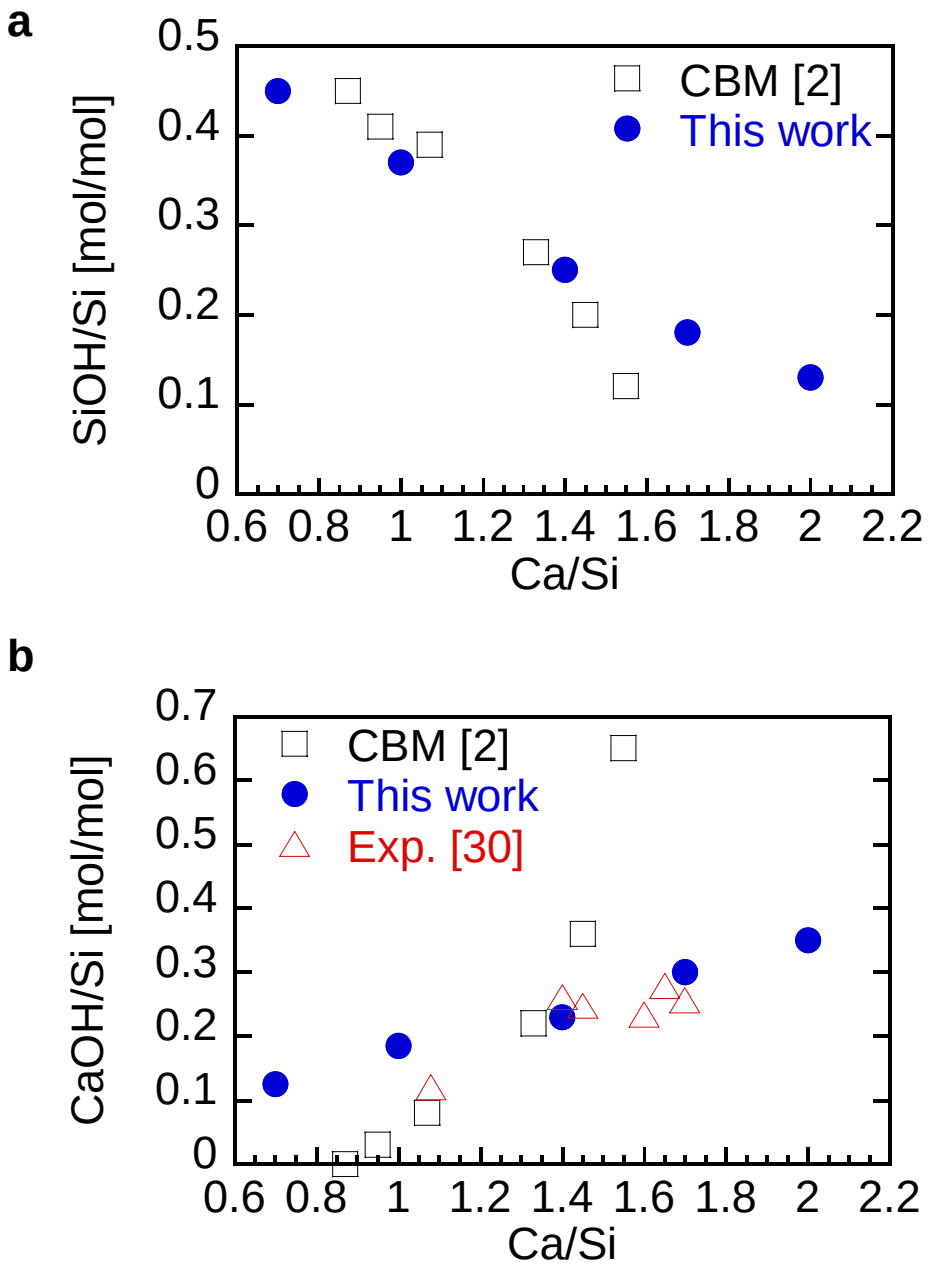
Comparison to NMR and INS experiments.

A previous work of the authors [19] studied the effect of C/S on the connectivity of the silicate chains of C-S-H gel and the number of Si-OH and Ca-OH bonds. In particular, four Ca/Si ratios were studied, namely Ca/Si=0.7, Ca/Si=1, Ca/Si=1.4 and Ca/Si=2. Present study adds a new case, Ca/Si=1.7, though in a much bigger simulation cell.



To study the connectivity of the silicate chains of C-S-H gel we have analysed the so called Q factor [SR1], which is up to a factor of two, the inverse of the mean chain length (MCL). SFig. 1 shows the new complete set of results obtained from our simulations (solid points) in comparison with the data obtained through ^{29}Si NMR

measurements by Cong&Kirkpatrick [2]. Our simulations give a good agreement with the experiments and confirm that our computational scheme accounts well for the local ordering of silicon atoms.



Likewise we also counted the number of Ca-OH and Si-OH bonds, as they are important fingerprints of the presence of tobermorite- and jennite-like features. SFig. 2 shows the results concerning the contents of Si-OH/Si (a) and Ca-OH/Ca (b) bonds as a

function of the Ca/Si ratio. We also show in SFig.2 the estimations given by the charge-balance model (CBM) presented in [2]. In Figure SR3 (b), the data obtained by Thomas et al. [30] by inelastic neutron spectroscopy (INS) over leached pastes are also shown. Keeping in mind that there are no Si-OH bonds for perfect jennite crystals, while there are no Ca-OH bonds for 1.4-nm tobermorite crystals, it can be concluded that our values are consistent with a C-S-H particle which concurrently contains tobermorite- and jennite-like environments. Regarding to the Ca-OH bonds, it is worth noting that our values are fairly consistent with the inferences gained by Thomas et al. [30] by Inelastic Neutron Spectroscopy (INS) experiments.

[SR1] Thomas, J. J. & Jennings, H. M. Free-energy-based model of chemical equilibria in the CaO-SiO2-H2O system. *J. Am. Ceram. Soc.* **1998**, 81 [31], 606.

SUPPLEMENTARY FIGURE CAPTIONS

Supplementary Figure 1.- Connectivity of the silicate chains present in C-S-H gel. This figure shows the Q factor as a function of the Ca/Si ratio. Our simulations (solid are compared with the experimental data provided by Cong and Kirkpatrick [2]

Supplementary Figure 2.- Presence of Si-OH and Ca-OH bonds a) Number of Si-OH/Si bonds as a function of the Ca/Si ratio, as determined by the charge balance model (CBM) proposed by Cong and Kirkpatrick [2], and those calculated in this work. (b) Number of Ca-OH/Ca bonds as a function of the Ca/Si as determined by CBM

proposed by Cong and Kirkpatrick [2], the experimental data of Thomas et al. [30], and those calculated in this work.