

# Aluminium substitution in C-S-H: ab initio calculations

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## Abstract

Calcium Silicate Hydrate (C-S-H) in formulations incorporating Supplementary Cementitious Materials (SCM's) is different from that in traditional cements, with a lower Ca/Si ratio and consequent propensity to incorporate Al. There is evidence that this has sizeable effects on the stability, solubility and ion uptake properties of C-S-H (e.g., Andersen *et al.*, 2003; Haas, 2012), but still relatively little is known about such systems. Molecular modeling studies of Al substituted C-S-H are highly desirable, in particular in what comes to adequate structural models, which can then constitute the basis for a myriad of further investigations (e.g., simulation of ion sorption isotherms).

We have studied the mechanism of aluminium incorporation in the surface of C-S-H with periodic Density Functional Theory (DFT) calculations. The emphasis was on preferential positions and the relative energies between different configurations. C-S-H was modeled based on a single structural layer-module of the natural mineral tobermorite,  $[\text{Ca}_4\text{Si}_6\text{O}_{14}(\text{OH})_4] \times 2\text{H}_2\text{O}$ , with so-called silicate dreierketten chains of alternating one bridging and two pairing tetrahedra on both surfaces.

Comparing the energy of a tobermorite "plate" with a single Al substitution in a bridging versus in a pairing position, it is found that the former is more stable by 18 Kcal/mol. The study was extended to configurations with two Al substitutions, be it both in bridging positions, both in pairing, or one of each, and including substitutions in the same or different dreierketten chains (next neighbour and second next neighbour). The global picture also shows clearly that the system becomes more unstable the more pairing Al it has. It also appears that there are no major correlations in the location of the Al for a given combination (e.g., two bridging Al). Exceptions are the configurations with two Al next to each other in the same dreierketten chain. There is therefore strong computational evidence that Al in C-S-H sits preferentially in bridging positions, in agreement with experimental information (e.g., Pardal *et al.*, 2012). The picture does not change even in the case where one Al is in a pairing position in the "end of a chain", i.e., adjacent to a missing bridging tetrahedron ("defect"), neither when it is in a dimer (two adjacent pairing tetrahedra isolated from the rest of the chain by two defects).

Andersen, M. D., Jakobsen, H. J. and Skibsted, J. (2003)

Incorporation of aluminium in the calcium silicate hydrate (C-S-H) of hydrated Portland cements: A high-field Al-27 and Si-29 MAS NMR Investigation. *Inorg. Chem.* 42, 2280.

Haas, J. (2012)

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Pardal, X., Brunet, F., Charpentier, T., Pochard, I. and Nonat, A. (2012)

<sup>27</sup>Al and <sup>29</sup>Si Solid-State NMR Characterization of Calcium-Aluminosilicate-Hydrate. *Inorg. Chem.* 51, 1827-1836.