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An atomistic building block description of C-S-H - Towards a realistic C-S-H model

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ABSTRACT

Understanding the atomistic structure of Calcium silicate hydrate (C-S-H), the main product of cement hydration, is of paramount importance to better formulate sustainable cement. The existing atomistic models are not in total agreement with experimental results and fail to explain the nanosized nature of C-S-H. Here, we present a new approach for describing the complexity of these structures at the molecular level, enabling a detailed comparison of C-S-H models. The new methodology encodes a full, large scale atomistic C-S-H structure by a simple, readable string of characters, similar to the way the base sequence in DNA encodes a vast range of different proteins. We then use the methodology to assess 14 Å tobermorite-defect structures and their stabilities using DFT and classical molecular dynamics. Finally we highlight how the model may be extended to develop reliable atomistic C-S-H models for a range of Ca/Si ratios and conditions.

1. Introduction

Hydrated cement is the binder or glue that holds together the sand and aggregates that all together make up concrete - the most used material in the world. Although per kg cement is inherently a low carbon material [1,2], the vast quantities used mean that cement is responsible for about 5–8 % of global CO_2 emissions. The optimisation of the mechanical properties and durability of concrete can therefore aid in the reduction of CO_2 emissions. This would be greatly aided by a better fundamental knowledge of the material at the atomistic structure level.

A better understanding of cementitous systems is complicated by the fact that the exact atomistic and nanoscale structure of the main hydration product (C-S-H) is poorly known. One reason for this is that both X-ray diffraction (XRD) and selected area diffraction show only two weak signals, indicating repeat distances of about $\sim 1.82 - 1.83$ Å and $\sim 2.7 - 3.2$ Å [3,4]. This implies that C-S-H does not have any 3D long range order. It also means that the exact atomistic structure of C-S-H cannot be resolved by conventional XRD techniques.

A further complication is the varying chemical composition of C-S-H. The composition varies significantly not only between different samples but also within one and the same sample. In neat tricalcium silicate (C_3S) pastes local energy dispersive X-ray analysis (EDS) has shown that on a scale of 100 nm $\frac{Ca}{Si}$ varies between 1.2 and 2.1, with an average calcium to silica ratio $\left\langle \frac{Ca}{Si} \right\rangle$ of 1.75 [5].

The type of silicate species present in C-S-H was first studied by Mohan et al. with trimethylsilylation followed by chromatography [6]. This technique revealed that only silica chains with a length of $3n - 1$ (i.e. dimers, pentamers, octamers and some longer chains) are present in C-S-H. This indicates a so called dreierketten structure with silicate dimers that can be linked by bridging silicate tetrahedra (see Fig. 1). Subsequent NMR studies revealed, that no connectivity larger than 2 exists between the different silicate chains [7–13]. In other words the silicate species in C-S-H are composed of linear chains without cross-linking. Also NMR distinguishes between different species within the linear chains: so called non-bridging chain tetrahedra Q^2 and the bridging tetrahedra Q^{2b}[8,13]. The ratio between the two in C-S-H being 2:1. This confirms the dreierketten structure where only chains of length $3n - 1$ can exist.

Additionally, transmission electron microscopy (TEM) images of carefully dried samples show different morphologies of C-S-H, often with a pronounced texture [4]. The smallest characteristic dimension of C-S-H, corresponding to both the size of the solid regions [4,14,15] and of the crystallites [16,17] is in the order of 3–6 nm. The largest characteristic dimension is less clear. For the crystalline domains in OPC the largest characteristic dimension is typically in the order of 6–15 nm [16,17], however some order can persist over much longer length scales of > 100 nm [4,18], which could be either due to a

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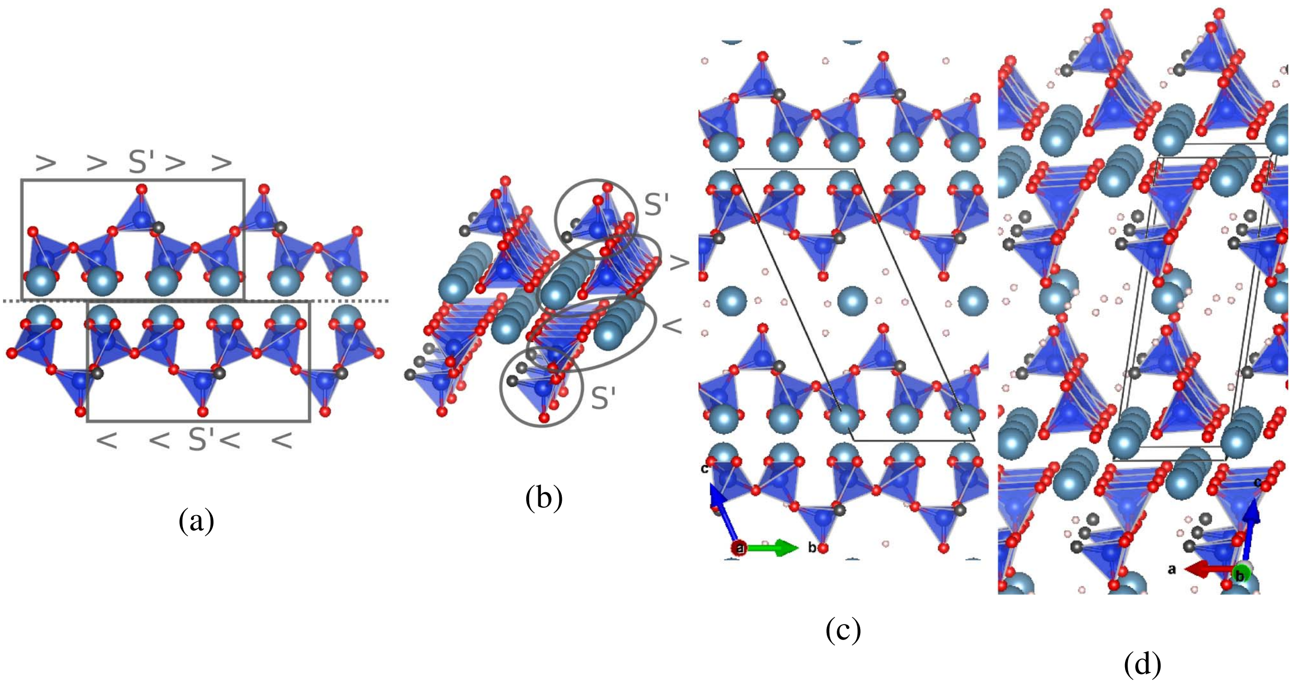

Fig. 1. Ca-Si layer of 14 Å tobermorite with characteristic linear dreierketten structure of silicate chains ((a) and (b)) as well as their stacking in 14 Å tobermorite ((c) and (d)). Si: blue, Ca: turquoise, O: red, OH: black. Also shown is the structural abbreviation introduced in Section 3.1.1.

partially continuous structure [19] or to a colloidal material [20] with long length scale ordering similar to that observed in e.g. liquid crystals. TEM images with an even higher resolution have revealed layering of the material with an approximate interlayer distance of ~ 12–14 Å [21].

Different water containing, layered calcium-silicate crystal structures containing linear silicate-“dreierketten” have been reported in the literature. The ones most commonly compared to C-S-H are the different tobermorites (e.g. 14 Å tobermorite: $\frac{Ca}{Si} = 0.83$, interlayer distance 14 Å molar water content: 42%) and jennite ($\frac{Ca}{Si} = 1.5$, molar water content: 42%). Both 14 Å tobermorite and jennite consist of calcium-silicate layers separated by an interlayer space containing both water and calcium. The main layer calcium ions in 14 Å tobermorite form a planar sheet, the calcium layer in the jennite structure is corrugated.

However the calcium to silicon ratio Ca/Si of all these minerals is significantly smaller than that observed for C-S-H. An indication as to what structural trends lead to an increase of the Ca/Si ratio in C-S-H can be gleaned from experimental observations. In C-S-H produced from tricalcium silicate (C_3S) pastes cured for 12 months, about 60% of the silicate species are present as dimers and 40% as longer chains [6] with a mean chain length (MCL) of 3.3. Similar results are found for ordinary Portland cement paste (OPC)[4]. The chain length continues to increase over the next couple of decades but even for ~ 20 year old pastes there are still a lot of dimers (~ 40 %[6]) and the MCL is still less than 5 [4]. This means that, compared to the model structures with infinite silicate chains, a significant part of the bridging silicate tetrahedra are missing in C-S-H, which will increase the Ca/Si.

Additionally both $^{1}H - ^{29}Si$ NMR measurements [8] and infrared spectroscopy [22] indicate the existence of Ca-OH groups in C-S-H. Thomas et al. used inelastic neutron scattering to quantify the amount of Ca-OH bonds in C-S-H [23]. They found that at a calcium to silicon ratio of 1.7 about 23% of the charge of the Ca^{2+} ions in C-S-H are compensated by hydroxyl groups. This value is in between that of tobermorite (no $Ca - OH$ groups) and that of jennite (33%). Thus these results indicate either a mix between jennite and tobermorite or additional $Ca - OH$ groups incorporated in a tobermorite like structure would be needed to give the appropriate Ca/Si ratio. Additionally the number of Si-OH groups decreases with increasing Ca/Si. In contrast to a non-defective 14 Å tobermorite, the number of silanol groups in a C-S-H with a Ca/Si ratio of 1.7 is below the detection limit of different experimental techniques [11,22].

While these results would indicate a closer resemblance of C-S-H with a typical Ca/Si ratio of 1.7 to jennite than to tobermorite, structural measurements such as XRD and Raman spectroscopy [16,24,25] as well as theoretical work [26] indicate a closer resemblance of the C-S-H structure to tobermorite rather than to jennite.

In summary, from these results we infer that C-S-H is composed of defective, nanocrystalline tobermorite with missing bridging silicate tetrahedra, leading to a decreased silicate chain length, and deprotonated silanol groups, the charge of which is compensated by additional calcium ions in the water-interlayer and with additional Ca-OH groups. Furthermore, experimental measurements revealed that the Ca-O and Si-O nearest neighbour distances in C-S-H with Ca/Si up to 1.75 are similar to the ones in tobermorite while the Ca-O coordination number decreases almost linearly with increasing Ca/Si (6.0 ± 0.2 at $Ca/Si = 1.75$, as compared to 7.1 ± 0.2 for $Ca/Si = 0.6$ and 7.0 ± 0.2 at $Ca/Si = 0.8$) [27,28]. The approximate stoichiometry is estimated to be $Ca_{1.7}SiO_{3.7} \cdot 1.8H_2O$ with a density of about 2.6 $\frac{g}{cm^3}$, excluding the water at the surface [15,29]. XRD measurements indicate that the interlayer distance may be smaller than 14 Å in C-S-H with $Ca/Si = 1.7$ (around 11 or 12 Å [11,16,27]).

An atomistic model should take into account all the experimental evidence presented above. Additionally it should give some indications as to why C-S-H displays the rather unique properties it does: How can we explain the consistently nanoparticulate nature of C-S-H? And why does the stoichiometry vary extensively within one and the same C-S-H sample? In recent years, several atomistic models for C-S-H have been proposed [21,30-33]. Despite capturing some of the salient features of C-S-H, none of the models are entirely satisfactory, when confronted with the experimental evidence available and they leave several questions regarding the properties and behaviour of C-S-H unresolved.

Recently, Pellenq et al. [21,31] and Kovačević et al.[32,34] used the Hamid [35] and the Merlino [36] 11 Å tobermorite respectively as the base structure to model C-S-H using classical molecular dynamics