



Review

A comprehensive review of the models on the nanostructure of calcium silicate hydrates



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HIGHLIGHTS

- The state-of-the-art of the nanostructure of C–S–H is clarified and updated.
- The descriptive and predictive key models for C–S–H are organised.
- The way in which water in C–S–H affects creep and shrinkage is reviewed.
- The role of nanotechnology in advances in cement research is considered.

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ABSTRACT

The need to master factors affecting the performance of concrete has sparked research on its basic constituent, cement, whose properties are determined by one of the most critical cement hydration products, the calcium silicate hydrate. The present paper discusses the evolution of models describing the nanostructure of the calcium silicate hydrate (C–S–H) over the past century (descriptive models), with a focus on the models presented in the last fifteen years, 2000–2014 (descriptive and predictive models), marked with the breakthrough of nanotechnology. The purposes and outcomes of the suggested models are discussed, along with their limitations. The article concludes that notwithstanding the enormous potentials nanotechnology and advanced molecular modelling have offered in the field, modern models are, in essence, still expanding on the colloidal or layered models suggested in the 60s, rather than providing a ground breaking new approach. However, it is generally recognised that nanotechnology and molecular modelling have, facilitated the shift from descriptive to predictive models, saving time and resources by extrapolating results of very lengthy experiments, e.g. sorption isotherms, or by mathematically manipulating the C–S–H components to derive different structures and assemblages, that would have been difficult or impossible in practice. In that sense, the new experimental methods available, paired with analytical models are able to provide further justification of the pioneering studies and advance cement nanoscience, paving the way to the production of innovative, nanomodified cements, with minimum Portland cement content.

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1. Introduction

The mechanical, chemical and transport properties of hydrating cement are controlled by the principal product of cement hydration and primary binding phase, the calcium silicate hydrate (C–S–H, the dashes denoting the versatile stoichiometry) [1]. Taking into consideration that the way to enhance the macroscopic mechanical properties of hydrated cement (strength and durability as affected by porosity, creep, shrinkage and ageing) is by understanding and modifying the structure of the C–S–H gel at atomic level [2] it can be realised that cement science cannot go far without mapping and quantitatively understanding the structure of C–S–H at the atomic to the 100 nm level [1]. In addition to this, with the emergence of nanotechnology and the use of advanced analytical techniques, not only the observation, but also the manipulation of matter at the nanolevel can be achieved and therefore the resolution of the nanostructure of C–S–H will lay the ground for further research and evolution of advanced cements and cementitious materials. This raises the question as to whether nanotechnology has managed to raise the barriers set by the older techniques and by how far has the envelope been pushed in recent research.

The atomic structure of C–S–H is still not fully determined and the nanostructure of the C–S–H continues to be explored and is still being debated on [2,3]. Taylor [4] has published a review with the models on the nanostructure of C–S–H presented until 1993 and Scrivener and Kirkpatrick have shed more light on a number of more recent models [1]. Two main obstacles to the atomic resolution of C–S–H have been identified; (i) the fact that the hydrated phases are difficult to separate and (ii) the low diffraction of C–S–H [5]. New experimental techniques (for example nuclear magnetic resonance and neutron scattering) have been devised and the older ones (for example electron, atomic force or field emission microscopy enhanced with X-ray energy dispersive spectroscopy) and analytical techniques (for example molecular modelling or quantum simulations) have been further developed. Notwithstanding these advances over the decades, there is still controversy and dispute as to whether C–S–H is made of globules [6–10], platelets [11] or disks [12] 5 nm thick or a morphology derived from a foil-like growth mechanism [13], a branched structure of less than 6 nm dimensions [14], or a clay-like structure of layers 1–5 nm thick, stacking up to form compounds [2,15]. Consequently, the following questions are pertaining; is the structure of the C–S–H colloidal or continuous, amorphous and up to what scale, “very poorly crystalline” or nanocrystalline and how has it emerged? [4,5,16,17]. What

is the role of water in the C–S–H, what are the characteristics of the different forms in which it is encountered and how do humidity changes at the nanolevel affect the macroscopic behaviour of pastes?

To address the issue of the nanostructure of the C–S–H in the hydrated cement paste, a comprehensive review was carried out to: (i) identify the key features of a selection of models, constituting schools of thought, some of which have been historically confused with each other, (ii) discuss the purpose for which they were developed and the limitations emerging from the techniques used at that time, including the latest advancements offered with nanotechnology-derived descriptive (experimental methods) or predictive techniques (mathematical simulations) available and (iii) compare the different approaches with regard to the form in which water is found in the nanopores. This latter aspect was of particular importance, as the movement of water, leading to drying shrinkage and creep, affects the characteristics of the C–S–H, while being one of the most difficult items to be encompassed in the suggested models. (iv) Clarify the state-of-the-art in order to define the basis for future work towards nanomodified cements; that is to say, innovative blended cements incorporating foreign nanoparticles, such as nano- SiO_2 , nano- TiO_2 , nano- Fe_2O_3 , nanoclays or others, as a counterbalance to the (a) decrease in Portland cement (PC) content and (b) an increase in supplementary cementitious materials' content. The selected descriptive models and some key aspects are summarised in Table 1. The computational models, developed, in order to predict the response of the C–S–H phase under different conditions and for entirely different purposes, were denoted as predictive computational models and are summarised in Table 2.

2. Background concepts and methods

In this section a short reference to the hydration and hardening of cement is made. The development of the parameters on which the comparisons of the models was based has been discussed, i.e. the C/S ratio, the crystal, quasicrystals and amorphous structures and the colloidal nature of gels. In addition to this, a short reference to the advancements in experimental and computational techniques, employed for the development of the models under discussion, was also made to facilitate later discussion.

2.1. Formation of C–S–H and C/S ratio

When the silicate phases of the Portland cement clinker (alite – C_3S and belite – C_2S), come into contact with water, two products are formed; crystalline calcium hydroxide and the almost amorphous or highly disordered C–S–H, which comprises

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