



Reactive molecular simulation on the ordered crystal and disordered glass of the calcium silicate hydrate gel

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Abstract

Modifying the properties of modern concrete highlights the decoding the molecular structure of C–S–H gel, which is the main binding phase in the cementitious materials. In this paper, the structural, dynamical and mechanical properties were investigated by using C–S–H glassy model and its crystal analog tobermorite 11 Å to represent the disordered and ordered molecular structure. By using reactive force field molecular simulation, the structural discrepancy for ordered and disordered phase was illustrated in respect of silicate chain skeletons, local structure of the calcium oxygen octahedrons and hydroxyl distribution. In the glassy model, the local structure of C–S–H gel, with defective silicate chains and distorted calcium sheet, is similar to the silicate glass phase of metallic ions. Furthermore, to predict the mechanical properties of the C–S–H gel and tobermorite, uniaxial tension testing by the reactive force field coupled with both the mechanical response and chemical response during the large tensile deformation process. During the tensile process, water molecules, attacking the Si–O and Ca–O bond, are detrimental to the cohesive force development in the C–S–H gel.

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1. Introduction

The cement paste is a porous and hierarchical material, containing different components and multi-scale pore structures. When dry cement powders are mixed with water, the hydration reaction gives birth to main chemical products: Calcium silicate hydrate (C–S–H), calcium hydroxide (CH), ettringite and mono-sulpho-aluminates as well as various pores [1]. The pores in cement-based material have a wide length range from less than 1 nm to larger than 1 mm, which can be categorized into capillary pores and gel pores [2]. The smallest gel pores with characteristic size around 1 nm, defined as the interlayer space or interlayer pore, exist in the C–S–H gel which takes up approximately 50–70% of the fully hydrated

products. The structure of the C–S–H gels is closely related with the properties of cement, including the cohesive force between different phases, the shrinkage or creep. Due to the complex Ca/Si composition, density variation and the multi-scale nature of the C–S–H gel, many experimental and computational techniques have been employed to intensively study the features of the nano-structure of the C–S–H gel.

The molecular structure of C–S–H has been studied for more than half a century, particularly using a variety of experimental techniques. The understanding of the molecular structure of C–S–H started from two crystal phases in nature. X-ray diffraction (XRD) investigation [3,4] indicated that the C–S–H gel is the analog of two types of crystals: Tobermorite [5,6] or Jennite [7] and exhibits layered nature. However, by comparing with other layered structures, the line broadening and asymmetry in the XRD spectroscopy of the C–S–H gel are attributable to distorted calcium silicate layers with short crystal size. The diffraction maximum exhibiting the strongest variation in position is the

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reflection between 13.5 and 11.2 Å which corresponds to interlayer space [8]. Based on great efforts from XRD testing [4,9–15], it can be concluded that at low Ca/Si ratio (< 0.9), interlayer distance is close to 13.5 Å while with increasing Ca/Si ratio, this distance reduces down to 11.2 Å for Ca/Si = 1.7. In addition, it can be inferred from Si²⁹ MAS NMR spectra that the silicate chains in the C–S–H gel follow the Dreierketten arrangement, with the dimeric chain occupying predominant percentage [16]. Mean silicate chain length, describing the polymerization degree, decreases as the Ca/Si ratio increase [16–18]. According to the morphology features detected from experiment, a series of theoretical models are proposed to explain the molecular structure variation for the C–S–H gel. Taylor proposed that C–S–H in cement paste is evidently a disordered layer structure and is a mixture of structures based on both 1.4 nm tobermorite and jennite [19]. This was theoretically one of the possible ways to explain the high Ca/Si ratio of C–S–H in cement paste (1.7–2.0) as dimeric 1.4 nm tobermorite and jennite type structures could have a C/S ratio of about 1.25 and 2.25 at early ages, respectively. Moreover, the water to calcium ratio of the C–S–H at 11% RH lies between that of the suggested structural representatives. Richardson and Groves [20] have proposed a two-fold classification to clarify C–S–H chemistry, which references tobermorite/jennite (T/J) models and tobermorite/calcium hydroxyl (T/CH) models.

With the development of the computational technology, the atomic simulation has been introduced to unravel the molecular structure of cement materials. Recently, with the increasing knowledge of the density and chemical composition of C–S–H gel obtained by SANS [21], Pellenq et al. [22] employed the Molecular Dynamic (MD) method to construct a C–S–H model and is defined as a “realistic model”. By using the model, the atomic order in the C–S–H gel has been further elucidated: despite an intermediate degree of order, the hydrated species are completely amorphous [23]. The realistic model has also illustrated the disordered characteristic for the calcium silicate hydrate in many respects. The model has been widely applied to explain the glassy nature for the water molecules highly confined in the nano-pores [24], the thermodynamic properties for the C–S–H gel [25], the comparison between different water models [26] and the alumina introduction in the C–S–H (CASH) [27].

In order to describe the C–S–H gel at the nano-scale more accurately, the “realistic model” has been improved in some important respects. To achieve the proper Ca/Si ratio, many Q_0 species, representing the monomer silicate structures, remained 13% in calcium silicate sheet, which is more than 3 times larger than the results obtained from the ²⁹Si and ¹⁷O cross-polarized NMR test [28,16]. To reduce the percentage of Q_0 species, the temperature annealing method has been employed to re-polymerize the defective silicate chains. Another structural limitation is that in the “realistic model”, OH bonds are only in the water molecules and neither the Ca–OH bonds nor the Si–OH bonds are present in the interlayer region, which is not consistent with the detecting of the Ca–OH bonding by INS [29]. This limitation results from the fact that the CSHFF, the empirical force field, cannot allow “hydrolytic reaction” for

water molecules confined in the C–S–H gel. Fortunately, the hydroxyl issue has been solved by using a reactive force field and DFT to dissociate the water molecules completely [30].

In this study, our simulation aims to give insights on the relationship between ordered and disordered phases in the C–S–H. Molecular simulation by the reactive force field is utilized to construct the improved “realistic model”. The structure, dynamics and mechanical properties for the newly constructed C–S–H model are investigated and the tobermorite 11 Å, as the mineral analog of C–S–H gel, is simulated for comparison. Furthermore, uniaxial tension testing is performed on the C–S–H gel and the tobermorite to obtain the mechanics, such as Young's modulus and tensile strength. It is valuable to note that the reactive force field, coupling the mechanical and chemical responses for the layered structure, can unravel the failure mechanism at the molecular level.

2. Method

2.1. Reactive force field

The reactive force field (ReaxFF), developed by van Duin et al. [31], is utilized to simulate the chemical reaction for both atomic structure construction and uniaxial tensile testing. The reactive force field provides an advanced description of the interaction between Ca, Si, O and H atoms in the C–S–H gel. The short-range interactions for the Reax force field are determined by a bond length-bond order scheme so that the bonds can be broken and formed, with the potential energy transforming into a smooth state [32]. On the other hand, the long-range coulombic interactions are determined by a 7th order taper function, with an outer cut off radius of 10 Å. The reactive force field has been widely utilized in silica–water interfaces [33], calcium silicate hydrate gel [34] and nanocrystals [35]. The parameters of the force field for Ca, Si, O and H can be directly obtained from previous published reference data [31,36].

2.2. Tobermorite and the C–S–H model

Tobermorite 11 Å [6,37,38] is used for the crystal phase simulation. The molecular structure for the tobermorite is shown in Fig. 1a.

For the C–S–H gel, the model construction in the present study is based on the procedures that combine the method proposed by Pellenq [22] and Manzano [30]. Firstly, the layered analog mineral of C–S–H, tobermorite 11 Å without water, was taken as the initial configuration for the C–S–H model [37]. Silicate chains were then broken to match the Q species distribution with $Q_1=73.9\%$, $Q_2=21.4\%$ and $Q_0=4.7\%$. The mean silicate chain length (MCL = $2(Q_2/Q_1 + 1) = 2.58$) is consistent with the results obtained both from NMR testing [16] and molecular dynamics simulation [39]. It is worth noting that the Q_0 percentage is controlled to less than 5%, also matching well with experimental results [28]. Meanwhile, the Ca/Si ratios range from 0.7 to 2.3 with an

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