



Structure, reactivity and mechanical properties of water ultra-confined in the ordered crystal: A case study of jennite



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ABSTRACT

Jennite is an important structural prototype of C–S–H gel that is the major component of the cement hydrate. The structure, dynamics and mechanical properties of jennite were investigated by reactive force field molecular dynamics simulation. Water molecules, confined between the neighboring calcium silicate sheets, dissociate and form the Si–OH bonds with the oxygen atoms in the bridging silicate tetrahedron, which is consistent with the strong signal of Si–OH linkage from NMR testing (Cong and Kirkpatrick, 1996) [1]. Dynamically, the high diffusion rate and the dissociation reaction of water molecules reduce the stability in the interlayer region. Additionally, uniaxial tensile testing, applied to the jennite structure in the *x*, *y* and *z* direction, exhibited the an-isotropic nature of the layered crystal. While Si–O bonds, acting in a skeleton role, contribute to the mechanical behavior in the *y* direction, the unstable H-bonds connectivity weakens the tensile strength and stiffness in the *z* direction. More importantly, the reactive force field accompanied together both the mechanical response and chemical response during the large tensile deformation process. On the one hand, the silicate chains de-polymerize to enhance the loading resistance and on the other hand, water molecules, attacking the Si–O and Ca–O bonds, dissociate into hydroxyls, which are detrimental to the cohesive force development.

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1. Introduction

Even though jennite crystals are rare minerals in nature, the layered structure of jennite resembles that of the calcium silicate hydrate (C–S–H) gel, the major component in cement-based materials. Like many mineral analogues of the C–S–H gel, jennite crystal has some structural features: the solid skeleton is calcium silicate clay-like layer; with water molecules in the inter-laminar space. Since the interlayer distance is around 1 nm, the jennite crystal provides a medium for investigation on the water and ions ultra-confined in the nano-pore. In biological, industrial and geological systems, water molecules in confinement have been extensively investigated. From water molecules in biological cells to molecules diffusing between the gel pores in the cement hydrate, water molecules, influenced by the geometrical and electronic confinement, demonstrate dramatically different properties from the bulk counterpart [2–4]. On the other hand, due to the existence of

interlayer water, the reactivity, mechanics and dynamic properties of the ultra-confining material are changed significantly [5].

As an important structural prototype of C–S–H gel, the molecular structure of jennite crystal has been investigated by both the experimental and computational efforts for many years [6,2,1,7,8]. In particular, by using multi-techniques, such as NMR [1] and single crystal X-ray diffraction [7], the crystal structure has been found to have three distinct features: ribbons of edge sharing calcium octahedrons, silicate chains of wollastonite-type running along the *b* direction, and additional calcium octahedrons on the inversion centers. Even though the structure of the calcium silicate skeleton has been determined, the orientation and position of the water molecules, Si–OH and Ca–OH groups remain undefined. Since the H-bonds that are inter-connected by the hydroxyl groups and water molecules significantly influence the mechanical and thermodynamic properties of the layered structure [9,10], it is necessary to have a comprehensive understanding of the H-bonds connectivity in the jennite.

By solving and refining the data achieved from single X-ray diffraction, Bonaccorsi et al. [7] proposed that the hydrogen atoms are in the form of Ca–OH and water molecules and that no Si–OH

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groups are included in the crystal structure of the jennite. However, ^1H – ^{29}Si CP MAS NMR studies suggested that some protons in the structure are associated with the Si–OH linkage. In addition, Churakov et al. [6] further investigated the H-bond connectivity in the jennite structure by ab initio MD simulation. During the MD simulation process within 10 ps, hydrogen atoms are only associated with the Ca–OH bonds and water molecules, which is consistent with the theory of Bonaccorsi. Both Churakov and Bonaccorsi's explanation on the strong NMR signal of Si–OH is the strong H-bond connectivity between the water molecules and dangling Si–O⁻. Therefore, it is necessary to further analyze the local structure of the water molecules in the jennite to accommodate any contradictory issues.

In this study, molecular simulation by the reactive force field is utilized to study the structure, dynamics and the mechanical properties of the jennite crystal. A new H-bond connectivity has been proposed according to the water reaction in the jennite structure. Additionally, uniaxial tension testing was performed on the jennite to obtain the mechanical properties, 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. Computational method

2.1. Reactive force field

The reactive force field (ReaxFF), developed by van Duin et al. [11] was 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 the Ca, Si, O and H atoms in the jennite structure. The short-range interactions for the reactive 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 [12]. 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 [13], calcium silicate hydrate gel [14] and nano-crystals [15]. The parameters of the force field for Ca, Si, O and H can be directly obtained from previous published reference data [11,16].

2.2. Jennite model

The accuracy and transferability of the reactive force field have been tested against the jennite unit cell. As shown in Table 1, the calculated lattice parameters agree with the experimental values within 2.9%. The jennite model, with a composition $12 \times [\text{Ca}_9\text{Si}_6\text{O}_{18} \cdot 8\text{H}_2\text{O}]$, constructed by $2 \times 3 \times 2$ unit cells of jennite, was subsequently used for the structure and dynamics simulation. The reactive force field molecular dynamic simulations under constant pressure and temperature (NPT) for 300 ps give the structures of the jennite at equilibrium states. A further 100 ps NPT run was employed to achieve the equilibrium configurations for structural and dynamic analysis.

Table 1
Lattice constants from the simulated jennite crystal and experimental result.

Lattice constants	<i>a</i>	<i>b</i>	<i>c</i>	α	β	γ
ReaxFF	10.28	7.35	11.11	101.09	96.70	108.57
Exp	10.58	7.27	10.93	101.30	96.98	109.65

2.3. Uniaxial tension testing

Uniaxial tension testing is employed to investigate the mechanical behavior of jennite. A super-cell, obtained by periodically extending the simulation model in Section 2.2 by a factor two, underwent uniaxial tension in the *x*, *y* and *z* direction. The super-cells were composed of 6624 atoms, with size around $44 \text{ \AA} \times 44 \text{ \AA} \times 44 \text{ \AA}$. It should be noted that using a large number of atoms in this study can give stable statistical simulation results, especially in regard to reliable failure modes. In order to explore the failure mechanism of the layered structure, the stress–strain relation and the change of molecular structure were investigated in the loading process.

To obtain the stress–strain relation, the structure was subjected to uniaxial tensile loading through gradual elongation at constant strain rate of 0.08/ps. In the whole simulation process, NPT ensembles are defined for the system. Taking the tension along the *x* direction, for example, the super-cells were firstly relaxed at 300 K and coupled to zero external pressure in the *x*, *y*, *z* dimensions for 100 ps. Then, after the pressures in the three directions reached equilibrium, the jennite structure was elongated in the *x* direction. Meanwhile, the pressures in the *y*, *z* directions were kept at zero. Pressure evolution in the *x* direction was taken as the internal stress σ_{xx} . Setting the pressure perpendicular to the tension direction to zero allowed the normal direction to relax un-isotropically without any restriction. The setting, considering Poisson's ratio, can eliminate artificial constraints in the deformation.

3. Results and discussion

3.1. Local structure of water molecules

The simulated jennite sample is shown in Fig. 1a. Correspondingly, the intensity profiles of the different atoms are plotted in Fig. 1b versus the distance in the *z* direction. It can be clearly observed in Fig. 1a that the jennite structure is composed of the calcium silicate sheet and interlayer region. The calcium atoms (Ca_s) and the surrounding oxygen atoms (O_s) form $\text{Ca}_s\text{--O}_s$ octahedrons, and construct the Ca_s sheet; continuous silicate chains graft on both sides of the Ca_s sheets; between the neighboring calcium silicate sheet distribute the interlayer calcium atoms (Ca_w) and water molecules (H_w , O_w). As shown in Fig. 1b, the sharp peaks of Ca and Si in density profile suggest the ordered structure of calcium silicate sheet, while the broad distribution of H atom reflects the disordered arrangement of interlayer water molecules. In addition, the intensity peaks of Si and H atoms overlap in the interlayer region, and are attributed to the silicate hydroxyl formed as a result of the hydrolytic reaction.

Water molecules, confined between the neighboring calcium silicate sheets, dissociate and form Ca–OH and Si–OH bonds. The hydrolytic reaction rate is quite fast; during less than 0.1 ns, 25% of the water molecules in the jennite dissociate. As shown in Fig. 1c, seven important states are utilized to describe the pathway of the reaction between water molecules and neighboring silicate tetrahedron. In general, the reaction mechanism is that water molecules dissociate into H^+ and OH^- , the H^+ ions diffuse to associate with the O_{NB} atoms in the bridging silicate tetrahedron, while the OH^- ions form Ca–OH bonds with neighboring interlayer calcium atoms. Actually, two types of water molecule react with the bridging silicate tetrahedron. Type 1 water molecule donates H-bond with the non-bridging oxygen (O_{NB}) atoms in the silicate chains, while O_w atom in the type 2 water molecule is the coordinated atom of O_{NB} in the tetrahedron. Initially, type 1 water molecule, close to the silicate tetrahedron, is strongly attracted by the O_{NB} atoms, which results in water dissociation into H^+ and OH^- . Then

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