Assessment of structural, thermal, and mechanical properties of portlandite through molecular dynamics simulations

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ABSTRACT

The structural, thermal, and mechanical properties of portlandite, the primary solid phase of ordinary hydrated cement paste, are investigated using the molecular dynamics method. To understand the effects of temperature on the structural properties of portlandite, the coefficients of thermal expansion of portlandite are determined in the current study and validated with what reported from the experimental tests. The atomic structure of portlandite equilibrated at various temperatures is then subjected to uniaxial tensile strains in the three orthogonal directions and the stress-strain curves are developed. Based on the obtained results, the effect of the direction of straining on the mechanical properties of portlandite is investigated in detail. Structural damage analysis is performed to reveal the failure mechanisms in different directions. The energies of the fractured surfaces are calculated in different directions and compared to those of the ideal surfaces available in the literature. The key mechanical properties, including tensile strength, Young's modulus, and fracture strain, are extracted from the stress-strain curves. The sensitivity of the obtained mechanical properties to temperature and strain rate is then explored in a systematic way. This leads to valuable information on how the structural and mechanical properties of portlandite are affected under various exposure conditions and loading rates.

1. Introduction

To improve the available models of cementitious materials at macro-, micro-, and nano-scale, it is necessary to determine the intrinsic properties of the ordinary hydrated cement paste (HCP) products. Among the HCP products, portlandite is known as the primary solid phase, which constitutes 20–25% of the volume of ordinary cement paste [24]. In cementitious materials, such as concrete and mortar, portlandite is formed as a result of reactions between water and cement clinkers, i.e., tricalcium silicate (alite) and dicalcium silicate (belite). During the exothermic hydration reactions, thermal stresses are generated, causing early-age cracks and structural damage. This highlights how critical it is to determine the temperature-dependent structural and mechanical properties of the HCP products, particularly portlandite. The thermo-elastic properties of portlandite were investigated first by Fukui et al. [7] using in-situ X-ray diffraction. Xu et al. [40] studied the anisotropic thermal expansion and hydrogen bonding behavior of portlandite via high-temperature neutron diffraction tests. There was a substantial difference between the coefficients of thermal expansion (CTEs) reported by Xu et al. [40] and Fukui et al. [7]. This was attributed to the fact that Fukui et al. [7] calculated the

lattice parameters using the conventional least-squares analysis of selected individual reflection lines, whereas Xu et al. [40] employed the more accurate whole-pattern Rietveld method to calculate the same quantities. Beyond these two studies, no other investigation on the thermal properties of portlandite was found in the literature. This was one of the main motivations of the current study to characterize the changes in the structural and mechanical properties of portlandite as a function of temperature.

A number of experimental and theoretical studies have been conducted to determine the elastic properties of portlandite. The initial experimental studies include Brillouin interferometry [15], tests of compacted powder samples with different porosities [2,37], and compression tests [20]. Based on the experimental test results, Monteiro and Chang [25] calculated the elastic properties of portlandite from the mathematical morphology of concrete; Laugesen [18] calculated the elastic constants of portlandite using density functional theory (DFT); Constantinides and Ulm [5] performed nano-indentation experiments to directly find the Young's modulus and Poisson's ratio of portlandite; and Speziale et al. [34] estimated the elastic properties of natural calcium hydroxide, including all the adiabatic elastic constants and acoustic velocities using the Brillouin spectroscopy. In the most

recent studies, Manzano et al. [21] and Qomi et al. [31] estimated the elastic properties of portlandite using the molecular mechanics (MM) method. Despite the contribution of the listed studies, the mechanical behavior of portlandite beyond the elastic range is still under question. Considering that this is critical to capture the onset of permanent deformations and fracture, the current study provides the first-known effort to address this research gap. The outcome of this effort also contributes to estimate the tensile strength and failure strain of portlandite subjected to extreme external loads.
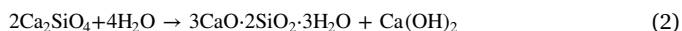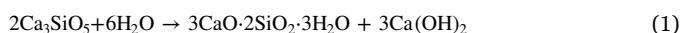
The structure, energetics, and reactivity of the portlandite's surfaces have been investigated in the literature. Kalinichev and Kirkpatrick [16] performed molecular dynamics (MD) simulations to study the binding of chloride ions to the surfaces of various HCP phases, including portlandite. It was observed that the chloride binding capacity of portlandite is significantly higher than that of tobermorite and ettringite, the other two abundant phases of the HCP. Through a set of MD simulations, Wang et al. [36] reported that for water at the portlandite's (001) surface, the $Ca_3^{VI}OH$ surface functional groups serve as both H-bond donors and acceptors. Galmarini et al. [8] performed systematic experimental tests and atomistic simulations to study the change in the morphology of portlandite in the environments where various ions, such as chlorides, nitrates, sulfates, and silicates exist. It was revealed that the portlandite particles have a regular facetted shape in the presence of chloride and nitrate ions, whereas the sulfate groups result in the formation of portlandite particles with a hexagonal platelet shape. Moreover, it was found that the addition of silicates leads to the formation of large agglomerated particles with irregular shapes. The hydration of CaO was investigated using reactive MD simulations by Manzano et al. [22]. It was reported that the CaO (001) surface is highly reactive toward water and maintains its structure only up to 0.75 water monolayer content. For a higher water content, however, the surface is altered drastically, which results in the formation of disordered calcium hydroxide. The listed studies contribute to provide a more detailed insight on how the properties of the fractured surfaces of portlandite identified in the current study are compared with those of the ideal surfaces available in the literature.

In this study, the Molecular Dynamics (MD) method is utilized to investigate the structural, thermal, and mechanical properties of portlandite. To this end, the crystalline structure of portlandite is constructed at the nano-scale. The effect of temperature on the lattice parameters and unit cell volume of portlandite is investigated. The CTEs are then determined and compared to those available in the literature. Subsequently, uniaxial tensile strains are applied in the x, y and z axis of the equilibrated super cells and the stress-strain data are recorded. A separate structural damage analysis is performed to reveal the correlation between the structural damage and the stress-strain relationships obtained from MD simulations. The failure mechanism for portlandite elongated in the three orthogonal directions is identified and discussed in detail. To understand the plastic energy required for fracture, the energies of the fractured surfaces are calculated and compared with those for the ideal surfaces. From the stress-strain curves, the tensile strength, Young's modulus, and fracture strain of portlandite are fully characterized as well. As the algorithm used in this study allows for anisotropic relaxation in the directions perpendicular to the direction of straining, the Poisson's effect can be simulated without imposing any artificial constraints. To investigate the sensitivity of the mechanical properties of portlandite to temperature and strain rate effects, an extensive set of MD simulations are conducted under different temperatures and strain rates. From the obtained results, the relationship between the fracture stress of portlandite and strain rate is determined at various temperatures. The outcome of this study provides the information needed to understand the key mechanical properties of portlandite at both elastic and plastic ranges. This directly contributes to improve the models available for cementitious materials at different length scales.

2. Computational methodology

2.1. Crystalline structure

Portlandite is the mineral name of crystalline calcium hydroxide, $Ca(OH)_2$, and is the calcium analogue of brucite ($Mg(OH)_2$). In cementitious materials, portlandite is produced through the hydration of tricalcium silicate (Ca_3SiO_5) and dicalcium silicate (Ca_2SiO_4) as shown in Eqs. (1) and (2), respectively:

$$2Ca_3SiO_5 + 6H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2 \qquad (1)$$

$$2Ca_2SiO_4 + 4H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2 \qquad (2)$$

where the first product in both reactions ($3CaO \cdot 2SiO_2 \cdot 3H_2O$) is the calcium-silicate-hydrates (C–S–H) gel, which is another important component of the HCP. While the two chemical reactions are similar in terms of the compounds produced (i.e., C–S–H gel and portlandite), they demonstrate different reaction rates. This is why the first reaction is known to be responsible for early-age strength, while the second one, which has a lower reactivity, contributes to the strength of the HCP in later stages. Portlandite is expected to decompose into calcium oxide and water when it is heated to 500 °C [9]:

$$Ca(OH)_2 \overset{\Delta}{\rightarrow} CaO + H_2O \qquad (3)$$

The crystalline structure of portlandite is well known and has been identified by both X-ray spectroscopy [3,28] and neutron diffraction [4]. The position of hydrogen atoms in the crystalline structure of portlandite has been determined using X-ray diffraction and Fourier synthesis techniques [29] and ^1H nuclear magnetic resonance (NMR) [14]. While portlandite has a hexagonal morphology, the crystalline structure is trigonal with space group of $P\bar{3}m1$. The crystallographic parameters of the unit cell of portlandite is $a = b = 3.5925$ Å, $c = 4.905$ Å, $\alpha = \beta = 90°$, and $\gamma = 120°$. Fig. 1 illustrates the unit cell of portlandite, which contains a total of five atoms. The calcium atoms are octahedrally coordinated with six oxygen atoms. The oxygen atoms are tetrahedrally coordinated with three calcium atoms and one hydrogen atom. The structure of portlandite consists of layers lying in the (001) plane and interacting mainly by weak H-mediated dispersive forces. The oxygen and hydrogen atoms form hydroxyl groups running along the c-axis. In this study, the crystalline structure of portlandite is adopted based on the experimental data by Henderson and Gutowsky [14].

2.2. Molecular dynamics simulations

The MD simulations are conducted using the large-scale atomic/molecular massively parallel simulator (LAMMPS) package [30]. As
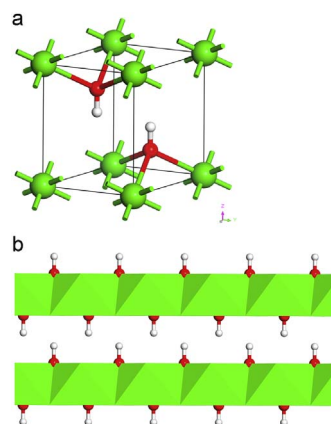

Fig. 1. (a) The trigonal unit cell and (b) the layered structure of portlandite. (Green: Calcium; Red: Oxygen; White: Hydrogen). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)