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A molecular dynamics investigation of hydrostatic compression characteristics of mineral Jennite

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ABSTRACT

This paper focuses on the study of mechanical behavior and deformation of mineral Jennite, under isothermal hydrostatic compression using Molecular Dynamics (MD) modeling. Atomistic structure of mineral Jennite is considered as a choice for representing calcium silicate hydrate (C-S-H), a key constituent in hydrated cement paste. The present work focuses and presents a molecular dynamics simulation approach to ascertain hydrostatic compression characteristics of mineral Jennite. The pressure–specific volume, and specific internal energy–specific volume relationships under isothermal hydrostatic compression conditions were determined. For the pressures ranging from 0.0001 GPa to 5 GPa, computational modeling results indicated that a linear relationship may be sufficient when describing the pressure–specific volume relationship. The results obtained in this study compared well with experimental and theoretical results recently published by other researchers. Additionally, a quadratic function was found to be appropriate to describe the specific energy–specific volume relationship, for the same pressure range used for studying the pressure–specific volume relationship. The pressure–specific volume, and specific internal energy-specific volume relationships reported in this paper are useful for further estimation of pressure–specific volume constitutive Hugoniot of the nanoscale mineral Jennite. Additionally, MD approach discussed and presented in this paper can be applied to understand hydrostatic compression behavior and deformation characteristics of other atomistic structures representing C-S-H. Further, the computational material modeling approach discussed in this paper provides an alternative methodology that can aid in the understanding of the deformation mechanisms and developing constitutive relationships from atomistic structures of materials.

1. Introduction

Several military applications involve cementitious-based concrete materials being subjected to shock and penetration loading conditions. Cementitious materials possess a complex hierarchical structure that span across several length scales. From an engineering perspective, concrete is a composite material in which cement paste binds together the coarse/fine aggregates and other fiber/nanoparticle reinforcement [1]. The discrete phases, nano-to-micro in geometrical size are the constituents that determine the mechanical response for the cementitious based mixtures [2]. The strength of the binder is dictated by the chemical reactions occurring between water and cement, a process known as hydration. Hydration occurs when unhydrated cement clinkers dissolve in water and later form a solid composite system. When cement hydrates, a semi-crystalline material is formed that is comprised of Calcium Silicate Hydrate (C-S-H), along with Calcium Hydroxide (CH), and other components that vary according to the composition of the clinkers [3]. The molecular structure of hydrated components continuously evolves throughout the service-life of the cement paste [3,4]. However, the cement paste's structure and its mechanical properties are considered to be sufficiently developed after 28 days of hydration [3].

Among the hydrated products generated when standard Portland Type I cement is used, the most abundant phase is the C-S-H [3,4]. Since C-S-H is the most abundant phase by volume in cement paste, its properties are thought to be the most dominant of the hydrated phases [3–5]. It is believed that C-S-H controls the strength and deformation behavior of cement paste [6,7]. Due to the complex hierarchical

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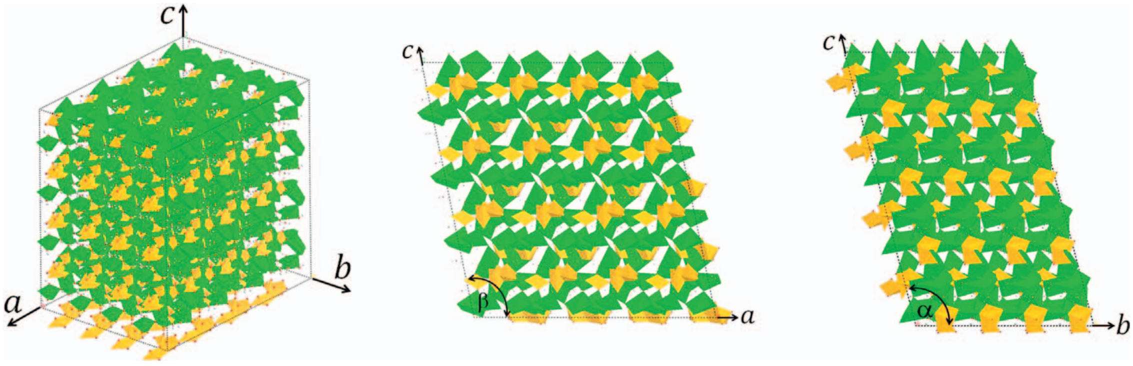

(a) Isometric view of mineral Jennite. (b) View from b-axis, (ac) plane. (c) View from a-axis, (cb) plane.

Fig. 1. Molecular structure of nanoscale mineral Jennite viewed from the different crystallographic directions: (a) isometric, (b) from *b*-axis onto (*ac*)-plane, and (c) *a*-axis onto (*cb*)-plane.

structure of the cement paste, changes in cement chemistry at the nanoscale level strongly influence the microstructural and global mechanical property evolution of cement binder [8].

Although uniquely defining C-S-H molecular structure has proven elusive and many different molecular models have been proposed [9–12], the C-S-H has been frequently represented using molecular models based on the atomistic structure of mineral Tobermorite and/or mineral Jennite [12–14]. Additional detailed discussion of C-S-H molecular structure representations can be found in [9,10,15,16–20]. The present work investigates the hydrostatic compression characteristics of mineral Jennite used as a choice for representing C-S-H, with the goal of presenting a MD modeling methodology that can be used to study other atomistic structures representing C-S-H. Further, present paper sheds light on the mechanical phenomena during hydrostatic compression that is occurring in mineral Jennite, which has been employed in the literature as a choice for representing C-S-H, and understanding hydrated cement paste C-S-H characteristics.

At the nanoscale, properties of cementitious materials are typically studied using atomistic models based on molecular dynamics (MD) techniques. Previous research efforts have focused on using atomistic/molecular dynamics modeling to estimate the elastic properties of molecular structures representing C-S-H in cement paste [17–20]. To date, limited studies have been conducted to investigate the hydrostatic compression deformation mechanisms that occur in the hydrated cement paste molecular structure [9–11,21]. Recently, Moon et al. [22] published experimental results of hydrostatic compression of mineral Jennite, along with theoretical predictions based on first principles calculations. This paper presents the first direct comparison of MD predictions with the experimental results and the first principles calculations reported by Moon et al. [22].

The main objective of this paper is to investigate and understand the mechanical deformation behavior of mineral Jennite under hydrostatic compression, and present a viable MD modeling approach. Such a MD computational material modeling approach for hydrostatic compression provides an alternative methodology that can aid in the understanding of the deformation mechanisms and developing constitutive relationships starting from atomic structures of materials. The hydrostatic pressure vs. specific volume $(P - \nu)$ and specific internal energy vs. specific volume $(\varepsilon - \nu)$ relationships can be used to estimate the Hugoniot relations for mineral Jennite as well as other representations of C-S-H. The Hugoniot relations are necessary when investigating the high strain rate deformation behavior of materials [23,24]. Determining the pressure vs. specific volume, specific energy vs. specific volume relationships from physical experiments is generally a difficult and cost prohibitive task. The present work provides an option for developing these constitutive material relationships using molecular dynamics modeling methods.

The Hugoniot relations are relationships between pairs of thermodynamic properties of a material that provide the minimum amount of thermodynamic state information required to estimate the response of a one-dimensional shock wave propagation through a material [23,24]. Typical Hugoniot relations are pressure vs. specific volume, $(P - \nu)$, shock wave velocity vs. particle velocity, $(U_s - \dot{x})$, longitudinal stress vs. specific volume, $(\sigma_{11} - \nu)$, and longitudinal stress vs. particle velocity, $(\sigma_{11} - \dot{x})$. The pressure vs. specific volume Hugoniot relation for a material can be estimated using isothermal relationship between pressure and specific volume, and between specific internal energy and specific volume based on [23,24].

$$P^{(H)}(\nu) = P^{(\theta)}(\nu, \theta_0) + \frac{\gamma(\nu)}{\nu}\left(\varepsilon^{(H)}(\nu) - \varepsilon^{(\theta)}(\nu, \theta_0)\right) \qquad (1)$$

where P, ε, γ, and ν indicate pressure, specific internal energy, Grüneisen parameter (a material property), and specific volume, respectively. The superscripts H and θ indicate that the properties are either measured along the Hugoniot or along an isothermal path at temperature θ_0. Present work, focuses on determining the relationships $(P^{(\theta)} - \nu)$ and $(\varepsilon^{(\theta)} - \nu)$ at room temperature (298 K) based on molecular dynamics simulations.

2. Computational model development of mineral Jennite

The molecular structure of mineral Jennite (a choice of representation employed for C-S-H in hydrated cement paste) for this work was obtained from American Mineralogist Crystal Structure Database (AMCSD), which corresponds to the structure proposed by Bonaccorsi et al. [25]. The MD modeling analyses were performed using the Discover module of Accelrys Material Studio. The interatomic interactions were modeled using COMPASS force field, which was developed to describe general atomic interactions in condensed-phase materials [26].

The molecular structure of mineral Jennite is described as a triclinic unit cell of dimensions $a = 10.6$ Å, $b = 7.3$ Å, $c = 10.9$ Å, and angles $\alpha = 101.3^\circ, \beta = 97.0^\circ, \gamma = 109.7^\circ$ [25]. In Fig. 1, a crystal of mineral Jennite, consisting of 64 unit cells in a 4 × 4 × 4 arrangement, is illustrated. The molecular structure is layered, formed by sheets of calcium oxide connected to long silica chains. These long silica chains are not bonded to each other but only to the calcium oxide sheets. The calcium oxide sheets are linked to each other by additional calcium octahedral sites. The layers containing the calcium octahedral sites connecting the calcium oxide sheets also contain most of the bonded water molecules in the structure [25].

3. Isothermal hydrostatic compression

Isothermal compression was simulated in the pressure range from 0.0001 GPa (1 atm) to 5 GPa (∼49 atm). The simulation scheme