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Molecular dynamics study on the mechanical properties of Portland cement clinker phases

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ABSTRACT

Recent advances in concrete industry have highlighted the need for accurate knowledge about its nano-structure and mechanical properties. Cement, as the main material of concrete, is of great importance. Additionally, using nano-scale calculation methods have led to better understanding of materials functionalities. In this paper, it is tried to estimate the mechanical properties of cement clinker phases by atomistic simulation and via molecular dynamics method. To achieve this goal, C_2S, C_3S, C_3A, and C_4AF were studied as major phases and periclase, calcium oxide, arcanite, aphthitalite, and thenardite were also selected as minor phases. Furthermore, the eight COMPASS, COMPASSII, CLAYFF, Dreiding, Universal, CVFF, PCFF and INTERFACE force fields were used for atomistic simulations. Finally, the bulk modulus, shear modulus, Young's modulus, Poisson ratio and compressibility properties were calculated by formulas of elasticity theory. Obtained results were compared with those in the pertinent literature. The results revealed that using molecular dynamics method was suitable in estimating mechanical properties of cement phases. These findings might be applied in larger scales and also multi-scale simulations.

1. Introduction

Concrete, as the most important material in building construction, has always been taken into consideration by researchers [1,2]. Numerous advances have been made in knowing the micro structure of concrete in recent years those have led to producing high-performance concrete. Concrete consists of cement, water, and aggregate and therefore, knowing its components and products resulted from chemical reactions will help researchers to have better comprehension about it [3]. Among these components, cement, as the main ingredient, is of great importance compared to other constituents. The raw materials of cement are clay and limestone which mostly include calcium oxide, silica, and alumina. Cement production method directly has some considerable effects on the cement hydration and its products properties. The most important phase of Portland cement clinker is C_3S. It has great influence on short-term cement properties. The second most important phase is C_2S which has more influence on long-term cement properties. C_3A and C_4AF are the other main Complexes. These are of secondary importance in comparison to C_3S and C_2S on cement properties [4]. In addition to these chemical compounds, some other phases are also formed in clinker. They are results of existence of less-important oxides in the primary materials. These phases, however, do not play significant roles on the final mechanical properties of cement paste; but they are important in the durability and some physical properties. Regarding this issue the most important phases are: thenardite, aphthitalite, arcanite, free lime and periclase [5].

Understanding the effects of these complex compounds on clinker properties is crucial to improve the cement hydration products.

Moreover, given the experimental limitations and also the necessity of speeding up the research studies in this area, it is important to use simulation methods. Molecular dynamics is one of the best methods for nano-scale simulation [6]. Atomistic-scale simulation by considering molecule and atom interactions is done through two ways: (1) molecular dynamics (MD), (2) Monte Carlo (MC) method [7]. The literature survey has indicated that the molecular dynamics is a very effective method to simulate different compounds, and it also is suitable to find the mechanical properties of materials. This method has recently been used in various structures and scientific works [8–12].

This paper deals with the mechanical properties of the phases of cement by using molecular dynamics method. The conducted studies on mechanical properties of cement clinker phases are rare. Velez et al. calculated the modulus of elasticity and hardness for the four main phases of cement [13]. They produced the four main clinker complex phases under experimental conditions. Then they used nanoindentation method to find out nano scale mechanical

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properties. The modulus of elasticity of the main phases were estimated to be between 125 GPa and 145 GPa. Another study was conducted by Boumiz et al. in which the transmission of ultrasonic wave method was employed to calculate the C_3S elastic modulus [14]. Granju et al. also dealt with the mechanical properties of C_3S phase. The C_3S modulus of elasticity was reported to be 117 GPa [15].

Regarding simulation studies, only few fundamental studies have been conducted. Manzano investigated the mechanical properties of C_2S and C_3S. He estimated the modulus of elasticity of these two phases by using molecular dynamics method [16]. In this simulation, no investigation was done on other major and minor phases. In another study by Wu et al. the mechanical properties of C_2S, C_3S, and C_3A were taken into consideration by molecular dynamics method [17]. In this study, the minor phases were not examined and the main phase of C_4AF was not studied either. The reported results of modulus of elasticity were not consistent and had a wide range. This difference in results is due to different used force fields, simulation engines and supercell sizes.

In another study, Wang et al. calculated the modulus of elasticity of C_2S by using density functional theory (DFT) and Reaxx FF molecular dynamics simulation [18]. Manzano et al. used the combination of classical and quantum–mechanical simulation methods to study the detailed physicochemical changes of the clinker phases alite and belite when guest ions are incorporated into their structure [19]. In this study indentation modulus was also studied. In another study, molecular dynamics simulation was done to estimate properties of C_3S [20]. Structural, mechanical, and reactivity Properties of C_3S were conducted with DFT by Manzano et al. [21]. C_3S hydration and dissolution mechanism were studied by them. In this study ReaxFF Force field was used for molecular simulation [22]. In another work a force field for surface properties of C_3A was modified [23].

Furthermore, a set of limited experimental research studies have also been conducted on clinker minor phases [24–28]. Isaak et al. measured elastic modulus of MgO [26] and Oda et al. calculated elastic properties of CaO [27]. In these studies, however, clinker minor phases were not considered as their real structures and only some natural minerals were studied to find out their mechanical properties. Regarding theoretical and simulation studies, only few significant works have been carried out. Elastic properties of CaO and MgO were studied with MD, DFT, ab initio and linearized-Muffin-Tin orbital methods [29–33]. Mechanical properties of thenardite were conducted with DFT by Arbeck et al. [34]. No reliable theoretical study on arcanite and aphthitalite has been done.

Based on the few conducted studies and lack of any final certain conclusion concerning the mechanical properties of clinker phases, in this paper it was tried to estimate the mechanical properties of the above-mentioned phases using molecular dynamics simulations. Moreover, given the importance of selecting the suitable force field in simulations, eight force fields of COMPASS, COMPASSII, CLAYFF, Dreiding, Universal, CVFF, PCFF and INTERFACE were used. Then, the simulation process was carried out, and the mechanical properties were determined. Results were compared with those in related literature. Finally some conclusions were made.

2. Portland cement clinker phases

Portland cement consists of four major phases and a set of minor phases.

2.1. Major phases

Portland cement clinker is composed of four main phases: alite, belite, tricalcium aluminate and ferrite [3].

Alite (C_3S) is a name for tricalcium silicate (Ca_3SiO_5), sometimes formulated as $3CaO{\cdot}SiO_2$. It is the most important portion of Portland cement clinker. It constitutes 50–70% of Portland cement clinker [35]. Alite reacts quickly with water, and it is in charge of setting and development of early strength (at ages up to 28 days). The crystalline structure of C_3S is built up from independent tetrahedra with Ca^{2+} in the corners and oxygen in the center. Tetrahedra are placed in the following manner: three calcium ions and three SiO_4 tetrahedra are lying on ternary axis. They are linked by two triplets of calcium ions [36]. At room temperature, C_3S has a triclinic unit cell with $P\bar{1}$ space group. Fig. 1a depicts C_3S atomistic structure.

Belite (C_2S), dicalcium silicate (Ca_2SiO_4), sometimes is formulated as $2CaO{\cdot}SiO_2$. It is another important constituent of Portland cement clinker. It constitutes 15–30% of normal Portland cement clinkers [35]. C_2S also has various polymorphs: α-C_2S, β-C_2S and γ-C_2S. It is normally formed as the β polymorph. All C_2S phases are formed of independent SiO_4 tetrahedra linked by calcium atoms, but the structural arrangement is changing in individual polymorphs. Belite is the mineral in Portland cement responsible for development of late strength [5,37].

It reacts slowly with water, thus contributing little to the strength during the first 28 days. But substantially it is responsible for long-term strength. The unit cell of β-C_2S is monoclinic with $P21/c$ space group. Fig. 1b depicts C_2S atomistic structure.

It should be noted that alite and belite react with water to form calcium silicate hydrates (C-S-H) and portlandite ($Ca(OH)_2$) [3].

Tricalcium aluminate $Ca_3Al_2O_6$, often formulated as $3CaO{\cdot}Al_2O_3$ to highlight the proportions of the oxides from which it is made, is the most basic of the calcium aluminates. Despite being a significant mineral phase in Portland cement, Tricalcium aluminate does not exist in nature. The aluminate phase constitutes 5–10% of most normal Portland cement clinkers. The C_3A structure is composed of $[AlO_4]^{5-}$ tetrahedra forming rings $[Al_6O_{18}]^{18-}$ composed of six AlO_4 groups sharing corners [38].

It reacts quickly with water, and can cause undesirably rapid setting unless a set-controlling agent, usually gypsum, is added. Sulfate ions in solution lead to the formation of an insoluble layer of Ettringite [3,5]. C_3A has a cubic unit cell with $Pa\bar{3}$ space group. Fig. 1c depicts C_3A atomistic structure.

The ferrite phase (C_4AF) is an important phases in clinker with chemical formula of Ca_2AlFeO_5. It also exists in nature as the rare mineral Brownmillerite. It makes up 5–15% of normal Portland cement clinkers. The ferrite phase can be prepared with any composition in the solid solution series $Ca_2(Al_xFe_{x-1})_2O_5$, where $0 < x < 0.7$. The composition C_4AF is only a point in this series, with $x = 0.5$. C_4AF has a little effect upon the physical properties of cement [3].

The unit cell of C_4AF is orthorhombic with Ibm 2 space group. Fig. 1d depicts C_4AF atomistic structure.

2.2. Minor phases

Calcium Oxide, periclase, thenardite, aphthitalite and arcanite are the most important minor phases in Portland cement clinker.

Calcium oxide (CaO), in cement industry generally known as free lime, is a widely used chemical compound. It is a white, alkaline, caustic, crystalline solid at room temperature [39]. CaO forms in general agglomerations of round particles. Two types of calcium oxide can be recognized in clinker. Primary free lime which did not react with other components because of errors in raw mix preparation. For example, coarse limestone grains or insufficient homogenization, or at least inadequate burning conditions or to high lime saturation factor are responsible for free lime existence in clinker. Second type is the secondary free lime. It is formed as a result of