

# Molecular simulations of cement based materials: A comparison between first principles and classical force field calculations



Sylvia M. Mutisya<sup>a</sup>, James M. de Almeida<sup>a</sup>, Caetano R. Miranda<sup>b,\*</sup>

<sup>a</sup>CCNH, Universidade Federal do ABC, Santo André, SP 09210-580, Brazil

<sup>b</sup>DFMT, Instituto de Física, Universidade de São Paulo, São Paulo, SP 05508-090, Brazil

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## ABSTRACT

The heterogeneity and complexity of the cement structure and processes makes the interpretation of experimental data challenging. Atomistic simulations allow investigations at the atomic level of interactions, thus having the potential to provide complementary information to experiments. In this regard, the investigation of the transferability of the available force fields as well their ability to predict the properties of interest is an important prerequisite. In this work, we compare CLAYFF force field against first principles Density Functional Theory (DFT) calculations focusing on its ability to predict structural, vibrational and thermodynamic properties of cement phases differing in the degree of hydration. The systems studied include tobermorite 9 Å, 11 Å, 14 Å, gypsum, tricalcium aluminate and ettringite. Our results indicate that CLAYFF describes well the lattice parameters within acceptable errors. However for the vibrational properties, there is a significant alteration in the silicate, sulfate, water and OH frequencies in comparison to DFT and experimental results. DFT Bader charge analysis indicate that the charge on the interlayer calcium ions in tobermorite does not change with increase in hydration, implying that the nature inter-atomic bonding within the layers remain unchanged. For the thermodynamic quantities investigated (*i.e.* Helmholtz free energy, entropy and specific heat), CLAYFF results are in agreement with DFT calculations. Our findings indicate that water enhances the stability of the hydrated phases based on the lower values of the Helmholtz free energy. We demonstrate that CLAYFF can capture consistently the thermodynamic properties of cement phases.

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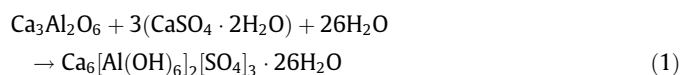
## 1. Introduction

Cement is one of the most consumed material in the world and its manufacturing process is responsible for about 8% of the total world CO<sub>2</sub> emissions [1,2]. Most of the cement produced is used to prepare concrete in addition to other applications such as a barrier for nuclear wastes [3,4] and for solidification/stabilization of a broad range of contaminated materials [5]. To improve the durability of concrete structures as well as produce novel cements for applications in extreme environments, it is important to understand the structure and thermodynamic properties of cement at a molecular level.

One of the major challenges in cement science is the limited understanding of the structure of the main hydration phase, calcium silicate hydrate (CaO·SiO<sub>2</sub>·H<sub>2</sub>O or C-S-H) [6]. C-S-H is known to be poorly crystalline to almost amorphous material, with structure organized over sizes less than 100 Å [7]. It has a complex

pore structure spanning over tens and hundreds of nanometers [8–10]. Nanoindentation analysis by Constantinides et al. [11] have shown that mechanically, C-S-H behaves as a nanogranular material composed of two distinct densities. A recent study has unveiled an extended pore network and a continuum distribution of local densities [12] beyond the colloid model [13,14] based on two distinct local densities. The atomic structure of C-S-H is not yet fully described, but XRD experiments have showed its similarities with the naturally occurring crystalline mineral, tobermorite [15–17].

Although C-S-H is associated with most of the properties observed in cement, other hydrated cement phases play a role in durability. One such phase is ettringite (Ca<sub>6</sub>[Al(OH)<sub>6</sub>]<sub>2</sub>[SO<sub>4</sub>]<sub>3</sub>·26H<sub>2</sub>O) which is produced from the hydration of tricalcium aluminate (3CaO·Al<sub>2</sub>O<sub>3</sub> or C<sub>3</sub>A) in the presence of gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O). The chemical reaction of C<sub>3</sub>A and gypsum is shown in Eq. (1).



\* Corresponding author.

E-mail address: [cmiranda@if.usp.br](mailto:cmiranda@if.usp.br) (C.R. Miranda).

Ettringite formation both controls the kinetics of hardening as well as maintains a good workability at early ages [18]. On the other hand, the presence of ettringite in mature cement paste is associated with degradation of concrete structures [19–21]. Delayed ettringite formation can be due to the availability of sulfate [22,23] or if the concrete mixture is under steam curing conditions with subsequent moist conditions [24]. It is believed that the formation of ettringite is a volume expanding reaction which causes damage to the cement paste [25,26]. However, the damage caused by sulfate attack cannot be explained solely by ettringite precipitation, and the link between ettringite formation and expansion is not clear [27,28].

The complexity of the cement structure and the processes responsible for the observable properties makes the interpretation of experimental data challenging. Atomistic simulations have the potential to provide useful information on understanding the structure of materials, since they allow investigations at the atomic level of interactions. Since the accuracy of atomic simulations is dependent on the choice of force field, detailed tests of the force field's description of the properties of interest is necessary.

A number of force fields have been optimized for cementitious materials including CSH-FF [29], INTERFACE [30] and REAXFF [31] force fields. In this work, we focus on CLAYFF [32] which was tested on a variety of systems including boehmite, portlandite, kaolinite, pyrophyllite, montmorillonite and hydrotalcite. In CLAYFF formulation, most interatomic interactions are treated as non-bonded. This allows the force field to be used for a wide variety of phases and to properly account for energy and momentum transfer between the fluid phase and the solid, while keeping the number of parameters small enough to allow modeling of relatively large and highly disordered systems. Over the years, CLAYFF force field has been used widely in the study of clays [33–35] and cement materials [36–38]. In this study, we investigate CLAYFF's accuracy in the description of structural, vibrational and thermodynamic properties for hydrated and anhydrous cement phases. Of interest here is the main hydration phase (C-S-H) which is responsible for the majority of the cement mechanical properties and the hydration reaction which produces ettringite due to its link to concrete deterioration. We model the C-S-H atomic structure with tobermorite crystal and in this regard, we investigated three phases of tobermorite (tobermorite 9 Å, 11 Å and 14 Å) which differ in the degree of hydration. In relation to the ettringite formation, we studied gypsum, tricalcium aluminate and ettringite.

Investigation of the vibrational frequencies reveals the stability of the relaxed systems and the frequencies can be directly compared to infrared and Raman spectra experiments. In addition, thermodynamic properties are useful in establishing stability relationships in terms of fluid composition, temperature and pressure. Experimentally, this ability is limited due to uncertainties in the quality of data especially for cementitious materials. Experimental data obtained by different approaches such as calorimetry, phase equilibria and solubility experiments is often conflicting due to problems intrinsic to the methods employed. Some sources of thermodynamic experimental data of cement phases include the compilations by Sarker et al. [39], Glasser et al. [40] and Taylor [41]. On the other hand, theoretical investigation of thermodynamic properties of minerals is challenging because it involves the comparison of anhydrous mineral which is governed by ionic and covalent interactions with a molecular liquid or crystal depending on the water reference state which may involve many interactions. Few theoretical studies have been conducted on the thermal properties of cement [42–44], thus verifying the performance of classical force fields in the description of these properties is important for future investigations.

## 2. Computational details

### 2.1. First principles calculations

First principles calculations were performed within the Density Functional Theory (DFT) [45,46] using the plane-wave projector augmented wave method [47] and the generalized gradient approximation in the Perdew-Burke-Ernzerhof [48] as implemented in the Vienna Ab-initio Simulation Package (VASP) [49,50] simulation package. After thorough convergence tests, the plane wave energy cutoff was found to be 450 eV. Initial configurations of all the structures were obtained from experimental data and then the unit cell parameters and atomic positions optimized with a force convergence criterion of  $10^{-4}$  eV/Å. Atomic charges on all atoms were obtained by performing a Bader analysis on the charge density calculated from VASP using the Bader analysis code by Henkelman et al. [51].

### 2.2. Molecular mechanics calculations

Classical molecular mechanics (MM) simulations were performed using LAMMPS [52] simulation package. The ion-ion, water-water and ion-water interactions were described using the CLAYFF [32] force field. The bonded interaction parameters describing the bond stretching and angle bending of the sulfate anion in gypsum and ettringite were adopted from the work by Kalinichev et al. [53]. Long range coulombic interactions are calculated using the PPPM method [54] with a cut-off radius of 10 Å. The search for local minima followed the conjugate gradient [55] procedure. More strict convergence criterion was applied for tobermorite 11 Å, tobermorite 14 Å and ettringite due to the large number of water molecules and OH groups.

### 2.3. Phonon calculations

The minimized structures from both first principles and classical MM simulations were used as input for the phonon calculations. The finite difference method using the Phonopy code [56] with a uniform displacement of 0.01 Å was used for the calculation of the harmonic vibrational frequencies. The phonon spectrum was computed by using supercells of  $2 \times 2 \times 2$  for tobermorite 9 Å, tobermorite 11 Å, tobermorite 14 Å and gypsum. The  $2 \times 2 \times 2$  supercells were not optimized because the sizes of the unitcells are relatively large, thus we do not expect a considerable change of the properties of interest after replication. The  $C_3A$  and ettringite unit cells did not need to be replicated, as the unit cells are already large enough to avoid spurious interactions with neighboring cells. During the forces calculation by both first principles or MM techniques, the cell volume and atomic positions were fixed. A major challenge in the calculation of phonons using first principles approach in these systems is the high computational cost because of the large supercell sizes.

The thermodynamic quantities (Helmholtz free energy ( $F$ ), specific heat at constant volume ( $C_v$ ) and entropy ( $S$ )) were obtained from the phonon frequencies by the following relations:

$$F = \sum_{\mathbf{qj}} \left[ \frac{1}{2} \hbar \omega_{\mathbf{qj}} + k_B T \ln [1 - \exp(-\hbar \omega_{\mathbf{qj}}/k_B T)] \right] \quad (2)$$

$$C_v = \sum_{\mathbf{qj}} k_B \left( \frac{\hbar \omega_{\mathbf{qj}}}{k_B T} \right)^2 \frac{\exp(\hbar \omega_{\mathbf{qj}}/k_B T)}{[\exp(\hbar \omega_{\mathbf{qj}}/k_B T) - 1]^2} \quad (3)$$

$$S = \frac{1}{2T} \sum_{\mathbf{qj}} \hbar \omega_{\mathbf{qj}} \coth[\hbar \omega_{\mathbf{qj}}/2k_B T] - k_B \sum_{\mathbf{qj}} \ln [2 \sinh(\hbar \omega_{\mathbf{qj}}/2k_B T)] \quad (4)$$

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