Understanding the Reactivity of Dicalcium Silicate by Density Functional Theory

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Abstract. *Ordinary Portland Cement (OPC) is a mixture consisting of various phases. Because of mineralogical complexity, the relationship between chemical reactivity of the mixture and each individual phase is still unanswered question. In this study, computational method based on Density Functional Theory (DFT) was applied to investigate the chemical reactivity of different polymorphs of dicalcium silicate crystals. At first, computationally generated dicalcium silicate crystals were geometrically optimized to achieve targeted convergence criteria for computing the total internal energy, lattice parameters, and atomic arrangement at 0K. The simulations performed explain well the thermodynamic stability as well as the synthesis temperatures of the different polymorphs of dicalcium silicate.*

Keywords: *Ordinary Portland Cement, Dicalcium Silicate, Reactivity, Density Functional Theory.*

1 Introduction

Ordinary Portland Cement (OPC) is one of the most manufactured materials in the world. Cement presents a mixture of various minerals as the elevated temperature decreases during the cement manufacturing process (Taylor, 1997). Because of the mineralogical complexity of clinker materials and complicated chemistry at high temperature, the origin of different reactivity of various minerals or different polymorphs in cement is still an open question. For instance, the reactivity of dicalcium silicate, which accounts for the second largest portion in typical OPC can be a key issue to produce high performance cement or reduce carbon dioxide emissions in cement manufacturing. However, the origin of the different reactivity of the polymorphs of dicalcium silicate has not been studied yet. Dicalcium silicate forms five different polymorphs (α-C_2S, α'_H-C_2S, α'_L-C_2S, β-C_2S, γ-C_2S) depending on sintering temperatures (Balonis and Glasser, 2009; Cuberos *et al.*, 2009; Taylor, 1997). It is well known that these polymorphs have identical chemical formula and mineral composition, albeit with slightly different ion substitution rates. They exhibit different crystal structures and reactivity characteristics which determine the entire chemical reaction kinetics of cement particles containing dicalcium silicate.

Several experimental methods have been conducted to study the reactivity of dicalcium silicate. Bensted (1978) found that γ-C_2S has significantly lower reactivity than β-C_2S by studying X-Ray Diffraction and Differential Thermal Analysis. The results of Cuberos et al.

(2009) and Fukuda and Taguchi (1999) suggest that the order of reactivity between the polymorphs of dicalcium silicate is α-C_2S > α'$_H$-C_2S > β-C_2S > α'$_L$-C_2S > γ-C_2S. These experimental methods, however, have limitations in terms of the difficulty of synthesizing pure polymorphs with and without ion substitution and the quantitative interpretation of the order of reactivity.

To accurately and quantitatively determine the reactivity among the different polymorphs of dicalcium silicate, the effect of foreign ion substitution should be eliminated. Recently, the reactivity of pure polymorph states has been studied through simulations. Among the simulation methods, DFT calculation has an advantage of high accuracy in simulating the crystal structures. Recent works on the reactivity of dicalcium silicate using the DFT calculation have been mainly conducted through identifying the Density of States (DOS). Wang et al. (2014) proposed the reactivity of α'$_H$-C_2S, β-C_2S and γ-C_2S in terms of Partial DOS (PDOS) and Local DOS (LDOS) based on data obtained using DFT calculation. Other results (Rejmak, Dolado, Aranda, and Ayuela, 2019; Tao, Zhang, Li, Wang, and Hu, 2019; Wang, Manzano, López-Arbeloa, and Shen, 2018) also show efforts to use DFT calculations in the reactivity studies of dicalcium silicate. However, as a result of the combined peak data from the PDOS, it is difficult to grasp the behavior of individual atoms, thus it is still difficult to find the origin of the difference in reactivity.

In this study, the relationship between the order of reactivity of different polymoprhs of dicalcium silicate and its total energy was investigated by DFT calculation. In addition, the effects of sintering temperature and the total energy of each polymorph are discussed.

2 Computational Methods

Quantum Espresso DFT package was used to perform the basic modeling and analysis of crystals of dicalcium silicates (Giannozzi *et al.*, 2009). The initial model of dicalcium silicate was taken from the lattice parameters and crystal structures published for all cement phases by Balonis and Glasser (2009). In the two crystal structures of α-C_2S and α'$_H$-C_2S, the atoms with occupancies were removed due to the duplicate positions with other atoms. Figure 1 shows α-C_2S which has duplicate atoms in a unit cell. All of the crystal structures were relaxed by Quantum Espresso pw.x executable to obtain a basically stable crystal structure at 0K. The DFT calculations were performed by Perdew-Burke-Ernzerhof (PBE) Generalized-Gradient-Approximation (GGA) functionals. The pseudopotentials made out of ultrasoft-postprecessing (USPP) were used to obtain the electronic information of each atom. The force convergence threshold and energy convergent threshold were 10^{-4} Ry/au and 10^{-3} Ry, respectively. The plane-wave biases set was converged by the energy cutoff of 800 Ry. The crystal structures of all polymorphs were relaxed with Broyden-Fletcher-Goldfarb-Shannno (BFGS) algorithm. Due to the large scale of unit cell, gamma-point sampling was used.
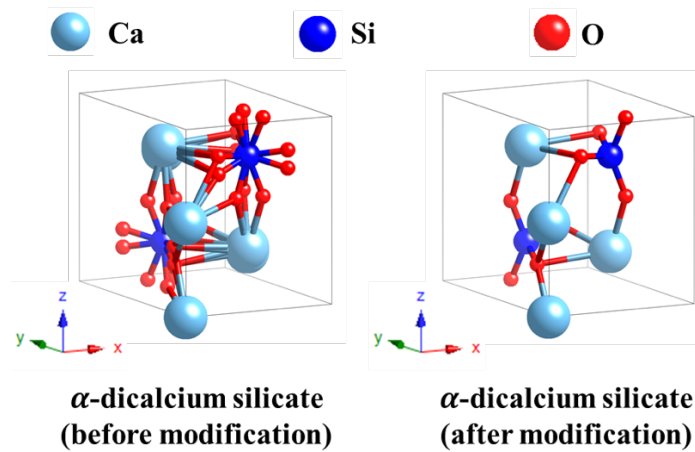
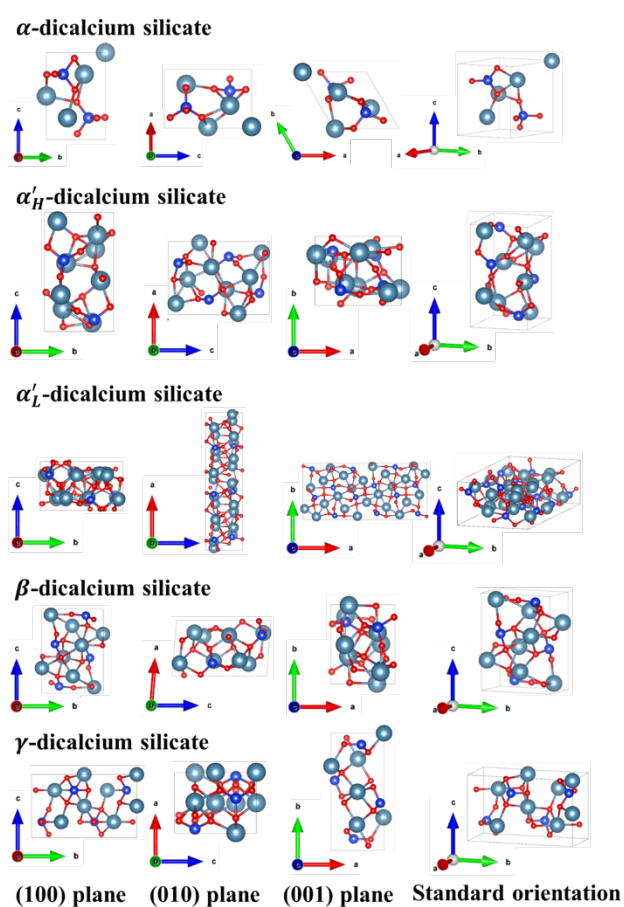**Figure 1.** The crystal structure of α-C$_2$S before and after modification.

3 Results and Discussion

3.1 Relaxation of Polymorphs

The crystal structures of all polymorphs of dicalcium silicate were relaxed from the original crystal structure starting from the lattice parameters and positions taken from the data of cement phases as shown in Table 1 (Balonis and Glasser, 2009). Figure 2 shows the crystal structure viewed from (100), (010) and (001) planes and the standard orientation for the five relaxed dicalcium silicate crystal structures. Since the relaxation method was used which did not change the lattice parameter itself, the basic crystal shape did not change significantly.

Table 1. Cell parameters of dicalcium silicate unit cells.

Polymorphs	Crystal Structure	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Z
α-C$_2$S	Hexagonal	5.579	5.579	7.15	90	90	120	2
α'$_H$-C$_2$S	Orthorhombic	6.85	5.49	9.49	90	90	90	4
α'$_L$-C$_2$S	Orthorhombic	20.871	9.496	5.6	90	90	90	12
β-C$_2$S	Monoclinic	5.502	6.745	9.297	90	85.45	90	4
γ-C$_2$S	Orthorhombic	5.081	11.224	6.778	90	90	90	4

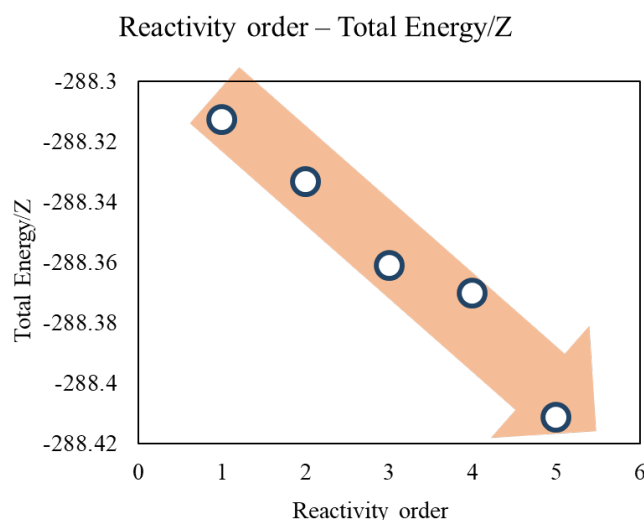**Figure 2.** Relaxed crystal structures of the polymorphs of dicalcium silicate.

3.2 Total Energy

The total energy value from the DFT calculation was used to explain the origin of different reactivity among the five polymorphs of dicalcium silicate. A significant difference was found in the total energy values of the five polymorphs of dicalcium silicate. The total energy values of each crystal structure are shown in Table 2. The total energy values were divided by the Z values for comparison between each formula. Figure 3 shows that the higher the total energy value of the crystal structure, the higher the reactivity. This phenomenon can be explained by the high total energy possessed by the crystal structure which causes the instability of the structure, leading to higher reactivity.

Table 2. The total energy values of the polymorphs of dicalcium silicate.

Polymorphs	Crystal Structure	Total Energy/Z (Ry)	Reactivity Order
α-C_2S	Hexagonal	-288.31	1st
α'_H-C_2S	Orthorhombic	-288.33	2nd
α'_L-C_2S	Orthorhombic	-288.37	4th
β-C_2S	Monoclinic	-288.36	3rd
γ-C_2S	Orthorhombic	-288.41	5th

Reactivity order – Total Energy/Z

Figure 3. The relationship between the total energy and the order of reactivity.

3.3 Sintering Temperature

This can be also linked to the order of sintering temperature. It is well known that the polymorphs of dicalcium silicate forms at different sintering temperatures. Table 3 shows the relationship between the sintering temperature and the order of reactivity. As the sintering temperature required for the formation of each crystal structure increases, more unstable polymorphs are produced. This is observed for α'_H-C_2S, α'_L-C_2S and γ-C_2S. For these three polymorphs having the same orthorhombic structure, it can be inferred that the orders of sintering temperature, total energy, and reactivity match well. The reversed reactivity order of α'_L-C_2S and β-C_2S can be explained due to the different crystal structures.

Table 3. The sintering temperature and the order of reactivity of polymorphs of dicalcium silicate.

Polymorphs	Crystal Structure	Sintering Temperature (°C)	Reactivity Order
α-C_2S	Hexagonal	>1425	1st
α'_H-C_2S	Orthorhombic	1160-1425	2nd
α'_L-C_2S	Orthorhombic	680-1160	4th
β-C_2S	Monoclinic	500-680	3rd
γ-C_2S	Orthorhombic	<500	5th

4 Conclusion

-   This study presents a new perspective to quantitatively explain the order of total energy, instability, and the reactivity of dicalcium silicate crystals in cement.
-   In summary, the relationship between the total energy and the reactivity order of the five dicalcium silicate polymorphs was revealed by DFT calculation. The order of α-C_2S > α'_H-C_2S > β-C_2S > α'_L-C_2S > γ-C_2S, which is the well-known order of reactivity for dicalcium silicate, matches well with the order of the total internal energy calculated from the DFT. This indicates a C_2S polymorph with a higher total energy is more

unstable and thus shows higher reactivity.
- In addition, the order of sintering temperature which plays an important role in cement production was shown to be almost identical with the order of reactivity or the order of total internal energy. In particular, the sintering temperatures of α'_H-C_2S, α'_L-C_2S and γ-C_2S correspond exactly to the order of reactivity. Possible explanation is that materials which are stable at higher temperatures present a more unstable structure at lower temperature, thus resulting in higher reactivity.

Acknowledgement

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