Understanding the Reactivity of Dicalcium Silicate by Density Functional Theory

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1 Introduction

Ordinary Portland Cement (OPC) is one of the most manufactured materials in the world. 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.

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). Several experimental results 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. 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). All of the crystal structures were relaxed by Quantum Espresso pw.x executable to obtain a basically stable crystal structures at 0K. More detail procedure on the simulation can be found in the submitted conference article.
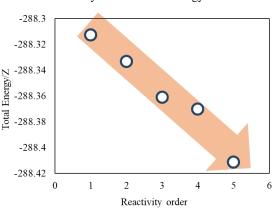
3 Results and Conclusion

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 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.

This can be also linked to the order of sintering temperature. 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.

Table 1. The total energy values of the polymorphs of dicalcium silicate.

Polymorphs	Crystal Structure	Sintering Temperature (°C)	Total Energy/Z (Ry)	Reactivity Order
α-C_2S	Hexagonal	>1425	-288.31	1st
α'_H-C_2S	Orthorhombic	1160-1425	-288.33	2nd
α'_L-C_2S	Orthorhombic	680-1160	-288.37	4th
β-C_2S	Monoclinic	500-680	-288.36	3rd
γ-C_2S	Orthorhombic	<500	-288.41	5th

Reactivity order – Total Energy/Z

Figure 1. The relationship between the total energy and the order of reactivity.

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