AB-INITIO MOLECULAR DYNAMICS STUDY
ON CRYSTAL STRUCTURE OF BETA-DICALCIUM SILICATE

R Sakurada*, Akita National College of Technology, Japan
A K Singh, Rice University, U.S.A.
B Yakobson, Rice University, U.S.A.
M Uzawa, Taiheiyo Cement Co., Ltd., Japan
Y Kawazoe, Tohoku University, Japan

33rd Conference on OUR WORLD IN CONCRETE & STRUCTURES: 25 - 27 August 2008, Singapore

Article Online Id: 100033043

The online version of this article can be found at:

http://cipremier.com/100033043

This article is brought to you with the support of

Singapore Concrete Institute

www.scinst.org.sg

All Rights reserved for CI-Premier PTE LTD

You are not Allowed to re-distribute or re-sale the article in any format without written approval of CI-Premier PTE LTD

Visit Our Website for more information

www.cipremier.com
AB-INITIO MOLECULAR DYNAMICS STUDY
ON CRYSTAL STRUCTURE OF BETA-DICALCICUM SILICATE

R Sakurada*, Akita National College of Technology, Japan
A K Singh, Rice University, U.S.A.
B Yakobson, Rice University, U.S.A.
M Uzawa, Taiheiyo Cement Co., Ltd., Japan
Y Kawazoe, Tohoku University, Japan

Abstract

The crystal structures and hydraulic activities of β and γ- form dicalcium silicates (β-C₂S, γ-C₂S) were analyzed by ab-initio calculation based on quantum mechanics. The mean distances less than 4 Å to the neighboring Ca atoms for all of independent Ca atoms were calculated within unit cell. Ca-Ca mean distances are 3.56 Å in β-C₂S and 3.75 Å in γ-C₂S. The shortening of Ca-Ca distance causes instability of a structure leading to a higher hydraulic activity. The interatomic bond lengths of the dicalcium silicates from the ab-initio calculations agree well with X-ray diffraction analysis. The substitution of Ca atom with Sr atom obtains an interest result that β-C₂S substituted Ca(2) having eight-fold coordinates with Sr is unstable than β-C₂S substituted Ca(1) having seven-fold coordinates with Sr.

Keywords: dicalcium silicate, belite, ab-initio calculation, crystal structure, hydraulic activity

1. Introduction

Belite C₂S (2CaO·SiO₂) has five polymorphs known as α-form, α′-form, α″-form, β-form and γ-form by the temperature of the cement clinker minerals during cooling process. Ordinary Portland cement usually contains β-form C₂S which reacts slower with water and results in lowest rate of heat evolution in four major compounds (C₃S, C₂S, C₃A, C₄AF). β-C₂S contributes to gain strength development in long-term age. On the contrary, γ-form C₂S, produced by a transformation of the crystal structure in slower cooling, scarcely reacts with water in comparison with β-form C₂S. The difference in hydraulic activity between β-form and γ-form Belites depends on the stability of inherent crystal structure. The hydraulic activities of β-C₂S and γ-C₂S have been estimated from crystal structures based on X-ray crystallographic measurements [1]. The experimental result elucidates that shorter Ca-Ca interatomic bond length closely relates to the higher hydration activity of cement clinker minerals. However, little has been made theoretically clear in crystal structure of Belites and in the relationship between the crystal structure and hydraulic activity.

Nowadays, new clinker mineral appears in newly developed cement, “Eco-cement”, that is made from garbage ash of city disposals. The garbage ash contains useful minerals for cement production and high concentrated-chlorides. Calcium chloroaluminate, C₁₁A₇·CaCl₂ that is replaced by aluminate phase (C₃A), is one of clinker minerals of Eco-cement. The high concentrated-chlorides in garbage ash were removed in the form of calcium chloroaluminate, C₁₁A₇·CaCl₂. The fixing of chloride enables one to reduce the chloride content in a commercially available concentration of 300 ppm and to prevent a largest trouble in production of cement.

“Eco-cement” is a modified Portland cement in which aluminate phase (C₃A) is replaced by a new
compound, calcium chloroaluminate, C₁₁A₇CaCl₂. This chloride-rich cement provides a short setting time and early strength gain comparable to an early strength Portland cement. The heating temperature of a kiln for the Eco-Cement is 1350°C, about 100°C lower than that of the kiln for the ordinary Portland cement. The lower heating temperature contributes to energy savings.

As a promotion of such ecological cement production, different types of waste are possibly used as a raw material of cement in the near future. This means that such a new compound, which never exists in conventional ordinary Portland cement, will be yielded and that the ionic exchange of foreign metallic ions with Ca and/or Si ions takes place simultaneously. The decrease of the heating temperature of a kiln may also influence on polymorphs of belite C₂S(2CaO·SiO₂).

Therefore, it is useful to predict the hydraulic activity of cement clinker minerals including newly born compounds as chloroaluminate, C₁₁A₇CaCl₂, in advance. The difference in hydraulic activity between β-C₂S and γ-C₂S was analyzed by numerical simulation using the self-consistent-field discrete variational Xα method (DV-Xα method) [2]. The calculation reveals that the higher hydraulic activity of β-C₂S lies in the weaker Ca-O ionic bond. DV-Xα method has been widely used to investigate solids, clusters and molecules. However, the exchange potential in Hartree-Fock equation is determined using a statistical approximation, i.e., the exchange potential constant that is adjustable from 2/3 to 1.0.

It is required to calculate the crystal structure theoretically without any other intended fitting parameters. Ab-initio molecular dynamics method employs no other statistical assumptions such as above fitting parameters and phenomena-based calculation model. The calculation of molecular electronics from first-principles is conducted directly solving Schrödinger’s equation on the quantum level. The theoretical approaches on atomic level using first-principles calculations have been performed to analyze crystal structure and elastic characteristics of calcium-silicate-hydroxide (C-S-H) so far. J. L. Laugesen calculated Young’s moduli of Portlandite and Forshagite as calcium-silicate-hydroxide (C-S-H) by using density functional method [3]. The first-principles density functional calculations have been mainly carried out in the investigation of electronic structure and band structure of nano-scale electronic devices: magnetism in metal-doped silicon nano-tubes [4] and magnetic behavior of Mn clusters [5].

This work therefore carried out the first-principle calculations based on only quantum mechanics to analyze the hydraulic activity of β-C₂S and γ-C₂S from the inherent characteristics of the crystal structure. Emphasis is given to the bond lengths of Ca-Ca, Ca-O and Si-O to estimate hydraulic activity of β and γ-dicalcium silicates. The bond-lengths less than 4 Å to the neighboring Ca atoms for all of independent Ca atoms were calculated within unit cell. The effect of substitution of Ca atom with Si atom as a trace mineral on hydraulic activity and Ca-Ca bond length has also been calculated.

2. β-C₂S and γ-C₂S

Five distinct crystalline polymorphs of Belite C₂S (2CaO·SiO₂) have been known to α-form, α₁′-form, α₂-form, β-form and γ-form in order of decreasing temperature of stability (Fig.1). Slower cooling at a temperature of 400-500°C may cause the transformation from β-C₂S to γ-C₂S which scarcely reacts with water. β-C₂S in metastable is formed only during cooling, and is not yielded from γ-C₂S on heating. The usual form of dicalcium silicate in ordinary Portland cement is β-C₂S, which reacts more slowly with water and results in lowest rate of heat evolution in four major compounds (C₃S, C₂S, C₃A, C₄AF). β-C₂S contributes to gain...
The structure of β-C₂S has been studied by X-ray diffraction analysis [1]. This structure belongs monoclinic space group \( P2_1/n \) (C\(_{5h}\)) with lattice constants of \( a_m = 5.502 \) Å, \( b_m = 6.745 \) Å, \( c_m = 9.297 \) Å, and the monoclinic angle \( \beta = 94.59^\circ \). The atom coordinates of the monoclinic cell are tabulated in Table 1. The crystal system of γ-C₂S is orthorhombic, and its space group belongs Pbnm with lattice constants of \( a_o = 5.081 \) Å, \( b_o = 11.224 \) Å, \( c_o = 6.778 \) Å from X-ray diffraction data [6]. The atom coordinates are listed in Table 2. The structures of β-C₂S and γ-C₂S are illustrated in Fig. 2 and Fig. 3, respectively.

### Table 1 Atomic coordinates for β-C₂S

<table>
<thead>
<tr>
<th>atom</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(1)</td>
<td>0.2738</td>
<td>0.3428</td>
<td>0.5694</td>
</tr>
<tr>
<td>Ca(2)</td>
<td>0.2798</td>
<td>0.9976</td>
<td>0.2981</td>
</tr>
<tr>
<td>Si</td>
<td>0.2324</td>
<td>0.7814</td>
<td>0.5817</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.2864</td>
<td>0.0135</td>
<td>0.5599</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.0202</td>
<td>0.7492</td>
<td>0.6919</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.4859</td>
<td>0.6682</td>
<td>0.6381</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.1558</td>
<td>0.6710</td>
<td>0.4264</td>
</tr>
</tbody>
</table>

Monoclinic
\( a_m = 5.502 \) Å, \( b_m = 6.745 \) Å, \( c_m = 9.297 \) Å
\( \beta = 94.59^\circ \)

### Table 2 Atomic coordinates for γ-C₂S

<table>
<thead>
<tr>
<th>atom</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(1)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Ca(2)</td>
<td>-0.0099</td>
<td>0.2809</td>
<td>0.2500</td>
</tr>
<tr>
<td>Si</td>
<td>0.4275</td>
<td>0.0966</td>
<td>0.2500</td>
</tr>
<tr>
<td>O(1)</td>
<td>-0.2543</td>
<td>0.0937</td>
<td>0.2500</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.2974</td>
<td>-0.0384</td>
<td>0.2500</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.2985</td>
<td>0.1624</td>
<td>0.0575</td>
</tr>
</tbody>
</table>

Orthorhombic
\( a_o = 5.081 \) Å, \( b_o = 11.224 \) Å, \( c_o = 6.778 \) Å

### 3. Density functional theory and computational procedure

First-principle molecular dynamics is based on the density functional theory and the norm-conserved pseudopotentials. The density functional theory has been most popular for calculation of the electronic structure of many-body systems. The total energy of electron system \( E[\rho(r)] \) is expressed as a functional of electronic charge density \( \rho(r) \) at a particular point of \( r \) in Eq. (1). This energy functional \( E[\rho(r)] \) gives the minimum value of energy in ground-state for the real electronic charge density. The electronic charge density at the exact ground-state \( \rho(r) \) is given by Eq. (2).
\[ E[\rho(r)] = T[\rho(r)] + \int V_{\text{ext}}(r)\rho(r)\,dr + \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|}\,dr\,dr' + E_{xc}[\rho(r)] \]  

(1)

\[ \rho(r) = \sum_{i=1}^{n} |\psi_i(r)|^2 \]  

(2)

Here " \( r \) " indicates coordinate vector in the real space and \( \psi_i(r) \) denotes the one-electron spatial orbital for \( i = 1, 2, 3, \ldots, n \). The terms on right-hand side of Eq.(1) are the kinetic energy of a system of non-interacting electrons, the potential energy by electron-nucleus attraction, the Coulomb interaction energy between the total charge distribution and the exchange-correlation energy of the system, respectively.

By applying the variation principle to the total energy functional \( E[\rho(r)] \) of the electronic charge density \( \rho(r) \) in Eqs.(1)-(2), the Kohn-Sham equation in a similar form of the Schrödinger equation can be easily obtained for the one-electron orbital in Eqs.(3)-(4)

\[ \left(-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(r)\right)\psi_i(r) = \epsilon_i \psi_i(r) \]  

(3)

\[ V_{\text{eff}}(r) = V_{\text{ext}}(r) + \int \frac{\rho(r')}{|r-r'|}\,dr' + \mu_{xc}[\rho] \]  

(4)

where \( \hbar \) is Planck’s constant (\( \hbar = \hbar/2\pi \)), \( m \) is mass of electron, \( \epsilon_i \) are the Kohn-Sham orbital energies, and \( V_{\text{eff}}(r) \) is effective potential involving the external potential, interaction potential between electrons and the exchange-correlation potential \( \mu_{xc}[\rho] \) which is the functional derivative of the exchange-correlation energy \( E_{xc}[\rho(r)] \):

\[ \mu_{xc}[\rho] = \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)} \]  

(5)

The solutions of Eq.(3) can be easily founded by solving the Schrödinger equation for non-interacting particles moving under an effective potential \( V_{\text{eff}}(r) \). The ab-initio calculations of Eqs.(3)-(5) were carried out using Vienna ab-initio simulation package, VASP. The calculations were performed using a plane wave method employing the ultrasoft pseudopotentials for Ca, Si and O, and the generalized gradient approximation (GGA) for the exchange-correlation potential in Eq.(5) is employed. \( \Gamma \)-point sampling and 27 k-points samplings were used for calculations.

4. Results and Discussions

The interatomic distances less than 4 Å to the neighboring O atoms for all of independent Si atoms were obtained within unit cell from the results of ab-initio calculations. Si-O mean distances are 1.62 Å in \( \beta \)-Ca\(_2\)S and 1.65 Å in \( \gamma \)-Ca\(_2\)S. Si-O mean distance in \( \beta \)-Ca\(_2\)S is 0.03 Å shorter than that of \( \gamma \)-Ca\(_2\)S. The experimental value of the bond length gave 1.63 Å in \( \beta \)-Ca\(_2\)S and 1.65 Å in \( \gamma \)-Ca\(_2\)S, respectively [1]. Si atoms have short distances to oxide atoms, with half the Ca-O distance as mentioned below. This means that Si atoms forming Si-tetrahedra lie in more stable positions than Ca atoms.

Si-O chemical bonding was analyzed by covalent and ionic bond orders on \( \beta \) and \( \gamma \)-Ca\(_2\)S. Both bond orders were evaluated by overlapping population through the calculation of DV-Xα molecular orbital method for Si(OH)\(_4\) [2]. This analysis reveals that there are only small differences in covalent and ionic bond orders between both dicalcium silicates. Therefore the differences in hydraulic activity between \( \beta \) and \( \gamma \)-Ca\(_2\)S are not from the difference of Si-O chemical bonding. However, further investigation is required on this point because the DV-Xα
Ca-O bond lengths give less information on the hydraulic activity of the Belites. The shortening of Ca-Ca distance increases linearly with an increase of the coordination number of Ca and that the larger Ca(4)-O distance suggests weak bonding between oxygen and Ca(4) atoms accompanying with low occupation rate[7]. These hypotheses cause several contradictions on hydraulic activity between β-C₆ and γ-C₇.

From Ca-O bond lengths, we cannot yet find an exact correlation between the bond length and the hydraulic activity of cement clinker minerals. The longer bond should be advantage to split Ca-O bond resulting in dissolve Ca ions. M. Yashima et.al also suggest that in CaO polyhedron of tricalcium phosphates, Ca(3)(PO₄)₂, Ca-O distance increases linearly with an increase of the coordination number of Ca and that the larger Ca(4)-O distance suggests weak bonding between oxygen and Ca(4) atoms accompanying with low occupation rate[7]. These hypotheses cause several contradictions on hydraulic activity between β-C₆ and γ-C₇.

K.H. Jost et al. pointed out on this point that there is less difference on Ca-O bond length between the clinker minerals reacting faster and slower with water and that the connexion of CaO polyhedra by common faces. In contrast there is a connexion by common edges and corners for polyhedra in γ-C₇. Therefore only values of Ca-O bond lengths give less information on the hydraulic activity of the Belites.

Therefore, we focused on the distances less than 4 Å to the neighboring Ca atoms for all of independent Ca atoms within unit cell. Table3 presents the calculated values of Ca-Ca bond length in comparison with experimental results conducted by K.H.Jost et al.[1]. Ca-Ca mean distances in this work are 3.56 Å in β-C₆ and 3.75 Å in γ-C₇. These distances agree well with the experimental ones [1]: 3.58 Å in β-C₆ and 3.75 Å in γ-C₇. The shortening of Ca-Ca distance causes instability of a structure because of repulsion between cations. From Table3, Ca-Ca distance of alite (C₆) that is most active in hydration among cement clinkers is 3.47 Å and 3.40 Å in CaO.

Ca-Ca bond-length of β-C₆ substituted Ca atom with S atom are 3.59 Å for substitution of Ca(1) atom having seven-fold coordinates and 3.32 Å for substitution of Ca(2) atom having eight-fold coordinates. Ca-Ca mean distance of β-C₆ substituted Ca(1) atom having seven-fold with S atom are 0.03 Å longer than that of β-C₆ without substitution by S atom. On the contrary, Ca-Ca mean distance of β-C₆ substituted Ca(2) atom

<table>
<thead>
<tr>
<th>Cement Compounds</th>
<th>Ca-Ca dis. Mean dis. Å unless 4 Å this work</th>
<th>Ca-Ca dis. Mean dis. Å unless 4 Å this work</th>
<th>Ca-Ca dis. Mean dis. Å unless 4 Å this work</th>
<th>Ca-Ca dis. Mean dis. Å unless 4 Å this work</th>
<th>Total energy eV</th>
<th>Number of Atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₅S</td>
<td>Ca₃SiO₅</td>
<td>Alite</td>
<td>3.47</td>
<td>3.16</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>β-C₆</td>
<td>β-C₆</td>
<td>Belite</td>
<td>3.39</td>
<td>3.38</td>
<td>-195.56</td>
<td>28</td>
</tr>
<tr>
<td>γ-C₇</td>
<td>γ-C₇</td>
<td>Belite</td>
<td>3.32</td>
<td>3.31</td>
<td>-204.86</td>
<td>28</td>
</tr>
</tbody>
</table>

**Table3** Interatomic distances of β-C₆S and γ-C₇S
having eight-fold with S$_r$ atom are 0.24 Å shorter than that of β-C$_2$S without substitution by S$_r$ atom. Ca atoms have short distances to the neighboring Ca atoms, and the shortening of Ca-Ca distance causes instability of a structure because of repulsion between cations. The total energy are −781.2 eV for β-C$_2$S substituted Ca(1) atom with S$_r$ atom and −780.6 eV for β-C$_2$S substituted Ca(2) atom with S$_r$ atom. This means that β-C$_2$S substituted Ca(2) atom having eight-fold coordinates with S$_r$ atom is unstable than β-C$_2$S substituted Ca(1) atom having seven-fold coordinates with S$_r$ atom.

The crystal structure analysis in this work reveals that shorter Ca-Ca distance results in higher hydraulic activity of dicalcium silicates. The crystallographic analysis of the calcium silicates based on the ab-initio calculations without any other assumptions based on only quantum mechanics is one index to predict the hydraulic activity of cement compounds in advance. However, further theoretical calculations will be required to explore the hydration mechanism of dicalcium silicates substituted Ca atom with other atoms.

5. Conclusions

The conclusions that can be drawn from ab-initio calculations on crystal structure of Belites are as follows:

(1) The interatomic mean distances less than 4 Å to the neighboring O atoms for all of independent S$_i$ atoms is 1.62 Å in β-C$_2$S and 1.65 Å in γ-C$_2$S from the results of ab-initio calculations. S$_i$ atoms have short distances to oxide atoms with half the Ca-O distance. S$_i$ atoms forming S$_i$-tetrahedra lie in more stable positions than Ca atoms.

(2) Ca-O bond lengths in this work provide 2.46 Å in β-C$_2$S and 2.38 Å in γ-C$_2$S, respectively. There is less correlation between Ca-O bond length and the hydraulic activity of cement clinker minerals.

(3) The mean distance less than 4 Å to the neighboring Ca atoms for all of independent Ca atoms within unit cell are 3.56 Å in β-C$_2$S and 3.75 Å in γ-C$_2$S, respectively. The calculated Ca-Ca bond lengths agree well with the experimental ones. The shorter distance in β-C$_2$S results in closely arrangement of Ca atoms than that of γ-C$_2$S. The shortening of Ca-Ca distance causes instability of a structure because of repulsion between cations. The crystallographic analysis of the dicalcium silicates based on the quantum mechanics is one index to predict the hydraulic activity of cement compounds in advance.

(4) Ca-Ca bond-lengths of β-C$_2$S substituted Ca atom with S$_r$ atom are 3.59 Å for substitution of Ca(1) atom having seven-fold coordinates and 3.32 Å for substitution of Ca(2) atom having eight-fold coordinates. β-C$_2$S substituted Ca(2) atom having eight-fold coordinates with S$_r$ atom is unstable than β-C$_2$S substituted Ca(1) atom having seven-fold coordinates with S$_r$ atom.

The authors would like to gratefully acknowledge the supercomputing resources from the Center for Computational Materials Sciences of the Institute for Materials Research, Tohoku University.

References


