Application of DV-Xα Method to Hydraulic Properties of α-Ca₂SiO₄

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DV-X α method, which is one of the quantum chemical method, has been applied to the hydration of a cement compound Ca₂SiO₄ (C₂S) with interesting hydraulic activity. The bonding state has been evaluated for the high temperature phase (α -C₂S) with hydraulic activity, compared with the room temperature phase (γ -C₂S) without hydraulic activity. For the bulk state, the calculated density of states for valence band agrees with the measured one by XPS. The Ca-O bond length in α -C₂S ranges from 0.194 to 0.324 nm, whereas that in γ -C₂S is nearly constant (0.24 nm). The calculated bond strength of Ca-O decreases with increasing bond length. By placing OH on the surface of the model cluster, the bonding properties of hydrated state have been calculated. The longer Ca-O bond is weakened by the hydration.

Key words: Quantum chemical calculation, DV-X α method, α -Ca,SiO₄, Hydration, Overlap population

1.INTRODUCTION

In spite of the good stock of knowledge in field of cement chemistry, the origin of hydraulic activity of cements has not been cleared yet. The difference of hydration activity among polymorphs such as Ca_2SiO_4 is not so well understood.

DV-X α method, which is one of the calculation method for quantum chemistry, is useful in the field of inorganic chemistry. For example, DV-X α method has been applied to solubility of atom in the solid state,¹) mechanochemical reaction,²) dielectric substance³ and adsorption phenomenon of molecules⁴) and so on. However, there are few reports on the application of DV-X α method to the hydration of cement compounds.

In this study, DV-X α method was applied to the hydration of a cement compound (α -Ca₂SiO₄) to discuss the hydraulic properties. The results are compared with those for γ -Ca₂SiO₄ without hydraulic activity at room temperature.

2. CALCULATION METHOD

2-1 Bulk state

The atomic arrangement in the model cluster of α -Ca₂SiO₄ were based on the crystal structure data with a space group P6₃/mmc by Udagawa et al.⁵⁾SiO₄ tetrahedron sets one's face toward up and down stochastically. Two model clusters were constructed, noticing at the direction of SiO₄ tetrahedron; (1) P3m1-model with the alternate orientation of SiO₄ tetrahedron (Fig.1-a) and (2) P6₃mc-model with the fixed orientation of SiO₄ tetrahedron (Fig.1-a). These model clusters have composition (Ca₉Si₁₂O₆₀)⁵⁴⁻ and (Ca₉Si₆O₅₁)⁶⁰⁻ for P3m1-model and P6₃mc-model, respectively. The point charges were distributed at virtual atomic sites around the model cluster to represent the bulk state. Total charge of model cluster and point charges is zero.

The validity of model cluster for the bulk state was evaluated by comparing the calculated density of states (DOS) with that measured by X-ray photoelectron spectroscopy (XPS). The validity of y



Fig.1 Model clusters used in the calculation of the bulk state for α -C₂S. (a) $P\overline{3}m1$ -model and (b) P6₃mc-model.

phase has been already reported.⁶⁾ The bonding states of Ca-O and Si-O were also discussed.

2-2 Surface state

The surface model cluster was constructed base on the $P\overline{3}m1$ bulk model cluster, which has an alternate arrangement of SiO₄ tetrahedron. The composition of the model cluster is $(Ca_8Si_6O_{39})^{38}$. The surface state was calculated without point charges above the (001) surface.

2-3 Hydration state

The hydration model was constructed by placing OH on the surface of the model cluster used in section 2-2. Three hydroxyls were placed at 0.24 nm above each Ca atoms at the surface (Fig.2). The differences of hydraulic properties between α and γ phases were discussed by comparing the surface state



Fig.2 A model clusters used in the calculation of the hydrated state for α -C₂S (hydration-model).



Fig.3 Density of states obtained by XPS (a) and the calculation (b,c) for α -C₂S. (b) $\overline{P3m1}$ -model and (c) P6₃mc-model. The composition of the sample used in XPS measurement is (Ca_{0.7}Ba_{0.3})₂SiO₄.

of the hydration model and the unhydration model.

3. RESULTS AND DISCUSSION

3-1 The validity of the bulk model

Figure 3 shows the density of states (DOS) profiles around the valence band calculated by DV-X α method and obtained by X-ray photoelectron spectroscopy (XPS) measurement. The relative peak positions in the range from -25 to -20 eV and from -10 to -5 eV for both P3m1 and P6₃mc models agree with experimental data obtained by XPS. However, there are some peaks at around -30 and -15 eV in XPS spectrum (marked

each model			
Model	P3ml	P6₃mc	γ

BOP 0.703 0.654 0.685

 Table I
 Bond overlap population (BOP) of Si-O for

by arrow), while these peaks are not found in the calculated patterns. The composition of the sample for XPS was (Ca_{0.7}Ba_{0.3})₂SiO₄. And then, DOS was also calculated for a model cluster (Ca₂Ba₂Si₆O₄₈)⁵⁴⁻ with space group P3m1, in which Ca atoms are partially substituted by Ba atoms. Those peaks are found to be from Ba atoms added to the sample as a mineralizer for α phase at room temperature. The calculated band gap energy for P3m1-model and P6₁mc-model were 6.2 and 4.4 eV, respectively. Both models reproduce the insulating state.

From the above results, the both models were found to well reproduce the bulk state of real crystal.

3-2 The bonding state of the bulk model

The calculated bond overlap population (BOP) of Si-O for P3m1-model, P6,mc-model and y phase is shown in Table I. BOP represents the magnitude of covalent bond. For α and γ phases, Si-O bond strength was similar, because SiO₄ tetrahedra in both phases are isolated (describe as "Q⁰" in field of NMR).

The Ca-O bond length for α phase ranges from 0.194 to 0.324 nm. The relationship between bond strength (BOP) and bond length for Ca-O is shown in Fig.4. The results for y phase are also shown in the same figure. BOP of Ca-O decreases with increasing bond length. The bond strength of y phase is similar to that of α phase with nearly equal bond length.

The coordination number of Ca atoms in α-phase ranges from 6 to 12. The relationship between BOP and coordination number of Ca is shown in Fig.5. The average bond strength of Ca-O decreases with increasing coordination number. The product of BOP and coordination number is shown in the same figure. The product means the number of covalent electrons per a Ca atom. The product does not depend on the coordination number, and is nearly constant (about 0.45). We have already reported the same relation between BOP and coordination number for AI-O bonds in calcium aluminate compounds.⁷⁾ For



Fig.4 Relationship between bond overlap population and bond length for Ca-O. \bigcirc : α -phase, \blacksquare : γ -phase.



Fig.5 Relationship between bond overlap population for 1-bond and coordination number for Ca-O. ○,● : α -phase, \Box , \blacksquare : γ -phase.

compounds with high coordination number, average bond strength should be weakened due to the increase of shared covalent electrons. Bredig⁸) has reported that hydraulic activity of compound with high coordination number is higher than that of low coordination number. The results of the present study agree with the Bredig's report.

3-3 The changes in bonding state on hydration

We have reported a DV-X study on the difference of hydraulic activity between γ -Ca₂SiO₄ and γ -Ca₂GeO₄.⁹⁾ The differential total overlap population (Δ TOP), which is the difference of bond strength between hydrated and unhydrated states, found to be a



Fig.6 Relationship between bond overlap population and bond length for Ca-O in α -C₂S. \bigcirc :unhydrated state, -:hydrated state.

good measure for estimation of hydraulic activity for compounds with the same crystal structure.

In this study, however, the composition of calculated model cluster is different, because the crystal structures of α and γ phases are different. Then calibration of composition was carried out so that the Ca/Si atomic ratio becomes to be 2. The Δ TOP after calibration was -0.303 and -0.294 for α and γ phases, respectively. α phase with hydraulic activity showed slightly smaller Δ TOP than γ phase without hydraulic activity. The distinct difference of Δ TOP was not confirmed for α and γ phases. This result should be caused by low hydraulic activity of α phase in other cement compounds.

Next, in order to discuss the influence of crystal structure, the change in the Ca-O bond strength before and after hydration is shown in Fig.6. The bond strength at long bond length became weak by hydration. This result indicated that the Ca-O bond with long length should play the trigger of hydration, and corresponded to a quantitative expression¹⁰ that the hydraulic activity of the compound with longer bond length is higher than that of shorter bond length.

From above results, it was found that DV-X α method is applicable to the study for the cement hydration, and that the hydration of α phase depends on the Ca-O bond length.

4. CONCLUSION

DV-X α method was applied to study the hydraulic activity of α and γ -C₂S phases with different crystal structures. The results are summarized as follows;

- 1) DV-X α method can be applied to α phase, because DOS calculated by this method was similar to that measured by XPS.
- For the bulk state, the bond strength of Ca-O for α phase became weak with increasing bond length. At the same bond length, the bond strength of α phase is nearly equal value as that of γ phase.
- 3) The change in the bond strength (Δ TOP) for α phase was slightly bigger than that of γ phase, and then α phase is hydrated more easily than γ phase. In α phase, the bond strength for the long bond length became weak on hydration, and the Ca-O bond with long length should play the trigger of hydration.
- 4) DV-Xα method is applicable to the evaluation of hydration of cement compounds.

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