Stability and Phase Relations of Dicalcium Silicate Hydrates under Hydrothermal Conditions

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In the system of CaO–SiO$_2$–H$_2$O (C–S–H) system$^{[14]}$ includes more than 40 compounds ranging from amorphous to crystalline compounds with various compositions in a wide range of calcium/silicon (C/S) ratio between 0.44–3.00. All of C–S–H compounds are classified as nesosilicates, and phyllosilicates by the modified Strunz classification$^5$ in terms of polymerized silicate anion structure. Calcium silicate hydrates play an essential role in the hydration process of cements and cement-based materials. α-dicalcium silicate hydrate (α-C$_2$SH), hillebrandite, and dellaite (Ca$_2$(SiO$_4$)OH)$_2$ and deliliane (Ca$_6$(SiO$_4$)(SiO$_2$)OH)$_2$ are three phases with the same molar ratio of C/S = 2.0 in this system.

α-C$_2$SH with isolated silicate tetrahedrons possesses the lowest degree of polymerization, and is one of members of the nesosilicates. It consists of [HSiO$_4$]$^{3–}$ anion groups connected with hydrogen bond; and here silicon in this structure is coordinated with three oxygen atoms and one hydroxyl group. α-C$_2$SH is the primary product of the hydrothermal treatments of β- and γ-dicalcium silicate (C$_2$S, Ca$_2$SiO$_4$) at temperatures between 140–160°C, and α-C$_2$SH and calcium hydroxide (CH) are also obtained from tricalcium silicate (C$_3$S, Ca$_2$SiO$_5$) at 200°C for 7 d. $^9$ Thus α-C$_2$SH is a common product resulting from hydrothermal treatments of ordinary Portland cement pastes. $^2$ α-C$_2$SH was also prepared by hydrothermal reactions of lime-amorphous silica, $^7$ lime-quartz or -silicic acid $^6$ at temperatures between 120–160°C, and 150–200°C, respectively.

The formation of α-C$_2$SH causes the decrease of mechanical strength of cement and cement-based materials$^2$ in industry, and so it is necessary to investigate stability of α-C$_2$SH under hydrothermal conditions. Thus, stability of α-C$_2$SH have been studied by several researchers.$^6$–$^8$ Assarsson$^7$ showed that α-C$_2$SH was formed from mixture of lime and amorphous silica below 160°C but hillebrandite above 160°C. Kalousek$^1$ also showed α-C$_2$SH and hillebrandite were synthesized from CH and quartz at 175°C for 3 d and 200°C for 12 d, respectively. Heller and Taylor$^6$ described from the results of hydrothermal reactions of β-C$_2$S at 100–200°C that α-C$_2$SH was not a stable compound in comparison with a mixture of afwillite (Ca$_6$(SiO$_4$)(OH)$_2$) and CH below 140°C and hillebrandite above 140°C.

Hillebrandite with a monoclinic structure comprises single silicate chains containing three silicate tetrahedrons per unit cell, $^9$ belonging to nesosilicates with [SiO$_4$]$^{4–}$ groups. It is a common product obtained by hydrothermal treatments of ordinary Portland cement pastes, and was synthesized from a mixture of C$_3$S and silicic acid$^{10}$ and from a mixture of CaO and SiO$_2$ (Aerosil), quartz$^{11,12}$ or silicic acid$^{11}$ by hydrothermal reactions. It is reported that hillebrandite is very stable under hydrothermal conditions at temperatures around 200°C.$^2,13$

According to the results given by these researchers, $^6$–$^8,13$ hillebrandite seems to be a transformation product from α-C$_2$SH, but the phase transformation was not clearly understood because they did not use α-C$_2$SH as a starting material. The transformation of α-C$_2$SH and the stability of hillebrandite need further investigation in detail.

Dellaite is a mineral named by Roy in the honor in her research history. It was, however, named as Phase Y by Roy and Taylor$^{21}$ in the early stage. Dellaite belonging to sorosilicates with [SiO$_4$]$^{4–}$ and [SiO$_2$]$^{5–}$ structures, forms short prismatic crystals elongated along a-axis.$^{14}$ Hydrothermal synthesis of dellaite from γ-C$_2$S needed high temperatures (> 800°C) and pressures (> 100 MPa). $^4,15$ Dellaite was also synthesized from α-C$_2$SH at 450°C by Flint et al.,$^{19}$ and from β-C$_2$S at 350–370°C for 3 weeks by Cooksley.$^{17}$ These results indicate that formation of dellaite requires high temperatures.

Even though these three types of calcium silicate hydrates with the same molar ratio C/S = 2.0 had been studied widely but separately by many researchers, the phase relationship of these phases has not been investigated systematically. In the

Key-words: Phase transformation, α-C$_2$SH, Hillebrandite, Dellaite, Hydrothermal treatment
present study, phase transformations of $\alpha$-C$_2$SH, hillebrandite and dellaite under hydrothermal conditions were investigated in detail. The formation conditions, stability, phase relations of these three phases under hydrothermal conditions were discussed, and the formation region of dellaite from different precursors were determined.

2. Experimental

The raw materials were CaCO$_3$ and amorphous SiO$_2$ powder (Aerosil) (both from Wako Pure Chem. Ind., Ltd., > 99.9%). $\beta$-C$_2$S was synthesized by solid state reaction of the mixture of CaCO$_3$ and amorphous SiO$_2$ powder corresponding to C/S = 2.0 at 1000°C for 3 h in air in a platinum crucible, and ground after the heat treatment to get a powder with specific surface area of 7.7 m$^2$/g. Pure $\alpha$-C$_2$SH was synthesized by hydrothermal treatments of $\beta$-C$_2$S in 50 cm$^3$ stainless steel autoclaves with agitation under an autogenous pressure at 150°C for 1 d. The ratio of water/solid (w/s) was fixed to be 20 (w/s = 20 g/1 g) in all hydrothermal reactions. After hydrothermal treatment at 150°C for 1 d, the autoclave was cooled by air quenching to room temperature, and was fixed to 210°C for further hydrothermal treatments of $\alpha$-C$_2$SH.

Hillebrandite was synthesized from stoichiometric mixtures of CaO (freshly prepared from CaCO$_3$ by heat treatment at 1050°C for 3 h) and amorphous SiO$_2$ by hydrothermal reaction at 220°C for 1 d. After hydrothermal treatment at 220°C for 1 d, the autoclave was cooled by air quenching to room temperature, and was fixed to 350°C for further hydrothermal treatments of hillebrandite. The stability of dellaite prepared by hydrothermal treatment of hillebrandite at 400°C for 2 d was investigated at lower temperatures under hydrothermal conditions.

After the scheduled hydrothermal treatments, the autoclave was cooled by air quenching to room temperature, and products were dried in vacuum. Powder X-ray diffraction (XRD, Rigaku RTP-300RC, Tokyo) with Cu Kα radiation (40 kV and 100 mA) was used to identify the crystalline phases. A scanning electron microscope (SEM; Hitachi S-530, Tokyo) was used to observe the morphology of the products.

3. Results and discussion

3.1 Phase transformation of $\alpha$-C$_2$SH

The formation of $\alpha$-C$_2$SH by hydrothermal treatment of $\beta$-C$_2$S at 150°C for 1 d was confirmed by XRD (Fig. 1(a)) and SEM (Fig. 2(a)). After the hydrothermal treatment at 150°C for 1 d, the autoclave was further heated to higher temperatures to treat $\alpha$-C$_2$SH under hydrothermal conditions. The results are summarized in Table 1, and XRD patterns and SEM photographs of the reaction products are shown in Figs. 1 and 2, respectively.

When $\alpha$-C$_2$SH was further treated at 180°C for 8 d under hydrothermal conditions; no phase changes were detected by XRD, and amorphous SiO$_2$ powder corresponds to C/S = 2.0 at 1000°C for 3 h in air in a platinum crucible, and ground after the heat treatment to get a powder with specific surface area of 7.7 m$^2$/g. Pure $\alpha$-C$_2$SH was synthesized by hydrothermal treatments of $\beta$-C$_2$S in 50 cm$^3$ stainless steel autoclaves with agitation under an autogenous pressure at 150°C for 1 d. The ratio of water/solid (w/s) was fixed to be 20 (w/s = 20 g/1 g) in all hydrothermal reactions. After hydrothermal treatment at 150°C for 1 d, the autoclave was cooled by air quenching to room temperature, and was fixed to 210°C for further hydrothermal treatments of $\alpha$-C$_2$SH.

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3.1 Phase transformation of $\alpha$-C$_2$SH

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Table 1. Reaction Products Obtained by Hydrothermal Treatments of α-C2SH

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α: α-C2SH, Ca3(SiO2OH)(OH)2, J: jaffeite, Ca6(SiO2)3(OH)6, R: reinhardbraunsite, Ca10(SiO4)2(OH)2, D: dellaite, Ca6(SiO4)(Si2O7)(OH)3.

* detected by SEM observation.

XRD (Fig. 1(b)), but SEM observation showed that the surface of α-C2SH crystals became rough and small fibrous crystals were formed on the surface of the plate crystals of α-C2SH as shown in Fig. 2(b). The result indicated that α-C2SH was very slowly changed to other phase even at 180°C. The amount of small fibrous crystals increased by the treatment at 210°C for 7 d (Fig. 2(c)), but the XRD patterns (Fig. 1(c)) did not show the formation of the other phase. The first evidence of the formation of the other phase was observed in XRD pattern of the product obtained by the hydrothermal treatment at 230°C for 2 d, which clearly showed the formation of jaffeite (Ca6(SiO2)3(OH)6) (Fig. 1(d)). Jaffeite belongs to sorosilicates with [Si2O7]3− groups and crystallizes to form long fibrous crystals,2,4 which suggests that fibrous crystals obtained by hydrothermal treatment of α-C2SH at low temperatures between 180°C and 220°C are jaffeite.

At 250°C, decomposition of α-C2SH was clearly observed (see Table 1), and α-C2SH disappeared after the treatment for 2 d. By the decomposition of α-C2SH, reinhardbraunsite (Ca10(SiO4)2(OH)2) and dellaite were formed together with jaffeite. It is reported that reinhardbraunsite is formed by decomposition of jaffeite at high temperatures.2 The amount of dellaite increased with the increase in reaction temperature and reaction time (see Table 1, Figs. 1 and 2). Dellaite must be the final stable phase. At 400°C, the pure dellaite was formed just after the reaction for 10 min (Fig. 1(h)). With the increase in reaction time, the dellaite crystals grew larger (Figs. 2(e) and (f)).

These results showed that α-C2SH did not change to hillebrandite under hydrothermal conditions, but was transformed to jaffeite (C/S = 3.0), even though α-C2SH and hillebrandite had the same chemical formula. In fact, it must be difficult to form hillebrandite with single silicate chains from α-C2SH with isolated silicate tetrahedrons. Polymerization of silicate tetrahedrons is required to form hillebrandite from α-C2SH. Some analogous metastable phases might be formed during hydrothermal processing of α-C2SH.

The formation mechanism from α-C2SH to dellaite was hypothesized as the following. When α-C2SH is placed in water at high temperatures, SiO2 tetrahedrons migrate into solution faster than Ca2+ due to the high solubility of SiO2 in comparison with that of Ca(OH)2 at high temperatures above 220°C,3 and Ca concentration increases at the surface of α-C2SH crystals to the level to stabilize Ca-rich jaffeite (C/S = 3.0). This assumption is supported by the fact that jaffeite fibrous crystals precipitated on the α-C2SH plate crystals (Fig. 2(b)). Jaffeite is decomposed to reinhardbraunsite (C/S = 2.5) and Ca(OH)2 in the system of C–S–H with C/S less than 3.0.5 Thus, reinhardbraunsite also exists with jaffeite during the early stages of the decomposition of α-C2SH. Though jaffeite and reinhardbraunsite are stable phases at their own C/S molar ratio even at high temperatures, they react at higher temperatures with SiO2 supplied by dissolution of α-C2SH to form dellaite (C/S = 2.0). At higher temperatures, dellaite is quickly formed due to the fast decomposition of α-C2SH.

3.2 Phase transformation of hillebrandite
Hillebrandite synthesized from CaO and amorphous SiO2 by hydrothermal reaction at 220°C for 1 d, was further treated under hydrothermal conditions at high temperatures above 300°C. The formation of hillebrandite was confirmed by XRD (Fig. 3(a)) and SEM (Fig. 4(a)). XRD patterns and SEM photographs of the products are shown in Figs. 3 and 4, respectively. The synthesized hillebrandite consisted of fibrous crystals with the length of about 20 μm (Fig. 4(a)). Hillebrandite was a stable phase under hydrothermal conditions at low temperatures below 350°C. Dellaite just began to appear by the reaction at 350°C for 1 d (Fig. 3(c)), but the intensity of its X-ray diffractions was very weak. Even when hillebrandite was treated at 350°C for 2 d, hillebrandite was still major phase (Fig. 3(d)), but bulky crystals of dellaite were clearly observed by SEM (Fig. 4(c)). This result indicat-
The single phase of dellaite was obtained by the reaction at 400°C, but the transformation rate was very slow. Dellaite was formed readily from hillebrandite by the reaction at 400°C (Figs. 3(e), (f) and Figs. 4(d), (e)). The dellaite crystals grew larger by a long time reaction (Fig. 4(f)). Dellaite must be a stable phase at 400°C.

The direct formation of dellaite from hillebrandite can be explained as follows: Hillebrandite comprises single silicate chains belonging to inosilicates. Dellaite belongs to sorosilicates including [SiO₄]⁴⁻ and [Si₄O₁₁]⁶⁻ groups. The dissolution of hillebrandite by destroying Si–O bond in single silicate chains may easily result in formation of [SiO₄]⁴⁻ and [Si₄O₁₁]⁶⁻ ions to form dellaite.

3.3 Formation region of dellaite

It has been shown that dellaite was obtained from α-C₂S•H and hillebrandite by hydrothermolysis. Different precursors such as β-C₂S and mixtures of lime and silica with C/S = 2.0 were used to prepare dellaite. As a conclusion, dellaite could be prepared from α-C₂S•H, hillebrandite, β-C₂S, and mixtures of lime and silica, but the formation region was different depending on the precursors.

The formation of dellaite from α-C₂S•H and hillebrandite was investigated in detail in this study. Here the results were briefly summarized. From α-C₂S•H, jaffeite was first formed as an intermediate phase by decomposition of α-C₂S•H, and then unstable jaffeite was decomposed to form reinhardbraunsite and Ca(OH)₂. Dellaite started to crystallize by the reaction at 250°C for 1 d, and was obtained as a single phase by the reactions at 350°C for 1 d or at 400°C for 10 min. From hillebrandite, dellaite was directly formed without any intermediate phases by the reactions at temperatures above 350°C, but the transformation at this temperature was so slow that only a small amount of dellaite was formed by the reaction for 2 d. The single phase of dellaite was obtained by the reaction at 400°C for 1 d.

When lime and silica (quartz or amorphous silica) with C/S = 2.0 were hydrothermally treated at temperatures between 200°C and 260°C for 1 d, hillebrandite was formed as a main phase. At higher temperatures above 280°C, dellaite started to crystallize. Dellaite was the main phase by the hydrothermal treatment at 400°C for 1 d but coexisted with a small amount of hillebrandite or jaffeite (Figs. 5(a) and (b)). Dellaite must be formed as a single phase by further hydrothermal treatments at higher temperature for a longer time. When the mixture of lime and silica was hydrothermally treated, many kinds of reactions might occur during heating process because of heterogeneity of the starting materials. Thus, the formation of the pure dellaite phase was kinetically restricted from the mixture of lime and silica.

The metastable phases of reinhardbraunsite (Ca₆(SiO₄)₂(Si₂O₆)(OH)₂) and kilchoanite (Ca₆(SiO₄)₂(OH)₂) were formed by the hydrothermal treatment of β-C₂S at temperatures above 260°C for 1 d. These phases were stable even at high temperatures, and only a small amount of dellaite was formed even by the treatment at 400°C for 5 d (Fig. 5(c)). It is reported...
that dellaite was synthesized by treating $\beta$-$\text{C}_2\text{S}$ at 350–370°C for 3 weeks\cite{Taylor, Garbev} or $\gamma$-$\text{C}_2\text{S}$\cite{Taylor} at higher temperatures than 800°C under hydrothermal conditions. It is concluded that formation of dellaite from calcium silicate anhydrates needs high temperatures for a long time due to the formation of stable intermediate phases.

3.4 Phase transformation of dellaite

Dellaite prepared by hydrothermal treatment of hillebrandite at 400°C for 2 d was treated at lower temperatures to investigate the phase transformation of dellaite under hydrothermal conditions. Figure 6 shows the XRD patterns of the reaction products. When dellaite was hydrothermally treated at 300°C for 1 d, hillebrandite was formed with a very small amount of kilchoanite (Fig. 6(a)). This result suggested that hillebrandite and dellaite were reversibly transformed to each other depending on temperature. When dellaite was hydrothermally treated at 150°C for 10 d, hillebrandite was formed as a main phase with killalaite ($\text{Ca}_2\text{H}_6\text{Si}_4\text{O}_{10}\text{(OH)}_2$) (OH). The amount of killalaite decreased with the increase in reaction temperatures up to 280°C (Fig. 6(b)). The chemical formula of killalaite was recently reported to be $\text{Ca}_9\text{Si}_9\text{O}_{18}\text{H}_2\text{O}$\cite{Taylor} and it was formed under hydrothermal conditions above 180°C. Garbev et al.\cite{Garbev} described that the set aphyllite ($\text{Ca}_3\text{Si}_4\text{O}_{10}\text{(OH)}_6$)–killalaite–kilchoanite with C/S ratio of 1.5 has a direct relationship between the degree of polymerization and the temperature of formation, and higher synthesis temperatures are required, reading from left to right. The formation of C–S–H compounds with C/S ratio of 1.5 from those with C/S ratio of 2.0 at lower temperatures may be explained by the increase in solubility of Ca(OH)$_2$ at lower temperatures. Though dellaite was stable even by the treatment at 100°C for 14 d (Fig. 6(d)) without formation of any other phases, it may be kinetically stable at low temperatures but not thermodynamically.

$\alpha$-$\text{C}_2\text{SH}$ was not formed by hydrothermal treatments of dellaite at low temperatures. This result agreed with that reported by Heller and Taylor.\cite{Taylor} It can be concluded that $\alpha$-$\text{C}_2\text{SH}$ is a metastable phase.

4. Conclusions

The phase transformation of $\alpha$-$\text{C}_2\text{SH}$ and hillebrandite was kinetically investigated under hydrothermal conditions. The results are schematically summarized in Fig. 7. $\alpha$-$\text{C}_2\text{SH}$ was stable at low temperatures and started to decompose at 180°C to form Ca-rich jaffeite and finally changed to dellaite at 350°C. Form $\alpha$-$\text{C}_2\text{SH}$, hillebrandite was never formed. Hillebrandite was a stable phase at lower temperatures than 350°C, but was transformed directly to dellaite at higher temperatures than 350°C. Dellaite was reversibly transformed to hillebrandite at lower temperatures below 300°C with formation of a small amount of the C–S–H compounds with C/S ratio of 1.5. In order to get the single phase of dellaite from hillebrandite required higher temperature (400°C) than from $\alpha$-$\text{C}_2\text{SH}$ because of the high stability of hillebrandite under hydrothermal conditions at high temperatures in comparison with $\alpha$-$\text{C}_2\text{SH}$. It was very difficult to prepare dellaite from $\beta$-$\text{C}_2\text{S}$ due to the high stability of intermediate phases of reinhardbraunsite and kilchoanite. From lime and silica, dellaite started to crystallize at 280°C and was the main phase at 400°C with a small amount of hillebrandite and/or jaffeite which existed due to heterogeneity of the starting materials.

References

2) Taylor, H. F. W., "Proceedings of the Fourth International


