Hydrothermal Synthesis of Dicalcium Silicate Based Cement

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Abstract. It is imperative to develop low energy alternative binders considering the large amounts of energy consumed as well as carbon dioxide emissions involved in the manufacturing of ordinary Portland cement. This study is on the synthesis of a dicalcium silicate based binder using a low temperature hydrothermal route. The process consists of synthesizing an intermediate product consisting of a calcium silicate hydrate phase with a Ca:Si ratio of 2:1 and further thermal treatment to produce the $\beta$-Ca$_2$SiO$_4$ (C$_2$S) phase. Effect of various synthesis parameters like water to solid ratio, dwell time and temperature on the formation of the desired calcium silicate hydrate phase is reported along with effect of heating conditions for formation of the $\beta$-C$_2$S phase. Around 77.45% of $\beta$-C$_2$S phase was synthesized by thermal treatment of the intermediate phase at 820°C.

1. Introduction

Ordinary Portland cement clinker is composed of 50-70% of alite or Ca$_3$SiO$_5$ (C$_3$S) and 15-30% of belite or Ca$_2$SiO$_4$ (C$_2$S). The manufacturing process to produce these phases in clinker requires very high temperatures (~ 1450°C) leading to significant consumption of fuel as well as carbon dioxide emissions. As per the International Energy Agency (IEA) [1], such emissions amount to about 5% of all anthropogenic CO$_2$ emissions. The overall energy consumption could be reduced if a clinker rich in the belite phase, Ca$_2$SiO$_4$ (C$_2$S) rather than the alite phase, Ca$_3$SiO$_5$ (C$_3$S) is produced as C$_2$S forms at a lower temperature than that of C$_3$S [2]. Additionally, a clinker rich in belite can be produced using a lower lime saturation factor (LSF) than that of alite and hence would lead to lower carbon dioxide emissions due to decarbonation of lower amount of calcium carbonate used.

However while the alite phase is responsible for the early age strength of cement, the belite phase contributes mainly to the late age strength of cement i.e. after 28 days. Dicalcium silicate is known to exist in five polymorphic forms which are $\alpha$, $\alpha'$, $\alpha''$, $\beta$ and $\gamma$. The $\beta$ polymorph of dicalcium silicate is usually present in ordinary Portland cement. $\gamma$-C$_2$S polymorphism regularly coordinated and non-hydraulic. The reactivity of C$_2$S with water is known to be dependent on a number of factors which include crystal imperfections, crystal size as well as polymorph in which it exists. Hence it is imperative to develop forms of belite phase with higher early age reactivity.

Reactive form of $\beta$-C$_2$S has been synthesized in the past [3,4,5] using low temperature hydrothermal synthesis route. The hydration of the synthesized $\beta$-C$_2$S was found to be complete at 28 days with curing at room temperature while $\beta$-C$_2$S synthesized by reaction of lime and quartz at 1400°C with stabilizing agents, at 50 days has been reported to be less than 40% [5]. Ishida et al. [4] synthesized $\beta$-C$_2$S using hydrothermal route with a specific surface area of 7 m$^2$/g and found its hydration to be complete at 28 days with a water to solid ratio of 0.5. On the other hand, Shibata et al. [6] synthesized...
pure $\beta$-C$_2$S by solid state reaction with a specific surface area of 1.59 to 2.10 m$^2$/g and found the degree of hydration to be 80 % after 168 days with a water to solid ratio of 0.5 at 20°C. The higher reactivity of $\beta$-C$_2$S prepared using hydrothermal synthesis has been attributed to the high surface area. Unlike conventional kiln process, hydrothermal synthesis can be carried out at comparatively lower temperatures. The intermediate products from hydrothermal reaction consist of crystalline calcium silicate hydrates which are further heated to produce the dicalcium silicate phase. $\alpha$-C$_2$S hydrate Ca$_2$(HSiO$_4$)(OH)$_2$, Hillebrandite Ca$_2$(SiO$_3$)(OH)$_2$ and Dellaite Ca$_6$(Si$_2$O$_7$)(SiO$_4$)(OH)$_2$ are the three known forms of calcium silicate hydrates having a Ca/Si ratio of 2/1 [7]. Since researches in the past have observed a high reactivity of hydrothermally synthesized $\beta$-C$_2$S phase, in this work we have studied the parameters of the hydrothermal process controlling the synthesis of calcium silicate hydrate phase with a Ca:Si ratio of 2:1. Further, we have studied the effect of the heating conditions on formation of the $\beta$-C$_2$S phase from the intermediate hydrate phase.

2. Material and methods

The starting materials used for hydrothermal synthesis were Ca(OH)$_2$ (Sigma Aldrich), SiO$_2$ (Evonik) and water. The molar ratio of Ca(OH)$_2$ to SiO$_2$ was maintained at 2:1. The synthesis was carried out in a 500 ml autoclave (Amar Equipments, India) under saturated steam pressure at different temperatures, water to solid ratios and dwell times. After autoclaving, the intermediate products from hydrothermal synthesis were vacuum filtered and oven dried at 105°C. The phase composition of the hydrothermally synthesized as well as the final calcined samples were investigated using powder X-ray diffraction (XRD). The data were collected using Bruker’s D8 advance diffractometer in a $\theta$-2$\theta$ configuration employing CuK$_\alpha$ radiation ($\lambda = 1.54$) with a fixed divergence slit 0.298° and a rotating sample stage at 40kV and 40 mA. The samples were scanned between 5 and 80° with a counting time of 0.1 second/step. Selected samples were analyzed by the Rietveld method using Bruker’s TOPAS version 3 software.

Surface areas of the thermally treated sample at 820°C were determined by Brunauer–Emmett–Teller (BET) analysis using Quantochrome Nova 1000e analyzer with Nitrogen gas as the adsorbate. Powder sample of 0.5 gm was employed and degassed for 2 hours at 80 ± 5°C. The hydrothermally synthesized sample with the desired intermediate phase was heated at different temperatures in a high temperature Carboline BLF furnace in platinum crucibles to produce the desired C$_2$S phases. The samples were placed in platinum crucibles and put in the preheated furnace at different temperatures (520°C, 570°C, 670°C, 720°C, 770°C, 820°C) and held there for 1 hour and taken out at that temperature itself and air quenched.

3. Results and Discussion

3.1 Effect of parameters of hydrothermal synthesis

Different parameters like dwell time, water to solid ratio and temperature of the hydrothermal synthesis process would have an effect on the product formed. Hence, we have studied the effect of each of these parameters on the formation of the desired calcium silicate hydrate phase with a Ca:Si ratio of 2:1.

3.1.1 Effect of dwell time. Hydrothermal reactions were initially started with a water: solid ratio of 5:1 at 200°C and 400 rpm for 1 hour and 5 hours respectively to observe the effect of dwell time on the formation of the intermediates. As shown in Figure 1, longer duration was observed to increase the formation of C-S-H type intermediates. The intensities of the peaks of calcium hydroxide and calcium carbonate were observed to be considerably reduced on the increase of dwell time to 5 hours. At a dwell time of 1 hour, a hump at around 2$\theta$ of 30° was observed which could be attributed to the unreacted amorphous silica present in the product. Also it was observed that calcium silicate hydrate phases with Ca:Si ratio of 2:1 were formed which included hillebrandite (ICSD 80127) and dellaite (ICSD 20148). Reinhardbraunsite, Ca$_3$(SiO$_4$)$_2$(OH)$_2$(ICSD 31275) and jaffeite, Ca$_6$(Si$_2$O$_7$)(OH)$_6$(ICSD 39725) were formed along with the other dicalcium silicate hydrates and had a Ca:Si ratio of 2.5:1 and 3:1 respectively.
3.1.2 Effect of water to solid ratio. Hydrothermal reactions were carried out at water to solid ratios of 2:1, 3:1 and 5:1 at a temperature of 250°C for 5 hours at 400 RPM. Figure 2A shows the XRD patterns of the products formed from the hydrothermal synthesis carried out with these three water to solid ratios. At water to solid ratios of 2:1 and 3:1, peaks of unreacted calcium hydroxide along with calcium carbonate were observed. At a water to solid ratio of 2:1, calcium silicate hydrates with Ca:Si ratio less than and equal to 1 were observed to be formed, which included rosenhahnite, Ca₃(Si₃O₈(OH)₂) (ICSD 100074), xonotlite, Ca₆Si₆O₁₇(OH)₂ (ICSD 20702) and truscottite, Ca₁₄Si₂₄O₅₈(OH)₈·2H₂O (ICSD 5126). With an increase in the water to solid ratio to 3:1, peaks of calcium silicate hydrates with Ca:Si ratio above 1 were also observed to be formed, which included killalaite, Ca₃₂(H₂O₆Si₂O₇)(OH), (ICSD 200124). With further increase in the water to solid ratio to 5:1, peaks of calcium silicate hydrates with Ca:Si ratio of and above 2 were observed, which included jaffeite, dellaite and reinhardbraunsite. Hence, increasing water to solid ratio was observed to favor the formation of calcium silicate hydrates with a Ca:Si ratio of 2:1.

3.1.3 Effect of temperature. In order to observe whether the desired calcium silicate hydrate phases formed at lower temperatures or not, hydrothermal synthesis was carried out at 150°C with a water to solid ratio of 5:1 at 400 RPM for 5 hours. Figure 2B shows the XRD patterns of the products obtained from the hydrothermal synthesis carried out at 150°C and 250°C. Peaks of unreacted calcium hydroxide and calcite were mainly observed in the product synthesized at 150°C, indicating that the initial reactants did not take part in the reaction at that temperature.

3.2 Effect of thermal treatment on β-C₂S formation
Since the hydrothermal synthesis at 250°C for 5 hours with a stirring rate of 400 RPM was observed to favor the formation of a product with desired calcium silicate hydrate phases with Ca:Si ratio of 2:1, this product was used for further thermal treatment to synthesize C₂S. The product was heated at different temperatures ranging from 520°C to 820°C to study the effect of thermal treatment on the formation of the desired β-C₂S phase. The phases observed in the thermally treated samples have been presented in Table 1. The XRD patterns of the thermally treated product at 670°C, 720°C, 770°C and 820°C have been shown in Figure 3A.
Figure 2. XRD patterns of hydrothermal synthesis product formed at− A) water to solid ratios of 2:1, 3:1and 5:1; B) temperatures of 150°C and 250°C

Table 1. Phases present in thermally treated samples at different temperatures.

| Phases          | 570°C | 620°C | 670°C | 720°C | 770°C | 820°C |
|-----------------|-------|-------|-------|-------|-------|-------|
| Dellsite        | ✔     | ✔     |       | ✔     | ✔     | ✔     |
| Reinhardbraunite| ✔     | ✔     | ✔     | ✔     | ✔     | ✔     |
| Ca₈Si₅O₁₈        | ✔     | ✔     | ✔     | ✔     | ✔     | ✔     |
| Calcite         | ✔     | ✔     | ✔     | ✔     | ✔     | ✔     |
| Calcium Hydroxide| X     | X     | ✔     | ✔     | ✔     | ✔     |
| β-C₂S           | ✔     | ✔     | ✔     | ✔     | ✔     | ✔     |
| a₁H–C₂S         | ✔     | ✔     | ✔     | ✔     | ✔     | ✔     |
| γ-C₂S           | ✔     | ✔     | ✔     | ✔     | ✔     | ✔     |

As shown in Table 1, jaffeite and hillebrandite present in the hydrothermal synthesized sample are seen to decompose below a temperature of 570°C leading to the formation of β-C₂S, a₁H–C₂S, γ-C₂S and Ca₈Si₅O₁₈. On heating the sample to a temperature of 670°C, peaks of dellite were observed which indicated that the phase has not been completely decomposed at that temperature. Peaks of calcite were not observed while peaks of calcium hydroxide appeared, indicating the decarbonation of
calcium carbonate at a temperature of 670°C. Peaks of β-C\textsubscript{2}S (ICSD 280995) and γ-C\textsubscript{2}S (ICSD 81095) were detected along with peaks of calcium silicate, Ca\textsubscript{8}Si\textsubscript{3}O\textsubscript{18}. Peaks of this Ca\textsubscript{8}Si\textsubscript{3}O\textsubscript{18} were observed to have disappeared on heating the sample at a temperature of 770°C. This possibly could have been due to the reaction between this phase and the excess calcium oxide present to form C\textsubscript{2}S at a temperature of 770°C. The calcium silicate hydrate phases present in the hydrothermal synthesis product with a Ca: Si ratio above 2:1, jaffeite and reinhardbraunsite, were observed to be decomposed to the C\textsubscript{2}S phases. Reaction of the decomposed product with any excess silica present in the system could have led to this formation of the C\textsubscript{2}S phase at the heated temperature. Peaks of α\textsubscript{H}–C\textsubscript{2}S (ICSD 81097) known to be a reactive form of belite, were detected on heating the sample at 670°C, 720°C and 770°C. Intensities of peaks of β-C\textsubscript{2}S were observed to be maximum for the product obtained by heating the sample at 820°C. Phases present in the thermally treated products at 770°C and 820°C were quantified using Rietveld analysis as presented in Table 2. Figure 3B shows the phase quantification done for the thermally treated sample at 820°C. As evident from the phase quantification, α\textsubscript{H}–C\textsubscript{2}S phase is observed to transform to the β-C\textsubscript{2}S at 820°C. The BET surface area of the thermally treated sample at 820°C was found to be 8 m\textsuperscript{2}/g. Due to the large surface area obtained using the hydrothermal synthesis route, it has been observed in the past that the reactivity of β-C\textsubscript{2}S synthesized is much higher as compared to that obtained by solid state reaction between CaO and SiO\textsubscript{2} [4].

| Temperature (°C) | β-C\textsubscript{2}S | γ-C\textsubscript{2}S | α\textsubscript{H}–C\textsubscript{2}S | Calcium Hydroxide |
|-----------------|---------------------|----------------------|--------------------------|-------------------|
| 770             | 49.97               | 24.25                | 22.55                    | 3.24              |
| 820             | 77.45               | 19.67                | -                        | 2.87              |

Table 2. Rietveld phase quantification of thermally treated samples at 770°C and 820°C
4. Conclusions
In this work, we have utilized the hydrothermal process to synthesize calcium silicate hydrate phases with a Ca: Si ratio of 2:1. The synthesis reaction has been found to be favored at a water to solid ratio of 5/1 at a temperature of 250°C and a dwell time of 5 hours with a stirring rate of 400 RPM. At lower temperatures and dwell times, degree of reaction has been found to be low with unreacted initial components present in the product. At lower water to solid ratios, formation of calcium silicate hydrate phases with lower Ca: Si ratio is favored.

The desired β-C2S phase is formed by heating the hydrothermally synthesized sample. At and above 820°C, the product comprised of 77.45% of β-C2S along with 19.67% of γ-C2S and 2.87% of calcium hydroxide. Another known reactive phase, α-H′-C2S was observed to be formed on heating the sample at 670°C, 720°C and 770°C. The BET surface area of the thermally treated sample at 820°C was found to be 8 m²/g.

Hence, a hydrothermal assisted calcination route can be used to synthesize a β-C2S phase with a high specific surface area. This phase can be utilized by blending with ordinary Portland cement to render a higher early age strength contribution than what is contributed by the β-C2S phase in ordinary Portland cement. This can be further leveraged by reducing the alite/belite ratio in cement and therefore reducing the overall energy consumption as well as the carbon dioxide emissions. Waste materials rich in lime and silica such as lime sludge, fly ash etc. can be explored further to synthesize this active belite phase.

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