Influence of Na₂Si₂O₅ on the Hydration of Tetracalcium Aluminoferrite

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Abstract: The hydration of C₄AF was retarded by the addition of Na₂Si₂O₅ of up to approximately 0.1 mass% and the hydration completely stopped when it exceeded 0.1 mass%. Metastable phases, such as Ca₄Al(OF)₄·3H₂O and Ca₀₅Al₀₅O₂·8H₂O, etc., were produced when C₄AF was hydrated in Na₂Si₂O₅ solution, whereas hydrogarnet was formed as the main hydration product when C₄AF was hydrated in water. The ion concentrations of Ca and Al in the liquid phase decreased, and at the same time the period for hydrogarnet formation in the paste was delayed with an increase in the amount of Na₂Si₂O₅ added to the liquid phase.

Keywords: Hydration reaction, Tetracalcium Aluminoferrite, Sodium Silicate, Hydrogarnet, Retardation, Solubility

1. INTRODUCTION

Portland cement consists mainly of alite, belite, aluminate and aluminoferrite [1]. The aluminate and aluminoferrite phases of the major cement phases are often referred to as the interstitial phases, and are known to exhibit a broad range of compositions in Portland cement [2]. The aluminoferrite phase also exists as a solid solution, the composition of which varies from C₄A₂F to C₄AF. In some cases, the typical composition of the ferrite phase was found to be C₄A₂Fe₃O₆·MgO·SiO₂·TiO₂O₅ in Portland cement [3]. The content of the ferrite phase in ordinary Portland cement ranges from 5 mass% to 10 mass% with an average of approximately 8 mass% [4]. The ferrite phase is commonly expressed in terms of its ideal composition: C₄AF. It has been reported that the hydration products of C₄AF comprise the cubic compound Ca₄Al₄(OH)₁₂(C₂AH₈), called hydrogarnet, which is probably the only stable hydrated calcium aluminium silicate similar to that in the CaO-Al₂O₃-H₂O system above 30°C [5]. Hydrogarnet is formed slowly at room temperature by conversion from metastable mono-, di- and tetracalcium aluminate hydrates, probably by a 'through-solution mechanism' involving the crystallization of C₂AH₈ from solution [5]. This transformation process is promoted by increasing temperature or pH [5]. Sersale [6] reported the transformation process of the crystalline habits of calcium aluminum hydroxide under the influence of various factors including temperature, CaO:Al₂O₃ ratio in the mother liquid and pH, etc. However, the hydration reaction of C₄AF in Portland cement has not yet been clarified. Although C₄AF reacts very rapidly with water, it has been accepted that the ferrite phase in Portland cement has low hydraulic reactivity. It is considered that the hydration reaction of C₄AF in Portland cement is affected by other ions, i.e., the diffused silicate ions from calcium silicate compounds in the liquid of hydration. Therefore, the influence of silicate ions on the hydration of C₄AF was investigated in this study.

2. EXPERIMENTAL

C₄AF was prepared in a laboratory furnace from a mixture of a reagent-grade CaCO₃, Al₂O₃ and Fe₂O₃. Pure C₄AF was obtained by heating the mixture at 1300°C for 10 h. C₄AF, ground to powder form with a specific surface area of 1000 cm²·g⁻¹, was used in this study. A solution of silicate ions was prepared by addition of the reagent-grade Na₂Si₂O₅. The amount added was expressed as mass% of the solution. The hydration rate of C₄AF was measured by a conduction calorimeter. The W/C (water/cement) ratio of the paste in the experiment using the conduction calorimeter was 1. The behavior of Ca and Al ions concentrations during C₄AF hydration was measured by atomic absorption spectrophotometry (AAS). The concentration of Fe was not detectable because the solubility of Fe³⁺ is very low at the pH of the hydration solution [7]. The W/C ratio of the paste used in the liquid analysis experiment was 10. After mixing C₄AF with Na₂Si₂O₅ solution at certain time intervals, the solution was extracted and filtered rapidly to analyze the concentrations of Ca and Al ions. X-ray diffraction and scanning electron microscope (SEM) were also used to identify the hydration products of the separated solid phases. The ion concentrations of Ca and Al obtained in the liquid analysis experiment were included to the CaO-Al₂O₃·H₂O phase diagram with respect to the maximum supersaturation curve of hydrogarnet, C₂AH₈ [8].

3. RESULTS AND DISCUSSION

3.1. Results of Conduction Calorimetry

Figure 1 shows the results of the experiment using the conduction calorimeter. The hydration of C₄AF was retarded with increasing amount of Na₂Si₂O₅ added.
Hydration of C₄AF with Na₂Si₂O₅

When the amount of Na₂Si₃O₅ exceeded 0.1 mass%, the hydration reaction of C₄AF did not occur even after hydration for 7 d. The samples measured by the conduction calorimeter were used to identify the hydration products by X-ray diffraction. The X-ray diffraction patterns of the pastes are shown in Fig. 2. Only the X-ray diffraction peak of C₆AH₈ appeared in the C₄AF hydrated in pure water, while the peak of C₆AH₁₃(C₆A₁₂(OH)₂•3H₂O) and C₆AH₄(C₆A₁₂O₃•8H₂O) were observed in the diffraction Na₂Si₃O₅ solution (C) and (D). In contrast, no hydrates appeared in the paste with 0.1 mass% Na₂Si₃O₅ solution. SEM observation of the morphology of the hydration products revealed that the cubic phase of hydrogarnet was present in the paste of C₄AF hydrated in water, and the hexagonal foliated masses of C₆AH₁₃ and C₆AH₄ were observed in the paste of C₄AF hydrated in 0.03 and 0.05 mass% Na₂Si₃O₅ solution. There was no hydration product in the paste in 0.1 mass% Na₂Si₃O₅ solution.

Fig. 1. Comparison of rate of heat liberation during hydration reaction of C₄AF in various solutions.

Fig. 2. X-ray diffraction patterns obtained from pastes of C₄AF hydrated in various solutions; A) unhydrated C₄AF, B) in water, C) in 0.03 mass% Na₂Si₃O₅ solution, D) in 0.05 mass% Na₂Si₃O₅ solution, and E) in 0.1 mass% Na₂Si₃O₅ solution.

Fig. 3. Changes of the concentration of Ca in various solutions during hydration of C₄AF.

Fig. 4. Changes of the concentration of Al in various solutions during hydration of C₄AF.
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Fig. 5. Variation of Al₂O₃/CaO ratio in the various pastes of C₄AF. Dotted line is maximum supersaturation curve of hydrogarnet. The underlined time presents the time just exceeded the saturation curve of hydrogarnet for the concentrations of CaO and Al₂O₃.

Fig. 6. Comparison of X-ray diffraction intensity of hydrogarnet in various pastes of C₄AF.

3.2. Solubility of C₄AF and Diagram for the Ternary CaO-Al₂O₃-H₂O

Changes in the concentrations of Ca and Al ions in the liquid phase during the hydration of C₄AF are shown in Figs. 3 and 4, respectively. The concentrations of Ca and Al ions in the liquid phase were decreased with the increase in the amount of Na₂Si₂O₅ in the liquid phase.

Fig. 7. Morphology of the hydration products, (A) in the C₄AF hydrated in water for 4 h and (B) in that of 0.015 mass% Na₂Si₂O₅ for the same time of hydration.
 Particularly, the concentration of Ca ions became zero in the 0.1 mass% Na$_2$Si$_2$O$_5$ solution. It was deduced from those results that the solubility of C$_4$AF is affected by the addition of Na$_2$Si$_2$O$_5$, and when a sufficient amount of Na$_2$Si$_2$O$_5$ is added, the solubility of C$_4$AF is markedly reduced.

Figure 5 shows the CaO-Al$_2$O$_3$-H$_2$O phase diagram with respect to the maximum supersaturation curve of hydrogarnet, C$_3$AH$_6$. The above-mentioned changes in the concentrations of Ca and Al in various C$_4$AF pastes with time are plotted in the diagram. The time for hydrogarnet formation from a liquid phase is estimated from this diagram. The dotted line represents the saturation curve of hydrogarnet. Therefore, when the concentrations of Ca and Al ions exceed this saturation curve, hydrogarnet is produced from this liquid phase. For example, the time for hydrogarnet formation is expected to be 30 min in the paste of C$_4$AF hydrated in water, but in 0.005 mass% Na$_2$Si$_2$O$_5$ solution, the formation of hydrogarnet begins after 2 h of hydration. It was also deduced from this phase diagram that when more Na$_2$Si$_2$O$_5$ is added, the time needed to produce hydrogarnet in the paste becomes longer; i.e., the formation of hydrogarnet in the solutions of 0.015 and 0.03 mass% Na$_2$Si$_2$O$_5$ is expected after 5 and 24 h of hydration, respectively. This diagram reveals that when the amount of Na$_2$Si$_2$O$_5$ added exceeds 0.05 mass%, no hydrogarnet is produced in the liquid phases even after 7 d of hydration. X-ray diffraction analysis was performed to establish the presence of hydrates in the hydrated pastes at a given time. The results are shown in Fig. 6. The Y-axis, I/I$_0$, represents the ratio of the X-ray diffraction intensity (I) of C$_4$AF (at 6.1 $^\circ$ /degree) to the intensity (I) of hydrogarnet (at 19.1 $^\circ$ /degree) in the same paste. The time for hydrogarnet formation almost agrees with the above predicted time from the CaO-Al$_2$O$_3$-H$_2$O phase diagram. The results indicate that the time for hydrogarnet formation is affected by silicate ion concentration in the solution. The mechanism of C$_4$AF hydration in the presence of silicate ions will be discussed in our forthcoming paper.

Figure 7 shows the morphology of the hydration products. Metastable phases were observed in the paste of C$_4$AF in 0.015 mass% Na$_2$Si$_2$O$_5$ solution, while cubic hydrogarnet was observed in the paste of C$_4$AF hydrated in distilled water over the same period of hydration.

4. CONCLUSION

The hydration of C$_4$AF was retarded by silicate ions, and the solubility of C$_4$AF was reduced by increasing the amount of silicate ions in the liquid phase. And the hydration of C$_4$AF did not occur in the liquid phase with a high concentration of silicate ions. Therefore, the reason why the hydration of C$_4$AF in Portland cement has low hydraulic reactivity is attributable to the high concentration of silicate ions during the hydration of Portland cement. The time for hydrogarnet formation was also delayed with the increase in the concentration of silicate ions.

REFERENCE