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INFLUENCE OF QUARTZ PARTICLE SIZE ON THE CHEMICAL AND MECHANICAL PROPERTIES OF AUTOCLAVED AERATED CONCRETE (I) TOBERMORITE FORMATION

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ABSTRACT

The chemical reactions in the hardening of autoclaved aerated concrete (AAC) block were investigated using ground quartz of different particle sizes. The samples were prepared at 180 ℃ under saturated steam pressure for various times from 0.5 to 64 h. Autoclaving for 0.5 h yielded 1.1-nm tobermorite, suggesting that the utilization of finer quartz has the advantage of reducing the processing time. The tobermorite formed had higher crystallinity with coarser quartz. The degree of reaction of finer quartz was higher than that of coarser quartz after shorter periods of autoclaving, but lower after longer periods of autoclaving. Gyrolite was formed after 64h when finer quartz was used.

Introduction

Autoclaved aerated concrete (AAC) with 1.1-nm tobermorite ($5CaO{\cdot}6SiO_2{\cdot}5H_2O$) as a binder is a lightweight construction material having a bulk density of 500 kg/m^3 and a volume porosity of 80 %. AAC is normally manufactured from calcareous materials (cement and lime) and siliceous materials (quartz sand) with a trace of Al as the foaming agent. These are mixed with water and molded to make a cellular green body by H_2 gas generation at atmospheric pressure, and then autoclaved at 180 ℃ under saturated steam pressure for several hours. Mitsuda et al. [1,2] examined the tobermorite formation

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process in AAC by analytical TEM. The results were: (1) the initial reaction product consists of fibrous Ca-rich C-S-H aggregates. (2) With an increase of autoclaving time, C-S-H reacts with silica dissolved from the quartz, reducing the Ca/(Al+Si) ratio, and is crystallized to tobermorite. (3) After the formation of highly crystalline tobermorite, the reaction is retarded, and some quartz remains as an unreacted residue. Many studies have been reported that the hydrothermal reactions in the CaO-quartz systems are controlled by the dissolution of the quartz [3-6], and this reaction determines the AAC processing time. Mitsuda et al. have suggested that the finer quartz as the starting material reduces AAC processing time [4]. However, very little has been reported regarding the mechanical properties of AAC, and especially on the influence of the quartz particle size.

The objective of the present work was to investigate the influence of the quartz particle size on the formation of tobermorite during the autoclaving process based on the actual industrial AAC recipe for reducing the processing time.

Experimental Procedure

Quartz Sample and AAC Preparation

The quartz samples used were of four different particle sizes (quartz A, B, C and D). They were from the same source and ground by ball mill. All the quartz samples contained about 99.7 wt% SiO_2 (Table 1). The mean particles size diameters were: (A) 4.3 μm (1.65 m^2/g, BET specific surface area), (B) 7.5 μm (1.28 m^2/g), (C) 12.4 μm (0.91 m^2/g) and (D) 32.3 μm (0.55 m^2/g) (Fig. 1).

AAC block-samples A, B, C and D were made using quartz A, B, C and D, respectively. The starting materials were a mixture of 60.4 wt% quartz, 20 % normal Portland cement, 15.6 % lime and 4 % gypsum with a trace of Al as the foaming agent, these mixes being based on the raw materials and proportions used to produce AAC. The bulk compositions of all AAC samples were almost the same, having a bulk Ca/(Al+Si) ratio of 0.48 and an Al/(Al+Si) ratio of 0.02. The starting mixtures with water (W/S=0.7) were cast in a 300×300×300 mm mold to make the cellular green body by hydrogen gas generation. All AAC blocks were made to be of bulk density 500 kg/m^3. After 4 h molding, the green bodies were demolded and autoclaved at 180℃ under saturated steam pressure for specified times of 1 to 64 h. The rate of temperature increase was 0.67℃/min.

Examination of Products

All the samples were examined by X-ray diffraction to identify the reaction phases. The 002 peak of tobermorite was used for the calculation of crystallite size. The atomic

TABLE 1
Chemical Compositions of Quartz Samples determined by XRF

wt%	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Ig-loss	Total
A	99.69	-	0.15	0.01	0.04	0.00	0.02	-	0.09	100.00
B	99.69	-	0.15	0.01	0.06	0.00	0.02	-	0.07	100.00
C	99.75	-	0.14	0.00	0.02	0.04	0.01	-	0.04	100.00
D	99.73	-	0.15	0.00	0.03	0.04	0.01	-	0.04	100.00

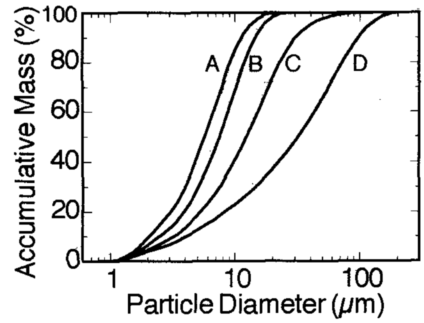

FIG. 1
Integrated particle size distribution of quartz samples A, B, C and D.

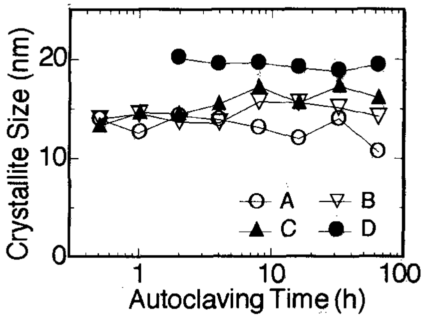

FIG. 2
Crystallite size of tobermorite of the samples autoclaved for various times.

ratios in the tobermorite and C-S-H relative to Si were determined by analytical TEM. The methods used were described by Mitsuda et al. [1].

The fraction of the quartz reacted was determined by wet chemical analysis [3], and then the degree of reaction of the quartz (reacted quartz/ total quartz) was calculated.

Results and Discussion

Reaction Product

Before autoclaving, all the green bodies contained C-S-H and $Ca(OH)_2$ as hydration products, and alite, belite, and almost all the quartz as unreacted starting materials were identified by XRD. After autoclaving, with increase of the specific surface area of the quartz, tobermorite tended to form earlier and to show lower reflection intensity. For all the samples except sample D made using the coarsest quartz, 0.5 h autoclaving yielded tobermorite with a small amount of C-S-H, shown by TEM. For sample D, tobermorite was formed after 2 h, while C-S-H was the major constituent up to 1 h. This result suggests that the finer quartz reduces the AAC processing time.

Figure 2 shows the crystallite size of the tobermorite. The coarser quartz tends to yield a larger crystallite size, indicating higher crystallinity. Using the finest quartz (A), the crystallite size decreased with the autoclaving time. For samples B and C, the crystallite size increased with autoclaving time up to around 8 h, and then slightly decreased. For sample D, the crystallite size remained nearly constant after 2 h, indicating that the highly crystalline tobermorites were formed on short periods of autoclaving.

Regarding the starting materials, the intensities of the quartz reflections in all the samples decreased with autoclaving time. Small amounts of alite and belite were observed up to 2 h in all the samples. Except when the coarsest quartz was used, $Ca(OH)_2$ was not observed even after 0.5 h, while it remained up to 2 h in sample D. These results suggest that the coarser quartz delayed the formation of tobermorite, and shows good agreement with previous reports [3-6]. Gyrolite was formed in samples A and B using finer quartz after 64 h autoclaving. The intensities of the gyrolite reflections were stronger for the finer quartz, indicating that gyrolite is formed readily by decomposition of tobermorite when the finer quartz is used [6].

Chemical Compositions of Reaction Products

Figure 3 shows the variations in the major element ratios of tobermorite obtained by ATEM measurements. In this figure, the selection of Ca/(Al+Si) is based on the tobermorite structure. Tobermorite formed by using the coarser quartz tends to have a higher mean Ca/(Al+Si) ratio after short periods of autoclaving, as Mitsuda et al. reported [4]. The mean ratio of the tobermorite decreased with autoclaving time, to an extent that was higher with the coarser quartz. After 64h autoclaving, the mean Ca/(Al+Si) ratio of tobermorite made using the finest quartz (A) was 0.85, while those in the other samples were 0.77-0.79. Long periods of autoclaving generally yielded tobermorite with a mean Ca/(Al+Si) ratio of 0.73-0.76, which is lower than the stoichiometric value (Ca/Si=0.83) [1,2,4]. These results suggest that the finer quartz retarded the decrease in Ca/(Al+Si) ratio. The mean Al/(Al+Si) ratio of tobermorite, which is the substitution ratio of Al for Si, was nearly constant at 0.02 until 64 h autoclaving for all the samples. The values were nearly equal to the bulk Al/(Al+Si) ratio of AAC.

In the factory products, the mean ratio of Ca/(Al+Si) and Al(Al+Si) of tobermorite were in the 0.77 to 0.83 range and in the 0.03 to 0.06 range, respectively [7]. The Ca/(Al+Si) ratio of tobermorite attained the range of factory products faster when the coarser quartz was used. The mean Al/(Al+Si) ratio of the tobermorite correlated with the bulk Al_2O_3 content [7]. The tobermorite made using quartz A, B, C or D had a lower Al/(Al+Si) ratio than that of the factory products due to the high purity of the quartz.

The mean Ca/(Al+Si) ratio of the gyrolite formed in samples A and B after 64 h was 0.68, which nearly equals the ideal gyrolite composition (Ca/Si=0.67). The mean Al/(Al+Si) ratio of the gyrolite was comparable to that of tobermorite.

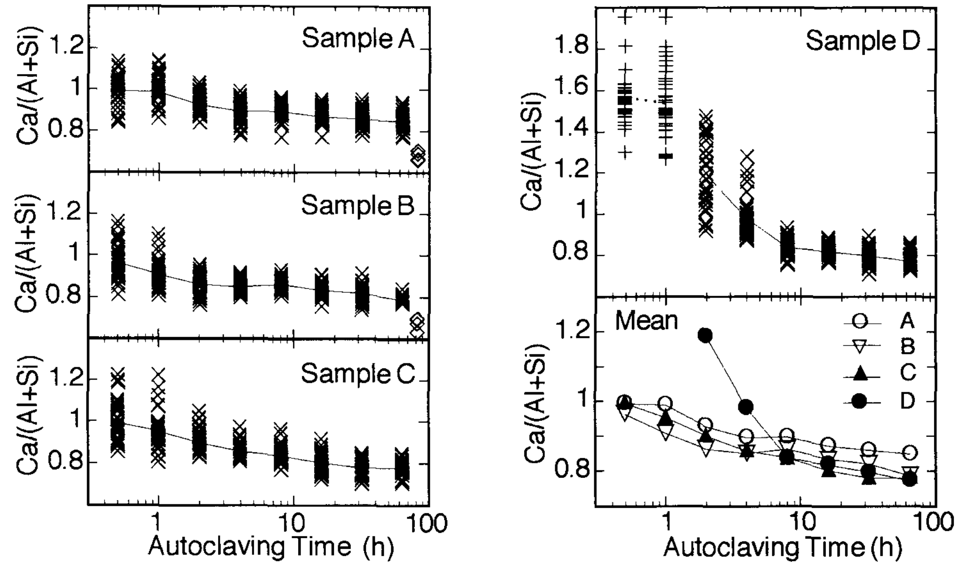

FIG. 3

Variations in Ca/(Al+Si) of C-S-H(+), tobermorite(×) and gyrolite(◇) for the block-samples (A, B, C and D) and their mean ratios.

Degree of Reaction of the Quartz

Figure 4 shows the degree of reaction of the quartz. During the initial stage of the reaction, the degree of reaction was less with the coarser quartz [4,5]. As the reaction proceeded, the relation was inverted; the degree of reaction being greater with the coarser quartz. This indicates that the amounts of tobermorite formed increase with increase in the particle size of the quartz after longer periods of autoclaving. The degree of reaction of the quartz became nearly constant after 2 to 4 h on using the finer quartz (A and B), while it took more than 16 h to be constant by using the coarser quartz (C and D). This agrees well with the ATEM results.

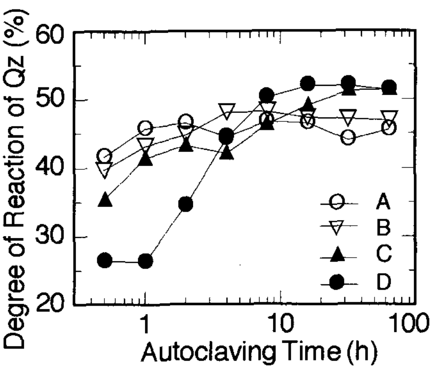

FIG. 4
Degree of reaction of the quartz (reacted quartz / total quartz) as a function of autoclaving time.

Influence of the Particle Size of the Quartz on the Tobermorite Crystallinity

The tobermorite formed using the finer quartz was of lower crystallinity than that formed using the coarser quartz. After short periods of autoclaving, the tobermorite initially formed with finer quartz had a lower mean Ca/(Al+Si) ratio, and the degree of reaction of the quartz was higher. After longer periods of autoclaving, however, the relations become inverted; the tobermorite showed a higher mean Ca/(Al+Si) ratio and the degree of reaction of the quartz was lower.

Taylor suggested that the hydrothermal reactions of lime with quartz occur in solution and not by a topochemical mechanism [6]. Regarding the crystal growth in solution, high supersaturation generally yields a large number of nuclei, thus giving crystals smaller than those from low supersaturation. The finer quartz with higher specific surface area could supply larger amounts of dissolved silica simultaneously, and thus producing a higher degree of supersaturation. This resulted in the formation of smaller crystals with lower crystallinity.

Influence of the Quartz Particle Size on the Degree of Reaction

In the hydrothermal reaction of the $CaO-SiO_2$ system, the reaction products have lower solubility than that of the starting materials [8]. That causes the apparent separation of reaction products from the reaction system without re-dissolution of the products. The formation of reaction products reduces the concentrations of the Ca- and Si- components in the solution., and is followed by further dissolution of the starting materials. Provided that the reaction product is stable, when either of the starting materials is wholly consumed, the other dissolves until the solubility is reached and the reaction is then retarded. Therefore, although the Ca/(Al+Si) ratio of the bulk AAC (in this case 0.49) is much lower than that of ideal tobermorite (Ca/Si=0.83), AAC consists of tobermorite and residual quartz without the formation of other phases having a lower Ca/Si ratio.

With the finer quartz, the degree of reaction of the quartz was retarded faster. This suggests that free Ca-component was consumed rapidly with the formation of a less crystalline tobermorite having a higher Ca/(Al+Si) ratio.

Gyrolite Formation

AAC factory products usually contain no gyrolite. For the lime-quartz reaction at a low Ca/Si ratio, C-S-H and tobermorite were formed successively in the initial stage of reaction, and the conversion of the tobermorite or C-S-H to gyrolite was slow [9]. Gyrolite was readily formed with amorphous silica at a low bulk Ca/Si ratio, but was hard to form with quartz [6,10]. This phenomenon was thought to be caused by the silica concentration in the solution [6,10]. Gyrolite was slowly and readily formed when the quartz used was finer (B and especially A). This is attributable to the lower crystallinity tobermorite with the finer quartz, being less stable to decompose. In addition, the contact frequency of tobermorite with quartz is larger for the finer quartz, indicating higher possibility of gyrolite formation due to higher silica concentration around the quartz particles.

Conclusions

(1) With finer quartz, tobermorite was formed after 0.5 h autoclaving, indicating that the finer quartz reduces the autoclaving processing time.
(2) The crystallinity of the tobermorite increased with increase of the quartz particle size.
(3) The degree of reaction of finer quartz was higher than that of coarser quartz after short periods of autoclaving, while it became lower after longer periods of autoclaving.
(4) Gyrolite was formed after longer periods of autoclaving when finer quartz was used.

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