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EFFECTS OF QUARTZ PARTICLE SIZE ON HYDROGARNET FORMATION DURING AUTOCLAVING AT 180°C IN THE $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O$ SYSTEM

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ABSTRACT

The effects of quartz particle size on the nature of hydration products in unstirred, autoclaved metakaolin-lime-quartz slurries with Ca/(Al + Si) and Al/(Al + Si) ratios of 0.80 and 0.13 were investigated. While hydrogarnet invariably appeared before 11 Å tobermorite when using either fine or coarse quartz, its formation was more prominent in the presence of coarse quartz. The breakdown of hydrogarnet and the formation of 11 Å tobermorite were delayed in the presence of coarse quartz, suggesting that when using aluminous additives under autoclaving conditions, quartz fineness is a deciding factor. The amount of hydrogarnet formed during autoclaving followed by its breakdown is significant in relation to the formation of 11 Å tobermorite. *© 1998 Elsevier Science Ltd*

Introduction

In our previous communication on unstirred, autoclaved metakaolin (MK)-lime-quartz slurries, hydrogarnet ($C_3AS_{3-x}H_{2x}$, $x = 0$ to 3) was reported to have preceded 11 Å tobermorite ($C_5S_6H_5$) with both low and high levels of MK addition (1). The continued existence of hydrogarnet depends on reaction time and bulk composition (1–3). A better understanding of additional factors that may affect formations of both hydrogarnet and 11 Å tobermorite is warranted from the viewpoint of cement-and/or lime-based building products, as hydrogarnet is considered to affect their strength adversely (4). Furthermore, hydrogarnet formation could play a significant role in relation to the formation of 11 Å tobermorite, which is one of the principal binders desired in certain autoclaved cured products (5). This paper presents new findings on the formation and breakdown of hydrogarnet during autoclaving in the presence of quartz of different particle size.

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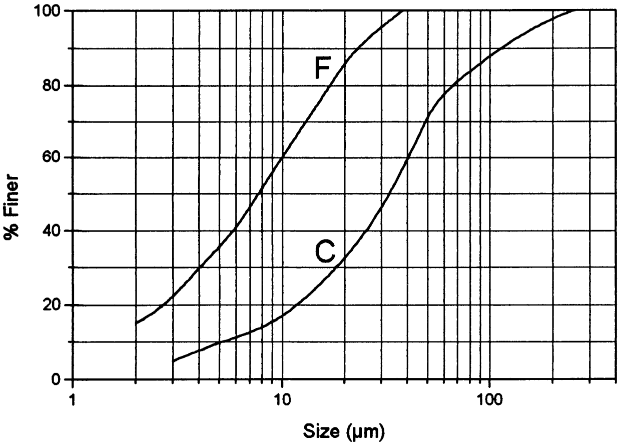

FIG. 1.
Particle size distribution by sedimentation for fine (*F*) and coarse (*C*) quartz.

Experimental

The starting materials were mixtures of CaO, MK, and ground quartz. Two mixtures were prepared, one with fine quartz (99.8% SiO_2) and the other with coarse quartz (99.0% SiO_2). Quartz particle size distributions, as per supplier specifications, are shown in Figure 1. Both mixtures were prepared at Ca/(Al + Si) and Al/(Al + Si) ratios of 0.8 and 0.13, respectively. The chemical composition of MK, preparation of the CaO, slurry preparation, and hydrothermal conditions were the same as those previously reported (1).

All specimens were vacuum dried at 60°C for a minimum of 24 h followed by grinding using a mortar and pestle and an additional drying period. Samples were examined by the following techniques:

1. X-ray diffraction (XRD) with CuK_α radiation at a scanning speed of 1.2° $min.^{-1}$ between $2\theta = 2$ up to 80° and an 8 s count time per step (Siemens D-5000 X-ray diffractometer).
2. Differential thermal and thermogravimetric analysis (DTA-TGA) between 40 and 1100°C under flowing nitrogen (100 mL min^{-1}) at a heating rate of 10°C $min.^{-1}$ (TA-instruments SDT 2960 simultaneous DTA-TGA thermal analyser).
3. Scanning electron microscopy (SEM) on carbon coated specimens at an accelerating voltage of 8kV (Jeol 6300 SEM fitted with energy dispersive X-ray microanalysis system (EDS)).
4. The amount of acid-insoluble residue was used as a measure of unreacted material as described previously (6) with modifications as follows: the centrifugal method described by Asaga et al. (7), was employed instead of the filtration method.

Results and Discussion

Figure 2a and b show the X-ray powder patterns of the two mixtures investigated. From Figure 2 it is evident that hydrogarnet invariably appeared before 11 Å tobermorite, irre-

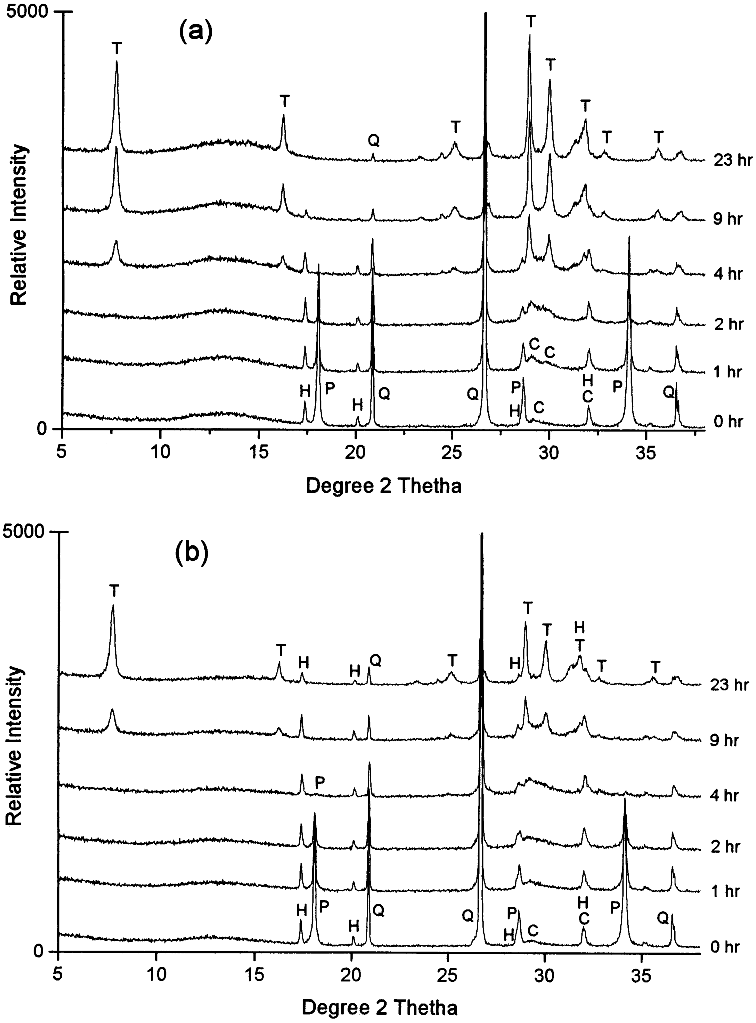

FIG. 2.

XRD patterns of autoclaved MK-lime-quartz mixtures prepared with: *a*) fine quartz, *b*) coarse quartz. H, hydrogarnet; T, 11 Å tobermorite; Q, quartz; C, calcium silicate hydrate (C-S-H); P, portlandite.

spective of the particle size of quartz. It is also evident that the formation of tobermorite was delayed when coarser quartz was used. This can be attributed at least partly to the lower reactivity/solubility of the coarser quartz particles, which slow down the lime-quartz and C-S-H-quartz reactions (8). The lower reactivity of coarse quartz in comparison to fine quartz is manifested by the acid-insoluble residue data (Fig. 3). An additional factor which may have retarded or delayed 11 Å tobermorite formation is the prevalence of hydrogarnet formation. This view is supported by the data depicted in Figure 4, which shows the mass loss

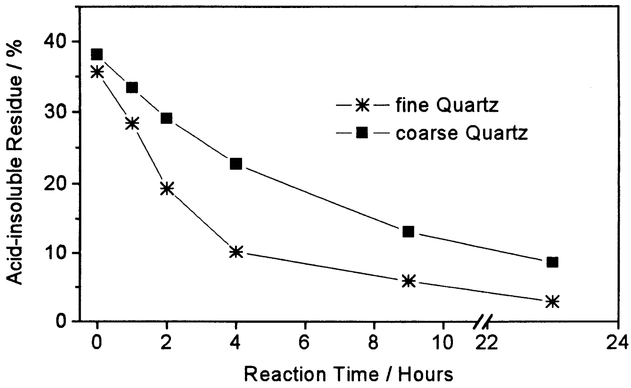

FIG. 3.

Percent acid-insoluble residue with reaction time when using fine or coarse quartz.

determined from TGA between 260 and 350°C attributable to hydrogarnet. The method employed for mass loss determination has been given elsewhere (9).

From these results the following are apparent:

1. In the presence of coarse quartz, the amount of hydrogarnet formed was generally greater than that when fine quartz was used. This indicates that the lime-MK reaction prevailed over the lime-quartz reaction more in the presence of coarse quartz due to its lower reactivity. SEM examination of samples prepared with coarse quartz and autoclaved for 1 h revealed hydrogarnet agglomerates to be ubiquitous, displaying complex three-dimensional growth patterns (Fig. 5). In contrast, hydrogarnet agglomerates were less common and appeared smaller when fine quartz was used; an example is shown in Figure 6.

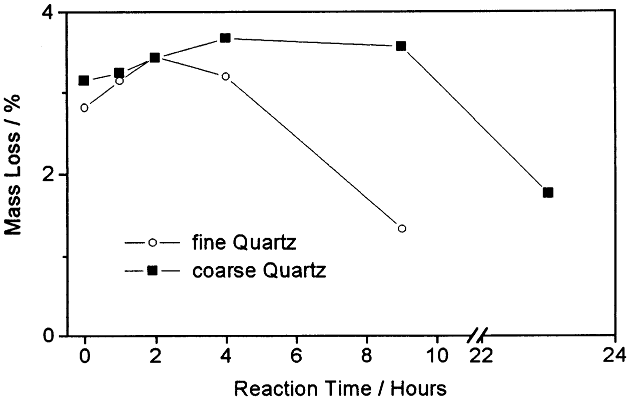

FIG. 4.

Percent mass loss due to hydrogarnet with reaction time when using fine or coarse quartz.

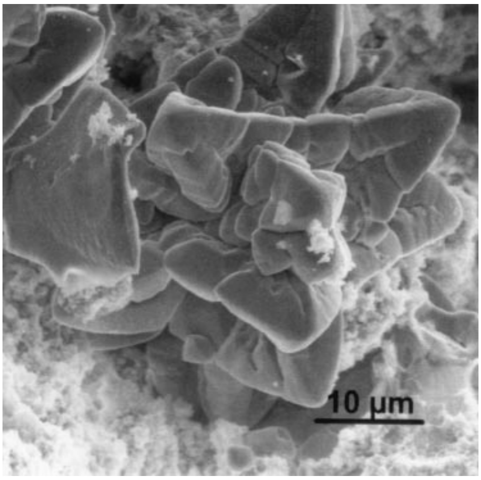

FIG. 5.
Hydrogarnet agglomerates in samples prepared with coarse quartz after 1 h of autoclaving.

2. In the presence of coarse quartz, the breakdown of hydrogarnet was significantly delayed and was evident after 9 h of autoclaving. This is in contrast with the breakdown of hydrogarnet after only 4 h of autoclaving when fine quartz was used. This indicates that quartz solubility, i.e. the release of silicate anions, is an important factor in relation to the onset of the breakdown of hydrogarnet under hydrothermal conditions.
3. The onset of the breakdown of hydrogarnet coincided with the appearance of 11 Å tobermorite (Figs. 2 and 4). SEM examination of samples prepared with fine quartz and

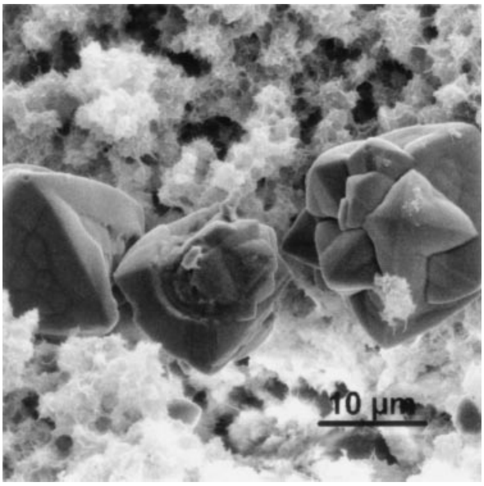

FIG. 6.
Hydrogarnet(s) in samples prepared with fine quartz after 1 h of autoclaving.

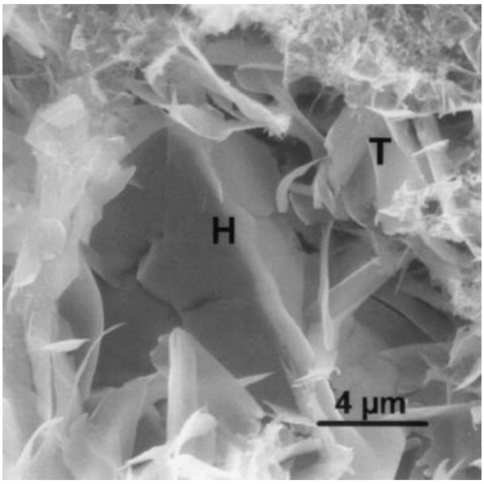

FIG. 7.
Hydrogarnet (H) breaking up and its close association with lath-type 11 Å tobermorite (T) observed when fine quartz was used and after 4 h of autoclaving.

after 4 h of autoclaving revealed lath-type 11 Å tobermorite in close association with hydrogarnet (Fig. 7). An example of a hydrogarnet agglomerate observed after 9 h of autoclaving in samples prepared with coarse quartz is shown in Figure 8. It is clear that hydrogarnet breakdown has begun while 11 Å tobermorite has formed. A close-up view of 11 Å tobermorite reveals characteristic flat plate and lath-type morphologies (Fig. 9).

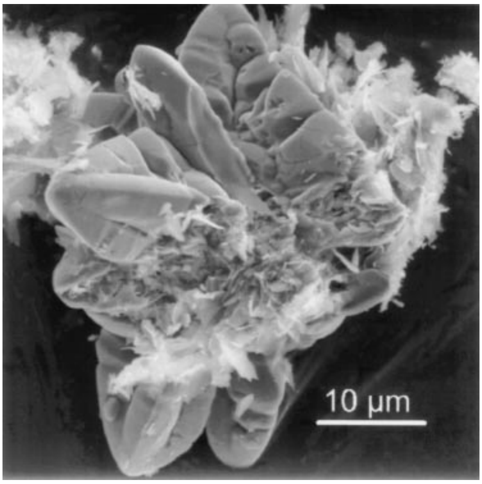

FIG. 8.
Hydrogarnet agglomerate breaking up, observed when coarse quartz was used and after 9 h of autoclaving.

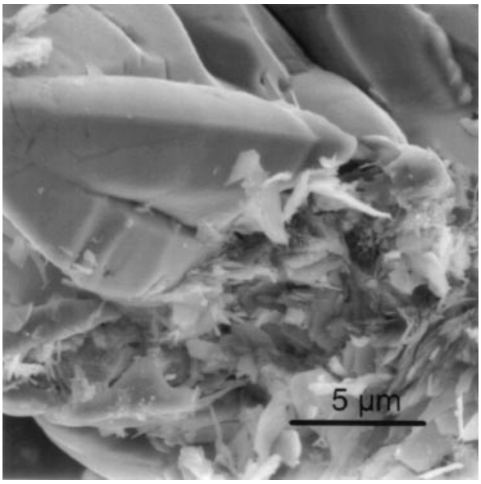

FIG. 9.
Close-up view of 11 Å tobermorite observed in samples prepared with coarse quartz and after 9 h of autoclaving.

4. Hydrogarnet remained and coexisted with 11 Å tobermorite after 23 h of autoclaving when using coarse quartz. The presence of hydrogarnet after 23 h of autoclaving when using fine quartz could not be ascertained with certainty by either DTA or XRD.

From these findings it is clear that in the presence of highly reactive aluminous additives such as MK, quartz fineness is of significance as this affects the hydrogarnet formation and its subsequent breakdown. It is also clear that these factors have a direct influence on the formation of 11 Å tobermorite.

Conclusion

This study has shown the following:

1. In the presence of highly reactive aluminous additives such as MK, quartz fineness is an influential factor and affects the formation and the breakdown of hydrogarnet during autoclaving. These phenomena are significant in relation to the formation of 11 Å tobermorite.
2. The formation of hydrogarnet was more prominent after all reaction times when using coarse quartz in comparison to fine quartz. This indicates that the lime-MK reaction prevailed over the lime-quartz reaction more in the presence of coarse quartz due to its lower reactivity.
3. The breaking down of hydrogarnet and the formation of 11 Å tobermorite were delayed when coarse quartz was used. This indicates that the release of silicate anions is an important factor in relation to the onset of the breakdown of hydrogarnet under hydrothermal conditions.

4. Hydrogarnet remained and coexisted with 11 Å tobermorite after 23 h of autoclaving when using coarse but not fine quartz.
5. SEM was an invaluable tool in providing direct evidence of both hydrogarnet breakdown and 11 Å tobermorite formation, as well as of their close association.

Acknowledgment

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