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EFFECTS OF QUARTZ PARTICLE SIZE AND KAOLIN ON HYDROGARNET FORMATION DURING AUTOCLAVING

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ABSTRACT

The effects of quartz particle size on the formation of hydrogarnet in unstirred, autoclaved kaolin-lime-quartz slurries with Ca/(Al + Si) and Al/(Al + Si) ratios of 0.8 and 0.13 were investigated. The initial lime-kaolin reaction was retarded only when fine quartz was used. The slower release of silicate anions from coarse quartz prolonged the stability of hydrogarnet while retarding the formation of 11Å tobermorite. Both the type of aluminous source and the extent of release of silicate anion from the silica source influence the formations of hydrogarnet and 11 Å tobermorite as well as the stability of the hydrogarnet. The interdependency between aluminous and siliceous sources is evident. *© 1998 Elsevier Science Ltd*

Introduction

In a recent communication on unstirred, autoclaved lime-quartz slurries prepared with thermally activated kaolin (metakaolin, MK) the authors reported that hydrogarnet ($C_3AS_{3-x}H_{2x}$, $x = 0$ to 3) formation always preceded 11 Å tobermorite ($C_5S_6H_5$) formation when using either fine or coarse quartz (1). Quartz fineness was a deciding factor in the lime-MK reaction, which prevailed over the lime-quartz reaction more in the presence of coarse quartz due to the slower release of silicate anions from the latter. In further studies it was demonstrated that the reactivity of the aluminous source also affected the extent of hydrogarnet formation (2). In order to investigate a possible interdependency between the aluminous and the siliceous sources, the effect of a variety of aluminous sources of different reactivity should be studied. This paper presents new findings on hydrogarnet formation during autoclaving in the presence of quartz of different particle size when using a less reactive aluminous source such as kaolin.

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Experimental

The starting materials were mixtures of CaO, kaolin and ground quartz. Quartz particle size distributions were the same as those reported previously (1). Kaolin, with particle size of 85 weight % < 2 μm (as per supplier specification), was supplied by ECC International (Europe). Its chemical composition as determined by XRF (ignited sample) was: 48.1% SiO_2, 37.3% Al_2O_3, 0.52% Fe_2O_3, 0.11% P_2O_5, 1.99% K_2O, and 0.02% CaO with a loss on ignition of 11.84%. Two mixtures were prepared, one with fine quartz (99.8% SiO_2) and the other with coarse quartz (99.0% SiO_2). Both mixtures were prepared at Ca/(Al + Si) and Al/(Al + Si) ratios of 0.8 and 0.13 respectively. The preparations of both the CaO and the slurry as well as the hydrothermal conditions were the same as those previously reported (3).

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 thermal analyses (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 (1).

Results and Discussion

Figures 1a and b show the X-ray powder patterns of the two mixtures investigated. Results for mass loss determinations (Figs. 2a–c) for the endotherms observed are ascribed to the following:

~60 to 260°C	presence of calcium silicate hydrates, C-S-Hs (Fig. 2c);
~260 to 350°C	presence of hydrogarnet a member of the series, $C_3AS_{3-x}H_{2x}$, $x = 0$ to 3 (Fig. 2a);
~350 to 500°C	presence of portlandite, $Ca(OH)_2$, (Fig. 2b).

It should be noted that calcium silicate hydrates are known to dehydrate gradually and variably over a wide temperature range up to ~800°C (4), their dehydration behaviour being a function of composition and structure (5). Consequently mass losses attributed to hydrogarnet and portlandite may be subject to overlap. From the data the following are nonetheless apparent:

1. Irrespective of the particle size of quartz, hydrogarnet appeared before 11 Å tobermorite. When coarse quartz was used, hydrogarnet was already present after 0 h of autoclaving (Fig. 1), i.e., upon completion of the 40 min. temperature ramp from 100°C to 180°C, as discussed previously (3). An example of hydrogarnets observed after 0 h is shown in

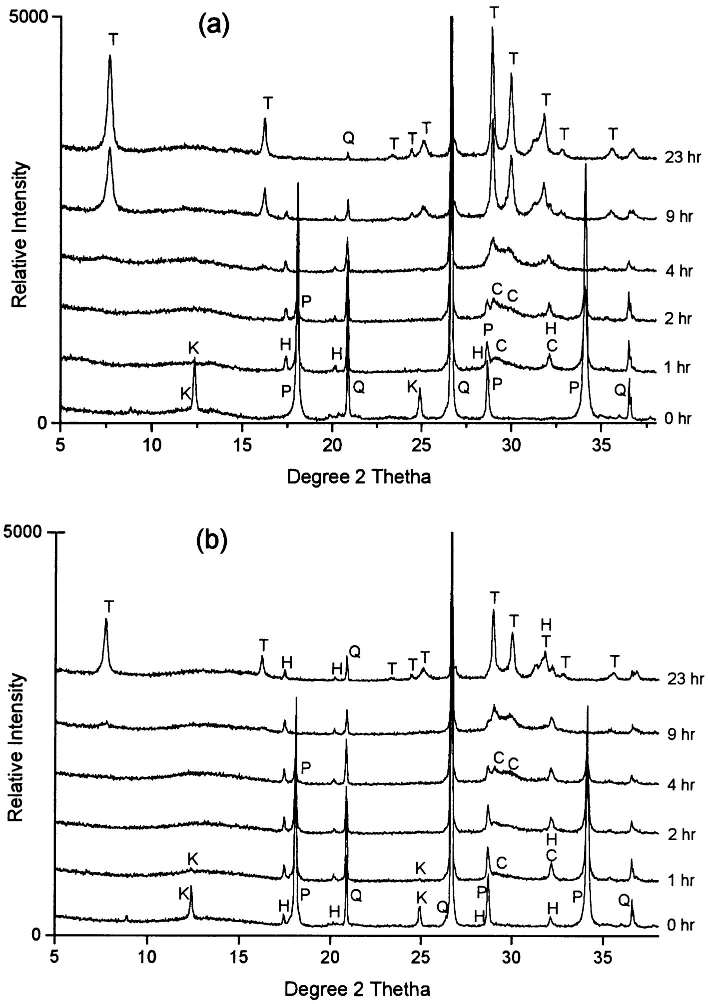

FIG. 1.

XRD patterns of autoclaved kaolin-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; *K*, kaolin.

Figure 3. In contrast, when fine quartz was used hydrogarnet was first detected after 1 h of autoclaving. Hydrogarnet morphology observed after 1 h is depicted in Figure 4. These findings indicate that initially the lime-fine quartz reaction prevailed over the lime-kaolin reaction while the presence of coarse quartz did not retard the lime-kaolin reaction. This is also manifested by XRD results (Fig. 1) and the acid-insoluble residue data (Fig. 2d) indicating that while kaolin remained after 0 h of autoclaving irrespective of the particle size of quartz, its amount was smaller when coarse quartz was used. Therefore, in the presence of coarse quartz, hydrogarnet formation was initially favoured indicating that the lime-kaolin reaction prevailed over the lime-coarse quartz reaction.

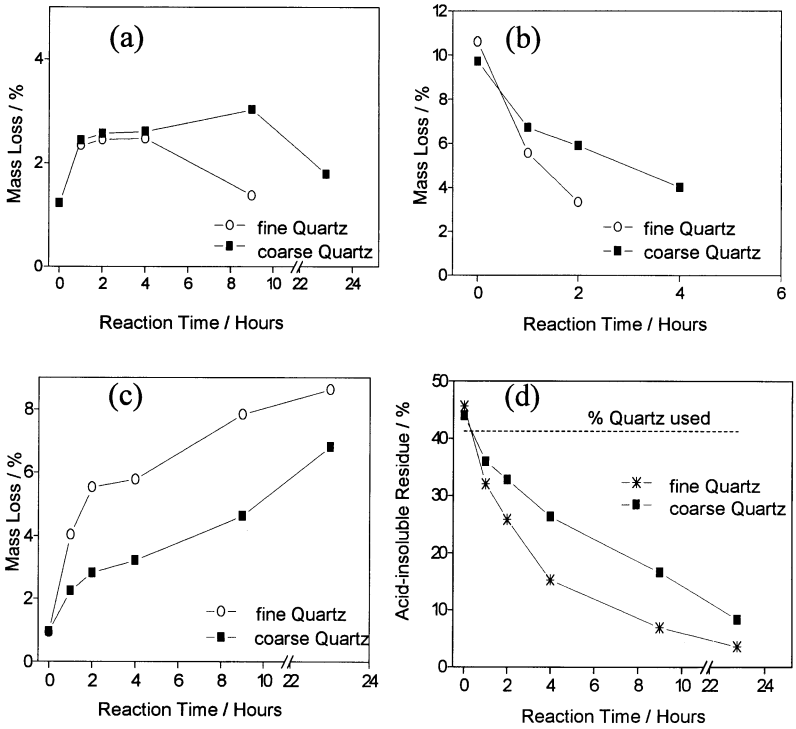

FIG. 2.

Amount of mass loss ascribed to: (*a*) hydrogarnet, (*b*) portlandite, and (*c*) calcium silicate hydrates and (*d*) amount of acid-insoluble residue vs. reaction time.

A possible explanation is the extent of removal of CH from the solution. Greenberg's (6) studies on the chemisorption of CH by quartz has shown that the initial reaction of CH is with the surface SiOH groups on quartz and that the amount of CH removed from solution is proportional to the surface area of quartz.

It is clear that, the effective available surface area being lower for coarse quartz, the amount of CH removed from solution will naturally be lower initially when coarse quartz was used. This in turn will result in "more" CH to be available to react with kaolin. Thus at the phase boundary of kaolin-lime solution the accumulation of OH^- and Ca^{2+} ions near the kaolin surface will facilitate the breakdown of the latter and the formation of hydration products.

2. Data for mass loss due to portlandite (Fig. 2b) were slightly lower when coarse quartz was used after 0 h of autoclaving due to the initial lime-kaolin reaction. With continued reaction time however, portlandite consumption was significantly lower in the presence of coarse quartz when compared with fine quartz. Portlandite remained for up to 4 h of autoclaving when coarse quartz was used in contrast to up to 2 h only in the presence of fine quartz (Fig. 2a). Hydrogarnet amount remained essentially constant for up to 4 h when either fine or coarse quartz was used. The observed decrease in lime consumption is clearly a consequence of the lower reactivity/solubility of coarse quartz. This view is

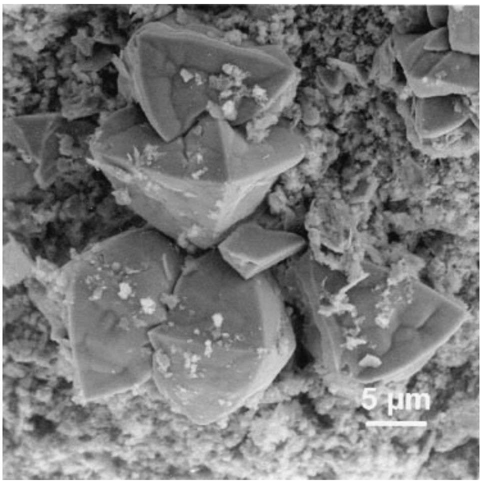

FIG. 3.
Hydrogarnets observed in samples prepared with coarse quartz after 0 h of autoclaving.

supported by the acid-insoluble residue data (Fig. 2d) and the significantly smaller mass loss due to C-S-Hs formed (Fig. 2c).

3. Hydrogarnet remained and coexisted with 11 Å tobermorite after 23 h of autoclaving with coarse quartz but not with fine quartz.
4. With coarse quartz the onset of the breakdown of hydrogarnet was evident after 23 h of autoclaving (Fig. 2a). In contrast, the breakdown of hydrogarnet was already evident after 9 h when fine quartz was used. As noted previously (1), this trend indicates that the release of silicate anions, a consequence of quartz dissolution, is a significant factor in

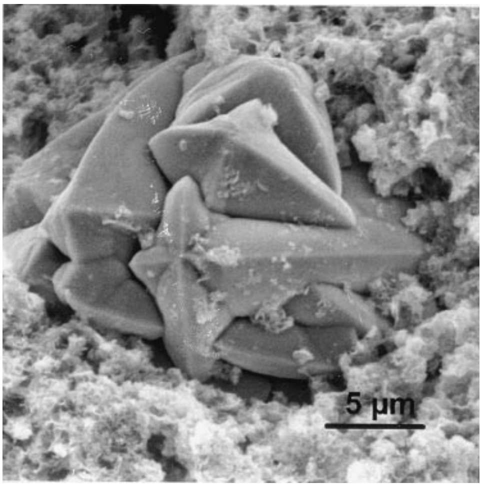

FIG. 4.
Hydrogarnets in samples prepared with fine quartz after 1 h of autoclaving.

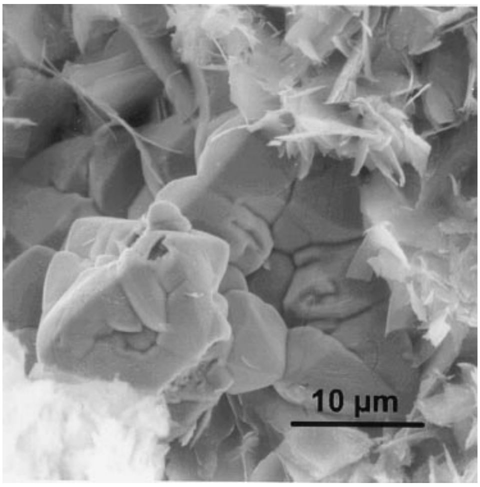

FIG. 5.
Hydrogarnet breakdown and 11 Å tobermorite observed after 23 h of autoclaving (coarse quartz).

relation to hydrogarnet stability. Examples of the breakdown of hydrogarnet and its close association with 11 Å tobermorite are given in Figures 5 and 6.

5. The appearance of 11 Å tobermorite coincided with the onset of the breakdown of hydrogarnet (Figs. 5 and 6). This agrees with our previous observations regarding the importance of the breakdown of hydrogarnet in relation to the formation of 11 Å tobermorite (1–3,7). The formation of 11Å tobermorite was significantly delayed and

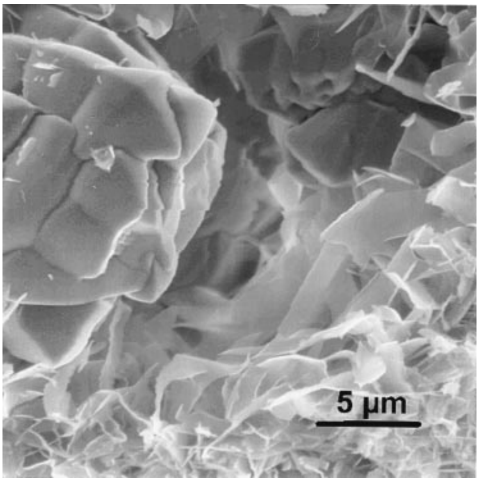

FIG. 6.
Hydrogarnet breakdown and 11 Å tobermorite observed after 9 h of autoclaving (fine quartz).

less prominent when coarser quartz was used, manifested in particular by the weaker peak intensities of the (002, 11.3 Å), (220, 3.08 Å), and (222, 2.98 Å) reflections. Again, this is a result of reduced solubility of coarser quartz.

The reduction in the release of silicate anions thus has a retarding effect on the formation of 11 Å tobermorite on the one hand while prolonging the stability of hydrogarnet.

6. Upon comparison with results reported for metakaolin (1,2), it is clear that metakaolin is a more reactive aluminous source, manifested in particular by its stronger effect on hydrogarnet formation initially. It is also clear that the effectiveness of the aluminous source is strongly dependent on the nature of the silica source as demonstrated by the authors' current and previous results. That an interdependency between aluminous and silica sources exists is thus evident.

From these studies it is clear that in the presence of less reactive aluminous additives, such as kaolin, quartz fineness is of significance as it affects the initial breakdown of kaolin and formation of hydrogarnet. More importantly however, quartz fineness is an influential factor in relation to both the breakdown of hydrogarnet and the formation of 11 Å tobermorite.

Conclusion

Our investigation has shown the following:

1. In the presence of coarse quartz, hydrogarnet formation was initially favoured, indicating that the lime-kaolin reaction prevailed over the lime-coarse quartz reaction.
2. Hydrogarnet remained and coexisted with 11 Å tobermorite after 23 h of autoclaving with coarse quartz but not with fine quartz.
3. The effectiveness of the aluminous source is strongly dependent on the nature of the silica source.
4. There exists an interdependency between the aluminous and the silica sources which influences the formations of both hydrogarnet and 11 Å tobermorite as well as the stability of the hydrogarnet.

Acknowledgment

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