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HYDROGARNET FORMATION DURING AUTOCLAVING AT 180°C IN UNSTIRRED METAKAOLIN-LIME-QUARTZ SLURRIES

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ABSTRACT

Autoclaved metakaolin-lime-quartz slurries with Ca/(Si+Al) composition of 0.8 and Al/(Si+Al) ratios between 0.03 and 0.38 were investigated. Hydrogarnet was always among the first phases formed and invariably appeared before 11 Å tobermorite. With increasing reaction time for Al/(Si+Al) ratios $\leq$ 0.13, the amount of hydrogarnet decreased and finally disappeared while 11 Å tobermorite increased concurrently. For Al/(Si+Al) ratios $>$ 0.13, hydrogarnet coexisted with 11 Å tobermorite after 4 h and beyond. Thus, in the presence of aluminous additives, hydrogarnet formation appears to play a more significant role in relation to 11 Å tobermorite formation than was thought previously. Increasing addition of metakaolin retarded the lime-quartz reaction, while enhancing the initial C-S-H formation. © *1998 Elsevier Science Ltd*

Introduction

Incorporation of aluminium ions in the crystal lattice of 11 Å tobermorite ($C_5S_6H_5$) in hydrothermally treated or autoclaved cured cement- and/or lime-based products is well known (1–6). The most widely studied aluminous materials and their effects on various aspects of tobermorite formation include: γ-Al_2O_3 (1,2), kaolin (3,4), zeolite (5) and $Al(OH)_3$ (4,6). The effect of another aluminous material, namely metakaolin (MK), in the autoclaved lime-quartz system, however, has received attention only in recent years (7–9). MK is an ultra-fine alumino-silicate, produced by the dehydroxylation of a kaolin precursor upon heating at a temperature range of ~700–800°C (10). The present work forms part of an investigation of the behaviour of MK in an autoclaved system. The method used in this study was based on that of Kalousek (3). This paperpresents new information on hydrogarnet ($C_3AS_3H_{2x}$ x = 0 to 3) formation during autoclaving in unstirred lime-quartz slurries in the presence of MK.

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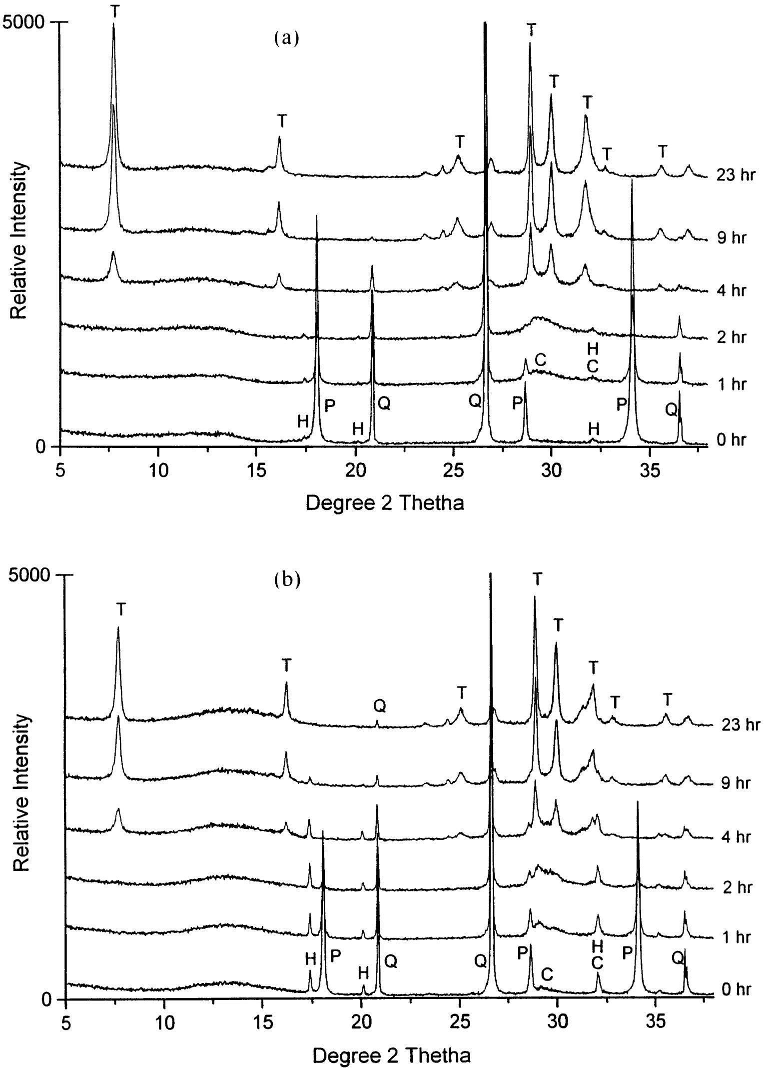

FIG. 1.
XRD patterns of autoclaved MK-lime-quartz mixtures with Al/(Si+Al) ratios of: *a*) 0.03, *b*) 0.13, *c*) 0.23, and *d*) 0.38. H, hydrogarnet; T, 11 Å tobermorite; Q, quartz; C, calcium silicate hydrate (C-S-H); P, Portlandite.

Experimental

The starting materials were mixtures of CaO, MK, and ground quartz. The percentages of oxides, as determined by XRF on ignited samples, are shown in Table 1. CaO was prepared by calcination of reagent-grade $CaCO_3$ (SIGMA, ACS reagent, assay 100.0%) at 1050°C for 5 h. The ground quartz (99.8% SiO_2) was from Ballarat, Victoria (Australia) with a particle size below 10 μm. MK, with particle size of 58 weight % < 2 μm (as per supplier specification), was supplied by ECC International (Europe). Its chemical composition, as

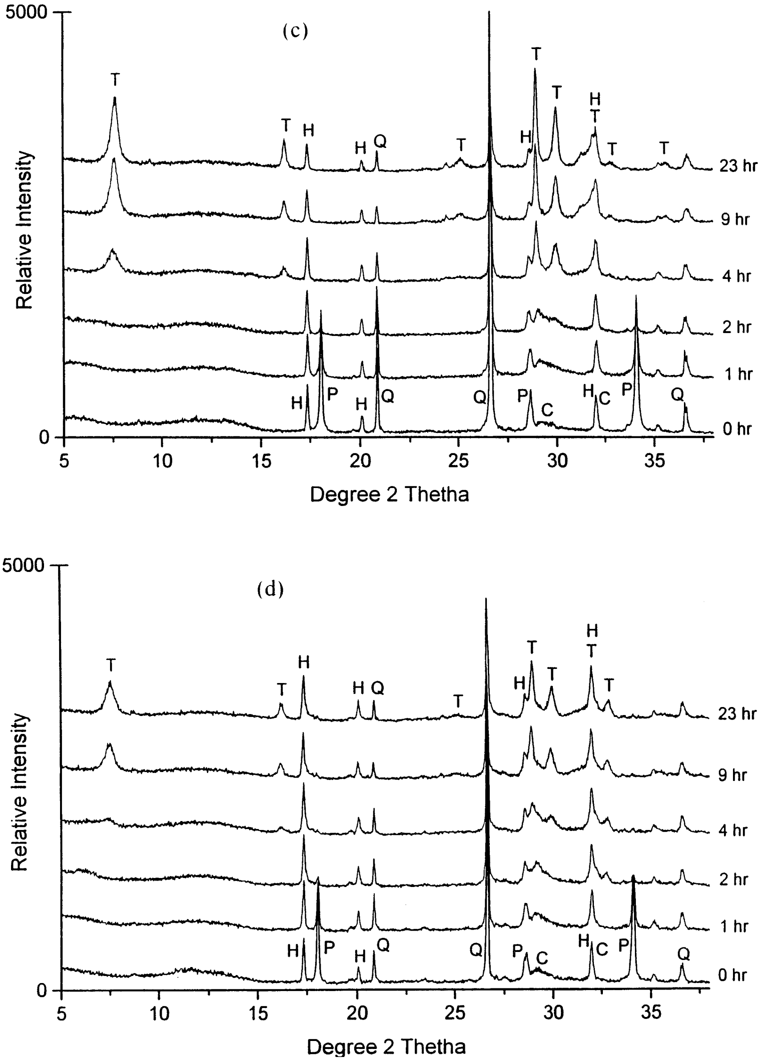

FIG. 1
Continued.

TABLE 1
Chemical composition of studied samples.

Atom ratios			Mass percent				
Al/(Si+Al)	Ca/(Si+Al)	Ca/Si	CaO	SiO_2	Al_2O_3	Fe_2O_3	K_2O
0.03	0.80	0.82	42.7	55.80	1.46	0.07	0.00
0.13	0.80	0.92	43.1	50.00	6.40	0.12	0.23
0.23	0.80	1.04	43.2	44.50	11.50	0.19	0.52
0.38	0.79	1.28	43.3	36.30	19.10	0.31	0.88

determined by XRF (ignited sample), was: 55.7% SiO_2, 41.5% Al_2O_3, 0.51% Fe_2O_3, 0.06% P_2O_5, 2.17% K_2O, and 0.02% TiO_2.

Slurries were prepared by hydrating CaO in six parts of freshly-boiled deionised water at 50–60°C with stirring for 3 min. The amount of water required to give a water/total solids ratio of 4.5 was then added, followed by addition of previously weighed and homogenised quartz-MK mixtures. Stirring was continued for another 5 min. at high speed. The resulting slurry was divided among 6 small Parr bombs (45 mL screw cap bomb fitted with needle valve) using a plastic syringe. These bombs were placed in a temperature-controlled oven, set at 100°C, and heated to 180°C in 40 min. They were removed from the oven after the following reaction times: 0 h (ie. upon completion of the 40 min. temperature ramp from 100°C to 180°C) then 1, 2, 4, 9, and 23 h at 180°C. Bombs were quenched in a bucket of water for 2 min., the steam released and the charge vacuum dried at 60°C for at least 24 h. After vacuum drying, samples were manually ground for 4 min. using a mortar and pestle followed by an additional vacuum drying period. Small pieces of material were retained for scanning electron microscope (SEM) evaluation. Slurry preparation, sample transfer and grinding were all conducted in a N_2-filled glove box to minimise the effects of atmospheric carbonation. Samples were examined by X-ray diffraction (XRD) using a Siemens D-5000 diffractometer and CuK_α radiation. SEM on carbon coated specimens was carried out using a Jeol 6300 fitted with EDS attachment using an accelerating voltage of 8kV.

Results and Discussion

Figures 1a-d show the X-ray powder patterns of the different mixtures investigated. It is evident that hydrogarnet was always among the first phases formed at all Al/(Si+Al) ratios studied and that it appeared before 11 Å tobermorite. At low MK additions, where Al/(Si+Al) ratios were 0.03 and 0.13, the amount of hydrogarnet increased slightly up to 2 h then decreased with increasing reaction time, but that of 11 Å tobermorite increased concurrently after 4 hours. Hydrogarnet was not detected by XRD after 4 and 23 h of autoclaving for starting Al/(Si+Al) ratios of 0.03 and 0.13, respectively.

Figures 2–4 are examples of hydrogarnet observed in samples, which had been removed from the oven after the 40 min. temperature ramp. "Near perfect" octahedral morphology of hydrogarnet occurring as single crystals is already evident in samples with the lowest Al/(Si+Al) ratio (Fig. 2.) The octahedral morphology of hydrogarnet crystals occurring in clusters is demonstrated by samples with Al/(Si+Al) ratio of 0.13 (Fig. 3.). An example of the growth pattern of octahedral crystals is shown in Figure 4.

After 4 h of autoclaving and at the lowest Al/(Si+Al) ratio, 11 Å tobermorite was found to be highly crystalline, displaying predominantly plate-like morphology (Fig. 5). In contrast, it was predominantly fibrous after 4 h and at a ratio of 0.13 (Fig. 6). SEM-EDS analyses revealed the presence of silicon in the hydrogarnet and aluminium in the 11 Å tobermorite.

At higher MK additions, with Al/(Si+Al) = 0.23, the amount of hydrogarnet remained essentially constant for up to 4 h followed by a decrease, while at the highest Al/(Si+Al) ratio the amount of hydrogarnet increased up to 4 h followed by a slight decrease (Figs. 1c–d). Hydrogarnet remained and coexisted with 11 Å tobermorite after 4 h of autoclaving and beyond at Al/(Si+Al) ratios of 0.23 and 0.38. Hydrogarnet and crystalline 11 Å tobermorite, observed after 23 h of autoclaving at the highest Al/(Si+Al) ratio, are depicted in Figures 7 and 8, respectively. The EDS analyses of numerous hydrogarnet grains and aggregates

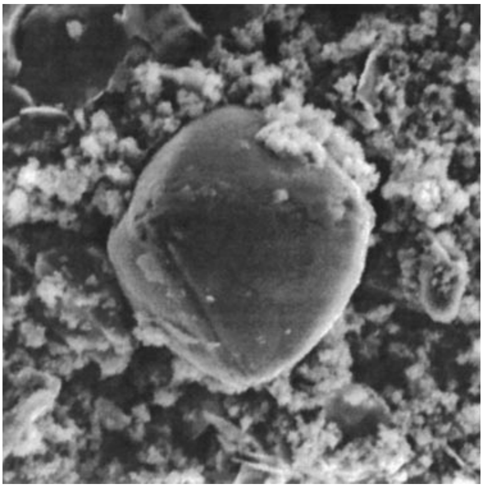

FIG. 2.
Hydrogarnet morphology observed after 0 h (Al/(Si+Al) = 0.03). Field of view (18.2 μm × 18.2 μm).

suggested that the hydrogarnet composition varied. It should be noted, however, that due to the nature of the samples, polished sections could not be prepared. Consequently, the observed variation in hydrogarnet composition could not be quantified.

11 Å tobermorite appeared after 4 h of autoclaving at all Al/(Si+Al) ratios, however, the rate of 11 Å tobermorite crystallisation clearly decreased or was retarded with increasing Al/(Si+Al) ratio (Figs. 1b–d). This is manifested particularly by the increasing line broadening of the (002) reflection of 11 Å tobermorite. The latter observation agrees with

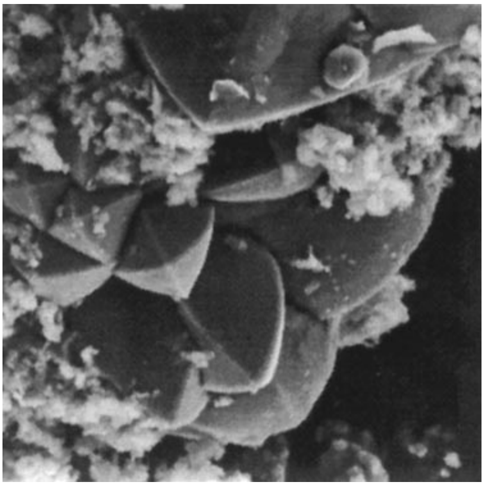

FIG. 3.
Hydrogarnet cluster observed after 0 h (Al/(Si+Al) = 0.13). Field of view (23.3 μm × 23.3 μm).

FIG. 4.
Example of the growth pattern of hydrogarnet after 0 h (Al/(Si+Al) = 0.13). Field of view (37 μm × 37 μm).

Kalousek's work (3), who found that 11 Å tobermorite crystallite size decreased with increasing Al/(Si+Al) ratio.

Our observations on hydrogarnet formation, however, are clearly different. It does not seem surprising that Kalousek (3) and Diamond et al. (4), for example, detected hydrogarnet only at "high" Al/(Si+Al) ratios after autoclaving for 24 and 19 h, respectively. At low Al/(Si+Al) ratios, at and below about 0.13, hydrogarnet decomposes or is consumed if the reaction time is increased, while at higher ratios it persists and coexists with 11 Å tobermorite

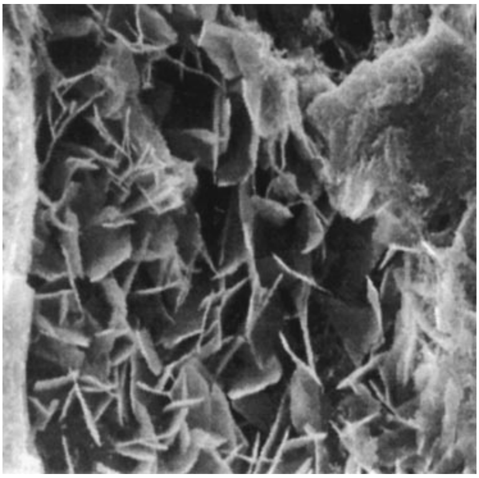

FIG. 5.
Crystalline platey 11 Å tobermorite after 4 h (Al/(Si+Al) = 0.03). Field of view (14.2 μm × 14.2 μm).

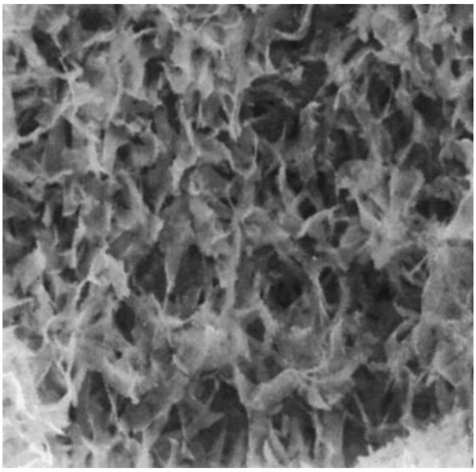

FIG. 6.
Fibrous 11Å tobermorite after 4 h ($Al/(Si+Al) = 0.13$). Field of view ($50\ \mu m \times 50\ \mu m$).

as demonstrated by our work. It is also clear that, at a $Ca/(Si+Al)$ ratio of 0.8, hydrogarnet is formed as a primary rather than a secondary phase.

Quartz was present after 23 h of autoclaving for $Al/(Si+Al)$ ratios > 0.03, the amount increasing with increasing MK used, indicating that the lime-quartz reaction had been affected. Initial C-S-H formation increased with increasing MK used. It has been observed (11), that with a mixture of CaO and quartz, the addition of kaolin or γ-Al_2O_3 markedly retarded the initial formation of C-S-H and this has been attributed to reduced solubility of quartz. While this may be valid also for MK addition in lime-quartz mixtures, the subject of the present investigation, other explanations seem equally plausible. For instance, the observed retardation of the lime-quartz reaction, may be due to:

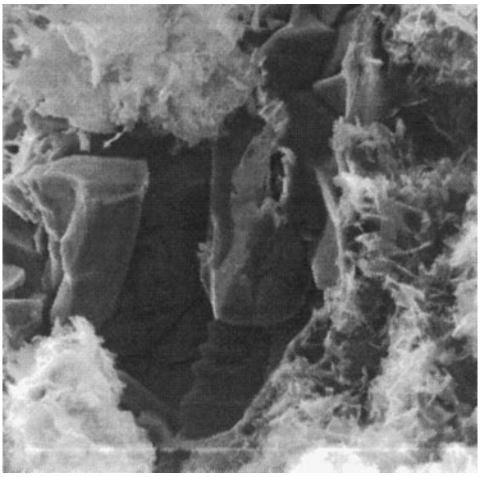

FIG. 7.
Hydrogarnet observed after 23 h ($Al/(Si+Al) = 0.38$). Field of view ($25\ \mu m \times 25\ \mu m$).

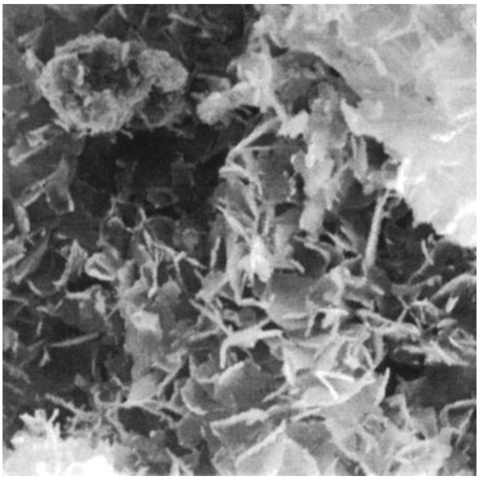

FIG. 8.
11 Å tobermorite observed after 23 h (Al/(Si+Al) = 0.38). Field of view (11.1 μm × 11.1 μm).

1. A lack of available lime in sufficient quantity. As the percent CaO was essentially the same for all Al/(Si+Al) ratios (Table 1) the increase in the amount of quartz with increasing MK addition, could be a consequence of hydrogarnet formation. The observed increase in hydrogarnet amount with increasing MK addition supports such a theory.
2. A more reactive silica source provided by MK in comparison with quartz. Thus initial C-S-H formation, at the shorter reaction times, increased as silica was readily available. The structure of the initial C-S-H, however, is known to influence the tobermorite crystallisation (12), suggesting that MK may affect the nature of the precursor C-S-H. A more detailed evaluation of the nature of hydration products formed is in progress, and we will report on this in future publications.

Conclusion

Our investigation has shown the following:

1. Hydrogarnet was always among the first phases formed at a Ca/(Si+Al) composition of 0.8 and Al/(Si+Al) ratios of 0.03 to 0.38 and appeared before 11 Å tobermorite.
2. At low MK additions, where Al/(Si+Al) ratios were 0.03 and 0.13, the amount of hydrogarnet decreased with increasing reaction time and was not detected after 4 and 23 h of autoclaving, respectively. 11 Å tobermorite increased concurrently after 4 h.
3. At higher MK additions, for autoclaving periods of up to 4 h, the amount of hydrogarnet remained essentially constant if the Al/(Si+Al) ratio was 0.23, and increased if this ratio was 0.38. Hydrogarnet remained and coexisted with 11 Å tobermorite at these Al/(Si+Al) ratios, after 4 h autoclaving and beyond.
4. With increasing MK addition, the lime-quartz reaction was retarded and initial C-S-H formation was enhanced, while the rate of 11 Å tobermorite crystallisation decreased or was retarded. A lack of available lime in sufficient quantity, due to increasing hydro-

garnet formation and/or a more reactive silica source provided by MK in comparison with quartz, perhaps affecting the nature of precursor C-S-H differently, may explain these phenomena.

5. Hydrogarnet formation may play a more significant role, particularly in relation to 11 Å tobermorite formation, than was thought previously.

Acknowledgments

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