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DTA–TGA of unstirred autoclaved metakaolin–lime–quartz slurries. The formation of hydrogarnet

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Abstract

DTA–TGA was used to monitor the evolution of hydration products in unstirred autoclaved metakaolin–lime–quartz slurries with reaction time. Hydrogarnet was always one of the first phases formed at all metakaolin additions and invariably appeared before 11 Å tobermorite. These findings explain apparent inconsistencies in the literature because the continued existence of hydrogarnet depends on such factors as reaction time and bulk composition. DTA–TGA indicated that the lime–quartz reaction was retarded and inferred differences in the precursor silicate anion structure of calcium silicate hydrates with increasing metakaolin addition. © 1998 Elsevier Science B.V.

Keywords: Autoclaving; Calcium silicate hydrate; Hydrogarnet; Metakaolin; Tobermorite

1. Introduction

Aluminium substituting for silicon into 11-Å tobermorite, under autoclaving conditions, is well documented [1–3]. Kalousek [1] in his classic work on this phenomenon used a combination of DTA and XRD to examine the nature of hydration products in lime–quartz–kaolin mixtures after autoclaving for 24 h. Kalousek noted that hydrogarnet had formed as a *second* phase when Al_2O_3 contents in the raw mix exceeded ~6.1%. Diamond et al. [2], examined lime–quartz specimens prepared with various aluminous additives after 19 h of autoclaving. While essentially confirming Kalousek's findings on Al-substituted 11 Å tobermorite, their observations on hydrogarnet formation appeared to be different. At $\%Al_2O_3$ contents comparable to those used by Kalousek, hydrogarnet was detected in some specimens while this phase was absent in others after autoclaving for 19 h. In view of these apparent inconsistencies on hydrogarnet formation, we have examined the evolution of hydration products in lime–quartz–metakaolin mixtures autoclaved for up to 23 h.

We report how DTA–TGA has been employed effectively in monitoring the evolution of hydration products, especially after short reaction times. We present evidence for hydrogarnet formation as a *primary*, rather than a secondary phase during autoclaving.

2. Experimental

The method used in this study was based on that of Kalousek [1]. The starting materials were mixtures of

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CaO, metakaolin (MK) and ground quartz. The starting composition with Ca/(Al+Si) bulk atom ratio of 0.8 and no added MK was 42.7% CaO and 57.3% quartz. Three additional mixtures prepared with MK and Ca/(Al+Si) bulk atom ratio of 0.8 contained 1.5, 6.4 and 11.5% Al_2O_3, respectively. 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 wt.% <2 μm (as per supplier specification), was supplied by ECC International (Europe). Its chemical composition, as 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 six 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 (i.e. upon completion of the 40 min temperature ramp from 100 to 180°C) then 1, 2, 4, 9 and 23 h at 180°C. Each bomb was quenched in a bucket of water for 2 min, the steam released and the charge vacuum dried at 60°C for a minimum of 24 h. After vacuum drying, samples were manually ground for 4 min using a mortar and pestle, followed by an additional vacuum-drying period. 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 DTA–TGA using a TA-instruments SDT 2960 simultaneous DTA–TGA analyser at a heating rate of 10°C/min under flowing nitrogen (100 ml/min) from 60–1100°C. Sample sizes were between 15 and 20 mg and were packed into a Pt–Rh crucible with 20 taps. All curves were evaluated using the TA-instruments software. Two-point rotations were carried out for all DTA curves as described previously [4]. Mass losses were determined by employing both TGA and DTG curves as described previously [4]. The second derivative differential thermal curve was used for peak temperature determinations [5]. Samples were also evaluated by X-ray diffraction (XRD) using a Siemens D-5000 diffractometer and CuK_α radiation [6].

3. Results and discussion

In the following discussion, the observed endotherms and corresponding mass losses are ascribed to:

- ~60–260°C: presence of calcium silicate hydrates;
- ~260–350°C: presence of a member of the hydrogarnet series, $C_3AS_{3-x}H_{2x}$, x=0 to 3, (hydrogarnet);
- ~350–500°C: decomposition of $Ca(OH)_2$, (portlandite);
- ~573°C: crystalline inversion of quartz.

3.1. Hydrogarnet formation

DTA curves of specimens retained after completion of the 40 min temperature ramp from 100 to 180°C (0 h) are shown in Fig. 1. The change in % mass loss versus % Al_2O_3, representing increasing addition of MK in the raw mix, for hydrogarnet and portlandite are shown in Fig. 2. In the presence of Al_2O_3 in the raw mix, the following are apparent:

- Hydrogarnet was always one of the first phases formed at all additions of MK, the amount increasing linearly with Al_2O_3 in the raw mix. Hydrogarnet could be detected by XRD [6] at all MK additions; however, peaks observed at the lowest MK addition were very weak while the presence of this phase was clearly manifested by the DTA curves even in samples with the lowest percentage of Al_2O_3.
- Unreacted portlandite decreased linearly with the percentage of Al_2O_3 in the raw mix as a consequence of having been consumed in reactions with MK and quartz.

The change in % mass loss due to hydrogarnet with reaction time is shown in Fig. 3. It should be noted that this mass loss is overlapped by calcium silicate hydrates, which are known to dehydrate gradually and differently over a wide temperature range up to

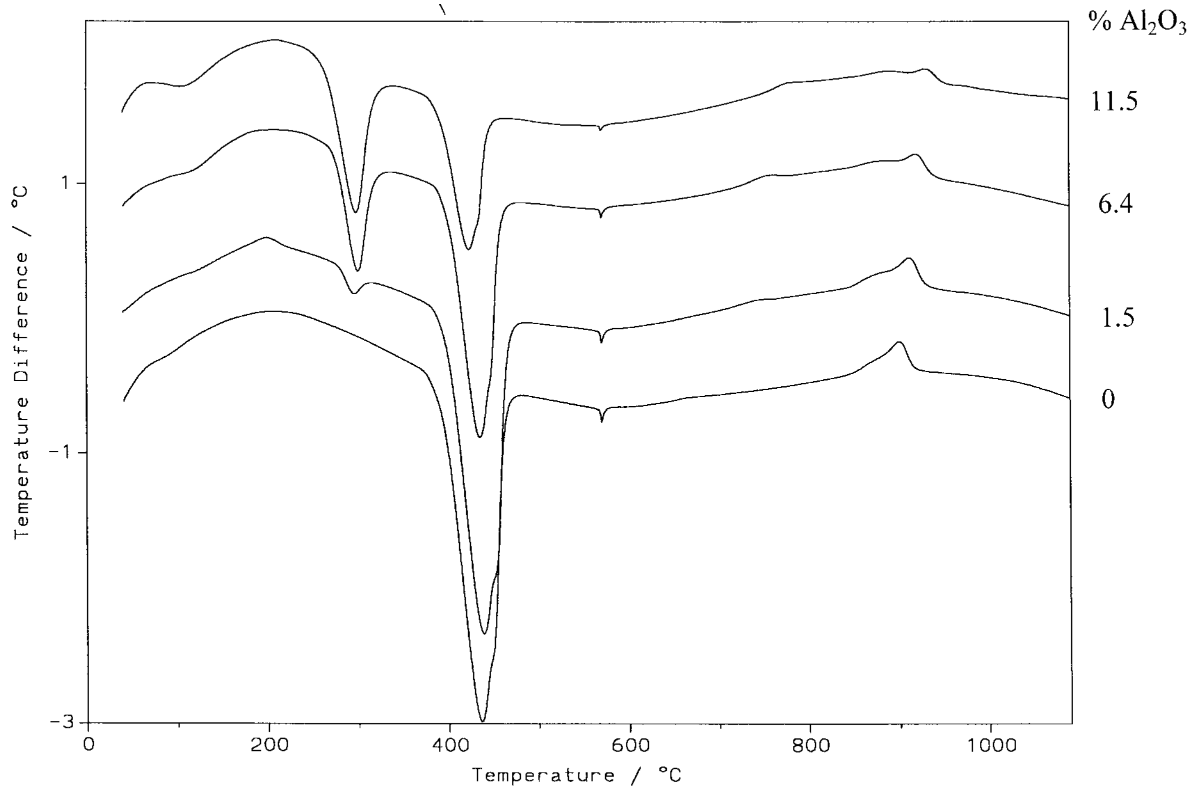

Fig. 1. DTA curves of specimens retained after completion of the 40 min temperature ramp.

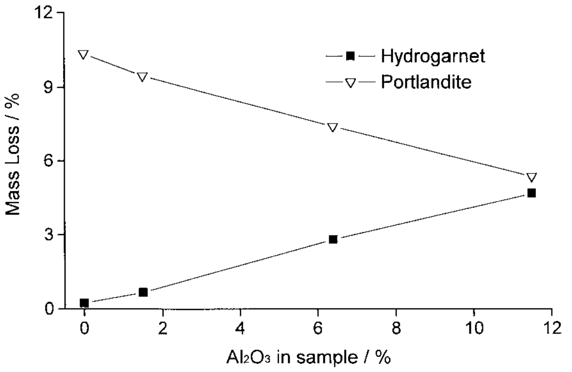

Fig. 2. Amount of mass loss vs. amount of Al_2O_3 for hydrogarnet and portlandite of specimens retained after the 40 min temperature ramp.

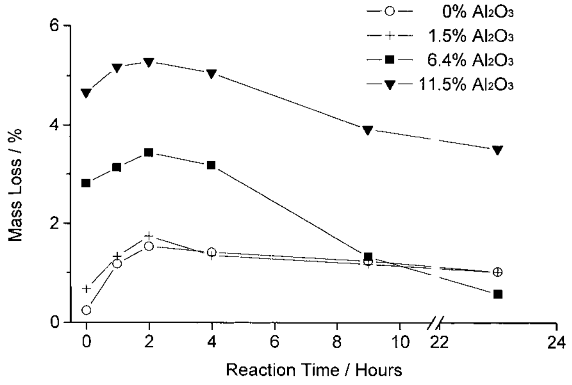

Fig. 3. Change in amount of hydrogarnet with reaction time for specimens containing increasing amounts of Al_2O_3.

~800°C [7]. Differences in their dehydration behaviour are due to compositional and structural variations [8]. From Fig. 3. the following is nonetheless apparent:

- Hydrogarnet amount increased slightly up to 2 h followed by a decrease clearly demonstrating that this phase was decomposed and consumed with reaction time. From DTA and XRD [6], hydrogarnet was no longer present after 4 and 23 h, respectively, of autoclaving for Al_2O_3 contents of 1.5 and 6.4% in the raw mix, while hydrogarnet remained with an Al_2O_3 content of 11.5% in the raw mix.

Our findings thus explain the apparent inconsistencies in the literature regarding the presence or absence of hydrogarnet [1,2]. From our results, it is clear that hydrogarnet is always one of the first phases formed; its continued existence in the final product depends on such factors, among others, as reaction time and bulk composition.

3.2. Calcium silicate hydrate and 11-Å tobermorite formation

Figs. 4 and 5 depict DTA curves after 1 and 2 h of autoclaving. From these and Fig. 1. the following are apparent:

- Calcium silicate hydrate formation was enhanced with increasing addition of MK, as is manifested by the size and presence of several endotherms between ~60 and 260°C, in comparison with the lime–quartz mixture with no Al_2O_3. This indicates that the silica source originating from MK is more reactive in comparison with quartz.
- More portlandite was consumed after 1 h of autoclaving; however, after 2 h it was still evident in samples containing Al_2O_3. This indicates that reactions with lime were perhaps retarded. The fact that quartz remained in increasing amounts after 23 h of autoclaving at Al_2O_3 additions exceeding 1.5% [6], indicates that it was the lime–quartz reaction which had been affected.

While 11-Å tobermorite appeared after 4 h of autoclaving at all Al_2O_3 contents in the raw mix and increased with reaction time, the ease of tobermorite

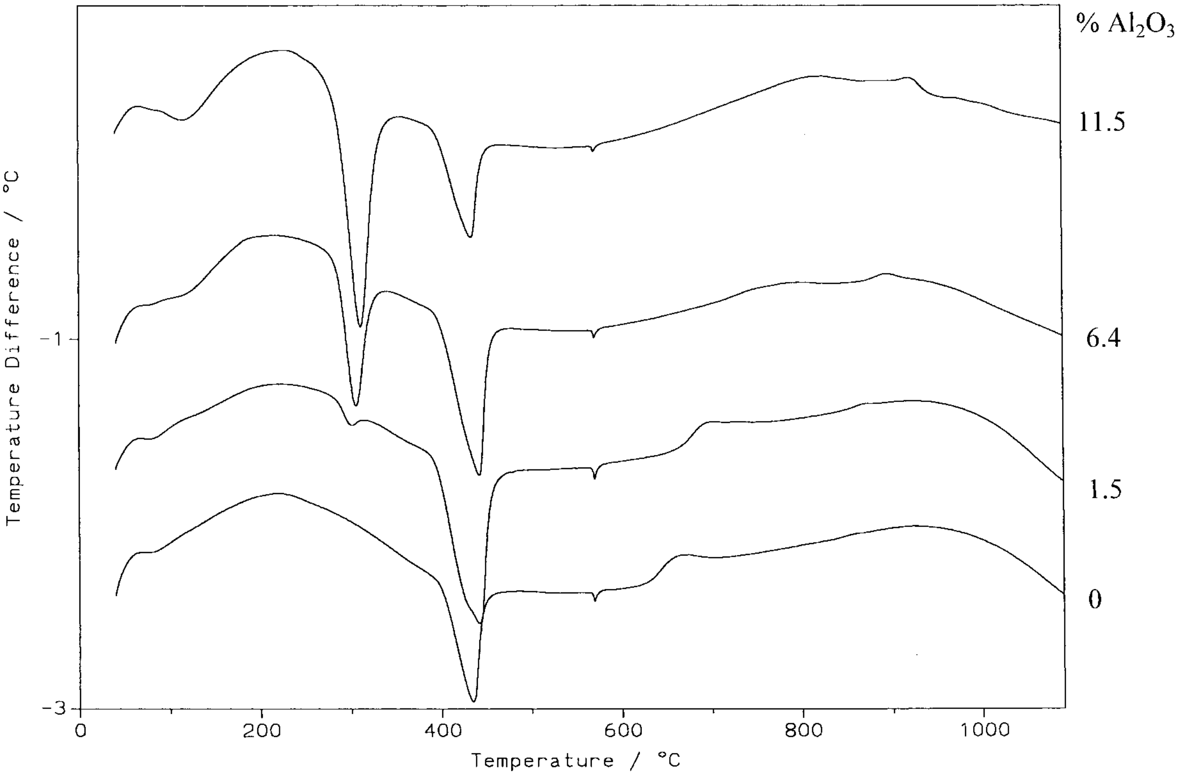

Fig. 4. DTA curves of specimens containing increasing amounts of Al_2O_3 after 1 h of autoclaving.

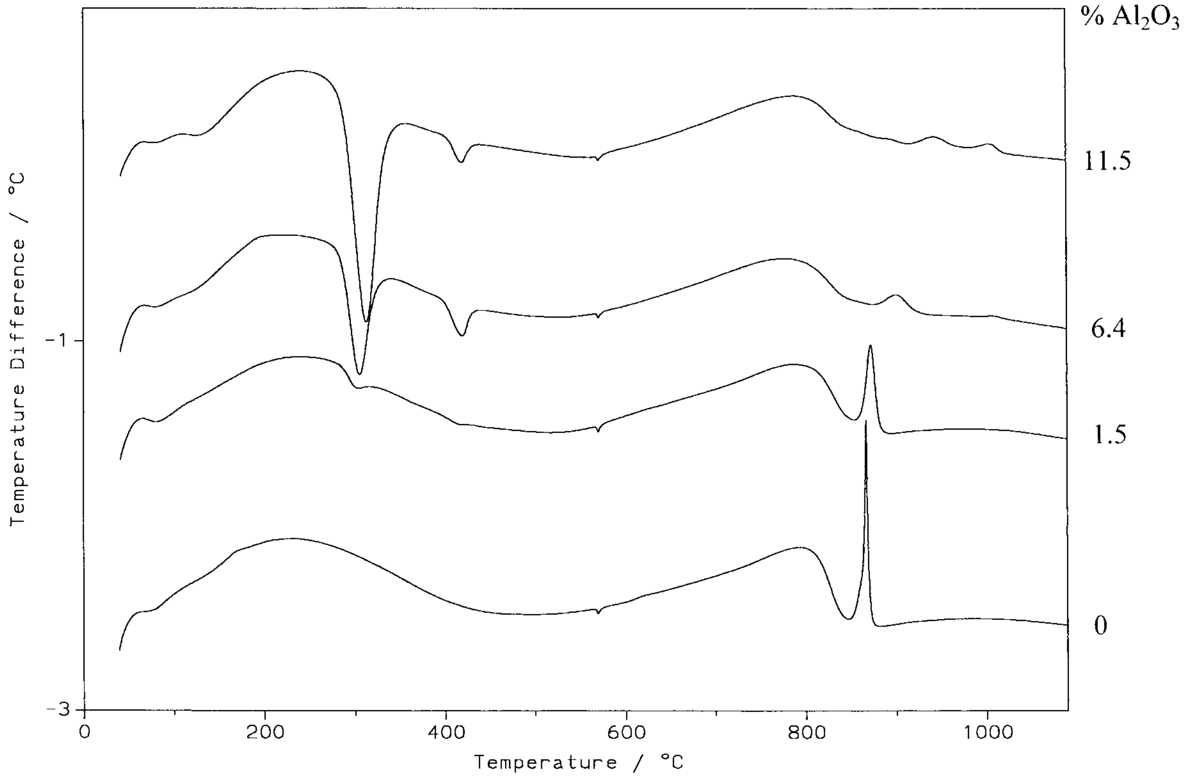

Fig. 5. DTA curves of specimens containing increasing amounts of Al_2O_3 after 2 h of autoclaving.

crystallisation decreased or was retarded at Al_2O_3 contents exceeding 1.5% [6]. Ease of tobermorite crystallisation is known to be affected by the precursor calcium silicate hydrate structure [9], i.e. the types of silicate anion structures. The types of silicate anion structures also affect the dehydration, dissociation and subsequent formation processes of β-C_2S [8] and/or β-CS [7,10]. The formations of the latter are manifested by exotherms at temperatures ranging between ~600 and 900°C [7,8]. From Figs. 1, 4, 5, mild-to-strong exotherms in the 600–900°C range are clearly evident. It is interesting to note that the exotherm temperature increased with Al_2O_3 content almost in a linear fashion, suggesting that there may be a relationship between these observed reactions and the precursor calcium silicate hydrate. This latter observation suggests that MK has affected the nature of the precursor calcium silicate hydrate. While the noted decrease in the ease of tobermorite formation with increasing MK additions seems to support such a theory, more detailed work is necessary. Additionally, interpretations of the noted exotherms are complicated by other possible phenomena, including:

- the presence of CaO, resulting from the portlandite decomposition may interact or interfere with the dehydrating calcium silicate hydrates [8];
- the possible interaction or interference of the hydrogarnet residue with the dehydrating calcium silicate hydrates; and
- the possibility of aluminium ions incorporated in the calcium silicate hydrates acting in a cationic manner during the dehydration reactions [11].

4. Conclusions

1. DTA–TGA was a very useful technique for monitoring the evolution of hydration products in the autoclaved lime–quartz–MK system, especially after short reaction times.

2. DTA–TGA results indicated that the lime–quartz reaction was retarded and inferred differences in the precursor silicate anion structure of calcium silicate hydrates with increasing MK additions.
3. DTA–TGA manifested the presence of small amounts of hydrogarnet more clearly than XRD.
4. Hydrogarnet was formed as a primary rather than a secondary phase and appeared before 11-Å tobermorite. This suggests that hydrogarnet formation may play a more significant role in relation to tobermorite formation than was thought previously.
5. The continued existence of hydrogarnet in the final product depends on factors such as reaction time and bulk composition, explaining apparent inconsistencies in the literature regarding its existence.

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