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DTA-TGA evaluations of the CaO–Al_2O_3–SiO_2–H_2O system treated hydrothermally

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Abstract

DTA-TGA in combination with XRD and wet chemical techniques was employed to explain the effect of chemical composition of the starting raw mix, maintaining the Al_2O_3 content constant, on the formations of hydrogarnet and Al-substituted 11 Å tobermorite. Three mixes with bulk Ca/(Al + Si) atom ratios of 1.0, 0.8, and 0.6 in the industrially important CaO–Al_2O_3–SiO_2–H_2O system were investigated following hydrothermal treatment at 180°C for up to 23 h. The stability of hydrogarnet decreased with increasing silica content in the bulk composition and was extended in the presence of portlandite and lime-rich calcium silicate hydrate. The formation of Al-substituted 11 Å tobermorite accelerated with decreasing bulk Ca/(Al + Si) atom ratio. Changes in the exotherm profiles, due to the crystallization of beta-wollastonite, with reaction time provided evidence for increasing incorporation of Al into the 11 Å tobermorite crystal lattice. The concurrent decrease in the hydrogarnet amount provided the proof that this phase supplied most of the Al for the formation of Al-substituted 11 Å tobermorite.

Keywords: Al-substituted 11 Å tobermorite; Anorthite; Beta-wollastonite; Hydrogarnet; Hydrothermal

1. Introduction

In a previous communication, the authors presented evidence that contrary to presumptions in the literature, in the industrially important hydrothermally treated CaO–Al_2O_3–SiO_2–H_2O system hydrogarnet is always one of the first phases formed and invariably appears before Al-substituted 11 Å tobermorite [1]. The continued existence of hydrogarnet depends on such factors as reaction time and initial Al_2O_3 content in the raw mix [1].

In the present investigation, we report how DTA-TGA in combination with X-ray diffraction and wet chemical techniques has been employed effectively in evaluating the effects of the initial chemical composition of the raw mix, maintaining a constant Al_2O_3 level, on the formations of hydrogarnet and Al-substituted 11 Å tobermorite. The changes in the exotherm profile above 800°C in relation to Al-substituted 11 Å tobermorites are also discussed.

2. Experimental

Three mixes were prepared of bulk Ca/(Al + Si) atom ratios as shown in Table 1. In this paper, ‘bulk

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Table 1
Chemical composition of studied samples

Bulk Ca/(Al + Si)	Bulk Al/(Al + Si)	Bulk Ca/Si	Quartz in mixture (%)
1.00	0.13	1.16	36.4
0.80	0.13	0.92	41.8
0.60	0.13	0.68	48.5

Ca/(Al + Si) atom ratio' is referred to simply as 'bulk ratio'. The starting materials were mixtures of CaO, metakaolin (MK) and ground quartz. Details of the raw materials used and the slurry preparation have been given elsewhere [1,2]. 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. Following this, the samples were manually ground for 4 min using a mortar and a pestle followed by an additional vacuum drying period at 60°C. 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 40° to 1150°C. Sample sizes were between 15 and 20 mg and were packed into a Pt–Rh crucible with 20 taps. All differential thermal (DT) and TG curves were evaluated using the TA instruments' software. Two point rotations were carried out for all curves as described previously [3]. Mass losses and peak temperatures were determined according to the methods described by Klimesch and Ray [3,4] by employing both TG and DTG (derivative thermogravimetric) curves [3] and second derivative DT curves [4], respectively. Samples were also characterised by X-ray diffraction (XRD) using a Siemens D-5000 X-ray diffractometer and CuK_α radiation. Details have been given elsewhere [2]. Selected samples were held for 1.5 h at specified temperatures up to 1100°C in air followed by cooling in a desiccator over silica gel and XRD examination (CuK_α radiation at a scanning speed of 1.8°/min between $2\theta = 5$ up to 65° using a 2 s count time per step).

The starting chemical composition for each mix was determined for one ignited sample (2 h at 1000°C) by X-ray fluorescence (XRF) using an ARL 8410 sequential spectrometer. The ignited samples were prepared as fused disks using flux 12–22 (35.2 wt% lithium tetraborate and 64.7 wt% lithium metaborate) with a sample to flux ratio of 1 : 10. The amount of acid-insoluble residue (AIR) was determined for all hydrothermally treated samples and served as a measure of unreacted material. The AIRs were determined according to the centrifugal method described by Asaga et al. [5] with the following modifications: the suspensions were digested for 0.5 h at room temperature and the residues were ignited at 1000°C for 2 h before weighing [6]. Following this, the AIR samples were fused in nickel crucibles using sodium peroxide followed by the addition of hydrochloric acid to dissolve the melt. The chemical compositions of the AIRs, including SiO_2% and Al_2O_3%, were determined by inductively coupled plasma optical (atomic) emission spectrometry (ICP) by Genalysis Laboratory Services, Western Australia. The amount of silica (SiO_2) reacted, expressed as 'SiO_2 reacted (mol)', was calculated according to Eq. (1).

$$\begin{aligned} SiO_2 \text{ reacted (mol)} &= [\text{total } SiO_2 \text{ in bulk mixture (mol), XRF}] \\ &\quad - [SiO_2 \text{ in AIR (mol), ICP}] \end{aligned}$$

3. Results and discussion

3.1. Hydrogarnet formation and its breakdown

Fig. 1(a)–(c) depict the DT curves after 0, 1, 2, 4, 9 and 23 h (bottom to top) of hydrothermal treatment for the samples prepared with bulk ratios of 1.0, 0.8 and 0.6, respectively. In the following discussion, the observed endotherms and corresponding mass losses are ascribed to:

- 260–350°C presence of hydrogarnet, a member of the series $C_3AS_{3-x}H_{2x}$, $x = 0–3$;
- 350–500°C decomposition of $Ca(OH)_2$ (portlandite).

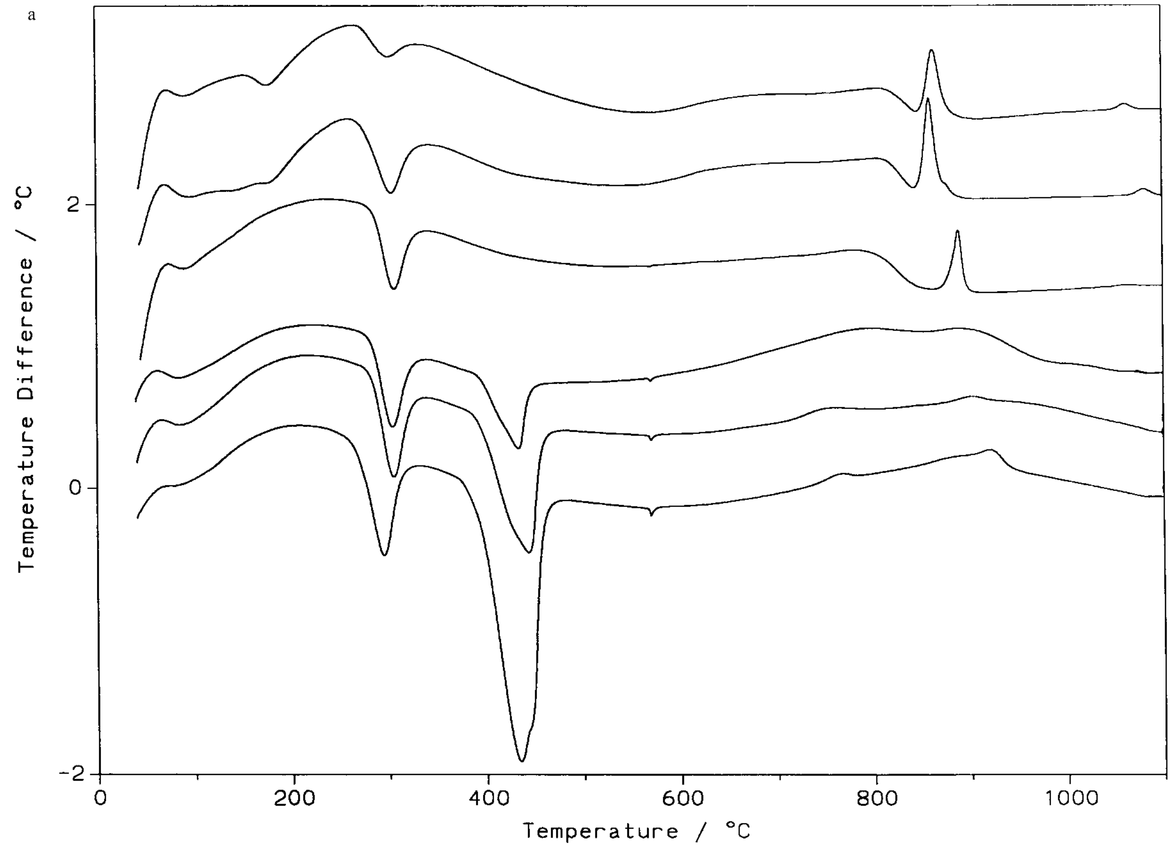

Fig. 1. DT curves after 0, 1, 2, 4, 9 and 23 h (bottom to top) of hydrothermal treatment at 180°C for samples prepared with bulk ratios of (a) 1.0, (b) 0.8, and (c) 0.6.

Data from the mass loss determinations for hydrogarnet and portlandite are shown in Fig. 2(a) and (b), respectively. Regarding hydrogarnet, the first noticeable decrease in the percent mass loss between consecutive reaction time was considered the indicator for the apparent onset of the breakdown of hydrogarnet (arrows in Fig. 2(a)). Although the mass losses attributed to hydrogarnet and portlandite are subject to overlap due to the concurrent dehydration reactions of calcium silicate hydrate (C–S–H) in these temperature ranges [7] and the mass loss due to portlandite may also be subject to overlap due to hydrogarnet [8], the following trends are clearly evident.

Hydrogarnet formation was comparable at all bulk ratios for up to 1 h (Fig. 2(a)) of hydrothermal treatment. The breakdown of hydrogarnet accelerated with decreasing bulk ratio, i.e. after 9, 4 and 2 h for bulk ratios of 1.0, 0.8, and 0.6, respectively. According to DTA and XRD [1], hydrogarnet was no longer present after 23 h of hydrothermal treatment for the 0.8 bulk ratio. In contrast, for the 0.6 bulk ratio, the hydrogarnet amount remained essentially constant after 9 h of hydrothermal treatment and beyond. Overall, it is apparent that hydrogarnet stability decreases with increasing silica content in the initial mix, which is expected to release a greater amount of silica to solution with reaction time. This view is supported by Fig. 3, which shows the amount of silica reacted, expressed as 'SiO_2 reacted (mol)', with reaction time.

It is interesting to note that the continuous decrease in the hydrogarnet amount (Fig. 2(a)) beyond 4 and 9 h for bulk ratios of 0.8 and 1.0, respectively, coincided with the continuous increase in the amount of silica reacted (Fig. 3). In contrast, for the 0.6 bulk

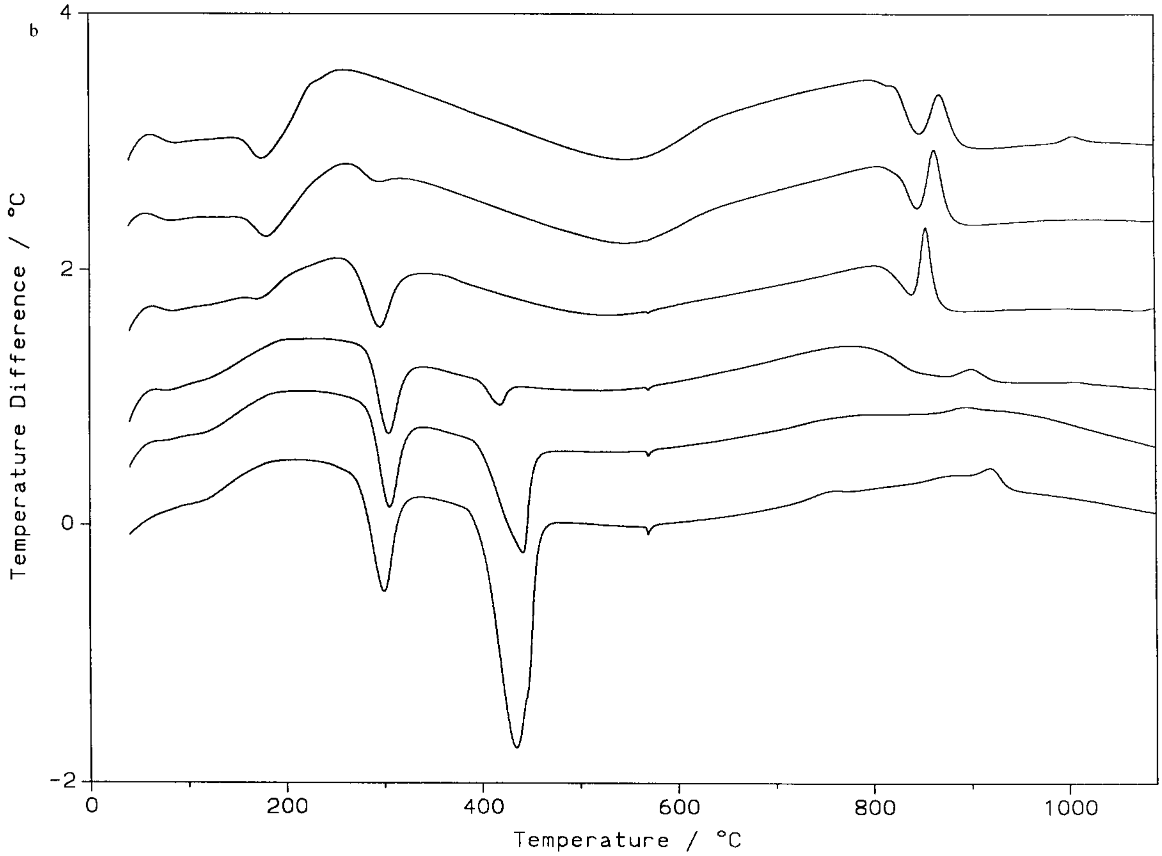

Fig. 1. (*Continued*)

ratio, the amount of silica reacted increased only slightly beyond 9 h of hydrothermal treatment explaining why the hydrogarnet amount remained essentially constant beyond 9 h (Fig. 2(a)).

Furthermore, it is apparent that the stability of hydrogarnet is extended in the presence of portlandite and lime-rich C–S–H. This view is supported by the data in Fig. 2(b) indicating complete portlandite consumption after only 4 h for the 1.0 and 0.8 bulk ratios in contrast to after 2 h for the 0.6 bulk ratio, i.e. no endotherm between ~350° and 500°C (Fig. 1(a)–(c)). In comparison to the 0.8 bulk ratio, the stability of hydrogarnet was extended for the 1.0 bulk ratio because lime-rich C–S–H prevailed for longer. This is evident from the corresponding DT curves revealing a main exotherm at ca. 889°C, that is characteristic of C–S–H having Ca/Si > 1.0 [9,10], after 4 h for the 1.0 bulk ratio (Fig. 1(a)). In contrast, for the 0.8 bulk ratio, the exotherm at 854°C indicates that Al-substituted 11 Å tobermorite having Ca/Si < ~1.0 [11], had already formed after 4 h (Fig. 1(b)). An interpretation supported by XRD evidence. A more detailed account of the exotherm temperatures in relation to C–S–H and 11 Å tobermorite has been given elsewhere [12].

3.2. Al-substituted 11 Å tobermorite formation

The formation of Al-substituted 11 Å tobermorite accelerated with decreasing bulk ratio and occurred after 9, 4 and 2 h of hydrothermal treatment for bulk ratios of 1.0, 0.8 and 0.6, respectively. The presence of this phase is manifested by the endotherms at ~180°, 174° and 177°C, due to the loss of molecular water, and the corresponding exotherms at 859°, 854° and 859°C, due to the crystallization of beta-wollastonite (β-CS), for bulk ratios of 1.0, 0.8 and 0.6, respectively.

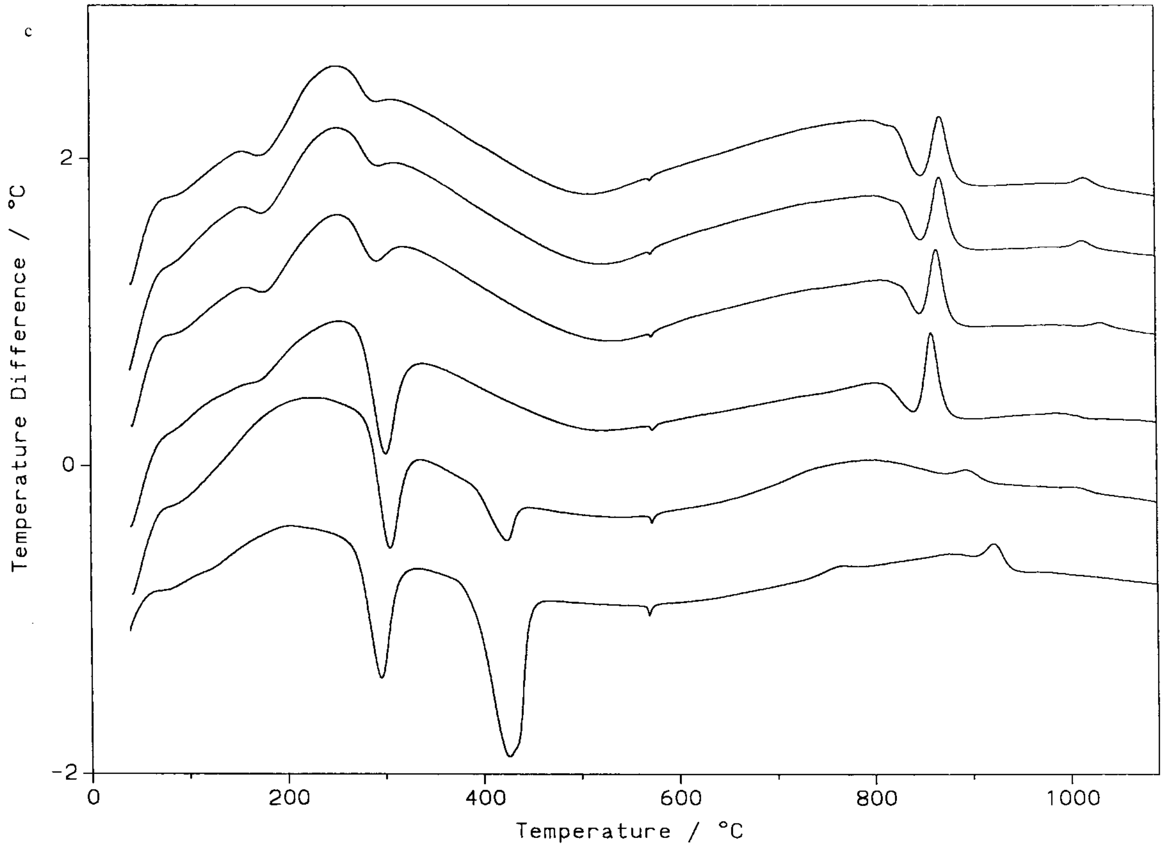

Fig. 1. (*Continued*)

For reference, the β-CS formation temperature of Al-free 11 Å tobermorite, treated hydrothermally at 180°C for 23 h and prepared with a bulk Ca/Si = 0.8 in an identical manner as described in Section 2, was 840°C [13].

Proof that hydrogarnet supplied the Al for the formation of Al-substituted 11 Å tobermorite comes from the appearance of the latter (Fig. 1(a)–(c)) coinciding with the onset of the breakdown of hydrogarnet (arrows in Fig. 2(a)). The authors have presented additional experimental proof for this phenomenon from solid-state ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR) data, which revealed a transformation of octahedrally coordinated Al (hydrogarnet) to a combination of tetrahedrally (Al-substituted 11 Å tobermorite) and octahedrally coordinated Al (hydrogarnet) with reaction time [2,13]. Evidence for the continued supply of Al from hydrogarnet for the formation of Al-substituted 11 Å tobermorite comes from the observed reduction in the percent mass loss, ascribed to hydrogarnet (Fig. 2(a)), correlating with the changes in the exotherm profile, due to the crystallization of β-CS, with reaction time. For instance, the increase in the β-CS formation temperature (Fig. 4) correlates with the decrease in the percent mass loss (Fig. 2(a)) with reaction time for all bulk ratios. Furthermore, the exotherm decreased in height and was broadened for all bulk ratios, very much so for the 0.8 bulk ratio (Fig. 1(a)–(c)). In addition, the endotherm preceding the exotherm became slightly larger in area and was broadened. These observations may be compared with the findings by Kalousek [14]. The author found that with increasing Al content in 11 Å tobermorite, the β-CS formation temperature increased and the exotherm became flatter and broader. The observed changes

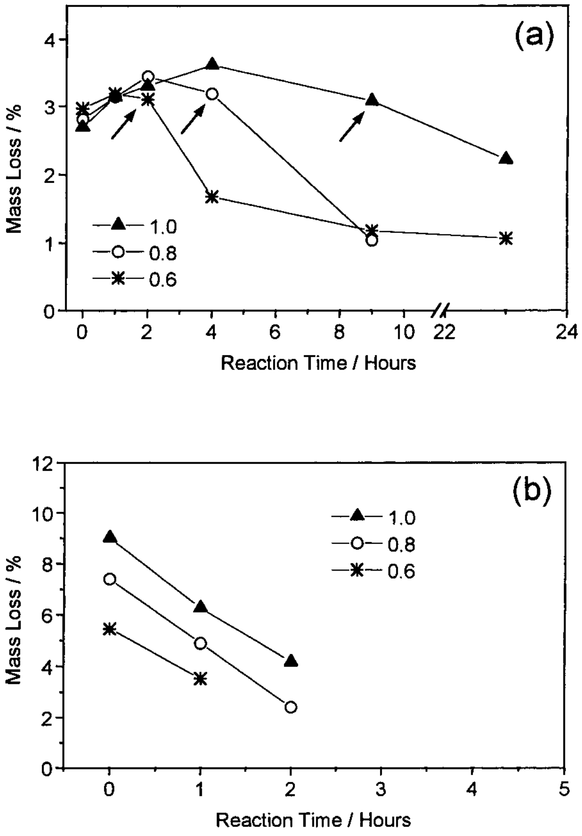

Fig. 2. Amount of mass loss ascribed to (a) hydrogarnet and, (b) portlandite versus rection time. The arrows in (a) signify the apparent onset of the breakdown of hydrogarnet as defined in the text.

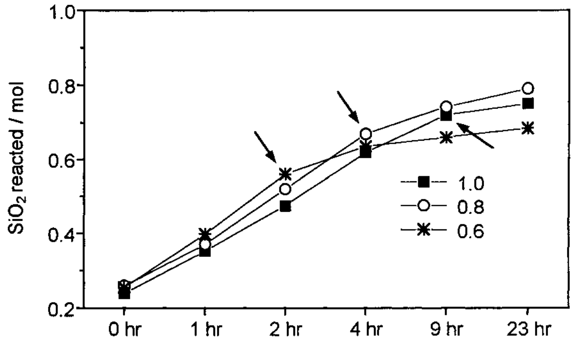

Fig. 3. Amount of silica reacted with reaction time for samples prepared with bulk ratios of 1.0, 0.8, and 0.6.

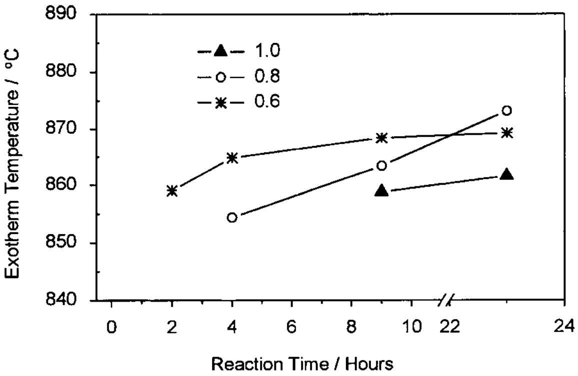

Fig. 4. Beta-wollastonite (β-CS) formation temperatures versus reaction time for samples prepared with bulk ratios of 1.0, 0.8, and 0.6.

in the exotherm profile could be due to stacking disorder caused by the Al for Si replacement as suggested by Hara et al. [15].

Overall, the changes in the exotherm profile also indicate that with increasing Al incorporation into the 11 Å tobermorite crystal lattice, the β-CS formation was obstructed. According to Taylor [16] the conversion of 9 Å tobermorite, formed upon dehydrating 11 Å tobermorite to ~300°C, into β-CS can be explained by the hypothesis of silicon migration, with the Ca-O framework remaining almost unchanged and the silicate anions being partly destroyed and rebuilt. It has also been noted that for 11 Å tobermorites having a highly ordered silicate anion structure, β-CS forms with comparative ease, since topotactic dehydration and crystallization reactions proceed at low energies [17]. Furthermore, it has been shown that the type of silicate anion structure influences the dehydration, dissociation, and the larnite (β-C_2S) formation process [18]. In addition, Sasaki et al. [17] reported that Al-substituted 11 Å tobermorites contain a larger number of monomeric silicate anions. Therefore, it is apparent that for the case of Al-substituted 11 Å tobermorites the β-CS formation process is obstructed because more structural rearrangement of the silicate anions is required. Accordingly, the β-CS formation process requires more energy as manifested by the increase in the area of the endotherm preceding the exotherm, i.e. increase in the heat absorption, and the increase in the β-CS formation temperature. From Fig. 4, it is also evident that the extent of Al incorporation into the 11 Å tobermorite crystal lattice was greatest for the 0.8 bulk ratio followed by the 0.6 and 1.0 bulk ratios

Table 2
High temperature exotherms versus reaction time observed for hydrothermally cured CaO–MK–quartz mixtures

Reaction time (h)	Bulk ratio = 1.0 exotherm (°C)	Bulk ratio = 0.8 exotherm (°C)	Bulk ratio = 0.6 exotherm (°C)
4	—	—	1033
9	1081	—	1015
23	1062	1008	1017

after 23 h of hydrothermal treatment. Again, this interpretation correlates with the percent mass loss data for hydrogarnet (Fig. 2(a)). For instance, for the 0.8 bulk ratio the data show that hydrogarnet was consumed after 23 h. In contrast, hydrogarnet coexisted with Al-substituted 11 Å tobermorite after 23 h for bulk ratios of 0.6 and 1.0, the amount of hydrogarnet remaining being greater for the 1.0 bulk ratio.

The temperatures for the second exotherm observed above 950°C, for samples containing Al-substituted 11 Å tobermorite (Fig. 1(a)–(c)), have been summarized in Table 2. For samples made with the 0.8 and 0.6 bulk ratios and heated to 1100°C, this exotherm can be attributed to the formation of anorthite as revealed by several X-ray reflections in the $2\theta = 27.5$–28.0° region. Anorthite was not detected in samples heated to 950°C. Samples made with the 1.0 bulk ratio and heated to 1100°C yielded poor quality XRD patterns, due to the limited amount of sample available, rendering identification of phases other than β-CS difficult. Nevertheless, the data reveal a near linear relationship between the temperatures for the second exotherm above 950°C and those due to the β-CS formation. This relationship, with a correlation coefficient of 0.91 together with 95% confidence bands (dashed lines), is shown in Fig. 5.

For comparison, Sakiyama et al. [19] reported a second exotherm at ~980–1000°C, attributed to anorthite, for Al-substituted 11 Å tobermorite samples made with bulk $Ca/(Al + Si) = 0.8$ and bulk $Al/(Al + Si) > 0.1$. The authors also noted that this exotherm increased in intensity with increasing Al content in 11 Å tobermorite. Based on the data provided by the present study and the observations by Sakiyama et al. [19], it appears that the second exotherm is an indicator for the extent of Al-substitution into the 11 Å tobermorite crystal lattice and is equivalent to bulk $Al/(Al + Si)$ ratios of at least 0.10.

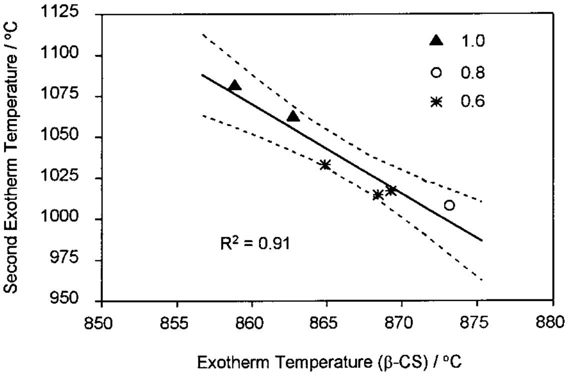

Fig. 5. Beta-wollastonite (β-CS) formation temperatures versus temperatures for the second exotherm observed above 950°C for samples prepared with bulk ratios of 1.0, 0.8, and 0.6. The dashed lines are 95% confidence bands.

4. Conclusions

From a combination of DTA-TGA, XRD and AIR evidences the authors conclude the following:

1. For up to 1 h of hydrothermal treatment at 180°C, hydrogarnet formation was comparable, irrespective of the bulk ratio.
2. The stability of the formed hydrogarnet decreased with increasing silica content in the bulk composition and was extended in the presence of portlandite and lime-rich C–S–H.
3. The appearance of Al-substituted 11 Å tobermorite coincided with the onset of the breakdown of hydrogarnet. The formation of Al-substituted 11 Å tobermorite accelerated with decreasing bulk ratio.
4. The thermal data firmly established that hydrogarnet supplied the Al to form Al-substituted 11 Å tobermorite during the hydrothermal treatment. The changes in the exotherm profiles, due to the crystallization of β-CS, with reaction time provided evidence for increasing incorporation of Al into the 11 Å tobermorite crystal lattice. The amount of Al incorporated into 11 Å tobermorite was greatest for the 0.8 bulk ratio followed by the 0.6 and 1.0 bulk ratios after 23 h of hydrothermal treatment. The reduced amount of Al incorporation observed for the 0.6 and 1.0 bulk ratios, was due to some Al remaining tied up in the hydrogarnet phase

which coexisted with Al-substituted 11 Å tobermorite.

Acknowledgements

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