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Reaction mechanism of the hydrothermally treated $CaO–SiO_2–Al_2O_3$ and $CaO–SiO_2–Al_2O_3–CaSO_4$ systems

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Mixtures of CaO, amorphous SiO_2 and kaolinite in the presence or absence of SO_4^{2-} ions (added as $CaSO_4{\cdot}2H_2O$) were treated in suspension under hydrothermal conditions at temperatures of 80–200 °C. Kaolinite was added to replace 3 and 10% of the total weight of the dry mix with the overall CaO/SiO_2 mole ratio being 0.83. The hydration products were investigated by XRD, IR spectroscopy and DTA techniques in order to elucidate their phase compositions. The results indicate that the presence of SO_4^{2-} ions leads to a marked increase in the reaction rate at all temperatures investigated. In the C–S–A* system, the detected hydration products are calcium silicate hydrate which is then transformed into 1.13 nm aluminium-substituted tobermorite and α-C_2SH by increasing the autoclaving temperature. In the C–S–A–$C\bar{s}$ system the hydrated products are calcium silicate hydrate, ettringite and monosulpho-aluminate. On increasing the hydrothermal temperature they decompose, recrystallize and 1.13 nm aluminium-substituted tobermorite, α-C_2SH and anhydrite II are formed. In both systems the excess Al_2O_3 appeared as a hydrogarnet phase, C_3ASH_4.

1. Introduction

The effect of Al^{3+} ions on the hydrothermal reaction of $CaO–SiO_2$ mixtures and the properties of the hydration products has been thoroughly studied [1–5]. The results generally indicate that the presence of Al^{3+} ions in the reaction mixture retards the lime–silica reaction sharply. However, it stabilizes the main desired binder, 1.1 nm tobermorite ($C_5S_6H_5$). Kalousek [1] has shown that the 1.1 nm tobermorite can accept up to 5% Al_2O_3 in its lattice, whereas Diamond *et al.* [2], Petrovic [3] and El-Hemaly [4] have found that this quantity is substantially higher, since the Al^{3+} ions can replace up to 15% of the Si^{4+} ions in the crystal structure of the tobermorite component. The incorporation or substitution of Si^{4+} by Al^{3+} ions in tobermorite is accompanied by considerable changes in the physico-mechanical properties and the morphology of the formed tobermorite [5].

The possibility of substitution of the SO_4^{2-} ions within the structure of tobermorite is still subject to controversy. At room temperature, 7.4% SO_3 could be substituted into high lime tobermorite gel [6]. Another study [7] on autoclaved paste of CH, tripoli and C$\bar{s}$H cured at 175 and 205 °C for 8 to 72 h indicated that 1.2 to 1.9% SO_3 entered the lattice of tobermorite.

Recently, an investigation [8] on autoclaved sand–lime brick has indicated that the presence of Al^{3+} ions has a negative effect on both the reaction rate and the mechanical properties of the products. The same effect is detected by the addition of SO_4^{2-} ions to the reaction mixture. The reverse effect on both the $CaO–SiO_2–H_2O$ reaction rate and the strength of sand–lime samples was detected by the addition of Al^{3+} and SO_4^{2-} ions together with the reaction mixture. For example, a complete consumption of lime in the $CaO–SiO_2–H_2O$ and Al_2O_3 (1–10% added as kaolinite) reaction is achieved at about 250×10^{-5} Pa h; this value is reduced to 64×10^{-5} Pa h with the addition of 1% $CaSO_4$ to the reaction mixture.

The main aim of the present work is to investigate more closely the influence of SO_4^{2-} ions on the hydrothermal reaction of $CaO–SiO_2–H_2O$ and Al_2O_3 system.

2. Experimental details

2.1. Materials

The CaO used was prepared by calcination of a BDH grade $CaCO_3$ at 1050 °C for soaking time of 3 h. Amorphous silica was obtained by calcination of green rice husk ash (RHA) at 500 °C for 6 h, using a very slow heating rate (2 °C min^{-1}) to avoid formation of silicon carbide (SiC) and in the presence of an oxidizing atmosphere. The green RHA was boiled for 1 h in 0.01 M HCl solution, then filtered off and washed several times using hot water until it was free from chloride ions. The calcined product is very white in colour. The SiO_2 content as estimated by the acid evaporation method [9] is 99%. The surface area of

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*Cement notations used are: C = CaO, S = SiO_2, A = Al_2O_3, H = H_2O, CH = $Ca(OH)_2$ and C$\bar{s}$ = $CaSO_4$.

TABLE I Chemical analysis of the kaolinite used

Al_2O_3	Fe_2O_3	TiO_2	CaO/MgO	SiO_2	L.O.I.	Total
36.60	0.60	0.35	0.05	49.25	12.95	100.00

the silica sample (S_{BET}) was 200 $m^2 g^{-1}$. The X-ray diffraction and infrared (IR) spectra reveal that the silica sample is amorphous in nature and free from carbon or silicon carbide. The chemical analysis of the kaolinite used as the source for Al^{3+} ions (supplied by AKW, Germany) is shown in Table I. $CaSO_4 \cdot 2H_2O$, BDH grade, of purity 99.00% was used as the source of SO_4^{2-} ions.

2.2. Preparation of samples and method of investigating the products

Five different mixes of CaO, SiO_2, kaolinite and calcium sulphate were prepared as shown in Table II. A fixed amount of water was used to prepare the suspended mixture before autoclaving (1:1 by weight) the well homogenized suspensions were hydrothermally treated in a high pressure autoclave at 80, 100, 120, 160 and 200 °C, respectively, for 24 h. After autoclaving, the samples were dried at 50 °C for 24 h and ground, to a powder that passed through a 0.063 mm sieve, for investigations. X-ray diffraction (XRD) performed with CuK_α radiation at a scanning speed of 1° min^{-1}, between $2\theta = 4$ up to 55°, IR spectra in the range 4000–200 cm^{-1} (Perkin Elmer 1430 Ratio Recording Infrared Spectrophotometer), and thermal analysis (Shimadzo Kyoto-Japan DTA) in the range of 25–1000 °C at a sensitivity of ± 50 μV, and with a heating rate of 20 °C min^{-1} were performed on some selected samples. Chemical methods were also used for unreacted $Ca(OH)_2$ determinations.

3. Results and discussion

3.1. Kinetics of hydration

The rate of reaction in the different mixes was followed by the determination of unreacted $Ca(OH)_2$. Fig. 1 shows the free lime (%) as a function of the autoclaving temperature. Examination of this figure indicates that the measured free lime in the $CaO–SiO_2–H_2O$ system (mix I) decreases sharply with increasing curing temperatures, indicating the high rapid consumption of lime due to the presence of amorphous silica. The addition of 3 and 10% kaolinite (mixes II_a and III_a) activates hydration at the lower temperatures of 80 and 100 °C. At higher temperatures above 100 °C, the presence of Al^{3+} ions retards the lime–silica hydrothermal reaction. The addition of SO_4^{2-} ions to the reaction mixture (mixes II_b and III_b) leads to an increase in the hydrothermal activity of the mixes at all temperatures investigated. This is clearly seen in the lower amounts of the measured unreacted $Ca(OH)_2$. The nature of formed hydration products, which depend on the mix composition as well as on the autoclaving temperature, will be discussed in the following sections.

TABLE II Five different mixes of CaO, SiO_2, kaolinite and calcium sulphate

Mix number	CaO (mole)	SiO_2 (mole)	Kaolinite (%)	$CaSO_4 \cdot 2H_2O$ (%)
I	83	100	–	–
II_a	83	100	3	–
II_b	83	100	3	3
III_a	83	100	10	–
III_b	83	100	10	10

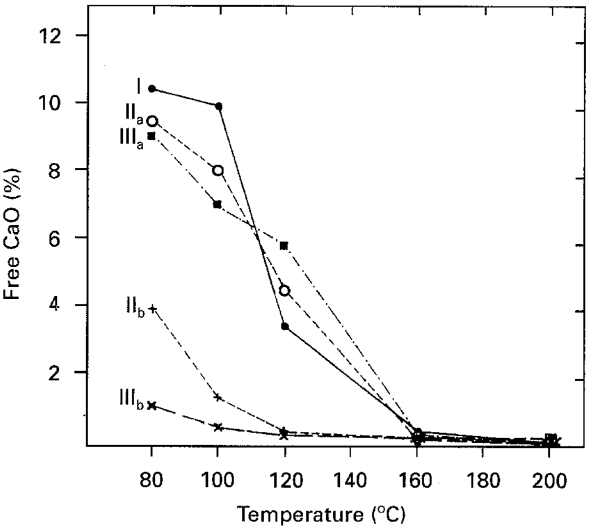

Figure 1 Unreacted lime as a function of the autoclaving temperature of the different mix compositions.

3.2. X-ray diffraction

X-ray diffraction analysis was performed on the products prepared at different autoclaving temperatures between 80 to 200 °C for 24 h. Only the mixes III_a ($CaO–SiO_2–Al_2O_3$) and III_b ($CaO–SiO_2–Al_2O_3$ and $CaSO_4$) are given in Figs 2 and 3, respectively. At lower temperatures, i.e. 80 to 120 °C, the formed hydration products in mix III_a (without sulphate) are C–S–H(I), C–S–H(II) in addition to the unreacted $Ca(OH)_2$ and kaolinite. The hydrogarnet phase $[Ca_3Al_2(SiO_4)(OH)_8]$, appeared at 120 °C. By raising the autoclaving temperatures to 160 and 200 °C the formed lime-rich phases C–S–H (I) C–S–H (II) are crystallized into 1.1 nm tobermorite and α-C_2SH, in addition to the hydrogarnet phase. These results are in good agreement with that obtained in [8].

The addition of $CaSO_4 \cdot 2H_2O$ to the reaction mixture, Fig. 3, affects the course of the hydrothermal reaction of the $CaO–SiO_2–Al_2O_3$ system considerably. At lower curing temperatures, 80 and 100 °C, most of the lime is consumed in the reaction and no reflections of free $Ca(OH)_2$ in the XRD appeared. This confirms the previous results in Fig. 1. The reaction seems to be activated with the addition of sulphate, and in fact, sulphate in this case cannot be considered as a simple activation catalyst but also as a main reactant, especially in the presence of kaolinite. At first, the formed hydration products are lime-rich calcium silicate hydrate phases and monosulpho-aluminate ($C_3A \cdot C\bar{s} \cdot H_{12}$). On autoclaving at 120 °C, the

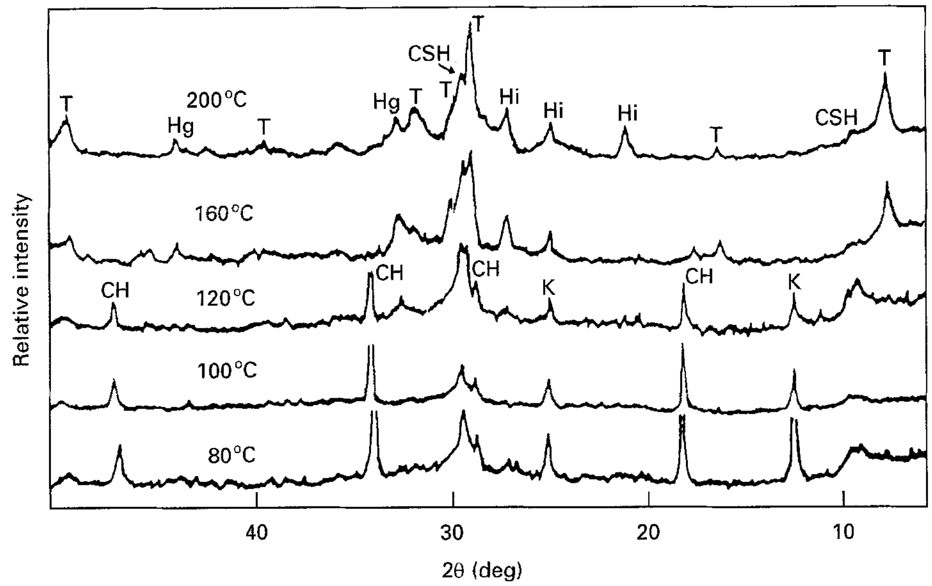

Figure 2 X-ray diffraction patterns of the autoclaved $CaO-SiO_2-Al_2O_3$ system (mix III_a). CH = calcium hydroxide, $Ca(OH)_2$; T = tobermorite, $C_5S_6H_5$; Hi = hillebrandite, C_2SH; CSH = calcium silicate hydrate; Hg = hydrogarnet, C_3ASH_4; K = kaolinite.

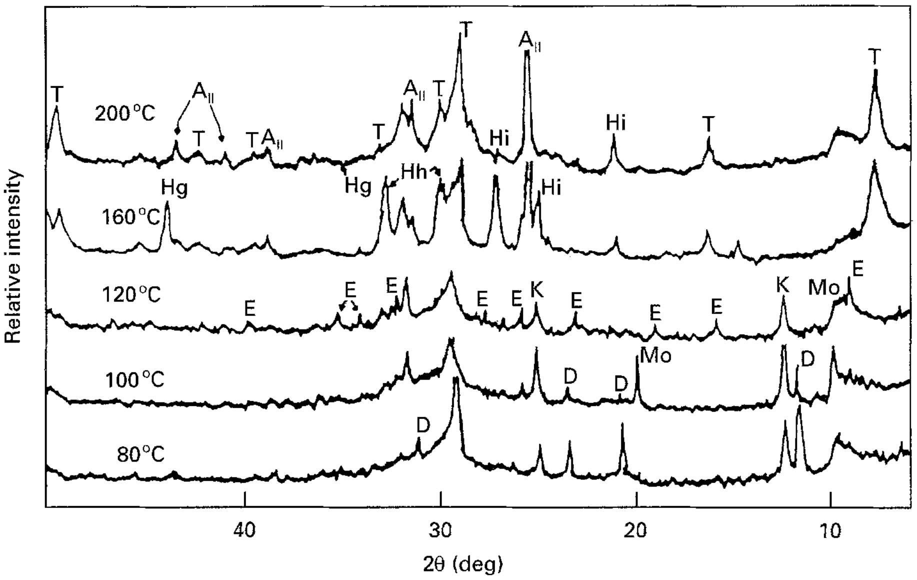

Figure 3 X-ray diffraction patterns of the autoclaved $CaO-SiO_2-Al_2O_3$ system in the presence of $CaSO_4 \cdot 2H_2O$ (mix III_b). T = tobermorite, $C_5S_6H_5$; Hi = hillebrandite, C_2SH; CSH = calcium silicate hydrate; Hg = hydrogarnet, C_3ASH_4; AII = anhydrite, $CaSO_4$; Hh = hemihydrate, $CaSO_4 \cdot 5H_2O$; D = dihydrate, $CaSO_4 \cdot 2H_2O$; E = ettringite, $C_3A \cdot 3C\bar{S} \cdot H_{32}$; Mo = monosulphate, $C_3A \cdot C\bar{S} \cdot H_{12}$; K = kaolinite.

latter reacts with excess sulphate to form the high sulphate phase, ettringite ($C_3A \cdot 3C\bar{S} \cdot H_{32}$), as seen in the following equation:

$$C_3A \cdot C\bar{S} \cdot H_{12} + 2CaSO_4 + 20H_2O \rightarrow C_3A \cdot 3C\bar{S} \cdot H_{32}$$

By raising the autoclaving temperatures to 160 and 200 °C, the formed ettringite reacts with the lime-rich CSH-phase to produce 1.1 nm tobermorite, in addition to hillebrandite, hydrogarnet and anhydrite II.

3.3. IR spectroscopic analysis

The IR spectra of the hydration products of the mixes III_a and III_b autoclaved for 24 h at different temperatures (80–200 °C) are given in Figs 4 and 5, respectively. The unreacted kaolinite is characterized by the absorption bands found at 3707–3703 and 3648–3647 cm^{-1} due to the valence vibration of OH groups, the double bands at 1030–1029, and 1007–1005 cm^{-1} due to the vibration of Si–O bonds, 935–930 cm^{-1} due to the deformation bonds of the Al–OH groups and the bands at 750 cm^{-1} are due to Al–O vibration [10–12]. The bands at 536–534 cm^{-1} are due to the bending vibration of Si–O–Si in silicates [12, 13]. The relative intensities of these bands decline with increasing autoclaving temperatures and in the presence of SO_4^{2-} ions in the reaction mixture. At higher temperatures (160 and 200 °C) these bands completely disappear.

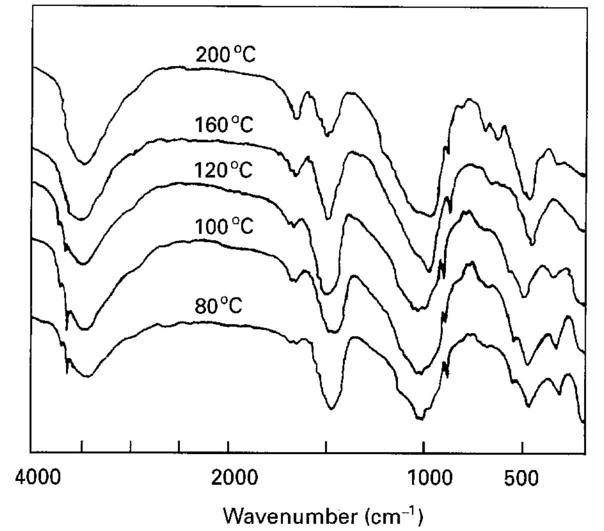

Figure 4 IR spectra of the autoclaved CaO–SiO_2–Al_2O_3 system (mix III_a).

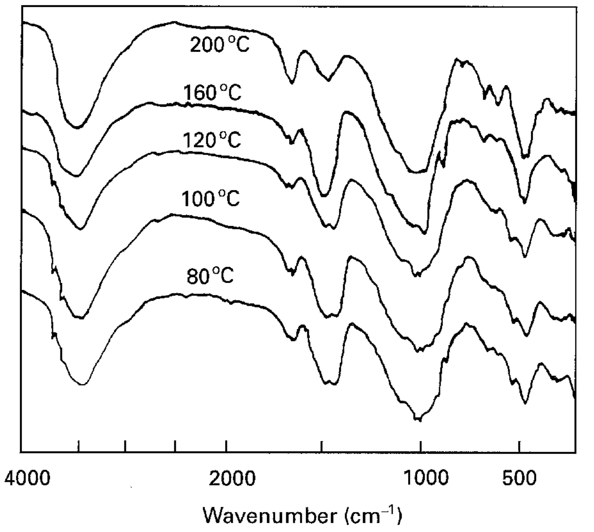

Figure 5 IR spectra of the autoclaved CaO–SiO_2–Al_2O_3 system (mix III_b).

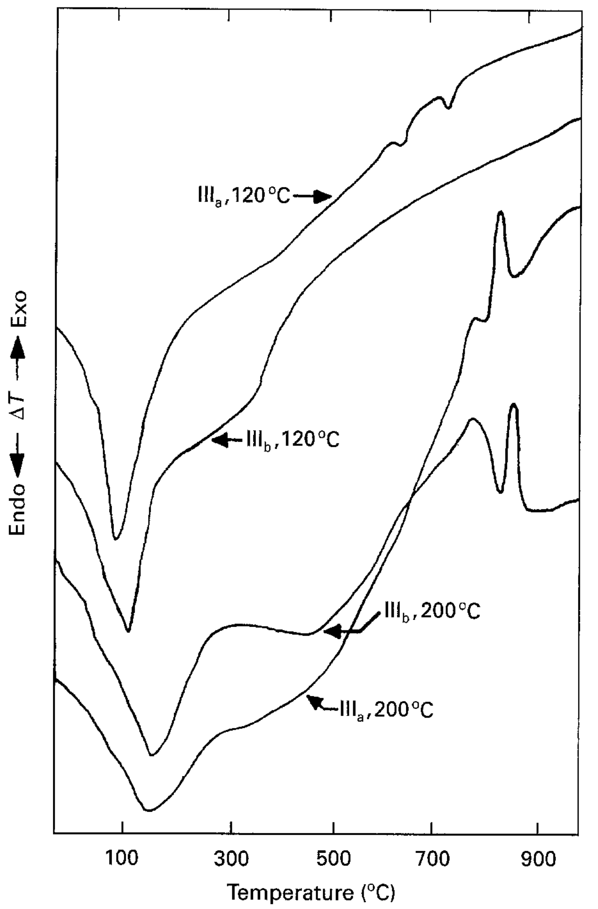

Figure 6 DTA curves of the III_a and III_b mixes autoclaved at 120 and 200 °C.

The free OH^- groups of the unreacted $Ca(OH)_2$ are detected in the sulphate-free specimens (Fig. 4) at the lower temperatures 80–120 °C, which confirms the previous results of Fig. 2. These bands appeared as sharp bands at 3648–3647 cm^{-1} and their relative intensities decrease with increasing autoclaving temperatures.

The bands detected at 1660–1630 cm^{-1} in all specimens are due to free water deformation [14] or water combined in the CSH phase [10, 15], while the broad bands located at 3520–3400 cm^{-1}, on the other hand, may be due to the OH^- valence vibrations of free and bonded water in the hydrated phases, mainly CSH phases. In a similar way, absorption broad bands at 1492–1466 and 1100–900 cm^{-1} were found in most of the hydrated silicates [10, 11, 15]. In SO_4^{2-}-containing specimens, the bands at 1107–1103, 650–644 and 603–619 cm^{-1} are due to the presence of $CaSO_4$, where the anhydrite is characterized by the strong band at 985–975 cm^{-1} [10, 14]. Moreover, these bands are also common with the strong absorption bands of 1.13 nm tobermorite [10, 15].

3.4. Differential thermal analysis (DTA)

The results of thermal analysis investigation of the prepared specimens under autoclaving temperatures of 120 and 200 °C in the absence and in the presence of SO_4^{2-} ions, which are given in Fig. 6, indicate the following:

1. At 120 °C steam curing temperature, the SO_4^{2-}-free sample reveals a very strong endotherm around 110 °C. This endotherm is shifted to 125 °C in SO_4^{2-}-containing specimens, accompanied by a wide shoulder at 230–320 °C. These thermal effects, may be due to the removal of free water and dehydration of the CSH phases, mainly CSH (II,I) [11, 16], in addition to the removal of bonded H_2O in $C_3A\cdot 3C\bar{s}\cdot 32H_2O$ (ettringite) in the SO_4^{2-}-containing specimens [17]. On the other hand, the SO_4^{2-}-free specimen reveals very weak shoulders located at 530 and 765 °C, respectively; the first may be due to dehydration of unreacted $Ca(OH)_2$ or dehydroxylation of the unreacted kaolinite mineral in the specimens [11], while the second one, may be due to the presence of a lime-rich phase (C_2SH) [11, 18] and/or decomposition of $CaCO_3$, which could be formed as a result of contamination with atmospheric CO_2.
2. At 200 °C steam curing, the SO_4^{2-} free specimen, shows, a strong and broad endotherm around 180 °C,

and a very weak shoulder at 855 °C accompanied by a sharp exotherm at 865 °C. While the SO_4^{2-}-containing specimen reveals almost a similar thermal behaviour, there is a small difference. The peak at 180 °C became a little stronger and was accompanied by a wide shoulder appearing at 380–470 °C. The thermal effect at 855 °C, became sharper, while the exotherm at 865 °C shifted to 875 °C. The endotherm detected at 180 °C and the exotherm at 865–875 °C may be due to the presence of 1.13 nm tobermorite and its crystallization into $CaO \cdot SiO_2$ (wollastonite) [11], respectively, while the wide shoulder at 380–470 °C and the endotherm at 855 °C may be due to the presence of C_2SH phase, mainly the α-form.

From the thermal analysis investigation, the presence of SO_4^{2-} ions may enhance the formation of the lime-rich phase (α-C_2SH) [11] especially at higher temperatures. This may be due to the increase of the ionic strength of Ca^{2+} ions during the reaction, resulting from the increasing solubility of $CaSO_4$ rather than Ca(OH) [19]. Taylor [20] reported that the normal type of tobermorite converts into 0.9 nm tobermorite around 300 °C. While El-Korashy [11] and Mistsude [21] suggested that the anomalous tobermorites exhibited no dehydration endotherm between 250 and 300 °C, the present study confirms this suggestion. Some authors [8, 22] reported the formation of hydroxyellistadite as a result of a hydrothermal reaction of the CaO–SiO_2–$CaSO_4$ system. The presence of Al^{3+} ions prevent the formation of this phase. This may be due to Al^{3+} ions reacting with most of the SO_4^{2-} ions and the formation of calcium sulphoaluminate and ettringite as metastable phases.

4. Conclusion

The reported experimental results can be epitomized as follows:

1. The presence of Al_2O_3 in the reaction mixture CaO–SiO_2 retards the hydrothermal reaction considerably, especially at lower temperatures, while the addition of $CaSO_4$ to the CaO–SiO_2–Al_2O_3-system acts as a good catalyst for the reaction.

2. The sequence of the formed hydration products in both systems investigated can be represented as follows:

(a) Without sulphate:

$$\begin{array}{lcl}
\mathrm{SiO_2} & & \\
+ & \text{lime-rich CSH} & \text{tobermorite} \\
\mathrm{CaO} \longrightarrow & & \longrightarrow (\mathrm{C_5S_6H_s}) \\
+ & + & + \\
\mathrm{Al_2O_3} & \text{hydrogarnet}^{\dagger} & \text{hydrogarnet} \\
 & (\mathrm{C_3ASH_4}) & (\mathrm{C_3ASH_4}) \\
 & & + \\
 & & \mathrm{C_2SH}
\end{array}$$

(b) With sulphate:

$$\begin{array}{lcc}
\mathrm{SiO_2} & \text{lime-rich CSH} & \text{tobermorite} \\
+ & + & (\mathrm{C_5S_6H_s}) \\
\mathrm{CaO} & & \\
+ \longrightarrow & \text{monosulpho-aluminate} \longrightarrow & + \\
\mathrm{Al_2O_3} & (\mathrm{C_3A \cdot C\bar{s} \cdot H_{12}}) & \\
+ & + & \\
\mathrm{CaSO_4} & \text{ettringite} & \text{hydrogarnet} \\
 & (\mathrm{C_3A \cdot 3C\bar{s} \cdot H_{32}}) & (\mathrm{C_3ASH_4}) \\
 & + & + \\
 & \text{hydrogarnet} & \text{anhydrite} \\
 & (\mathrm{C_3ASH_4}) & (\mathrm{CaSO_4}) \\
 & & + \\
 & & \mathrm{C_2SH} \\
 & \underbrace{\hphantom{\text{monosulpho-aluminate}}}_{\text{intermediate phases}} &
\end{array}$$

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