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Kinetics and mechanism of formation of tricalcium aluminate, $Ca_3Al_2O_6$

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Abstract

The kinetics of formation of tricalcium aluminate, $Ca_2Al_2O_6$ or C_3A, have been studied in the range 1150–1350 °C using quantitative X-ray diffraction (XRD) analysis of pellets made from powder mixtures (3:1 molar ratio) of calcite and α-alumina (α-Al_2O_3)(the alumina was replaced by gibbsite in some experiments). Dodecacalcium heptaaluminate, $C_{12}A_7$, and monocalcium aluminate, CA, were formed as intermediate phases, which persisted until the reaction to form tricalcium aluminate was nearly complete. No calcium dialuminate or calcium hexaaluminate was observed. The kinetic mechanism was identified with the aid of reduced time plots to be based on a diffusion-controlled step, described by the Ginstling–Brounshtein equation. There was a good fit to this equation up to a fraction reacted of at least 0.6. The activation energy for the reaction between calcite and α-Al_2O_3 was determined to be 216 ± 10 kJ mol^{-1}, while that between calcite and gibbsite was 224 ± 10 kJ mol^{-1}. It is proposed that the rate-determining step is the diffusion of Ca^{2+} ions through the layers of reaction products, while the Al^{3+} ions remain relatively immobile. Formation of $C_{12}A_7$ may be the first step. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Kinetics; Quantitative X-ray diffraction; Calcium aluminates; Reaction intermediates; Diffusion

1. Introduction

Portland cement is made by firing a mixture of limestone (or chalk) at about 1450 °C. Partial fusion occurs and a clinker is formed. The part that was solid at the clinkering temperature forms tricalcium silicate and dicalcium silicate, whereas the part that was liquid crystallises as an aluminate and a ferrite phase. The aluminate phase, which constitutes 5–10% of most normal Portland cement clinkers, is tricalcium aluminate, $Ca_3Al_2O_6$ or C_3A (C = CaO, A = Al_2O_3), with various other ions, e.g. K^+ and Fe^{3+}, in solid solution. C_3A is, therefore, produced around the world in huge quantities during the manufacture of Portland cement, yet its kinetics of formation have not often been studied.

Pure C_3A has a cubic unit cell with a very large cell parameter (15.263 Å). When foreign ions are incorporated, the symmetry drops to a lower form, but we are concerned in this paper with the kinetics of formation of pure cubic C_3A. The aim of the work was (a) to follow the course of the reaction in terms of any intermediate phases formed and (b) to determine the kinetic mechanism of the solid-state reaction from a quantitative study of the amounts of C_3A formed after various times on heating samples under isothermal conditions at various temperatures. These results complement those already published for the formation of monocalcium aluminate [1] and dodecacalcium heptaaluminate [2].

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2. Experimental

The requisite amounts for 3:1 molar proportions of AR reagent grade calcite and AR α-alumina (α-Al_2O_3) or gibbsite, $Al(OH)_3$, were accurately weighed and intimately mixed using boiled distilled water. The slurry was filtered using a vacuum pump and dried in an oven at 110 °C. Pellets (1 g each), with a diameter of about 12.5 mm, were made from each mixture by single-ended pressing using a steel die. Press loading of 326 MPa was used throughout the experiments.

The pellets were fired in a sintered alumina boat. They were heated to about 850 °C for 1 h to allow for evolution of carbon dioxide without the formation of any calcium aluminate phase, and then pushed into the hot zone of the furnace. The reactions were studied in the temperature range 1150–1350 °C for up to 24 h. After each run the alumina boat containing the samples was removed quickly from the furnace, a sample taken, and the boat pushed back into the hot zone. The fired samples were quenched in air, stored in plastic bags and kept in a desiccator to be analysed by X-ray diffraction (XRD).

Quantitative analysis of the calcium aluminate phases present in each reaction mixture after firing was carried out as follows. The quenched fired samples were ground to pass a 38 μm sieve. Randomly orientated samples were prepared by the back-loading technique to avoid preferred orientation. The amounts of all the reaction products formed during the reactions were determined by quantitative XRD, using rutile (TiO_2) as the initial standard. Each ground sample of fired reactants (1 g) was mixed with a fixed weight (0.2 g) of rutile, followed by grinding in an agate mortar under acetone. The mixture was dried and then examined on a Philips PW1710 diffractometer using monochromatic Cu Kα radiation operating at a voltage of 50 kV and current of 30 mA. A scanning speed of 0.25° 2θ min^{-1} and a step size of 0.02° were used to examine the samples in the range 10–70° 2θ.

A set of calibration curves was determined from pure, laboratory synthesised calcium aluminates, fired three times with intermediate grinding. The C_3A and $C_{12}A_7$ pellets were fired at 1350 °C for 6 h, the CA and CA_2 pellets at 1450 °C for 6 h, and the CA_6 pellets at 1600 °C for 6 h. The peaks used for the QXRD analysis are shown in Table 1.

Table 1
Reference peaks used for quantitative determination of the calcium aluminate phases

Phase	Miller index (hkl)	d (Å)	2θ	Relative intensity	Disturbing phase
α-Al_2O_3	113	2.085	43.36	100	–
	024	1.740	52.55	45	–
Rutile	110	3.247	27.44	100	–
C_3A	440	2.699	33.16	100	$C_{12}A_7$
C_3A	800	1.909	47.60	45	–
$C_{12}A_7$	211	4.890	18.13	95	–
CA	220	2.966	30.10	100	$C_{12}A_7$
CA	112	4.670	19.00	25	–
CA_2	020	4.440	19.98	55	–
CA_6	0110	2.007	45.14	60	–
CA_6	1112	1.533	60.32	65	–

3. Results

3.1. Intermediate phases formed in the reaction between α-Al_2O_3 and calcite

The kinetics of formation of C_3A was studied in the temperature range from 1150 to 1350 °C. At all five temperatures studied, three calcium aluminates, namely C_3A, $C_{12}A_7$ and CA, were formed initially and persisted until the reaction to form C_3A was nearly complete [Fig. 1]. The phases CA_2 and CA_6 were not detected in any of the reaction products. The amounts of the three calcium aluminates formed decreased in the sequence $C_3A > C_{12}A_7 >$ CA. At the lower temperatures studied (1150 and 1200 °C), substantial amounts of $C_{12}A_7$ and CA persisted throughout the length of the experiments, but at the higher temperatures (1250, 1300 and 1350 °C), they reached a maximum and subsequently decreased. CA was no longer observed after 5 h at 1300 and 1350 °C, and only small amounts of $C_{12}A_7$ remained [Fig. 1(d) and (e)].

It is concluded that $C_{12}A_7$ and CA are formed as intermediate phases during the synthesis of C_3A. There has been much confusion in the published literature about the reaction intermediates formed during the synthesis of the various calcium aluminate phases and this is discussed in Section 4.1.

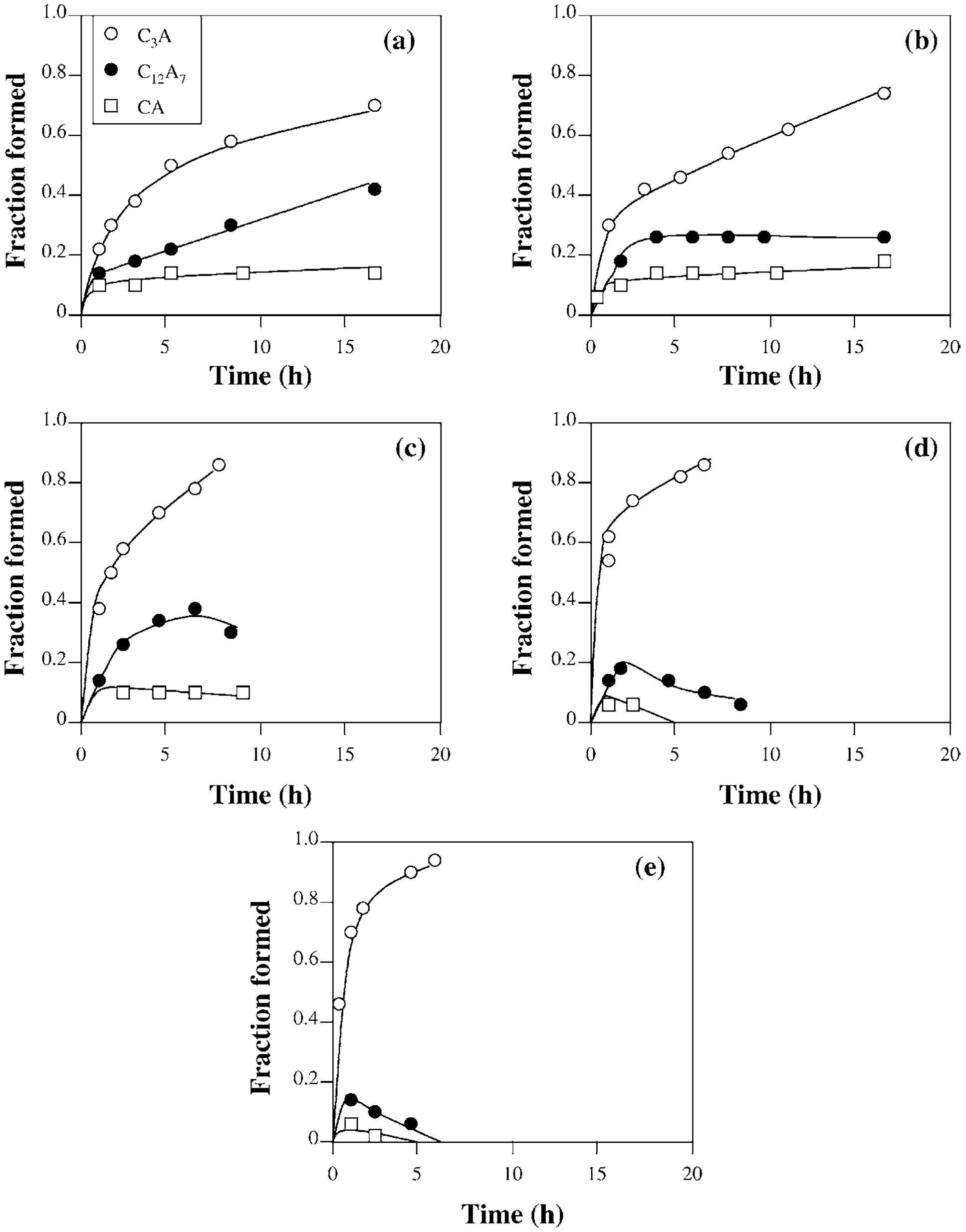

Fig. 1. Formation of the various calcium aluminate phases during reaction of 3:1 CaO with α-Al_2O_3 at (a) 1150 °C; (b) 1200 °C; (c) 1250 °C; (d) 1300 °C; (e) 1350 °C (○: C_3A; ●: $C_{12}A_7$; □: CA).

3.2. Kinetics of the reaction between calcite and α-Al_2O_3 or gibbsite

The amount of C_3A formed at various temperatures is plotted as fraction reacted, α, against time in Fig. 2. This amount always increased with increase in temperature and the reaction approached completion at the highest temperatures studied within 10 h. At 1200 °C, the time taken to reach half reaction ($t_{0.5}$) was about 5 h, but at 1350 °C it was only about

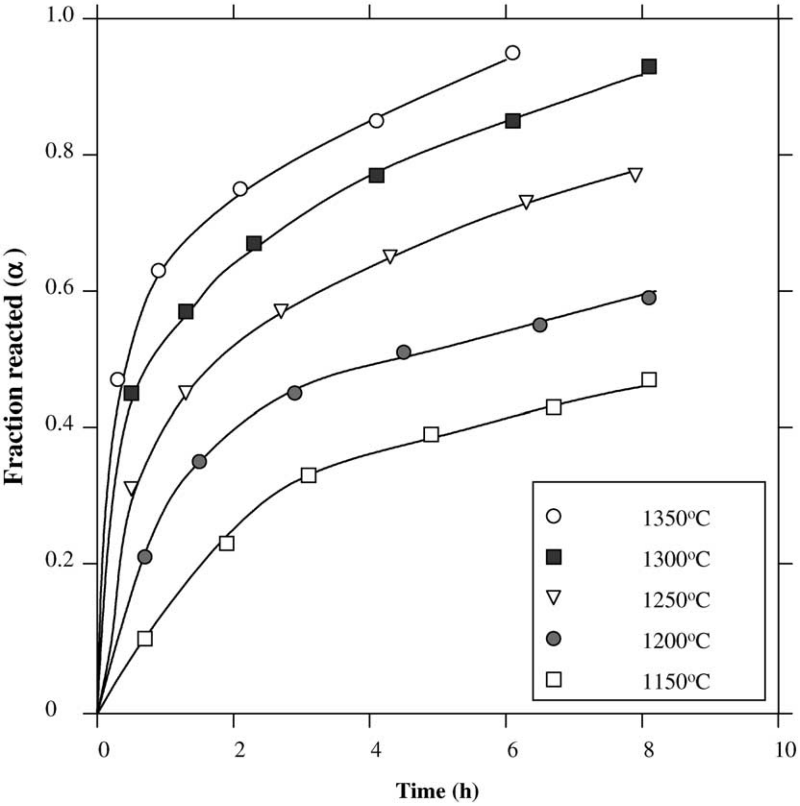

Fig. 2. Plots of fraction of C_3A formed vs. time from calcite and α-Al_2O_3 at various temperatures.

35 min. When α-Al_2O_3 was replaced by gibbsite, the rate of formation of C_3A was faster as can be seen from the data shown in Fig. 3, which indicate that $t_{0.5}$ was about 2.5 h at 1200 °C and about 25 min at 1350 °C.

The kinetic mechanism for the reaction of 3:1 C:A to form C_3A was determined from the amounts of C_3A formed using the master curves [3] of fraction reacted against reduced time, $t/t_{0.5}$. The time to reach 50% conversion was determined from plots of α against *t* shown in Figs. 2 and 3 at the reaction temperatures investigated. The reduced time plot for the data from the reaction between calcite and α-Al_2O_3 is shown in Fig. 4, but the data obtained at the highest temperature, 1350 °C, have been omitted because the value for $t_{0.5}$ is too much affected by the initial conditions before the sample had reached the isothermal temperature.

It can be seen from Fig. 4 that the experimental data are isokinetic since they follow a common curve. Furthermore, they give good agreement with the curve drawn up to α values of around 0.6, beyond which the experimental data fall below the curve. This curve is not the best curve that can be drawn through the experimental points, but a calculated curve based on the Ginstling–Brounshtein equation [4] for diffusion in a spherical particle:

$$D_4(\alpha) = 1 - 2\alpha/3 - (1-\alpha)^{2/3} = kt$$

where, $D_4(\alpha)$ is the Ginstling–Brounshtein function and k is the rate constant, which is temperature dependent. The agreement between the experimental data and the calculated curve is good at low values of α, and departs from it at high values because smaller particles have fully reacted. The reduced time plot obtained from the experimental data obtained from the reaction between calcite and gibbsite was, if anything, better than that shown in Fig. 4 and confirmed that the rate-determining step is a diffusion process.

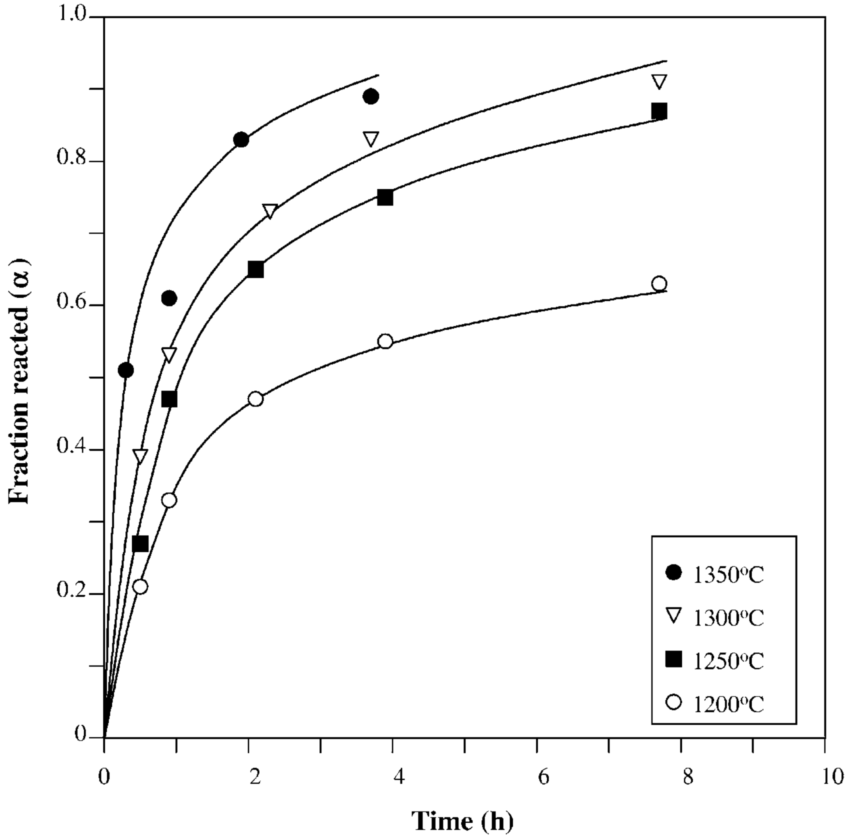

Fig. 3. Plots of fraction of C_3A formed vs. time from calcite and gibbsite at various temperatures.

Plots of the Ginstling–Brounshtein function, $D_4(\alpha)$, against time at various temperatures are shown in Fig. 5. The linearity of these plots confirms the validity of the kinetic model. Similar linear plots were obtained for the data obtained when α-Al_2O_3 was replaced by gibbsite.

From the slopes of the lines obtained when $D_4(\alpha)$ was plotted against time, rate constants were obtained at each temperature. These were used to construct Arrhenius plots of ln k versus $1/T$, as shown in Fig. 6. From the slope of this line the activation energy, E, for the formation of $Ca_3Al_2O_6$ formed from the reaction between α-Al_2O_3 and calcite was determined to be 216 ± 10 kJ mol^{-1} and the pre-experimental factor, determined from the intercept, was 2.1×10^{13} s^{-1}. A similarly good straight line was obtained for the data in which α-Al_2O_3 was replaced by gibbsite, leading to values of $E = 224 \pm 10$ kJ mol^{-1} and $A = 8.9 \times 10^{13}$ s^{-1}.

4. Discussion

4.1. Reaction intermediates

As stated above, the published literature includes conflicting reports about the reaction intermediates found during the synthesis of the various calcium aluminates, and specifically tricalcium aluminate. These reports fall into two main groups.

When reaction couples comprising sintered pellets of CaO and Al_2O_3 are fired and examined by scanning electron miscroscopy (SEM), several or even all of the five calcium aluminate phases (C_3A, $C_{12}A_7$, CA, CA_2 and CA_6) are formed in a sequence of parallel zones with the concentration of calcium gradually decreasing and that of aluminium increasing as the scan is made from the lime pellet to the alumina pellet (2, 5–7). The relative thickness of the layers is generally in the sequence $C_{12}A_7 > C_3A > CA > CA_2 > CA_6$.

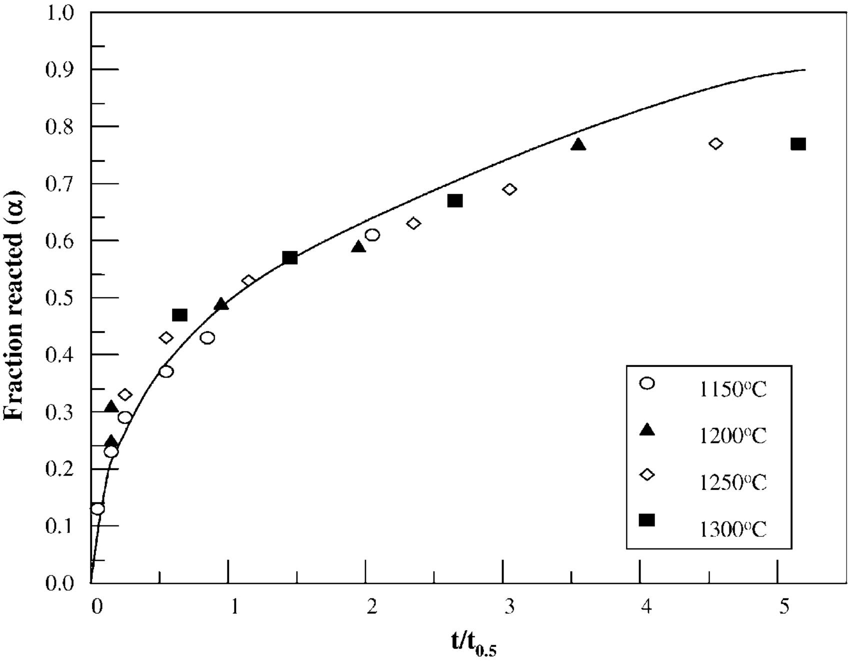

Fig. 4. Reduced time plot of (α) fraction reacted to form C_3A, against time for the reaction of calcite with α-Al_2O_3.

There is agreement that the observations can be interpreted in terms of the rate-determining step being the diffusion of Ca^{2+} ions through the reaction products towards the alumina pellet [5,7].

The second group of papers relate to studies in which mixed powders have been fired, as in the present investigation. Repenko [8] reported that CA is a reaction intermediate in the formation of C_3A,

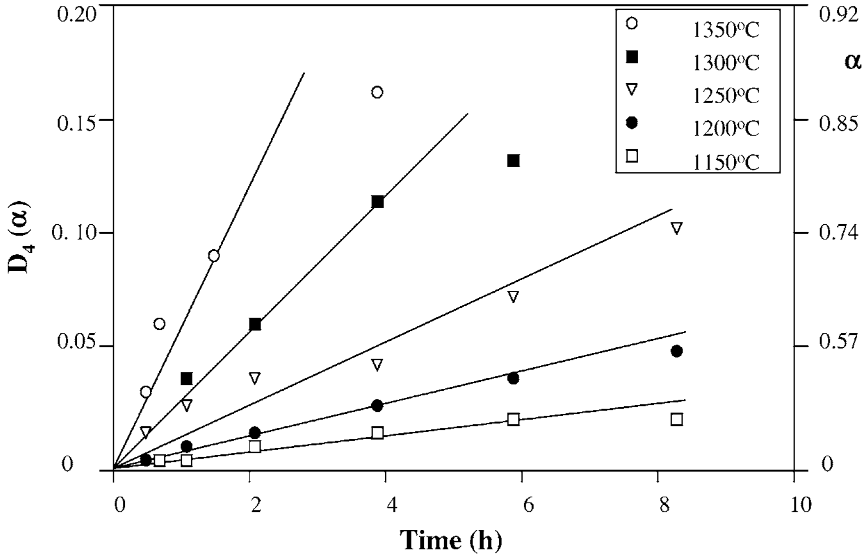

Fig. 5. Plots of $D_4(\alpha)$ vs. time for the formation of C_3A.

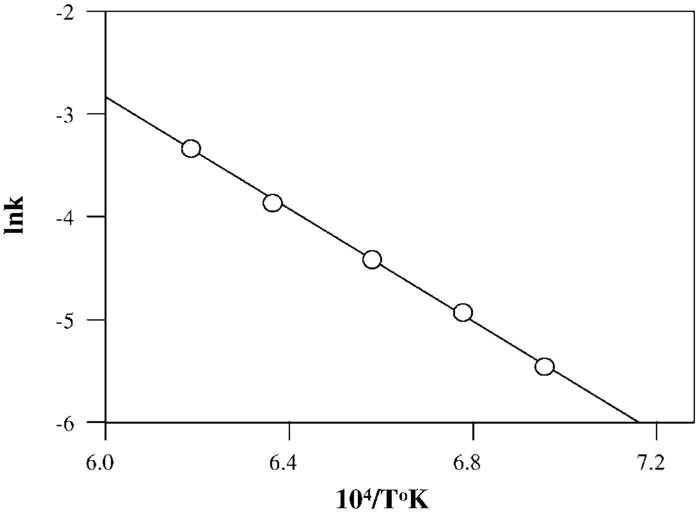

Fig. 6. Arrhenius plot for the formation of C_3A.

whereas Williamson and Glasser [9] reported $C_{12}A_7$ to be the principal non-equilibrium phase, although CA was also observed. MacKenzie and Banerjee [10] identified "C_2A", $C_{12}A_7$, CA, CA_2 and CA_6 during the synthesis of C_3A, but concluded that CA_2 and "C_2A" were reaction intermediates, whereas CA_6, $C_{12}A_7$ and CA should be considered as minor products. Singh et al. [11] also reported that several calcium aluminate phases formed when a 3:1 mix of $CaO:Al_2O_3$ was fired at 1380 °C for 240 min, but the evidence for the formation of CA and especially CA_2 is questionable, since the peak at 21.8° 2θ labelled CA_2 is attributable to C_3A, and the strongest peak of CA expected at 30.1° 2θ is absent. $C_{12}A_7$ was, however, clearly present as well as C_3A.

Chou and Burnet [12] observed a sequence of compounds in the reaction between CaO and Al_2O_3, although SiO_2 was also present in most of their reaction mixes. They suggested that $C_{12}A_7$ is likely to be the first compound formed, but the amount present initially does not grow to any appreciable extent. CA is then formed as the CaO continues to diffuse into the Al_2O_3. When the alumina particle has been converted into CA, the C_3A phase begins to form. Later, when both Al_2O_3 and CaO are used up, the $C_{12}A_7$ grows at the expense of CA and C_3A.

In another related study concerned with the sequence of phases formed during the formation of CA, Scian et al. [13] reported that the reaction proceeded through the formation of all the possible aluminates, except CA_6 and C_5A_3, but that $C_{12}A_7$ was first formed in considerable amounts and subsequently reacted with CA_2 and alumina to form CA.

We have recently reported on the kinetics and mechanisms of formation of CA [1] and $C_{12}A_7$ [2] as well as C_3A (present work). It is interesting to compare our observations with those published more than 30 years ago by Williamson and Glasser [9]. The phases reported as non-equilibrium reaction intermediates in these two investigations are compared in Table 2. Phases in parentheses were less evident than those not in parentheses. There is excellent agreement between these two investigations.

4.2. Kinetic mechanism

The reduced time plot (Fig. 4) and the plots of the Ginstling–Brounshtein function, $D_4(\alpha)$, against time

Table 2
Reaction intermediates observed during the formation of various calcium aluminates

Mixture	Non-equilibrium phases	
$CaO:Al_2O_3$	Williamson and Glasser	Mohamed and Sharp
3:1	12:7 (1:1)	12:7 (1:1)
12:7	3:1 (1:1)	1:1 and 3:1
1:1	12:7 and 3:1	12:7 and 3:1 (1:2)

(Fig. 5) clearly indicate that the kinetic mechanism is based on a diffusion-controlled rate-determining step. This conclusion is shared by almost all previous workers [10,11,14,15].

Whether the Ginstling–Brounshtein equation [4], or any of those reported by Jander [16], Zhuravlev et al. [17] or Carter [18] is used, makes little difference to the conclusions. As discussed elsewhere [3,18], unless control of the experimental variables, especially the particle size and shape of the reactants, approaches perfection, deviation will be observed from the model at high values of α, as observed in Figs. 4 and 5. All that can be established is that the experimental data follow any one of a group of related equations based on a diffusion process as the rate-determining step.

4.3. Activation energy for the formation of tricalcium aluminate

From the shape of the linear plot shown in Fig. 6 for the reaction between calcite and α-Al_2O_3, the activation energy for the formation of tricalcium aluminate was determined to be 216 ± 10 kJ mol^{-1}, and the pre-experimental factor determined from the intercept was 2.1×10^{13} s^{-1}. From similar data for the reaction between calcite and gibbsite, the activation energy was determined to be 224 ± 10 kJ mol^{-1}, and the pre-experimental factor was 8.9×10^{13} s^{-1}.

It can be seen from the data shown in Table 3 that these values correspond well with those reported by MacKenzie and Banerjee [10], and Chou and Burnet [14], but are lower than that reported by Repenko [8] and higher than that reported by Weisweiler and Ahmed [7]. In fact the estimates for the activation energy for the formation of C_3A do not vary as much as those reported for the formation of CA, as listed in Table 4.

Table 3
Reported values (kJ mol^{-1}) of the activation energy for the formation of tricalcium aluminate

Reference	Starting materials[a]	Method[b]	E
[8]	CA_2/C	KMP	285
[10]	CC/A	KMP	203
[14]	CC/A	KMP	191
[7]	CC/A	SEM	151
Present investigation	CC/A	KMP	216
Present investigation	CC/G	KMP	224

[a] C: CaO, A: Al_2O_3, CC: $CaCO_3$, G: $Al(OH)_3$.
[b] KMP: kinetics of mixed powders.

Table 4
Reported values (kJ mol^{-1}) of the activation energy for the formation of monocalcium aluminate

Reference	Starting materials[a]	Method[b]	E
[8]	CC/A	KMP	152
[14]	CC/A	KMP	376
[15]	CC/G	KMP	303–309
[6]	$C_{12}A_7$/A	SEM	502
[6]	CA_2/C	SEM	352
[1]	CC/A	KMP	205
[1]	CC/G	KMP	215

[a] C: CaO, A: Al_2O_3, CC: $CaCO_3$, G: $Al(OH)_3$.
[b] KMP: kinetics of mixed powders.

It is common for literature values of the activation energy for a solid-state reaction to vary widely. In the case of the formation of calcium aluminate phases, the method based on layer thicknesses observed by SEM in only a small number of experiments can lead to an approximate estimate at best. Although kinetic studies of mixed powders should give more reliable results, changes in the composition, and especially the particle size distribution, of powder reactants inevitably affects the rate of reaction at any given temperature.

In the present study, we had expected at the outset that the use of gibbsite, leading to a reactive alumina after its decomposition at ca. 300 °C, would lead to faster rates of reaction and perhaps a different value for the activation energy. In fact, similar rates of reaction and activation energies were observed for the systems incorporating gibbsite and α-Al_2O_3. These observations may be because the rate-determining step is the diffusion of Ca^{2+} ions (1, 2, 5–7) through the layers of reaction products, while the Al^{3+} ions remain immobile.

4.4. Mechanism of formation of tricalcium aluminate

The results of the present work and those reported by Williamson and Glasser [9] are in close agreement and indicate that $C_{12}A_7$ and to a lesser extent CA are formed as reaction intermediates during the synthesis of C_3A. Furthermore, the values for the activation energy of formation of CA, $C_{12}A_7$ and C_3A determined by the present authors, which are shown in Table 5, are similar, although that for the formation of

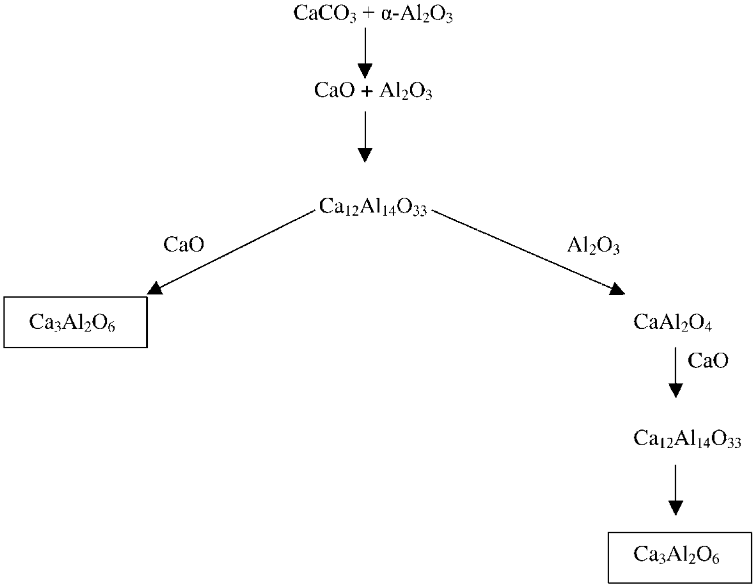

Fig. 7. Reaction scheme for the formation of $Ca_3Al_2O_6$.

Table 5
Values (kJ mol^{-1}) of the activation energy for the formation of calcium aluminates determined by Mohamed and Sharp

Compound	E	Reference
$CaAl_2O_4$	205–215	[1]
$Ca_{12}Al_{14}O_{33}$	182	[2]
$Ca_3Al_2O_6$	216–224	Present work

$C_{12}A_7$ is the lowest. The values of these activation energies are all within the range for the self-diffusion of Ca^{2+} ions in CaO (146–268 kJ mol^{-1}) determined by Gulgun et al. [19]. Scanning electron micrographs of lime-alumina reaction complex always show a thick layer of formation of $C_{12}A_7$ [2,5–7].

With all these observations in mind, it is possible to speculate about the mechanism of formation of C_3A, as shown schematically in Fig. 7. On heating to about 900 °C, the calcite decomposes into lime, which has a high surface area and hence is in a reactive form. On further heating, some of this lime reacts with alumina, where there is good geometrical contact between grains, to form $C_{12}A_7$, the principal reaction intermediate. According to the geometry of the system, reaction can then proceed in either of two directions. Where the $C_{12}A_7$ is formed in contact with grains of lime, the final product C_3A is readily produced. Where, however, the $C_{12}A_7$ is in contact with grains of alumina, it reacts first to form CA (also observed as an intermediate phase but in smaller amounts than $C_{12}A_7$, see Fig. 1) and subsequently C_3A. Monocalcium aluminate is, therefore, initially formed in a side-reaction, but then becomes a reaction intermediate.

5. Conclusions

(i) The phases $Ca_{12}Al_{14}O_{33}$ and $CaAl_2O_4$ are observed as reaction intermediates in the formation of $Ca_3Al_2O_6$.
(ii) The kinetics of formation of $Ca_3Al_2O_6$ from the oxides follow the diffusion-controlled model of Ginstling–Brounshtein [4].
(iii) The value for the activation energy obtained for the synthesis of $Ca_3Al_2O_6$ from calcite and α-Al_2O_3 is 216 ± 10 kJ mol^{-1}, and from calcite and gibbsite is 224 ± 10 kJ mol^{-1}, in good agreement with some of the values previously reported [10,14].
(iv) The sequence of reactions involving the intermediate phases is probably dependent upon geometrical factors affecting contacts between

grains, but formation of $C_{12}A_7$ is probably the first step.

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References

[1] B.M. Mohamed, J.H. Sharp, J. Mater. Chem. 7 (1997) 1595–1599.
[2] B.M. Mohamed, J.H. Sharp, in: R.J. Mangabhai, F.P. Glasser (Eds.), Proceedings of the 2nd International Conference on Calcium Aluminate Cements, Edinburgh, UK, 2001, pp. 65–76.
[3] J.H. Sharp, G.W. Brindley, B.N.N. Achar, J. Am. Ceram. Soc. 49 (1966) 379–382.
[4] A.M. Ginstling, B.I. Brounshtein, J. Appl. Chem. USSR 23 (1950) 1249–1259.
[5] I. Kohatsu, G.W. Brindley, Z. Phys. Chem. 60 (1968) 79–89.
[6] S. Ito, M. Kato, K. Suzuki, M. Inagaki, Z. Phys. Chem. 104 (1977) 147–154.
[7] W. Weisweiler, S.J. Ahmed, Zement-Kalk-Gips 33 (1980) 84–89.
[8] K.I. Repenko, Sb. Nauchn. Tr. Ukr. Nauchn. Issled Inst. Ogneuporov 7 (1963) 318–329.
[9] J. Williamson, F.P. Glasser, J. Appl. Chem. 12 (1962) 535–538.
[10] K.J.D. MacKenzie, R.K. Banerjee, Trans. J. Br. Ceram. Soc. 77 (1978) 88–92.
[11] V.K. Singh, M.M. Ali, U.K. Mandal, J. Am. Ceram. Soc. 73 (1990) 872–876.
[12] K.S. Chou, G. Burnet, Cem. Concr. Res. 11 (1981) 57–64.
[13] A.N. Scian, J.M. Porto-Lopez, E. Pereira, Cem. Concr. Res. 17 (1987) 198–204.
[14] K.S. Chou, G. Burnet, Cem. Concr. Res. 11 (1981) 167–174.
[15] A.N. Scian, J.M. Porto-Lopez, E. Pereira, Cem. Concr. Res. 17 (1987) 525–531.
[16] W. Jander, Z. Anorg, Allg. Chem. 163 (1927) 1–30.
[17] V.F. Zhuravlev, I.G. Lesokhin, R.G. Tempel'man, Zh. Prikl. Khim. (Leningrad) 21 (1948) 887–902.
[18] R.E. Carter, J. Chem. Phys. 34 (1961) 2010–2015;
R.E. Carter, J. Chem. Phys. 35 (1962) 1137–1138.
[19] M.A. Gulgun, O.O. Poplooler, W.M. Kriven, J. Am. Ceram. Soc. 77 (1994) 531–539.