

Effect of electric fields on solid-state reactions between oxides

Part 1 *Reaction between calcium and aluminium oxides*

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The solid-state reaction between CaO and Al₂O₃ in intimately mixed powders and pressed polycrystalline pellets to form a series of calcium aluminates is assisted by the application of external d.c. electric fields. The formation of all the aluminate phases is particularly enhanced in the vicinity of the positive electrode. The major effect of the electric field is probably to assist the diffusion of Ca into Al₂O₃, and the results can be qualitatively explained in terms of a simple diffusional model which takes account of the orientation of the reactant grains relative to each other and to the electric field vector. Possible effects of field-induced sintering and the anion packing density of the various product phases are also discussed.

1. Introduction

Many materials of practical usefulness are prepared by solid-state reactions between oxides, for example, ceramic materials for electronics, refractories and cements. Diffusion processes play an important part in reactions between oxides, and a knowledge of the role of various external factors in determining the mobility of the migrating species in oxides is essential if the course of these reactions is to be controlled or modified.

Recent experiments on the solid-state reactions occurring during the formation of Portland cement clinker [1] have shown that the reaction between the various constituent oxides in this system can be strongly influenced by the application of electric fields during firing, the formation of tricalcium aluminate being enhanced at the positive electrode. The theoretical interpretation of these results [2] is complicated by the number of components present in the clinker-forming system, but can be qualitatively explained in terms of factors such as the shift of the diffusion profile under an electric field gradient, the oxygen pack-

ing density of the phases through which diffusion must occur, and (in powder samples) the relative orientation of the reactant grains to the electric field direction [2].

The aim of this work is therefore to examine in more detail the effect of electric fields on a simpler system consisting of just two of the components of the cement clinker-forming assemblage, calcium oxide and aluminium oxide. The formation of the various calcium aluminates was studied in both powder and pellet samples of different oxide ratios by X-ray diffraction, using an internal standard. Throughout this paper, the various calcium aluminates will be referred to in terms of the standard cement chemistry nomenclature, in which C = CaO and A = Al₂O₃.

2. Experimental details

Calcium oxide was prepared by heating analytical reagent grade CaCO₃ at 1050°C for 0.5 h. The aluminium oxide was also of analytical reagent grade. Scanning electron microscopy of the unreacted oxides showed that the CaO consisted of well-defined cubelets of fairly uniform size

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(7 μm mean). The particle size of the Al_2O_3 was in the range 1 to 4 μm with a mean size of 2.5 μm . The CaO was stored in an oven at 120°C before use to prevent dehydration. Mixtures containing 3 mol CaO to 1 mol Al_2O_3 were thoroughly ground together immediately prior to an experiment, and reacted together at temperatures of 900 to 1300°C in an electrolysis cell consisting of a cylindrical alumina container 10 mm diameter, fitted with two platinum foil electrodes. The thickness of the powder sample was 8 mm. The top electrode was perforated with many small holes to allow free access between the sample and the furnace atmosphere. A weighted sample of reactant powder was lightly compacted into the cell under controlled and reproducible pressure, and the whole assembly placed in a pre-heated tube furnace. Two sets of experiments were carried out: (i) at various temperatures and constant field strength ($1.0 \times 10^5 \text{ V m}^{-1}$) and (ii) at various field strengths between 0.25 and $1.0 \times 10^5 \text{ V m}^{-1}$ and fixed temperature (1200°C). All powder firings were of 4 h duration, and the electric field was supplied by a Philips PE 4839 E.H.T. power supply. In each case, separate experiments were made in which the top electrode was respectively of negative and positive polarity, and control experiments were also made without the electric field.

Since control of shrinkage due to sintering is difficult in lightly compacted powders, another set of experiments was devised in which the contact between the reactant grains was increased by pressing the powders into pellets 20 mm diameter by 10 mm high at a pressure of $5.0 \times 10^3 \text{ kg cm}^{-2}$. The resulting increase in the conductance of pressed samples of 3CaO: Al_2O_3 composition was such that very large currents were drawn during electrolysis, resulting in some cases in melting of the sample due to internal electrical heating effects. For this reason, the experiments on pressed pellets were made with samples of smaller CaO content (mole ratio 1:1) and therefore of lower overall conductivity. These were reacted for 2 h between platinum foil electrodes at 900 to 1300°C under electric fields as in the powder experiments.

After firing, small samples of material were taken from the electrode regions, mixed thoroughly with 10% by weight of calcined rutile (TiO_2) as an internal standard, and examined by X-ray diffraction. The ratios of the diagnostic peaks

for the various aluminate phases to the internal standard peak were taken as an indication of the amount of phase present; since the aim of this work was to detect *changes* in the concentrations of each phase present, no attempt was made to relate the observed ratios to actual phase percentages via calibration curves. The X-ray peaks taken as diagnostic for the various phases were: C_3A , $d = 2.69$ and 1.91 \AA , CA_6 , $d = 2.48 \text{ \AA}$, C_{12}A_7 , $d = 2.186$ and 4.90 \AA , C_5A_3 , $d = 2.97 \text{ \AA}$, CA_2 , $d = 4.439$ and 3.68 \AA , CA , $d = 2.29$ and 2.13 \AA , CaO , $d = 2.41 \text{ \AA}$ and Al_2O_3 , $d = 2.09 \text{ \AA}$. The internal standard peak was at 3.51 \AA . Several of these peaks occur in close proximity to other peaks in the system; one of the C_{12}A_7 peaks lies near a CA peak at 2.196 \AA , the CA_6 peak is close to a rutile peak at 2.49 \AA and one of the C_3A peaks is close to a CA peak at 2.72 \AA . However, by using a slow scan speed and fast recorder speed, it was possible to resolve the peaks satisfactorily in most of the samples. In doubtful cases, a second peak of the same phase was also measured as a cross-check. The reproducibilities of the ratio determinations were in all cases better than 5%.

3. Results and discussion

3.1. Reactions in 3CaO: Al_2O_3 powder mixtures

The effect of the reaction temperature on the development of the various phases under an electric field of constant strength is shown in Fig. 1, which shows that within this temperature range, the greatest degree of development of all the aluminate phases occurs at the positive electrode.

All of the aluminate phases reported by Repenko [3] to be formed in the CaO- Al_2O_3 system were detected in the powder samples, as well as an additional phase, C_{12}A_7 . For all phases, the concentration at the negative electrode, although less than at the positive electrode, was greater than in the unelectrolysed control. These results are in agreement with those previously obtained on an actual cement clinker mix [1], although in those experiments, C_3A was the only aluminate phase analysed for. The close similarity in the shapes of the present curves both in the presence and absence of the electric field suggests that the effect of field is to increase the rate of reaction rather than to change the reaction mechanism.

Fig. 2 shows the effect of changing the field strength at a fixed reaction temperature (1200°C).

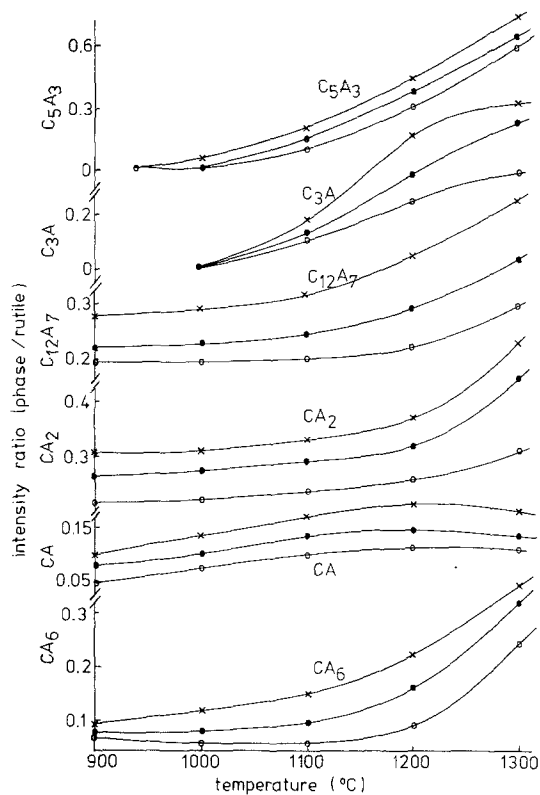


Figure 1 Effect of reaction temperature on phase formation in electrolysed and unelectrolysed $3\text{CaO}:\text{Al}_2\text{O}_3$ powders. Field strength $1.0 \times 10^5 \text{ V m}^{-1}$, reaction time 4.0 h. \circ = unelectrolysed, \bullet = -ve face, \times = +ve face.

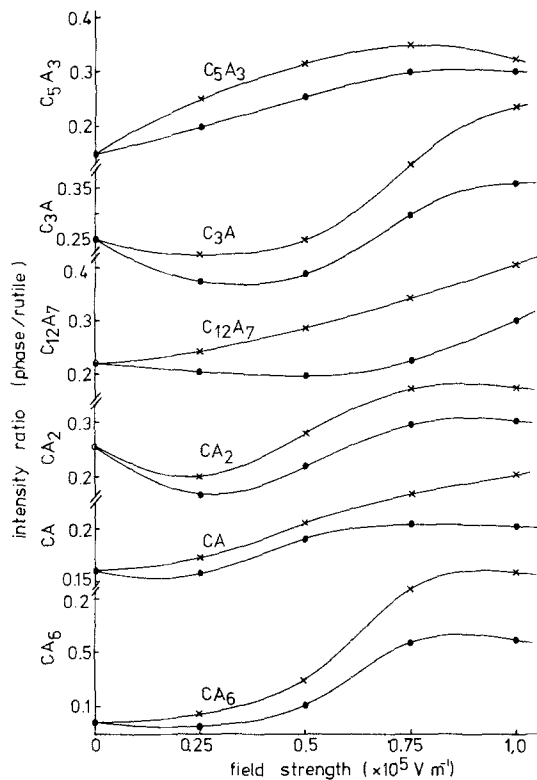


Figure 2 Effect of electric strength on phase formation in $3\text{CaO}:\text{Al}_2\text{O}_3$ powders. Reaction temperature 1200°C , reaction time 4.0 h. \bullet = -ve face, \times = +ve face.

Again, the greatest development of all the aluminate phases is observed at the positive electrode. At the highest field strengths, the effectiveness of the field in enhancing the formation of most phases falls off, either because under those conditions the reaction is approaching completion, or possibly because of some ionic saturation or blocking effect in the electrode regions.

During the course of a powder electrolysis

experiment, considerable variation was observed in the current drawn by the sample as a function of electrolysis time, especially in the early stages of the reaction. A typical current-time curve is given in Fig. 3, which shows that the current drops sharply within the first 15 min, probably due to a depletion of charge carriers such as residual protons or even carbonate ions originating from CO_2 pick-up from the atmosphere. The

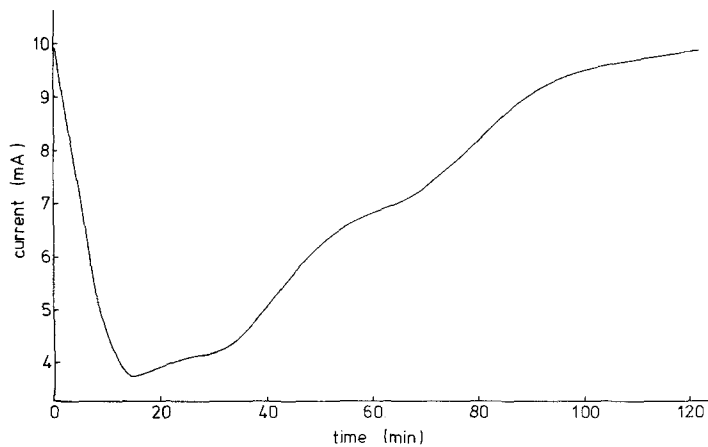


Figure 3 Variation of sample current with reaction time for $3\text{CaO}:\text{Al}_2\text{O}_3$ powder. Field strength $5.7 \times 10^4 \text{ V m}^{-1}$, reaction temperature 1200°C . Positive electrode surface in contact with ambient atmosphere.

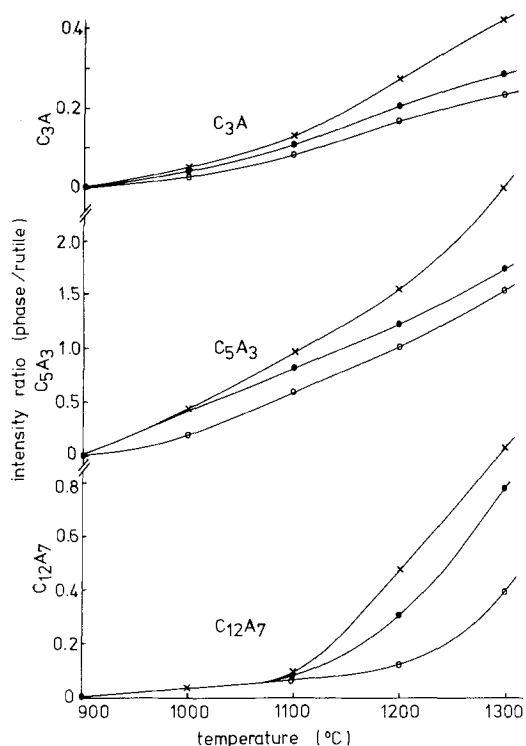


Figure 4 Effect of reaction temperature on phase formation in electrolysed and unelectrolysed $\text{CaO}:\text{Al}_2\text{O}_3$ pressed pellets. Field strength $3.0 \times 10^4 \text{ V m}^{-1}$, reaction time 2.0 h. \circ = unelectrolysed, \bullet = -ve face, \times = +ve face.

subsequent steady increase in current is possibly due to a continuous decrease in the contact resistance between the reactant grains resulting from sintering and the solid-state reaction processes occurring. The sintering process eventually reaches an equilibrium state and the current becomes steady.

3.2. Reactions in 1:1 $\text{CaO}:\text{Al}_2\text{O}_3$ pressed pellets

The effect of electrolysis temperature and field strength on the formation of the aluminate phases is shown in Figs. 4 and 5 respectively. The principal phases observed in this system were C_{12}A_7 , C_5A_3 and C_3A ; smaller amounts of CA and CA_2 were found but their concentrations were too low to detect significant field-related changes in their formation rates. The results of the experiments on pressed pellets again show that the principal aluminate phases are formed in greater amount at the positive electrode. Thus the qualitative effect of electric fields on the reactions between the oxides appears to be independent of the stoichiometry of the mixture and the

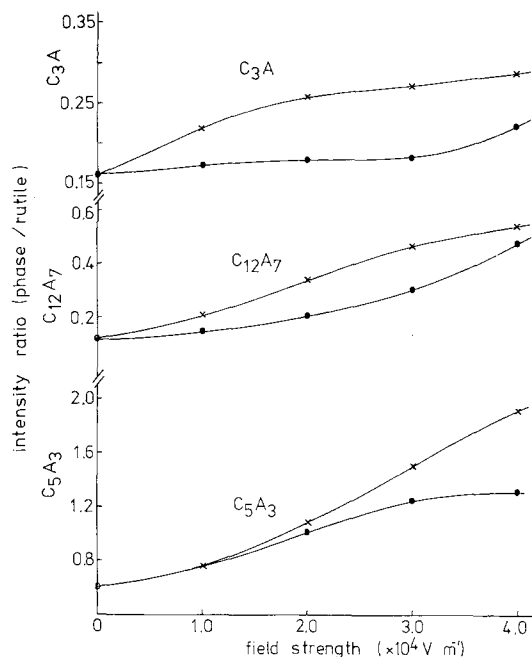


Figure 5 Effect of electric strength on phase formation in $\text{CaO}:\text{Al}_2\text{O}_3$ pressed pellets. Reaction temperature 1200°C , reaction time 2.0 h. \bullet = -ve face, \times = +ve face.

physical form of the sample, apart from the fact that these two factors affect the electrical resistance of the system, and hence the maximum field strength which can be applied.

3.3. Effect of electric fields on the reaction mechanism

The similarity in the shapes of the electrolysed and unelectrolysed growth curves of all the aluminate phases suggests that the reaction mechanism is unchanged by the electric field. In the absence of electric fields, this mechanism has been shown by Kohatsu and Brindley [4] to predominantly involve diffusion of Ca into Al_2O_3 rather than vice versa. There are several ways in which electric fields might influence this diffusion process in intimately mixed powders:

(i) by shifting the diffusion profile within the grains downfield by an amount related to the field strength, electrolysis time and effective electrical mobility of the migrating species,

(ii) by modifying the anion packing of the product phases through which subsequent diffusion must occur,

(iii) by influencing sintering processes in the compacted powder, thereby modifying grain-boundary diffusion.

The magnitude of the downfield shift of the diffusion profile has been crudely estimated by

indirect means for C_3A in a fired Portland cement clinker [2], but similar calculations have not been made for the other calcium aluminates. More detailed investigations of this parameter are reported in Part 2 of this paper. In general, however, the electric field vector should act to reinforce the diffusion of Ca into Al_2O_3 for all grain orientations where the Ca-containing component is more positive than the aluminium component. For all orientations where the reverse is the case, the field will act in opposition to the normal thermal diffusion direction, with the net effect that Ca probably undergoes relatively little displacement. The electric field vector should also promote some diffusion of Al into CaO under these conditions, but probably not to any significant extent, due to the relatively low diffusivity of Al. The net effect of the field should, therefore, be to promote enhanced diffusion of Ca into the Al_2O_3 grains at the positive electrode, resulting in the enhanced formation of all the calcium aluminate phases in that region. This crude qualitative picture takes no account of the relative grain sizes of the reactants, but merely assumes a reasonable number of point contacts between the reactant particles.

The role of oxygen ion packing density in determining the relative ease of diffusion of Ca through the various aluminate product phases in the contact zone between reactant grains was pointed out by Kohatsu and Brindley [4], who deduced on this basis that the relative ease of Ca diffusion should be greatest in $C_{12}A_7$ (oxygen packing density 1.03 g cm^{-3}), and should decrease in the order C_3A (1.17 g cm^{-3}), CA (1.21 g cm^{-3}), CA_2 (1.23 g cm^{-3}), CA_6 (1.75 g cm^{-3}). These conclusions were well supported by experimental diffusion measurements [4], except in the case of CA_6 , in which the ease of Ca diffusion was greater than predicted from the oxygen packing density of that phase. On the previous reasoning, the electric field may be assumed to reinforce the normal thermal diffusion processes, particularly in the region of the positive electrode. If the effect of the field on the formation of the various phases is defined as $(R_{(+)} - R_{(0)})$ where R is the intensity ratio for a particular phase and the subscripts refer to the electrolysis conditions, Fig. 2 shows that at the highest field strengths, the field exerts almost the same effect on all the aluminate phases except CA_6 , the formation of which is enhanced to a much greater

extent. A similar conclusion is also reached if $(R_{(+)} - R_{(-)})$ is taken as a measure of the effect of the field. On the basis of these ratio measurements, the field effect on the various aluminates decreases in the order $CA_6 > C_5A_3 > C_3A \approx C_{12}A_7 = CA > CA_2$, approximately following the order of the oxygen packing densities, with exception of CA_6 (C_5A_3 was not included in the calculations, as it was apparently not observed by Kohatsu and Brindley). The CA_6 phase was found by Kohatsu and Brindley [4] to exhibit anomalous diffusion behaviour similar to the present results, causing those authors to suggest that at higher oxygen densities, the bulk properties of a phase may become less important than the effects of grain-boundary diffusion, presumably because grain boundaries would present paths of lower diffusional resistance.

Although the complete sequence of phases was not observed under the conditions of the pellet experiments, Fig. 5 shows that of the three phases measured, the formation of $C_{12}A_7$ is most influenced by the electric field, followed by C_5A_3 and C_3A . This again follows the order of oxygen packing densities of Kohatsu and Brindley [4], with the exception of C_5A_3 .

If grain-boundary diffusion contributes significantly to the overall reaction process, the degree of sintering will become important in controlling the progress of phase formation. Electric fields can influence sintering in two ways, by assisting mass transfer across the contact zone between the grains, and by a local electrical heating effect in which the temperature of the contact zones is raised, even to the point where incipient melting may occur. By this reasoning, electric fields should increase the degree of sintering and thereby decrease the degree of grain-boundary diffusion. Electron micrographic evidence of field-enhanced sintering, particularly in the CaO component, is discussed in Part 2 of this paper, but the present results suggest that in mixed powders, field-induced sintering does not significantly interfere with the process of phase formation.

4. Conclusions

(1) The formation of all the phases resulting from reaction between CaO and Al_2O_3 is assisted by the application of a d.c. electric field, particularly in the region of the positive electrode. This result is true for both powders and pressed polycrystalline pellets and is also apparently independent of

the stoichiometry of the sample, having been observed in mixtures of both 1:1 and 3:1 mole ratio of CaO to Al₂O₃. The similarity in the temperature dependence curves for electrolysed samples suggests that the field does not change the formation mechanism but simply enhances the reaction rate. These results confirm the findings of previous experiments on Portland cement clinker raw mixes.

(2) In 3:1 powder mixtures, the phase whose formation is most enhanced by the field is CA₆, followed by C₅A₃, C₁₂A₇, CA and CA₂. This is approximately the order of increasing density of oxygen ion packing in the various aluminates, suggesting that even in electric fields, the diffusional process is strongly dependent on this parameter. The anomalously large effect of the field on the formation of CA₆ may indicate the importance of grain-boundary diffusion in the reaction process at higher oxygen densities.

(3) The particular enhancement of aluminate formation at the positive electrode can be qualitatively explained in terms of a field-induced shift of the diffusion profile of Ca in the Al₂O₃ grains, taking account of the relative orientation of the grains to each other and to the direction of the electric field vector.

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