Thermochimica Acta, 28 (1979) 161–173

THE FORMATION OF PORTLAND CEMENT CLINKER UNDER APPLIED ELECTRIC FIELDS. I. THERMAL REACTION SEQUENCE AND KINETICS OF CLINKER PHASE FORMATION

K. J. D. MACKENZIE AND R. A. FLETCHER
Chemistry Division, D.S.I.R., Private Bag, Petone (New Zealand)
(Received 17 February 1978)

ABSTRACT

The development of β-dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and "ferrite" phases (C_4AF) and the disappearance of free calcium oxide during the firing of a commercial Portland cement raw mix under the influence of d.c. electric fields was monitored by X-ray powder diffraction. Samples fired under electric fields contained increased amounts of C_3A and C_4AF, particularly at the positive electrode, in which region the consumption of calcium oxide was also enhanced. Electric fields also appear to assist the thermal decomposition of the calcium carbonate starting material, particularly at the positive electrode.

Measurements of the time-dependence at different temperatures of the formation of the various phases result in complex curves which are not amenable to conventional kinetic analysis, but determinations of the initial rate constants for both electrolysed and unelectrolysed samples show that the consumption of CaO by clinker phase formation is enhanced by the field at temperatures above 1200 °C. The occurrence of β-C_2S is decreased above about 1200 °C by electrolysis, due to the enhanced formation of the other phases at the expense of C_2S. Field-induced increases in C_3A and C_4AF contents become less marked at increasing temperatures, at which the normal thermal processes begin to predominate.

INTRODUCTION

Portland cement is formed by calcining an intimate mixture of $CaCO_3$ and a siliceous material, often containing a hydrous aluminosilicate. Mechanically held water evaporates at about 100 °C, while dehydroxylation of the aluminosilicate occurs at about 500–600 °C. Decarbonation of the limestone at 894 °C then produces in situ reactive CaO which combines with the silica and components of the dehydroxylated aluminosilicate to form the principal Portland cement phases β-Ca_2SiO_4, Ca_3SiO_5, $Ca_3Al_2O_6$ and Ca_2AlFeO_5 (in cement chemistry notation, in which the component oxides are abbreviated to C, S, A and F, these phases would be written β-C_2S, C_3S, C_3A and C_4AF, respectively). The precise formation sequence of these phases depends on the nature of the starting materials (particularly with respect to the fluxing agents present), but, in general, C_2S is the first stable product to be formed, followed by C_3A, which results from the decomposition of a precursor phase $C_{12}A_7$ at about 1100°C (ref. 1). At about 1100°C, the free lime content reaches a maximum as the decomposition of $CaCO_3$ is rapidly completed. Between 1100 and 1200°C, the so-called ferrite phase, C_4AF, forms, while at higher temperatures (1200–1300°C), C_3S is formed by reaction between C_2S and free lime. The phase composition of a typical Portland cement clinker is 42% C_3S, 34% C_2S, 9.5% C_4AF and 6.7% C_3A. The remaining 8% is composed of free lime and minor phases.

Studies of the mechanism by which these phases are formed are complicated by the fact that the process is a non-equilibrium one, and, furthermore, the higher-temperature reactions occur in the presence of a liquid phase which forms at about 1260°C.

Previous studies in other oxide and silicate systems have shown that the application of electric fields substantially enhanced solid-state reaction such as dehydroxylation of clay minerals[2], phase transformations[3] and sintering[4], and since similar reactions are involved in cement clinker formation, the present experiments were carried out to observe the effects of electric fields on the formation of the various clinker phases. The idea of applying electric fields to cement is not new, but most of the previous work has been directed towards the modification or acceleration of the setting properties (as in the electrocuring of cement/water pastes, or the "activation" of cements to render them especially reactive to water[5]). The one previously reported study of the effect of electric fields on clinker formation[6] used 67 kHz alternating fields; these experimental conditions were thought to change the mechanism of phase formation by eliminating the recrystallization of the intermediate oxides and promoting their simultaneous combination. In view of the a.c. fields used, the inductive heating effect within the samples would not have been insignificant. In the light of similar experiments in which a.c. fields were applied to kaolinite[7], the apparent lowering of the reaction temperature by 100°C could have been more than compensated for by temperature rises induced in the sample. No previous studies of clinker formation in a d.c. field have been reported.

The aim of the present experiments was to study the effect of d.c. fields on the thermal reactions leading to the formation of Portland cement clinker by measuring the effects of field strength and electrolysis temperature and time on the development of the various clinker phases. Although the time–temperature studies reported have are referred to as kinetics, the results are not in the form of the families of phase development curves normally associated with the term "kinetics". This is brought about by the complexity and interdependence of the reactions, in which one phase appears at the expense of another, and is in turn consumed by further reaction. This is the reason why virtually no kinetic studies of the complete system have been previously reported, except in special cases where, at higher temperatures in the presence of liquid, formation of the final phases may proceed to completion.

In addition to providing a possible practical means of controlling clinkering, the present experiments were also expected to provide further information on the clinkering process. Many of the previously reported fundamental studies of clinkering reactions were made on synthetic oxide mixtures, but the present work was carried out on an actual cements works raw mix, to eliminate possible changes in the reactivity of the system introduced by the mixing and grinding procedures employed in actual cement production.

EXPERIMENTAL

Materials

The starting material used in these experiments was obtained from the production line of a New Zealand cement works at the point just before introduction into the kiln. When obtained, it was in the form of a slurry, but was oven-dried at 100 °C for the purpose of these experiments. X-Ray powder diffraction of the dried material showed it to be composed principally of $CaCO_3$ and quartz, with small amounts of clay minerals, of which kaolinite was the only component to be positively identified. The mineralogical composition of the quarry clay used in this particular mix is approximately 31 % kaolinite and 45 % quartz, with the balance composed of minor amounts of feldspars, serpentine, calcite and hematite. The chemical analysis of the oven-dried raw mix is shown in Table 1.

Thermogravimetric (TG) curves of the oven-dried material show a plateau at 650 °C, corresponding to a weight loss of 2.49 %, representing the loss of mechanically held water and hydroxyl water from the kaolinite present. Decarboxylation occurs between about 680 and 850 °C, resulting in a weight loss corresponding to a carbonate

TABLE 1

CHEMICAL ANALYSIS OF PORTLAND CEMENT RAW MIX

Sample oven-dried at 100 °C.

Component	%
SiO_2	15.44
Al_2O_3	2.90
$CaCO_3$	75.94
$MgCO_3$	2.66
Fe_2O_3	1.37
Mn_2O_3	0.02
TiO_2	0.035
P_2O_5	0.025
H_2O (at 650 °C)	2.49
Na_2O	0.02
K_2O	0.08
Total	100.98

content of 72.25%, in good agreement with the value of 75.49% based on the chemical analysis figures for calcium. The magnesium content is also expressed as carbonate in Table 1, since this is its most likely form in the present mix. Making the simplifying assumption that all the aluminium is associated with the kaolinite component, the mineralogical composition of the raw mix is 78.6% carbonates, 12.0% quartz, 7.3% clay and 2.1% minor phases (hematite, etc.).

Electrolysis methods

The oven-dried powder samples were packed firmly into the specially fabricated electrolysis cell described elsewhere[3]. The electrolyses were carried out in still air, and three sets of experiments were made, in which the electrolysing voltage, temperature and time were respectively varied. Each experiment was conducted with the upper electrode positive, and repeated at reverse polarity. The electrolysing voltage was supplied from a Philips PW 4022 E.H.T. power supply. After electrolysis, the material in the region of the upper electrode was carefully removed and subjected to phase analysis by quantitative X-ray diffractometry. In order to provide a control, all of the experiments were repeated without electrolysis.

X-Ray analysis of the fired material

An X-ray powder diffraction analysis method was developed for five phases most commonly found in Portland cement clinkers, namely, CaO, C_2S, C_3A, C_4AF and C_3S. X-Ray analysis of these phases in the presence of each other is complicated by the fact that their X-ray patterns overlap extensively; although diagnostic peaks can be identified in mixtures of these phases, in some cases they are relatively minor peaks. Furthermore, some of these phases (e.g. C_2S) occur in several crystalline modifications, with different X-ray characteristics. Fortunately, this did not prove to be too serious a drawback in the present work, since a single starting material was used, which produced the same phases throughout the course of the experiments, allowing meaningful comparisons to be made.

The analytical method involved the addition of 10% reagent grade anatase (TiO_2) as an internal standard. After thorough mixing, the sample was slurried in acetone and deposited on to a glass slide. This method of grinding under a solvent is commonly used by IR spectroscopists to reduce the particle size without introducing undue crystalline strain. After evaporation of the solvent, the X-ray pattern was recorded in the range 25–40° 2θ, and the areas under the diagnostic peaks were measured by cutting them out of the chart and weighing. Because of the overlapping nature of the X-ray pattern, a slow scan speed ($1/4°$ 2θ/min at 400 counts/sec) was used to permit maximum resolution. The ratio of the peak areas to the area of the anatase peak at $d = 3.51$ Å were then calculated. For the purpose of this study, the following peaks were used for the analysis of the major phase (the angular values refer to CuKα radiation).

CaO 200 peak at $d = 2.405$ Å ($37.4°$ 2θ)
β-C_2S $12\bar{1}$ peak at $d = 2.878$ Å ($31.05°$ 2θ)

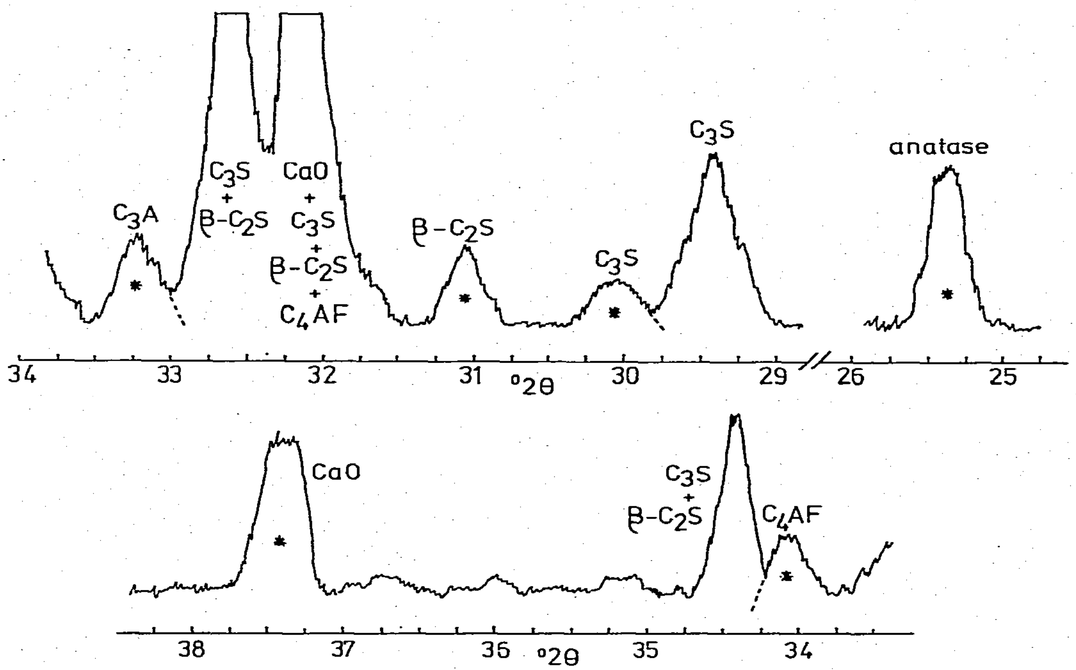


Fig. 1. Typical X-ray trace of fired clinker showing peaks used for phase analyses (marked*).

C_3A 440 peak at $d = 2.700$ Å ($33.18°\ 2\theta$)
C_4AF 141 peak at $d = 2.63$ Å ($34.1°\ 2\theta$)
C_3S 40$\bar{2}$ peak at $d = 2.966$ Å ($30.1°\ 2\theta$)

The anatase internal standard peak was the 101 peak at $d = 3.51$ Å ($25.38°\ 2\theta$).

Figure 1. shows a typical X-ray trace in the region used for analysis. It is seen that some extrapolation of the side of the peaks to the baseline was required, principally in the case of the C_3A peak. The choice of this peak for the C_3A analysis would have been invalidated by the presence of either $C_{12}A_7$ or spurrite ($2C_2S \cdot CaCO_3$), both of which phases have a major peak in this region. The absence of the $C_{12}A_7$ peak at 4.89 Å and the spurrite peaks at 3.81 and 2.66 Å indicated that the C_3A peak at 2.7 Å could confidently be used to estimate that phase. Using this procedure, it was possible to achieve reproducibilities within at least 5% for the same sample; in many cases, the reproducibilities were rather better than this (3%). (This reproducibility refers to the analytical method only, and does not include errors introduced during the firing and electrolysis, which were more variable. In general, however, a result was not considered acceptable unless it could be repeated to within the accuracy of the analytical method).

Since the purpose of this study was to detect *differences* in the degree of phase formation resulting from changes in the external firing conditions, the results are presented as intensity ratios rather than absolute phase compositions deduced via calibration curves.

RESULTS AND DISCUSSION

The effect of external electric fields

In this section, the effect of two variables, electrolysing field strength and electrolysing temperature, are studied. The purpose of the field strength dependence study was to ascertain the optimum field strength at which further studies should be made (this is not necessarily the highest possible field strength, since polarization and saturation effects can cause a marked decrease in electrolysing efficiency at higher field strengths[3, 4]). Once an optimum field strength has been determined for a particular electrolysing temperature and time (in this case 1200 °C for 2 h), the effect of varying the electrolysing temperature can be determined. These temperature-dependence studies are essential in a complex system such as the present one, since the formation of the various phases becomes kinetically optimal at different temperatures. Temperature-dependence studies therefore offer the only real hope of differentiating the effect of electrolysis on the different overlapping reactions. Experiments in which the electrolysis time is varied at different temperatures are described in the next section.

The effect of field strength. The percentage of each major phase formed after electrolysis for 2 h at 1200 °C is shown in Fig. 2 as a function of field strength. Two major points emerge from Fig. 2: (1) electrolysis exerts a considerable effect on the

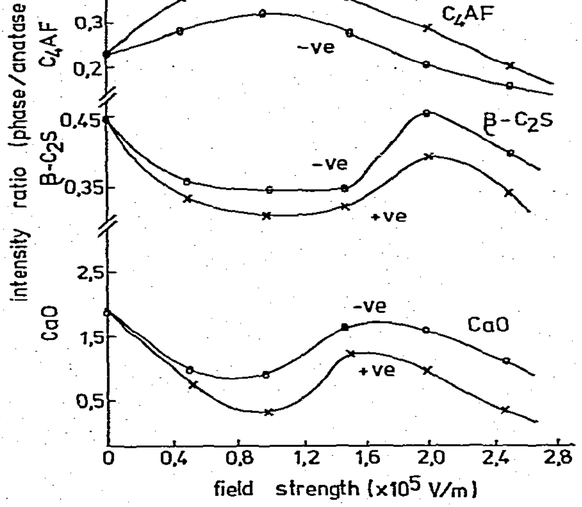


Fig. 2. Effect of electrolysing field strength on the development of clinker phases at 1200 °C for 2 h. Reaction atmosphere, air; electrode material, platinum.

consumption of CaO and the formation of some of the product phases, particularly C_4AF, and (2) the greatest effect, both on the consumption of reactant and the formation of new phases is observed at the positive electrode at all field strengths. The only apparent exception to both these results is β-C_2S, the amount of which is apparently depressed by electrolysis, particularly at the positive electrode. The behaviour of β-C_2S is, however, consistent with the other results, since this phase acts as an intermediate which is consumed by the formation of other phases. Thus, at the positive electrode, the greatest depletion of β-C_2S will occur, since this is where the greatest formation of other phases occurs.

Another point emerging from Fig. 2 is that the highest electrolysing field strength is not necessarily the best for promoting phase formation. Since the phases are interdependent, but with different formation kinetics, this result probably also reflects differences in the effect of the electric field on the formation kinetics of the various phases. To be on the safe side, field strengths of 2×10^5 V/m were used in all subsequent experiments.

Effect of electrolysis temperature. The effectiveness of electrolysis in assisting the ionic movements necessary for the formation of new phases will clearly vary differently with temperature for the different phases. Moreover, the optimum electrolysis temperature for the formation of a particular phase will be related to the unelectrolysed formation kinetics of that phase, since similar ionic movements are involved whether the material is electrolysed or not. In addition, however, the temperature dependence of electrical mobility of each migrating species becomes important; although, in the present system, there are only four major migrating cationic species (Ca^{2+}, Si^{4+}, Al^{3+} and Fe^{3+}) and one anionic (O^{2-}), there are several different oxide matrices through which these species must move.

Figure 3 shows the temperature dependence of the formation of product phases and the consumption of CaO, both in unelectrolysed samples and in the positive and negative electrode regions of electrolysed samples. It is seen that, over the whole temperature range, electrolysis affects the phase compositions, and, as in the field strength dependence studies, different phase compositions are recorded at the positive and negative electrodes.

In the case of CaO, the shape of the unelectrolysed curve can be understood in terms of an increase in the rate of $CaCO_3$ decomposition at about 1000 °C, followed by a decrease in CaO content as the rates of formation of the other Ca-containing phases become significant. Figure 3 shows that the consumption of CaO due to the formation of other phases occurs at lower temperatures under electrolysis (i.e. the electrolysed curves have been displaced to the left by about 100 °C) and, moreover, the process is most efficient at the positive electrode, consistent with the field strength dependence measurements.

The curves for β-C_2S show a slight increase in this phase at lower temperatures, the greatest increase being at the negative electrode. At 1200 °C, the situation is changed by the formation of other phases at the expense of β-C_2S, especially at the

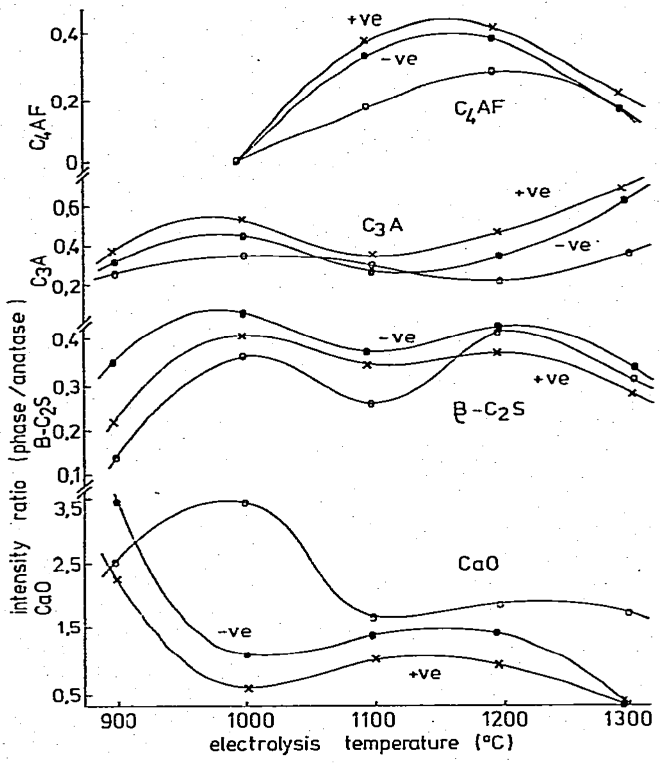


Fig. 3. Effect of electrolysis temperature on the development of clinker phases. Field strength = 2.0 × 10^5 V/m; time = 2 h. Reaction atmosphere, air, electrode material, platinum.

positive electrode; the concentration of β-C_2S at this electrode drops below the unelectrolysed control at higher temperatures.

The curves for C_3A and C_4AF are of similar shape to those of the unelectrolysed samples, but the amount of each has been increased by electrolysis, particularly at the positive electrode. The inter-relation of these two phases can be clearly seen from the curves of Fig. 3. Below 1000 °C, no C_4AF is detectable by X-ray in electrolysed or unelectrolysed samples, and the C_3A content increases with increasing temperature, especially at the positive electrode. Above 1000 °C, C_4AF formation begins, particularly under electrolysis, and simultaneously the C_3A content decreases. Above 1200 °C, the C_4AF content slowly decreases, and a simultaneous increase in C_3A content is recorded. All of these trends are more pronounced in the electrolysed samples, although the curve shapes (and therefore the reaction mechanisms) are unchanged by electrolysis. The theoretical implications of these results are considered further in Part II of this paper[11].

The effect of electric fields on phase formation kinetics

As in the case of the field strength and temperature dependence studies, the results of the time dependence studies at different temperatures are complex, representing a balance between the thermal generation of reactants such as CaO and the consumption of reactant and intermediate phases to form products. In general, the

TABLE 2

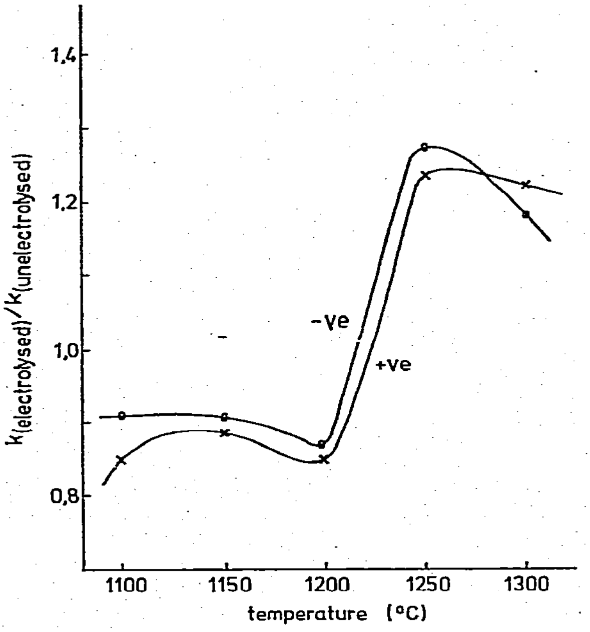
INITIAL RATE CONSTANTS FOR THE FORMATION OF CLINKER PHASES IN ELECTROLYSED AND UNELECTROLYSED SAMPLES

Phase	*Temperature* (°C)	*Initial rate constant* (min^{-1})		
		Unelectrolysed	+ve	−ve
CaO	1100	2.92	2.50	2.67
	1150	2.83	2.53	2.58
	1200	3.03	2.57	2.60
	1250	2.43	3.02	3.08
	1300	2.58	3.15	3.05
β-C_2S	1100	1.50	1.25	0.82
	1150	0.55	1.10	1.10
	1200	0.88	1.10	1.28
	1250	1.67	0.97	1.33
	1300	1.15	0.58	0.98
C_3A	1200	0.03	0.20	0.08
	1250	0.50	0.77	0.48
	1300	0.47	0.62	0.55
C_4AF	1100	0.06	0.37	0.20
	1150	0.10	0.30	0.60
	1200	0.42	0.36	0.50
	1250	0.42	0.33	0.42
	1300	0.42	0.13	0.45

results of these experiments confirm the conclusions of the previous experiments.

Although, because of their complexity, these kinetic results are not amenable to conventional kinetic treatments (the extraction of activation thermodynamics, etc.), an evaluation of the reaction rates at short reaction times is instructive. Since the initial portions of all the curves are approximately linear, the initial rate constants can be approximated to the slopes of these lines. The resulting rate constants are shown in Table 2.

Since the system undergoes a number of concurrent and sequential reactions over the temperature range of Table 2, plots of the natural logarithm of these rate constants vs. reciprocal temperature are not linear, but the ratios of the rate constants for electrolysed and unelectrolysed samples illustrate clearly the manner in which the effect of the field varies with temperature. Such plots of $k_{(\text{electrolysed})}/k_{(\text{unelectrolysed})}$ are shown for CaO, β-C_2S, C_3A and C_4AF in Figs. 4–7 respectively. It should be noted that the data for CaO are expressed in terms of $(1\text{-}\alpha)$, where α is the fraction reacted; i.e. these results refer to the rate of consumption of CaO. In Figs. 4–7, values of the ratio of rate constants greater than unity indicate an enhancement of the reaction rate by the field, whereas ratios less than unity indicate retardation by the field. Figure 4, therefore, indicates that only above 1200°C does the field become effective at short



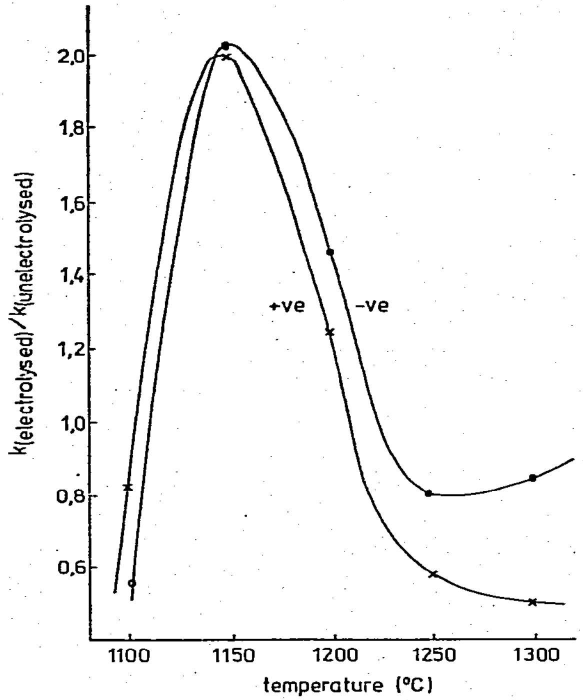


Fig. 4. Variation of the ratio of electrolysed to unelectrolysed initial rate constants with temperature for CaO depletion in clinker.

Fig. 5. Variation of the ratio of electrolysed to unelectrolysed initial rate constant with temperature for β-C_2S formation in clinker.

times in promoting the consumption of CaO by the formation of products. (At lower temperatures, the field is more beneficial in promoting the production of CaO than its consumption.)

The curves for β-C_2S (Fig. 5) show that the formation of this phase is enhanced by the field only in the relatively narrow temperature range between about 1125 and 1200 °C; at higher temperatures, the field becomes more effective in bringing about the formation of other Ca-containing phases at the expense of β-C_2S.

Figure 6 shows that, at all temperatures, the formation of C_3A is enhanced by the field, but the effect is more noticeable at lower temperatures, decreasing with increasing temperature as the normal thermal processes of the reaction become increasingly significant. Differences in C_3A content at the two electrodes also becomes less marked with increasing temperature.

A similar trend is seen in the behaviour of C_4AF (Fig. 7), except for the cross-over in electrode properties between 1100 and 1150 °C. This curious result may be due either to (a) the retention to higher temperatures of protons in the spinel phase formed from the kaolinite component, or (b) the temperature-dependent reduction of Fe^{3+} at the negative electrode. In the first case, proton retention up to > 1100 °C in dehydroxylated kaolinite has been reported[8]. These species are eventually evolved as water, or, in the presence of reducing agents, as molecular hydrogen[8]

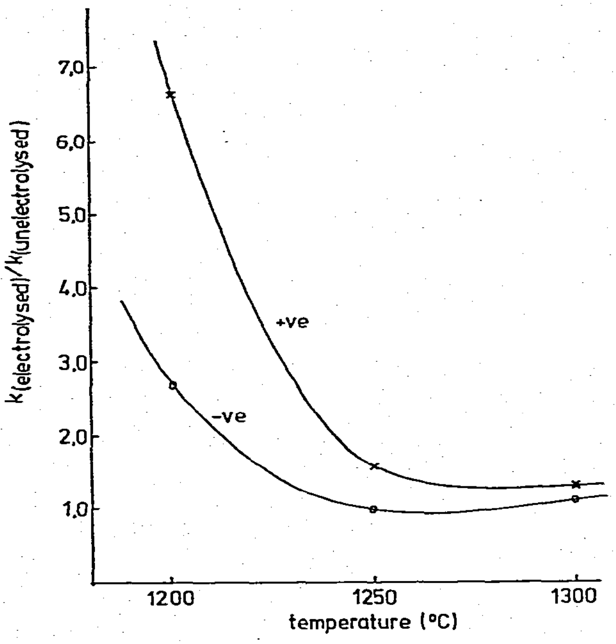


Fig. 6. Variation of the ratio of electrolysed to unelectrolysed initial rate constant with temperature for C_3A formation in clinker.

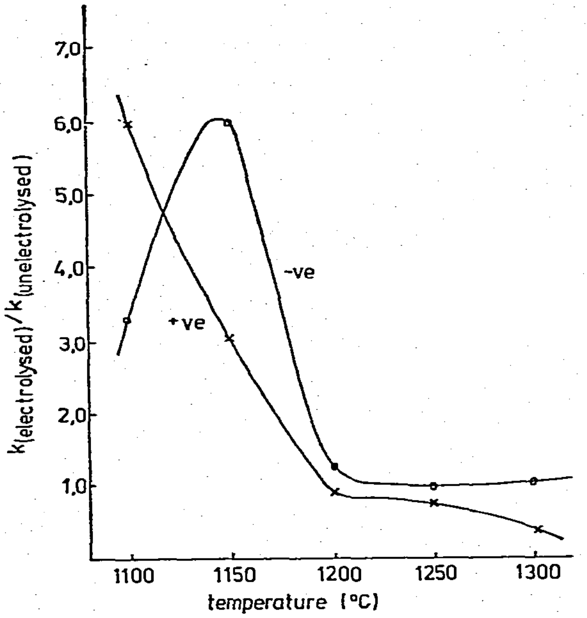


Fig. 7. Variation of the ratio of electrolysed to unelectrolysed initial rate constant with temperature for C_4AF formation in clinker.

$$2\,H^+ + 2\,e^- \rightarrow H_2 \qquad (1)$$

Such a reaction is feasible at the negative electrode in the present case. The presence of either water or hydrogen at the negative electrode will enhance the formation of C_4AF at that electrode[12].

In case (b), the effect of electrical reduction of Fe^{3+} is difficult to predict, although the result might be similar to that of mild chemical reduction, which has been reported[9] to assist the formation of C_4AF by repressing the solid solution of C_3A in C_4AF. On the other hand, more extensive chemical reduction of C_4AF results in its decomposition to Fe metal, C_3A, CaO and H_2O (ref. 10); this would account for an observed decrease in C_4AF content in electrolysed samples at 1300 °C. At intermediate temperatures, a balance appears to be maintained between the field-induced reactions which tend to enhance C_4AF formation on the one hand, and its decomposition on the other. In these cases, little difference is found between the C_4AF content of the electrolysed and unelectrolysed samples except at the shortest firing times.

CONCLUSIONS

Electrolysis markedly affects the amount of the various phases formed, particularly at higher field strengths. The overall reaction sequence is unchanged by electrolysis, but the reaction processes are accelerated, occuring at shorter times or lower temperatures.

The generation of CaO by the thermal decomposition of $CaCO_3$ is enhanced by electric fields, particularly at the positive electrode, at which the development of all product phases is also greatest.

Determinations of the initial rate constants for electrolysed and unelectrolysed samples show that the consumption of CaO by formation of the clinker phases is significantly facilitated by the field above 1200 °C. Below this temperature, this process is offset by the field-enhanced generation of CaO by thermal decomposition of $CaCO_3$.

The formation of β-C_2S is most markedly enhanced by electric fields between about 1120 and 1220 °C. A higher β-C_2S content is observed at the negative electrode than at the positive, due to enhanced formation in the latter region of other phases at the expense of C_2S.

The formation of C_3A is most enhanced by electric fields at temperatures below 1250 °C, the greatest enhancement being at the positive electrode at all temperatures. With increasing temperature, the effectiveness of the field in promoting C_3A formation decreases, and the difference in C_3A content between the two electrodes becomes less marked.

The formation of C_4AF is most enhanced by electric fields at temperatures below 1200 °C. The electrode at which greatest enhancement occurs depends on the temperature, possibly due to competing temperature-dependent electrode reactions involving protons, or the reduction of Fe^{3+}.

REFERENCES

1 A. J. Majumdar, *Silic. Ind.*, 32 (1967) 297.
2 K. J. D. MacKenzie, *J. Therm. Anal.*, 5 (1973) 5.
3 K. J. D. MacKenzie, *Trans. J. Br. Ceram. Soc.*, 74 (1975) 121.

4 K. J. D. MacKenzie, *Trans. J. Br. Ceram. Soc.*, 74 (1975) 127.
5 O. P. Mchledlov-Petrosyan and M. G. Stephanenko, *Dokl. Akad. Nauk SSSR*, 141 (1961) 172.
6 G. D. Uryvaeva, A. T. Logvinenko and A. S. Tretyakova, *VI Int. Congr. Chem. Cement, Moscow, 1974*, Suppl. Paper, Sect. I, 1–4.
7 K. J. D. MacKenzie, *Proc. Brit. Ceram. Soc.*, 19 (1971) 207.
8 K. J. D. MacKenzie, *J. Inorg. Nucl. Chem.*, 32 (1970) 3731.
9 I. F. Ponomarev, A. N. Grach'yan and P. P. Gaidzhurov, *Issled. Obl. Khim. Silik. Okislow*, Akad. Nauk SSSR, Sb. Statei, 1965, p. 271.
10 V. G. Matyash, L. I. Leontev and G. I. Chufarov, *Dokl. Akad. Nauk SSSR*, 207 (1972) 1413.
11 K. J. D. MacKenzie, *Thermochim. Acta*.
12 K. J. D. MacKenzie, to be published.