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EFFECTS OF MINOR COMPONENTS AND HEATING RATES ON THE FINE TEXTURES OF ALITE IN PORTLAND CEMENT CLINKER

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ABSTRACT

The fine textures of alite vary sensitively with heating rates and minor components in clinker. The phase constitution (the ratio of M_3 to M_1) and the morphology of alite do not necessarily change monotonously with the heating rate. MgO and Na_2O favor the formation of the M_3 phase whereas P_2O_5 and SO_3, especially the former, enhance the occurrence of the M_I phase. The heating rate and the minor component interact with respect to the phase constitution of alite. These results were explained systematically in terms of the growth environment of alite in clinker and the replacement of minor elements in the structure of alite. © *1997 Elsevier Science Ltd*

Introduction

The fine textures of the constituent minerals in Portland cement clinker vary to a considerable extent with the processing conditions, exerting a great influence on the quality of resulting cement (1-3). Accordingly, the evaluation of the fine textures is important to the process and quality control in clinker manufacturing. Alite crystals in portland cement clinker, which are precipitated from the interstitial liquid supersaturated as regards CaO and C_2S (4,5), usually occur in M_3 or M_1 or in their hybrid at ambient temperature (6-8). The phase constitution of alite depends primarily on the amount and kind of impurities incorporated into alite during crystallization from the interstitial liquid (9-11). The concentration of minor components in alite depends on the growth rate as well as on their concentration in the interstitial liquid. The crystal growth of alite can be divided into two modes, stable and unstable, with widely different fine textures (5,7). The unstable growth, in which alite crystals grow at high rate entrapping a large number of inclusions, leads to the large size and irregular outer shape of alite crystals. M_1 tends to occur because of a high concentration of impurities as Al_2O_3 and Fe_2O_3 in solid solution. In the stable growth, on the other hand, faceted crystals occur with a scarcity of inclusions. The impurity concentration is relatively low in favor of the occurrence of M_3. Taking into account the fine texture change of alite as mentioned above, the growth environment of alite in the early stage of clinkering was classified into the following three categories in order of decreasing initial supersaturation of C_3S (7,10).

1. High nucleation and low growth rate (nucleation predominant)
2. Low nucleation and high growth rate (growth predominant)
3. Low nucleation and low growth rate (extended nucleation and growth)

Based on this classification, the present study deals quantitatively with the influence of heating rates and minor components on the phase constitution and the grain size of alite.

Materials

The raw mixes were prepared with limestone, clay and chemical reagents. The chemical composition of the standard clinker to be obtained after burning was: SiO_2 22.5, Al_2O_3 5.3, Fe_2O_3 3.1, CaO 66.0, MgO 1.4, P_2O_5 0.2, SO_3 0.7, Na_2O 0.39 and K_2O 0.56 by weight percent. HM, SM, IM and LSD were 2.14, 2.70, 1.70 and 0.93, respectively. A series of raw mixes with increased concentration of Mg, Na, P and S were prepared by adding reagent $MgCO_3$, $NaCO_3$, $CaSO_4 \cdot 2H_2O$ and $Ca(H_2PO_4) \cdot 2H_2O$ to the standard raw mix. The raw mixes, after being pelletized and calcined at 1000°C for 30 minutes, were heated up to 1600°C at given rates between 10 and 50°C/min, retained for 5 minutes, cooled down to 1450°C at 38°C/min and then quenched. Clinker specimens isothermally burnt at 1600°C were also prepared for comparison. The atmosphere during burning and quenching was air.

Experimental

The volume ratio of M_3 to M_1 in alite was determined by the XRD method developed by the authors (3). This method is based on the decomposition of the X-ray diffraction peaks between 51.0 and 52.5° (2θ for CuKα) into those of M_1 and M_3. The X-ray intensity ratios of M_3 to M_1 were calibrated by the ratios obtained by the point counting technique under the microscope. M_1 and M_3, widely different in birefringence, can easily be distinguished under the microscope. The grain size of alite crystals were measured on the polished sections for

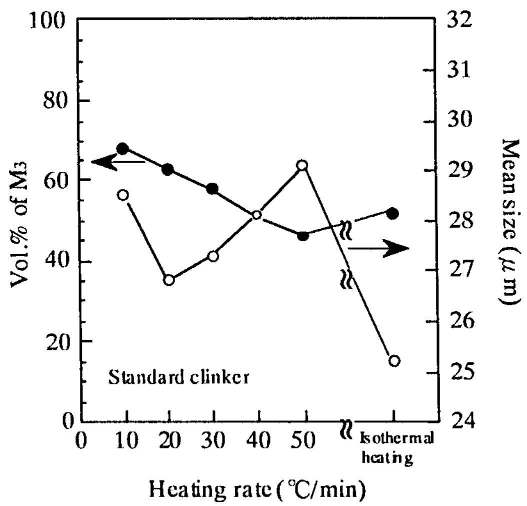
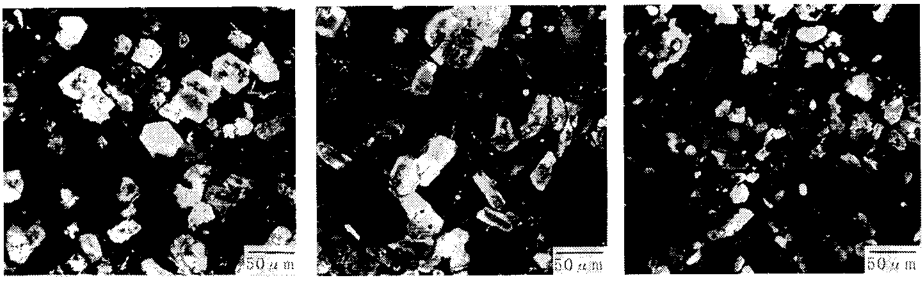


FIG. 1.
Variation of phase constitution and grain size of alite with heating rate.



(a) 10°C/min. (b) 50°C/min. (c) Isothermal heating

FIG. 2.
Variation of fine textures of alite with heating rate.

approximately 1000 grains. The average size was expressed by [Σ(longer diameter × shorter diameter)/number of grains]$^{1/2}$. The morphological instability of alite crystals was also observed. The concentrations of P and S in alite were determined with EPMA.

Results and Discussion

Figure 1 shows the variation of the ratio of M_3 and the mean grain size of alite with increasing heating rate for the standard clinker. M_3 continues to decrease up to 50°C/min, which, as shown in Fig. 2, corresponds to increasing occurrence of zoned crystals with M_1 in the core. Between 20°C/min and 50°C/min, the crystals became large and irregular in shape, especially in the core. These changes in the phase constitution and grain size of alite are considered to be due to the high rate of dissolution of CaO and C_2S into the interstitial liquid and the resultant increase of supersaturation in the early stage of clinkering, i.e., the growth environment of alite changed from category 3 to 2 with increasing heating rate (7,10). In

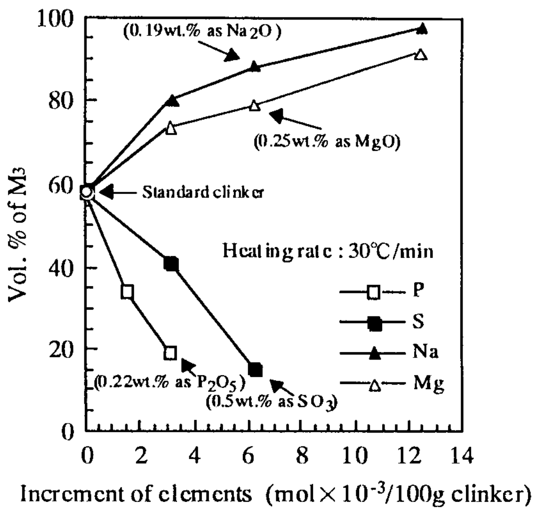
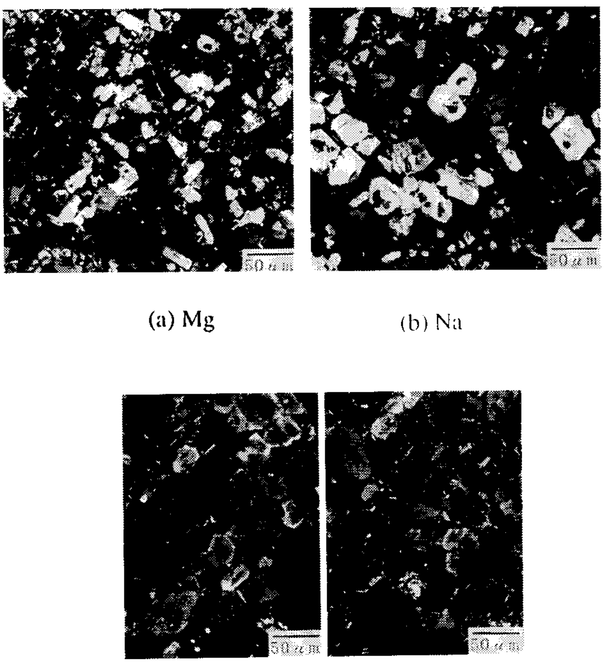


FIG. 3.
Increment of minor elements and the occurrence of the M_3 phase.

other words, the growth rate of alite, as compared with the nucleation rate, was kept high during the initial stage of clinkering. In isothermal burning at 1600℃, the growth environment of alite approximated category 1 and M_3 increased in quantity with a decrease in grain size. At 10°C/min, the alite crystals grew large with facets due to the Ostwald ripening of the crystals formed under category 3 with prolonged retention at elevated temperatures (12). Thus the heating rate exerts a significant influence on the growth environment of alite with the intermediate heating rate promoting the growth process. For a wide range of heating rates, therefore, the monotonous decrease in grain size with increasing heating rate as mentioned by Ono (1) is not necessarily expected.

Fig. 3 shows the effect of the concentration of minor components in clinker on the M_3/M_1 ratio of alite. The increment of the cationic elements was given by mol per 100g clinker. The raw mixes different in impurity concentration were burnt at constant heating rate of 30°C/min between 1000 and 1600°C. Mg and Na promoted the formation of the M_3 phase, while P and S, especially the former, encouraged the occurrence of the M_1 phase. As shown in Fig. 4, the phase change was accompanied by morphology change. The results can be explained in terms of the influence of those minor components on the physical properties of the interstitial liquid and the resultant growth environment of alite in clinker (10,13). The increase of Mg raises the surface tension and lowers the viscosity of the interstitial liquid. These changes of the physical properties promote the dissolution of CaO and C_2S grains (14), causing the increase of supersaturation in the early stage of clinkering. As a result, the



(a) Mg (b) Na

(c) S P

FIG. 4.

Effect of minor elements on the fine textures of alite. Heating rate: 30°C/min; Increment: 6.25×10^{-3} mol/100g clinker for Mg, Na, S and 3.13×10^{-3} mol/100g clinker for P.

TABLE 1

Distribution of P and S into Alite

	P	S
	(mol × 10^{-3}/100g clinker)	
alite (n=10)	5.7 (4.0-6.9)	2.2 (1.1-4.0)
clinker	5.9	7.9

( ) : deviation

nucleation process is encouraged producing a large number of small faceted crystals grown stably and made up mostly of M_3 (Fig. 4a). On the contrary, the increase of Na raises the viscosity and lowers the surface tension of the interstitial liquid, thus depressing both nucleation and growth rates of crystallization. The crystals grew stably throughout with M_3 as the constituent phase (Fig. 4b). P and S lower both the viscosity and the surface tension of the liquid to a considerable extent. The growth environment of alite was such as represented by category 2 in which a small number of nuclei grew at high rate. The growth mode in the early stage of clinkering was unstable in favor of the occurrence of M_1. M_3 was observed only in the periphery of the crystals (Fig. 4c). Despite the similarity in their effect on the physical properties of the interstitial liquid (13), P is much more effective than S in producing M_1. This can be ascribed to the higher solubility of P into alite (M_1 part) as illustrated in Table 1; P is distributed to alite in nearly 2.5 times as much concentration as S though the bulk concentration of P in clinker chemically analyzed is a little lower.

The raw mixes with increased concentration of minor components were burnt at different heating rates. The increment of cationic elements was 6.25×10^{-3} mol per 100g clinker for Mg, Na and S and 3.13×10^{-3} mol per 100g clinker for P. The increment of P was halved

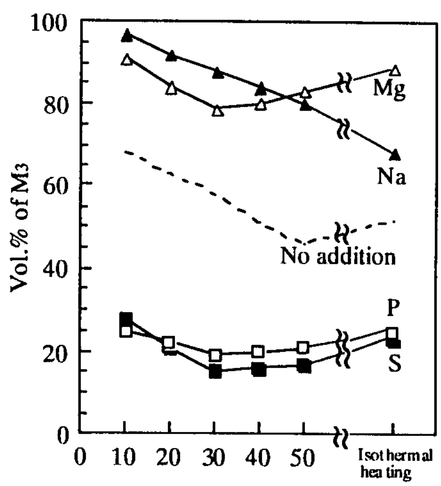


FIG. 5.
Effect of heating rates on the occurrence of M_3 phase with the increment of minor elements.

considering its concentration in alite as mentioned before. Fig. 5 shows the phase constitution of alite. In the case of Mg, M_3 turned to increase beyond 30°C/min. This suggests that with the increment of Mg the initial supersaturation increased as compared with the standard clinker (Fig. 1). With the increment of Na, M_3 decreased steadily with increasing heating rate. The rise in initial supersaturation was so small that the growth process remained predominant in the crystallization of alite. No remarkable phase change was observed with the increment of P and S. The slight increase in the M_3 content at higher rats can be ascribed to a small increase of the initial supersaturation.

Comparison of Figs. 1, 3 and 5 shows that concerning the influence on the phase constitution of alite the minor component is superior in effect to the heating rate. This indicates that the minor components in solid solution are most influential on the phase constitution of alite at ambient temperature, i.e., the replacement of the Ca sites by Mg and Na encourages the occurrence of M_3 and that of the Si sites by P and S the occurrence of M_1 (11,15). The transition elements (d-block elements) were shown to be amphoteric in effect according to their redox state (10).

Summary

1) The heating rate of clinker influences the growth environment of alite, especially the supersaturation in the early stage of clinkering, and changes the resultant phase constitution and grain size of alite. The relations of heating rate to the phase constitution and the grain size are not necessarily monotonous.
2) Minor elements widely change the physical properties of interstitial liquid and thus influence the growth environment of alite. Minor elements replacing the Ca and the Si sites in alite structure favor respectively the occurrence M_3 and M_1 at ambient temperature.

Acknowledgments

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