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Communication

Effect of CaF_2 and MgO on sintering of cement clinker

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Abstract

CaF_2 (0.25, 0.50, and 1%) and MgO (1, 2, and 3%) was added to a mixture composed from limestone, sand, and loam, then burned at 1410°C for 112 min. Clinker samples were cooled to room temperature and the amount of free lime (CaO_f) was determined by titration while the relative amounts of alite and belite were determined by X-ray diffraction (XRD). Microstructure was investigated by scanning electron microscopy (SEM). The amount of alite decreased in CaF_2-added samples and the amount of belite increased. The CaO_f content of the sample containing 1% MgO was less than that of the pure sample. For the other MgO-added samples, due to the increase in lime saturation factor value no evident change was detected in the amount of CaO_f. Both XRD and SEM analyses showed a decrease of the amount of alite and an increase of the amount of belite in MgO-added samples when compared to pure samples. The reason for the decrease in amount of alite in MgO-added samples is believed to be coarse belite crystals. Due to the prolonged holding time at the alite formation temperature, coarse belite crystals were formed. Because of the high diffusion rate at this period, belite crystals lose their surface activity and consequently alite formation was hindered. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Clinker; Fluoride; MgO; Admixture

1. Introduction

CaF_2 and MgO are added to the raw mix to improve the raw mix burning. These materials decrease the formation temperature of the clinker minerals by increasing the calcination, solid-state reaction, melt, and alite formation rate [1–4]. It is possible to reduce the specific burning heat without decreasing the clinker quality in this manner [5].

CaF_2 lowers the alite formation temperature by improving solid-state diffusions. CaF_2 also reduce the liquid phase viscosity and surface tension. Low viscosity has a positive effect on liquid phase reactions. Low surface tension causes porous and fine-grain clinker formation. This type of clinker has low sintering shrinkage and good grindability. However, clinker dustiness increases and it affects the thermal gradient negatively during technical processes [6]. CaF_2 addition changes the clinker constituents. Alite with fluorine or $C_{11}A_7CaF_2$ may form during sintering. Pseudoalite ($3C_3S \cdot CaF_2$) and Fluore-Spurrite ($2C_2SCaF_2$) form only as intermediate phases and these compounds accelerate the indirect lime bonding [6]. Compounds of tentative compositions $(3CaO \cdot SiO_2) \cdot CaF_2$ and $(2CaO \cdot SiO_2)_2CaF_2$ have been characterized [7,8]. $\beta \rightarrow \gamma$-C_2S conversion may increase, especially in slow-cooled clinkers when the CaF_2 addition is higher than 2%. Fluorine amount must be limited in raw mix, because the properties of cement may change. Cements with clinker containing fluorine solidify slowly. Generally, C_3S formation increases with the addition of fluorine. However, fluorine addition to raw mix should not be more than 0.5% (no reaction acceleration and decrease in strength) and, at the same time, clinker should have a high lime saturation factor [9]. The maximum fluorine amount is approximately 0.25–0.6% (0.5–1.2% CaF_2) by weight. Fluorine evaporates easily, like alkalies and sulfates do. Fluorine in clay minerals turns into gas phase by thermal decomposition and circulates in the furnace [10]. Condensation occurs in the cool region of the kiln and fluorine reacts with excess CaO to form CaF_2. The entrance rate of fluorine to the clinker was measured to be 88–98% according to the Bilanz measurements [11].

MgO also decreases the liquid phase viscosity and provides the formation of liquid phase at lower temperature. In addition, the amount of liquid phase increases. These factors play an important role in the acceleration of clinker phase formation. Generally, the amount of MgO is up to 2% in clinkers. Free periclase appears when the addition ex-

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Table 1
Addition amount (weight %) and modules of samples

Sample	A	B	C	D	E	F	G
CaF_2	–	0.25	0.50	1.00	–	–	–
MgO	–	–	–	–	1	2	3
Lime saturation factor	93.74	93.76	93.75	93.76	95.40	96.16	96.20
Alumina module	2.10	2.10	2.10	2.10	2.10	2.10	2.10
Silica module	2.85	2.85	2.85	2.85	2.85	2.85	2.85

ceeds 2.5% by weight. The solubility of MgO in clinker increases with temperature. In a study at 3.2% MgO and 1400°C burning temperature conditions, it was found that 1.6% MgO was free [12]. Since the volume expansion of MgO hydrating to $Mg(OH)_2$ appears over a longer time than free lime, it is more dangerous. If the MgO content is greater than 2.5% with a high cooling rate (greater than 40 K/min), free MgO appears as a fine crystalline periclase [13]. With a slow cooling rate (10–20 K/min), all periclase may crystallize. At a medium cooling rate, periclase does not have sufficient time for idiomorphic crystallisation, and dentritic and fine crystallisation takes place [14]. In this study, the effect of different amounts of CaF_2 and MgO addition on the sintering of raw mix have been investigated.

2. Methods

The CaF_2 and MgO additions to the limestone, loam, and sand raw mix are given in Table 1. A drop of diethylene glycol was added as a dispersant to the raw mix; it was then homogenized in a laboratory-type ceramic grinder until the 90-μm residue sieve 10% is reached. The raw mix was granulated using a granulation plate with 10% water addition. After drying the granules (3–10 mm in diameter), they were weighed in a platinum basin. The raw mix was burned at 1410°C for 112 min (36.9 K/min up to 1200°C at the first period, 5.3 K/min up to 1410°C at the second period, holding for 40 min at 1410°C at the third period) in a gradient furnace. Clinker samples were cooled at room temperature. The amounts of CaO_f in the samples were determined by the Schlaepfer-Bukowsk titration method. Relative amounts of alite and belite in CaF_2 and MgO mixed and unmixed samples were compared by X-ray diffraction (XRD) analyses. Microstructures of the samples were investigated by scanning electron microscopy (SEM).

3. Results and discussion

The CaO_f amounts of the mixed and unmixed clinker samples are given in Fig. 1. It was found that the amount of CaO_f decreases with increasing CaF_2 content. The reason for the CaO_f reduction is the increase in the speed of the solid-state reaction due to the easy diffusion effect of fluorine and the acceleration of the necessary reactions for clinker phase formation due to the low-viscosity fluorine melts. Similar results were not obtained in MgO-added samples. To find the reason for the low CaO_f content in sample E, microprobe analysis was conducted of samples A and E. The Ca/Si ratio of C_3S and C_2S crystals in sample E was lower than that in sample A. The Ca/Al ratio of calcium aluminate in sample E was again lower than that in sample A. The reason for the lower amount of CaO_f in sample E may be the increase in the amount of belite. Relatively higher amounts of belite were observed by XRD analysis in MgO-added samples compared to sample A. The reason for the high amount of CaO_f in samples F and G may be the increase in lime saturation factor due to the change in the chemical composition with the addition of MgO so that burning time of high lime saturation factor clinker should be longer.

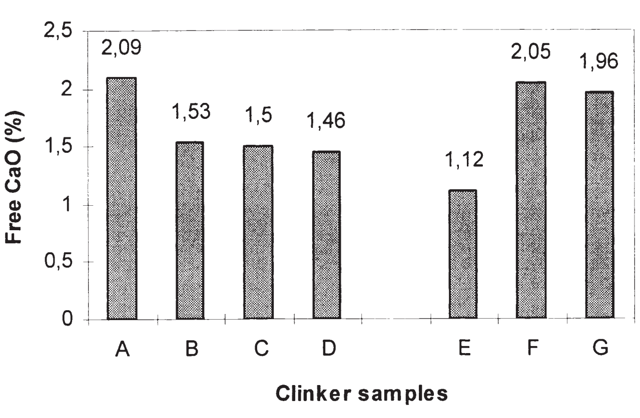

Fig. 1. Free amounts CaO in clinker samples.

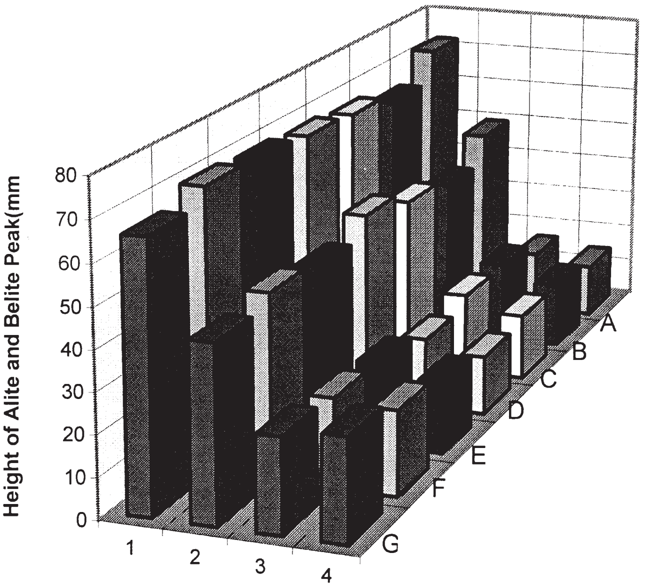

Fig. 2. Height of alite (1: $d = 2.606$ Å, 2: $d = 2.184$ Å) and belite (3: $d = 2.403$ Å, 4: $d = 2.091$ Å) peaks of clinker samples (A–G).

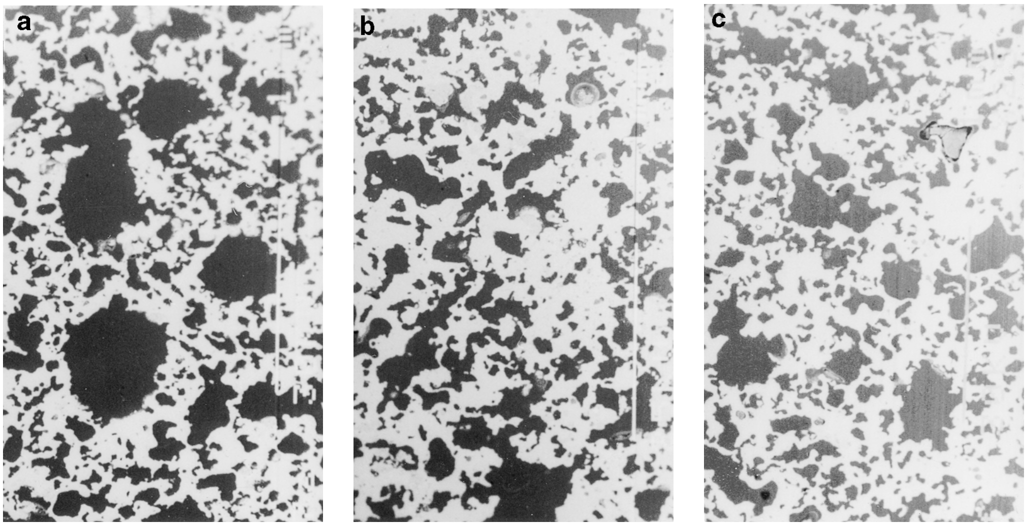

Fig. 3. SEM of clinker samples (a) A, (b) B, and (c) E.

To compare the relative amount of alite in mixed and unmixed samples, intensities of nonoverlap alite XRD peaks were investigated. Alite forms are observed as monoclinic. Absolute amount of alite cannot be determined here. Lower alite peak height was observed in MgO-added samples (E, F, and G) with respect to sample A (Fig. 2). The burning time (112 min) of the samples having high lime saturation factor was not sufficient for sinterisation due to the addition of MgO. The reason for the lower amounts of alite and CaO_f in sample E may be coarse belite crystals. Accumulative crystallization (Sammelkristallisation) under the alite formation temperature may be why coarse belite crystals formed. Belite peak height of sample E was higher than that of sample A. The reduction of alite content with an increase in amount of belite in sample E is shown in Fig. 2. An increase in the relative amount of alite and a decrease in the amount of CaO_f in CaF_2-added samples was expected. A low amount of alite with a low amount of CaO_f in CaF_2-added sample may again be due to the coarse belite crystals. The relatively high amount of belite crystals observed in XRD analysis was proved by SEM.

The microstructures of samples A ,B, and E were investigated by SEM (Fig. 3). Sample E has a lower porosity than sample A, because the high liquid phase quantity causes easy sintering and consequently lowers the porosity. The quantity of coarse pores was reduced and the ratio of fine pores decreased in sample E. These pores have a round and elongated shape. Irregular pores are connected in some situations. No important differences were observed between samples B and A. However, sample B has a higher amount of fine pores. The sintering of CaF_2-containing samples was improved.

CaO_f crystals are randomly distributed individually (10–60 μm) and as groups (up to 250 μm). No important differences were observed in CaO_f crystal size and distribution in mixed and unmixed samples. Periclase crystals in the samples containing added MgO were mostly less 1 μm in size and distributed homogeneously. Periclase crystals up to 8 μm do not show magnesia coarsening. No important differ-

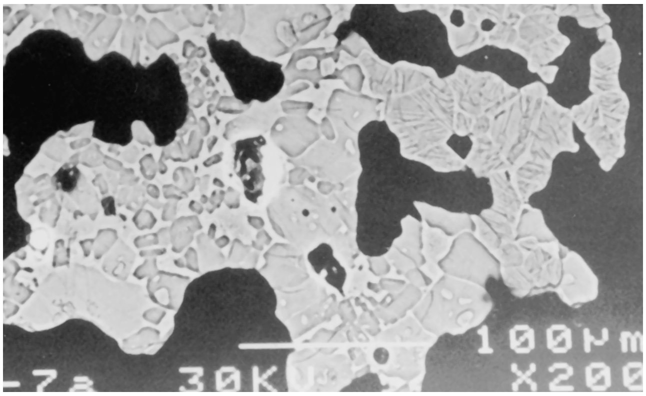

Fig. 4. SEM of clinker sample A.

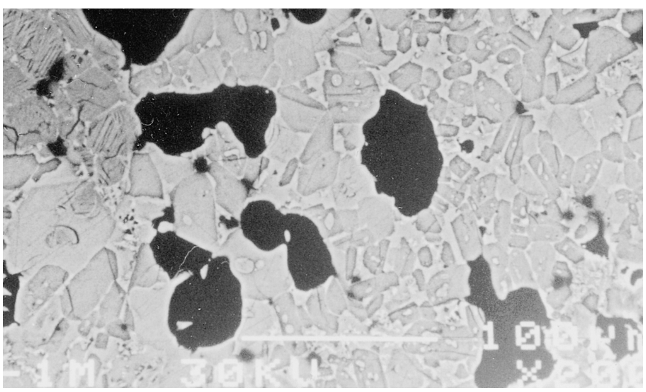

Fig. 5. SEM of corroded alite crystals of clinker sample F.

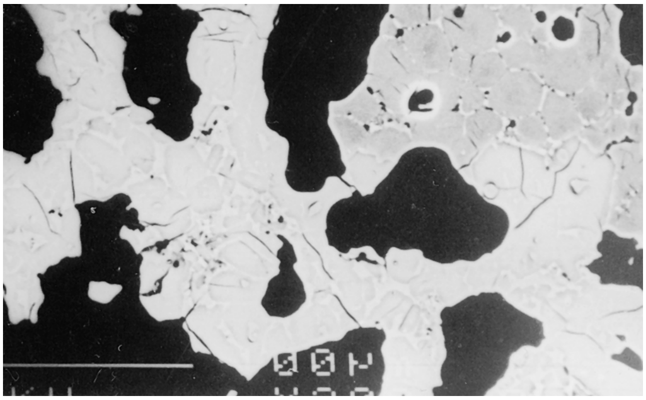

Fig. 6. SEM of lamellar belite of clinker sample F.

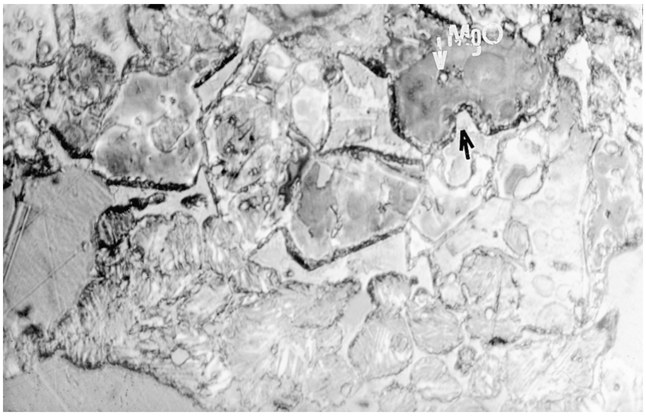

Fig. 7. Belite particles showing parallel (L) and cross-lamellar (K) structures of sample C.

ences were observed between samples A, B, and E (Fig. 4). However, higher amounts of intermediate phases are present in sample E due to the MgO addition, which causes an increase in liquid phase. In Fig. 5, the corroded alite crystals in sample F are shown. Small belite crystals that surround the alite were formed due to the redissolution of alite during slow cooling. Lamellar belites in sample F (Fig. 6) were formed because of the tendency toward accumulative crystallization of belite.

Some lamellar belites begin to grow and as a result coarse belite crystals formed. Similar big belite groups having parallel and cross-lamellar structures appeared around the pores in sample C (Fig. 7). Similar structures have been observed by other researchers [15,16].

4. Conclusions

Because of the high diffusion rate of belite suspended for a long time in the second period of the heating cycle, which has a temperature lower than alite formation temperature, no fault zone and surface activity could take place. Thus alite formation was hindered. The reason for low alite content and high belite content was the short waiting time at the third period. Homogenous distribution of CaO_f proved this conclusion. The second period of the heating cycle should be shortened, while the third period should be lengthened. The best sintering was obtained in the 0.25% CaF_2- and the 1% MgO-added samples.

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