LOW-TEMPERATURE BURNT PORTLAND CEMENT CLINKER USING MINERALIZER

Makio YAMASHITA*1 and Hisanobu TANAKA*1

*1 MITSUBISHI MATERIALS CORPORATION, Cement Research Institute (2270, Yokoze, Yokoze-machi, Chichibu-gun, Saitama 368-8504, Japan)

ABSTRACT: Decreasing the burning temperature of cement clinkers leads to a rational reduction of CO₂ emitted from the cement industries. This study examines the use of CaF₂ and CaSO₄ as a mineralizer or flux. It was possible to reduce the burning temperature 100 °C below that of the current process (1450 °C) by controlling the fluorine and sulfur trioxide in the clinker. The setting and hardening properties of the low-temperature cement equal those of ordinary Portland cement. It was also found that the coating effect of additional mineralizer components on the preheater was insignificant.

KEY WORDS: Low-temperature burning, Mineralizer, Flux, Fluorine, Sulfur trioxide, Clinker mineral, Cement properties, Preheater coating

1. INTRODUCTION

The cement industry consumes much energy and accounts for six percent of the total carbon dioxide (CO₂) emissions from stationary sources1). The reduction of CO₂ and the conservation of energy are social demands for the cement industry. However, in the cement industry, appreciable amounts of energy have been saved or conserved over time2). At this point, cost-effective ways of conserving energy are difficult to find. Lowering the burning temperature of clinker could be regarded as a pathway to reduce CO₂ emissions.

Clinker burning requires high temperatures because the stabilization of alite requires a high temperature, and alite forms more slowly than other clinker minerals. The rate of alite formation is controlled by the dissolution and the diffusion of CaO through the melt. Lower melting temperature and viscosity and increased liquid phase accelerate alite formation. A mineralized or flux agent changes the properties of the melt phase. In general, as the flux agent becomes more electronegative, the melt becomes more viscous.

Fluorinated salts accelerate the formation of clinker minerals because of their high electronegativity3) 4). In addition, sulfur, chloride, and heavy metal (e.g., lead) behave as flux in clinker production. However, these components may affect cement properties, stable plant operation, and the environment.

Many studies have focused on reducing the burning temperature by adding salts containing fluoride, on a percent order5). However, few have addressed the problems mentioned above. Chloride input in a clinker production system is restricted not only by compliance with quality standards of cement, but also by the need to avoid preheater kiln operational problems that result from a high concentration of chloride in the preheater. Also, increased heavy metals (e.g., lead) in cement may dissolve from concrete or mortar products. In this study, we used calcium fluoride (CaF₂) and calcium sulfate (CaSO₄) as the mineralizer or flux for ordinary Portland cement clinker burning. We investigated the conditions of the mineralizer, which enables a 100 °C reduction in clinker burning temperature. Also, clinker and cement properties obtained at low burning temperature were investigated. Fluoride volatility in the burning process was examined in order to determine its condensation in the area between the rotary kiln and the preheater, which may result in coating formation.

2. EXPERIMENTAL

2.1 Fabrication of Clinkers

Each clinker was prepared in such a way that the moduli were the same as those of ordinary Portland cement clinker. Raw metal from a cement plant and commercially available reagents (e.g., calcium carbonate, silicon oxide, aluminum oxide, iron oxide, calcium sulfate, alkali carbonate, and calcium fluoride) were used as starting materials to adjust the clinker moduli,
along with sulfur oxide, alkali oxide, and fluorine in the clinker. A minimal amount of reagents (10%) was used to adjust the clinker’s moduli and minor elements. The mixture of starting materials was calcined at 1000 °C for 60min and then burned at 1450 °C for 90min in an electric furnace, and quenched in air.

JIS R 5204 : 2002 “Chemical analysis method of cement by X-ray fluorescence” and Japan Cement Association Standard (JCAS I-01 : 1997 “Determination method for free calcium oxide” were used to determine the chemical composition and the free lime (f.CaO) amount of the clinker. Florine (F) content in clinker was determined in accordance with spectrophotometry in combination with steam distillation (JCAS I-51 : 1981).

2.4 Fabrication of Cement
The obtained clinker was crushed in a jaw crusher and roughly ground with a ball mill under constant conditions. Reagent gypsum was added to adjust the total sulfur oxide (SO₃) content in cement to 2.1 % when the SO₃ content in the clinker was less than 1.3 %. When the SO₃ content in the clinker was more than 1.3 %, reagent gypsum addition was constant at 0.8 % SO₃. The mixture was further ground with a ball mill to a Blaine specific surface area (Blaine value) of 3250 ± 50cm²/g.

2.5 Physical Testing of Clinker and Cement
The bulk density of the clinker was determined by filling a 400mL container and weighing the amount of clinker with a particle size of 2 to 5mm to fill the container. The number of revolutions of the finishing mill required to obtain the intended Blaine value was used to evaluate the grindability of the clinker. Fewer revolutions indicated superior grindability. Bruker’s D8 ADVANCE and TOPAS Version 3 were used to acquire an X-ray diffraction (XRD) profile and used for the Rietveld calculation of the mineral composition. The sample preparation, XRD measurement conditions, and Rietveld analysis method were the same as in the reference⁶. Tests for setting time and compressive strength of the cement were carried out in accordance with JIS R 5201 : 1997 “Physical testing method for cement.”

3. RESULTS AND DISCUSSION
3.1 Effect of the Mineralizer
Figure 1 illustrates the relationship between F content and f.CaO content in clinker at burning temperatures of 1300 °C and 1350 °C. The f.CaO content in clinker that is burned at the same temperature decreases with an increase in F. This result demonstrates the effect of CaF₂ as a mineralizer. Furthermore, SO₃ content in clinker enhances burnability and strengthens the effect of mineralization of CaF₂. The improved burnability of a high F and high SO₃ clinker can be explained not only by reduced viscosity and surface tension of the oxide melt, but also by increased melt due to eutectic formation of fluoride and sulfate mixtures, which enables alite to form at low temperatures⁷,⁸.

In the present study, the degree of burnability was evaluated by the f.CaO in clinker. When the mineralized clinker was burned at 1350 °C, the F content increased from 0.024% to 0.067%, and the SO₃ content increased from 0.6 % to 2.2 %, thus achieving the same burnability as the normal clinker burned at 1450 °C. In addition, in the clinker burned at 1300 °C, as the F content was increased up to 0.27 % and the SO₃ content was increased up to 2.2 %, the burnability was equal to that of the normal clinker burned at 1450 °C.

Table 1 presents the chemical composition of mineralized clinkers burned at 1350 °C and 1300 °C in which mineralizer content was adjusted to same burnability as normal clinker burned at 1450 °C.

Although the Na₂O and K₂O contents in the raw
mix of all clinkers were adjusted in the same way, the mineralized clinkers burned at low temperatures had somewhat higher alkali content, due to their reduced volatility.

3.2  Clinker minerals

Conventional clinker minerals (e.g., alite, belite, aluminate, and ferrite) were easily identified in all clinkers by XRD. Other minerals containing F or SO₃ such as fluoroaluminates (C₃A · CaF₂) and calcium langbeinite (K₂SO₄ · 2CaSO₄) were not identified with XRD methods. However, the alite polymorphs differed in the samples studied here. In commercial clinker, alite exists in two crystal systems (M₁ and M₂), in which the polymorphic state is reflected in the diffraction peak at 2θ = 51.5° (CuKα radiation)⁹,¹⁰. The M₁ phase gives a single peak, and M₂ phase gives a double peak. Figure 2 presents their XRD profiles. Alite in mineralized clinker burned at 1350 °C or 1300 °C resulted in M₅, and alite in the normal clinker burned at 1450 °C resulted in M₅. The M₁ phase of the alite in mineralized clinker may be attributed to the high SO₃ content, since it has been demonstrated that doping with SO₃ stabilizes M₀ polymorphs¹¹.

Figure 3 indicates the mineral composition of the mineralized clinkers burned at different temperatures, determined by the XRD/Rietveld method. The mineralized clinker had higher belite and ferrite contents and lower alite and aluminate contents than the normal clinker, mostly due to the influence of higher F and SO₃ in clinker¹²,¹³.

3.3  Physical Properties of Clinker and Cement

(1) Bulk density and grindability of clinker

The bulk density of the clinker was measured since there was a significant difference in shrinkage of the clinker after burning (Figure 4). The mineralized clinker burned at 1350 °C had higher bulk density than the normal clinker burned at 1450 °C, primarily because of increases of SO₃. However, the bulk density of the mineralized clinker burned at 1300 °C was lower than that of other clinkers due to insufficient clinker sintering. Decreasing fCaO in clinker may not necessarily improve the clinker sintering characteristics.

Figure 5 presents the number of test mill revolutions required to achieve a specified Blaine surface area. The grindability of clinker was primarily reflected in the bulk density.
(2) Setting time

Cement was fabricated using mineralized clinkers and gypsum. Figure 6 indicates the setting time of cement burned at different temperatures with or without mineralizer. Setting time differed only slightly between cement burned at 1450 °C and that burned at 1350 °C. However, the setting time of cement burned at 1300 °C was retarded to 50min. In the past study, the setting time was retard to 60min with a 0.1 % increase of F [22].

(3) Compressive strength

Figure 7 illustrates the relationship between clinker burning temperature and cement compressive strength. Compressive strength after three days was not influenced by the clinker burning temperature or the mineralizer in the clinker. However, the cement burned at 1300 °C had lower compressive strength than those burned at 1350 °C and 1450 °C.

From the results of this study, we could not determine a clear reason for the large strength gap between the two cements burned at 1300 °C and burned at 1350 °C. Several studies have focused on the effect of F on cement compressive strength. Most report that F in cement does not negatively affect the strength of cement up to the order of 1 % [22]. In this study, the F content in the cement burned at 1300 °C was at most 0.27 %. We assumed that the decreasing strength of the mineralized cement at 28days was due to the relatively low burning temperature, which decreases active alpha-C2S in the high-temperature phase.

Despite lower alite content in the mineralised clinker burned at 1350 °C, the compressive strength of the cement is the almost same as the one burned at 1450 °C. The reason for this seems to be lower gypsum addition to the mineralised clinker since the gypsum amount in the cement lower compressive strength [14], and particle size of mineralised clinker was smaller than normal one at the same Blaine value of the cement.

3.4 Influence of Mineralizer on Preheater Coating

(1) Influence of fluorine

Chloride in the raw materials and fuels of the clinker burning process causes coating problems in preheater cyclones. The chloride that condenses on the kiln feed or kiln gas reacts with sulfates, resulting in a low melting point composition so that the materials become adhesive and adhere to the preheater equipment. In this section, we discuss the chemical reactivity of fluorine with sulfate, as well as the volatility of fluorine compared with that of chloride. The influence of mineralizers on preheater coating is then investigated.

Figure 8 depicts the phase diagram for the CaSO4–CaCl2–CaF2 system [10]. Fluoride forms a eutectic system with sulfate as well as chloride : eutectic liquid thus appears below the melting point of CaF2. The ternary eutectic temperature is 597 °C. The amount of eutectic liquid increases with fluoride, the same as chloride on a molar basis. Therefore, increasing the fluoride content
in raw material could lead to the emergence of coating or build-up in the upper preheater cyclone stage, as well as chloride.

The F content in the clinker tended to increase linearly with the addition of CaF₂. Here, the burning temperature and SO₃ content in clinker affected the F content in clinker, with the same CaF₂ addition. Figure 9 indicates that the volatilization ratio of F increased with temperature and decreased with SO₃ content in clinker. The volatilization ratio increased 7% per 100 °C as the temperature increased from 1300 to 1450 °C. The decrease of F volatility with high SO₃ content in clinker was due to the lower vapor pressure of the fluoride salt in eutectic liquid with sulfate.

If F combines with alkalis to form alkali fluorides as well as chloride in the preheater, significantly higher F should be volatilized in the burning process. Figure 10 illustrates the relationship between the F content and the alkali content in clinker. The alkali content did not change with an increase in CaF₂ addition. Therefore, F exists in other compounds (e.g., CaF₂).

(2) Influence of sulfur

Increasing SO₃ in clinker may seriously increase the coating or build-up in the preheater. In a general cement plant, SO₃ in clinker is supplied by the fuel (e.g., high sulfur petroleum cokes). However, cement plants have already developed techniques to reduce SO₃ in the preheater and in exhausted gas. Since we did not examine the influence of SO₃ on the coating or build-up, coating problems due to increased SO₃ in the process could be avoided by using existing technology.

4. CONCLUSION

We investigated the conditions of CaF₂ and CaSO₄ as a mineralizer or flux to lower the clinker burning temperature. We also examined the properties of clinker and cement fabricated used these components and obtained the following results.

(1) Controlling the F content at 0.067 % and the SO₃ content at 2.2 % achieved clinker burning at a temperature 100 °C below that of the current process (1450 °C).

(2) The setting and hardening properties of mineralized cement burned at 1350 °C equal those of ordinary Portland cement burned at 1450 °C.

(3) Coating or build-up on the preheater cyclone may form due to the condensation of fluoride vapors, in the same way as for chloride. However, lowering burning temperature and increasing SO₃ content in clinker to decrease the volatilization of fluoride and then increasing the fluorine content to 0.067 %

**Fig. 8** The system CaF₂-CaCl₂-CaSO₄

**Fig. 9** Relationship between burning temperature and volatilization of F

**Fig. 10** Relationship between CaF₂ addition and alkali content in clinker

did not significantly influence coating formation.

**REFERENCES**

p. 81 (2005)


5) V. Johansen, N. H. Christensen: “Rate of formation of C₃S in the system CaO-SiO₂-Al₂O₃-Fe₂O₃-MgO with addition of CaF₂,” Cement and Concrete Research, Vol. 9, pp. 1-5 (1979)


