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Communication

Effect of cooling performance on the mineralogical character of Portland cement clinker

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Abstract

The mineral compositions, crystal features, and microstructures of the low-quality cement clinker from a cement plant were investigated with X-ray diffraction, scanning electron microscopy (SEM), and reflected light microscopy. X-ray diffraction shows that the clinker contains additional phases ($C_{12}A_7$ and α-C_2S) besides the four normal minerals [alite (C_3S), β-C_2S, ferrite (C_4AF), and aluminate (C_3A)]. Microscopic observations indicate that there are microcrackles on belite (C_2S) crystal surfaces, leaflike texture of C_2S aggregates, and droplets of crystalline black interstitial minerals, which suggest the clinker was produced under reducing conditions and underwent a rapid cooling process. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Microstructure; Clinker; X-ray diffraction; SEM

1. Introduction

Portland cement clinker is typically composed of 50–75% alite (C_3S), 10–20% belite (C_2S), 5–10% aluminate (C_3A), and about 10% ferrite (C_4AF). However, incorrect operation would not only lead to the generation of some unexpected phases, which are harmful to the clinker performance, but also exert a significant influence on the microscopic textures and the crystal characters of the principal clinker minerals.

Usually, rapid cooling is favorable to produce high-quality clinker. Cooling rate of the clinker was changed to improve the properties of its product in a cement plant in Hubei province recently. However, the result was unsatisfactory. In order to interpret the relationship between cooling rate and its product, studies on phase components and microstructure of the minerals of the clinker were undertaken, and the discussion was made with reference to the phase equilibrium diagram of the system SiO_2–CaO–Al_2O_3.

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2. Analyses

2.1. X-ray diffraction analyses

Powder diffraction analyses were done on a Rigaku IIIA diffractometer with Co K_α radiation. The analyses were performed at 40-kV X-ray tube voltage and 35-mA tube current with the silt conditions, DS = SS = 1°, RS = 0.22 mm.

The clinker samples were ground with an agate pestle in a small agate mortar to about 10 μm in particle size, which were then mounted onto a sample plate.

2.2. Scanning electron microscopy (SEM) and reflected light microscopy analyses

Small clinker nodules were glued with sulfur, polished with fine sand paper, and then etched with a solution of nitric acid in ethyl alcohol for about 1 min. Optical microscopic observation was performed on a Leitz Metallux III reflected light microscope. For SEM observation, small clinker nodules were polished and then carbon-coated. The analyses were undertaken on a SX-40 SEM at 20-kV accelerating voltage and a beam current in the range of 1–3 nA.

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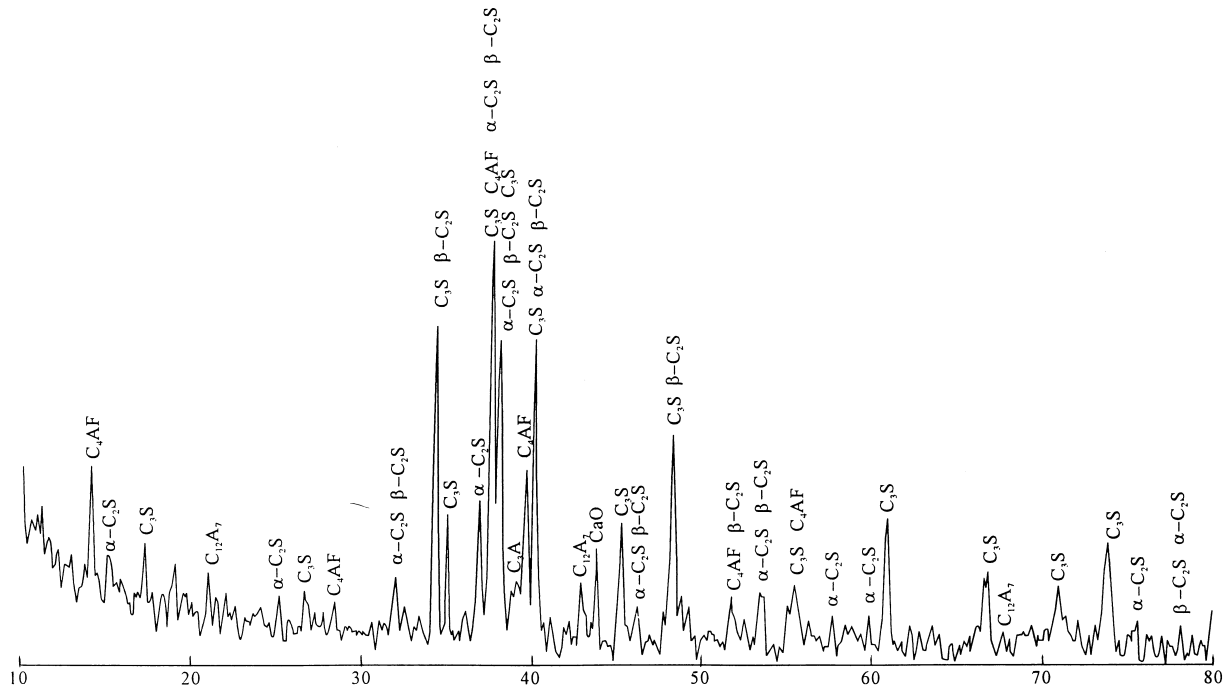


Fig. 1. X-ray diffraction pattern of the cement clinker.

3. Results and discussion

3.1. X-ray diffraction of the cement clinker

The X-ray diffraction pattern of the sample is shown in Fig. 1, which indicates that the mineral components of the cement clinker are composed of C_3S, β-C_2S, C_4AF, C_3A, and minor α-C_2S and $C_{12}A_7$. However, α-C_2S is generated in the temperature condition above 1425°C, whereas, β-C_2S exists in the temperature below 690°C. The coexistence of both α- and β-C_2S suggests that α-C_2S was not able to transform fully into β-C_2S due to a very rapid decrease in

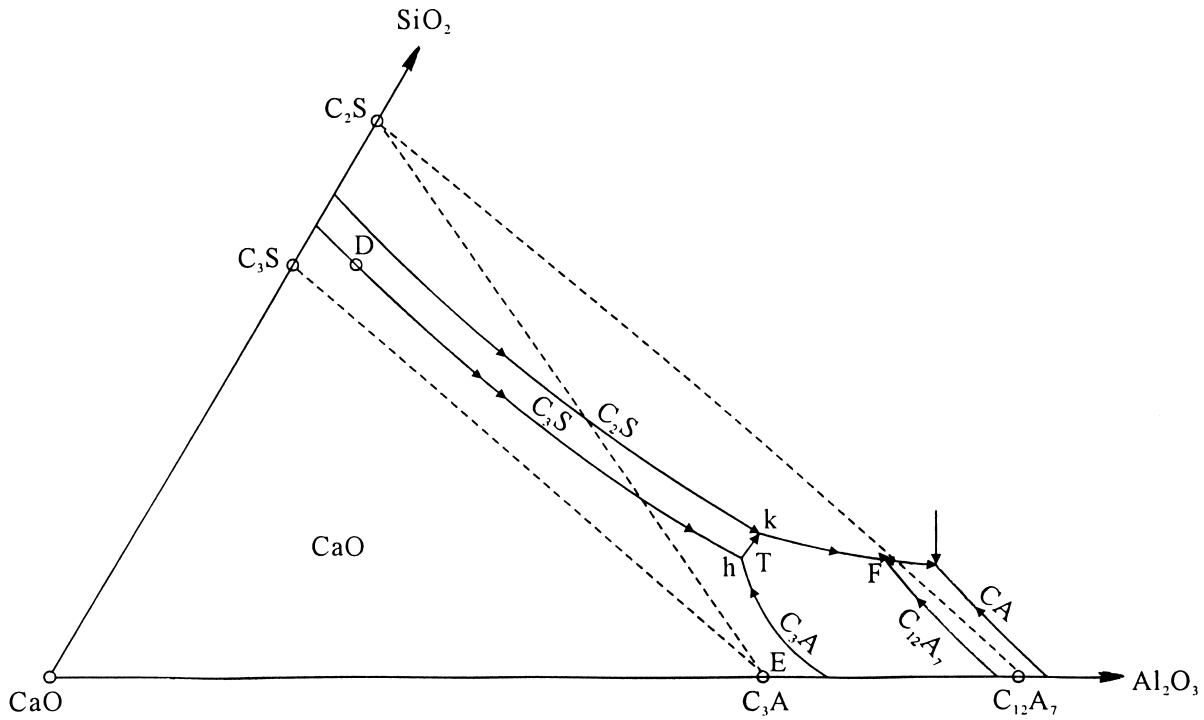
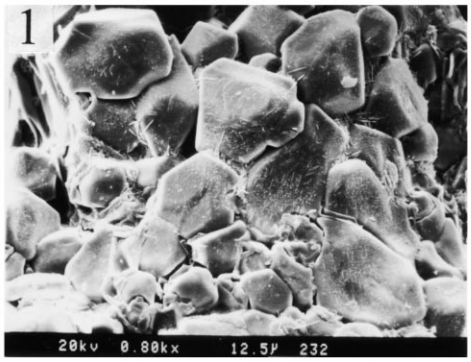
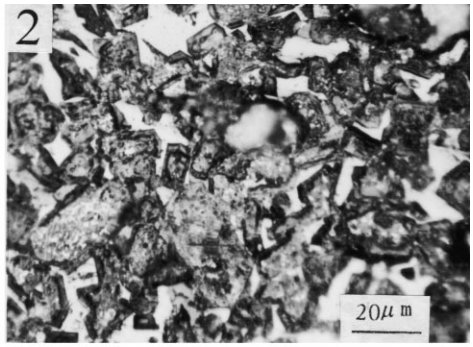
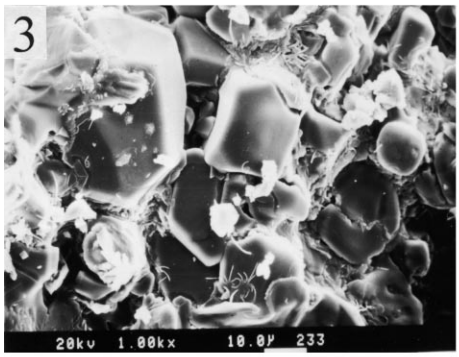
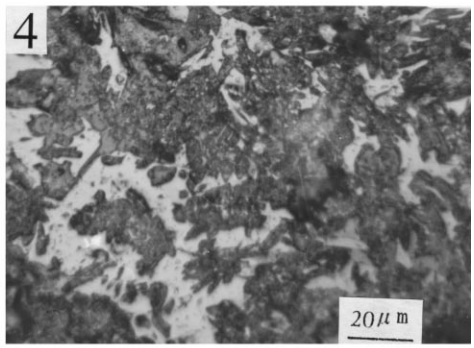


Fig. 2. Equilibrium diagram of ternary system CaO-Al_2O_3-SiO_2 after E.F. Osborn and Arnulf Muan.









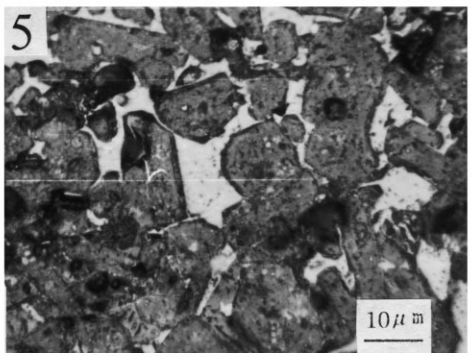


Plate 1. C_3S crystal occurs as thin basal plate of hexagonal outline (SEM). Plate 2. A large number of C_2S inclusions occur within the C_3S crystals; and a ring structure appears in the rims of C_2S crystals. White interstitial material C_4AF is among the C_3S and C_2S crystals (Reflected light microscope). Plate 3. Most of the C_2S crystals have a rounded smooth outline. However, there are microcrakles on some of the crystal surfaces (SEM). Plate 4. The C_2S aggregates show a leaflike structure (Reflected light microscope). Plate 5. Black interstitial materials $C_{12}A_7$ and C_3A, some of which occur as droplets in the bright C_4AF among the C_3S and C_2S crystals (Reflected light microscope).

temperature at the early stage of the cooling process; some of which were retained in the clinker.

The relative chemical composition of the raw material is plotted in the $CaO-SiO_2-Al_2O_3$ ternary system, after Osborn and Muan [1], at Point D in Fig. 2, which shows the phase equilibrium diagram of the system $C_3S-C_2S-C_3A-C_{12}A_7$. On cooling, the liquid phase in clinker precipitates C_3S and changes its composition toward the C_3S-C_2S boundary line. Under equilibrium crystallization, the liquid phase assimilating part of the solid C_3S and precipitating C_2S and C_3A changes its composition across the boundary line toward the invariant point H (1470°C). However, as mentioned by Wei and Wenxi [2], the equilibrium cooling can hardly be realized; particularly for rapid cooling, the liquid would precipitate C_2S and C_3A without significantly assimilating of the crystallized C_3S and change its composition across the primary phase field of C_3S and reach the $C_2S-C_3A-C_{12}A_7$ zone, as shown in Fig. 2. In such a case, $C_{12}A_7$ would occur in the clinker, again, part of the α-C_2S phase may probably be kept in the product after the clinkering process.

3.2. SEM and reflected light microscopy analyses

The morphology of the clinker minerals was observed with SEM, and the microstructure of the clinker minerals was observed with a reflected light microscope. SEM observations show that only C_3S and C_2S can be identified by their crystal characteristics. The C_3S occurs as thin basal plates of hexagonal outline with distinct pyramidal faces with particle size ranging from 10 to 20 μm (Plate 1). Generally, the C_2S crystal has a smooth and round appearance with particle size of about 10 μm. On some of the C_2S crystal surfaces, there exist some microcrackles (Plate 3), which are indicative of a stress process due to rapid cooling. On the other hand, reflected light microscopic observation shows that there are a large amount of inclusions within the C_3S crystals, and almost all the C_3S crystals have a clear reaction rim (Plates 2 and 3). The C_2S aggregate usually shows a leaflike structure (Plate 4), which suggests that the clinker minerals were produced under reducing conditions. In addition to C_3S and C_2S, other minerals, such as $C_{12}A_7$, C_3A, and C_4AF, are difficult to be identified by their crystal characters in the optical microscope. As mentioned by Shao [3], in the reflected light microscope, the black interstitial droplets are composed of $C_{12}A_7$ and C_3A (Plate 5), and the white interstitial consists of C_4AF (Plate 2).

As shown in the plates, the C_3S crystals show euhedral, hexagonal-shaped plate or short prism outline, which indicates that crystallization of C_3S was in an unrestricted environment, and the reaction rim of the crystals attests that crystallization of C_3S took place under unequilibrated conditions. During the process, the chemical composition of a crystal gradually changes from the center to the rim, the inside of a grain was kept apart from the solution, and only the rim reacted with the solution and led to the formation of the reaction rim. The smooth and round appearance of C_2S reflects that the crystallized C_2S underwent dissolution during the clinker process, for the edges were first dissolved into the solution, and the residual, as a result, became smooth and round.

Moreover, the clinker contains rarely black interstitial minerals, which suggests that the clinker underwent a rapid cooling process [4], and droplets of crystalline black interstitial minerals are also the characteristic of separation of crystalline solution during rapid cooling process.

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