Characterization of Portland Cement Clinker by Image Processing Technique

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Abstract

With the developing technology, devices that can fully control the quality of cement and clinker in cement production have been produced. These devices can give accurate results in a short time and with minimum error margins, with all necessary analyzes and phase compositions. Although these methods are very useful for cement factories in practice, they cannot fully reveal some parameters such as crystal structure and morphology of clinker phases, size distribution and clinker porosity. In microscopic studies, the formation, size, distribution and amount of clinker phases in the examined cross-sectional area can be determined. In this study, optical microscope examination and image processing techniques were used to determine the clinker characteristics. Raw meal was formed by mixing limestone and clay from cement raw materials in certain proportions. Then, clinker was obtained as a result of burning the raw meal at approximately 1400 °C. In addition to performing rapid phase analysis using image processing programs, information about the crystal properties of the phases was obtained. The size, number, average equivalent diameter, distribution of clinker phases and porosities can also be examined with the help of image processing programs. According to the result of the image processing method, Portland cement clinker with easy burning properties, high alite and low belite content was obtained.

Keywords: Optical microscope, Clinker, Characterization, Quality, Alite, Belite

Portland Çimento Klinkerinin Görüntü İşleme Tekniği ile Karakterizasyonu

Öz

Gelişen teknoloji ile çimento üretiminde çimento ve klinker kalitesini tam olarak kontrol edebilen yeni cihazlar üretilmiştir. Bu cihazlar, gerekli tüm analizler ve faz kompozisyonları ile kısa sürede ve minimum hata payı ile doğru sonuçlar verebilmektedir. Bu yöntemler pratikte çimento fabrikaları için çok faydalı olmasına rağmen, klinker fazlarının kristal yapısı ve morfolojisi, boyut dağılımı ve klinker gözenekliliği gibi bazı parametreleri tam olarak ortaya koyamamaktadır. Mikroskobik çalışmalarda incelenen kesit alanındaki klinker fazlarının oluşumu, boyutu, dağılımı ve miktarı belirlenebilir. Bu çalışmada, klinker özelliklerini belirlemek için optik mikroskop incelemesi ve görüntü işleme teknikleri kullanılmıştır. Çimento hammaddelerinden kireçtaşı ve kilaşı belirli oranlarda karıştırılarak farin hazırlanmıştır. Daha sonra farinin yaklaşık 1400 °C'de pışırılması sonucu klinker ürünü elde edilmiştir. Optik mikroskop tekniği ve görüntü işleme programları kullanılarak faz analizinin hızlı yapılmasının yanı sıra fazların kristal özellikleri hakkında bilgiler elde edilmiştir. Görüntü işleme programları yardımıyla boyut, ortalama eşdeğer çap, klinker fazlarının dağılımı ve gözenekler de incelenebilmiştir. Görüntü işleme yönteminin sonucuna

göre kolay pişme özelliklerine sahip, yüksek alit ve düşük belit içeriğine sahip Portland çimentosu klinkeri elde edilmiştir.

Anahtar Kelimeler: Optik mikroskop, Klinker, Karakterizasyon, Kalite, Alit, Belit

1. Introduction

The first meaning that comes to mind for engineers and scientists is the use of light or optical microscopy to study the microstructure of materials. The first microstructure study dates back to 1880. It is frequently used by materials scientists in the study of metallic materials and is called metallography. It is the basic instrument used in the microstructural investigation of metals, ceramics and polymers [1].

Many destructive and non-destructive methods are traditionally applied in the quality control of cementitious materials, especially concrete. These methods are very useful in terms of giving an idea about the general quality of the concrete and are widely used. However, classical methods may be insufficient in many cases to obtain information about the internal structures of cementitious materials, and different approaches may need to be preferred in order to obtain the desired data. Some of the most important of these techniques are macroscopy and complementary methods related to microscopy [2].

In microscopic studies, the formation, size, distribution, and amount of clinker phases in the examined cross-sectional area can be determined. It is not possible to distinguish unetched clinker phases in clinker bright sections. By etching (eg 1% HNO₃ solution in ethyl alcohol) silicate crystals become evident. Each clinker phase becomes distinct with different etching chemicals. Besides etching with different chemical solutions, clinkers can be processed by titration and steam diffusion to reveal different phases. At the same time, optical microscope examinations give information about porosity, size and shape of pores, sintering conditions. However, in order to obtain a statistically significant result, data must be obtained from a large number of points. This can only be possible by using image processing programs. By using image processing programs, besides performing rapid phase analysis, information about the crystal properties of the phases can also be obtained [3].

In this study, phase determination calculations of typical Portland cement clinker will be made under the optical microscope and the results will be compared with the phase determinations calculated with the Bogue formula. In literature studies, phase determinations of clinkers produced at industrial scale were investigated under optical microscope [4]. In this study, a new clinker was produced from clay and limestone material from raw material quarries under laboratory conditions. Phase determinations of clinker produced under laboratory conditions were determined by optical microscope and image processing technique. In this way, the phase determinations of the clinker produced under laboratory conditions and the production process of the clinker produced at industrial scale will be controlled and process errors will be minimized.

2. Material and Method

2.1. Material

In the study, fireability analysis was carried out on 1 limestone and claystone samples. The chemical and mineralogical compositions of limestone and clay samples were determined. Burnability test was carried out on the raw meal sample prepared in line with the analysis results obtained from the raw material samples. Within the scope of the analysis, one clinker sample was produced under laboratory conditions. Chemical, mineralogical, and microscopic analyzes of the obtained clinker sample were made and its fireability properties were determined.

2.2. Method

X-ray diffraction (XRD) analysis of the raw material samples were conducted using Bruker Brand D 8 Advance model X-ray diffraction (XRD) instrument with Cu K α rays ($\lambda = 1.54 \text{ \AA}$). The chemical analyses were determined using ARL-8680+ Model X-ray spectrophotometer device according to TS EN 196-2 Turkish Standard.

2.2.1. Optical Polarized Microscope Method

Clinker granules are cut with a diamond saw to obtain a cross section. Clinker granules are fixed by embedding in polyester. The surfaces of the clinker frozen in polyester are sanded. With the help of aluminum paste, the sanded surface is polished. The cross-sectional surface is colored by being exposed to hydrofluoric acid vapor [5].

Figure 1. Diamond saw method (a) Surface sanding method (b).

2.2.2. The Method of Determining the Color Distribution of Phases and Porosity in Optical Microscope Examinations

The prepared clinker bright section samples were etched using 1% HNO₃ solution in ethyl alcohol. With the etching process, the colors and geometries of the alite and axitic phases became clear. When etching in nitric acid solution, alite and alite phases become evident, and the intermediate phases emerge as a whole, but the distribution of the interphases among themselves cannot be clearly determined by nitric acid etching. For this reason, etching with different chemicals is required in order to distinguish between C₃A and C₄AF intermediate phases [6]. Coloring and optical microscope imaging works of the clinker cross-sectional surface are given in Fig. 2.

Figure 2. Section surface coloring process (a) Optical microscopic imaging process (b)

A section was taken from the clinker granules of different sizes and appearances, whose polished sections were prepared, and their surfaces were etched by contacting with HF acid vapor. As a result of etching, each clinker phase has its own color [(alite (C₃S) brown, belite (C₂S) blue, liquid phase (C₃A + C₄AF) dark gray + white part on the ground and free lime white)]. Allite (C₃S), belite (C₂S) and liquid phase (C₃A+C₄AF) ratios were found by dot counting method in the polarized microscope device. It is a more robust and reliable method than the Bogue formula [7].

3. Results and Discussion

3.1. Chemical analysis

Chemical analyzes of raw material samples were made using TS EN 196-2, Flame Photometer, UV Spectrophotometer, XRF and ICP-OES method and the results are given in the table below. In order to learn the chemical contents of the raw materials, the oxide ratios were determined in the XRF device. The silicate modules and aluminum modules of the cement raw materials were calculated by using their chemical contents (Table 1).

Table 1. Chemical analysis of raw material samples

Chemical component	Clay stone	Limestone
	%	%
Loss of igniton	6.24	43.68
SiO ₂	65.83	0.24
Al ₂ O ₃	11.44	0.07
Fe ₂ O ₃	4.98	0.05
CaO	4.01	55.45
MgO	1.88	0.49
SO ₃	0.05	<0.01
Na ₂ O	2.60	<0.01
K ₂ O	1.46	<0.01
TiO ₂	0.65	-
P ₂ O ₅	0.12	-
Cr ₂ O ₃	0.03	-
Mn ₂ O ₃	0.09	-
SIM	4.01	2.00
ALM	2.30	1.40

It is seen that the chemical contents of limestone and claystone raw materials are suitable for cement production and can be used for cement production (Table 1).

3.1. Mineralogical Analysis

As a result of the evaluation of the peak intensities, it can be said that the claystone unit has a high grade in terms of quartz, muscovite and cola. It is known that quartz, calcite, albite are minerals that make firing difficult and muscovite, chlorite and montmorillonite group clay minerals have positive effects on burning (Fig. 3).

Mineralogical analysis was performed for the cement limestone sample taken from the quarry using a high resolution X-Ray Diffractometer. As a result of the XRD analysis of the limestone sample used in the experiments, it was determined that its component was calcite (CaCO₃) mineral, and no other mineral was found (Figure 4.1). In the limestone quarry where the sample was taken, siliceous structures are found in very small amounts, especially in the metamorphosed and altered veins. In the results of chemical analysis (XRF), siliceous structures within the limestone veins do not exceed 5% (Fig. 4).

Figure 3. Claystone XRD image

Figure 4. Limestone XRD image

3.2. Clinkerization

Free CaO ratios were measured at each temperature by subjecting the raw meal sample to programmed heating at temperatures of 1200-1300-1350-1400 and 1450°C. The results are given in Table 2.

Table 2. Variation of Free CaO values with temperature in raw meal sample during clinkerization

(%) Free Lime	1200 °C	1300 °C	1350 °C	1400 °C	1450 °C
Clinkerization	14.51	4.45	4.42	2.66	1.60

Mineralogical analysis of the obtained clinkerization sample was made and it was observed that basic clinker phases were formed. The fact that the Free CaO values are 1.60 in the clinker formed at 1450°C indicates that the prepared raw meal has an easy burning character (S.CaO: less than 2.00). The mineralogical results of the metastasis sample used also confirm the easy-firing property of raw meal.

The chemical properties and the calculated modules and phase percentages of the clinker sample produced at 1450°C are given in Table 3.

Table 3 Chemical analysis of clinker sample obtained after clinkerization (1450 °C)

Chemical components	%
Loss of igniton	0.42
SiO ₂	20.19
Al ₂ O ₃	6.88
Fe ₂ O ₃	2.86
CaO	65.11
MgO	1.63
SO ₃	0.01
K ₂ O	1.28
Free Lime	1.60
LSF	97.90
SİM	2.07
ALM	2.41
C ₃ S	54.80
C ₂ S	16.55
C ₃ A	13.39
C ₄ AF	8.70
Liquid Phase	29.64

3.3. Microscopic Analysis Results

The phase amount was determined by point counting method with the help of polarized light microscope. For the aforementioned process, two different granules of the clinker sample obtained as a result of the firing process were placed in polyester and fixed by freezing. The phase amounts determined for the clinker sample are given in Table 4.

Table 4. Determination of Clinker Sample Phase Amount with Microscope

Clinker phases	%
Alite - C ₃ S	51.68
Belite - C ₂ S	17.31
C ₃ A+C ₄ AF+Free CaO+ Alkaline Sulphate)	31.01

In order to produce good quality cement clinker, the firing of the clinker provides the formation of a large amount of alite on the other hand. It is necessary to keep the growth and coarsening of the crystals under control. Thus, for a certain raw material mixture, it is necessary to optimize the kiln regime that will minimize the crystal size and ensure the formation of the appropriate composition [8]. The image of the produced clinkers is shown in figure 5.

Figure 5. exterior view (a) and cut interior view of clinker (b)

Figure 7. Clinker optical microscope phase images (Brown: alite; blue: belite)

Blue crystals are alite, brown-orange crystals are alite. In the clinker sample, partly cumulated belite crystals were encountered. Homogeneous phase distribution is desired in clinker samples. However, this situation can be achieved if raw material homogenization is done well, and it is unlikely that such a situation will occur in a clinker produced in a laboratory environment. In addition, the clustered structure shows free lime crystals. The amount of free lime is not very high in the clinker sample. In general, the clinker sample shows good burning.

When we look at the clinker phase distribution in general, it is seen that the alite mineral is more dense and the belite mineral is less (Fig. 7a). The intense alite phase has a positive effect on Grindability [9,10]. It facilitates grinding and reduces energy consumption. Belite minerals are found in clusters in some regions, and in most of them they are dispersed among the alites. This situation requires coarse-grained minerals in the clay stone raw mixture and requires finer grinding in order to fully homogenize it (Fig. 7b). When the crystal sizes of the clinker granules were examined, it was observed that the alite and belite crystals were of variable size (5-40 microns) in general. Large sized alite and belite crystals were also observed in some granules in the clinker. For this reason, the burning ability can be increased with the improvements to be made in the process [11, 12].

4. Conclusions and Recommendations

When the limestone sample was examined from a mineralogical point of view, the presence of calcite, which causes difficulty in firing, was found in its composition. When the mineralogical analysis result of the clay sample is evaluated in terms of fireability, it is known that quartz, calcite and albite detected in the structure of the clay sample make firing difficult, and the clay minerals montmorillonite, muscovite and chlorite affect firing positively.

The fact that the Free CaO values are 1.60 in the clinker formed at 1450°C indicates that the prepared raw meal has an easy burning character (S.CaO: less than 2.00). Mineralogical results of the claystone sample used also confirm the easy-burning feature of raw meal.

When the clinker produced is examined in terms of quality parameters, it is observed that it has a relatively lower quality than the optimum quality ($C_3S < 60.0\%$). The amount of liquid phase (29.64) in the clinker shows a height (around 27 optimum) due to low SIM and high ALM modulus values, depending on the raw material characteristics. In the use of this raw meal, it is important to pay attention to the liquid phase in terms of belt formation. It is thought that the clinker quality and the amount of liquid phase will be positively affected in the clinker that is formed by bringing SIM and ALM to the optimum point (additional use of correcting agents, such as iron ore and sand).

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