Free lime quantification in clinker with simultaneous wavelength dispersive X-ray fluorescence spectrometer

Mitsuru Watanabe*

1. Introduction

Cement is used for concrete in construction and architectural structures. Clinker, which is an intermediate material for cement, is produced by mixing and calcinating cement raw materials such as limestone, clay and silica in a rotary kiln at a high temperature.

The unreacted calcium oxide remaining after calcination of the clinker is called free lime (f.CaO). When calcination in a rotary kiln is insufficient, limestone, the main raw material, does not react sufficiently with silicon dioxide, aluminum oxide, etc., and the amount of free lime increases, resulting in the cement not meeting the expected composition. Furthermore, free lime changes to calcium hydroxide and calcium carbonate by reacting with moisture and carbon dioxide in the air, causing volume expansion. Thus, process control of clinker is important because it directly affects the quality of the cement product(1).

There is no difference in the X-ray fluorescence peak profile of the Ca Kα line between free lime and other calcium compounds; therefore, the concentration of free lime cannot be determined by X-ray fluoresce (XRF) analysis. Free lime is therefore generally analyzed by wet chemical analysis like titration or by an X-ray diffractometer (XRD). This paper introduces the Rigaku simultaneous wavelength dispersive X-ray fluorescence (WDXRF) system Simultix 15 equipped with a free lime diffraction channel, enabling both XRF analysis and free lime quantification by XRD. Quantitative analysis of free lime is also described.

2. Instrument

For over 40 years, the Rigaku simultaneous WDXRF spectrometer Simultix systems have been widely used as elemental analytical tools for process control in industries that require high throughput and precision analysis, such as steel and cement. Over 1200 Simultix systems have been delivered to customers around the world. Along with technical progress over these years, customer requirements have advanced and diversified as well. Simultix 15 was developed to meet these changing needs. It offers significantly improved performance, functions and usability. Recently, the Simultix systems have also been integrated with sample preparation machines and used as complete automation systems. The compact and intelligent Simultix 15 is a powerful analytical tool that demonstrates superior performance across many industrial sectors.

3. Sample Preparation

Since free lime in clinker reacts with moisture and carbon dioxide in the air, samples must be measured immediately after calcination. In this paper, standard samples were prepared by adding calcium oxide to cement supplied by the Japan Cement Association. The cement is produced for research purposes.

The calcium oxide reagent (FUJIFILM Wako Pure Chemical, 99.9% purity) used for the addition was first pulverized in an alumina vessel for 2 minutes and then calcined at 1050°C for 5 hours. After calcination, it was stored at 110°C in an electric furnace. The cement was first dried as well at 110°C for 2 hours.

The cement and weighed calcium oxide mixture was pulverized in an aluminum vessel for 3 minutes. Then, the mixed powder sample was pressed in an aluminum ring (inner diameter, 32 mm) at 10 tons.

4. Measurement

Measurements were performed using a Simultix15 equipped with a free-lime diffraction channel. The measurement conditions are shown in Table 1. For XRD measurement, the sample is irradiated with a collimated X-ray beam through a slit. A fixed Rh Lβ1 line channel is arranged at the diffraction angle for the crystal plane of CaO(200), and the diffracted X-rays are detected.

5. Result

A calibration curve for free lime from 0 to 3 mass%, shown in Fig. 1, was prepared. Good correlation was obtained.

Table 1. Measurement condition.

Component	f.CaO
Crystal plane	CaO(200)
X-ray tube	end-window Rh
kV-mA	40 kV-70 mA
Slit for XRD	In
Diameter	30 mm
Measurement line	Rh Lβ1
Crystal	RX9
Detector	F-PC
PH	Differential
Measurement time	40 s
Atmosphere	Vacuum

* SBU WDX, X-ray Instrument Division, Rigaku Corporation.

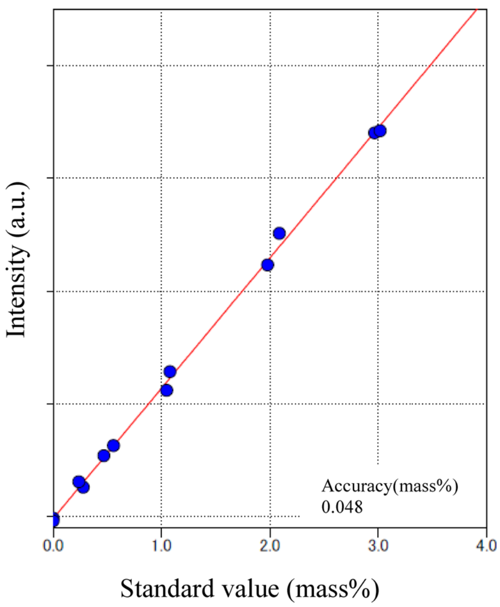

Fig. 1. Free lime calibration curve.

6. Standard Testing Methods for Free Lime

Many standard testing methods for free lime analysis have been proposed over the years, two of which are ASTM C114-18 and JCAS I-01: 1997 issued by the Japan Cement Association. Both describe two distinct methods shown in Table 2 below[(2), (3)].

The ethylene glycol method is generally used because of its short elution time, but it should be noted that not only free lime but also hydrated $Ca(OH)_2$ is extracted.

Table 2. Standard testing methods for free lime.

	Method A	Method B
ASTM C114-18	ethyl acetoacetate–isobutyl alcohol	alcohol–glycerin
JCAS I-01: 1997	ethylene glycol	alcohol–glycerin

7. Conclusion

Simultix15 equipped with a diffraction channel was used to set up a free lime calibration with good correlation for the quantitative analysis of free lime in clinker. By integrating both XRF and XRD methods in a single equipment, quantitative analysis of chemical composition and free lime concentration can be performed in one measurement. Compared to conventional wet chemical analysis, the sample preparation is simpler and analysis time is shorter with higher accuracy, making this system optimal for process and quality control in cement plants.

References

(1) H. Homma: *Rigaku Journal (English version)*, **35** (2019), No. 1, 17–23.
(2) ASTM C114-18, *Standard Test Methods for Chemical Analysis of Hydraulic Cement.*
(3) JCAS I-01: 1997, *Method for Determination of Free Calcium Oxide*.