Cement analysis by wavelength dispersive XRF spectrometry

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1. Cement manufacturing process

Cement is one of the most essential materials in modern construction. In this article, the term “cement” means Portland cement, which is typically a grayish powder to be solidified by a hydration reaction. Portland cement comprises most of the total cement production.

The cement manufacturing process is composed of three basic steps: raw meal preparation, clinker production and cement milling(1). In the raw meal preparation process, raw materials such as limestone, clay, shale, silica sand and iron oxides are blended together in suitable proportions to make raw meal. During the clinker production process, preheated and precalcined raw meal is fed into a rotary kiln for sintering at up to 1450°C to form clinker minerals, then the hot clinker is cooled. In the cement process, small quantities of gypsum are added to clinker. They are then milled together to make final cement products.

Production of uniformly high-quality cement requires advanced process control and blending quality based on accurate chemical composition obtained by prompt and reliable chemical analysis methods.

2. Chemical composition of cement and process control parameters

2.1. Major components

Table 1 shows typical chemical compositions of Portland cement and clinker(2).

Cement is mainly composed of CaO and SiO_2. Relatively small quantities of Al_2O_3 and Fe_2O_3 are added to the above two components. These four components account for over 90 mass% of the chemical composition of cement. Differences in content among these four components cause changes in properties of the cement, such as hydration rate and hardening strength.

Cement properties depend on the proportion of the four minerals making up the clinker: two calcium silicate phases, an aluminate phase and a ferrite phase. The calcium silicate phases are tricalcium silicate (C_3S, $3CaO \cdot SiO_2$, alite) and dicalcium silicate (C_2S, $2CaO \cdot SiO_2$, belite). The aluminate phase mineral is tricalcium aluminate (C_3A, $3CaO \cdot Al_2O_3$) and the ferrite phase is calcium aluminoferrite (C_4AF, $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$). The content of each of these minerals can be calculated from the oxide chemical compositions and simple formulae (Bogue calculation(3)).

$$
\begin{aligned}
C_3S &= 4.07 \times CaO - (7.60 \times SiO_2 + 6.72 \times Al_2O_3 \\
&\quad + 1.43 \times Fe_2O_3 + 2.85 \times SO_3) \\
C_2S &= 2.87 \times SiO_2 - 0.754 \times C_3S \\
C_3A &= 2.65 \times Al_2O_3 - 1.69 \times Fe_2O_3 \\
C_4AF &= 3.04 \times Fe_2O_3 \\
CaSO_4 &= 1.70 \times SO_3
\end{aligned}
$$

*In clinker, SO_3 is not included.

Based on practical experience and the process of production in cement manufacturing, it has been found that relationships exist between cement quality and proportions of oxide components, CaO, SiO_2, Al_2O_3 and Fe_2O_3. These relationships were established as formulae called the cement modulus to control the quality of raw meal and clinker. The cement modulus are as follows:

Lime Saturation Factor (LSF);

$$LSF = \frac{CaO - 0.7 \times SO_3}{2.8 \times SiO_2 + 1.2 \times Al_2O_3 + 0.65 \times Fe_2O_3}$$

Silica Ratio (SR);

$$SR = \frac{SiO_2}{Al_2O_3 + Fe_2O_3}$$

Alumina Ratio (AR);

$$AR = \frac{Al_2O_3}{Fe_2O_3}$$

Hydraulic Modulus (HM);

$$HM = \frac{CaO - 0.7 \times SO_3}{SiO_2 + Al_2O_3 + Fe_2O_3}$$

*In clinker, SO_3 is not included.

Table 1. Typical composition of Portland cement and clinker(2).

(mass%)

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O
Portland cement	63−67	19−23	3−7	1.5−4.5	0.5−2.5	2.5−3.5	0.07−0.4	0.1−1.2
Clinker	67.7	21.7	5.3	2.6	1.3	0.7	0.2	0.5

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When the LSF is higher than 1.0, CaO can remain as free lime in the clinker. Typical values of LSF in clinkers is 0.92–0.98(4) or 0.92–0.96(5). (There are slight differences in the typical range of these cement modulus depending on the literature.) Typical SR ranges are 2.0–3.0(4), 2.4–2.8(5) or 1.9–3.2(6). AR indicates the ratio of aluminate to ferrite phase in clinker, which typically ranges from 1–4(4) or 1.5–2.5(6). AR is controlled to be within 1.9–2.1(5) in typical Japanese cement manufacturing. HM is typically maintained between 1.7 to 2.3(6). In a Japanese plant, HM is controlled between 2.0 to 2.2(5).

2.2. Other components

Clinker minerals generated in the clinkering process contain minor and trace components from raw materials. The calcium silicate phase contains trace Al, Fe, Mg, Na, K, Ti and Mn. The aluminate and aluminoferrite phases contain minor Si, Mg, Na and K. These minor and trace components also must be controlled.

Alkali in cement can react with excess reactive silica in concrete aggregates, resulting in expansion. Therefore, a low alkali cement regulation was established to control alkali content. In Europe and USA, the maximum alkali content should be 0.6 mass% expressed as sodium oxide equivalent (see formula below). The Japanese regulation specifies total alkali content in sodium oxide equivalent as 0.75 mass% applied to all Portland cement(6).

$$Na_2O_{eq}=Na_2O+0.658\times K_2O$$

Chloride ions in cement corrode reinforcing bars in concrete to deteriorate the reinforced concrete structure. Chlorine content in Portland cement is regulated to $\leq$0.035 mass%(6).

Magnesium oxide (MgO) in the raw meal promotes clinkering, but excess MgO forms magnesium hydroxide during hydration of cement, which causes volume expansion in concrete. Therefore, MgO content is also regulated. The maximum MgO content in Portland cement should be 6 mass% in USA and 5 mass% in Europe and Japan(6).

Sulfur trioxide (SO_3) in cement originates from gypsum in the cement milling process. Excess SO_3 causes expansion after the hydration of cement. SO_3 in cement is controlled to less than 3.5 mass% (6).

When industrial waste and by-products contain major cement components such as CaO, SiO_2, Al_2O_3 and Fe_2O_3, these materials can be used as raw materials or fuels in the cement manufacturing process. In cement manufacturing plants currently, industrial waste such as coal fly ash, waste incineration residue, plastics, sludge, casting sand and waste tire, and by-products such as gypsum and blast furnace slug are accepted as constituents and fuels. For modern cement companies, it is essential to operate plants in an environmentally friendly manner. In addition to controlling major components, it is also necessary to analyze materials for trace heavy elements that are harmful to human health and/or cause high environmental load.

In Japanese cement plants, it is necessary to determine and control almost 20 chemical components in cement. Using a wavelength dispersive XRF spectrometer, which is rapid, accurate and has high performance, is a useful method for process control in cement plants.

3. Analysis standard of cement

ASTM C114(8) is a standard for chemical analysis of Portland cement and is used in numerous countries and regions as a *de facto* standard. In Asia, the Japanese industrial standard is JIS R 5204(9), and the Chinese national standard GB/T 176(10) is issued by the Standardization Administration of China.

ASTM C114 standardizes chemical analysis of hydraulic cement; the current version is ASTM C114–18 as of 2018. An XRF method is included in the "Rapid Test Methods" described in ASTM C114.

In the Rapid Test Methods in ASTM C114, limits on precision and bias are described for qualification, but the sample preparation and analysis methods are not specified. Both of the fusion bead method and the pressed powder method are available in XRF analysis according to ASTM C114.

The standard ASTM C114 has the following descriptions about "Rapid Test Methods"(8):

"Using the test method chosen, make single determinations for each analyte under consideration on at least seven CRM (Certified Reference Material) samples." "Complete two rounds of tests on different days repeating all steps of sample preparations. Calculate the differences between values and averages of the values from the two rounds of tests."

"When seven CRMs are used in the qualification procedures, at least six of the seven differences between duplicates obtained of any single analytes shall not exceed the limits shown in Table 1 and the remaining differences by no more than twice that value."*

"For each analyte and each CRM, the average obtained shall be compared to the certified concentrations. When seven CRMs are used in the qualification procedure, at least six of the seven averages for each analytes shall not differ from the certified concentrations by more than the value shown in Table 1, and the remaining average by more than twice that value."* (* see Table 2 in this article)

The maximum permissible variations in analysis results defined in ASTM C114 are listed in Table 2. Table 3 shows a summary of a number of CRMs required to meet the limits of ASTM C114 qualification.

JIS R 5204 is a cement analysis standard by XRF analysis method using the fusion bead method. As the fusion bead method can eliminate some error factors in powder samples such as particle size and mineralogical effects, JIS R 5204 can be applied to analysis of raw materials such as limestone and blast furnace slug as well as cement and clinker. JIS R 5204 describes limits of permissible tolerance for measurement of standard sample (bias) and repeatability (precision). The

Table 2. Maximum permissible variations defined in ASTM C114(8).

(mass%)

Component	Maximum difference between duplicates	Maximum difference of the average of duplicates from CRM certificate values
SiO_2	0.16	±0.2
Al_2O_3	0.20	±0.2
Fe_2O_3	0.10	±0.10
CaO	0.20	±0.3
MgO	0.16	±0.2
SO_3	0.10	±0.1
Na_2O	0.03	±0.05
K_2O	0.03	±0.05
TiO_2	0.02	±0.03
P_2O_5	0.03	±0.03
ZnO	0.03	±0.03
Mn_2O_3	0.03	±0.03
Cl	0.003	±0.005

Table 3. Number of samples required for qualification of ASTM C114(8).

	Number of samples used for test	
	=7	>7
Number of samples meet the limits	≧6	≧77%
Number of samples less than twice of limits	≦1	Remaining above

Table 4. Repeatability limit in JIS R 5204(9).

(mass%)

Average of duplicates	Limit
<0.5	0.020
0.5	0.023
1	0.032
2	0.044
3	0.054
4	0.062
5	0.069
7	0.081
10	0.096
15	0.116
20	0.134
25	0.149
(Omitted.)	(Omitted.)
65	0.235
70	0.244
75	0.252
80	0.260

maximum permissible limits in analysis results defined in JIS R 5204 are listed in Tables 4 and 5.

Table 5. Permissible tolerance for measurement of standard sample in JIS R 5204(9).

(mass%)

Analysis result	Limit
0−0.49	0.02
0.50−0.99	0.03
1.00−9.99	0.08
10.00−29.99	0.15
30.00−49.99	0.20
50.00−79.99	0.25
80.00−100	0.30

Table 6. Maximum permissible variation in GB/T 176(10).

(mass%)

Component	Maximum difference between duplicates	Maximum difference of the average of duplicates from CRM certificate values
SiO_2	0.20	0.25
Al_2O_3	0.20	0.30
Fe_2O_3	0.15	0.20
CaO	0.25	0.40
MgO	0.15	0.25
SO_3	0.15	0.20
Na_2O	0.05	0.10
K_2O	0.10	0.15
TiO_2	0.05	0.10

GB/T-176 is a Chinese standard for chemical analysis of cement and defines limits of precision and bias as well as other standards. Table 6 shows permissible limits for cement analysis, which is dedicated to XRF methods.

4. XRF analysis

In the cement analysis using XRF methods, either the fusion bead method or the pressed powder method are available for sample preparation.

In this article, certified reference materials of Portland cements supplied by National Institute of Standards and Technology (NIST) were analyzed by the fusion bead method and pressed powder method respectively and then analysis results were evaluated according to ASTM C114. The certified reference materials and measurement components used in this test are listed in Table 7. The measurement spectrometer is the Rigaku sequential WDXRF ZSX Primus IV equipped with a high-performance 4 kW X-ray tube. The Rigaku benchtop WDXRF, Supermini200 equipped with 200 W Pd X-ray tube was also used for the test by the pressed powder method. Evaluation for Rigaku benchtop WDXRF with the fusion bead method was reported by Watanabe(11).

When it is necessary to obtain phase compositions using the Bogue calculation and cement modulus together with oxide content by XRF analysis, a process parameter function, which can automatically calculate these parameters from analytical results, is available as a standard function in the software of all Rigaku sequential and multi-channel WDXRF spectrometers.

4.1. Fusion bead method

Fusion beads for the test were prepared as follows.

Table 7. Measurement component and NIST cement CRMs.

Sample preparation	CRM	Measurement component
Fusion bead method	9 CRM 1881a, 1882a, 1883a, 1884a, 1885a, 1886a, 1887a, 1888a, 1889a	11 component CaO, SiO_2, Al_2O_3, Fe_2O_3, SO_3, MgO, K_2O, TiO_2, Na_2O, P_2O_5, Mn_2O_3
Pressed pellet method	7 CRM 1881a, 1884a, 1885a, 1886a, 1887a, 1888a, 1889a	13 component CaO, SiO_2, Al_2O_3, Fe_2O_3, SO_3, MgO, K_2O, TiO_2, Na_2O, P_2O_5, Mn_2O_3, Cl, ZnO

Table 8. Measurement condition of fusion bead (ZSX Primus IV).

Element	Si	Al	Fe	Ca	Mg	S	Na	K	Ti	P	Mn
Measurement line	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα
Attenuator	1/1	1/1	1/1	1/1	1/1	1/1	1/1	1/1	1/1	1/1	1/1
Slit	S4	S4	S2	S4	S4	S4	S4	S4	S2	S4	S2
Analyzing crystal	PETH	PETH	LiF (200)	LiF (200)	RX25	GeH	RX25	LiF (200)	LiF (200)	GeH	LiF (200)
Detector	F-PC	F-PC	SC	F-PC	F-PC	F-PC	F-PC	F-PC	SC	F-PC	SC
Counting time (sec)											
Peak	20	20	10	10	20	20	40	20	20	20	20
Background	10	10	5	5	10	10	10	10	10	10	10
Atmosphere	Vacuum										
kV−mA	50 kV−50 mA										
Measuring diameter	30 mm										

Table 9. Results of precision test (Fusion bead, ZSX Primus IV).

(mass%)

Component	Range*	Difference between duplicates											
		Limit	Result (total)		Result (individual)								
			Maximum	Pass/Fail	1881a	1882a	1883a	1884a	1885a	1886a	1887a	1888a	1889a
SiO_2	0.24−22.72	0.16	0.118	Pass	0.073	0.021	0.008	0.042	0.006	0.118	0.007	0.070	0.081
Al_2O_3	3.933−69.76	0.20	0.094	Pass	0.028	0.051	0.094	0.005	0.038	0.016	0.012	0.015	0.001
Fe_2O_3	0.078−14.73	0.10	0.037	Pass	0.004	0.037	0.004	0.014	0.004	0.002	0.001	0.004	0.009
CaO	29.40−68.89	0.20	0.215	Pass	0.188	0.021	0.037	0.024	0.056	0.215	0.079	0.041	0.109
MgO	0.19−4.529	0.16	0.054	Pass	0.029	0.004	0.006	0.035	0.054	0.019	0.006	0.008	0.009
SO_3	2.117−4.701	0.10	0.015	Pass	0.015	0.001	0.001	0.009	0.008	0.012	0.010	0.001	0.013
Na_2O	0.021−1.093	0.03	0.042	Pass	0.023	0.023	0.012	0.023	0.042	0.017	0.002	0.002	0.014
K_2O	0.014−1.248	0.03	0.006	Pass	0.002	0.000	0.001	0.001	0.003	0.001	0.001	0.002	0.006
TiO_2	0.020−1.793	0.02	0.008	Pass	0.005	0.006	0.003	0.000	0.008	0.006	0.007	0.007	0.003
P_2O_5	0.003−0.311	0.03	0.002	Pass	0.000	0.000	0.001	0.001	0.002	0.001	0.002	0.001	0.002
Mn_2O_3	0.003−0.2676	0.03	0.001	Pass	0.001	0.000	0.001	0.001	0.000	0.001	0.001	0.001	0.000

* Certified values are normalized except for ignition loss.
Underline is a value exceed the limit.

Samples calcined at 1050°C were exactly weighed 0.4 g and mixed with 4.0 g flux (the mixed flux; 67% $Li_2B_4O_7$ and 33% $LiBO_2$). The mixed samples were fused by a fusion machine at 1050°C. Nine fusion beads were prepared for calibration standards and calibrations were performed with ZSX Primus IV. Table 8 shows measurement conditions. A correction for matrix effects was applied to all calibration curves using theoretical alpha coefficients generated by the fundamental parameter program. Normalized values excluding ignition loss were used as standard values for calibrations.

Duplicate test beads were analyzed and evaluated according to ASTM C114. Results of the test are shown in Tables 9 and 10. The XRF results using the fusion bead method are shown to meet the requirements defined in ASTM C114.

4.2. Pressed powder method

Sample powders of cement CRMs were well-pulverized by a tungsten carbide vessel. Before pulverization, N-hexane was added as a grinding aid. Then, well-dried samples were pressed into aluminum rings at 150 kN to form pressed powder briquettes. ZSX Primus IV and Supermini200 were calibrated by the briquettes of seven CRMs. Correction for inter-element effects was applied to each calibration using theoretical alpha coefficients.

Table 10. Results of bias test (Fusion bead, ZSX Primus IV).

(mass%)

Component	Range*	Difference of the average of duplicates from CRM											
		Limit	Result (total)		Result (individual)								
			Maximum	Pass/Fail	1881a	1882a	1883a	1884a	1885a	1886a	1887a	1888a	1889a
SiO_2	0.24−22.72	±0.2	−0.09	Pass	0.07	0.04	−0.01	0.00	−0.09	0.08	−0.01	−0.05	−0.01
Al_2O_3	3.933−69.76	±0.2	−0.16	Pass	0.02	−0.16	0.11	0.04	0.01	0.01	−0.02	0.05	−0.04
Fe_2O_3	0.078−14.73	±0.10	−0.056	Pass	−0.020	0.029	0.042	−0.056	0.001	0.028	−0.023	0.014	0.007
CaO	29.40−68.89	±0.3	$\underline{-0.45}$	Pass	0.21	−0.18	0.17	−0.16	$\underline{-0.45}$	0.13	−0.10	−0.06	$\underline{0.31}$
MgO	0.19−4.529	±0.2	0.02	Pass	0.00	0.00	0.00	−0.01	0.02	0.01	−0.02	−0.01	−0.02
SO_3	2.117−4.701	±0.1	0.05	Pass	0.00	—	—	−0.04	−0.05	0.05	−0.02	0.03	0.05
Na_2O	0.021−1.093	±0.05	0.012	Pass	0.001	−0.005	0.002	0.012	−0.001	0.001	−0.002	−0.007	0.004
K_2O	0.014−1.248	±0.05	$\underline{-0.061}$	Pass	−0.009	0.009	0.005	$\underline{-0.061}$	0.025	−0.024	$\underline{0.051}$	−0.011	0.017
TiO_2	0.020−1.793	±0.03	−0.007	Pass	−0.002	−0.007	−0.002	0.001	0.003	−0.001	−0.004	−0.004	0.002
P_2O_5	0.003−0.311	±0.03	0.003	Pass	−0.002	0.002	0.000	0.003	0.000	−0.001	−0.002	−0.002	0.001
Mn_2O_3	0.003−0.2676	±0.03	−0.018	Pass	0.000	−0.018	0.000	0.002	0.000	0.001	0.000	0.000	0.002

* Certified values are normalized except for ignition loss.
Underline is a value exceed the limit.

Table 11. Measurement condition of pressed pellet (ZSX Primus IV).

Element	Si	Al	Fe	Ca	Mg	S	Na	K	Ti	P	Zn	Mn	Cl
Measurement line	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα
Attenuator	1/10	1/1	1/1	1/10	1/1	1/1	1/1	1/1	1/1	1/1	1/1	1/1	1/1
Slit	S4	S4	S2	S4	S4	S4	S4	S4	S2	S4	S2	S2	S2
Analyzing crystal	PETH	PETH	LiF (200)	LiF (200)	RX25	GeH	RX25	LiF (200)	LiF (200)	GeH	LiF (200)	LiF (200)	GeH
Detector	F-PC	F-PC	SC	F-PC	F-PC	F-PC	F-PC	F-PC	SC	F-PC	SC	SC	F-PC
Counting time (sec)													
Peak	20	10	10	20	20	10	20	10	10	20	10	20	20
Background	—	—	—	—	—	—	—	—	—	—	—	—	—
Atmosphere	Vacuum												
kV−mA	50 kV−50 mA												
Measuring diameter	30 mm												

Table 12. Measurement condition of pressed pellet (Supermini200).

Element	Si	Al	Fe	Ca	Mg	S	Na	K	Ti	P	Zn	Mn	Cl
Measurement line	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα
Analyzing crystal	PET	PET	LiF (200)	LiF (200)	RX25	PET	RX25	LiF (200)	LiF (200)	PET	LiF (200)	LiF (200)	PET
Detector	F-PC	F-PC	SC	F-PC	F-PC	F-PC	F-PC	F-PC	SC	F-PC	SC	SC	F-PC
Counting time (sec)													
Peak	40	40	20	40	60	40	60	40	20	40	60	60	60
Background	—	—	—	—	—	—	—	—	—	—	—	—	—
Atmosphere	Vacuum												
kV−mA	50 kV−4 mA												
Measuring diameter	30 mm												

Measurement conditions are listed in Tables 11 and 12.

Duplicate test briquettes were analyzed in the same way as the fusion bead method. Test results from the ZSX Primus IV are shown in Tables 13 and 14. Results from the Supermini200 are shown in Tables 15 and 16. The pressed pellet method was also demonstrated to meet the requirements of ASTM C114.

5. Free lime analysis using an XRF spectrometer

When all CaO is not combined during the clinkering process, calcium can remain as free lime (f.CaO) in clinker. Excess f.CaO causes expansion after hydration of cement, so f.CaO degrades concrete. Therefore, f.CaO in clinker must be controlled to a low level.

As f.CaO is indistinguishable from other calcium compounds in clinker by the spectrum of X-ray fluorescence, analysis of f.CaO is impossible by the XRF method. In general, f.CaO content is determined by chemical analysis or X-ray diffraction. The X-ray intensity of the diffraction peak of f.CaO is proportional

Table 13. Results of precision test (pressed pellet, ZSX Primus IV).

(mass%)

Component	Range	Limit	Difference between duplicates								
			Result (total)		Result (individual)						
			Maximum	Pass/Fail	1881a	1884a	1885a	1886a	1887a	1888a	1889a
SiO_2	18.637−22.38	0.16	0.103	Pass	0.103	0.034	0.005	0.069	0.102	0.09	0.067
Al_2O_3	3.875−7.06	0.20	0.038	Pass	0.026	0.003	0.038	0.029	0.013	0.032	0.017
Fe_2O_3	0.152−3.09	0.10	0.003	Pass	0.003	0.000	0.003	0.000	0.003	0.001	0.003
CaO	57.58−67.87	0.20	0.119	Pass	0.050	0.037	0.018	0.063	0.071	0.069	0.119
MgO	0.814−4.475	0.16	0.035	Pass	0.012	0.007	0.012	0.001	0.014	0.035	0.005
SO_3	2.086−4.622	0.10	0.045	Pass	0.008	0.022	0.011	0.007	0.045	0.045	0.008
Na_2O	0.021−1.068	0.03	0.017	Pass	0.005	0.001	0.017	0.001	0.014	0.002	0.002
K_2O	0.093−1.228	0.03	0.003	Pass	0.002	0.000	0.001	0.000	0.003	0.001	0.001
TiO_2	0.084−0.366	0.02	0.006	Pass	0.002	0.006	0.001	0.000	0.000	0.003	0.001
P_2O_5	0.022−0.306	0.03	0.004	Pass	0.003	0.002	0.001	0.003	0.004	0.003	0.002
ZnO	0.001−0.107	0.03	0.001	Pass	0.001	0.000	0.001	0.000	0.000	0.001	0.001
Mn_2O_3	0.007−0.259	0.03	0.001	Pass	0.001	0.000	0.001	0.001	0.000	0.000	0.000
Cl	0.0019−0.013	0.003	$\underline{0.005}$	Pass	0.003	0.001	0.002	0.002	$\underline{0.005}$	0.001	0.000

Underline is a value exceed the limit.

Table 14. Results of bias test (pressed pellet, ZSX Primus IV).

(mass%)

Component	Range	Limit	Difference of the average of duplicates from CRM								
			Result (total)		Result (individual)						
			Maximum	Pass/Fail	1881a	1884a	1885a	1886a	1887a	1888a	1889a
SiO_2	18.637−22.38	±0.2	0.19	Pass	0.00	0.19	−0.11	−0.04	−0.03	0.04	0.03
Al_2O_3	3.875−7.06	±0.2	0.14	Pass	0.07	−0.03	0.08	0.14	−0.12	−0.08	−0.05
Fe_2O_3	0.152−3.09	±0.10	0.04	Pass	0.000	−0.040	0.010	0.010	0.000	0.040	−0.020
CaO	57.58−67.87	±0.3	−0.15	Pass	0.09	−0.01	−0.15	0.11	0.05	−0.04	0.00
MgO	0.814−4.475	±0.2	0.07	Pass	−0.07	0.07	0.07	0.00	−0.02	−0.02	0.05
SO_3	2.086−4.622	±0.1	0.08	Pass	0.06	−0.08	−0.03	0.08	0.03	0.01	−0.02
Na_2O	0.021−1.068	±0.05	0.007	Pass	−0.007	−0.007	0.000	−0.004	0.007	0.000	0.005
K_2O	0.093−1.228	±0.05	0.005	Pass	−0.004	0.005	0.003	−0.003	0.002	−0.002	0.004
TiO_2	0.084−0.366	±0.03	0.005	Pass	0.005	−0.001	0.002	0.001	−0.003	−0.004	−0.003
P_2O_5	0.022−0.306	±0.03	−0.004	Pass	0.002	0.001	−0.003	−0.001	−0.002	−0.004	0.001
ZnO	0.001−0.107	±0.03	−0.002	Pass	−0.002	0.000	0.001	0.000	0.000	0.001	−0.001
Mn_2O_3	0.007−0.259	±0.03	0.002	Pass	0.001	0.002	−0.001	−0.001	−0.001	−0.001	0.001
Cl	0.0019−0.013	±0.005	$\underline{-0.007}$	Pass	$\underline{-0.007}$	0.001	0.000	0.000	−0.003	0.000	0.000

Underline is a value exceed the limit.

Table 15. Results of precision test (pressed pellet, Supermini200).

(mass%)

Component	Range	Limit	Difference between duplicates								
			Result (total)		Result (individual)						
			Maximum	Pass/Fail	1881a	1884a	1885a	1886a	1887a	1888a	1889a
SiO_2	18.637−22.38	0.16	0.080	Pass	0.020	0.047	0.012	0.021	0.052	0.080	0.014
Al_2O_3	3.875−7.06	0.20	0.027	Pass	0.004	0.016	0.004	0.010	0.027	0.019	0.006
Fe_2O_3	0.152−3.09	0.10	0.011	Pass	0.011	0.009	0.000	0.000	0.008	0.007	0.001
CaO	57.58−67.87	0.20	0.117	Pass	0.117	0.123	0.025	0.023	0.008	0.051	0.039
MgO	0.814−4.475	0.16	0.032	Pass	0.004	0.018	0.014	0.000	0.019	0.032	0.003
SO_3	2.086−4.622	0.10	0.055	Pass	0.010	0.011	0.023	0.017	0.048	0.055	0.024
Na_2O	0.021−1.068	0.03	0.005	Pass	0.002	0.005	0.003	0.001	0.003	0.003	0.001
K_2O	0.093−1.228	0.03	0.011	Pass	0.011	0.004	0.002	0.000	0.005	0.002	0.001
TiO_2	0.084−0.366	0.02	0.002	Pass	0.001	0.003	0.001	0.001	0.002	0.002	0.001
P_2O_5	0.022−0.306	0.03	0.003	Pass	0.000	0.001	0.001	0.000	0.003	0.001	0.001
ZnO	0.001−0.107	0.03	0.001	Pass	0.000	0.000	0.001	0.000	0.000	0.000	0.000
Mn_2O_3	0.007−0.259	0.03	0.002	Pass	0.001	0.001	0.000	0.000	0.001	0.000	0.002
Cl	0.0019−0.013	0.003	0.001	Pass	0.001	0.000	0.000	0.000	0.000	0.000	0.000

Table 16. Results of bias test (pressed pellet, Supermini200).

(mass%)

Component	Range	Difference of the average of duplicates from CRM									
		Limit	Result (total)		Result (individual)						
			Maximum	Pass/Fail	1881a	1884a	1885a	1886a	1887a	1888a	1889a
SiO_2	18.637−22.38	±0.2	0.20	Pass	0.05	0.20	−0.04	−0.14	−0.14	−0.02	0.05
Al_2O_3	3.875−7.06	±0.2	0.13	Pass	0.07	−0.05	0.07	0.13	−0.11	−0.07	−0.04
Fe_2O_3	0.152−3.09	±0.10	0.041	Pass	0.005	−0.036	0.016	0.007	−0.005	0.041	−0.021
CaO	57.58−67.87	±0.3	0.18	Pass	0.18	0.01	0.07	0.12	0.00	0.13	0.03
MgO	0.814−4.475	±0.2	−0.08	Pass	−0.08	0.07	0.03	−0.02	−0.03	−0.04	0.07
SO_3	2.086−4.622	±0.1	0.08	Pass	0.03	−0.07	0.00	0.08	0.03	0.03	−0.01
Na_2O	0.021−1.068	±0.05	0.009	Pass	−0.004	−0.004	0.001	−0.006	0.001	0.009	−0.001
K_2O	0.093−1.228	±0.05	0.006	Pass	0.006	0.005	0.004	−0.001	−0.001	−0.003	0.001
TiO_2	0.084−0.366	±0.03	−0.004	Pass	0.002	0.001	0.001	0.002	−0.004	−0.003	−0.001
P_2O_5	0.022−0.306	±0.03	0.003	Pass	−0.001	0.003	0.000	0.000	−0.002	−0.002	0.001
ZnO	0.001−0.107	±0.03	−0.002	Pass	−0.002	0.000	0.000	0.000	0.000	0.001	0.000
Mn_2O_3	0.007−0.259	±0.03	0.002	Pass	0.000	0.002	0.000	0.000	−0.001	−0.001	0.001
Cl	0.0019−0.013	±0.005	−0.001	Pass	0.000	−0.001	0.001	0.000	0.000	0.001	0.000

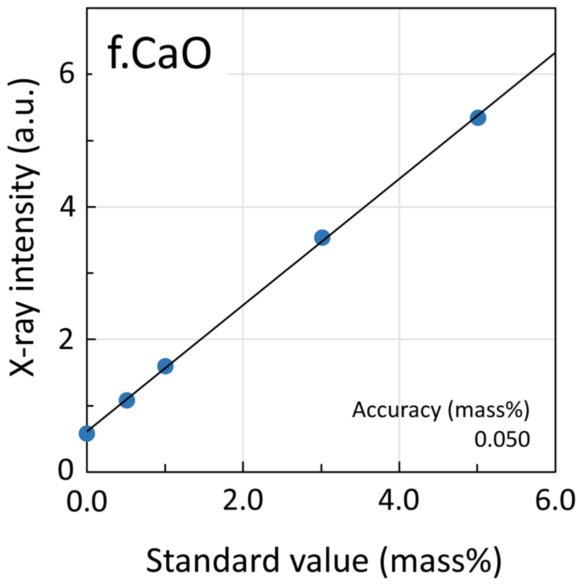

Fig. 1. Calibration curve of free lime.
Load: 40 kV–70 mA
Counting time: 10 sec.

to the quantity of f.CaO, so the XRF spectrometer enables the quantification of f.CaO content in clinker by measurement of the intensity of the diffraction peak.

Figure 1 shows a calibration curve of f.CaO using the Rigaku multi-channel simultaneous WDXRF spectrometer Simultix 15 equipped with a special fixed channel for diffraction peak measurement. Although careful sample handling and measurements are necessary because free lime is easily influenced by moisture and CO_2 gas in the air, the calibration curve shows good correlation between intensity of diffraction peak and quantity of f.CaO.

6. Summary

Certified reference materials of Portland cement were analyzed using WDXRF spectrometers and the analysis results were evaluated according to ASTM C114. It was proved that the results for a high performance WDX spectrometer and a benchtop WDX spectrometer both meet the requirements of ASTM C114.

In the cement manufacturing process, sample analysis is performed at regular intervals to control each process. Since the number of analyses for each process increases with the number of kilns and plant size, high-throughput analysis is required in cement manufacturing plants with a large production volume. For most of the components tested in this article, differences between duplicates (precision) and differences between certificates and averages of duplicates (bias) were sufficiently smaller than permissible limits defined in ASTM C114. XRF performance demonstrated in this article indicates that XRF analysis can be performed in a shorter time than the measurement conditions in this article to meet the practical use in modern cement plants.

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