Determination of refractory products with the XRF quantitative application package

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1. Introduction

Refractory products are materials that can withstand high temperatures, above 1500°C. They are used in a wide range of applications, including as the lining of furnaces that perform melting and heating processing of materials for metallurgical, chemical, ceramic, machine, glass industries and so on. There are many types of refractories, including shaped refractories that have been molded and fired beforehand in the form of the final products, powder granules, or paste-like monolithic refractories that are formed into a specific shape at a construction site. Furthermore, refractory products can have different chemical properties. For example, there are acidic refractories that mainly consist of acidic oxides such as SiO_2 and ZrO_2, basic refractories that mainly consist of basic oxides such as MgO and CaO, and neutral refractories. The type of refractory is chosen depending on its intended use. In order to maximize the performance of such refractories, it is necessary to precisely control their elemental composition to meet the needs of specific applications(1).

Analysis of refractories can be performed according to standardized methods prescribed by Japanese Industrial Standards (JIS R 2216)(2) and ISO 12677 (2011)(3), utilizing X-ray fluorescence (XRF) spectrometry, which is known as a rapid and accurate quantitative analysis method for elemental analysis(2). To obtain accurate analysis results, samples are prepared by the fusion bead method to eliminate grain size and mineralogical effects.

In order to meet customer needs, Rigaku was the first company to release quantitative application packages, including for refractories. These application packages have been well received for their ability to easily and accurately perform quantitative analysis without any specialized technical skills.

This paper describes an analysis example using an application package for quartzite refractory products, an acidic refractory. Quartzite refractories are effective for repeated heating and cooling cycles due to their small change in volume above 600°C. In addition, due to their excellent heat properties, they are widely used as construction furnaces for coke ovens, hot stoves, and glass melting chambers. It is necessary to add 4 to 5 mass% of Al_2O_3 or Fe_2O_3 etc. as a sintering aid to quartzite refractories. However, when used in a glass melting chamber, it is necessary to use a low-porosity Al_2O_3 or other low-alkali component to avoid attack by alkaline vapor in the atmosphere, and accurate analysis of coexisting elements is also required.

2. Sample preparation

The analysis used certified reference materials (CRMs) of quartzite refractory (JRRM 220 series) issued by the technical association of refractories (Japan). These CRMs are used in the application package produced by Rigaku (refer to Rigaku Journal, etc. for general information on fusion bead production) (2)–(5). The sample preparation method was according to the method of JIS R 2216. The fusion machine used is the benchtop fusion sampler with high-frequency induction technology (produced by Rigaku). Melting conditions were performed at 1150°C for 7 minutes. In order to perform accurate analysis by fusion bead, it is necessary to examine the masses of the beads and the reproducibility of the beads to determine the optimum conditions, such as fusion method, fusion temperature, fusion time. Table 1 shows measured data of fusion bead masses using JRRM221 refractory CRM. Masses of the crucible (fusion bead preparation container) and the sample, flux, and oxidizing agent were measured in advance. After making each fusion bead, measure the mass of the crucible with the fusion bead to determine the mass of the fusion bead itself. A total of six beads were prepared in the same manner. The coefficient of variation of the fusion bead masses was calculated using Eq. (1), and the test criterion is $CV_m<0.1\%$.

$$CV_m = \frac{\sqrt{\dfrac{\sum\left(m_i - \bar{m}\right)^2}{6-1}}}{\bar{m}} \qquad (1)$$

Where, CV_m: coefficient of variation of masses of beads (%)
m_i: Mass of bead i (g)
$\bar{m}$: Average of mass of bead (g)

The evaluated result obtained by Eq. (1) using the data in Table 1 was $CV_m=0.02\%$, which complies with JIS R 2216.

Table 1. Measured masses of beads for measurement condition evaluation.

Fusion bead number, i	1	2	3	4	5	6
Mass, g	4.3953	4.3949	4.3962	4.3942	4.3945	4.3943

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Table 2. Measured intensities for reproducibility test.

Component	Number of measurement, i	1	2	3	4	5	6	Average	σ
SiO_2	Measured values, integrated counts	7638800	7647120	7640120	7640720	7656680	7637080	7643420	0.08
Al_2O_3	Measured values, integrated counts	1073784	1072972	1095972	1073604	1082300	1069852	1078081	0.09

Table 3. Analytical conditions.

Component	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO
Analyte line	Kα	Kα	Kα	Kα	Kα	Kα	Kα
Power (kV–mA)	50–50						
Primary beam filter	Out						
Slit	S4	S4	S2	S4	S2	S4	S4
Attenuator	Out	Out	Out	Out	Out	Out	Out
Analyzing crystal	PETH	PETH	LiF (200)	LiF (200)	LiF (200)	LiF (200)	RX25
Detector	F-PC	F-PC	SC	F-PC	SC	F-PC	F-PC
Measurement time (sec)	40	40	40	40	40	40	40

Component	Na_2O	K_2O	P_2O_5	Cr_2O_3	ZrO_2
Analyte line	Kα	Kα	Kα	Kα	Lα
Power (kV–mA)	50–50				
Primary beam filter	Out				
Slit	S4	S4	S4	S2	S4
Attenuator	Out	Out	Out	Out	Out
Analyzing crystal	RX25	LiF (200)	GeH	LiF (200)	GeH
Detector	F-PC	F-PC	F-PC	SC	F-PC
Measurement time (sec)	40	40	40	40	40

The following is an example of the verification of fusion bead reproducibility. The measured X-ray intensities fully satisfied the criteria. The test is applied to components with 8 mass% or more. Table 2 shows the measured intensities in integrated counts of JRRM 221 for SiO_2 with 83.85 mass% and Al_2O_3 with 10.03 mass%.

$$\sigma = \frac{\sqrt{\frac{\sum\left(Y_i - \bar{Y}\right)^2}{6-1}}}{\bar{Y}} \times Z \tag{2}$$

Where, σ: Standard deviation of measurement component [mass%]

Z: Content of measurement component [mass%]

Y_i: X-ray intensity of bead i for evaluation [counts]

$\bar{Y}$: Average of measured X-ray intensity [counts]

The result of calculations using the data in Table 2 according to Eq. (2) were σ (SiO_2)=0.08 and σ (Al_2O_3)=0.09. According to JIS R 2216, bead reproducibility is evaluated according to Eq. (3).

$$\left.\begin{array}{ll} \text{Where,} & Z > 40, \sigma < 0.15 \\ \text{Where,} & 8 < Z < 40, \sigma < 0.10 \end{array}\right\} \tag{3}$$

The results satisfied the criteria for the reproducibility test. This preparation procedure produces fusion beads with good reproducibility.

3. Apparatus and measurement condition

The XRF spectrometer was the Rigaku ZSX Primus IV wavelength dispersive X-ray fluorescence spectrometer. Table 3 shows the analytical conditions, which are provided by the quantitative application package. According to JIS of refractories, the minimum accumulated X-ray counts were specified for each concentration level in JIS R 2216, and the conditions in Table 3 satisfied the criteria.

4. Calibration curves

The standard samples for calibration curves were JRRM 220 series of CRMs refractory for XRF (distribution start date: July 3, 2017). The generated calibration curves are shown in Fig. 1. The accuracy results are shown in the calibration curves, respectively.

Coexisting components in a sample affect the

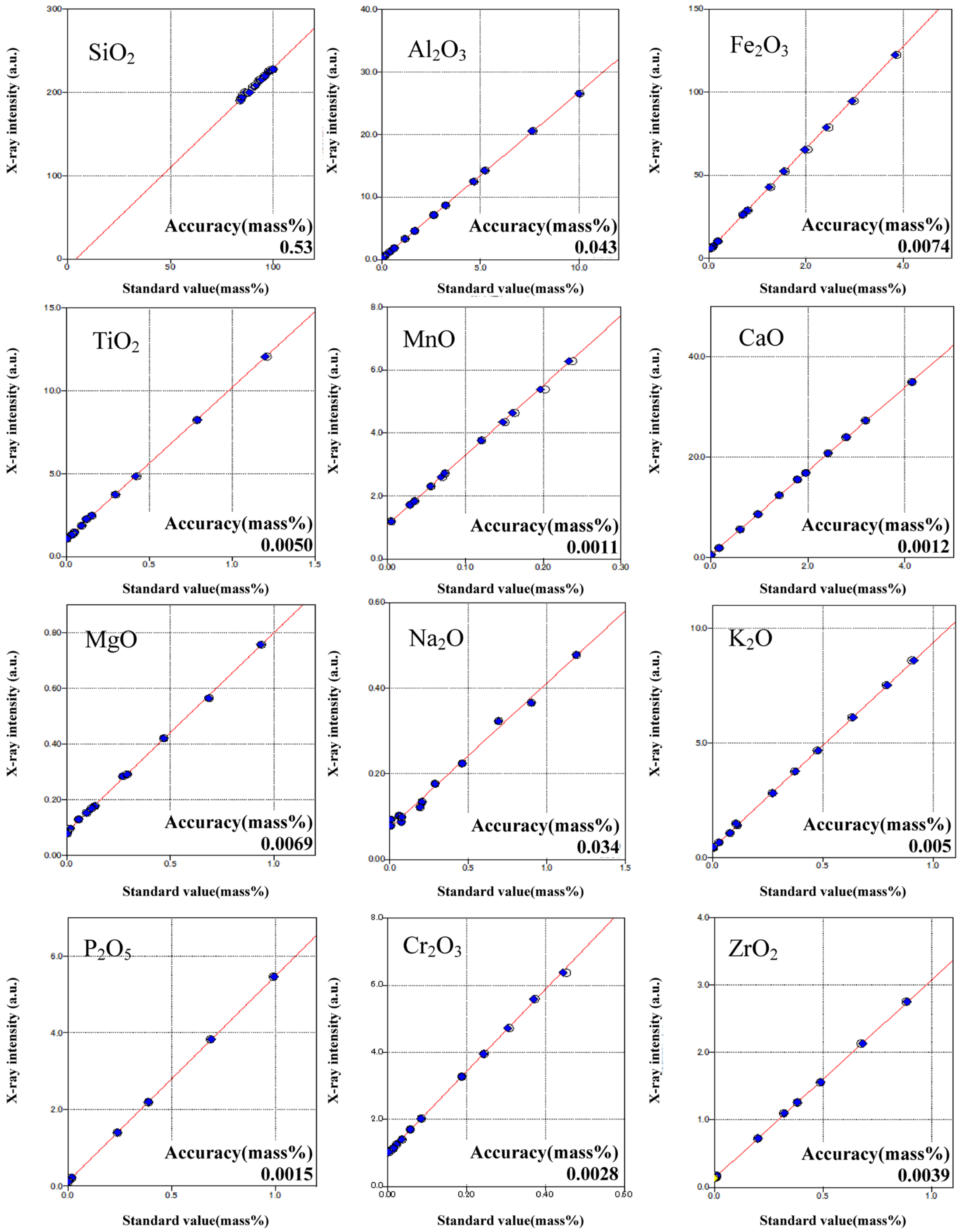

Fig. 1. Calibration curves for quartzite refractory.

fluorescent X-ray intensities of the analytical components because these materials absorb or enhance the fluorescent X-rays generated in the sample. Absorption and enhancement effects are called matrix effects, which can be corrected by a matrix correction[(6)–(8)]. The correction coefficients can be obtained by calculating the theoretical fluorescent X-ray intensities using fundamental parameters. This procedure is specified in JIS R 2216[(9)–(11)].

5. Quantitative results

Table 4 shows the results of quantitative analyses of JRRM 221 repeated 10 times to confirm measurement precision. These results show good precision.

Table 5 shows the results of quantitative analysis of a silica brick, CRM (BAS 314), as an unknown sample. The result shows good agreement with the certified values and demonstrates that the quantitative application package is available for the quartzite refractory analysis with good accuracy.

6. Conclusion

In this paper, a quantitative application package for quartzite refractory was introduced. Quantitative

Table 4. Quantitative results of JRRM221 (10 times measurement).

Unit [mass%]

Component	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	Na_2O	K_2O	P_2O_5	Cr_2O_3	ZrO_2
n=1	83.30	9.931	1.574	0.041	0.149	2.797	0.674	0.405	0.265	0.014	0.022	0.007
2	83.29	9.950	1.579	0.042	0.150	2.795	0.672	0.421	0.264	0.013	0.022	0.009
3	83.30	9.965	1.577	0.041	0.150	2.789	0.675	0.406	0.265	0.014	0.021	0.009
4	83.32	9.959	1.577	0.041	0.149	2.794	0.684	0.401	0.265	0.013	0.021	0.008
5	83.35	9.970	1.576	0.041	0.150	2.795	0.688	0.426	0.264	0.014	0.021	0.008
6	83.35	9.966	1.578	0.040	0.149	2.791	0.689	0.417	0.264	0.014	0.022	0.007
7	83.36	9.945	1.578	0.042	0.149	2.792	0.684	0.401	0.264	0.014	0.021	0.008
8	83.41	9.962	1.574	0.041	0.150	2.794	0.683	0.422	0.264	0.014	0.022	0.009
9	83.27	9.961	1.574	0.041	0.149	2.789	0.683	0.419	0.264	0.014	0.021	0.009
10	83.36	9.963	1.578	0.040	0.148	2.790	0.668	0.400	0.264	0.014	0.022	0.009
Average	83.33	9.957	1.576	0.041	0.149	2.793	0.680	0.412	0.264	0.014	0.021	0.008
Standard deviation	0.042	0.012	0.002	0.001	0.001	0.003	0.007	0.010	0.0003	0.0004	0.000	0.001

Table 5. Quantitative result of BAS314.

Unit [mass%]

Component	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	K_2O	P_2O_5	Cr_2O_3	ZrO_2
Analytical value	96.4	0.75	0.48	0.19	0.004	1.80	0.05	0.08	0.02	0.006	0.07
Certified value	96.2	0.77	0.53	0.19	<0.01	1.81	0.05	0.09	—	—	—

Table 6. Precision data of clay bricks.

Unit [mass%]

Component	analytical range	Low Conc.	Middle Conc.	High Conc.
	mass%	(Std.dev.[σ]/mass%)	(Std.dev.[σ]/mass%)	(Std.dev.[σ]/mass%)
SiO_2	37–86	0.027/42	0.033/62	0.039/81
Al_2O_3	6.1–49	0.014/10	0.023/28	0.03/45
Fe_2O_3	0.25–4.5	0.0013/0.67	0.0023/2.4	0.0029/4
TiO_2	0.056–3.4	0.0015/0.39	0.0028/1.7	0.0037/3
MnO	0.008–0.37	0.00048/0.044	0.00077/0.19	0.00096/0.33
CaO	0.11–2.8	0.0015/0.38	0.0027/1.5	0.0034/2.5
MgO	0.084–3.1	0.0054/0.39	0.0098/1.6	0.013/2.8
Na_2O	0.072–3.2	0.0096/0.39	0.017/1.6	0.023/2.9
K_2O	0.23–3.1	0.0016/0.52	0.0027/1.7	0.0035/2.8
P_2O_5	0.046–4.9	0.0022/0.53	0.0046/2.5	0.0061/4.4
Cr_2O_3	0.01–1.3	0.00099/0.14	0.0018/0.64	0.0025/1.2
ZrO_2	0.023–1.1	0.0016/0.13	0.003/0.57	0.0039/1
SiO_2(RX4)	37–86	0.018/42	0.022/62	0.026/81
MgO(RX35)	0.084–3.1	0.0032/0.39	0.0055/1.6	0.0072/2.8
Na_2O(RX35)	0.072–3.2	0.0056/0.39	0.0093/1.6	0.012/2.9

analysis can be performed easily and accurately by the quantitative application package. Finally, Table 6 and 7 show the measurement precision data of typical acid refractory clay bricks and basic refractory chromium and magnesia bricks. The precision table also includes the data with the high-sensitivity analyzing crystals RX35 (for Na and Mg) and RX4 (for Si).

Rigaku will be releasing the quantitative application packages for refractory products soon. It is believed that these packages can contribute to elemental analysis of refractory products that are essential for many industries. Recently, we have also developed pre-application packages that can be set up with databases without the need for standard samples, and have commercialized OXIDE-FB-PAK for various oxide samples[12]. We will continue to develop

Table 7. Precision data of chromium and magnesia bricks.

Unit [mass%]

Component	analytical range	Low Conc.	Middle Conc.	High Conc.
	mass%	(Std.dev.[σ]/mass%)	(Std.dev.[σ]/mass%)	(Std.dev.[σ]/mass%)
SiO_2	0.93–11	0.0092/1.9	0.016/5.7	0.021/9.6
Al_2O_3	2.9–29	0.015/5.6	0.025/16	0.033/27
Fe_2O_3	1–27	0.004/3.6	0.0079/14	0.011/24
TiO_2	0.006–1.2	0.0016/0.13	0.0025/0.61	0.0032/1.1
MnO	0.006–0.18	0.00052/0.023	0.00068/0.091	0.00081/0.16
CaO	0.071–4.1	0.0023/0.47	0.0043/2.1	0.0056/3.7
MgO	11–88	0.045/18	0.075/49	0.096/80
Cr_2O_3	2.8–52	0.0083/7.8	0.017/28	0.022/47
SiO_2(RX4)	0.93–11	0.0064/1.9	0.011/5.7	0.014/9.6
MgO(RX35)	11–88	0.026/18	0.042/49	0.054/80

application packages so that users can obtain more accurate quantitative analysis more easily for variety of applications.

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