XRF1052 - Accurate determination for elements in laterite ores by pressed powder method

Introduction

Nickel laterite is one of the two types of ores for nickel extraction. The other type of ore is sulfide. Currently, 40% of the world's nickel production is obtained from laterite ores. Its share is however likely to increase since most ore reserves and a majority of nickel mining projects currently under development are laterite deposits.

In nickel laterite mining, nickel and cobalt are target metals that represent ore grade. Iron and magnesium in laterite ore are indicative elements to determine extraction method, which is hydrometallurgical or pyrometallurgical process.

In modern resource industries, demand for accurate and quick determination of elements in ores is increasing in order to efficiently operate mining and processing. Wet chemical analysis, which is the traditional analytical technique for elemental determination, requires time and expertise for sample preparation and is therefore not suited for the rapid analysis of large number of samples.

X-ray fluorescence spectrometry (XRF) with pressed powder method can overcome these problems. For the analysis of laterites by XRF, to detect trace amount of cobalt, high spectral resolution is required since a large iron peak is present adjacent to the cobalt peak in the spectrum. In addition, high sensitivity is required for the analysis of light elements such as magnesium.

Wavelength dispersive XRF (WDXRF) can meet both of these requirements.

This note demonstrates an improved method to determine multiple elements in nickel oxide ores by pressed powder method.

Instrument

The Supermini200 is a unique benchtop sequential WDXRF spectrometer with high spectral resolution and high sensitivity for light elements. The spectrometer is designed to minimize installation utilities such as cooling water, power supply and installation space. For the analysis of light elements, the newly developed sealed proportional detector (S-PC) can be substituted (option) for the conventional flow proportional detector (F-PC). Since the S-PC eliminates the need for an external P10 (detector) gas cylinder, the Supermini200 can be a truly utility-free WDXRF instruments. It is equipped with an air-cooled 200W X-ray tube and up to three analyzing crystals allowing analysis of element oxygen to uranium.

The functionally versatile software allows easy setup of various types of applications. In particular, the flowbar guides the user step by step for the setting up of quantitative and qualitative analysis conditions.

The user friendly interface of the semi-quantitative analysis program "SQX" allows quick elemental determination of unknown samples without the need for reference materials.

Quant Scatter FP function

"Quant Scatter FP" is a unique function integrated Rigaku Fundamental Parameter (FP) system. The function is able to generate dedicated theoretical alphas to correct for matrix effects in empirical calibration curve by the internal standard method using scattering X-rays. The internal standard method using scattering X-rays (Compton scattering X-ray) without theoretical alphas has been preferred for heavy element analysis in some ores because of its ease of use. However, this conventional method does not fully correct for matrix effects especially for ore samples with high heavy element content. Rigaku's correction scheme overcomes this problem by integrating the Compton scattering internal standard correction method with theoretical alpha correction by FP method. This advanced correction method for powder samples provides improved analysis results of ores.

"Quant Scatter FP" function (optional) is available for Supermini200 as well as Rigaku Simultix and ZSX Primus family.

Standard and sample preparation

The standard samples used for calibration are commercially available 14 certified reference materials (CRMs). These standards are composed of typical nickel laterites including saprolite and transitional type ores. This implies that these references cover ores from almost the entire stratigraphic profile in typical laterite deposits. Concentration range of nickel and cobalt in these CRMs is from 0.37 to 2.9 and 0.021 to 0.090 mass%. Iron and magnesium content ranges from 8.9 to 47 mass%, 1.2 to 17 mass%, respectively. Careful and consistent pulverization is quite essential to obtain good results because mineral assemblages are different depending on ore type. In addition, since laterite ores are highly hydroscopic, it is recommended to measure the specimen immediately after pelletization.

The well-dried (2 hours at 105°C) samples were ground and then pressed at 200 kN using sample cup. Generally, adding binder for pelletization introduces a potential source of analytical error in internal standard method using Compton scattering X-rays. Therefore, applications requiring high degree of accuracy should avoid use of binder.

Measurement and calibration

Supermini200 was used for the measurement of Ni, Co, Cu, Zn, Cr, Fe, Na, Mg, Si, Al, P, S, Ca, K, Ti and Mn element lines. Pd-Kα Compton scattering X-ray which is used for correction was also measured.

The calibration equation for nickel, iron and zinc is as follows:

$$W_i = (AI_R^2 + BI_R + C) \cdot (1 + \sum \alpha_j W_j)$$

$I_R = \frac{I_i}{I_{Compton}}$

α_j : theoretical alpha of element j

W_j : weight fraction of element j

I_i : intensity of element i line

$I_{Compton}$: intensity of Pd-Kα Compton line

A, B, C : constant

Calibration for other components uses the following equation:

$$W_i = (BI_i + C) \cdot (1 + \sum \alpha_j W_j)$$

α_j : theoretical alpha of element j
W_j : weight fraction of element j
I_i : intensity of element i line
B, C : constant

Matrix correction coefficients (alpha) applied to the calibrations are theoretically calculated by the FP software. The theoretical alphas for nickel, iron and zinc calibration are calculated by taking the Compton scattering internal standard into consideration by the Quant Scattering FP function integrated in the software.

Results

Calibration curves for Ni, Co, Fe, Mg, Al and Ca are shown in Figure 1. Aluminum, calcium and magnesium are elements of interest as well. It is preferred that the content of these elements are low, since they cause excessive consumption of sulfuric acid during the metal extraction process when the laterite ore is leached.

Calibration accuracies for all measured elements are listed in Table 1.

The accuracy of calibration is calculated by following the equation:

$$Accuracy = \sqrt{\frac{\sum_i (C_i - \hat{C}_i)^2}{n-m}}$$

C_i: calculated value of standard sample
$\hat{C}_i$: reference value of standard sample
n : number of standard samples.
m: degree of freedom (linear 2, quad. 3)

The Rigaku correction method is compared to the conventional internal standard method and theoretical alpha correction. Results are shown in Table 2.

One saprolite and a transitional type ore were measured 10 times to demonstrate the instrument's high precision. Results are summarized in Table 3 and 4. From rough estimation on the basis of these repeatability tests, 0.1 mass% of LOQ (limit of quantitation) is expected in magnesium analysis.
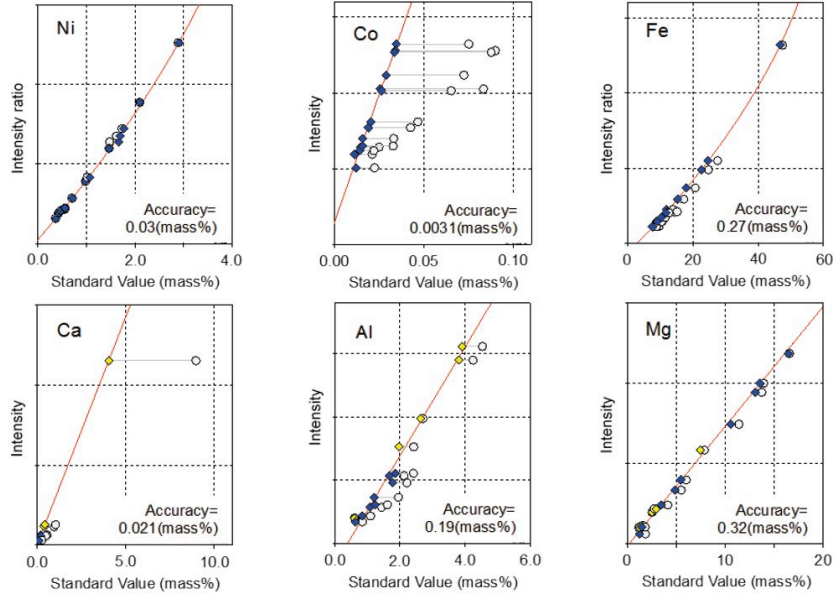
Figure 1: Calibration curves of representative elements in nickel laterite ores. Calibration curves of nickel, iron and zinc use Compton scattering internal standard combined with theoretical alpha correction. Blue: Corrected (certified), Yellow: Corrected (uncertified), Circle: Uncorrected.

Table 1: Accuracy of calibration curves (unit: mass%)

Element	Concentration range	Typical accuracy of calibration
Ni	0.37 - 2.9	0.030
Co	0.002 - 0.090	0.0031
Fe	8.9 - 47	0.27
Mg	1.2 - 17	0.32
Na	0.006 - 0.47	0.016
Al	0.62 - 4.5	0.19
Si	3.2 - 33	0.71
P	0.002 - 0.017	0.0010
S	0.002 - 1.3	0.016
K	0.009 - 0.28	0.0018
Ca	0.095 - 9.0	0.021
Ti	0.012 - 0.21	0.0014
Cr	0.14 - 1.8	0.022
Mn	0.009 - 0.28	0.0067
Cu	0.085 - 0.58	0.0019

| Zn | 0.005 - 0.14 | 0.0017 |

Table 2: Comparison among correction methods for iron (unit : mass%)

Standard Sample	Chemical value (Fe)	Correction method		
		Rigaku correction	Theoretical alpha	Conventional internal standard
A	47.46	47.49	47.73	47.45
B	14.4	14.1	14.3	13.7
C	9.68	9.66	9.52	9.33
D	14	14.8	15.2	14.4
E	15.2	14.8	14.9	13.7
F	10.6	10.9	10.8	10.7
G	20.72	20.66	20.23	20.48
H	8.90	9.00	9.10	9.18
I	27.57	27.72	27.60	27.45
J	10.45	10.44	10.60	10.75
K	24.76	24.75	24.16	25.20
L	17.23	16.99	17.17	17.37
M	11.48	11.41	11.69	11.98
N	12.70	12.54	12.80	13.41
Standard error of estimate		0.28	0.49	0.55

Table 3: Result of precision test for saprolite ore (unit : mass%)

Element	Certified value	Average of 10 measurements	Std. dev.	RSD%
Ni	2.10	2.15	0.007	0.32
Co	0.0424	0.0399	0.0006	1.5
Fe	11.48	11.45	0.02	0.19
Mg	13.73	13.27	0.02	0.19
Na	0.020	0.029	0.003	12
Al	1.44	1.39	0.003	0.23
Si	20.05	19.87	0.04	0.20
P	0.0018*	0.0018	0.0003	14
S	-	0.010	0.001	12

K	0.0093*	0.0108	0.0008	7.5
Ca	0.229	0.215	0.0008	0.38
Ti	0.020	0.021	0.0006	3.0
Cr	0.557	0.525	0.003	0.56
Mn	0.203	0.202	0.001	0.57
Cu	0.0041	0.0058	0.0002	2.9
Zn	0.0184	0.0170	0.0002	1.0

* Uncertified

Table 4: Result of precision test for transitional ore (unit : mass%)

Element	Certified value	Average of 10 measurements	Std. dev.	RSD%
Ni	1.02	1.01	0.005	0.49
Co	0.0899	0.0873	0.0007	0.85
Fe	27.57	27.88	0.1	0.41
Mg	1.81	1.91	0.009	0.49
Na	0.0056	0.0050	0.003	63
Al	2.42	2.19	0.003	0.14
Si	19.71	19.53	0.04	0.20
P	0.0074	0.0078	0.0004	4.9
S	-	0.012	0.001	10
K	0.0086*	0.0083	0.0008	9.1
Ca	0.165	0.184	0.0008	0.46
Ti	0.035	0.036	0.0007	1.87
Cr	1.20	1.22	0.006	0.5
Mn	0.525	0.516	0.003	0.56
Cu	0.0060	0.0040	0.0002	5.9
Zn	0.0287	0.0277	0.0003	0.97

*: Uncertified

Conclusions

This application note demonstrates that it is possible to accurately analyze nickel oxide ores with wide concentration ranges from low to high grade nickel laterite by the pressed pellet method.

The results also indicate that Supermini200 is applicable to ore characterization and discrimination analysis for most stratigraphic profiles in typical laterite deposits.

The pressed powder method with Rigaku's advanced correction technology can play a valuable role in various fields such as elemental analysis in exploration, metal extraction as well as quality and process control in mining and mineral processing.

Related products

Supermini200

Benchtop tube below sequential WDXRF spectrometer analyzes O through U in solids, liquids and powders