Application Note: 41703

Analysis of Metallurgical Slags

ARL OPTIM'X WDXRF Simultaneous Configuration

Key Words

- ARL OPTIM'X
- Iron & Steel
- Slags
- X-Ray Fluorescence

Introduction

Slags originate from various stages in the iron & steel process, e.g. blast furnace, converter, basic oxygen furnace (BOF also referred to as BOS = basic oxygen steelmaking), electric arc furnace or ladle.

In the blast furnace, slag is formed from impurities in the iron ores (known as the gangue), the flux and coke ashes. It is a complex silicate of aluminum, calcium and magnesium containing small quantities of manganese and iron oxides as well as calcium sulfide. Slag has a double role: it permits removal of the gangue thanks to its fusibility and fluidity. It also allows exchange reactions with the liquid metal and permits a control of the process in order for the desirable elements to stay in the melt while the others are removed. As an example, in an electric arc furnace the slag formation process can be controlled by adding oxygen, carbon and slag formers to the melt. This will promote formation of CO instead of MnO and FeO and help keep these elements in their metallic form in the melt. The basic slag formers like lime (CaO) and magnesia (MgO) will help neutralize the acidity of the slag in order to save the refractory bricks of the furnace.

Instrumentation

The Thermo Scientific ARL OPTIM'X is an entry level WDXRF instrument designed for ease of use and minimal operating and maintenance costs. An ARL OPTIM'X XRF spectrometer configured with eight fixed channels for the elements/oxides as listed in Table 1 was used to obtain the results presented in this application note. The instrument is fitted with a low power Rh anode X-ray tube; its geometry is optimized to provide the highest sensitivity. It does not require external or internal water cooling. Detector gas supply is not needed in this configuration. It has about 10 times better spectral resolution than a conventional EDXRF instrument as well as superior precision, short and long term stability. It can analyze Na and Mg without any problem. Ease of operation is obtained through OXSAS, our modern, powerful and user-friendly software supporting instrument operation and data handling.

Sample preparation

Slags samples were crushed and ground in a mill to less than 50 microns to avoid particle size effects. Magnetic separation of metallic residues is performed on the milled fractions before further preparation. In general the pressed powder method is used for routine elemental determinations in slags, especially when fast reporting is important.

Calibration and results

Eleven standard reference materials have been used for calibration of the ARL OPTIM'X: BCS 174/2, BCS 381, BCS 382/2, BS 100, BS 101/1, BS 101/3, BS 101/4, BS 101/5, JK S1, JK S3, JK S8. These standard samples allow the concentration ranges shown in Table 1 to be covered.

A working curve is established for each element using the Multi-Variable-Regression incorporated in the OXSAS software package. The Standard Error of Estimate (SEE) is a measure of the accuracy of analysis. It is the average error between the certified concentration of the standard samples and the calibration curve of a given oxide. Table 1 shows the limits of detection for the various elements/oxides derived from the calibration curves.

ELEMENTS/ OXIDES	CALIBRATION RANGES	SEE (%)	LOD FIXED CHANNELS (3 SIGMA) (120S)
Fe_2O_3	0.4% - 20%	0.16	15 ppm
Al_2O_3	0.5% - 10%	0.05	n.r.
MgO	1.0% - 12%	0.15	72 ppm
P_2O_5	0.2% - 16%	0.06	12 ppm
SO_3	0.1% - 1.5%	0.025	12 ppm
SiO_2	8% - 40%	0.18	n.r.
CaO	32% - 55%	0.5	n.r.
K_2O	0.05% - 1.5%	0.007	9 ppm

Table 1: Summary of performance – Fixed channels

LoD = limit of detection (3 sigma) in 120 s counting time
SEE = Standard error of estimate : it is a measure of the accuracy
n.r. = not relevant in view of the high concentration range

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Stability tests

In order to show the excellent repeatability of the ARL OPTIM'X for the analysis of slags, both short and long term stability tests were performed. A counting time of 30 seconds was chosen with the fixed channels. For short term repeatability, 10 consecutive measurements were performed on two pressed standards. Average concentration and standard deviations are shown in Table 2.

		BCS 382/1		BS 100	
ELEMENTS	ANALYTICAL DEVICE	AVERAGE CONCENTRATION %	TYPICAL STD.DEV. %	AVERAGE CONCENTRATION %	TYPICAL STD.DEV. %
Al_2O_3	Fixed	3.78	0.012	9.69	0.026
CaO	Fixed	40.49	0.05	35.92	0.04
Fe_2O_3	Fixed	19.98	0.02	0.52	0.0018
K_2O	Fixed	0.0089	0.0006	0.60	0.0032
MgO	Fixed	3.54	0.042	14.41	0.038
P_2O_5	Fixed	3.01	0.0042	0.033	0.001
SO_3	Fixed	0.39	0.002	1.47	0.0034
SiO_2	Fixed	12.99	0.024	36.40	0.094

Table 2: Results of a repeatability test (10 runs) for a simultaneous configuration: 30 s counting time

For long term repeatability test, one of the pressed standard specimen was analyzed every 30 minutes over 12 hours. Average concentration and standard deviations are shown in Table 3.

	BCS 382/1	
ELEMENTS	AVERAGE %	ST.DEV. %
Al_2O_3	3.78	0.016
CaO	40.49	0.052
Fe_2O_3	19.98	0.024
K_2O	0.0089	0.0006
MgO	3.54	0.042
P_2O_5	3.01	0.009
SO_3	0.39	0.0018
SiO_2	12.99	0.046

Table 3: Reproducibility over 12 hours: 30 s counting time

Conclusion

The ARL OPTIM'X low power WDXRF instrument successfully analyzed various elements in slags.
The limitation in terms of accuracy is not due to the instrument, but to the pressed pellet sample preparation and the variety of slags used in this test. In order to get the best accuracy with slags of different origins it is necessary to prepare the samples as fused beads with lithium tetraborate (see application note nr. 41702) in order to avoid grain size effects and mineralogical effects.

The limits of detection obtained are sufficient in view of the concentration ranges of slags. Excellent repeatability and reproducibility is obtained with 30 seconds counting time. This fast analysis is obtained as fixed channels are fitted for the eight elements considered. If necessary even better results can be obtained by increasing the counting time. Should additional elements need to be analyzed a SmartGonio™ can be used in parallel with two fixed channels (see application note nr. 41704).

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