Application Note: 41704

Analysis of Metallurgical Slags

ARL OPTIM'X WD-XRF Sequential-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 oxides of manganese and iron 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 reaction 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 a WD-XRF instrument designed for ease of operating and low maintenance costs. An ARL OPTIM'X XRF spectrometer configured as a sequential-simultaneous unit was used to obtain the results presented in this application note. The instrument was fitted with a SmartGonio™ covering elements from Al (Z=13) to U (Z=92) and with fixed channels for elements Mg (Z=12) and Na (Z=11). The ARL OPTIM'X XRF spectrometers are fitted with a low power Rh anode X-ray tube and the geometry of the instrument is optimized to provide the highest sensitivity. The instrument does not require external or internal water cooling, and has 10 times better spectral resolution than a conventional EDXRF instrument as well as superior precision, short and long term stability. It can analyse Na and Mg without any problem, or even F in slags if necessary. Ease of operation is obtained through the state-of-the-art WinXRF software running under Windows® XP Professional environment.

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

Ten secondary slag standards were used for calibration of the ARL OPTIM'X. 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 WinXRF 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.

ELEMENTS/ DEVICE	ANALYTICAL RANGES	CALIBRATION RANGES	SEE (%)
Fe_2O_3	SmartGonio™	1.6% - 34%	0.27
Al_2O_3	SmartGonio™	1% - 52%	0.19
MgO	Fixed	3.1% - 12.2%	0.22
P_2O_5	SmartGonio™	0.021% - 0.9%	0.012
S	SmartGonio™	0.035% - 0.21%	0.0067
SiO_2	SmartGonio™	4.2% - 16.3%	0.22
CaO	SmartGonio™	30% - 58%	0.33
MnO	SmartGonio™	1.5% - 4.9%	0.027

Table 1: Summary of performance

Stability tests

In order to show the excellent repeatability of the ARL OPTIM'X for the analysis of slags, both in short and long term, stability tests were performed. A counting time of 20 seconds was chosen for each element measured on the SmartGonio™. Mg on the fixed channel was analyzed in parallel during 140 seconds. For short term repeatability 10 consecutive measurements were performed on two pressed standards. Average concentration and standard deviations are shown in Table 2.

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ELEMENT/ OXIDE	ANALYTICAL DEVICE	COUNTING TIME	SLAG A AVERAGE CONCENTRATION %	SLAG A TYPICAL STD.DEV. %	SLAG B AVERAGE CONCENTRATION %	SLAG B TYPICAL STD.DEV. %
Al_2O_3	SmartGonio™	20 s	38.52	0.028	1.16	0.02
CaO	SmartGonio™	20 s	46.49	0.055	35.57	0.035
Fe	SmartGonio™	20 s	2.51	0.01	32.7	0.04
MnO	SmartGonio™	20 s	1.69	0.006	2.17	0.007
MgO	Fixed channel	Fixed	6.25	0.02	7.21	0.04
P_2O_5	SmartGonio™	20 s	0.033	0.0036	0.476	0.01
S	SmartGonio™	20 s	0.069	0.0018	0.061	0.001
SiO_2	SmartGonio™	20 s	5.99	0.03	6.92	0.028

Table 2: Results of a repeatability test (10 runs) for a sequential-simultaneous configuration: total counting time per run is 140s in this example

For long term repeatability test, one of the pressed standard specimen was analyzed every 8 minutes over 12 hours. The total counting time per run was set at 140s. Average concentration and standard deviations are shown in Table 3.

ELEMENTS	ANALYTICAL DEVICE	COUNTING TIME	SLAG C AVERAGE CONCENTRATION %	SLAG C ST.DEV. %
$Al_2 O_3$	SmartGonio™	20 s	3.78	0.023
CaO	SmartGonio™	20 s	34.49	0.04
Fe	SmartGonio™	20 s	25.25	0.028
MnO	SmartGonio™	20 s	2.82	0.01
MgO	Fixed channel	Fixed	7.11	0.024
P_2O_5	SmartGonio™	20 s	0.5	0.008
S	SmartGonio™	20 s	0.06	0.0017
SiO_2	SmartGonio™	20 s	16.3	0.054

Table 3: Results of an overnight reproducibility test over 12 hours

Conclusion

The ARL OPTIM'X low power WD-XRF instrument successfully analyzed various elements in slags.
The limitation in term of accuracy is not due to the instrument, but to the pressed pellet 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. Good repeatability and reproducibility is obtained with 140s of total counting time with the SmartGonio™ working in parallel to the fixed channels. If better results are required for any element the counting time for that particular element can be increased.

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