

SCOPE

The analysis of major oxides iron, calcium and silicon in electric arc furnace slag (EAFS) is demonstrated for screening purposes, furnace control and slag quality control. Performance for other oxides is also summarized.

BACKGROUND

Electric arc furnace steelmaking, also called EAF, typically uses Direct reduced iron or ferrous scrap as the feed materials. In the electric arc furnace lime (calcium) is added to remove silicates and phosphorus. With the addition of oxygen the ferrous materials are essentially melted, while the remaining material is changed to oxide forms. The slag by-product, also called EAFS, contains relatively constant levels of these oxides and variable amounts of iron, calcium and silicon oxides. Monitoring the FeO levels indicates the efficiency of the process, while monitoring the ratio of CaO to SiO₂ gives information on the basicity of the slag. The slag is then collected and either refined to be fed back into the steelmaking system, or sold as an aggregate. The high iron and low silicate content and hardness of the EAFS make it unsuitable as a cement raw material, but make it an excellent aggregate in asphalt and construction usage.



INSTRUMENTATION

Model:	Rigaku NEX QC ⁺
X-ray tube:	4 W Ag-anode
Detector:	SDD
Sample Type:	Slag
Film:	Mylar
Analysis Time:	200 sec
Environment:	Air
Optional:	Autosampler Manual Sample Press



SAMPLE PREPARATION

For quick screening, grind or break up the sample to a particle size approximately 1mm or less. Light element analysis may be improved by grinding to <60 mesh, with optimum grind being <200 mesh. The results shown here use a grind of approximately 60 mesh (~0.3mm particle size). EAFS has a hardness between 5-7 on the Mohs scale, and so grinding tools should be a harder material such as tungsten carbide or zirconia (hardness ~8). Once in homogeneous semi-powder or powder form, each sample was prepared by transferring 7g of loose powder to an XRF sample cup and compressing to 250 inch-pounds torque using a Manual Sample Press.

CALIBRATION

Standards were ground to ~60 mesh. Eleven assayed calibration standards were used to develop empirical calibrations for FeO, CaO and SiO₂. In this example the other oxides present did not need to be measured, as their concentrations remained relatively constant and did not cause variations in X-ray absorption properties.

Component	Concentration Range (mass%)	Standard Error of Estimate (SEE)	R ² Confidence
FeO	26.00 – 50.00	0.545	0.99517
CaO	17.74 – 24.41	0.251	0.98733
SiO ₂	12.47 – 14.43	0.083	0.98575

REPEATABILITY

To demonstrate repeatability (precision), the high and low calibration standards were selected and measured in 10 repeat analyses using an analysis time of 200 sec per sample without moving the sample between measurements. The sample grind was ~60 mesh.

Sample ID: Standard 681				
Component	Standard Value	NEX QC ⁺ Average Value*	STD Dev	% Relative
FeO	49.89	49.83	0.11	0.2
CaO	17.74	17.62	0.03	0.2
SiO ₂	12.47	12.40	0.02	0.2

Sample ID: Standard 624				
Component	Standard Value	NEX QC ⁺ Average Value*	STD Dev	% Relative
FeO	25.96	25.86	0.04	0.2
CaO	24.41	24.14	0.03	0.2
SiO ₂	14.43	14.34	0.01	0.1

* Average value reflects the fitted measured value from the calibrations.

DETECTION LIMITS (LLD – Lower Limit of Detection)

The empirical method was used to determine the detection limits for FeO, CaO and SiO₂. Boric acid powder was used as a blank sample. In the empirical method, 10 repeat analyses of a blank sample are taken with the sample in static position, and the standard deviation (σ) is determined. The LLD (Lower Limit of Detection) is then defined as 3σ . The measurement time for LLDs shown below is 200 sec per analysis. The LLD is determined by the analysis time, the concentrations of other elements present and the concentration range of a calibration.

LLD from Blank Standard	
Component	LLD
FeO	0.003
CaO	0.018
SiO ₂	0.018

FULL CHARACTERIZATION

Iron, calcium and silicon oxides are the main components of interest for optimum furnace control and slag quality. Other oxides may also be measured using NEX QC⁺. To calibrate, a set of standards that characterizes the particular EAF slag is obtained and assayed for the oxides present. Given a good set of matrix-matched calibration standards that models the slag of interest, the following typical performance can be expected.

Typical Analytical Ranges and Precision

Component	Concentration Range	Relative Precision (repeatability)
SiO ₂	2 – 5%	0.3 – 0.6% rel
Total Fe	0.45 – 0.65%	0.2 -0.4% rel
Al ₂ O ₃	30 – 40%	0.3 – 0.6% rel
CaO	50 – 60%	0.1 – 0.2% rel
TiO ₂	0.1 – 0.2%	4 – 9% rel
MgO	5 – 8%	1.7 – 2.2% rel
Cr ₂ O ₃	0.04 – 0.05%	2 – 5% rel
MnO	0.04 – 1.5%	2 – 4.5% rel
P ₂ O ₅	0.01 – 0.02%	3 – 8% rel
S	0.2 – 0.8%	0.4 – 1.4% rel

Typical Detection Limits using 200 sec total Analysis Time

Component	Empirical LLD	Condition Count Time
SiO ₂	0.029%	100 sec
Al ₂ O ₃	0.040%	100 sec
TiO ₂	0.037%	100 sec
Total Fe	0.001%	100 sec
CaO	0.022%	100 sec
MgO	0.262%	100 sec
Cr ₂ O ₃	0.003%	100 sec
MnO	0.009%	100 sec
P ₂ O ₅	0.001%	100 sec
S	0.009%	100 sec

DISCUSSION

EAFS samples originate as large, hard chunks. Some sample preparation is required to either break the sample or grind to a powder. For screening and monitoring for general trends, larger particle size up to ~1mm is suitable. Performance is improved by grinding to powder ~60 mesh. Powder samples are typically compacted using the Manual Sample Press to minimize variations in X-ray scatter caused by large particle size. Optimum results and optimum light element performance are achieved by grinding powder to <200 mesh (<75um particle size) and making a hydraulically pressed pellet using 20 tons pressure. Optimum light element performance is also achieved using Prolene film and helium purge atmosphere.

Larger particle sizes may affect accuracy to a greater extent than precision. In cases of larger particle size, a sample spinner is recommended to help even out variations in X-ray scatter. The same sample preparation should be used for calibration standards and unknown samples being measured.

CONCLUSION

The NEX QC⁺ offers technicians and non-technical operators a simple yet powerful and versatile system for quantifying elemental composition using the empirical approach. The results of this study indicate that given stable samples, proper sample handling and proper calibration technique, the Rigaku NEX QC⁺ EDXRF can achieve excellent results in screening and monitoring the concentration of FeO, CaO and SiO₂ in electric arc furnace slag and other similar matrices. Given suitable calibration standards other elements and oxides may be measured by EDXRF, as well, including MgO, Al₂O₃, TiO₂, Cr₂O₃, MnO, P₂O₅ and S.