DETERMINATION OF SULPHUR CONTENTS IN METALLURGICAL SLAGS

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Abstract

Metallurgical slag is a waste product of metallurgical processes and an important raw material, for example, in the construction industry or road building. The use of slag depends, among other things, on its chemical composition. Sulphur is an undesirable element in most metallurgical products. This paper deals with determining sulphur content in different types of metallurgical slags by two different methods - X-ray fluorescence spectrometry and combustion elemental analysis. Using standards, it statistically compares the results of the two methods, evaluates the repeatability of the measurements, and assesses the amount of sulphur in different types of slags.

Keywords: Metallurgical slags, XRFS, elemental analysis, determination of sulphur content

1. INTRODUCTION

Sulphur is an undesirable element in most metallurgical products [1]. It enters steel from steelmaking raw materials. At high temperatures, it causes a phenomenon called hot cracking in steel, which occurs due to the formation of crystallisation cracks [2]. Sulphur also impairs weldability and reduces corrosion resistance [3]. Therefore, sulphur is removed from the steel by a refining process and is transferred to the slag. The high temperature positively affects desulphurisation and the high basicity, large quantity, and low oxidisability of the refining slag [4].

Sulphur is also an undesirable ingredient in pig iron production. Slag is used for the removal of sulphur impurities or desulphurisation. Slag is used for desulphurisation of pig iron and has the physical properties and chemical composition to remove the sulphur impurities from the pig iron as completely as possible. By controlling the volume and chemical composition of the blast furnace slag, the sulphur content of the molten metal can be controlled [5].

Metallurgical slags are divided into blast furnace slags and steel slags [6]. In more detail, they are designated according to the type of furnaces where they are produced. The slag from metallurgical processes has a varied composition. It consists mainly of alkaline earth metal oxides and minor components, phosphorus compounds, metal particles and sulphur [7]. In all types of metallurgical slags, the sulphur content ranges from 0.05% to 1.5% [8].

The chemical composition of the slag produced from the blast furnace depends on the origin of the ore, the coke consumption, the composition of the limestone flux and the type of iron produced. Smelter ore deposits and technology can vary over the years; these variations, therefore, change the representation of the four main oxides: CaO, SiO_2, Al_2O_3 and MgO. Other oxides that slag may contain are TiO_2, Na_2O and K_2O. Minor constituents include sulphides, FeO and MnO [9].

The chemical composition of steel slag is more variable than that of blast furnace slag. In most steel slags, the four most abundant oxides are CaO, MgO, FeO, and SiO_2. The ratio of these oxides and secondary oxides is highly dependent on the furnace conditions, the raw material, and the type of steel produced. Slag from a converter furnace generally has a lower silicon content and a higher manganese and iron content. Ladle slag differs from other steelmaking slags in that it has the most significant variance in the abundance of individual constituents [8].

Air-cooled blast furnace slag is used as a road base material. This slag has no risk of alkaline reactions, does not contain clay or organic impurities; therefore, it is used as a concrete admixture in the same way as natural admixtures. It is also used as a raw material for producing stone wool or as a calcium silicate-based fertiliser [10].

Granulated blast furnace slag has excellent hydraulic properties, so it is used in products such as Portland blast furnace slag cement, which has the same properties as ordinary Portland cement. Around 70% of the total production of blast furnace slag is used only as a substitute for Portland cement. The advantages of this blast furnace slag cement are its low heating rate when reacted with water, high chemical resistance, and increasing strength with time. Therefore, this slag is used in many areas, including the construction industry. Like air-cooled slag, it is used as a calcium silicate-based fertiliser but also for improving soil quality [10,11].

Steel slag is used as a material for road base layers due to its good hydraulic properties and high load-bearing capacity. These slags also have excellent wear resistance and are used as aggregate for asphalt concrete. They can also be used in agriculture for soil cultivation or as fertilisers. Furthermore, they are applied as an admixture in cement clinker or as a material for construction and site improvement [10,12].

Sulphur is an undesirable admixture in slag. It comes mainly from pyrite, used as a raw material in blast furnaces and as fuel. In molten slag, sulphur is contained in the form of the anion S^{2-} and during quenching, most of it is removed as H_2S with water vapour [13]. The content of S^{2-} anion in blast furnace slag ranges from 0.5% to 3.8%. According to the European standard EN 15167-1 [14], the sulphate and sulphide slag content should be ≤2.0% and <2.5%, respectively. Exceeding this amount results in delayed formation of ettringite, which has a negative impact on the mechanical properties of the slag. If the slag contains large amounts of sulphur, it cannot be reused in production or recycling [13,15].

The aim of the research published in this paper is a statistical comparison of methods suitable for the determination of sulphur content in different types of metallurgical slags, namely X-ray fluorescence spectrometry and elemental combustion analysis, and verification of their accuracy and precision.

2. EXPERIMENTAL MATERIAL

To validate the methodology for the determination of sulphur and, in the case of elemental analysis, carbon contents, 12 commercially available slag standards were selected (see **Figure 1** for an example), and 45 samples of 5 slag types were selected for comparison of the two sulphur determination methods (see **Table 1**). The slags were ground to a grain size of <0.1 mm (see **Figure 1** for an example).

Figure 1 Certified standard sample (left) and ladle slag sample (right)

Table 1 Distribution of slag samples

Sample number	Type of slag
1-12	granulated blast furnace slag (GBFS)
13-25	ungranulated blast furnace slag (UgBFS)
26-29	furnace slag - tandem (FST)
30-33	furnace slag - converter (FSC)
34-45	ladle slag (LS)

3. EXPERIMENTAL METHODS

This paper compares two methods for determining sulphur in metallurgical slags, namely X-ray fluorescence spectrometry and elemental combustion analysis.

The determination of sulphur content in the induction furnace of an elemental combustion analyser (EA) is one of the most sensitive and accurate methods. The ELTRA CS 2000 analyser was used for this purpose. It can be used to determine the total sulphur (and simultaneously, also carbon) content of steels [16], cast irons, non-ferrous alloys [17], ceramic materials [18], bentonite binders [19] and slags, as well as organic and nanomaterials. Ceramic crucibles were used for the analysis, which had to be pre-annealed in a furnace at 1000 °C. Approximately 0.25 g of slag was weighed into the crucible, and 0.8 g of powdered iron and 1.6 g of tungsten as a flame accelerator were added. For the calibration of the analyser, the Automatstal NR 6A standard with a sulphur content of 0.150% was used.

X-ray fluorescence spectrometry (XRFS) is a non-destructive instrumental method used for qualitative and quantitative elemental analysis based on the measurement of the wavelength of X-rays and the evaluation of spectral line intensities [20]. XRFS was performed on a Rigaku Supermini 200 analyser. The sample had to be converted into tablet form prior to analysis by creating a mixture of 4 g of finely ground slag sample (grain size <0.1 mm) and 1 g of binder (Hoechst wax C). This mixture was subsequently homogenised in a shaking pan, placed in a mould and then placed in a press where the tablet was pressed. The prepared tablet was then placed in the automatic feeder of the spectrometer and measured. The EasySken method was used for the measurement, which was set up and calibrated by the manufacturer of the analyser.

4. RESULTS AND DISCUSSION

In order to validate the sulphur determination methodology, 12 purchased certified slag standards were used. The following figures show a graphical comparison and pairwise comparison of the amount of sulphur detected in the standards by the two methods with the certified amount. QC-Expert software (module “Comparison of two selections - Paired test”) and MS Excel were used for the evaluation.

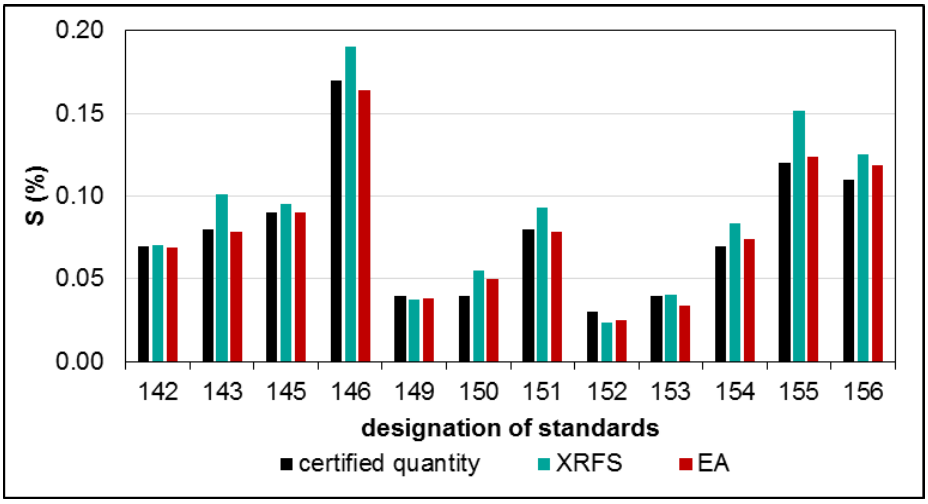

Figure 2 Comparison of the determined amount of sulphur with the certified

A bar chart showing the differences between the measured values of the two methods and the certified sulphur content of the standards is shown in **Figure 2**. The following graph, **Figure 3**, shows the deviations identified by the linear regression method, which again compares the measured values with the certified values. Based on the equation of the regression line and the correlation coefficient, it can be concluded that the EA method gives more correct results.

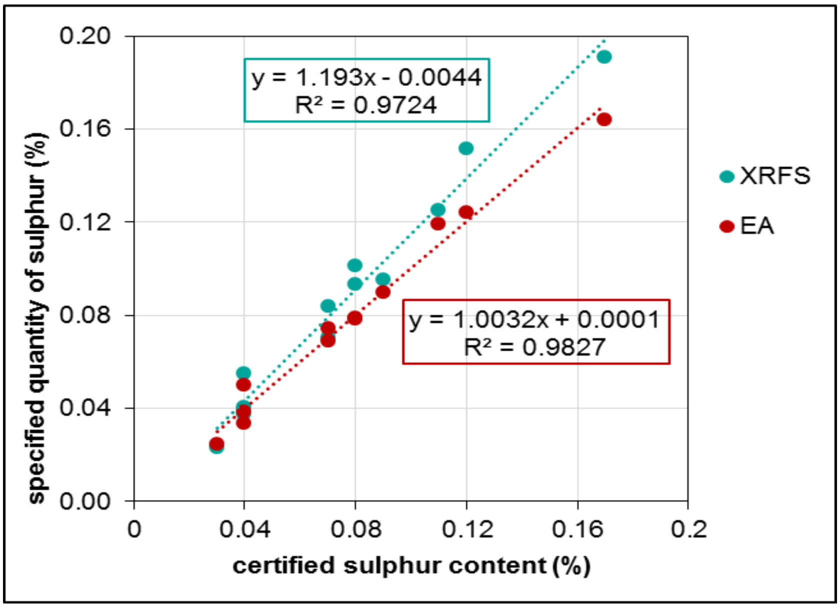

Figure 3 Linear regression - determination of S in standards by both methods

The most frequently used method for determining the agreement of measured data with certified data is the paired test, which is performed in this work using QC-Expert software. From the graphical representation of the density of the normal distribution of differences for the EA method (**Figure 4**), it can be seen that the vertical line corresponding to zero difference lies within the confidence interval of the mean difference. This implies that the differences are insignificant. A graphical representation of the density of the normal distribution of differences for the XRFS method can be seen in **Figure 5**. The vertical line does not lie within the confidence interval of the mean of the difference. Hence the differences are significant. From these graphs (and the conclusions of the paired test according to QC-Expert software), it can be concluded that the elemental combustion analysis is suitable for the determination of the sulphur content of slags. The XRFS method can also be used, but with the caveat that the results are burdened with a systematic error, the value of which increases with increasing sulphur content of the sample.

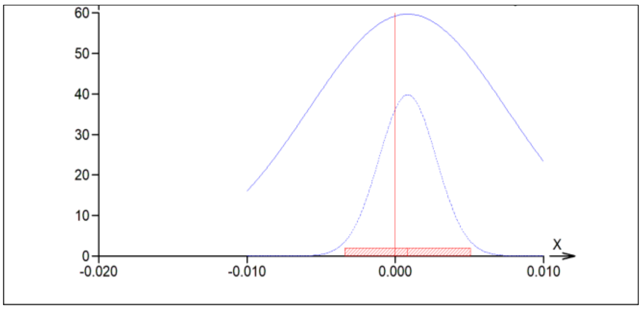

Figure 4 Comparison: EA - certified quantity

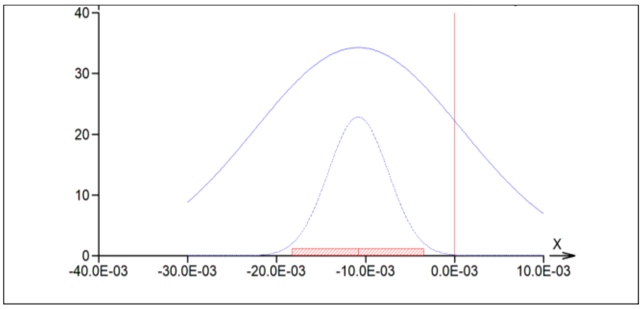

Figure 5 Comparison: XRFS - certified quantity

Since elemental combustion analysis was selected as the more appropriate method for the determination of sulphur content in slag, its repeatability was evaluated. To verify the repeatability of the EA method, sample No. 37 (ladle slag) (see **Figure 1**) was selected and measured 20 times over the course of one day. The QC-Expert software (module “Basic Statistics”) was used for the evaluation. From the generated plots, a scatter plot with quantiles was selected as one of the most versatile and most frequently used exploratory plots, which is used to assess the skewness of the distribution and the occurrence of outliers. In **Figure 6**, the individual rectangles expressing each quantile of values are symmetrically inside each other. From this plot and other tests, it can be concluded that the data exhibit a Gaussian, symmetric distribution with no outliers.

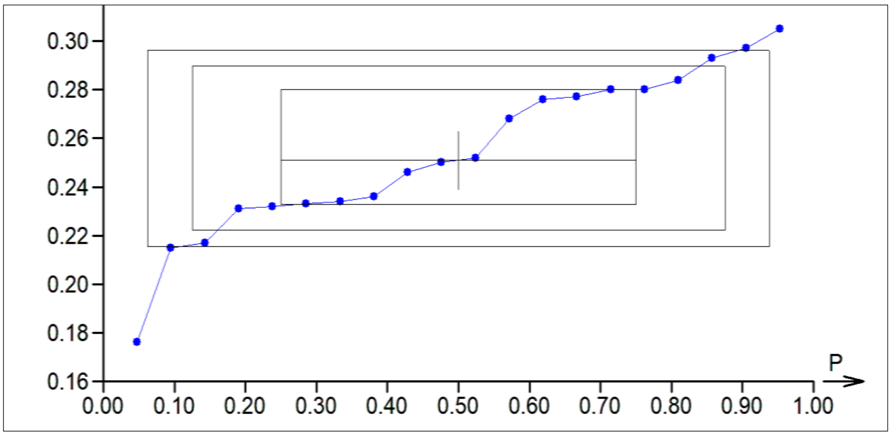

Figure 6 Scatter plot with quantiles - results of determination of sulphur content in sample No 37 by EA

The following figures show a graphical comparison of the average sulphur content found in granulated blast furnace slag, ungranulated blast furnace slag, tandem furnace slag, converter furnace slag, and ladle slag (**Figure 7**) as determined by the two methods. This graph shows that blast furnace slags (granulated and ungranulated) have significantly higher sulphur contents than steel slags.

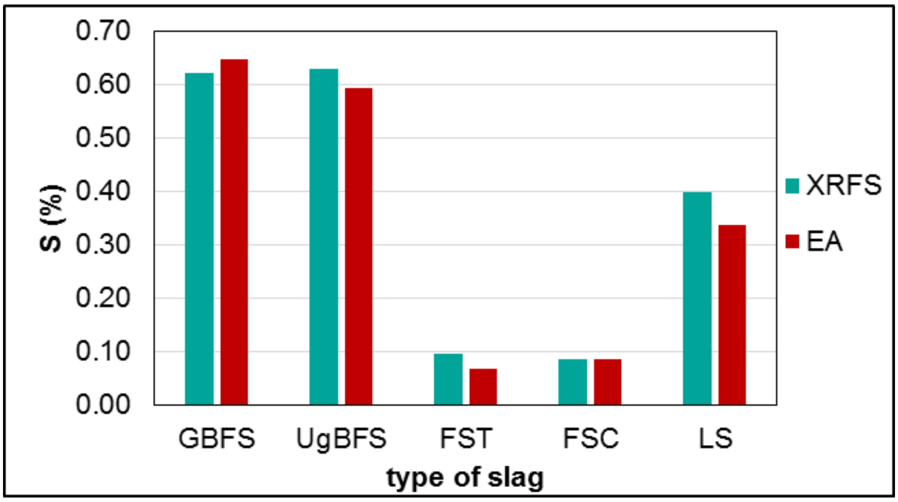

Figure 7 Comparison of average sulphur contents determined by XRFS and EA

5. CONCLUSION

The main objective of the work was to verify two methods used to determine sulphur content in metallurgical slags. Statistical methods were used to show that the elemental combustion analysis method is more suitable for this determination because it gives more correct results than X-ray fluorescence spectrometry. Repeated measurements (20 times) of a real sample of metallurgical slag also demonstrated the repeatability of the EA measurement. In agreement with the literature, it was shown that the sulphur content is higher in blast furnace slags than in steelmaking slags and that steelmaking slags have higher compositional variability.

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