Comparison of X-Ray Fluorescence and Infrared Spectrometry for Determination of Trace Amounts of Sulfur in Smelter Grade Alumina and Study of Thermal Desulfurization

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Abstract

National Standard GOST 30558-2017 does not regard sulfur as an identified or specified impurity in smelter grade alumina (SGA). Moreover, no state standard reference samples or quality control samples are available for sulfur, and consequently it is virtually impossible to determine the sulfur balance in the reduction process. Thus, a method for measurement of sulfur trace amounts in SGA was needed. Research was conducted to compare two methods of measuring the sulfur content (including trace amounts) in SGA, i.e., X-ray fluorescence (XRF) and infrared (IR) spectrometry. The influence of SGA sample preparation methods on XRF determination of sulfur trace amounts and the effect of a fluxing agent on (higher-melting-point) alumina decomposition were analyzed. The experiments proved the consistency/traceability of the results obtained using two methods of measuring the sulfur trace amounts provided that the SO_3 content is ≥ 0.006 mass. %. Quality control samples for measuring the sulfur content in SGA were developed. Furthermore, the experimental set-up was used to study the possibility of SGA desulfurization depending on a process temperature and gaseous phase composition.

Keywords: Alumina, Sulfur trace amounts, IR spectrometry, X-ray fluorescence, Desulfurization.

1. Introduction

National standard GOST 30558-2017 Smelter grade alumina [1] does not regard sulfur as an identified or specified impurity in smelter grade alumina (SGA). For this reason, no reference documents on determining sulfur content in alumina or standard reference samples with known sulfur content are available. This paper aims to elaborate a method to determine sulfur content in alumina during the incoming quality control to be performed by central laboratories at RUSAL's smelters, as well as generate the quality control samples (QC samples).

Additionally, the present studies determine the possibility of alumina desulfurization during its preliminary treatment before feeding to the cells.

2. Development of a Method to Measure Sulfur Content and Production of the Quality Control Samples

Previously the physical and chemical laboratory of RUSAL ETC's technology department used three methods to measure total sulfur (expressed as SO_3):

- Gravimetric analysis;
- Inductively coupled plasma-atomic emission spectrometry (ICP-AES) using Optima 8000 Perkin Elmer instrument;
- Infrared spectroscopy using LECO CS-744 carbon\sulfur analyzer.

Gravimetric analysis. To determine total sulfur (expressed as SO_3) by gravimetric analysis weighted 5 g samples were decomposed as per standard GOST R 50332.1-92 Methods for the decomposition of test sample and the preparation of test solution [2]. Upon decomposition, a method of sulfur gravimetric analysis was applied. Samples were fused in platinum crucibles, all reagents were pure, and high-quality filters were used for ignition.

Atomic emission spectrometry. No specialized method is available for measuring total sulfur by inductively coupled plasma-atomic emission spectrometry. Analysis of trace amounts of sulfur (< 0.1 wt.%) requires specific purging of the instrument and high amounts of argon. Alumina shall be fused with lithium tetraborate of high purity. For the analysis a weighted sample of 0.1 g is used.

Infrared spectroscopy. LECO CS-744 carbon\sulfur analyzer is used to measure a weight fraction of carbon and sulfur in inorganic materials [3]. The principle of operation lies in the sample combustion in the induction furnace in the flow of oxygen followed by measuring gaseous oxides of sulfur and carbon by infrared spectroscopy method. Thus, such analyzers consist of an induction furnace and analytical unit comprising gas columns and infrared sensors.

The comparative evaluation of the methods showed the following:

- ICP-AES method has number of disadvantages, i.e. long analysis time , high consumption of argon for purging, need for high purity reagents for fusing samples, availability of alumina reference sample with a known sulfur content, small sample for analysis (0.1 g) which makes an alumina sample unrepresentative in terms of sulfur content;
- The non-instrumental (chemical) method also has some drawbacks, i.e. long time of the analysis; besides, it cannot be used for measuring trace amount of sulfur in alumina;
- The optimal method for measuring total sulfur is infrared spectroscopy using carbon\sulfur analyzer (in our case LECO CS-744 analyzer is used).

X-ray fluorescence (XRF) spectrometry. XRF method was used to determine small amounts of sulfur in alumina [4]. Our laboratory used Zetium 2.4 kW instrument (Malvern Panalytical B.V.), which is equipped with 2.4 kW X-ray tube, to analyze pressed pellets. The method requires the use of additional equipment. To obtain reliable measurements, two sample preparation steps are essential, namely:

- Alumina grinding to required fineness in the laboratory mill (our lab uses Desktop swing mill HK40), whereas to avoid contamination of the sample a specialized lining is applied.
- Pressing of the grinded sample material using a high-pressure press (our lab uses HERZOG pelletizing press) to obtain a pressed pellet with a diameter of 40 mm in a steel ring.
- When alumina is grinded to a fraction of < 63 μm it displays good pressing properties, therefore use of a binding agent is not strictly required.

To comply with the international Standard method of measurement (SMM), a method was developed to analyze alumina using fused beads prepared by fusing alumina with a mixture of lithium tetraborate and metaborate (for Zetium 2.4 kW). ISO 23201-2015 Aluminium oxide primarily used for production of aluminium – Determination of trace elements – Wavelength dispersive X-ray fluorescence spectrometric method [5] was used to elaborate the said method. The fused beads for analyzing the alumina samples by this method are prepared as follows:

- Samples are fused with the fine flux (without granules), i.e. with 50 : 50 mixture of lithium tetraborate anhydrous and metaborate LB-H5050;
- Alumina sample is blended with said mixture at the ratio of 1 : 2 in a beaker and placed into the platinum crucible. The crucible is placed into the muffle furnace at a fusion temperature of 1050 °C for 15 minutes. Furthermore, the melt is poured into the steel ring, which is placed on the stainless-steel surface and compacted.

5. References

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