

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 SO₃ 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 SO₃):

- 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 SO₃) 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.

The obtained results showed that XRF analysis (using Zetium 2.4 kW) is quite acceptable for measuring total sulfur (expressed as SO₃) in alumina.

In addition, optimal conditions for sample analysis were determined for LECO CS-744 analyzer. The analysis was performed with iron chip accelerators enabling to fully analyze (decompose) a sample.

Comparison of the methods. All measurement results obtained by two methods (IR spectroscopy and XRF) were used to compare the data of sulfur content in alumina. Table 1 and Table 2 present the measurement results of alumina samples with different sulfur content.

Table 1. Comparison of the results of sulfur measurement in alumina by two methods.

Alumina	IR spectroscopy (LECO CS-744 carbon/sulfur analyzer)	(XRF) (Zetium 2.4 kW)
	SO ₃ , %	SO ₃ , %
Fluorinated sandy alumina	0.60	0.59
Modified alumina	0.58	0.55
Aughinish alumina (initial)	0.005	0.006

Table 2. Comparison of the results of sulfur measurement in an international sample of SMM alumina by two methods.

Alumina	SMM results	IR spectroscopy (LECO CS-744 carbon/sulfur analyzer)	(XRF) (Zetium 2.4 kW)
	SO ₃ , %	SO ₃ , %	SO ₃ , %
Hydro Bauxite & Alumina Support	0.03	0.025	0.03

Quality control samples. To calibrate the instruments, QC samples CO 11-2020 and CO 12-2020 were generated containing minimum and maximum amounts of sulfur. Two smelter grade alumina samples were used as initial materials, i.e. CO 11-2020 from Aughinish alumina refinery (Ireland) and CO 12-2020 from Friguia alumina refinery (Guinea). The materials for reference samples were prepared according to the standard GOST 25389-93 (ISO 802-76) Alumina. Sample preparation [6].

The uniformity of sulfur in the samples was tested by XRF method using Zetium instrument as per standard GOST R 55410-2013 (ISO 12677:2011) Refractory. Chemical analysis by X-ray fluorescence [7]. Measurements were carried out in compliance with Measurement procedure No. 7 – 2020 “Method of measuring the concentration of sulfur oxide in alumina by Infrared spectrometry” by the Engineering and technology directorate (alumina), RUSAL ETC LLC [8]. 40 mm pressed pellets were prepared with HERZOG pelletizing press. Samples were ground to obtain a 63 µm fraction.

To calibrate the LECO CS-744 analyzer, state standard samples CO LECO 502-870 with a known sulfur content of 0.0135 % and CO 502-868 with a sulfur content of 0.0160 % were used. Measurements were carried out in compliance with Measurement procedure No. 7 – 2020 “Method of measuring the concentration of sulfur oxide in alumina by Infrared spectrometry” by the Engineering and technology directorate (alumina), RUSAL ETC LLC [9].

Table 3. Metrological properties of the QC samples for a confidence probability of P = 0.95.

QC sample	Qualifiable property	Certified value (A), wt. %	Allowable error due to non-uniformity, Δ_h^{adm} , %	Specified error value due to non-uniformity, Δ_h , %
CO 11- 2020	Sulfur	0.0019	0.0010	0.0010
CO 12- 2020		0.134	0.008	0.008

3. Results of x Preliminary Alumina Desulfurization Tests

Sorption of SO₂ on smelter grade alumina is well researched [9, 10]. Under refinery conditions, sulfur content in alumina after dry scrubbing can reach ≥ 0.5 % (expressed as SO₃) [11]. Sulfur removal from alumina is poorly researched and literature references are scarce and non-systematic [11, 12].

A laboratory unit was installed to carry out tests on removing sulfur from initial smelter grade alumina by heat treatment with gas purging under controlled atmosphere conditions. Figure 1 shows a process flow diagram of the said lab unit.

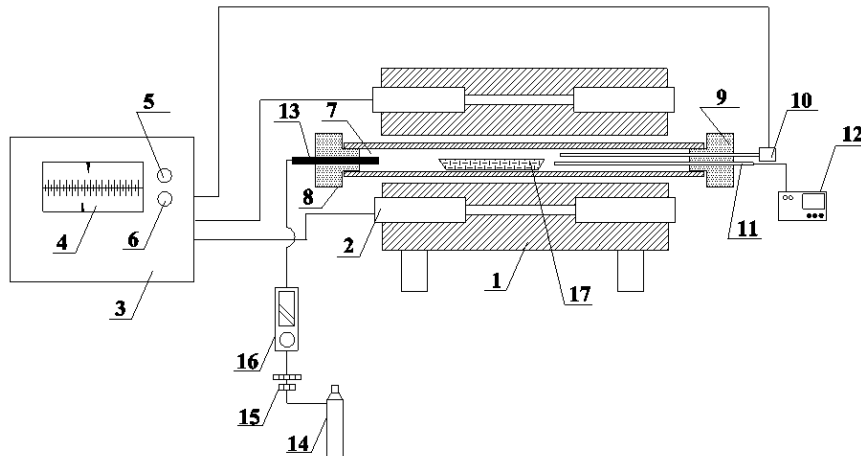


Figure 1. Laboratory unit for sulfur removal from initial smelter grade alumina.

The laboratory unit consists of the following equipment: tube furnace (1) heated by six silicon carbide heating elements (2). To maintain the required temperature the furnace is equipped with a control unit (3) with temperature indicator (4) and controls for zero setting (5) and required temperature setting (6). Silica reactor (7) is used for roasting. Reaction chamber is equipped with covers (8) and (9) made from light chamotte. Cover (9) is equipped with thermocouple (10) of the control unit and sampling probe (11) of Polar-T multi-component gas analyzer (12). Nitrogen flow connection (13) is mounted in plug (8). Nitrogen is supplied from cylinder (14) via reduction

gearbox (15). The gas flow rate is monitored with MASS-VIEW MV-308 flow meter (16). The material is roasted in corundum tray (17), which is placed in the reaction chamber (7).

Table 4 presents the obtained results.

Table 4. Results of S measurements in alumina samples under various conditions.

Sample description, measurement conditions	S, wt. % (analysis method)	
	IR spectroscopy, LECO CS 744 with chip accelerators	KRF, pressed pellets Zetium 2.4 kW
Friguia alumina (raw sample)	0.056	0.060
Friguia alumina after roasting in a lab unit for 60 minutes at 200 °C in nitrogen atmosphere	0.052	0.053
Friguia alumina after roasting in a lab unit for 60 minutes at 200 °C in air	0.049	0.051
Aughinish alumina (raw sample)	0.0053	0.0053
Aughinish alumina after roasting in a lab unit for 60 minutes at 200 °C in nitrogen atmosphere	0.0052	0.0052
Aughinish alumina after roasting in a lab unit for 60 minutes at 200 °C in air	0.0049	0.0050

The obtained results did not confirm the recommendations of Patent US009248396B2 [12] on possibility of desulfurization of smelter grade alumina in the gas flow at a temperature of + 200 °C. Presumably, desulfurization performance should be tested using a fluidized bed reactor.

It would make sense to test the sulfur content reduction by removal of fine fractions from alumina after gas scrubbing as it is suggested by Burkat and Drukarev [11].

4. Conclusions

The research has experimentally proven the traceability of the results of measuring the trace amounts of sulfur by two methods, i.e. infrared spectroscopy using LECO CS-744 carbon/sulfur analyzer and X-ray fluorescence using Zetium 2.4 kW instrument.

A method was developed to determine the sulfur content in smelter grade alumina during the incoming quality control to be performed by the central laboratories at RUSAL's aluminium smelters.

The quality control samples (QC samples) were generated and are available to calibrate the instrument for sulfur measurements.

The method should be certified and introduced for the quality control at aluminium smelters.

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