Measuring sulphur in the electrolyte of aluminium reduction cells

Rauan Meirbekova[1], Jomar Thonstad[2] and Gudrun Saevarsdottir[3]
1. Project Manager
Reykjavik University, School of Science and Engineering, 101, Reykjavik, Iceland
2. Emeritus Professor
3. Associate professor and dean of the school of science and engineering
Department of Materials Science and Engineering, NTNU, NO-7491 Trondheim, Norway
Corresponding author: rauan@ru.is

Abstract

Impurities are known to affect aluminium production. To study the effect of impurities in this industry, it is important to accurately quantify their concentration. This work focuses on sulphur quantification in cryolite-alumina melts. X-Ray Fluorescence (XRF) was selected as a method and its performance was evaluated by adding predetermined amounts of sulphur to the melt in the form of sodium sulphate (Na_2SO_4). The amount of added total sulphur ranged from 100 to 1200 ppm. Based on linear regression analysis, XRF exhibited a coefficient of determination of 0.99. Systematic overestimate by a factor of 1.1 for sulphur was observed. XRF performance was compared with Ion Chromatography (IC) and Inductive Coupled Plasma Optical Emission Spectrometry (ICP-OES). Comparison with IC and ICP-OES revealed discrepancies of up to 70 % in concentration, which may be due to sample preparation techniques. To obtain representative samples with least contamination of carbon dust, a modified sampling device with a closing mechanism was adapted from Rolseth [1] and tested. The device delivered reproducible samples with a sulphur concentration of 94.8 ± 11.0 ppm. The iron spatula used as a standard sampling tool at the aluminium plant produced 461 ± 370.2 ppm from the same cell. Samples were analysed for phosphorous in the XRF along with the sulphur. Phosphorus is one of the known detrimental impurities in aluminium production. The phosphorus concentration was not influenced by the sampling technique.

Keywords: Sulphur; sodium sulphate; phosphorus; analytical methods.

1. Introduction

Some impurities have negative effects on aluminium production both on the production process and the final products. Depending on their nature, impurities can cause excess carbon consumption or deterioration of materials, change electrolyte composition, reduce current efficiency, and affect metal quality [2]. One of the most studied impurities, known for its detrimental effect on current efficiency, is phosphorus. Current efficiency can be reduced by as much as 1 % for each 100 ppm of phosphorus present in the electrolyte [3 - 9]. Within the last decade, another impurity – sulphur – has been receiving increased attention. This was spurred by a change in crude oil quality, which resulted in higher sulphur concentrations in anodes [10]. Moderate levels of sulphur in the anodes have been considered beneficial as sulphur protects the anodes from air burn and CO_2 reactivity [11 - 14]. However, recent work studying the effect of sulphur on current efficiency shows that sulphur also may reduce current efficiency by 1.8 % for every wt% of sulphur in the anode (sulphur concentrations ranged from 0 to 3.82 wt% of sulphur for these experiments) [15]. As sulphur in anodes was shown to have an effect in a laboratory cell, it is also of interest to study the effect of sulphur in the electrolyte on the electrolysis. For this end, reliable measurements of sulphur concentration are required.

Literature treating the analysis of sulphur in cryolite-alumina samples is scarce [16 - 19]. Available literature uses either wet chemistry or ion chromatography. These methods are time consuming and more suitable for measuring high levels of sulphur. Sample preparation is complex and can introduce significant uncertainties into the measurements. The objective of our study was to test a different method for sulphur analysis in cryolite-alumina melts, X-Ray Fluorescence (XRF) which is available at many aluminium plants. Sulphur, because of its atomic number and associated radiation energies, is particularly well suited for XRF [20]. XRF provides fast multi-elemental analysis, without involvement of chemical attack accurate values are consistently obtained for total sulphur regardless of the sulphur mineral species [20 - 22]. Samples are not destroyed during the analysis and can thus be used for comparison with other methods. XRF has been widely used in a number of other fields. Of particular interest are measurements of sulphur in petroleum products, which contain sulphur within their structure [23, 24].

To achieve our goal, we added known amounts of sodium sulphate into solidified electrolyte samples taken from aluminium cells and analysed the samples by XRF. We compared the results to measurements obtained by different analytical techniques, in particular Inductive Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Ion Chromatography (IC). A recently published paper [19] has verified the accuracy of IC for measurements from cryolite melts and reported satisfying results for concentrations below 1000 ppm with 1.1 % uncertainty. ICP-OES has been recognized by having far superior detection limits and for providing accurate, rapid results for sulphur [25, 26]. To exclude the possibility of sample incompatibility, identical samples were utilized for three methods.

In order to collect representative samples from the cryolite-alumina melts, a sampling device design equipped with a sampling mechanism was adopted from Rolseth [1], modified and tested. This sampling device can take samples from a predetermined location, for example from the bulk of the electrolyte where least carbon dust is present, and the closing mechanism prevents mixing during extraction. Since XRF can also measure phosphorus concentration during the sulphur analysis, the effect of the sampling device on phosphorus content is also reported.

2. Experimental procedure

Automated equipment from Herzog Maschinenfabrik was used for sample preparation. The device is equipped with a sample magazine (Mach.No: MA12683-1-1), a metal detector (HP-CA/M/TD (Mach-No.: 12683-3-1), a miller (HP-MA (Mach.-No.: MA12683-6-1), and a tablet press (HP-PA (Mach.-No.: MA12683-10-1). A cellulose preparation pallet weighing 0.20 g for each 25 g of sample was added to improve grinding and binding during tablet pressing.

Verification of XRF accuracy: After the samples were milled and well mixed, 5 representative samples were taken for measurement of background sulphur concentration. The remaining samples were spiked with known quantities of sulphur. The following samples were created: 5 samples spiked with 100 ppm of sulphur, 10 samples with 200 ppm of sulphur, 8 samples with 300 ppm of sulphur, and 5 samples with 1 000 ppm of sulphur. The last 3 samples contained 1 180 ppm of sulphur in the crushed bath. All the 31 samples were analyzed by XRF. The 5 reference samples without additional sodium sulphate were also analyzed by XRF, and the amount of sulphur from these samples was subtracted from the sulphur concentration in the spiked samples.

Comparison of XRF with other methods: The solidified electrolyte was crushed into powder and well mixed. Five reference samples (without additional sodium sulphate) were taken. Subsequently, 0.44 wt% of sodium sulphate (1000 ppm of sulphur) was added into the powder and well mixed. The spiked samples were divided equally into 9 samples. Then 5 samples were analysed by XRF and ICP-OES and IC each of them analysed 2 samples.

Time dependency of samples: Electrolyte samples were taken by the modified Rolseth sampling device from the same cell. The samples were crushed and well mixed. The obtained powder was equally sub-divided into 6 samples. Three of the samples were analysed immediately by XRF. The remaining 3 samples were left at ambient temperature in the open air next to a glass of water for three months. XRF analysis was performed on these samples at the end of the 3 months.

2.1. XRF

PANalytical AXIOS X-Ray Fluorescence Spectrometer (Almelo, Netherlands), model number PW4400/xx, was utilized. Measurements were performed inside a vacuum chamber. The detection limits for sulphur and phosphorus with this instrument are 40 and 20 ppm, respectively.

After milling the samples, 25 g of each sample was pressed into tablets by an automated tablet press (HP-PA (Mach.-No.: MA12683-10-1).

2.2. ICP-OES

Inductive coupled plasma optical emission spectrometry was used to perform ICP-OES analysis. To prepare samples, 0.2 g of sample was mixed with 1 g of lithium metaborate ($LiBO_2$) in a Pt crucible and heated up to 1000 °C for 15 min. After cooling the crucible was boiled in a 100 mL of 5 % HNO_3 until glass was dissolved. The solution was diluted to 200 mL with deionized water. The samples were then filled into ICP-OES tubes for analysis. The ICP-OES instrument used in this study has a detection limit of 20 ppb both for sulphur and phosphorus.

2.3. Ion Chromatography

Ion Chromatograph 761 Compact IC (Metrohm Ltd., Switzerland) equipped with an IC anion column (MetroSep A supp. 3 for analysis with chemical suppression) was used.
The detection limit for sulphur is 1 ppb. The sample preparation procedure is described in detail in an article published by Ambrova et al. [19].

Determination of sulphates: Approximately 0.5 g of sample was dissolved in deionized water and stirred for 1 hour at ambient temperature. The sample was filtered and a solution of Na_2SO_4 (concentration of sulphate = 10 ppm) was added to bring the volume up to 100 mL (standard addition). Thus prepared sample was analysed by IC.

Determination of sulphides (total sulphur): Approximately 0.5 g of sample and 0.3 g of NaOH were dissolved in 30 mL of deionized water. The aqueous suspension was then oxidised by adding 40 mL of 15 wt % hydrogen peroxide (H_2O_2). After 1 hour of stirring, HCl solution (1:1) was added until the pH reached 1.5. Sulphide oxidation was allowed to continue at ambient temperature under stirred conditions for an additional 1 hour in the acidic solution. This treatment should ensure all sulphides were oxidised to sulphates. After this treatment, the solution was neutralised by NaOH to precipitate aluminium ions (required for the IC procedure) and boiled for 20 min to decompose any traces of H_2O_2. The cooled solution was then filtered and a solution of Na_2SO_4 (to adjust to 10 ppm sulphate) was added to bring the final volume to 100 mL (standard addition). The prepared sample was analysed by IC.

2.4. Reagents

Analytical grade sodium sulphate (Sigma-Aldrich, Germany) was used for experiments comparing added sodium sulphate and analytically determined sulphur concentrations. Food grade sodium sulphate (Abbey Chemicals, UK) was the reagent added to the industrial pot. All chemicals used for laboratory experiments were analytical grade chemicals (Merck, Germany). All chemicals were dried in a closed furnace at 200°C.

3. Results and Discussion

To verify the XRF instrument, a known amount of sodium sulphate was spiked into samples. A plot showing the amount of added sulphur versus the analytically determined sulphur concentration is shown in Figure 1. Based on linear regression analysis, XRF showed a coefficient of determination $R^2 = 0.99$ and p-value of 1.8×10^{-41}. The slope of the linear fit is 1.109 with a standard error 0.009.

The systematic overestimate by factor of 1.1 is difficult to trace. It may be due to addition of more sodium sulphate than targeted. The reference used for sulphur calibration may be another source of this error.

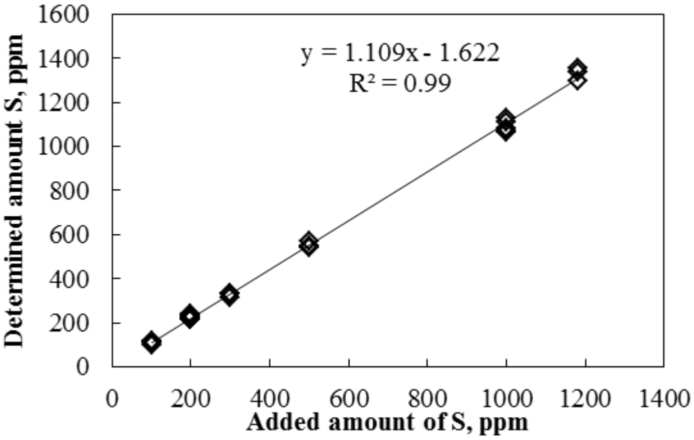

Figure 1. Comparison of spiked and analytically determined sulphur amounts by XRF.

After XRF was verified at different concentrations, it was compared with ICP-OES and IC. These methods were compared by adding predetermined amounts of sodium sulphate into crushed solidified industrial bath samples. Each method analysed three samples (a reference and two spiked samples) and the results of the analysis are shown in Table 1. The systematic error reported in Figure 1 for XRF samples was subtracted, but both raw and corrected XRF values are reported here for completeness. The difference in sulphur concentration between the reference and the spiked samples should equal the spiked sulphur content (1 000 ppm). The discrepancy in sulphur concentration in reference samples between XRF and IC or ICP-OES are up to 70 %, however discrepancy is reduced to 16 % for the second samples with much higher sulphur concentrations. The differences in the amount of sulphur recovered by the three techniques are difficult to interpret. Some differences may have arisen from sample inhomogeneity, but the samples were well mixed and both IC and ICP-OES utilized the same samples as XRF. The problem might be in sample preparation procedure for each technique. Samples might not have been well digested (especially carbon particles, which contain sulphur in their structure). For instance, the ICP-OES sample preparation procedure was later changed due to bad recoveries of sulphur from lithium motaborate digestion. In the new procedure the sample is melted with a 1:3 mixture of boric acid and sodium carbonate. XRF does not require sample digestion; therefore it might have an advantage over the other methods. In order to verify this statement, more data is needed to understand the error associated with each analytical method. In the next experiments, combustion methods such as Leco can be used, as it would burn all the carbon dust and only the remaining sulphur would be measured. In this study Leco was not considered, because it has a detection limit of 100 ppm for sulphur.

No phosphorus was added into the crushed bath samples discussed above in Table 1, but since XRF and ICP-OES can simultaneously analyse both these elements, phosphorus measurements with normal concentrations in industrial samples are shown in Table 2. These two methods (XRF and ICP-OES) seem to be in agreement, even though only a few samples were analysed.

Table 1. S concentrations determined by IC, ICP-OES and XRF.

N sample	S, ppm			
	IC	ICP-OES	XRF	XRF-sys.error
1	128* 95	221* 220	412.4±15.4	373.4±15.4
2	1265* 1222	1269* 1251	1503.6±27	1357.6±27
Sample 2- Sample 1 = 1 000 ppm	1137	1048	1091.2	984.6

*Same sample utilized for XRF analysis

Table 2. Natural phosphorus concentration in industrial electrolyte samples, given in ppm.

N sample	Phosphorus, ppm	
	XRF	ICP-OES
1	70	68*
2	70	81*
3	55	47
4	55	41

*Same sample utilized for XRF analysis

In a paper where IC was used to determine the sulphur concentration in solidified electrolyte [19], the authors claimed that sulphur levels can change after some time due to oxidation or the presence of moisture. To test it these samples were analysed after 3 months. The results of XRF analysis are shown in Table 3. The results indicate that the change in sulphur concentration over time is within its standard deviation and therefore cannot serve as an explanation for the deficit of sulphur observed in IC (see Table 1). All the samples in Table 1 were analysed within a month period.

Table 3. Change in S concentration in the crushed powder over three month's period.

Sample	S in powder analysed 8th January 2014, ppm	Sample	S in powder analysed 7th March 2014, ppm
1	186	4	168
2	186	5	180
3	176	6	184
Average	183±7.0	Average	177±7.0

Finding a suitable sampling device for taking electrolyte samples from industrial cells is crucial, especially since the electrolyte may contain carbon dust. Carbon dust typically accumulates near the surface of the electrolyte, and it can serve as nucleation site for impurities. The standard procedure for collecting electrolyte samples at aluminium plants is by using an iron spatula. This is an easy and fast sampling technique, especially when a large sample is required. The Alcoa Fjarðáal plant uses XRF and X-Ray Diffraction (XRD) spectroscopy for analysis of electrolyte samples. Both methods require a sample weight of 20 grams, and this is considered a large sample compared to other techniques such as ICP-OES or IC (these techniques only require up to 1 g of sample).

For this study, a sampling technique for taking large samples was adopted from Rolseth [1] and tested at the plant. Figure 2 shows a photograph of the original sampling device built according to Rolseth's design. The body of the sampling device consists of a cup with a lid and a height adjuster. The cup can be positioned at different heights by regulating the height adjuster. The sampling device is closed while entering the electrolyte. The lid is then lifted for a few seconds to allow electrolyte to flow in. The lid is then quickly closed, and the sampling device is lifted out. An electrolyte sample weighing up to 30 grams can be obtained with this device.

The disadvantage of the original Rolseth design is that it is heavy (7.1 kg). Due to all the bulk mass around the cup, cooling of the sampling device took at least 20 min, and sometimes the lid would not open due to heat expansion. To address these shortcomings, the sampling device was modified by removing any unnecessary material. This resulted in a lighter device (3.3 kg), making sample collection easier. The stability of sampling device was also improved as the device was less prone to be disturbed by magnetic fields. The maximum sampling frequency was also increased due to faster cooling compared to the original design. The amount of sample collected was increased to 40 grams, which enabled duplicate sample analysis. A photo of the modified sampling device is shown in Figure 3.

Figure 2. Original sampling device from Rolseth [1].

Figure 3. Modified sampling device.

In order to test the effectiveness of the modified sampling device and compare it with the use of iron spatula, fifteen samples were extracted from the same cell: 5 samples were withdrawn by the modified sampling device and 10 samples were collected by the iron spatula. A photo of the prepared samples pressed into tablets is shown in Figure 4. The samples in the third row collected by iron spatula are black due to the presence of carbon dust in them.

Table 4 shows the results of XRF analysis for phosphorus and sulphur for the 15 collected samples. The concentration of phosphorus was unaffected by the sampling technique: 64.0 ± 4.2 ppm and 65.2 ± 5.0 ppm was obtained for the modified Rolseth design and the iron spatula, respectively. This was unexpected as phosphorus has previously been found to correlate with the carbon concentration [9, 27]. It has been hypothesized that carbon serves as a nucleation site for phosphorus [28]. The reason might be that carbon dust contains much less phosphorus than sulphur [29].

Figure 4. Electrolyte samples pressed into tablets for XRF analysis. First row- modified Rolseth device, second and third row- iron spatula.

In contrast to phosphorus, the sulphur concentration changed dramatically depending on the sampling technique. The average sulphur concentration in samples collected by the modified Rolseth design and by the iron spatula was 94.8 ± 11.0 ppm and 461.4 ± 370.2 ppm, respectively (see Table 4). Analysis of the samples for sulphur and carbon content confirmed that the concentration of sulphur depends on the concentration of carbon dust particles in the electrolyte (see Figure 5).

Carbon dust originates from the carbon anodes, which are made of petroleum coke and recycled butts bound with coal tar or petroleum pitch. All these materials contain sulphur as a part of their structure [5]. As carbon levels in the sample increase, sulphur concentration is likewise expected to increase as a result. This highlights the importance of the sampling device for correct interpretation of the results.

Table 4. Average phosphorus and sulphur concentrations (and standard deviations) in samples collected by the two sampling devices.

Sampling device	P, ppm	S, ppm
Mod. Rolseth Device	64.0±4.2	94.8±11.0
Iron Spatula	65.2±5.0	461.4±370.2

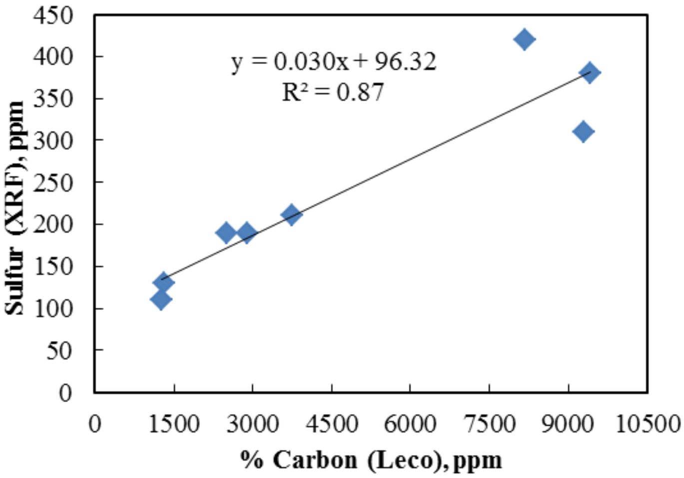

Figure 5. Sulphur concentration in the electrolyte determined by XRF as a function of the carbon content in the electrolyte determined by LECO.

4. Conclusions

Determining the sulphur concentration in cryolite melts was found to be very challenging. Carbon dust has the largest influence on the concentration of sulphur in the electrolyte. XRF showed a coefficient of determination R^2 = 0.99 and an overestimate by a factor of 1.1 was observed. However, when compared with IC or ICP-OES methods discrepancies of up to 70 % between sulphur analyses were observed. More work has to be done to check the reliability of IC and ICP-OES implemented here. A modified Rolseth sampling device can help to eliminate carbon dust and obtain representative samples with good reproducible results. The sulphur concentration was 94.8 ± 11.0 ppm using the modified Rolseth device. However, the standard iron spatula used at aluminium plants produced 461.4 ± 370.2 ppm from the same cell.

The phosphorus concentration in the electrolyte did not show any dependency on the sampling technique and the presence of carbon dust.

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