

DEVELOPMENT OF TECHNIQUES FOR MEASURING THE COMPOSITION OF LOW TEMPERATURE ELECTROLYTES

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Abstract

Low temperature, cryolite-based electrolytes for the Hall-Heroult process continue to be of interest to the aluminium industry. In a conventional Hall-Heroult cell, lower temperature operation could increase energy efficiency and improve materials performance. Low temperature electrolytes may also facilitate the operation of an inert anode, since the solubility of many metal oxides decreases with temperature.

The ability to measure bath composition (aluminium fluoride, alumina and other components) quickly and accurately will be critical to successful operation of low temperature electrolytes because liquidus temperature becomes more sensitive to small changes in concentration as AlF_3 concentration increases. Also the measurement and control of alumina would be particularly important to operation with inert anodes because the solubility of many oxides is highly dependant on the alumina concentration.

In this paper the use of x-ray fluorescence and its combination with an electrochemical alumina sensor for the analysis of high AlF_3 electrolytes for low temperature operation is discussed. Comparisons with x-ray diffraction analyses are also presented. The combination of x-ray fluorescence and alumina probe is promising in the sense that the difference between the values measured will indicate any undissolved alumina suspended in the bath.

1. Introduction

The use of low temperature baths is promising for inert anode operations since the solubility of oxide species are reduced and materials performance may be increased. However, the solubility of alumina is reduced when decreasing temperature and the liquidus curve is more sensitive to aluminium fluoride variation. Therefore the development of a system allowing rapid measurements of alumina and aluminium fluoride is important for successful low temperature bath operations.

It was shown that x-ray fluorescence (XRF) can be used to measure bath composition in high temperature baths (excess AlF_3 6-12 wt%) (1,2). In the present paper XRF analyses were made, using an Applied Research Laboratories x-ray fluorescence spectrometer ARL-Advant'XP, to measure excess aluminium fluoride and alumina content in electrolytic bath with typical compositions 24-32 wt% excess AlF_3 and 2-6 wt% Al_2O_3 (these compositions correspond to BR between 0.83-0.65). The XRF Advant'XP instrument combines all the latest developments in X-ray instrumentation intended for increased sensitivity. In particular, since this application involves analysis of light elements such as oxygen which has very low fluorescence yield, the key instrument components like X-ray tube window, primary collimators, multilayer crystals and detector windows have all been optimised to get the highest sensitivity. To insure a better accuracy on the alumina measurement a special crystal, called AX06+, has been installed on the spectrometer. This crystal reduces the second order K_{α} line of sodium, which is interfering with the K_{α} oxygen reflection. Since a large amount of sodium is present in cryolite baths the suppression of this interference can improve the analysis. Calibrations curves were made for the different elements present in the bath (O, F, Na, Al, Ca), allowing the complete composition of a bath sample to be determined in a single measurement. Note that impurities can also be measured without calibration by using the semi-quantitative programs Quantas or Uniquant.

Measurements to monitor the alumina level in these low melting electrolytes were also successfully made using the alumina sensor developed by Haverkamp and Welch (3).

2. Results

2.1 X-Ray Fluorescence Measurements

2.1.1 Sample preparation

The sample preparation for XRF analyses (alumina and excess AlF_3) was made using the following procedure: A support pellet is made by pressing a mixture of boric acid with 10% wax. The bath sample to be analysed is ground in a grinding mill (Herzog HSM 100) and 1.5 g of the ground powder are pressed on the boric acid-wax support pellet. This procedure insures a sufficient adherence of the ground bath to the pellet to avoid desegregation of the pellet during the analysis. When analysing fluorine care must be taken to apply a constant and sufficiently high pressure because of the sensitivity of the fluorine signal with the applied pressure (4).

The chemicals used for the preparations of the standard bath samples used in the calibration are sodium fluoride (Cerac 99.9 wt%), aluminium fluoride (Cerac 99.9 wt%) and alumina (Cerac 99.99 wt%). The standard bath samples were prepared by mixing NaF , AlF_3 and Al_2O_3 in required proportions (total weight 50g). The mixed powders were placed in a graphite crucible covered by a graphite disc and melt at a temperature 50°C higher than the melting point for minimum 2 hours. The whole of each standard was ground to avoid errors due to non-uniform cooling.

2.1.2. XRF alumina measurements

The alumina concentration is calculated on the basis that the total oxygen measured in the bath is present as alumina. Since the other elements, which may be present as oxides, are usually below 100 ppm the error introduced by this hypothesis can be neglected.

The main concern when analysing oxygen in cryolite bath is the interference of the second order line of sodium K_α . The oxygen-sodium interference on a typical multilayer crystal (AX06 type) can be easily observed on an energy profile of the signal measured at the 2θ angle of the K_α line of oxygen. An energy profile is based on the fact that the detector's signal is dependent on the intensity of the incident x-ray photon. Since, according to Bragg's law, at a fixed 2θ angle a second order reflection has an energy double than a first order reflection, a scan of the intensity measured as a function of the energy of the incident photons will give information regarding the order of the photon detected.

When using an AX06 crystal the energy profile measured at the 2θ oxygen angle is shown in Fig. 1.

The intensity due to the oxygen is maximum when using a pulse height discrimination (PHD) of 900 mV. Most of the intensity measured for a PHD scale higher than 1200 mV is due to the second order reflection of the sodium, this reflection having its maximum intensity at a PHD scale of 1800 mV.

As can be seen in Fig. 2 the use of an AX06+ crystal allows the suppression of most of the intensity from the second order sodium reflection. The calibration was made using a series of bath samples with a constant aluminium fluoride excess of 27.5 wt% and with an alumina concentration between 0 wt% and

5 wt%. The calibration curve obtained when using the AX06 or the AX06+ crystal is shown in Fig. 3. It can be seen that, although the oxygen signal intensity is reduced when using the AX06+ crystal a better calibration is obtained, as indicated by the standard estimated errors and limits of detection given in Table I. Another advantage of the AX06+ crystal is that the oxygen measured is less sensitive to possible sodium variations which may be created by bath ratio modifications.

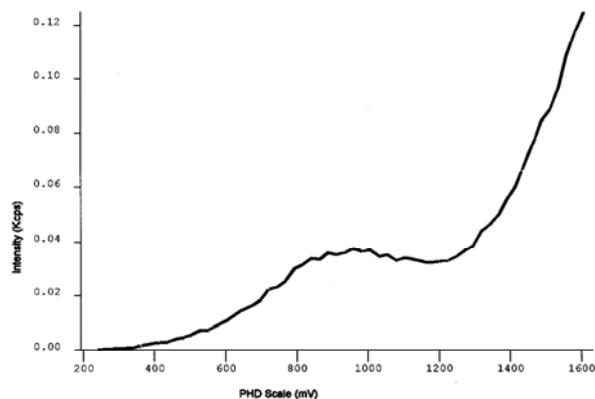


Fig. 1. Energy profile measured at the 2θ angle of oxygen using AX06 crystal (Bath composition: 27.5 wt% AlF_3 , 2 wt% Al_2O_3 , 70.5 wt% Cryolite).

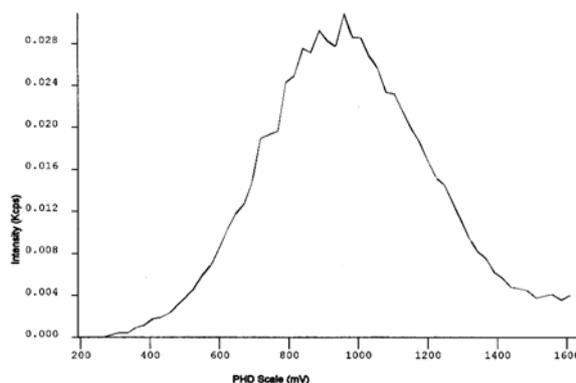


Fig. 2. Energy profile measured at the 2θ angle of oxygen using AX06+ crystal (Bath composition: 27.5 wt% AlF_3 , 2 wt% Al_2O_3 , 70.5 wt% Cryolite).

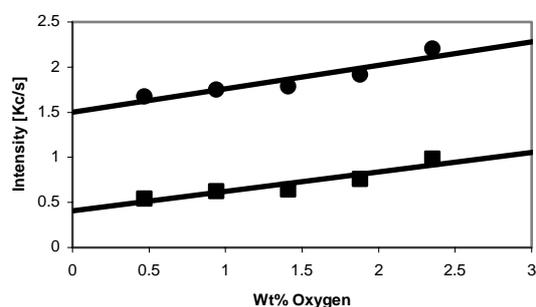


Fig. 3. Calibration curve of oxygen in bath with 27% excess AlF_3 . ● = measurement using the AX06 crystal, ■ = measurements using the AX06+ crystal.

Table I. Parameters of the calibration curves obtained with the AX06 and AX06+ crystals

Crystal	Limit of detection [ppm]	Standard Estimated Errors [%]
AX06	391.5	0.338
AX06+	247.6	0.2932

This calibration was used to measure alumina dissolved in cryolite-based bath. A series of eight samples sample was taken in a bath without electrolysis, with a 10 min delay between each sample. Average concentration was found to be 7.8 ± 0.5 wt%, the error being in agreement with the precision of the calibration curve.

2.1.3. XRF Excess aluminium fluoride measurements

In low-temperature electrolytes the use of XRF to measure the aluminium fluoride in excess is interesting because the usual x-ray diffraction technique is not suitable. This is due to the fact that the excess aluminium fluoride is usually derived from the chiolite content. The problem is that the composition of solid mixtures from bath with an AlF_3 excess higher than 24% consists of chiolite and AlF_3 instead of cryolite and chiolite (see, for example, (5)). A possible solution for this problem is to add sodium fluoride to the sample, to make a thermal treatment to reduce the excess AlF_3 to a part of the phase diagram where cryolite and chiolite are in equilibrium, to measure the chiolite and then to calculate the initial excess AlF_3 . However, this method is time consuming and adds the possibility of errors.

When using the XRF technique the excess AlF_3 can be measured according to the following formulas:

$$F(\text{AlF}_3) = \text{Total F measured} - F(\text{Na}_3\text{AlF}_6) - F(\text{CaF}_2) \quad (1)$$

Where $F(\text{AlF}_3)$ is the fluorine in the excess AlF_3 , $F(\text{cryolite})$ represents the fluorine from the cryolite and $F(\text{CaF}_2)$ represents the fluorine from the calcium fluoride

$$\text{Al}(\text{AlF}_3) = \text{Total Al measured} - \text{Al}(\text{Na}_3\text{AlF}_6) - \text{Al}(\text{Al}_2\text{O}_3) \quad (2)$$

Where $\text{Al}(\text{AlF}_3)$ is the aluminium in the excess AlF_3 , $\text{Al}(\text{Na}_3\text{AlF}_6)$ represents the aluminium from the cryolite and $\text{Al}(\text{Al}_2\text{O}_3)$ represents the aluminium from the alumina

When using Eq. 1 the fluorine from the cryolite is calculated on the assumption that the totality of the sodium measured consists of cryolite and that the totality of the calcium is present as calcium fluoride. So, a stoichiometric calculation allows the determination of the fluorine from the cryolite. When using Eq. 2 the aluminium from the cryolite is also calculated using the sodium measured, while the alumina is calculated using the oxygen measured.

Calibration curves were made with samples containing variable amounts of sodium, aluminium, fluorine and calcium. The concentration ranges, in atomic weight percent, used were for sodium 22.2 to 31.5, for aluminium 14.46 to 20.25, and for fluorine 52.11 to 57.48. Alumina in these samples was constant at 4 wt%. This concentration range corresponds to BR between

1.5 and 0.7. Calibrations curves obtained for fluorine, sodium and aluminium are given, respectively, in Figs 4, 5 and 6. The calibration curve for calcium, shown in Fig. 7, was made in baths with constant aluminium fluoride at 27.5 wt% and alumina at 4 wt%. The parameters for the calibration curves obtained for these four elements are given in Table II.

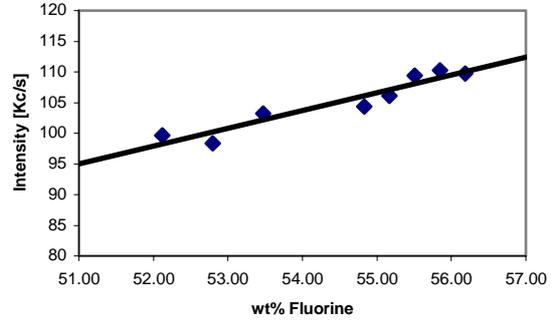


Fig. 4: Calibration curve for fluorine with a constant alumina concentration at 4.0 wt%.

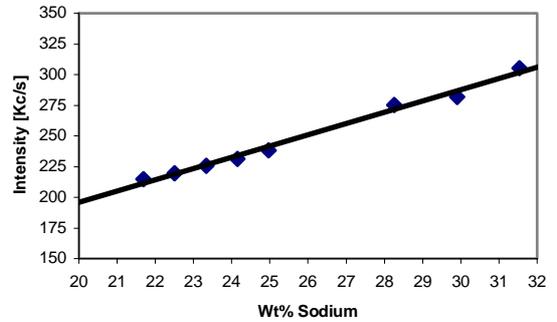


Fig. 5: Calibration curve for sodium with a constant alumina concentration at 4.0 wt%.

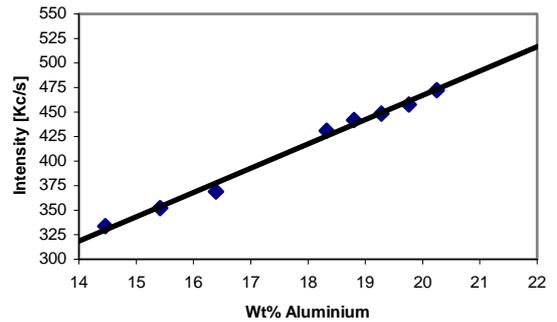


Fig. 6: Calibration curve for aluminium with a constant alumina concentration at 4.0 wt%.

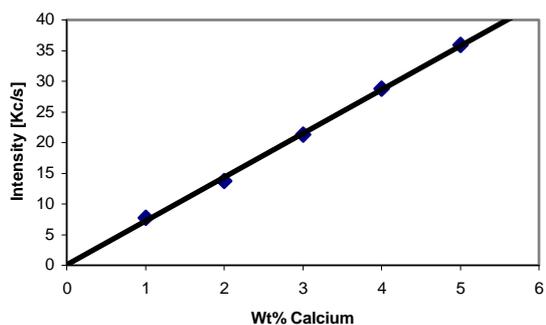


Fig. 7: Calibration curve for calcium with a constant alumina concentration at 4.0 wt%.

Table II. Parameters of the calibration curves obtained for fluorine, sodium, aluminium and calcium

Element	Limit of detection [ppm]	Standard Estimated Errors [%]
Fluorine	123.6	0.66
Sodium	58.9	0.39
Aluminium	35.4	0.20
Calcium	29.7	0.25

With a view to investigate if different accuracies are obtained when using Eq.1 or Eq.2 measurements of excess AlF_3 were made on commercial certified bath samples (provided by VAW Aluminium AG). The correlation factor between certified and measured excess AlF_3 is 0.98 when using Eq. 1 and only 0.78 when using Eq. 2. Another series of sample was taken in a bath with the cover partially opened, which creates an important evaporation of the aluminium fluoride. We therefore monitor the level of excess AlF_3 with time. The values measured using both equations are shown in Fig. 8. It can be seen that a better correlation is obtained when using Eq. 1. The reason for having better correlations when using Eq.1 is probably related to the fact that this equation does not involve measurement of oxygen, which, in our samples, is the most difficult element to measure.

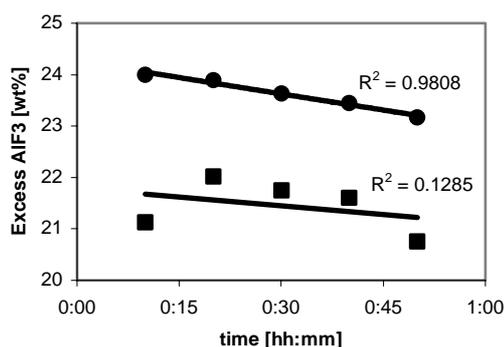


Fig. 8: Excess AlF_3 measured versus time with equation 1 (●) or equation 2 (■).

2.2 Electrochemical Alumina Measurements

The details of the operation of the alumina sensor are described more fully elsewhere (6). The sensor uses modified linear sweep voltammetry (3,7) with a carbon anode and a stainless steel or inconel cathode. During this process an anode effect, on a very minor scale, is achieved. The applied potential at which the anode effect occurs is due, among other things, to the concentration of dissolved alumina in the electrolyte. It is possible to correlate this potential with the alumina concentration within a defined range of parameters.

The nature of the voltammogramme is very different in high AlF_3 low melting electrolytes than in standard electrolytes (8,9). This has led to the need to modify the analysis software to be able to correctly detect the position of the anode effect. The anode effect is less sharply defined in high AlF_3 electrolyte with the current dropping more gradually and to a higher minimum value as can be seen in Figure 9. This is due to the mechanism of formation of the anode effect as outlined elsewhere (8,9). However the detection of a reproducible but somewhat arbitrary anode effect point is possible.

A calibration curve can be constructed to relate the measured potential of the anode effect to the dissolved alumina concentration. The calibration curve is dependent on the ratio of NaF to AlF_3 in the electrolyte so that a calibration curve needs to be constructed for each electrolyte type of interest. Two calibration curves that have been used for a particular model of the alumina sensor are shown in Figure 10. These calibration curves do not have any absolute significance but are relevant only to this particular analysis setup. The calibration is affected by the voltage sweep rate used, the spacing between the anode and cathode and other factors for a particular configuration. If the electrolyte composition is maintained within a relatively broad band (say $\pm 3\%$ excess AlF_3) then one calibration curve can be used and gives results within about 5% of the value ($\pm 0.15\% \text{Al}_2\text{O}_3$ at 3% alumina).

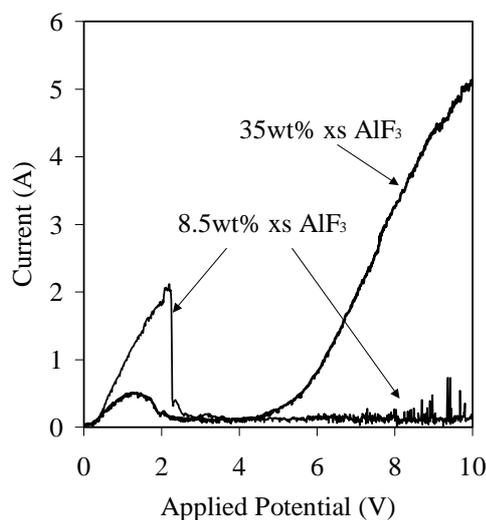


Figure 9. Voltammogrammes in 8.5 wt% excess AlF_3 (at 980 °C) and in 35 wt% excess AlF_3 (at 730 °C).

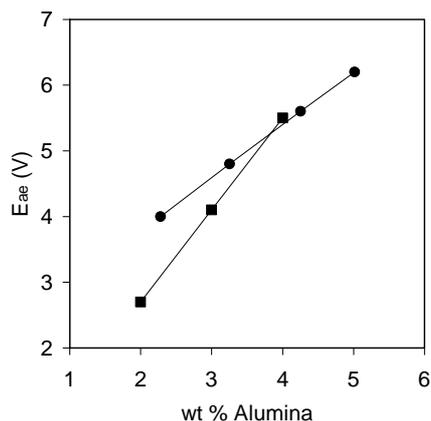


Figure 10. Calibration curves for the potential of the anode effect (E_{ae}) with alumina concentration for ■ 8.5 wt% AlF_3 excess (+5% CaF_2 , 980°C) and ● 24 wt% AlF_3 excess (at 850°C).

The calibration curve is dependant on but not highly sensitive to temperature. Therefore if the cell operating temperature is known and is maintained within a relatively broad band (say $\pm 20^\circ C$) then one calibration curve can be used and gives results within about 5% of the correct value ($\pm 0.15\% Al_2O_3$ at 3% alumina).

Individual measurement of dissolved alumina concentration can be taken at around one second intervals. There is some scatter in the values obtained as shown in Figure 11. The scatter in the values obtained is always higher at higher alumina concentrations. However by averaging over a number of readings quite a precise value for the alumina concentration can be obtained. The precision is sufficient for the monitoring and control of high AlF_3 electrolytes.

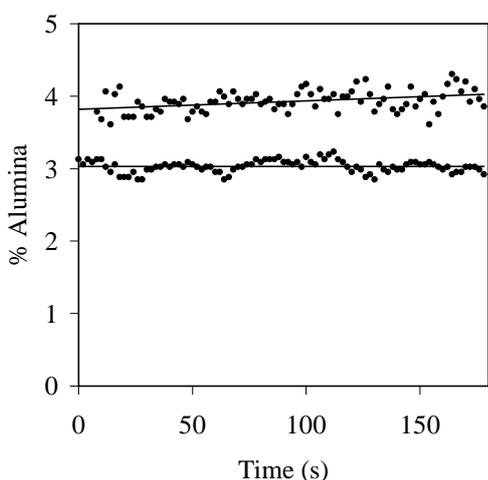


Figure 11. Successive measurements of alumina in a cell with static alumina concentration and 24% excess AlF_3 . The standard deviation at 3% Al_2O_3 is 0.08 % Al_2O_3 (3 %) and at 4% Al_2O_3 it is 0.15 % (4%). Data points are taken at 1 second intervals.

3. Conclusion

It was shown that x-ray fluorescence can be used to measure bath composition (excess AlF_3 , Al_2O_3 , CaF_2) in low temperature bath with excess AlF_3 up to 32 wt%. It was also found that, provided that the adequate calibration curve is prepared, an electrochemical alumina sensor can be used to measure dissolved alumina in AlF_3 rich baths.

The simultaneous use of both methods is very promising since the difference between the alumina measured by XRF and by the alumina probe will indicate possible alumina suspended in the bath. This is important because when operating in low-temperature baths the alumina solubility is reduced resulting in a narrower range of concentration. The combination of these two analysis methods may help overcome possible difficulties in remaining within this concentration range.

References

1. F.R. Feret, "Characterization of Bath Electrolyte by X-Ray Fluorescence", *Light Metals*, (1988), 697-702.
2. S. Baggio, and C. Foresio, "An X-Ray Method for Measuring the Alumina Content in Reduction Cells for Aluminum Production", *Aluminium*, 56(4) (1980), 276-278.
3. R.G Haverkamp, and B.J. Welch inventors, Auckland Uniservices assignee, "Measurement of Alumina in Reduction Pots" *US Patent 6 010 611*, 4 January 2000.
4. K. Grjotheim, and B.J. Welch, *Aluminium Smelter Technology* (Aluminium-Verlag Düsseldorf, 1980), p. 115.
5. K. Grjotheim, C. Krohn, M. Malinovsky, K. Matiasovsky, and J. Thonstad, *Aluminium Electrolysis* (Aluminium-Verlag, Düsseldorf, 1982), p. 28.
6. R.G.Haverkamp, B.J.Welch, and A. McMullen "Real Time Alumina Measurement in Industrial Cells" *Light Metals*, 2001.
7. R.G. Haverkamp, B.J. Welch., and J.B. Metson, "An Electrochemical Method for Measuring the Dissolution Rate of Alumina in Molten Cryolite", *Bull. of Electrochem.*, 8 (7), (1992), 334-340.
8. R.G. Haverkamp, S.Rolseth, J. Thonstad, and H. Gudbrandsen, "A Voltammetric Study Of The Anode Effect In $NaF-AlF_3-CaF_2-Al_2O_3$ Mixtures" *Proceedings of the 198th Electrochemical Society Conference*, Phoenix, USA, 22-27 October 2000.
9. R.G. Haverkamp, S. Rolseth, J. Thonstad, and H. Gudbrandsen, "Voltammetry And Electrode Reactions In AlF_3 -Rich Electrolyte" *Light Metals*, 2001.