AN EVALUATION OF XRD AND XRF METHODS USED IN AN ALUMINIUM BATH ANALYSIS.

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ABSTRACT

The paper deals with the application of X-ray fluorescence and diffraction for the routing control of a chemical content of an electrolysis cell in aluminum reduction plants. Among two approaches XRD meets technological requirements on accuracy, time limit and the cost of analysis. XRF demonstrates insufficient accuracy because of sample preparation problem.

INTRODUCTION

The electrolysis cell used in the production of aluminum is a dynamic system. The concentration of main components in the electrolyte must be rigidly controlled in order to maintain optimum conditions during the production process. The electrolyte consists of a molten mixture of sodium and aluminum fluorides and other calcium, magnesium and lithium fluorides whose function is to decrease the solidus temperature. It is necessary to use optimum analytical method to measure the concentration in order to determine when a certain point in a 6 component system (Al-Na-Ca-Mg(Li)-F-O) where the concentrations of the elements are ~14\%, Na ~25\%, F ~54\%, Ca ~3\%, Mg(Li) ~ 2\%, O ~ 2\% is reached. A mineralogical content a sample of cooling electrolyte may include the following phases: cryolite (Na$_3$AlF$_6$), cholite (Na$_5$Al$_3$F$_{14}$), Ca-cryolite (Na$_2$Ca$_3$Al$_2$F$_{14}$), fluorite (CaF$_2$), weberite (Na$_2$MgAlF$_7$), neiborite (NaMgF$_3$), corund (Al$_2$O$_3$), spinel (MgAl$_2$O$_4$), viliamite (NaF). In actual practice, control of the electrolyte concentration of the bath is done measuring the cryolite ratio (CR), or bath ratio BR, where BR=1/2CR. CR is equal to the ratio of the main chemical components of electrolyte NaF and AlF$_3$:

\[
CR = \frac{C(\text{NaF}, \text{ mol})}{C(\text{AlF}_3, \text{ mol})}
\]

CR value can range from 1.67 to 3.3. The accuracy required is 0.02-0.03 CR units. The others parameters which must be controlled are concentrations of added CaF$_2$, MgF$_2$ or LiF. The range of concentration of these added materials is 0 to 8\%, relative accuracy is of ~10\%. The concentration Al$_2$O$_3$ also requires control. Measurement of the bath is done every 2 or 3 days. Industrial production requires that the bath analysis does not take longer than about 2 to 3 minutes because there are often several hundred or even thousands of cells to measure.

THE USE OF XRF IN BATH CONTROL

Several analytical methods have been used over the years in bath ratio: wet chemistry, optic methods, XRD, XRF and others [1-4]. Wet chemistry is the most accurate method, however, it takes too much time to be applied as a routine control. Wet chemistry is however, used as a reference method. Optical methods cannot cover a large range of concentrations and therefore are not, at this time, used (fig.1). XRF analysis is the least expensive, however, the limiting factor in
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XRF analysis is specimen preparation and it is difficult to prepare a specimen from a bath. Possible XRF analysis might consist of the following procedure. The measurement of the numerator in the expression for CR, below, requires the measurement of total sodium concentration. In order to this the Na should be measured in the cool sample of electrolyte because Na forms crystalline fluoride phases. Aluminum also crystallizes into fluoride or oxygen salt; only very little oxide is formed. The denominator of the CR expression is the mole concentration of total Al minus the concentration of the oxides of Al.

$$CR = \frac{C(\text{Na, mol})}{C(\text{Al(tot), mol})-C(\text{Al(O), mol})}$$

Although XRF has the advantage of being a rapid method of analysis, it is not used in the production of aluminum. Efforts have been made to use XRF, however, without success [5]. XRF cannot be used to measure Na or O with great accuracy. Our measurement of the e.s.d of repeat measurements did not produce results better than 1% (rel) and the e.s.d of replicate measurements is more than 3% relative. These kind of errors results in an error in CR greater than 0.10 CR units. Specimen inhomogeneity is a major problem in the XRF analysis of the bath constituents. XRF therefore restricted to measurement of Mg and Ca-concentration in the bath.

THE USE OF XRD BATH CONTROL

Several different XRD methods can be used in the bath control. Use of X-ray diffractometer to measure elemental concentrations requires the determination of the concentration of crystalline phases and then the calculation of the concentrations of the elements or combinations of the elements. Phase content of a sample of cooled electrolyte however depends on CR and cooling speed. High speed of cooling induces that alumina and some Ca-contained phases are amorphous and invisible for the XDR analysis. Typical XRD patterns of electrolytes containing Ca, Mg can be seen in Figure 2a, and 2b.

Fig. 1. Optical data versus chemical analysis data. Black dots represent the expected concentrations.

Fig. 2a. The XRD pattern of an electrolyte with CR= 3.28, C(CaF$_2$)=0.6%, C(MgF$_2$)=4.23%. 
The diffraction peaks from several minor phases are overlapped by larger peaks. This makes it difficult to measure the intensities of the small peaks. A high resolution X-ray diffraction equipment is required to get accurate measurements. There is also a claim in d-spacing availability at least in the range 1.6-5.2 Å.

Fig. 2.b. A typical XRD of pattern of electrolyte containing Ca-Mg with CR=2.35, C(CaF$_2$)=5.6%, C(MgF$_2$)=2.7%.

A lot of information concerning the structure of crystallized phases containing calcium became available during the last decade [7]. It makes possible the application of the multiphase Rietveld’s technique [6] can be to the task. Figure 3 is a final Rietveld plot of the magnesium rich electrolyte containing 6 phases. As a rule, the fitting procedure was not too difficult. The procedure provided results which were in good agreement with chemical analysis in the case of slowly crystallized samples and when special correction coefficients were used. We recommend the use of this procedure for the characterization calibration samples. There are some disadvantages to this procedure. It is time consuming, requires manpower, specimen preparation is made difficult by the existence of preferred orientation in the specimen.

FIG. 3. The Rietveld plot of an electrolyte containing a lot of magnesium.

Chung’s or RIR method [8] are not discussed in the paper because we feel that it is not suited for a routine industrial application, however, a variation of it has been used to prepare calibration samples.

In our opinion, the external standard method is best suited for this application. It is the most widely used method for such samples and analyses. The work described in this paper was designed for electrolytes containing magnesium, which are in the use in Russia. The method assumes that the X-ray diffractometer will be used to calibrate all the phases to be measured. In the case of magnesium at least eight calibration are necessary. We obtained samples of known phases and known concentrations to use in this study: Na$_5$Al$_3$F$_{14}$, AlF$_3$, NaF, CaF$_2$, MgO. In
synthesizing the calibration materials our objective was to maintain stoichiometry and the proper crystallization conditions to have the least number of phases in each calibration standard. We also attempted to produce materials which had a microstructure similar to that of industrial materials. We found that it was necessary to synthesize about 30 standards in order to be able to produce an adequate number of calibration curves. Figure 4 is a plot of XRD and Chemical analysis CR values for electrolytes containing Ca and Mg using a direct calibration method. The X-ray instrument was a Philips PW1800.

The first bath chemistry control procedure for industrial application so called Potflux analysis was developed by Philips Analytical [9]. This method used XDR and XRF. PW1800 diffractometer was equipped with special Ca-XRF channel to measure a total Ca content. The procedure was used in a number of aluminum smelters all over the world. The results of a bath control measurement at an Aluminium plant in Krasnoyarsk, Russia are shown in table I [10] A large set of calibration samples is necessary for this kind of work.

<table>
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<tr>
<th>Table 1. The characteristics of the PotFlux procedure based on PW1800 (Philips) at Krasnoyarsk Aluminum plant (Russia).</th>
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<td>Convergence of parallel Measurements ($\sqrt{S^2}=\sigma$)</td>
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**REVERSE CALIBRATION XRD APPROACH**

The literature contains methods which suggest ways to minimize the problem of having to use such a large number of calibration samples [11]-[13]. We have developed a so called reverse calibration method to reduce the need for use of large set of calibration samples in order to create sufficient calibration curves. The method uses a combination of XRD and chemical analyses. It treats the mineral content as unknown and attempts to derive it. The following equations are used to calculate concentrations. The relation between intensity $I_{ij}$ and concentration $C_{ij}$ [14]:

$$I_{ij} = KC_{ij}/\mu_j$$

$i$-numerates phases, $j$ – samples in the present case with $\mu_j = \text{constant}$. This equation can be converted to:

$$C_{ij} = a_i I_{ij},$$

where $a_i$ – calibration coefficient for the $i$-phase. Using the last equation the magnitude of $CR_{j,\text{chem}}$ obtained from chemical analysis can be correlated with X-ray intensities:
\[
CR_j = \frac{\sum_i \alpha_i C_{ij}}{\sum_i \beta_i C_{ij}} \approx CR_{j,chem}
\]

\(\alpha_i\) and \(\beta_i\) – indicate the fractions of NaF and AlF\(_3\) correspondingly in presenting phases. This equation can be used to generate a set of equations which can be used to make calculations of concentrations. Additionally at least three type of balance equations for total CaF\(_2\), MgF\(_2\) and total mass balance can be derived:

\[
C_j(CaF_2) = \sum_i \gamma_i C_{ij} \approx C_{j,chem}(CaF_2)
\]

\[
C_j(MgF_2) = \sum_i \eta_i C_{ij} \approx C_{j,chem}(MgF_2)
\]

\[
\sum_i C_{ij} \approx 1.0
\]

Using an LS-formalism four functionals can be written:

\[
\Phi_1 = \sum_j (CR_j - CR_{j,chem})^2 \rightarrow 0
\]

\[
\Phi_2 = \sum_j (\sum_i \gamma_i C_{ij} - C_{j,chem}(CaF_2))^2 \rightarrow 0
\]

\[
\Phi_3 = \sum_j (\sum_i \eta_i C_{ij} - C_{j,chem}(MgF_2))^2 \rightarrow 0
\]

\[
\Phi_4 = \sum_j (\sum_i C_{ij} - 1.0)^2 \rightarrow 0
\]

The total minimizing functional is the sum of the weighted functions:

\[
\Phi_{total} = w_1 \Phi_1 + w_2 \Phi_2 + w_3 \Phi_3 + w_4 \Phi_4
\]

New functionals, presenting other conditions, may be added to the final equation. An iteration is required to compensate for the non-linearity of CR-function. Calibration coefficients are treated as a refinement parameters. A convergent series of \(\Delta a_i\) corrections to the calibration coefficients \(a_i\) are calculated. Chemically defined \(CR_{j,chem}\), \(C(CaF_2)_{chem}\), \(C(MgF_2)_{chem}\) as well as X-ray intensities of analytical lines \(I_{ij}\) provide the experimental data needed to make calculations of concentrations of the unknowns. This method requires a lot fewer calibration samples than the methods described above. This is because of every sample with the same kind of material can provide 4 equations including 12 experimental values. The set of calibration samples can be created by new samples which have been properly crystallized and for which there is accurate chemical data concerning the concentrations in the samples. The advantage of the approach is in lower requirements to the phase distributions in the samples. Figure 5 contains a graph showing the results of the reverse calibration method. The estimated standard deviation is 0.008 in CR units.
CONCLUSIONS
Specimen preparation for XRF analysis is so difficult that it makes impossible to achieve the desired accuracy. The XRD methods produces results of satisfactory accuracy, but the method is complex due to the phase contents in the electrolytes and is too cumbersome because it requires such a large set of calibration standards. We find that our reverse calibration procedure is accurate and a much easier can be provided calibration samples.

Fig.5. Plot of XRD data and chemical analysis of Cryolite ratios in the case of reverse calibration.

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REFERENCES