Explorer

Aluminum Electrolytic Bath monitoring by XRD

Introduction

Aluminum is the most abundant metal on the Earth, being about the 8% of its crust; moreover, it is the second largest used metal in the world, thanks to its light weight, high strength and recyclability[1]. Besides, it easily binds with other elements, which on the one hand allows the formation of a huge number of compounds and alloys; on the other hand, it prevents its occurrence in pure form, so that energy is required to recover it.

The main Aluminum source is Bauxite, a mineral that mainly consists of Aluminum Hydroxides, Iron Oxides, Kaolinite and Titania.

The production of Aluminum is a two-step process: first Aluminum Oxide (*Alumina*) is extracted from Bauxite through the Bayer process, then Aluminum is recovered by electrolytic reduction through the Hall-Héroult one[2]. The latter consists of Alumina decomposition in a molten Cryolite (Na_3AlF_6) electrolyte at 1230 K, which is more economically sustainable with respect to direct production from Alumina alone. Despite this advantage, the electric current demands are still large and proper electrolytic cell (bath) tuning is mandatory in order to keep the efficiency at maximum and greenhouse gas emissions at minimum.

The presence of additional compounds in the bath has both positive and negative effects on its properties. Typical additives are: MgF_2, CaF_2, AlF_3, LiF, KF, NaF. In general, additives reduce the liquidus temperature, which is beneficial to energy consumption reduction, but detrimental to process efficiency, due to Alumina solubility decrease. Moreover, Alumina content has to be above a concentration threshold in order to avoid the anode effect, which causes the interruption of Al production and generates greenhouse gases. It is thus important to optimize the bath operating conditions by monitoring the Cryolite-Alumina-Additives system.

X-Ray Diffraction (XRD) quantitative analysis has proved to be effective in determining the bath conditions for several years[3]: a sample of the molten electrolyte is taken from each cell and after solidification is reduced to powder form and pressed into steel rings before analysis. Typical mineral phases are reported in Table 1 (Theory section), although certain variability is expected depending on additives. The most important parameters to be monitored are the Bath Ratio (BR) and the Excess AlF_3 ($ExAlF_3$).

Given the large number of cells and sampling frequency, the time available for analysis is limited to some minutes: this target can be reached by using Explorer diffractometer coupled with Multi Task Solution (MTS) software.

[1] http://www.aluminiumleader.com

[2] http://www.hydro.com/en/About-aluminium/How-its-made/

[3] S. Kirik, I. Yakimov, *An evaluation of XRD and XRF methods used in an Aluminium bath analysis, Adv.X-Ray Analysis* Vol 44

Summary

The optimization of Aluminum production process by electrolytic reduction (Hall-Héroult) requires constant monitoring of the bath parameters: X-Ray Diffraction has been an effective technique to determine Bath Ratio and Excess AlF_3 for several years. The Explorer MTS configuration with XRD Linear detector, XRF detector and automated sample holder allows to cope with short available time for measurement and analysis in an easy-to-use way. Besides, the use of a Silicon Drift Detector for XRF allows to monitor the content of both Ca and other elements of interest (e.g. K) at the same time, which can be very useful for an unconventional bath chemistry.

Theory

BR is defined as the *weight* ratio between total NaF and total AlF_3 in the sample, while $ExAlF_3$ is the Aluminum Fluoride in excess with respect to pure Cryolite for each phase.
Cryolite Ratio (CR) parameter is used as well as of BR:

$$BR = \frac{NaF}{AlF_3} \;;\; CR = 2BR \;;\; Ex\,AlF_3 = \sum AlF_{3j}^{EX}$$

For pure Cryolite BR=1.5 (CR=3.0), $ExAlF_3$=0.

The cell working range is between BR=1.1-1.4 (CR=2.2-2.8)

The weight amount contribution from each phase to BR and $ExAlF_3$ is related to the intensity of one (or more) reference XRD peak through a calibration curve, which is built by using reference samples with known parameters (e.g. determined by Wet Chemistry).

Besides XRD, XRF signal is collected at the same time for Ca element in order to overcome difficulties in Calcium Cryolite (CaCryo 1 and 2) contribution estimation, due to poor crystallinity and peak overlaps:

$$Tot_{CaF_2} = Fluorite + 0.383 NaCaAlF_6 + 0.482 Na_2Ca_3Al_2F_{16}$$

where total Calcium is taken as CaF_2.

Table 1. List of common phases in congealed electrolyte with corresponding Cryolite and $ExAlF_3$ fraction

Phase	Formula	Cryolite fraction	AlF_{3j}^{EX} fraction
Cryolite	Na_3AlF_6	1	0
Chiolite	$Na_5Al_3F_{14}$	0.758	0.242
CaCryo 1	$NaCaAlF_6$	0.343	0.274
CaCryo 2	$Na_2Ca_3Al_2F_{16}$	0.288	0.230
Li Cryolite	Na_2LiAlF_6	0.722	0.144
Fluorite	CaF_2	0	0
Corundum	Al_2O_3	0	0
Neighborite	$NaMgF_3$	0	0
Weberite	Na_2MgAlF_7	0.608	0.121

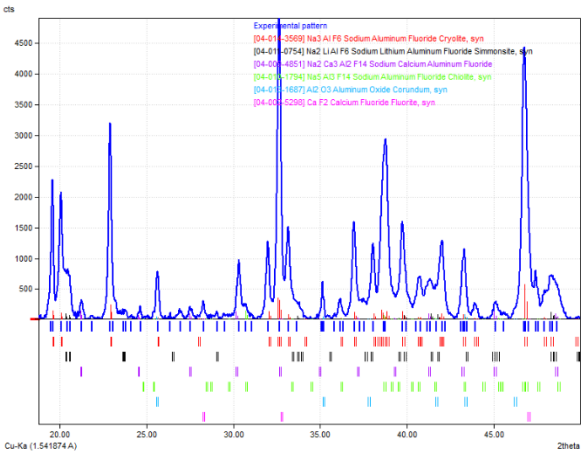
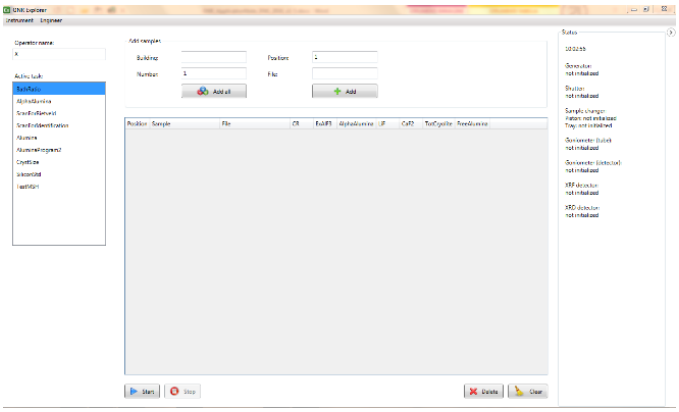


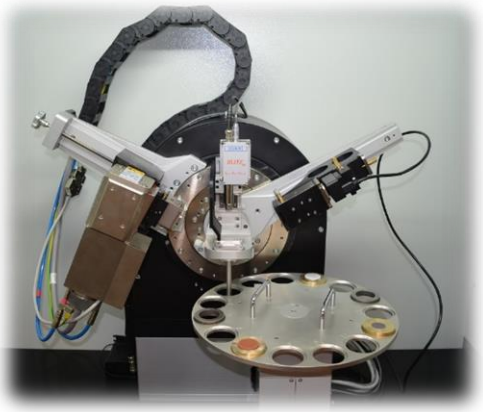
Figure 1. XRD pattern for an Electrolytic Bath standard sample

Product Specifications

Explorer MTS couples the performances of Explorer Theta/Theta diffractometer with the versatility and ease of use of MTS software: this makes it a suitable solution for production control



The unit consists of:
- Explorer Theta-Theta goniometer;
- rotating multi sample holder (MSH);
- Piston;
- Trays;
- XRD linear detector;
- XRF Silicon Drift detector.



Depending on the bath chemistry and number of phases, a typical measurement can last from 1 to 3 minutes per sample. In addition to Ca, it is possible to monitor K fluorescence signal too, which may be required in case KF is present as an additive.

MTS allows to create Tasks and corresponding calibration curves in a simple way; once a Task is created, the operator has only to load the unknown samples and wait for results, which can then be sent automatically to a remote repository in the plant. Moreover, data can be exported for further analysis with other software (e.g. Rietveld refinement).

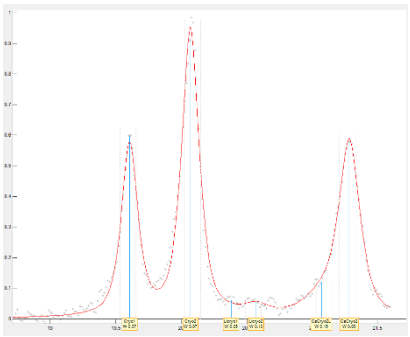


Figure 2. Cryolite and Ca-Cryolite representative peaks

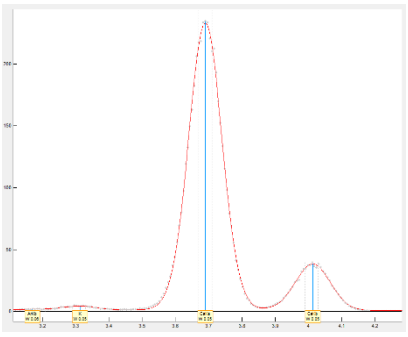


Figure 3. XRF Ca (K_α and K_β) and K signal

Experimental

Goniometer radius [mm]:	215		
X-Ray Source:	Cu LFF	Filter:	Nickel 0.02 mm
Divergence slit[°]:	0.5	Detector:	XRD: Mythen 2
			XRF: XGlab SDD 25 mm^2

First, in order to show the instrument capabilities, 10 Alcan bath standards were pressed into 51.5 mm steel rings to realize the calibration curve. The sample holder tray is compatible with most common hydraulic press rings.

In a second time, calibration curves were performed by using 32 custom-reference samples (Wet Chemistry).

Goodness of calibration is represented by RSD value:

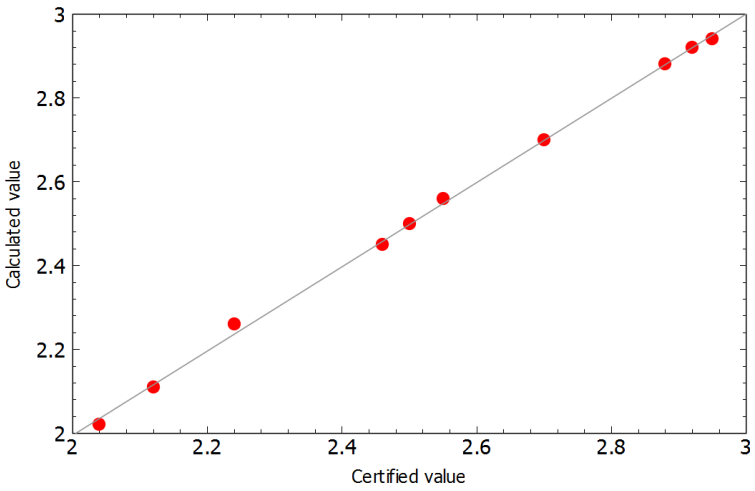
$$RSD = \left(\frac{1}{N} \sum_{i=1}^{N} \left(f_{calc,i} - f_{cert,i} \right)^2 \right)^{1/2}$$

where N is the number of samples, $f_{calc,i}$ the calculated value and $f_{cert,i}$ the known value.

Results

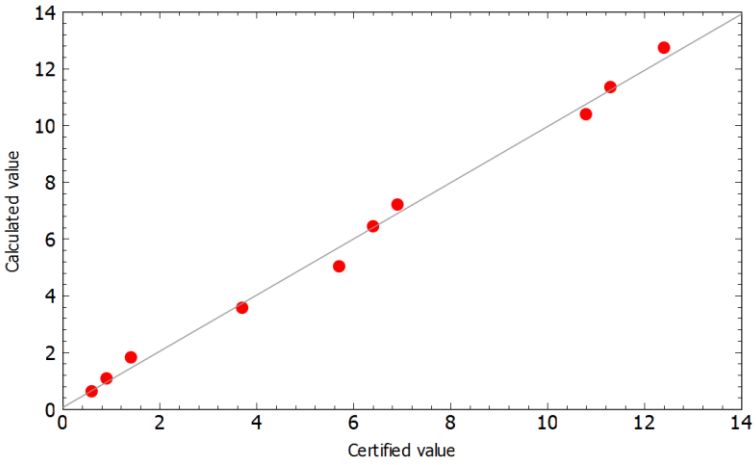
CR calibration curve with Alcan standards.

RSD=0.01



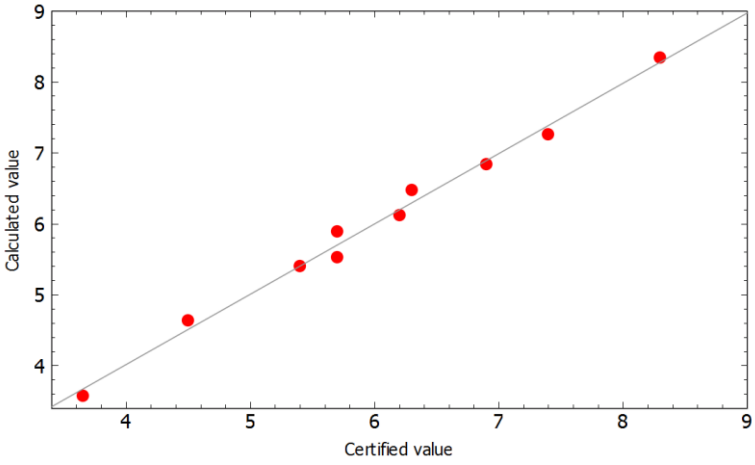
$ExAlF_3$ calibration curve with Alcan standards.

RSD=0.33



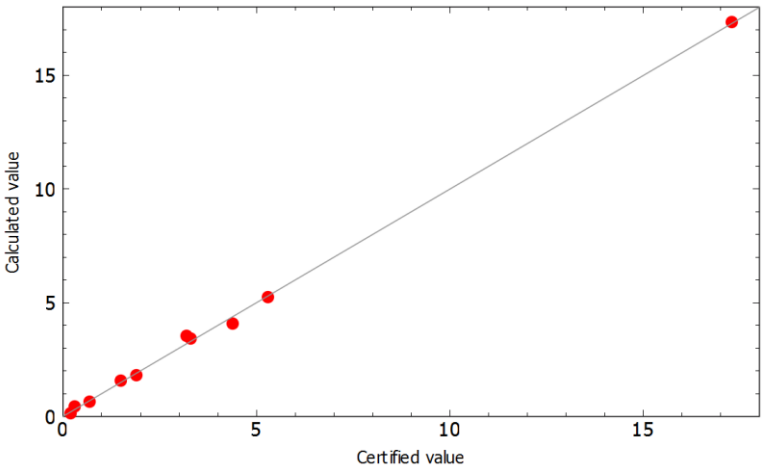
CaF_2 (XRF) calibration curve with Alcan standards

RSD=0.13



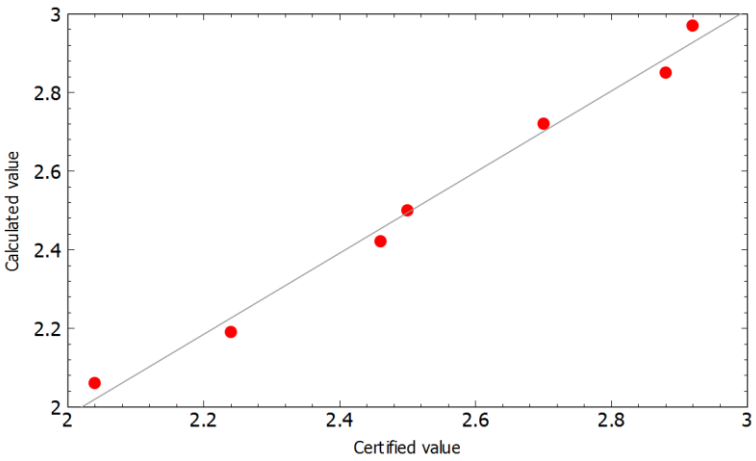
Alpha Alumina calibration curve with Alcan standards

RSD=0.16



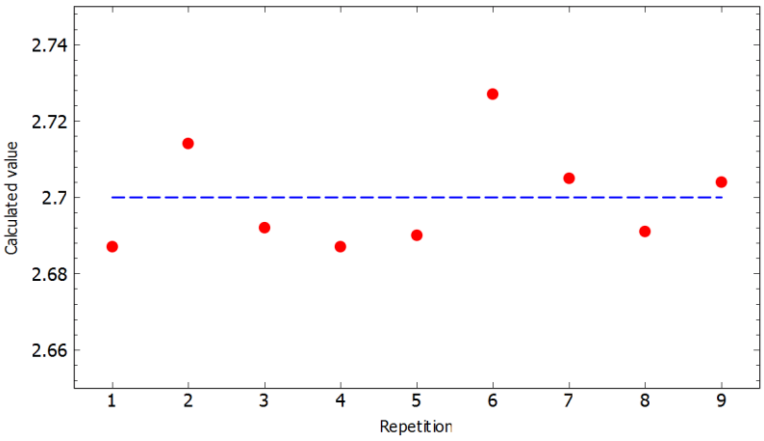
CR calculated values for some Alcan standards prepared and loaded again as "unknown" samples on the instrument. Alcan calibration curve parameters were applied.

RSD=0.03



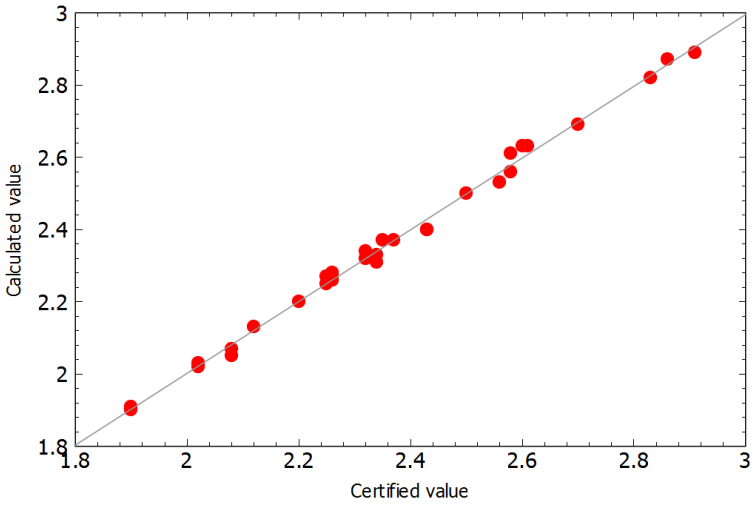
CR values for one sample prepared and loaded 9 times. Certified value is 2.7

RSD=0.01



CR calibration curve with customer standards.

RSD=0.02



The correlation between reference values and calculated ones is pretty good.

In general, it is preferable to have custom-reference standards in order to build calibration curves with sample compositions as close as possible to production ones.

Conclusions

Explorer MTS configuration allows to determine electrolytic bath parameters (BR, CR, ExAlF_3) in a fast and easy way: after calibration curves have been prepared by using reference samples, the user loads production samples and waits for results. Successful testing was performed with both Alcan Electrolytic Bath standards and custom-reference standards.

Authors

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About GNR SRL

With 30 years of technological experience, GNR is a worldwide market manufacturer of advanced analytical instruments in Optical Emission Spectrometer and XRD / XRF domain, developing procedures of analysis for various applications, supplying the corresponding laboratory equipment and providing consulting and customer support worldwide.

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