Fully Automated XRD Analysis of Electrolytic Bath– An Advanced and Flexible Approach for Rapid and Accurate Process Monitoring

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Abstract

A rapid and accurate process monitoring is crucial for any industry especially aluminum smelters due to immense electricity consumption during the aluminum electrolysis process. Over the last decades, due to relatively quick sample preparation and analysis, and the use of Rietveld method for phase quantification, X-Ray Diffraction (XRD) has become a standard analytical tool from bauxite mining to alumina refining, aluminum smelting, and even valorization of red mud. This study presents a coupled XRD-full pattern Rietveld technique in combination with a well-established statistical algorithm (Partial Least Squares Regression: PLSR) that simultaneously quantifies all mineral phases present in an electrolytic bath sample and calculates bath parameters (e.g., excess AlF_3, total CaF_2, total Al_2O_3). To create a global solution able of predicting process parameters in any types of bath samples, the PLSR calibration was built based on over 70 standard bath samples, including the Alcan B-1 to -31. The prediction results of total CaF_2 contents of 85 samples show above 99.9% accuracy. This technique was developed using Aeris compact diffractometer and the measurements and results reporting can be done in a fully automatic mode. This is a fast (95s scan time), accurate and reproducible technique, that in contrary to the conventional approach, does not require an X-Ray Fluorescence (XRF) channel nor further calibration.

Keywords: Electrolytic bath, Bath parameters, excess AlF_3, Quantitative XRD, PLSR.

1. Introduction

The aluminum industry plays a crucial role in sectors such as aerospace, automotive, construction, and packaging. However, maintaining efficient operations poses challenges. X-ray diffraction (XRD) can be utilized to gain mineralogical insights at every stage of the aluminum production process, starting from bauxite to alumina and aluminum. Its applications span across the entire aluminum production chain, encompassing tasks such as grading the ore, evaluating the available alumina content, assessing reactive silica levels, optimizing recovery processes, monitoring phase composition and structural changes, reducing energy consumption, determining optimal bath composition, analyzing anodes, and ensuring quality control of alumina.

Aluminum smelting is a complex industrial process that demands precise control over numerous parameters to ensure optimal efficiency and product quality. Among these parameters, the electrolytic bath is a critical component within the electrolytic cell, where the electrochemical reduction of alumina takes place. Monitoring electrolytic bath samples in aluminum smelters is particularly important for controlling the electrolysis process and accurately determining key parameters like excess AlF_3 ($xsAlF_3$) and total CaF_2, which are essential for achieving optimal aluminum production.

To achieve precise control and optimization in aluminum smelting, monitoring techniques are essential for providing accurate and real-time information about the characteristics of the electrolytic bath. Among these techniques, X-ray diffraction (XRD)-Rietveld analysis (also known as quantitative XRD or QXRD) has emerged as a powerful tool for analyzing electrolytic bath samples, enabling comprehensive investigations into their crystalline structure and composition. XRD-Rietveld analysis basically combines XRD with the Rietveld refinement method, a mathematical technique that enables detailed quantitative analysis of diffraction patterns from crystalline materials [1].

Feret [2, 3] and König et al [4] showed that mineralogical analysis of electrolytic bath samples through QXRD plays a crucial role in determining important parameters such as the liquidus temperature, abundance of different phases (e.g., cryolite, chiolite) at a certain temperature, bath ratio, and bath temperature. Additionally, it provides insights into how the amount of CaF_2 and $xsAlF_3$ can control the efficiency of the bath or in other words influence the bath ratio, which represents the ratio of alumina to bath material. It is worth mentioning that CaF_2 acts as a fluxing agent, helping to lower the melting point of the bath and improving its conductivity. $XsAlF_3$ also affects the bath efficiency by influencing the electrical conductivity and the dissolution kinetics of alumina. Excessive levels of AlF_3 can lead to increased electrical resistivity and reduced alumina dissolution rate, negatively impacting the smelting process. By accurately determining the amounts of CaF_2 and $xsAlF_3$ through mineralogical analysis, smelters can adjust the bath composition to ensure efficient and stable operation.

Following König et al [4] approach, this article explores the significance of QXRD analysis as a monitoring tool in aluminum smelters, shedding light on its role in process optimization, troubleshooting, and overall quality control. By delving into the practical applications and benefits of this technique, we aim to highlight its relevance in the aluminum industry and its potential to enhance the efficiency and sustainability of aluminum smelting operations.

Furthermore, this article presents an innovative approach that combines QXRD with partial least squares regression (PLSR). By utilizing PLSR, simultaneous quantification of mineral phases and determination of bath parameters can be achieved [4]. The XRD-PLSR approach offers advantages for process monitoring, including rapid analysis, quick sample preparation, high accuracy, and reproducibility. A key advantage of this approach is the creation of a comprehensive calibration using standard bath samples, such as well-known Rio Tinto Alcan Electrolytic Bath Standards, which allows for the prediction of process parameters in different bath samples. Moreover, the proposed technique eliminates the need for an additional X-Ray Fluorescence (XRF) channel, simplifying the setup and reducing costs. By using a single XRD instrument for both phase quantification and bath parameter determination, the analysis process is streamlined, optimizing efficiency and productivity.

Finally, we will discuss the key parameters and considerations involved in conducting QXRD on electrolytic bath samples. These parameters include sample preparation, instrument setup, data acquisition, and data interpretation. Understanding these fundamental aspects is crucial for effectively implementing this analytical method and extracting valuable information from the obtained XRD patterns.

2. Materials and Methods

2.1 Sampling

To establish a global predictive solution applicable to real-world scenarios and diverse bath samples, this study investigated a total of 85 samples, of which 69 samples originated from industrial baths. In this approach, PLSR calibration incorporated XRD data from 16 Alcan standard samples (B-1 to -31), along with data from 54 bath samples serving as in-house standards in different aluminum smelter plants. Additionally, 15 industrial bath samples were employed for presents the mean composition of various bath phases obtained from the 15 separate analyses, accompanied by their corresponding standard deviations.

The small standard deviation (Std) reported (Table 1) indicates a high level of repeatability of the whole procedure and intensity stability in during the measurements. Given the importance of intensity stability, a correction must be applied using a monitor sample when the X-ray tube intensity declines through time. However, the Aeris diffractometer's low energy consumption (energy settings: 40kV, 15 mA) guarantees an almost unlimited tube lifetime. This advantageous feature of the instrument ensures high-quality data over an extended period of time, and makes it a reliable analytical device for process monitoring in smelter plants.

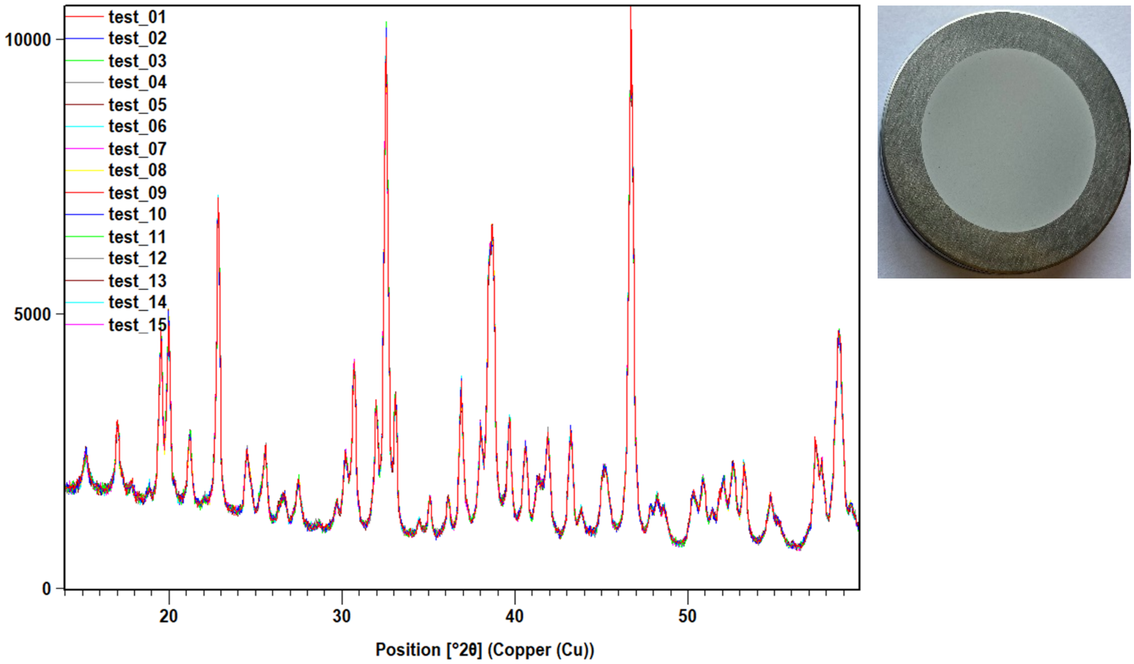

Figure 5. A compare-view of 15 scans of a bath sample in Aeris compact XRD system showing the stability of intensity during the measurements.

Table 1. Mean composition and corresponding standard deviation (Std) measured from 15 times analysis of an electrolytic bath sample. Bath ratio (BR), xsAlF$_3$ were measured from phase compositions by Rietveld refinement, whilst the total CaF$_2$ and Al$_2$O$_3$ were predicted by PLSR model. The liquidus temperature (LT) is calculated based on the outcome of both Rietveld and PLSR methods.

n=15	**BR**	**xsAlF3 (wt%)**	**total-CaF$_2$ (wt%)**	**total-Al$_2$O$_3$ (wt%)**	**LT (°)**
mean	1.26	6.65	8.75	4.20	946.90
Std	0.00	0.04	0.03	0.12	0.30

4. Conclusions

Knowing the mineralogical composition of the electrolytic bath in aluminum smelters is crucial for optimizing the smelting process, ensuring bath stability, detecting impurities, troubleshooting issues, and driving process development and innovation. It complements the understanding gained from chemical analysis, enabling a more comprehensive understanding of the electrolytic bath and facilitating improved control and performance in aluminum smelting operations.

This paper demonstrates that modern XRD equipment can rapidly determine the phase composition of an electrolytic bath, along with vital process parameters such as bath ratio, xsAlF$_3$,