

AL28 - 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

PLSR prediction validation. Adhering to confidentiality agreements and privacy commitments, specific customer names have not been disclosed in the paper.

2.2 Sample Preparation

Achieving precise outcomes in XRD analysis relies on appropriately preparing powder samples, just like any other techniques. It is essential to standardize and optimize the sample taking process to ensure maximum accuracy tailored to the specific application requirements. To guarantee reproducibility and consistency in sample preparation for XRD measurements, automatic sample preparation equipment (Herzog HP-MP) was utilized. In this regard, the sample materials underwent a 30-second milling process at 750 rpm, followed by a 30-second pressing phase under a 100 kN load into a 51.5 mm steel ring sample holder. To enhance the grinding and pressing processes, we incorporated four polysius Mahlhilfe tablets into the material as a grinding aid. The recommended proportion for the grinding aid is approximately $10 \pm 3\%$ of the total sample weight. The addition of grinding aids significantly improves the mechanical stability of the pressed pellets, resulting in better grinding and pressing outcomes. This meticulous preparation technique resulted in a particle size below 60 μm , ensuring uniformity and reliability in the obtained XRD data. With this technique, a total of 85 pressed pellets of bath samples were produced for mineralogical investigation.

2.3 XRD Measurements

The XRD scans were collected using the Metals Edition of the Aeris compact X-Ray diffractometer from Malvern Panalytical. The instrument was equipped with an Emyrean copper-anode X-ray tube and had power settings of 40 kV and 15 mA, and a goniometer radius of 145 mm. The optics used included 0.04 soller slits, a 1° divergence slit, a 20 mm mask, and a pre-calibrated beam-knife. The step size was set to 0.04° with an acquisition time of 18 seconds per step (total measurement time of 95-seconds). In addition, the instrument featured a linear PIXcel^{1D} Medipix3 detector with a 5.54° 2θ active length, enabling rapid scan acquisition. The Bragg-Brentano measurement covered a range of $10\text{-}60^\circ$ 2θ encompassing the peak positions of all potential phases present in an electrolytic bath sample.

Although it was feasible to analyze each bath sample in as little as 24 seconds using the Aeris instrument while maintaining an acceptable level of precision, achieving accurate Rietveld refinement necessitates XRD scans of a specific quality. These quality scans should exhibit a low and flat background and high diffraction intensities, particularly at the most intense peak where counts should exceed 10,000. In this study, all scans of the required quality were collected within a measurement time of 95 seconds.

Detectability of signals relies on achieving a certain signal-to-noise ratio. A signal that is three times above the noise level can be detected, while a signal that is ten times above the noise level is necessary for precise QXRD analysis. In the collected XRD scans, the average signal-to-noise ratio was measured to be 120, indicating that all minor and trace phases present in the studied samples were detectable and quantifiable.

2.4 Data Analysis

2.3.1 Cluster Analysis and Rietveld Refinement

For phase identification and quantification, Malvern Panalytical's HighScore Suite software version 5.1 [5] was employed, utilizing the ICDD PDF-4 database [6]. To streamline the analysis process for bath samples, the phase identification of 85 XRD patterns was performed using specific XRD scans selected through an extended cluster analysis and 3-dimensional Principal

Component Analysis (3D-PCA) implemented in HighScore Plus (Figure 1). The cluster analysis module in the HighScore Plus incorporates various algorithms resulting in creation of a correlation matrix, agglomerative hierarchical cluster analysis, grouping, and visualization of the scans (Figure 1a) [7, 8]. These algorithms offer a valuable tool for simplifying the analysis of large datasets. Despite the formation of four major groups observed in the 3D-PCA plot of 85 XRD scans of electrolytic bath samples, the extent of variation and compositional diversity within each group is visually depicted by the distances between individual data points (Figure 1b). By automatically categorizing closely related scans from an experiment into distinct groups, the module identifies the most representative scan within each group, as well as any exceptional or outlying scans. This selection process ensures the development of a Rietveld refinement routine that can be employed in automatic mode for data analysis.

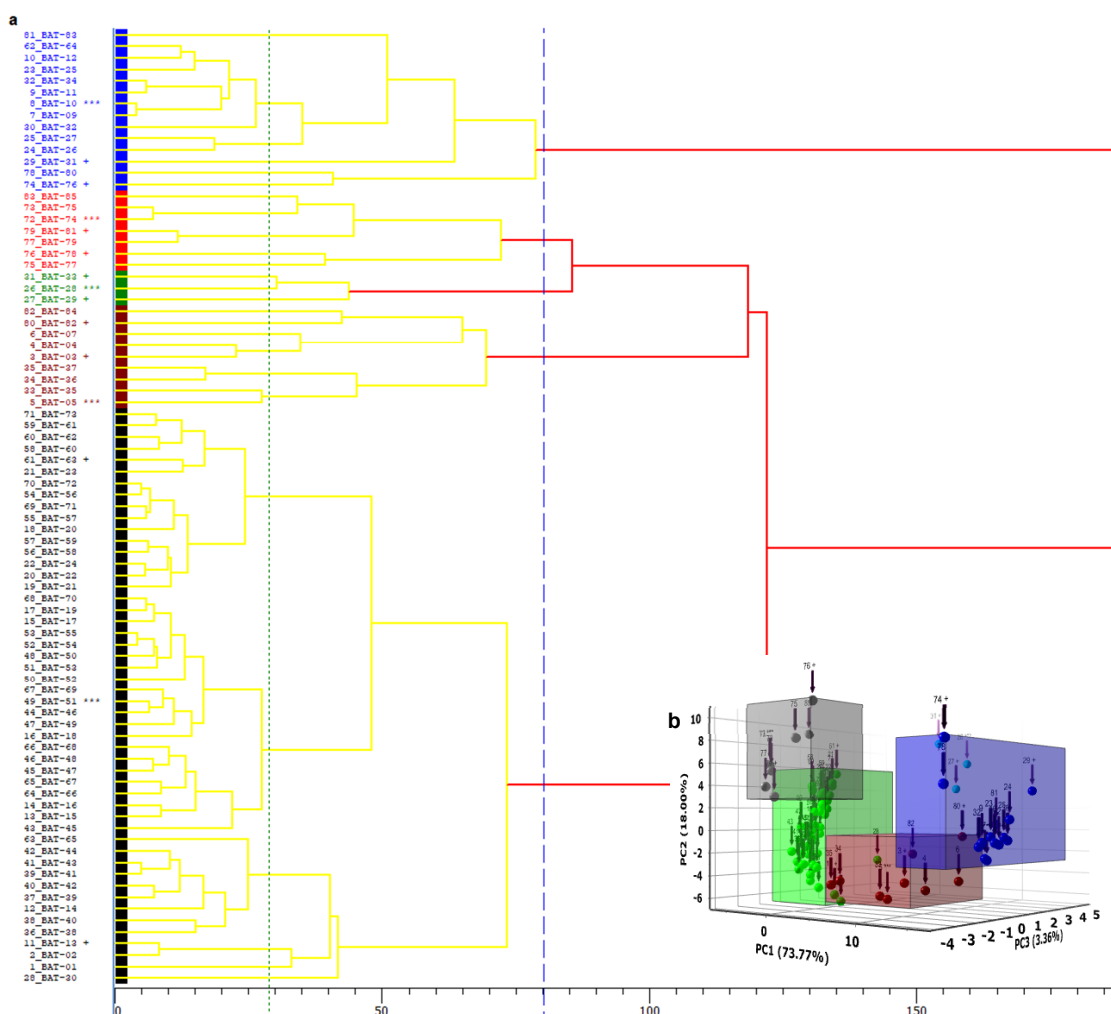


Figure 1. An extended cluster analysis of the XRD patterns of the 85 studied samples in HighScore Plus. a) dendrogram displaying the results of cluster analysis based on the correlation matrix of 85 studied samples. The X-axis represents the dissimilarity of the tie bars, indicating the degree of dissimilarity between clusters. The most representative scan from each cluster is indicated by ***. b) three-dimensional Principal component analysis (3D-PCA) of the XRD patterns capturing > 95.1% of the variation in the dataset.

2.3.2 Partial Least Squares Regression Calibration

PLSR, also known as soft modeling, is a widely used statistical method that enables the prediction of "hidden" properties directly from raw data. PLSR enables the extraction of meaningful relationships between variables, allowing accurate predictions of properties of interest based on the variability in data matrices. Once the model is calibrated using independent determination of reference values, it can be employed to predict the property of unknown samples. PLSR, developed by Wold [9], allows for the direct prediction of any defined property, denoted as Y , by leveraging the variability in a data matrix X . This matrix typically contains non-systematic variations (such as sample preparation, impurities, and different grain sizes) as well as systematic "measurable" variations (such as different quantities). The objective is to establish a correlation between the systematic variation and a known property, Y . In the case of XRD data, PLSR adopts a full pattern approach that disregards profile shapes while utilizing the complete information in the XRD data sets. HighScore Plus employs the SIMPLS algorithm for PLSR. The PLSR module is user-friendly, with semi-automatic evaluation and optimization of the regression model, requiring minimal knowledge of the method.

The PLSR module in HighScore Plus offers two scaling modes to determine the optimal calibration model. In the "center" scaling mode, variables are centered by subtracting the mean value from each variable, while in the "standardize" scaling mode, variables are standardized by subtracting the mean and dividing by the standard deviation.

Cross-validation was employed to estimate the errors of a particular PLSR calibration model when a set of independent samples is unavailable for validation. During cross-validation, one sample was omitted from the calibration set and used as a validation sample. This process was repeated until all samples have been predicted. The root mean square error of prediction (RMSEP) provides an absolute value indicating the expected variation in the analyzed property after applying cross-validation. However, using an independent test set remains the most reliable approach for validating any PLSR model [4, 8].

3. Results and Discussions

As mentioned above, a combined analysis approach involving QXRD-PLSR was employed to determine the mineralogical composition of the bath and various process parameters, including the bath ratio, total CaF_2 , xsAlF_3 , free Al_2O_3 , and liquidus temperature. Specifically, Rietveld full-pattern fitting was utilized to ascertain the mineralogical composition, bath ratio, and xsAlF_3 . Simultaneously, the PLSR method was applied to determine the total CaF_2 , total Al_2O_3 , and liquidus temperature. An alternative method involves calculating the CaF_2 content based on the Rietveld phase composition (Figure 2). Furthermore, the Rietveld method allows for accurate determination of crystalline $\alpha\text{-Al}_2\text{O}_3$ (corundum). However, the total Al_2O_3 content, including amorphous and semi-crystalline Al_2O_3 , cannot be fitted within the Rietveld model. Nonetheless, similar to CaF_2 , total Al_2O_3 can be predicted using the PLSR method with a pre-calibrated model. Figure 2 illustrates a case of Rietveld quantification performed on a standard composition electrolytic bath sample, where no magnesium, lithium, or potassium was added. The quantification process considered nine phases. If required, based on the specific bath chemistry, supplementary phases containing magnesium, lithium, or potassium can be incorporated into both the Rietveld model and the associated calculations. Upon the development of a reliable Rietveld model, a large number of XRD scans of electrolytic bath samples can be automatically analyzed using a smart batch known as MultiRiet in HighScore Plus. The mineralogical similarity or dissimilarity between different samples can be examined by analyzing the generated histograms (Figure 3) or the outcome data table.

3.1 Prediction of CaF₂ Contents using PLSR Calibration

In order to verify the precision of the predictions of the CaF₂ contents made by the developed PLSR model, a comprehensive comparison was performed against the reference values obtained from XRF analysis. Figure 4a shows the comparison between the CaF₂ contents predicted by PLSR and reference data for 85 electrolytic bath samples. The findings revealed an exceptional level of agreement between the CaF₂ contents obtained from both techniques. Impressively, the coefficient of determination (r-squared) for the PLSR model stood at 0.9997, reaffirming the model's outstanding correlation and remarkable predictive capability. This outcome demonstrates a better accuracy of CaF₂ measurement through the XRD method compared to the previous approach where XRD systems were equipped with an XRF channel were utilized for Ca quantification in the bath samples [1]. Nevertheless, Feret [1] reported a strong correlation (98.0%) between reference values and Rietveld determined CaF₂ concentrations.

It is worth emphasizing that the precision of PLSR results, like any other techniques, hinges on the quality of the calibration model. Incorporating a diverse range of standard samples enables the PLSR model to effectively learn and establish correlations between XRD-derived sample characteristics and CaF₂ contents. Consequently, the impressive agreement observed between PLSR predicted and XRF reference values can be attributed to the robustness of the PLSR calibration, which utilized 70 standard samples representing various mineralogical compositions. Notably, the PLSR model exhibits the capability to predict CaF₂ contents in electrolytic bath samples beyond the specific calibration set.

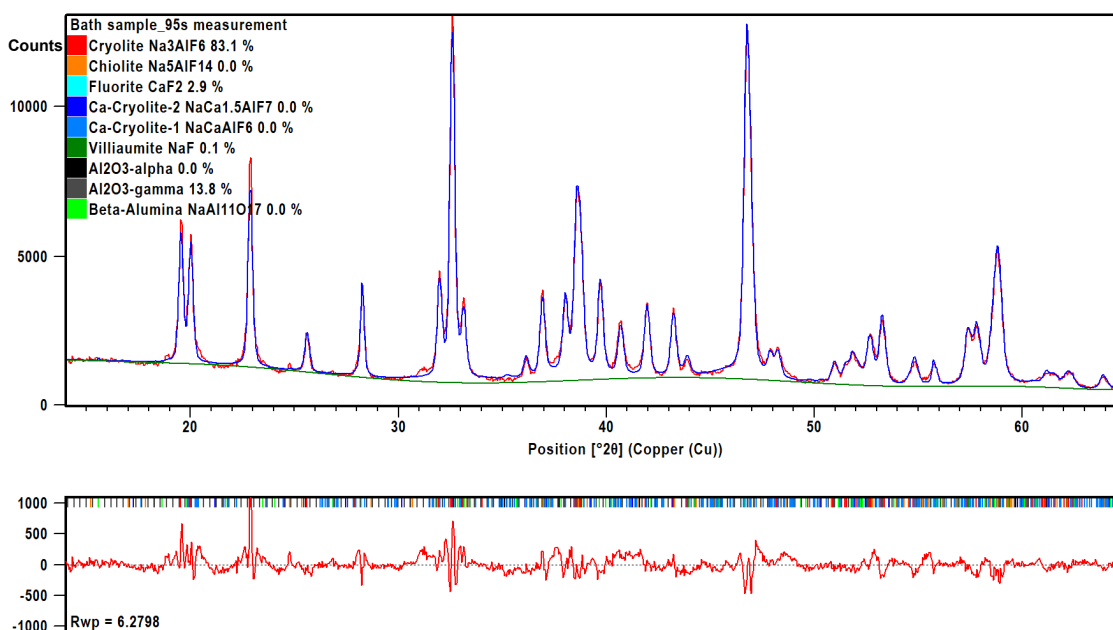


Figure 2. An example of Rietveld refinement conducted on an electrolytic bath sample, presenting the measured (pattern in red) and calculated patterns (pattern in blue) along with the difference plot (below) and the Rietveld agreement index Rwp.

3.2 Comparison of xsAlF₃ from XRD with Reference Values

As mentioned above, the xsAlF₃ can be directly estimated from the phases' composition through Rietveld refinement of XRD patterns. To evaluate the XRD-Rietveld data precision, the acquired data was plotted against the reference values obtained from XRF as a conventional approach. The comparison results in Figure 4b reveal a remarkably high level of agreement (r-squared: 0.9982) between the two techniques, underscoring the reliability and accuracy of XRD analysis in determining xsAlF₃ content. Given the importance of monitoring xsAlF₃ in aluminum smelters

for optimizing energy efficiency, ensuring bath stability and maintaining consistent product quality, the adoption of a faster (95 seconds instead of several minutes) and reliable technique like XRD offers substantial benefits including facilitating a prompt response to any alteration in bath composition.

It is important to note that this study considered the contribution of two distinct types of Ca-cryolite (alpha and beta Ca-cryolite) identified and quantified by QXRD into $xsAlF_3$ estimation [10]. This is in contrary to the commonly used algorithm for determining $xsAlF_3$. The conventional approach incorrectly relies solely on the composition of chiolite and CaF_2 . As a result, the accuracy of $xsAlF_3$ determination is compromised because the phase composition of reference materials and plant samples often exhibit dissimilarities. This also impacts the precision of estimating other bath parameters [10].

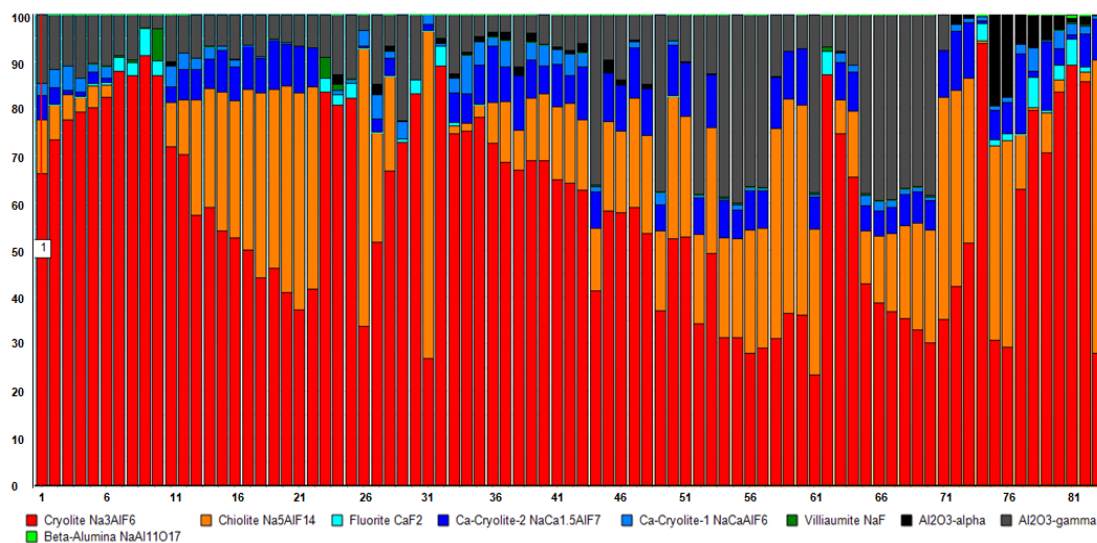


Figure 3. Histograms depict the phase quantification (wt%; normalization to 100%) results of 85 bath samples characterized by diverse mineralogical variations.

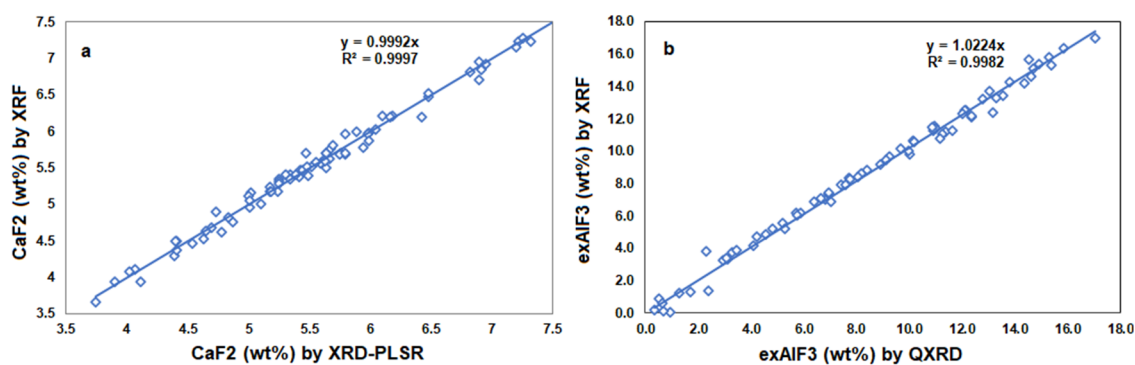


Figure 4. A comparison between a) the total CaF_2 and b) $xsAlF_3$ measured predicted by XRD-PLSR versus reference values from XRF for 85 bath samples. Strong correlations and agreements are seen between the values obtained from both techniques.

3.3 Estimation of Other Critical Bath Parameters

Bath ratio (BR): Along with $xsAlF_3$, the bath ratio plays a crucial role in controlling the composition of the electrolyte in aluminum production. BR, in brief, is determined by the weight ratio of NaF to AlF_3 in the electrolyte. BR can be calculated through QXRD by analyzing the quantities of mineral phases present in the solidified electrolyte. This estimation takes into

account the known stoichiometry of cryolite, chiolite, and two types of Ca-cryolites. QXRD analysis of the 85 studied samples demonstrated a range of variation in the bath ratio from 0.9 to 1.5.

Liquidus temperature (LT): LT is another critical parameter that represents the temperature at which the electrolytic bath composition begins to solidify. Determining the liquidus temperature is essential for maintaining a stable and efficient bath composition, as operating below this temperature can also lead to increased energy consumption and reduced productivity. LT can be determined by utilizing the contents of the corresponding bath parameters such as $x\text{sAlF}_3$, CaF_2 , and total Al_2O_3 in thermodynamic models or phase diagrams.

Traditionally, the composition of electrolytic bath has been determined using various analytical techniques, such as XRF and wet chemical analysis. However, XRF cannot provide mineralogical information, while wet chemistry requires significant manpower resources. Consequently, the QXRD method has emerged as a primary and universal technique for phase determination and quantification in electrolytic baths due to its efficiency and quick results.

In the literature, multiple approaches have been proposed to estimate the liquidus temperature and associated superheat of electrolytic baths based on specific bath parameters [11]. This study employed the models developed by Peterson et al. [12] and Solheim et al. [13] to estimate LT. The results showed a range of liquidus temperature variations among the samples, spanning from 855 to 985°C. This range is wider than the typical range for an efficient aluminum electrolytic bath indicating potential deviations from the optimal operating conditions.

A liquidus temperature as low as 855°C can lead to reduced electrical conductivity and potentially impact the efficiency of the aluminum production process. It may also indicate a different composition of the bath or the presence of impurities that affect the melting characteristics.

König et al. [4] determined the LT and calculated the corresponding superheat, which represents difference between the measured bath temperature and the theoretical liquidus temperature. Positive superheat values indicate inefficient energy utilization, while negative values indicate the potential risk of bath solidification. König et al. [4] used a PLSR model to predict the bath temperature using XRD raw data, with thermocouple data from the bath serving as reference values.

3.4 Repeatability of the QXRD-PLSR Technique

The repeatability of the whole procedure depends on several factors: 1) Reproducible sample preparation technique: A consistent and uniform sample preparation technique is crucial, including factors such as controlling particle size, ensuring sample homogeneity, and proper handling to minimize errors due to sample height and prevent strong preferred orientation of crystallites within the sample. 2) Stability of XRD intensity, which is controlled by factors such as instrument calibration, the stability of the X-ray source, detector performance, and correct alignment of the instrument components. 3) Stability and precision of automatic Rietveld refinement, and 4) robustness and reliability of the PLSR calibration model.

To assess the repeatability of the QXRD-PLSR analysis for the electrolytic bath, one of the studied samples was randomly selected and measured 15 times using the 95-second program in Aeris. The measurements were automatically analyzed using a Rietveld-PLSR routine (also known as a control file) executed by the RoboRiet software included on the diffractometer's internal computer, and data was transferred to a shared folder. Figure 5 displays an overlay of the 15 collected scans measuring a pressed pellet of bath sample prepared in a 51.5 mm ring. Table 1

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.

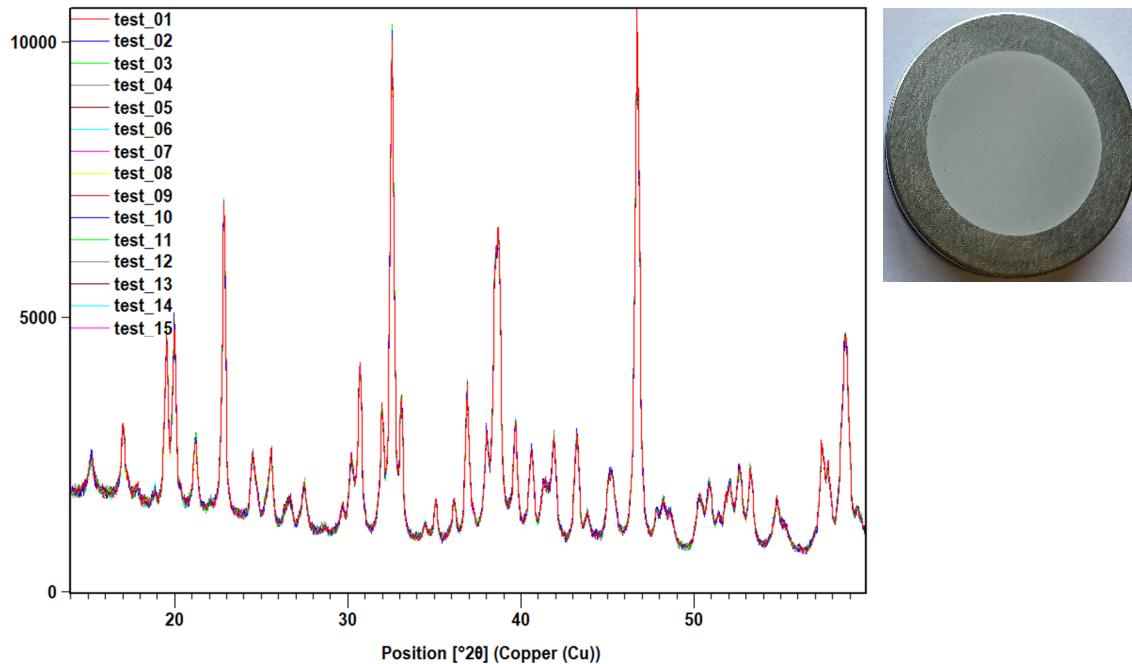


Figure 5. A compare-view of 15 scans of a bath sample in Aeris compact XRD system showing the stability of intensity during the measurements.

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_2O_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	$xsAlF_3$ (wt%)	total- CaF_2 (wt%)	total- Al_2O_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, $xsAlF_3$,

total CaF₂, total Al₂O₃, and liquidus temperature. Moreover, this study revealed that employing PLSR (Partial Least Squares Regression) on X-ray diffraction data can provide even more valuable insights for process control in aluminum industries. Both the Rietveld and PLSR methods take into account the full XRD pattern, allowing them to be applied to the same measurement without incurring additional costs or time requirements.

The findings of this study also highlighted the crucial role of XRD as a tool for optimizing energy usage in aluminum production. By offering short measurement times (95 seconds), high sample throughput, and frequent monitoring of electrolytic bath parameters, XRD enables smelters to minimize operational costs effectively.

5. References

1. H.M. Rietveld, A profile refinement method for nuclear and magnetic structures, *Journal of Applied Crystallography* 2 (2), 1969, 65-71.
2. Frank R. Feret, Breakthrough in analysis of electrolytic bath using Rietveld-XRD Method, *Light Metals* 2008, 343-346.
3. Frank R. Feret, Selected applications of Rietveld-XRD analysis for raw materials of the aluminium industry, *Powder Diffraction* 2013, Vol. 28 (2), 112-123.
4. Uwe König, Nicholas Norberg and Luciano Gobbo, X-ray diffraction (XRD) – from bath composition towards superheat, *Proceedings of the 36th International ICSOBA Conference*, Belem, Brazil, 29 October - 1 November 2018, *TRAVAUX* 47, 1013-1019.
5. Thomas Degen, Mustapha Sadki, Egbert Bron, Uwe König and Gwilherm Nénert, The high score suite, *Powder Diffraction* 29, 2014, S13-S18.
6. Stacy Gates-Rector, Thomas Blanton, The powder diffraction file: a quality materials characterization database, *Powder Diffraction* 34, 2019, 352-360.
7. Mark Paine, Uwe König, Emma Staples Application of Rapid X-Ray Diffraction (XRD) and Cluster Analysis to Grade Control of Iron Ores, *Proceedings of the 10th International Congress for Applied Mineralogy (ICAM)*, Springer: Berlin/Heidelberg, Germany, 2012, 495-501.
8. Matteo Pernechele, Ángel López, Diego Davoise, Maria Maestre, Uwe König and Nicholas Norberg, Value of rapid mineralogical monitoring of copper ores, *Minerals* 2021, 11(10), 1142.
9. H. Wold, Estimation of principal components and related models by iterative least squares, In P.R. Krishnaiah (Ed.), *Multivariate Analysis*, 1966, 391-420.
10. Frank R. Feret, Effect of Ca in characterization of bath electrolyte by X-ray methods, *Light Metals* 2007, 373-377.
11. Peter Entner, <http://peter-entner.com/E/Theory/EIProp/LiquTemp.aspx>
12. Ray D. Peterson and Alton T. Tabereaux, Liquidus curves for the Cryolite-AlF₃-CaF₂-Al₂O₃ system in aluminium cell electrolytes, *Light Metals* 1987, 383-388.
13. A. Solheim, S. Rolseth, E. Skybakmoen, L. Støen, Å. Sterten and T. Støre, Liquidus temperature and alumina solubility in the system Na₃AlF₆-AlF₃-LiF-CaF₂-MgF₂, *Light Metals* 1995, 451-460.