X-ray Diffraction (XRD) – from Bath Composition towards Superheat

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Abstract

Varying raw material qualities, the use of different fluxes and increasing prices require a better control of processes and a more efficient use of energy. X-ray diffraction (XRD) is a process-critical tool to efficiently use energy during aluminium production. Traditionally quality control of electrolytic bathes, alumina and bauxites have relied on calibration-based single peak methods or more advanced full pattern techniques. Recent tests showed that the same XRD measurement used to determine composition and bath parameters can be used to predict the bath temperature and to calculate liquidus temperature and superheat. This technique saves valuable time and costs for additional temperature monitoring and allows fast counteractions on changing conditions to prevent bath solidification.

The paper shows possibilities to predict bath temperature and calculate liquidus temperature and superheat on a real-life test sample set of 69 samples together with the determination of phase composition, excess AlF_3, CaF_2 and total Al_2O_3. Measurement time per sample can reach less than one minute.

Keywords: XRD; electrolytic bath, process control, bath and liquidus temperature, superheat, PLSR.

1. Introduction

XRD analysis is a recognized analytical tool for production control in aluminium industries. Especially during the last decades with increasing analysis speed and with the use of modern techniques such as the Rietveld method XRD became a standard tool [1, 2]. Typical applications are the analysis of the mineral composition in bauxite and red mud, the alpha-alumina during the alumina extraction and the phase composition, bath ratio and excess aluminium in electrolytic bathes.

Speed of analysis and use of XRD in an automated environment are important to receive frequent feedback from the process and allow fast counteractions on changing bath conditions.

The use of statistical methods enables the handling of large data sets and extracts the maximum amount of information in the shortest possible time.

2. Methods

A first trial was set up to test if the bath temperature, liquidus temperature and superheat of an electrolytic bath can be predicted directly from the XRD measurement. A test set of 69 measurements (10 - 75 °2θ) of electrolytic bath samples with known bath compositions and corresponding bath temperatures was used to test the accuracy of the XRD analysis. The range of the bath temperatures was 931 - 1025 °C, measured with a thermocouple type k of Tyrotec and Fluke thermometer. The CaF_2 (total) content varied in the range of 6.0 - 7.6 % whereas the excess AlF_3 of the measured samples ranged from 3.3 to 13.1 % for the test set of 69 samples. Reference values for CaF_2 and excess AlF_3 for all 69 samples were determined by X-ray diffraction using the classical straight-line calibration methodology. Furthermore, an additional set of 29 bath samples with known total Al_2O_3 contents determined via oxygen combustion analysis using a Leco-O analysis for total oxygen and total alumina was used to calibrate a partial least square regression model to determine the total Al_2O_3 from the above-mentioned test set.

A Malvern Panalytical *CubiX*^{3} *Potflux* industrial diffractometer was used for the measurements, featuring measurement times of less than 90 seconds per scan. Similar tests were run on an Aeris benchtop X-ray diffractometer featuring measurement times of less than 1 minute. Data evaluation was done using the software package HighScore Plus version 4.7, incorporating the **p**artial **l**east **s**quares **r**egression (PLSR) analysis of XRD data. A combined analysis approach was used for the determination of the bath composition as well as the bath temperature, liquidus temperature and corresponding superheat. Rietveld full-pattern fitting was used to determine the phase composition, bath ratio, excess AlF_3 and liquidus temperature. In addition, simultaneously to the Rietveld analysis, the PLSR method was applied to determine total CaF_2, total Al_2O_3 and bath temperature. Alternatively, the CaF_2 content can also be calculated from the Rietveld phase composition. In addition, crystalline α-Al_2O_3 (corundum) can be accurately determined with the Rietveld method. The total Al_2O_3 content, however, including amorphous and semi-crystalline Al_2O_3, cannot be fitted as part of the Rietveld model but (like CaF_2) it can be predicted with the PLSR method [8] using a pre-calibrated model.

Partial least squares regression is a popular statistical method to predict properties directly from raw data. After calibration using a set of independently analyzed reference samples the model can be used to predict the property from unknown samples. Using PLSR [3] it is possible to predict any defined property *Y* directly from the variability in a data matrix *X*. The matrix *X* typically contains non-systematic variations (sample preparation, impurities, different grain sizes) and systematic 'measurable' variations (different quantities). Aim is to correlate the systematic variation with one known property Y. PLSR for XRD data is a full-pattern approach that totally dismisses profile shapes but still uses the complete information present in the XRD data sets. For this study, the PLSR method was used to correlate and extract the bath temperature from XRD raw data. Liquidus temperatures and superheat were calculated using the determined bath compositions from both the Rietveld and PLSR method and formulas given in the literature [6, 7].

3. Results

3.1. Bath Composition and Parameters

Prior to the tests for the prediction of the temperatures, composition and bath parameters (bath ratio, excess AlF_3) where determined applying the Rietveld method to the full XRD pattern. Figure 1 shows an example of a Rietveld quantification of an electrolytic bath sample with a standard composition, without any addition of magnesium, lithium or potassium. Eight phases were taken into account for the quantification. Depending on the bath chemistry, additional

phases containing magnesium, lithium or potassium can be added to both the Rietveld model and the corresponding calculations if needed.

The phase quantification was performed for all 69 samples. Figure 2 gives an overview about the different compositions for all samples. The analyzed samples have a broad range of varying phase content, from zero chiolite and the presence of fluorite (low excess AlF_3) till baths with high chiolite and excess ALF_3 content (up the 13 %).

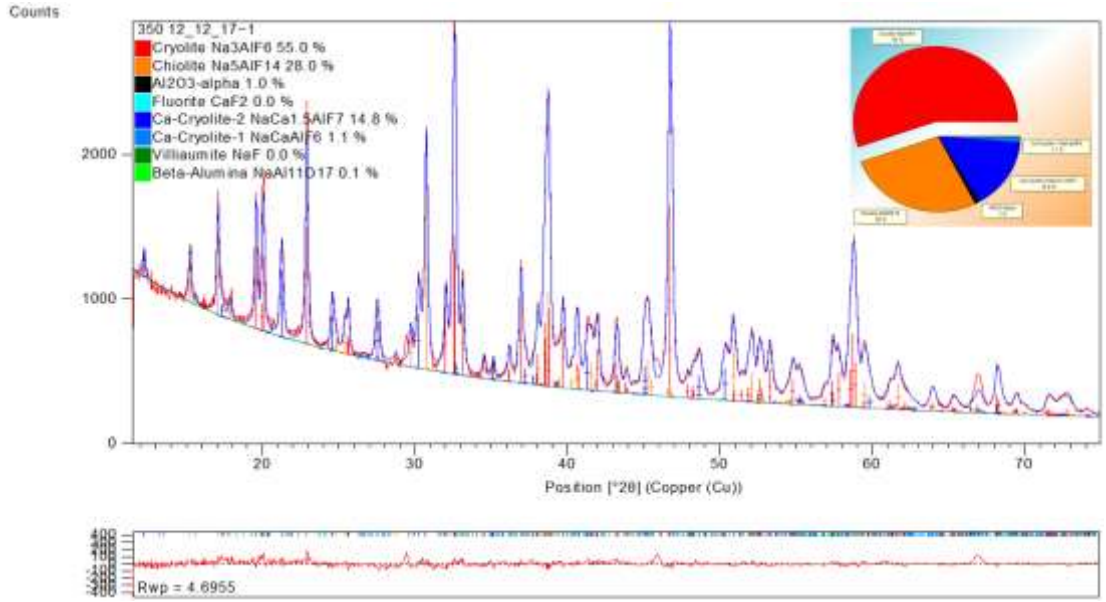

Figure 1. Rietveld refinement of an electrolytic bath sample; measured and calculated patterns (above), difference plot (below).

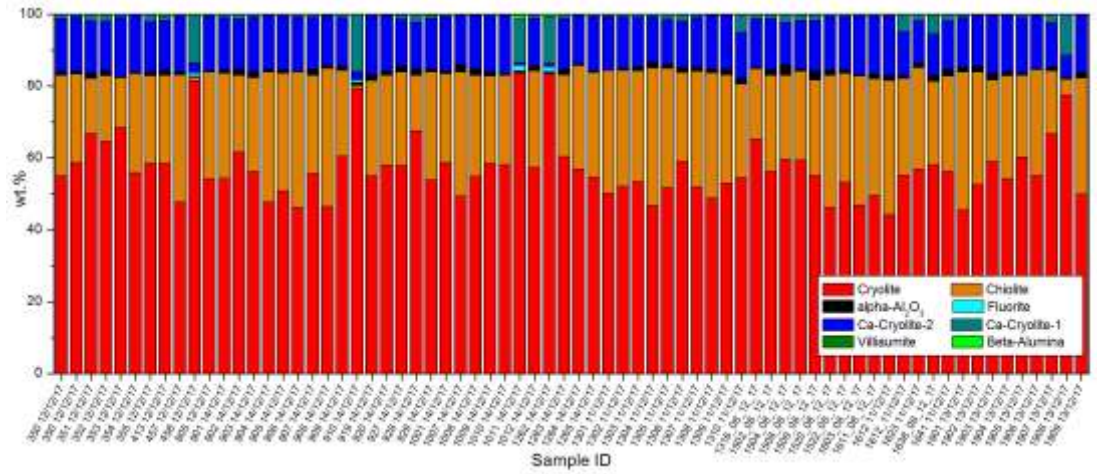

Figure 2. Phase quantification of 69 samples using Rietveld method.

Figure 3 gives an overview about the excess AlF_3 (also known as $XsAlF_3$), CaF_2, and total Al_2O_3 contents of all 69 analyzed samples. The excess AlF_3 was calculated from the phase composition obtained with the Rietveld method. Simultaneously, the CaF_2 and total Al_2O_3 were predicted using the PLSR approach. A comparison of reference and measured values for excess ALF3 and CaF2 is plotted in Figure 4. In both cases XRD and reference values are in good agreement.

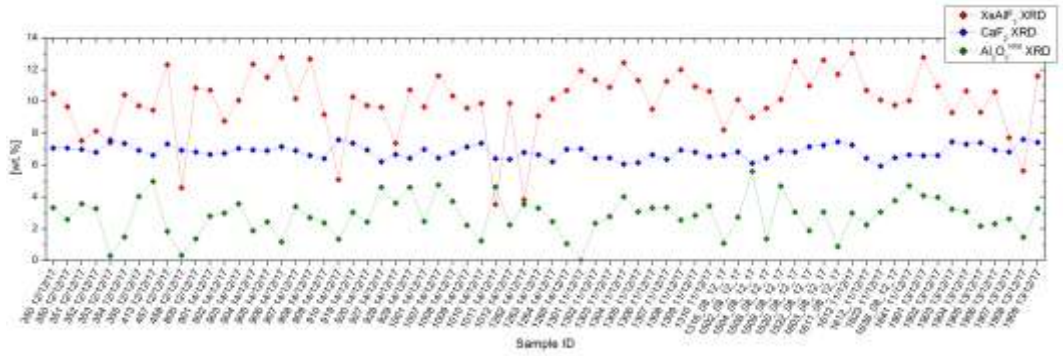

Figure 3. Excess AlF_3 and CaF_2 and total Al_2O_3 determined with XRD.

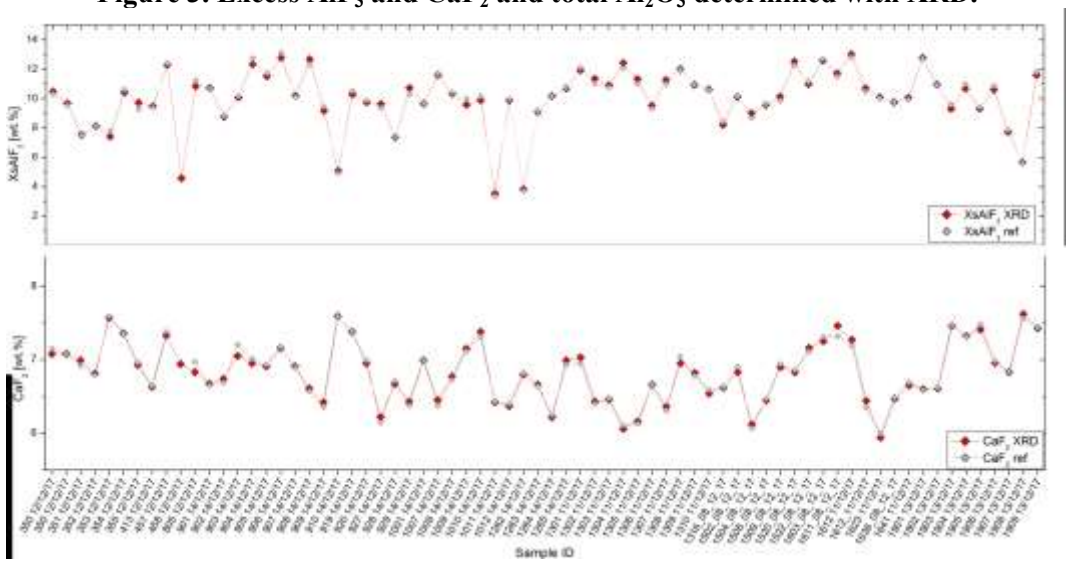

Figure 4. Excess AlF_3 and CaF_2 measured and compared with reference values.

3.2. Prediction of Bath Temperature

The liquidus temperature (T_L) is the temperature at which solid material is precipitating when a liquid is cooled. It can be calculated from the respective bath parameters (excess AlF_3, CaF_2, total Al_2O_3) obtained with XRD. For the calculation of T_L, various formulas are available [6, 7, 9]. In contrast, the bath temperature (T_B) is the temperature of the liquid electrolyte in an electrolysis cell that is measured during normal pot operation. Bath temperatures are traditionally measured directly in the electrolytic bath using a shielded thermocouple or a fiber optic device. For this study, the results of the measurements with the thermocouple were used as reference values to create a PLSR model to predict the bath temperature using XRD raw data. Figure 5 shows the comparison of the predicted bath temperatures from PLSR with the directly measured reference temperatures for all 69 samples. The difference between the measured bath temperature and the theoretical liquidus temperature is called superheat (ΔT) as shown in Equation (1). ΔT should be as low as possible to effectively use energy but avoid bath solidification. The usual values used in the industry are in the range of 5 – 15 °C.

$$\Delta T = T_B - T_L \quad (1)$$

where:

ΔT Superheat (°C)
T_B Bath temperature (°C)
T_L Liquidus temperature (°C).

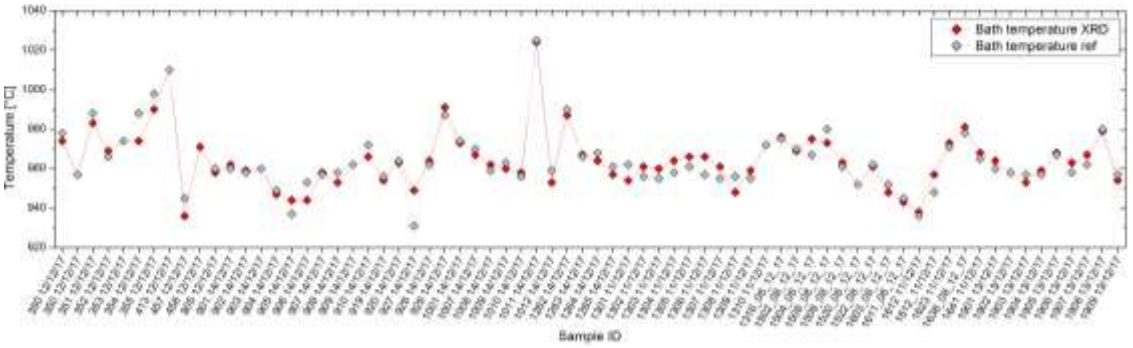

Figure 5. Measured bath temperatures and predicted temperatures with XRD.

For the direct prediction of the bath temperature, a PLSR model was created with the XRD raw data from 63 of the 69 measurements. The results of this test show an expected error (RMSEP = root mean square error of prediction) of the PLSR model of 8.6 ºC for a calibrated temperature range from 931 °C to 1025 °C. Figure 6 shows a screenshot of the PLSR module as part of the software package HighScore. The plot illustrates predicted bath temperatures versus the reference values measured with the thermocouple used as input for the model. On the right side of the screenshot the RMSEP is displayed, giving a direct indication about the expected error of the model. Both, Figure 5 and Figure 6, show a very good agreement between measured and predicted bath temperatures from XRD. This strongly suggests that the PLSR approach is not only suited to predict CaF_2 and total Al_2O_3 directly from the obtained XRD raw data [8] but also the bath temperature.

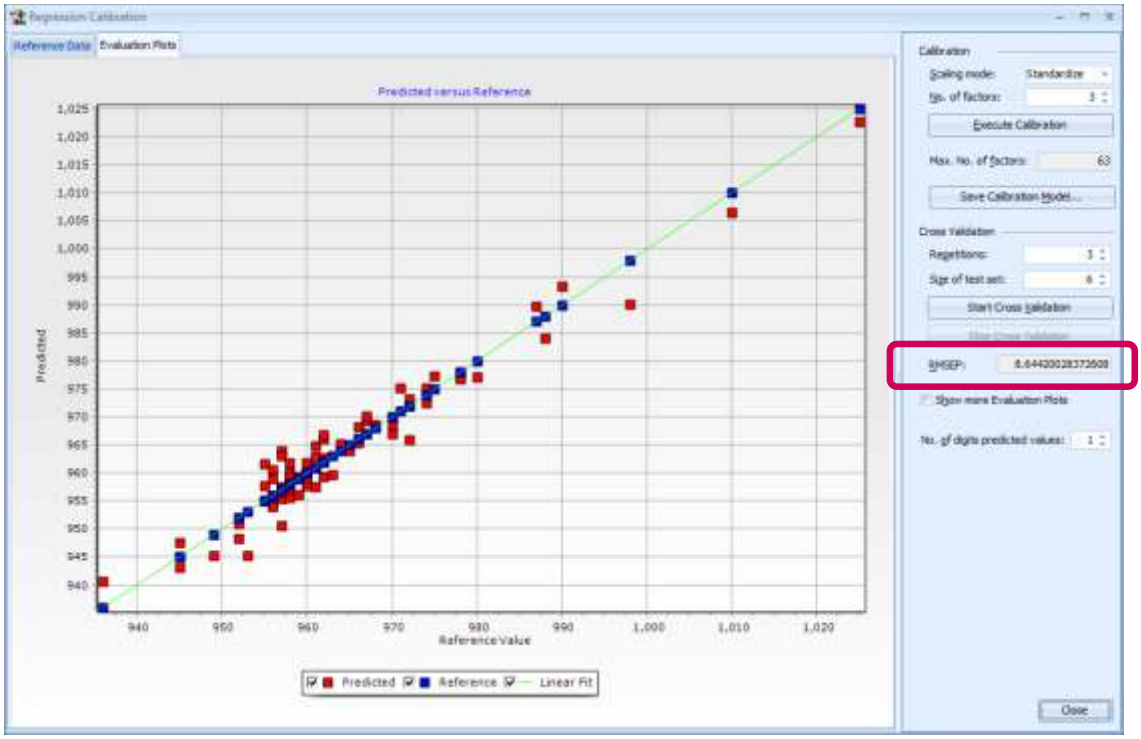

Figure 6. PLSR prediction model (screenshot) for the prediction of the bath temperature of electrolytic baths, root mean square error of prediction (RMSEP) = 8.4 °C, temperature range of PLSR model 931 – 1075 °C.

3.3. Calculation of Liquidus Temperature and Superheat

Several models can be found in the literature to calculate the liquidus temperature and corresponding superheat of electrolytic baths from the bath parameters [9]. For this study the models from Peterson et al. (1987) and Solheim et al. (1995) were used, [6, 7]. Solheim's model additionally takes the addition of LiF, MgF_2 and KF into account (in this study all 0.0 wt%).

Figure 7 gives an overview about the bath temperatures predicted with the PLSR model, the liquidus temperatures calculated from the bath parameters and the superheat. The upper plot shows the results from the Peterson model whereas the lower plot indicates the results obtained with the model from Solheim. The differences of the results between the two models are very small as expected since the analyzed baths have a standard composition without addition of LiF, MgF_2 and KF.

The plot of the superheat indicates for positive ΔT values an inefficient use of energy and for negative ΔT values the risk of bath solidification. The expected error of the PLSR model for the bath temperatures of 8.6 °C needs to be considered to draw conclusions of the plots in Figure 7.

Nevertheless, several bath samples show superheat values significantly deviating from the targeted zero line with values significantly higher than the expected error of prediction.

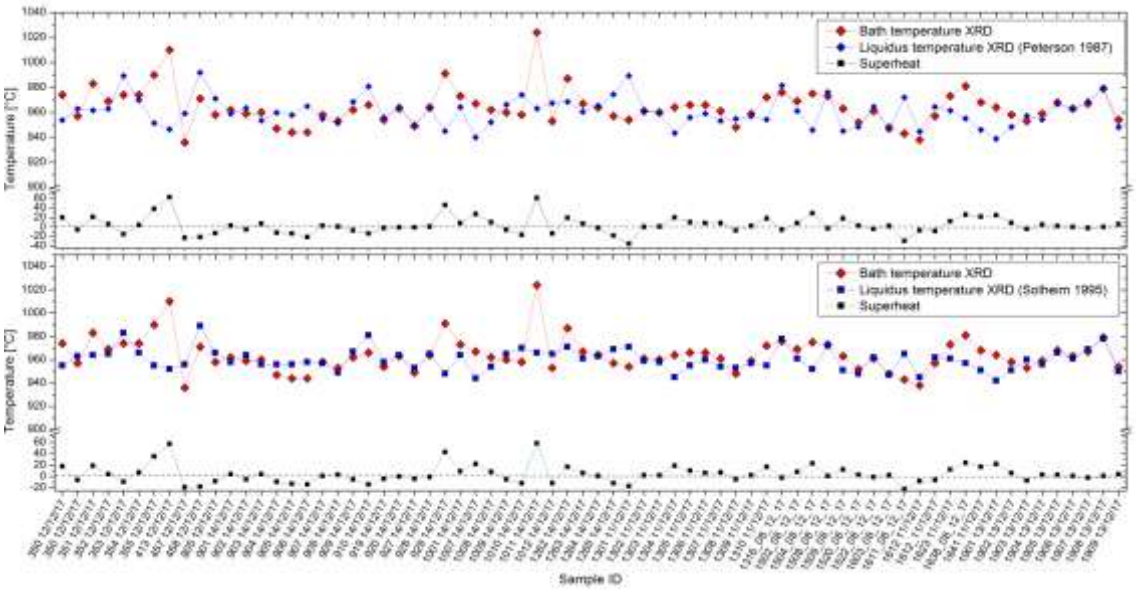

Figure 7. Liquidus temperature and superheat calculated bath parameters obtained from XRD measurements.

4. Conclusions

This study shows that XRD is a process critical tool to efficiently adjust the use of energy during the aluminium production. Short measurement times, high sample throughput and frequent monitoring of electrolytic bath parameters are important to ensure minimum costs for smelter operation.

This paper shows that modern XRD equipment can be used to determine within minutes the phase composition as well as important process parameters such as excess AlF_3, CaF_2, total Al_2O_3, bath temperature, liquidus temperature and the superheat of an electrolytic bath.

It is shown that PLSR on X-ray diffraction data can be used to provide even more information for process control of aluminium industries. Both methods, Rietveld and PLSR, take the full XRD pattern into account and can be therefore applied on the same measurement without additional costs and time.

5. References

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