Process Control in Aluminium Industry - News in the XRD Tool Box

Uwe König[1] and Nicholas Norberg[2]
1. Global Mining Segment Manager,
2. Application Specialist
Malvern Panalytical B.V, Almelo, Netherlands
Corresponding author: uwe.konig@panalytical.de

Abstract

Efficient use of energy requires fast and accurate feedback about composition and condition of each electrolytical bath of an aluminium smelter. X-ray diffraction (XRD) is a standard tool for process control in aluminium industries. Traditionally quality control of electrolytic bathes has relied on calibration based single peak methods or more advanced full pattern techniques. This paper describes the use of new statistical methods (PLSR) in combination with full pattern phase analysis to control electrolytic baths measured on a high-speed benchtop X-ray diffractometer. Measurements in less than a minute allow monitoring of the mineralogical phase composition and, simultaneously, bath parameters such as excess AlF_3, CaF_2 and the total Al_2O_3 content. First trials prove that the same XRD measurement can be used to track the liquidus temperature of the bath under safe conditions, making time- and cost intensive traditional analysis obsolete.

Keywords: XRD; electrolytic bath, process control, liquidus temperature, 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 baths.

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

To guarantee a reproducible and constant sample preparation for the XRD measurements, the samples for this study were prepared using automatic sample preparation equipment. All samples were milled for 30 seconds and pressed 30 seconds with 10 Nm load into steel ring sample holders.

A Malvern Panalytical *Aeris Minerals* industrial benchtop diffractometer was used for the measurements, featuring measurement times of less than 1 minute per scan. Data evaluation was done using the software package HighScore Plus version 4.6, incorporating the Partial **L**east-**S**quares **R**egression (PLSR) analysis of XRD data.

PLSR (also called soft modelling) is a popular statistical method to predict “hidden” properties directly from the raw data. After “training” the model can be used to predict the property from unknown samples. Training requires an independent determination of the “standard values”. 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.

The software HighScore Plus version 4.6 uses the SIMPLS algorithm [4,5]. It is easy to use; evaluation and optimization of the regression model is semi-automatic and requires little knowledge of the method.

3. Results

3.1. Ultrafast Bath Monitoring

Eleven certified reference materials from Alcan (BA-01 to BA-11) were used to test several measurement times and the influence on the accuracy and repeatability of the results. Measurements of 0:48 min, 1:36 min and 3:12 min were performed (figure 1) to test the influence of measurement time on accuracy of the results for excess AlF_3, CaF_2, total Al_2O_3 and the phase composition. Figure 1 shows a comparison of the XRD pattern measured within different times.

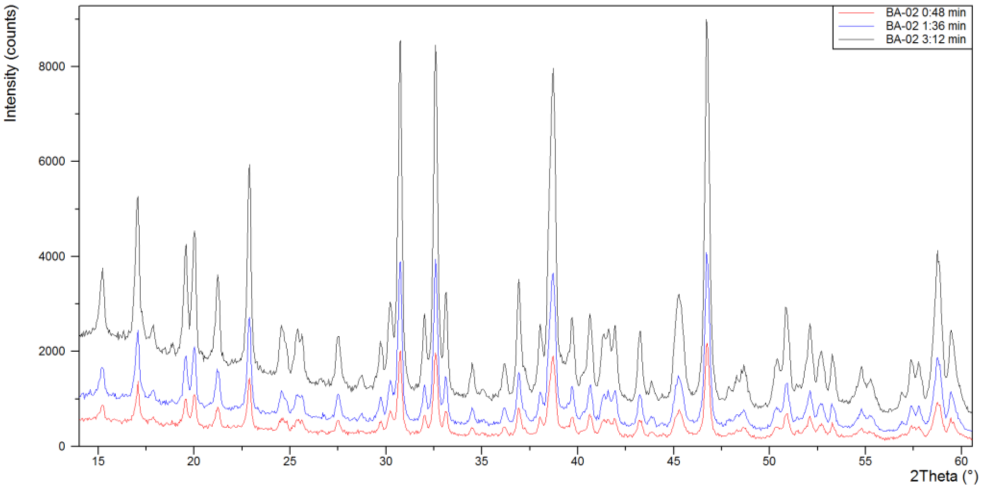

Figure 1. Comparison of full pattern XRD measurements with three different measurement times, measured on a benchtop Aeris diffractometer (Cu radiation).

To test the influence of the measurement time on the accuracy of the prediction of process parameters and phase composition, reference material BA-02 was measured 10 times with three different measurement times. Figure 2 shows the results for the determination of $exAlF_3$ and the ESD (2σ), indicated in the error bars in the graph. The $exAlF_3$ content was calculated from the results of the phase composition.

For a measurement time of 48 seconds an estimated standard deviation ESD (2σ) of 0.12 % was calculated, showing that even with high-speed measurements, accurate process control is possible. The ESD (2σ) improves as expected with increasing measurement time towards 0.07

% for 1:36 minutes and 0.06 for 3:12 minutes.

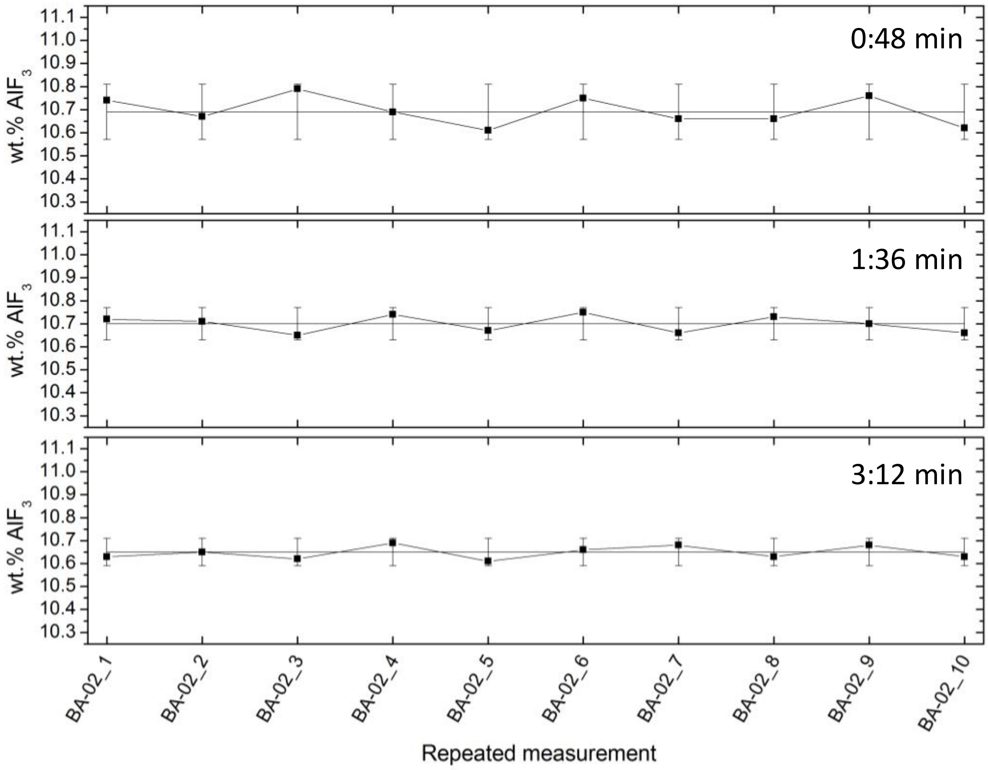

Figure 2. Repeatability of exAlF_3 compared on three different measurement times (one sample measured 10 times, error bars = 2 σ).

Table 1. Repeatability of excess AlF_3 compared on three different measurement times.

		Cryolite Na_3AlF_6	**Chiolite** Na_5AlF_{14}	**Ca-Cryolite** $NaCaAlF_6$	**Ca-Cryolite** $NaCa_{1.5}AlF_7$	**Villiaumite** NaF	**β-Alumina** $NaAl_{11}O_{17}$	**α-Al_2O_3** Al_2O_3	***exAlF_3*** *XRD*	***exAlF_3*** *Reference*
0:48 min	Average	54.56	33.16	0.25	11.42	0.06	0.04	0.52	*10.69*	*10.80*
	ESD [2σ]	0.53	0.37	0.25	0.35	0.12	0.06	0.14	*0.12*	*0.30*
1:36 min	Average	54.67	33.08	0.31	11.34	0.03	0.02	0.55	*10.70*	*10.80*
	ESD [2σ]	0.32	0.24	0.15	0.10	0.06	0.04	0.12	*0.07*	*0.30*
3:12 min	Average	54.74	32.89	0.30	11.44	0.06	0.01	0.55	*10.65*	*10.80*
	ESD [2σ]	0.17	0.19	0.16	0.14	0.05	0.03	0.06	*0.06*	*0.30*

Besides the results for the determination of the excess AlF_3, Table 1 shows the ESD's (2σ) for the different bath phases present in the samples, quantified using the Rietveld method, Figure 3.

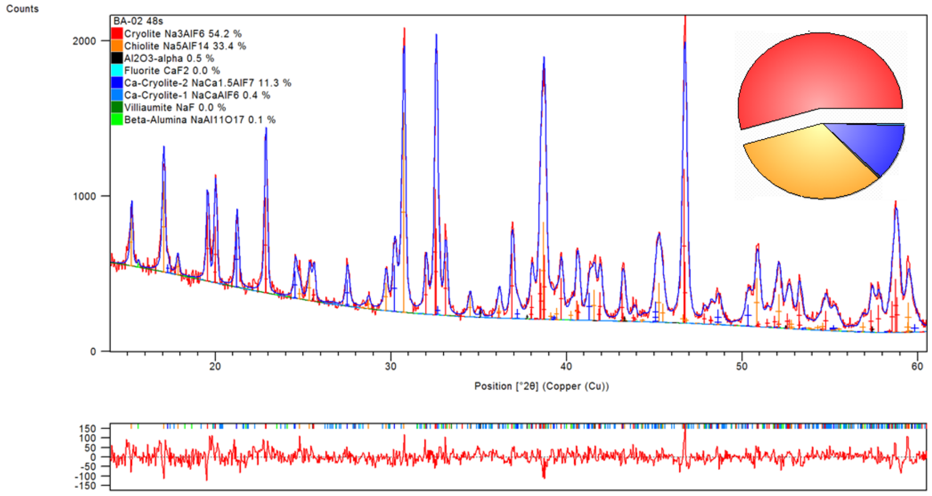

Figure 3. Rietveld refinement of sample BA-02, measured and calculated patters (above), difference plot (below).

The PLSR method was used to predict the CaF_2 content of the same samples. Figure 4 gives an overview about exAlF_3 and CaF_2 of all 11 reference samples. Certified and measured values are plotted as well as the error bars for the ESD's (2σ). In both cases XRD and certified values are in good agreement.

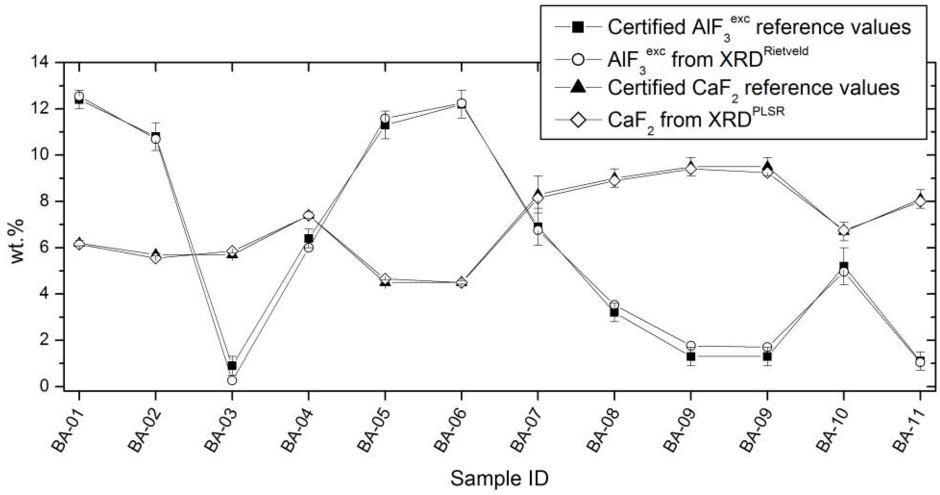

Figure 4. Excess AlF_3 and CaF_2 measured on Alcan reference samples (BA-01 to BA-11), comparison with certified values (measurement time 48 seconds).

Simultaneously to all analysis mentioned before, the crystalline Al_2O_3 content (corundum) and total Al_2O_3 content were analysed. Crystalline Al_2O_3 can be easily analysed with the Rietveld method. The total Al_2O_3 content, including amorphous and semi-crystalline Al_2O_3, was predicted with the PLSR method, Figure 5. The difference of both curves in Figure 5 represents the amount of semi-crystalline or amorphous Al_2O_3 and, if present, oxygen bound in other aluminium phases.

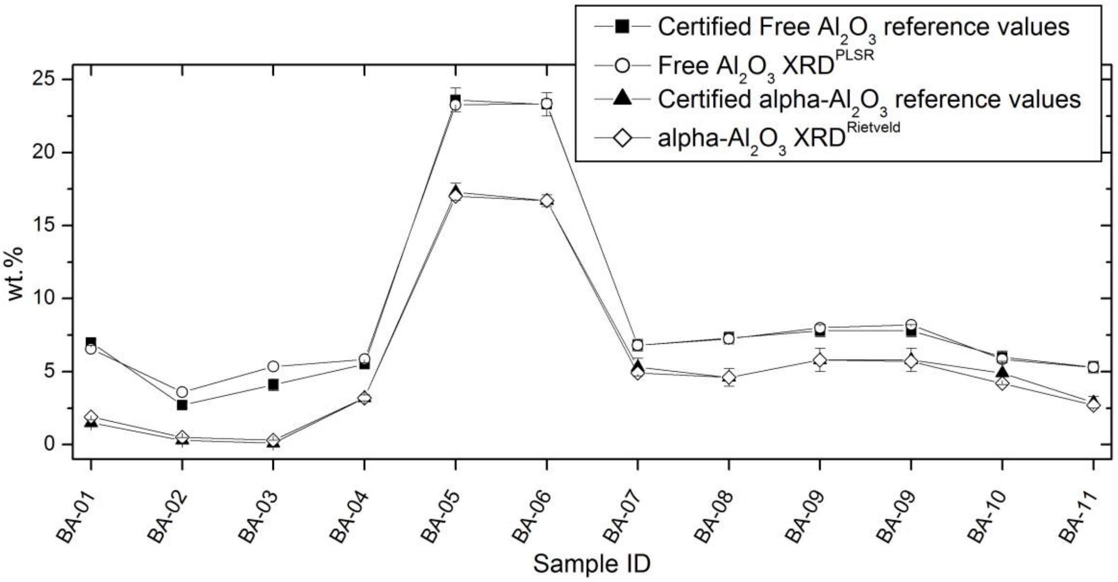

Figure 5. Crystalline and total Al_2O_3 determined on Alcan reference samples (BA-01 to BA-11), comparison with certified values (measurement time 48 seconds).

3.2. Determination of the Liquidus Temperature from XRD Data

A first trial to predict the liquidus temperature of an electrolytic bath directly from the XRD measurement was setup. A test set of measurements with corresponding temperatures was available. The PLSR method was used to predict the liquidus temperature. The results of a first feasibility study gave an expected error (RMSEP) of the PLSR model of 3.3 ºC.

Figure 6 illustrates the results for the prediction of the temperatures and the corresponding exAlF_3 content. Measured and calculated temperatures match within the expected error of 3.3 ºC. Higher temperatures correspond with lower exAlF_3 values.

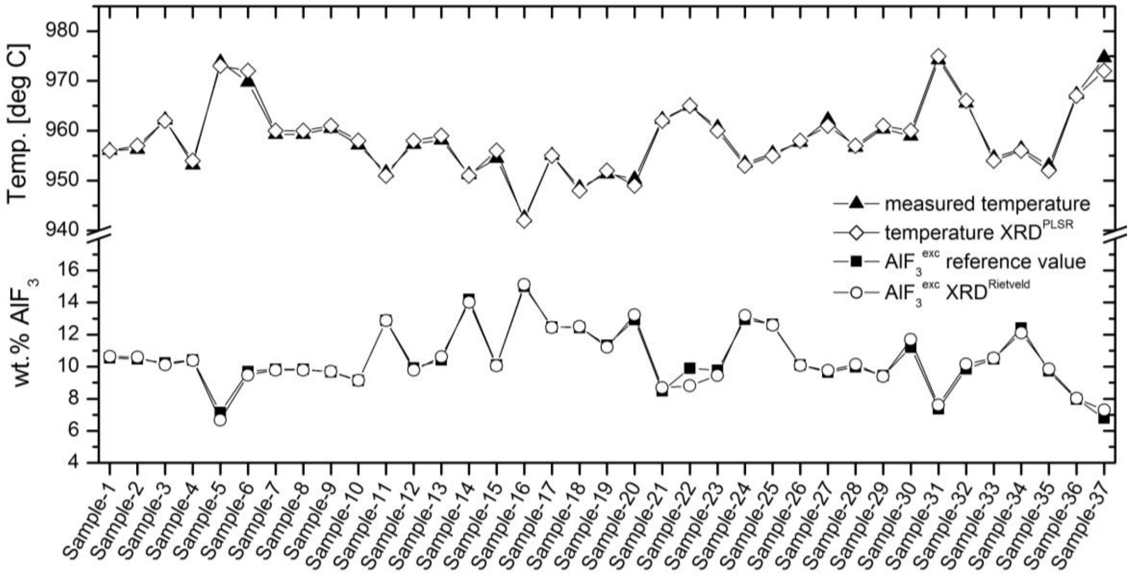

Figure 6. Determination of the liquidus temperature direct from XRD measurements, comparison with the excess AlF_3 content.

4. Conclusions

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 benchtop XRD equipment can be used to determine within 48 seconds the phase composition as well as important process parameters such as AlF_3, CaF_2, total Al_2O_3 and the liquidus temperature 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. Today's optics, detectors, and software can provide rapid and accurate analyses, suitable for process control environments as well as research.

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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