

# Alternative Methods for Process Control in Aluminium Industries - XRD in Combination with PLSR

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## Abstract

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X-ray diffraction (XRD) is a standard tool for process control in aluminium industries. 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. Traditionally quality control of electrolytic baths, alumina and bauxites has relied on calibration based single peak methods or more advanced full pattern techniques. A common method is the Rietveld quantification which uses structural information to predict information from the full pattern using physical models and fitting techniques. Sometimes this approach is stretched to its limits, especially when no realistic physical model is available, or when the model is either too complex or does not fit to reality. In such cases there is an elegant alternative: multivariate statistics and **Partial Least-Squares Regression (PLSR)**, a method that does not require pure phases, crystal structures or complex modelling of peak shapes. This paper describes the advantages of using PLSR and shows new results for the determination of electrolytic baths and bauxite directly from the XRD pattern.

**Keywords:** XRD; PLSR; electrolytic bath; bauxite; process control; X-ray diffraction.

## 1. Introduction

During the last decades XRD became a analytical standard tool in aluminium industries due to increasing analysis speed and the use of modern techniques such as the Rietveld method for quantification of the total phase content of a sample [1], [2].

Typical applications are the analysis of the mineral composition in bauxite and red mud, the determination of alpha-alumina during the alumina extraction and the monitoring of bath ratio and excess aluminium in electrolytic baths.

Traditional calibration based methods rely on one peak only and do not analyse the total phase composition. The Rietveld quantification uses structural information to predict information from the full pattern using physical models and fitting techniques. This requires crystallographic knowledge and realistic physical models that fit with the specific materials.

This paper deals with the analysis of the complete XRD pattern using **Partial Least-Squares Regression (PLSR)** that requires neither crystal structures nor complex modelling techniques.

## 2. Methods

### 2.1. Sample preparation

Sample preparation of powder samples is an important factor to obtain correct results. In order to maximize the accuracy, the sample taking should be standardized and optimized to the special needs of the application. To guarantee a reproducible and constant sample preparation for XRD measurements, the samples were prepared using automatic sample preparation

equipment. All samples were milled for 30 seconds and pressed for 30 seconds with 10 Nm load into steel ring sample holders resulting in a particle size <73  $\mu\text{m}$ .

## **2.2. Data collection and analysis**

For the studies presented in this paper, a PANalytical *CubiX<sup>3</sup> Minerals* industrial diffractometer with Co anode, incident iron filter and high-speed *X'Celerator* detector was used, featuring measurement times of less than 8 minutes per scan.

Data evaluation was done using the software package HighScore Plus version 4.5, incorporating the **Partial Least-Squares Regression (PLSR)** analysis of XRD data.

## **2.3. Partial Least Squares Regression (PLSR)**

PLSR (also called soft modelling) is a popular statistical method to predict “hidden” properties directly from the raw data. After “calibration” the model can be used to predict the property from an unknown sample. Calibration requires an independent determination of the “reference values”. Using PLSR, as developed by Wold [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). The aim is to correlate the systematic variation with a 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 4.1 uses the SIMPLS algorithm [4], [5]. The PLSR module is easy to use, evaluation and optimization of the regression model is semi-automatic and requires little knowledge of the method.

The PLSR module in the software package HighScore Plus uses two different scaling modes to find the optimal calibration model. For the scaling mode “center” the variables are centered by subtracting the mean from each value of the particular variable whereas for scaling mode “standardize” the variables are standardized by subtracting the mean and dividing by the standard deviation [5].

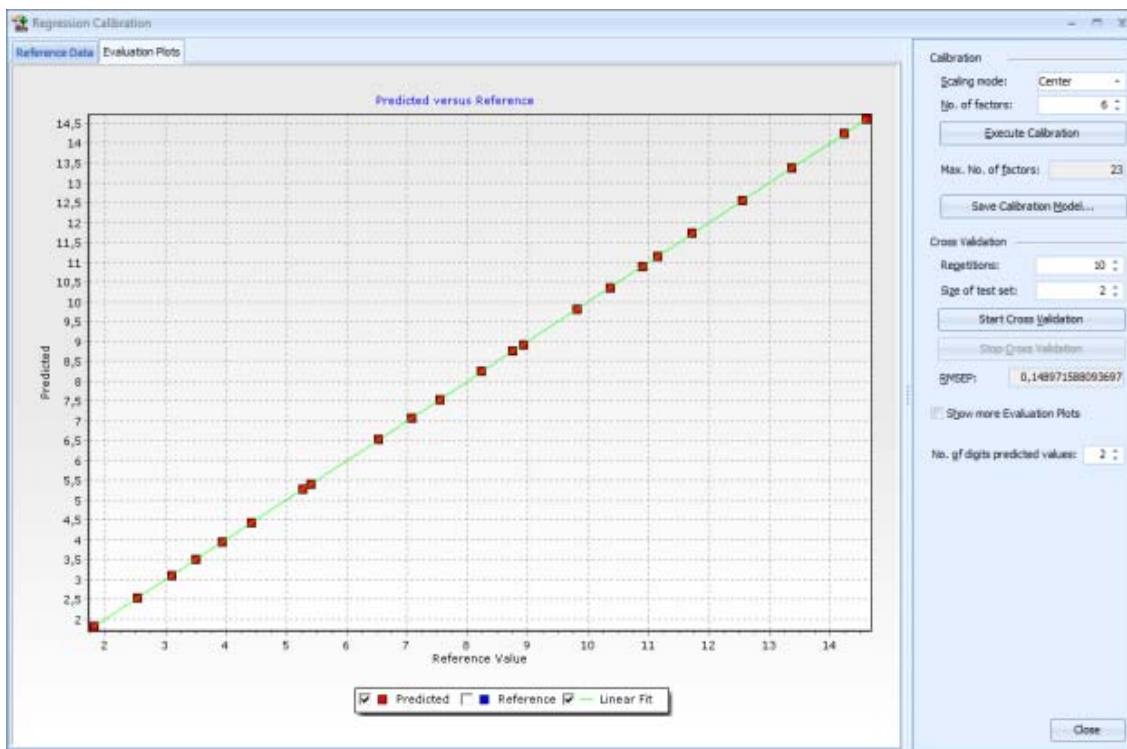
Cross-validation is used to estimate the errors of a certain PLSR calibration model when a set of independent samples is not available for validation. While performing cross validation one sample is left out of the calibration and this one sample is then used as a validation sample. The process is repeated until all samples have been predicted. The root mean square error of prediction (RMSEP) gives an absolute value of the expected variation of the property analyzed after cross validation was applied. However, an independent test set is still the best approach to validate any PLSR model.

## **3. Results**

### **3.1. Analysis of available alumina in bauxite**

Seventeen samples from one bauxite deposit located in the northeastern part of the state of Pará in Northern Brazil were chosen for the analysis of available alumina and reactive silica using PLSR. For the calibration of the PLSR model the reference values from wet chemical digestion of the samples were used. 11 samples were used to create a PLSR model whereas 6 samples were measured as unknowns to crosscheck the model.

Cross validation was applied in 2 different ways to estimate the errors of the PLSR calibration model. A) using the cross validation function as part of the HighScore software package and B)



**Figure 5.** Screen shot of the PLSR module as implemented in the HighScore software package, showing the regression plot, reference values (X-axis) versus predicted values (Y-axis) of  $\text{exAlF}_3$  for the calibration of 23 electrolytic bath samples.

#### 4. Conclusions

It is shown that PLSR on X-ray diffraction data can be used to provide valuable information for process control of aluminium industries. Today's optics, detectors, and software can provide rapid (within minutes) and accurate measurements, suitable for process control environments.

An advantage of the PLSR method is that no pure phases, crystal structures or complex modelling of peak shapes are required. PLSR is relatively simple, rapid and accurate compared with other modelling techniques. The full pattern variation is taken into account for the quantification. PLSR is less sensitive to non-ideal sample preparation and measurement setup as long as these are constant. The method needs a set of samples for calibration and validation.

The Rietveld method quantifies the total phase composition of the samples and can give a more detailed information about the phase composition of the samples, if required.

Both methods take the full XRD pattern into account and can be therefore applied on the same measurement without additional costs and time.

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