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

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Abstract

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 **P**artial **L**east-**S**quares **R**egression (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 **P**artial **L**east-**S**quares **R**egression (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 μm.

2.2. Data collection and analysis

For the studies presented in this paper, a PANalytical *CubiX*^{3} *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 **P**artial **L**east-**S**quares **R**egression (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

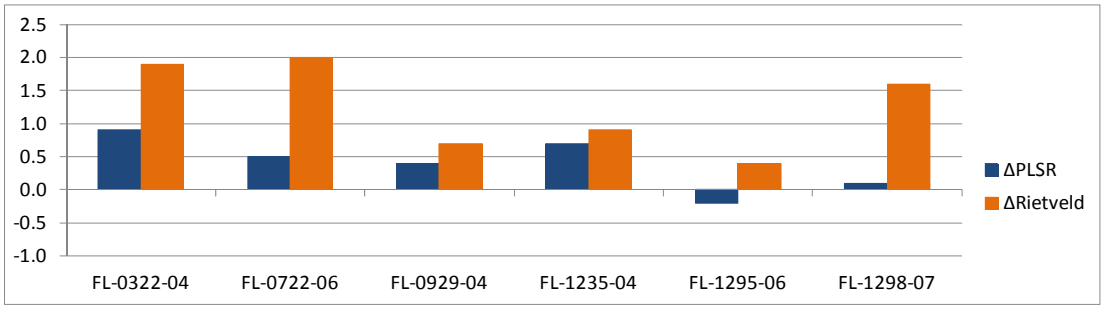
3.1. Analysis of available alumina in bauxite

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)

by measuring unknown test samples.

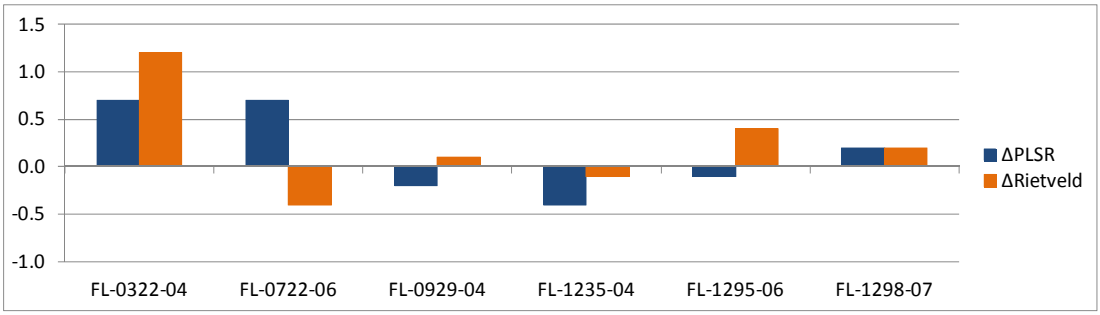
Based on the cross validation function in the software module the RMSEP was found to be 0.7 % available alumina. This is in line with the results of the errors from the test set. Figure 1 shows the comparison of the reference values, the obtained results using PLSR and the results calculated with the mineralogical quantification (Rietveld method, Table 1) for the available alumina content in the 6 unknown test samples.



Available aluimina					
Sample	Reference	PLSR	Rietveld	ΔPLSR	ΔRietveld
FL-0322-04	52.6	51.7	50.7	0.9	1.9
FL-0722-06	47.9	47.4	45.9	0.5	2.0
FL-0929-04	48.9	48.5	48.2	0.4	0.7
FL-1235-04	51.0	50.3	50.1	0.7	0.9
FL-1295-06	50.8	51.0	50.4	-0.2	0.4
FL-1298-07	50.1	50.0	48.5	0.1	1.6

Figure 1. Comparison of the available alumina content (range 46.5 % - 56.9 %) analyzed with wet chemical digestion, PLSR and the Rietveld method.

The PLSR method was also tested for the determination of the reactive silica content of the same samples in the range from 0.6 % to 10.3 % (Figure 2). The RMSEP was calculated with 0.4 %.



Reactive silica					
Sample	Reference	PLSR	Rietveld	ΔPLSR	ΔRietveld
FL-0322-04	4.1	3.4	2.9	0.7	1.2
FL-0722-06	6.4	5.7	6.8	0.7	-0.4
FL-0929-04	2.6	2.8	2.5	-0.2	0.1
FL-1235-04	0.6	1.0	0.7	-0.4	-0.1
FL-1295-06	1.7	1.8	1.3	-0.1	0.4
FL-1298-07	1.5	1.3	1.3	0.2	0.2

Figure 2. Comparison of the reactive silica content (range 0.6 % - 10.3 %) analyzed with wet chemical digestion, PLSR and the Rietveld method.

The results show that PLSR can be used as fast method to determine the available alumina and reactive silica content in Bauxites. Expected errors for available alumina are smaller compared to the calculated from the mineralogical content. However, constant sample preparation and measurement conditions are mandatory for the PLSR method.

Table 1. Reference values and mineralogical analysis of 16 bauxite samples, in grey are the samples used for cross validation.

	Reference		XRD Rietveld					
Sample	Available aluimina	Reactive silica	Gibbsite	Kaolinite	Hematite	Quartz	Anatase	Rutile
FL-0250-03	52.2	3.2	77.9	13.2	5.1	1.3	1.4	1.2
FL-0307-08	53.4	1.0	78.2	8.1	9.8	1.1	1.8	1.0
FL-0322-04	52.6	4.1	77.6	13.1	5.1	1.7	1.5	0.9
FL-0435-04	39.4	10.3	63.0	24.6	7.5	1.4	2.1	1.4
FL-0507-06	56.9	1.6	83.7	9.7	3.1	2.4	1.1	0.0
FL-0722-06	47.9	6.4	70.2	20.5	5.2	1.6	1.6	0.9
FL-0929-04	48.9	2.6	73.7	12.0	10.7	1.3	1.7	0.7
FL-0932-04	46.5	2.8	68.5	14.0	14.1	1.2	1.5	0.7
FL-0940-04	49.1	3.6	72.9	14.5	8.6	1.3	1.8	0.8
FL-0997-05	50.2	3.7	75.8	15.8	5.2	1.5	1.4	0.4
FL-1235-04	51.0	0.6	76.7	5.7	14.7	1.3	1.2	0.4
FL-1295-06	50.8	1.7	77.1	8.1	11.6	0.5	2.1	0.6
FL-1298-07	50.1	1.5	74.2	8.3	14.5	0.6	1.5	0.8
FL-1298-09	55.6	3.2	82.5	11.9	2.7	2.2	0.7	0.1
FL-1299-08	55.1	2.6	80.0	12.2	3.9	3.0	0.9	0.0
FL-1493-07	55.4	2.1	83.6	11.4	2.9	1.2	0.7	0.3
FL-1501-06	50.6	0.7	75.8	7.1	12.5	1.2	2.1	1.3
Maximum	56.9	10.3	83.7	24.6	14.7	3.0	2.1	1.4
Minimum	39.4	0.6	63.0	5.7	2.7	0.5	0.7	0.0

3.2. Analysis of total Al_2O_3 in electrolytic bath samples using PLSR

Total Al_2O_3 is assumed to be all oxidic bound aluminium in a bath sample, it consists of α-alumina (corumdum, crystalline Al_2O_3), semicrystalline or amorphous Al_2O_3 (difficult to analyze with XRD for low amounts < 5 %) and other oxidic aluminium phases such as diaoyudaoite $NaAl_{11}O_{17}$.

The amount of total Al_2O_3 is traditionally analyzed based on oxygen determination with a combustion analyzer. This method assumes that all oxygen in a sample is bound to Al_2O_3. The existence of other oxidic Al_2O_3 phases such as diaoyudaoite $NaAl_{11}O_{17}$ is not taken into account. Since traditional XRD methods can only determine crystalline Al_2O_3 directly (the amount of semi crystalline and amorphous Al_2O_3 is too low for direct analysis), PLSR was tested as an alternative.

29 electrolytic bath samples were measured whereas 22 were used to create the PLSR model and 7 samples were taken as validation samples to test the model. Reference values were

supplied from two different external laboratories using a combustion analyzer. The range of the total Al_2O_3 values varies from 1.7 % to 7.4 % (Figure 3).

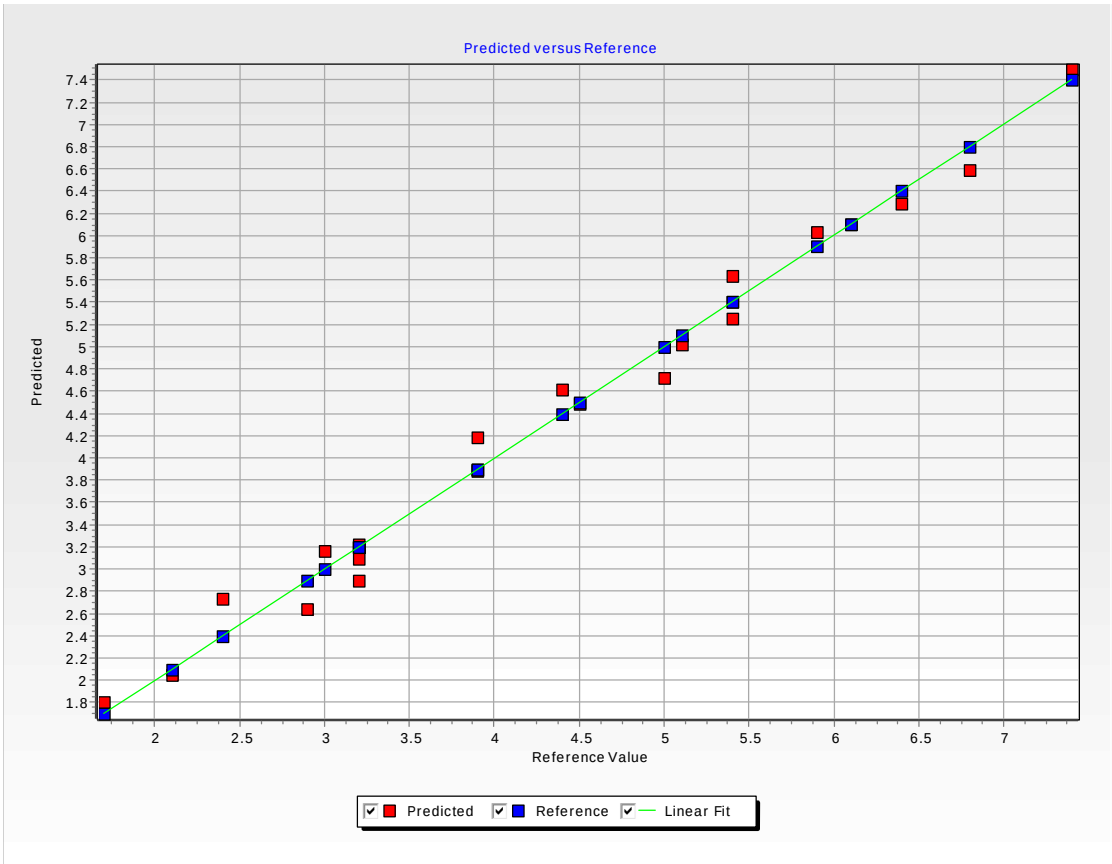
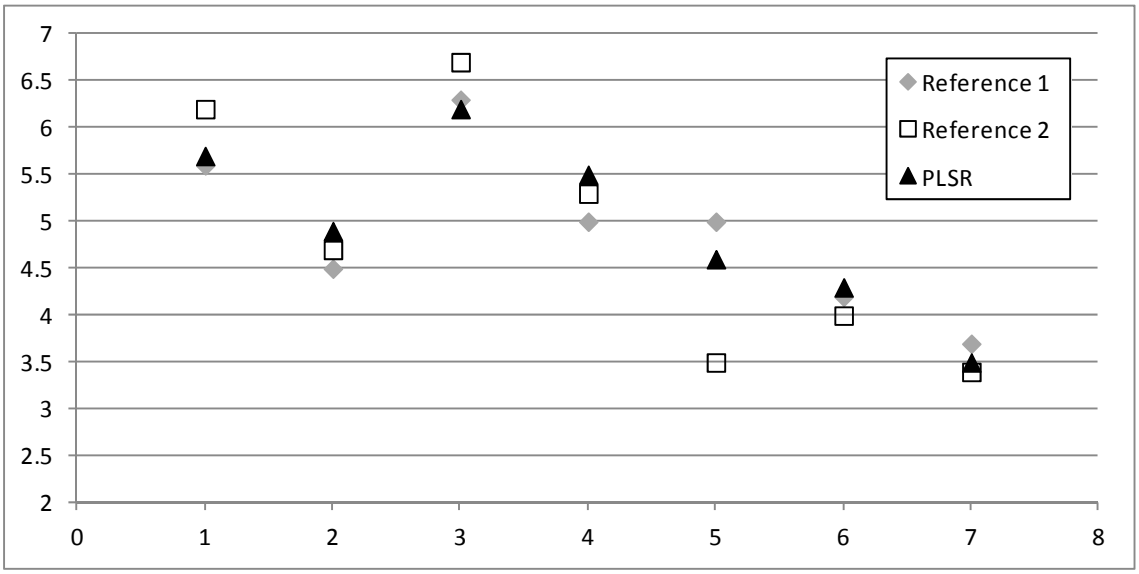


Figure 3. Evaluation plot for the analysis of total Al_2O_3 in 22 electrolytic bath samples.

The Root Mean Square Error of Prediction (RMSEP) using the cross validation tool in HighScore was found to be 0.7 % total Al_2O_3 which is in line with the deviation found from the 7 test samples, Figure 4.



Test sample	Reference 1	Reference 2	PLSR	Δ Reference 1-PLSR
1	5.6	6.2	5.7	-0.1
2	4.5	4.7	4.9	-0.4
3	6.3	6.7	6.2	0.1
4	5.0	5.3	5.5	-0.5
5	5.0	3.5	4.6	0.4
6	4.2	4	4.3	-0.1
7	3.7	3.4	3.5	0.2

Figure 4. Results of the analysis of total Al_2O_3 using XRD in combination with PLSR compared to 2 independent reference values obtained by combustion analysis.

3.3. Analysis of electrolytic bath samples

XRD is nowadays a standard tool for the characterization electrolytic baths. Process parameter such as $exAlF_3$, bath ratio, CaF_2 and undissolved Al_2O_3 are determined by either standard calibration based methods or full pattern Rietveld refinement. Especially if additional information about the total phase composition of the baths is required, the Rietveld method is the preferred tool, [1].

If only one process parameter is required, PLSR might be an option since no crystallographic input has to be given. PLSR was tested on 23 electrolytic bath samples from one smelter plant to determine the $exAlF_3$ content (present in the range 1.82 - 14.6 %). Figure 5 shows a screen shot of the PLSR module of the HighScore software package with the regression plot for the calibration of $exAlF_3$ based on the measurement and calibration of 23 samples with known $exAlF_3$ content.

Cross validation was applied to estimate the errors of a the PLSR calibration model. The optimal number of PLSR factors was found to be 6 with the scaling mode “center” with a RMSEP of 0.15 % $exAlF_3$.

The PLSR methods was also tested for the determination of the calcium content (as CaF_2, present in the range 6.3 - 8.2 %) and the bath ratio (in the range 1.01 - 1.43). The RMSEP was determined to be 0.25 % for CaF_2 and 0.008 for the bath ratio.

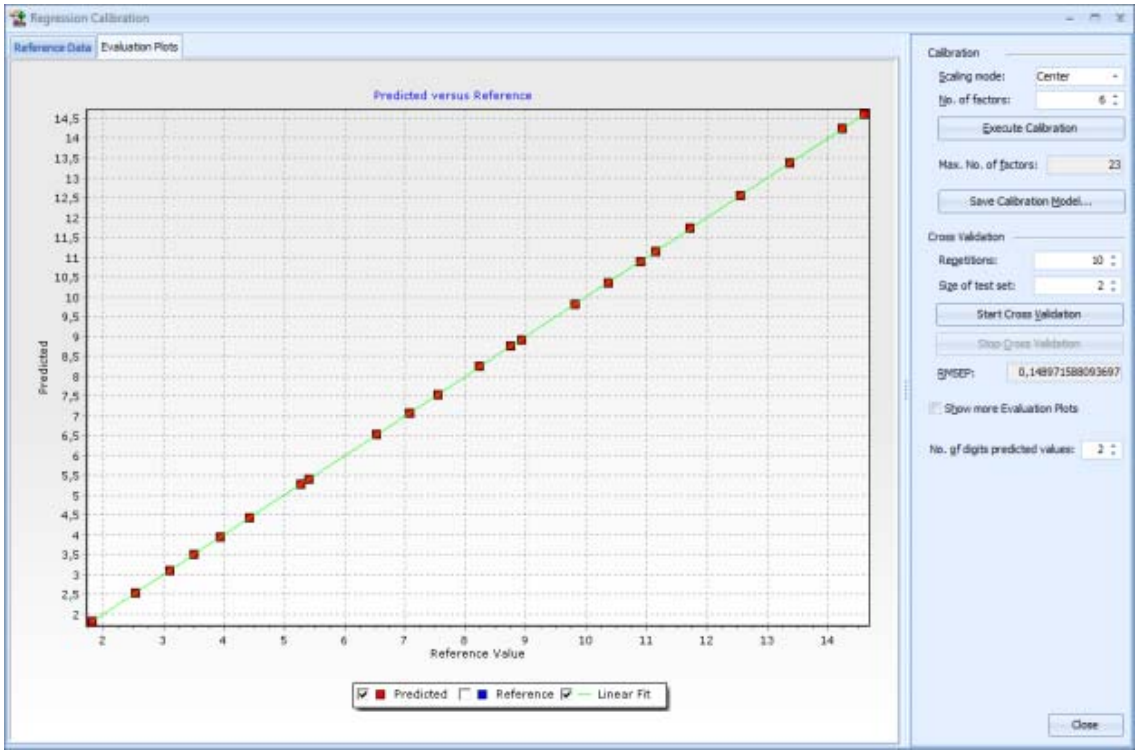


Figure 5. Screen shot of the PLSR module as implemented in the HighScore software package, showing the regression plot, reference values (X-axis) versus predicted values (Y-axis) of exAlF_3 for the calibration of 23 electrolytic bath samples.

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.

5. References

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