

## Estimation of $AvAl_2O_3$ and $RxSiO_2$ by Partial Least Square Regression (PLSR) on XRD data: A Case Study Using Low Grade Bauxites

Caio César A. Melo<sup>1</sup> and Simone P. A. Paz<sup>1,2</sup>

1. Programa de Pós-Graduação em Engenharia de Recursos Naturais da Amazônia (UFPA).

2. Laboratório de Caracterização Mineral, Instituto de Geociências, Universidade Federal do Pará, Campus do Guamá, 66075-110, Belém, Pará, Brasil

Corresponding author: eng.caiomelo@hotmail.com

### Abstract

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Wet chemistry used for grade control of bauxites is an industry standard for quantification of available alumina ( $AvAl_2O_3$ ) and reactive silica ( $RxSiO_2$ ), but very costly and time-consuming. Alternative methods for these determinations are constantly studied with the aim of providing speed and practicality. In this work, X-ray diffraction data using the statistical tool of Partial Least Square Regression (PLSR) analysis was used to predict the amount of available alumina and reactive silica, related to gibbsite and kaolinite respectively, in several samples of four bauxite lithologies from the Paragominas Mine in Pará State, Northern Brazil. Rietveld refinement was carried out in some of the analyzed samples and both estimates were compared with wet chemistry data. Results have shown that it was possible to achieve a good prediction of reactive silica content, even for those bauxites with higher silica content. The quality of XRD data required for prediction applying PLSR is also discussed. The tool has proven to be very powerful in predicting these values, and it may be an alternative for the grade control of bauxites.

**Keywords:** bauxite, reactive silica, partial least square regression, powder XRD.

### 1. Introduction

The production of bauxite is increasing every year, and as reported by U.S. Geological Survey [1] world production reached about 300 Mt in 2017, where more than 90 % is refined by the Bayer process. In this scenario, Brazil plays an important role, having the 4th largest deposits and production in the world. Brazilian bauxites are concentrated mainly in the Amazon region, more specifically in the state of Pará, where about 35.7 million tonnes of bauxite are produced per year, representing more than 93 % of the national production [2].

One of the greatest challenges faced by the alumina industry is the high levels of reactive silica ( $RxSiO_2$ ) in bauxites, which leads to a costly loss of caustic soda during Bayer refinery processing [3]. Due to the formation of insoluble sodium-alumino-silicate phases (DSP – Desilication Product), the more  $RxSiO_2$  present in the bauxite, the more caustic soda is lost in the process as fixed soda in the solid residue. Despite the amount of available alumina ( $AvAl_2O_3$ ), the presence of high  $RxSiO_2$  results in many of the world's reserves of bauxite being sub-economic.

The high levels of  $RxSiO_2$  in some of Brazilian bauxites, such as those from Paragominas (in the Miltonia region of the State of Pará, Northern Brazil), require good quality control to ensure that the ore fed to the Bayer process is within the acceptable limits of  $AvAl_2O_3$  and  $RxSiO_2$ , avoiding economic penalties. Currently, the grade control relies on the consolidated wet chemistry methods [4]. Such methods consist of simulating the Bayer process on a laboratory scale and then determining the levels of  $AvAl_2O_3$  and  $RxSiO_2$ , providing indirectly the approximate contents of gibbsite and kaolinite respectively [5, 6]. Apart from their known accuracy and uncertainty, these traditional methods are time-consuming and demand a large quantity of

chemicals, manpower and laboratory space [4, 7]. In addition, it is essential to know the mineralogy and texture of the minerals, since these determine the physicochemical interactions occurring in the processes. There are no guarantees that only the wet chemical determinations will allow high efficiency control in the metallurgical processes [7, 8].

Other methods have been proposed for mineralogical classification and quantification of bauxites based on statistical tools and X-ray diffraction data [4, 6, 7, 9, 10]. These methods are proposed as fast, practical and relatively reliable alternatives for obtaining bauxite mineralogy, for optimizing the operation of mining and processing plant.

Since the pioneer works on partial least square (PLS) by Wold [11], this method has become widely used in many fields of applied science like chemometrics, bioscience and social science [12, 13, 14]. As stated by Geladi E Kowalski [15] PLS is a good alternative to multiple linear regression (MLR) and principal component regression (PCR) methods due its robustness. Such methods are well suited when data is strongly collinear, and the numbers of variables is greater than observations, which is common for analytical data such as UV-visible, infra-red and Raman spectra and XRD patterns [16, 17, 18].

The PLS method provides a prediction of hidden information (latent variables) from the raw data, which can be of great interest for industrial process control. The advances in XRD detectors allows obtaining good quality data within a few minutes [14, 18]. In this context, application of the PLS method directly to the XRD raw data appears to be an interesting alternative for the industrial grade control of ores and processes [14, 19, 20]. This study aimed to evaluate the applicability of the PLS regression on XRD data of several bauxite samples, including low grade samples (high silica content) to predicting the principal parameters required for process control.

## **2. Experimental**

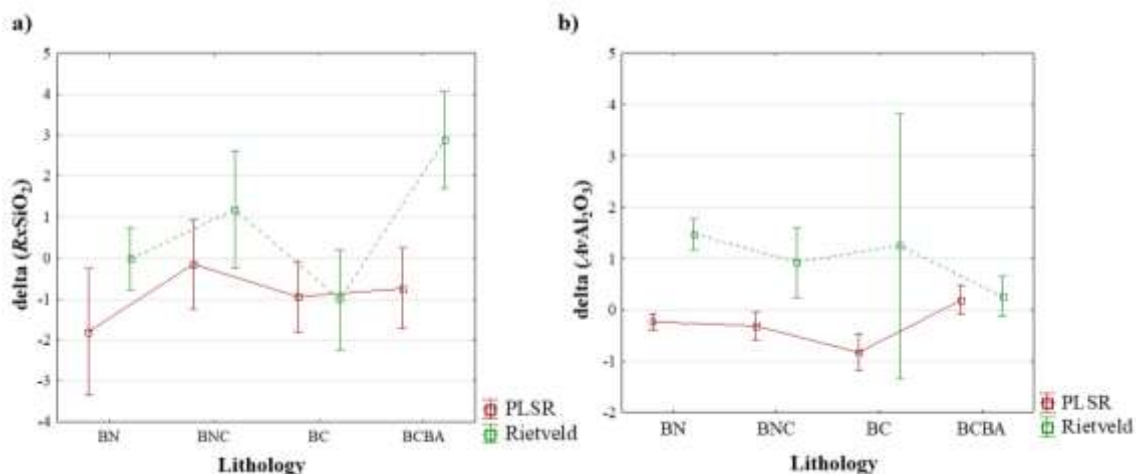
### **2.1. Materials**

A total of 64 samples of bauxites were used, randomly selected from sampling boreholes at the Miltonia 3 plateau. Both the samples and the quantification their extractables ( $AvAl_2O_3$  and  $RxSiO_2$ ) were provided by Hydro Paragominas. According to the typical lateritic profile of the plateau, the samples correspond to four lithologies: BN (Nodular Bauxite), BNC (Nodular/Crystalized Bauxite), BC (Crystalized Bauxite) and BCBA (Crystalized/Amorphous Bauxite). More details of borehole sampling, localization and grid size, sample preparation, and description of the lithologies are given in Melo et al [10] and Silva et al [21].

### **2.2. XRD data**

The powder XRD data were collected using a PANalytical *Empyrian* diffractometer, equipped with a  $\theta$ - $\theta$  goniometer, Co X-ray tube ( $K\alpha_1 = 1.78901 \text{ \AA}$ ), Fe  $K\beta$  filter and a PIXel<sup>3D</sup> 2x2 area detector (linear scanning mode) with active length of  $3.3473^\circ 2\theta$  (255 channels). Analyses were carried out under the follow conditions: 40 kV and 35 mA; soller slit of 0.04 rad;  $\frac{1}{4}^\circ$  and  $\frac{1}{2}^\circ$  divergent and anti-scattering slits respectively;  $0.02^\circ 2\theta$  step size; sample spinning with 1 rotation per second. Two scan ranges and time per step were adopted resulting in different times of measurements (Table 1). The main idea was to optimize the measurement time while maintaining a good prediction.

Rietveld refinement was performed using the PANalytical software HighScore Plus v7.4. The CIF files were: 6162 – Gibbsite; 87771 – Kaolinite; 170915 – Hematite; 109411 – Al-Goethite; and 202242 – Anatase. Background was fitted for each XRD pattern and the following



**Figure 5. Plot of delta of PLSR and Rietveld prediction vs lithology. a) expressed for  $RxSiO_2$ . b) expressed for  $AvAl_2O_3$ . Bars denote the SD.**

#### 4. Conclusions

Available alumina and reactive silica contents, the main parameters for grade control of bauxites, were successfully determined from several samples using the PLSR method directly from raw XRD data. It shows to be robust at the rapid prediction of wet-chemical determinations ( $AvAl_2O_3$  and  $RxSiO_2$ ) from unknown samples.

The quality of the XRD data needed to achieve satisfactory predictions were evaluated. It was concluded that by reducing the scan range  $2\theta$  from  $5^\circ - 70^\circ$  to  $13^\circ - 45^\circ$ , the measurement time is optimized without loss of accuracy. The optimal conditions for XRD data collection were found to be: *scan range*:  $3^\circ - 45^\circ$  ( $2\theta$ ), and *time per step*: 56.865 s. However, satisfactory results were obtained even for the measurement time of 2 min 30 s.

The model constructed using both high and low-grade bauxites allowed the prediction of  $AvAl_2O_3$  and  $RxSiO_2$  values from all lithologies including those of marginal bauxites and gangues. This can improve process control in mining, streamlining communication between the laboratory and the mine, when there is a mineralogical change in the feedstock.

#### 5. References

1. E. L. Bray. Bauxite and alumina. *Mineral Commodity Summaries*. USGS, (2018), 30–31.
2. Brasil. Departamento Nacional de Produção Mineral. *Sumário Mineral* / Coordenadores T. M. Lima, C. A. R. Neves. Brasília: DNPM, 2018, 131 p.
3. P. Smith. The processing of high silica bauxites – review of existing and potential processes. *Hydrometallurgy* Vol. 98, (2009), 162–176.
4. Uwe König et al., Rapid X-ray diffraction (XRD) for grade control of bauxites. *International Committee for Study of Bauxite, Alumina & Aluminium – ICSOBA*, November 2012, Belém. Papers, Bauxite Program BX14-T, 11 p., CD-ROM.
5. S. Ostap. Control of silica in the Bayer process used for alumina production. *Can. Metall.* Vol. 25, (1986), 101–106.
6. R. S. Angélica, H. Kahn, S. P. A. Paz. A proposal for bauxite quality control using the combined Rietveld-Le Bail-Internal Standard PXRD method – Part 2: Application to a gibbsitic bauxite from the Paragominas region, northern Brazil. *Minerals Engineering*, Vol. 122, (2018), 148–155.

7. S.P.A. Paz, H. Kahn, R.S. Angélica, A proposal for bauxite quality control using the combined Rietveld – Le Bail – Internal Standard PXRD method – Part 1: *hkl* model developed for kaolinite. *Minerals Engineering* Vol. 118, (2018), 52–61.
8. D. J. O’Connor. Alumina Extraction from Non bauxitic Materials. *Aluminium Verlag*, Sydney, (1988), 370 p.
9. Bulent Tutmez, Bauxite quality classification by shrinkage methods. *Journal of Geochemical Exploration*. Vol. 191, (2018), 22–27.
10. C. C. A. Melo et al., Cluster Analysis from X-ray Diffraction data: A practical tool for mineralogical classification of bauxites and related products from the Bayer digestion. *Holos*, Vol. 6, (2017), 32–42.
11. H. Wold, Estimation of principal components and related models by iterative least squares, in P.R. Krishnaiah (Editor), *Multivariate Analysis*, Academic Press, New York, 1966, 391-420.
12. Agnar Höskuldsson. PLS regression methods. *Journal of Chemometrics*. Vol. 2, (1988), 221–228.
13. M. C. F. Ferraro, P. M. Castellano, T. S. Kaufman. A spectrophotometric-partial least squares (PLS-1) method for the simultaneous determination of furosemide and amiloride hydrochloride in pharmaceutical formulations. *Journal of Pharmaceutical and Biomedical Analysis*. Vol. 26, (2001), 43–451.
14. Uwe König, Thomas Degen, Nicholas Norberg. PLSR as a new XRD method for downstream processing of ores: – case study: Fe 2+ determination in iron ore sinter. *Powder Diffraction*. Vol. 29, (2014),
15. Paul Geladi, Bruce R. Kowalski. Partial least-squares regression: a tutorial. *Analytica Chimica Acta*. Vol. 185, (1986), 1–17.
16. S. Wold, et al., The collinearity problem in linear regression, the partial least squares approach to generalized inverses, *SIAM J. Sci. Stat. Comput.* Vol.5, (1984), 735–743.
17. S. Wold, M. Sjöström, L. Eriksson. PLS-regression: a basic tool of chemometrics. *Chemometrics and Intelligent Laboratory Systems*. Vol. 58, (2001), 109–130.
18. Thomas Degen et al., The HighScore suite. *Powder Diffraction*, Vol. 29, (2014) 13–18.
19. Uwe König, Nicholas Norberg, Process Control in Aluminium Industry – News in the XRD Tool Box. *Proceedings of 35<sup>th</sup> International ICSOBA Conference, Travaux No. 46*, Hamburg, Germany, October 2017, 2–5.
20. N. A. S. Webster et al., Predicting iron ore sinter strength through partial least square regression (PLSR) analysis of X-ray diffraction patterns. *Powder Diffraction*. Vol. 32, (2017), 66–69.
21. H. M. Silva et al., Geology, mining operation and scheduling of the Paragominas bauxite mine. *Proceedings of the 8<sup>th</sup> International Alumina Quality Workshop*. Darwin, Northern Territory, Australia. September 2008, 11–16.
22. Sijmen de Jong. SIMPLS: an alternative approach to partial least squares regression. *Chemometrics and Intelligent Laboratory Systems*. Vol. 18, (1993), 251–263.
23. S. Wold, Multivariate Data Analysis in Chemistry. in B. Kowalski (Ed.), *Chemometrics: mathematics and statistics in chemistry*. Reidel, Dordrecht, (1984), 17–95.
24. Yvonne M. Mos et al., X-ray diffraction of iron containing samples: the importance of a suitable configuration. *Geomicrobiology Journal*. Vol. 35, (2018), 511–517.
25. Mark G. Aylmore, Graham S. Walker. The quantification of lateritic bauxite minerals using X-ray powder diffraction by the Rietveld method. *Powder Diffraction*, Vol.13(03), (1998), 136–143.
26. S. P. A. Paz, et al, Synthesis, Rietveld refinement and DSC analysis of Al-goethite to support mineralogical quantification of gibbsitic bauxites. *J Therm Anal Calorim*, Vol. 128, (2017), 841–854.