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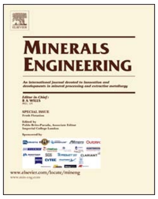

A proposal for bauxite quality control using the combined Rietveld – Le Bail – Internal Standard PXRD Method – Part 1: *hkl* model developed for kaolinite

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ABSTRACT

In the bauxite industry – exploration, beneficiation and refinery – two main chemical parameters are used for the quality control: available alumina ($AvAl_2O_3$) and reactive silica ($RxSiO_2$). Both are determined using a procedure that simulates the Bayer process at the laboratory scale. For gibbsitic bauxites, the subject of this study, the available alumina is associated with gibbsite, and the reactive silica is associated with kaolinite. Significant quantities of kaolinite increase the operational costs because under the conventional conditions of the Bayer process, kaolinite reacts with NaOH (leaching agent) to form a sodalite-type desilication product, which results in irreversible NaOH losses. In Northern Brazil (Pará State), where the world's largest metallurgical alumina refinery (Hydro Alunorte) is located, the loss of caustic soda due to sodalite formation has been reported to be much higher than the estimated value based on the amount of reactive silica that has been measured by quality control. However, the estimated experimental errors are usually within the deviations expected by the certified values, and thus has prevented obtaining a clear answer to this problem. A great innovation for this industry would be to make this control by mineralogical parameters, i.e., the wt% of gibbsite and wt% of kaolinite via Powder X-ray Diffraction Analysis (PXRD). Even with the fast increase in the last years of studies related to mineralogical phase quantification using PXRD analysis, there are still some challenges related to bauxite quantification. For instance, the lack of crystal structure information related to kaolinite, which has been underestimated when trying to apply the Rietveld method with available Crystallographic Information File (CIF). In this work, a combination of the Rietveld, Le Bail and Internal standard methods was tested, and the results were very promising for a Brazilian gibbsitic bauxite. This combination not only improved the quality of gibbsite and kaolinite quantification, but also decreased computer processing time, making it a more convenient and fast procedure, both requirements for an industrial control method.

1. Introduction

In mining, chemical data, rather than mineralogical, data have traditionally been used as the main parameters for the quality control of ore and mineral and metallurgical processes with a few exceptions. Chemical data are used more often because systems for quantitative chemical analysis, such as wet methods, instrumentation, and analytical techniques, quick, cheap and are accessible. Mineralogical analysis systems are still in development, including imaging analytical techniques and X-ray diffractometry (Baroni et al., 2000; Scarlett et al., 2002; Scarlett and Madsen, 2006; Reed, 2005; Moen, 2006; Kern, 2008; Hestnes and Sørensen, 2012).

Even if the method used to determine a chemical parameter has a low uncertainty and/or high reproducibility, only knowing the chemical content does not guarantee the high performance of mineral and metallurgical processes because the mineralogy and texture of the minerals determine the physicochemical interactions in the processes (O'connor, 1988; Solymár et al., 2005; Ou et al., 2007; Smith, 2009).

The current quality control methods for bauxite intended for the production of primary aluminum also rely on chemical parameters. The two chemical parameters used as the main quality and process indices are the available alumina ($AvAl_2O_3$) and reactive silica ($RxSiO_2$). These two parameters are used since the early stages of bauxite deposits exploration, passing through mining and beneficiation until entry into the refinery (Bayer process). They are determined in accordance with a procedure that simulates Bayer digestion on a laboratory scale (Paz

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et al., 2017a; Ostap, 1986).

For gibbsitic bauxites, which are of interest in this work, the available alumina is associated with gibbsite, and the reactive silica is associated with kaolinite. Therefore, they are referred to as gibbsitic alumina and kaolinitic silica. *High-grade* bauxite contains > 41 wt% $AvAl_2O_3$ and < 5 wt% $RxSiO_2$; *low-grade* bauxite contains < 41 wt% $AvAl_2O_3$ and 5–20 wt% $RxSiO_2$ (Andrews, 1984; Rayzman et al., 2003). In terms of operating cost, the gibbsitic type is preferred because the refining process requires less energy consumption, since the digestion of gibbsite occurs at low temperatures (130–160 °C). Significant amounts of kaolinite increase the operating cost since kaolinite reacts with NaOH (leaching agent) to form a sodalite-type desilication product under the conventional conditions of the Bayer process, which results in irreversible losses of NaOH (Barner et al., 1999; McCormick et al., 2002; Croker et al., 2008; Smith, 2009).

Bayer sodalite, which has the general formula $3(Na_2O{\cdot}Al_2O_3.2SiO_2{\cdot}nH_2O).2NaX$, where X is an anionic species, such as OH^-, Cl^-, CO_3^{2-}, SO_4^{2-}, and $0 < n < 2$ (Whittington, 1996), is a sodium aluminosilicate that is insoluble in the Bayer medium. It is discarded along with other insoluble gangue minerals (in general, hematite, goethite, anatase and quartz) in red mud, and the caustic soda incorporated in the sodalite is not recovered (Barner et al., 1999; McCormick et al., 2002; Croker et al., 2008; Smith, 2009).

Rachel et al. (2012) simulated caustic soda consumption to show that 2% more reactive silica than the maximum required significantly increased the operating cost. These authors considered a refinery with a capacity of 3 million metric tons per year (Mt/yr), a bauxite/alumina ratio of 2.5 and a bauxite feed equal to 7.5 Mt/yr. For every ton of reactive silica, 0.89 ton of NaOH is lost to the formation of sodalite. NaOH is valued at $450 per ton, and the difference between processing bauxite with 5% reactive silica vs. 7% is 0.133 Mt/yr of NaOH, which is approximately 60 million dollars a year.

Brazil's three largest operating bauxite mines (> 90% of Brazilian production) and the world's largest metallurgical alumina refinery (Hydro Alunorte), are located in northern Brazil (State of Pará). In this refinery, the loss of caustic soda due to the formation of sodalite was far greater than estimated using the reactive silica value measured by quality control. This was especially true for the Paragominas bauxite, which typically has a high concentration of reactive silica before mineral beneficiation. These discrepancies show the weaknesses of the quality control method concerning the raw material (Paz et al., 2017a; 2017b).

A major innovation in the sector would be to base the control of bauxite ores on mineralogical parameters, “wt% gibbsite and wt% kaolinite”, determined using Powder X-ray Diffractometry (PXRD). Although its use has already been tried, there are still many uncertainties associated with the technique even for simple geological matrices (mineralogy with only a few phases). The challenge has been to refine the complex crystalline structure (poor crystallinity/small crystallite size, abundant solid-solutions and mineral intergrowth) of the constituents of bauxite ores, besides that strong effects of preferred orientation and overlapping reflections.

Some discrepancies have been observed between the measured diffraction pattern and the CIF-ICSD models (Crystallographic Information File of the Inorganic Crystal Structure Database), which have made difficult the quantification of phases using the conventional Rietveld methodology, one of the most used methods for quantifying polycrystalline mixtures via PXRD (Scarlett and Madsen, 2006; Paz et al., 2012; Paz, 2016).

The Rietveld method (Rietveld, 1969) makes it possible to deal with a large number of sample-related effects by using the full diffraction pattern (whole-profile). However, this is only reliable when all the phases in a given mixture have known crystalline structures. This is not the case of bauxites, since crystallographic information related to their various phases is absent, e.g., kaolinite, Al-goethite, and the presence of amorphous material. This has greatly hindered the success of PXRD quantification.

New paths open to the possibility of achieving this goal by using combinations of diffractometric methods, such as *Rietveld - RIR*, *Rietveld - Le Bail*, *Rietveld - Internal standard*, and *Rietveld - Le Bail - Internal standard* (Rietveld, 1969; Klug and Alexander, 1974; Le Bail, 1988; Gualtieri, 2000; Scarlett and Madsen, 2006; Kern, 2008; Paz et al., 2012). It is in this context that the present work was designed, which is a methodological approach that used the combined *Rietveld - Le Bail - Internal Standard* Method for quality control of gibbsitic bauxites.

Table 1
Standard minerals.

Mineral	Formula	Manufacturer	Purity (%)	Particle size (μm)/D90
Kaolinite	$Al_2Si_2O_5(OH)_4$	Imerys	97.9	< 10
Quartz	SiO_2	–	99.1	< 80
Fluorite[a]	CaF_2	Sigma-Aldrich	99.0	< 40

[a] This mineral was used as an internal standard in the combined Rietveld-Le Bail-Internal Standard Method, and not in the standard mixtures.

2. Materials and methods

2.1. Materials

High-purity quartz and kaolinite samples (Table 1) were used to prepare the binary standard mixtures presented in Table 2. The kaolinite sample was donated by Imerys Rio Capim Caulim Company. The sample is the final product of the company for paper coating.

The kaolinite came from the mines in the Capim region (State of Pará, North Brazil), and it is geologically similar to the bauxite deposits in the Paragominas region (State of Pará, North Brazil), which were used as the bauxite test material in this work. The latter is a reference material certified by the Mineral Technology Center (Centro de Tecnologia Mineral – CETEM, Brazil) via a proficiency testing scheme featuring thirty-five specialized laboratories using methods of their choice. The reference material, BXPA-4, is a washed bauxite sample with a grain size < 150 μm (Cetem, 2016). Table 3 shows the certified chemical analysis: total oxides, loss on ignition and the two chemical parameters used in the quality and process control of gibbsitic bauxite ($AvAl_2O_3$ and $RxSiO_2$).

Quartz samples used in this work and routinely in the laboratory are centimetric to decimetric pieces of Rock crystal quartz from pegmatites. They were prepared by grinding for 1.5 min on a ringmill.

Table 2
Codes and mineral proportions for each standard mixture.

Mixture code	Wt%		
	Kaolinite	Quartz	Impurities
Calibration of the hkl model			
KQ8020	78.3	19.8	1.9
Validation of the hkl model			
KQ9901	96.9	1.0	2.1
KQ9010	88.1	9.9	2.0
KQ8020	78.3	19.8	1.9
KQ7030	68.5	29.7	1.8
KQ6040	58.7	39.6	1.7
KQ5050	49.0	49.6	1.4
KQ4060	39.2	59.5	1.3
KQ3070	29.4	69.4	1.3
KQ2080	19.6	79.3	1.1
KQ1090	9.8	89.2	1.0
KQ0199	1.0	98.1	0.9