

Optimization of the reactive silica quantification method applied to Paragominas-type gibbsitic bauxites



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ABSTRACT

This study presents an optimization of the method used to quantify reactive silica (R_xSiO₂) in gibbsitic bauxites, specifically those which contain no (or insignificant) quartz. In this work they are named as Paragominas-type Bauxites. A factorial design of experiments was used. The variables included the temperature, caustic concentration and time for two cases: bauxites with low and high R_xSiO₂ contents. Temperature is the most important factor and has a positive influence on R_xSiO₂. First-order empirical models were properly obtained to predict the amount of R_xSiO₂ as a function of temperature, caustic concentration and time, which responded to the following optimal conditions: (1) without significant amount of quartz – 180 °C, NaOH 10% w/v and 60 min for low R_xSiO₂ and 25 min for high R_xSiO₂, and (2) with significant amount of quartz – 150 °C, NaOH 20% w/v and 60 min for both situations.

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1. Introduction

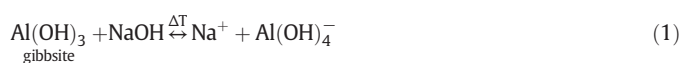
Global bauxite production in 2014 was 234 million tons. The largest global bauxite producer is Australia, which produces approximately 81 million tons per year, followed by China (47 million tons per year), and Brazil, which produces 32.5 million tons per year (Bray, 2015).

>90% of the bauxite produced since 1890 has been used in the aluminum metal industry, the conventional process of which involves two stages. First, bauxite is subjected to alkaline leaching with NaOH at moderate temperatures and pressures to produce alumina (Al₂O₃) with >99% purity; this hydrometallurgical step is known as the Bayer Process. Then, alumina from the Bayer process is dissolved in a molten cryolite bath and reduced to metallic aluminum by the electrolytic Hall-Héroult process. Depending on the quality of the bauxite ore, the stoichiometry of aluminum production uses 4 to 7 tons of bauxite to produce 2 tons of alumina, and 2 tons of alumina are required to produce 1 ton of aluminum (Barrand et al., 1967; The Aluminum Association, 2016).

In general, attention and studies have been primarily directed at lateritic bauxites (mostly gibbsite) due to their large proportion of global reserves (approximately 90%). Their composition is generally associated with four main elements, Al, Si, Fe and Ti, which are related to eight

major minerals (Table 1). These minerals can be soluble or insoluble under the conditions of the Bayer process at low temperatures (130–160 °C; low-temperature digestion (LTD)) or at high temperatures (200–270 °C; high-temperature digestion (HTD)) (Ostap, 1984; Whittington, 1996; Authier-Martin et al., 2001; McCormick et al., 2002; Rayzman et al., 2003; Smith, 2009).

The Bayer process is the main method used to produce metallurgical alumina from bauxite throughout the world. The modern version of the Bayer Process still uses the primary steps that exploit the solubility of aluminum minerals in the caustic solution (at moderate temperatures and pressures) and the insolubility of the remaining minerals. Under LTD conditions, gibbsite can dissolve to the point of saturation of the liquor according to Eq. (1). Once dissolved, the aluminum, in the form of aluminate, is surrounded by OH⁻ groups and has a tetrahedral symmetry in a dilute solution.



In addition to the gibbsite dissolution reaction, two other reactions occur consecutively from the clay minerals, primarily kaolinite. First, the clay mineral is dissolved in the Bayer liquor (Eq. (2)), and the dissolved silica reprecipitates as sodium aluminosilicate, which is known as the desilication product (DSP) or Bayer sodalite (Eq. (3)). The “X” in the sodalite formula represents a variety of inorganic anions. The most

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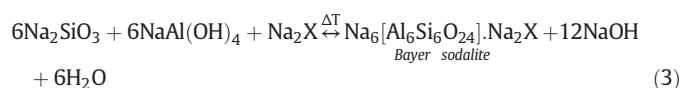
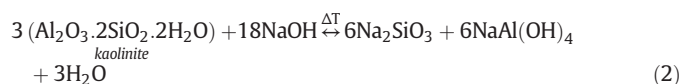
Table 1

Typical chemical and mineralogical compositions of lateritic bauxites.

Source: Authier-Martin et al. (2001).

Component	wt%	Mineral	Formula
Al ₂ O ₃	30–60	Gibbsite	Al(OH) ₃ or Al ₂ O ₃ ·3H ₂ O
SiO ₂	<0.5–10	Boehmite	AlO(OH) or Al ₂ O ₃ ·H ₂ O
Fe ₂ O ₃	1–30	Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄ or Al ₂ O ₃ ·2SiO ₂ ·2H ₂ O
TiO ₂	<0.5–10	Quartz	SiO ₂
		Hematite	Fe ₂ O ₃
		Al-Goethite	(Fe,Al)OOH or (Fe,Al) ₂ O ₃ ·H ₂ O
		Anatase	TiO ₂
		Rutile	TiO ₂

common anions are SO₄²⁻, CO₃²⁻, 2Cl⁻, and 2OH⁻.



Sodalite is insoluble under the conditions of the Bayer process and is therefore discarded along with other insoluble minerals in the LTD process (hematite, Al-goethite, anatase, rutile and quartz) as red mud. Thus, the alumina associated with the clay minerals is not recovered. Additionally, as shown in Eqs. (2) and (3), the formation of sodalite represents a significant loss of caustic soda (a minimum of 1 mol of NaOH per mol of reactive silica). This loss of soda is the source of contract fines and is linearly correlated with the reactive silica content in the bauxite (Ostap, 1984; Whittington, 1996; McCormick et al., 2002; Rayzman et al., 2003; Croker et al., 2008; Smith, 2009).

In this context, the main question is: how is the quality control of the bauxite ore carried out? Since early steps of mineral exploration up to processing prior to the Bayer process, the primary quality and process indices to date have been two chemical parameters: the available alumina (AvAl₂O₃) and reactive silica (RxSiO₂). Both are determined using a procedure that simulates the Bayer process at the lab scale (Ostap, 1986).

For gibbsitic bauxites, subject of this study, the available alumina is associated with gibbsite, and the reactive silica is associated with kaolinite. For this reason, they are also referred to as gibbsitic alumina and kaolinitic silica. High-grade bauxites contain >41 wt% AvAl₂O₃ and <5 wt% RxSiO₂, while low-grade bauxites contain <41 wt% AvAl₂O₃ and 5–20 wt% RxSiO₂ (Andrews, 1984; Rayzman et al., 2003). Gibbsitic bauxites are most valuable in terms of operational cost; the refining process of these bauxites consumes less energy because gibbsite digestion occurs at low temperatures (130–160 °C). However, 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 (Barnes et al., 1999; McCormick et al., 2002; Croker et al., 2008; Smith, 2009).

Rachel et al. (2012) simulated caustic soda consumption to show that the presence of 2% more reactive silica than is required can significantly increase the operational costs. They considered a refinery with a capacity of 3 Mtpa, a bauxite/alumina ratio of 2.5 and a bauxite feed of 7.5 Mtpa. For each ton of reactive silica, 0.89 tons of NaOH is lost due to the formation of sodalite. Processing bauxite with 7% reactive silica requires 0.133 Mtpa more NaOH than processing bauxite with 5% reactive silica, which is equivalent to \$60 million per year at a NaOH cost of U\$450 per ton.

Northern Brazil contains the three largest bauxite mines in the country (>90% of Brazilian production) and the largest metallurgical alumina

refinery in the world (Hydro Alunorte). The loss of caustic soda due to sodalite formation in the Hydro Alunorte refinery has been reported to be much higher than is estimated based on the amount of reactive silica that has been measured by quality control, primarily in bauxites from Paragominas (region of Miltônia, State of Pará), which typically have high reactive silica contents prior to washing. However, the estimated experimental errors are usually within the deviations expected by the certified values, which has prevented obtaining a clear definition of the problem. A working hypothesis was therefore established: “The physical-chemical conditions of the standard method are not optimal for determining the reactive silica content in Paragominas-type bauxites, so the contents are underestimated”.

To test this hypothesis, a statistical significance test was performed by comparing the values estimated by the standard method to those estimated by a modified method using a certified reference material. Once it was statistically proven that the control method should be modified, the method was optimized based on a full factorial design and regression by least squares.

2. Materials and methods

2.1. Materials

The certified reference material BXPA-4 is a washed bauxite sample from the Paragominas region, which is located in the State of Pará, Brazil. This material was certified by Centro de Tecnologia Mineral - CETEM through an interlaboratory program that included thirty-five specialized laboratories using their methods of choice (including the Alcan and Alcoa methods, which are the most commonly used methods for the determination of AvAl₂O₃ and RxSiO₂). The particle size of the material is <150 μm (Cetem, 2016).

A mixture with 60% gibbsite and 40% kaolinite, which represents a “simulating bauxite” with a high reactive silica content (known as sample Gbs60Kln40), was used. The certified gibbsite was 98.8% pure with a particle size below 150 μm and was obtained from Merck, and the kaolinite was 97.9% pure with a particle size below 10 μm donated by Imerys Rio Capim Caulim. The kaolinite comes from mines in the Capim region that are in the same geological context as the bauxite deposits in the Paragominas region.

Analytical grade (PA) sodium hydroxide (Merck) was used in this study. The Bayer sodalite was synthesized from the Imerys kaolinite and NaOH under conditions similar to those of the standard Alcan method (Ostap, 1986).

2.2. Equipment

The digestions were performed in 50 mL steel batch reactors (Parr bombs) placed in a direct contact metallic electric oven operating at 18 rpm rotation (known as digestion block).

2.3. Experimental procedure

2.3.1. Digestion

Standard Method (Alcan): a 3.25 g sample of the representative bauxite was dried at 105 °C for 2 h and then digested in a solution of NaOH 10% (w/v) at 150 °C for 25 min.

Modified Method (this study): a 3.25 g sample was digested with 10, 15 or 20% (w/v) NaOH solutions at 150, 165 and 180 °C, respectively, and digestion times of 25, 42.5 and 60 min, respectively, according to the combinations described in the two factorial designs in Section 3.4.

The mass of each of the samples was mixed with 25 mL of NaOH solution directly in the Parr bomb. The closed bomb was shaken and placed in the digestion block at each of the specified temperatures. A waiting time of approximately 10 min was necessary to reestablish the block temperature, and the digestion time of each of the planned assays was recorded.

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