STUDY ON ORE DRESSING AND CHARACTERIZATION OF DIFFERENT GRANULOMETRIC FRACTIONS THAT COMPOUND BauxITE FROM PARÁ/BRAZIL

Fernanda A.N.G. Silva1,2, Rachel D. Santos1,2, João A. Sampaio2, Francisco M. S. Garrido1, Marta. E. Medeiros1

1Universidade Federal do Rio de Janeiro, Instituto de Química, Avenida Athos da Silveira Ramos, 149, Cidade Universitária; Rio de Janeiro, RJ, 21941-909, Brazil.
2Centro de Tecnologia Mineral / CETEM-MCT, Avenida Pedro Calmon, 900, Cidade Universitária; Rio de Janeiro, RJ, 21941-908, Brazil.

Keywords: Bauxite, Mineralogical and Chemical Characterization, Thermal Analysis

Abstract

Bauxite from Paragominas (Pará/Brazil) was ore dressed and characterized by XRD, XRF, chemical and thermal analysis. XRD was performed to determine the mineral content. This bauxite is essentially gibbsitic and has been associated with kaolinite, aluminum-goethite, goethite and iron and titanium compounds. XRF analysis was carried out in order to determine the sample’s chemical composition and how its content varied after ore dressing. However, the chemical content of Al\textsubscript{2}O\textsubscript{3}available and SiO\textsubscript{2}reactive was determined by back titration and flame atomic absorption. The results found for the Bayer Process’ sample were 47.2% and 5.3%, respectively. Thermal analysis was performed as a supplemental technique in order to observe the bauxite decomposition in the mineralogical phases. Thus, based on stoichiometric relations of the bauxite components decomposition and the mass loss observed in the thermal analysis, it was possible to confirm the following phases: gibbsite, aluminum-goethite and kaolinite.

Introduction

The bauxite rock is composed of a mixture of aluminum minerals having as its most important components: gibbsite (γ-Al(OH)\textsubscript{3}), diaspore (γ-AlO(OH)) and boehmite (α-AlO(OH)). These minerals are known as aluminum oxi-hydroxides and their proportions in the rock vary according to the deposits. Kaolinite (Al\textsubscript{2}(Si\textsubscript{4}O\textsubscript{10})(OH)\textsubscript{8}), quartz (SiO\textsubscript{2}), hematite (Fe\textsubscript{2}O\textsubscript{3}), goethite (FeOOH), aluminum-goethite (α-Al-Fe)(OH)\textsubscript{2}, ilmenite (Fe\textsubscript{2}TiO\textsubscript{3}), rutile and anatase (TiO\textsubscript{2}) are among the main impurities that compose this rock.

In 2007 the world’s bauxite reserves were estimated in 34 billion tons. Brazil holds approximately 10.6% out of this total and is the third in the world classification [1].

Brazil’s annual bauxite production is estimated in 25 million tons from which 95% are used in alumina production by the Bayer process, followed by the Hall-Héroult process. The other 5% are applied in the production of refractory, abrasive materials, ignition candles, ceramic, etc. [2].

The State of Pará holds around 95% of the Brazilian reserves. The bauxite of this region is divided into five layers and its iron contents, gibbsite and kaolinite, vary according to the profile depth [3-5]. In the outcrop top, the iron content is higher than in the bottom whereas an opposite behavior is observed for the kaolinite content [4,5]. For a bauxite to be considered economically useful for the Bayer process, the available Al\textsubscript{2}O\textsubscript{3} content should be between 45-55% whilst the reactive SiO\textsubscript{2} content should be between 4-6%. Therefore, only the fraction called crystallized bauxite(CB) of the bauxitic outcrop from NE Pará is used in the Bayer process [4-6].

NE Pará’s bauxite was ore dressed by the processes of crushing, grinding, washing and classification by cyclone [6] whereas its quality was determined by means of chemical analysis for the measurement of available Al\textsubscript{2}O\textsubscript{3} and reactive SiO\textsubscript{2}. X-ray Fluorescence (XRF) was carried out to determine the total contents of Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} [5].

Dump way analysis simulates the material behavior in the Bayer process for alumina production and involves hardworking procedures [5], giving a slow pace to ore dressing process control and mineral research. Therefore, different characterization techniques have been incorporated to chemical analysis with the objective of completing and/or reaching results related to the chemical and mineralogical composition in a shorter period of time. Among them, the thermal analysis technique has been given attention recently [7-10].

In this context, the aim of this work was to ore dress and characterize the chemical, structural and mineralogical layers of NE Pará’s bauxite, which has the necessary quality to be used by the Bayer process. The techniques applied in this study were: chemical analysis for potentiometric titration and flame atomic absorption spectroscopy, X-ray fluorescence, X-ray diffraction and, as a complementary technique to chemical analysis, thermal analysis was carried out.

Materials and Methods

1 - Sample Preparation

The bauxite ore was crushed in a jaw crusher. The crushed product was classified with the use of a sieve (1.65 mm). The coarse fraction was crushed by crushing rolls in a closed circuit. The -1.65 mm fraction was classified to remove particles -37 µm (sludge). The +37 µm fraction was homogenized with the product of the crushing rolls and two samples of 20 kg and 5 kg, respectively, were separated for wet granulometric analysis. For grinding, samples of 20 kg were homogenized and separated into piles of 1kg. Figure 1 shows the block diagram used in the bauxite beneficiation [5].

Samples (1 kg) of the final product of the preparation stages were wet ground in a stainless steel mill bar with 10 stainless steel bars of 20 mm diameter. The slurry in water was prepared using a bauxite solid concentration of 1000 g L\textsuperscript{-1}. The time of grinding varied from 0 to 40 minutes. A wet granulometric analysis was carried out after each grinding to adjust the sample to the necessary conditions for the Bayer process [5].
The granulometric analysis were carried out with samples of 1kg, according to the damp method [11]. A vibratory siever (684,5 rpm), equipped with a group of sieves with openings from 3,350 mm to 37 µm, was used according to the Tyler series. All the granulometric analysis fractions obtained in these tests were dried (100ºC) and weighed.

2 – Chemical and Mineralogical Characterization

The bauxite ore was submitted to chemical and mineralogical analysis with the use of: X-ray diffraction, X-ray fluorescence, potentiometric titration, flame atomic absorption spectrometry and thermal analysis.

During the ore dressing tests, four different samples were obtained: work sample (WS) obtained after crushing, two work sample fractions (833 and 208 µm) and the sludge (~37 µm fraction obtained after screen size desliming of the −1,65 mm fraction). These samples were submitted to the same characterization techniques of the crude sample.

2.1 – X-ray Fluorescence (XRF)

The samples were fused with lithium tetraborate at 1100ºC, in the proportion of 1:6 sample/fluxing agent. The melted bead was analyzed in X-ray fluorescence spectrometer by dispersive energy (BRUKER-AXS model S4-Explorer), equipped with Rh tube. To obtain the semiquantitative chemical analysis, the sample spectrum was evaluated by Spectra plus v.1.6 software, in the standardless method mode, without curve of specific calibration.

2.2 – Determination of Available Alumina and Reactive Silica

The method for determination of available alumina (the amount that will be refined to obtain Al₂O₃ in the Bayer Process) and reactive silica (kaolinite), consisted of bauxite digestion in alkaline medium (NaOH) under controlled pressure and temperature, simulating the Bayer process. For the determination of available aluminum, sodium gluconate solution was added to the supernatant to form an aluminum hydroxide gluconate complex. The excess of NaOH, used in the digestion step, was neutralized with the addition of HCl solution. Then, a KF solution was added and back titration was carried out. Afterwards, an excess of HCl standardized solution was titrated with a NaOH standardized solution. The solid phase, resulting from the stage of the ore’s digestion, was dissolved in a HNO₃ solution [5]. The concentration of reactive silica was determined by flame atomic absorption spectrometry (FAAS).

2.3 – Flame atomic absorption spectrometry (FAAS).

Chemical analysis was performed by flame atomic absorption spectrometry in an AA6 Varian equipment with 248.3 nm wave number, 0.5 nm slit and with air/acetylene.

2.4 – X-ray Diffraction (XRD)

Samples were examined by XRD in a Bruker-AXS D5005 diffractometer, with Co Kα (35 kV/40 mA) radiation, 0,02° goniometer velocity and 2θ by path with 1 s by path counting time and data collected from 5 to 80° 2θ.

2.5 – Thermal Analysis (ATD/AGT)

Thermal analysis were carried out in a Shimadzu TA-50WSI equipment (thermogravimetric analysis), DTA-50 (differential thermal analysis) in a heating grade of 10ºC/min, from room temperature to 1200ºC under flow of air.

Results and Discussion

In this work, among the bauxite layers that form the bauxite horizon in NE Pará, only the fraction used by the Bayer Process (crystallized bauxite) was studied. The mineralogical phases that compose this rock were determined by X-ray diffraction (XRD), Figure 2. Therefore, this bauxite is essentially gibbsitic and is associated with kaolinite (Al₄(Si₄O₁₀)(OH)₈), aluminum-goethite ([αFe₃Al]OOH), goethite (FeOOH) and hematite ([αFe₂O₃]). In order to determine the sample’s chemical composition and how its content varied after ore dressing, XRF was carried out, Table I.
According to the results, Table II, it was observed that the content of available alumina is higher in the coarse fractions whereas the content of reactive silica is higher in the finer fractions. This behavior is similar to the one observed through XRF. However, it allowed us to determine the exact quantity of available alumina and reactive silica of this sample. The bauxite sample that is sent to the Bayer Process, according to the ore dressing steps described, contains 47.5% of available alumina and 5.9% of reactive silica. It can be observed that, after sample adjustment to the Bayer Process (30 minute grinding), the contents of available alumina and reactive silica do not suffer greater variations in relation to work sample as well as no significant alterations in the spectrum IV and in the XRD figures are observed [5]. These results indicate that grinding does not cause mineralogical changes or great alterations in the crystalline structure of the phases present in this bauxite. However, these little differences may be attributed to the mecanochemical activation of the minerals present in it [4,5,12].

Table II. Chemical contents of $\text{Al}_2\text{O}_3\text{total}$ and $\text{SiO}_2\text{reactive}$ for XRF and of $\text{Al}_2\text{O}_3\text{available}$ and $\text{SiO}_2\text{reactive}$ for potentiometric titration and atomic absorption bauxite ore and its fractions obtained during ore dressing.

<table>
<thead>
<tr>
<th>Samples</th>
<th>XRF (in mass)</th>
<th>Chemical Analysis (in mass)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{Al}_2\text{O}_3\text{total}$</td>
<td>$\text{SiO}_2\text{reactive}$</td>
</tr>
<tr>
<td>Bauxite Ore</td>
<td>49.78</td>
<td>12.60</td>
</tr>
<tr>
<td>WS</td>
<td>55.44</td>
<td>5.61</td>
</tr>
<tr>
<td>WS 833 µm</td>
<td>56.52</td>
<td>4.00</td>
</tr>
<tr>
<td>WS 208 µm</td>
<td>51.04</td>
<td>9.05</td>
</tr>
<tr>
<td>Sludge</td>
<td>37.74</td>
<td>30.90</td>
</tr>
<tr>
<td>BP</td>
<td>54.10</td>
<td>6.47</td>
</tr>
</tbody>
</table>

The thermal behavior of different bauxites has been the object of study due to the possibility of determining the rock’s mineralogical composition through the dehydroxylation of the minerals that compose it [7]. A bauxite’s thermal analysis varies according to the deposits of origin, impurities and sample crystallinity. Thus, thermal analysis (DTA/TGA) was carried out in this work as a complementary technique to chemical analysis and XRD was performed in order to obtain a complete characterization as well as a better knowledge of the rock that composes the geological profile of NE Pará.

Bauxite dehydroxylation during calcination leads to one or more alumina transitions ($\chi$, $\gamma$, $\delta$, $\theta$ and $\alpha$-$\text{Al}_2\text{O}_3$) with structures partially disordered. With the raise in temperature, the structures become more ordered and at the end of calcination a more stable $\alpha$-$\text{Al}_2\text{O}_3$ [8] occurs. Such dehydroxylation can happen in two distinct sequences, Figure 3. A sequence by means of boehmite formation and another one through the formation of $\chi$-$\text{Al}_2\text{O}_3$.  

\[ 6\text{Na}_2\text{SiO}_3(\text{aq}) + 6\text{NaAlO}_2(\text{aq}) + \text{Na}_2\text{X}(\text{aq}) + 12\text{H}_2\text{O}(\text{v}) \xrightarrow{\Delta T} 3\text{[Na}_2\text{OAl}_2\text{O}_3\cdot 2\text{SiO}_2\cdot 3\text{H}_2\text{O}]}(\text{aq}) + 12\text{NaOH(aq)} \]

\[ X = (\text{CO}_3)^2-, (\text{SO}_4)^2-, 2(\text{AlO}_2)^-, 2\text{OH}^-, \text{among others}; n = 0 - 2 \]

(3)

Results analysis, Table 1, indicated a higher content of SiO$_2$ in the finer fractions than in the coarse fractions, whereas an opposite behavior was observed in the content of Al$_2$O$_3$. However, in order to evaluate such behavior in relation to the contents of available alumina, Equation 1, and reactive silica responsible for the consumption of NaOH and the formation of de-silicification product (DSP) by the Bayer Process, Equations 2 and 3 respectively, a chemical analysis for potentiometric titration and flame atomic absorption spectroscopy was carried out.

\[ \text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}(\text{s}) + 2\text{NaOH}(\text{aq}) \xrightarrow{\Delta T} \text{Na}_2\text{OAl}_2\text{O}_3\cdot 3\text{H}_2\text{O}(\text{aq}) + 4\text{H}_2\text{O}(\text{v}) \] 

(1)

\[ \text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}(\text{s}) + 6\text{NaOH}(\text{aq}) \leftrightarrow 2\text{Na}_2\text{O}(\text{aq}) + \text{SiO}_3(\text{aq}) + 2\text{NaAlO}_2(\text{aq}) + 5\text{H}_2\text{O}(\text{v}) \] 

(2)
Both sequences happen simultaneously at temperature band between 200 and 500ºC, leading to the formation of $\alpha$-$\text{Al}_2\text{O}_3$ around 1200 ºC [8-10].

![Figure 3. Gibbsite dehydroxylation sequences way $\chi$-$\text{Al}_2\text{O}_3$ and AlO(OH).](image)

According to the results obtained through DTA/TGA for the bauxite ore sample, Figure 4, three events were observed:

i. The first event, between 230 and 290ºC, is related to Al(OH)$_3$ dehydroxylation, with the formation of a AlO(OH) and $\chi$-$\text{Al}_2\text{O}_3$ mixture, Equations 4 and 5, respectively.

ii. The second one corresponds to ($\alpha$(Al-Fe)OOH) ($\cong$ 360ºC) dehydroxylation, Equation 6, since among the mineralogical phases identified through XRD, this is the only phase where it can be decomposed at such temperature.

iii. The third event, at approximately 490ºC, is related to a AlO(OH) dehydroxylation combination formed in the first event and (Al$_4$(Si$_4$O$_{10}$)(OH)$_8$) dehydroxylation, as shown in Equations 7 and 8.

\[
\frac{1}{2}\text{Al(OH)}_3\text{(s)} \rightarrow \frac{1}{2}\text{AlOOH}\text{(s)} + \frac{1}{2}\text{H}_2\text{O}\text{(v)} \quad (4)
\]

\[
\frac{1}{2}\text{Al(OH)}_3\text{(s)} \rightarrow \frac{1}{4}\text{Al}_2\text{O}_3 + \frac{3}{4}\text{H}_2\text{O}\text{(v)} \quad (5)
\]

\[
2\text{FeOOH}\text{(s)} \rightarrow \text{Fe}_2\text{O}_3\text{(s)} + \text{H}_2\text{O}\text{(v)} \quad (6)
\]

\[
\text{AlOOH}\text{(s)} \xrightarrow{\Delta T} \frac{1}{2}\text{Al}_2\text{O}_3\text{(s)} + \frac{1}{2}\text{H}_2\text{O}\text{(v)} \quad (7)
\]

\[
\text{Al}_4[\text{Si}_4\text{O}_{10}]\text{(OH)}_8\text{(s)} \rightarrow 2\text{Al}_2\text{O}_3\text{(s)} + 4\text{SiO}_2\text{(s)} + 4\text{H}_2\text{O}\text{(v)} \quad (8)
\]

In figure 5, DTA/TGA results can be observed for the WS and Sludge samples. Table III contains the data related to the samples’ mass loss obtained during ore dressing. Results analysis show that in the coarse fractions there is a bigger mass loss related to the first event when compared to the finer fractions. However, the latter present a bigger mass loss related to the third event. These results can be explained based on Equations 4, 5, 7 and 8, if we consider that the fractions with higher granulometry contain a bigger amount of gibbsite and, in the finer fractions, a bigger amount of kaolinite. These results are in accordance with those obtained through the chemical analysis for available alumina and reactive silica, respectively, Table II.

![Figure 4. DTG/ATG of the Bauxite Ore.](image)

![Figure 5. DTA/AGT of the WS and Sludge samples.](image)
Table III. Mass loss related to thermal events of bauxite sample and the fractions of its ore dressing.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Mass Loss (%)</th>
<th>Events</th>
<th>Mass Loss (%)</th>
<th>Events</th>
<th>Mass Loss (%)</th>
<th>Events</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st</td>
<td>2nd</td>
<td>3rd</td>
<td>4th</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al(OH)₃</td>
<td>FeOOH</td>
<td>Al₂O₃</td>
<td>SiO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bauxite Ore</td>
<td>16.2</td>
<td>1.2</td>
<td>3.2</td>
<td>3.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WS</td>
<td>20</td>
<td>1.2</td>
<td>4.1</td>
<td>1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WS 833μm</td>
<td>22.5</td>
<td>1.9</td>
<td>4.5</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WS 208 μm</td>
<td>18.5</td>
<td>1.4</td>
<td>3.7</td>
<td>2.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sludge</td>
<td>4</td>
<td>1.5</td>
<td>1.0</td>
<td>9.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Mass loss values obtained after deconvolution of DTA/AGT curves (Table IV) are in agreement with the data obtained through the chemical analysis (Table II). By means of a semiquantitative analysis, as shown in Table IV, it can be observed that Equations 4, 5, 7 and 8 are good models to describe the thermal behavior of the bauxite studied.

Table IV. Chemical contents of Al₂O₃ available and SiO₂ reactive for potentiometric titration and atomic absorption and for values obtained after deconvolution of the thermal analysis curves for crude sample and its fractions obtained during ore dressing.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Chemical Analysis (%)</th>
<th>Thermal Analysis (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al₂O₃ available</td>
<td>SiO₂ reactive</td>
</tr>
<tr>
<td></td>
<td>(s ≤ 0.3%)</td>
<td>(s ≤ 0.1%)</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃</td>
<td>SiO₂ reactive</td>
</tr>
<tr>
<td>Bauxite Ore</td>
<td>36.7</td>
<td>10.4</td>
</tr>
<tr>
<td></td>
<td>36.6</td>
<td>10.3</td>
</tr>
<tr>
<td>WS</td>
<td>47.2</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>45.5</td>
<td>5.2</td>
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<tr>
<td>WS 833 μm</td>
<td>51.2</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>51.1</td>
<td>3.9</td>
</tr>
<tr>
<td>WS 208 μm</td>
<td>42.0</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>41.9</td>
<td>7.9</td>
</tr>
<tr>
<td>Sludge</td>
<td>8.4</td>
<td>32.1</td>
</tr>
<tr>
<td></td>
<td>9.4</td>
<td>31.1</td>
</tr>
</tbody>
</table>

*Based on Equations 4, 5, 7 and 8.

Conclusion

The ore dressing stages aimed at the adaptation and characterization of the fractions that compose the bauxite sample of NE Pará that is used in the Bayer process. According to the results, crushing stages, screening, removal of fine fractions and 30 minutes of grinding adjusted the sample to the Bayer process (BP) in the context Al₂O₃ available and SiO₂ reactive content, which in this sample was 47.5 and 5.9%, respectively. This work also allowed us to understand how the minerals that compose this rock are distributed in different granulometric fractions enhancing that the coarse fractions are composed mostly of gibbsite and the finest ones mainly of kaolinite, and that the iron minerals are distributed in all the fractions studied.

XRD informed us the mineralogical composition of this bauxite. Therefore, the studied bauxite is essentially gibbritic and is associated with the minerals kaolinite, aluminum-goethite, goethite and hematite.

XRF provided information related to the chemical composition of the sample, but did not inform the chemical content of Al₂O₃ available and SiO₂ reactive, making necessary the chemical analysis for potentiometric titration and flame atomic absorption spectroscopy.

Thermal analysis helped us confirm the occurrence of aluminum-goethite and it allowed us to identify the events related to dehydroxylation of the components present in this sample: gibbsite, aluminum-goethite and kaolinite. The differences in the thermal behavior of the samples are in agreement with the quantity of their constituents, that is, in the coarse fractions gibbsite is predominant whereas in the finer fractions there is a bigger quantity of kaolinite.

Acknowledgments

We would like to thank technician Odilon da Silva, CNPq and CAPES for their financial support.

References


