

STUDY ON THE CHARACTERIZATION OF MARGINAL BAUXITE FROM PARÁ/BRAZIL

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Abstract

Bauxite from Pará is divided into five different layers. However, only one is processed. The crystallized-amorphous (CAB) phase is considered a marginal bauxite because it presents a high quantity of $\text{SiO}_{2\text{reactive}}$ and its use depends on special technologies. CAB was characterized and the results were compared with the bauxite used nowadays in the alumina plant. Characterization was performed by XRD, IR, XRF, chemical analysis, TGA and SEM. XRD determined the mineral content: such bauxite is gibbsitic and has been associated with kaolinite and hematite. IR data supported the XRD results. XRF was used to determine the sample's chemical composition. The chemical content of $\text{Al}_2\text{O}_{3\text{available}}$ and $\text{SiO}_{2\text{reactive}}$ was determined by potentiometric titration and FAAS. The results found for the Bayer process sample were 41.7% and 7.1%, respectively. TGA observed the bauxite decomposition and SEM supplied chemical and thermal analysis. Thus, based on stoichiometric relations of the bauxite components decomposition, it was possible to confirm the presence of the following phases: gibbsite and kaolinite.

Introduction

Bauxites are usually considered to be of two major types: (1) lateritic (sometimes called equatorial) and (2) karst, both being weathered products from the underlying parent rock: lateritic bauxites. [1]

Lateritic bauxites, formed in equatorial climates, comprise 90% of the world's exploitable bauxite reserves [1]. The weathering process has resulted in a typical profile in which the valuable aluminous material lies atop of an aluminosilicate base (often clay) and has formed from it through the leaching of silica. The main silicate mineral is kaolinite which is often associated with goethite as the iron mineral. Aluminous minerals are predominately gibbsite and to a lesser extent boehmite [1].

Bauxite from NE Pará is divided into five layers: (1) nodular (NB), (2) crystallized nodular (CNB), (3) crystallized (CB), (4) crystallized amorphous (CAB) and (5) amorphous (AB) (Figure 1) [3]. The NB, CNB, CAB and AB layers present a high quantity of iron minerals, reactive SiO_2 and others impurities. [2-3]. These bauxites are considered marginal and their ore dressing requires special technologies arising from their content of impurities.

Bauxite mining methods vary according to the nature of the mineralized field bodies, but in most of the cases a strip or block of bauxite is exposed and surface-mined [3]. Although the mining process is selective and only the layer of crystallized bauxite is removed, for a bauxite to be considered economically useful for the Bayer process, the available Al_2O_3 content should be between 45-55% whilst the reactive SiO_2 content should be between 4-6%. [4-6].

In this context, the aim of this work was to: ore dress, provide the chemical, structural and mineralogical characterization of crystallized amorphous bauxite (CAB) and compare its behavior and characteristic with the bauxite processed by the Bayer process, such as crystallized bauxite (CB). The techniques applied in this study were: chemical analysis by potentiometric titration and flame atomic absorption spectroscopy, X-ray fluorescence, X-ray diffraction, infrared spectroscopy, scanning electron microscopy and thermal analysis.

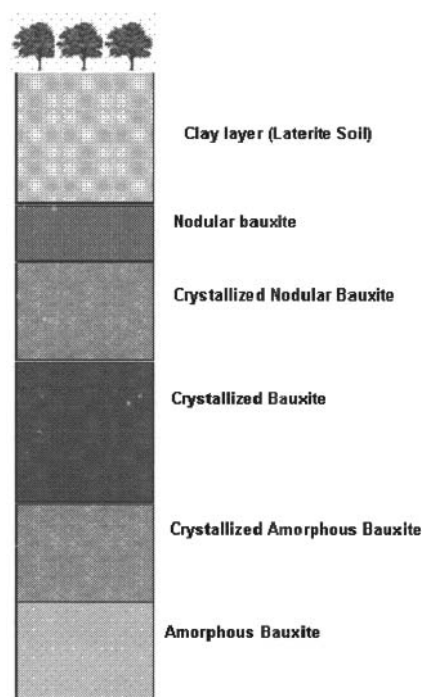


Figure 1. Bauxite geological profile from Northern Pará/Brazil.

Materials and Methods

1 – Sample Preparation

The bauxite ore was crushed in a jaw crusher and the product was classified with the use of a sieve (1.65 mm). The coarse fraction was crushed (crushing rolls) in a closed circuit. The -1.65 mm fraction was classified to remove the -37 μm particles (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 2 shows the block diagram used in the bauxite beneficiation [7].

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⁻¹. Grinding time varied from 0 to 30 minutes. A wet granulometric analysis was carried out after each grinding to adjust the sample to the necessary conditions for the Bayer process [7].

The granulometric analysis was carried out with samples of 1kg, according to the damp method [8]. A vibratory sifter (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 (100°C) and weighed.

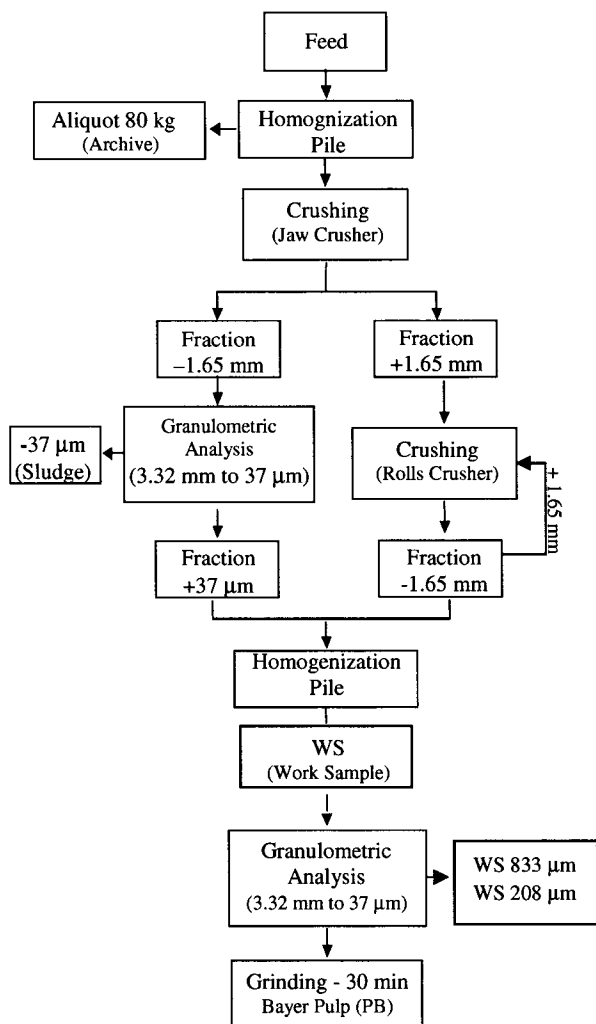


Figure 2. Block diagram of the stages used in the beneficiation of bauxite samples.

2 – Chemical and Mineralogical Characterization

The bauxite ore was submitted to chemical and mineralogical analysis with the use of: X-ray diffraction, infrared spectroscopy and X-ray fluorescence.

During the ore dressing tests, four different samples were obtained: a work sample (WS) obtained after crushing, two work sample fractions (833 and 208 μm) and the sludge (-37 μm fraction obtained after desliming of the -1.65 mm fraction). These samples were submitted to the same characterization techniques of the crude sample.

The BP sample (the sample ground to the Bayer process requirement) was characterized with the same techniques used in the crude sample followed by potentiometric titration, flame atomic absorption spectrometry, thermal analysis and scanning electron microscopy.

2.1 – X-Ray Diffraction (XRD)

Samples were examined by XRD in a Bruker-AXS D5005 diffractometer, with Co K α (35 kV/40 mA) radiation, 0.02° goniometer velocity and 2 θ by path with 1 s by path counting time and data collected from 5 to 80° 2 θ .

2.2 – Infrared Spectroscopy (IR)

Infrared spectra (FTIR) was performed in a Nicolet Magna 750 Fourier transform spectrometer, from 4000 to 400 cm⁻¹, with resolution of 4 cm⁻¹, with sample mounting using KBr discs.

2.3 – X-Ray Fluorescence (XRF)

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

2.4 – Thermal Analysis (DTA/TGA)

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

2.5 – Determination of Available Alumina and Reactive Silica

The method to determine the amount of available alumina (the amount that will be refined to obtain Al₂O₃ in the Bayer process) and the amount of 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 alumina, a 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 an HCl solution. Then, a KF solution was added and back titration was carried out. Afterwards, an excess of HCl in the standardized solution was

titrated with a NaOH standardized solution. The solid phase, resulting from ore digestion stage, was dissolved in an HNO₃ solution [5]. The concentration of reactive silica was determined by flame atomic absorption spectrometry (FAAS).

2.6 – 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.

2.7 – Scanning Electron Microscopy (SEM)

Bauxite morphology was determined by scanning electron microscopy in high vacuum SEM (Leica/F440). The sample was embedded in resin epoxy and polished. The resin was covered again by vaporized carbon to be used as a conductor.

Results and Discussion

In this work, the fraction of crystallized amorphous bauxite (CAB) was characterized and the results were compared with crystallized bauxite (CB). The mineralogical phases that compose the crystallized bauxite (CB) were determined by X-ray diffraction (XRD), Figure 3. Therefore, this bauxite is essentially gibbsitic and is associated with kaolinite (Al₄(Si₄O₁₀)(OH)₈ and hematite (αFe₂O₃).

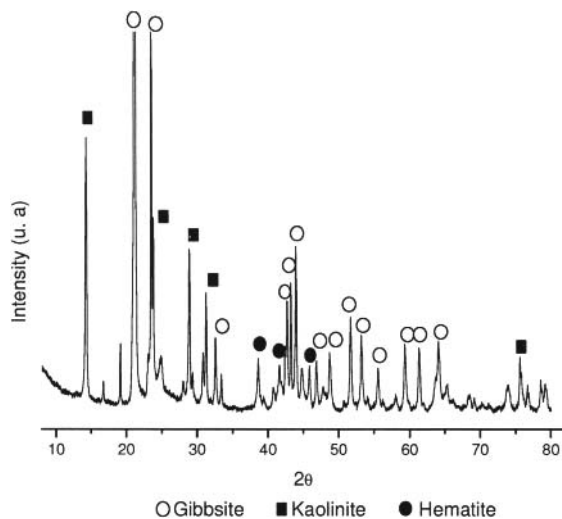


Figure 3. XRD of crystallized amorphous bauxite (CAB)

Infrared spectroscopy was used as a support to the XRD results. The infrared spectra analysis of crystallized amorphous bauxite (CAB), Figure 4, shows the bands related to the stretching vibration of Al–O–H groups observed at around 3620 cm⁻¹. This band is related to gibbsite and kaolinite minerals [9]. The bands around 3526, 3460 and 3390 cm⁻¹ are assigned to O–H stretching of gibbsite. The band at 914 cm⁻¹ is due to Al–O–H group deformation vibration [10], the bands observed around 1.100–1.030 cm⁻¹ are related to the deformation vibrations of OH and are characteristic a gibbsite bauxite ore [11]. Bands appearing at around 450, 540, 660, 1100 cm⁻¹ are assigned to the Si–O

vibration [9, 12,13] and the bands near 3695 are attributed to OH stretching of kaolinite [14].

In order to compare the mineralogical phases between CAB and CB, it is possible to observe that in CB there are more phases related to iron minerals, such as aluminum-goethite (α(Fe,Al)OOH), goethite (FeOOH) and hematite (αFe₂O₃) [7] than in CAB. These results are associated with the distribution of the layers in the bauxite’s profile since the CB layer is near the NB layer, which is composed essentially of iron minerals. For the dissolution of gibbsitic bauxite, the temperature in the Bayer process must be between 140-150°C. At this temperature the iron minerals are inert and do not react during the process.

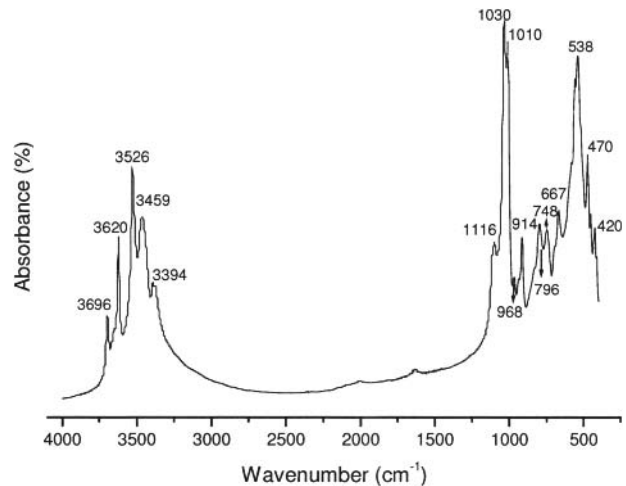


Figure 4. Infrared spectra of CAB bauxite

In order to determine the sample’s chemical composition and how its content varied after ore dressing, XRF analysis was carried out, Table I.

Table I. Chemical composition of the bauxite ore

Samples	Components (% in mass)				
	Al ₂ O ₃	Fe ₂ O ₃	MnO	SiO ₂	SO ₃
Bauxite Ore	46.06	14.64	0.03	9.11	-
WS	53.10	8.77	0.04	9.08	-
WS 833 μm	56.54	2.25	-	5.86	-
WS 208 μm	50.70	10.77	0.15	11.70	-
Sludge	40.94	12.95	-	35.70	0.13
Samples	Components (% in mass)				
	TiO ₂	WO ₃	ZrO ₂	PF	Total
Bauxite Ore	1.84	-	0.22	28.10	100.00
WS	1.79	-	0.25	26.97	100.00
WS 833 μm	1.37	0.36	0.36	27.26	100.00
WS 208 μm	3.92	-	0.77	21.99	100.00
Sludge	2.03	-	0.28	7.97	100.00
WS: sample obtained after crushing (final product of ore dressing);					
Sludge: -37 μm fraction obtained from the removal of the -1.65 mm fraction					

The analysis of the results in Table 1, indicated a higher content of SiO₂ in the finer fractions than in the coarse fractions, whereas

the opposite behavior was observed in the content of Al_2O_3 . The same behavior could be observed in the CB bauxite. Nevertheless, the values of the chemical content are different because CAB has a higher amount of kaolinite than CB, according to its geological profile [7]. However, in order to evaluate such behavior in relation to the contents of available alumina and reactive silica responsible for the consumption of NaOH and the formation of desilication product (DSP) by the Bayer process, a chemical analysis by potentiometric titration and flame atomic absorption spectroscopy was carried out. These analyses were done after adjusting the CAB sample to the Bayer process.

The grinding study showed that after a period of 20 min., the bauxite particle size distribution was similar to the optimum particle size for the Bayer process. The grinding curve, Figure 5, showed that around 90% of the particles had grain size lower than 0.208 mm and 50% under 0.043 mm.

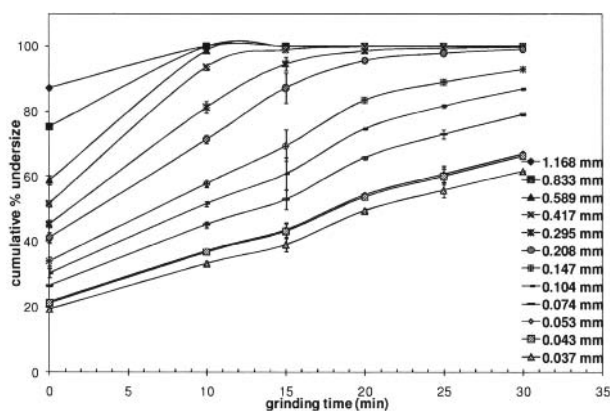


Figure 5. Grinding curve of CAB bauxite.

The time used to mill CAB was shorter than the time used to mill CB, at 20 and 30 min., respectively [5]. This result was in agreement with the results obtained from XRF, since this analysis showed that in CAB there was a larger amount of finer particles when compared with the CB. Considering that the finer fractions were composed essentially of kaolinite, according to the XRD and IR results, the time of mill was short because this mineral presented particle size smaller than $43 \mu\text{m}$.

After adjusting the CAB sample to the Bayer process requirement (20 minutes of grinding), this bauxite was characterized by thermal and chemical analysis. The chemical analysis used the following techniques: potentiometric titration and flame atomic absorption spectroscopy.

Thermal analysis of the bauxite varied according to the sample's origin, impurities and crystallinity. Thus, thermal analysis (DTA/TGA) was carried out in this work as a complementary technique to XRD, IR, XRF and chemical analysis, in order to obtain a complete characterization as well as a better knowledge of the rock that composes the geological profile of NE Pará [4, 5, 7].

According to the results obtained through DTA/TGA for the CAB sample to the Bayer process (Figure 6) three events were observed:

i. The first event was related to $\text{Al}(\text{OH})_3$ dehydroxylation, with the formation of a $\text{AlO}(\text{OH})$ and $\chi\text{-Al}_2\text{O}_3$ mixture [7].

ii. The second one corresponded to $\alpha\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ dehydroxylation, since among the mineralogical phases identified through XRD, this was the only phase where it could be decomposed at such temperature [7].

iii. The third event was related to a $\text{AlO}(\text{OH})$ dehydroxylation combination formed in the first event and $(\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_8)$ dehydroxylation [7].

Table II contains the data related to the samples' mass loss obtained to the Bayer process sample (BP) to both bauxites. Results analysis showed a bigger mass loss related to the first and third events. These results can be explained based on explanations i and iii [7].

In order to evaluate Table II, it can be observed that the CAB bauxite had a larger mass loss related to the third event (kaolinite) when compared with the CB bauxite. An opposite behavior was observed for the mass loss related to alumina (first and third events), in which CB presented a larger mass loss than CAB. These results were in agreement with those obtained through XRD, IR and XRF, which showed that the DTA/TGA analysis could be used to observe the relationship between gibbsite and kaolinite in bauxites.

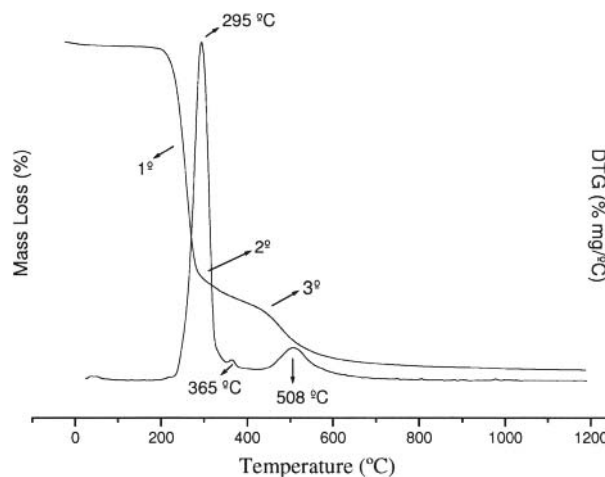


Figure 6. DTG/TGA of Bauxite Ore.

Table II. Mass loss related to thermal events of CAB and CB samples.

Samples	Mass Loss (%)			
	Events			
	1 st	2 nd	3 rd	
	$\text{Al}(\text{OH})_3$	Fe_2O_3^*	(AlOOH)	$\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$
CAB BP	18.4	2.0	3.7	2.1
CB BP	21.0	1.2	4.2	1.8

BP: sample ground to Bayer process.
*To CABA $\alpha\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$
*To CB ($\alpha(\text{Fe,Al})\text{OOH}$)

Thermal analysis results were in accordance with those obtained through the chemical analysis for available alumina and reactive silica, 41.7% and 7.1%, respectively (Table III). The ratio between Al_2O_3 available and SiO_2 reactive in the CB bauxite was 8:1. When this ratio is below the conditions recommended by the Bayer process, 10:1, it causes a reagents and products loss during the process of bauxite dissolution. Therefore, CAB cannot be used in the Bayer process because its ratio is 6:1 and it provides a high loss to the process.

Table III. Chemical contents of Al_2O_3 available and SiO_2 reactive of CAB and CB samples by potentiometric titration and atomic absorption.

Samples	Chemical Analysis	
	(% in mass)	
	Al_2O_3 available ($s \leq 0.3\%$)	SiO_2 reactive ($s \leq 0.1\%$)
CAB BP	41.7	7.1
CB BP	47.5	5.9

BP: sample ground to Bayer process.

Scanning electron microscopy (SEM) was used to support the aforementioned analyses. Figure 7 illustrates the SEM of the Bayer process sample. This sample was divided into two different particles: pure gibbsite with smooth surface (A) and gibbsite associated with kaolinite particles with rugous surface (B).

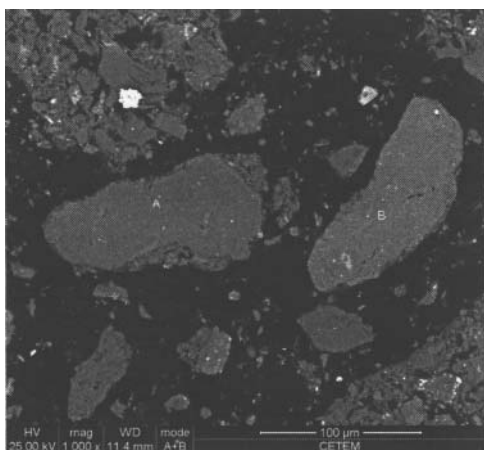


Figure 7. Scanning electron microscopy imaging of the CAB BP sample: (A) pure gibbsite and (B) gibbsite associated with kaolinite.

With the use of EDS (Energy Dispersive Spectrometer), Figure 8A and 8B to gibbsite particle and gibbsite with kaolinite, respectively, it was possible to observe the semiquantitative composition of those minerals.

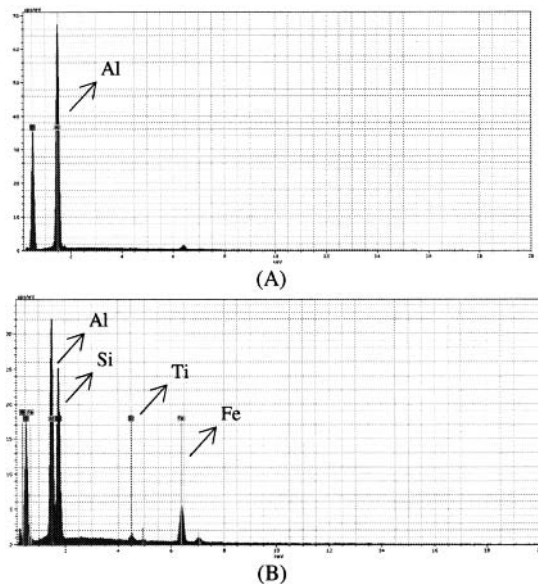


Figure 8. Energy Dispersive Spectrum to the CABA BP sample: (A) pure gibbsite and (B) gibbsite associated with kaolinite.

After the ore dressing stages, it was possible to observe that the prepared sample for the Bayer process had kaolinite particles associated with gibbsite through a physico-chemical interaction as well as in the finest fractions that comprised the sample.

Conclusion

The ore dressing stages aimed at the adaptation and characterization of the fractions that compose the bauxite sample of NE Pará that is not currently used in the Bayer process. According to the results, the sample was adjusted to the Bayer process (BP) requirements after crushing stages, screening, removal of fine fractions and 20 minutes of grinding.

XRD indicates the mineralogical composition of this bauxite. Therefore, the studied bauxite is essentially gibbsitic and is associated with the minerals kaolinite and hematite.

XRF provided information related to the chemical composition of the sample, but did not inform the chemical content of Al_2O_3 available and SiO_2 reactive making it necessary a chemical analysis by potentiometric titration and flame atomic absorption spectroscopy.

Thermal analysis helped us confirm the events related to dehydroxylation of the components presented in the sample: gibbsite, hematite and kaolinite.

The contents of Al_2O_3 available and SiO_2 reactive in the sample were 41.7 and 7.1%, respectively. The ratio between Al_2O_3 available and SiO_2 reactive was below the quantity recommended for the Bayer process (10:1). Thus, the 6:1 rate caused a lot of loss in the process.

This work has allowed us to understand why CAB bauxite is not used in the Bayer process. The reason is related to the high amount of reactive silica. This problem is likely to be associated with the presence of gibbsite particles associated with kaolinite

particles, possibly, by a chemical surface interaction, even after the ore dressing steps.

Acknowledgments

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