

MECHANOCHEMICAL ACTIVATION OF BAUXITE

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Abstract

The crystallized layer that compounds the bauxite's geological profile from NE Pará was ore dressed through the processes of crushing, screening, washing and grinding, in order to reach the same size distribution of that in the alumina production industry. After the preparation process, the sample (90%, < 0.21 mm) containing 5.3% reactive silica and 47.2% available alumina was submitted to mechanochemical activation with different kinds of reagents (CaO, Ca(OH)₂, CaCO₃, CaO+HCl), in different concentrations, which resulted in the formation of a calcium aluminum hydrosilicate (hydrogarnet). This phase was formed in the first 30 min of grinding with the use of CaO and Ca(OH)₂. However, chemical characterization showed that the principal phase obtained, katoite hydrogarnet, had high aluminum content in its chemical composition thus proving that its formation is not good for the Bayer process.

Introduction

Bauxite from Northern Brazil is characterized by a geological profile that consists of five layers with different forms of crystallization: nodular, crystallized nodular, crystallized, crystallized-amorphous and amorphous [1], whose contents of iron, gibbsite and kaolinite vary according to the profile's depth [1, 2, 3]. The content of iron is higher at the top of the outcrop than at the bottom whereas an opposite behavior is observed for the content of kaolinite [4, 5].

Among the layers that compound this geological profile, only the fraction called crystallized bauxite is used by the Bayer process [2, 4, 6] and its ore dressing consists of crushing, semi-autogenous grinding, washing, hydrocyclone classification and thickening [6]. However, this process does not remove all the reactive silica (kaolinite) present in the bauxite.

The lack of processes capable of removing kaolinite, the largest carrier of reactive silica, limits, significantly, the reuse of several aluminum ores, as it happens in the nodular, crystallized nodular, crystallized-amorphous and amorphous layers [3]. Moreover, the reutilization of such aluminum ores would mean that bauxite reserves in Brazil could be doubled [7].

It is believed that the removal of the remaining kaolinite after washing is possible through physical and/or physicochemical processes of beneficiation, in which the steps of washing and screening, flotation of gangue minerals, and mechanochemical activation can be used, among others [2, 7, 8, 9].

Mechanochemistry is a field that studies materials science and solid state chemistry, where chemical reactions happen due to the deformation and breakage of such solids when activated by means of a mechanical power, i.e., grinding [10], which allows the occurrence of chemical reactions considered difficult or impossible with the use of conventional routes [11, 12].

Mechanochemical studies with bauxites were carried out by [11, 13, 14, 15].

[13, 15] studied the removal of reactive silica from bauxites by adding CaO. The authors claimed that the process consisted in the formation of two compounds of the hydrogarnet type, hydrated grenades, calcium-aluminum-hydrosilicate (Ca₃Al₂(SiO₄)(OH)₈) and calcium-aluminum-iron-hydrosilicate (Ca₃AlFe(SiO₄)(OH)₈). According to them, these compounds converted the contents of reactive silica and iron present in the bauxite into a non-reactive and stable compound before adding NaOH in the digestion stage of the Bayer process, thus reducing the consumption of alumina and NaOH. However, the results obtained by Picaro and McCormick are doubted by other authors [9, 11]

[14] studied the mechanochemical activation of bauxites with a high content of reactive silica, diasporite (γ -AlO(OH)) and boehmite (α -AlO(OH)), by adding Na₂O (sodium oxide). Boehmite bauxite was composed by low contents of gibbsite, chlorite and mica, and diasporite was associated with the minerals goethite, hematite and gibbsite. According to the results, the mechanochemical activation of bauxite minerals promoted a structural deformation that affected the O-H bond of the boehmite bauxite after 5 min. activation. This result was important because it allowed this bauxite, after activation, to undergo dissolution in contact with NaOH thus increasing the amount of Al₂O₃ drawn by the Bayer process, which did not happen before the mechanochemical activation.

The same result was found for diasporite bauxite. Thus, diasporite became more reactive after the mechanochemical study. However, the highest extraction of Al₂O₃ obtained through mechanochemical activation occurred in the boehmite bauxite. [11] evaluated the behavior of gibbsite and boehmite bauxites in the Bayer process, with and without mechanochemical activation. According to X-ray diffraction (XRD) results, the content of reactive silica before and after mechanochemical activation, in contact with CaO, was the same and there were no changes in the peaks related to kaolinite. This result showed that the formation of the hydrogarnet compound did not occur, as mentioned by [13, 15]. However, mechanochemical activation was important once

kaolinite's dissolution time was shorter. Therefore, this study pointed out that, by activating bauxite through mechanochemistry, it facilitated the exposure of the kaolinite's surface, its reaction and, consequently, a shorter residence time for the precipitation of DSP. This DSP showed an amount of reactive silica higher than expected.

According to the aforementioned works, mechanochemical activation of bauxite provides the Bayer process with a lower reagent consumption (NaOH) and less product loss ($\text{Na}_2\text{OAl}_2\text{O}_3$), be it through the formation of an insoluble compound or through the shorter residence time for the precipitation of DSP.

Within this context, the aim of this work was to perform the mechanochemical study of crystallized bauxite (CB) using different reagents (CaO, $\text{Ca}(\text{OH})_2$, CaCO_3 and $\text{CaO}+\text{HCl}$), through the steps of grinding, seeking to form a compound that would incorporate reactive silica and become insoluble during the Bayer process.

Materials and Methods

1 – Sample Preparation

The layer of crystallized bauxite from Northern Brazil was beneficiated according to the methodology described in [5]. The improvement stages were crushing, washing and grinding.

Particle size distribution of this bauxite was based on industrial transport conditions of the bauxite pipeline and on the Bayer process conditions, where particle size distribution in 90% of the particles were with a grain size lower than $208\ \mu\text{m}$ and 40% under $43\ \mu\text{m}$ [4]. Therefore, grinding times for crystallized bauxites took 30 minutes and this sample was called Bayer pulp (BPCB).

2 – Mechanochemical Activation

After the sample fit the Bayer process conditions, mechanochemical activation was initiated through grinding of the Bayer pulp (BPCB) with different reagents and in different concentrations. Grinding was carried out following the methodology described in [4], for 180 min. Aliquots were removed every 30 min. to verify the pulp's pH, followed by the steps of sieving, drying and studies of characterization.

The conditions used in the tests of mechanochemical activation are summarized in Table 1.

2 – Characterization

Samples obtained after mechanochemical tests were characterized through X-ray Diffraction (XRD), Infrared Spectroscopy (IR), Scanning Electron Microscopy (SEM) and chemical analysis (potentiometric titration and atomic absorption).

2.1 – X-ray Diffraction (XRD)

Samples were examined by XRD in a Bruker-AXS D5005 diffractometer, with $\text{Co K}\alpha$ (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 $80^\circ 2\theta$.

Table 1. Conditions used in the tests of mechanochemical activation

| Tests | Reagents | Concentrations (%m/m) | Activation Time (min.) | Initial pH |
|-----------------|--------------------------|-----------------------|------------------------|------------|
| Grinding | | | | |
| 1 | CaO | 4 | 180 | 12.60 |
| 2 | | 7 | 180 | 12.53 |
| 3 | | 9 | 180 | 12.29 |
| 4 | | 12 | 180 | 12.32 |
| 5 | $\text{Ca}(\text{OH})_2$ | 4 | 180 | 12.48 |
| 6 | | 7 | 180 | 12.61 |
| 7 | | 9 | 180 | 12.53 |
| 8 | | 12 | 180 | 12.35 |
| 9 | CaCO_3 | 4 | 180 | 7.80 |
| 10 | | 7 | 180 | 7.83 |
| 11 | | 9 | 180 | 7.52 |
| 12 | | 12 | 180 | 7.79 |
| 13 | CaO + HCl | 4 + 272 mL at 8 mol/L | 180 | 10.67 |
| 14 | | 7 + 515 mL at 8 mol/L | 180 | 9.91 |

2.2 – Infrared Spectroscopy (IR)

Infrared spectra (FTIR) was performed in a Nicolet Magna 750 Fourier transform spectrometer, from 4000 to $400\ \text{cm}^{-1}$, with resolution of $4\ \text{cm}^{-1}$, using KBr disc.

2.3 – Scanning Electron Microscopy (SEM)

Bauxite samples were embedded in epoxy resin and then polished to obtain a smooth edge. This way, particles' morphology was determined through a Leica scanning electron microscope, model F440, high vacuum mode. Samples were analysed by back-scattered electrons.

The scanning electron microscope was coupled with an energy dispersive spectrometer (EDS) to allow the qualitative determination of chemical elements.

2.4 – Determination of Available Alumina and Reactive Silica

The method for the determination of available alumina (the amount to be refined to obtain Al_2O_3 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, 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 a 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 ore digestion, was dissolved in a HNO_3 solution [4]. The concentration of reactive silica was determined by flame atomic absorption spectrometry (FAAS) [4].

2.5 – 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.

Results and Discussion

The study of mechanochemical activation was carried out aiming to convert reactive silica, present in bauxite, into a non-reactive and stable compound before the addition of NaOH in the digestion step of the Bayer process, thus reducing the consumption of sodium hydroxide and sodium aluminate.

The results for mechanochemical activation tests in aqueous medium, developed by [4], were employed to evaluate if using a grinding time above that determined for the Bayer process would cause mineralogical changes or significant alterations in the crystalline structure of the phases present in this bauxite. It was observed that in the time interval 210 min., the pulp's pH varied from 6.46 (BPCB) to 7.04 (210 min. grinding) and the temperature ranged from 29 to 34°C. By examining the diffractograms for the products of this grinding at different times, no significant variations were proven in the phases gibbsite and kaolinite present in this bauxite sample.

Therefore, tests with the addition of different types of reagents were performed, as described in Item 2 and Table 1. In this study, the parameters considered were the variation in the concentration of reagents and the pulp's pH. The aim of these tests was to promote the dissolution of kaolinite before that of gibbsite to favor the formation of a hydrogarnet phase with a higher content of silica. It is worth mentioning that only the results that presented relevant data were taken into account.

Tests began by grinding the BPCB sample with CaO. During activation, it could be observed through XRD the formation of a new phase (Figure 1), with peaks at 20.06 and 37.09° (2θ). According to the literature, this phase was the hydrogarnet katoite (Ca_{2,93}Al_{1,97}(Si_{0,64}O_{2,56})(OH)_{9,44}) (CRYSMET 2009, code 49772) [16]. This compound was formed in the first 30 min. of grinding, according to the chemical reaction, Equation 1.

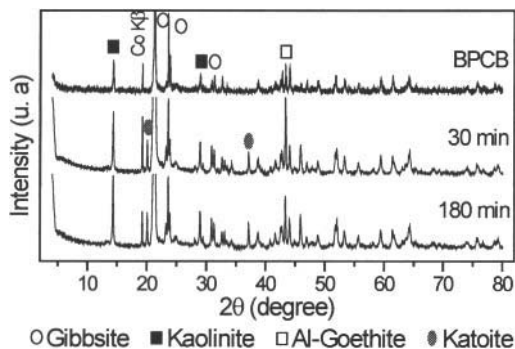
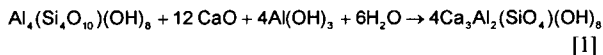


Figure 1 – X-ray diffractograms for the samples obtained after grinding BPCB bauxite with 4% m/m of CaO at 30 and 180 min. Radiation Co K α .

In order to reinforce the results obtained through XRD, infrared spectroscopy (IR) and scanning electron microscopy coupled with EDS were used as complementary techniques. According to IR results, Figure 2, it can be observed the appearing of a band near 3.660 cm⁻¹ attributed to the OH stretching of katoite, formed at 30 min. of grinding, corroborating the XRD data.

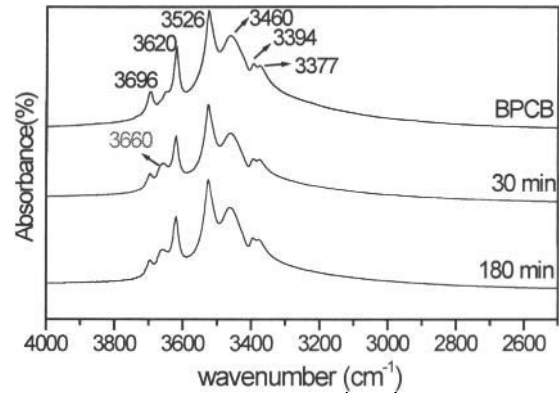


Figure 2 – Infrared spectroscopy for the samples obtained after grinding BPCB bauxite with 4% m/m CaO at 30 and 180 min.

By using SEM coupled with EDS, it was possible to observe the formation of a particle constituted by the elements Al, Si and Ca, Figure 3. This particle could be attributed to the katoite phase obtained during mechanochemical activation. It is important to mention that the katoite particles were found isolated and not associated with other particles.

Therefore, the combination of XRD, IR spectroscopy and SEM/EDS allowed to confirm the formation of the katoite phase after 30 min. of grinding. However, they did not provide the amount of kaolinite and/or of gibbsite that was incorporated to the phase formed. Thus, it became necessary to perform chemical analysis for Al₂O₃ available and SiO₂ reactive. The data, Table 2, indicated that both the content of Al₂O₃ available and that of SiO₂ reactive decreased with grinding. Moreover, it could be affirmed that the formation of the hydrogarnet compound (grinding with 4% m/m of CaO), took up approximately 17% of alumina and 29% of silica.

It was observed that there was a consumption of silica higher than that of the alumina in the formation of the hydrogarnet. However, the consumption of alumina was higher than expected, indicating the formation of a hydrogarnet phase with a high content of aluminum (katoite). Thus, the formation of this phase implied a high consumption of gibbsite, as shown in Equation 1.

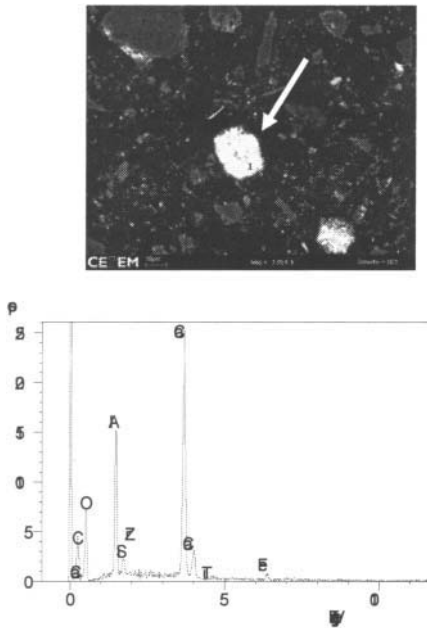


Figure 3 – Image for the particle constituted by Ca-Al-Si, formed through grinding BPCB sample with 4% m/m of CaO for 30 minutes, obtained through scanning electron microscopy by secondary electrons, coupled with EDS.

Table 2 – Contents of Al_2O_3 available and SiO_2 reactive for the samples obtained during mechanochemical activation of BPCB bauxite with 4% m/m of CaO.

| Samples | pH | Al_2O_3 available | SiO_2 reactive |
|---------|-------|---------------------|------------------|
| | | (%) | |
| BPCB | 6.85 | 47.5 | 5.9 |
| 30 min | 12.60 | 40.7 | 4.2 |
| 180 min | 12.52 | 40.1 | 4.5 |

It is important pointing out that the same behavior was observed for the concentrations of CaO 7, 9 and 12% m/m., i.e., a high consumption of available alumina that became higher as the reagent concentration increased. On the other hand, the content of reactive silica could not be measured for results showed disparities. Such behavior was due to the possibility of katoite dissolution by HNO_3 during the chemical analysis for reactive silica, as described in item 2.4. Table 3 shows that the contents of available alumina decreased as the concentration of CaO increased.

Table 3 – Contents of Al_2O_3 available for the samples obtained during mechanochemical activation of BPCB bauxite with CaO in concentrations 7, 9 and 12% m/m.

| Samples | CaO (%m/m) | pH | Al_2O_3 available (%) |
|----------|------------|-------|-------------------------|
| 30 min. | 7 | 12.60 | 35.6 |
| 180 min. | | 12.58 | 35.2 |
| 30 min. | 9 | 12.29 | 32.4 |
| 180 min. | | 12.47 | 32.4 |
| 30 min. | 12 | 12.32 | 32.9 |
| 180 min. | | 12.65 | 28.7 |

Figure 4 shows X-ray diffractograms for the test of mechanochemical activation of bauxite with CaO in concentrations 4, 7, 9 and 12% m/m. According to the results, the peaks related to the katoite compound (20.06, 30.87, 37.09, 45.86, 52.01° (2 θ)) became more intense as CaO concentration increased.

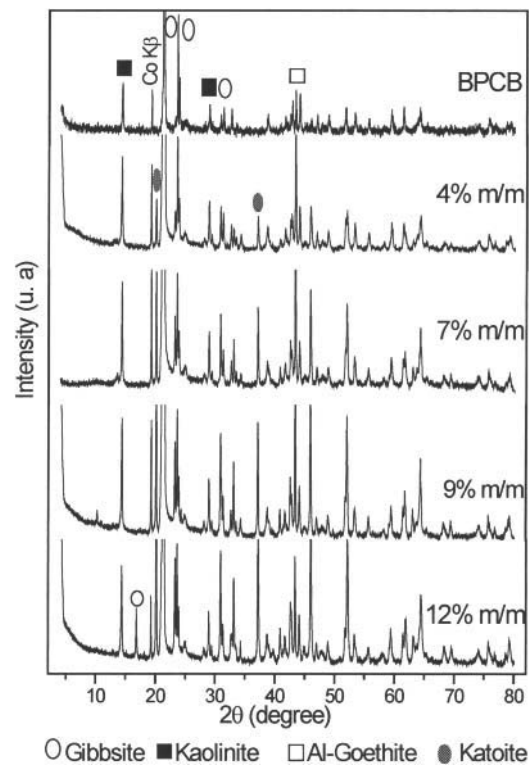


Figure 4 – X-ray diffractograms for samples obtained after grinding BPCB bauxite with 4, 7, 9 and 12% m/m at 30 min. Radiation Co K α .

In order to form a hydrogarnet phase that would take a smaller amount of alumina, like hibschite, grinding studies were carried out using the following reagents: $Ca(OH)_2$, $CaCO_3$, in the same concentrations (m/m) of the tests run with CaO and CaO + HCl. The aim in using these reagents was to reduce the pH of reaction thus avoiding gibbsite dissolution.

The pulp that was formed after mechanochemical activation with $\text{Ca}(\text{OH})_2$ presented a pH value near that obtained by using CaO . $\text{Ca}(\text{OH})_2$ was used for it has higher solubility in aqueous medium than CaO . This reaction could favor the formation of the desired hydrogarnet, the hibschite, $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$, whose X value can vary between 1.5 and 3. Thus, the investigation of the data obtained through XRD, Figure 5, revealed the formation of katoite and results for chemical analysis of Al_2O_3 available, Table 4, showed a significant consumption of available alumina due to the formation of katoite hydrogarnet.

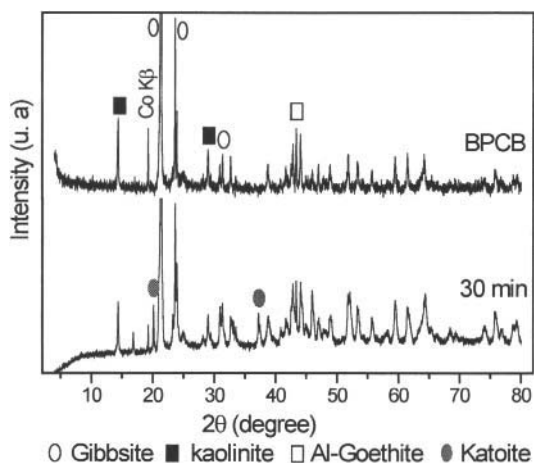


Figure 5 – X-ray diffractogram for sample obtained after grinding BPCB bauxite with 4% m/m of $\text{Ca}(\text{OH})_2$ at 30 min. Radiation $\text{Co K}\alpha$.

Table 4 – Contents of Al_2O_3 available for samples obtained during mechanochemical activation of BPCB bauxite with $\text{Ca}(\text{OH})_2$ in concentrations 4, 7, 9 and 12% m/m.

| Samples | $\text{Ca}(\text{OH})_2$ %m/m | pH | Al_2O_3 available (%) |
|----------|-------------------------------|-------|---------------------------------------|
| 30 min. | 4 | 12.48 | 39.0 |
| 180 min. | | - | - |
| 30 min. | 7 | 12.61 | 37.5 |
| 180 min. | | 12.15 | 37.0 |
| 30 min. | 9 | 12.53 | 36.6 |
| 180 min. | | 12.46 | 36.5 |
| 30 min. | 12 | * | 33.0 |
| 180 min. | | * | 32.8 |

* no electrode answer

Mechanochemical activation with CaCO_3 did not favor the formation of a hydrogarnet phase. The pulp's pH, after activation, was approximately 8.0. A peak in the XRD at 34.29° (2θ) was attributed to calcite, Figure 6, which indicated that the reagent was not totally solubilized thus not favoring the conditions to form the desired species.

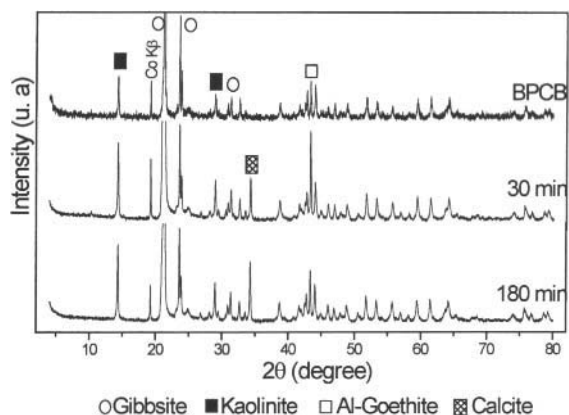


Figure 6 – X-ray diffractogram for samples obtained after grinding BPCB bauxite with 4% m/m of CaCO_3 at 30 and 180 min. Radiation $\text{Co K}\alpha$.

After evaluating mechanochemical activation at pH values near 12, by using CaO and $\text{Ca}(\text{OH})_2$, and at values near 8, by using CaCO_3 , new tests were carried out to keep the pulp's pH below 12 and above 8 in order to favor the formation of the hibschite hydrogarnet. Thus, the mechanochemical study was performed with the BPCB sample in the presence of a CaO pulp with pH adjusted with HCl . After activation, the pH values reached 11.70 (4% m/m of CaO and 272 mL of HCl 8 mol/L) and 9.90 (7% m/m of CaO and 515 mL of HCl 8 mol/L). According to XRD results, Figure 7, the katoite phase was not formed which indicated that the formation of hydrogarnets occur at a pH value higher or near 12.

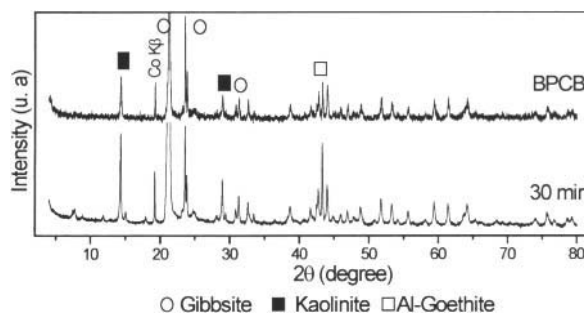


Figure 7 – X-ray diffractogram for sample obtained after grinding BPCB bauxite with $\text{CaO} + \text{HCl}$ (4% m/m + 272 mL of HCl 8 mol/L) at 30 min. Radiation $\text{Co K}\alpha$.

Conclusion

The mechanochemical study of CB bauxite led to the formation of katoite hydrogarnet, which presented high aluminum content in its chemical composition. This compound was formed in the first 30 minutes of grinding, at pH values higher than 12. However, none of the conditions used in the mechanochemical activation led to the formation of a hydrogarnet phase with a lower content of aluminum. Therefore, the formation of katoite hydrogarnet during mechanochemical activation in the presence of calcium compounds makes this approach unfeasible for the reduction of reactive silica in the bauxite from Northern Brazil.

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