

## Kaolinite Reduction on Bauxite through Mechanochemical Activation with Lime

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### Abstract

Bauxite is the primary ore for metallic aluminium production, consisting of aluminium, iron oxides, and kaolinite, a clay mineral commonly found in Amazonian bauxites, as the main carrier of reactive silica. Kaolinite is especially relevant in this context as it reacts with sodium hydroxide in the Bayer process, increasing reagent consumption. This work aimed to investigate the inertization of this silica through the mechanochemical activation of bauxite with lime. The study was conducted in a bench ball mill with different lime dosages. Hydrogarnet formation was observed in conditions with lime dosages higher than 0.5 %. Reactive silica concentration was reduced from 4.1 % to 3.4 % on the conditions when hydrogarnets were formed. In contrast, when lime dosages were increased, the available alumina concentration was decreased from 47.4 % without mechanochemical activation to 47.2 % and 45.6 % with 0.5 % and 2.0% lime dosage, respectively. Among the evaluated scenarios, the better balance between achieving reactive silica reduction through the formation of grossular, and minimizing the impacts in available alumina grade, with minimum formation of katoite, was obtained with 0.5 % lime dosage.

**Keywords:** Bauxite, Mechanochemical activation, Reactive silica, Lime, Hydrogarnet.

### 1. Introduction

Kaolinite, a common impurity in Amazonian bauxite, poses challenges during the Bayer process for alumina extraction due to its high reactivity and tendency to form undesirable by-products. The presence of kaolinite increases the consumption of caustic soda and generates more bauxite residue, complicating waste management and increasing operational costs [1,2].

Several technologies have been developed to reduce the impact of this reactive silica source on the process, primarily based on strategies for reducing the reactive silica content in the bauxite and modifying the process to lower soda consumption [3]. Despite promising results, most have not been implemented, indicating that the hurdles to implementation are mainly due to the specific characteristics of the different ores and plants.

By integrating lime into the mechanochemical activation process, researchers have demonstrated a significant reduction in kaolinite content, and thus reduced caustic consumption on Bayer process. This approach not only enhances the quality of the bauxite but also contributes to more sustainable and cost-effective production processes [3–7].

Mechanochemical activation is a process that enhances the reactivity of minerals through the application of mechanical energy. This technique has gained significant attention for its potential to improve the efficiency of mineral processing and material synthesis [8, 9]. When applied to bauxite, mechanochemical activation can notably alter its mineralogical composition, forming inert hydrogarnet phases in digestion conditions and reducing caustic soda consumption. Recent studies have highlighted the effectiveness of mechanochemical activation in reducing kaolinite content in bauxite by using different additives, with lime being particularly effective due to its chemical properties and availability [4-6].

Smith [3] argues that bauxite mechanochemical activation with lime could not be an economical way of reducing caustic losses due to a) the costs associated with the implementation of the ultra-fine grinding and downstream requirements for solid-liquid separation and b) costs associated with a high lime charge required (essentially based on McCormick et al. [4] data, in which > 9 % CaO on bauxite converted significant quartz into hydrogarnet). However, the context of Hydro's pipeline transported bauxite and low temperature alumina operations in Brazil is a particular case where there would be an opportunity to use this technology.

The bauxite processed in Paragominas must be subjected to grinding to adjust the particle size, ideally for its transport as pulp in the pipeline. The bauxite must be dewatered in hyperbaric filters before being fed to the process at the refinery [10, 11]. Also, the quartz content is minimal in the bauxite and often not detected in X-ray diffraction analysis. In contrast, the kaolinite content tends to increase over the years. An additional benefit would be the eventual pH increase of the bauxite pulp pumped in the pipeline, which is demonstrated to reduce pipeline corrosion and improve dewatering performance [11, 12].

In this context, this work aims to investigate the opportunity to reduce the kaolinite content in the bauxite by mechanochemical activation with lime, considering the actual Paragominas milling operation conditions.

## 2. Methodology

This study was developed using reagent grade CaO and two different Amazonian bauxite samples from Hydro Paragominas, a mine located northeast of Para state, Brazil. Over two distinct periods, incremental samples from the beneficiation plant grinding mill fresh feed were taken every 4 hours for five days. Each campaign's combined sample was homogenized and quartered in a rotary sample splitter to generate aliquots for further characterization and tests. The chemical composition of the bauxite samples is shown in Table 1.

**Table 1. Bauxite samples chemical composition.**

Element	Sample #1 (%)	Sample #2 (%)
Al <sub>2</sub> O <sub>3</sub> – Total	55.08	52.03
Available Alumina	50.57	47.37
SiO <sub>2</sub> – Total	5.13	4.71
Reactive Silica	4.25	4.14
Fe <sub>2</sub> O <sub>3</sub>	8.37	13.40
TiO <sub>2</sub>	1.56	1.69
Loss on ignition (LOI)	29.13	27.61

Two sets of tests were carried out. Sample #1 was submitted to a screening test covering a broader range of lime dosage, from 0 % to 16%. Sample #2 tests seek a finer tuning on lime dosage. It

was defined after the screening test covering the range between 0 % and 2 % of lime by weight. Testing conditions regarding lime dosage for Samples #1 and #2 are shown in Table 2.

**Table 2. Testing conditions, lime dosage (wt%).**

Sample #1	Sample #2
0.00	0.00
1.30	0.13
2.70	0.25
4.00	0.50
8.00	0.75
16.00	1.25
-	2.00

All samples were submitted to wet milling, with water, in a laboratory-scale tumbler ball mill for 20 minutes. The grinding conditions, described in Table 3, were defined aiming to reproduce Hydro Paragominas ball milling design and operational.

**Table 3. Testing conditions, grinding mill**

Diameter (cm)	30.48
Length (cm)	30.48
Total filling (%)	30.00
Ball charge (kg)	31
% of solids in weight	55.00
Bauxite charge (kg)	2.26
Water volume (L)	1.85
Mill speed (rpm)	56.60
Specific energy (kWh/t)	10.50

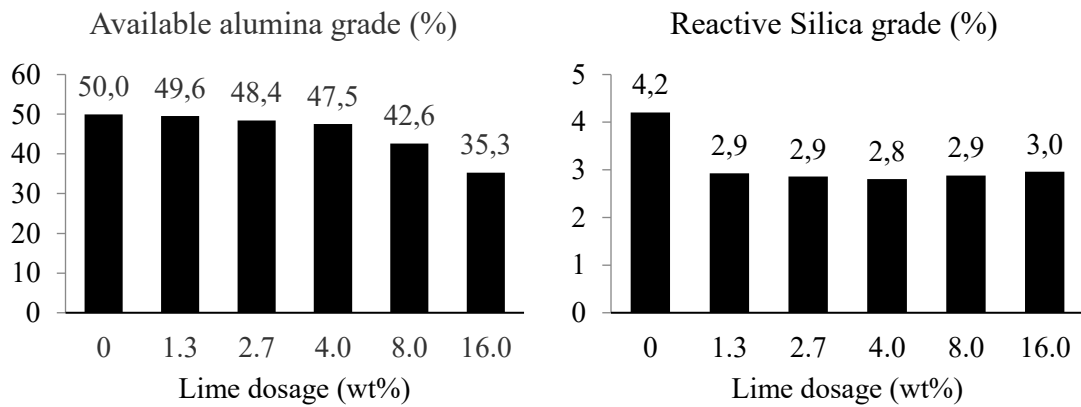
The products were dried and then subjected to chemical analysis using X-ray fluorescence and digestion at 145 °C to simulate the Bayer process and identify the grades of alumina and reactive silica available. Specific samples were analyzed by X-ray diffraction to determine the different phases present and support the investigation of patterns observed in the results.

### 3. Results and discussion

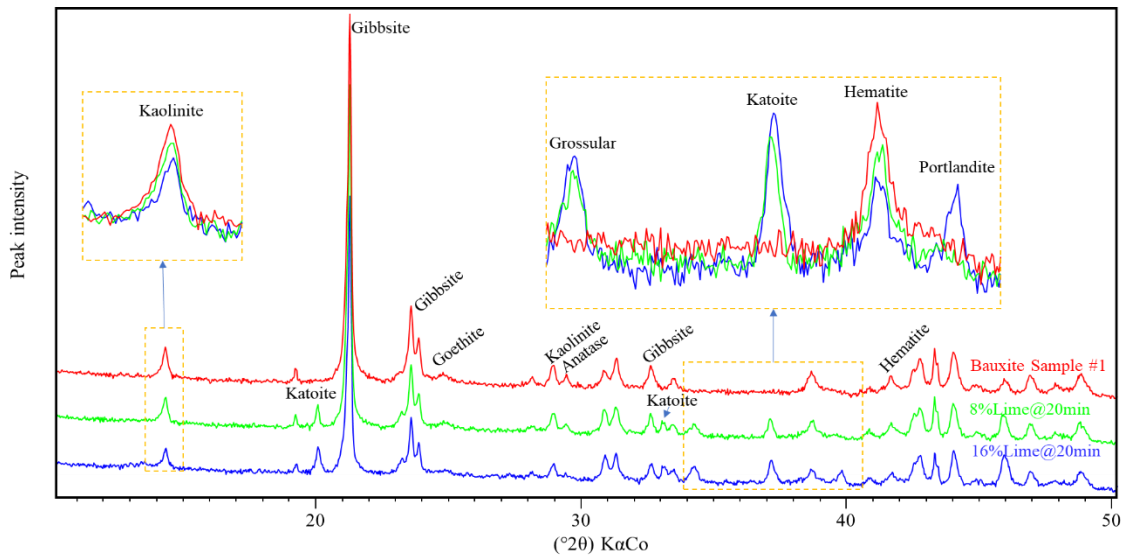
Available alumina and reactive silica grades of Sample #1 milled without lime and with different lime dosages are shown in Figure 1, respectively. A pattern of decreasing available alumina grade as lime dosage increases was observed. In contrast, a reduction of approximately 1.3 percentual points was observed for the lower lime dosage tested for reactive silica grade and remained constant for higher dosages.

The X-ray diffraction patterns of the bauxite Sample #1 and products from the mechanochemical activation with 8% and 16% lime are shown in Figure 2. The main phases of the raw bauxite – gibbsite, kaolinite, hematite, Al-goethite, and anatase remained present in the products. It is observed that at lower lime dosages, grossular ( $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$ ), a hydrogarnet with silica in the chemical structure, forms from the reaction of kaolinite with lime (see decreasing of kaolinite peak intensity in the highlighted box in Figure 2), reducing the reactive silica grade in the bauxite. At higher lime dosages, an increasing mass fraction of katoite ( $\text{Ca}_3\text{Al}_2\text{O}_6(\text{OH})_4$ ), a silica-free hydrogarnet, was observed, causing the reduction of available alumina grade in the bauxite likely due to the reaction of gibbsite with lime (as a slight decreasing of the gibbsite peaks

intensities are observed). In the diffractograms of samples with lime addition of 16 %, the presence of portlandite ( $\text{Ca}(\text{OH})_2$ ) indicates an excess of Ca source non-reacted with the bauxite.



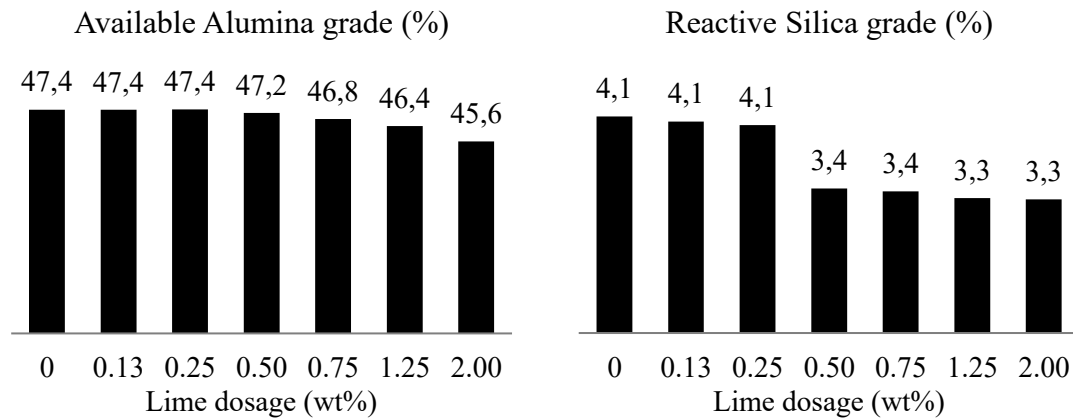
**Figure 1. Digestion results from different lime dosages with Sample #1: Left: Available Alumina grade, Right: Reactive Silica grade.**



**Figure 2. Comparison of the X-ray diffractograms of Sample #1 and the test products with lime dosages of 8 % and 16 %. Note: Diffractograms are depicted as stacked for better visualization, while in the highlighted boxes, they are shown as overlapped raw data to compare the peak intensities.**

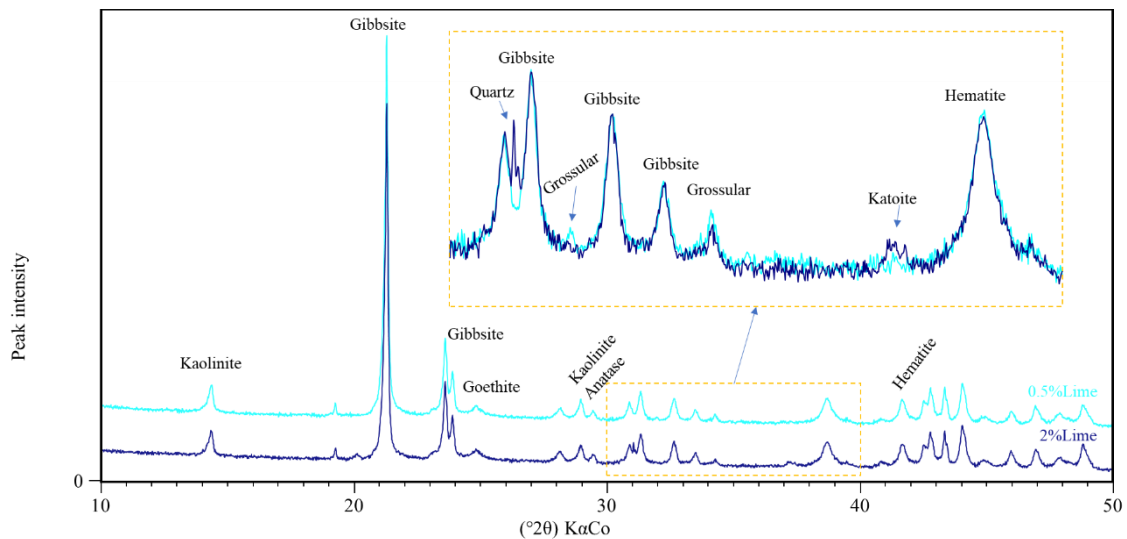
Tests with Sample #2 were carried out to seek an optimized lime dosage that maximizes grossular formation, promoting the reduction of the reactive silica content while minimizing the katoite formation (avoiding the reduction of available alumina grade). This optimized condition was based on the tests with Sample #1. Thus, a narrow lime dosage was defined between 0 and 2 %. Results of Available Alumina and Reactive Silica are depicted in Figure 3.

Comparing results of Sample #2 to #1 shows a similar graph pattern. The available alumina grade decreases as lime dosage increases. In contrast, reactive silica grade presents two different trends, one with higher silica in the absence and low lime concentrations and a second one with lower silica grade associated with higher lime dosages.



**Figure 3. Digestion results from different lime dosages with Sample #2: Left: Available Alumina grade, Right: Reactive Silica grade.**

Among the tested conditions, the better balance between achieving the desired reactive silica grade reduction and minimizing the undesired reduction on available alumina grade was found with a lime dosage of 0.5 %. A mineralogy comparison between the products with lime dosages of 0.5 % and 2 % is shown in Figure 4. It can be noticed that when the mechanochemical activation is carried out with 0.5 % of lime, grossular is the primary phase formed, while katoite is negligible. It suggests that katoite is a secondary phase formed in this system, and hence, any additional lime charge would react with the gibbsite, reducing the available alumina content or remaining unreacted and precipitating as portlandite (as observed in Figure 2).



**Figure 4. Comparison of the X-ray diffractograms of the test products with lime dosages of 0.5 % and 2 %. Note: Diffractograms are depicted as stacked for better visualization, while in the highlighted box, they are shown as overlapped raw data to compare the peak intensities.**

The results obtained on tests with Sample 1# and #2 shows that mechanochemical activation with lime could be a solution to reduce caustic losses from reactive silica in Amazonian bauxite through the formation of unreactive grossular hydrogarnets. The estimated reduction on caustic consumption at the refinery associated to mechanochemical activation with 0.5 % of lime is 5.4 kg/tonne of bauxite. Under the tested conditions there were alumina losses as dosage increased, further studies would be necessary to fine-tune lime dosage seeking to understand the mechanisms to minimize alumina loss.

The formation of insoluble calcium hydrogarnets in the present work is consistent with studies reported by other authors [4, 13], despite with lower lime dosage. Lime dosage of 0.5 % is one order of magnitude lower than the minimum dosage for hydrogarnet formation of 9 % reported by McCormick et al. [4] and 4 % reported by Santos et al. [13]. Further studies should be developed to understand whether this result is associated to the grinding condition with lower residence time in the present work or to other characteristics intrinsic to the different bauxite mineralogy.

#### 4. Conclusions

On laboratory-scale, bauxite mechanochemical activation with lime and water, reproducing the grinding conditions from Hydro Paragominas industrial plant, resulted in the formation of hydrogarnets, such as grossular and katoite. Katoite, an alumina substituted hydrogarnet was the predominant phase formed in higher lime dosages, resulting in relevant loss of alumina when lime dosages were higher than 0.5 %. Among the tested conditions, 0.5 % was the optimum lime dosage, reducing reactive silica grade by 0.7 percentual points, with only 0.2 percentual points reduction on available alumina grade.

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