PILOT TEST OF BAUXITE RESIDUE CARBONATION WITH FLUE GAS.
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Abstract
The Bayer process alumina production generates 0.7 to 2.0 ton of bauxite residue (BR) and an average of 1.0 ton of CO₂ per ton of alumina produced. The direct use of exhaust gases to react and reduce the alkalinity of BR may allow a triple gain: improve the storage conditions, open a range of new applications for BR and sequester from 33 to 102 kg of CO₂ per ton of alumina. This paper shows a pilot scale reaction of a suspension of bauxite residue in water with flue gas, produced from direct oil burning. Three different types of reactors were used: one spray tower and two packed columns. The inlet and exhaust gases were analyzed using electrochemical and non dispersive infrared sensors. The pH of the suspension was monitored during and after the reaction to evaluate the buffer effect.

Introduction
The alumina is mainly produced from the refining of bauxite by the Bayer process which consists in the extraction of aluminum oxide through its dissolution in caustic soda and the separation of insoluble residues. The bauxite residue (BR) although not particularly toxic, poses risks to the environment due to the large volume and its reactivity. According to the latest technology it is stored in sealed deposits specially constructed. To date the immense majority of the bauxite residue that has been produced was stored and were not incorporated into existing production processes to any significant amount with exception to some extent of the sintering process residue at Russia and China [1]. On the other hand, a strategic goal was set in 2010 by the Bauxite and Alumina Committee of the International Aluminium Institute (formed by most industries) to reuse 20% of BR in 2025 [2]. China has established the same objective for 2015[1]. This paper shows the design, construction and first results of a pilot plant for reaction of cooled flue gas without any previous treatment and BR. It shows tests and results of substantially reducing the reactivity of the bauxite residue by reaction with the gaseous effluents similar to the refining process. As an additional gain there is a reduction on the emission of carbon dioxide and sulfur dioxide. This pilot plant was designed to consume minimal power and use the effluent as efficiently as possible in different reactors from low cost to ultra high performance. The process is designed for minimizing the energy consumption and equipment investment.

Three models of test reactors were designed to pilot scale the reaction with the gases produced from burning fossil fuel. So far, 25 experiments were held and the results were analyzed with electrochemical cells and non dispersive infrared sensors. The smaller reactivity reduces the risk of storage as well as facilitates the use of BR in different applications [3-5]. However the neutralization behavior of the BR is highly complex. The buffering action of multiple alkaline solids makes the pH to continue changing with time after the completion of the experiment. For this reason, the pH evolution of the reacted BR was also monitored after the experiment in different conditions.

Bayer Process for Alumina Production
The Bayer process to obtain alumina from bauxite can be divided in four steps:

Digestion
The minerals containing aluminum at the bauxite are selectively extracted from the non soluble components through the dissolution in sodium hydroxide.

\[\text{Al(OH)}_3 + \text{Na}^+ + \text{OH}^- \rightarrow \text{NaAlO}_2 + 2\text{H}_2\text{O}\]  

Clarification
Crystalline aluminum trihydroxide “hydrate” is precipitated from the liquor.

\[\text{NaAlO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + \text{Na}^+ + \text{OH}^-\]  

Precipitation
The hydrate is fed into the calcination kiln.

Calcination
The hydrate is calcined to form alumina trough the separation of the water.

\[2\text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}\]  

Bauxite Residue
Alumina production through Bayer process generates from 0.7 to 2.0 tons of residue per ton of alumina produced. It is usually called Bauxite Residue (BR) also called red mud. The BR composition include hematite and e other iron oxides, quartz and titanium oxides. On the BR treatment only part of the sodium hydroxide is removed. The BR has a considerable amount of sodium hydroxide and several concentrated ores. On the other hand, the bulk of its alkalinity is in the solids and reacts slowly after the pH of the liquid is lowered. The addition of lime and other additives during the Bayer process contributes to this solid alkalinity. It is done with the objective of avoiding silica dissolution, helping the settling and improving the production. Not integrating BR in other

processes is a waste of mineral resources, but it must be done in an energetic and economically viable way. Table 1 shows the chemical analysis of the BR from Alumina do Norte do Brasil S/A (ALUNORTE – Belém-PA-Brazil).

Table 1 - Dry BR Composition [6].

<table>
<thead>
<tr>
<th>CONTENT</th>
<th>%</th>
<th>CONTENT</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>18.3</td>
<td>Na₂O</td>
<td>9.31</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>22.6</td>
<td>V₂O₅</td>
<td>0.28</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>34.9</td>
<td>K₂O</td>
<td>0.13</td>
</tr>
<tr>
<td>TiO₂</td>
<td>5.56</td>
<td>MgO</td>
<td>0.04</td>
</tr>
<tr>
<td>CaO</td>
<td>1.32</td>
<td>FL</td>
<td>7.56</td>
</tr>
</tbody>
</table>

**BR Complex Alkalinity and the Reaction with Carbon Dioxide**

Complex chemical reactions govern the alkalinity of BR and its neutralization behavior. The pH and the time are the two key variables. The pH is dominated by the presence of alkaline solids. BR solutions pH average is 12.3, with standard deviation of 1.0 and ranges between 9.7 and 12.8. Therefore BR although not particularly toxic is highly alkaline [7], and as such hazardous. The pH neutralization process is buffered by the presence of hydroxides, carbonates, aluminates and polyacrylates [7-8]. These solids that are formed on the desilication process, on the Bayer process and also by addition of lime. The buffering action of this multiple alkaline solids causes the neutralization behavior of BRs to be complex with several steps and time dependant. Washing with water is not a practical way to remove the alkalinity from BR [9]. This chemistry and alkalinity impact on different aspects of BR. Storage requirements are affected by the reactivity with sealants. Bulk density, sedimentation rates, compaction, hydraulic conductivity, drying rates, dusting behavior, and physical strength are also alkalinity impacted [10]. The reuse as a raw material other process requires at least reduced reactivity to facilitate handling and transport.

The carbonation neutralizes the alkalinity according to the following equations:

\[ \text{CO}_2 (g) + \text{OH}^- \leftrightarrow \text{HCO}_3^- \]  
\[ \text{HCO}_3^- (aq) \leftrightarrow \text{H}^+ + \text{CO}_3^{2-} (aq) \]

As pH decreases the following reaction occur:

\[ \text{NaAl(OH)}_4 (aq) + \text{CO}_2 \leftrightarrow \text{NaAl(OH)}_2\text{CO}_3 (s) + \text{H}_2\text{O} (l) \]

**The BR Pilot Test Plant**

**Design and construction.**

The test plant was designed and constructed by the authors for this research. It is mounted at the Chemical Engineering Laboratory at UFPA and will serve as long term research facility. The concept was to test the feasibility of amend BR, capture CO₂ and explore the possibilities of reuse of this and other residues in a low cost and low energy consumption process. The first premise was to use real flue gas produced from oil burning.

The experimental system used in this study whose schematic and layout are shown at Figures 1 and 2, consists of three different reactors. Additionally we have reservoir, pump, blower, valves and measurement equipment. The suspension is transported from the reservoir by the pump to the distribution system inside one of the reactors. These reactors objective was to promote the reaction between the flue gases with the water and the alkaline ions present in the liquid-solid phase. The gas stream is fed by direct entry of gas at the bottom of the reactors, which comes into contact in countercurrent with the recirculating suspension of RM.

**Gas Supply Preparation System.**

The gases are produced at a burner chamber of a boiler. From the chimney they are deviated through a specially designed heat exchanger where they are cooled to 70°C with a countercurrent water mist spray. Pumped by a centrifugal fan the gases pass across a manifold and go to the input of the chosen reactor.

**Reactors:**

The main function of the reactors is to provide contact between the two phases (liquid and gas), thereby occurring the transfer of CO₂ and other gases from the flue gas to the RM suspension. First one (Figure 12) is a washer type spray tower, with cylindrical geometry that operates vertically. It consists of a cylindrical shell of fiberglass 10 mm thick. It has 2 meters height, 0.6 m in diameter and is divided into two symmetrical parts (1m). The suspension is sprayed by ten hollow cone centrifugal type nozzles on two levels. The second one is a packing tower filled with saddles (Figures 13-14). The third is a packing tower identical to the second but filled with structured high surface filling (Figures 13-14). The suspension is distributed on the top of the packing material. The packing towers were designed and constructed specifically for this experiment. They consist of cylindrical shells (0.38 m diameter), one top and one bottom cap. They were made of stainless steel and were provided with two glass windows. They were equipped with bottom internal screens for supporting the random saddles or the structured filling. The gas inlet is in the bottom below the screen and the outlet is on the top.

**BR Suspension Circulation System.**

The water-BR suspension was prepared at a tank. The preparation include adjust of the water content and the circulation through a screen box to remove the coarse particles. During the experiment the solution was pumped from the recirculation tank and return to it. The pH was measured by digital equipment that allows monitoring throughout the experiment in order to identify the saturation point of the suspension.

**Definition of measuring points.**

We defined three measurement points shown in the diagram of Figure 1 below:

At point 1, return of the reacted suspension to the box was measured flow of suspension using a beaker and a stopwatch, the temperature of the suspension and the pH evolution throughout each experiment.

At point 2, exit of the exhaust gases from heat exchanger were measured chemical composition % -v and gas temperature upstream of the reactors.

At point 3, gas exit of the reactors were measured temperature, volume flow and chemical composition % -v of the gases.