

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.



Clarification

After the extraction, the insoluble residue must be separated through a settling and filtering process. The aluminum containing liquor is transferred to the precipitators.

Precipitation

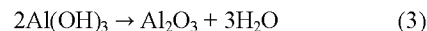
Crystalline aluminum trihydroxide "hydrate" is precipitated from the liquor.



The hydrate is fed into the calcination kiln.

Calcination

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



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 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 a 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).

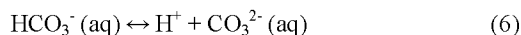
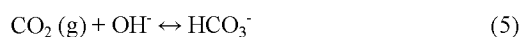
Table 1 - Dry BR Composition [6].

CONTENT	%	CONTENT	%
SiO ₂	18.3	Na ₂ O	9.31
Al ₂ O ₃	22.6	V ₂ O ₅	0.28
Fe ₂ O ₃	34.9	K ₂ O	0.13
TiO ₂	5.56	MgO	0.04
CaO	1.32	FL	7.56

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:



As pH decreases the following reaction occur:



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.

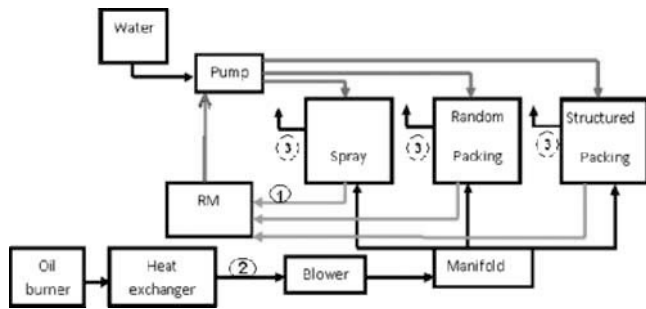


Figure 1 – Process flowsheet with measurement points.

Equipment.

At Figure 11 we have the gas analyzers capable of measuring O_2 , SO_2 and CO_2 . At Figures 2 to 14 we can see the layout and the equipment used for the experiments.

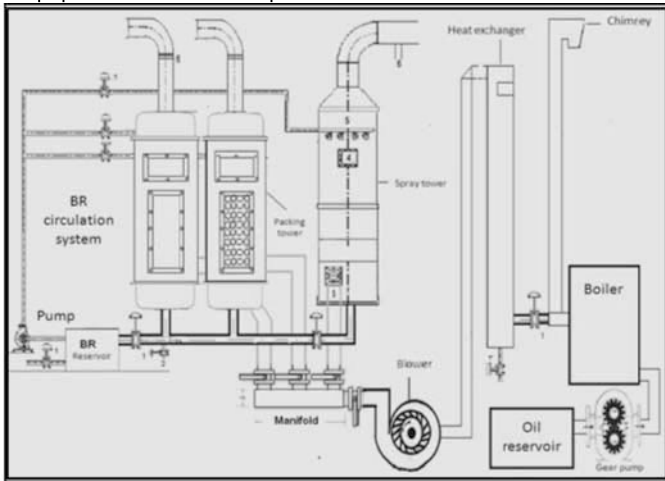


Figure 2 – Equipment layout



Figure 3 – Heat exchanger

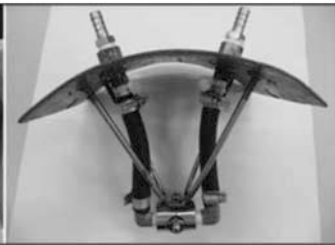


Figure 4 – Mist generator



Figure 7 – Gas manifold.

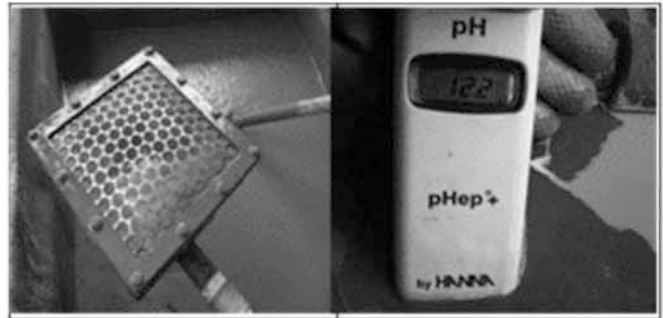


Figure 8 – BR reservoir and sand screen box.

Figure 9 – pH measuring.

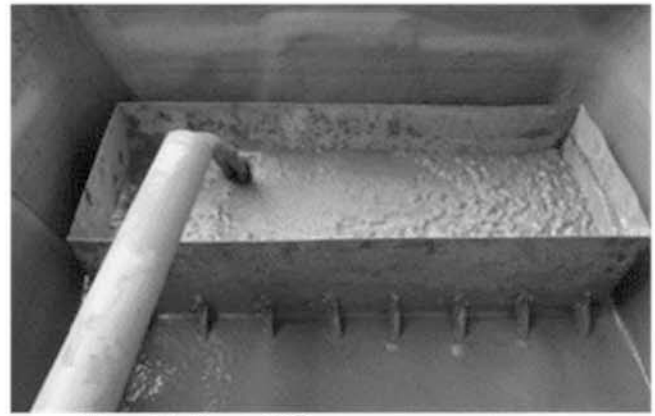


Figure 10 – Reacted BR return on supernatant test.



Figure 5 – Oil burner.

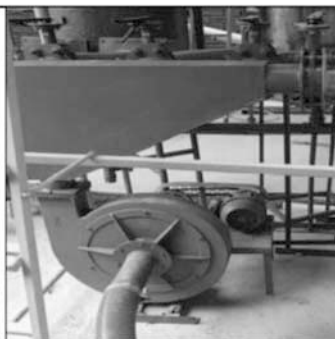


Figure 6 – Gas blower



Figure 11 – Electrochemical and infrared gas analyzers.

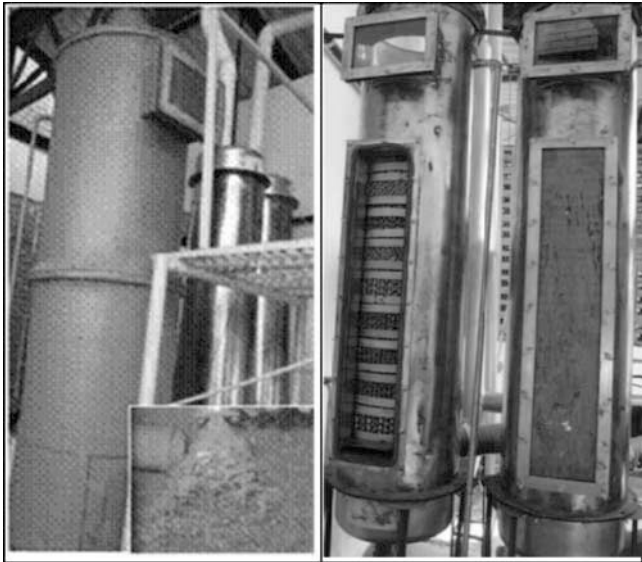


Figure 14 – Fillings of random and structured packing towers..

Evolution of pH during experiments.

At Figure 15 we can see the average results of each tower model during the experiment. We can observe that the reaction is faster at the structured packing tower followed by the random fillings packing tower.

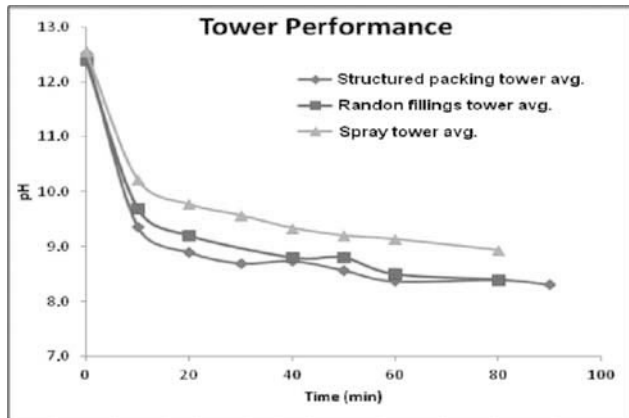


Figure 15 – Performance of the reactors during the experiments

pH Buffering and the Long Term pH

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. We can see an example at the Figure 16. In light of these facts we decided to monitor what we called the long term pH of the samples of each experiment conserved in flasks with caps. This is the pH measured after the experiment was

completed. We can see the further evolution at Figure 17. In parallel we begin monitoring samples of reacted BR with open contact to the air, kept on flasks without caps. The results can be seen at Table 3 and Figure 18. At Figure 19 we see the average evolution of the pH of BR at open flasks compared the results with the capped samples.

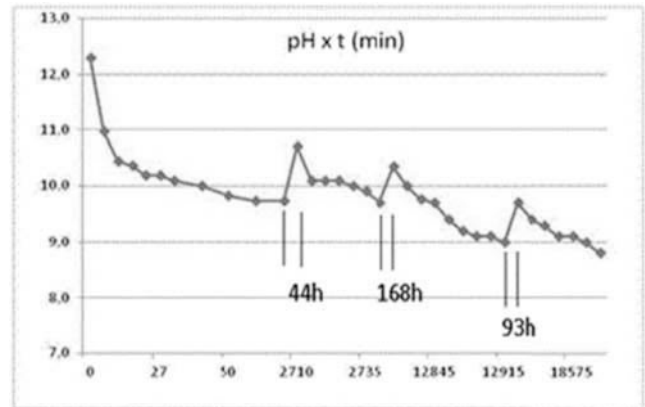


Figure 16 - Buffer effect at several stages experiment [9].

Samples of reacted BR were kept at closed and opened flasks. The long term pH results are shown at Tables 2 and 3.

Table 2 - Average results of the long term pH closed flasks.

Reactor Type	Long term pH	Standard deviation
Spray	10.5	0.5
Random fillings	10.4	0.6
Structured packing	10.4	0.4
Average	10.4	0.3

At Figure 14 lowest line, we can see the pH evolution of the sample from experiment shown at Figure 13. This experiment was conducted along four steps and a total of 13 days.

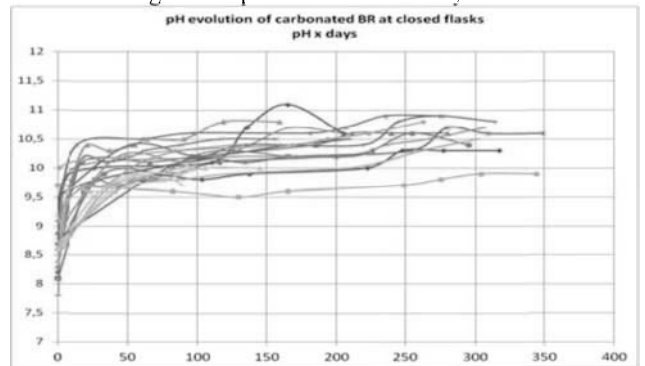


Figure 17 – Tendency of the pH evolution on lidded flasks.

As can be seen at Table 3 and Figure 18, although not stabilized yet, the pH evolved to an average of 11.1 when the material is fully exposed to the atmosphere. At Figure 19 we can see the averages of open and closed flasks.

Table 3 – Average results of the long term pH open flasks.

Reactor Type	Long term pH	Standard deviation
Spray	10.9	0.1
Random fillings	11.1	0.3
Structured packing	11.2	0.3
Average	11.1	0.2

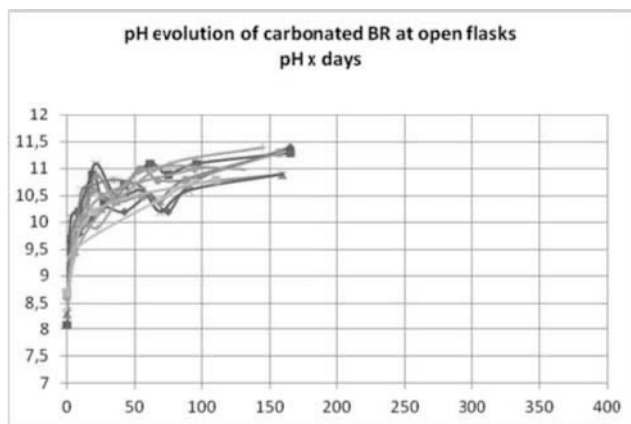


Figure 18 - Tendency of the pH evolution on open flasks.

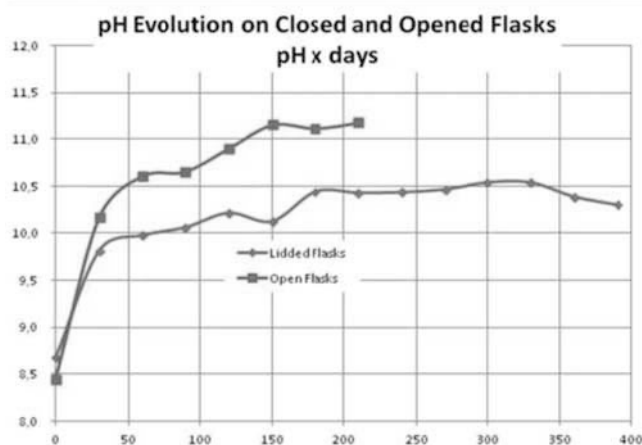


Figure 19 – Comparison of average pH evolution on closed and open flasks

Experiment with Supernatant

As shown on the Table 4 four experiments with the supernatant were realized. The pH reached averaged 8.4 at the end. However the average long term pH returned to the original before the beginning of the experiments.

Table 4 – Carbonation of supernatant

Reactor Type	pH begin	pH end	pH long
Spray	12.8	8.4	11.7
Spray	12.8	8.8	12.9
Random fillings	12.7	8.2	13.0
Structured packing	12.5	8.3	12.4

This fact stems from two factors: first is that the main part of the alkalinity being in the solid part of the BR and the second is that the absence of circulation of the solid of BR substantially hinders the reaction of CO₂ with alkali ions present the solid part.

CO₂ Capturing

The amount of CO₂ at entry and exit was measured using a non dispersive infrared equipment shown at Figure 11. A mass balance was calculated for each experiment integrating the rate captured at each interval and taking into account the temperature at entry and exit. Each experiment with 37 kg of BR on dry basis captured a

minimum of 1.22 and a maximum of 3.79 kg of CO₂ with an average of 1.84 kg. The amount of captured CO₂ is directly related to the duration of each experiment. Although this is a reversible reaction, the preliminary results of the long term behavior of pH show a lower elevation with increasing reaction time. As can be seen at Table 5 (converted to kg CO₂/ ton BR), each experiment with BR suspension at 27% -w (37 kg on dry basis) captured a minimum of 1.22 kg and a maximum of 3.79 kg of CO₂ with an average of 1.84 kg.

Table 5 – CO₂ captured during each experiment.

	Kg CO ₂ / ton BR
Average	49.8
Standard Deviation	17.7
Minimum	33.0
Maximum	102.5

SO₂ Absorption Experiment.

An experiment was conducted to evaluate the capture of SO₂ (one in each reactor type). Bottled SO₂ was injected in amounts ranging from 100 to 700 PPM and the reactors have performed as shown at the table 6.

Table 6 – Experiment of SO₂ capture in parallel with the flue gas.

Reactor type	Entry avg SO ₂ (PPM)	Std dev (PPM)	Exit avg SO ₂ (PPM)	Std dev (PPM)
Spray	246	88	15	5
Random fillings	134	84	21	13
Structured packing	488	203	82	10

Conclusions

The main objective of this experiment was to demonstrate the feasibility of the BR reaction with gases from the combustion of fossil fuels similar to the produced by the refinery itself without any prior processing was fully achieved with the long-term pH reaching 10.4.

At this point the spray tower has overall lower cost of capital for construction, operation and much simpler maintenance. From the environmental point of view, it has the advantage of not requiring chemical cleaning, which prevents the generation of new waste.

The result of the long-term pH on the experiments with the supernatant shows clearly that most of the alkalinity is located in the solid part of the BR. The fact that the long-term pH is on average 12.8 after the experiments with supernatant compared with 10.4 in experiments with the suspension of mud clearly demonstrates that the alkalinity concentrated in the solid do not take part on the reaction. This has direct impact on future industrial applications of this technology because making the reaction with the supernatant implies in the need to mix again with the decanted several times generating a waste of energy and capital to the process.

The fact that the long term pH has a standard deviation of 0.3 clearly indicates that it is being buffered by the slow release of certain ions of the solid part of the BR. The low Ca content of this BR points to other components controlling the pH. However the long term pH has a similar evolution with the BR with high content of Ca.

The addition of sources of calcium and magnesium to the BR may allow the precipitation of stable compounds, reducing the overall alkalinity.

The differences of the long term pH shown at Tables 3 and 4 are caused by the partial pressure of CO₂. This demonstrates the partial reversion of the carbonation. On a real dry stacking storing, the partial pressure probably is in between the situation of closed and opened flask. Since the reversion of the carbonation is very slow and the successive deposition of new layers of carbonated BR should increase the partial pressure of CO₂ on the bottom layers.

BR suspension can be used to remove SO₂ from gas streams in substitution of other alkaline solutions.

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