Bauxite Residue Flotation as an Alternative for Iron Concentration and Sodalite Removal

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Abstract

Bauxite residue (BR) is a byproduct of the alumina production by Bayer process. BR generated from gibbsitic bauxite usually presents iron as major element associated with hematite and goethite phases (40.8 % Fe_2O_3). The other typical phases found are sodalite, gibbsite, anatase and quartz. In general, gibbsitic bauxite generates a BR with particle size distribution typical of silt and clay ranges. Such fine distribution normally makes physical separation process unfeasible for a specific mineralogical phase concentration. It is well known that conventional flotation process is limited by particle size, however, considering the surface charge difference mainly between hematite and sodalite, it is worthwhile to investigate if this differentiability property could enhance flotation efficiency. Desliming and reverse cationic flotation operations were carried at under bench scale for hematite concentration from BR by removing sodalite as floated. The results were promising. The mass recovery of BR reported as concentrate was 20 %, the iron and sodium contents were 58.22 % Fe_2O_3 and 0.60 % Na_2O, in addition, sodalite was not detected by X-ray diffraction and SEM, resulting in a final pH of 6.6 on this stream.

Keywords: Bauxite residue valorization, Circular economy, Elutriation, Flotation, Sodalite.

1. Introduction

Bauxite residue (BR) is the solid mixture remaining after aluminium phases lixiviation from bauxite added to compounds formed during other steps of the Bayer process. Based on 2020 alumina production data, it is estimated that 170 million tonnes per year of dry bauxite residue are generated and only about four million is used productively [1]. The variability in BR properties makes it a very challenging material for broad use or individual element concentration. Since iron is one of the main constitutes of BR, it is one of most promising elements for reducing BR inventory [1, 2]. However, BR is not considered a competitive raw material for iron-making process due to its low Fe_2O_3 content (27–47 %) comparing to the conventional iron ores (>60 %) [3], so operations for iron concentration should be investigated.

Considering BR as a potential “mine” for iron extraction, the feasibility of iron concentration needs to be evaluated from the perspective of mineral concentration. The requisites for mineral concentration can be summarized in three topics: (i) mineral liberation, (ii) differentiability and

(iii) dynamic separability [4]. The first two topics are related to the mineral, i.e., if the target phase is present as free particles (liberated) and if the mineral has properties that can be handled to allow its concentration. The last subject concerns equipment technology, meaning that the equipment should be able to achieve the conditions that will result in the concentration of the target phase [4].

In terms of liberation, as a rule of thumb, mineral liberation is lower in coarser size ranges, and it increases in finer size ranges [4]. BR studied in this work presents fine particle size distribution, where more than 80 % is smaller than 38 µm [5]. For the purpose of this study and due to insufficient data, one will assume that the main constituents of the BR, such as iron oxides (hematite and goethite), aluminous compounds (gibbsite), silicon compounds (sodalite and quartz), titanium oxides (anatase) [1, 5, 6] exist as individual particle and are able to be handled in a concentration process. Regarding to differentiability, properties such as broader size range, pronounced differences of properties as density and magnetic susceptibility do not occur among the solids present in BR. However, surface charge may be a potential property to be explored. Both pH-dependent surface charge (variable) and pH-independent surface charge (permanent) exist in BR [6, 7]. Sodalite is the only pH-independent charge, being permanently negative, while the other solids present in BR have a pH-dependent charge [6]. Based on that, charge development in mineral-solution phases regulates, for instance, adsorption reactions of ions at the mineral-water interface; the hydrophobic/hydrophilic character induced or modified by the adsorption of reagents can be very opportune and may result in substantial differentiation property between the various solids. Furthermore, the principle of concentration by flotation is related to the difference between the wettability of a specific mineral or its hydrophobic/hydrophilic character [4]. Flotation is about dynamics of liquid, solid and gas phases. Reagents are used to modify the wettability of a specific mineral, changing selectively its hydrophobic/hydrophilic character. Hydrophilic particles have a strong affinity to water while hydrophobic particles combine with bubbles, so they float [4].

In terms of the dynamic separability, the third and last topic mentioned above and related to the requisites of mineral concentration, handling very fine particle is an issue for mineral processing. Flotation of fine particles is being studied specially because of the declining of mineral grades, which results in comminution until finer sizes to improve liberation, and also, as a potential concentration process to recover minerals from tailings, such as recovery of iron from iron slimes [8, 9, 10]. Therefore, development of flotation equipment for small size particles can be a solution for dynamic separability issues related to handling fine material such as BR [5, 11]. For the moment, a deep discussion about equipment dynamic improvement is out of the scope of this work since the aim is a first exploratory assessment of how the solids present in BR will answer to a conventional flotation cell at bench scale.

Flotation is a well-known process in iron ore mining; in particular, cationic reverse flotation route is very effective in separating quartz from hematite [12]. BR holds similarities to iron slimes generated after iron ore beneficiation. Iron slimes has hematite as the main iron host phase (35 – 45 % Fe), a fine particle size distribution (99 % < 45 µm), and silicate gangue minerals (quartz and kaolinite) [13]. Several researches remark that development in flotation may be a possible alternative for iron concentration from slimes [13, 14, 15]. Therefore, in the present work, a BR sample from a gibbsitic bauxite processing was tested to investigate conventional flotation for iron oxides concentration. The reagents, process conditions and parameters were similar to those used in iron ore processing.

2. Experimental

Norsk Hydro Alunorte Refinery provided the bauxite residue (1500 g) studied in this work. The refinery is located in the state of Pará, northern Brazil. The study was conducted at the SENAI Innovation Institute for Mineral Technologies (ISI-TM) and SENAI Innovation Institute for Mineral Processing (ISI-PM).

2.1 Analyses and Instruments

Bauxite residue (head sample) and the product streams were characterized for chemical content, mineralogy, morphology and particle size distribution.

Chemical analyzes were performed by energy dispersive X-ray Fluorescence (EDXRF: Epsilon 3XLE, PANalytical Spectrometer) using an X-ray Rhodium (Rh) tube, and anode at 1.5 W.

Mineral phases were determined by powder method and X-ray Diffraction (XRD: Empyrean PANalytical Diffractometer, Almelo, The Netherlands). Powder XRD patterns were obtained (5°–80°, 40 kV, 20 mA, Kα 1.78901 Å, step size 0.02°, 55 s/step).

Morphological micrographs were obtained by Scanning Electron Microscopy (SEM: Vega 3 LMU, Tescan), operated at 20 kV and 10 µA with a focal distance between 8 and 15 mm. Mineral samples were coated with a thin gold layer using a Desk V metallizer (Denton Vacuum) before SEM.

Particle size distribution (PSD) was determined by laser diffraction in a Malvern Mastersizer 3000 using water as dispersant.

pH was measured using an Orion Star (Thermo) pH meter in a 1:1 BR/water solution.

2.2 Desliming and Flotation

Conventional flotation in the iron ore industry operates with particle size ranging between 10 µm and 150 µm, and the slimes (< 10 µm) are removed [13, 16, 17]. To achieve the feed specification and to allow a proper reagent mixing, the experiment was carried out in three equipments: attrition scrubber, elutriator and flotation cell.

A Denver attrition scrubber (1500 mL) was used to promote proper reagents mixing and dispersion of the particles. Agitator speed was maintained at 1200 rpm for 5 minutes and pH controlled at 11. For desliming, an elutriator of 135 mm diameter and 630 mm height was used. The water flowrate was controlled to achieve a particle cut size of 10 µm. The overflow was dried and held for analysis while the underflow was filtered and submitted to flotation. Flotation tests were thereafter carried out in a Denver (D 2) flotation cell (1500 mL), where airflow rate was held at 200 Nl/h and impeller speed at 1200 rpm. Table 1 summarizes the reagents list, function and dosage used in each experiment step, where corn starch was gelatinized with a starch/NaOH ratio of 1:10 and the collector EDA C was diluted in distilled water (1 %).

Table 1. Process stage and list of reagents (function and dosage).

Experiment	**Reagent**	**Function**	**Dosage**
Attrition	NaOH	pH adjustment	As needed
	HCl	pH adjustment	As needed
	Na_2SiO_3	Dispersant	200 g/t
Elutriation	Corn starch	Depressant	100 g/t
	Na_2CO_3	Buffering agent	68 mg/l
Flotation	NaOH	pH adjustment	As needed
	HCl	pH adjustment	As needed
	EDA-C / Clariant	Collector	25 g/t[1]
	Corn starch	Depressant	1000 g/t

[1] Dosage added after each foam removal

3. Results and Discussion

Conventional flotation in the iron ore industry operates with particle size range between 10 µm and 150 µm, and slimes fraction (<10 µm) are removed [13, 16]. The presence of slimes results in deleterious effects on recovery, selectivity and reagent consumption, mainly due to small mass of the particles leading to low probability of collision with a bubble and particle entrainment in froth [8]. Therefore, prior to flotation, elutriation of BR was carried out for desliming. The concentration of hematite and other iron oxides in iron ore beneficiation usually occurs by cationic reverse flotation [13, 16, 17], where the gangue minerals (tailings) are removed in the floated stream and the product (concentrate) is the underflow stream. The same approach was made in flotation of the deslimed BR (underflow of the elutriator), cationic reverse flotation was applied, and the final product were the concentrate from the bottom of the flotation cell.

Table 2 presents the overall mass balance and chemical analysis for the BR (head sample) and the resulting streams. The overflow stream from the elutriator was weighted and determinations were performed, the underflow from elutriator were conditioned for flotation. A semi-batch flotation was carried out, where the floated material was removed until insignificant mass was detected and finally, the concentrate (CO) was removed from the flotation cell bottom. As expected, a higher mass of BR (66 %) reported to the overflow stream from the elutriator since BR typically presents a very fine size distribution where more than 80 % is smaller than 38 µm [5]. In terms of chemical analysis, the overflow presents a slight decrease in iron and increase of aluminium and silicon elements. Since the differentiability properties of this operation are particle size and density, a high sensibility is not expected in terms of elements as investigated in a previously reported work [11]. However, even a small variation in contents combined with a pronounced mass removed from the original BR will result in a different material reporting to flotation with more iron and less silicon and aluminium bearing solids. About 34 % of BR reported to the elutriator underflow and this material was fed in the flotation cell. A semi-batch operation of the flotation cell resulted in four tailings streams (FT1, FT2, FT3 and FT4). After the fourth foam removal, insignificant mass floated, so the flotation experiment was stopped. The chemical analysis of the tailings shown a considerable iron content; the probable hypotheses about it will be discussed after further analyses. Looking at the product, the iron content of the concentrate increased significantly (58.22 %) while Na_2O decreased substantially down to 0.60 %.

Table 2. Overall mass balance and chemical analysis.

	BR	**Elutriation**	**Flotation**				
	Feed	Overflow	Tailings				Product
			FT1	FT2	FT3	FT4	CO
Mass Balance	100 %	66 %	5 %	3 %	3 %	2 %	20 %
Chemical Analysis							
% Fe_2O_3	40.80	37.16	43.90	40.25	42.71	42.26	58.22
% Al_2O_3	17.32	21.15	17.98	19.60	18.33	18.76	11.92
% SiO_2	14.01	15.71	14.51	15.68	14.79	14.95	9.54
% Na_2O	9.68	8.66	6.53	7.34	6.45	6.44	0.60
% TiO_2	5.93	4.93	6.12	5.40	5.57	5.26	8.05
% CaO	1.43	1.15	1.16	1.07	1.05	1.13	0.59
% ZrO_2	0.92	0.46	1.32	0.59	0.61	0.66	2.26
% V_2O_5	0.16	0.13	0.16	0.14	0.16	0.15	0.22
% SO_3	0.14	-	-	-	-	-	-
% MnO	0.12	-	-	-	-	-	-
% P_2O_5	0.11	-	-	-	-	-	-
% LOI	9.12	10.19	7.79	9.40	9.80	9.85	7.93

Figure 1 shows XRD diffractograms of all streams. The predominant phases present in the BR were: hematite (Hem), aluminous goethite (Al-Gth), gibbsite (Gbs), sodalite (Sdl), anatase (Ant), quartz (Qz) and calcite (Cal). All of that was detected in the other streams, except in the concentrate from flotation cell bottom (CO). In this stream, sodalite was not noticed which corroborates with the chemical characterization where Na_2O content was near zero; in addition, if sodalite is not present, the silicon (9.54 %) and aluminium (11.92 %) contents are related to quartz and gibbsite. Chlorite (Chl) and illite (Ill) are clay minerals and they were detected only in one floated stream (FT3) and in the overflow of elutriator (OVER), probably due to concentration effect. Hematite was detected in all streams.

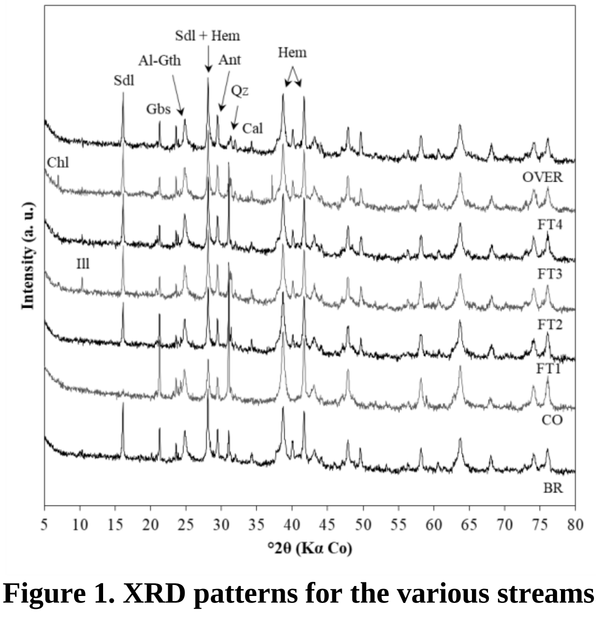


Figure 1. XRD patterns for the various streams.

As an exploratory study, the parameters of the experiments were based on common practices in reverse cationic flotation for iron ore concentration. Sodium silicate may be used as a dispersant of silicate gangue minerals, such as quartz and kaolinite but it can also have an agglomeration effect at a specific range of pH [14, 18]. EDA-C (Clariant) is used as cationic collector and adsorbs strongly on quartz making its surface hydrophobic [13] while gelatinized starch is used as the hematite depressant with enhancement of its hydrophilic character [13, 16, 17]. Therefore, the data present in Table 2 and Figure 1 indicate that sodalite was the principal solid to combine to the collector; quartz was still present in the concentrate, so it did not float properly. A high content of iron was still present in the tailings, which rises questions about the cell dynamics (fines are entrapment in the froth) and liberation (does the mineral phases exist as free particle?).

Figure 2 and Figure 3 present the particle size distribution of BR (head sample) compared with overflow from elutriation (OVER) and streams from flotation, respectively. BR presents clearly two population, a relatively coarser and a finer one. The overflow and floated (FT) streams present a higher proportion of fines and particles of bigger size than the original BR, which is not possible. Therefore, agglomeration is probably taking place. For the concentrate (CO), the complete removal of small size particles is clear, so the dynamics of the conventional flotation cell may be limited to handle this material.

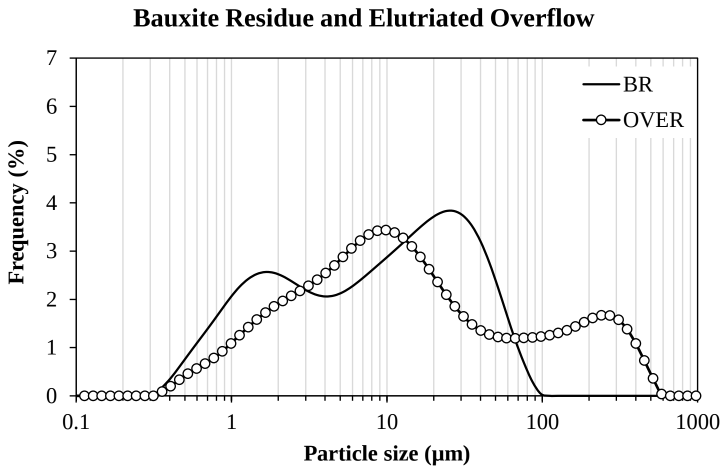


Figure 2. Particle size distribution for bauxite residue and elutriated overflow.

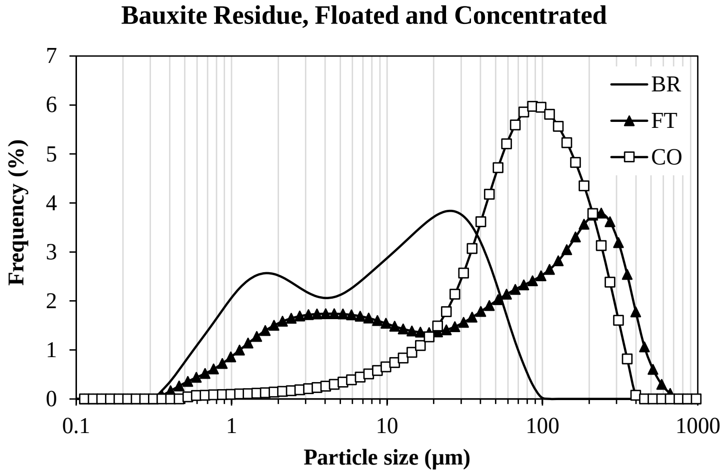
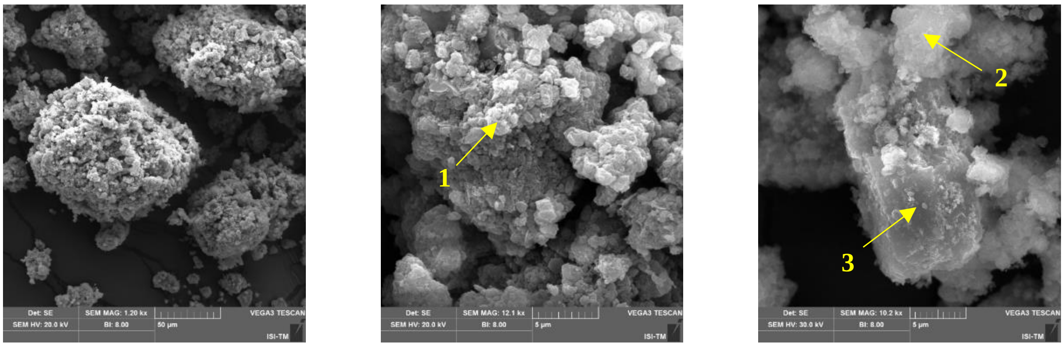


Figure 3. Particle size distribution for bauxite residue and products from flotation.

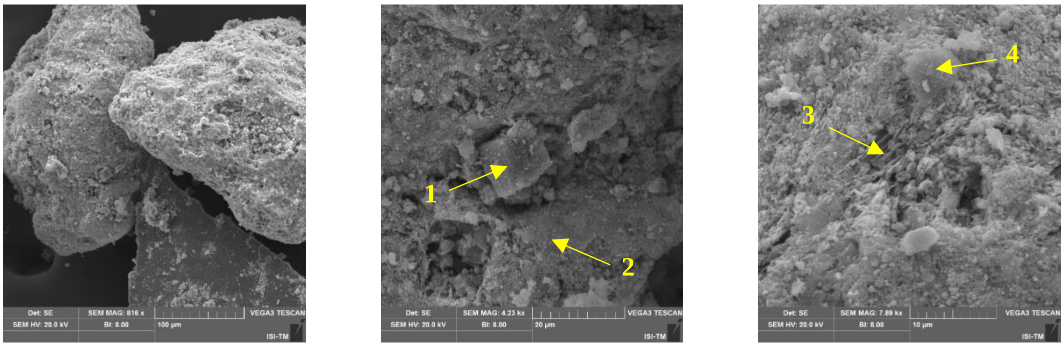
Scanning electron micrographs (SEM) showing the morphology of BR and the concentrate from flotation are shown in Figures 4 and 5, and energy dispersive spectroscopy (EDS) was performed at the points indicated by the yellow arrows. The initial assumption is that each particle has only one individual mineral type (good mineral liberation) may have faults. In Figure 4 (a), it is possible to observe the presence of clusters covering the surface of several particles. EDS executed at points marked in Figures 4 (b) and (c) indicated "arrow 1" aluminium, sodium, silicon and oxygen (sodalite); by "arrow 2" aluminium, sodium, silicon and oxygen (sodalite) and by "arrow 3" aluminium and oxygen (gibbsite). Therefore, it is not possible to confirm the liberation degree of the BR solids and how strong is the inter-connection between the minerals, further studies about it should be undertaken to assess the limitations of element concentration from BR.

Micrographs of the concentrate are shown in Figure 5 where one can observe clean particles and degraded parts. From Figure 5 (b), EDS performed in point "1" indicated the presence of aluminium, oxygen and iron, and in "2" iron, titanium and oxygen. The lamellar forms indicated by the arrow "3" presented iron and oxygen, and at point "4", silicon and oxygen (quartz). The micrographs did not show the typical morphology of sodalite which confirms the XRF and XRD results. Again, the identification of elements such as iron and titanium, which belong to different minerals in a same particle, reaffirm the need for more studies concerning mineral liberation in BR.



(a) (b) (c)

Figure 4. Bauxite residue micrographs.



(a) (b) (c)

Figure 5. Concentrate from flotation.

For pH determinations, elutriation overflow, combined flotation tailings and concentrate were washed with distilled water, filtered and dried; about 3 g of each stream were then suspended in distilled water in 1:1 proportions. Elutriation overflow and combined flotation tailings presented pH values of 10.24 and 9.95, respectively. The concentrate presented a pH value of 6.60. As the pH value of the concentrate was significantly different from the others, the sample was reserved for a new determination. After three months, the pH was 7.9. The first and last pH measurement of concentrate show a slight variation, but it remains near neutral value. Therefore, since the concentrate does not contain sodalite, it is possible to confirm that sodalite is the only responsible for the BR alkalinity: without sodalite, there is no caustic adsorbed on the other solids present in BR.

4. Conclusions

Flotation is a concentration operation based on the wettability as the differentiability property. Reagents are used to change or enhance the hydrophilicity or hydrophobicity characteristics of the particle surface, so each solid will combine to liquid or to gas phase (bubbles), allowing a proper material split and its concentration.

As a first and exploratory trial, BR from a gibbsitic bauxite processing was submitted to the reverse cationic flotation where the reagents and process conditions were similar as usually applied during iron ore beneficiation. An attrition scrubber, an elutriator and a conventional flotation cell were used for desliming and flotation tests. The chemical analyses for the final product (concentrate), showed an Fe_2O_3 concentration of 58.22 % while one of the major contaminants, Na_2O, decreased to 0.60 %, suggesting the absence of sodalite. XRD diffractograms confirmed that sodalite was removed from the concentrate stream, which presents strong evidence that charge surface may be a strong property to be manipulated for solids concentration from BR. In addition, since a stream from BR without sodalite was obtained and lead to the measurement of a neutral pH (6.60 and 7.9), it confirmed that DSP is responsible for the alkalinity of the BR in study.

It is also important to note that, evaluating the iron concentration from BR under the perspective of mineral concentration (liberation, differentiability, and dynamic separability), the main bottlenecks may stand clearly. The liberation degree of the solids present in BR needs to be determined, so a complete assessment about the limits of concentration potential would be known. This work has shown that surface charge of the BR solids can be explored for concentration proposes. As for dynamic separability, handling particle of small size is a major concern everywhere, and developments are being made, especially in operations such as flotation.

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