Original Article

Feldspar production from dimension stone tailings for application in the ceramic industry

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\textbf{A R T I C L E  I N F O}

Article history:
Received 20 September 2017
Accepted 4 February 2018
Available online 26 September 2018

Keywords:
Granite
Syenite-feldspar
Magnetic separation
Froth flotation
Ceramic industry

\textbf{A B S T R A C T}

Brazil has one of the largest reserves of granite in the world and is in part of the top ten producers of dimension stone. The dimension granite extensive mining in this country generates expressive volumes of tailings, among them rock fragments and fine particles, accounting for more than 50% of the material extracted from the quarries. The dimension stone, commercially known as Marrom-Guáiba granite, is an alkali-feldspar quartz syenite rich in potassium and sodium exploited by Serra Geral Mining in the southern part of Brazil. Due to its chemical composition, Marrom-Guáiba tailings have potential application in the ceramic industry. However, the grade of iron bearing minerals (considered a contaminant) is too high. Tailings samples were ground, milled, chemical analyzed and tested using magnetic separation and froth flotation in order to reduce the iron and quartz content. The results show that the magnetic separation reduced the iron content from 3.20 to 0.48% and increased the feldspar content from 72.20 to 81.23% with 65.31% of mass recovery and 73.48% of metallurgical recovery. Flotation provided small decreased in quartz content, from 4.40 to 3.90%. A suitable feldspar concentrate for ceramic industry was obtained.

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1. Introduction

In 2014, the world production of dimension stone reached 136,500 Mt, leaded by China with approximately 31.1%. Brazil is the fourth in the world ranking, contributing with 7.4% of the world’s production. In the same year the Brazilian’s granite exportation reached 2547 Mt [1]. Granite extensive mining generates an expressive volume of tailings, accounting for more than 50% of the extracted material, causing many environmental impacts. Due to its mineralogical and physical characteristics, some granites present significant feldspar and quartz concentrations [2].

Ceramic and glass industries are the main consumers of feldspar in Brazil. In glass manufacture, feldspar is used as fluxing agent and as a source of alumina (Al\textsubscript{2}O\textsubscript{3}), alkali (Na\textsubscript{2}O $\textsuperscript{a}$ Corresponding author.
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https://doi.org/10.1016/j.jmrt.2018.02.011
2238-7854/© 2018 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
and K₂O), and silica [3]. Fluxing agents are substances, usually oxides, used in glasses, glazes and ceramic bodies to lower the high melting point of the main glass forming constituents, usually silica and alumina. These materials play a key role in the vitrification of clay bodies by reducing the overall melting point and the most common fluxes used in clay bodies are potassium oxide and sodium oxide, which are found in feldspars. In the manufacture of ceramics, feldspar is the second most important ingredient after clay. They improve the strength, toughness, and durability of the ceramic body and cement the crystalline phase of other ingredients, softening, melting and wetting other batch constituents. In the flooring sector, feldspar is the main constituent in the body composition [4].

Brazilian’s feldspar gross production in 2014 was 497 kt, which represented an increase of 41% over the previous year. The State of Paraná was responsible for 40.5% of the gross production, followed by Minas Gerais (35.9%), Santa Catarina (10.6%), Bahia (5.2%), Paraíba (4.4%), Rio Grande do Norte (3.1%), and São Paulo (0.3%). Processed production totalled around 418 kt [3].

One of the main characteristics to be considered of feldspar for ceramic industry is the grade of iron bearing minerals (oxides or silicates) present on it. Although the ceramic industry requirements for raw material are quite diversified, since they depend on the type of material to be produced, if the grade of this contaminant is higher than 0.5% it promotes a dark colouring and other irregularities in the final product, detrimental to the processes and to the quality of the ceramic. In the production of white dishes, the maximum iron content (evaluated as Fe₂O₃) is 0.1%. However, if the product brightness is not important, which happens in cases where the ceramic receive a colourful pigmentation in the last stages of the process, the Fe₂O₃ content can reach 2 or 3%. Regarding the granulometry, feldspar used in the ceramic industry must be smaller than 74 μm because its fluxing power is inversely proportional to its size [5].

This paper describes the tests in bench scale performed with samples from Marrom-Guaiba granite tailings in order to obtain a feldspar concentrate with chemical and granulometric properties suitable for use in the ceramic industry. A dry high-intensity magnetic separator was used in order to reduce the iron bearing minerals content on the sample. Cationic flotation of feldspar using amine and HF was used to reduce the quartz content.

2. Methodology

A sample of 20 kg of Marrom-Guaiba granite tailings was received in pieces with size between 25 and 50 mm, donated by Serra Geral Mining Company, located in the Piquiri District, municipality of Cachoeira do Sul, State of Rio Grande do Sul, Brazil. The rock was characterized in the SED-FUNMINERAL mineral laboratory using an Atomic Absorption Spectrophotometry (AAS) Analyst 200 (Perkin Elmer). Samples were comminuted bellow 74 μm and sent to XRD analysis using Ultima IV (Rigaku). The quartz content was determined semi-quantitatively by the solubilization of the silicates with hydrofluoric acid to a concentration of 30% using 10 g of sample during 10 min of reaction. Two samples of pure quartz were tested under the same conditions to generate a calibration curve for the rock samples silicates solubilization. A petrographic analysis was done for determining the composition and texture of the rock.

2.1. Sample preparation and milling tests

The rock samples were crushed in a jaw crusher, to obtain particles below 10 mm, and then milled in a HPGR mill, resulting in 80% of the particles bellow 3 mm. The material was mixed and quartered in a longitudinal Chevron pile, assembled with three passes and aliquots withdrawals of 1 kg.

To determine the optimum time for the rock comminution (100% below 600 μm), milling tests were carried using a bar mill and three different residence times (5, 10, and 15 min). The mill had 400 mm length and 200 mm diameter and operated with 6 bars of 25 mm, 7 bars of 20 mm, and 8 bars of 10 mm diameter. The solids percentage in the mill was 55% and the rock mass was 1 kg. The mill product was deslimed through wet sieving for 10 min using a 38 μm sieve, without dispersant. The resulting material (retained in 38 μm) was dried in oven at 80 °C for 4 h.

2.2. Magnetic separation tests

A high-intensity (22 kG) dry magnetic separator was used in an attempt to separate mica from feldspar present in a feldspathic sand. The authors were able to reduce the mica content of the initial sample by 95% [6]. In order to test the presence of high magnetic minerals in the rock a magnetic separation test was performed in the fraction above 38 μm using a manual ferrite magnets with magnetic field approximately 1 kG. Since some material was separated with a low magnetic field, a Frantz Isodynamic Separator was tested operating with magnetic field of 12 kG. The chute inclination was set to 25° longitudinal and 20° transversal. A vibration intensity level 6 was adopted in all tests.

2.3. Cationic flotation of feldspar (amine + HF)

After the magnetic separation, the non-magnetic particles @ 12 kG field were sent to froth flotation bench tests using a Denver laboratory machine with a 2.51 cell. The direct flotation was opted in order to separate feldspar from quartz. Triameen Y12D, an amine with CAS name N,N-Bis(3-aminopropyl) dodecylamine, supplied by AkzoNobel was used as collector with dosage of 200 g/t. The collector’s alkyl chain distribution, according to the supplier, was maximum 1% for alkyl chain length C10 or C14 and minimum 98% for C12. Kerosene was used as feldspar activator and frother in a dosage of 50 g/t. Hydrofluoric acid was used as silica depressant and feldspar activator [7] and to adjust the pulp pH to 2.5. The pulp density was 35 wt% solids and the impeller speed 1400 rpm. The conditioning time was 5 min and the flotation time 5 min. Tap water was used throughout the experiments. The flotation tests were performed in two sequential stages at the same conditions: rougher and scavenger.
3. Results and discussion

Feldspar contents were calculated by stoichiometry based on sodium and potassium contents, as can be observed in Fig. 1. According to the petrographic analysis, the sample of Marrom-Guaíba granite, as shown in Fig. 2, corresponds to an igneous rock, classified as alkali-feldspar quartz syenite. The rock cannot be characterized as a granitic rock due to quartz low grade (5.7%). Granitic rocks normally have quartz modal composition ranging from 20 to 60% [8]. The macroscopic description of the rock is a reddish-brown rock, phaneritic textures, equigranular grains with average granulation, predominantly constituted by K-feldspar and amphibole (black colour), subordinately by titanite and rarely pyrite [9]. The sample presented moderate magnetism, which could be related with the presence of magnetite on it. In structural terms, it is anisotropic, featured by the preferred orientation of the crystals of feldspar and amphibole.

The microscopic description showed that the Marrom-Guaíba granite was constituted predominantly by K-feldspar and amphibole, which agrees with the macroscopic description, having secondarily titanite, apatite, and opaque minerals, and traces of clinopyroxene. The rock texture was a stacked arrangement of K-feldspar crystals, which showed preferred alignment. The modal composition estimated was 66% K-feldspar, 24% amphibole, 4% quartz, 3% titanite, 2% opaque minerals, and 1% apatite. The rock was classified as a syenite alkali-feldspar [12].

3.1. Milling residence time tests

Fig. 3 presents the results of the bar mill tests. After 5 min, 100% of the rock was below 600 μm, with P80 approximately 280 μm. The rock showed P80 around 160 μm only after 15 min of milling. Since Frantz Isodynamic Magnetic Separator usually shows better results for particles above 74 μm no additional tests were performed for higher residence time than 15 min. It is also possible to notice that the amount of fine particles (bellow 38 μm) produced in all tests were similar, ranging from 5 to 10%. No finer milling was necessary once there was no presence of sulphides in the samples.

3.2. Magnetic separation

Fig. 4 shows the Frantz Isodynamic Separator results for the three milling residence times tested. It is possible to notice that 5 and 15 min milling showed the high non-magnetic minerals content (feldspar, quartz and silicates) in weigh, 62.13 and 51.14% respectively. This result could be explained because some magnetic particles could be remained lock or associated at 5 min milling. For 15 min milling the higher amount on fine particles present in the sample (above 74 μm) could be lead to a poor separation at the Frantz Isodynamic Separator.

Fig. 5 shows the chemical composition of the magnetic and non-magnetic materials produced at 12 kG magnetic field for the three tested milling times. It was possible to enhance the grade of Fe2O3 from 3.20 to 11.2% with 5 min of milling and to 15.90% with 15 min. This result proves, as expected, that a higher milling time lead to a high liberation degree of the iron bearing particles. The Fe2O3 grade in the non-magnetic was 0.48% after 15 min of milling, achieving the goal of reduce the iron content to levels below 0.5%. The Fe2O3 mass recovery was 17.64% and the metallurgical 87.85% for the same milling time (see Table 1).

Regarding the K2O, it was possible to enhance its grade from 6.41 to 8.18%, with mass recovery of 60.22% and metallurgical recovery of 76.85%. The total alkali mass recovery for 15 min milling was 63.57% and the metallurgical recovery was 73.56%. The feldspar mass and metallurgical recovery reached the maximum after 15 min milling, 65.31 and 73.48% respectively. On the other hand, the grade of feldspar on the paramagnetic flow was 55.20% for the same milling condition. The presence of this material in the magnetic stream could be explained due to the action of mechanical drag force present in the equipment.

Fig. 6 shows the X-Ray diffraction results for the magnetic and non-magnetic products produced at a 12 kG magnetic field after 15 min of milling. The magnetic product was identified as hornblende, anorthoclase, microcline, albite, and quartz and the non-magnetic product was composed by anorthoclase, microcline, albite, quartz, and cummingtonite.

3.3. Flotation results

Fig. 7 shows the mass fraction (in g) and recovery (in %) for the froth flotation bench tests regarding the three tested milling
Fig. 2 – (a) Macroscopic aspect of the sample with preferred minerals orientation on the horizontal axis. (b) Photomicrograph in binocular magnifying glass showing titanite crystals. (c) Photomicrography in natural and (d) polarized light of amphibole grains containing inclusions of clinopyroxene in association with opaque minerals and apatite. (e) Photomicrography in natural and (f) polarized light showing a Carlsbad germination and perthitic intergrowths in K-feldspar. (g) Photomicrography in natural and (h) polarized light of a quartz grain among a K-feldspar.

<table>
<thead>
<tr>
<th>Milling (min)</th>
<th>Fe$_2$O$_3$ Mass (%)</th>
<th>Fe$_2$O$_3$ Metal. (%)</th>
<th>K$_2$O Mass (%)</th>
<th>K$_2$O Metal. (%)</th>
<th>Feldspar Mass (%)</th>
<th>Feldspar Metal. (%)</th>
</tr>
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<tbody>
<tr>
<td>5</td>
<td>25.72</td>
<td>90.02</td>
<td>49.07</td>
<td>61.71</td>
<td>63.11</td>
<td>70.15</td>
</tr>
<tr>
<td>10</td>
<td>23.99</td>
<td>91.45</td>
<td>48.79</td>
<td>61.65</td>
<td>58.96</td>
<td>64.93</td>
</tr>
<tr>
<td>15</td>
<td>17.64</td>
<td>87.65</td>
<td>60.22</td>
<td>76.85</td>
<td>65.31</td>
<td>73.48</td>
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times. The flotation was not efficient for coarser particles, since for 5 min milling the mass recovery was around 50%. However, after 15 min milling the mass recovery reached 93%, an increase of 86%. On one hand the feldspar metallurgical recovery was around 91% (see Table 2) for the same milling time, but in the other hand the recovery of quartz in the concentrate was also high (82%). Those results confirm that the feldspar and quartz floated together. This result could be related with particle association between feldspar and quartz or a low concentration of the hydrofluoric acid.
Chemical analysis of the flotation concentrate were inconsistent for milling times of 5 and 10 min, (see Fig. 8), since the grade of K$_2$O and feldspar were similar in both concentrate and tailings. There was a slight increase in the feldspar grade in the concentrate for 5 and 10 min milling, but a reduction for 15 min (from 67.3 to 66.2%), which was unexpected. It is possible to notice the enrichment of quartz in the tailings, indicating an interaction between feldspar and amine and the depression of quartz due the hydrofluoric acid. The tailings chemical analysis results for 15 min milling resulting in a low grade of alkalis (5.2%) and high grade of quartz (47.8%).
addition, we would like to thank the companies Metago and Serra Geral Mining and the support of the Federal University of Goiás and Goiano Federal Institute.

REFERENCES


Table 2 – Froth flotation bench tests metallurgical recovery.

<table>
<thead>
<tr>
<th>Milling (min)</th>
<th>Metallurgical recovery (%)</th>
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<tbody>
<tr>
<td></td>
<td>K$_2$O</td>
</tr>
<tr>
<td>5</td>
<td>50.55</td>
</tr>
<tr>
<td>10</td>
<td>76.83</td>
</tr>
<tr>
<td>15</td>
<td>91.93</td>
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</table>

4. Conclusions

Marrom-Guaíba granite corresponds to an igneous rock, classified as alkali-feldspar quartz syenite due to its low amount of quartz (5.7% on petrographic and 8.4% on the semi-quantitative analysis). Therefore, the rock cannot be considered as a granitic, or a granitoid, geologically speaking.

The feldspar concentrate production with chemical and granulometric specifications suitable for the manufacture of ceramics, porcelain tiles, sanitary wares, glasses, and insulators was investigated in this work. After 15 min of milling and a magnetic separation with a 12 kG field the iron content (expressed as Fe$_2$O$_3$) was reduced from 3.20 to 0.48% and the feldspar content increased from 72.20 to 81.23% with 65.31% of mass recovery and 73.48% of metallurgical recovery, being this concentrate suitable to be used as ceramic raw material.

Flotation tests were not efficient for coarser particles (lower milling time). However, there was a slight increase in the alkalis content and consequently in the feldspar grade and a decrease in quartz content in those conditions, which could not be observed for 15 min milling. A deficit in hydrofluoric acid or an association between quartz and feldspar could explain the found results.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

The authors gratefully acknowledge the financial support of the Brazilian agencies CNPq, CAPES, FAPEG and FUNAPE.