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Limestone Briquette Production and Characterization

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Abstract**—**Modern agriculture requires productivity, efficiency and quality. Therefore, there is need for agricultural limestone implementation that provides adequate amounts of calcium and magnesium carbonates in order to correct soil acidity. During the limestone process, fine particles (with average size under 400#) are generated. These particles do not have economic value in agricultural and metallurgical sectors due their size. When limestone is used for agriculture purposes, these fine particles can be easily transported by wind generated air pollution. Therefore, briquetting, a mineral processing technique, was used to mitigate this problem resulting in an agglomerated product suitable for agriculture use. Briquetting uses compressive pressure to agglomerate fine particles. It can be aided by agglutination agents, allowing adjustments in shape, size and mechanical parameters of the mass. Briquettes can generate extra profits for mineral industry, presenting as a distinct product for agriculture, and can reduce the environmental liabilities of the fine particles storage or disposition. The produced limestone briquettes were subjected to shatter and water action resistance tests. The results show that after six minutes completely submerged in water, the briquettes where fully diluted, a highly favorable result considering its use for soil acidity correction.

Keywords**—**Agglomeration, briquetting, limestone, agriculture.

I. Introduction

MINING is one of the basic sectors of Brazil's economy; it contributes decisively to the well-being and improving the quality of life for present and future generations. It is essential for the development of an equitable society, provided it is operated with social responsibility, and while the principles of sustainable development are always present, considerable environmental impacts are caused by the same [1]. Intense mining activities alter both the mined and the surrounding areas, where waste and tailings deposits build up [2].

Limestone, most commonly used materials in liming, generally varies in mineralogical; the chemical and textural composition jointly determines the overall capacity of soil acidity neutralization. Among the features relating to the quality of limestone, only two have been considered: the neutralizing content and grain size. In evaluating these products, with respect to the aspect particle size, the same has been done in terms of responsiveness on the ground (for short periods), disregarding the residual effect [3].

The current Brazilian's Normative Instruction No. 35 of 2006 from MAPA, discuss how to perform the analysis to classify soil acidity corrective agents, and is based on level of calcium, magnesium and the Effective Neutralizing Power (ENP) of the agent [4].

The Brazilian production of agricultural limestone in 2013 showed unimpressive growth (less than 0.2%) compared to 2012, with the regions and states that produced more agricultural limestone shown in Fig. 1. The import and export of agricultural limestone are missing, confirming the self-sustainability of Brazil in the production of this input [4].

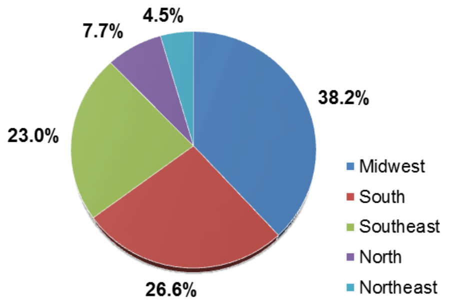

Fig. 1 Production of agricultural limestone per region in 2013 [4]

Mineral processing is performed through industrial processes for concentrates production, as minerals are almost never present in nature with the properties, such as size and facility, suitable for direct use in industry [5]. During limestone processing, a milling step of the same step which generates this fine material (size less than 400 #) is required, which has no economic viability in production agriculture, coking and calcining. Either this is because such a particle size may be carried by the wind, therefore constitute an environmental liability when used in agriculture, or reduce the percolation of gas in blast furnaces because of slow sedimentation [6].

The importance of studying the particle size is linked to the negative effects of these materials. When particles are smaller than 1 μm they can be hazardous for human beings, particularly for the respiratory system. Although being solid, fine particles (smaller than 1 μm) behave as a gas when disperse in the atmosphere and are subject to Brownian motion (random motion). The American Lung Association indicates that particles suspended in air with a diameter smaller than 10 micrometers, the so-called respirable particles are the most harmful to human health [7].

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The agglomeration processes intend to recover fine particles from mineral processing and the choice of this process depends on a careful and thorough analysis [8]. Pelletizing is the agglomeration method used to transform fine fractions of iron ore into a suitable product (pellet) to supply blast furnaces and direct reduction reactors, which will be transformed into pig iron and sponge iron, respectively [9]. Sintering, the main raw material of which are fine iron ore particles, is used in the metallurgical industry to turn ore and other raw materials through heat agglomeration into a product called sinter [10], and finally briquetting, which is a very efficient way to concentrate the available energy in biomass [11].

The briquetting process is an agglomeration process that consists of applying pressure through a mechanical press in a mass feedstock transforming it into a compact cylindrical solid with high density [12].

The first patent relating to briquetting was granted to William Easby in 1848 with the development of a process that allowed the formation of solid agglomerates of varying size and shape from fine fractions of any kind of coal, through pressure exerted on the material [8].

Briquette production, besides being a form of waste reuse, has the economic advantage of income generation for industry, through the marketing of this product [13]. Other advantages offered are reducing the volume of waste stored on site and reduced transport costs, as the briquettes can be stored to reduce the gaps in transit. In Brazil, interest in the briquetting process has always been focused on the use of thin steel coming from vegetable coal, constituting most of the research for the development of briquettes for use in this secondary activity [14]. Therefore, an alternative is proposed to mitigate the fine particles problem. The briquetting offers a workable and efficient solution, for both the limestone industry and the environment. The proposed agglomeration process could reduce environmental liabilities and generate profits for the mineral industry by developing a coproduct, using limestone fine particles, also known as limestone fines (particles smaller than 400#).

II. Methodology

The experiments were performed in the Modeling and Research Laboratory in Mineral Processing at the Federal University of Goiás using limestone fines (typically under 400#), from the Lagamar region. The limestone samples used in this work were donated by Cala Limestone Lagamar Company.

A. Limestone Characterization

In order to characterize the particle size to be used, limestone fines samples were prepared and subjected to tests to determine density, grain size and chemical analysis. The mass was determined by pycnometer. The granulometric analysis of the limestone was performed with a laser particle analyzer Mastersizer 3000 from Malvern in triplicate. This device uses the technique of laser diffraction for analyzing particle size [15].

A chemical analysis was performed to determine the limestone's Effective Neutralizing Power (ENP) and its reactivity, in order to calculate the Total Neutralizing Power (TNP, which is the same as calcium carbonate equivalent, TNP=CCE). TNP is an index commonly used in the selection of agricultural limestone in Brazil. Knowledge of these values is necessary from the context that incorrect usage can be harmful for farmers, who often do not have the expertise to apply limestone according to the requirements of the soil.

According to the technical report of studies conducted by the Agronomic Institute of Campinas, the calcium/magnesium ratio in the soil is irrelevant as long as the levels of these nutrients are suitable for a specific crop. Thus, based on soil analysis the correct usage is easy to define. This analysis was performed in order to classify the limestone regarding its neutralization strength according to its particle size. Both analyzes were performed by the Institute of Agricultural Sciences, Federal University of Uberlândia.

B. Production of Briquettes

The potential of limestone agglomeration was evaluated by briquetting using water as a binder agent and 15 g of limestone for each prepared composition. After homogenization, the mixture of limestone and water was placed in a mold (see Fig. 2) and applied 3 tons of uniaxial compression to it for 2 minutes, in order to promote the agglomeration. The uniaxial compression was applied using a hydraulic press.

The addition of water to the limestone was carried out using a graduated pipette to guarantee the correct volume and the desired amount of water. To a 250 mL beaker was added to 15 g of the limestone and water divided into three allotments to ensure that the homogenization of the mixture was optimal. The water dosage used was 0%; 5%; 7.5%; 10% and 12.5% by weight of water. The manufactured were then briquettes were weighed and measured (diameter and height using a digital caliper) to determine their variations in density.

C. Shatter Test

The Shatter Test determines the briquette strength to withstand repeated drops, simulating impacts that occur naturally during handling and transportation. The strength can be determined by dropping the briquette from a height of 0.3 m, using a steel plate with 10 mm thickness to stop the fall. If the briquette is subjected to a thermic treatment (or curing) to increase its mechanical strength, the height of the test will should be increased to 1.5 m [8].

The impact resistance is determined by the number of consecutive drops the briquette can withstand without fragmenting when released at standardized heights (30, 60, 90, 120 and 150 cm). For the uncured briquettes, three releases are considered a reasonable number, while for the heat-treated briquettes, the number of releases exceeds 10. The briquettes were subjected to successive drops until 5% of the initial mass is lost.

In order to analyze the water loss during the aging and its influence on the mechanical strength briquettes with 7.5% moisture content were made. This percentage was chosen because of the shatter test results. The briquettes weight was monitored for seven days and the relative air humidity was monitored using a thermo-hygrometer Minipa MT-241. After that, the briquettes were subjected to the shatter test.

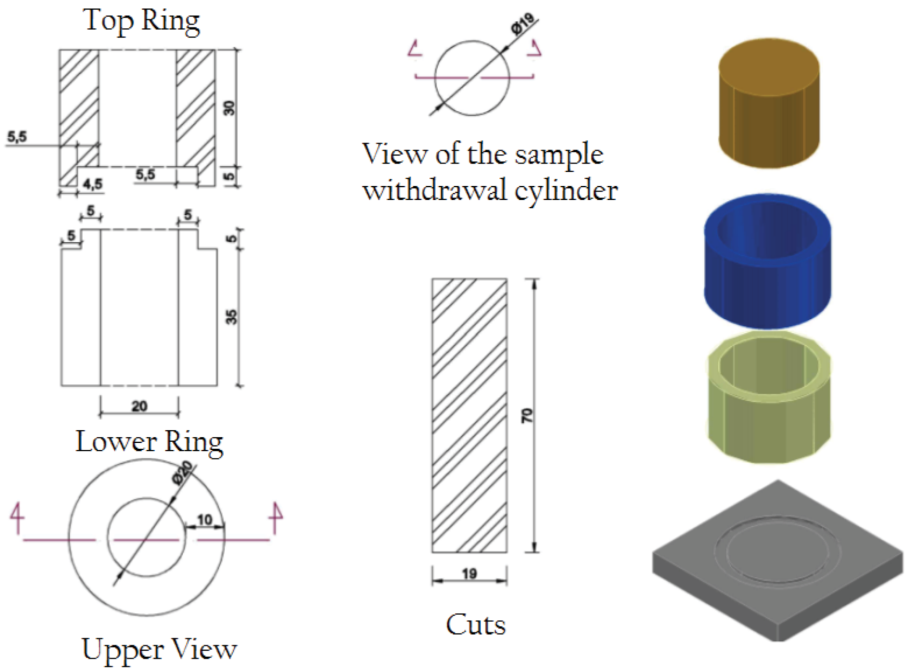


Fig. 2 Views of the cylinder used for the briquettes production

D. Briquettes Water Resistance

One way of assessing the quality of the briquettes is regarding their water resistance. This information is of great importance for cases where the briquettes can be stored in an open environment. One way to measure the water absorption by the briquettes is through immersion in water, being common determine the weight variation over time [8]. Tests must be conducted for 24 hours [16]. This test was also necessary to understand how briquettes would behave when coming in contact with water after being applied to the soil for the purpose of pH correction.

Five briquettes with the highest water percentage tested (water 12.5%) were manufactured and placed in five 25 mL beakers filled with water. The test ended when the briquette lost its cohesiveness and the immersion time was noted.

E. Limestone Morphology Analyzes through Scanning Electron Microscope (SEM)

Information on the morphology and characterization of limestone fines microstructure were obtained using a SEM model JEOL JSM - 6610, equipped with Energy-dispersive X-ray spectroscopy (EDS), Thermo Scientific NSS Spectral Imaging.

III. Results and Discussion

The average density of the limestone found in the pigmentary tests was 2.76 +/- 0.05 g/cm^3. The results are in agreement with the values found in literature (2.72 g/cm^3 and 2.87 g/cm^3) [17].

Fig. 3 shows the average particle size using data obtained by testing in triplicate performed on Mastersizer 3000 equipment. It is noted that approximately 99.5% of the limestone has particle size less than 74 µm (purple line).

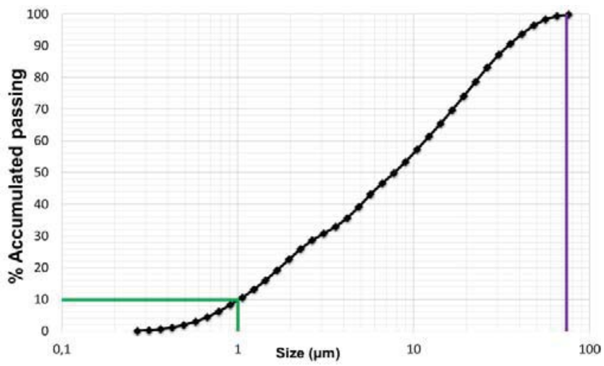


Fig. 3 Particle size analysis average limestone fines

The limestone fines have a low mass because they have particles below 1 µm. During application to the soil, this becomes an important feature, due to the health concerns associated with inhaling particulate matter. If the proper precautions are not taken, it can lead to pulmonary diseases. From the agriculture application point of view, the fine particulates can present huge losses as a result of wind [18]. According to the particle size analysis, around 10% of the limestone fine particles are colloidal (less or equal to 1 µm.)

The type of limestone to be used in agriculture depends on the calcium and magnesium ratios in the soil determined by chemical analysis. Table I shows the results of the chemical analysis of the limestone sample. The obtained value ENP was 100% and the reactivity equal to 99.6%. The calculated TNP was equal to 99.6%. The limestone was rated according to its MgO content and its ENP as a dolomitic limestone, since the MgO value was greater than 5%. With regard to the ENP, it was classified as group D, since the ENP was greater than 90%.

TABLE I
CHEMICAL ANALYSIS OF LIMESTONE SAMPLE

Oxide	CaO	$CaCO_3$	MgO	$MgCO_3$
%	33.6	59.8	11.1	23.3

Fig. 4 shows the side and top views of briquettes with water additions of 0; 5; 7.5; 10 and 12.5% (by weight) before and after the shatter test at 30 cm height. It was observed that there were fractures mostly at the edges of the briquettes. Large fragments were obtained for briquettes without water. A difference in color was also noticed in the absence of water.

The briquettes produced had average diameter of 1.93 cm and height of 2.36 cm. Briquettes with 12.5% of water addition presented a difficult mechanical conformation, mainly because the water drains out of the mold when compression was applied, although the removal of the briquette from the mold was still possible.

According to the analysis of Fig. 5, the results show a reduction in the number drops as the height of the fall was increased. Without the addition of water (see Fig. 5 (a)), the briquettes were fragile, supporting less than five drops from a height of 30 cm. However, with the addition of water as a binder (Figs. 5 (b)-(f)), the briquettes had higher mechanical strength in the first two tested heights (30 cm and 60 cm). In some tests, the briquettes past the shatter test for drops from a height of 90 cm (Figs. 5 (b) and (c)).

The higher performance of the briquettes with water addition can be explained by the bond formation between the particles and the water. The water provides the necessary cohesive strength for the particles adhesion and agglomeration. This force also depends on the capacity of adsorption of water by the particles [13]. To further analyze the briquettes, strength testing was conducted after seven days of aging (as shown in Fig. 5 (f)) and compared to the results of the tests performed immediately after manufacture.

It can be seen that there was no difference between the results of tests performed immediately after manufacture and the results of the shatter test conducted after seven days of drying. The briquettes with moisture (7.5%) showed the same pattern of resistance even when subjected to mechanical strength testing seven days after manufacture. Thus, even losing moisture, initially used as a binding agent, the product continues to maintain its strength. Table II shows the average data loss of mass in grams and percent, this loss can be justified due to moisture variation of the air recorded on the weighing days.

H_2O %	Before shatter test Upper	Before shatter test Side	After the shatter test Upper	After the shatter test Side
0				
5				
7.5				
10				
12.5				

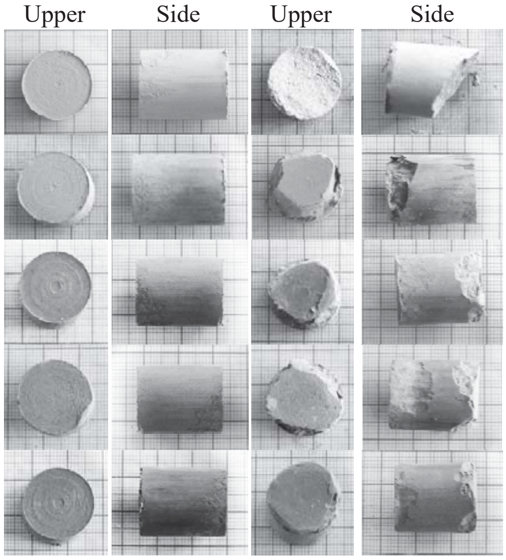
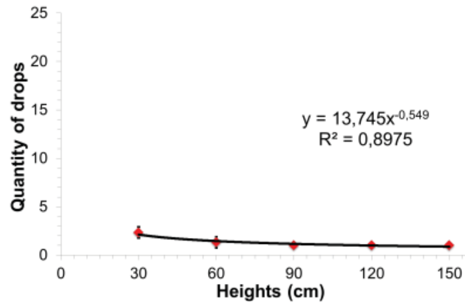
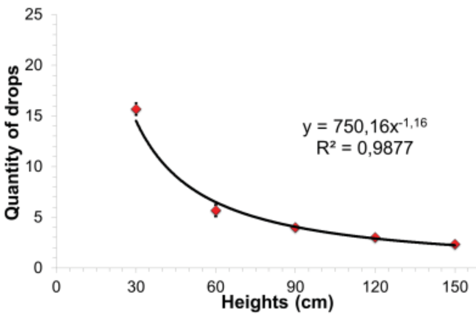


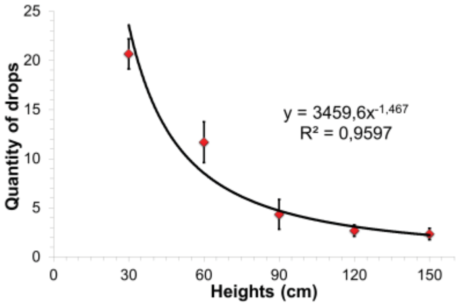
Fig. 4 Top and side views of the briquettes before and after the outputs of the shatter test on 30 cm



(a)



(b)



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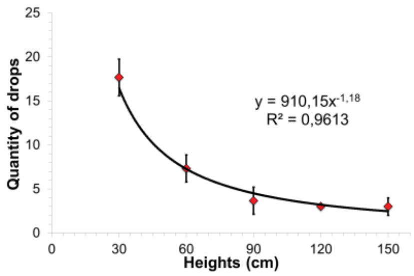
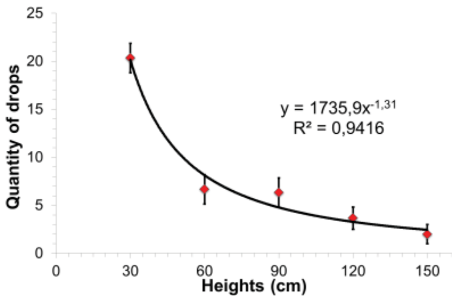
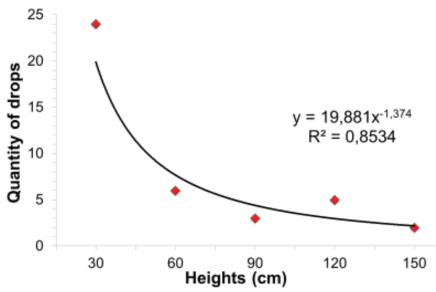


(d)



(e)



(f)

Fig. 5 Quantity of drops in relation to heights of fall: (a) 0; (b) 5; (c) 7.5; (d) 10; (e) 12.5% humidity and (f) shatter test with the briquette 7.5% after 7 days of drying

The porosity reduction occurred over the briquetting and the expulsion of air bubbles due the pressure applied were responsible for the increase in the density of the briquettes. Even more, the water adhered to the limestone fines due to capillary forces reduced the empty pores. Those mechanisms acting together increased the mechanical strength of the briquettes. The variation of the briquettes density over the water content can be seen in Fig. 6.

TABLE II
WEIGHT LOSS (%) OF THE BRIQUETTES AFTER 7 DAYS DRYING

Days	Initial Average Mass (g)	Average Loss (g)	Average Loss (%)	Air humidity (%)
0	15.347	-	-	-
3	14.363	0.984	6.41	81
4	14.341	0.022	0.14	73
6	14.330	0.011	0.08	75
7	14.309	0.021	0.14	45.5

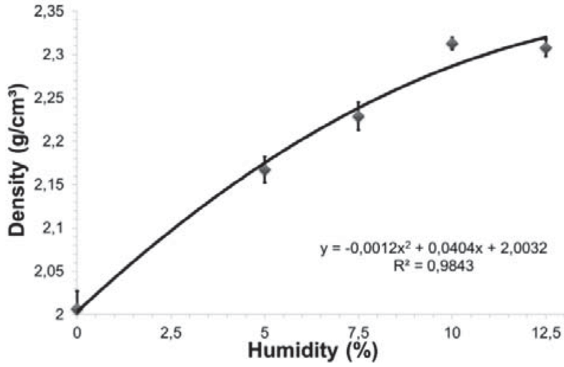
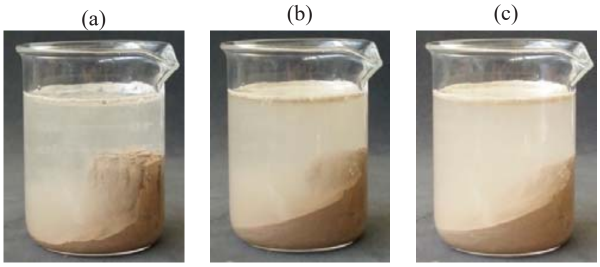


Fig. 6 Variation of the density of briquettes relative humidity

Fig. 7 shows that the briquettes did not retain their shape and constitution when submerged in water. The briquettes showed rapid disintegration, fully dissolving at an approximate average of 4.5 minutes.

One of possible practical use for limestone briquettes is soil acidity correction. For this purpose, the found dilution time is acceptable. When subjected to rain or irrigation water for longer than five minutes the briquettes would disolve and permeate into the soil to enhance its pH levels.

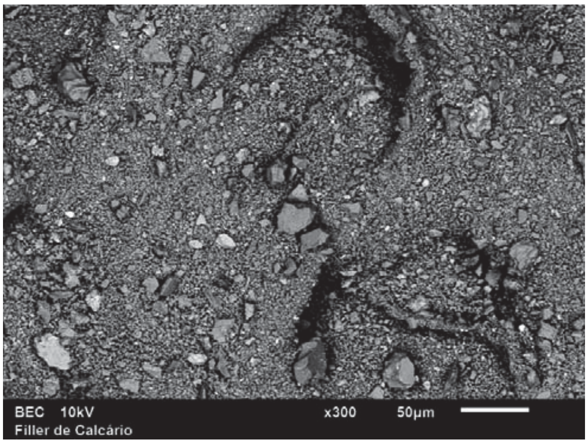
(a) (b) (c)



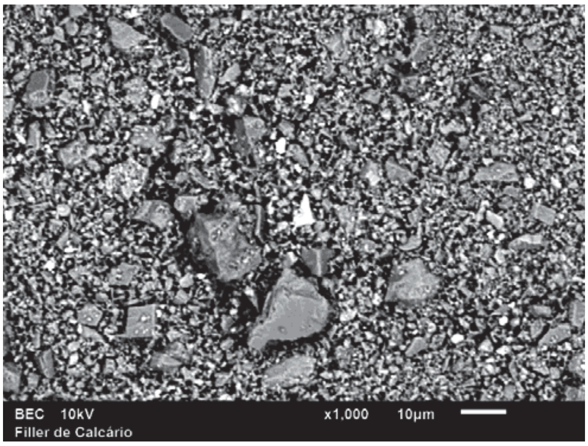
(d) (e) (f)

Fig. 7 Briquette of immersion time in water: (a) 4 seconds; (b) 1 minute; (c) 1 minute and 30 seconds; (d) 2 minutes; (e) 3 minutes and (f) 4 minutes

Fig. 8 shows the SEM results for the limestone fines samples. It is possible to see that the morphology of the particles is not similar, justifying the result obtained by granulometric analysis, which showed that 10% of the material is below 1 μm, and the particles were not clear because the shortest distance without losing the quality of the images was of 10 μm.



(a)



(b)

Fig. 8 SEM results for the distances (a) 50 μm and (b) 10 μm limestone sample

IV. Conclusion

From an analysis of the results, it can be proved that limestone briquetting is an option both quantitative and qualitative regarding the need for reuse of limestone fines. This is due the fact that briquettes assign value to the fine particles, and as well minimize the level of losses and exposure caused by wind, as well as reducing the tailing from discarded residue.

The fine limestone particles generated through mineral limestone treatment show chemical and physical characteristics suitable for briquette production. Instead of sending the fine particles to tailings dams (generating an everlasting environmental impact) the limestone briquettes can be a revenue source for the mining companies.

Since the amount of fine particles smaller than 1 μm is relatively high (around 10%), they can severally affect the health of workers (either in mining companies or in agriculture). To solution for this lies on agglomeration too, even if only to dispose these fine particles in a storage area. Considering the use of the fine particles in agriculture, they are extremely vulnerable to wind and rain action, which does not occur with the briquettes.

Another possible use for the limestone briquettes is the production of Calcium oxide (CaO), commonly known as quicklime or burnt lime. Quicklime is a widely used chemical compound produced by thermal decomposition of limestone. If the particles are too fine, the lost in the oven through the exit gases are too high. In this case, the briquetting of the fines can also become a feasible solution.

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