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DETERMINATION OF THE EFFICIENCY OF THE CALCINATION PROCESS THROUGH THE CHEMICAL COMPOSITION OF THE LIMESTONE OF A MIDWSTERN MINING INDUSTRY

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Abstract. *The present article aims at determining the efficiency of the process of calcination of an industry located in the Central-West region of Minas Gerais. To determine the chemical composition of the limestone and lime were held two chemical analyses: weight loss for ignition and the analytical method of titration.The choice of analysis method of weight loss on ignition is due be an analysis of easy reproduction in the laboratory, not requiring sophisticated equipment. And the analysis by titration allows for greater accuracy in the data. Was compared different granulometries of limestone calcined at different temperatures. After this, it was possible to conclude that the limestone calcítico compared to Dolomite (limestone) showed better results, because the limestone calcítico lost less weight to contain lower levels of impurities. It was also possible to conclude that a smaller particle size of limestone and a higher temperature increases the efficiency of the process.*

Keywords: *calcination, efficiency, ignition, titration, lime industry*

1. INTRODUCTION

According to data from the Brazilian Association of Cal, Brazil is one of the largest producers of lime in the world, occupying the fifth position in the ranking of lime producers, with a production of 7,425 thousand tons/year (ABPC, 2014).

The lime, also called quicklime, is produced by the dissociation reaction of calcium carbonate ($CaCO_3$) in calcium oxide (CaO). When the surface of the rock hits the calcination temperature dissociation process starts from the surface to the center of the rock, completing the process of calcination (OCHOA et al., 2010). For this reaction to occur the limestone must be heated to temperatures above 1173.15 K (SILVA, 2009).

The approximate chemical equation for this process is:

$$CaCO_3 + heat \rightarrow 56\ CaO + 44\ CO_2 \tag{1}$$

The State of Minas Gerais in the Southeast region of focus, one of the largest mineral reserves of the country. One of the main economic activities of the mid-western region of that State, is the production of lime in this region, there are 140 calcination industries, being mostly small businesses (SILVA, 2009). In the industries of the Central-West region of Minas Gerais, this process usually occurs in vertical blast furnaces.

The goal of this article is to determine the efficiency of the process of calcination of an industry located in the Central-West region of Minas Gerais. To determine the amount of calcium oxide present in the raw material were carried out two types of chemical analyses: weight loss for ignition and titration. With the results of these analyses it was possible to determine the efficiency of the process of calcination.

2. CHEMICAL ANALYSIS FOR WEIGHT LOSS ON IGNITION

A method that can be used to determine the calcium oxide content present in the limestone is the method of chemical analysis for ignition. This method presents advantages as being simple, fast, low cost, easy reproduction in the laboratory and can be used for a large number of samples. Knowing the mass of the sample it is possible to determine the percentage of calcium oxide from the determination of volatile and non-volatile mass (Dean, 1974 *apud* VERES, 2002).

Temperature action removes carbon dioxide (CO_2), organic matter and moisture and is obtained as residue calcium oxide and magnesium, along with other silicates and oxides. In this work, we considered that the percentage of silicates and other oxides is despicable, by having very small percentage.

The limestone can be classified according to their percentage of magnesium oxide as: calcítico limestone (less than 5 %) and magnesium (5 to 20 %) or dolomitic (above 12 %). The industries located in the Centre West miner using limestone and dolomitic limestone calcítico.

The Eq. (2) describes the process of calcination of calcitic limestone:

$$CaCO_3 + heat \rightarrow CaO + CO_2 \tag{2}$$

The Eq. (3) describes the process of calcination of dolomitic limestone:

$$CaCO_3 \cdot MgCO_3 + heat \rightarrow CaO + MgO + CO_2 \tag{3}$$

2.1 Equipment and materials to be used

2.1.1 Necessary equipment

- Muffle burnace Quimis, Q318M (Diadema, SP, Brazil);
- Analytical balance, GEHAKA, model AG 200 (Bradford, MA, EUA).

2.1.2 Glassware

- Porcelain crucibles.

2.2 Experimental procedure

Samples of limestone and lime were provided by an industry located in the Central-West region of Minas Gerais and transported and analyzed in the laboratory of chemistry of the Federal Institute of Mines-General-Campus Ant.

In chemical analysis the steps taken were:

- Measure the weight of the Crucible (without sample) using the analytical balance.
- After this, tara the scales and measures the sample sample before the limestone calcination. The experiment was done for different particle sizes of limestone before being calcined in muffle furnace at different temperatures.
- Using tweezers takes samples to muffle furnace with the temperature scorching the sample in furnace during a one-hour period.
- Afther this period, using tweezers, remove the muffle and weigh the sample calcined with the crucible (mass of the sample – burned + crucible).

To know the final mass after calcination, simply subtract the weight of the sample added to the Crucible calcined (obtained at the beginning of the experiment) of the weight of the crucible.

2.3 Example of calculation for determination of calcium oxide content by weight loss on ignition

Table 1. Lower calorific value of fuel.

Measurement	Weight [Kg]
Inicial mass of the sample:	0.0062
Mass do crucible:	0.0843
Inicial mass of set (crucible + sample):	0.0905
Final mass of the set (crucible + sample):	0.0088
Final mass of sample (after calcination):	(0.0878 – 0.0843) = 0.0035

$$\% \ CaO = \left(\frac{Final\ mass\ of\ sample\ (after\ calcination)}{Mass\ of\ the\ sample\ prior\ to\ calcination} \right) \times 100\ \% \tag{4}$$

Considering the data from example:

$$\% \, CaO = \frac{0.0035 \times 100\,\%}{0.0062} = 56.45\,\% \tag{5}$$

3. CHEMICAL ANALYSIS BY TITRATION

Another technique that was used to determine the percentage of calcium oxide and magnesium oxide is titration.

The advantages of this technique include besides economy and precision, simple, quick reactions, stoichiometry and known. Also has chemical and physical changes (pH, temperature, conductivity), the equivalence point (HARVEY, 1956).

This type of technique according to the changes of pH, monitors the volume of a solution with defined chemical characteristics, to determine the percentage of calcium oxide and magnesium oxide in the limestone (HARVEY, 1956).

In this process the measured volume of a solution of known concentration (NaOH solution, the 0.1 mol L^{-1}), necessary to react quantitatively with a solute (the solute is the solution of HCl, the 0.1 mol L^{-1}).

In practice, they were able to analyze multiple samples and determine the amount of calcium oxide in the same from the knowledge of the techniques of volumetric analysis

The Eq. (6) and (7) describe the titration process is:

$$CaCO_3 + 2\,HCl \rightarrow H_2O_{(l)} + CO_{2(g)} + CaCl_{2(aq)} \tag{6}$$

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)} \tag{7}$$

3.1 Determination of the pH of the turn of hydrochloric acid solution (HCl) to 0.1 mol L^{-1}

The indicator used in this work to determine the moment when the quantities of the analyte and the titrant molars are equal, also called the equivalence point, was the bromothymol blue. The choice of this indicator is due the same present transition interval of pH between 6.0 and 7.6. The pH of turning chemical reactions studied in this work is around 7.

3.2 Determination of the mass of the sample of calcium carbonate ($CaCO_3$) that really reacted with 0.025 L of HCl in 0,1 mol L^{-1}

The Eq. (8), (9), (10), (11) and (12) describe the process of titration:

$$n_{HCl} = n_{CaCO_3} + n_{NaOH} \tag{8}$$

$$n_{HCl} = n_{HCl\ in\ excess} - n_{NaOH} \tag{9}$$

$$n_{CaCO_3} = C_{HCl}\ x\, V_{HCl} - C_{NaOH}\ x\, V_{OH}^{-} \tag{10}$$

$$m_{CaCO_3} = MM_{CaCO_3}\ x\,(C_{HCl}\ x\, V_{HCl} - C_{NaOH}\ x\, V_{OH}^{-}) \tag{11}$$

$$m_{CaCO_3} = 0.1\,Kg \cdot mol^{-1}\ x\,(0.1\,mol \cdot L^{-1}\ x\,0.05\,L - 0.1\,mol \cdot L^{-1}\ x\, V_{OH}^{-} \cdot L) \tag{12}$$

3.3 Materials to be used

3.3.1 Reagents

All reagents used were of analytical grade.

- Hidrochloric acid, HCl, MM = 0.0375 Kg mol^{-1}, LABIMPEX (Diadema, SP, Brazil);
- Sodium hydroxide, NaOH, MM = 0.0400 Kg mol^{-1}, VETEC, (Duque de Caxias, RJ, Brazil).

3.3.2 Glassware

- Erlenmeyer flask;
- Burettes;
- Volumetric pipettes;
- Beakers.

3.4 Experimental procedure

Titration analysis followed the following steps:

- In na Erlenmeyer flask, weigh 0.000125 Kg of residue (CaO).
- Added to the Erlenmeyer flask 0.0500 L of HCl in 0,1 mol L^{-1}.
- In a burette measure 0.0500 L of NaOH in 0,1 mol L^{-1}.
- The mass of calcium carbonate ($CaCO_3$) that really reacted with 0.025 L of HCl 0.1 mol L^{-1}, using the Eq. (12).

4. DETERMINATION OF PROCESS EFFICIENCY

HILL, 1997, defined that process efficiency (η) can be calculated using the following relationship:

$$\eta = \frac{Hc \cdot Ls}{PCL \cdot Mc} \tag{13}$$

Where:

η – Calcination process efficiency.
Hc – Obtained by calculating the energy required for ash the fraction of calcitic limestone and the energy required to calcine the dolomitic fraction (MJ/tonne de CaO).
Ls – Calcium oxide contente avaliable at lime.
PCL – Lower calorific value of the fuel used (MJ/Kg).
Mc – Mass of fuel used per tonne of lime produced (Kg of fuel/tonne of lime produced).

4.1 The parameter Hc

Recent work (HILL, 1997), in practical applications can be assumed the value of Hc for the calcitic limestone of 3,200 MJ/tonne of CaO and dolomitic of 3,020 MJ/tonne of CaO.

4.2 The parameter Ls

This parameter represents the calcium oxide content. To determine that we use two chemical analyses: weight loss for ignition and titration. These analyses were described in the Sections (2) and (3) (HIIL, 1997).

4.3 The lower calorific valuer (PCL)

The calorific value is defined as the amount of heat that escapes during the complete combustion of the fuel mass unit, the difference between the PCS and PCI is the energy required to evaporate the moisture present in the fuel and energy from oxidation of hydrogen present in the same. The calorific value of the fuel can be obtained in practice using a calorimetric bomb (CORTEZ et al., 1997).

The values of lower calorific value (PCL) used in this article were obtained according to the Tab. (1):

Table 1. Lower calorific value of fuel.

Combustível	PCL (kJ/Kg)
Firewood (40% water)	10,048.32
Firewood (dry) (12% water)	15,407.42
Coffe husks	15,909.84

Source: Adapted from AALBORG, 2015.

4.4 Fuel consumption

The fuel consumption is given by the fuel mass in kilogram used per tonne of lime produced. To determine this parameter you must register for a period of time the fuel consumption (HILL, 1997).

The industry studied in this article has a consumption of 0.390 pounds of eucalyptus / Kg of lime and 0.0012 Kg of coffee husk / Kg of lime.

4.5 Example of calculation of the efficiency of the process of calcination

The efficiency of a sample of calcitic limestone, with 57.41 % content of calcium oxide (CaO), calcined temperature of 1,273.15 K, for a process with fuel consumption (eucalyptus) of 0.390 Kg of the eucalyptus / Kg of lime produced can be calculated using the Eq. 14:

$$\eta = \frac{Hc \cdot Ls}{PCI \cdot Mc} \tag{14}$$

$$\eta = \frac{3{,}200 \cdot 0.57514102}{\left(\frac{3{,}680}{10^{-3}} \frac{4.18}{\cdot 10^{6}}\right) \cdot 390} = 0.30678 = 30.678\ \% \tag{15}$$

5. CASE STUDY

In this work it was determined the efficiency of the process of calcination of a calcination industry using two chemical analyses. The first step was to determine the percentage of calcium oxide for each type of limestone. With the determination of calcium oxide was unable to determine the efficiency of the process of calcination.

Chemical analysis considering weight loss by trusted results not in ignition temperature of 1,073.15 K, as shown in Fig. 1 and Fig. 2. This is because, at this temperature the sample not yet completely calcined limestone.

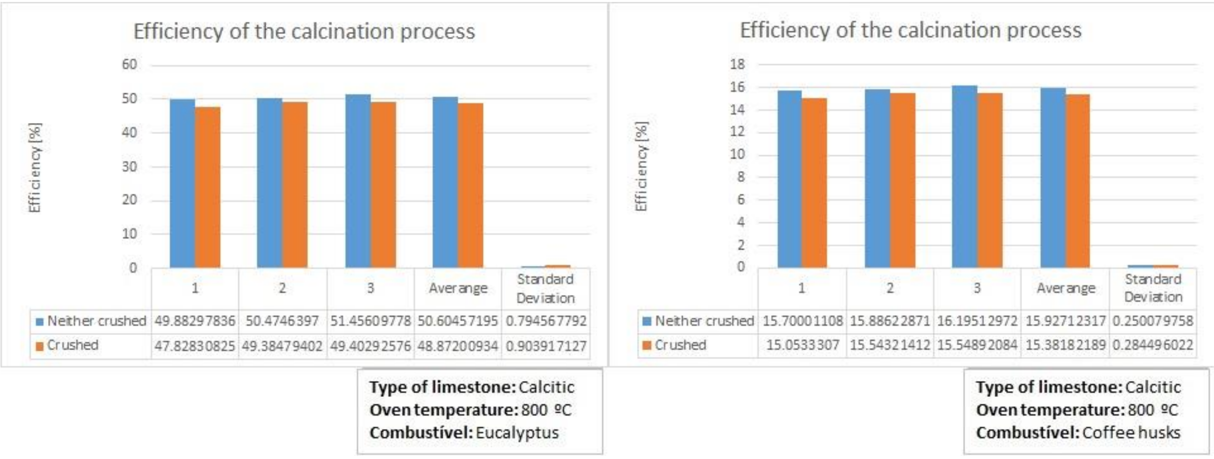

Figure 1: Calcination process efficiency for the method of the loss on ignition for the calcitic limestone to 1,073.15 K.

Figure 2. Calcination process efficiency for the method of the loss on ignition for the dolomitic limestone to 1,073.15 K.

At the temperature of 1,273.15 K, calcined limestone sample completely. At this temperature it was possible to assess that the sample of crushed limestone presented greater efficiency, this is because there has been greater formation of calcium oxide.

The calcitic limestone calcined at the temperature of 1,273.15 K and using the eucalyptus as fuel, obtained an efficiency of 28.4809 % for samples crushed and 30.8347 % for crushed samples as show the Fig. 3. For the coffee pods in the same temperature, the efficiency was of 8.9640 % for samples crushed and 9.6418 % for crushed samples.

Figure 3. Calcination process efficiency for the method of the loss on ignition for the calcitic limestone to 1,273.15 K.

For the calcined dolomitic (limestone) in the temperature of 1,273.15 K and using the eucalyptus as fuel, obtained an efficiency of 25.0602 % for samples crushed and 28.3618 % for crushed samples, as show the Fig. 4. For the coffee pods in the same temperature, the efficiency was of 7.8873 % for samples crushed and 8.9265 % for crushed samples.

Figure 4. Calcination process efficiency for the method of the loss on ignition for the dolomitic limestone to 1,273.15 K.

Chemical analysis by titration, obtained rellable results when the limestone is calcined to 1,073.15 K temperature because this type of analysis determines the calcium oxide contente presente in the sample taking into account the calcium oxide contente presente in the sample taking into account the calcium oxide contente that really reacted in chemical reaction of titration, does not require that the limestone calcine completely. Fig. 5 shows the process efficiency for the calcitic limestone and the Fig. 6 shows the process efficiency for the dolomitic limestone in the temperature of 1,073.15 K.

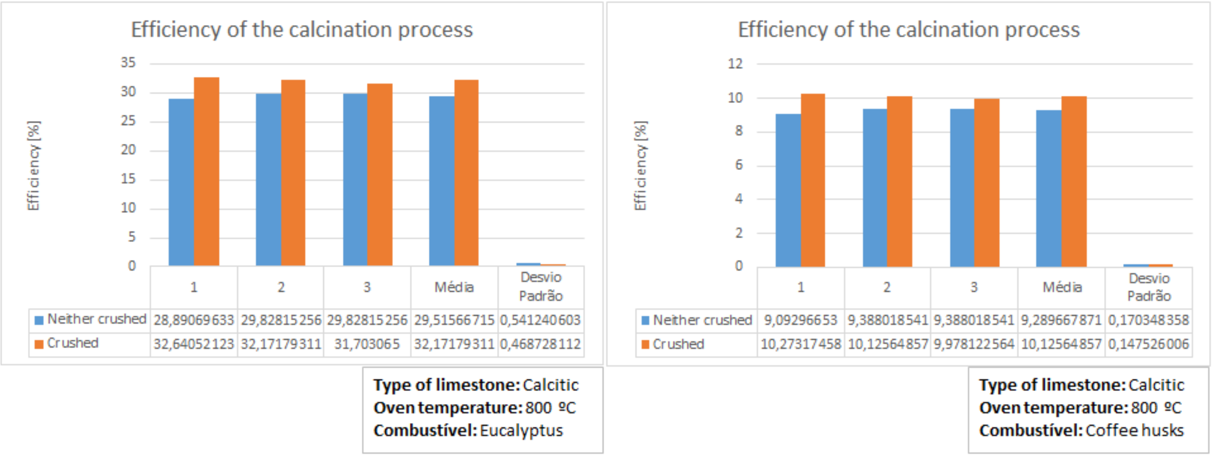

Figure 5. Calcination process efficiency for the chemical analysis of the titration for the calcitic limestone to 1,073.15 K.

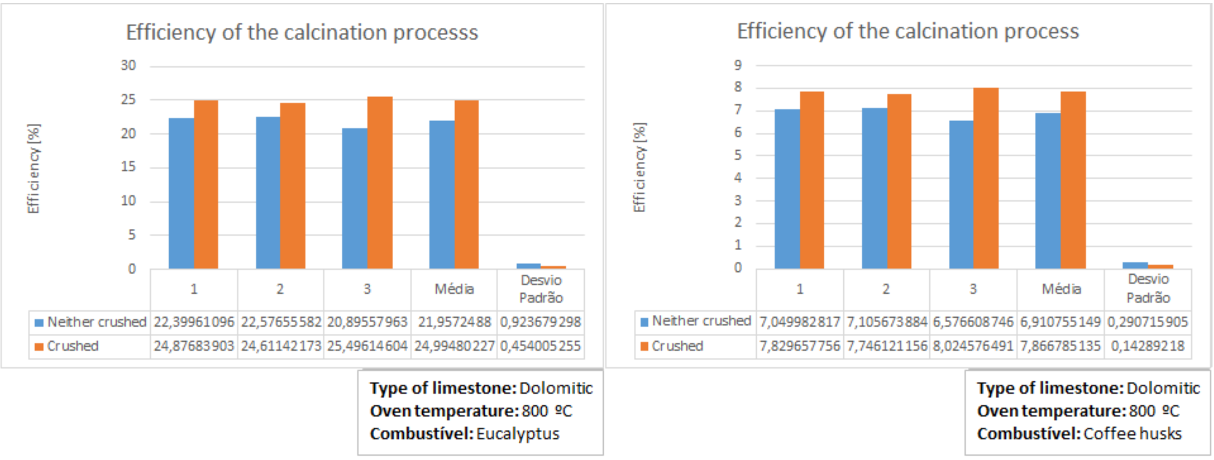

Figure 6. Calcination process efficiency for the chemical analysis of the titration for the dolomitic limestone to 1,073.15 K.

Figure 7 and the Fig. 8 shows the efficiency of the calcination process considering the calcium oxide content determined by chemical analysis by titration for the two types of limestone calcined at a temperature of 1,273.15 K. Figure 7 shows the calcination process efficiency for the calcitic limestone. And the Fig. 8 shows the efficiency of the process of calcination to dolomitic limestone.

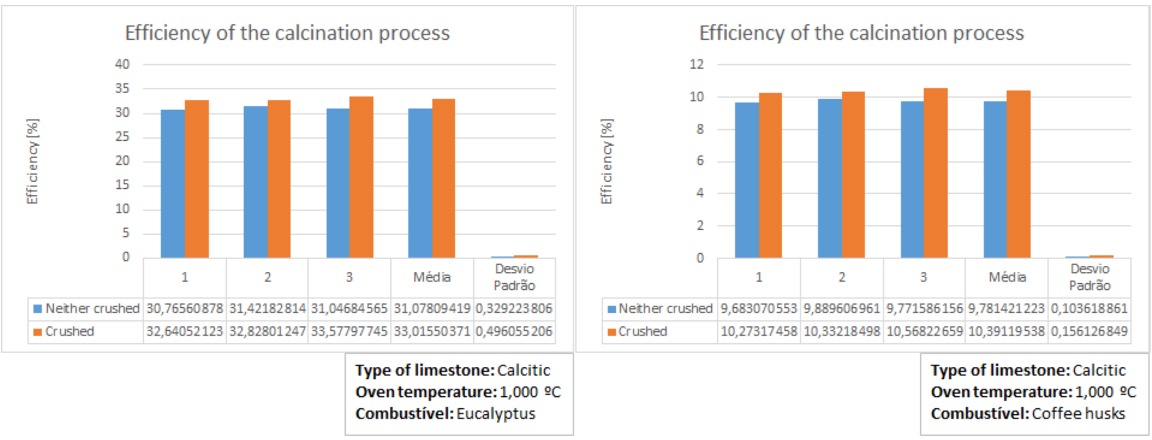

Figure 7. Calcination process efficiency for the chemical analysis of the titration for the calcitic limestone to 1,273.15 K.

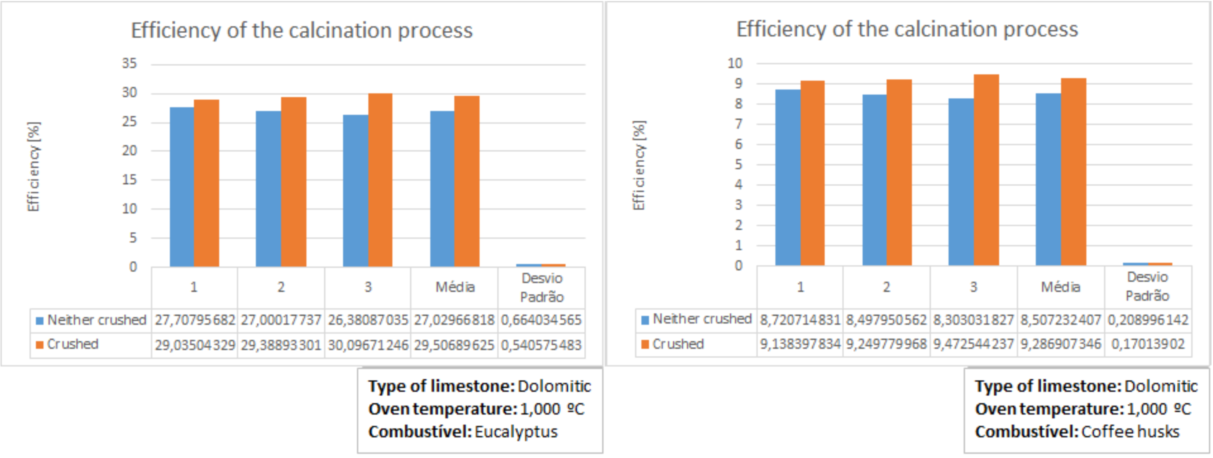

Figure 8. Calcination process efficiency for the chemical analysis of the titration for the dolomitic limestone to 1,273.15 K.

6. CONCLUSIONS

Most lime industries located in the Central-West region of Minas Gerais still operate with low efficiencies.

A diameter of limestone feeding in the blast furnace should be smaller. This is because a smaller particle size, implies increased contact surface, increasing the chemical reaction. The chemical composition of the limestone influences the efficiency of the process of calcination. The calcitic limestone compared with dolomitic limestone presented a greater efficiency in the process of calcination, because it presents a greater calcium oxide content in its chemical composition.

The type of fuel used is eucalyptus, which presented better efficiency. The experiment conducted in the laboratory of chemistry of IFMG-Ant Campus considered small sample masses, but best results can be obtained on an industrial scale of large masses of samples.

The crushed samples obtained better results, because increased contact surface increases the speed of chemical reaction. For a lower fuel consumption, higher efficiency of the process of calcination and consequent greater efficiency from the calcination process indicates that the limestone goes through a crushing process for reducing the size of the rock that enters the blast furnace, utilization of eucalyptus as main fuel and coffee pods as secondary fuel.

The temperature rise resulted in an increase in the speed of chemical reaction and therefore an increase in the efficiency of calcination.

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