

# Experimental study applied to the lime hydration process, in a thermoelectric coal power plant unit

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## Case study

**Keywords:** temperature dependence, calcium hydroxide, limestone, flue gas desulfurization, mineral coal

**Posted Date:** September 2nd, 2020

**DOI:** <https://doi.org/10.21203/rs.3.rs-66834/v1>

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# Experimental study applied to the lime hydration process, in a thermoelectric coal power plant unit

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**Abstract:** Coal Power Plants need to control SO<sub>2</sub> emissions to the atmosphere from the boiler flue gases, in order to reach standards according to guidelines determined by the Conselho Nacional de Meio Ambiente - CONAMA. For this purpose hydrated lime is used, which is, in fact, produced from lime at the power plant. Hydrated lime is injected into the equipment called desulphuriser that operates capturing the sulfur dioxide from the boiler flue gas. Due to the importance of this process, the present work aimed to evaluate several points that involve: the production of hydrated lime from lime, the analysis of the quality of lime received, the study of the hydration process. Moreover it was evaluated the impact of the temperature of reaction through to the hydration efficiency according to the methodology and routine proposed. In addition, complementary analysis were carried out on the characterization of lime and hydrated lime and the correlation between the main process parameters measured and recorded in lime hydration control system. In relation to the results of hydration efficiency, it was possible to observe its increase when the maximum temperature of the reaction stage was lower, reaching results up to 85%.

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**Keywords:** temperature dependence, calcium hydroxide, limestone, flue gas desulfurization, mineral coal.

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## 1. Introduction

The *Companhia de Geração e Transmissão de Energia Elétrica do Sul do Brasil - Eletrobras CGT Eletrosul* is a subsidiary company Eletrobras whose one of its activities is the power energy based generation on mineral coal. Its coal power plant complex is located in Candiota, 400 km from Rio Grande do Sul capital. In 2011, the commercial operation of UTE Candiota III was initiated. Candiota III Power Plant has an installed capacity of 350 MW with a 3-stage turbine, natural circulation boiler with tangential direct burning (Eletrobras 2020). The superheated steam is produced with 200 bar, 541 °C and 150 t/h. For the environmental control of the boiler flue gases, two electrostatic precipitators are used to reduce ash content carried by the gas. In the middle of these equipments, a Semi Dry Circulating Fluidized Bed Flue Gas Desulfurizer (Semi Dry CFB FGD) system is used to control sulfur dioxide (SO<sub>2</sub>) emissions. The Environmental Operating License 991/2010 granted by the “Instituto Brasileiro do

Meio Ambiente e dos Recursos Naturais Renováveis – IBAMA”, define that the daily average of SO<sub>2</sub> atmospheric concentration is limited to 1700 mg/Nm<sup>3</sup>, among other flue gas concentration control parameters. For this reason, to control this parameter, due to the high coal sulfur content, it is essential the FGD operation. The desulfurizer installed at UTE Candiota III performs a reduction of sulfur dioxide from calcium hydroxide, according to the following simplified reaction.



On the other hand, for the production of Hydrated Lime (basically Ca(OH)<sub>2</sub>), reagent in Equation 1, which is produced at the company itself, quicklime rich in calcium oxide (CaO) is used as raw material. This is mixed with water in an equipment called hydrator, to obtain hydrated lime. As a consequence, considering that the boiler flue gas desulphurization requires the production of hydrated lime for its operation, the hydration process study becomes relevant. In general, three factors are fundamental for the quicklime

Received: MM DD, 2020; Accepted: MM DD, 2020; Published: MM DD, 2020

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hydration process analysis: the study of the process parameters (to find the optimum values in the equipment), the characterization of the received input and the product generated. The general objective of this article aims to study the production process of hydrated lime from lime proposing points of improvement to guarantee greater hydration efficiency. Specifically, it was proposed a new methodology for the collection of lime and hydrated lime to obtain and analyze hydration efficiency results.

In the industrial dry hydration process, equipment installed at UTE Candiota III, the mixture of calcium oxide and water, in the first stage of the equipment, produces a liquid mass. Such as  $\text{Ca}(\text{OH})_2$  formation reaction is exothermic, part of the added water is evaporated. The process is regulated with enough water to ensure that water liquid is present until the reaction is practically complete. Then the last trace of liquid water is evaporated to produce a finely divided powder, practically free of moisture (Tsimas 2015).

The relationship between the hydration efficiency and the temperature of the thermocouple located in the hydrator central part (Figure 1), in the reaction stage (T5) showed an improvement trend when this temperature was lower, with a negative correlation of 0.82. T5 is the temperature measured in the center of the hydrator.

Another important item to be considered is that it was possible to achieve hydration efficiencies between 80% - 85% at temperatures closer to 100 °C in T5. Thus, we can suppose that the indicator created in the present work satisfactorily represented the process condition of the studied equipment. By knowing the material received in more depth, improvements in control parameters can be sought in order to establish more favorable conditions for the hydration process. Microcrystalline impurities, for example, contained in limestones, the raw material to obtain lime -and in consequence the hydrated lime- could shown a marked effect promoting grain sintering in calcination condition (Souza, F. D. and Braganca, 2017). In addition, by ensuring greater efficiency in the hydration process of quicklime, the greater the use of the input and, consequently, the better the capture of  $\text{SO}_2$ . Based on a better understanding of the behavior of the hydration system process parameters, it was possible to verify which points have the greatest influence on the process and, with this, improve operational procedures and create updated training in order to increase the knowledge of operators and raise their awareness. The importance of this process, guaranteeing better results, reducing operating costs and continuous improvement using control tools with indicators that represent the studied process.

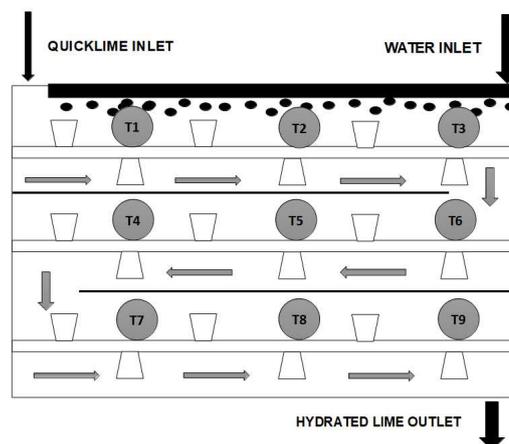


Figure 1: Schematic Diagram: Hydration Equipment for FGD reagent production.

In order to identify the similarities or dissimilarities between the different thermostats with regard to the influence of temperature on the lime hydration process, the analysis (multivariate) was performed by hierarchical grouping. For the purpose of establishing the comparison between the groups, the high degree of intra-group homogeneity and low-grade inter-group are measured, in general, by the concept of distance (Soler 2013).

In this work, Euclidean distance was used as a grouping measure. Such a metric is characterized by assessing the dissimilarity between two elements. The dendrograms resulting from the hierarchical grouping were produced by the most distant neighbor-complete linkage method (Charikar et al., 2019; Rajalingam and Ranjini, 2011).

## 2. Methodology

### 2.1. Sampling points to determine hydration efficiency and quicklime characterization.

Figure 2 below shows the boiler flue gases desulphurization process at Candiota III Power Plant. The diagram details since the reception of quicklime from trucks, hydrated lime production as well as the desulfurization process itself. In this figure are presented 3 sampling points that were used for the characterization of both quicklime and the hydration process, which will be presented as follows.

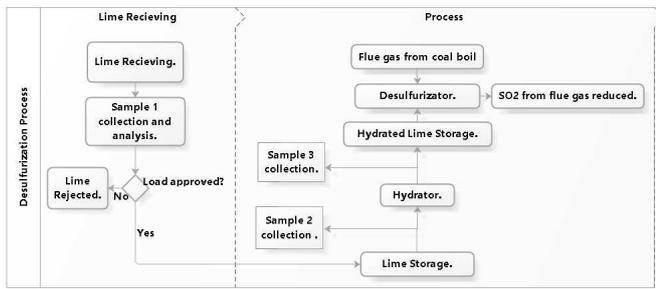


Figure 2: Desulfurization process and sampling points

The sampling locations are indicated according to Figure 2, as described below:

- **Sample Point 1:** Lime Sampling that is carried out for approval or rejection of material in compliance with current contracts with supplier company. This sample is carried out for each load received.

- **Sample Point 2:** Quicklime Sampling at the hydrator inlet. This sampling routine was implemented with the objective to calculate the hydration efficiency. The result of analysis of the material at this point differs from the result of Sample Point 1 because there is a storage silo that receives different loads and this device mix their loads.

- **Sample Point 3:** Hydrated lime sampling at the outlet of the hydrator. This routine, also was implemented in order to obtain the calculation of the efficiency of hydration. Between Points 2 and 3, water is injected to produce hydrated lime. For the collection of Point 3, it was proposed, designed and made for the present study a manual sampling device that was hermetically adjusted to a ball valve so that this equipment could be closed during sampling moment, allowing the material to be collected. This was necessary to enable the collection of hydrated lime at the outlet of the hydrator, which is kept at negative pressure. The amount withdrawn from this point for carrying out the analyzes was around 100g.

## 2.2. Tests for characterization of quicklime and hydrated lime

### 2.2.1. Reactivity in 3 minutes

For the reactivity analysis for quicklime, 100 g of a quicklime sample was added in 400 ml of CO<sub>2</sub> - free demineralized water at 25 ° C ± 1°C in a Dewar flask shaking at 400 rpm for 3 minutes. This analysis was performed according to the procedure ASTM C110 (2016), Standard Test Methods for Physical Testing of Quicklime, Hydrated Lime, and Limestone. The following equation shows how reactivity is calculated:  $\Delta T = T_2 - T_1$  (4)

Since Temperature T<sub>1</sub> is the initial temperature which is 25°C and T<sub>2</sub> is the temperature measured after 3 minutes.

### 2.2.2. Available calcium oxide

For the analysis, 0.5 g of quicklime or hydrated lime sample was weighed, transferred into a 250 ml Erlenmeyer flask and immediately afterwards it was added 20 ml of demineralized water. The sample was stirred and boiled for

two minutes. After this step, another 150 ml of CO<sub>2</sub>-free demineralized water was added and plus 15 g of sucrose. The sample was stirred with a magnetic stirrer for 30 minutes. Then, 2 to 5 drops of 11% phenolphthalein were placed and then a titration with 0.5M hydrochloric acid standard solution. It was noted the volume spent during the procedure. The analysis of available calcium oxide, which is part of standard NBR 6473 (2003) "Lime and hydrated lime – Chemical Analysis" is presented by the following equation (Equation 2).

$$CaO_d = (0,01402 \times V_{HCL} \times F_{HCL} \times 100) / m \quad (2)$$

Where:

**CaO<sub>d</sub>** = It is the content of calcium oxide and hydroxide available in percentage

**V<sub>HCL</sub>** = is the spent volume of HCl (ml)

**F<sub>HCL</sub>** = is the correction factor for hydrochloric acid.

**m** = mass of the sample in grams

0.01402 = corresponds to the g equivalent of CaO / (cm<sup>3</sup> hydrochloric acid 0.5N)

### 2.2.3. Moisture

For the determination of moisture (ABNT NBR 6473, 2003) it was necessary to take approximately 5g of sample, in a porcelain capsule with 80 cm<sup>3</sup> capacity to 100 cm<sup>3</sup>, with an oven previously adjusted to 110 ± 5°C and approximately 15 minutes keeping the sample for 1h. After that period, the sample was placed in a desiccator and cooled for approximately 30 min to determination of its mass (m<sup>3</sup>). The moisture content of virgin lime and hydrated lime were calculated using the equation 3:

$$Moisture = ((m_1 + m_2) - m_3) / m_1 \quad (3)$$

Where:

**m<sub>1</sub>**: mass of the sample, in grams;

**m<sub>2</sub>**: mass of the capsule, in grams;

**m<sub>3</sub>**: mass of the capsule plus sample after drying, in grams.

### 2.2.4. Lost of Ignition

For the analysis of loss of ignition (ABNT NBR 6473, 2003) 1.0 g of sample was weighed in a crucible previously calcined and tared on an analytical balance. The material was calcined in a muffle furnace at 1000 ° C ± 50 ° C for 1h and then cooled in a desiccator to measure its mass. Loss of Ignition (LOI) is calculated by the Equation 4, as follows:

$$PF = ((m_4 - m_3) \times 100) / m_2 \quad (4)$$

Where:

**m<sub>4</sub>** = Mass of the crucible with the sample before calcination, in grams (g);

$m_3$  = Mass of the crucible with the sample after calcination, in grams (g);

$m_2$  = Initial mass of the sample in grams (g).

For the present work, the loss of ignition test was used to measure the percentage of  $CO_2$  of the quicklime sample as well as the percentage of combined water from the hydrated lime. The loss of ignition analysis was used to calculate the efficiency of hydration of quicklime.

### 2.2.5. Determination of Hydration Efficiency

From the samples collected of quicklime and hydrated lime at Points 2 and 3, it was possible to calculate the hydration efficiency. To obtain this parameter, an analysis routine was performed according to the diagram shown in Figure 3.

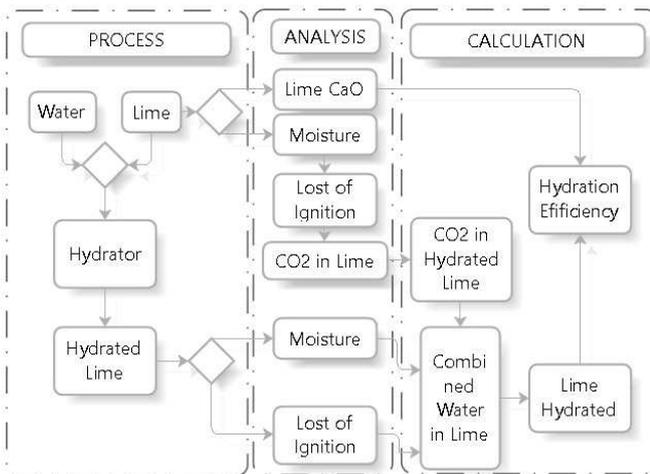


Figure 3: Determination of Hydration Efficiency

For this route to determine hydration efficiency, it was assumed that the result of lost of ignition obtained from quicklime corresponds to the percentage of  $CO_2$  contained in the hydrated lime.

### 2.2.6. Combined water and hydrated CaO

For the route to determine hydration efficiency, only two equations will be used to determine the combined water and hydrated CaO parameters present in NBR 7175 (2003), according to the following equations 5 and 6:

$$\text{CombinedWater} = \% - (CO_2 - \%) \quad (5)$$

$$CaO_{Hydrated} = \%Water \times 3,11 \quad (6)$$

The equations presented are derived from this standard and are part of the implemented methodology that performs the calculation of the hydration efficiency of quicklime in hydrated lime. Due to this, it is possible

determine the amount of water that combined with the calcium oxide, that is, the amount of water that reacted with the calcium oxide, forming calcium hydroxide. On the other hand, refers to the amount of calcium oxide that was hydrated. The “3.11” factor is nothing more than the stoichiometric relationship between the molar mass of water and the molar mass of calcium oxide (56gmol / 18gmol).

### 2.2.5. Determination of hydration efficiency

With the determination of hydrated CaO results, it was possible to establish hydration efficiency, according to the Equation 7, below.

$$\text{Efficiency of Hydration} = \%_{Hydrated} / \%_d \quad (7)$$

Therefore, the hydration efficiency is the amount of calcium oxide hydrated over the total amount of calcium oxide available in the sample.

### 2.2.6 Hydrator Operational Temperature x Hydration Efficiency

With the consolidation and application of the routine to define hydration efficiency, it was possible to study the correlation between the process operating temperature and the proposed methodology.

The results of hydration efficiency were compared with the average temperature in the period from 8 am to 12 pm of T5 (same sampling period) which is located in the second stage, in the central position of the equipment (Figure 1). The data were collected in average values every 5 minutes through the Hydration monitoring system. The T5 thermocouple was chosen as a reference because it was observed that at this point the highest average temperature among the nine temperature sensors were presented. Several samplings were performed at the inlet and outlet of hydrator in order to correlate the hydration efficiency with the temperature at T5, in the second stage.

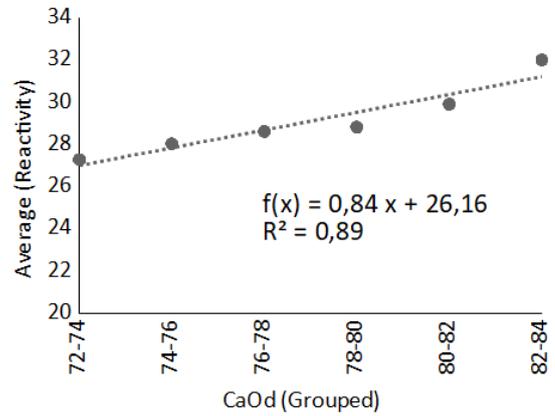
The equipment chosen for the analysis was Hydrator 1, due to its longer operating time. In order to compare the hydration efficiency results with the T5 temperature, technical and statistical criteria for sample exclusion was considered.

### 2.2.7. Control parameters of the hydration process.

The quicklime hydration monitoring system, among other functions, allow the control of the following parameters: first stage mixers rotation, water flow, lime flow or the water / lime ratio, according to the behavior of the reaction temperature observed by the operator. Next, Table 1 presents the main parameters measured and registered in the Hydration Monitoring System.

**Table 1:** main parameters measured and registered in the Hydration Monitoring System

Symbol	Meaning
T1	Temperature 1 of the 1 <sup>st</sup> stage.
T2	Temperature 2 of the 1 <sup>st</sup> stage
T3	Temperature 3 of the 1 <sup>st</sup> stage
T4	Temperature 1 of the 2 <sup>nd</sup> stage.
T5	Temperature 2 of the 2 <sup>nd</sup> stage
T6	Temperature 3 of the 2 <sup>nd</sup> stage
T7	Temperature 1 of the 3 <sup>rd</sup> stage.
T8	Temperature 2 of the 3 <sup>rd</sup> stage
T9	Temperature 3 of the 3 <sup>rd</sup> stage
t/h of CaO	Quicklime flow (t/h)
l/h water	Water flow (l/h)
CaO/Water	Quicklime water ratio



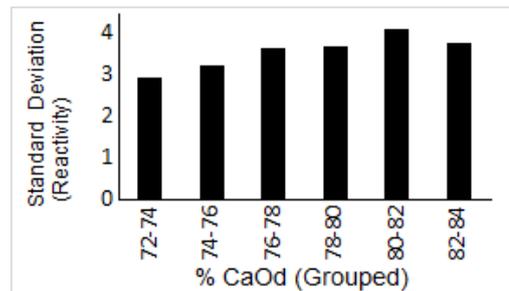
**Figure 4:** Average Reactivity x CaOd (Grouped)

In addition, it was evaluated what is the behavior of the standard deviation according to the grouped results of the available calcium oxide according to the reactivity. From the statistical graphs presented, it is possible to consider that an increase in the CaOd content generated not only an increase in the average reactivity but also an increase in its standard deviation (standard deviation correlation = 0.88).

### 3. Results and discussions

#### 3.1. Relationship between Available Calcium Oxide x Reactivity

Considering that the available calcium oxide and reactivity may present a relationship between the values obtained, Figure 4 shows a bivariate analysis of these two parameters. This relationship was performed considering the samples collected at Point 1. In this graph the data was grouped in bands every two percent to obtain the average reactivity for each group.



**Figure 5:** Reactivity Standard Deviation x Available Calcium Oxide

The greater deviation pattern in the results of reactivity (figure 5) may indicate greater difficulties in adjusting parameters in the calcination process when the limestone fed in the kiln has higher calcium contents and, consequently, higher calcium oxide content available in quicklime. This condition may be related to the increased incidence of quicklime sintering resulting in a reduction in surface area and porosity, which would justify the incidence of lower reactivity results even with a higher available calcium oxide content.

#### 3.3.3. Hydration Efficiency

With the methodology of collecting samples of

quicklime and hydrated lime at points two and three in the installed hydrator, as well as the consolidation of laboratory routine to carry out the analyzes, it was possible to obtain the results of hydration efficiency. In relation to analyzes carried out to determine hydration efficiency, as in several analyzes made of quicklime, the values of moisture and loss of ignition were practically zero, the existence of combined water in form of calcium hydroxide at the entrance of the hydrator and the water combined in the calcium oxide came exclusively from the hydration reaction. In order to assess the behavior of hydration efficiency with the temperature (Figure 6), the result obtained was compared with the T5 equipment temperature.

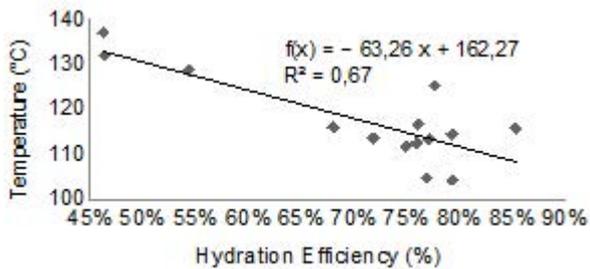


Figure 6: Temperature at T5 x Hydration Efficiency

There is a negative relationship between the hydration efficiency and the T5 temperature of the second stage, that is, the lower the hydration temperature in the reaction stage, the better its efficiency. In other words, when the hydration reaction is controlled at lower temperatures, there is a tendency to increase the conversion of calcium oxide into calcium hydroxide. The determination coefficient indicated that 66.72% of the hydration efficiency results are explained by the average temperature T5. Another statistical measure, the correlation coefficient indicated a strong and negative relationship between the study variables, which was -0.82.

It is also observed that there was a concentration of data in the temperatures below 120 °C. This concentration of data is due to the request that was made for the hydrators to operate at temperatures in this range, which in fact occurred. It is also possible to check three samples that showed low efficiency and are distant from the others. However, these results correspond to 21.43% of the total samples collected, which justifies the maintenance of these data within the study. In addition, in the study of outliers, these were not removed, that is, they are included between the minimum and maximum values.

As presented in the methodology for data exclusion inconsistent, more than 50% of the results obtained had to be removed from the dispersion due to technical and

statistical conditions. For the correlation to be improved, it is necessary to carry out this analysis with a larger number of results. Regarding the method of quantifying hydration efficiency, it is important to note that the results observed in Figure 36 allowed a satisfactory relationship between temperature and efficiency to be established, and this method can be maintained as an analysis routine for the operational assessment of the hydration system of the quicklime.

### 3.3.4. Correlation between the main parameters of the hydration process

In order to verify the existence of correlation between the first stage and the second stage to try do predict the maximum possible temperature at T5, the graph below show a day of operation between 12:00 am and 5:15 pm, in six different periods (Figure 7). The T2 temperature was chosen for this evaluation due to its intermediate positioning in the first stage as well as the possibility of predicting the T5 result in advance. In view the presented information, the diversity of the reactivity results provided different correlation periods between T2 and T5 during the period studied, i.e. the temperature elevation profile in the hydration process depends on the average reactivity in that period during the hydration process. In most the presented curves, a small temperature variation in T2 generates a large variation in temperature in T5. Even though it is not possible to directly predict the T5 temperature, noting that the lower for temperature T2, the greater the probability of having T5 temperature results closer to 100 °C.

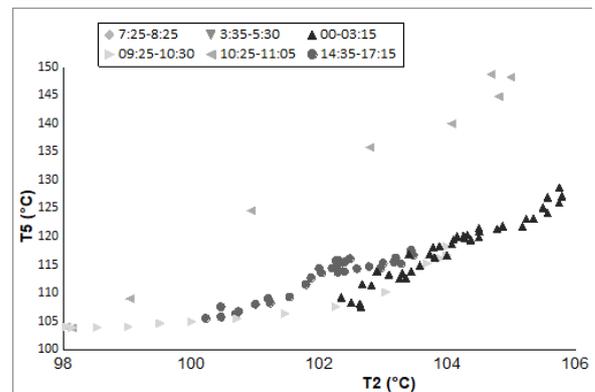


Figure 7: Temperatures T2 and T5 in six different tables

In most the presented curves, a small temperature variation in T2 generates a large variation in T5. Even though it is not possible to directly predict the T5 temperature, noting that the lower for temperature T2, the

greater is the probability of having T5 temperature results closer to 100 °C. Even with this results dynamicity, the graph demonstrates that when T2 is close to 100 °C, the temperature in T5 does not have such a sudden variation and also approaches 100 °C. For this reason, to achieve the best hydration efficiency it is important to take into account the temperatures of the mixing stage of the moisturizer (in the case T2) seeking between 98°C and 100°C for the situation studied without prejudice in the operation of the equipment.

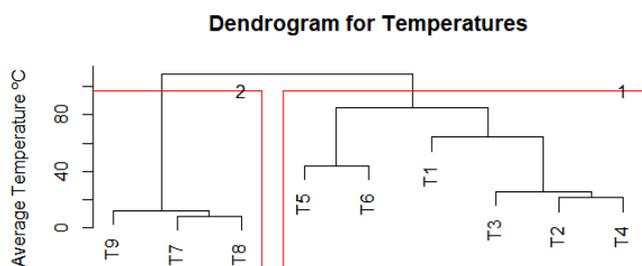


Figure 8: dendrogram of temperatures hierarchical clustering, read in the thermostat

Furthermore, it was generated a dendrogram ( Figure 8) aims to analyze the hierarchical clustering formatted between the temperatures read in the thermostat. The Figure 8 displays the results from cluster being identified two groups. The first group (called group 1) built by six temperatures (T1,T2,T3, T4, T5 and T6). The second one, sets the three temperatures (T7, T8, T9). Based on dendrogram it can be observed that the temperature T2 and T5 belong to same group, pointing out the existence the some correlation between them.

## 4. Conclusions

Quicklime received at UTE Candiota III, a raw material used for the production of hydrated lime, a reagent used in the process of desulphurization of the boiler flue gases, is subjected to routine analyzes in order to verify its quality. When an analysis of the relationship between reactivity and available calcium oxide is carried out through result ranges, it is possible to conclude that there is a positive correlation, that is, there is an increase in the mean reactivity when the available calcium oxide content increases. The curve that sought to represent the dispersion presented a coefficient of determination ( $R^2$ ) of 0.9. The increase in reactivity due to the increase in the available calcium oxide content can be justified, because the greater the amount of calcium oxide available to react, the greater is the quantity of energy released during the hydration reaction.

Statistical analyzes revealed a slight increase in the standard deviation of reactivity with an increase in the

available calcium oxide content. This result suggest that when there are higher values of calcium oxide available, it was more difficult to adjust the parameters during the limestone calcination process, which would indicate the greatest variability in the reactivity results.

Another item of great importance in this work was the proposal for determining hydration efficiency. The relationship between hydration efficiency and the temperature of the thermocouple located in the central part, in the reaction stage (T5) showed an improvement trend when this temperature was lower, presenting a negative correlation of 0.82. Another important item to be considered is that it was possible to achieve hydration efficiencies between 80% - 85% at temperatures closer to 100 ° C in T5. Thus, we can conclude that the indicator created in the present work satisfactorily represented the process condition of the studied equipment.

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## Acknowledgements

The authors gratefully acknowledges the support given by UNIPAMPA and Eletrobras CGT Eletrosul.

## Funding

Not applicable

Duarte Ferreira: orientations and data analyses

### **Authors' contributions**

Rodrigo Saraiva Dantas and Rodrigo Bortoluzzi data collection. Maria Alejandra Liendo and Vera Lucia

# Figures

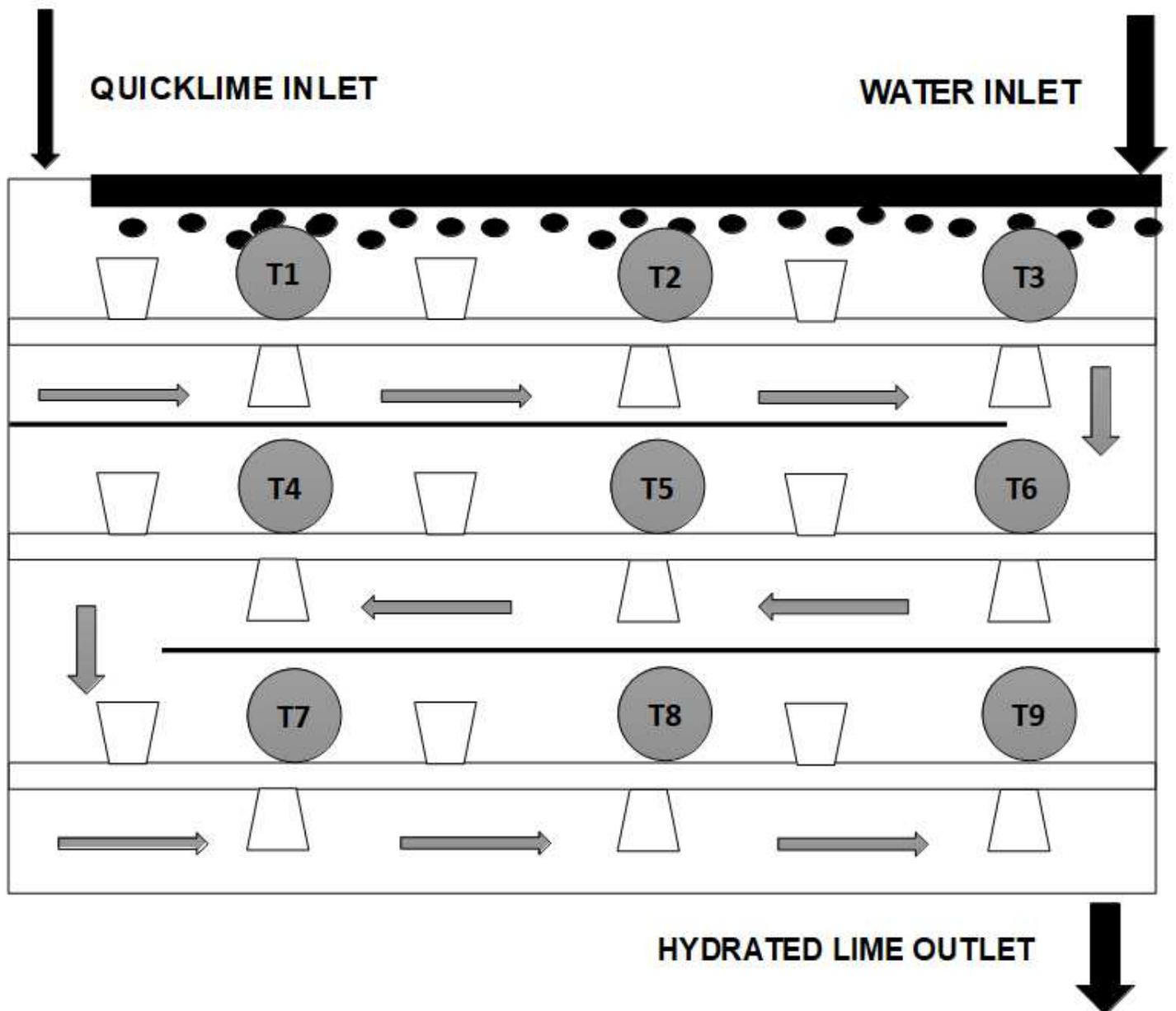


Figure 1

Schematic Diagram: Hydration Equipment for FGD reagent production.

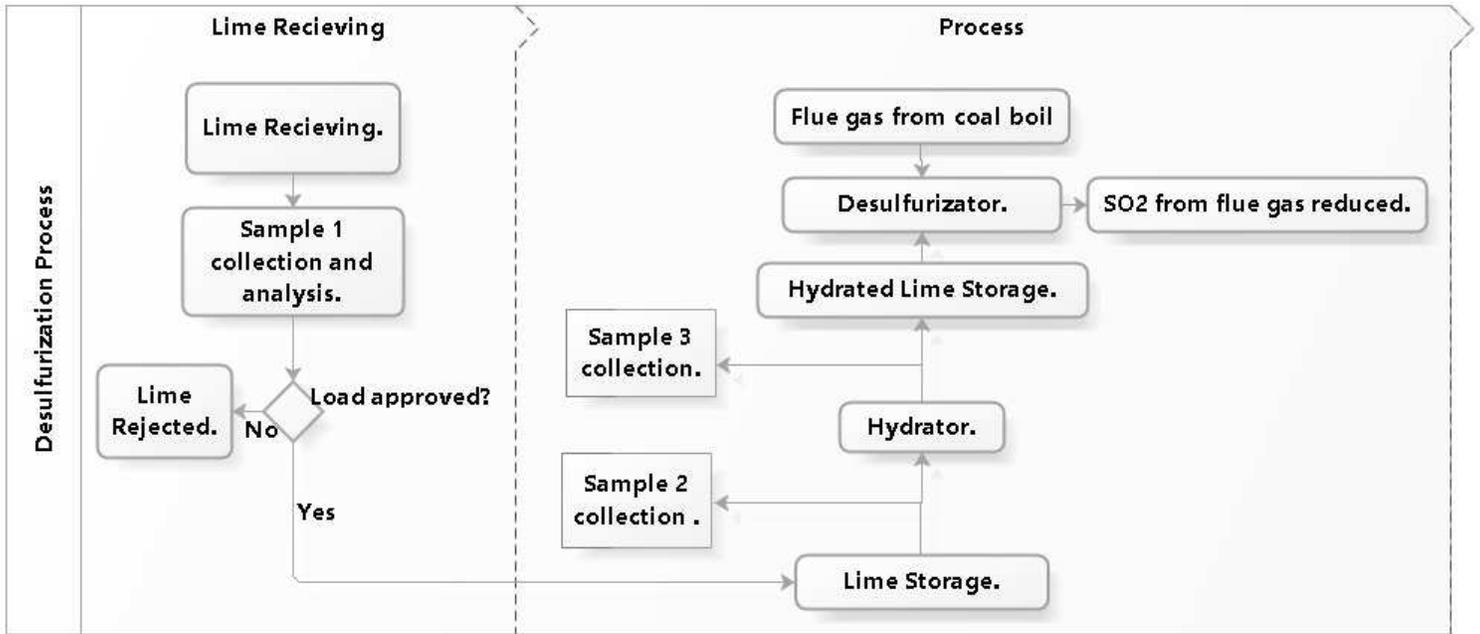


Figure 2

Desulfurization process and sampling points

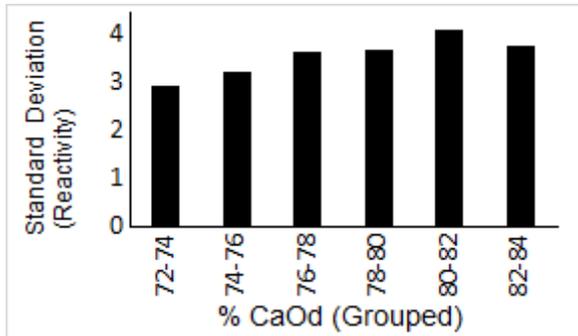


Figure 3

Determination of Hydration Efficiency

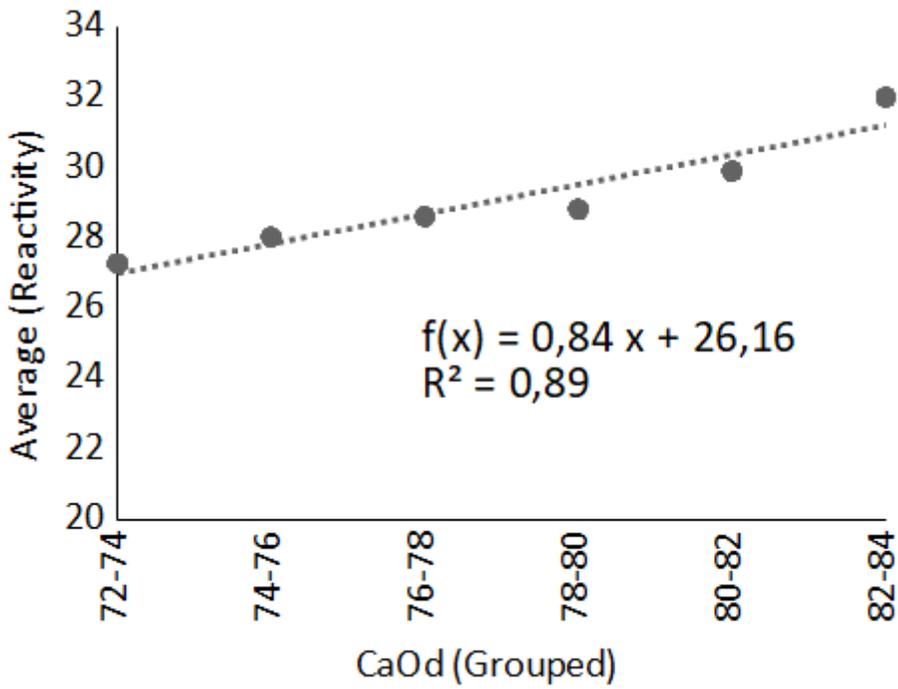


Figure 4

Average Reactivity x CaOd (Grouped)

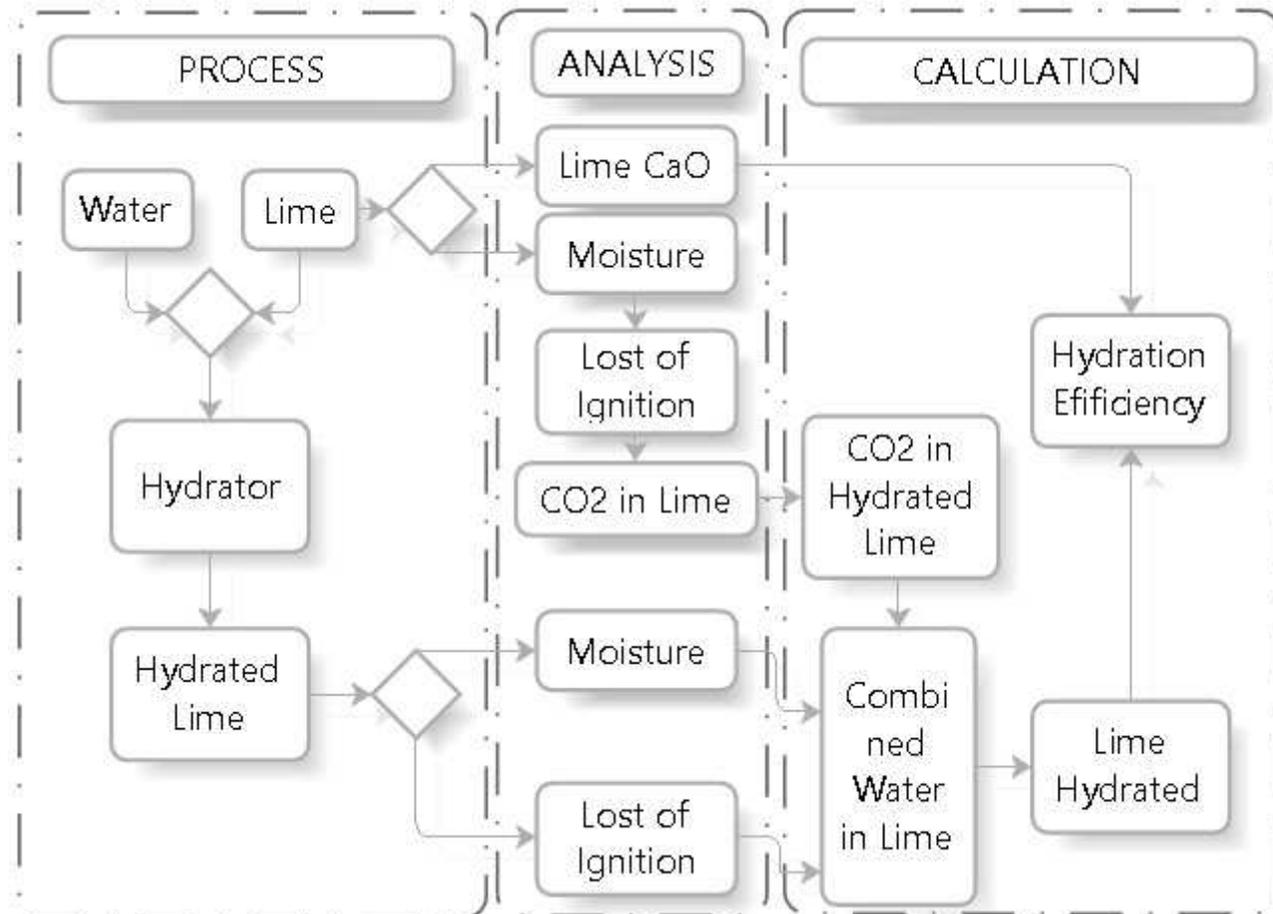


Figure 5

### Reactivity Standard Deviation x Available Calcium Oxide

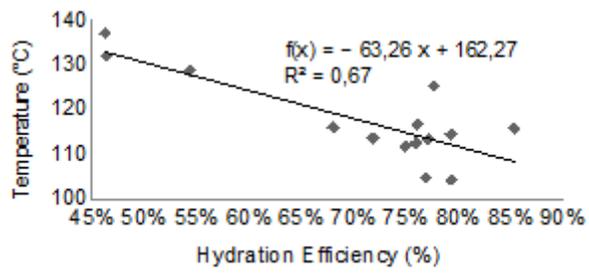


Figure 6

### Temperature at T5 x Hydration Efficiency

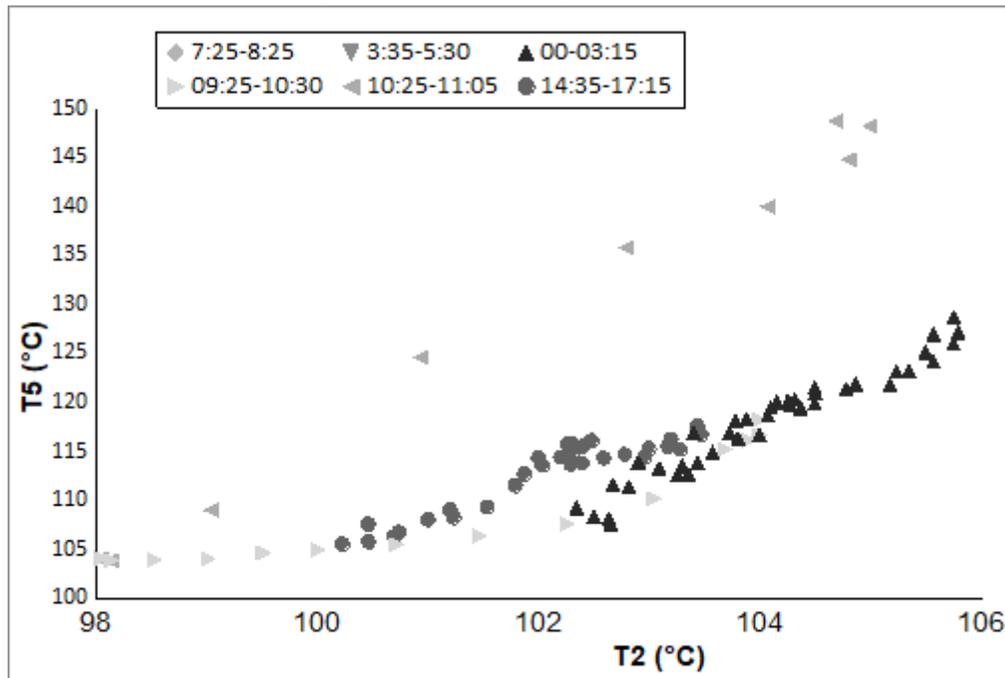


Figure 7

### Temperatures T2 and T5 in six different tables

## Dendrogram for Temperatures

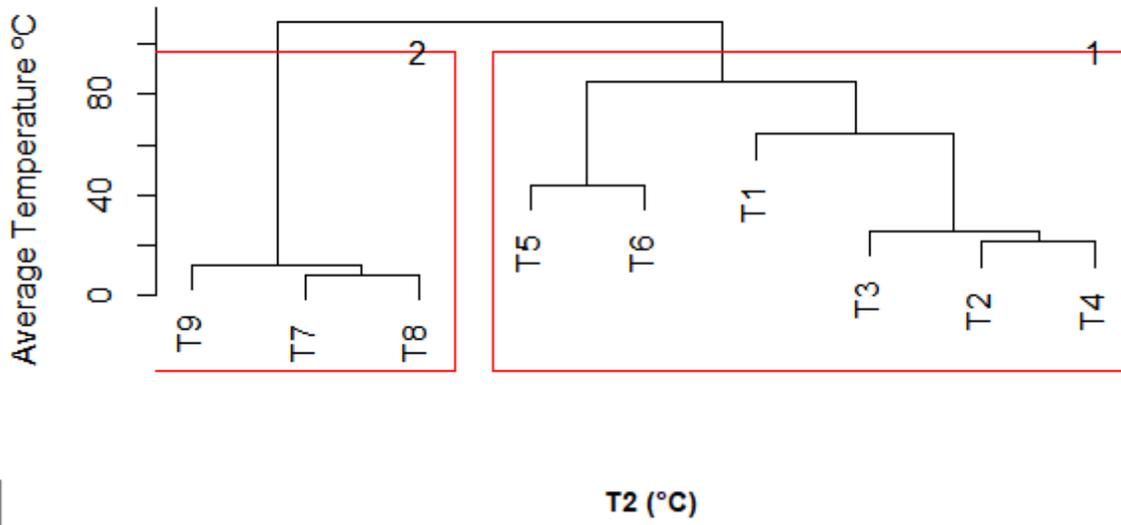


Figure 8

dendrogram of temperatures hierarchical clustering, read in the thermostat