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STUDY OF CALCIUM LOOPING TECHNOLOGY FOR CARBON CAPTURE

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Abstract. Carbon capture and storage technologies (CCS) are essential for mitigating the effects of climate change caused by CO_2 emissions in the atmosphere. The application based on the reversible calcination/carbonation reactions of limestone materials, called Calcium Looping (Ca-L), is a promising CCS technology. In this study, thermal analysis was applied to evaluate the Cal-L process using Brazilian limestones as CO_2 sorbents. As experimental design was considered the variables that affect the conversion of the reactions of carbonation. X-Ray Fluorescence and thermal analysis were performed for the characterization of the limestones in the calcination and carbonation process. The treatment by hydration was applied to improve the CO_2 conversion. The results showed that after the treatment the limestone studied obtained a conversion of 72,5 % de $kmol_{CO2}/kmol_{Ca + Mg}$.

Keywords: Calcium Looping, Carbonation, Ca-L, Thermal analysis, Combustion. Limestone.

1. INTRODUCTION

Carbon capture and storage (CCS) is a potential option for the reduction of anthropogenic CO_2 (IPCC, 2005). All suggest that Calcium Looping (CaL) could be a pioneering technology in future climate change mitigation strategies (MUTCH; ANDERSON; VEGA-MAZA, 2017).

The process of CO_2 capture by CaL is an absorption / desorption process using a solids circulation system in a post-combustion CO_2 capture process (SHIMIZU; KOSEKI, 2017).

The combustion gases react with CaO particles in a carbonation reactor to produce $CaCO_3$, where a stream of purified CO_2 is produced for transport, storage or use (MUTCH; ANDERSON; VEGA-MAZA, 2017). The estimated costs for the final disposal of CO2 (transport, sequestration and storage) are lower than in the separation phase (capture) (LYNGFELT; LECKNER; MATTISSON, 2001), making capture the most challenging phase (RIDHA et al., 2013).

One of the CCS technologies that is nearby for commercial use is the amine scrubbing. Other promising CCS are those designated by Chemical-Looping Combustion, Calcium Looping Cycle or Ca-Looping (Ca-L) and oxyfuel combustion. The main disadvantage of CaL is the deactivation of the sorbent related to morphology and reactivity alterations (MUTCH; ANDERSON; VEGA-MAZA, 2017).

Through the carbonation reaction, calcium sorbents in the form of CaO can capture CO_2 from burning fossil fuels, forming carbonates $CaCO_3$, Eq. (1), which can subsequently be decomposed thermally, Eq. (2), forming CaO and CO2 (BLAMEY et al., 2010; DEAN et al., 2010; WANG et al., 2014).

$$CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)} \tag{1}$$

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \tag{2}$$
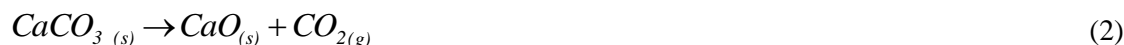
The carbonation reaction, Eq. (1) occurs at temperatures between 600-700 °C, while a calcination reaction, Eq. (2), at temperatures between 850-950 °C (WANG et al., 2014).

Figure 1 shows the Cal-L process diagram. In this process, the calcium based sorbents recirculate between the carbonation and the calcination reactor until the sorbent is inactive and the CO_2 is concentrated and purified, being suitable for compression before transportation and final storage (DIEGO; ALONSO, 2016).
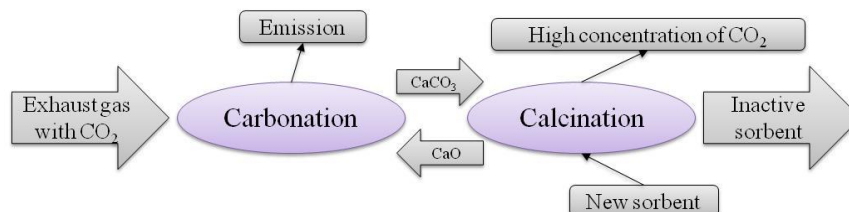

Figure 1: Diagram of the process Ca-L (Adapted WANG et al. (2014)).

2. MATERIALS AND METHODS

2.1 Materials

For the study, as CO_2 sorbent samples of two Brazilian limestones were used. Dolomitic limestone (DP) (Fig.2a), from Ipeúna (SP) and calcitic limestone (CI) (Fig. 2b), from Itaú (MG).

(a)   (b)

Figure 2: Limestones: (a) Dolomite (DP); (b) Calcitic (CI).

2.2 Methods
. First, a separation of the particle sizes was made, which are related as average granulometries between two consecutive screens series ASTM. In this case, values of 82.5-327.5 and 655 μm were used, which refer to the means of the sieves 75-90, 300-355 and 500-600 μm, respectively. To characterize and study the structure of dolomitic and calcitic limestone, X-ray fluorescence (FRX) analyzes were performed to identify the elements of the samples.

The calcination and carbonation process is evaluated in thermal analysis. Thermal analysis was performed on a simultaneous TA Instruments, SCT TGA-DSC Q600 system. It was used an alumina melting pot for withstanding high temperatures. The two limestones were evaluated in the calcination process in the different granulometries 82.5-327.5 and 655 μm, with sintetic air or nitrogene, in heating rate of 30 °C/min, mass of 10 ± 0.05 mg and heating range from 30°C to 1200°C.

In order to evaluate calcination and carbonation, in calcination stage the analysis was performed from 30 °C to the temperature of 850 °C in a heating rate of 20 °C/min and after an isotherm of 5 min. For the carbonatation, the sample cooled to the test carbonatation temperature of the test (650-700 °C) and mantein an isotherm of 15 min.

The design of experiment proposed for Taguchi will be used as exploratory. Is was applied the Taguchi Orthogonal Array L4, that present the smaller number of experiments proposed for the method. The L4 array considers up to three factos, called by A, B e C, and two nivels each one (high and low). The tests were realized in aleatory form to avoid systematical errors. In this first time, no replicas were performed, because the exploration was realize in order to understand as the raw material behave, therefore the calculus and results was evaluated only about the average.

In carbonatation stage, opted to undestand the cabonatation methodology first using the DP limestone, due to availability of the material. The factors employed were: carbonation temperature (650-700 ºC); granulometry (82.5 – 327.5 – 655 µm) and sample mass (5-10 ± 0.05 mg) (Tab. 1).

Table 1. Orthogonal L4 arrangement with factors for carbonation.

Test	Coded Factors			Numerical Factors (Carbonation)		
	A	B	C	T_{Carb} (ºC)	Φ µm (mm)	Mass (mg)
1	1	1	1	650	82.5	5
2	1	2	2	650	327.5	10
3	2	1	2	700	82.5	10
4	2	2	1	700	327.5	5

For the measure the factors effects upon the response variable was used the Eq. (3), being the average of the response variables – j is the factor (A,B and C) and k factor's level (1, 2 and 3). The variable n refers to a number of repetitions of the k level represent in j factor.

$$M_{j,k} = \frac{\sum(Y_i)}{n} \tag{3}$$

In order to evaluate the sorption capacity of the limestones, it is necessary to realize the conversion calculations using thermal analysis. The CO_2 injection in the thermal analyzer promotes the carbonation of the calcined limestone, causing a mass increase. Thus, the conversion due to the carbonation of the already calcined sample is given by the global reaction presented in Eq. (4), where W is the atomic or molecular mass of the relative species; MF is the mass of the final sample after carbonation, and MC is the mass of the calcined sample; MA is the initial mass of the limestone sample and y is the mass fraction of the relative species. The conversion results are given in $kmol_{CO2} / kmol_{Ca + Mg}$.

$$X = \frac{\dfrac{M_F - M_C}{W_{CO2}}}{Ma\left(\dfrac{y_{Ca}}{W_{Ca}} + \dfrac{y_{Mg}}{W_{Mg}}\right)} \cdot 100 \tag{4}$$

After finding the best fit condition proposed by the Taguchi method the treatment of DP limestone was performed by hydration. For hydration treatment, 1 g of limestone was used for 50 mL of deionized water (4 times the amount of stoichiometric). The deionized water was added in a beaker with magnetic stirring (300 rpm), after limestone was added and the solution was shaken for 15 min at room temperature. After simple filtration the sample was dried at 105 °C in an oven. The treatment was carried out in natura sample for later calcination and carbonation.

3. RESULTS AND DISCUSSIONS

The elemental chemical composition of the limestones was determined by x-ray fluorescence and is presented in Tab. 2. It is observed that the less granulometry presents a higher percentage of CaO and MgO available for carbonation.

Table 2. FRX analysis of DP and CI limestones.

Oxides	DP			CI		
	82.5 (µm)	327.5 (µm)	655 (µm)	82.5 (µm)	327.5 (µm)	655 (µm)
MgO	11.4	6.4	6.4	1.5	3.6	3.8
Al_2O_3	Nd	Nd	1.1	0.5	0.8	0.5
SiO_2	18.4	10.7	12.4	1.6	2.2	1.4
P_2O_5	Nd	Nd	0.2	Nd	Nd	Nd
SO_3	0.6	Nd	0.5	Nd	Nd	Nd
K_2O	0.4	0.2	0.1	Nd	Nd	Nd
CaO	25.2	20.7	19.3	66.6	45.2	41
TiO_2	0.3	0.2	0.1	Nd	0.1	0
MnO	0.2	0.2	0.2	Nd	Nd	Nd
Fe_2O_3	2.3	2.2	1.6	0.3	1.4	0.5
SrO	Nd	0.1	0.1	0.2	0.1	0
In_2O_3	0.6	0.5	0.5	0.9	1.1	0.8

Nd: Not identified

In Figure 3, Figure 4 and Figure 5 evaluate calcination of the limestone from differential thermal analysis (DTG) and thermogravimetric analysis (TG). It is observed that for DP limestone calcination at temperatures lower than 765ºC, and for CI limestone calcination occurs around 800 ºC. Thus, to evaluate the calcination the temperature of 850 ºC is used for the two limestone.

In Figure 3 and Figure 5 it is possible to observe the phenomenon called decreptation for CI limestone, which occurs in temperature around 400 ºC. Decreptation is a phenomenon that creates high energy points on the outer surface and increases the reactive surface because it gives access to gaseous diffusion within the limestone grains. It can be described as the ejection of limestone particles due to the high internal pressure created by the release of water within the crystalline lattice. The tension exerted by the release of water is greater than its walls, to the point of provoking this phenomenon (CRNKOVIC, 2003).
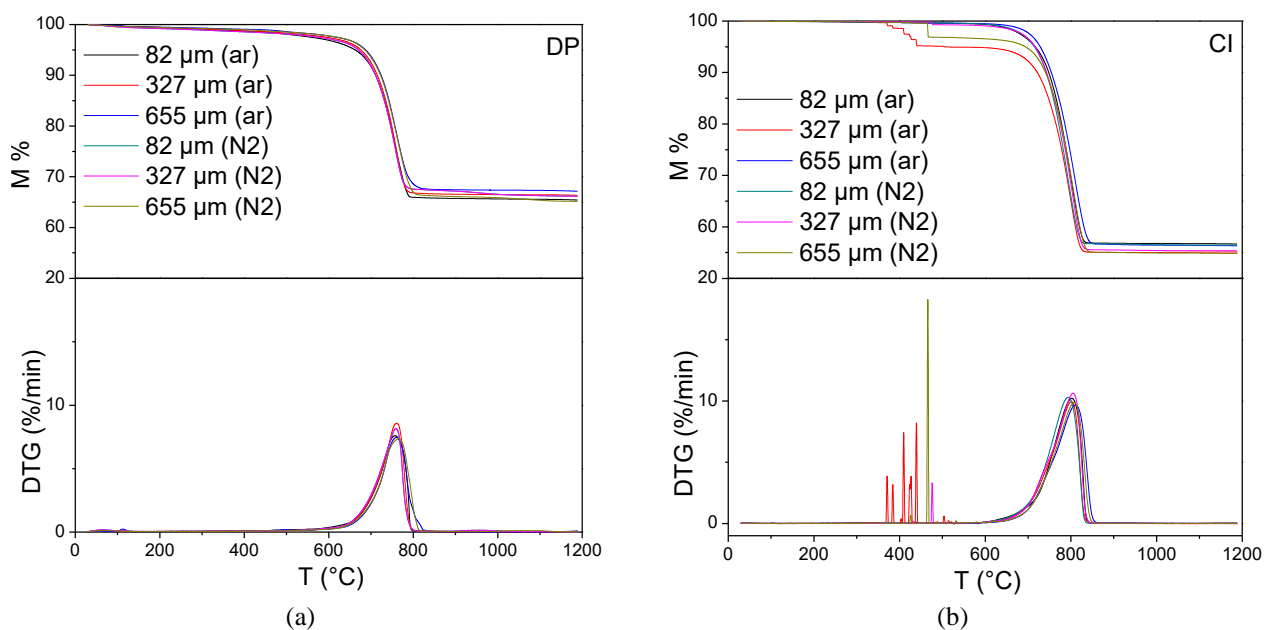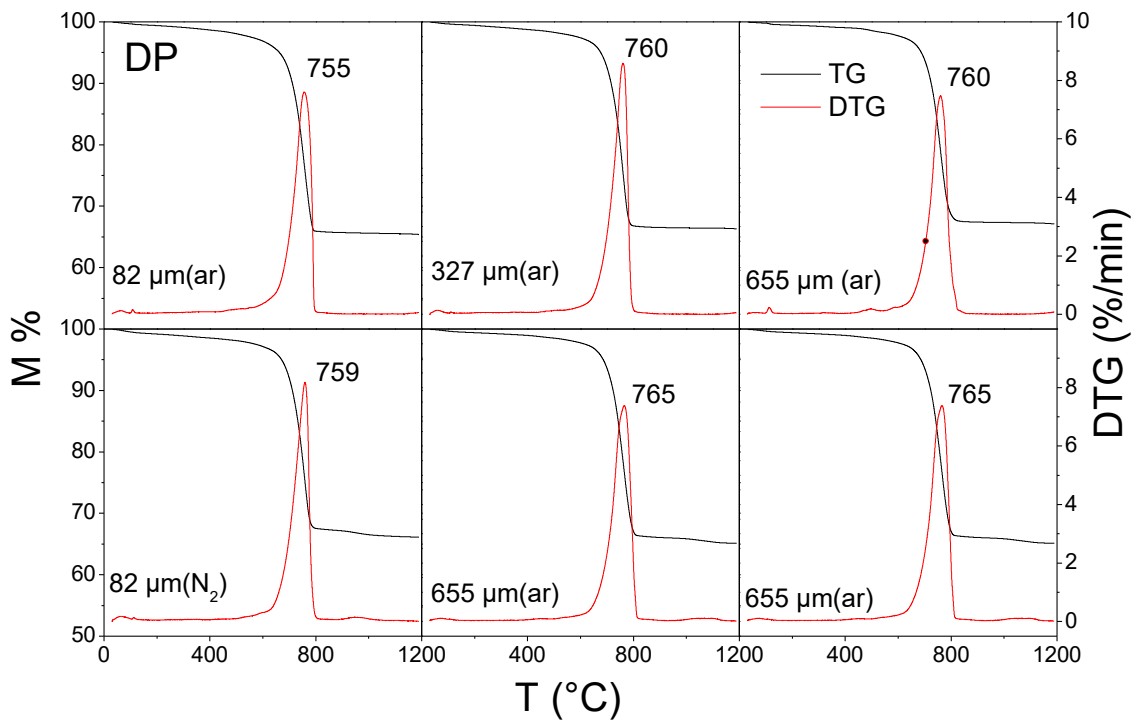

Figure 3: TG e DTG: (a) DP; (b) CI.
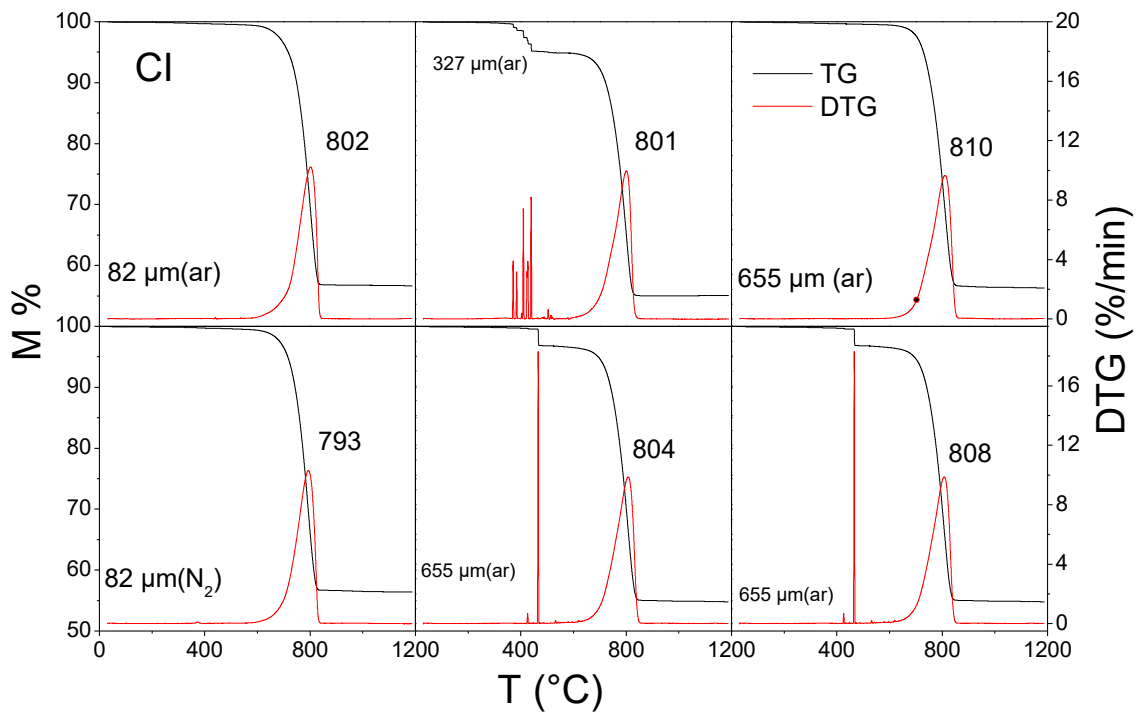
Figure 4: TG e DTG do calcário DP.

Figure 5: TG e DTG CI limestone.

Figure 7a shows the mass loss (TG) and the DTG peaks of the calcination and carbonation tests of the DP limestone. The first mass loss refers to the release of CO_2 from the limestone and formation of CaO and the second event occurs by the gain of mass referring to the incorporation of CO_2 by CaO.

For the analysis of the factors on the CO_2 conversion response variable, Eq. (4) was used. Table 3 shows the L4 array and the response variable of the carbonation process of DP limestone.

For the knowledge of the behavior of the response variable as a function of factor levels, the effect for each factor on the mean was calculated using Eq. (3) (Table 4).

For the construction of Figure 6, the global average was calculated, calculated by the average of all CO_2 conversion values (dashed line), being equal to 52.19 %.

Table 3. L4 and response variable CO_2 conversion.

Test	Coded Factors			Numerical Factors (Carbonation)			TG data			CO_2 Conversion
	A	B	C	T_{Carb}	Φ	Mass	Ma	Mc	Mf	
				(°C)	(µm)	(mg)	(mg)	(mg)	(mg)	
1	1	1	1	650	82.5	5	5.02	3.09	3.85	46.32
2	1	2	2	650	327.5	10	9.87	6.58	7.98	60.82
3	2	1	2	700	82.5	10	10.49	7.07	8.37	38.55
4	2	2	1	700	327.5	5	4.95	3.22	3.95	63.05
Best condition (BC)										
BC	1	2	1	650	327.5	5	5.27	3.44	4.22	63.33

Table 4. Effect of the factors on the response variable (average).

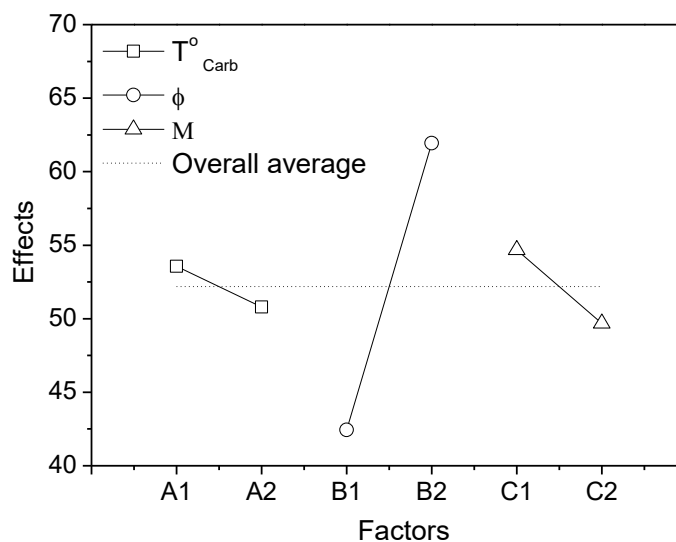| Effect of the factors on the average					
M_{A1}	M_{A2}	M_{B1}	M_{B2}	M_{C1}	M_{C2}
53.57	50.8	42.44	61.94	54.69	49.69

Figure 6: Graphic effect of the factors on the average.

The factors combined with the levels that generate the best fit proposal are those in which their averages are higher than the global mean value, since it is considered that better results refer to the CO_2 conversion values, thus, it was possible to find the combination of A1B2C1 (Factor A at the low level, factor B at the high level and factor C at the low level).

The best condition (BC) requires a confirmatory test to assess whether the response variable encompasses higher CO_2 conversion rates. Figure 7 and Figure 8b present the thermal analysis of the best fit condition test. The best fit condition presented the best CO_2 conversion value of the tests covered in the experimental matrix L4 (Table 3).

After evaluating the best adjustment condition (BC), a test under the same conditions was carried out under nitrogen atmosphere (BC II), a test that obtained a higher conversion of CO_2 than in an atmosphere of synthetic air (Table 5). The BC III test was performed after hydration treatment using the same conditions of thermal analysis of the best fit condition (BC II). The highest conversion found for this work occurred for the limestone according to the best fit condition (Carbonation temperature of 650 ºC, 327.5 μm and mass of 5 mg), under nitrogen atmosphere and after hydration treatment (Table 5) (Figure 8b).

Table 5. Best condition of carbonation.

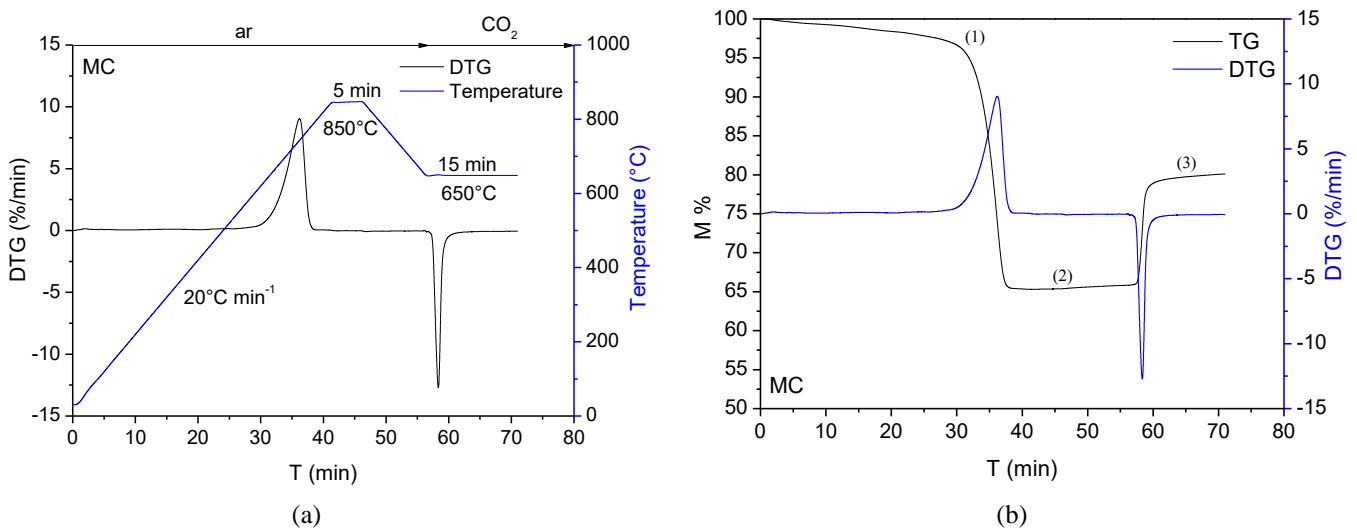|	Coded Factors			Numerical Factors (Carbonation)			TG data			CO$_2$ Conversion
	A	B	C	T$_{Carb}$ (ºC)	Φ (μm)	Mass (mg)	Ma (mg)	Mc (mg)	Mf (mg)	
BCII	1	2	1	650	327.5	5	5.16	3.14	3.97	69.07
BCIII	1	2	1	650	327.5	5	5.04	3.19	4.05	72.5

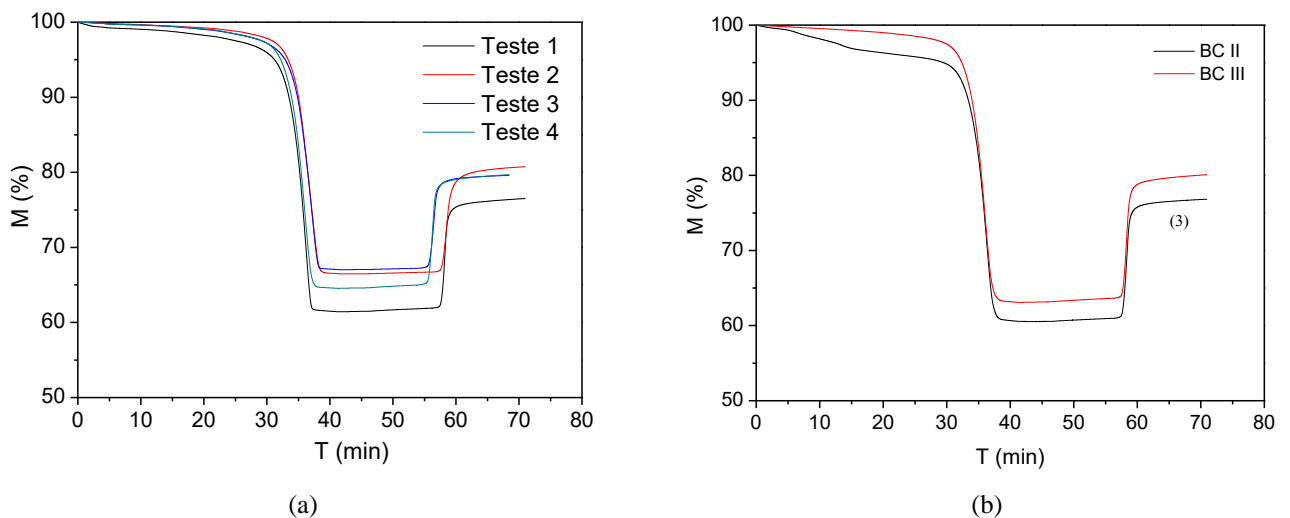Figure 7: (a) DTG and temperature ramp; (b) TG and DTG of BC.

Figure 8: TG: (a) Matriz L4; (b) BC II e III.

4. CONCLUSIONS

Selection and characterization of limestones were performed for the application of calcium looping technology (Ca-L). The difference in composition of the limestones was observed according to Ca and Mg percentages. Taguchi methodology was applied to evaluate the variables that most influence the Ca-L process. After finding the best fit condition, limestone treatment was performed by hydration. The results of the thermal analysis obtained a conversion of 72.5 % of $kmol_{CO_2}/kmol_{Ca+Mg.}$.

5. ACKNOWLEDGEMENTS

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