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STUDY OF TREATMENTS FOR CALCIUM LOOPING SORBENTS FOR CO_2 CAPTURE

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Abstract. *From the need for the development of new technologies for Carbon Capture and Sequestration (CCS), the study of Calcium Looping technology (CaL) is necessary. In order to study the use of Brazilian limestone in CaL processes, as well as the application of acidification and hydration treatments in these limestones, calcination/carbonation cycles are evaluated in order to obtain better carbon conversions in the process. The results of the thermal analysis obtained the conversion of 71.10 % of* $kmol_{CO2}/kmol_{Ca\ +\ Mg}$ *to the CMG limestone after the hydration process.*

Keywords: *Calcium Looping, CaL, Thermal analysis, Combustion. Limestone, Carbon Capture.*

1. INTRODUCTION

From the need to reduce CO_2 emissions, the implementation of appropriate Carbon Capture and Sequestration (CCS) technologies will contribute significantly to meet greenhouse gas emission reduction targets (DIETER et al., 2014; PEREJÓN et al., 2016). The development of CCS technologies aims to reduce the economic and efficiency penalties (ERANS; MANOVIC; ANTHONY, 2016)

One of the promising CCS technologies of CO_2 capture and storage is called for Calcium Looping, this technology has the following main processes carbonation and calcination for carbon capture.

The carbonator is fed with the flue gases, where the CO_2 contained in these gases is absorbed from the CaO to form $CaCO_3$. $CaCO_3$ is transferred to the calciner where it is regenerated to CaO. The gas containing CO_2 is directed to use or storage after processing and compression (DIETER et al., 2014). This process occurs in successive carbonation / calcination cycles.

The Ca-L technology is based on the reuse of materials containing calcium. For the process to be economically feasible, the sorbent must be capable of being regenerated and reused repeatedly (RIDHA et al., 2013). Among the methods to activate the absorbers, the treatment with the hydration of CaO and the modification by organic acids is currently studied.

The hydration process, Eq. (1), the calcium-based material is calcined and then reacts with water, in liquid or vapor state. The hydration of the calcium oxide induces the formation of $Ca(OH)_2$, altering the morphology of the surface of the material and increasing the surface area and volume of the pores (YIN et al., 2012).

$$CaO_{(s)} + H_2O_{(l.g)} \rightarrow Ca(OH)_{2(s)} \quad (1)$$

The acidification reaction using acetic acid is presented in Eq. (2):

$$CaCO_{3\ (s)} + 2CH_3COOH_{(aq)} \rightarrow Ca(CH_3CO_3)_{2(g)} + H_2O_{(l)} \quad (2)$$

When it is heated, it decomposes into acetone and carbonate ($CaCO_3$), according to Eq. (3).

$$Ca(CH_3CO_3)_{2(g)} \rightarrow CaCO_{3(s)} + C_3H_6O_{(g)} \quad (3)$$

The objective of this work is to evaluate two Brazilian limestones for use in the carbon capture from the calcium looping process. From the studies of calcination/carbonation cycles, treatments are applied for evaluation of process improvement.

2. MATERIALS AND METHODS

An application of two Brazilian calculations as CO_2 sorbents was evaluated. A dolomitic limestone (DSP) made available by the company Calcário Diamante of Piracicaba / Tietê (SP) and a calcitic limestone (CMG) made available by the company Calcário Vitória of São João del Rei (MG).

Thermal analysis was performed on a simultaneous TA Instruments - SCT TGA-DSC Q600 system. To perform the CaL cycles, the sorbents were subjected to heating (10 °C/min) to the calcination temperature studied, and the temperature was maintained at a 5 min isotherm; subsequent to cooling (20 ºC/min), and the carbonation consisting of a 20 min isotherm at 650 ºC. In the isotherm were connected the controlled gas flow, and inserted the CO_2 into the lateral entrance of the thermobalance.

For the sorbent treatment tests, the limestone sample was weighed in the granulometry used in the test (327.5 μm), the reagent volume (acid or distilled water), the insertion of the limestone sample in the erlenmeyer, volume of reagent and introduction of the magnetic stirring with rotation at about 200 rpm.

For the acidification of the sorbents, 20 mL of 10% acetic acid solution (v/v) and 2.5 g of limestone (327.5 μm) were used. The test lasted 5 min and after that period the material was left in a glass petri with 24-h film, a procedure adopted from the works of Ridha et al. (2013) (RIDHA et al., 2013)

In the hydration treatment, the calcined sorbents were hydrated with a 1:20 ratio, for the 15 min shaking period. After the end of the test the solution was filtered using a simple filtration system and drying of the materials retained in the film paper in a petri for 1 h in the oven with a temperature of 105.5 °C. This procedure was adopted from the works of Yin et al. (2012) (YIN et al., 2012).

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 $kmol_{CO2}$ / $kmol_{Ca+Mg}$.

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

Microscopies were obtained using Zeiss MEV-EDS / EBDS from EVO LS 15 equipped with Oxford INCA Energy 250 EDS / EBDS System (Oxford Instruments, Abingdon, Oxfordshire, United Kingdom) for dispersive energy microanalysis, operating between 0,2 and 30 kV acceleration and using Everhart - Thornley secondary electron detector at 8.5 mm working distance.

3. RESULTS AND DISCUSSIONS

After finding the calcination temperature of the sorbents, the Ca-L cycles were performed. The 5 cycles of calcination/carbonation of the sorbents are shown in Fig. 1 and Fig. 2. In Fig. 3, the final conversion curve was generated as a function of the carbonation cycles. It is observed that the DSP sorbent obtained better conversions and less decrease with the passage of the cycles.

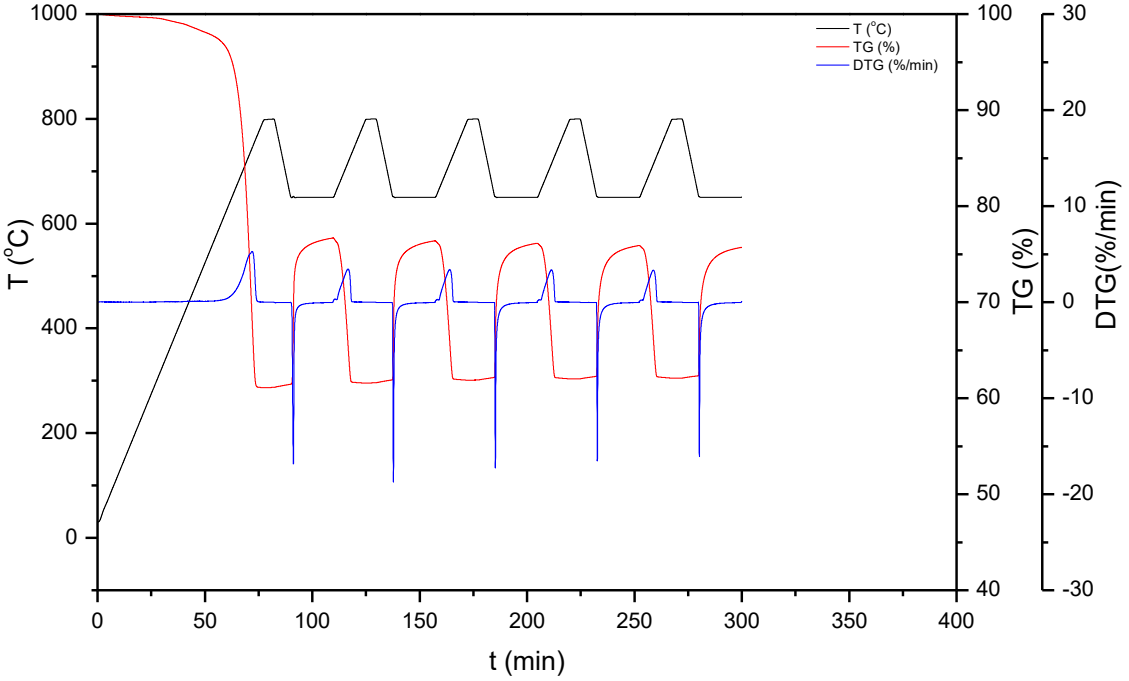


Figure 1. Cycles Ca-L DSP (TG/DTG) e temperature.

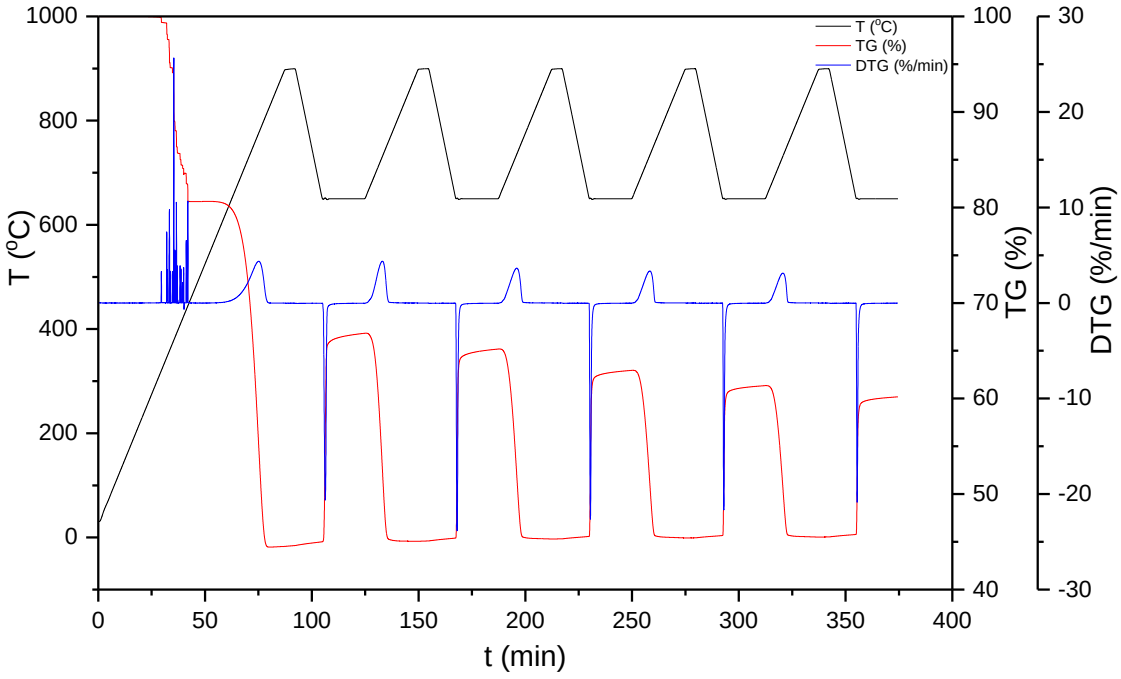


Figure 2. Cycles Ca-L CMG (TG/DTG) e temperature.

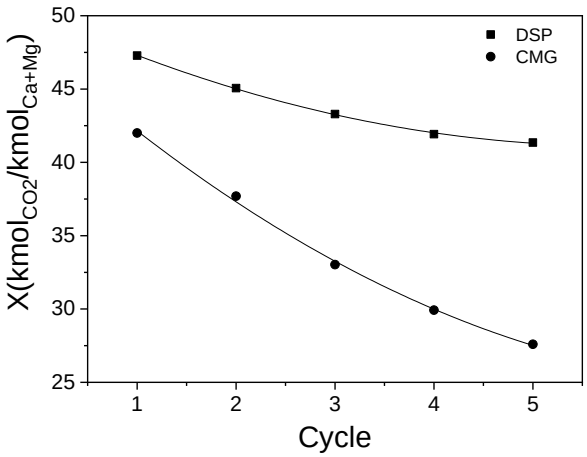
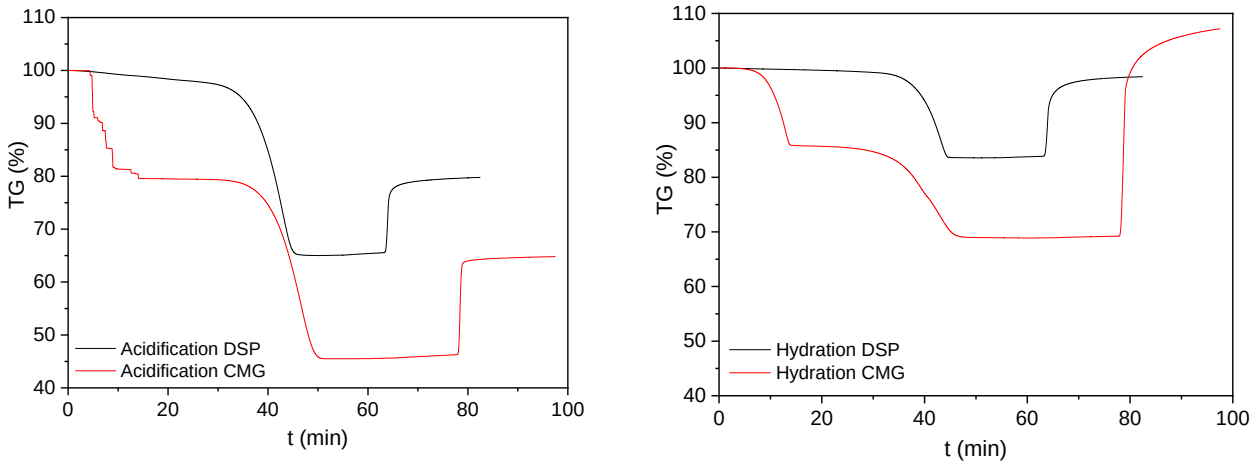


Figure 3. Adjustment curve of the final conversion according to the number of calcination / carbonation cycles.

In order to improve the conversion of CO_2, it was observed that the DSP obtained a higher conversion after the acidification process than the CMG, but after the treatment by hydration the sorbent CMG obtained the highest percentage of conversion equal to 71.10 ($kmol_{CO2}/kmol_{Ca+Mg}$). Figure 4 shows TG curves of the samples after treatment by acidification and hydration. By analyzing the CMG sorbent sample it is possible to observe two mass losses, the first mass loss can be related to $Ca(OH)_2$ dehydration occurring around 400 ºC, which can also be observed in the DSP sample. From the acidification test curves a predominant curve is also found around 400 ºC which may be related to the decomposition of calcium acetate ($Ca.(CH_3COO)_2$) and the release of acetone C_3H_6 (Ridha, Manovic, Wu, Macchi, & Anthony, 2013).



(a) (b)

Figure 4. TG after treatment: (a) Acidification; (b) hydration.

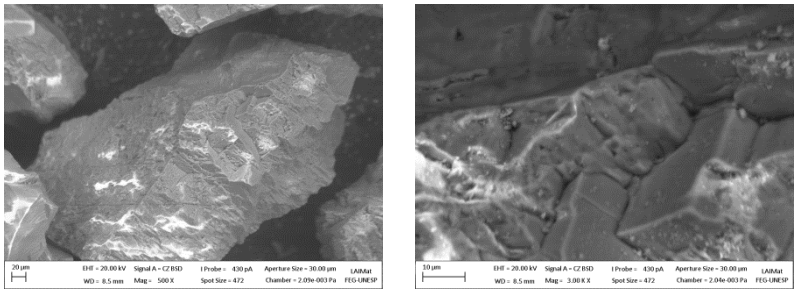
SEM-EDS analyzes of natural limestone DSP (Figure 5) and CMG (Figure 6) samples were performed. Hydration treatment (Figure 7 and Figure 8) was also considered in the microscopy analysis.

DSP limestone particles showed higher compaction and lower roughness when compared in the fresh condition with CMG limestone particles (Figure 5b and Figure 6b). Crystal roughness, pore type distribution and structure compaction are due to the parameters of limestone formation.

The hydration process consisted of increasing the amount of reactive area from the formation of granules on the crystal structure, as can be seen in Figure 7 and Figure 8.

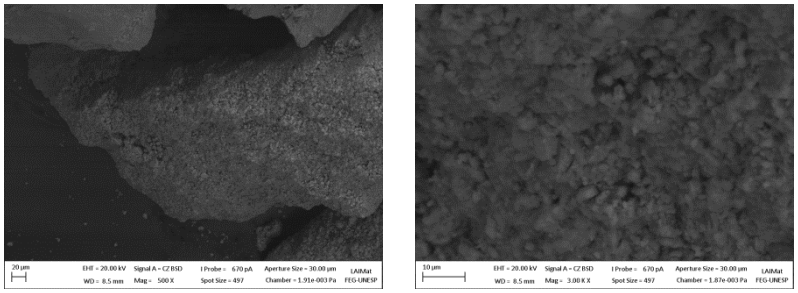
During CMG hydration, there may have been higher adsorption and consequent higher $Ca(OH)_2$ formation on the outer surface. The EDS analysis indicates the formation of $Ca(OH)_2$ in the CMG, since there was a 7 % variation of

Oxygen in the sample, compared to the small variation of the DSP sample, when analyzing the natural and after hydrated conditions.



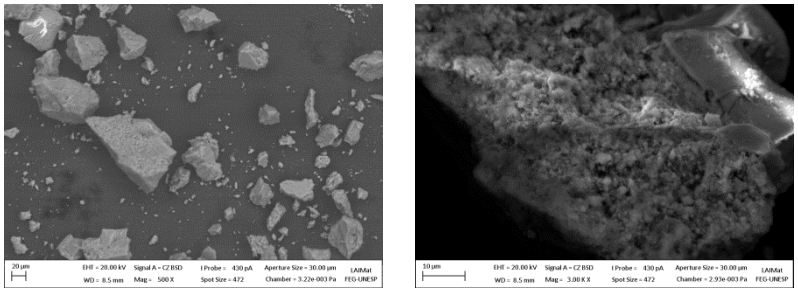
(a) (b)

Figure 5. SEM images of DSP particles with a grain size of 327.5 µm natural: (a) 500x; (b) 3000x.



(a) (b)

Figure 6. SEM images of CMG particle size 327.5 µm natural: (a) 500x; (b) 3000x.



(a) (b)

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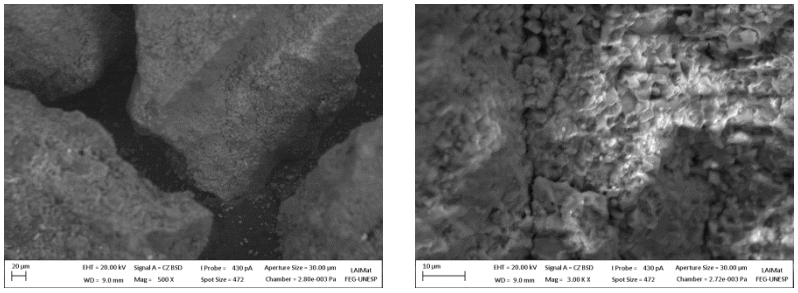
Figure 7. SEM images of DSP particles after hydration: (a) 500x; (b) 3000x.



(a) (b)

Figure 8. SEM images of CMG particles after hydration: (a) 500x; (b) 3000x.

4. CONCLUSIONS

Two limestones were analyzed in order to capture CO_2 from CaL processes. After studies of the CaL cycles, treatments were applied to evaluate the improvement of the percentage of carbon capture in the process. The results of

the thermal analysis obtained the conversion of 71.10 % of $kmol_{CO2}/kmol_{Ca + Mg.}$ for the limestone CMG after the hydration process.

5. ACKNOWLEDGEMENTS

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7. RESPONSIBILITY NOTICE

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