

THE CALCIUM LOOPING CYCLE STUDY FOR CAPTURING CARBON DIOXIDE APPLIED TO THE ENERGY GENERATION

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Abstract. *The calcium looping process (Ca-L) is a promising technology to reduce of the carbon dioxide (CO₂) emissions when applied in energy generation systems. Ca-based materials (usually limestone) are used in this process as CO₂ sorbents. Thus, the CO₂ capture occurs by the reversible reaction between calcium oxide (CaO) and CO₂, resulting in the calcium carbonate form (CaCO₃). Compared to other technologies applied to carbon sequestration process, the Ca-L offers additional advantages such: the use of fluidized bed technology that is already well established; this process occurs at high temperature, and the excess of heat generated can be recovered; the cost of limestone sorbents is low because of its wide availability. However, in the applying the Ca-L process is essential to understand the mechanism and the effect of partial pressure of CO₂ in both, calcination and carbonation processes; to investigate the effect of sintering and to evaluate the sorbent activity decay. In this paper, empirical technique such as thermogravimetry is applied to investigate the reactivity of limestone sorbents and the effect of CO₂ high concentrations in both calcination/carbonation processes.*

Keywords: *calcium looping, carbon capture, dolomite, thermogravimetry.*

1. INTRODUCTION

The effect of CO₂ partial pressure on the calcination of carbonate sorbent is a determining factor to define the reactivity of the calcined rocks for SO₂ sorption in coal combustion processes. The knowledge of the decomposition mechanism may provide useful ways for establishing relevant coefficients that describe intra-particle diffusivity, thermal conductivity, and heat and mass transfer. It may also provide information for understanding changes in the physical structure that may account for a limited utilization of the limestone in the sulfation.

At low CO₂ partial pressures dolomite (Equation 1) decompose in a single step. However, at high CO₂ partial pressures it has often been assumed that dolomite decomposes in two stages (Bandi and Krapf, 1976; McIntosh et al. 1990; Samtani et al., 2001): decomposition of double calcium carbonate and magnesium, forming calcium carbonate and magnesium oxide, and decomposition of calcium carbonate (Equation 2).



Oxy-fuel combustion is a promising technological option for the reduction of CO₂ emissions, as the fuel is burned in an oxygen-rich atmosphere with a portion of the flue gas being recycled, generating high CO₂ concentrations ready for sequestration (Buhre et al., 2005; Arias et al., 2008). Several characteristics are different between oxy-fuel combustion and air combustion, especially the proportions of CO₂ in the furnace. Conventional combustion power plants are characterized by the low concentration of CO₂ (typically between 6% and 15%) in flue gases due to nitrogen presence in the air. In oxy-fuel technology the concentration of CO₂ in the flue gas is increased from approximately 17% to 70% (Buhre et al., 2005) or up to 95% (Arias et al., 2008) by mass. The use of limestone sorbents in oxy-fuel processes is desired because other gases, such as SO₂ and NO_x are also accumulated. However, under oxy-fuel combustion the calcination mechanism must be evaluated due to the special environment with high CO₂ content (Toftgaard et al., 2010).

The calcium looping cycle (Ca-L) is another developing technology for CO₂ capture. In calcium looping systems the carbonation reaction of CaO with CO₂ (Equation 3) is followed by the reverse calcination reaction of CaCO₃ to regenerate CaO (Equation 4) in a pure atmosphere of CO₂ or CO₂/H₂O (Arias et al., 2010; Blamey et al., 2010). According to Blamey et al. (2010), in order to produce a suitable gas for CO₂ sequestration it is of interest to understand how the decomposition rate of CaCO₃ varies with partial pressure of CO₂.



The Ca-L process was proposed by Shimizu et al. (1999) for CO₂ removal from flue gas using the reaction CaO+CO₂ → CaCO₃. The process consists of two fluidized bed reactors connected by solid transportation lines. In one reactor (absorber), CO₂ in the flue gas is captured by CaO at 873K and the produced CaCO₃ is transported to another reactor (regenerator), in which CaCO₃ is decomposed to CaO at 1223 K. The produced CaO is transported to the absorber again. The heat of decomposition in the regenerator is supplied by feeding coal and pure oxygen, thus the flue gas from the regenerator is high purity CO₂ (>95%, dry base).

Based on the literature, in this paper an empirical technique, such as thermogravimetry, is applied to investigate the reactivity of limestone sorbents and the effect of CO₂ high concentrations in both calcination/carbonation processes.

2. MATERIAL AND METHODS

A Brazilian natural dolomite from Ipeúna/SP with an average particle size of 545 μm was used for all tests. Table 1 shows the elementary chemical compositions of dolomite determined by atomic emission spectrometry (ICP-AES).

Table 1. Partial elementary chemical composition (% mass/mass) of the dolomite.

Ca	Mg	Fe	Al	Sr	K	Mn
17.07	11.73	0.32	0.42	0.08	0.13	0.09

The thermogravimetric experiments are performed in a Shimadzu TGA-51H analyzer. Samples of 10±0.5 mg were used in all experiments. In the calcination study, the tests are carry out under non-isothermal conditions, with temperature ranging from room temperature up to 850 °C, applying five different heating rates (5, 10, 20, 30 and 40 °C min⁻¹) in dynamic atmospheres of air with 0% and 15% CO₂. For the carbonation study, the tests are performed in two steps: (1) calcination tests at different heating rate (30, 40 and 50 °C min⁻¹) from room temperature up to 850 °C under a flow rate of 80 mL min⁻¹ of synthetic air; (2) carbonation tests at different temperatures, heating rates and concentrations of CO₂.

For the calcium looping cycle study, calcination and carbonation experiments in successive cycles, were carried out in a vertical tubular furnace with volume of 3817 cm³. The same experimental conditions of heating rate, gas flow rate and temperature of process adopted in thermogravimetry tests were used. Thus, in carbonation experiments, natural dolomite samples were positioned within the furnace (electrically heated and controlled) and subjected to a heating rate of 50°C min⁻¹ under a flow rate of 80 mLmin⁻¹ of synthetic air. When the desired temperature of 650°C had been reached, the isothermal conditions were maintained. Under these conditions CO₂ was injected at a flow rate of 20 mL min⁻¹.

After each carbonation cycle, an aliquot of samples was taken and analyzed in thermogravimetry conditions to evaluate the conversion. The conversion (*X*) of a reactant is the ratio between the number of moles of the species which reacts and the number of moles of the species fed in the process. The injection of CO₂ in the thermogravimetric analyzer promotes the carbonation, causing a mass increase. Thus, the total mass variation due to the carbonation of the already calcined sample is given by the global reaction presented in equation 1. Then, the conversion is given by:

$$X = \frac{\frac{M_F - M_C}{W_{CO_2}}}{M_A \left(\frac{Y_{Ca}}{W_{Ca}} + \frac{Y_{Mg}}{W_{Mg}} \right)} \times 100 \quad (5)$$

where *W* is the atomic or molecular mass of the concerning species; *M_F* is the final sample mass after carbonation, and *M_C* is the mass of the sample after calcination; *M_A* is the initial sample mass of the natural dolomite and *Y* is the mass fractions. The conversion results are given at kmol_{CO₂}/kmol_{Ca+Mg}.

3. RESULTS AND DICUSSION

3.1 Study of Calcination Reaction

Previously to the carbonation study it is important understand the behavior of calcination. Figure 1 shows the TG curves of calcination in atmosphere of air with 0% (Figure 1a) and 15% CO₂ (Figure 1.b) for the dolomite.

From Figure 1 it is evident that the remaining mass of the samples is different at 0% of CO₂ and at 15% of CO₂. It is reasonable that the CO₂ slows down the reaction so that at the same temperature a core of CaCO₃ remains inside the particle, but an opposite behavior was observed. However, the difference between the remaining mass was very small (0.9% for DP), possibly due to the heterogeneity of the samples.

Moreover, the curves in Figure 1 show that in atmosphere without CO₂, the decomposition occurred in only one step (Equation 2). On the other hand, with 15% CO₂, the decomposition occurred in two stages (Equation 3). In agreement with the observations of McIntosh et al. [12], for DP with 15% CO₂ the first decomposition temperature was lower in the presence of CO₂ than without CO₂, and the second decomposition temperature increased with the increase in the CO₂ partial pressure.

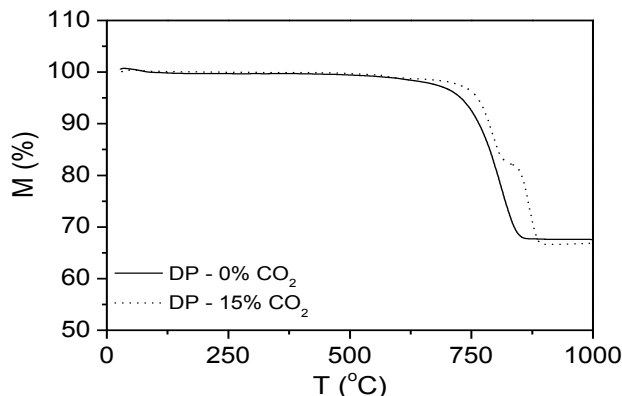


Figure 1. Mass (M) versus temperature (T) for dolomite with average particle sizes of 545 μm in samples of 10 ± 0.5 mg in dynamic air atmosphere with 0% and 15% CO₂ at heating rate of 30 °C min⁻¹.

In the Ca-L conditions, it is necessary to submit the dolomite samples at high concentrations of CO₂. Thus, TG tests of calcination were performed at four different concentrations of CO₂ (15, 50, 80 and 90%) and two different heating rates (30 or 50°C·min⁻¹). TG and DTG curves obtained in these tests are shown in Figure 2a and Figure 2b, respectively.

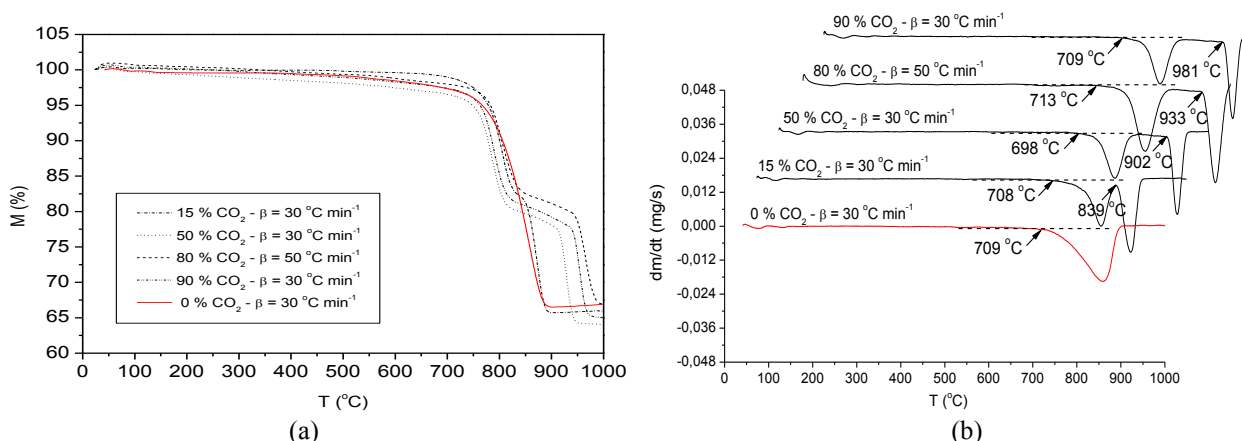


Figure 2: (a) TG and (b) DTG curves for dolomite samples with average particle sizes of 545 μm in samples of 10 ± 0.5 mg in air atmosphere with 15%, 50%, 80% and 90% of CO₂ at heating rate of 30°C·min⁻¹ or 50°C·min⁻¹.

Figure 2 show TG/DTG curves obtained in which are observed that the calcination process occurred even when concentration of CO₂ applied were higher. The initial temperatures of the first stage of dolomite decomposition (formation of MgO) resulted close and, considering the experimental errors, it can be affirmed that the increased of CO₂ concentration did not affect the initial temperature of the first stage of decomposition. However, the onset temperature of the second stage of decomposition (formation of CaO) was significantly affected. In this case the initial temperature of the second decomposition was 17% higher when the concentration of CO₂ in the system increased from 15 to 90%.

3.2 Study of Carbonation Reaction

Figure 3 shows the result of the carbonation test performed for one of the considered temperatures (650 °C) in atmosphere of 80% of air and 20% of CO₂. The TG and DTA curves show both the calcination and the carbonation events. The sets of curves for all the other experiments resulted similar.

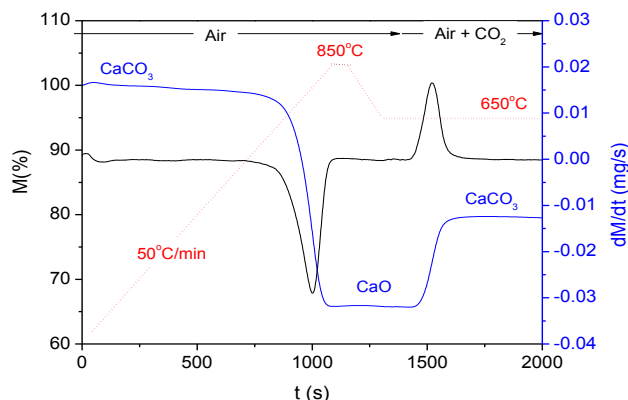


Figure 3. TG (M) and DTG (dM/dt) curves versus time (t) obtained for dolomite samples of 10 ± 0.5 with average particle sizes of $545 \mu\text{m}$.

The tests were performed to evaluate the carbonation conditions. Different conditions of temperature (T), heating rates (β) and CO_2 concentrations in the atmosphere (C_{CO_2}) were applied. Table 2 shows the results obtained for thirteen tests in the carbonation of dolomite samples. For these tests, the calcination was performed in synthetic air atmosphere with a flow rate at 80 mLmin^{-1} and temperature of 850°C . After calcination, the carbonation tests were carried out in different experimental conditions and the conversion was calculated applying the equation 5.

Table 2. Results of conversion (X) obtained in the thermogravimetry tests.

Tests	Carbonation			TG Data			
	T ($^\circ\text{C}$)	β ($^\circ\text{C}/\text{min}$)	C_{CO_2} (mL/min)	M_A (mg)	M_C (mg)	M_F (mg)	$X \pm 0.63$ ($\text{kmol}_{\text{CO}_2}/\text{kmol}_{\text{Ca+Mg}}$)
<i>Effect of reaction temperature</i>							
1	550	50	20	9.91	6.37	6.52	3.85
2	600	50	20	10.09	6.92	8.25	32.95
3	650	50	20	9.85	6.50	7.71	30.81
4	700	50	20	9.72	6.49	7.78	33.26
<i>Effect of heating rate</i>							
5	750	30	20	10.03	6.43	7.84	35.29
6	650	40	20	9.96	6.32	7.67	33.86
7	650	50	20	9.87	7.73	7.99	31.87
<i>Effect of CO_2 concentration</i>							
8	650	50	20	10.03	6.67	7.9	30.75
9	650	50	40	10.09	6.63	8.02	34.40
10	650	50	50	10.01	6.38	7.89	37.71
11	650	50	60	10.04	6.49	7.84	33.65
12	650	50	80	9.78	6.33	7.65	33.64
13	650	50	100	10.25	6.85	8.28	34.93

It was observed that in the temperatures below at 550°C and above 700°C , the carbonation reaction does not occur. Table 2 shows that to the tests performed at 550°C (test 1) the conversion values were very low and the conversion values obtained at 600°C , 650°C and 700°C were close. In addition, at high concentration of CO_2 (100% - tests 13) the conversion values was similar those obtained to the other tests. There were no significant differences in conversion results due to the different heating rates applied.

3.3 Study of Calcium Looping Cycle

Thus, it was defined to evaluate the deactivation of dolomite during the carbonation reaction after successive

calcination/carbonation cycles, considering the following methodology: (1) calcination tests were carry out under non-isothermal conditions, with temperature ranging from room temperature up to 850 °C, applying a heating rate of 50°C min⁻¹ in dynamic atmosphere of air; (2) for the carbonation study the tests were performed under isothermal conditions at 650°C during 14 min.

Figure 4 shows the conversion (increase in % of mass), behavior after each carbonation cycle. It is observed that significant differences in the conversion values occurred after the 1st and 2nd cycles (> 20%). However, after the 3rd cycle of carbonation these differences were less significant (< 15%).

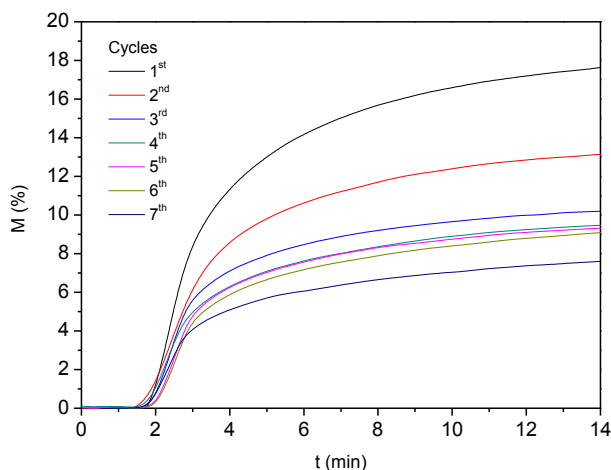


Figure 4. Conversion (%mass) as a function of time of carbonation for dolomite samples previously calcined/carbonated in VTF at temperatures of 650°C.

To evaluate the decrease in the sorbent reactivity after each calcination/carbonation cycle in the samples prepared in VTF, conversion values (X) were plotted as a function of number of cycles considering the carbonation for 14 min of reaction in thermogravimetry analyzer conditions (Figure 5).

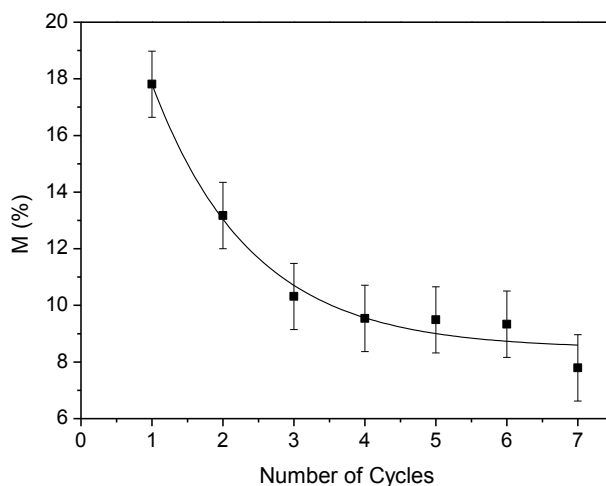


Figure 5. Fit curves to the experimental data considering 14 min of carbonation as a function of number of cycles for dolomite samples previously calcined and carbonated in VTF at temperatures of 650°C.

The equation that best fitted the experimental points was obtained by a first-order exponential decay (Equation 6).

$$X_{(\%Mass)} = 19.107 \cdot \exp\left(-\frac{x}{1.398}\right) + 8.470 \quad R^2 = 0.97 \quad [6]$$

Good correlation coefficient were obtained ($R^2 > 0.95$), considering the methodology applied. Moreover, the present study has provided mathematical expression that quantifies the behavior of the sorbent activity with increasing cycles of carbonation/calcination, indicating a decay of the carbonation activity.

4. CONCLUSIONS

The thermal decomposition of a dolomite by thermogravimetry analyzer conditions was investigated considering the influence of the carbon dioxide partial pressure on the reacting atmosphere. Moreover, it was possible evaluate the carbonation reaction through the TG experiments.

The observed dependence of sorbent activity on the cycle number can be viewed as the dependence on the duration of sorbent regeneration. The residual activity of the sorbent after a large number of cycles may be simply determined with single calcination and carbonation test runs. This can greatly reduce the amount of work for evaluation of long-term sorbent activity, and for screening materials for sorbent synthesis.

Mathematical expression was also obtained to quantify the reactivity decrease behavior of sorbent activity over large number of carbonation/calcination cycles.

5. ACKNOWLEDGEMENTS

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