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 (CO_2) emissions when applied in energy generation systems. Ca-based materials (usually limestone) are used in this process as CO_2 sorbents. Thus, the CO_2 capture occurs by the reversible reaction between calcium oxide (CaO) and CO_2, resulting in the calcium carbonate form ($CaCO_3$). 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 CO_2 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 dolomite as CO_2 sorbent. The effect of CO_2 high concentrations in both calcination/carbonation processes is also investigated.

NOMENCLATURE

M_A initial mass, mg
M_C mass after calcination, mg
M_F mass after carbonation, mg
T   temperature, °C
W   atomic or molecular mass
X   conversion, $kmol_{CO2}/kmol_{Ca+Mg}$
Y   mass fractions

Greek symbol
β   heating rate, °C/min

INTRODUCTION

Considering the importance of fossil fuels for the world's economy, there is urgency to develop effective technologies for the management of carbon emissions due to energy generation. Thus, there are some suggestions or technologies to reduce those dioxide carbon emissions, e.g., increasing the energy efficiencies applied to existing technologies, and replacing the fossil fuels by using renewable energy sources (Wall, 2007).

The products that are derived from fossil fuel combustion can be captured and sequestered. On the other hand, technologies and strategies to reduce carbon emissions can be assessed using three criteria: (1) a minimum impact on both, availability and cost, (2) the possibility of a large-scale application and expansion of technology, and (3) a minimum environmental impact (Arce, 2012).

The processes known as carbon sequestration are those used to capture and sequester CO_2 emissions in an environmentally safe manner. The sequestration and fixation through geological, oceanic, and mineral methodologies have been suggested to reduce CO_2 emissions.

The concept of mineral sequestration technology with accelerated kinetics for CO_2 sequestration is commonly called as mineral carbonation (Lackner, 2002; Park et al., 2003; Sipilä et al., 2008). It is a technology based on a natural process of CO_2 sequestration, known as rocks weathering.

The carbon sequestration technology through mineral carbonation allows the formation of solid inorganic carbonates by a reaction between CO_2 and silicate minerals. This process involves a gas-solid reaction between finely ground minerals with CO_2 to form geologically stable carbonates. Magnesium and calcium containing silicate ores are identified to react with CO_2 to form stable carbonates.

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

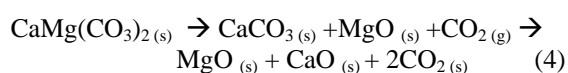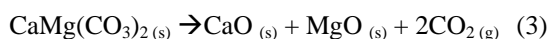$$CaCO_{3\,(s)} \rightarrow CaO_{\,(s)} + CO_{2(g)} \qquad (2)$$
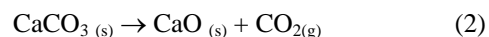
The calcium looping cycle (Ca-L) is another developing technology for CO_2 capture. In calcium looping systems the carbonation reaction of CaO with CO_2 (Eq. 1) is followed by the reverse calcination reaction of $CaCO_3$ to regenerate CaO (Eq. 2) in a pure atmosphere of CO_2 or CO_2/H_2O (Arias et al., 2010; Blamey et al., 2010).

The Ca-L process was proposed by Shimizu et al. (1999) for CO_2 removal from flue gas using the reaction shown it Eq. 1. The process consists of two fluidized bed reactors connected by solid transportation lines. In one reactor (absorber), CO_2 in the flue gas is captured by CaO at 873 K and the produced $CaCO_3$ is transported to another reactor (regenerator), in which $CaCO_3$ 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 CO_2 (> 95%, dry base).

The effect of CO_2 partial pressure on the calcination of carbonate sorbent is a determining factor to define the reactivity of the calcined rocks for CO_2 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 (Ávila et al., 2011).

It may also provide information for understanding changes in the physical structure that may account for a limited utilization of the limestone in the Ca-L process. According to Blamey et al. (2010), in order to produce a suitable gas for CO_2 sequestration it is of interest to understand how the decomposition rate of $CaCO_3$ varies with partial pressure of CO_2.

$$CaMg(CO_3)_{2\,(s)} \rightarrow CaO_{(s)} + MgO_{(s)} + 2CO_{2\,(g)} \quad (3)$$

$$CaMg(CO_3)_{2\,(s)} \rightarrow CaCO_{3\,(s)} + MgO_{(s)} + CO_{2\,(g)} \rightarrow MgO_{(s)} + CaO_{(s)} + 2CO_{2\,(s)} \quad (4)$$

At low CO_2 partial pressures dolomite decompose in a single step, Eq. 3. However, at high CO_2 partial pressures it has often been assumed that dolomite decomposes in two stages: decomposition of double calcium carbonate and magnesium, forming calcium carbonate and magnesium oxide, and decomposition of calcium carbonate, Eq. 4 (Bandi and Krapf, 1976; McIntosh et al. 1990; Samtani et al., 2001).

Considering the importance of the use of CO_2 capture technologies, in this paper thermogravimetry is applied to investigate the reactivity of limestone sorbents and the effect of CO_2 high concentrations in both calcination/carbonation processes.

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 of the dolomite (% m/m).

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

The thermogravimetric experiments were 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 (β = 5, 10, 20, 30 and 40 °C min^{-1}) in dynamic atmospheres of air with 0% and 15% CO_2. 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 CO_2.

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 cm^3. 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 CO_2 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.

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

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

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 CO_2 in the thermogravimetric analyzer promotes the carbonation, 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. 5.

RESULTS AND DISCUSSION

Study of Calcination Reaction

Previously to the carbonation study it is important understand the calcination behavior of the dolomite. Figure 1 shows the TG curves for the dolomite in atmosphere of air with 0% and 15% CO_2. It is evident that the remaining mass of the samples is different in atmosphere with 0% and 15% CO_2. According Ávila et al. (2011), it is reasonable that the CO_2 slows down the reaction so that at the same temperature a core of $CaCO_3$ remains inside the particle, but an opposite behavior was observed. However, the difference between the remaining mass was very small (0.9%), possibly due to the heterogeneity of the samples.
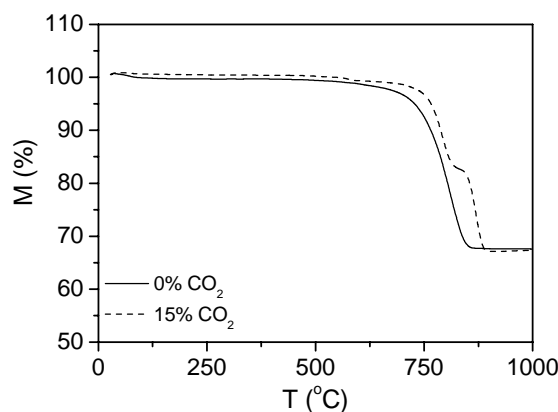

Figure 1. Mass (M) versus temperature (T) for dolomite with average particle sizes of 545 µm in samples of 10±0.5 mg in dynamic air atmosphere with 0% and 15% CO_2 at heating rate of 30 $^{\circ}$C min^{-1}.

Moreover, the curves in Fig. 1 show that in atmosphere without CO_2, the decomposition occurred in only one step (Eq. 3). On the other hand, with 15% CO_2, the decomposition occurred in two stages (Eq. 4).

In the Ca-L conditions, it is necessary to submit the dolomite samples at high concentrations of CO_2. Thus, TG tests of calcination were performed at four different concentrations of CO_2 (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 Figs. 2 and 3, respectively in which are observed that the calcination process occurred even when concentration of CO_2 applied were higher. It is also noted that the initial temperatures of the first stage of dolomite decomposition (formation of MgO) resulted

close. Considering the experimental errors, it can be affirmed that the increased of CO_2 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 CO_2 in the system increased from 15 to 90%.
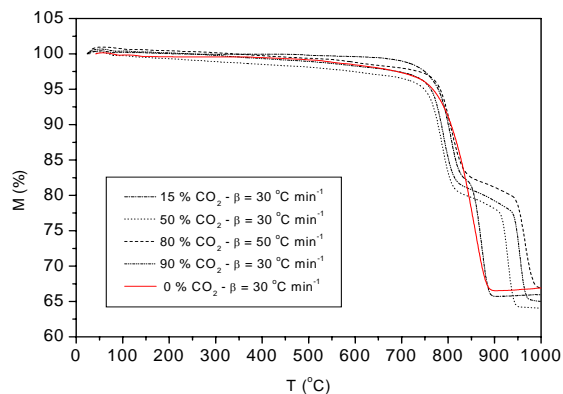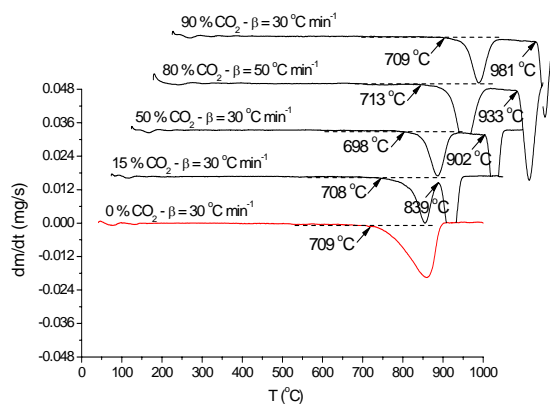

Figure 2. TG curves for dolomite samples with average particle sizes of 545 µm in samples of 10±0.5 mg in air atmosphere with 15%, 50%, 80% and 90% of CO_2 at heating rate of 30°C·min^{-1} or 50°C·min^{-1}.

Figure 3. 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 CO_2 at heating rate of 30°C·min^{-1} or 50°C·min^{-1}.

Study of Carbonation Reaction

TG tests were performed to assess the carbonation conditions. After calcination, the carbonation tests were carried out in different experimental conditions of temperature (T), heating rates (β) and CO_2 concentrations (C_{CO2}) in the atmosphere were applied.

Figure 4 shows the result of the carbonation test performed for one of the considered temperatures

(650 ^{o}C) in atmosphere of 80% of air and 20% of CO_2. The TG and DTA curves show both the calcination and the carbonation events. The sets of curves for all the other experiments resulted similar.
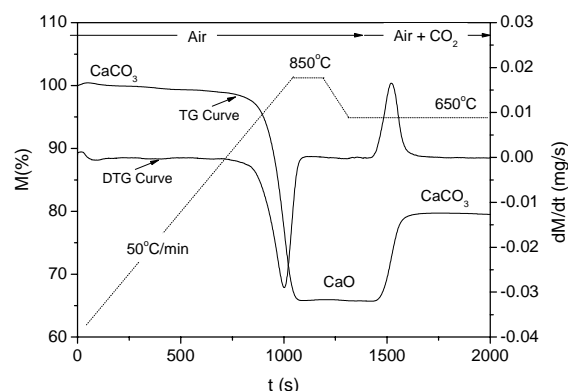

Figure 4. TG (M) and DTG (dM/dt) curves versus time (t) obtained for dolomite samples of 10±0.5 with average particle sizes of 545 µm.

From TG/DTG curves, the conversion was calculated applying the Eq. 5. 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.

Thus, it was concluded that for the applied conditions, the carbonation reaction did not occur significantly at temperatures below 550°C and above 700°C.

In addition, at high concentration of CO_2 (100% - test 13), the conversion values were similar to those obtained to the other tests. There were no significant differences in conversion results due to the different heating rates applied. Moreover, the TG tests showed that 14 min is enough to complete the carbonation process.

Study of Calcium Looping Cycle

Considering the results obtained in Tab. 2, it was assessed the deactivation of dolomite during the carbonation reaction after successive calcination/ carbonation cycles in a vertical tubular furnace (VTF).

The following methodology was applied: (1) calcination tests were carry out under non-isothermal conditions, with temperature ranging from room temperature up to 850 ^{o}C, using 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.

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

Tests	Carbonation			TG Data			
	T (°C)	β (°C/min)	C_{CO2} (mL/min)	M_A (mg)	M_C (mg)	M_F (mg)	X ± 0.63 ($kmol_{CO2}$/$kmol_{Ca+Mg}$)
Effect of reaction temperature							
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
Effect of heating rate							
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
Effect of CO_2 concentration							
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

Figure 5 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%).
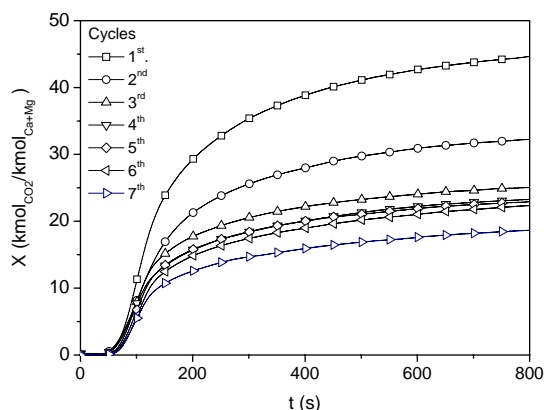

Figure 5. Conversion (%mass) as a function of time of carbonation for dolomite samples previously calcined/carbonated in VTF at temperatures of 650°C.

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 (Fig. 6).
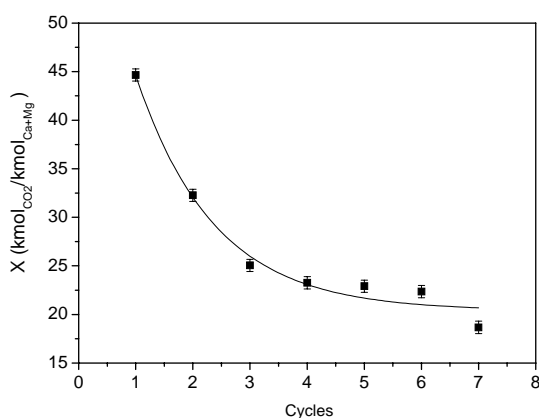

Figure 6. Fit curves to the experimental data considering 14 min of carbonation as a function of number of cycles for dolomite samples previously calcined and carbonated in VTF at temperatures of 650°C.

The equation below that best fitted the experimental points was obtained by a first-order exponential decay.

$$X_{(\%Mass)} = 50.34 \cdot exp\left(-\frac{x}{1.368}\right) + 20.38 \qquad (6)$$

$$R^2 = 0.97$$

Good correlation coefficient were obtained

($R^2 = 0.97$), 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.

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 dependence of sorbent activity was studied as a function of the several cycles of the dolomite regeneration. The residual activity of the sorbent after a large number of cycles was determined from the calcination and carbonation tests.

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

REFERENCES

Arce, G. L. A. F., 2012, Assesment of the Potential for Carbon Mineral Sequestration Applied to Power Plants in Brazil, Doctoral Thesis, Faculdade de Engenharia do Campus de Guaratinguetá, UNESP - Univ Estadual Paulista, Guaratinguetá.

Arias, B., Grasa, G. S., and Abanades, J. C., 2010, Effect of Sorbent Hydration on the Average Activity of CaO in a Ca-looping System, Chemical Engineering Journal, Vol. 163, No. 3, pp. 324-330.

Ávila, I., Crnkovic, P. A., Milioli, F. E., and Luo, K. H., 2011, Thermal Decomposition Kinetics of Brazilian Limestones: effect of $CO_2^=$ partial Pressure, Environmental Technology, Vol. 32, pp. 1-8.

Bandi, W. R., and Krapf, G., 1976, The Effect of CO_2 Pressure and Alkali Salt on the Mechanism of Decomposition of Dolomite, Thermochimica Acta, Vol. 14, No. 1-2, pp. 221-243.

Blamey, J., Anthony, E. J., Wang, J., and Fennell, P. S., 2010, The Calcium Looping Cycle for Large-scale CO_2 Capture, Progress in Energy and Combustion Science, Vol. 36, No. 2, pp. 260-279.

Lackner, K. S., 2002, Carbonate Chemistry for Sequestering Fossil Carbon, Annual Review of

Energy and the Environment, Vol. 27, pp. 193-232.

McIntosh, R. M., Sharp, J. H., and Wilburn, F. W., 1990, The Thermal Decomposition of Dolomite, Thermochimica Acta, Vol. 165, No. 2, pp. 281-296.

Park, A-H. A., Jadhav, R., and Fan, L. S., 2003, CO_2 Mineral Sequestration: Chemically Enhanced Aqueous Carbonation of Serpentine, The Canadian Journal of Chemical Engineering, Vol. 81, pp. 885-890.

Samtani, M., Dollimore, D., Wilburn, F. W., and Alexander, K., 2001, Isolation and Identification of the Intermediate and Final Products in the Thermal Decomposition of Dolomite in an Atmosphere of Carbon Dioxide, Thermochimica Acta, Vol. 367-368, pp. 285-295.

Shimizu , T., Hirama, T., Hosoda, H., Kitano, K., Inagaki, M., and Tejima, K., 1999, A Twin Fluid-bed Reactor for Removal of CO_2 from Combustion Processes, Chemical Engineering Research and Design, Vol. 77, No. 1, pp. 62-68.

Sipilä, J., Teir, S., and Zevenhoven, R., 2008, Carbon Dioxide Sequestration by Mineral Carbonation - Literature Review Update 2005–2007, Åbo Akademi University Faculty of Technology Heat Engineering Laboratory, Turku, Finland, Report VT 2008-1.

Wall, T., 2007, Combustion Processes for Carbon Capture, Proceedings of the Combustion Institute, Vol. 31, No. 1, pp. 31-47.