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

I. Ávila\textsuperscript{a,b}, A. Mortarib, A. M. Santos\textsuperscript{b}, and P. M. Crnkovic\textsuperscript{b}

\textsuperscript{a}UNESP - Universidade Estadual Paulista, Departamento de Energia, Faculdade de Engenharia de Guaratinguetá, São Paulo, Brasil. iavila@unesp.br
\textsuperscript{b} USP – Universidade de São Paulo Núcleo de Engenharia Térmica e Fluidos, Escola de Engenharia de São Carlos, São Carlos, Brasil.

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ABSTRACT

The calcium looping process (Ca-L) is a promising technology to reduce of the carbon dioxide (CO\textsubscript{2}) emissions when applied in energy generation systems. Ca-based materials (usually limestone) are used in this process as CO\textsubscript{2} sorbents. Thus, the CO\textsubscript{2} capture occurs by the reversible reaction between calcium oxide (CaO) and CO\textsubscript{2}, resulting in the calcium carbonate form (CaCO\textsubscript{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\textsubscript{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\textsubscript{2} sorbent. The effect of CO\textsubscript{2} high concentrations in both calcination/carbonation processes is also investigated.

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

NOMENCLATURE

\begin{align*}
M_a & \quad \text{initial mass, mg} \\
M_c & \quad \text{mass after calcination, mg} \\
M_f & \quad \text{mass after carbonation, mg} \\
T & \quad \text{temperature, } ^\circ\text{C} \\
W & \quad \text{atomic or molecular mass} \\
X & \quad \text{conversion, kmol}_{\text{CO}_2}/\text{kmol}_{\text{Ca+Mg}} \\
Y & \quad \text{mass fractions} \\
\beta & \quad \text{heating rate, } ^\circ\text{C/min}
\end{align*}

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\textsubscript{2} emissions in an environmentally safe manner. The sequestration and fixation through geological, oceanic, and mineral methodologies have been suggested to reduce CO\textsubscript{2} emissions.

The concept of mineral sequestration technology with accelerated kinetics for CO\textsubscript{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\textsubscript{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\textsubscript{2} and silicate minerals. This process involves a gas-solid reaction between finely ground minerals with CO\textsubscript{2} to form geologically stable carbonates. Magnesium and calcium containing silicate ores are identified to react with CO\textsubscript{2} to form stable carbonates.

\begin{align*}
\text{CaO}(s) + \text{CO}_2(g) & \rightarrow \text{CaCO}_3(s) \quad (1) \\
\text{CaCO}_3(s) & \rightarrow \text{CaO}(s) + \text{CO}_2(g) \quad (2)
\end{align*}
The calcium looping cycle (Ca-L) is another developing technology for CO₂ capture. In calcium looping systems, the carbonation reaction of CaO with CO₂ (Eq. 1) is followed by the reverse calcination reaction of CaCO₃ to regenerate CaO (Eq. 2) in a pure atmosphere of CO₂ or CO₂/H₂O (Arias et al., 2010; Blamey et al., 2010).

The Ca-L process was proposed by Shimizu et al. (1999) for CO₂ removal from flue gas using the calcium looping systems. In developing technology for CO₂ capture, the carbonation reaction of CaO with CO₂ (Eq. 1) is applied to investigate the reactivity of limestone to produce a suitable gas for CO₂ sequestration. In calcium looping systems, the carbonation reaction of CaO with CO₂ (Eq. 1) is followed by the reverse calcination reaction of CaCO₃ to regenerate CaO (Eq. 2) in a pure atmosphere of CO₂ or CO₂/H₂O (Arias et al., 2010; Blamey et al., 2010).

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The effect of CO₂ partial pressure on the decomposition of carbonate sorbent is a determining factor to define the reactivity of the calcined rocks for CO₂ 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 (Avila 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 CO₂ sequestration, it is of interest to understand how the decomposition rate of CaCO₃ varies with partial pressure of CO₂.

\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \quad (1)
\]

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 carried 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% 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 mL min⁻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 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 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% CO₂. It is evident that the remaining mass of the samples is different in atmosphere with 0% and 15% CO₂. According Ávila et al. (2011), 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%), possibly due to the heterogeneity of the samples.

Moreover, the curves in Fig. 1 show that in atmosphere without CO₂, the decomposition occurred in only one step (Eq. 3). On the other hand, with 15% CO₂, 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 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 Figs. 2 and 3, respectively in which are observed that the calcination process occurred even when concentration of CO₂ 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 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%.

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 CO₂ 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 °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.

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 CO₂ (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 carried out under non-isothermal conditions, with temperature ranging from room temperature up to 850 °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>
<thead>
<tr>
<th>Tests</th>
<th>Carbonation</th>
<th>TG Data</th>
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<tbody>
<tr>
<td></td>
<td>T (°C)</td>
<td>β (°C/min)</td>
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<tr>
<td>Effect of reaction temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>550</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
<td>50</td>
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<td>3</td>
<td>650</td>
<td>50</td>
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<tr>
<td>4</td>
<td>700</td>
<td>50</td>
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<tr>
<td>Effect of heating rate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>750</td>
<td>30</td>
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<tr>
<td>6</td>
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<td>40</td>
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<tr>
<td>7</td>
<td>650</td>
<td>50</td>
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<tr>
<td>Effect of CO₂ concentration</td>
<td></td>
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<tr>
<td>8</td>
<td>650</td>
<td>50</td>
</tr>
<tr>
<td>9</td>
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<td>13</td>
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</tbody>
</table>

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.](image)

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.](image)

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

\[
X_{\%\text{Mass}} = 50.34 \cdot \exp\left( -\frac{x}{1.368} \right) + 20.38
\]

\[R^2 = 0.97\]

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.

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