Kinetics of the Carbonation Reaction of Lithium Orthosilicate Using a Typical CO₂ Concentration of Combustion Gases

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The aim of this work was to investigate the carbonation kinetics of lithium orthosilicate (Li4SiO4) by thermogravimetry and via thermodynamic simulations, using CO₂ concentrations of 15 vol.% (typical of combustion gases) and 100 vol.%.

Tests were performed in a thermogravimetric analyzer, in two sequential steps: (1) pre-treatment at 750 ºC with N₂ and (2) thermal analysis, non-isothermal (at 10 ºC min⁻¹ up to 1000 ºC) or isothermal (at 550 ºC, 600 ºC and 650 ºC). According to the non-isothermal results, the carbonation of Li4SiO4 occurs in the range of 450-746 ºC and the decarbonation above it. Also, it was possible to capture up to 24.9 wt.%CO₂. The isothermal kinetics showed that an increase in temperature promotes an increase in the reaction rate. Yet, the adsorption capacity is limited by the thermodynamics at higher temperatures and the kinetics is slow at low CO₂ concentrations.

Keywords: Carbon dioxide, carbonation kinetics, lithium orthosilicate, combustion gas.

1. Introduction

In the medium term, carbon capture and storage (CCS) is an essential technology for reducing CO₂ emissions through its capture in fossil fuel-fired power plants. Several technologies are applied to remove CO₂ from exhaust gases; however, many still have economic and operating limitations. The main restricting factor is the high temperature at which the CO₂ is generated. Hence, the development of technologies capable of removing this gaseous product at high temperatures, without the need of cooling the gaseous stream, is extremely desirable.

The technique applied to capture CO₂ from an exhaust of a power station includes the use of a calcium based sorbent (usually derived from natural limestone), which is repeatedly carbonated and calcined during the process. Calcium oxide (CaO) owns a high CO₂ capture capacity at temperatures of 600-700 ºC; however, it presents low stability during repeated carbonation and decarbonation cycles, and requires high energy for its complete regeneration at 950 ºC: problems that must be surpassed in order to improve the process efficiency. The sintering of CaO sorbent during calcination leads to a drastic reduction in the surface area, which can affect the adsorption reaction rates. The carbonation reaction for CaO is given by Eq. 1.

$$\text{CaO} + \text{CO}_2 \rightleftharpoons \text{CaCO}_3$$

Ceramics of alkali metals (Li, Na, K, etc.) are included in another group of CO₂ sorbents suitable for high temperatures and greatly studied in recent years. Among these, lithium containing materials such as lithium zirconate (Li₂ZrO₃) and lithium orthosilicate (Li₄SiO₄) seem to be promising CO₂ acceptors in the temperature range of 450-700 ºC, being the Li₄SiO₄ the most reactive. The CO₂ uptake on Li₄SiO₄ is almost 50 wt.% greater than the weight change for Li₂ZrO₃. The reaction of Li₄SiO₄ is attributed to the mechanism by which lithium oxide (Li₂O) within the crystalline structure of Li₂SiO₄ reacts reversibly with CO₂ according to the reaction given by Eq. 2.

$$\text{Li}_4\text{SiO}_4 + \text{CO}_2 \rightleftharpoons \text{Li}_2\text{SiO}_3 + \text{Li}_2\text{CO}_3$$

Advantages of using lithium orthosilicate in high temperature processes include the high sorption rate and capacity, excellent cyclability properties and raw materials of low cost. It also requires a much lower temperature to be recovered when compared to the CaO. According to Amorim et al. (2016), the advantages of Li₂SiO₃ also include the fast carbonation and decarbonation kinetics, the use in 48-repeated reaction cycles, as well as the good mechanical properties.

In general, a higher concentration of CO₂ is beneficial for the CO₂ sorption of Li₂SiO₃ sorbents. Still, the sorption performance of Li₂SiO₃ sorbents decays with the decrease of CO₂ concentration and the suitable temperature to the desorption process depends on the CO₂ concentration.
From the viewpoint of kinetics, the diffusion of Li$_2$O on the sorbent surface has been considered as the rate-limiting step at higher CO$_2$ concentrations, while the superficial sorption becomes the rate-limiting step for lower CO$_2$ concentrations$^{17,27,28}$.

Despite these findings, tests of Li$_2$SiO$_4$ sorbent performance under realistic conditions (temperature, CO$_2$ concentration, pressure, flow rate, etc.) and apparatus are scarcely reported in the literature$^{17,29}$. It is known that the CO$_2$ concentration in flue gases depends on the fuel such as coal (12–15 vol.%CO$_2$) and natural gas (3–4 vol.%CO$_2$), and the effect of CO$_2$ concentration in the sorption performance of Li$_2$SiO$_4$ should be deeply studied.

In this work, the carbonation kinetics of lithium orthosilicate was studied in non-isothermal and isothermal tests by thermogravimetry, and also, via thermodynamic simulations, in order to evaluate the carbon capture at concentrations of 100 vol.% and 15 vol.%CO$_2$ (typical of flue gases).

2. Procedures

2.1 Material preparation and characterization

Lithium orthosilicate (Li$_2$SiO$_4$) was supplied by Chemetall Company (Frankfurt, Germany) with purity of 97.5% and is presented as a crystalline powder with a particle diameter up to 350 μm and density of 2.4 g cm$^{-3}$. The specific surface area of Li$_2$SiO$_4$ was calculated using the Brunauer-Emmett-Teller model$^{30}$, being the isotherm of adsorption/desorption obtained in a New 2200E by Quantachrome. The particles morphology was determined by scanning electron microscopy (SEM) using a JEOL JSM-6390LV microscope. Crystalline phases of the solid were found by X-ray diffraction (XRD) analysis, conducted in an X’Pert diffractometer by Philips, with a scan of 0.038/s and Cu Kα radiation.

Gases used in the thermogravimetric tests were nitrogen (purity 99.996 vol.%) and industrial carbon dioxide, both supplied by White Martins company (Santa Catarina, Brazil).

2.2 Thermogravimetric measurements

Thermogravimetry is still the most widely used technique to determine the adsorption kinetics and provides accurate real-time data under well-controlled conditions. Accordingly, in this work, carbonation tests with CO$_2$ were carried out in a thermogravimetric analyzer model DTG-60 (Shimadzu, Japan). Reactions were conducted in two sequential steps$^{24,31}$: (1) pre-treatment and (2) thermal analysis ((i) non-isothermal and (ii) isothermal conditions):

(i) Non-isothermal analysis were conducted immediately after cooling the solid down to room temperature, under N$_2$, and then by heating at a rate of 10 °C min$^{-1}$ up to 1000 °C, with 15 vol.%CO$_2$ (0.15 atm) or 100 vol.%CO$_2$ (1 atm). The aim of this experimental set was to identify the operating temperature range for Li$_2$SiO$_4$ carbonation;

(ii) Isothermal analysis were conducted after cooling the solid down to the final carbonation temperature of 550, 600 or 650 °C, under N$_2$, and then by replacing the inert gas to the CO$_2$ gas, also with 15 or 100 vol.%CO$_2$. Reactions occurred until there was no more weight variation.

Both N$_2$ and CO$_2$ flow rates were set to 100 mL min$^{-1}$ during all experiments. The CO$_2$ partial pressure of 0.15 bar was selected to simulate a typical concentration of flue gases (combustion gases).

2.3 Thermodynamic data

Thermodynamic equilibrium reactions between Li$_2$SiO$_4$ and CO$_2$ at different temperatures were theoretically determined using the FactSage® 6.3 program (FACT – Facility for the Analysis of Chemical Thermodynamics). This software has a thermodynamic database that allows calculating the conditions for multicomponent equilibrium by minimizing the Gibbs free energy.

The equilibrium partial pressure of CO$_2$ (for the carbonation reaction with Li$_2$SiO$_4$, Eq. 2) was calculated at different temperatures. Then, the changes in Gibbs free energy (ΔG) were evaluated for the carbonation reactions of both CaO (for comparison) and Li$_2$SiO$_4$ (Eq. 1 and 2, respectively) as function of temperature for CO$_2$ partial pressures of 1 atm and 0.15 atm. According to the thermodynamics, the reaction proceeds when ΔG < 0. In the case of adsorption of CaO and Li$_2$SiO$_4$, ΔG depends on both temperature and CO$_2$ concentration, and becomes larger with the increase of these two parameters. The temperature at which the carbonation and decarbonation processes are “balanced” is called the equilibrium temperature, and is the temperature when ΔG equals zero.

3. Results and Discussion

3.1 Characterization

Porous structure analysis of Li$_2$SiO$_4$ generated an N$_2$ adsorption–desorption isotherm of type II, corresponding to a non-porous or macroporous sorbent. The specific surface area determined by the BET method was 0.56 m$^2$/g which is a characteristic value found for other compounds as Li$_2$ZrO$_3$ and CaO$^{32-34}$. 
The low surface area can be a limiting feature to the carbonation reaction, once the CO₂ has no access to the entire active area of the solid, thus requiring the gas diffusion through the product layer 35. SEM analysis for Li₄SiO₄ with different approximations are shown in Fig. 1. The solid is basically composed of agglomerates of granular particles, mostly in polyhedral shape 23,24. In addition, the solid surface possess a smooth feature, confirming the low surface area found by the porous structure analysis.

The XRD pattern presented in Fig. 2 showed characteristic peaks of crystalline phases of lithium orthosilicate (Li₄SiO₄ - JCPDS 37-1472), lithium metasilicate (Li₂SiO₃ - JCPDS 83-1517), lithium carbonate (Li₂CO₃ - JCPDS 83-1454), hydrated lithium hydroxide (LiOH·H₂O - JCPDS 76-1073) and silicon dioxide (SiO₂ - JCPDS 82-1568), as reported by Amorim et al. 24. According to Cruz et al. 36, depending on the synthesis method, the Li₂SiO₃ can be generated during the process. However, the presence of the LiOH·H₂O, Li₂CO₃ and SiO₂ compounds are explained by the reaction of Li₄SiO₄ with steam 37 and/or CO₂ 13, at room temperature.

3.2 Simulation results

The thermodynamic equilibrium reactions between Li₄SiO₄ and CO₂ at 1.0 atm of CO₂ are presented in Tab. 1. It is verified that the sorbent reacts generating different products, depending on the temperature range. Furthermore, it is observed that the stoichiometric ratio CO₂:Li₄SiO₄ decreases with increasing temperature, which is a negative aspect from the viewpoint of CO₂ capture kinetics.

<table>
<thead>
<tr>
<th>T (°C) range</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>25-228</td>
<td>Li₄SiO₄ + 2CO₂ = 2Li₂CO₃ + SiO₂</td>
</tr>
<tr>
<td>229-262</td>
<td>2Li₄SiO₄ + 3CO₂ = 3Li₂CO₃ + Li₂SiO₃</td>
</tr>
<tr>
<td>263-723</td>
<td>Li₄SiO₄ + CO₂ = Li₂CO₃ + Li₂S</td>
</tr>
<tr>
<td>724-1000</td>
<td>Decarbonation</td>
</tr>
</tbody>
</table>

The variation of the equilibrium partial pressure of CO₂ as function of temperature is shown in Fig. 3. It can be seen that the amount of adsorbed CO₂ increases with temperature and, e.g., at a CO₂ pressure of 1.0 atm the equilibrium temperature of Li₄SiO₄ is equal to 723 °C. It is important to note that the adsorption process (for both Li₄SiO₄ and CaO) is strongly dependent on CO₂ partial pressure in the product flow, in a specific reaction temperature.
The changes in the Gibbs free energy ($\Delta G$) to the carbonation reactions of Li$_4$SiO$_4$ and CaO are shown in Fig. 4 as a function of temperature. Negative values indicate the direct order of the reaction. The equilibrium temperature difference between the two sorbents was found to be equal to 170 °C (723 °C to Li$_4$SiO$_4$ and 893 °C to CaO) at 1.0 atm of CO$_2$ (Fig. 1a). The Li$_4$SiO$_4$ requires a considerably lower regeneration temperature when compared to the CaO, and, thus, the reaction between CO$_2$ and Li$_4$SiO$_4$ is more easily reversible. Also, according to Fig. 4 (b), for 0.15 atm of CO$_2$, the sorbents Li$_4$SiO$_4$ and CaO have equilibrium temperatures of 596 °C and 777 °C, respectively, indicating that the CO$_2$ capture is expected to occur at temperatures lower than these.

3.3 Thermal decomposition

The thermogravimetric profile for the thermal decomposition of Li$_4$SiO$_4$ under N$_2$ atmosphere is shown in Fig. 5. It is possible to identify two main steps of mass loss: (1) from room temperature up to 300 °C, attributed to the elimination of the water present on the solid surface (dehydration) and to the dehydroxylation process of Li$_4$SiO$_4$; (2) from 400 °C up to 750 °C, related to the decarbonation process, once the sorbent is capable of capture CO$_2$ even at room temperature. A total weight loss of 2.93 wt.% was verified, which is very close to the impurity content provided by the supplier, of 2.5 wt.%.

3.4 Non-isothermal carbonation

Thermogravimetric results for the non-isothermal analysis of the pretreated Li$_4$SiO$_4$ are shown in Fig. 6. According to Fig. 6 (a), at 1.0 atm of CO$_2$, the carbonation reaction occurs in the temperature range of 500-746 °C, with a CO$_2$ uptake of 24.9 wt.%, which is lower than the maximum theoretical capacity for this solid (36.7 wt%, 8.34 mmol CO$_2$/g Li$_4$SiO$_4$). Here, the maximum experimental temperature for carbonation reaction was higher than the theoretical value of 723 °C. It is important to emphasize that both the temperature at which the maximum CO$_2$ capture occurs and the adsorption capacity may depend on the experimental conditions of the analysis.

3.5 Isothermal carbonation

Thermogravimetric results for the isothermal kinetics of the pretreated Li$_4$SiO$_4$ are shown in Fig. 7. For a reaction time of 180 min, at temperatures of 550 °C, 600 °C and 650 °C, the lithium orthosilicate captured a total of 8.2 wt.%, 12.1 wt.% and 14.6 wt.% of CO$_2$, respectively, at 1.0 atm of CO$_2$. Accordingly, at temperatures of 550 °C and 600 °C, the sorbent captured 4.4 wt.% and 5.5 wt.% of CO$_2$, respectively, at 0.15 atm of CO$_2$. Thought, the experimental decarbonation temperature is much lower than that found for CaO, as previously described. According to Fig. 6 (b), at 0.15 atm of CO$_2$, the carbonation reaction occurs in the temperature range of 450-640 °C, with a CO$_2$ uptake of 2.8 wt.%. Thus, the isothermal capture experiments should be performed at temperatures lower than 640 °C. In addition, the temperature of 750 °C is adequate to guarantee the decarbonation reaction of the solid, independent of the CO$_2$ concentration in the gas stream.

The abrupt weight decrease at the temperatures of 723 °C and 640 °C, respectively for 1.0 atm and 0.15 atm of CO$_2$, is attributed to the decarbonation reaction. The reduction of initial decarbonation temperature (at 0.15 atm of CO$_2$) can be related to both thermodynamic (Fig. 4) and kinetic aspects, as discussed below.
The kinetics of the carbonation reaction is faster at the beginning due to the reaction of CO$_2$ on the exposed surface of Li$_4$SiO$_4$, which is practically pure. As the reaction proceeds, the carbonation rate decreases, possibly due to diffusive limitations. At 1.0 atm of CO$_2$ (Fig. 7a), the carbonation reaction rate increases with temperature due to the decrease of the influence of the diffusive process $^{24}$ (kinetics is favored). The same behavior is observed at 0.15 atm of CO$_2$ (Fig. 7b) when increasing the temperature from 550 °C to 600 °C. However, the carbonation process is thermodynamically unfavored ($\Delta G > 0$) at temperatures higher than 600 °C (Fig. 4b); thus, the CO$_2$ adsorbed at 0.15 atm of CO$_2$ and 650 °C is almost negligible.

The mechanism for capturing CO$_2$ in lithium compounds appears to occur in two steps. First, the reaction of CO$_2$ on the solid surface occurs until the complete formation of the product layer, mainly composed by lithium carbonate (Li$_2$CO$_3$). In the second step, the reaction is controlled by diffusive processes, either by the diffusion of lithium in the reaction products or the diffusion of CO$_2$ in the Li$_2$CO$_3$ layer $^{38}$.

4. Conclusion

It was found that the lithium orthosilicate is a non-porous sorbent, with low surface area, which may be a limiting factor for the carbonation reaction. According to the non-isothermal results, the carbonation of Li$_4$SiO$_4$ occurs in the range of 450-746 °C and the decarbonation is favorable above it. Also, it was possible to capture up to 24.9 wt.%CO$_2$, which is lower than the maximum theoretical capacity of 36.7 wt.%CO$_2$. The isothermal kinetics showed that an increase in temperature promotes an increase in the reaction rate. According to the experimental results and the thermodynamic simulations, the lower is the CO$_2$ gas concentration, the lower is the amount captured and also the equilibrium temperature of adsorption, thus limiting the carbon capture in exhaust gases.

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6. References


