Kinetics of the Carbonation Reaction of Lithium Orthosilicate Using a Typical CO_2 Concentration of Combustion Gases

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The aim of this work was to investigate the carbonation kinetics of lithium orthosilicate (Li_4SiO_4) by thermogravimetry and via thermodynamic simulations, using CO_2 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 N_2 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 Li_4SiO_4 occurs in the range of 450-746 ºC and the decarbonation above it. Also, it was possible to capture up to 24.9 wt.%CO_2. 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 CO_2 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 CO_2 emissions through its capture in fossil fuel-fired power plants [1,2]. Several technologies are applied to remove CO_2 from exhaust gases; however, many still have economic and operating limitations. The main restricting factor is the high temperature at which the CO_2 is generated [3]. 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 CO_2 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 [4–7]. Calcium oxide (CaO) owns a high CO_2 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 [8–11]. The sintering of CaO sorbent during calcination leads to a drastic reduction in the surface area, which can affect the adsorption reaction rates [1]. The carbonation reaction for CaO is given by Eq. 1 [1,4,12].

$$CaO + CO_2 \rightleftharpoons CaCO_3 \qquad (1)$$

Ceramics of alkali metals (Li, Na, K, etc.) are included in another group of CO_2 sorbents suitable for high temperatures and greatly studied in recent years [10,13,14]. Among these, lithium containing materials such as lithium zirconate (Li_2ZrO_3) and lithium orthosilicate (Li_4SiO_4) seem to be promising CO_2 acceptors in the temperature range of 450-700 ºC, being the Li_4SiO_4 the most reactive [15–19]. The CO_2 uptake on Li_4SiO_4 is almost 50 wt.% greater than the weight change for Li_2ZrO_3 [13,20]. The reaction of Li_4SiO_4 is attributed to the mechanism by which lithium oxide (Li_2O) within the crystalline structure of Li_4SiO_4 reacts reversibly with CO_2 according to the reaction given by Eq. 2 [3,13,14,20]. The lithium orthosilicate can theoretically adsorb up to 36.7 wt.% of its own weight.

$$Li_4SiO_4 + CO_2 \rightleftharpoons Li_2SiO_3 + Li_2CO_3 \qquad (2)$$
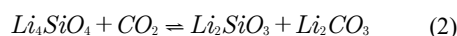
Advantages of using lithium orthosilicate in high temperature processes include the high sorption rate and capacity, excellent cyclability properties and raw materials of low cost [13,14,20–24]. It also requires a much lower temperature to be recovered when compared to the CaO. According to Amorim et al. (2016) [24], the advantages of Li_4SiO_4 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 CO_2 is beneficial for the CO_2 sorption of Li_4SiO_4 sorbents [17,25,26]. Still, the sorption performance of Li_4SiO_4 sorbents decays with the decrease of CO_2 concentration and the suitable temperature to the desorption process depends on the CO_2 concentration [16,26].

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From the viewpoint of kinetics, the diffusion of Li_2O 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_4SiO_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_4SiO_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_4SiO_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} [3]. The specific surface area of Li_4SiO_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):

(1) The pre-treatment was applied for all procedures, by heating the sorbent (10 mg, placed as a thin layer into a platinum pan) from room temperature up to 750 °C, under N_2 atmosphere. The aim of this stage was to eliminate impurities on the solid surface;

(2) The thermal analysis was carried out as follows:

(ii) 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_4SiO_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_4SiO_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_4SiO_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_4SiO_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_4SiO_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_4SiO_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_2ZrO_3 and CaO [32–34].

The low surface area can be a limiting feature to the carbonation reaction, once the CO_2 has no access to the entire active area of the solid, thus requiring the gas diffusion through the product layer [35]. SEM analysis for Li_4SiO_4 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 (Li_4SiO_4 - JCPDS 37-1472), lithium metasilicate (Li_2SiO_3 - JCPDS 83-1517), lithium carbonate (Li_2CO_3 - JCPDS 83-1454), hydrated lithium hydroxide ($LiOH.H_2O$ - JCPDS 76-1073) and silicon dioxide (SiO_2 - JCPDS 82-1568), as reported by Amorim et al. [24]. According to Cruz et al. [36], depending on the synthesis method, the Li_2SiO_3 can be generated during the process. However, the presence of the $LiOH.H_2O$, Li_2CO_3 and SiO_2 compounds are explained by the reaction of Li_4SiO_4 with steam [37] and/or CO_2 [13], at room temperature.

3.2 Simulation results

The thermodynamic equilibrium reactions between Li_4SiO_4 and CO_2 at 1.0 atm of CO_2 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 CO_2:Li_4SiO_4 decreases with increasing temperature, which is a negative aspect from the viewpoint of CO_2 capture kinetics.

Table 1. Reactions between Li_4SiO_4 and CO_2 at different temperatures.

T (°C) range	Reaction
25-228	$Li_4SiO_4 + 2CO_2 \rightleftharpoons 2Li_2CO_3 + SiO_2$
229-262	$2Li_4SiO_4 + 3CO_2 \rightleftharpoons 3Li_2CO_3 + Li_2Si_2O_5$
263-723	$Li_4SiO_4 + CO_2 \rightleftharpoons Li_2CO_3 + Li_2S_3$
724-1000	Decarbonation
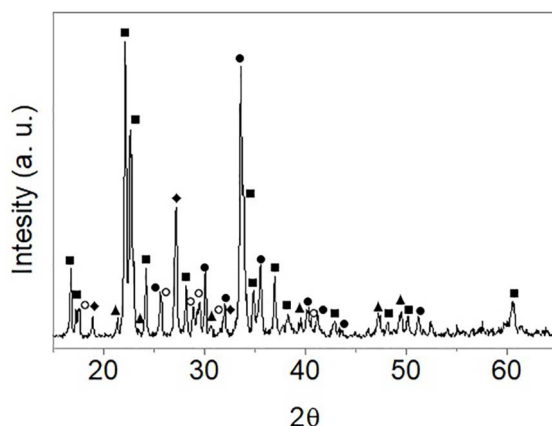
Figure 2. XRD pattern of the raw Li_4SiO_4. Crystalline phases Li_4SiO_4 (■), Li_2SiO_3 (♦), Li_2CO_3 (▲), $LiOH.H_2O$ (●) and SiO_2 (○) were identified.

The variation of the equilibrium partial pressure of CO_2 as function of temperature is shown in Fig. 3. It can be seen that the amount of adsorbed CO_2 increases with temperature and, e.g., at a CO_2 pressure of 1.0 atm the equilibrium temperature of Li_4SiO_4 is equal to 723 °C. It is important to note that the adsorption process (for both Li_4SiO_4 and CaO) is strongly dependent on CO_2 partial pressure in the product flow, in a specific reaction temperature.
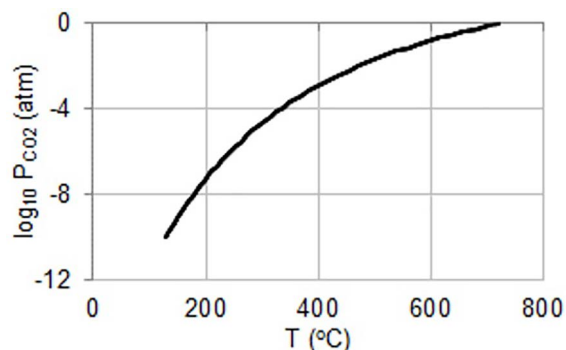

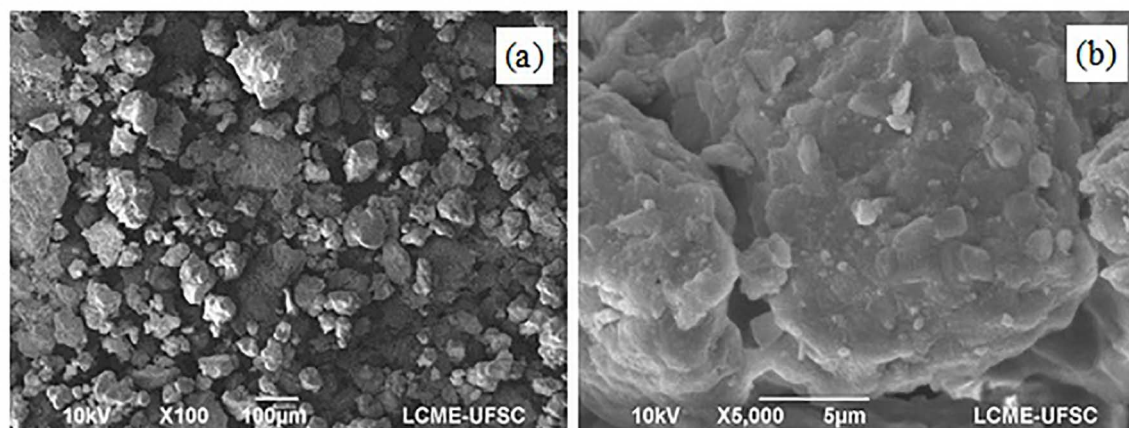**Figure 3.** Equilibrium partial pressure of CO_2 as a function of temperature for Li_4SiO_4 sorbent.

Figure 1. SEM analysis for Li_4SiO_4 with approximations of 100x (a) and 5000x (b).

The changes in the Gibbs free energy (ΔG) to the carbonation reactions of Li_4SiO_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_4SiO_4 and 893 °C to CaO) at 1.0 atm of CO_2 (Fig. 1a). The Li_4SiO_4 requires a considerably lower regeneration temperature when compared to the CaO, and, thus, the reaction between CO_2 and Li_4SiO_4 is more easily reversible. Also, according to Fig. 4 (b), for 0.15 atm of CO_2, the sorbents Li_4SiO_4 e 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_4SiO_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_4SiO_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 [13,20,23,37]. 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_4SiO_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_4SiO_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.
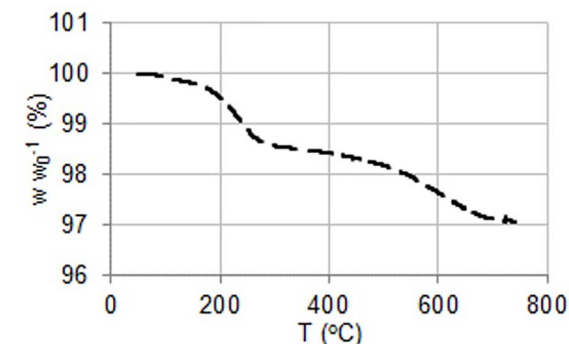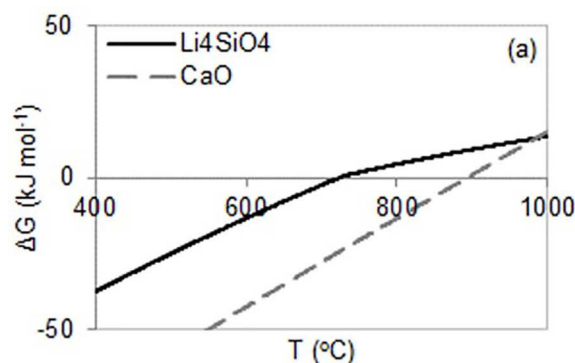

Figure 5. Thermal decomposition of Li_4SiO_4 under N_2 atmosphere.

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 [24].

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.

3.5 Isothermal carbonation

Thermogravimetric results for the isothermal kinetics of the pretreated Li_4SiO_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.% CO_2, respectively, at 0.15 atm of CO_2.
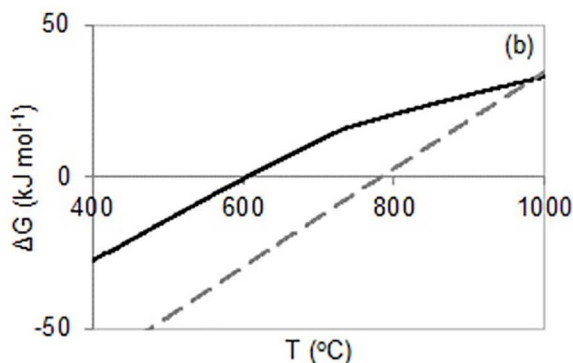

Figure 4. Changes in the Gibbs free energy to Li_4SiO_4 and CaO as a function of temperature, for CO_2 partial pressures of 1.0 atm (a) and 0.15 atm (b).
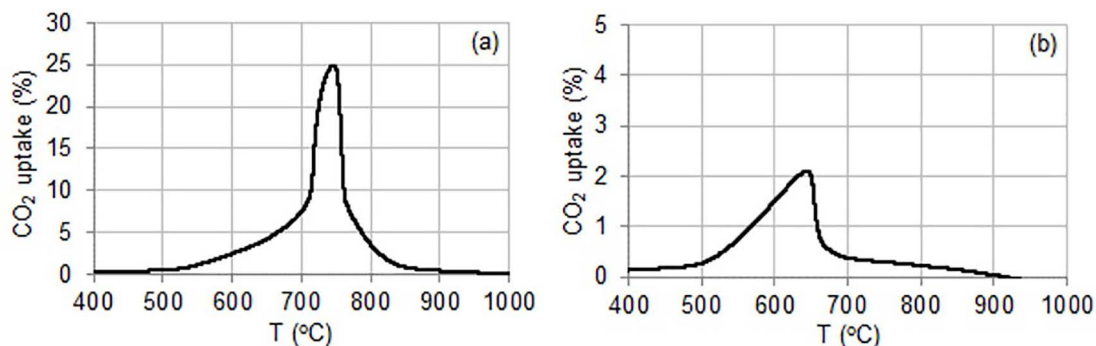
Figure 6. Non-isothermal carbonation to Li$_4$SiO$_4$ as a function of temperature, for CO$_2$ partial pressures of 1.0 atm (a) and 0.15 atm (b).
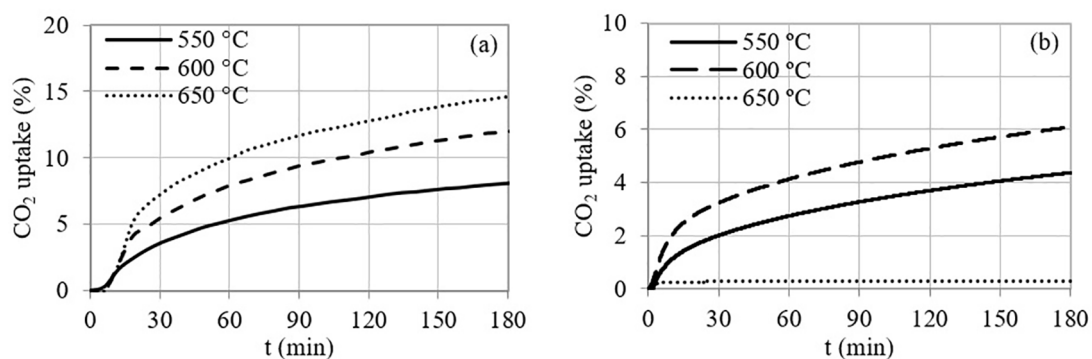

Figure 7. Isothermal carbonation to Li$_4$SiO$_4$ as a function of temperature, for CO$_2$ partial pressures of 1.0 atm (a) and 0.15 atm (b).

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.

5. Acknowledgments

6. References

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