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

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Received: December 13, 2018; Revised: June 06, 2019; Accepted: July 16, 2019

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.

\[ \text{CaO} + \text{CO}_2 \leftrightarrow \text{CaCO}_3 \]  

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. 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. 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 Li₄SiO₄ reacts reversibly with CO₂ according to the reaction given by Eq. 2. The lithium orthosilicate can theoretically adsorb up to 36.7 wt.% of its own weight.

\[ \text{Li}_4\text{SiO}_4 + \text{CO}_2 \leftrightarrow \text{Li}_2\text{SiO}_3 + \text{Li}_2\text{CO}_3 \]  

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 Li₄SiO₄ reacts reversibly with CO₂ according to the reaction given by Eq. 2.

In general, a higher concentration of CO₂ is beneficial for the CO₂ sorption of Li₄SiO₄ sorbents. Still, the sorption performance of Li₄SiO₄ 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$_4$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$_4$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$_4$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$_4$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 ((ii) 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:
   (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$_4$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$_4$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$_4$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$_4$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$_4$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$_4$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. SEM analysis for Li₂SiO₃ with different approximations are shown in Fig. 1. The solid is basically composed of agglomerates of granular particles, mostly in polyhedral shape. 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. 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 and/or CO₂ 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 1. Reactions between Li₄SiO₄ and CO₂ at different temperatures.**

| T (°C) range | Reaction                                      |
|-------------|-----------------------------------------------|
| 25-228      | Li₄SiO₄ + 2CO₂ = 2Li₂CO₃ + SiO₂                |
| 229-262     | 2Li₄SiO₄ + 3CO₂ = 3Li₂CO₃ + Li₂SiO₃            |
| 263-723     | Li₄SiO₄ + CO₂ = Li₂CO₃ + Li₂S                  |
| 724-1000    | Decarbonation                                 |

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.

**Figure 1.** SEM analysis for Li₄SiO₄ with approximations of 100x (a) and 5000x (b).

**Figure 2.** XRD pattern of the raw Li₄SiO₄. Crystalline phases Li₄SiO₄ (■), Li₂SiO₃ (♦), Li₂CO₃ (▲), LiOH.H₂O (●) and SiO₂ (○) were identified.

**Figure 3.** Equilibrium partial pressure of CO₂ as a function of temperature for Li₄SiO₄ sorbent.
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$_4$ 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$_4$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 $^{13,20,23,37}$. 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$_4$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.

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$_4$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.% CO$_2$, respectively, at 0.15 atm of CO$_2$. 
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 (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.

**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**

This research was supported by the Coordination for the Improvement of Higher Education Personnel (CAPES-Brazil) and the National Council of Technological and Scientific Development (CNPq-Brazil). The authors would like to thank LCME-UFSC for the technical support provided in the electron microscopy analysis.
6. References

1. Fennell PS, Davidson JF, Dennis JS, Hayhurst AN. Regeneration of sintered limestone sorbents for the sequestration of CO₂ from combustion and other systems. Journal of the Energy Institute. 2007;80(2):116-119.

2. Costa CC, Melo DMA, Martinelli AE, Melo MAF, Medeiros RLBA, Marconi JA, et al. Synthesis Optimization of MCM-41 for CO₂ adsorption Using Simplex-centroid Design. Materials Research. 2015;18(4):714-722.

3. Domenico MD, Amorim SM, Collazzo GC, José HJ, Moreira RFPM. Coal gasification in the presence of lithium orthosilicate. Part I: Reaction kinetics. Chemical Engineering Research and Design. 2019;141:529-539.

4. Sun H, Wu C, Shen B, Zhang X, Zhang Y, Huang J. Progress in the development and application of CaO-based adsorbents for CO₂ capture—a review. Materials Today Sustainability. 2018;1-2:1-27.

5. Zhang Y, Gong X, Chen X, Yin L, Zhang J, Liu W. Performance of synthetic CaO-based sorbent pellets for CO₂ capture and kinetic analysis. Fuel. 2018;232:205-214.

6. Erans M, Manovic V, Anthony EJ. Calcium looping sorbents for CO₂ capture. Applied Energy. 2016;180:722-742.

7. Kierzkowska AM, Pacciani R, Müller CR. CaO-Based CO₂ Sorbents: From Fundamentals to the Development of New, Highly Effective Materials. ChemSusChem. 2013;6(7):1130-1148.

8. Florin NH, Harris AT. Reactivity of CaO derived from nano-sized CaCO₃ particles through multiple CO₂ capture-and-release cycles. Chemical Engineering Science. 2009;64(2):187-191.

9. Abanades JC. The maximum capture efficiency of CO₂ using a carbonation/calcination cycle of CaO/CaCO₃. Chemical Engineering Journal. 2002;90(3):303-306.

10. Yong Z, Mata V, Rodrigues AE. Adsorption of carbon dioxide at high temperature—a review. Separation and Purification Technology. 2002;26(3-195):205-206.

11. Pecharumproporn P, Wongsakulphasatch S, Glirunr T, Maneedaeng A, Hassan Z, Assabumrungrat S. Synthetic CaO-based sorbent for high-temperature CO₂ capture in sorption-enhanced hydrogen production. International Journal of Hydrogen Energy. 2019;44(37):20663-20677.

12. Hougen OA, Ragatz RA, Watson KM. Chemical Process Principles. Part 2: Thermodynamics. 2nd ed. New York: John Wiley and Sons; 1959. 624 p.

13. Kato M, Nakagawa K, Essaki K, Maezawa Y, Takeda S, Kogo R, et al. Novel CO₂ Absorbents Using Lithium-Containing Oxide. International Journal of Applied Ceramic Technology. 2005;2(6):467-475.

14. Nakagawa K, Kato M, Yoshikawa S, Essaki K, Uemoto H. A Novel CO₂ Absorbents Using Lithium-Containing Oxides. In: Proceedings of the 2nd Annual Conference on Carbon Sequestration; 2003 May 5-8; Alexandria, VA, USA.

15. Izquierdo MT, Gasquet V, Sansom E, Ojeda M, Garcia S, Maroto-Valer MM. Lithium-based sorbents for high temperature CO₂ capture: Effect of precursor materials and synthesis method. Fuel. 2018;230:45-51.

16. Lee SC, Kim MJ, Kwon YM, Chae HJ, Cho MS, Park YK, et al. Novel regenerable solid sorbents based on lithium orthosilicate for carbon dioxide capture at high temperatures. Separation and Purification Technology. 2019;214:100-127.

17. Hu Y, Liu W, Yang Y, Qu M, Li H. CO₂ capture by Li₂SiO₄ sorbents and their applications: Current developments and new trends. Chemical Engineering Journal. 2019;359:604-625.

18. Kwon YM, Chae HJ, Cho MS, Park YK, Seo HM, Lee SC, et al. Effect of a Li₂SiO₄ phase in lithium silicate-based sorbents for CO₂ capture at high temperatures. Separation and Purification Technology. 2019;214:104-110.

19. Wang K, Guo X, Zhao P, Wang F, Zheng C. High temperature capture of CO₂ on lithium-based sorbents from rice husk ash. Journal of Hazardous Materials. 2011;189(1-2):301-307.

20. Kato M, Yoshikawa S, Nakagawa K. Carbon dioxide absorption by lithium orthosilicate in a wide range of temperature and carbon dioxide concentrations. Journal of Materials Science Letters. 2002;21(6):485-487.

21. Essaki K, Kato M, Nakagawa K. CO₂ Removal at High Temperature Using Packed Bed of Lithium Silicate Pellets. Journal of the Ceramic Society of Japan. 2006;114(1333):739-742.

22. Saggiani M, Puccini M, Vitolo S. High-temperature and low concentration CO₂ sorption on Li₂SiO₄ based sorbents: Study of the used silica and doping method effects. International Journal of Greenhouse Gas Control. 2011;5(4):741-748.

23. Zhang Q, Han D, Liu Y, Ye Q, Zhu Z. Analysis of CO₂ sorption/desorption kinetic behaviours and reaction mechanisms on Li₂SiO₄. AlchE Journal. 2013;59(3):901-911.

24. Amorim SM, Domenico MD, Dantas TLP, José HJ, Moreira RFPM. Lithium orthosilicate for CO₂ capture with high regeneration capacity: Kinetic study and modeling of carbonation and decarbonation reactions. Chemical Engineering Journal. 2016;283:388-396.
25. Essaki K, Kato M, Uemoto H. Influence of temperature and CO$_2$ concentration on the CO$_2$ absorption properties of lithium silicate pellets. *Journal of Materials Science*. 2005;40(18):5017-5019.

26. Kaniwa S, Yoshino M, Niwa E, Yashima M, Hashimoto T. Analysis of chemical reaction between Li$_2$SiO$_3$ and CO$_2$ by thermogravimetry under various CO$_2$ partial pressures—Clarification of CO$_2$ partial pressure and temperature region of CO$_2$ absorption or desorption. *Materials Research Bulletin*. 2017;94:134-139.

27. Pacciani R, Torres J, Solsona P, Coe C, Quinn R, Hufton J, et al. Influence of the Concentration of CO$_2$ and SO$_2$ on the Absorption of CO$_2$ by a Lithium Orthosilicate-Based Absorbent. *Environmental Science & Technology*. 2011;45(16):7083-7088.

28. Quinn R, Kitzhoffer RJ, Hufton JR, Golden TC. A High Temperature Lithium Orthosilicate-Based Solid Absorbent for Post Combustion CO$_2$ Capture. *Industrial & Engineering Chemistry Research*. 2012;51(27):9320-9327.

29. Jeoung S, Lee JH, Kim HY, Moon HR. Effects of porous carbon additives on the CO$_2$ absorption performance of lithium orthosilicate. *Thermochimica Acta*. 2016;637:31-37.

30. Brunauer S, Emmett PH, Teller E. Adsorption of Gases in Multimolecular Layers. *Journal of the American Chemical Society*. 1938;60(2):309-319.

31. Di Domenico M. Gaseificação de carvão mineral brasileiro na presença de ortossilicato de litio visando a produção aumentada de hidrogênio. [Thesis]. Florianópolis: Federal University of Santa Catarina; 2013.

32. Nikulshina V, Gálvez ME, Steinfeld A. Kinetic analysis of the carbonation reactions for the capture of CO$_2$ from air via the Ca(OH)$_2$–CaCO$_3$–CaO solar thermochemical cycle. *Chemical Engineering Journal*. 2007;129(1-3):75-83.

33. López Ortiz A, Escobedo Bretado MA, Guzmán Velderrain V, Meléndez Zaragoza M, Salinas Gutiérrez J, Lardizábal Gutiérrez D, et al. Experimental and modeling kinetic study of the CO$_2$ absorption by Li$_2$SiO$_3$. *International Journal of Hydrogen Energy*. 2014;39(29):16656-16666.

34. Xiong R, Ida J, Lin YS. Kinetics of carbon dioxide sorption on potassium-doped lithium zirconate. *Chemical Engineering Science*. 2003;58(19):4377-4385.

35. Romero-Ibarra IC, Ortiz-Landeros J, Pfeiffer H. Microstructural and CO$_2$ chemisorption analyses of Li$_2$SiO$_3$: Effect of surface modification by the ball milling process. *Thermochimica Acta*. 2013;567:118-124.

36. Cruz D, Bulbulian S, Lima E, Pfeiffer H. Kinetic analysis of the thermal stability of lithium silicates (Li$_2$SiO$_3$ and Li$_4$SiO$_4$). *Journal of Solid State Chemistry*. 2006;179(3):909-916.

37. Ortiz-Landeros J, Martínez-dlCruz L, Gómez-Yáñez C, Pfeiffer H. Towards understanding the thermoanalysis of water sorption on lithium orthosilicate (Li$_2$SiO$_3$). *Thermochimica Acta*. 2011;515(1-2):73-78.

38. Ortiz-Landeros J, Ávalos-Rendón TL, Gómez-Yáñez C, Pfeiffer H. Analysis and perspectives concerning CO$_2$ chemisorption on lithium ceramics using thermal analysis. *Journal of Thermal Analysis and Calorimetry*. 2012;108(2):647-655.