



# Lithium orthosilicate for CO<sub>2</sub> capture with high regeneration capacity: Kinetic study and modeling of carbonation and decarbonation reactions



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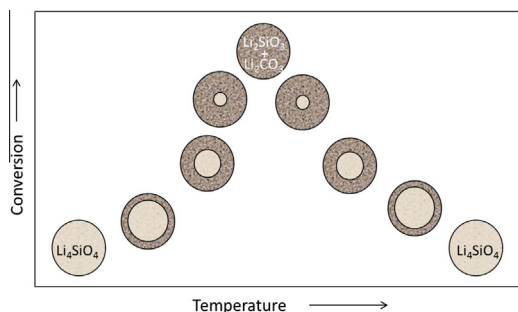
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## HIGHLIGHTS

- This work presents a kinetic study and modeling of the CO<sub>2</sub> capture of Li<sub>4</sub>SiO<sub>4</sub>.
- After 48 carbonation/decarbonation cycles the solid showed an activity decay of 20%.
- The shrinking core model was firstly applied to Li<sub>4</sub>SiO<sub>4</sub> decarbonation.
- This model adequately described both kinetics of carbonation and decarbonation.

## GRAPHICAL ABSTRACT



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## ABSTRACT

One of the most promising techniques for CO<sub>2</sub> capture at high temperatures consists in its separation by the carbonation reaction with an inorganic solid. Lithium orthosilicate (Li<sub>4</sub>SiO<sub>4</sub>) is considered one potential material due to its high capture capacity and thermal stability. In this study, the kinetics of carbonation and decarbonation of Li<sub>4</sub>SiO<sub>4</sub> was evaluated at atmospheric pressure, isothermal and non-isothermal conditions and in cycling experiments. According to the non-isothermal test, carbonation occurs within 500–715 °C and decarbonation above it. Isothermal tests showed that the reaction rates increased with increasing temperature and at high temperatures it was possible to capture up to 35 wt% CO<sub>2</sub>. Kinetics of both carbonation and decarbonation was adequately described by the shrinking core model. The Li<sub>4</sub>SiO<sub>4</sub> presented an excellent durability comparing to other materials for CO<sub>2</sub> capture, with an activity decay of 20% after 48 cycles.

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## 1. Introduction

There is a growing interest in the concept of a hydrogen economy, in which H<sub>2</sub> along with electricity can become the main energy carriers. Advantages of this type of energy include the

low environmental impact in addition to the application on fuel cell technology aiming the generation of electricity.

Processes to produce hydrogen, as the conventional steam reforming and coal gasification, are operated at a high temperature range (700–900 °C) and have carbon dioxide as one of the products. The removal of CO<sub>2</sub> from the reaction stream can both increase the concentration of the desired products and improve the overall efficiency [1–4].

One of the most promising techniques for CO<sub>2</sub> capture consists in its separation by the reversible reaction with a sorbent. Three

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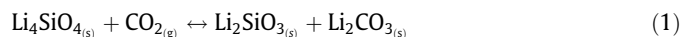
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suitable materials are known to have good capacities for the sorption of CO<sub>2</sub> at high temperatures: CaO-based materials [5–7], hydrotalcites (HT) [2,4,8,9] and lithium based materials [10,11]. Activated carbons and zeolites have been widely used, though the low equilibrium temperature for adsorption (25–150 °C) limits their application.

Calcium oxide (CaO) presents high CO<sub>2</sub> capture capacity in temperatures of 600–700 °C; however, the solid shows poor stability during extended carbonation/decarbonation cycles and requires high energy for complete regeneration (950 °C) [12–14]. Hydrotalcites are more suitable to use in the cyclic process (carbonation/decarbonation) than CaO, but they have lower adsorption capacity [5,15].

The lithium-based ceramics such as lithium oxide (Li<sub>2</sub>O), lithium zirconate (Li<sub>2</sub>ZrO<sub>3</sub>), lithium silicate (Li<sub>4</sub>SiO<sub>4</sub>), lithium aluminate (Li<sub>5</sub>AlO<sub>4</sub>), lithium ferrite (LiFeO<sub>2</sub>) and lithium titanate (Li<sub>4</sub>TiO<sub>4</sub>) have also been used for CO<sub>2</sub> capture [16]. Li<sub>2</sub>O has the highest theoretical capacity (147.3 wt%), but the high reactivity of the solid and corrosion may limit its use [17]. Li<sub>5</sub>AlO<sub>4</sub> has also a high capture capacity (70.0 wt%) and wide operating range (200–700 °C), but the sintering during its regeneration can reduce the surface area, and thus, the solid reactivity [17]. Although the Li<sub>2</sub>SiO<sub>3</sub> presents a good capture capacity (48.9 wt%) it has a low equilibrium temperature for carbonation (260 °C) [11]. Li<sub>4</sub>TiO<sub>4</sub>, Li<sub>2</sub>ZrO<sub>3</sub> and LiFeO<sub>2</sub> present the lower theoretical CO<sub>2</sub> uptakes (31.5, 23.2 and 28.7 wt%, respectively). Finally, the equilibrium temperature of the carbonation reaction for LiFeO<sub>2</sub> is relatively low (510 °C) when compared to other ceramics such as Li<sub>2</sub>ZrO<sub>3</sub> (715 °C) and Li<sub>4</sub>SiO<sub>4</sub> (720 °C) [11].

Among the lithium-based compounds, Li<sub>4</sub>SiO<sub>4</sub> appears as a suitable material for CO<sub>2</sub> capture at high temperatures. The reaction of this solid is attributed to the mechanism by which the Li<sub>2</sub>O within the crystal structure of Li<sub>4</sub>SiO<sub>4</sub> reversibly reacts with CO<sub>2</sub>, as given by Eq. (1). The advantages of this solid include a relatively high capture capacity (theoretical value of 36.7 wt%) at temperatures of 450–700 °C, fast kinetics of carbonation/decarbonation, good mechanical properties and also the possibility of use in repeated carbonation/decarbonation cycles [18–20]. Still, there is not enough knowledge related to the regeneration potential of this material [20–22].



Understanding the physical and chemical processes that occur during CO<sub>2</sub> capture is extremely important for the proper application of the sorbent, but its regeneration has not been studied in details [16,18,23,24]. The possibility of regenerating the Li<sub>4</sub>SiO<sub>4</sub> along with its reuse, make the study of the decarbonation mechanism equally important as the carbonation mechanism and fundamental in the economic point of view. Up to now, it was found that only Qi et al. [23] and Amorim [25] studied the kinetics of both carbonation and decarbonation reactions of Li<sub>4</sub>SiO<sub>4</sub>. Qi and others [23] tested the fitting of three different models to the experimental data of carbonation: shrinking core model with chemical reaction as the rate-limiting step, double exponential model and Avrami–Erofeev model. The latter presented the best fitting to the results, being later applied to the experimental data of decarbonation.

The Avrami–Erofeev model describes the kinetics of crystallization of solids and, despite presenting a good fit to the experimental data, there is no clear physical interpretation of the model constants [23]. The double exponential model is widely used to describe the carbonation of Li<sub>4</sub>SiO<sub>4</sub> [18,21,26,27] since it generally presents good agreement with the kinetic data. In this model, the constants values correspond to the chemical reaction of CO<sub>2</sub> on the particle surface and the chemical reaction controlled by diffusion processes through the layer of products. Although the good fit

presented for the carbonation of Li<sub>4</sub>SiO<sub>4</sub>, there is no other compelling experimental evidence that could validate this model [24].

The shrinking core model has been tested to fit the experimental results for the carbonation reaction of Li<sub>2</sub>ZrO<sub>3</sub>, considering the internal diffusion in the product layer as the rate-limiting step [28,29]. In this case, limitations by the external diffusion in the gas layer and chemical reaction were excluded. Jimenez and others [30], on the contrary, proposed the fitting of the shrinking core model considering the three rate-limiting steps to the carbonation reaction of Na<sub>2</sub>ZrO<sub>3</sub>. Ortiz and others [24] applied the same methodology as Jimenez and others [30] to the experimental data of lithium orthosilicate carbonation. Both research groups found excellent results using this approach.

This work presents a kinetic study and modeling of the carbonation and decarbonation reactions of Li<sub>4</sub>SiO<sub>4</sub>. The regeneration capacity of Li<sub>4</sub>SiO<sub>4</sub> for 48 cycles was evaluated in cyclic carbonation/decarbonation experiments in a thermogravimetric analyzer. Isothermal and non-isothermal tests were also carried out and the experimental results were fitted to the shrinking core model considering the three rate-limiting steps: chemical reaction, external diffusion and internal diffusion.

## 2. Fundamentals of the kinetic model

The mechanism proposed by the shrinking core model assumes the particles as uniform non-porous grains. Initially, the reaction occurs in the grain surface and then the reaction zone moves into the solid leaving a product layer behind. The total radius of the particle remains constant, while the radius of the unreacted core and the layer of products vary over time as a function of conversion.

The approximate solution of the shrinking core model applied in this work is a combination of the resistances that can simultaneously occur in a particle under reaction [31]: CO<sub>2</sub> diffusion in the gas layer surrounding the particle, CO<sub>2</sub> diffusion through the product layer around the unreacted core and chemical reaction on the unreacted core surface. The algebraic solution that relates the conversion as a function of time for a spherical particle is given by:

$$t = \frac{1}{S_m} X + \frac{1}{S_g} [1 - 3(1 - X)^{2/3} + 2(1 - X)] + \frac{1}{S_r} [1 - (1 - X)^{1/3}] \quad (2)$$

where the terms  $S_m$ ,  $S_g$  e  $S_r$  represent the resistances to the external mass transfer, product layer diffusion and chemical reaction, respectively, and  $X$  is fractional conversion. Carbonation/decarbonation parameters are calculated separately according to the equations presented in Table 1. The model was derived considering carbonation and decarbonation reaction orders of 1 and 0, respectively, with respect to carbon dioxide [24].

In Table 1,  $b$  is the stoichiometric coefficient determined by the ratio of moles of Li<sub>4</sub>SiO<sub>4</sub> per mol of CO<sub>2</sub> in the carbonation reaction,  $c$  is the stoichiometric coefficient determined by the ratio of moles of Li<sub>2</sub>CO<sub>3</sub> per mol of CO<sub>2</sub> in the decarbonation reaction,  $k_g$  is the

**Table 1**  
Equations used to determine the parameters of the shrinking core model for carbonation/decarbonation reactions of Li<sub>4</sub>SiO<sub>4</sub>.

Parameters	Equations	
	Carbonation	Decarbonation
$S_m$	$\frac{3bk_g C_{CO_2,0}}{r\rho_{Li_4SiO_4}}$	$\frac{3ck_g C_{CO_2}}{r\rho_{Li_2CO_3}}$
$S_g$	$\frac{6bD_g C_{CO_2,0}}{r^2 \rho_{Li_4SiO_4}}$	$\frac{6cD_g C_{CO_2}}{r^2 \rho_{Li_2CO_3}}$
$S_r$	$\frac{bk_g C_{CO_2,0}}{r\rho_{Li_4SiO_4}}$	$\frac{bk_g}{r\rho_{Li_4SiO_4}}$
$X$	$\frac{m_0 - m_t}{m_f}$	$\frac{m_0 - m_t}{m_f}$

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