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CO_2 Capture in a Fixed Bed Reactor: Experimental and Simulation Study of Adsorption Process Using Li_4SiO_4-based Sorbents

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One of the most pressing challenges facing the energy sector is the urgent need to reduce anthropogenic CO_2 emissions while simultaneously meeting the increasing energy demands of a growing global population. Among the various strategies to mitigate point-source CO_2 emissions, post-combustion carbon capture stands out as one of the most straightforward and widely applicable methods. This study focused on modeling a fixed bed reactor utilizing K_2CO_3-doped Li_4SiO_4 porous pellets as the adsorbent material. The pellets were tested in a lab-scale fixed bed reactor under conditions simulating the exhaust gases of power plants, specifically at a low CO_2 concentration (4 vol%) and an adsorption temperature of 515 °C. A one-dimensional model was developed using COMSOL Multiphysics® to simulate the CO_2 adsorption process within the pellet bed. The model incorporated modified shrinking core reaction kinetics, which accounted for the presence of a molten carbonate mixture and a nucleation phase to capture the adsorption process accurately. Simulation results showed good agreement with the experimental data, confirming the model's ability to predict the adsorption performance under the specified conditions.

1. Introduction

The increasing CO_2 concentration in the atmosphere, which has recently exceeded 400 ppm, has raised significant concern for its potential effects on Earth's ecosystems. Achieving net-zero carbon emissions by 2050 requires scalable and efficient decarbonization strategies, particularly in energy-intensive industries, which are crucial for limiting global temperature rise. Among these efforts, carbon capture and storage (CCS) technologies are emerging as essential approaches to mitigate emissions from industrial processes and power generation that continue to depend on fossil fuels (Chu et al., 2024). The removal of CO_2 from industrial flue gas streams at high temperatures is traditionally realized by liquid-phase absorption methods using amine-based sorbents, which require cooling the gas to temperatures below 100 °C for effective capture, resulting in significant energy losses (Chao et al., 2021). In contrast, high-temperature regenerable solid sorbents have gained significant attention due to their ability to capture CO_2 from hot flue gas streams directly (Nedoma & Netušil, 2021). A promising sorbent is lithium orthosilicate (Li_4SiO_4) since it can adsorb CO_2 at high temperatures (450-600 °C) with a reversible reaction (Eq(1)), even at low concentrations (2-5 vol%), typical of industrial operating conditions in natural gas power plants. The main advantages of Li_4SiO_4 lie in its high theoretical adsorption capacity of 367 mg CO_2/g sorbent, fast reaction kinetics, and excellent stability that make it suitable for use in several adsorption/desorption cycles.

$$Li_4SiO_{4\,(s)} + CO_{2\,(g)} \leftrightarrow Li_2CO_{3\,(s)} + Li_2SiO_{3\,(s)} \quad (1)$$

However, low CO_2 concentrations could significantly hinder Li_4SiO_4 adsorption capacity and kinetics due to CO_2 diffusion resistance through the reaction products' solid layer that forms on the particle surface. Its performance could be improved by doping Li_4SiO_4 with alkali carbonates such as potassium carbonate (K_2CO_3), thanks to the formation of a molten carbonate layer, which reduces CO_2 diffusion resistance. Several studies have been

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carried out on CO_2 capture by Li_4SiO_4-based sorbents; however, only very few of them report the dynamic adsorption performance of the sorbent in a packed bed system (Hu et al., 2019). Furthermore, modeling the chemical adsorption process of CO_2 in a fixed bed reactor provides valuable insights into the transport and reaction mechanisms (Zedda et al., 2024), enabling optimization of reactor design and operational parameters for process scale-up. This study investigated the CO_2 adsorption process at high temperature by K_2CO_3-doped Li_4SiO_4 sorbents, focusing on the modeling of a fixed bed reactor of pellets. A mathematical model based on the equations of mass conservation and energy balance was developed to simulate the adsorption breakthrough results obtained from experimental tests carried out in a lab-scale fixed bed reactor.

2. Experimental

2.1 Sorbents production

Li_4SiO_4-based sorbents in pellet form were produced by employing a fabrication method developed in collaboration with Industrie Bitossi S.p.A., as described in detail in our previous work (Stefanelli et al., 2025). First, Li_4SiO_4 powders were synthesized using a solid-state method assisted by wet milling. Then, the sorbent was mixed with 30 wt% of K_2CO_3 (by weight of Li_4SiO_4) as the activity promoter and 20 wt% of cellulose fibers and mechanically compressed to obtain cylindrical pellets (6 mm diameter, 2.5 mm height). A final thermal treatment allowed cellulose combustion to obtain macro-porous pellets.

2.2 Fixed bed reactor CO_2 capture tests

CO_2 adsorption properties of the pellets were investigated in a lab-scale fixed bed reactor (Figure 1a), composed of a quartz tube filled with a packed bed of K_2CO_3-doped Li_4SiO_4 pellets (Figure 1b) and placed in a vertical tubular furnace, analyzing the CO_2 outlet concentration in line with an infrared spectrometer. The adsorption experiments were conducted at low CO_2 concentration in the feed gas (4 vol% CO_2, balance nitrogen), varying the interstitial gas velocity and the sorbent height. The temperature of 515 °C was chosen for the adsorption tests as a case study since it is included in the adsorption range of such sorbent (Yang et al., 2023). The reactor key parameters and the test conditions for the case study analyzed are listed in Table 1.

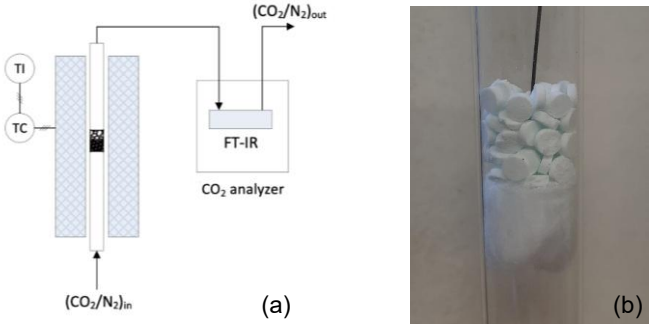

Figure 1: Lab-scale fixed bed reactor system (a) simplified scheme and (b) packed bed of Li_4SiO_4-based pellets.

Table 1: Reactor parameters and CO_2 adsorption test conditions

Packed bed diameter, d_{bed} (cm)	Packed bed height, L (cm)	Void fraction, ε_b	Gas flow rate, G_{in} (mL/min)	Interstitial gas velocity, u_g (cm/s)	GHSV* (h^{-1})
2.5	2.5	0.44	260	2	2270

* Gas Hourly Space Velocity.

3. Mathematical modeling

A numerical model for gas-solid flow was developed and used to study the CO_2 adsorption process by K_2CO_3-doped Li_4SiO_4 sorbents. The packed bed reactor of doped Li_4SiO_4 pellets was modeled as a one-dimensional domain using COMSOL Multiphysics®, simplifying the geometry to reduce the computational cost of the simulations. This approach assumes negligible radial transport within the pellet bed, focusing exclusively on variations along the axial direction. The model incorporates a system of equations comprising time-dependent partial differential equations (PDEs) along the reactor length, coupled with time-dependent ordinary differential equations (ODEs) and algebraic equations to describe the relevant physicochemical processes. The primary governing equations used for the packed bed simulation are the mass conservation (Eq(2)) and the energy conservation (Eq(6)) equations, which account for the transport and transformation of species as well as the

thermal behavior within the reactor. A uniform velocity profile is assumed throughout the reactor bed, with the gas phase velocity set equal to the inlet velocity. This assumption simplifies the fluid dynamics while maintaining sufficient accuracy for the system under consideration. The CO_2 mass balance along the axial direction of the reactor is shown in Eq(2):

$$\frac{\partial(\varepsilon_b \cdot C_{CO_2})}{\partial t} + \frac{\partial}{\partial z}\left(D_{CO_2} \cdot \frac{\partial C_{CO_2}}{\partial z} + u_z \cdot C_{CO_2}\right) = -\varphi_{CO_2} \tag{2}$$

where C_{CO_2} is the CO_2 concentration in the gas phase (mol/m^3), ε_b is the void fraction of the pellets bed, D_{CO_2} is the CO_2 diffusivity in the gas phase (m^2/s) along the axial direction (*z* coordinate), u_z is the superficial gas velocity (m/s), and φ_{CO_2} is the mass exchange term of CO_2 from the bulk gas phase to the solid adsorbed phase per unit of volume. The CO_2 mass flux from the bulk phase to the packed bed of pellets, approximating the pellets to a spherical shape, can be expressed as:

$$\varphi_{CO_2} = \frac{\rho_{bulk}}{MW_{Li_4SiO_4}} \cdot \frac{3(1-\varepsilon_b)}{R_0} \cdot \frac{dr_c}{dt} \tag{3}$$

where ρ_{bulk} is the bulk density of pellets, which considers their macro-porosity (experimentally evaluated as 1152 kg/m^3), $MW_{Li_4SiO_4}$ is the molecular weight of Li_4SiO_4 (119.85 g/mol), R_0 is a pellet equivalent radius (calculated as about 2 mm), and r_c is the unreacted radius of a pellet (mm). The dr_c/dt term of Eq(3) is evaluated assuming a gas-solid reaction between CO_2 and Li_4SiO_4, which follows shrinking core kinetics. The adsorption process is described as a combination of three steps: the CO_2 external diffusion through the gas layer surrounding the particles, the CO_2 diffusion across the products layer, and the CO_2 surface reaction with Li_4SiO_4. However, the resistance to the external mass transfer for the CO_2 adsorption process on doped Li_4SiO_4 has been found negligible (Stefanelli et al., 2020), obtaining Eq(4):

$$\frac{dr_c}{dt} = -\frac{\frac{MW_{Li_4SiO_4}}{\rho_{bulk}} \cdot C_{CO_2}}{\frac{(R_0 - r_c) \cdot r_c}{R_0 \cdot D_{eff}} + \frac{1}{k'}} \tag{4}$$

where D_{eff} is the effective CO_2 diffusion coefficient through the layer of reaction products surrounding the sorbent particles (m^2/s) and k' is the surface reaction rate (m/s). D_{eff} and k' depend on the reaction progress and include corrections to take into account the presence of a molten eutectic phase of Li_2CO_3/K_2CO_3 in the product layer and an initial nucleation stage of the reaction products, respectively, as found by the authors in a previous kinetic study of CO_2 adsorption on doped Li_4SiO_4 (Stefanelli et al., 2025). The final kinetic equation that has been implemented in the numerical model is reported in Eq(5):

$$\frac{dr_c}{dt} = -\frac{\frac{MW_{Li_4SiO_4}}{\rho_{bulk}} \cdot C_{CO_2}}{\frac{(R_0 - r_c) \cdot r_c}{R_0 \cdot D_0} \cdot \left[1 + e^{\alpha\left(1-\left(\frac{r_c}{R_0}\right)^3\right)-\beta}\right] + \frac{1}{k_0 \cdot \left(1 - e^{-\gamma \cdot \sqrt{2(R_0 - r_c)}}\right)}} \tag{5}$$

where D_0 is the CO_2 diffusion coefficient in the initial molten product layer (m^2/s), k_0 is the kinetic constant for the surface reaction (m/s), α, β, and γ are kinetic parameters. The first denominator term represents the diffusion resistance while the second one is the chemical reaction resistance, and both depend on r_c.

The enthalpy balance along the axial direction of the reactor, considering the assumption of local thermal equilibrium, is shown in Eq(6). $(\rho c_p)_{eff}$ and k_{eff} represent the effective heat capacity and the effective thermal conductivity considering both the gas (CO_2/N_2 mixture) and the solid matrix (Li_4SiO_4/K_2CO_3 mixture), and are defined in Eq(7) and Eq(8), respectively:

$$(\rho c_p)_{eff} \frac{\partial T}{\partial t} + \rho_g c_{p,g} u_z \cdot \nabla T - \nabla(k_{eff} \cdot \nabla T) = (-\Delta H_r) \cdot \varphi_{CO_2} \tag{6}$$

$$(\rho c_p)_{eff} = \varepsilon_b \rho_g c_{p,g} + (1-\varepsilon_b)\rho_s c_{p,s} \tag{7}$$

$$k_{eff} = \varepsilon_b k_g + (1-\varepsilon_b) k_s \tag{8}$$

where ρ is the density (kg/m^3), c_p is the specific heat (J/(kgK)), k is the thermal conductivity (W/(mK)), and $(-\Delta H_r)$ is the enthalpy of the adsorption reaction (kJ/mol). *g* and *s* subscriptions refer to the gas phase and the solid matrix, respectively. k_s and $c_{p,s}$ have been estimated as the weighted average on mass fractions of Li_4SiO_4

and K_2CO_3. Li_4SiO_4 thermal conductivity and heat capacity have been obtained from Löbbecke et al. (2009) and Kleykamp (1996), respectively. K_2CO_3 thermal conductivity and heat capacity have been estimated by Navarrete et al. (2022). The same procedure has been applied for the estimation of k_g.

3.1 Boundary conditions

The initial conditions refer to $t = 0$. For the gas phase, the initial concentration is set to zero throughout the reactor length (Eq(9)), while the initial reactor temperature is set as the adsorption temperature, T_r (Eq(10)).

$$C_{CO_2}\big|_{t=0} = C^0_{CO_2} = 0 \tag{9}$$

$$T|_{t=0} = T_w|_{t=0} = T_r \tag{10}$$

The boundary conditions are set for $z = 0$ and $z = L$. At the reactor inlet, the Danckwerts boundary condition type is supposed to be valid for the mass conservation, while for the enthalpy balance the temperature is specified as the adsorption temperature (Dirichlet boundary condition):

$$\boldsymbol{n} \cdot \left(D_{CO_2} \boldsymbol{\nabla} C_{CO_2} + \boldsymbol{u} \cdot C_{CO_2}\right) = \boldsymbol{n} \cdot (\boldsymbol{u} \cdot C^{in}_{CO_2}) \text{ for } z = 0 \tag{11}$$

$$T|_{z=0} = T_r \text{ for } z = 0 \tag{12}$$

At the exit of the reactor, the Neuman boundary condition has been applied to ensure no concentration gradients normal to the boundary and, therefore, no backflow effect (the CO_2 is assumed to leave the reactor entirely with the convective flow):

$$\boldsymbol{n} \cdot D_{CO_2} \boldsymbol{\nabla} C_{CO_2} = 0 \text{ for } z = L \tag{13}$$

For the enthalpy balance, the Neuman boundary conditions are assumed at the exit of the reactor, considering no net heat transfer across the outlet of the reactor:

$$-\boldsymbol{n} \cdot \boldsymbol{q} = 0 \text{ for } z = L \tag{14}$$

where $\boldsymbol{q}$ is the heat flux in (W/m^2).

4. Results and discussion

4.1 Parameters estimation

For the simulation of the CO_2 adsorption process in the fixed bed reactor, the kinetic parameters defined in section 3 must be determined. These parameters depend on both CO_2 concentration and temperature; thus, they vary spatially along the bed and over time. Given the small reactor size, the packed bed of pellets has been assumed to be isothermal (a hypothesis later confirmed through a posteriori analysis). However, the parameters' dependence on CO_2 concentration results complex: as the CO_2 is adsorbed from the gas phase into the pellets, the concentration along the bed length decreases, leading to non-linear changes in the kinetic parameters. The values of the diffusion coefficient and reaction-related parameters were estimated by performing a polynomial fitting of the kinetic data obtained by a previous study (Stefanelli et al., 2025) testing the pellets to CO_2 adsorption in a gas flow-controlled environment (i.e., thermogravimetric analysis) at different CO_2 concentrations (0.5-4 vol%) and temperatures (495-615 °C). The obtained equations were implemented in the COMSOL Multiphysics® simulation.

4.2 Adsorption simulation and model validation

The CO_2 adsorption experiment in the fixed bed reactor at 4 vol% CO_2 and 515 °C (L= 2.5 cm, G_{in}=260 mL/min) and the model simulation results are reported in Figure 2a in terms of CO_2 outlet concentration versus time of adsorption. As shown, by comparing simulation results with experimental data, the model demonstrates excellent agreement with the experimental breakthrough curve, particularly for the first 140 min of adsorption. Whereas, after this point, the model exhibits a lower accuracy in the prediction of the experimental data. Figure 2b depicts the temperature profile along the reactor length at various times predicted by the model. As displayed, the temperature of the pellet bed after 50 min of adsorption is increased of about 1.5 °C in the first 5 mm due to the exothermic behavior of the adsorption reaction. With increasing the time of adsorption, the temperature increases along the bed height due to the occurrence of the adsorption throughout the bed. The maximum temperature increase observed is approximately 7 °C after 300 min of adsorption, when the pellet bed is saturated, providing strong support for the isothermal assumption used for the kinetic parameter's estimation.
The chemical and diffusion resistances have been evaluated as a function of time at two positions within the reactor: z=0 (inlet) and z=L (outlet), and the results are reported in Figure 3. At the reactor inlet, the chemical

resistance exceeds the diffusional resistance only during the first 10 minutes of adsorption (Figure 3a). In contrast, at the outlet, the chemical resistance remains dominant for nearly 140 minutes (Figure 3b). This highlights the critical importance of accurately modeling the chemical term to capture the system's behavior. Furthermore, comparing Figure 2a and Figure 3 shows that the breakthrough time corresponds to the time for which the chemical and diffusion resistances become comparable in magnitude at the reactor outlet. Therefore, in the first 140 min, the adsorption process is controlled by the chemical reaction (chemical regime), while after this point the diffusion resistance takes control (diffusion regime). This relationship underscores the interaction between these resistances in determining the breakthrough dynamics of the reacting bed.

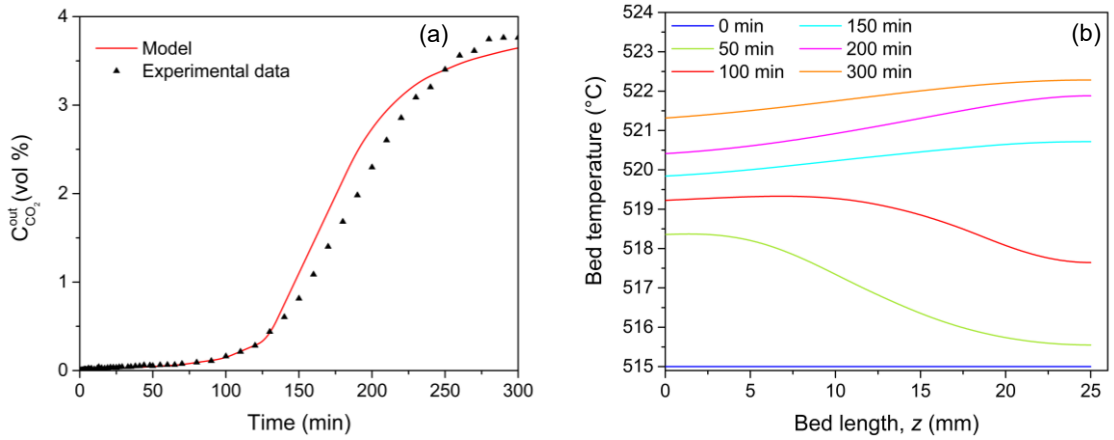

Figure 2: CO_2 adsorption by K_2CO_3-doped Li_4SiO_4 pellets in the fixed bed reactor: (a) breakthrough curve and (b) temperature profiles along the packed bed at different adsorption times

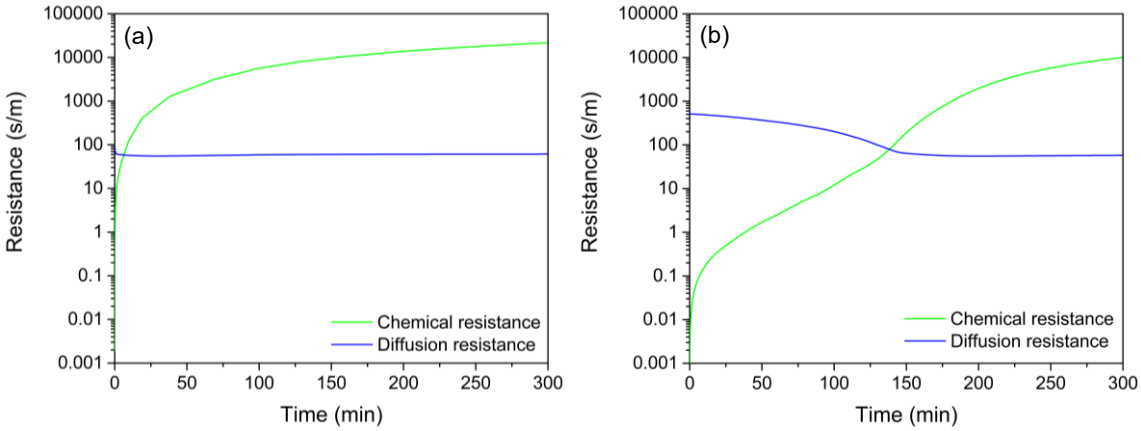

Figure 3: Chemical and diffusion resistance profiles as a function of adsorption time for (a) z=0 and (b) z=L

4.3 Sensitivity analysis

Once the proposed model had been validated, its physical behavior was investigated under different adsorption conditions, varying the gas flow rate (i.e., the surface velocity in the packed bed) and the bed length. The results of this analysis are reported in Figure 4. As shown, by increasing the gas flow rate, and thus the gas surface velocity, the breakthrough time decreases (Figure 4a), suggesting a faster saturation of the sorbent bed. This performance is expected since increasing the gas flow rate in the adsorption bed reduces residence time, thus decreasing CO_2 adsorption efficiency and causing earlier breakthroughs due to mass transfer limitations. Conversely, increasing the bed height provides more adsorbent material available for CO_2 adsorption reaction, enhancing the overall adsorption capacity and delaying the breakthrough occurrence, thus improving the CO_2 removal efficiency. As shown in Figure 4b, the model is able to predict this behavior since the breakthrough time increases for greater bed height. It is important to highlight that this model framework is a first step towards a more complete simulation of a fixed bed reactor composed of doped Li_4SiO_4 pellets. Future works may concern a 2D model framework and the implementation of the momentum balance equation to better fit the pellet bed behavior, especially in the diffusion stage. Furthermore, additional study is needed to obtain the kinetic parameters more easily, potentially directly from the breakthrough curves.

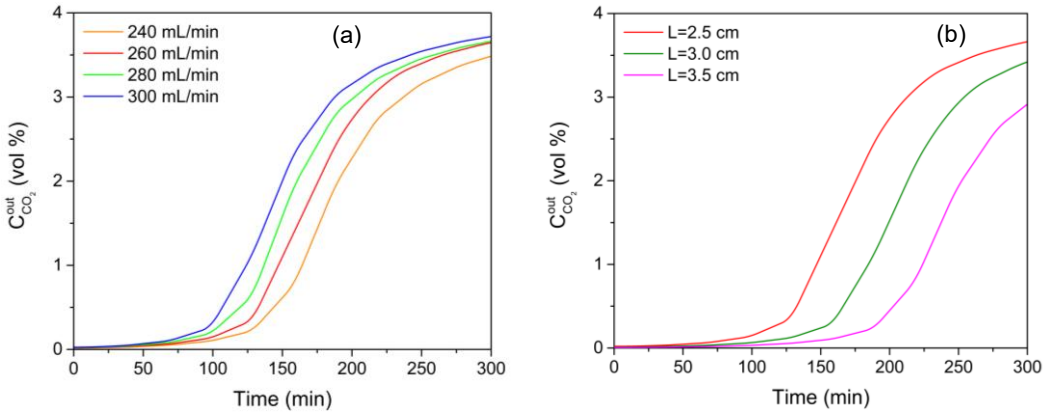

Figure 4: CO_2 adsorption breakthrough curves: (a) effect of different gas flow rates and (b) effect of different bed heights

5. Conclusions

In this study, the CO_2 adsorption process at high temperature and low CO_2 concentration (4 vol%) in a fixed bed reactor composed of a packed bed of K_2CO_3-doped Li_4SiO_4 pellets was experimentally investigated and numerically simulated using COMSOL Multiphysics®. A one-dimensional mathematical model was successfully developed, which implements shrinking core reaction kinetics suitably modified to consider the presence of a K_2CO_3/Li_2CO_3 molten mixture and a reaction product nucleation phase. The model exhibited good agreement with the experimental breakthrough curves, representing a good trade-off between computational cost and accuracy. Moreover, the model allowed a detailed analysis of the relationship between chemical and diffusion resistances and their influence on the breakthrough behavior of the pellets bed. It was observed that the breakthrough occurred when the controlling resistance shifted from chemical to diffusion, highlighting the dynamic interaction between them during the adsorption process.

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References

Chao C., Deng Y., Dewil R., Baeyens J., Fan X., 2021, Post-combustion carbon capture, Renewable and Sustainable Energy Reviews, 138, 110490.

Chu H., Huang Z., Zhang Z., Yan X., Qiu B., Xu N., 2024, Integration of carbon emission reduction policies and technologies: Research progress on carbon capture, utilization and storage technologies, Separation and Purification Technology, 343, 127153.

Hu Y., Liu W., Yang Y., Qu M., Li H., 2019, CO_2 capture by Li_4SiO_4 sorbents and their applications: Current developments and new trends, Chemical Engineering Journal, 359, 604–625.

Kleykamp H., 1996, Enthalpy, heat capacity, second-order transitions and enthalpy of fusion of Li_4SiO_4 by high-temperature calorimetry, Thermochimica Acta, 287, 191–201.

Löbbecke B., Knitter R., Rohde M., Reimann J., 2009, Thermal conductivity of sintered lithium orthosilicate compacts, Journal of Nuclear Materials, 386–388, 1068–1070.

Navarrete N., Nithiyanantham U., Hernández L., Mondragón R., 2022, K_2CO_3–Li_2CO_3 molten carbonate mixtures and their nanofluids for thermal energy storage: An overview of the literature, Solar Energy Materials and Solar Cells, 236, 111525.

Nedoma M., Netušil M., 2021, CO_2 Separation from Flue Gases by Adsorption, Chemical Engineering Transactions, 88, 421–426.

Stefanelli E., Francalanci F., Vitolo S., Puccini M., 2025, Insights into adsorption mechanism and kinetic modeling of K_2CO_3-doped Li_4SiO_4 pellets for CO_2 capture at high temperature and low concentration, Fuel, 380, 133161.

Stefanelli E., Puccini M., Vitolo S., Seggiani M., 2020, CO_2 sorption kinetic study and modeling on doped-Li_4SiO_4 under different temperatures and CO_2 partial pressures, Chemical Engineering Journal, 379, 122307.

Yang Y., Dai P., Chen Z., Sun X., Ren X., 2023, Kinetic and thermodynamic investigations on the cyclic CO_2 adsorption-desorption processes of lithium orthosilicate, Chemical Engineering Journal, 468, 143679.

Zedda F., Casu M., Atzori F., Orrù R., Cao G., Concas A., 2024, Comprehensive Mechanistic Modelling of Non-isothermal CO_2 Adsorption in Fixed Packed Bed, Chemical Engineering Transactions, 111, 553–558.