

CO₂ capture using lithium-based sorbents prepared with construction and demolition wastes as raw materials

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Abstract

CO₂ capture was tested using lithium silicates prepared with construction and demolition waste materials (CDWM) to climate change mitigation. Four types of CDWM with high silicon and aluminum content were evaluated: sand, block, ceramic sanitary ware (CSW), and concrete wastes. CDWM were characterized by XRF, XRD and SEM-EDS; subsequently, the non-conventional precursors were mixed with LiOH and thermally treated in two stages: at 250 and 550 °C. Li₄SiO₄ was synthesized using conventional SiO₂, applying the same synthesis method, and used as a reference. Li₄SiO₄, Li₂SiO₃ and LiAlO₂ crystalline phases were obtained from all CDWM. Additionally, Li₂CaSiO₄ was detected in the case of wastes with high calcium content (block and concrete). The prepared Li₄SiO₄ samples were

evaluated using the TGA technique for CO₂ capture in dynamic and isothermal modes. The bulk CO₂ adsorption in the Li₄SiO₄ prepared with CDWM started at a lower temperature (380 °C) than the material prepared with conventional precursors (500 °C). The temperature of CO₂ sorption maxima was estimated at around 600 °C, being the Li₄SiO₄ prepared with block waste the material with the best performance. According to the isothermal analysis, the block-derived lithium silicate achieved a maximum CO₂ capture capacity of 183 mg/g at 580 °C with P_{CO₂}=0.2; the desorption was observed above this temperature. The kinetic results (Avrami Eroffev model) were similar to those of Li₄SiO₄ prepared with conventional SiO₂. Moreover, the stability of the materials was demonstrated during 20 cycles of the sorption-desorption process, displaying a constant sorption capacity of 180 CO₂ mg/g.

Keywords: waste valorization; lithium silicate; greenhouse gases; alkaline fusion treatment.

Introduction

The problems generated by increased greenhouse gas (GHG) emissions have produced severe affectations worldwide. Extreme climate episodes occur daily, occasioning loss of biodiversity, economic affectations, and social impacts, among others [1]. In the future, migrations of people toward hemispherical zones are expected due to warm equatorial zones [2]. Governments and United Nations have implemented several actions to mitigate global warming, such as the Sustainable Development Goals (SDG), to decrease greenhouse emissions. Moreover, the Paris Agreement, adopted in 2015, aims to strengthen the global response to the threat of climate change by keeping a global temperature rise below two

degrees Celsius above the pre-industrial levels this century. According to the SDG, the reduction of CO₂ emissions (main GHG) is considered one of the most important challenges to overcome. The technologies to replace fossil fuels used to obtain energy and other services are not yet ready due to high economic, social, technical, and political aspects, mainly in underdeveloped and emerging countries. i.e., electric cars are now a reality; however, some countries still use traditional fuels for transportation. The industry also causes serious problems because natural gas, the main source of energy used to reduce CO₂, is not fully implemented. In this concern, there has been an increase in the research and implementation of CO₂ capture technology with promising results; in fact today direct CO₂ capture is a reality [3,4].

The CO₂ capture is carried out by the gas sweetening process using liquid solutions of amines [5]. However, the main disadvantages of the CO₂ chemical absorption using alkanolamines are equipment corrosion, degradation by acid gases in the flue gas, which requires previous removal of NO_x and SO₂ from the flue gas stream and the energy penalty, as the gas must be cooled to 40 °C before coming into contact with the liquid [6]. Alternatively, CO₂ sorption with solid materials has gained significant attention due to its versatility compared to the sweetening process [6,7]. There are many solid sorbents useful under different operating conditions. Among the critical properties desired are sorption/desorption kinetics, simple regeneration, wide operating temperature range, stability toward other gases, high sorption capacity, and long functional life [8–10].

Among the sorbent materials for high-temperature CO₂ capture, alkaline silicates have shown important achievements. Specifically, lithium orthosilicate (Li₄SiO₄) has a high CO₂ sorption capacity, adsorbing approximately 36 wt% of CO₂ forming lithium carbonate at temperatures

between 550-680 °C [11–16]. The capture of CO₂ from lithium silicate involves the regeneration of lithium orthosilicate by decomposing lithium carbonate (Li₂CO₃) at approximately 700 °C. CO₂ capture at elevated temperatures requires extra energy to regenerate the material; however, combustion gases in a typical fuel oxidation process can reach temperatures higher than 1000 °C [17], making this process affordable.

The Li₄SiO₄ is synthesized mainly by solid-state reaction, however, other preparation methods are modified combustion, hydrothermal and sol-gel methods; nevertheless, they all involve the calcination step. Pfeiffer et al. (1998) reported three routes to prepare lithium silicate: solid-state reaction, precipitation and sol-gel [18]. By the solid-state reaction using amorphous silica and LiCO₃; by precipitation utilizing amorphous silica with LiOH; and by sol-gel, dissolving in isopropyl alcohol tetraethyl orthosilicate and lithium methoxide, or LiOH, all of them followed by calcination at 900 °C. The calcination step is crucial in the preparation of lithium silicate because the heating rate and time can affect the final performance of the product. Li:Si ratio and the silicon precursor are other factors to consider in the preparation of lithium silicate. Varying the Li source, ortho- or meta-silicate can be formed while modifying the source of silicon, quartz, or other isomorphous SiO₂ compounds can be obtained [19]. In addition, in all the studies, a single grinding step and thermal treatment have been implemented to optimize the homogenization of precursors. Lately, the utilization of a cheap lithium source for the preparation of Li₄SiO₄ was investigated by Tong et al. [16] They proposed a route to synthesize low-cost Li₄SiO₄ as CO₂ sorbents from spent lithium-ion batteries, obtaining a material with a stable CO₂ capacity of 0.19 g/g (15 vol%) for 80 cycles.

Silicon precursors have drawn special attention because waste or natural materials, as non-conventional precursors, can be used to prepare lithium-based sorbents, including Li_4SiO_4 [20]. The use of wastes and by-products has important advantages, e.g., availability, abundance, the possibility of reuse, reactivity and low costs. Among them, rice husk ashes [21], fly ashes [22], synthetic spent zeolites [23], agricultural and forestry waste [24] and steel metallurgical slags [25–27] stand out for preparing lithium silicates. Moreover, several natural materials such as diatomite [28], sepiolite [29], vermiculite [30] and lake sediments [31] have also been used to prepare lithium silicates. The synthesis of Li_4SiO_4 using wastes such as walnut shell ashes has also been reported; the silicate was obtained in several stages involving calcination at $750\text{ }^\circ\text{C}$ for 3h. The product was mixed with nitric acid and lithium nitrate and subjected to thermal treatment ($650\text{ }^\circ\text{C}/3\text{h}$) to obtain a mixture of lithium silicates [32]. In another report, fly ashes were treated with Li_2CO_3 at $950\text{ }^\circ\text{C}/8\text{h}$, resulting in a mixture of lithium silico-aluminates [33]. Recently, lithium silicates were obtained using iron and steel slags, steel slags were mixed with Li_2CO_3 and treated at $850\text{ }^\circ\text{C}$ for 8 hours [26]. In other work, glass wastes mixed with LiOH were used to obtain lithium metasilicate from hydrothermal treatment at $100\text{ }^\circ\text{C}$ for five days obtaining 67 wt% of Li_2SiO_3 [34]. Recently, the formation of a lithium silicate using four types of CDWM was reported. The synthesis was carried up in two steps: the grinding of the waste and the alkaline fusion treatment at $550\text{ }^\circ\text{C}$ for two hours [35]. However, lithium silicates prepared from CDWM as unconventional sources of silicon have not been tested as CO_2 sorbent materials for high temperatures.

According to Wu et al. (2021), ten billion tons/year of CDWM are generated worldwide. CDWM comprises asphalt, bricks, concrete, rubble, plasterboard cement sheeting, steel, aluminum, non-ferrous materials, garden organics timber, paper, cardboard, plastics, glass,

textiles, and other unclassified materials [36]. They are used in several applications, such as aggregate to prepare concrete, construction of roads and highways, preparation of geopolymers, binders, and even in the synthesis of porous materials [35]. Some CDWM have been used for CO₂ uptake in aqueous solutions, mainly cement and concrete waste [37–39]. Therefore, in this study, lithium-based sorbents were prepared using different CDWM (ceramic sanitary waste, sand, concrete and block) by alkaline fusion treatment at 550 °C, characterized and tested in the CO₂ capture process.

Materials and methods

Sand, concrete, CSW, and building block waste were obtained from Querétaro, México, ground in a ball mill for one hour, and sieved through a 60 mesh. CSW composition was analyzed by X-ray fluorescence using a Rigaku Primus II spectrometer. The major elements were determined in pellets prepared with a 10% sample and 90% Li₂B₄O₇ and the loss of ignition (LOI) by heating 1 g of the sample (dry basis) at 950 °C for one hour. XRD technique was carried out in a diffractometer Bruker AXS Model D8 Advance. The Bragg Brentano configurations were executed with a step size of 0.02 in a range of 5-60 2θ. After characterization, the alkaline fusion treatment was used to prepare lithium silicates using CDWM as a silica source and LiOH. Waste was mixed with LiOH (Sigma-Aldrich, >98% of purity) in a mass ratio of 1:1.5 and calcined at 250 °C for two hours. Further, the product was subjected to a mechanical milling process for one hour and calcined again at 550 °C for two more hours. In the last stage, the formation of Li₄SiO₄ was preferentially promoted. To compare the effect of the silicon source, Li₄SiO₄ was also prepared using pure SiO₂ (Sigma-

Aldrich, 99.9% of purity) and LiOH reagents under the above described conditions. All obtained materials were homogenized in an agate mortar, and the mineralogical phases were identified by XRD. XRD quantitative phase analysis was carried out by Rietveld using Topas software. Crystallographic information was obtained from Crystallography Open Database (<http://www.crystallography.net/cod/search.html>). Refinement was executed following the typical routine, starting with unit cell parameters, background and instrumental information; the preferred orientation was also considered. A Jeol JSM-6510 LV device with a Bruker XFlash 6I10 EDX detector was used to determine the morphology and the elemental composition. The microstructural characterization was complemented with the N₂ adsorption-desorption analysis using a Bel-Japan Minisorp II instrument at 77 K by the multipoint technique (N₂ from Praxair, grade 4.8); the specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method. Before the analysis, the samples were pretreated overnight by heating at 120°C in a N₂ flow (40 mL/min).

The CO₂ sorption behavior of the resultant lithium silicates was evaluated by thermogravimetric and temperature-programmed techniques. Before the CO₂ sorption tests, the samples were pretreated in N₂ flow (60 mL/min) at 800 °C to eliminate any previous carbonation. Then, temperature-programmed experiments were carried out in a Belcat B (Bel Japan) equipped with a thermal conductivity detector (TCD), which records the changes in CO₂ concentration in the outlet gas stream. In these experiments, 50 mg of sorbents were kept in contact with a 5 % mol CO₂ gas stream (He balance, Praxair, certificated standard) and heated up to 900 °C using a temperature ramp of 5 °C min⁻¹. Moreover, thermogravimetric experiments were performed on a Labsys Evo TG analyzer from Setaram, using 20 mg of sample. The dynamic performance of CO₂ sorption was obtained by heating

the samples from room temperature to 850 °C at 10 °C min⁻¹ using a partial pressure of CO₂ (P_{CO_2}) of 0.2 (balanced with N₂). After, the CO₂ sorption over time was measured between 500 and 600 °C. In each test, the temperature was increased in the N₂ flow (60 mL min⁻¹); afterwards, and then the flow was switched to the desired P_{CO_2} (0.2-0.05) for 180 min.

The stability of the block-derived lithium silicates was studied through consecutive sorption-desorption cycles. The sorption step was carried out using the best sorption conditions, while the desorption temperature (T_d) was studied between 580 and 650 °C to determine the proper T_d of the material. For each sorption-desorption cycle, 20 mg of the sample was subjected to 60 min of CO₂ sorption followed by a desorption step in N₂ flow for 30-40 min. Once the best T_d was determined, 20 cycles were performed, and the CO₂ sorption-desorption employed material was analyzed by XRD.

Results and discussion

CDWM characterization

The chemical composition of CDWM obtained by XRF is shown in Table 1. It should be noted that no previous treatment was carried out to eliminate impurities. SiO₂ is the main component in the CDWM, followed by Al₂O₃ and CaO. CaO is more abundant than Al₂O₃ in the block and concrete due to its cement Portland content. In CSW, the CaO content is very low, and Al₂O₃ is more abundant since kaolin is used to manufacture these ceramic materials [40]. Na₂O and K₂O are present at low percentages (1-5 wt%), Fe₂O₃ and Mg₂O are between 0.3 and 2wt%, and S and Ti are lower than 0.5 wt%.

Table 1. Chemical composition of CDWM by X-ray fluorescence (wt%).

	Sand	Block	CSW	Concrete
SiO₂	70.77	58.38	66.84	49.12
Al₂O₃	11.96	9.32	20.66	9.51
TiO₂	0.28	0.29	0.96	0.47
Na₂O	2.74	1.92	2.96	1.83
K₂O	5.22	4.25	2.94	2.46
MgO	0.46	0.62	0.30	1.34
CaO	1.50	10.44	2.30	16.92
MnO	0.03	0.04	0.02	0.06
Fe₂O₃	2.40	3.22	2.22	3.95
P₂O₅	0.04	0.04	0.02	0.10
LOI	4.58	11.46	0.94	14.21

LOI: loss on ignition

According to the XRD results depicted in Fig. 1, several types of silicates were identified in all wastes. Furthermore, a broad signal between 20° and 40° indicates the amorphous nature of compounds, possibly of disordered silicates [41]. The XRD patterns of CSW and concrete show a low signal of amorphous material presence because both materials are thermally treated at high temperatures (>1000 °C). In CSW and concrete, crystalline compounds with high stability were identified. Mullite (Al₆Si₂O₃, PDF-15-0776) and quartz (PDF-46-1045) were identified in the CSW. Mullite is a neosilicate commonly found in ceramic materials. Other silicates were also identified, such as nepheline (NaAlSiO₄, PDF-35-0424), a sodium aluminate tectosilicate, sanidine (K,Na)(Si,Al)₄O₈ (PDF-19-1227) a potassium tectosilicate that belongs to the group of feldspars as well as to albite (NaAlSi₃O₈, PDF-10-0393). Calcium minerals come from the cement or mortar used to manufacture the blocks. Calcite was also identified in the XRD pattern of concrete (Fig. 1d). This waste has the highest Ca content of all studied wastes. Ca is part of a mineral formed by calcium carbonate (CaCO₃)

that is widely used to manufacture mortars and cement. Albite and anorthite (PDF-41-1486) were also found, which can be derived from the sand content in the concrete waste.

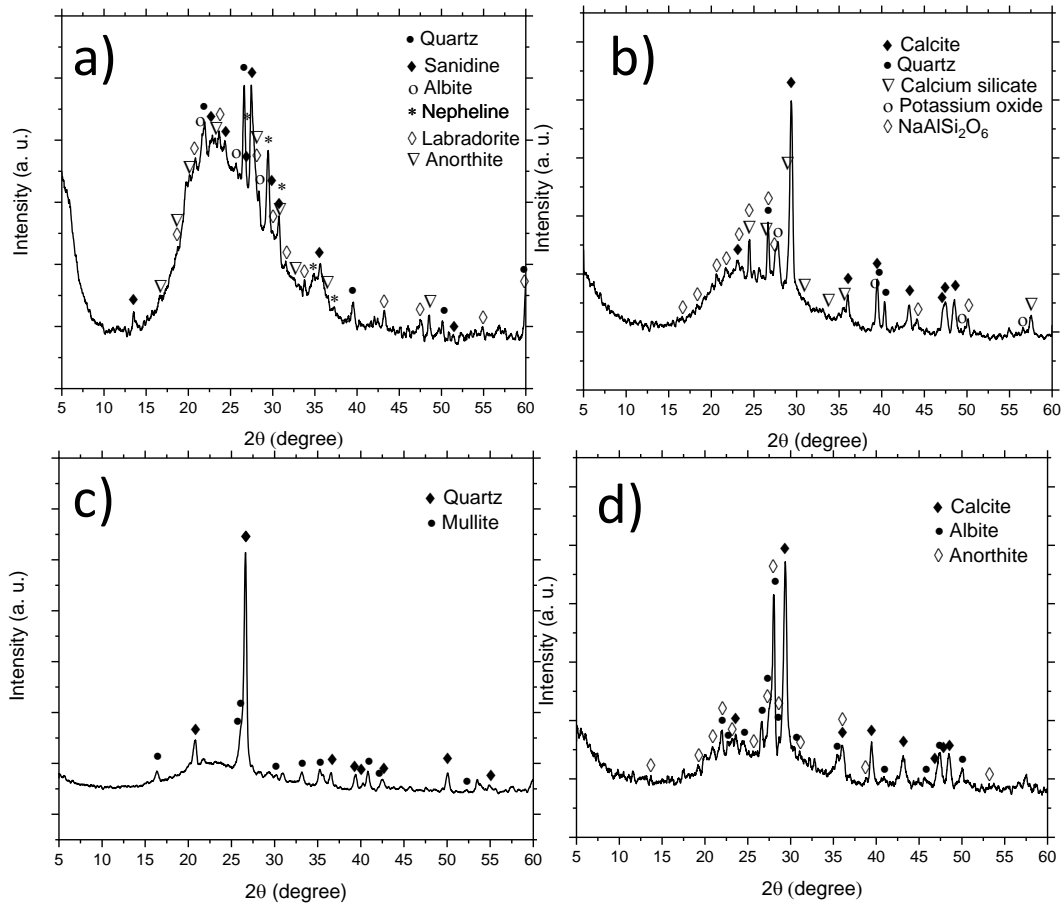


Fig. 1. XRD patterns of CDWM: a) sand, b) building block, c) CSW and d) concrete.

Li₄SiO₄ characterization

The materials obtained with different CDWM were analyzed by XRD, and the results are shown in Fig. 2.

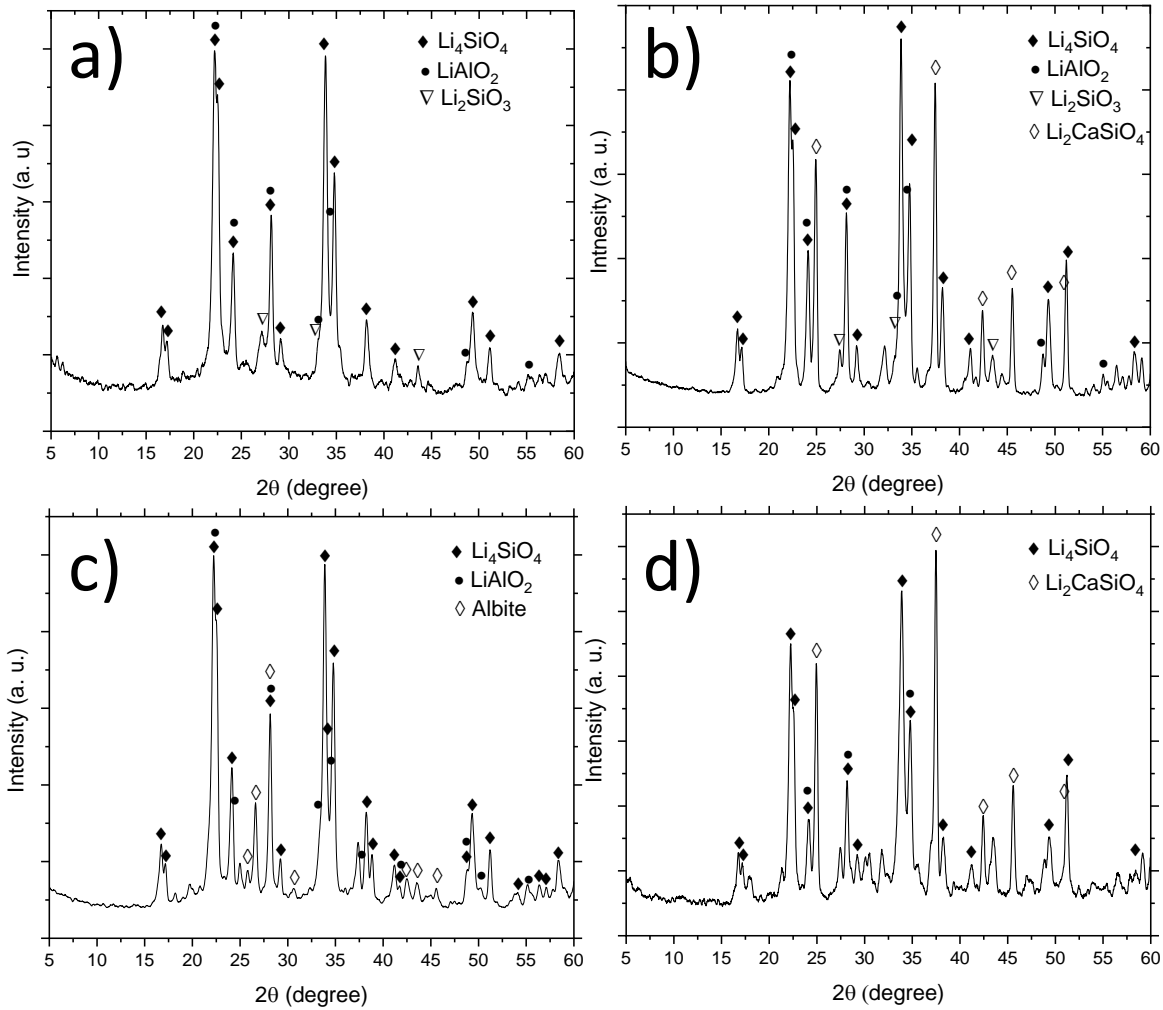


Fig. 2. XRD patterns of the lithium silicates prepared with CDWM: a) sand, b) building block, c) CSW and d) concrete.

The formation of lithium orthosilicate (Li_4SiO_4) was observed in all materials obtained from alkaline fusion treatment. Besides, Li_2SiO_3 was also identified except in concrete-derived material. LiAlO_2 was formed in the silicates prepared from CDWM with aluminum content (sand, block and CSW, the last one in less amount). $\text{Li}_2\text{CaSiO}_4$ phase was observed in sand-, block- and concrete-derived silicates because of the medium-high CaO content in these

wastes (1.50, 10.44-16.92 wt%). According to Chen et al. (2016), the presence of $\text{Li}_2\text{CaSiO}_4$ helps in the transfer of CO_2 in the Li_4SiO_4 particles favoring a fast CO_2 sorption. [42] Semi quantitative analysis of crystalline phases was achieved by applying the Rietveld method, and the results are shown in Table S1 and Fig. S1 (refinement diffractograms of XRD). Li_4SiO_4 phase predominates in the composition of the prepared materials, indicating the high reactivity of LiOH with each CDWM; moreover, Li_2SiO_3 was identified and quantified. Then, lithium silicates, as well as the lithium aluminate, were formed under the following reactions:



Gibbs free energy (ΔG) of the reactions was estimated to explain the formation of lithium silicates with the wastes. Calculated ΔG would give an approximation of the reactivity of original silicates (quartz, sanidine, nepheline, albite, anorthite, calcite and mullite): more negative ΔG indicates that the reaction can occur spontaneously. Then, reaction 1 is thermodynamically more favorable in comparison with reaction 2 and 3 according to Gibbs free energy calculated. However, the mineralogical composition can affect the formation due to different activation temperatures of the pristine silicates. Furthermore, lithium silicate formation is assumed to occur from the outside of the particle; that is, the Li ions diffuse into the SiO_2 particles [43]. Then, the original distribution of silicates in the CDWM is also important for understanding the formation of lithium silicates and the other identified phases. The heterogeneous composition of CDWM could affect the amount and velocity of lithium

silicate formation. Fig. 3 shows the crystalline phases quantified by Rietveld method compared to Si, Al, and Ca content in the CDWM estimated by XRF.

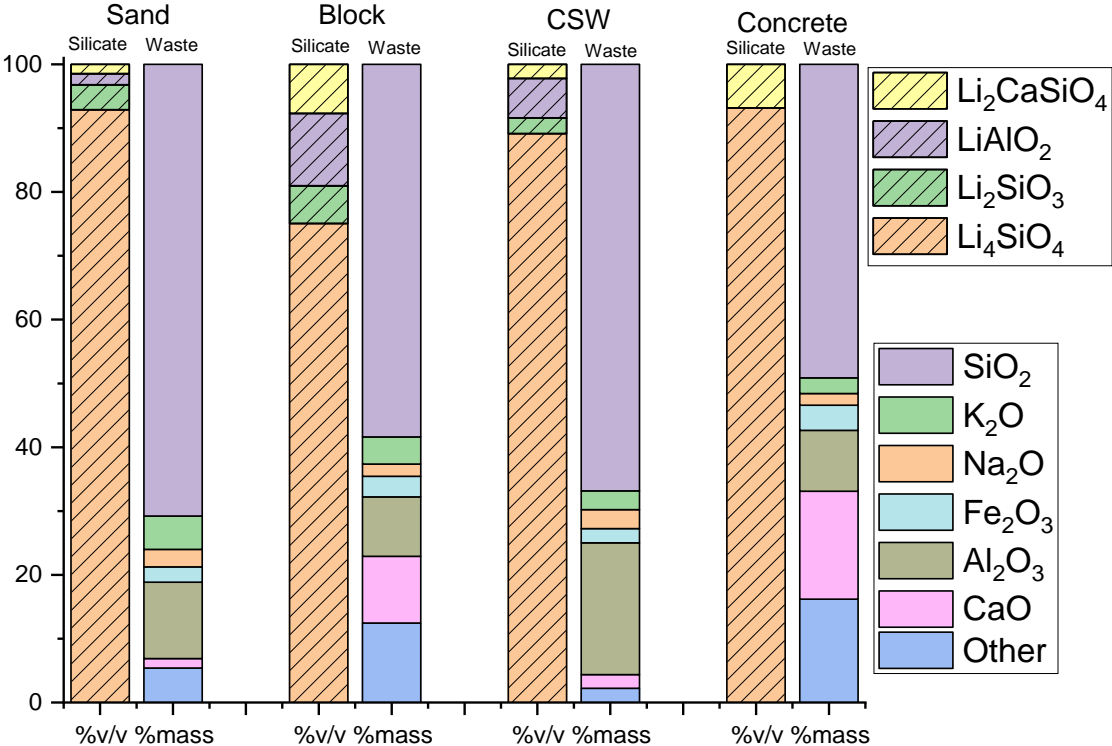


Fig. 3. Comparison between phases quantified by Rietveld method in lithium silicates and the composition of the CDWM determined by XRF.

Li_4SiO_4 formation was preferred over the other crystalline phases, while Li_2SiO_3 was less than 5%, except in the concrete-derived silicate where it was not identified. Almost 90% of Li_4SiO_4 was obtained in the silicates prepared from sand, CSW, and concrete, in which the Si content was 40-70%. While 60% of Si content in the block waste led to the formation of 75% of Li_4SiO_4 . LiAlO_2 and $\text{Li}_2\text{CaSiO}_4$ were observed in a low proportion (<10%) due to the presence of Al and Ca in the wastes. With the relatively high content of Ca, the formation

of $\text{Li}_2\text{CaSiO}_4$ was promoted, while, in the case of Al content, there is no correlation with the percentage of Al crystalline phases.

The conventional silicon source was used to prepare Li_4SiO_4 under the same synthesis conditions as a comparison. Fig. 4 shows the XRD results of Li_4SiO_4 prepared with SiO_2 and LiOH pure reagents. The Li_4SiO_4 formation was confirmed, and it is important to highlight that many works report solid-state synthesis at temperatures close to $800\text{ }^\circ\text{C}$ [18,26,44,45], while in this work, the alkali fusion treatment allowed obtaining this phase at $550\text{ }^\circ\text{C}$. Therefore, the effectiveness of alkali fusion treatment to prepare Li_4SiO_4 using conventional and unconventional silica sources was demonstrated.

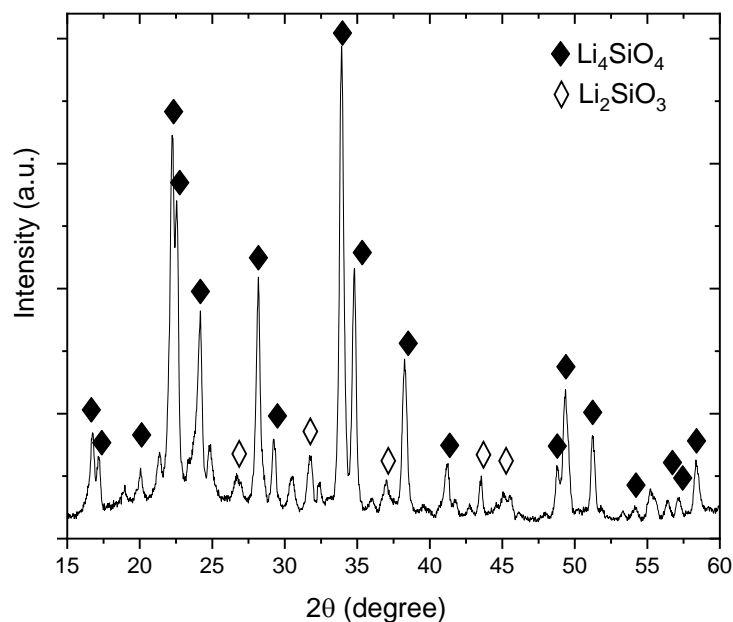


Fig. 4. XRD pattern of Li_4SiO_4 prepared with conventional reagents.

Izquierdo et al. (2018) prepared Li_4SiO_4 with fly ash (FA) and conventional SiO_2 with Li_2CO_3 and LiOH by solid-state and precipitation methods, respectively. They reported the low formation of Li_4SiO_4 with the FA and LiOH at $600\text{ }^\circ\text{C}$ due to the relatively high proportion of CaO that hindered the main reaction [46]. Herein, the preparation of a high proportion of Li_4SiO_4 from the $550\text{ }^\circ\text{C}$ alkaline fusion method using silica waste materials was demonstrated. However, it is important to point out that the thermal treatment was implemented in two stages: the first at $250\text{ }^\circ\text{C}$ for 2 hours following a milling step and the second at $550\text{ }^\circ\text{C}$ for 2 hours. Thus, this process allowed to maximize the formation of Li_4SiO_4 and lowered the preparation temperature, so this method could be potentially used with other silicon-rich waste materials.

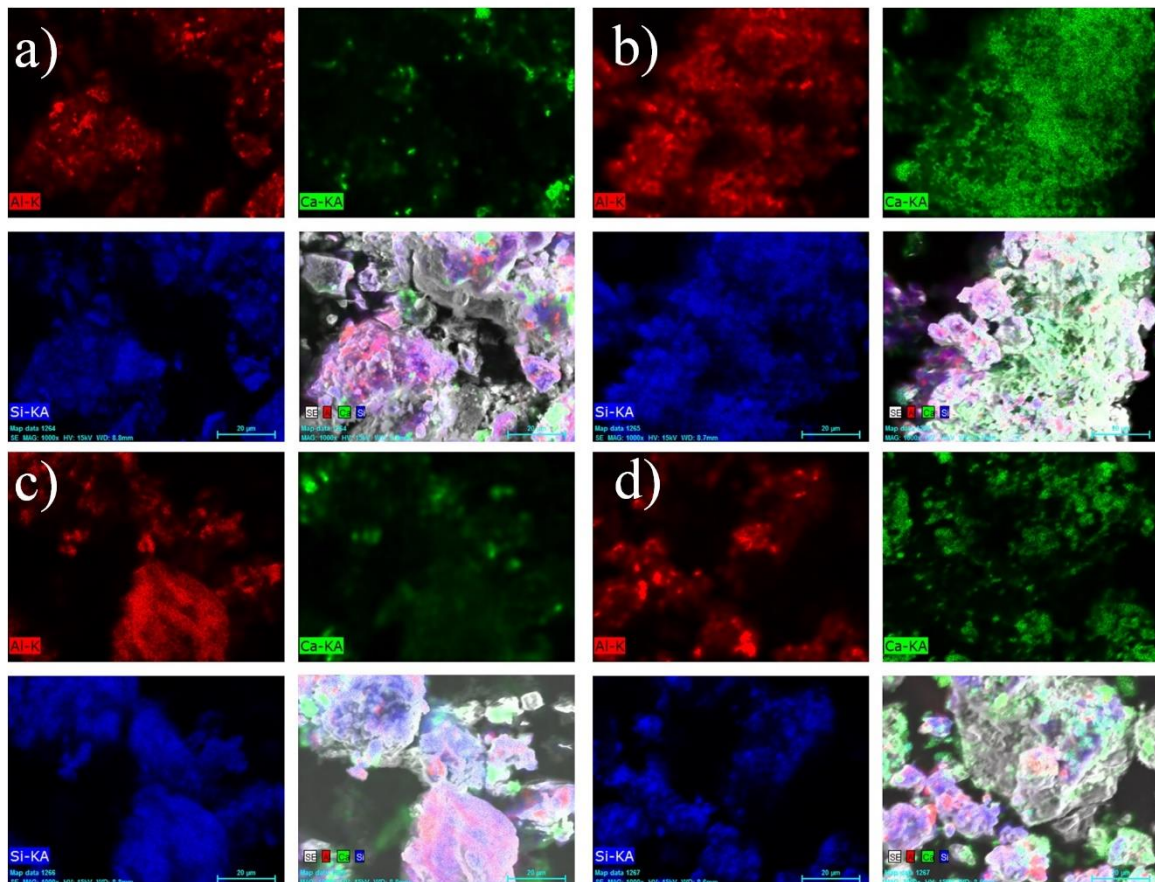


Fig. 5. Distribution of Si, Al, and Ca in the lithium silicates samples prepared with a) sand, b) block, c) SWD and d) concrete.

Additionally, Fig. 5 shows the Si, Al, and Ca distribution in the lithium silicates prepared with wastes. Si (blue) distribution in all samples is relatively homogeneous, while Al (red) appears heterogeneously in the sand and concrete as compared to the block and CSW materials. The homogeneous distribution of Si appears in the following order: block>CSW>sand>concrete. This distribution of Si is related to the lithium silicates formed. Ca (green) is the third element with low concentration and distribution. The silicates derived from block and concrete have a homogeneous distribution and a high proportion of Ca due to the cement-derived calcium silicates present in the waste. To complete the characterization, N₂ adsorption-desorption isotherm of lithium silicate prepared from block waste is depicted in Fig. S2. The isotherm corresponds to the type II form of non-porous solids, although the hysteresis in the desorption is observed, possibly due to mesoporous formed interparticle (interparticle condensation). According to the BET model, the surface area is about 1.23 m²/g.

CO₂ capture study

The CO₂ capture study starts with temperature-programmed experiments, which are useful for determining the CO₂ sorption-desorption capacity and the inversion temperature. As illustrated in Figure 6, the sorption process for Li₄SiO₄ prepared with conventional SiO₂ starts at 380 °C and shows a peak at 428 °C, followed by the desorption process at 485 °C. In the case of sand-, block- and CSW-derived silicates, the CO₂ sorption starts above 342 °C with

a double peak; the first (472-488 °C) is assigned to the CO₂ sorption on the surface and the second (388-400 °C) to the CO₂ sorption in the bulk of the material controlled by diffusive processes. The CO₂ sorption in the concrete-derived silicate presented two peaks, starting at 295 °C, then at a temperature above 496 °C, the inversion point was observed. It is important to highlight that block- and CSW-derived silicates display a second sorption process (after the first inversion temperature) at 546 and 535 °C, respectively, followed by a small second desorption stage. This behavior could be associated to the high calcium content in the block and CSW wastes, 10-16 wt%.

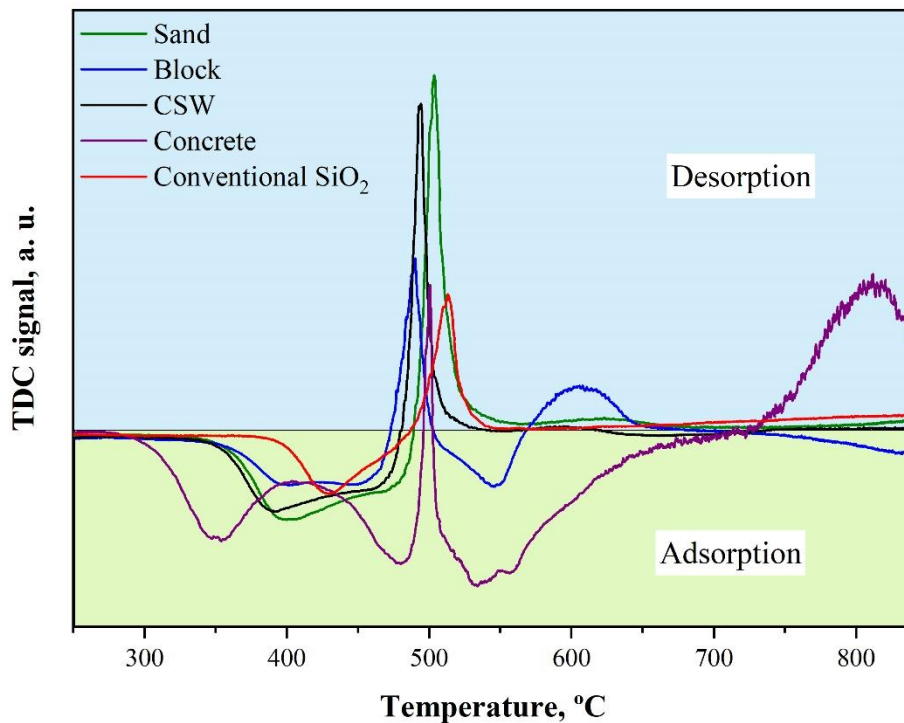


Fig. 6. Temperature-programmed CO₂ sorption-desorption of Li₄SiO₄ prepared with CDWM and conventional SiO₂.

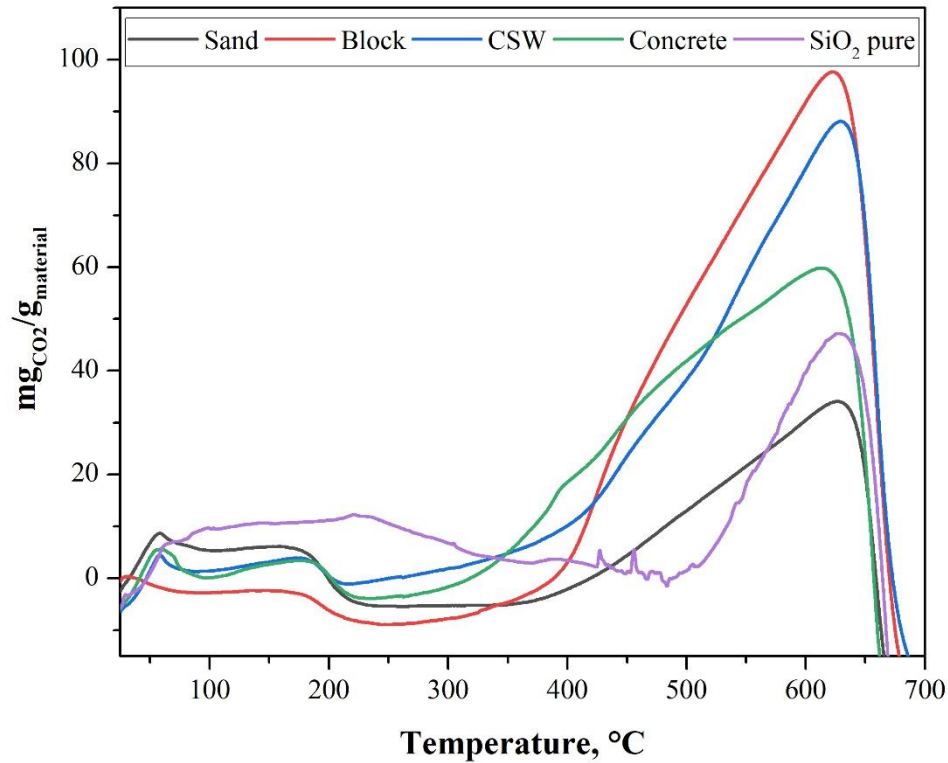


Fig. 7. Dynamic sorption of CO₂ with the Li₄SiO₄ prepared with CDWM and conventional SiO₂, with $P_{CO_2}=0.2$.

Figure 7 shows the CO₂ capture with respect to the temperature increase. The CO₂ sorption experiments suddenly increased above 300 °C in all cases except in the sample prepared with conventional SiO₂. The maximum CO₂ capture was achieved at around 600° C for all the materials, being the block-derived silicate the one that reached the maximum, 100 mg CO₂/g. The Li₄SiO₄ prepared with conventional SiO₂ presents a maxima sorption of 47 mg CO₂/g. The lowest CO₂ capture was observed in the sand-derived material, 35 mg CO₂/g. The sudden increase in CO₂ sorption at 500 °C agrees with that reported by several authors for Li₄SiO₄

prepared by sol-gel and solid-state methods and conventional and unconventional SiO₂ sources [42,47–49]. The desorption occurred between 614 and 629 °C; the mass loss was even higher than the original weight sample due to the decomposition of carbonates in the starting material or another mineral. Lithium silicate prepared with block waste showed the maxima sorption capacity followed by the derived from CSW. From this point, the next tests were carried out with block-derived silicate, as this material shows the best preliminary results.

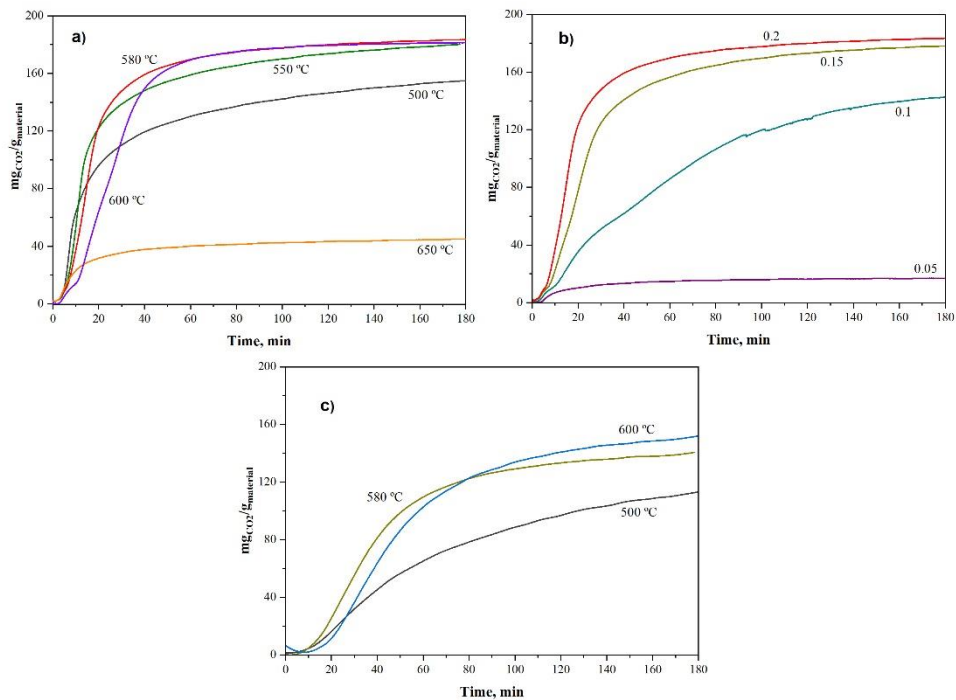


Fig. 8. CO₂ capture capacity over time of Li₄SiO₄ prepared from block waste: a) at different temperatures with $P_{\text{CO}_2} = 0.2$ and b) at 580 °C with different P_{CO_2} ; and (c) conventional SiO₂ with $P_{\text{CO}_2} = 0.20$.

TG analysis were conducted on the block-derived silicate and Li_4SiO_4 prepared with conventional SiO_2 at different temperatures and P_{CO_2} , and the weight change was plotted in Figures 8. TG curves under $P_{\text{CO}_2}=0.2$ is shown in Figure 8a; the capture rate gradually rises with the increase in temperature and reaches the highest value (183 mg CO_2/g) between 550 and 600 °C. The CO_2 capture rate at 550 and 580 °C are higher than at 600 °C in the first 30 min, but after 3h, the sorption value was the same. At temperatures above 600 °C, CO_2 desorption starts; at 650 °C, the CO_2 capture was only 44.6 mg CO_2/g . The capture capacity reaches approximately 50% of the Li_4SiO_4 theoretical sorption value in 3h. These results are similar to those obtained using other sources of silica, such as metallurgical slags, rice husk ash, and fly ash [21,25,26,45]. According to Li et al. (2022), from the kinetics perspective, increasing temperature promotes the sorption reaction; however, from the chemical equilibrium perspective, the CO_2 sorption process is not favored at high temperatures. Therefore, kinetic and chemical equilibrium factors compete at high temperatures, giving rise to the results obtained. In Figure 8b, the influence of the CO_2 concentration was studied by TG tests at 580 °C. As the CO_2 partial pressure decreases, the CO_2 capture capacity also decreases. A lesser effect was observed when the P_{CO_2} decreased from 0.20 to 0.15, and the CO_2 capture was 178 mg CO_2/g . However, with $P_{\text{CO}_2} = 0.1$, the CO_2 sorption rate was significantly affected, and the process was notably slow, reaching 141 mg CO_2/g . Finally, the CO_2 capture was only 16.5 mg CO_2/g with $P_{\text{CO}_2} = 0.05$.

For comparison purposes, the CO_2 capture capacity of Li_4SiO_4 prepared from conventional SiO_2 is shown in Figure 8c. The differences in the sorption rate between block-derived silicate and Li_4SiO_4 prepared with conventional SiO_2 are notable. Although the increase in temperature favors the sorption rate in Li_4SiO_4 prepared with conventional SiO_2 , it is very

Li ₄ SiO ₄ , block waste	500	0.20	3.0110	4.71x10 ⁻²	0.9926	0.2213	4.14x10 ⁻⁵	0.9831
	550	0.20	2.3860	3.72x10 ⁻²	0.9929	0.1561	1.63x10 ⁻⁵	0.9850
	580	0.20	2.3031	3.12x10 ⁻²	0.9980	0.0852	1.51x10 ⁻⁷	0.9770
	650	0.20	1.7453	2.05x10 ⁻²	0.9813	0.1196	6.64x10 ⁻¹²	0.9910
	580	0.15	1.7650	1.69x10 ⁻²	0.9938	0.1400	7.53x10 ⁻⁶	0.9673
	580	0.10	1.5664	8.90x10 ⁻³	0.9877	0.6641	1.08x10 ⁻³	0.9733
	580	0.05	3.9676	4.45x10 ⁻²	0.9651	0.3426	4.89x10 ⁻⁷	0.9832
Li ₄ SiO ₄ ,	500	0.20	2.1705	8.50x10 ⁻³	0.9633	0.6507	4.02x10 ⁻⁴	0.9678
conventional	580	0.20	2.1729	9.73x10 ⁻³	0.9528	0.2007	2.63x10 ⁻⁶	0.9276
SiO ₂	600	0.20	3.1156	1.30x10 ⁻²	0.9624	0.3737	1.24x10 ⁻⁴	0.9343

To compare the CO₂ capture of Li₄SiO₄ prepared with non-conventional materials, some previously reported works are shown in Table 3.

Table 3. Previous CO₂ capture studies using lithium silicates prepared with non-conventional sources of silicon: wastes and natural materials.

Precursors	Synthesis conditions			Product obtained	CO ₂ sorption capacity, wt% (Temperature, %CO ₂)	Ref.
	Temperature, °C	Time, h	Li source			
Diatomite	700	2	Li ₂ CO ₃	Li ₄ SiO ₄ LiAlSi ₂ O ₆	28.62 (620 °C, 20%)	[28]
Expanded vermiculite	750	6	LiNO ₃	Li ₄ SiO ₄	18.5 (650 °C, 20%)	[30]
Sepiolite	750	6	LiNO ₃	Li ₄ SiO ₄	27.27 (650 °C, 100%)	[29]
Sediments	750	6	LiNO ₃	Li ₄ SiO ₄ Li ₂ SiO ₃ Li ₃ HSiO ₄ LiOH	27.93 (650 °C, 100%)	[31]

Synthetic zeolites	750	6	LiNO ₃	Li ₄ SiO ₄	29.1 (650 °C, 100%)	[23]
Bagasse ash	900	4	Li ₂ C ₂ O ₄	Li ₄ SiO ₄ Li ₂ CaSiO ₄	32.0 (700 °C, 100%)	[24]
Iron slags	850	8	Li ₂ CO ₃	Li ₄ SiO ₄ Li ₂ CaSiO ₄ Ca ₃ SiO ₅ CaO LiAlSiO ₄	13.4 (650 °C, 5%)	[26]
Fly ash	900	4	Li ₂ C ₂ O ₄	Li ₄ SiO ₄ Li ₂ CaSiO ₄ LiAlO ₂	25 (700 °C, 100%)	[50]
Rice husk ash	900	4	Li ₂ CO ₃	Li ₄ SiO ₄	36.57 (680 °C, 100%)	[51]
Building block waste	250 and 550	Two steps of 2	LiOH	Li ₄ SiO ₄ Li ₂ SiO ₃ LiAlO ₂ Li ₂ CaSiO ₄	18.3 (580 °C, 20%)	This work

According to Table 3, the preparation temperature to obtain lithium silicate was up to 700 °C for a long period in all cases, except for the work of Yun et al. (2012), who synthesized lithium silicate during 2h, obtaining Li₄SiO₄ as well as LiAlSi₂O₆.

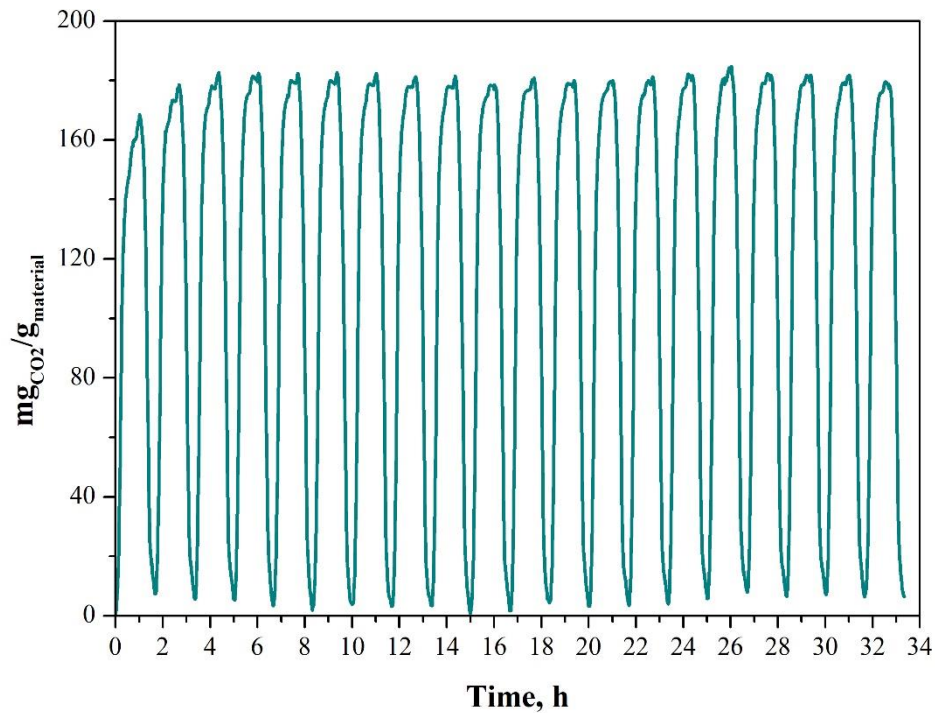


Fig. 9. Sorption-desorption cycles of block-derived lithium silicate: sorption was achieved at 580 °C with 20 vol% CO₂ balanced with N₂ (60 mL min⁻¹); desorption was conducted with a N₂ flow of 60 mL min⁻¹.

To complete the study, the cyclic behavior of block-derived silicate is shown in Figure 9. The performance of the material during 20 cycles indicates that, after the first cycle, the sorption capacity was practically constant (178-183 mg/g), and complete desorption was achieved at the same temperature (580 °C). Also, SEM images (Figure S4) show no significant changes in the morphology of lithium silicate before and after the CO₂ capture, indicating the chemical stability of the material during the 20 cycles of sorption-desorption. To understand the gas-solid interaction, XRD analysis was carried out after the CO₂ sorption on the Li₄SiO₄ prepared with block waste (Figure 10).

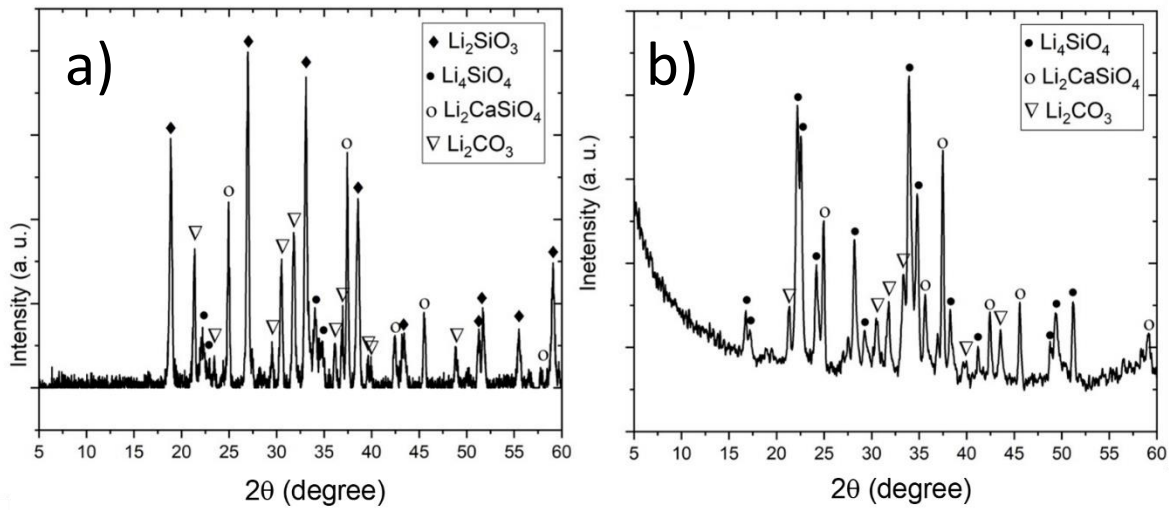
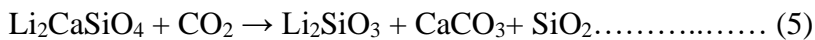
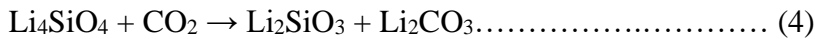


Fig. 10. XRD patterns of Li_4SiO_4 prepared with block waste a) after a CO_2 sorption step at $580\text{ }^\circ\text{C}$ with $P_{\text{CO}_2}=0.2$, b) after 20 CO_2 sorption cycles.

In Figure 10a, the intensities of Li_4SiO_4 signals are in a low proportion compared to Li_2SiO_3 , indicating that reactions 4 and 5 occurred. Li_2CO_3 was also identified as a principal product of the sorption process. According to Chen et al. (2016) the formation of $\text{Li}_2\text{CaSiO}_4$ favored the transferring of CO_2 from the Li_4SiO_4 surface to the core, reducing the diffusional resistance and improving the CO_2 sorption [42].



After the cyclic test (Figure 10b), low crystallinity was observed due to the small amount of sample used in the experiment. Moreover, the presence of Li_4SiO_4 and $\text{Li}_2\text{CaSiO}_4$, crystalline phases also identified in the fresh materials, confirmed the regeneration process during the

desorption step. However, a small amount of Li_2CO_3 suggests that complete regeneration (reaction 4) was not achieved at the end of the process. Li_2SiO_3 signals were not observed, possibly due to the formation of amorphous phases.

Conclusions

Li_4SiO_4 was successfully prepared from LiOH and CDWM, sand, block, ceramic sanitary ware and concrete waste. Experimental results indicated that the CO_2 capture capacity of the lithium silicates prepared with CDWM was as follows: block > CSW > concrete > sand. While, the Li_4SiO_4 prepared with a conventional SiO_2 source presented a maximum sorption of $35 \text{ mgCO}_2/\text{g}$ under the same experimental conditions. In addition to Li_4SiO_4 , the formation of $\text{Li}_2\text{CaSiO}_4$ was observed due to the presence of Ca in the block and concrete waste, increasing the sorption capacity. The Li_4SiO_4 prepared with block waste was able to capture $183 \text{ mgCO}_2/\text{g}$ at $580 \text{ }^\circ\text{C}$, with $P_{\text{CO}_2}=0.2$. Moreover, the block-derived silicate exhibits chemical stability during 20 cycles of sorption-desorption, keeping the maximum CO_2 sorption between 178 and $183 \text{ mgCO}_2/\text{g}$. All these results showed that the Li_4SiO_4 prepared with the evaluated construction and demolition wastes were acceptable to underpin a sustainable process to capture CO_2 and help climate change mitigation.

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