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Effect of milling mechanism on the CO_2 capture performance of limestone in the Calcium Looping process

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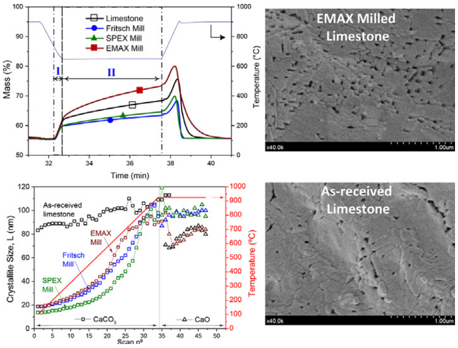
HIGHLIGHTS

- Limestone samples were subjected to mechanical milling using diverse mills based on different mechanisms.
- The multicycle Calcium Looping performance of the samples depends critically on the milling mechanism.
- Shear and impact based dry-millings promote sintering of the nascent CaO after calcination, which hinders CO_2 capture.
- In contrast, highly energetic dry-milling combining impact and shear forces (EMAX) promotes CO_2 capture.
- CaO porosity and solid-state diffusion of CO_2 during carbonation are enhanced by EMAX ball mill.

GRAPHICAL ABSTRACT



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ABSTRACT

This work analyzes the relevant influence of milling on the CO_2 capture performance of CaO derived from natural limestone. Diverse types of milling mechanisms produce contrasting effects on the microstructure of the CaO formed after calcination of the milled limestone samples, which affects crucially the kinetics of carbonation at conditions for CO_2 capture. The capture capacity of CaO derived from limestone samples milled using either shear or impact based mills is impaired compared to as-received limestone. After calcination of the milled samples, the resulting CaO porosity is increased while crystallinity is enhanced, which hinders carbonation. Conversely, if the material is simultaneously subjected to intense impact and shear stresses, CaO porosity is promoted whereas CaO cristanillity is reduced, which enhances carbonation in both the reaction and solid-state diffusion controlled regimes.

1. Introduction

The 21th conference on global warming (COP21) was ended with a commitment to limit the increase of the global average temperature to 2.0 °C in 2100 [1]. Such a great challenge would be feasible by promoting the share of renewable energies, a rational use of fossil fuels and the use of carbon capture technologies to reduce the emissions of CO_2 in power plants. In this regard, the Calcium Looping (CaL) process has

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lastly received considerable interest as a potentially cheap, environmentally friendly and efficient CO_2 capture technology at the necessarily large scale that involves retrofitting commercial fossil fuel fired power plants [2–5].

The CaL process for CO_2 capture, which has been already demonstrated at large pilot scale (1–2 MW_{th}) [6–9], is based on the reversible carbonation/calcination reaction of CaO:

$$CaO_{(s)} + CO_{2(g)} \rightleftarrows CaCO_{3(s)}; \quad \Delta Hr^0 = -178\ kJ\ mol^{-1} \tag{1}$$

Thus, the flue gas stream from a combustion plant (carrying a concentration of CO_2 close to 15 vol% in the case of coal) is used to fluidize a bed of CaO particles at atmospheric pressure, where quick carbonation takes place at around 650 °C. The carbonated particles are transferred to a second fluidized bed reactor where calcination occurs under high CO_2 concentration (above 70 vol%) at temperatures ~930–950 °C in short residence times, which is achieved by oxy-fuel combustion to avoid CO_2 dilution [6,10]. Calcination serves to regenerate the CaO particles and produces a concentrated CO_2 gas stream, which is extracted from the calciner, compressed and stored or employed for other uses. A schematic diagram of the process is shown in Fig. 1.

Among the different CaO-based materials to be employed in the CaL process, natural limestone (near 100% $CaCO_3$) is a preferred CaO precursor due to its low price (about 10€/ton), abundance and nontoxicity [11,12]. However, the CaO derived from natural limestone calcination exhibits a progressive decay of its CO_2 capture capacity as the number of carbonation/calcination cycles is increased [13–16], which makes it necessary to introduce a make-up flow of fresh limestone while the spent sorbent is periodically purged from the system. A drastic reduction of the CaO surface area due to marked sintering in the calcination stage at the harsh conditions of the process is a main limiting mechanism for carbonation as widely reported in the literature [17–19].

Many different strategies to mitigate CaO sintering have been pursued in recent works such as the use of thermally stable inert additives [4,11,12] and the use of pelletizing methods to maintain a porous structure [20–22]. An alternative simple and cost-effective method to produce porous Ca-based sorbents scalable to the industrial level is mechanical milling. Mechanical milling leads to a reduction of $CaCO_3$ crystallinity, thus favoring the kinetics of calcination, which reduces the temperature needed to achieve full calcination in short residence times [23,24]. Nevertheless, the literature on the effect of milling on the performance of CaO-based materials for CO_2 capture is yet scarce [23,25,26]. The use of different types of CaO precursors (limestone, dolomite, etc.) [23,26], calcination conditions (mild or harsh as would be the case for CO_2 capture) [24–26], and milling media (dry or wet) [25,26], lead to diverse results. Some of these works point out to the reduction of particle size as the main cause for the enhancement of CaO activity [25,26], whereas others highlight the role of milling on CaO crystallinity [23,24]. On the other hand, milling has been shown to enhance the multicycle CaO activity in [24] whereas the opposite effect is reported elsewhere [23]. This work is focused on getting a grip on the relevant mechanism involved on the CO_2 capture capacity of milled limestone in order to reconciliate these apparently contradictory results. To this end, several mills have been employed, which operate by applying different types of stress on the sample. As will be seen, the behavior of limestone in the CaL process previously subjected to mechanical milling depends on the type of stress acting on the sample predominant during the milling process, which affects critically the reactivity of the milled solids.

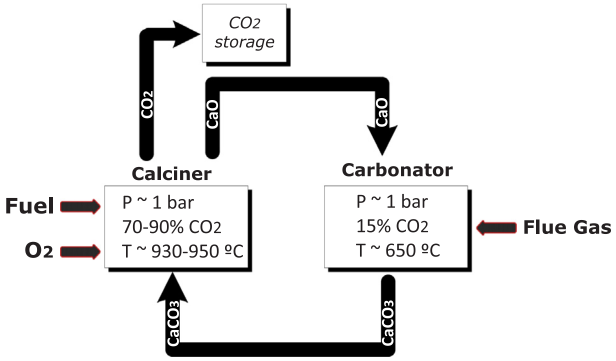

Fig. 1. Schematic representation of the Ca-Looping process for CO_2 capture.

2. Material and methods

High-purity natural limestone from Matagallar quarry (Sevilla, Spain) (99.5% wt $CaCO_3$) was employed in the present work. The as-received limestone was supplied in powder form (particle size < 45 μm) by Segura S.L. Company. Samples were mechanically milled in a very high-energy ball mill EMAX (Retsch), which achieves maximum intensity ball grinding in short times by the joint action of impact and shear stresses. 100 cm^3 steel jars and 50 steel balls per jar with a diameter of 10 mm were employed for milling. The limestone sample weight to ball ratio was set to 1:20 and the sample mass in each jar was 10 g. The limestone sample was milled at 1500 rpm for 90 s under dry air. This short milling time was selected attending to the results on the evolution of $CaCO_3$ crystallite size with the milling time (Fig. 2). As can be seen in Fig. 2, for the EMAX mill the coherent crystal length (crystallite size) reaches a minimum value after just about 90 s milling. This milling time is much smaller as compared with the time required by the other different milling procedures employed in the present work as briefly described below. Crystallite size of the milled samples was estimated using the Scherrer equation applied to the maximum intensity (1 0 4) Bragg reflection peak.

For the sake of comparison, results obtained in a recently published work [23], where samples were grinded in other mills, are used in the present manuscript. In that work, a centrifugal ball mill (Fritsch Pulverisette) was employed, which subjects the sample to mainly shear stresses. Besides, a SPEX 8000 ball mill was also employed, which creates high energy impact forces on the limestone particles. Further details on the milling conditions in these mills can be seen in [23].

Particle size distributions (PSDs) were analyzed by laser granulometry, using a Mastersizer 2000 (Malvern). For this purpose, samples were previously dispersed in 2-propanol and sonicated for 30 s to loose particle agglomerates.

Measurements on the multicycle CaO conversion were performed using a Q5000IR thermogravimetric analyzer (TA instrument), equipped with a high sensitive balance (< 0.1 μg) and a furnace heated by IR halogen lamps, which allows achieving very high heating and cooling rates (up to 300 °C/min) as well as stable isotherms. Each experiment was started by a calcination step from room temperature to 900 °C (at 300 °C/min, and held for 5 min) under high CO_2 concentration (70% CO_2/30% air vol/vol) at atmospheric pressure. The milled samples exhibited full calcination at this relatively reduced temperature (900 °C) as compared with as-received limestone (> 930 °C) [23]. The precalcination stage was followed by a carbonation stage quickly decreasing the temperature to 650 °C at 300 °C/min, which was held for 5 min under 15% CO_2/85% air vol/vol. As discussed in detail in previous works, achieving quick transitions between both stages is of paramount importance to mimic realistic CaL conditions for CO_2 capture necessarily involving high CO_2 concentration in the calcination stage [27]. A total of 20 carbonation/calcination cycles were run in which a fixed and small mass (10 mg) was used for avoiding undesired effects due to CO_2 diffusion resistance across the sample bulk. The scheme of the procedure is shown in Fig. S1 (Appendix), where temperature curves recorded for the program and sample are compared. As can be seen, there is a quite good match in the ramps and a high temperature accuracy at the isotherms, which complies with the specifications provided by the manufacturer (± 1 °C).