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# Increasing $CO_2$ carrying capacity of dolomite by means of thermal stabilization by triggered calcination

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## HIGHLIGHTS

- We developed a novel pre-treatment to improve dolomite $CO_2$ capture performance.
- The pre-treatment was tested under different operational conditions.
- We examine the effect of combining different pre-treatments in the sorbent.
- An indirect model to characterize textural properties of the sorbent was developed.
- Triggered calcination improves carrying capacity and shows promising integration potential.

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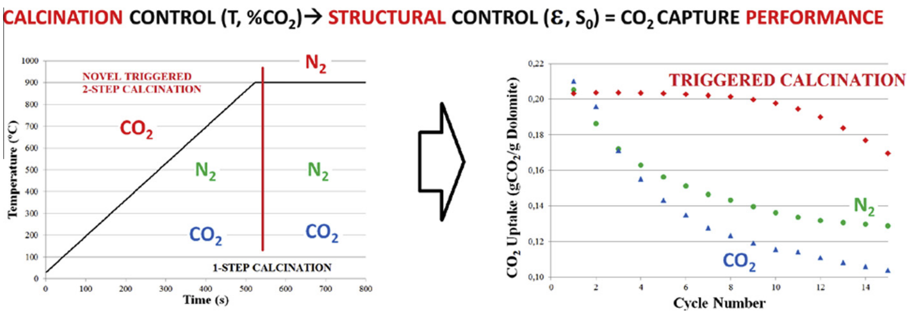
## GRAPHICAL ABSTRACT



## ABSTRACT

The high-temperature, solid chemical looping for $CO_2$ capture is a promising technology to mitigate greenhouse gases emission. The choice of a high-performance sorbent is a fundamental need to improve the $CO_2$ uptake in solid regeneration systems. Calcium-based sorbents have demonstrated a good compromise between cost, performance and environmental impact. In particular, calcined dolomite is selected as $CO_2$-acceptor in pre-combustion processes due to its good experimental capacity for $CO_2$ uptake. Moreover, among the solid acceptors investigated in scientific literature, naturally occurring sorbents (e.g. calcite and dolomite) are not considered as potentially hazardous substances, as they are not toxic either to the environment or to humans. This work presents the effect on $CO_2$ carrying capacity of different compositions of the calcination atmosphere, from 100% $N_2$ to 50/50% $CO_2$–$N_2$, as well as a novel pre-treatment (here called triggered calcination) by means of half-calcination in $CO_2$ with subsequent flash $N_2$ calcination. This new decomposition method improves $CO_2$ capture up to 24% in prolonged carbonation/calcination cycling (over 150 cycles). Other factors have been studied such as heating rate, $CO_2$ concentration and carbonation time, as well as other pre-treatments. Increased and sustained rates of $CO_2$ uptake can be explained as a result of changes in the internal structure of sorbent particles. In order to explain them, a study of the surface area has been carried out by means of an indirect method based on TGA experiments.

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## 1. Introduction

CaO-based chemical looping is being studied as a promising technological option for reducing $CO_2$ emission to the atmosphere. Some of the key advantages of this option, which make it a valuable route in gas decarbonization, are the low cost and wide availability of the starting material, as well as its high reactivity with $CO_2$. Moreover, CaO-based solid sorbents are more environmentally benign compared to other state-of-the-art solutions (e.g. amine-based liquid solvents), thus paving the way towards a solution for a sustainable development. Implementation of such a technology allows the use of fossil fuels in order to produce clean energy vectors, such as decarbonized electricity in low-rank fossil-fuelled power plants or hydrogen in methane reforming plants. System analyses and technical feasibility studies [1–3] have shown that the integration of $CO_2$-carbonate looping in iron, steel-making factories and cement industries will lead to higher efficiencies and lower energy penalties than conventional $CO_2$ capture technology. Additionally, integrating $CO_2$-carbonate looping into mature technologies will allow process intensification, reduction of the reactor size and an increase in the efficiency of the whole system. Being mature at industrial scale, these plants could accelerate the transition of high carbon technologies towards low carbon technologies. Then, the issue of concentrating, capturing and sequestering of $CO_2$ must be comprehensively addressed in the near future.

Naturally occurring carbonates are currently attracting considerable attention as $CO_2$ acceptors for decarbonizing reformed/shifted fuel gases or flue gases, e.g. limestone ($CaCO_3$) and dolomite ($CaCO_3{\cdot}MgCO_3$). When the material is exposed to $CO_2$, the fresh CaO grains that compose the sorbent are converted into $CaCO_3$. When the sorbent is completely carbonated or the gas–solid reaction shows negligible extent, calcination under atmospheric pressure and temperature greater than 850 °C allows obtaining a regenerated material for further $CO_2$ uptake cycles. The main drawback of such a process is the marked decrease of $CO_2$ uptake during the first few repeated cycles of carbonation/sorbent regeneration [4–6]. This loss of reversibility is due to the CaO sintering and ensuing pore-mouth blockage that occurs during the high-temperature regeneration step [7,8], albeit dolomite shows greater resistance to this effect when compared to limestone under oxy-fuel calcination conditions [9]. Its higher reversibility is probably due to the presence of MgO, which acts as an inert binder during the carbonation of calcined dolomite, inhibiting sintering of the active phase grains (CaO) and pore closure. Due to this ability to retain pore volume through carbonation/calcinations cycles, dolomite has been widely studied, showing the best results among the naturally occurring carbonates, in spite of the lower calcium content with respect to limestone [8,10,11]. However, regardless of the demonstration of limestone as $CO_2$ acceptor under industrially relevant conditions [12], the $CO_2$ uptake decay with cycling exhibited by naturally occurring sorbents counteracts the advantage of their low cost and limits their life. Thus, there is a need to find sorbent materials that show no or little decay after repeated cycling.

Generally, in order to achieve a high and stable $CO_2$ uptake capacity, two main routes have so far been adopted: synthesis of new materials [13–18] and thermal/chemical pre-treatment of naturally occurring carbonates for improving their stability during cyclic operation [19–26]. As for synthetic materials, efforts are being made to manufacture materials in an economically viable way with longer useful life and, consequently, smaller environmental footprint [27,28]. In spite of the promising results, most of the thermally stabilized natural materials have so far been exposed to regeneration only under a 100% nitrogen atmosphere, without taking into account the effects of $CO_2$ on sintering. However, when dolomite and limestone are calcined in a $CO_2$-containing atmosphere, sintering processes can occur [29–31].

Dolomite is mainly composed of $CaCO_3$ and $MgCO_3$, which present different decomposition behavior than their respective oxides. Calcination of $MgCO_3$ takes place at lower temperature and much more rapidly than $CaCO_3$ [32] according to the reaction:

$$\mathrm{MgCO3} \cdot \mathrm{CaCO_3} \rightarrow \mathrm{MgO} \cdot \mathrm{CaCO_3} + \mathrm{CO_2} \tag{1}$$

The reaction product is called half-calcined dolomite. During the half-calcination process, the porosity of the dolomite structure largely increases. This extra pore volume is formed due to the lower molar volume of MgO when compared to $MgCO_3$. As the temperature increases, full calcination of the dolomite takes place:

$$\mathrm{MgO} \cdot \mathrm{CaCO_3} \rightarrow \mathrm{MgO} \cdot \mathrm{CaO} + \mathrm{CO_2} \tag{2}$$

and the particle achieves its maximum porosity and specific surface area. It is important to note that $CaCO_3$ calcination takes place once $MgCO_3$ is completely calcined. The decomposition of calcium carbonate occurs in the boundary between CaO and $CaCO_3$ phases, and depends on sorbent structure [33]. Furthermore, the calcination temperature of each species depends on $CO_2$ partial pressure [5,33].

This paper presents the experimental investigation of a new thermal treatment to increase dolomite $CO_2$ capture performance. During calcination, $MgCO_3$ decomposes faster than $CaCO_3$, changing the particle structure. Hence, an accurate control of early calcination conditions improves the performance of sorbents as $CO_2$ acceptors.

## 2. Materials and methods

### 2.1. Characterization of the solid sorbent

A Mettler Toledo TG/DSC thermogravimetric analyzer (TGA) was used for cyclic $CO_2$ capture tests at atmospheric pressure. *Bianca di Zandobbio* dolomite was selected for this study, which contains 55.61% $CaCO_3$ by weight, 44.20% $MgCO_3$ and 0.07% $SiO_2$ and other impurities. For all tests, the dolomite particle diameter was pre-screened and a solid sample ranging from 400 to 600 μm was used, according to the particle size proposed by Manovic and Anthony [19] for thermal treatments in order to avoid self-activation effects. In a previous work, it was observed that global conversion and kinetics (for the first 50 s) of dolomite are practically independent of particle size, provided it is lower than 780 μm [34]. The gas flow was set at 60 ml/min. In order to select the mass sample which offers negligible diffusional resistance through the sample, a number of experiments were conducted with 3, 8 and 16 mg samples. The 3 and 8 mg samples did not present external mass transfer resistance of $CO_2$ through the height of the sample, contained on the 70 μl alumina crucible. However, in the 16 mg sample tests, the external diffusion effect could not be considered negligible. Therefore, the mass sample selected for all experiments was 8 mg, which produces a less noisy signal than that of 3 mg in a well-dispersed thin-layer sorbent bed. As part of the experimental procedure, blank runs were conducted with an empty crucible, in order to record and subtract the disturbances in mass change and reaction heat readings when switching the atmosphere between the calcination and carbonation processes.

The specific surface was analyzed in a Micromeritics Accelerated Surface Area and Porosimetry System ASAP 2000 using BET method. Particle morphology and textural pattern of the samples were observed by SEM images obtained by a Philips XL30 CP.