CO_2 Capture Performance and Particle Comminution Behavior of Brazilian Dolomite in a Lab-scale Dual Interconnected Fluidized Bed for Calcium Looping Application under Simulated Natural Gas Combustion Conditions

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Abstract. In this work, a Brazilian dolomite was investigated as a CaO-based sorbent in a Calcium Looping (CaL) process under a simulated natural gas exhaust atmosphere, to evaluate its potential for efficient CO_2 capture in low-concentration flue gas. The campaign was carried out in a bench-scale Dual Interconnected Fluidized Bed (DIFB) reactor, and the obtained key experimental parameters were optimized by a Rotatable Central Composite Design (RCCD) method. The performance in terms of sorbent capture capacity and its particle comminution by impact fragmentation was evaluated, considering the influence of gas velocity and temperature. Carbonation temperature was identified as the dominant operational parameter. When assessing overall performance, tests conducted in the presence of a simulated combustion gas derived from natural gas yielded trends in line with a typical CaL process but showing a reduced CO_2 capture efficiency compared to other data reported in the literature, although for different conditions. Under the most favorable operating conditions, at 675 °C and for a fluidization velocity of 0.5 m/s, a capture efficiency of 0.0177 $g_{CO2}/g_{sorbent}$, affected by sorbent thermal degradation and its rather severe elutriation behavior, was measured.

1. Introduction

Despite the increasing efforts towards the energy transition and the reduction of greenhouse gas emissions, fossil fuels will continue to play a relevant role in the global energy scenario over the coming decades [1].

In Brazil, where the role of fossil fuels is consistent with the global picture, the natural gas consumption is expected to rise in the coming years, given the policies aimed at promoting the development of offshore reserves and the industrial use of natural gas [2].

In this context, Carbon Capture, Utilization, and Storage (CCUS) technologies represent strategic short-term alternatives for mitigating CO_2 emissions while maintaining the reliance on fossil resources. Among these approaches, CaL represents a post-combustion CO_2 capture process based on the reversible reaction between calcium oxide (CaO) and carbon dioxide, forming calcium carbonate ($CaCO_3$) during carbonation and regenerating CaO during calcination. CaL is traditionally carried out in DIFB reactors with a carbonator where CO_2 is captured from the flue gas at temperatures around 600–650 °C, and a calciner, operating at approximately 900–950 °C to regenerate the sorbent and produce a concentrated CO_2 stream suitable for storage or utilization [3].

The advantages of this technology rely in the use of low-cost, abundant and eco-friendly sorbents such as limestone and dolomite, and in a straightforward retrofitting of existing plants and relatively low efficiency penalties [4].

Several studies, focused on fluidized bed reactors, which allow solids circulation between the reactors and are favorable to provide efficient gas–solid contact, and heat and mass transfer, have addressed process intensification strategies, including indirect heating systems, integration with renewable energy sources, and the development of synthetic sorbents with improved cyclic stability [5].

One of the main technical challenges of CaL is represented by the sintering of the sorbent at high temperatures, especially during the calcination stage, with the consequent decay in CO_2 capture capacity over iterated cycles. In addition to sorbent deactivation, the sorbent loss due to comminution (attrition and fragmentation) occurring in fluidized beds calls for continuous fresh sorbent make-up. Among the various

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comminution mechanisms, fragmentation by impact damage – comparatively less scrutinized – due to high velocity collisions between fluidized particles and targets, can generate both elutriable and non-elutriable fragments [6].

Despite the extensive research conducted, the application of CaL to natural gas-fired power plants, that is, under low CO_2 concentrations (close to 4%), remains less explored when compared to coal-fired systems and derived flue gases with CO_2 concentrations above 12–15 vol.% [7].

Although most CaL studies had been focused on limestone performance, dolomite, a calcium–magnesium carbonate, is a cheap natural material with a price roughly 10% higher than limestone, presenting a more elevated resistance toward sintering, although its use implies larger sorbent feed rate to obtain the required Ca/S ratio and larger extent of attrition phenomena [8].

In this context, the present study investigated a Brazilian dolomite exposed to CaL tests at low CO_2 concentrations in a lab-scale DIFB apparatus, focusing on CO_2 capture and particle comminution by impact fragmentation.

2. Experimental

The experimental setup, specifically developed for looping experiments, consists of a laboratory-scale DIFB including two identical bubbling FB reactors (ID 40 mm), serving as the calciner and the carbonator, respectively. The reactors, although operating in batch mode, are interconnected by a transfer line enabling the rapid pneumatic transport of the sorbent between the two units by means of a valve-controlled system [9].

Each CaL test consisted of ten consecutive calcination/carbonation cycles, followed by a final calcination step performed prior to the spent sorbent discharge.

In both reactors, inert silica sand with a particle size of 0.8–1 mm was used as fluidizing and thermal ballast material. A dolomite sample of m_0=20 g, with particle size in the range 0.4–0.6 mm, was loaded at the calciner at the beginning of each test. Each stage lasted 10 minutes.

Calcination was conducted at 940 °C under oxy-combustion-like conditions, using a gas mixture containing 70% CO_2 in air. The superficial gas velocity during fluidization was maintained at 0.5 m/s.

The carbonator was fed with 4% of CO_2 (balance air) in tests investigating the effect of different carbonation temperatures and fluidization velocities on sorbent performance, according to a Rotatable Central Composite Design (RCCD) model.

The RCCD 2^k model (with k=2 in our experimental design) investigated two factors at five coded levels: a central (with replicated central experiments used to estimate experimental error), factorial and axial points, employed to characterize the curvature of the response surface. The experimental data were fitted with a quadratic regression model using matrix regression analysis, and response surface methodology was employed to evaluate the interaction between variables and process performance. Finally, analysis of variance (ANOVA) was applied to assess the statistical significance of the parameters investigated. The methodology is described more in detail elsewhere [10]. Table 1 shows the design with the total number of experiments [11].

The amount of CO_2 captured during each carbonation step was determined by integrating the outlet CO_2 concentration profile, monitored using a mobile NDIR analyzer, over time. The CO_2 capture capacity (ξ) was defined as the mass of CO_2 captured per unit mass of the initial sorbent, according to the following expression:

$$\xi = \frac{\int_0^t \left[W_{CO_2}^{in} - W_{CO_2}^{out}(t)\right] \mathrm{d}t}{m_0} \quad (1)$$

where $W_{CO_2}^{in}$ and $W_{CO_2}^{out}(t)$ are the CO_2 inlet and outlet mass flow rates, respectively, as a function of time t.

Since the DIFB could not reproduce the high-velocity conditions of industrial-scale systems, comminution by impact fragmentation was studied at room temperature using a dedicated apparatus [8]. Fragmentation experiments were carried out at five impact velocities ranging from 10 to 45 m/s using 1.2 grams of the pre-processed sample previously subjected to CaL test, re-sieved into the initial particle size range of 0.4–0.6 mm. After impact, considering as "fragments" the impacted particles finer than 0.4 mm, the mass fraction of fragments f, defined as follows, can be obtained for each sample as a function of velocity:

$$f = \sum_{d_i<40\ \mu m} [x(d_i)] \quad (2)$$

where $x(d_i)$ is the mass fraction of particles that fall into a size range with an average diameter d_i.

The fragmentation data were fitted using a linear model in which the slope represents the fragmentation intensity as a function of impact velocity. This parameter was selected as the response variable in the RCCD analysis.

3. Results

Overall, it should be noted that severe fragmentation and elutriation were observed throughout the tests, causing filter clogging and substantial material losses, which significantly affected the experimental methodology. Despite these challenges, the RCCD experimental design provided consistent data and enabled evaluation of the effects of temperature (T) and fluidization velocity on CO_2 capture performance. The sorbent exhibited a typical CaL deactivation trend, with higher CO_2 capture during the first cycles followed by rapid decay and stabilization after approximately five cycles (Figure 1). However, the overall capture capacity was considerably lower than values reported in the literature for CaO-based (i.e., limestone) sorbents. Moreover, unlike dolomites, which generally show a smoother deactivation trend and higher long-term stability, the dolomite sorbent investigated in this work behaved more similarly to limestone, displaying a pronounced decay in capture performance. These discrepancies may be associated with differences in operating conditions and sorbent composition. Particularly, the higher silica content of the Brazilian dolomite investigated here, around 27%, may have

negatively affected both capture efficiency and mechanical resistance compared to the dolomite tested in the reference study by Coppola et al. [12], for which the SiO_2 content was 0.91%. Among the tested conditions, the best performance was obtained at low fluidization velocity (0.23 m/s) and 675 °C, where longer gas residence time enhanced gas–solid interaction and improved carbonation, while no carbonation occurred at T of 750 °C or above, as thermodynamic equilibrium shifted toward calcination under these conditions.

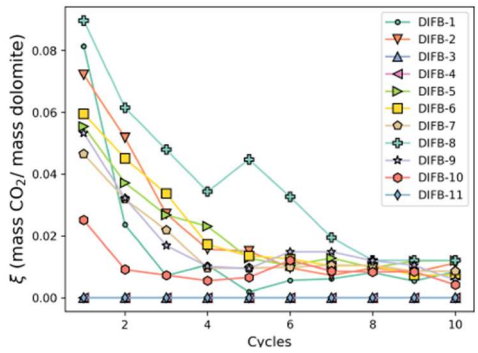

Figure 1. Specific CO_2 capture performance ξ (in g/g) as a function of the number of carbonation stages for DIFB tests.

In Figure 1, the tests numbered '1' through '11' in Table 1 are labeled 'DIFB-1' through 'DIFB-11'. Test 11 was not conducted, but the capture capacity was assumed to be equal to 0 since the scheduled test was at the highest T considered (780 °C) and the experimental capture capacity for the test at 750 °C was already zero.

Response surface analysis revealed a saddle-shaped behavior, indicating the absence of a clear global optimum. Temperature was identified as the dominant parameter affecting process performance, whereas velocity showed a weaker statistical influence. Although the quadratic RCCD model captured the general trends, it could not accurately represent the sharp thermodynamic transition between carbonation and calcination at high temperatures. Response surface plot of ξ_{mean} experimental data by v and T is not reported here for the sake of brevity, while the values of ξ_{mean} can be found in Table 1 (where ξ_{mean} has been calculated as the average of ξ values referring to cycles from 6 to 10, i.e. when the sorbent capture capacity reaches a plateau).

The second-order polynomial used to model the response variable ξ_{mean} provided a moderate fit to the experimental data, with temperature emerging as the only statistically significant factor in the ANOVA analysis, suggesting that broader operating ranges or additional variables, such as fragmentation intensity, may be necessary to better describe and optimize the system. Impact tests to investigate particle comminution by fragmentation were designed with the label IPT. IPT-1 was performed on sorbent particles after having experienced 10 CaL cycles under DIFB-1 conditions, and so on up to IPT-10. The impact test-fitted results, with the fragmentation index (f) plotted as a linear function of impact velocity, are presented in Figure 2, being the angular coefficient the response for the RCCD model applied. In Figure 3, the response surface plot is then reported.

Table 1. RCCD matrix of actual values and codification for two parameters, fluidization velocity (v) and carbonation temperature (T); and average CO_2 capture capacity (ξ_{mean}) for the tests in the DIFB system.

#	v (m/s)	T (°C)	x1	x2	ξ_{mean} ($\cdot 10^3$ g/g)
1	0.30	600	-1	-1	6.7
2	0.70	600	1	-1	9.2
3	0.30	750	-1	1	0.0
4	0.50	750	0	1	0.0
5	0.50	675	0	0	11.3
6	0.50	675	0	0	10.6
7	0.50	675	0	0	9.6
8	0.23	675	-1.41	0	17.7
9	0.78	675	1.41	0	11.6
10	0.50	570	0	-1.41	8.3
11	0.50	780	0	1.41	0.0

The figure highlights a region of low fragmentation occurring at T between 580–680 °C, which is the range where the experimental results give the higher capture capacities. When considering, in fact, the impact tests of Figure 2, the higher fragmentation was observed at the highest and lowest T considered, 750 °C (IPT-3, IPT-4) and 570 °C (IPT-10), where the capture capacities are essentially zero. In the range where the CO_2 capture occurs more significantly, with the formation of larger amount of in-bed fragment as well, presumably, the fragmentation index turns out to be the lowest, in particular at 675 °C, for the highest velocities considered of 0.5 and 0.78 m/s. When considering the fluidization velocity effect, the results show a reduction in the impact fragmentation tendency as the velocity increases. From the experimental impact tests, when considering the tests carried out at 600 °C, the curve of the test at the higher fluidization velocity, 0.7 m/s, such as IPT-2, is located in the low fragmentation indexes zone, whereas the IPT-1 test, at a velocity of 0.3 m/s, results in larger amount of fragments. This trend is also observed for the test at 675 °C, at the lowest velocity considered (0.23 m/s), which behaves differently from the tests at 0.5 and 0.78 m/s.

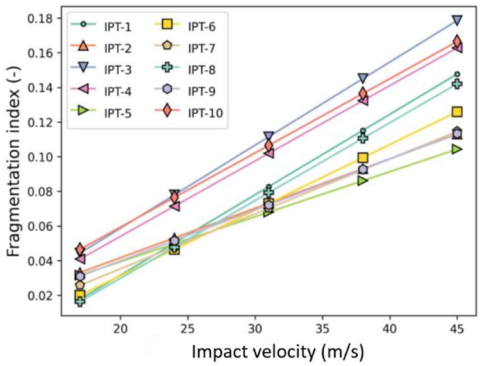

Figure 2. Linearly interpolated fragmentation index (f) curves as a function of impact velocity.

It is plausible that elevated fluidization velocities promoted the removal of fragile external layers by attrition or chipping, thereby exposing a mechanically more robust surface for the subsequent impact tests.

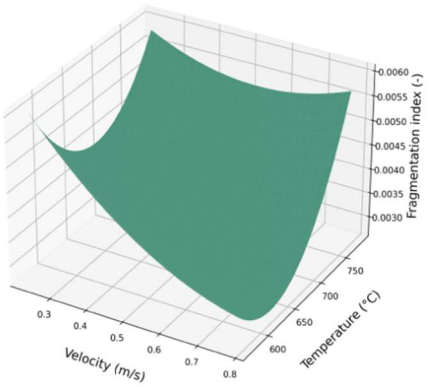

Figure 3. Response surface plot of fragmentation index (*f*) experimental data as a function of fluidization velocity and temperature.

4. Conclusions

This study evaluated a Brazilian dolomite as a sorbent for CO_2 capture in a CaL process using a bench-scale DIFB reactor under simulated natural gas exhaust conditions. The experimental campaign, designed through an RCCD model, enabled systematic assessment of the effects of carbonation temperature and fluidization velocity on sorbent performance and comminution by fragmentation behavior. Results showed that carbonation temperature is the dominant operating parameter governing CO_2 capture. The overall CO_2 uptake remained low compared to literature values for CaO-based materials, most of which, however, were obtained in experimental campaigns involving higher CO_2 concentrations. This reduced performance may also be attributed to thermal degradation, severe elutriation, and the high silica content of the dolomite, which likely weakened both chemical reactivity and mechanical stability. More in detail, the mean carbonation degree showed a strongly non-monotonic dependence on *T*, with a maximum around 675 °C and complete suppression above 750 °C, where the equilibrium of the exothermic CaO–CO_2 reaction is approached. The effect of the fluidization velocity *v* was non-linear and coupled with *T*: at the optimal temperature, lower *v* favoured conversion through the longer gas residence time, whereas at lower *T* higher *v* enhanced ξ through better mixing, suggesting a possible shift from kinetic and mass-transfer control to thermodynamic control as *T* increases. The optimum operating window is narrow and lies at moderate *T* combined with low *v*, with the highest measured conversion obtained at 0.23 m/s and 675 °C.

Impact tests revealed a non-trivial relationship between operating conditions and particle resistance, although it is necessary to emphasize that severe fragmentation and material losses significantly affected reactor operation. At intermediate temperatures (around 675 °C), associated to higher CO_2 capture capacities, and higher fluidization velocities, the extent of impact fragmentation resulted to be reduced, suggesting a partial surface "conditioning" effect due to attrition of weak external layers. The most carbonated particles showed the lowest fragmentation, suggesting that a denser $CaCO_3$ layer mechanically stabilizes the sorbent. Secondary effects were also evident: a high *v* during carbonation enhanced in-bed attrition damage, while high *T* can degrade the microstructure, both raising particle fragility. The response surface analysis highlighted the limitations of a purely quadratic model in capturing the transition between chemical reactions regimes, suggesting that future optimization should consider other coupled performance variables, alongside classical parameters used to evaluate CO_2 capture.

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