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Influence of Fluidised Bed Inventory on the Performance of Limestone Sorbent in Calcium Looping for Thermochemical Energy Storage

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Abstract: This research work deals with the application of the calcium looping concept for thermochemical energy storage. Experiments were carried out in a lab-scale fluidised bed reactor, which was electrically heated. An Italian limestone (98.5% CaCO3, 420–590 µm) was present in the bed alone, or in combination with silica sand/silicon carbide (this last material was chosen as per its high absorption capacity in the solar spectrum). Calcium looping tests (20 calcination/carbonation cycles) were carried out under operating conditions resembling the “closed-loop” scheme (calcination at 950 °C, carbonation at 850 °C, fluidising atmosphere composed of pure CO2 in both cases). Carbonation degree, particle size distribution, and particle bulk density were measured as cycles progressed, together with the application of a model equation to relate carbonation degree to the number of cycles. Mutual relationships between the nature of the bed material and possible interactions, the degree of CaO carbonation, the generation of fragments, and changes in particle density and porosity are critically discussed. An investigation of the segregation behaviour of the bed material has been carried out through tests in a devoted fluidisation column, equipped with a needle-type capacitive probe (to measure solid concentration).

Keywords: thermochemical energy storage; fluidised bed; calcium looping; limestone; silicon carbide; segregation; particle size distribution; particle density

1. Overview

Among the several renewable energy sources, solar energy is intended to play a strategic role in reducing the massive production of greenhouse gases. However, for effective large-scale deployment, research is aimed at finding appropriate solutions to overcome the highly intermittent nature of solar energy. One option is by Concentrated Solar Power (CSP) integrated with Thermal Energy Storage (TES) systems [1–3]. This integration is capable of storing solar energy in a secondary medium and releasing it where/when required [4,5]. The main TES systems exploit the thermal accumulation through sensible heat, using molten salts (a binary mixture of NaNO3 and KNO3) as heat transfer medium, with an operating temperature range of $T = 290–565 ^\circ C$ (higher temperatures lead to the degradation of salts). Drawbacks are represented by low: (i) operating temperatures, (ii) efficiency of energy storage density, and (iii) duration of utilisation. To overcome these limitations, the recent literature has focused on ThermoChemical Energy Storage (TCES) processes, which are based on reversible reactions with high enthalpy variation, in which...
the heat needed to sustain the endothermic stage is provided by solar energy, which is then accumulated in the noble form of chemical bonds. When required, the reaction products are brought together to conduct the exothermic stage, release the previously accumulated energy, regenerate the reagents, and start a new thermochemical cycle [6–11].

In this context, increasing interest has been shown in decomposition reactions, characterised by high enthalpy variations following the dissociation of a chemical compound (hydrides, carbonates, oxides, hydroxides) into two products, typically a gas and a solid, characterised by high values of energy storage and easy separation. Several studies have been carried out on the use of solid particles as solar receivers and thermal storage media in TCES, leading to the possibility of operating temperatures of over 1000 °C [12,13].

Since solid–gas reactions are favoured in TCES processes, Fluidised Bed (FB) reactors appear to be excellent particle receptors, able to exceed the characteristic limits of the molten salt technologies currently used, thanks to the very good mass and heat transfer coefficients ensured by FB fluid dynamics [14–17]. A reversible reaction of interest is the calcination/carbonation of limestone ($\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$). This reaction, which is also the basis for Calcium Looping (CaL), has been widely investigated in recent decades for post-combustion and atmospheric CO$_2$ capture, and for its subsequent release in concentrated form for geological sequestration or chemical reuse [18–29]. Nowadays, CaL is also of particular interest for energy purposes, thanks to the high reaction enthalpy ($\Delta H_r^\circ = 178$ kJ/mol) and low cost of the raw material. On the contrary, this process is inhibited by the rapid deactivation of the sorbent induced by a loss of porosity following thermochemical sintering, mecha-chemical deactivation, pore plugging, and low absorption of solar radiation, due to the typical high light reflectance of limestone [30–32]. For this reason, different processes have been investigated to improve the performance of the starting material, such as mechanical activation [33], thermal pre-treatments [34], synthesis of composite materials with inert stabilisers such as ZrO$_2$, Al$_2$O$_3$, SiO$_2$, TiO$_2$ [35–37], coating procedures [38].

Novel strategies to directly absorb solar energy using calcium-based composite TCES materials are under scrutiny [39], with the aim of simultaneously boosting solar absorption and improving cycling stability in integrated CaL-CSP systems. The introduction of inert materials in synthetic Ca-based sorbents with the aim of improving their optical performance in terms of solar energy absorptivity, through the use of particles with better light absorption properties in the reactor atmosphere, is being addressed as well [40–43].

Moreover, different reactor configurations have been proposed to improve the efficiency of the CaL-TCES process. Tregambi et al. [31] distinguish between open-loop and closed-loop conditions regarding CO$_2$ sent to the reactor. In the open-loop conditions, sorbent calcination is performed at 850 °C using air. Otherwise, in closed-loop conditions, calcination is performed at 950 °C under a CO$_2$-rich atmosphere, which can then be recycled in the process. Experimental tests performed in a FB heated by a solar simulator have shown that the harsher closed-loop conditions induce a greater loss of reactivity. Pascual et al. [44,45] conceptually proposed a closed-loop plant scheme with carbonation/calcination conducted at 850/950 °C under pure CO$_2$, inserting a Solid Separation Unit (SSU) after the carbonator to separate converted and unconverted particles, and to increase the efficiency of the process. Sarrion et al. [46] also suggested process configurations for a closed-loop CO$_2$ cycle applied to TCES.

A review of the literature showed that integration between CaL and CSP is a widely investigated topic, but the effect of the FB reaction environment on the process performance still deserves investigation. When TCES conditions are used, the process is mainly studied in thermogravimetric analysers [47–50], while there are few studies in which it is assessed in fluidised bed reactors [31,34,51–53]. Thus, the present study is not limited to the assessment of the deactivation of CaO in general terms, but it focuses on the specific process conditions of CaL coupled with concentrated solar radiation for energy storage. In the companion paper of this article [52], the study of the effect of FB fluid dynamics on the performance of an Italian limestone for TCES applications was investigated, consider-
ing carbonation/calcination at 850/950 °C under pure CO₂ (i.e., the closed-loop scheme illustrated in Figure 1). From that work (focusing on energetic aspects as well), we have borrowed some data referring to an FB composed of limestone only (or with sand). Instead, the aim of the present manuscript is to extend the performances comparison when particles with a higher absorption coefficient in the solar spectrum (silicon carbide-based) are present in the bed. The focus was on the degree of CaO carbonation, and its effects on generation of fragments, particles bulk density and porosimetric characteristics as the bed composition changes. Furthermore, insights concerning possible interactions among sorbent, sand, and/or silicon carbide have been critically discussed. An investigation of the segregation behaviour of the bed material complements the work.

Figure 1. Conceptual scheme of calcium looping closed-loop cycle applied to thermochemical energy storage.

2. Materials, Methods, Equipment, and Operating Conditions

Experimental tests were carried out in semi-batch mode using a single lab-scale FB reactor, operated either as carbonator or calciner (Figure 2). The reactor is electrically heated by semicylindrical radiant heaters (driven by a PID controller; maximum \( T = 1200 \) °C; total power = 6.2 kW); its ID = 0.04 m and total height is 1.4 m (subdivided into windbox, bed, and freeboard). A lateral port, located few millimetres above the distribution grid, allows for temperature measurement inside the reactor, by means of a K-type thermocouple. Electronic mass flow controllers are used for gas feeding. Further details can be found in the companion paper [52].

Figure 2. Electrically heated lab-scale fluidised bed reactor.
Three materials were adopted in the experimental process (Table 1, where the corresponding values for the minimum fluidisation velocity \( u_{mf} \) are given at the temperatures of interest):

- Limestone from Sardinia (Italy)—very rich in CaCO\(_3\) (98.5%wt.), with initial particle size range between 420 and 590 µm;
- Silica sand from the Ticino River (Italy), mostly silico-aluminous, initial size range 850–1000 µm;
- Reagent grade silicon carbide (purity in SiC = 98.80%wt.; size range 600–850 µm). This material was chosen due to its high emissivity/absorption in the solar spectrum [40], making it a very good candidate to improve the opto-thermal properties of the limestone bed.

<table>
<thead>
<tr>
<th>Material</th>
<th>Size Range [µm]</th>
<th>( u_{mf} @ 850–950 ^\circ C ) [m/s]</th>
<th>Main Chemical Composition [%wt.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone (Sardinia, Italy)</td>
<td>420–590</td>
<td>0.12–0.11</td>
<td>98.5% CaCO(_3)</td>
</tr>
<tr>
<td>Sand (Ticino River, Italy)</td>
<td>850–1000</td>
<td>0.35–0.33</td>
<td>83.9% SiO(_2); 8.4% Al(_2)O(_3); 2.4% K(_2)O; 1.8% Na(_2)O</td>
</tr>
<tr>
<td>Silicon carbide (r.g.)</td>
<td>600–850</td>
<td>0.32–0.30</td>
<td>98.80% SiC; 0.20% C; 0.19% Fe</td>
</tr>
</tbody>
</table>

CaL tests (Table 2) were carried out at atmospheric pressure fluidising the bed under 100% CO\(_2\) during both carbonation and calcination stages, to simulate closed-loop conditions. A test consists of a first calcination (“calcination 0”), plus \( N = 20 \) cycles of carbonation/calcination. Each calcination or carbonation stage lasted 20 min, a time long enough to observe practical completion of the reactions. Calcination was carried out at 950 °C, while carbonation was carried out at 850 °C. As a matter of fact, looking at Figure 3, which reports the regions of thermodynamic stability for CaCO\(_3\) (i.e., the region where CaO carbonation is active) and CaO (i.e., the region where the reverse CaCO\(_3\) calcination is active), under 1 atm of total pressure and 100% CO\(_2\), carbonation can be brought up to 850 °C thanks to the high CO\(_2\) concentration (this is positive in terms of process thermal efficiency), while one would need \( T\) higher than 900 °C to attain calcination conditions.

Three cases were investigated (total initial bed inventory = 180 g):

- A bed consisting of limestone only (under both calcination and carbonation, superficial gas velocity \( u_g = 0.6 \) m/s);
- A bed consisting of a 1:1 mixture of silica sand and limestone (under both calcination and carbonation, \( u_g = 0.7 \) m/s);
- A bed consisting of a 1:1 mixture of silicon carbide and limestone (under both calcination and carbonation, \( u_g = 0.7 \) m/s).

<table>
<thead>
<tr>
<th>Bed</th>
<th>Calcination Temperature and Atmosphere</th>
<th>Carbonation Temperature and Atmosphere</th>
<th>Value of ( u_g ) for Calcination and Carbonation at Reaction Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>950 °C; 100% CO(_2)</td>
<td>850 °C; 100% CO(_2)</td>
<td>0.6 m/s</td>
</tr>
<tr>
<td>Limestone + Sand (1:1)</td>
<td></td>
<td></td>
<td>0.7 m/s</td>
</tr>
<tr>
<td>Limestone + Silicon carbide (1:1)</td>
<td></td>
<td></td>
<td>0.7 m/s</td>
</tr>
</tbody>
</table>

The actual fluidisation velocities were chosen so to obtain a good compromise between acceptable fluidisation (cf. Table 1) and limited elutriation phenomena.

At the end of each calcination and carbonation stage, the material was retrieved from the bed. If sand or silicon carbide were present, they were separated from the sorbent via gentle sieving. The sorbent material was then weighed. The weighing procedure allowed us to calculate, for each carbonation stage, the CaO carbonation degree:
with a sufficient degree of carbonation (i.e., richer in CaCO$_3$) and to deduce the pore size distribution. For its bulk density, $\rho$, the lower the solid concentration. Segregation tests have been carried out, at the actual fluidisation velocities were chosen so to obtain a good compromise between acceptable fluidisation (cf. Table 1) and limited elutriation phenomena. A bed consisting of a 1:1 mixture of silicon carbide and limestone (under both calcination and carbonation, superficial gas velocity $u = 0.7$ m/s); desorption isotherms were post-processed with the Barrett–Joyner–Halenda (BJH) theory to deduce the pore size distribution.

For its Particle Size Distribution (PSD), via sieving in the size ranges of 0–100, 100–200, 300–420, and 420–590 $\mu$m, so as to obtain the mass fraction for particles falling in a size bin with mean diameter $d_i$, $x(d_i)$. PSD data reported in this work refer, in particular, to sorbent samples after calcination stages. PSD characterisation served as a means to analyse particle fragmentation, which is related to FB fluid dynamics;

- For its bulk density, $\rho$, by pouring the material into a 50 mL graduated cylinder and measuring the mass and the occupied volume.

$$X_{Ca}(N) = \left( \frac{m_{carb} - m_{calc}}{m_{calc}x_{CaO}} \right) \frac{MW_{CaO}}{MW_{CO_2}}$$

where $m_{carb}$ and $m_{calc}$ represent the overall mass of the carbonated and calcined sample, respectively, $x_{CaO}$ is the mass fraction of CaO in the calcined sorbent, assuming complete calcination and the composition in Table 1 ($x_{CaO} = 0.973$), while $MW$ stands for molecular weight. After weighing and before being re-fed to the FB reactor for the following stage, the sorbent material was further characterised:

- For Particle Size Distribution (PSD), via sieving in the size ranges of 0–100, 100–200, 300–420, and 420–590 $\mu$m, so as to obtain the mass fraction for particles falling in a size bin with mean diameter $d_i$, $x(d_i)$. PSD data reported in this work refer, in particular, to sorbent samples after calcination stages. PSD characterisation served as a means to analyse particle fragmentation, which is related to FB fluid dynamics;

- For its bulk density, $\rho$, by pouring the material into a 50 mL graduated cylinder and measuring the mass and the occupied volume.

Finally, after 20 cycles of carbonation/calcination, the bed material retrieved from the reactor was scrutinised via Scanning Electron Microscopy (SEM) complemented with Energy Dispersive X-ray (EDX) analysis, at magnifications from 70× to 10,000×, and via $N_2$-intrusion porosimetric analyses. SEM-EDX was performed using an FEI Inspet S instrument, while porosimetry was carried out through an Autosorb iQ apparatus (Quantachrome Instruments, Boynton Beach, FL, USA); desorption isotherms were post-processed with the Barrett–Joyner–Halenda (BJH) theory to deduce the pore size distribution.

On a parallel line, the conceptual possibility of separating, in the carbonator, material with a sufficient degree of carbonation (i.e., richer in CaCO$_3$, to be sent to the calcination stage) from that which remains unconverted (i.e., still rich in CaO, to be recycled to the carbonator for the improvement of the process performance) has been investigated through devoted segregation tests. The underlying idea is to exploit the difference in density between more and less carbonated particles, though having similar particle size. In such cases, the material with a lower density (“flotsam”) is characterised by lower $u_{mf}$ and, therefore, tends to segregate in the upper part of the bed; the material with a higher density (“jetsam”) is characterised by higher $u_{mf}$ and tends to segregate at the bottom of the bed [54,55]. To this end, preliminary segregation tests have been carried out in an ID = 40 mm Plexiglas fluidisation column. The column is provided with a needle-type capacitive stainless-steel probe, immersed in the bulk of the bed. The probe central electrode has OD = 1.6 mm. This system allows the solid concentration to be indirectly determined, through the measured voltage $V$: the higher $V$ (data acquired via a NI 9215 module through LabVIEW), the lower the solid concentration. Segregation tests have been carried out, at
room temperature, with a 50 mL bed, fluidised via \( \text{N}_2 \), consisting of (i) sorbent material after the first calcination stage; (ii) sorbent material after the first carbonation stage; (iii) a mix (1:1 by vol.) of the two. This choice originates from preliminary results reported in the companion paper [52] where, through analysis of the minimum fluidisation velocity, it can be seen that (a) \( u_{mf} \) for the carbonated material is higher than for calcined one; (b) \( u_{mf} \) for the carbonated material tends to decrease with \( N \), while \( u_{mf} \) for the calcined material, it tends to increase with \( N \); (c) the maximum gap between values of \( u_{mf} \) for calcined and carbonated material is for the sorbent after its first calcination and carbonation. In segregation tests, the \( \text{N}_2 \) flow is sent in a range of \( u_g = 0-0.33 \text{ m/s} \), large enough to sound out both fixed and fluidised bed conditions.

3. Results and Discussion

3.1. CaO Carbonation Degree and Interaction of Sorbent with Sand and Silicon Carbide

Figure 4 presents \( X_{Ca}(N) \) trends. Starting from the case of a bed composed of only limestone, it can be seen that \( X_{Ca} \) decreases from 0.63 (\( N = 1 \)) to 0.14 (\( N = 20 \)), because of thermal sintering deactivation, with a more marked effect up to \( N = 8 \) (after which, it seems that a stabilisation of the sorbent properties occurs). In the presence of silicon carbide, the performance is lower: \( X_{Ca}(N = 1) = 0.61, \) and \( X_{Ca}(N = 20) = 0.11 \). The average value for \( X_{Ca} \) is, in this case, \( X_{Ca,av} = 0.21 \) (over \( N = 20 \) carbonation stages) vs. 0.24 for the previous case. Differences in sorbent carbonation performance are not relevant up to \( N = 5 \): in the first cycles, the reactivity of the limestone in the two cases is very similar. Even after that, the presence of silicon carbide adds to thermal sintering in surface deactivating the sorbent material (see discussion below). Even worse is the situation when a bed of limestone and sand has been used: \( X_{Ca} \) decreases from 0.63 (\( N = 1 \)) to 0.07 (\( N = 20 \)), averaging at \( X_{Ca,av} = 0.16 \). If one takes into account this case vs. the previous two, it can be seen that the sorbent reactivity is comparable up to \( N = 5 \); then, in the case of sand, \( X_{Ca} \) decreases quickly. This would suggest a stronger surface deactivation effect related to the presence of sand vs. silicon carbide.

A potential chemical interaction between sand and sorbent particles might be at work. If we refer to the carbonation stage, the following reaction network could be postulated by assuming dicalcium silicate as the possible product of the reaction between sand and sorbent:

\[
\begin{align*}
\text{CaO}(S) + \text{CO}_2(G) & \to \text{CaCO}_3(S) & \text{(R1: carbonation)} \\
2\text{CaO}(S) + \text{SiO}_2(S) & \to 2\text{CaO}_2\text{SiO}_2(S) & \text{(R2: formation of dicalcium silicate from CaO)} \\
2\text{CaCO}_3(S) + \text{SiO}_2(S) & \to 2\text{CaO}_2\text{SiO}_2(S) + 2\text{CO}_2(G) & \text{(R3: formation of dicalcium silicate from CaCO}_3) 
\end{align*}
\]

Figure 4. Trends for the CaO carbonation degree (Equation (1)) vs. number of carbonation stages for the three cases under investigation.
Re-working kinetic data published by Alonso et al. [56], it can be seen that at 850 °C (the carbonation temperature adopted in this work), the kinetic constant for R2 and R3 is in the order of, respectively, $3.8 \times 10^{-5}$ s$^{-1}$ and $4.2 \times 10^{-6}$ s$^{-1}$. Characteristic reaction times associated with R2 and R3 are, therefore, in the order of 450 min and 4500 min, respectively, well longer that the characteristic time (tens of minutes) that we experimentally observed for CaO carbonation. Thus, the formation of dicalcium silicate from either CaO or CaCO$_3$ during carbonation can be safely neglected. On the other hand, when we increase $T$ to 950 °C (the calcination temperature in this work), while the kinetic constant for R3 values are $2.3 \times 10^{-5}$ s$^{-1}$ (characteristic reaction time of about 700 min), the kinetic constant for R2 increases to $6.5 \times 10^{-4}$ s$^{-1}$, i.e., a characteristic reaction time of the order of tens of minutes, well comparable with the time scale of calcination (the reverse of R1). The more marked increase in the kinetic constant for R2 vs. R3 is related to its higher activation energy (325 kJ/mol for R2 vs. 195 kJ/mol for R3), which makes the R2 kinetic constant more sensitive to increases in $T$. The following reaction scheme in series

$$\text{CaCO}_3 \rightarrow \text{CaO} \rightarrow \text{dicalcium silicate}$$

cannot be excluded during calcination, with the formation of dicalcium silicate that subtracts reactive CaO and/or induces a loss of reactive porosity, for a material that is subsequently used as CO$_2$ sorbent in the carbonation stage. In the companion paper of this article [52], XRD data on limestone samples at the 20th cycle of calcination seem to rule out a bulk chemical interaction between sand and lime, since no peaks related to new crystalline phases were detected. A quantitative XRD analysis was also performed to assess the extent of dicalcium silicate formation, which was not detected. It is likely that a potential chemical interaction takes place only at the particle surface, given the sizes of sorbent and sand particles used in these studies.

Figure 5 illustrates a comparison (at different magnifications) among SEM micrographs for the material retrieved from the bed after 20 cycles, referred to the bed of limestone vs. bed of limestone and sand cases. Fragmentation and agglomeration phenomena are clearly visible. To gain further insights, the material retrieved from the bed after 20 cycles (in the case of limestone and sand bed) was also characterised via EDX, as shown in Figure 6. When the analysis concerns the whole surface, the presence of Si, together with a Ca:O molar ratio much lower than unity, indicates either the possibility of surface formation of compounds containing Si and Ca (as dicalcium silicate) in addition to CaO, as obtained from the above kinetic observations (it should be noted that the sample under scrutiny issues the reactor in its calcined state), or the possible presence of fine sand particles in the lime meso- and macro-pores. In fact, in an FB system one might expect less silicate conversion than in a fixed bed, due to shorter contact times among particles. When, instead, the EDX analysis concerns a detail in a zone showing fractures, one can observe the absence of Si and a Ca:O molar ratio much closer to unity to indicate that, if present, dicalcium silicate mostly concentrates in the outer periphery of the particles, while fractures are composed of CaO only.

The effect of SiC can be related to its potential to interact with oxidising agents [57]. Under our operating conditions, SiC could subtract oxygen present in the CaO structure (yielding silicon oxides and carbon, and/or carbon oxides and silicon), leaving calcium/calcium carbide no more active toward CO$_2$ capture. Obviously, the presence of fine SiC particles in the lime pores could also arise in this case. As, on the other hand, SiC is characterised by a generally high thermal stability, the actual occurrence of such phenomena needs further clarification in future experimental research. Altogether, the stronger deactivation effect related to the presence of sand vs. silicon carbide should be related to the formation of surface dicalcium silicate, which is deemed to be possible in the presence of sand, while unlikely in the presence of SiC.
To gain insights on the sorbent deactivation tendency, the following Initial Activity & Decay (IAD) equation been postulated:

$$X_{Ca}(N) = k_1 N^{-k_2}$$  \hspace{1cm} (2)

where $k_1$ is the initial activity constant, which measures the efficacy of the sorbent when $N = 1$ ($X_{Ca}(N = 1) = k_1$), and $k_2$ is the decay constant that considers the resistance of the sorbent to sintering phenomena (the higher $k_2$, the worse the sintering resistance). While Figure 7 shows data fitting, Table 3 lists the best-fitting values for $k_2$ (along with the values for the coefficient of determination). It is confirmed that $k_2$, with a value of 0.425 for the case of limestone only, increases by about 35% and 65% in the presence of, respectively, silicon carbide and silica sand.
3.2. Particle Size Distribution for Calcined Sorbent

Figure 8 illustrates the PSD for the sorbent samples retrieved after each calcination stage, from $N = 0$ to $N = 20$, in the case of a bed inventory composed of limestone only (Figure 8a), limestone and silicon carbide (Figure 8b), limestone and sand (Figure 8c). It should be noted here that the size range of the parent sorbent (termed “TQ” in figures) is (Table 1) 420–590 µm.

![Figure 8](image-url)

Figure 8. Particle size distribution for calcined sorbent as a function of the calcination stage in the case of a bed inventory composed of (a) limestone only, (b) limestone and silicon carbide, (c) limestone and silica sand; (d) cumulative mass percentage of fragments for the above three cases. The label, “TQ”, refers to the parent limestone.
Starting with the case of a bed of pure limestone, after \( N = 0 \) and \( N = 1 \), the mass fraction of particles falling in the 300–420 \( \mu \)m size bin results 0.05 and 0.10, respectively. After that, the PSD changes only little, to underline that fragmentation phenomena are mostly active in the first stages. Similarly, in the presence of silicon carbide in the bed, \( x(d_i = 300–420 \mu \text{m}) \) is 0.05 for \( N = 0 \), and 0.18 for \( N = 3 \), stabilising thereafter. Values for \( x(d_i < 300 \mu \text{m}) \) were not significant in both cases. A more pronounced fragmentation has been observed in the presence of silica sand. Values for \( x(d_i = 300–420 \mu \text{m}) \) increase up to 0.4, and non-negligible values for mass fractions related to finer sizes have been observed as well. Looking at the synoptical Figure 8d, reporting \( x(d_i < 420 \mu \text{m}) \), i.e., the cumulative mass fraction of “fragments” (defined as particles finer than the lower limit of the parent size range), and comparing with data in Figure 4, it can be observed that, the higher the mean \( X_{\text{Ca}, \text{av}} \) value, the lower the fragmentation propensity. Even though data refer to samples after calcination stages, their PSD is influenced by carbonation stages as well: when \( X_{\text{Ca,av}} \) is higher, the fractional content of CaCO\(_3\) in the particle is larger. Given that CaCO\(_3\) harder than CaO, this generally results in samples more resistant to fragmentation [58]. In addition, the presence of hard materials (such as those that are Si-based) could add to this effect, through mechanical interaction (and consequent surface wear) with sorbent particles. The relationship between \( X_{\text{Ca,av}} \) and the average value for \( x(d_i < 420 \mu \text{m}) \), termed \( x(d_i < 420 \mu \text{m})_{\text{av}} \), is illustrated in Figure 9.

![Figure 9. Relationship between average fraction of sorbent fragments (from Figure 8d) and average degree of CaO carbonation (from Figure 4) for the three cases under investigation (1: bed of limestone only; 2: bed of limestone and silicon carbide; 3: bed of limestone and silica sand), with expression for mathematical fitting.](image-url)

### 3.3. Bulk Density for Calcined and Carbonated Sorbent

Figure 10a illustrates, as a function of the relative stage, the values for the bulk density referred to calcined and carbonated sorbent, in the case of a bed inventory composed of limestone only. For values referring to carbonated samples, the corresponding \( X_{\text{Ca}} \) [%] measures have been added as figure label.

It is observed that \( \rho \) for the calcined material rapidly increases from 0.9 g/mL (\( N = 0 \)) to 1.09 g/mL (\( N = 1 \)), to practically stabilise thereafter. Thermal sintering should be active in decreasing particle porosity and, therefore, increasing the bulk density of the calcined material. On the contrary, \( \rho \) for the carbonated material decreases from 1.59 g/mL (as received limestone) to 1.46 g/mL (\( N = 1 \)), and, then, down to about 1.3 g/mL (\( N = 8 \)), to remain almost constant for subsequent carbonation cycles. As it can be inferred from the \( X_{\text{Ca}} \) values, the trend of \( \rho \) follows that of the CaO carbonation degree: stages characterised by lower degree of carbonation, in fact, yield material with a lower fraction of CaCO\(_3\) (denser than CaO), thus leading to a decrease in the bulk density of the carbonated material, with an effect which results of greater relevance than the sintering one.
Figure 10b illustrates the curves for \( \rho \), with reference to calcined samples, as a function of \( N \), for the three cases under investigation. While the general \( \rho(N) \) trend is also confirmed for the other cases, interestingly, the higher material reactivity (translated by \( X_{Ca,av} \) (i.e., lower \( k_2 \) (Table 3)) determines samples more resistant to thermal sintering and, therefore, lower mean values for \( \rho (\rho_{av}) \), referred to the calcined material. Figure 11 and Table 4 synoptically illustrate the concept.

![Figure 10](image1)

**Figure 10.** (a) Bulk density for calcined and carbonated material as a function of \( N \), for the case of a bed composed of limestone only (numbers in label refer to corresponding \( X_{Ca} \) [%] values); (b) bulk density for calcined material, as a function of \( N \), for the three cases under investigation.

![Figure 11](image2)

**Figure 11.** Relationship between average bulk density for calcined samples (from Figure 10b) and average degree of CaO carbonation (from Figure 4) for the three cases under investigation (1: bed of limestone only; 2: bed of limestone and silicon carbide; 3: bed of limestone and silica sand), with expression for mathematical fitting.
Table 4. General relationship between carbonation reactivity, fragmentation tendency, and bulk density for the calcined material, for the three cases under analysis.

<table>
<thead>
<tr>
<th></th>
<th>Carbonation Reactivity</th>
<th>Fragmentation Propensity</th>
<th>Bulk Density for Calcined Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>Higher</td>
<td>Lower</td>
<td>Lower</td>
</tr>
<tr>
<td>Limestone + Silicon carbide</td>
<td>Intermediate</td>
<td>Intermediate</td>
<td>Intermediate</td>
</tr>
<tr>
<td>Limestone + Sand</td>
<td>Lower</td>
<td>Higher</td>
<td>Higher</td>
</tr>
</tbody>
</table>

3.4. Reactive Porosity and Porosimetric Analysis

In the companion paper [52], starting from the bulk density of the calcined and carbonated material, it was possible to define a “reactive porosity” of the material itself, which represents the internal porosity of the particles which is occupied by the CO₂ molecules reacting with CaO to form CaCO₃ during the carbonation step:

$$\varepsilon_{pN}^{\text{react}} = \varepsilon_{pN-1}^{\text{calc}} - \varepsilon_{pN}^{\text{carb}}$$  (3)

where $$\varepsilon_{pN}^{\text{react}}$$ is the reactive porosity of particle at stage N, $$\varepsilon_{pN-1}^{\text{calc}}$$ is the porosity of particle in its calcined form at stage N − 1, and $$\varepsilon_{pN}^{\text{carb}}$$ is the porosity of particle in its carbonated form at stage N; $$\varepsilon_{pN-1}^{\text{calc}}$$ and $$\varepsilon_{pN}^{\text{carb}}$$ are calculated via values of density and degree of carbonation [52]. Figure 12 reports the reactive porosity as a function of the reaction stage N for the three cases under investigation. The reactive porosity trends along iterated cycles confirm what can already be observed in Figures 4 and 7 for the carbonation degree over cycles, and highlights a difference in the effective porosity in favour of the only limestone and limestone and silicon carbide cases, with respect to limestone and silica sand, where a stronger reduction of sorbent reactivity along the iterated cycles was observed.

![Figure 12. Reactive porosity of limestone particles for calcined and carbonated samples, for the three cases under investigation.](image-url)

The higher reactive porosity obtained from the tests with only limestone is demonstrated by the cumulative pore volume distribution of the calcined materials recovered after the 20th cycle, for the three cases (Figure 13). The sorbent obtained from the test with only limestone, which is the best in terms of mean carbonation degree and reactive porosity, is also characterised by a high value of total pore volume (0.165 cm³/g), most of which are mesopores. When the sorbent is processed together with silicon carbide,
total pore volume is very similar to the limestone-only case (0.171 cm$^3$/g) but slightly shifted to the macropores region. This shift leads to a small reduction in the specific surface of the sorbent and, consequently, a lower reactive porosity of the limestone along the cycles. Instead, the sample obtained from the test performed with limestone and silica sand, which has the worst performance in terms of mean carbonation degree, also has the lowest value of total pore volume (0.047 cm$^3$/g) and a significant share of both micropores and smaller mesopores, probably formed following sand/sorbent interactions, with an associated reduction in terms of sorbent reactivity.

![Figure 13](image)

Figure 13. Cumulative specific pore volume distribution for the three different samples, retrieved from the bed after the last calcination step (semi-log scale).

3.5. Segregation Tests

Figure 14 presents the results of the segregation tests, in terms of voltage acquired by the probe vs. superficial gas velocity (reported, for the ease of reading, in cm/s), for: (i) the sorbent material after the first calcination stage; (ii) the sorbent material after the first carbonation stage; (iii) a mix (1:1 by vol.) of the two. When the column is filled with calcined material only, or with carbonated material only, the following features can be observed:

- $V$ increases with $u_g$, starting from the onset of minimum fluidisation, that is, under fluidised conditions; the larger the gas velocity, the lower the solid concentration;
- $V$ for the calcined material is larger than for the carbonated sorbent; this reflects the circumstance that calcined particles are more porous and, therefore, material concentration is lower.

Furthermore, looking at the behaviour when the 1:1 mix is considered, up to about $u_g = 24$ cm/s, the values for $V$ are very similar to those for the case of carbonated material. Since the probe is immersed in the bed in the close proximity of the distribution grid, this is a clue that when the mixture is present and for lower values of $u_g$, a two-layer pattern is established, with carbonated material acting as jetsam and segregating at the bottom of the bed, while calcined material acting as flotsam is mostly concentrated close to the bed surface (Figure 14). This suggests that by choosing appropriate conditions for the superficial gas velocity, it would be possible to design an SSU able to allow the separation of the more carbonated material (to be sent to the calciner) from the material prevailingly unconverted (to be recycled to the carbonator). SSU embodied in the CaL process could, therefore, improve the overall efficiency of the system (Figure 15). It should be noted that values for $u_g$ should not be too high (in Figure 14, not higher than 24 cm/s), as this would
promote the mixing of the two materials (values of voltage for the mixture lie in between the two previous cases).

Figure 14 also reports the theoretical $V_{mix}^{th}(u_g)$ curve for our 1:1 mixture. It has been calculated as follows:

$$V_{mix}^{th} = \frac{V_{N_2}}{K_{mix}^{em}}$$

where $V_{N_2}$ is the voltage acquired by the probe in absence of solid (only nitrogen flowing in the column), while $K_{mix}^{em}$ is the relative dielectric constant of the FB emulsion phase in the presence of our mixture:

$$K_{mix}^{em} = (0.5K_{calcined} + 0.5K_{carbonated})(1 - \varepsilon_{mix}) + \varepsilon_{mix}$$

In Equation (5), on the right-hand side, $K$ indicates the relative dielectric constant referred to each type of solid:

$$K = \frac{K_{fixed\ bed} - \varepsilon}{1 - \varepsilon}$$

where $\varepsilon$ is a typical degree of voidage for a bed of limestone sorbent (0.41), while the relative dielectric constant of each system under fixed bed conditions is easily calculated from

$$K_{fixed\ bed} = \frac{V_{N_2}}{V(u_g = 0)}$$

with $V(u_g = 0)$ being the voltage we acquired under no flow, but with the reactor filled with solid. The parameter $\varepsilon_{mix}$ in Equation (5) is an average between the voidage degree of the calcined and that of the carbonated material, that is, for a 1:1 mix:

$$\varepsilon_{mix} = 0.5\varepsilon_{calcined} + 0.5\varepsilon_{carbonated}$$

The values for $\varepsilon_{calcined}$ and $\varepsilon_{carbonated}$ are calculated from

$$\begin{align*}
\varepsilon_{calcined} &= \frac{K_{calcined} - K_{calcined}}{1 - K_{calcined}} \\
\varepsilon_{carbonated} &= \frac{K_{carbonated} - K_{carbonated}}{1 - K_{carbonated}}
\end{align*}$$

where, finally, the relative dielectric constants of the FB emulsion phase are obtained from the experimentally acquired values of voltage in the case a bed of calcined or carbonated material, respectively:

$$\begin{align*}
K_{calcined}^{em} &= \frac{V_{N_2}}{V_{calcined}} \\
K_{carbonated}^{em} &= \frac{V_{N_2}}{V_{carbonated}}
\end{align*}$$

By iterating this procedure for each value of $u_g$, it is possible to obtain the $V_{mix}^{th}(u_g)$ curve represented in Figure 14. It shows that, under ideal conditions, the voltage lies in between the values obtained for the two distinct cases in the whole range of experienced superficial gas velocities. This corresponds to what we have observed for $u_g > 24$ cm/s (good mixing), but does not for lower gas velocities, to indicate that, under real conditions, the mixture would tend to segregate, at odds with theoretical findings. These results reinforce the possibility of adding an SSU to the CaL cycle (as schematised in Figure 15), although segregation tests have been conducted on materials at the beginning of their calcination and carbonation history, i.e., when the gap between fluidisation velocities is more favourable to segregation. Further insights must be given by the analysis of the segregation behaviour in the case of sorbent (calcined and carbonated) cycled for a longer time in the system.
Sintering has been observed as the carbonation stages progress, negatively affecting the degree of CaO carbonation. With respect to a bed made of limestone only, the detrimental effect related to the presence of sand was more pronounced than that related to silicon carbide. The surface formation of dicalcium silicate during the calcination stage in the presence of sand cannot be neglected, as well as the possible oxidation of SiC at the expense of the sorbent when the former is present, aspects that can be responsible for the loss of “free” CaO otherwise available for CO₂ capture. The application of an “initial activity & decay” equation to the conversion data confirmed the better resistance to sintering in the case of a bed of limestone only.

Samples showing higher values for the carbonation degree are also more resistant to fragmentation in a fluidised bed, due to the pronounced hardness of CaCO₃ vs. CaO; we found a linear relationship stating that the higher the average degree of carbonation, the lower the fraction of generated fragments. We observed that the bulk density of the calcined material increases with the number of cycles (as an effect of thermal sintering). Interestingly, the higher the material reactivity (i.e., the higher the sintering resistance), the lower the density of calcined particles, and the higher the reactive porosity and the total pore volume. Again, a linear relationship between a decreasing average density of calcined particles, and an increasing average degree of CaO carbonation, has been elucidated.

Segregation tests suggested that, by choosing appropriate conditions for the superficial gas velocity, it would be possible to design a solid separation unit (downward the carbonator) able to allow the separation of the more carbonated material (to be sent to the...
calciner) from the material which remains unconverted (to be recycled to the carbonator),
thanks to the establishment of a two-layer pattern, with carbonated material acting as jetsam and segregating at the bottom of the bed, while calcined material acts as flotsam, mostly concentrated close to the bed’s surface.


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Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to privacy restrictions.

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Conflicts of Interest: The authors declare no conflict of interest.

List of Symbols

\(d\) \(\) Particle diameter \([\text{length}]\)
\(k_1\) \(\) Initial activity constant \([\text{–}]\)
\(k_2\) \(\) Decay constant \([\text{–}]\)
\(K_{\text{calcined}}\) \(\) Relative dielectric constant for the calcined material \([\text{–}]\)
\(K_{\text{carbonated}}\) \(\) Relative dielectric constant for the carbonated material \([\text{–}]\)
\(K_{\text{em, calcined}}\) \(\) Relative dielectric constant for a bed of calcined material \([\text{–}]\)
\(K_{\text{em, carbonated}}\) \(\) Relative dielectric constant for a bed of calcined material \([\text{–}]\)
\(K_{\text{em, mix}}\) \(\) Relative dielectric constant of the emulsion phase in fluidised bed \([\text{–}]\)
\(n_{\text{calc}}\) \(\) Overall mass of the calcined sample \([\text{mass}]\)
\(n_{\text{carb}}\) \(\) Overall mass of the carbonated sample \([\text{mass}]\)
\(MW\) \(\) Molecular weight \([\text{mass}/\text{mole}]\)
\(N\) \(\) Cycles of carbonation/calcination \([\text{–}]\)
\(P_{\text{CO}_2}\) \(\) Partial pressure of \(\text{CO}_2\) \([\text{pressure}]\)
\(R^2\) \(\) Coefficient of determination \([\text{–}]\)
\(T\) \(\) Temperature \([\text{temperature}]\)
\(u_g\) \(\) Superficial gas velocity \([\text{length}/\text{time}]\)
\(u_{\text{mf}}\) \(\) Minimum fluidisation velocity \([\text{length}/\text{time}]\)
\(V\) \(\) Voltage \([\text{electric potential}]\)
\(V_{\text{calcined}}\) \(\) Voltage for a bed of calcined material \([\text{electric potential}]\)
\(V_{\text{carbonated}}\) \(\) Voltage for a bed of carbonated material \([\text{electric potential}]\)
\(V_{\text{th, mix}}\) \(\) Theoretical voltage for a mix of calcined/carbonated material \([\text{electric potential}]\)
\(V_N\) \(\) Voltage in absence of solid \([\text{electric potential}]\)
\(x\) \(\) Absolute granulometric fraction \([\text{–}]\)
\(x_{\text{av}}\) \(\) Average absolute granulometric fraction \([\text{–}]\)
\(x_{\text{CaO}}\) \(\) Mass fraction of CaO in the calcined sorbent \([\text{–}]\)
\(X\) \(\) Degree of carbonation \([\text{–}]\)
\(X_{\text{CaO}}\) \(\) Average degree of carbonation \([\text{–}]\)
\(\Delta H_r\) \(\) Reaction enthalpy \([\text{energy/mole}]\)
\(\epsilon\) \(\) Voidage degree for a bed of limestone \([\text{–}]\)
\(\epsilon_{\text{calcined}}\) \(\) Voidage degree for the calcined material \([\text{–}]\)
\(\epsilon_{\text{carbonated}}\) \(\) Voidage degree for the carbonated material \([\text{–}]\)
\(\epsilon_{\text{em, mix}}\) \(\) Voidage degree for a mix of calcined/carbonated material \([\text{–}]\)
\(\epsilon_{\text{pN}, 0\quad 1}\) \(\) Porosity of particle in its calcined form at stage \(N - 1\) \([\text{–}]\)
\(\epsilon_{\text{pN}, \text{calcined}}\) \(\) Porosity of particle in its calcined form at stage \(N\) \([\text{–}]\)
\(\epsilon_{\text{pN}, \text{carbonated}}\) \(\) Porosity of particle in its carbonated form at stage \(N\) \([\text{–}]\)
\(\rho\) \(\) Bulk density \([\text{mass}/\text{volume}]\)
\(\rho_{\text{av}}\) \(\) Average bulk density \([\text{mass}/\text{volume}]\)
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