

ATTRITION OF LIMESTONE DURING CO₂ CAPTURE IN A FLUIDIZED BED CALCIUM LOOPING PROCESS

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Abstract

Attrition of a limestone during calcium looping cycles for CO₂ capture was studied in a lab-scale fluidized bed apparatus. Batch experiments under alternating calcination-carbonation conditions were carried out to investigate the effect of chemical reactions and temperature changes on the attrition propensity of the sorbent particles. Attrition processes were characterized by following the modifications of bed sorbent particle size distribution and the elutriation rates of fines throughout conversion over repeated cycles. Different bed temperatures and CO₂ inlet concentrations were tested in the experiments.

Results show that relatively large attrition rates were experienced by the sorbent particles only during the first cycle. From the second cycle on the attrition rate progressively declines, also during the calcination stage where the softer CaO is produced. It is inferred that the combined chemical-thermal treatment affects the particle structure making it increasingly hard. At the same time the CO₂ capture capacity decays toward an asymptotic level, possibly related to the very same structural modifications. Bed temperature and CO₂ concentration both appear to influence the sorbent behavior in the tests.

Introduction

The increase of CO₂ concentration in the atmosphere is recognised as the main responsible for global warming [1]. Power plants firing fossil fuels represent the most important source of CO₂ emissions. A promising way for reducing such emissions is to separate CO₂ from flue gas to produce a concentrated CO₂ stream ready for sequestration. In general, there are three possible approaches to CO₂ capture: post-combustion, pre-combustion and oxy-fuel [2–4]. In a post-combustion process, CO₂ is separated from the flue gas by absorption with organic solvents such as monoethanolamine or by reaction with solid particles such as lime (CaO) [5]. The main advantage of the post-combustion process with respect to the others, is the possibility to easily retrofit existing plants.

Recently, several experimental activities have been reported on CO₂ capture using Ca-based looping cycles in fluidized bed systems [6–8]. The process is based on the reversible exothermic carbonation reaction:



The carbonation reaction proceeds with a satisfactory rate at temperatures in the range 650–700°C, while the reverse calcination reaction is carried out at 850–950°C. The calcium oxide sorbent, typically derived from natural limestone, is repeatedly cycled between two reactors (Fig. 1). In one reactor (the carbonator) carbonation of CaO particles occurs, capturing CO₂ from the flue gas. The sorbent particles are then circulated to another reactor (the calciner) where calcination takes place. The regenerated CaO particles are returned to the carbonator, leaving a concentrated stream of CO₂ ready for sequestration.

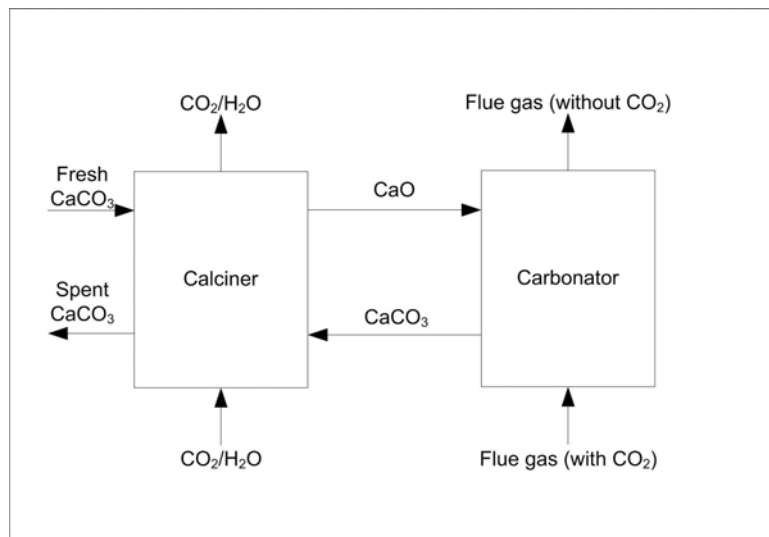
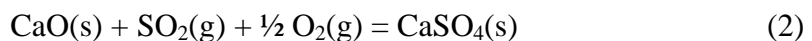


Figure 1. Typical scheme of a calcium looping process.

The typical reactor configuration for the calcium looping process consists of two interconnected fluidized beds. This configuration permits the circulation of the solids between the reactors and ensures an intimate contact between the solid and gas phases. The fluidizing gas in the carbonator is the flue gas coming from the combustion process, while the fluidizing gas in the calciner may be either CO_2 recycled from the outlet gas, or a $\text{CO}_2/\text{H}_2\text{O}$ mixture that enables a lower temperature in the calciner.

In an early work Barker [9] studied the effect of repeated cycles of carbonation and calcination of limestone and found that the CO_2 capture capacity of the sorbent decreased with the number of cycles. This result has been more recently confirmed by other authors [10–12]. The main cause of this decrease has been identified in sorbent sintering and in the associated changes of pore size, which depends on the process temperature and on the duration of the cycles. The CO_2 capture capacity of the fresh sorbent decreases quickly during the first cycles until an asymptotic value is reached, which then remains approximately constant over many cycles.

Another problem is represented by the possible presence of SO_2 in the flue gas, which reacts with lime to form CaSO_4 according to the following sulphation reaction:



A sulphated external layer is formed that hinders the diffusion of CO_2 in the pores and affects the mechanical properties of the material [6,11,13]. Unfortunately, reaction (2) is irreversible in the temperature range of interest so that the lime reacted with SO_2 is permanently lost. This reaction further reduces the CO_2 capture capacity of the sorbent.

In a fluidized bed reactor limestone particles are also subjected to attrition phenomena. Several studies on limestone attrition during calcination and sulphation in fluidized beds have been reported in the literature [14–17]. Three attrition/fragmentation mechanisms were identified: primary fragmentation, secondary fragmentation and attrition by abrasion. Primary fragmentation occurs immediately after injection of the particles in the hot reactor, as a consequence of thermal stresses due to fast heating of the particles and of internal overpressures due to CO_2 release upon calcination. It results in the generation of both coarse and fine fragments. Secondary fragmentation and attrition by abrasion are determined by the mechanical stresses due to collisions among particles and with the internals of the reactor.

Table 1. Chemical and physical properties of Massicci limestone.

Mineralogical analysis	100% calcite
<i>Chemical composition:</i>	
CaCO ₃	96.8%
MgCO ₃	2.4%
Others	0.8%
Loss on ignition (CO ₂)	43.9%
<i>Physical characteristics:</i>	
Porosity (initial rock)	6.15%
Porosity (after calcination)	38.0%
Surface area (initial rock)	0.247 m ² g ⁻¹
Surface area (after calcination)	10.5 m ² g ⁻¹
Density (initial rock)	2.42 g cm ⁻³
Density (after calcination)	1.65 g cm ⁻³

These phenomena can be classified on the basis of the typical size of the generated fragments: secondary fragmentation generates coarser fragments, while attrition by abrasion generates finer ones. In the context of the calcium looping process, particle attrition determines a net calcium loss from the circulating loop, as elutriable fines leaving the cyclone with the gas stream. This loss of material adds to sorbent deactivation and contributes to the required make-up of fresh sorbent.

The aim of this work was to study CO₂ capture by simulating the calcium looping process with repeated calcination/carbonation cycles in a lab-scale bubbling fluidized bed. The focus of this activity was to quantify the extent of particle attrition during the cycles and the effect of chemical reactions on the sorbent mechanical resistance. The influence of the calcination temperature and environment on sorbent attrition and CO₂ capture capacity was also investigated.

Experimental

Materials and experimental set-up. The raw sorbent used in the tests was an Italian high-calcium limestone, commercially referred to as Massicci, whose properties are given in Table 1. Gases used in the tests were either air or a mixture of CO₂ and air.

The experiments were carried out in a stainless steel bubbling fluidized bed reactor, 40 mm ID operated at atmospheric pressure (Fig. 2). The reactor consists of three sections: a) the preheater/premixer of the fluidizing gas, 0.66 m high; b) the fluidization column, 0.95 m high; c) the brass two-exit head placed on top of the reactor with a hopper to feed the solids in the reactor and connected with the exhaust line. The gas distributor is a perforated plate with 55 holes of 0.5 mm diameter in a triangular pitch. The reactor is electrically heated with two semi-cylindrical ovens placed around the upper part of the preheater/premixer and the lower part of the fluidization column. A type-K thermocouple, placed at 40 mm above the gas distributor, allows to measure the reactor temperature. The thermocouple is connected with a PID temperature controller which controls the electrical power supply for the ovens. The two-exit head is used to convey flue gases through either of two cylindrical sintered brass filters, whose filtration efficiency is 1 for >10 μm-particles. Alternated use of the filters enables time-resolved capture of elutriated fines at the exhaust. Fluidizing gases are supplied to the reactor by means of two mass flow meters/controllers. Downstream of the two-exit head, a fraction of the exhaust gas is continuously sampled to measure CO₂ concentration with a NDIR analyzer in order to monitor the progress of reactions. Concentration signals are logged on a PC at a sampling rate of 1 Hz.

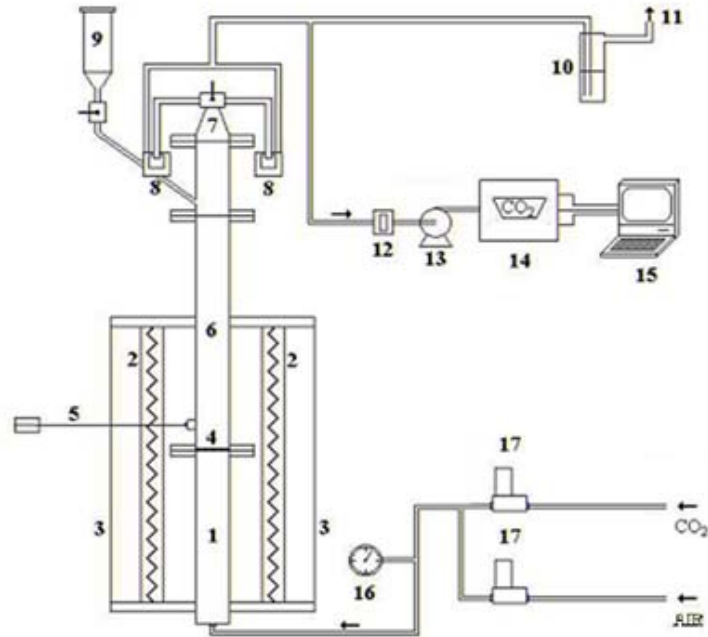


Figure 2. Experimental apparatus. (1) gas preheating/premixing section; (2) electrical furnaces; (3) ceramic insulator; (4) gas distributor; (5) thermocouple; (6) fluidization column; (7) two-exit head; (8) sintered brass filters; (9) hopper; (10) SO₂ scrubber; (11) stack; (12) cellulose filter; (13) membrane pump; (14) gas analyzer; (15) personal computer; (16) manometer; (17) mass flow meter/controller.

Procedure. Five calcination/carbonation cycles were carried out in all the experiments using an initial amount of 20 g of fresh limestone, sieved in the range size 0.4-0.6 mm. The bed consisted of 150 g of silica sand in the range size 0.85-1.0 mm and the fluidizing velocities were 0.7 and 0.6 m/s in the calcination and in the carbonation stages, respectively. The operating conditions of the experiments are given in Table 2.

Before each test the reactor was charged with the silica sand and heated up to the desired temperature (either 850°C or 900°C). When the set temperature was reached, the limestone particles were injected in the reactor by means of the hopper. After injection, the sorbent underwent rapid heating from ambient temperature to the reactor temperature, resulting in a thermal shock. The progress of calcination was followed during the run by measuring the CO₂ concentration at the exhaust. The run ended when calcination was complete. At this point the bed was rapidly discharged and cooled down. The sand was separated from the limestone by sieving and re-injected in the fluidized bed reactor. The temperature of the bed was then set to the carbonation temperature (700°C). When the new temperature was reached the carbonation reaction was started by fluidizing the bed with a mixture of air and CO₂ (16% v/v), and injecting the calcined sorbent particles through the hopper. The progress of carbonation was followed during the run by measuring the CO₂ concentration at the exhaust. Again, the run ended when carbonation was complete. The bed was rapidly discharged and cooled down (in 100% CO₂ to avoid possible calcination). The procedure described before was then repeated in all the cycles. The same duration of the first calcination stage was used for the successive calcination stages, and the same criterion was applied for the duration of the carbonation stages (Table 2).

Table 2. Operating conditions of the calcination/carbonation experiments.

Calcination/Carbonation	Condition 1	Condition 2	Condition 3
Duration [min]	15/15	35/15	20/15
Temperature [°C]	850/700	850/700	900/700
Inlet CO ₂ [% v/v] (balance air)	0/16	20/16	44/16

During the experiments the rates of fines generation were determined by measuring the amount of fines carried over by the fluidizing gas and elutriated from the reactor. Elutriated fines were collected by means of the two-exit head previously described by letting the flue gas flow alternately through sequences of filters for definite time periods. The difference between the weight of filters after and before operation, divided by the time interval during which the filter was in operation, gave the average fines elutriation rate (E) relative to that interval.

Particle size distribution (PSD) of the sorbent was determined by sieving the bed material, after each calcination and carbonation stage. The sieving operation was carried out gently to avoid further comminution of the particles, but rapidly, because of the propensity of the calcined sorbent to absorb moisture when in contact with ambient air.

The CO₂ capture capacity of the sorbent during the carbonation stage was evaluated from the CO₂ concentration profile at the exhaust. The total amount, by mass, of CO₂ uptaken during the experiment, divided by the initial amount of limestone (20 g), gave the sorbent capture capacity.

Two calcination temperatures were tested (850°C and 900°C). At these temperatures, the CO₂ equilibrium pressures for the calcination reaction are estimated to be 0.5 atm and 1.1 atm, respectively [6]. The CO₂ partial pressures during calcination in experiments in conditions 2 and 3 (Table 2) were chosen so as to obtain the same ratio between the partial pressure and equilibrium pressure, and consequently the same driving force for the calcination reaction. Experiments in condition 1 were conducted by calcining the limestone in air (0% CO₂). For all tests the inlet CO₂ concentration during the carbonation stage was set at 16% v/v (balance air), in order to simulate CO₂ concentrations in realistic flue gases.

Results and discussion

CO₂ capture capacity. Figure 3 reports the sorbent capture capacity as a function of the number of cycles, for the three conditions investigated. As expected, the capture capacity decreases with the number of cycles towards an asymptotic value. It is noted that the highest capture capacity was obtained in condition 1, i.e. when calcination was carried out in air. In condition 2 (calcination in 20% CO₂) a slightly lower capacity was found during all the cycles. A possible explanation for this result lies in the experimental evidence that the presence of CO₂ during calcination enhances sintering [18]. A higher calcination temperature (condition 3) determines a significant fall in the capture capacity at each cycle. This result underlines the important role of the thermal history of the sorbent particles. Again, this behaviour can be explained by an enhancement of sintering at higher temperature. It is also interesting to note that in this case the capture capacity reaches a plateau already after the fourth cycle.

Particle size distribution. Figure 4 reports the particle size distributions (PSD) of the limestone during a test in condition 1. The PSD was evaluated after every calcination and carbonation stage, but in the figure only the PSDs after the first calcination, the third carbonation and the fifth carbonation were plotted, for clarity, since all the other PSDs were very similar to each other.

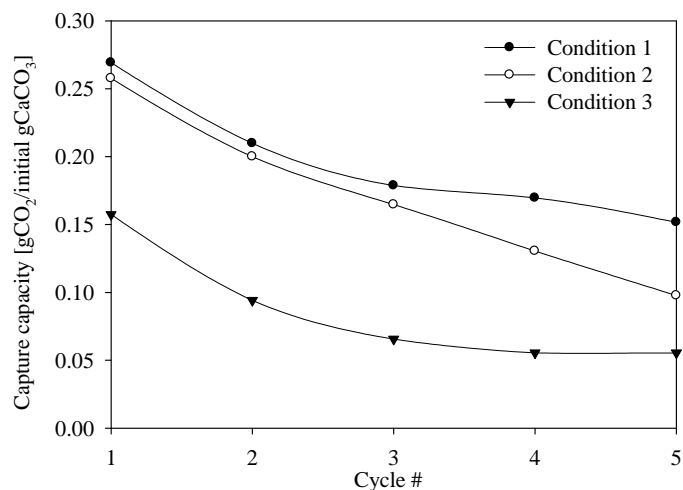


Figure 3. CO₂ capture capacity of the sorbent as a function of the number of cycles for the three experimental conditions investigated (Table 2).

It can be noted that the PSD does not change appreciably during the cycles, indicating a limited occurrence of particle fragmentation. Indeed, the qualitative features of the PSD after the first calcination remain approximately constant after the following cycles. The only significant difference is the amount of fines (<100 μm) appearing after the first calcination that was not found in the following cycles. This result is more evident in the figure at right, where the PSD refers only to particles (fragments) with a size below the initial feeding size range. Generation of fines is mostly due to particle rounding off of the fresh particles during the first calcination [14]. When rounding off is complete, less fines are generated by attrition, as it will be shown in the following section.

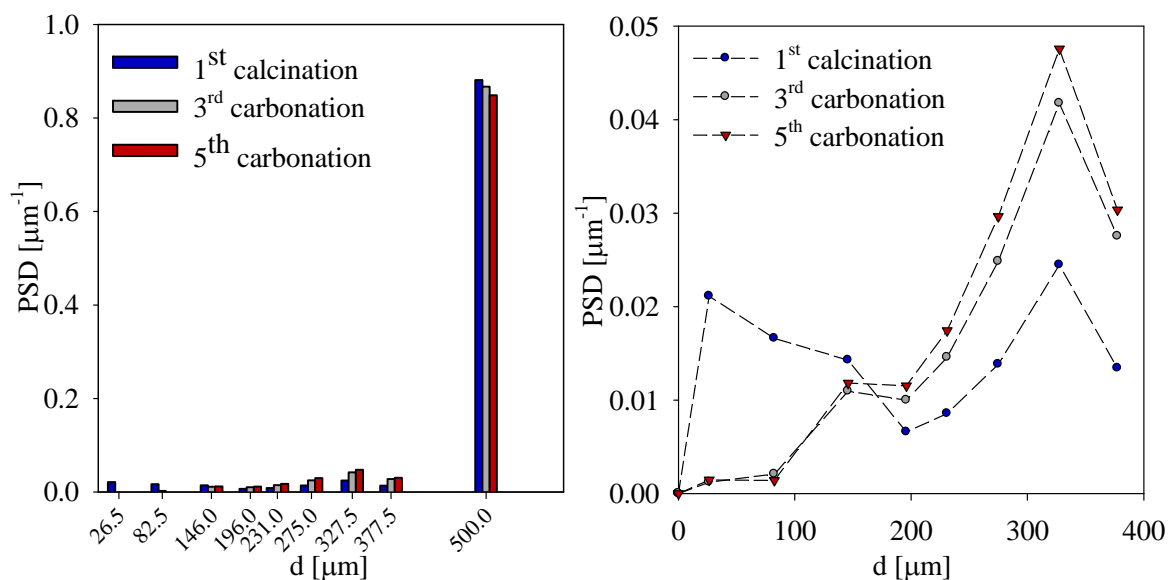


Figure 4. Particle size distribution of the sorbent during a test in condition 1 (Table 2), after 1st calcination, 3rd carbonation and 5th carbonation. Left: complete PSD. Right: PSD for particles with a size below 400 μm (fragments).

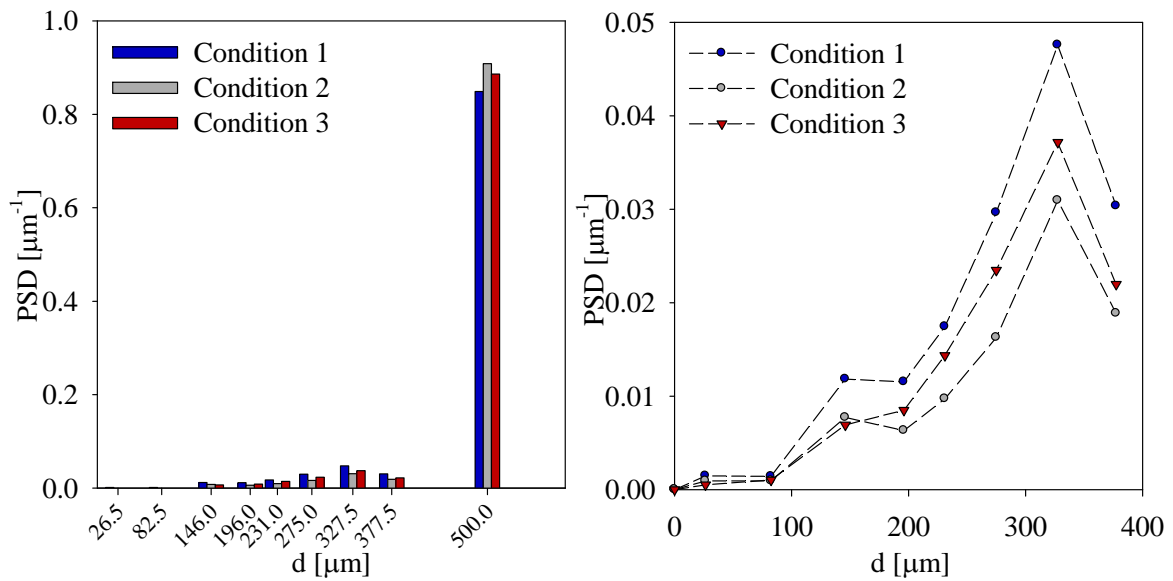


Figure 5. Particle size distribution of the sorbent during tests in all experimental conditions investigated (Table 2), after 5th carbonation. Left: complete PSD. Right: PSD for particles with a size below 400 μm (fragments).

Tests carried out under the other two experimental conditions showed the same qualitative trend. Fig. 5 compares the measured PSDs of the sorbent particles after the fifth carbonation in tests under the three operating conditions investigated. It can be observed that all the PSD curves have a similar shape, with only slight differences in the amount of produced fragments. Altogether, analysis of the PSD curves indicates that, irrespective of the operating conditions, only limited particle fragmentation occurs and the PSD remains approximately constant over the cycles.

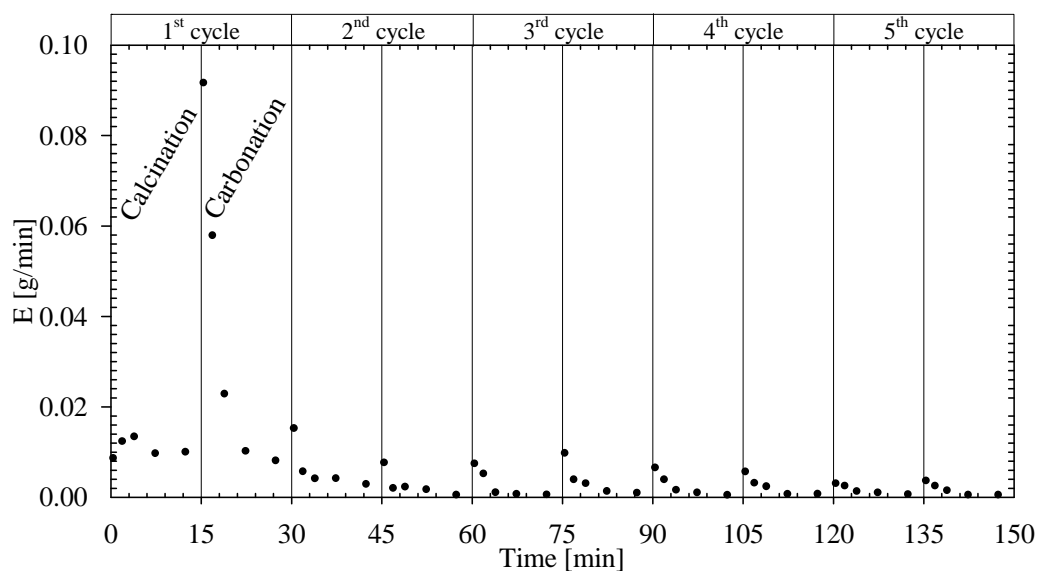


Figure 6. Sorbent elutriation rate as a function of time during alternated calcinations and carbonations for a test in condition 1 (Table 2).

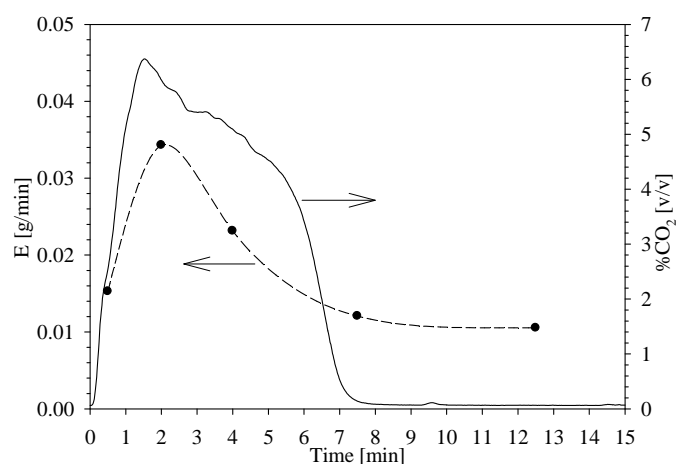


Figure 7. Sorbent elutriation rate and measured CO₂ outlet concentration as a function of time during the 1st calcination stage for a test in condition 1 (Table 2).

Elutriation rate. Figure 6 reports the fines elutriation rate (E) as a function of time, measured in a test carried out in condition 1. Similar results were obtained in the other two conditions. As a general trend, it is noted that the fines elutriation rate decreases with the number of cycles. This suggests that hardening of the particle surface takes place over the cycles, which is consistent with the progressive sintering of the sorbent. In each cycle the elutriation rate shows a typical trend with a peak of fines generation at the beginning. This peak is caused by a combination of the following effects: rounding off of the rough particles [14] and thermal shock after injection in the hot bed. During calcination, a further process is the rapid release of CO₂ that causes overpressures inside the particles and may change the mechanical properties of the solid. Figure 6 shows a remarkable feature: during the first calcination the elutriation rate shows a slightly different trend with a peak shifted to about 2 min after the beginning of the test. This behaviour was not observed in tests carried out under conditions 2 and 3, where CO₂ was present in the inlet gas stream and calcination was slower (Table 2). This finding suggests that the peak might be related to the large rate of CO₂ release during calcination in condition 1. Fig. 7 reports the measured fines elutriation rate and CO₂ concentration at the exhaust during the first calcination stage in condition 1. The figure clearly shows that the peak of the elutriation rate occurs approximately at the same time as the CO₂ concentration peak.

Fig. 8 (A–C) reports the total amount of fines (E_{tot}) collected during each calcination and carbonation stage as a function of the number of cycles. In all conditions the amount of fines decreases with the cycle number. When considering that the calcination stages have a different duration under the different experimental conditions (Table 2), the average fines elutriation rate is approximately the same during the calcination and the carbonation stages. The largest amount of fines was obtained in the tests carried out in condition 1 (Fig. 8A). Fines generation was much smaller under condition 2 (Fig. 8B), where the only difference was the presence of 20% CO₂ in the fluidizing gas during calcination. This behaviour is most likely due to the absence of CO₂ during calcination in condition 1, that determines on the one hand a fast release of CO₂ and a consequent higher overpressure in the particles, on the other hand a less pronounced sintering. When the calcination temperature is increased at 900°C (condition 3, Fig. 8C), a larger amount of fines was collected when compared with results obtained under condition 2. Again, this behaviour should be related to the faster release of CO₂ due to the higher temperature, and possibly to a more pronounced thermal shock.

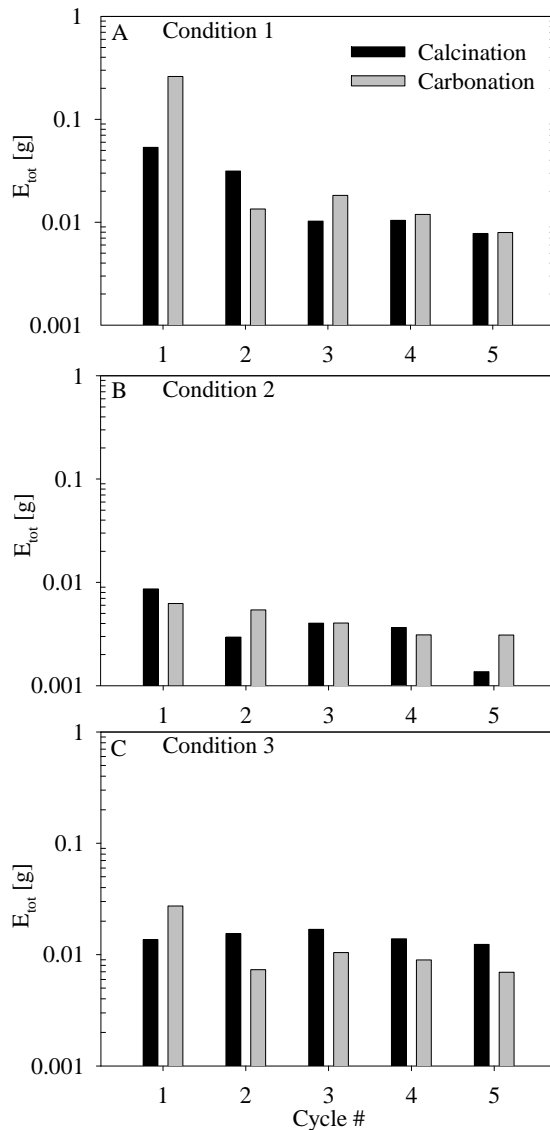


Figure 8. Total amount of elutriated fines as a function of number of cycles in each calcination and carbonation stage for the three conditions investigated (Table 2).

Conclusions

The CO₂ capture capacity and the attrition propensity of an Italian limestone have been assessed under cyclic calcination/carbonation conditions in a bubbling fluidized bed reactor. In particular, the effects of the calcination temperature and of the CO₂ partial pressure during the calcination stage have been investigated. Results showed that the limestone exhibited the typical decrease of the uptake capacity with increasing number of cycles. The presence of CO₂ during calcination and especially a higher calcination temperature determine a decrease of sorbent capacity for all the cycles, most likely due to the enhancement of particle sintering. The analysis of PSD of bed material over repeated calcination/carbonation cycles indicated that particle fragmentation was very limited in all the conditions investigated. The fines elutriation rate was relatively large during the first cycle and decreased with the number of cycles. The presence of CO₂ during calcination led to a significant decrease of fines generation, while a higher calcination temperature produced an increase of the particle attrition rate. These results may be explained by the competition of two opposed effects: on

the one hand sintering brings about hardening of the particle surface; on the other side a faster release of CO₂ leads to higher internal overpressures and, in turn, to increased propensity to particle breakage.

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