Role of particle size on the multicycle calcium looping activity of limestone for thermochemical energy storage

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Highlights

- Thermal energy performance of narrow particle size distribution limestones is studied.
- Multicyclic activity is better for small particles under all the different studied conditions.
- This effect is particularly relevant for particles smaller than 15 μm median particle size.
- Particle size effect is not relevant for particles between 15 and 900 μm.

Abstract

The calcium looping process, based on the reversible reaction between CaCO₃ and CaO, is recently attracting a great deal of interest as a promising thermochemical energy storage system to be integrated in Concentrated Solar Power plants (CaL-CSP). The main drawbacks of the system are the incomplete conversion of CaO and its sintering-induced deactivation. In this work, the influence of particle size in these deactivation mechanisms has been assessed by performing experimental multicycle tests using standard limestone particles of well-defined and narrow particle size distributions. The results indicate that CaO multicycle conversion benefits from the use of small particles mainly when the calcination is carried out in helium at low temperature. Yet, the enhancement is only significant for particles below 15 μm. On the other hand, the strong sintering induced by calcining in CO₂ at high temperatures makes particle size much less relevant for the multicycle performance. Finally, SEM imaging reveals that the mechanism responsible for the loss of activity is mainly pore-plugging when calcination is performed in helium, whereas extensive loss of surface area due to sintering is responsible for the deactivation when calcination is carried out in CO₂ at high temperature.

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Despite increasing effort in developing environmentally friendly technologies based on renewable energy sources, fossil fuel power plants still account for a significant share of the overall energy mix. Thus, greenhouse gas emissions from this type of facilities are still at unacceptable levels [2]. The main alternative renewable energy sources to replace fossil fuel power plants are wind and solar. Nonetheless, these technologies share an important shortcoming in their inability to provide a constant energy supply due to the intrinsic intermittency of wind and sunlight. Concentrated solar power plants (CSP) offer the possibility of integrating grid energy production with large-scale thermal energy storage (TES) thereby achieving dispatchability [3,4]. TES systems in commercial CSP plants include steam accumulators and high specific heat molten salts [4–6]. However, storing the heat produced by direct solar radiation as chemical energy entails several advantages [7,8]. For instance, the long-term storage of the products without radiative heat losses becomes possible. At the same time, the continuous energy consumption required to maintain the salts in molten state is avoided [9]. Finally, Current molten salts are limited to about 560 °C to avoid degradation, thereby limiting the maximum attainable efficiency [10]. Achieving higher temperatures could boost the efficiency of the thermodynamic power cycle as the difference between charge and discharge temperatures becomes larger [8,11]. Finally, exergy efficiency is enhanced due to the larger energy densities provided by reaction enthalpies as compared to sensible and latent heats [8,12,13]. Among several chemical looping alternatives, the calcium looping (CaL) process has attracted a great deal of interest as a very promising system for thermochemical energy storage (TCES) since it displays several advantages such as low cost, high reaction temperature, acceptable reversibility and high energy density [14–16].

In the last decades, the CaL process has been explored as an avenue to mitigate CO₂ emissions in fossil fuel power plants and cement manufacture facilities since it constitutes an effective technology for CO₂ capture and storage (CCS). The CaL process is based on the reversible calcination of CaCO₃ into CaO [17]:

\[
\text{CaCO}_3(s) = \text{CaO}(s) + \text{CO}_2(g) \quad \Delta H^0 = 178 \text{ kJ mol}^{-1}
\]  

(1)

This reaction has been widely studied since it is a fundamental step in cement production. Thus, it is relatively feasible to establish the optimum conditions for direct and reverse reaction depending on the application. CaCO₃ is inexpensive and abundant in the form of different minerals (limestone, marble, dolomite, etc) [18,19]. It exhibits a high reaction enthalpy that allows for a high theoretical energy density, ranging from 1 to 4 GJ/m³ depending on the author and estimation method [12,13,20]. In the last years, several schemes regarding the integration of the CaL process in CSP plants (CaL-CSP) [14,21–23]. These contemplate the calcination of CaCO₃ using direct solar radiation as heat source. Solar radiation can impinge directly on the storage material or it can be used to heat up the external walls of a solar particle receiver [14,24]. Stored energy is recovered through the reverse exothermic solid–gas reaction between CaO and CO₂ at higher temperatures in the carbonator. Excess CO₂ out of the carbonator is then circulated to power a CO₂ turbine and produce electricity on demand. The high temperature of the working gas would ensure higher efficiency as compared with that of TES plants [16].

The CaL process exhibits two significant drawbacks that penalize its large-scale implementation, the incomplete conversion of CaO and its progressive deactivation along the successive carbonation/calcination cycles [14,25]. The decay in CaO conversion is generally attributed to the extensive sintering and loss of surface area that occur at the high temperature and high CO₂ partial pressure required [26–28]. Moreover, it has been observed that, when calcination is carried out in inert gas, a blocking CaCO₃ layer rapidly forms on the CaO particles surface during the subsequent carbonation. This pore-plugging layer severely hinders further diffusion of CO₂ molecules and prevents achieving complete conversion [29–31]. Therefore, the optimum conditions for CSP storage would be those that maximize the discharge temperature in order to improve the efficiency of the thermodynamic cycle while avoiding excessive sorbent deactivation. Recent studies have shown that can be achieved by carrying out the calcination at the lowest possible temperature in inert gas, and the carbonation at the maximum attainable temperature in CO₂, normally about 950 °C [32,33]. However, pressurized carbonation (at ~3 bars) would allow to further extend the maximum carbonation temperature [16,34].

Being one of the relevant challenges to overcome towards making the CaL-CSP technology attractive at industrial level, a number of strategies have been devised to reduce CaO deactivation. Thus, it is well known that crystallinity [35], particle size [18,36], morphology [37,38] and the inclusion of additives [19,39] have a strong influence on Ca-based multicycle performance. Regarding the impact of particle size, it has been observed that large or highly crystalline particles exhibit substantially slower decarbonation kinetics, thereby requiring higher temperatures for the complete regeneration of CaO in short residence times [40]. Additionally, carbonation in large particles is hindered by pore diffusion and pore-plugging [30,41,42]. On the other hand, small particles exhibit faster calcination at lower temperatures, what eventually results in improved long term recyclability [18]. Moreover, the use of small particles would facilitate the integration with solar energy and decrease the cost in materials for constructing the solar receiver [43]. However, small particles are difficult to handle in industrial processes based on fluidised bed reactors. Trajectories and residence times of particles in cyclones strongly depend on their size while collection efficiency decays markedly for particles with sizes below 10 μm [44,45]. Thus, the usual particle size lower limit to ensure an acceptable efficiency of cyclones is about 50 μm. Overall, the optimum particle size in pilot plants based on fluidised bed reactors has been found to lie within the 100–300 μm range [46,47].

Despite its importance, the influence of particle size in CaL-CSP has yet to be explored in sufficient detail since most published works use material with very wide particle size distributions. In this study, multicycle CaL-CSP experiments have been carried out using limestone sample sets with well-defined particle sizes, ranging from small 4-μm particles to large 900-μm particles. At the same time, Scanning Electron Microscopy (SEM) has been used to observe the morphological changes undergone by the material during consecutive carbonation and calcination cycles, in order to assess the mechanism responsible of the loss of activity. The results herein shed light on the relationship between particle size, extent of conversion after each cycle and deactivation after repeated carbonation and calcination cycles. Two different CaL-CSP operation schemes have been considered. First, the calcination stage is carried out in helium (CSP-He) as originally conceived in [32]. This procedure takes advantage of the high thermal conductivity of helium and the high diffusivity of CO₂ in this gas to favour the calcination process so that full decarbonation is achieved in short residence times at temperatures as low as 700–750 °C. However, use of helium at industrial scale entails technical issues such as high cost, gas losses and the necessity of gas separation from CO₂ after calcination. Thus, the tests have also been carried out using an alternative operation scheme in CO₂ closed cycle. This second integration scheme would be less complicated to implement technically but would entail raising the calcination temperature up to 950 °C.
Table 1
PSD data of limestone samples. Adapted from [48].

| Sample | d_{10} | d_{50} | d_{90} | (d_{90}-d_{10})/d_{50} |
|--------|--------|--------|--------|------------------------|
| KO2    | 0.78   | 2.22   | 4.15   | 1.52                   |
| KO4    | 1.6    | 4.42   | 8.25   | 1.50                   |
| KO15   | 12     | 19     | 28     | 0.84                   |
| KO30   | 21     | 30     | 43     | 0.73                   |
| KO80   | 39     | 71     | 106    | 0.94                   |
| KO900  | 738    | 938    | 1148   | 0.44                   |

Experimental

Materials

The samples used in this work were limestone from standard Eskal series supplied by KSL Staubtechnik GmbH (Germany). The Eskal series are widely used in powder technology studies as standards for calibration of equipment and testing. Particle size distributions were determined by laser diffraction as reported in [48]. Five different samples with a well-defined average particle size were studied (2, 4, 15, 30 and 80 μm). An additional sample with larger particle size, ranging from 700 to 1000 μm, was also tested. Samples will be referred hereafter as KO2, KO4, KO15, KO30, KO80 and KO900. PSD data are listed in Table 1 while frequency distributions of particle sizes for all samples are plotted in Fig. 1.

Methods

Multicycle calcination/carbonation tests were carried out in a TA instrument Q5000IR TG analyzer equipped with a IR furnace composed of a SiC reaction chamber heated by IR lamps that allows high cooling and heating rates up to 300 °C min⁻¹. Such rates are necessary to emulate realistic Cal conditions in which the material is rapidly circulated between carbonator and calciner at different temperatures. All tests were run using small sample masses (≈10 mg) in order to avoid interfering mass and heat transfer phenomena as well as to facilitate exchanges with the surrounding atmosphere. The reaction chamber has a volume of just 20 cm³.

According to process simulations, the maximum efficiency in CaL-CSP plants, not considering pressurized conditions, is achieved when the carbonation reaction takes place in a high CO₂ concentration environment at about 850 °C [16]. Considering this, the samples were tested according to the energy storage conditions described below:

CSP-He

CSP-He experiments begin with a calcination step (from room temperature to 750 °C at 300 °C min⁻¹) under He atmosphere followed by a 5-min isothermal stage. After this first calcination, carbonation is initiated in pure CO₂ atmosphere by increasing the temperature at a rate of 300 °C min⁻¹ up to 850 °C, and keeping this temperature for 5 min. Then, a new calcination stage is triggered by reducing the temperature at 300 °C min⁻¹ down to 750 °C under He, followed by 5-min isotherm. An intermediate step is introduced after calcination by decreasing the temperature down to 300 °C under He for 2 min. This stage is intended to simulate the extraction of sensible heat from reaction products after calcination. After this cooling step a new cycle is started, for a total of 20 carbonation/calcination cycles.

CSP-CO₂

CSP-CO₂ experiments begin with a precalcination stage (from room temperature to 950 °C at 300 °C min⁻¹, held for 5 min) in high CO₂ concentration (95% CO₂/5% air vol/vol). Precalcination is followed by a carbonation stage without changing the atmosphere by quickly decreasing the temperature down to 850 °C at 300 °C min⁻¹ and maintaining this temperature for 5 min. A total of 20 carbonation/calcination cycles were run in these tests.

SEM micrographs of gold-sputtered samples (40 mA, 30 s) were taken employing a Hitachi S4800 FEG microscope at 5 kV. Nitrogen adsorption–desorption isotherms were measured using an ASAP2420 (Micromeritics) instrument. Samples degassing was carried out at 300 °C for 2 h. Total surface areas (S_{BET}) were determined using the BET equation. In order to prepare the amount of sample needed for BET measurements, a tubular furnace was employed. Samples were prepared in small batches (300 mg of CaCO₃ at a time) to minimize mass and heat transfer phenomena during the calcination and carbonation reactions. The experimental schemes were similar to that described in B.1 and B.2 but calcination times had to be extended to 30 min to ensure complete decarbonation.

Results and discussion

Multicycle conversion

Fig. 2 shows, as an example, the complete thermograms recorded in the multicycle tests in both CSP-He and CSP-CO₂ conditions for the KO30 sample. The main implication of the latter conditions is that calcination temperature needs to be raised up to 950 °C in order to achieve complete decarbonation within the scheduled 5-min step, as compared to just 750 °C required when helium is used as carrier gas. Fig. 3 includes a detail of the 1st, 10th and 20th cycles, highlighting the differences in the fast kinetic-driven and diffusion driven carbonation phases depending on particle size and operation scheme. It has been amply reported that the carbonation in Cal processes proceeds through two well differentiated stages [42]; first a rapid reaction controlled phase that depends on CaO available surface which is abruptly followed by a much slower diffusion controlled phase that triggers once a barrier layer composed of CaCO₃ product forms, hindering further diffusion of CO₂ molecules [49]. The diffusion controlled stage becomes rate-limiting step once the CaCO₃ product layer reaches the critical value that depends on reaction conditions [31]. Fig. 3 illustrates the influence of particle size, cycle number and operation scheme on the relative importance of fast reaction-
controlled and slow diffusion-controlled carbonation stages. It can be inferred from the plots in Fig. 3a and b that in CSP-He the carbonation reaction is mainly determined by the fast reaction regime, with negligible CO₂ uptake during the subsequent diffusion-controlled stage. This behaviour serves to highlight the pore-plugging phenomenon, since the rapid formation of a blocking CaCO₃ layer limits further CO₂ diffusion to the porous interior of the particle. Therefore, in CSP-He conditions, the conversion at each cycle depends mostly on the extension of the carbonation achieved during the fast stage since the relative contribution of diffusion-controlled carbonation is very small. In contrast, the relative contribution of each carbonation phase differs in CSP-CO₂. As shown in Fig. 3c and d, in CSP-CO₂ the weight of diffusion-controlled carbonation is much more relevant. The extension of the reaction-controlled stage during the first recarbonation is roughly independent of the particle size save for the largest KO900 particles, which displays an unusual behaviour that might be related to its substantially slower decarbonation kinetics. However, the diffusion-controlled regime is promoted in smaller particles. Finally, Fig. 3d shows a marked decrease of the reaction-controlled carbonation with the cycle number. After 10 cycles, the carbonation is mainly diffusive, what implies that the CaO is heavily sintered (Fig. 3d). Another important issue, illustrated in Fig. 4, is decarbonation kinetics. The measured reaction rate is much faster when calcining at CSP-CO₂ conditions due to the higher employed temperatures.

The CaO conversion (X) is used to quantitatively compare the performance of different materials and reaction conditions. This parameter provides a measure of the extension of the reaction at any given cycle. It is defined as the ratio of the mass of CaO converted in the carbonation stage of each cycle to the total CaO mass before carbonation [50]. In order to extrapolate at long term and determine the residual conversion after a large number of cycles,
the conversion plots can be fitted by the following semi-empirical equation [26,50]:

\[ X_N = X_r + \left( \frac{X_1}{K(N-1) + (1 - \frac{X_1}{K})} \right) \]

(2)

where \( X_r \) is the residual conversion, which converges asymptotically after a large number of cycles, \( K \) is the so-called deactivation constant, \( X_1 \) is the conversion at the first cycle and \( X_{20} \) the conversion at the 20th cycle. Best fitting parameters are included in Table 2. In summary, the data show that conversion achieved in CSP-He is in all cases higher than the conversion achieved in CSP-CO₂. However, the difference in residual conversion, the really relevant parameter for industrial purposes, is only significant for KO₂ and KO₄; the two smaller particle sizes tested.

Influence of particle size and reaction conditions on sample morphology

In order to gain a better understanding of the influence of particle size on multicycle performance, the morphological changes undergone during carbonation and calcination stages have been

**Table 2**

CaO conversion values (at 1st, 20th and residual conversion) and deactivation constants for limestone samples at CSP-He and CSP-CO₂ conditions. \( \Delta X_r \) is the difference in residual conversions estimates for each particle size and conditions employed.

| Sample  | KO2  | KO4  | KO15 | KO30 | KO80 | K0900 |
|---------|------|------|------|------|------|-------|
| Calcination Conditions | He   | CO₂  | He   | CO₂  | He   | CO₂  | He   | CO₂  | He   | CO₂  | He   | CO₂  |
| \( X_1 \) | 0.79 | 0.63 | 0.78 | 0.66 | 0.72 | 0.63 | 0.73 | 0.61 | 0.74 | 0.59 | 0.53 | 0.64 |
| \( X_{20} \) | 0.62 | 0.23 | 0.50 | 0.22 | 0.31 | 0.20 | 0.26 | 0.17 | 0.24 | 0.15 | 0.24 | 0.14 |
| \( X_r \) | 0.55 | 0.17 | 0.42 | 0.16 | 0.20 | 0.14 | 0.15 | 0.12 | 0.15 | 0.08 | 0.15 | 0.07 |
| \( \Delta X_r \) | 0.38 | 0.44 | 0.37 | 0.41 | 0.29 | 0.48 | 0.30 | 0.56 | 0.42 | 0.41 | 0.32 | 0.56 |
| \( K \) | 0.37 | 0.44 | 0.37 | 0.41 | 0.29 | 0.48 | 0.30 | 0.56 | 0.42 | 0.41 | 0.32 | 0.56 |

**Fig. 4.** Comparison of the decarbonation rate of KO80 sample measured at the 4th cycle under both CSP-He and CSP-CO₂.

**Fig. 5.** CaO conversion (X) as a function of the cycle number (N) for CaL tests of limestone of different particle sizes carried out at CSP-He (a) and CSP-CO₂ (b) conditions. Solid lines correspond to best fits of Eq. (2) to the experimental data.
structure after the initial carbonation (Fig. 7e), the subsequent carbonation stage leads to the rapid formation of a CaCO\(_3\) blocking layer preventing the diffusion of CO\(_2\) molecules to the interior of the particle. Subsequent calcination and carbonation stages eventually lead to the progressive sintering of the surface layer, which is ultimately the only part of the particle that undergoes repeated transformations. Fig. 7g and h show the porous core underneath the sintered surface created by the pore-plugging effect after 20 calcination and carbonation cycles. The grain growth and sintering occur mainly during the calcination stage as it is promoted by CO\(_2\). Actually, both KO2 and KO80 samples (Fig. 7b and f) evidence considerable grain growth even after the first recarbonation, with the formation of a mosaic structure, comprised of about 1 \(\mu\)m grains covering the entire particle surface. Therefore, the limited grain size observed underneath the external sintered layer in Fig. 7g and h proves the inner core has remained inactive during the cycles. In the inset of Fig. 7h, a fracture is shown to emphasize the marked differences between the surface CaCO\(_3\) shell and the inner unreacted CaO core. It should be noted that the inset in Fig. 7h was taken using identical magnification as the main image to better highlight the disparity in grain sizes. Finally, it is interesting how the conversion of CaCO\(_3\) into CaO exhibits a shape-memory feature; the shades of the previous CaCO\(_3\) grains are apparent in subsequent CaO (Fig. 7g). This shape-memory feature preserves the blocking layer along the carbonation and calcinations cycles and facilitates further sintering, leading to the progressive decay in CaO conversion.

The relationship between these morphological transformations and the multicycle behavior described is Fig. 5a is clear. The relevance of the pore-plugging effect depends on particle size; the larger the size, the higher the volume of material that remains inactive underneath the plugging layer. Hence the limited CaO conversion exhibited by the larger particle sizes in the multicycle tests. For smaller particles, a greater fraction of the material contributes to conversion each carbonation stage. Furthermore, the CaO arising from the calcination of the mosaic-like sintered structure shows a significant loss of surface porosity (Fig. 7g) with respect the starting material (Fig. 7a) leading to a decay in CaO conversion along ensuing cycles. Table 3 includes the BET surface area values measured for KO2 and KO80 samples after one calcination and after 5 carbonation and calcinations cycles. As expected, there is a reduction in surface area because of sintering after a few cycles. Surface available for carbonation decreases about 30% in the case of the small KO2 particles whereas the reduction reaches 50% for the larger KO80 particles. That difference can be attributed to the formation of the sintered surface layer. It is also interesting that the surface area for all 4 samples studied is quite similar after the first calcination.

### CSP-CO\(_2\)

As it will be discussed hereafter, sample behaviour is remarkably different when cycled in CSP-CO\(_2\) conditions, due to the harsher calcination conditions; pure CO\(_2\) and a high temperature of 950 °C. The overall effect on the multicycle conversion is a worsening of cycling performance with respect to CSP-He conditions, especially in the case of smaller particles. The sequence shown in Fig. 8a–d illustrate how small KO2 particles cycled in CSP-CO\(_2\) conditions endure progressive aggregation, eventually leading to the formation of a macroporous structure constituted of merged neighbouring grains. Also, while in CaCO\(_3\) form, well developed grains in mosaic structures are clearly distinguished. However, the morphology of subsequent CaO exhibits striking features that contrast with what previously observed in CSP-He. Instead of preserving the mosaic structure attained by CaCO\(_3\) grains in the preceding carbonation stage, CaO arising in CSP-CO\(_2\) conditions constitutes a macroporous globular structure containing large
channels. Moreover, no differences in morphology were observed between the surface and the interior of the particles. Thus, it seems that pore-plugging phenomenon is not that relevant in this CSP-CO₂ operation scheme as the formation of macroporous channels largely prevents the particles to be completely covered by the clogging carbonate layer. This arrangement is a consequence of the high temperatures attained, well over CaCO₃ Tamman temperature (about 500 °C), that strongly promote mass transfer by solid state diffusion [52]. That, coupled with the grain-growth promoting effect of CO₂ lead to extensive sintering all over the entire particle volume. In the case of samples with small average size, neighbouring particles merge as seen in Fig. 8c and 8d. After 20 carbonation and calcination cycles, the loss of surface area is substantial as observed in the insets of Fig. 8c and g. The surface of the CaO

![Image of SEM micrographs illustrating morphology changes during carbonation and calcination cycles in CSP-He conditions for limestone samples KO2 and KO80.](image)

Fig. 7. SEM micrographs illustrating morphology changes during carbonation and calcination cycles in CSP-He conditions for limestone samples KO2 and KO80. (a) KO2 CaO after first calcination; (b) KO2 CaCO₃ after the first recarbonation; (c) KO2 CaO after 20 cycles; (d) KO2 CaCO₃ after 20 cycles; (e) KO80 CaO after first calcination; (f) KO80 CaCO₃ after the first recarbonation; (g) KO80 CaO after 20 cycles and (h) KO80 CaCO₃ after 20 cycles. 
appears smooth (Fig. 8d and h) in contrast with the cracked surface evidenced in samples cycled in CSP-He (Fig. 7d and h). The progressive loss of micro and mesoporosity in CaO formed under CSP-CO₂ after repeated cycling might explain the reduction in relative weight of the fast reaction-controlled carbonation in relation to the diffusion-controlled carbonation. Besides, as illustrated in Fig. 4, decarbonation rate is at least five times faster at 950 °C in CO₂ than at 750 °C in helium. Sudden release of occluded gases in short times within a high mobility matrix might induce the for-

Table 3

| Sample   | S BET (m²/g) | 1 calcination | 5 carb/calc cycles |
|----------|--------------|---------------|--------------------|
| KO2-He   | 14.9         | 10.2          |
| KO2-CO₂  | 11.3         | 6.8           |
| KO80-He  | 16.3         | 8.5           |
| KO80-CO₂ | 15.3         | 3.9           |

Fig. 8. SEM micrographs illustrating morphology changes during carbonation and calcination cycles in CSP-CO₂ conditions for limestone samples KO2 and KO80. (a) KO2 CaO after first calcination; (b) KO2 CaCO₃ after the first recarbonation; (c) KO2 CaO after 20 cycles; (d) KO2 CaCO₃ after 20 cycles; (e) KO80 CaO after first calcination; (f) KO80 CaCO₃ after the first recarbonation; (g) KO80 CaO after 20 cycles and (h) KO80 CaCO₃ after 20 cycles.
mation of a globular-like or foamy structure, as it has been observed in a somewhat different systems, such as the pyrolysis of rice husk to form SiO₂ [53]. Contrary to what occurs in the case of CSP-He, under CSP-CO₂ operation conditions there is little advantage in using small-sized particles since the extensive sintering and particle merging rapidly destroy the relatively open structure displayed in CSP-He (Fig. 7b and d). Table 3 also includes the BET surface area values measured for KO2 and KO80 samples after one calcination and after 5 carbonation and calcination cycles in these experimental conditions. As it occurred in the previous CSP-He conditions, the decline in surface area after 5 consecutive carbonation and calcination reactions is more marked in larger particles, amounting to 75% and 40% for KO80 and KO2 samples respectively.

Conclusions

In this work, the influence of particle size on limestone multicycle chemical looping conversion has been studied under operation conditions relevant for thermochemical energy storage applications. Experimental multicycle tests have been carried out using calcination in helium at relatively low temperatures and calcination at high temperatures in 100% CO₂. Limestone particles of well-defined and narrow particle size distributions have been employed in the analysis. When calcination is carried out in helium at low temperature, the CaO conversion is substantially better for small particles as they are more resilient to pore-plugging, the main deactivation mechanism in CSP-He. Nevertheless, the enhancement is only substantial for particles below 15 μm, which might be difficult to employ in industrial applications involving fluidised bed reactors. Over that size, the formation of a blocking CaCO₃ layer on the particles surface prevents further diffusion of CO₂ to the inner particle core. Thus, a substantial volume of material remains inactive during the carbonation stage thereby limiting CaO conversion. On the other hand, when calcination is carried out in CO₂ at high temperatures, the deactivation of the material can be attributed to severe sintering all over the entire particle volume and the loss of surface porosity. Consequently, the improvement in conversion achieved by using particles with small average size is very limited. For particle sizes over 15 μm, the multicycle performance is relatively similar regardless the operation conditions. Thus, the CSP-CO₂ scheme of closed loop might be more advantageous for techno-economic reasons due to the high cost of helium and the simplicity of design. It has also been found that the carbonation process in CSP-He is mostly driven by fast kinetically controlled reaction while in CSP-CO₂ conditions solid-state diffusion has a relevant contribution. The residual CaO conversion attained in our experiments for particle-size usable at industrial level is still below 0.4, the critical value to make the technology competitive with respect to molten salts. Nevertheless, the sequence of morphological changes here presented brings valuable insight into the deactivation mechanism and can provide researchers a guide regarding the type of macroporous structures to be sought in order to minimise the sorbent deactivation.

Compliance with ethics requirements

This article does not contain any studies with human or animal subjects.

Declaration of Competing Interest

The authors have declared no conflict of interest.

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