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Thermal Activation of CaO-Based Sorbent and Self-Reactivation during CO₂ Capture Looping Cycles

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In this study, the thermal activation of different types of CaO-based sorbents was examined. Pretreatments were performed at different temperatures (800—1300 °C) and different durations (6—48 h) using four Canadian limestones. Sieved fractions of the limestones, powders obtained by grinding, and hydroxides produced following multiple carbonation/calcination cycles achieved in a tube furnace were examined. Pretreated samples were evaluated using two types of thermogravimetric reactors/analyzers. The most important result was that thermal pretreatment could improve sorbent performance. In comparison to the original, pretreated sorbents showed better conversions over a longer series of CO₂ cycles. Moreover, in some cases, sorbent activity actually increased with cycle number, and this effect was especially pronounced for powdered samples preheated at 1000 °C. In these experiments, the increase of conversion with cycle number (designated as self-reactivation) after 30 cycles produced samples that were ~50% carbonated for the four sorbents examined here, and there appeared to be the potential for additional increase. These results were explained with the newly proposed pore—skeleton model. This model suggests, in addition to changes in the porous structure of the sorbent, that changes in the pore—skeleton produced during pretreatment strongly influence subsequent carbonation/calcination cycles.

Introduction

Climate change, due in large measure to the use of fossil fuels, is a key problem that requires urgent solutions. Power plants that use fossil fuels are among the main emitters of CO₂, and reduction of their emissions may significantly decrease total emissions of greenhouse gases to the atmosphere. One possible approach is the separation of CO₂ from flue gas followed by its sequestration in a wide range of geological formations or perhaps on the ocean floor (*1–3*).

CO₂ looping cycles, which employ a solid CaO-based carrier, represent an important new class of technology that may inexpensively and effectively remove CO₂ from combustion or gasification gases, allowing it to be regenerated as a pure CO₂ stream suitable for use or, more likely, for sequestration (*4*). The use of solids also means that, in many cases, fluidized bed combustion (FBC) systems will represent optimal technology for such processes (*5–7*) since they permit

large amounts of solids to be transferred easily from one chemical environment to another (*8*). The deployment of such technologies has the added advantage that both large (>350 MWe) atmospheric and pressurized systems also exist (*9, 10*), and so the technical challenges of developing such systems for a number of possible looping cycle schemes are significantly reduced. Preliminary economic analyses (*11–13*) suggest that such processes are economically attractive, and an important advantage of using CaO is that limestone (CaCO₃) is abundant and a relatively inexpensive material when used at the industrial scale.

The process is based on the reversible chemical reaction

$$CaO + CO_2 = CaCO_3 \qquad (1)$$
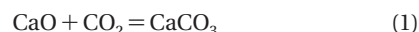
However, despite the simple chemistry, there are some restrictions to such processes related to the kinetics and thermodynamics of the reactions, along with undesirable side reactions such as sulfation and processes such as attrition and sintering. At atmospheric pressure, practical carbonation takes place in a narrow temperature window of 650—700 °C. At lower temperatures, the reaction rate is too slow for practical use. At higher temperatures, the capture efficiency decreases following the chemical equilibrium, which can be described by the equation $\log_{10} P_{CO_2}[atm] = 7.079 - (8308/T[K])$ (*14*) (i.e., the equilibrium concentration of CO₂ for the CaO/CaCO₃ system becomes too high). For regeneration, this equilibrium limits the minimum temperature (>900 °C) for fast calcination, in the presence of a nearly pure CO₂ stream. Flue gas from fossil fuel combustion typically contains SO₂, which under CO₂ looping cycle conditions irreversibly reacts with CaO, forming CaSO₄. A portion of CaO sorbent is, therefore, lost as CaSO₄, and more importantly, the CaO reaction surface is covered by this product, preventing the contact of CaO and CO₂ with a resulting rapid decrease of capture capacity (*15, 16*). Attrition of sorbent is a significant problem for FBC systems (*17*), leading to significant sorbent elutriation from the reactor, and this was confirmed in our first pilot-scale demonstration of the CO₂ looping cycle using a dual FBC reactor (*18*).

However, the major and most investigated challenge for CO₂ looping cycles is the decrease of reversibility for the carbonation reaction due to sorbent sintering (*19, 20*). During such cycles, the sorbent morphology changes, and the sorbent loses surface area and small pores, which are the main contributors to the rapid carbonation necessary for practical systems. The most important variable that determines sorbent activity decay is the number of reaction cycles, and this is the key parameter in empirical models describing the change in carbonation levels (*21, 22*). Other parameters such as temperature, duration of carbonation and calcination, sorbent type, and sorbent particle size are much less important in comparison to the number of calcination/carbonation cycles (*23, 24*).

Improvement of sorbent activity for extended use of sorbents in commercial plants is imperative since sorbent replacement strongly influences the cost of a Ca looping cycle process (*13*). Doping of sorbent by additives (*25, 26*) and hydration of spent sorbent (*15, 26, 27*) have been examined to see if they can improve sorbent reversibility, and current research shows that steam hydration in combination with the use of reactivated sorbent for SO₂ removal (perhaps in a separate reactor) may represent a promising method (*28, 29*) for improving the performance of such cycles. Recent work (*24*) has shown that, under certain conditions, the sorbent can "remember" a cycling history and pretreat-

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ment by physical methods. In this work, we present a new method for the enhancement of sorbent properties that includes activation by grinding and thermal treatment. A combination of these two pretreatments leads to the emergence of a remarkable new behavior for lime-based sorbent—increase of activity with increasing calcination/carbonation cycles—which we have called self-reactivation.

Materials and Methods

Four Canadian limestones were used in the experiments: Kelly Rock (KR), Cadomin (CD, formerly called Luscar), Graymont (GR), and Havelock (HV). The crushed limestone samples were sieved, three particle sizes of KR were tested here (75–150 μm (KR01), 300–425 μm (KR02), and 600–750 μm (KR03)), and particle sizes between 250 and 425 μm were used in the experiments with other limestones. The results of X-ray fluorescence (XRF) elemental analyses and data on BET pore surface area and BJH pore volume distributions for particle size fractions investigated were published in our earlier papers (15, 28, 29). Experiments were performed with original particle size fractions, with powders following grinding as well as with "spent" samples from CO_2 looping cycles after their reactivation.

The tests were made in two (atmospheric) thermogravimetric analysis (TGA) instrument/reactors: a Cahn Model C-1100 TGA instrument and a PerkinElmer TGA-7. Samples used for examination in a Cahn Model C-1100 TGA instrument were pretreated in a tube furnace (TF). Three types of pretreatment were carried out for the three particle size fractions of KR limestone: (i) During 20 CO_2 cycles, samples (2 g of calcined sample) were carbonated by 20% CO_2 (N_2 balance) for 30 min and calcined for 30 min under 100% N_2. The temperatures during calcination and carbonation were 850 and 650 °C, respectively, and gas flows were 1250 cm^3/min. (ii) Samples (4 g of original sample) were heated (sintered) for 24 h in 100% N_2 (1000 cm^3/min) at 1100 °C. (iii) Samples were calcined for 2 h at 850 °C in 100% N_2, sulfated at 850 °C for 2 h using synthetic flue gas (15% CO_2, 3% O_2, 1% SO_2, and N_2 balance), and cycled in the same manner as for samples i. Two carbonation cycles in the TGA instrument with pretreated sorbents were performed; each cycle was typically 40 min (10 min calcination at 850 °C and 30 min carbonation at 700 °C). Gas flow was 400 cm^3/min: 100% N_2 for calcination and 15% CO_2 (N_2 balance) for carbonation. The sample mass was monitored, and the degree of carbonation was calculated on the basis of observed mass changes, assuming that mass changes were only due to the formation/decomposition of $CaCO_3$. More details about TF pretreatment and TGA equipment and experiments are given elsewhere (15).

The samples examined in a PerkinElmer TGA-7 were pretreated in the TGA instrument and directly after pretreatment cycled in the same TGA run. The pretreatment involved heating at different temperatures (800–1300 °C) for different durations (6–48 h) in an atmosphere of nitrogen. Experiments were made with four limestone samples using original particle size fractions and powders (<50 μm) produced by grinding of the original particle size fractions and also with a sample of KR limestone that had undergone multiple TF CO_2 looping cycles followed by steam hydration. Samples were cycled at 800 °C (isothermally) after pretreatment. Carbonation was carried out for 30 min in 50% CO_2 (N_2 balance), and calcination was carried out for 10 min in 100% N_2. Gas flows, controlled by a flowmeter, were 40 cm^3/min. The sample (30 mg) was suspended in a quartz tube (i.d. of 20 mm) on a platinum pan (i.d. of 5 mm). The temperature and gas used were controlled by Pyris software. The data were monitored, and the degree of carbonation was calculated on the basis of mass changes.

(i)

(ii)

(iii)
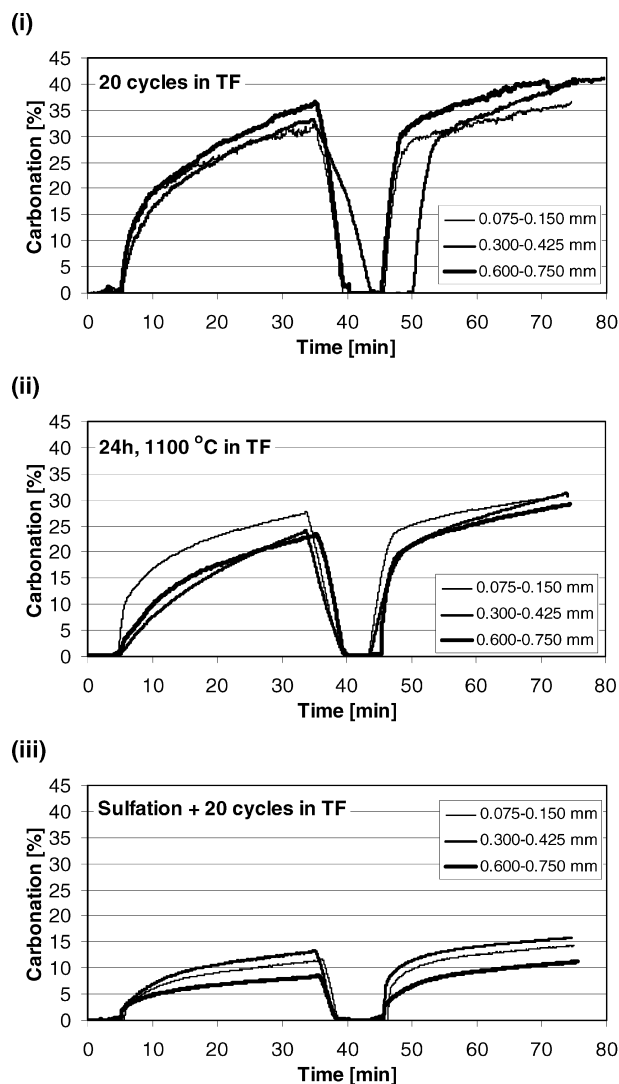
FIGURE 1. Increase of sorbent activity (KR limestone) after pretreatments in TF: (a) 20 CO_2 looping cycles, (b) sintering for 24 h at 1100 °C, and (c) sulfation and 20 CO_2 looping cycles.

Results and Discussion

Results on carbonation rates during the first two cycles in the Cahn Model C-1100 TGA are presented in Figure 1. It can be seen that the three different pretreatments in the TF (Figure 1a: CO_2 looping cycles b: sintering; and c: sulfation) resulted in sorbents with quite different behavior during the first two CO_2 cycles as compared to those shown for the original sorbents. Typically, conversion in the second cycle was ~5% higher than conversion in the first cycle. This result is surprising; normally, sorbents lose activity with increasing numbers of calcination/carbonation cycles. The shape of the carbonation curves for the two cycles is qualitatively different. In the first cycle, there is no obvious transition between the first, fast stage (limited by kinetics of the chemical reaction) and the subsequent, slow stage (limited by diffusion through the product layer of $CaCO_3$). Moreover, in the second cycle, after a shift to the slow stage, the carbonation rate is not negligible as is typical for natural sorbents.

The results presented in Figure 1 indicate that the enhancement of sorbent activity with increasing cycles may also be possible with other sorbent modifications. The phenomenon of increased sorbent activity (i.e., increase of maximum conversions) with increased cycle number is called self-reactivation. It should be noted that a recent study (24)
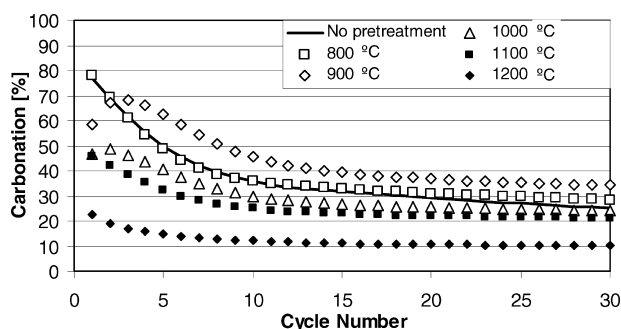
FIGURE 2. Preheating of original particle size fractions for 24 h at different temperatures and the influence on sorbent behavior in subsequent CO_2 cycles.
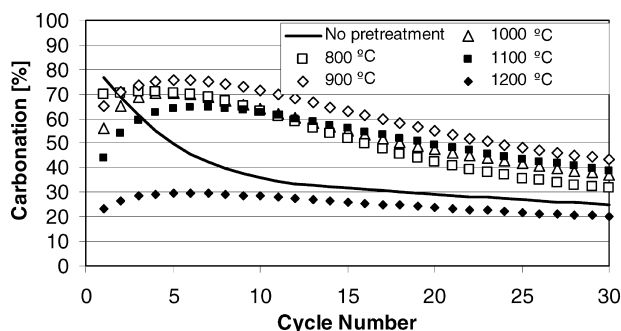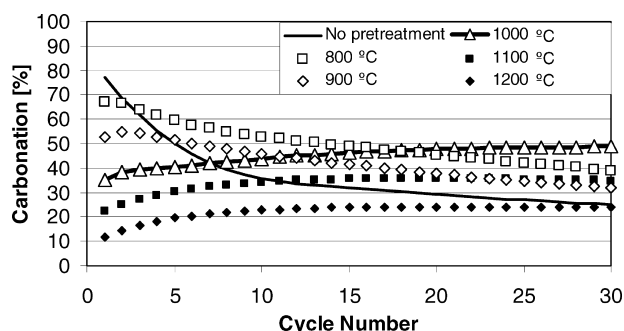

FIGURE 3. Carbonation conversions of KR samples (KR02) spent in 20 CO_2 cycles in TF, hydrated by steam, and preheated for 24 h at different temperatures.

FIGURE 4. Carbonation conversions of KR samples (KR02) powdered and preheated for 24 h at different temperatures.

FIGURE 5. Carbonation conversions of KR samples (KR02) powdered and preheated for 6 h at different temperatures.

also showed a beneficial effect of prolonged exposure of sorbent to calcination conditions under nitrogen.

In the PerkinElmer TGA-7 experiments, thermal pretreatment of a sorbent sample and subsequent CO_2 cycles were carried out during one TGA run to avoid other influences on the sample (i.e., reactions with atmospheric moisture and/ or CO_2) in the interim.

Figure 2 shows the influence of temperature during pretreatment in an atmosphere of nitrogen for 24 h. Here, the sorbent pretreated at 800 °C had similar carbonation properties to those of the original sorbent with no pretreatment. For the pretreated sorbent, a somewhat better activity was noted after the 20th cycle, while a sample treated at 900 °C had ∼20% lower conversion in the first cycle than for the original sample. However, conversion for the pretreated sample increased and in the third cycle was ∼8% higher than that of the original sample. In subsequent cycles, conversion was typically at least 10% greater than that for the original untreated sorbent. Pretreatment of the original samples did not show a significant self-reactivation effect but did indicate that a sorbent with better conversions in later cycles can be produced. Importantly, such pretreatment resulted in a sorbent with better mechanical properties (i.e., resistance to attrition), which is critical in FBC systems (17). Increasing the temperature to above 900 °C resulted in a decreased activity in the initial cycles, which stabilized at a relatively constant level in the later cycles. However, the maximum temperature of interest for practical use was about 1100 °C because at 1200 °C the resulting sorbents showed very low conversions, ∼10%.

Hydrated sorbent samples had better conversions (15) than the original samples, and this also was confirmed in this work (Figure 3). Additionally, preheating hydrated samples modifies their conversions during cyclic carbonation. Heat pretreatment at 800 °C has no noticeable effect, but with an increased temperature, carbonation conversions are significantly modified. Experiments performed with samples pretreated at higher temperatures show significant effects of
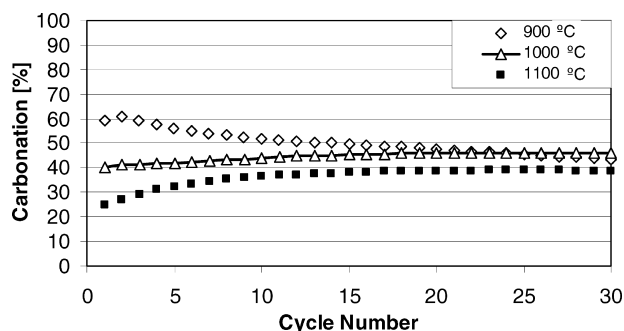
self-reactivation for the initial 6−7 cycles when conversions increase. Beyond this point, the decrease in activity is less pronounced, resulting in higher conversions in comparison to those seen for samples preheated at 800 °C or the original samples after hydration. It is also important to note that the falloff of conversions with calcination/carbonation cycles is lower for preheated samples. In this case, 1200 °C may be a promising temperature because conversions are >20% and showed little change during the next 30 cycles.

Perhaps the most interesting result is seen for powdered samples (<50 μm), presented in Figure 4. It can be seen that, for preheat temperatures ≥1000 °C, self-reactivation occurred for the entire next 30 cycles. The highest conversions were obtained at 1000 °C, for which 49% carbonation was achieved in the last cycle, with a mean value ∼45% for 30 cycles; this is very good for a natural sorbent that has not been chemically modified. These results (Figure 4) suggest that self-reactivation will continue in subsequent cycles (i.e., conversions will additionally increase). Lower conversions are obtained for samples pretreated at 1100 and 1200 °C, but given the effect of self-reactivation, these results are also interesting, especially if sorbent preheating at these temperatures (in combination with pelletization) results in better mechanical properties that could prevent undesirable attrition.

It was expected that the duration of pretreatment (along with temperature) would be an important parameter; thus, tests were performed for 6 h with powdered samples pretreated at 900, 1000, and 1100 °C (Figure 5). The same self-reactivation was obtained after 6 h of heat pretreatment; however, 24 h pretreatment produced only small differences. All three runs with 6 h pretreated samples began with higher conversions. The final (30th cycle) conversion for 1000 °C was higher for 24 h of pretreatment, while that for 900 and 1100 °C was higher for 6 h of pretreatment. Results obtained with samples pretreated for 6 h confirmed that the duration of pretreatment affected sorbent properties for CO_2 capture and that shorter time periods are effective, which may be important in practice.

The finding that a natural CaO-based sorbent may be modified by heat pretreatment to obtain increased conver-
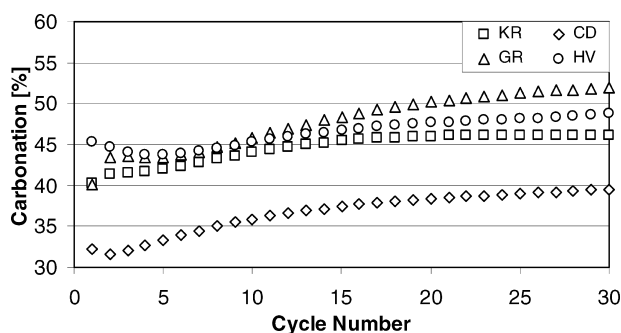
FIGURE 6. Carbonation conversions of four investigated limestones powdered and preheated for 6 h at 1000 °C.
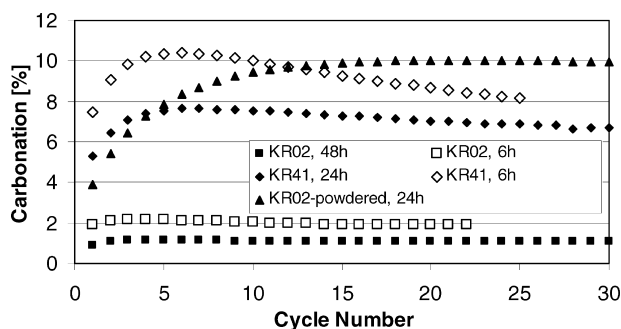
FIGURE 7. Influence of deep sintering (1300 °C, different durations) of CaO-based sorbents on their activity for CO_2 capture.

FIGURE 8. Schematic representation of proposed pore–skeleton model.

sions in longer series of cycles was supported by tests with three more limestones, and results are given in Figure 6. The original time-conversion curves are interesting, and they can be seen in Figures S1–S4 of the Supporting Information. CD limestone displayed ~10% lower conversions than the other samples, but the effect of self-reactivation was obvious for all limestones tested here. The conversion of GR limestone exceeded 50% in the 20th cycle and reached 52% in the 30th cycle with a tendency for further increase. Testing of samples in a longer series of cycles also would be interesting. However, in practice, the benefits associated with a longer series of cycles can be expected to be somewhat limited because it is difficult to avoid the negative effects on the sorbent after long exposure to a SO_2-containing atmosphere that can be expected in a real system.

To better understand the influence of heat pretreatment of CaO-based sorbents, tests also were carried out under extreme conditions (1300 °C), and results are presented in Figure 7. Here, the original samples (KR02) treated at 1300 °C for 6 and 48 h had conversions of 1 and 2%, respectively. These conversions were practically constant with increasing cycles, indicating no self-reactivation. Somewhat better conversions were obtained for hydrated and powdered samples but did not significantly exceed 10%. These results suggest that sorbent particles were strongly sintered and that carbonation occurred most likely only at the external particle surface.

The results presented in this paper show that sorbents can remember their thermal history, which can have a negative influence on behavior in carbonation/calcination cycles—this effect can be explained by sintering and a decrease of pore surface area. The favorable influence of sorbent thermal pretreatment and the effect of sorbent self-reactivation cannot easily be explained by considering sintering and pore distribution change models. For example, it is expected that exposure of sorbents to high temperatures leads to the formation of larger pores and the elimination of smaller pores, resulting in lower carbonation conversions. It is also interesting that, after a long series of cycles, sorbents
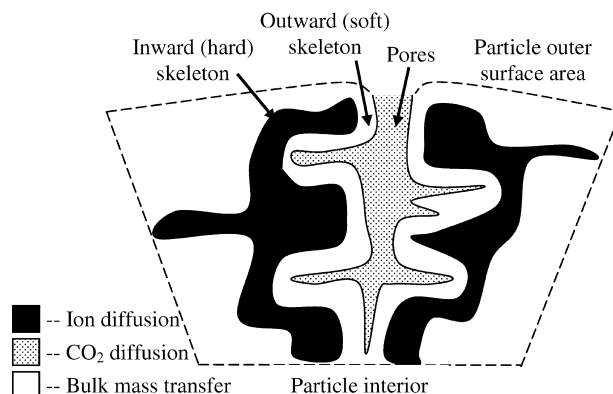
displayed final asymptotic conversions of 7–8% (23), while the original sorbent treated here at 1300 °C showed only 1–2% conversion, regardless of the number of reaction cycles. A somewhat different performance and higher conversions were obtained with powdered samples and with samples kept in the TF for over 20 cycles (see pretreatment i in the Materials and Methods), for example, KR41, which was hydrated before being heated at 1300 °C. This also demonstrates that, along with its thermal history, the sorbent can remember its physical (grinding) and chemical (hydration) pretreatments.

To explain our results, we propose that sorbent skeleton changes need to be considered (along with pore size changes) as these occur during calcination/carbonation cycling (30, 31). During cycling, two different types of mass transfer in the sorbent particles must occur in parallel: bulk diffusion connected to the formation/decomposition of $CaCO_3$ and ion diffusion in the crystal structure of CaO. Ion diffusion in CaO stabilizes its crystal structure but with no significant effect on particle morphology and corresponding carbonation conversions (24). Bulk mass transfer occurred during formation and decomposition of $CaCO_3$, and this led to major changes of morphology (i.e., to sintering and loss of small pores and sorbent activity). During CO_2 cycles, competition occurred between ion diffusion and bulk mass transfer, and two types of structure or skeleton were formed (i.e., an internal unreacted structure and an external structure in which carbonation/calcination proceeded). The internal skeleton can be considered as a hard skeleton that stabilizes and protects the particle morphology (i.e., its pore structure). The external structure or skeleton can be considered to be a soft skeleton that easily changes during $CaCO_3$ formation and decomposition, resulting in changes of particle morphology. Here, it should be noted that the terms internal and external skeleton are not related to the particle but to the pores: outer or external means that this part of the skeleton is exposed to pores and surrounded by the gas that fills pores. A schematic representation of the proposed pore–skeleton model is presented in Figure 8.

The presented model can explain the loss of sorbent activity with cycle number, activation of sorbent by heat treatment (better conversions in later cycles), self-reactivation, and other experimental data as well as data presented in the literature and cited here. Like other models, this model predicts that, as a result of CO_2 cycles, pore size distribution changes and that smaller pores transform into larger ones, leading to a loss of pore surface area and loss of activity.

During thermal pretreatment of sorbents, bulk diffusion occurs only during calcination, but when the decomposition of $CaCO_3$ is completed, ion diffusion continues, which leads to skeletal structure stabilization and the formation of a hard

skeleton. In parallel, a loss of pore surface area occurred, but such effects are less significant; however, they become more important as the pretreatment temperature is increased. At temperatures that are not too high (1200−1300 °C), the sorbent morphology is not totally destroyed. The porous structure with the hard skeleton is capable of significant carbonation. In the initial cycles, the reaction rate is slower, usually seen because the hard skeleton is less reactive—ion diffusion necessary for carbonation is more difficult in that type of skeleton because it is a more stable structure. In subsequent cycles, the outward or external (soft) skeleton is formed, which accelerates the carbonation rate. An increase of conversion with cycle number occurs because the soft part of the skeleton grows. At the same time, the inward hard skeleton keeps the particle morphology stable (i.e., reduction of sorbent surface is prevented). Moreover, the smooth surface area obtained during thermal pretreatment may be transformed during repeated carbonation/calcination cycles, also leading to increased conversions. The conversion for one sorbent after infinite cycles is the consequence of the competition between ion diffusion (formation of hard skeleton) and bulk mass transfer (sintering), which resulted in the formation of the final morphology with a stable skeleton that determines conversions.

The results presented here can have practical applications because they show that the thermal pretreatment of a sorbent can lead to better performance in a longer series of cycles. As a result of the self-reactivation effect, the sorbent activity can increase, which is also important for practical applications. The best results were obtained with the powdered sorbent, which implies that pelletization would be required for FBC systems. Only 30 cycles were examined here because we expect that under real conditions, the sorbent most likely would not survive more cycles due to sulfation and/or attrition losses.

Supporting Information Available

Four figures of original time-conversion TGA curves of pretreated powdered limestone samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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