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Parametric Study on the CO$_2$ Capture Capacity of CaO-Based Sorbents in Looping Cycles

Vasilije Manovic and Edward J. Anthony*

CANMET Energy Technology Centre-Ottawa, Natural Resources Canada, 1 Haanel Drive, Ottawa, Ontario, Canada K1A 1M1

An experimental parametric study on the CO$_2$ capture activity of four limestone-derived CaO-based sorbents has been performed. Experiments were done in a thermogravimetric analyzer (TGA) at temperatures ranging from 650 to 850 °C. Three particle-size fractions of Kelly Rock limestone and powders obtained by their grinding were also tested, while the influence of carbonation and calcination durations was examined at 750 and 850 °C. Calcination is typically performed in an atmosphere of N$_2$ and carbonation in 50% CO$_2$ (N$_2$ balance), and the influence of the effective CO$_2$ concentration surrounding reacting particles was examined by changing the sample mass in some experiments. The results indicated that increasing the calcination/carbonation temperature had a negative influence on the sorbent activity, while the influence of particle size was small, although larger particles have higher activity. This was unexpected, but it can be explained by the higher content of impurities in the smaller particles. Grinding enhances sorbent activity, and this appears to be more than simply due to increased external surface area of the sorbent particles in the powdered samples. Prolonged carbonation time has a negative effect on the sorbent performance. The formation and decomposition of CaCO$_3$ as well as its presence on the sorbent surface at higher temperatures appear to be key factors in the loss of surface area (i.e., decrease in sorbent activity). However, it is shown that the prolonged exposure to calcination conditions employed in this work (inert atmosphere) has a slightly beneficial effect on sorbent behavior as a function of the number of calcination/carbonation cycles. Experiments with larger sample masses typically resulted in better conversions. Analysis of scanning electron microscope (SEM) images of spent sorbent particles obtained from different reactor types indicated that thermal stresses are the main cause for sorbent particle fracture and attrition.

1. Introduction

CaO-based sorbents, in particular lime (CaO) produced from limestone, have been intensively investigated as sorbents for CO$_2$ capture during the last several years. To date, it appears that CaO is thermodynamically the best candidate among metal oxides for CO$_2$ capture in zero-emissions power generation systems,[1] and it is expected that this process may be economically competitive with classic monoamine processes.[2–4] The process appears particularly suitable for use with fluidized bed combustion (FBC) systems.[5–10]

The chemistry of the process is simple, and it is based on the carbonation reaction:

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s) \qquad \Delta H < 0 \qquad (1)$$
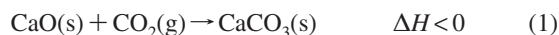
Here, the lime (CaO) is obtained from limestone (CaCO$_3$), which is both abundant and relatively inexpensive, via the calcination reaction:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \qquad \Delta H > 0 \qquad (2)$$
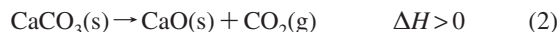
Calcination is the sorbent regeneration reaction, and the process is based on a looping cycle that can take place in a dual reactor, with a carbonator (CO$_2$ capture) and a calciner (sorbent regeneration). In principle, the same amount of sorbent circulates between the carbonator and calciner (apart from any regeneration of the sorbent), and the recovery of heat used for calcination is possible with an appropriately designed dual reactor.[9] A high-purity CO$_2$ stream, produced in the calciner, is suitable for

* To whom correspondence should be addressed. Telephone: (613) 996-2868. Fax: (613) 992-9335. E-mail: banthony@nrcan.gc.ca.

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liquefaction and storage in a wide range of geological formations or possibly in a deep ocean basin.[11,12]

Despite the fact that the chemistry of such a process is simple, there remain some practical challenges. They are mainly connected with the slow, decreasing reversibility of the reaction, which is usually explained by sorbent sintering.[13–16] As a result of sintering, the available surface area for carbonation decreases with the number of reaction cycles, leading to lower conversions corresponding to the thickness of the product layer ($CaCO_3$) on the reacting CaO surface.[17] Thus, a very fast initial carbonation reaction stage finishes with a lower level of conversion (typically less than 10%) and then shifts into a very slow reaction stage, which is practically useless and is controlled by the diffusion through the product layer of $CaCO_3$.[13,18] Also, it is plausible that the reduction of the pore volume as a consequence of sintering is a more important cause for the decrease of conversion with cycle number.[19] Reactivation by hydration currently appears to be the most promising method for recovery of the sorbent activity.[20–22] Unfortunately, doping of the sorbent by additives does not appear to significantly improve the sorbent activity during multiple carbonation cycles.[7,23] This is probably due to sintering, which is also enhanced by the presence of impurities in the sorbent.[24] Other challenges described in the literature include sorbent attrition that leads to its elutriation from a FBC system[25,26] as well as

irreversible loss of activity in the SO_2-containing atmospheres because of the formation of a thermally stable $CaSO_4$ product.[20,27]

In the literature, there are numerous equations that can fit experimental data for maximum CO_2 capture with the number of reaction cycles,[13,16,28,29] and some qualitative models have been proposed.[15,30] However, despite numerous experimental and theoretical investigations, there are no satisfactory answers for some questions. The rate of sorbent activity decay may be fitted, but the parameters used in the proposed formulas cannot be easily correlated with the sorbent characteristic(s) and/or process conditions. The final sorbent capacity after "infinitely" long cycling is not predictable. The proposed models are mainly qualitative with no numerical simulation or quantitative comparison with experiments. All of this demonstrates that the influence of different parameters on sorbent behavior with increasing numbers of reaction cycles needs additional investigation. This work provides an experimental investigation of the influence of different parameters: temperature, particle size, carbonation and calcination durations, choice of sorbent, CO_2/CaO ratio in the reactor, as well as the influence of the reactor type.

2. Experimental Section

Four Canadian limestones are used in these experiments: Kelly Rock (KR), Cadomin (CD, formerly called Luscar), Graymont (GR), and Havelock (HV). The crushed limestone samples were sieved, and three particle sizes of Kelly Rock were tested here: 75–150 μm (KR01), 300–425 μm (KR02), and 600–750 μm (KR03). Particle sizes between 250 and 425 μm were used in the experiments with other limestones. The results of the X-ray fluorescence (XRF) elemental analyses and the data on the BET (Brunauer–Emmett–Teller) pore surface area and the BJH (Barrett–Joyner–Halenda) pore volume distributions for investigated particle size fractions were described in our earlier papers.[20,21,31]

CO_2 looping cycles for samples of selected particle sizes were performed by thermogravimetric analysis (TGA) under different conditions. A Perkin-Elmer TGA-7 thermogravimetric analyzer was used for the experiments. The sample was suspended in a quartz tube (i.d. 20 mm) on a platinum pan (i.d. 5 mm). The gas flow rate, controlled by a flow meter, was 0.04 dm^3/min. The temperature and gas used were controlled by Pyris software. The data on sample mass during the experiments were monitored, and the degree of carbonation was calculated on the basis of the mass change, assuming that mass change occurs only due to formation/decomposition of $CaCO_3$.

The conditions for the benchmark looping tests were 750 °C (both calcination and carbonation), 90 min calcination, and 30 min carbonation, with 100% N_2 for calcination and 50% CO_2 (N_2 balance) for carbonation; 30 mg samples were used. To investigate the influence of different parameters, the following were varied: temperature, calcination and carbonation durations, particle size, and sample mass. The long calcination times (90 min) in the benchmark tests were chosen to ensure complete calcination in the experiments at the lowest examined temperature (650 °C). Ten cycles were typically performed with an additional one (11th) at 750 °C (30 min calcination +30 min carbonation) in order to

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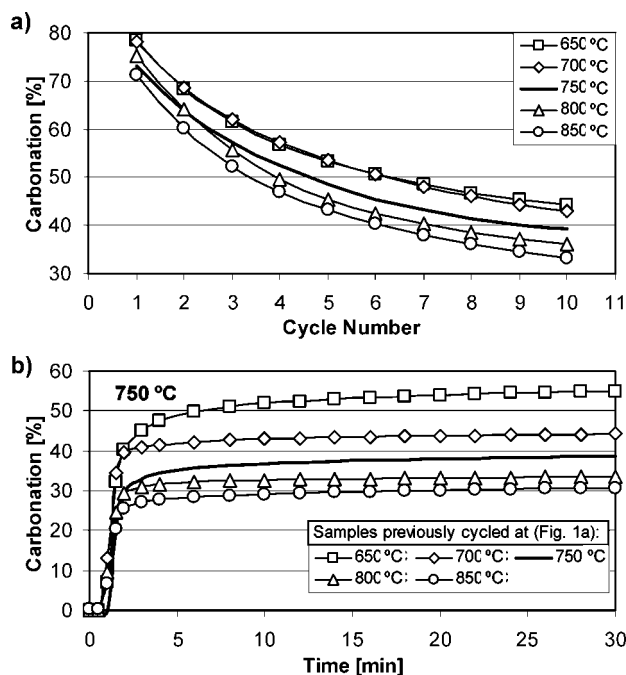
Figure 1. Influence of temperature on the sorbent activity decay of Kelly Rock limestone (KR01) with a particle size of 75–150 μm: (a) 10 cycles (90 min calcination +30 min carbonation) at different temperatures; (b) continued runs, 11th carbonation at the same temperature (750 °C).

compare the activity of the samples (under the same conditions) when they had different cycling histories.

An important difference between the TGA cycling conditions performed in this work and those in a real dual FBC reactor is temperature stress; that is, in experiments described here, the temperature is constant, but this is not the case in a real dual reactor.[26] Thus, sample morphologies were observed with a scanning electron microscope (SEM), and the SEM images obtained were compared with those obtained for samples obtained from a tube furnace (TF)[20] and under dual FBC reactor conditions.[26,32] A Hitachi S3400 SEM with 20 kV of accelerating voltage was used, and the samples were observed at different magnifications ranging from 20 to 10 000×.

3. Results and Discussion

Chemical analysis of the limestone particle-size fractions used indicated that the CaO contents in the samples were as follows: KR01 = 49.50%, KR02 = 51.61%, KR03 = 52.43%,[20] CD = 54.91%, GR = 53.42%, and HV = 51.51%.[21] It may also be important that the HV limestone tends to have some dolomitic characteristics and contains 3.09% MgO. Interesting differences can be seen for the CaO content in the KR particle-size fractions, where sample purity decreases with particle size.

3.1. Temperature. The influence of temperature, in the range 650–850 °C, on the sorbent capacity with calcination/carbonation cycles can be seen in Figure 1a. With increasing temperature, there is faster sorbent activity loss with increasing numbers of calcination/carbonation cycles. This is because both ion migration in the sorbent crystal structure and sintering are strongly influenced by temperature.[24] Furthermore, sintering results in decreased sorbent surface area and reduced conversion in reactions, with formation of a solid product layer on the surface of the solid reactant (CaO). In the case of carbonation, the product layer (CaCO₃) also reduces contact between gaseous

CO₂ and solid CaO, and it is known that the maximum conversions depend on the sorbent surface area.[17]

Solid state diffusion through the product layer is also enhanced by temperature,[18] which should lead to higher conversions with increased temperature; however, samples cycled at higher temperatures are more sintered and, hence, less active, as is demonstrated in Figure 1a. In other words, the influence of temperature on the sorbent sintering (and its resulting decay in carbonation activity) is masked by the enhanced carbonation at higher temperatures. The confirmation of this hypothesis is presented in Figure 1b. The difference between the conversions in the 11th cycle, when samples were carbonated at the same (750 °C) temperature, is 27% (55% at 650 °C and 28% at 850 °C), which is a significantly higher difference than for the 10th cycle (Figure 1a), ∼12%. This clearly shows that carbonation conversion (after 30 min) in the 11th cycle (at 750 °C) is better for material originally cycled at 650 °C (55% vs 45%) but worse for material originally cycled at 850 °C (28% vs 33%). These results—showing the considerable influence of temperature on the sorbent activity decay—are unfavorable, especially when considering a real FBC reactor where the temperature of calcination should be higher (>900 °C) to achieve calcination in a concentrated CO₂ stream in the calciner. Moreover, an atmosphere of concentrated CO₂ also amplifies sintering,[33,34] which reduces the sorbent activity with increasing reaction cycles.

3.2. Particle Size. The literature[13,14,29] shows that there are no significant effects of particle size when comparing maximum carbonation conversions under typical conditions, and only under extreme conditions can particle size be an important parameter.[35] Particle size influences only the rate of carbonation (the shift between the fast and slow reaction stages is more pronounced in the case of smaller particles), but with increasing cycle number this effect disappears; that is, larger pores are formed, enhancing CO₂ diffusion through the particle porous structure. Insensitivity of the maximum carbonation conversions to particle size is a direct consequence of the fact that carbonation inside the particle is typically uniform; that is, there is no radial conversion profile. However, in some cases,[14,20] it was noticed that there was an unexpected particle size influence: the conversion of smaller particles was lower. Similar results were obtained with three KR particle-size fractions as shown in Figure 2a. It can be seen that the decrease in the maximum carbonation is faster for the sample with the smallest particle size (KR01). This result cannot be explained on the basis of known carbonation mechanisms.

The decreased carbonation conversions obtained with smaller particles may be the result of parameters other than particle size. Thus, when all three samples are powdered (<50 μm) and cyclic carbonation experiments are performed on the powdered samples (see Figure 2b), one can see this effect more clearly, since the sample with the lowest particle size originally, performed significantly worse. This result can be correlated with elemental analyses of the samples of different particle size (see ref 20 and also the beginning of this section). Here, as particle size increases, the sample purity also increases; that is, the content of impurities decreases. The concept of better cyclic carbonation properties with decreasing impurities is in agreement with the

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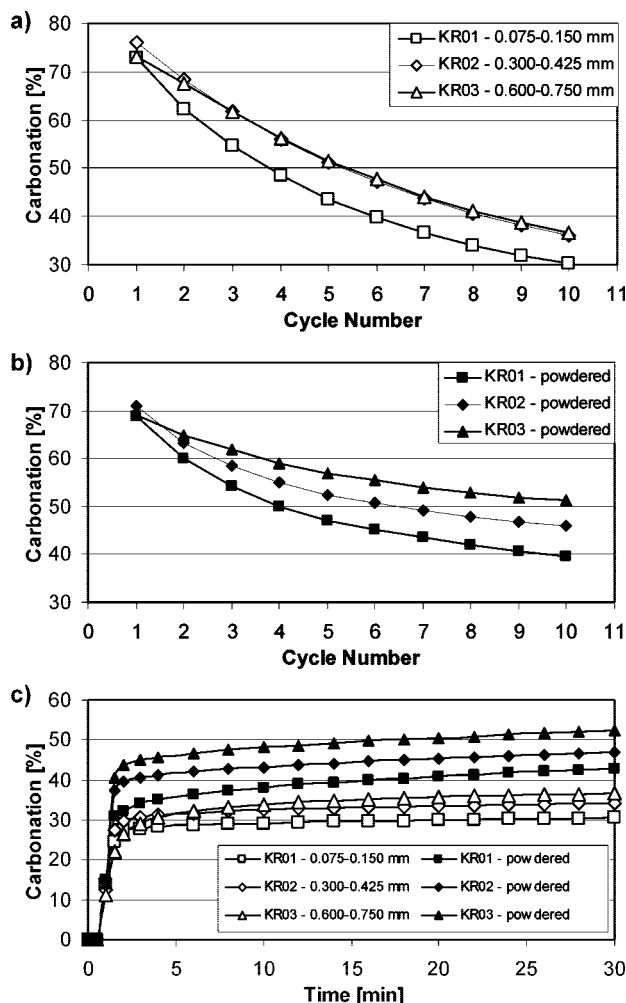
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Figure 2. Influence of the sorbent particle size on the sorbent activity decay of KR limestone: (a, b) 10 cycles at 800 °C, 15 min calcination + 15 min carbonation; (c) continued runs, 11th cycle at 750 °C for 30 min calcination +30 min carbonation.
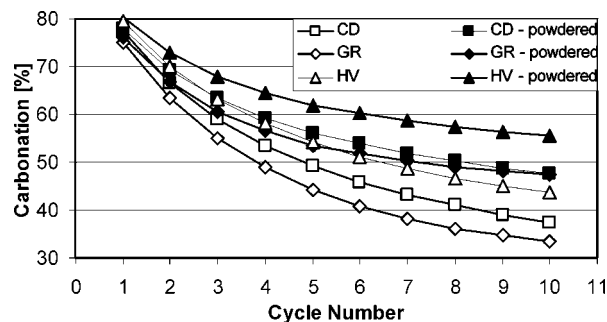

Figure 3. Influence of the sorbent particle size on the sorbent activity decay of the CD, the GR, and the HV limestones, with a particle size of 0.250–0.425 mm, 10 cycles at 800 °C, and 15 min calcination + 15 min carbonation.
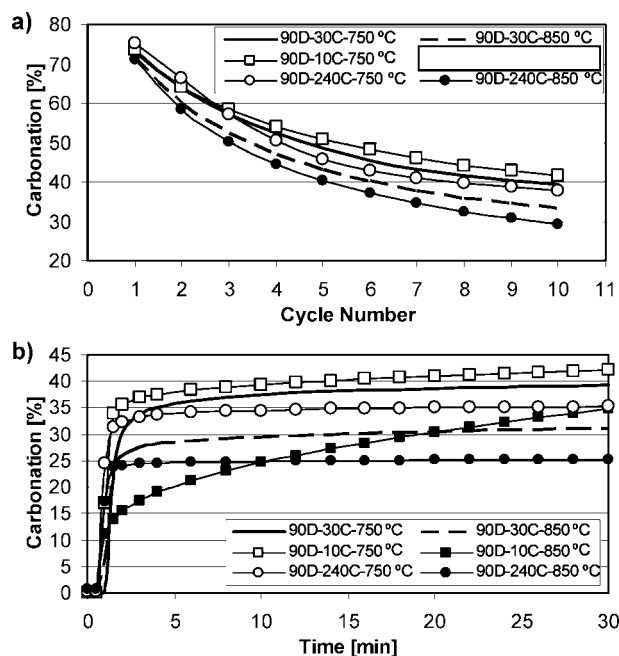

Figure 4. Influence of carbonation duration on the sorbent activity decay of KR01 limestone: (a) 10 cycles, 90 min calcination; (b) continued runs, 11th cycle at 750 °C for 30 min calcination +30 min carbonation. Designation: for example, 90D-30C-750 °C indicates a 90 min calcination (decomposition, D), a 30 min carbonation (C), and a temperature of 750 °C.

finding that impurities enhance sintering[24] because they provide defects in the sorbent crystal structure and, hence, enhance ion migration.

The differences between carbonation levels of the original (Figure 2a) and the powdered (Figure 2b) samples are also of interest. In the first cycle, carbonation levels are ∼70% (and, interestingly, somewhat higher for the original samples); however, the decrease in sorbent activity is faster for the original samples. The corresponding 11th-cycle data are presented in Figure 2c and show similar carbonation curve shapes, but the conversion of powdered samples is ∼12% higher. One possible explanation is that the exterior surface area obtained by grinding the samples (which may be assumed constant as a function of number of reaction cycles) becomes relatively more important in comparison to the interior surface area (which decreases with increasing reaction cycles) with increasing cycle number. However, the influence of the outer surface area formed by grinding (∼0.1 m^2/g maximum), in comparison to that of the interior surface area (∼1–10 m^2/g), appears to be insufficient to explain the significantly better behavior of the powdered samples. For example, the BET surface area of KR01 after the first calcination is 4.06 m^2/g, and after 20 cycles in the TF, it is 3.18 m^2/g.[31] It is difficult to imagine that ∼0.1 m^2/g of the outer surface area is important for a spent sample with a BET of ∼3 m^2/g but not important in the first carbonation of a sample with

a BET of ∼4 m^2/g; moreover, the first carbonation conversion is higher in the case of the original sample.

Similar experiments with the original and powdered samples were also performed with other limestones, and the results are presented in Figure 3. It can be seen that the first carbonation conversion is similar (75–80%) despite limestone type and sample grinding. The sorbent activity decay is significantly slower for the powdered samples. This also confirms activation of the sorbent by grinding. This finding may be important, for example, in efforts to produce a synthetic sorbent with enhanced properties. However, pelletization would be necessary prior to use of such powdered sorbents, and it also remains a possibility that some sort of pelletization may be necessary for the original sorbent, to prevent attrition.

3.3. Carbonation Duration. The influence of calcination/carbonation duration at two temperatures (750 and 850 °C) was also investigated here. Calcination for 90 min and three carbonation times (10, 30, and 240 min) were chosen, and the results are given in Figure 4a. The longer carbonation periods at both temperatures led to a faster loss of the sorbent activity. It should be noted that carbonation conversions after 10 min
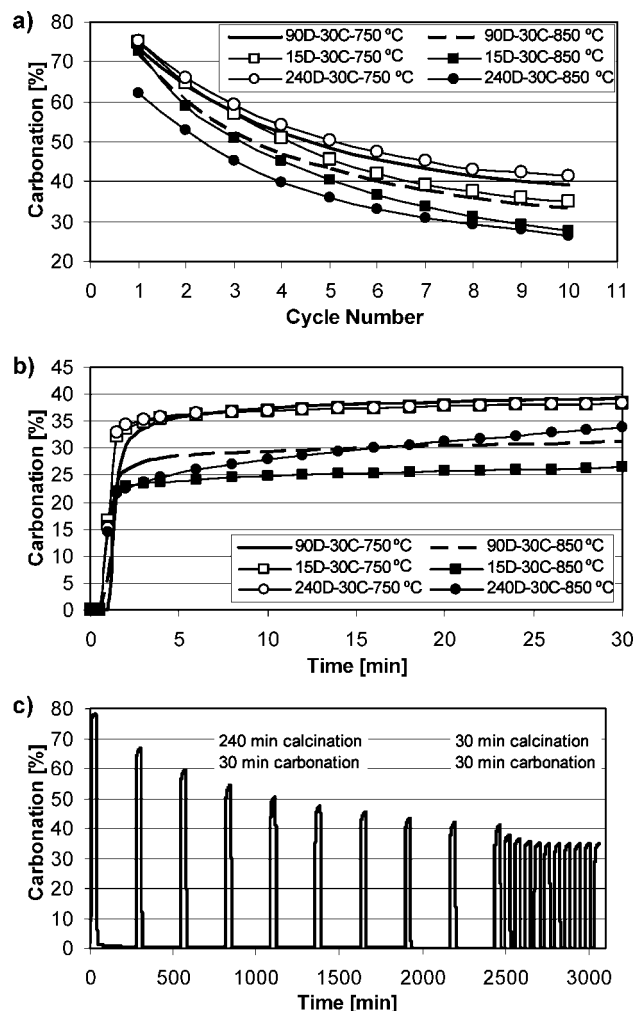
Figure 5. Influence of the calcination duration on the sorbent activity decay of KR01 limestone: (a) 10 cycles, 30 min carbonation; (b) continued runs, 11th cycle at 750 °C for 30 min calcination +30 min carbonation; (c) run 90D-30C-750 °C continued with 10 cycles at 750 °C for 30 min calcination +30 min carbonation. Note: The same type of designation is used as in Figure 4.

(in a cycle) are presented in the figure, while results for a 10 min carbonation at 850 °C are not presented, because uncharacteristic carbonation curves for this run were obtained, as can be seen in Figure 4b. This figure presents results for the 11th cycle at 750 °C for a 30 min calcination and a 30 min carbonation. The results obtained may be related to the influence of a CO_2 atmosphere on the sintering of CaO[33,34] and to the Tammann temperature, which is relatively low for $CaCO_3$, 533 °C.[30] On the basis of these results, it may be assumed that sintering with reaction cycles occurs as a result of mass transfer through the calcium carbonate phase, which is in agreement with results obtained elsewhere.[36] However, it should be noted that the differences presented in Figure 4a are not large and the sensitivity of the method (pore size distribution) may not be enough to see an effect in the calcined samples (after the first carbonation) for different carbonation times.[15]

3.4. Calcination Duration. The influence of the calcination time on the sorbent activity decay is presented in Figure 5a. Here, the carbonation time is fixed at 30 min, and the calcination times are varied as follows: 15, 90, and 240 min. It should be pointed out that the term "calcination time" is a non sequitur
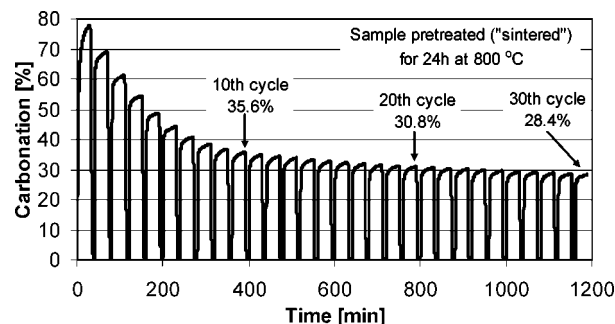
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Figure 6. Influence of thermal pretreatment ("sintering") at 800 °C for 24 h on the sorbent (KR02) activity along 30 cycles, 20 min calcination + 20 min carbonation at 800 °C.

because calcination is always finished in less than 15 min. It is interesting that with longer calcination times the sorbent has higher conversions, with the exception of the result for 240 min at 850 °C. However, under these conditions, different types of carbonation curves were obtained (Figure 5b). It is interesting that similar carbonation curves were obtained at 750 °C when the calcination time for the 11th cycle was the same (30 min). A favorable influence of the calcination time was unexpected and differed from the behavior presented in the literature. Grasa and Abanades[29] and Lysikov et al.[30] showed that the calcination time is not an important parameter, and Sun et al.[15] found that a longer calcination time actually reduced the pore volume for pores < 220 nm (which are most responsible for carbonation conversions).

To check these results, more experiments were performed. The cyclic carbonation run for 240 min calcination was continued for 10 cycles with a 30 min calcination (and a 30 min carbonation), and the results are shown in Figure 5c. It is interesting that the sorbent, after an initial loss of activity, displayed a constant CO_2 capture capacity of ~35% in additional cycles, which is a relatively high value after 20 cycles. This behavior of the sorbent during the additional 10 cycles suggests that it can "remember" its thermal history.

Sample KR02 (300–425 μm) was "calcined" for 24 h; that is, it was heat treated at 800 °C for that time and then cycled (Figure 6). After the usual rapid loss of activity over the first 10 cycles, the conversion was 35.6%. Subsequently, the loss of activity was very slow, and a high conversion (28.4%) was achieved after 30 cycles. This means that heat pretreatment of the sorbent can enhance its CO_2 carrying capacity. Moreover, it can be expected that some thermal pretreatment of the sorbent can reduce undesirable attrition in FBC systems because it is noticed in this work that pretreated particles have greater hardness.

A long-term cyclic carbonation run with the CD limestone is presented in Figure 7. The carbonation time is 60 min, and the calcination time is varied during the run. After four typical calcinations (60 min), a long period (600 min) under calcination conditions was employed. The differences in the maximum sample masses are designated in the chart presented in Figure 7. This test also confirms the observation that heating the sample under calcination conditions (in an inert atmosphere) has no negative effect on the sorbent activity. Moreover, long calcinations have a slightly favorable effect. This is illustrated by Δm9, Δm10, and Δm11, which show that the loss of activity is greater in the cycle before long-term calcination (Δm9) and in the second cycle after long-term calcination (Δm11) than it is after long-term calcination (Δm10). Finally, after the third long-term calcination, a decay of activity was not noticed (Δm15 ≈ 0).
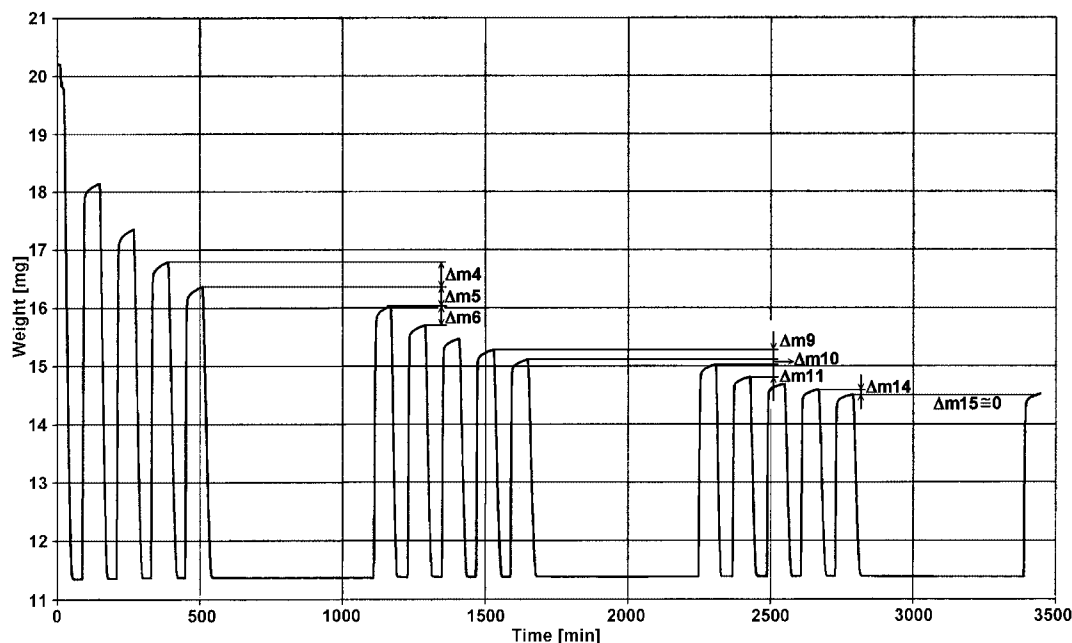
Figure 7. Influence of long-term calcination/sintering on the sorbent activity: CD limestone, 60 min calcination (5, 10, and 15th calcination 10 h), 60 min carbonation at 700 °C.
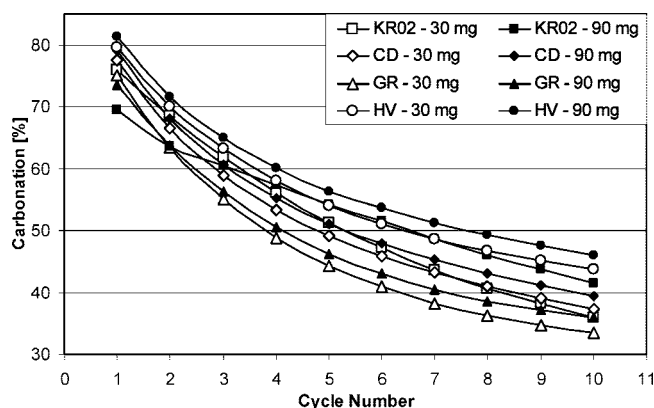

Figure 8. Influence of sample mass on the sorbent activity in the TGA runs: 10 cycles, 800 °C, 15 min calcination + 15 min carbonation.
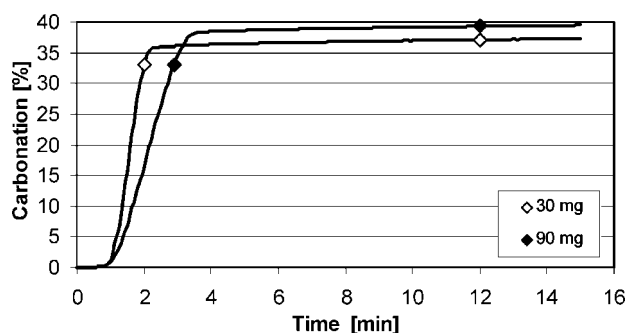

Figure 9. Typical difference between carbonation curves obtained with different sample masses under the conditions presented in Figure 8 (CD, 10th cycle).

The results presented in Figures 5–7 illustrate that the sorbent does not lose activity as a result of prolonged exposure to the calcination conditions, and it appears that this treatment may actually improve the sorbent behavior. A weakness of these experiments is that they were not performed under conditions that are characteristic of a real FBC reactor (where sorbent particles will experience a higher

calcination temperature because of the more concentrated CO_2 atmosphere). However, these results are interesting because they show that prolonged exposure of the sorbent to heat may stabilize its maximum carbonation level as a function of reaction cycles. There is no satisfactory explanation for this effect on the basis of sintering and pore distribution change models. However, a possible explanation may be found in the concept of sorbent skeleton changes. Previous research[32] has shown that skeleton densities after CO_2 looping cycles were higher than those after the first calcination. It may be assumed that, apart from changes in particle surface morphology, changes in the crystal structure of the sorbent skeleton occur and these stabilize its morphology. Nonetheless, the formation and decomposition of $CaCO_3$ have a strong effect on the sorbent sintering and the decay of activity, and this is confirmed by the fact that carbonation conversion is a clear function of reaction cycle number.

These results (Figure 4) also show that prolonged exposure to carbonation conditions has a negative influence on the sorbent activity as the number of cycles increases. By contrast, exposure to heat in prolonged calcinations has the effect of stabilization of the sorbent skeleton crystal structure, which becomes more resistant to change because of $CaCO_3$ formation/decomposition. During the same calcination duration (heating with no CO_2), significant sintering does not occur (given the thermal stability of CaO), and the sorbent obtained has a more stable skeleton, which is important for enhanced conversions in later cycles, for example, 35% after 20 cycles (Figure 5c) or 28.4% after 30 cycles (Figure 6). These findings strongly suggest that the sorbent modification by thermal pretreatment ought to be considered, as it is clear that the sorbent can remember its thermal history.

3.5. CO_2/CaO Ratio. The influence of sample mass in the TGA experiments on the sorbent activity is presented in Figure 8. It can be seen that conversions are typically higher for larger sample mass, with the exception of the first few cycles of sample KR02. Typical carbonation rate curves, presented in Figure 9, show that the reaction rate is slower for the heavier (90 mg) sample. This is a result of CO_2
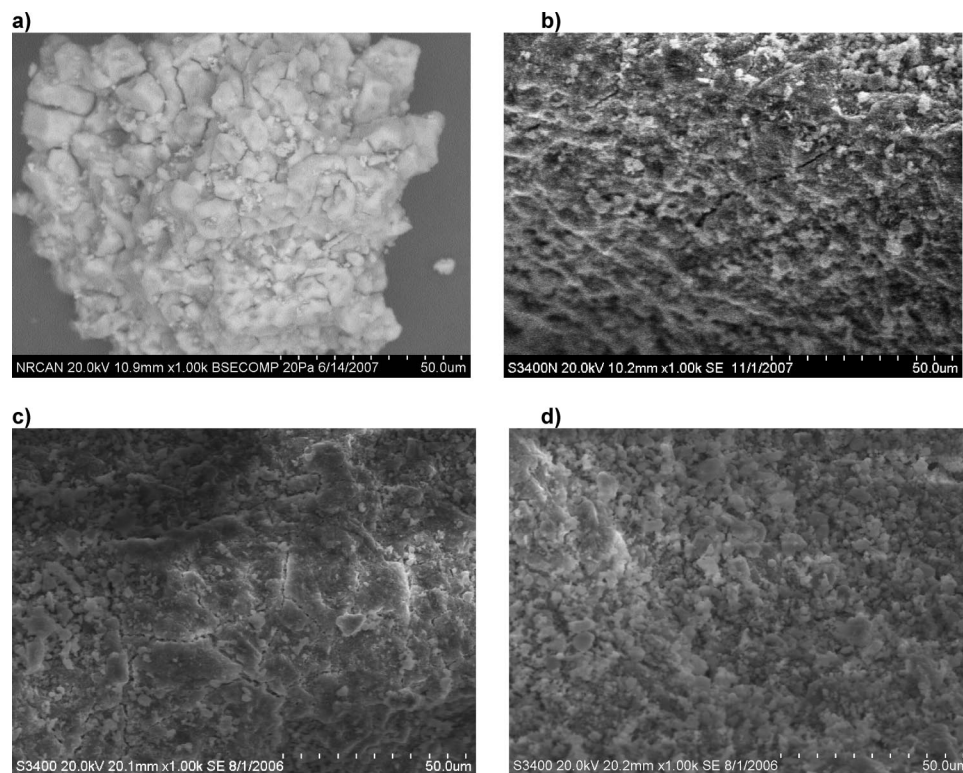
Figure 10. SEM images of spent sorbent samples obtained in different reactor types: (a) HV from the carbonator of a dual FBC reactor after 165 min of cycling (~6 cycles);[26] (b) HV from TGA after 10 cycles; (c, d) KR from TF after 20 cycles.[20]

diffusion between particles in bulky samples. This diffusion resistance leads to a lower concentration of CO_2 around the sorbent particles and a slower reaction rate, which is a possible explanation for slightly higher conversions. That is, a fast reaction rate may lead to formation of small local zones with unreacted CaO patterns surrounded with $CaCO_3$, which prevent further contact of CaO with CO_2. The effects of pore closure and narrow pore bottlenecks have been previously noticed and discussed elsewhere.[35]

3.6. Reactor Type. The results presented in this paper were obtained under isothermal conditions, which are clearly different than those in a real FBC reactor. An important difference might be the degree of thermal stress for samples circulating between the carbonator and calciner. Typical SEM images of samples (after the carbonation stage) obtained in different reactor types (over a period of 18 months of research) with varying intensities of thermal stress are presented in Figure 10. The differences in particle morphologies are clearly visible. Several large pores and cracks can be seen on particles from a FBC reactor (Figure 10a), which is quite different from particles obtained in a TGA under isothermal conditions at 750 °C. The particles from the TGA typically have no (or very few) cracks, as presented in Figure 10b. This means that under isothermal conditions cracks are not formed; that is, thermal stresses are responsible for their appearance. Samples from the TF (Figure 10c and d) display both types of particles (with and without cracks), but the cracks are noticeably less pronounced than those on the particles from the FBC reactor. This is most likely because the thermal stresses in the TF were not as great, since the time needed to change the temperature during heating and cooling in the TF (650–850 °C) was ~10 min, which is insufficient to produce significant stresses. It may,

therefore, be concluded that thermal stress is a significant cause of particle cracking and attrition in FBC systems.

4. Conclusions

An experimental parametric study of the CaO-based sorbent capacity under CO_2 looping cycles has been carried out. Here, the influence of various parameters was examined. These included particle size, impurities, limestone type, temperature, and influence of the effective CO_2 concentration surrounding reacting particles, as well as carbonation/calcination duration and temperature stresses in different reactor types. It was found that increasing temperature in the range of 650–850 °C has a negative effect on the sorbent activity. Particle size is unimportant in terms of the sorbent CO_2 carrying capacity, and any differences are likely to be a function of impurity content in samples of different particle size. The grinding of sorbent results in better reaction cycle properties for the powder obtained. This is unlikely simply due to the particle size decrease and suggests that it may be possible to achieve sorbent activation by grinding. Prolonged carbonation accelerates the sorbent activity decay, while an opposite effect is produced for the prolonged sorbent exposure to calcination conditions in an inert atmosphere. It is clear that the formation and decomposition of $CaCO_3$ is a critical step for sorbent sintering and its subsequent decay in activity. However, heating in an inert atmosphere stabilizes the sorbent skeletal structure, which leads to a slower decay of activity and higher conversions in later cycles. The slower carbonation rates obtained using larger sorbent sample mass typically led to slightly higher maximum conversions. A comparison of SEM images of spent sorbent samples obtained in different reactor types showed that thermal stresses are mainly responsible for sorbent particle fracture.