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# Steam Reactivation of Spent CaO-Based Sorbent for Multiple CO<sub>2</sub> Capture Cycles

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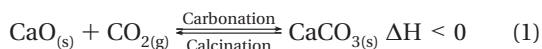
This study examines steam reactivation of sorbent to improve the reversibility of multiple CaO–CO<sub>2</sub> capture cycles. Experiments to obtain spent sorbent were performed in a tube furnace, and reactivation was achieved using steam in a pressurized reactor. Sorbent activity for CO<sub>2</sub> capture was then tested in a thermogravimetric analyzer (TGA), in multi-cycle carbonation tests. After reactivation the sorbent had even better characteristics for CO<sub>2</sub> capture than that of the natural sorbent. The average carbonation degree over 10 cycles for the reactivated sorbent approached 70%, significantly higher than for the original sorbent (35–40%). This means that the same sorbent may achieve effective CO<sub>2</sub> capture over a large number of cycles, in the absence of other phenomena such as attrition. Partially sulfated sorbents may also be reactivated, but hydration itself is also hindered by sulfation.

## Introduction

Fossil fuel combustion causes increasing atmospheric concentration of CO<sub>2</sub>, a major contributor to the greenhouse effect. Decrease of anthropogenic CO<sub>2</sub> emissions, especially from power plants, is an important goal. One of the new approaches is based on CO<sub>2</sub> capture from flue gas, followed by sequestration in a wide range of geological formations (1, 2).

Fluidized bed combustion (FBC) has successfully solved SO<sub>2</sub> and NO<sub>x</sub> emissions problems and is a candidate technology for future low- or zero-CO<sub>2</sub> emissions combustion (3). Additionally, if biomass is used as a fuel, FBC plants employing CO<sub>2</sub> capture technologies could have “negative” CO<sub>2</sub> emissions; i.e., serve as net CO<sub>2</sub> sinks. CaO-based sorbents are used for SO<sub>2</sub> retention (4) and recently intensive research is being directed to their use as possible sorbents for CO<sub>2</sub> capture (3, 5–8), and simultaneous CO<sub>2</sub>/SO<sub>2</sub> capture (9, 10).

CO<sub>2</sub> capture by CaO-based sorbents is based on the reversible chemical reaction



CO<sub>2</sub> separation from flue gas is possible in a multi-cycle process in a dual reactor. This involves reaction of CaO with CO<sub>2</sub> from flue gas in a carbonator, and regeneration of sorbent in a calciner (3). In the ideal case, carbonation–calcination cycles can be carried out indefinitely with the only limitations

due to the kinetics of the reactions and thermodynamics of the equilibrium system. The chemical equilibrium of the reaction depends on temperature, *T*, and CO<sub>2</sub> partial pressure, *P*<sub>CO<sub>2</sub></sub> (11):

$$\log_{10} P_{\text{CO}_2} [\text{atm}] = 7.079 - \frac{8308}{T[\text{K}]} \quad (2)$$

In practice, the use of the carbonation reaction (exothermic) is limited by the maximum temperature that allows CO<sub>2</sub> capture at the desired concentration in cleaned flue gas (according to eq 2) and the minimum temperature that allows a practical reaction rate. The calcination reaction is limited by the minimum temperature necessary to obtain sufficient CO<sub>2</sub> concentration at the calciner outlet. Operation at elevated pressure in the carbonator and at lower pressure in the calciner can improve cycle efficiency, i.e., increase the carbonation rate and obtain lower CO<sub>2</sub> concentrations in cleaned flue gas, allowing calcination under higher CO<sub>2</sub> concentrations.

However, experimental work has shown that the most important limitations of the process relate to the reversibility of reaction (1). Sorbents rapidly lose activity, i.e., the maximum degree of carbonation decreases quickly with the number of cycles (5, 11–13). The decrease of sorbent activity is explained by sintering—the available surface area diminishes as the number of calcination–carbonation cycles increases (14). Carbonation involves an initial fast stage, which is kinetically controlled, and a much slower second stage controlled by diffusion through the CaCO<sub>3</sub> layer (15, 16). The shift of controlling mechanisms depends on the available surface area and, with increasing cycle number, the practically useful initial stage becomes shorter because of sintering. Simple equations connecting cycle number and maximum (usable) value of conversion are available elsewhere (17, 18).

Practical use of the carbonation–calcination cycles depends on increasing conversion during the various cycles, resulting in decreasing consumption of fresh sorbent and storage of spent sorbent. Hydration of the spent sorbent used for CO<sub>2</sub> capture in multiple cycles is one possible approach for sorbent reactivation. Based on experience on reactivation of sorbent utilized for SO<sub>2</sub> retention (19, 20) and similar improvement of sorbent characteristics for use in CO<sub>2</sub> capture cycles (7), steam reactivation of sorbent sintered after a number of CO<sub>2</sub> capture cycles was investigated here.

## Materials and Methods

Kelly Rock limestone was chosen for experiments as it has been used extensively in our other studies on carbonation (6, 7). Ground limestone was sieved into particle size fractions. Three sizes were tested here: 75–150 μm (KR01), 300–425 μm (KR02), and 600–750 μm (KR03). The results of X-ray fluorescence (XRF) elemental analyses for these limestone fractions are shown in Table 1.

To produce sufficient amounts of spent/sintered sorbent samples, a tube furnace was employed since this, unlike thermogravimetric analysis (TGA), can easily produce large samples for a variety of tests and analyses. Samples produced in the tube furnace were subsequently used for steam reactivation and experiments on cyclic carbonation in a TGA (6). Also, some sample was reserved for Brunauer Emmett Teller (BET) surface area, TGA, and scanning electron microscope (SEM) analyses.

**Tube Furnace Experiments.** Two types of experiments were performed in the tube furnace: calcination/sintering of samples under different conditions, and cyclic carbonation

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**TABLE 1. XRF Elemental Analyses of Kelly Rock Limestone Samples Used**

component	KR01 (75–150 $\mu\text{m}$ )	KR02 (300–425 $\mu\text{m}$ )	KR03 (600–750 $\mu\text{m}$ )
SiO <sub>2</sub>	5.34 wt %	3.70 wt %	2.95 wt %
Al <sub>2</sub> O <sub>3</sub>	1.44 wt %	1.00 wt %	0.74 wt %
Fe <sub>2</sub> O <sub>3</sub>	0.48 wt %	0.37 wt %	0.32 wt %
TiO <sub>2</sub>	0.07 wt %	0.06 wt %	0.05 wt %
P <sub>2</sub> O <sub>5</sub>	0.012 wt %	0.011 wt %	<0.011 wt %
CaO	49.50 wt %	51.61 wt %	52.43 wt %
MgO	0.58 wt %	0.52 wt %	0.47 wt %
SO <sub>3</sub>	0.55 wt %	0.24 wt %	0.30 wt %
Na <sub>2</sub> O	<0.096 wt %	<0.096 wt %	<0.096 wt %
K <sub>2</sub> O	0.39 wt %	0.27 wt %	0.21 wt %
Ba	996 ppm	367 ppm	347 ppm
Sr	273 ppm	283 ppm	286 ppm
V	<50 ppm	<50 ppm	<0.50 ppm
Ni	80 ppm	113 ppm	<0.50 ppm
Mn	1139 ppm	1051 ppm	1023 ppm
Cr	<50 ppm	<50 ppm	<0.50 ppm
Cu	88 ppm	66 ppm	42 ppm
Zn	63 ppm	42 ppm	30 ppm
loss on fusion	40.59 wt %	41.69 wt %	42.05 wt %
sum	99.29 wt %	99.68 wt %	99.69 wt %

(production of spent sorbent) of both partially sulfated and unsulfated sorbents. The samples were calcined under nitrogen atmosphere and then weighed. Two calcination conditions were employed: 850 °C for 2 and 24 h, and 1100 °C for 24 h to produce a “deeply sintered sorbent”. The flow of N<sub>2</sub> was 1000 mL/min and samples used were ~4 g.

Sulfated sorbent samples were prepared using ~1 g of the calcine, which was produced by calcination under an atmosphere of nitrogen at 850 °C for 2 h. Two portions of calcined sorbent samples (2 g total) in two dishes were placed in the tube furnace, and sulfation was performed using synthetic flue gas (15% CO<sub>2</sub>, 3% O<sub>2</sub>, 1% SO<sub>2</sub>, and N<sub>2</sub> as balance) at 850 °C for 2 h. The partially sulfated samples were then carbonated using a gas mixture containing 20% CO<sub>2</sub> (N<sub>2</sub> balance) for 30 min. Calcination (for 30 min) and carbonation (for 30 min) were performed 20 times. The temperatures during calcination and carbonation were 850 °C and 650 °C, respectively, and the gas flows were 1250 mL/min for each cycle. The sample was weighed after sulfation and on the final experiment (20th carbonation).

Following a similar methodology, but without sulfation, samples of unsulfated spent sorbent were also produced. All experiments in the tube furnace were repeated in duplicate, and the samples obtained were merged into one sample and kept in a small, capped jar for subsequent experiments.

It should be noted that, during experimental work, particle size decrease after the initial calcination was noticed. After sulfation and/or carbonation, any eventual particle size increase was not apparent. Particle shrinkage during initial calcination reduces particle porosity and affects subsequent carbonation and, to a greater extent, sulfation because of the greater volume of the reaction product (CaSO<sub>4</sub>). This phenomenon of particle size changes was not investigated in more detail in this work.

The samples of both calcined/sintered and spent sorbent (partially sulfated and unsulfated) obtained in the tube furnace were hydrated in a 2-L Parr 4522M pressure reactor (21). Each sample was placed on filter paper in an aluminum sample dish within the vapor space of the pressurized reactor. The temperature in the vapor space (which contained saturated steam) was 200 °C. Air contained in the bomb was purged from the system after the temperature in the bomb exceeded 100 °C. Hydration durations were 30 min after

temperature in the reactor achieved 200 °C. These conditions were chosen to ensure that “deeply sintered sorbents” would be completely hydrated in a reasonable period of time. When the hydration experiment was complete, the sample was transferred to a vacuum oven and dried at 50 °C for 2 h. All free water was removed from samples, as confirmed by the TGA analyses. To prevent mass loss, change of particle size and morphology and additional free water in the sample, the sample was not washed before drying. Sample mass before hydration was typically 0.5 g, and samples were weighed after drying. Samples from two repetitions of the hydration process were merged.

**TGA Experiments.** Multiple carbonation cycles with both the parent (natural) and reactivated sorbents were performed using a Cahn model C-1100 TGA. The sample was suspended in a 316 stainless steel “hang-down” tube on a platinum pan. The sorbent masses were chosen such that masses of CaO in runs with different sorbent samples were the same, ~15 mg CaO. The temperature was measured using a type K thermocouple that was inserted axially into the “hang-down” tube below the sample pan. The temperature was controlled using a Lab-Temp tube furnace and controller. The heating rate used was typically 20 °C/min. The cooling rate was higher because the tube furnace was disconnected for the cooling step, so some tens of seconds was enough for the sample temperature to decrease to the desired level. N<sub>2</sub> and CO<sub>2</sub> feed rates were controlled using Matheson mass flow controllers. The gases flowed upward within the “hang-down” tube of the Cahn Thermo Balance. Data were recorded at 2-s intervals using a Keithley 2700 data acquisition system connected to a personal computer running Keithley Xlinx software. The experimental setup is described elsewhere in more detail (6).

Temperatures during multiple TGA cycles were 850 °C (calcination) and 700 °C (carbonation). Gas flow was 400 mL/min, 100% N<sub>2</sub> for calcination, and 15% CO<sub>2</sub> (N<sub>2</sub> balance) for carbonation. Each cycle was typically 40 min (10 min calcination + 30 min carbonation), except for some short-time-cycle experiments.

## Results and Discussion

Multiple carbonation cycles (usually 10 cycles) were performed in the TGA with the goal of comparing modified sorbents starting with typical or deeply sintered sorbents. Changes in the degree of carbonation were calculated on the basis of mass change, and it was assumed that no other process occurs, i.e., that the CaSO<sub>4</sub> itself does not decompose during carbonation cycles. This is ensured due to the thermal stability of CaSO<sub>4</sub> under the current operating conditions and confirmed by the constant and unchanging sample mass after calcination during cycles.

The carbonation degree (CO<sub>2</sub>/CaO molar ratio) vs time from the TGA runs for natural sorbent is shown in Figure S1, of the Supporting Information. As expected, the maximum value of the degree of carbonation rapidly decreases with increasing cycle number (6, 7) and this may be explained by sintering and associated reduction in surface area with cycles.

To more easily compare multiple-cycle carbonation runs, some parameters related to maximal values in the cycles are defined in Table 2. After two cycles the three size fractions examined had very similar values for maximum conversions, but there is a more noticeable decrease of activity after 10 cycles in the smallest particles. This was not expected because the mechanism of carbonation involves diffusional limitations. The limitations decrease with smaller particle sizes, which results in increase of reaction rate of smaller particles and usually (but not necessarily) in level of maximal conversions attained well after the end of the fast reaction period. A possible explanation may be found in the elemental analyses as sample 75–150  $\mu\text{m}$  contains the highest level of

**TABLE 2. Behavior of Natural and Reactivated Spent/Sintered Sorbents in Carbonation Cycles in TGA Experiments<sup>a</sup>**

sample	description	$X_{1-2}$ (%)	$X_{9-10}$ (%)	$X_{1-10}$ (%)
KR01 (75–150 $\mu\text{m}$ )	natural sorbent	67.97	34.26	45.99
KR02 (300–425 $\mu\text{m}$ )	natural sorbent	69.66	38.68	49.77
KR03 (600–750 $\mu\text{m}$ )	natural sorbent	67.08	39.52	49.12
KR37 (75–150 $\mu\text{m}$ )	sulfated, 20 cycles in TF, hydrated	52.22	41.94	46.40
KR38 (300–425 $\mu\text{m}$ )	sulfated, 20 cycles in TF, hydrated	58.70	43.67	50.98
KR39 (600–750 $\mu\text{m}$ )	sulfated, 20 cycles in TF, hydrated	61.62	44.02	51.88
KR40 (75–150 $\mu\text{m}$ )	20 cycles in TF, hydrated	77.85	54.19	66.74
KR41 (300–425 $\mu\text{m}$ )	20 cycles in TF, hydrated	76.06	63.14	70.91
KR42 (600–750 $\mu\text{m}$ )	20 cycles in TF, hydrated	75.38	61.54	69.51
KR43 (75–150 $\mu\text{m}$ )	sintered 24 h, 1100 °C, hydrated	60.64	45.00	51.58
KR44 (300–425 $\mu\text{m}$ )	sintered 24 h, 1100 °C, hydrated	60.03	43.95	52.34
KR45 (600–750 $\mu\text{m}$ )	sintered 24 h, 1100 °C, hydrated	61.54	44.84	54.02

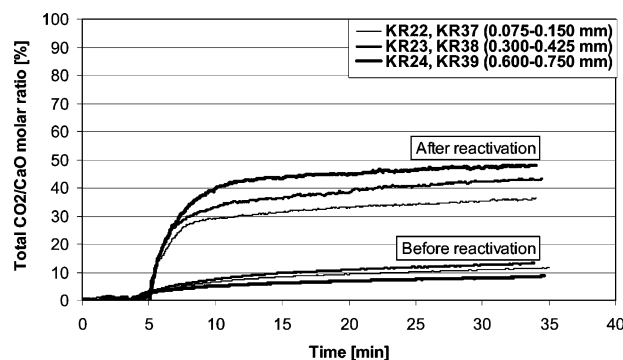
<sup>a</sup>  $X$  = Average value of maximum carbonation degrees for range of cycles indicated by subscript. For example,  $X_{1-10}$  is average value for all cycles. TF = tube furnace.

impurities, and it is known that impurities can enhance sorbent sintering, which in turn reduces porosity and pore surface area (22). This result may appear to be in disagreement with a higher level of sulfation for the 75–150  $\mu\text{m}$  sample (next paragraph). However, it should be noted that the 10  $\text{CO}_2$  cycles are of longer duration than the sulfation, and that sulfation is often improved by the presence of impurities (23).

Hydration by steam under pressure was examined as a method of reactivating sorbent spent in carbonation/calcination cycling. Reactivated samples were analyzed by TGA, and the results are given in Table S1, of the Supporting Information. The degree of sulfation decreases as particle size increases, from 29.8% (CaO in the form  $\text{CaSO}_4$ ) in the 75–150  $\mu\text{m}$  sample to 26.6% in the 600–750  $\mu\text{m}$  sample. Also, the amount of CaO carbonated was determined before reactivation to check the degree of carbonation for the final cycle in the tube furnace. It was found that samples after hydration contained more  $\text{CO}_2$  than those without hydration. This is probably due to sample handling after multiple cycles, during hydration, drying, and after drying. The main contribution to carbonation occurred during sample hydration because air in the bomb with the sample (during the heating process to bring the sample to 100 °C) necessarily contains  $\text{CO}_2$ . Moreover, the partial pressure of  $\text{CO}_2$  in the bomb was higher than might be expected on the basis of  $\text{CO}_2$  content in air because tap water (containing  $\text{CO}_2$ ) was used in the bomb to generate steam. However, to mitigate any further such reaction, the samples between different stages were kept in small, capped jars, and their exposure to air was reduced to the minimum possible.

The presented values on hydration (Table S1) are mainly due to hydration in the pressurized reactor, i.e., hydration by atmospheric moisture was negligible. The amounts of CaO (hydrated) present as  $\text{Ca}(\text{OH})_2$  were different for partially sulfated and unsulfated samples, which appears to be due to the lower porosity and pore surface area of sulfated samples as well as unavailability of CaO chemically bonded in  $\text{CaSO}_4$ . Similar values for hydration levels for different particle size fractions result from the net effect of opposite influences of higher level of sintering and/or sulfation of smaller particles, and dimensions of larger particles.

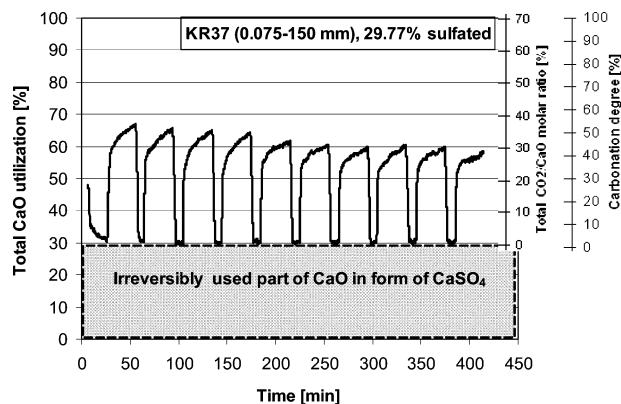
In order to examine the behavior of reactivated sorbents, multiple TGA carbonation cycle runs were performed with reactivated sorbents. The comparisons for  $\text{CO}_2/\text{CaO}$  molar ratios vs time during carbonation of sulfated spent sorbents before and after reactivation (in the first cycle) are shown in Figure 1. The values of  $\text{CO}_2/\text{CaO}$  molar ratio are calculated using recorded data on sample mass increment during the TGA carbonation and CaO content in the sample (Table 1). It may be seen that sorbent in the cycle after sulfation and cyclic carbonation in the tube furnace had very low activity

**FIGURE 1. Steam reactivation effect on sorbent activity during carbonation in the TGA—partially sulfated sorbent.**

for carbonation. The shapes of curves are uncharacteristic for carbonation because there are effectively no fast stages at the beginning of the carbonation process. Here, sintering and pore closure by  $\text{CaSO}_4$  ensure that carbonation was limited by product layer diffusion from the start of the run, which caused the disappearance of a well-defined fast carbonation stage. The final value of the  $\text{CO}_2/\text{CaO}$  molar ratios is about 11%. This is higher than values obtained in the last cycle in the tube furnace (4.08–4.86%, Table S1), and is likely due to the lower carbonation temperature in the tube furnace (650 °C) compared with the temperature in the TGA run (700 °C), as well as more significant inter-particle mass transfer resistance in the tube furnace because of the larger sample mass. After reactivation, the sorbent had significantly higher activity, with a clearly defined fast stage at the start of the carbonation process. Here, the activity of sorbent increases regularly with particle size, and  $\text{CO}_2/\text{CaO}$  molar ratio values at the finish of the first cycles were 36.24, 43.10, and 48.01%. This dependency is due primarily to the increase in sulfation with decrease in particle size, i.e., decreasing amounts of chemically available CaO.

Thus, the total  $\text{CO}_2/\text{CaO}$  molar ratio is not the best parameter for comparing carbonation levels of partially sulfated sorbents. In Figure 2, in addition to time (cycle number) vs total  $\text{CO}_2/\text{CaO}$  molar ratio, changes in total CaO utilization (sulfation + carbonation) and degree of carbonation are shown (here only chemically available CaO is taken into account). The carbonation cycles are shown here for the 75–150  $\mu\text{m}$  sample. (Corresponding curves for 300–425  $\mu\text{m}$  and 600–750  $\mu\text{m}$  samples are in Figure S2.) Similarly to the original sorbent (Figure S1) the loss of activity with cycle number is noticeable, but the decay is slower than in the case of original sorbent. This is especially important because of the fact that reactivation is not performed after every cycle (but performed only before the TGA cyclic run). The slower decay may be a consequence of the presence of  $\text{CaSO}_4$ , which



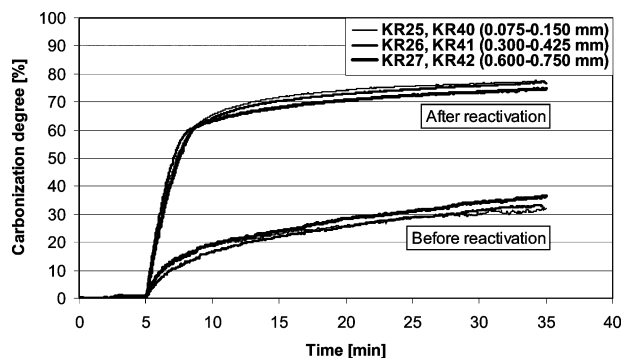


**FIGURE 2.** TGA calcination/carbonation results for reactivated partially sulfated spent sorbent, particle size 75–150  $\mu\text{m}$ .

may hinder sintering. However, we cannot demonstrate this on the basis of the present results because slower decay in the case of reactivated unsulfated samples was also noticed, (Figure S3). Parameters calculated on the basis of maximum carbonation degrees during cycles are given in Table 2. The carbonation characteristics at the beginning ( $X_{1-2}$ ) were significantly lower than in the case of natural sorbent. This is due to sulfation, which may also be confirmed by the increase of  $X_{1-2}$  with particle size, i.e., with decreasing degree of sulfation. However, more interestingly, Table 2 clearly shows the improved characteristics of reactivated sorbent at the end of multiple cycles ( $X_{9-10}$ ), with improved average carbonations ( $X_{1-10}$ ) for the chemically available CaO in the case of reactivated sorbent.

The results of multi-cycle carbonation for reactivated sorbent indicated that hydration by steam is potentially a very good method for sorbent reactivation for carbonation. The results also show the negative impact of sulfation, not only on carbonation of partially sulfated sorbent, but also on its characteristics with respect to hydration (Table S1) and subsequent carbonation. This arises because part of the sorbent is irreversibly combined as  $\text{CaSO}_4$ , which limits both hydration and carbonation of chemically available CaO. This led to the idea of examining the hydration of unsulfated spent sorbent and studying its impact for multi-cycle carbonation for the reactivated sorbent. The comparisons of time vs  $\text{CO}_2/\text{CaO}$  molar ratios (carbonation degree) during carbonation of unsulfated spent sorbents before and after reactivation are shown in Figure 3. It may be seen that sorbent after treatment in the tube furnace, at the end of the first cycle, had a carbonation degree  $\sim 35\%$ , regardless of particle size. The lower values obtained after the last cycle in the tube furnace may be explained similarly to the case of the partially sulfated sorbent, i.e., as being due to the lower temperature and greater sample mass in the tube furnace. The shapes of curves are uncharacteristic for carbonation (no initial fast stages). However, final values of the degree of carbonation were significantly higher than in the case of partially sulfated sorbent (about 11%, Figure 1). This highlights the problems of using sulfated sorbent carbonation. After reactivation, the sorbent had significantly higher activity, with a clearly visible fast stage at the start, and final value for the degree of carbonation in the first cycle above  $\sim 75\%$ , regardless of the particle size, which was significantly higher than related values for reactivated sulfated spent sorbent (Figure 2).

The behavior of reactivated unsulfated spent sorbent in multiple carbonation cycles is shown in Figure S3. The corresponding carbonation characteristics are given in Table 2. The results were exceptionally good. Carbonation in initial cycles ( $X_{1-2}$ ) was about 8% higher than for the natural sorbent. The reactivated sorbent had significantly better characteristics at the end of multi-cycle carbonation ( $X_{9-10}$  in the range



**FIGURE 3.** Steam reactivation effect on sorbent activity during carbonation in the TGA-unsulfated sorbent.

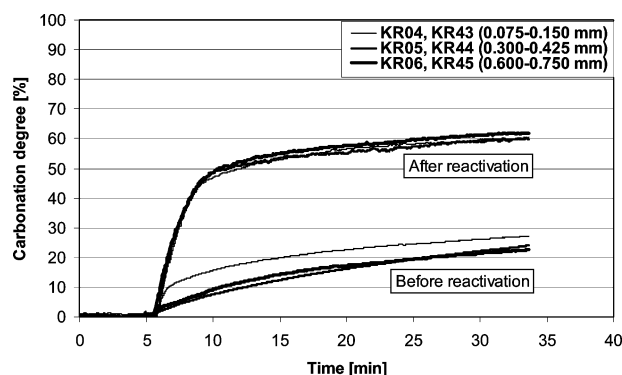
of 54.19–61.54% vs 34.26–39.52% for natural sorbent), which finally resulted in average carbonation ( $X_{1-10}$ ) of  $\sim 70\%$ . This analysis shows that steam reactivation actually improves sorbent characteristics in comparison to the original sorbent. This means that in the case of  $\text{CO}_2$  capture, separate  $\text{SO}_2$  capture, i.e., avoidance of sorbent sulfation, in combination with pressurized steam reactivation, may enable use of the sorbent for prolonged times, or at least until attrition phenomena dominate. This should aid in the commercialization of the process of  $\text{CO}_2$  separation by CaO-based sorbent in FBC systems.

Additional improvements in the process may also be achieved by using shorter times for carbonation cycles. The shape of carbonization curves shows two different stages: a short, fast stage at the beginning, comprising the majority of the  $\text{CO}_2$  capture; and a long, slow phase, responsible for only a few percent of  $\text{CO}_2$  capture. The behavior of sorbent in short-time multi-cycle carbonation tests is shown in Figure S4 (Supporting Information). Each carbonation step was stopped when it was determined that the first (fast) phase was finished, and each of the calcinations was stopped when sample mass achieved a minimal, constant value.

Mean duration of cycle depended on particle size and was 9.5, 11.7, and 12.3 min for three samples (increasing particle size). Characteristic values from multiple cycles are given in Table S2 (Supporting Information). Very similar values to those for cycles with 40 min duration (Table 2, natural samples: KR01, KR02, and KR03) were obtained, but these values are typically some few percent lower. This indicated that there is a (cycle number)-(sorbent characteristic) function, but not a (time)-(sorbent characteristic) function; thus it is not possible to reduce sintering by decreasing cycle times. However, significant improvement of the process is shown in that the same amount of sorbent may capture larger amounts of  $\text{CO}_2$  (3:1 here) over the same time period, i.e., the conversions in cycles are negligibly lower regardless of the shorter cycles (less than 1/3 the duration).

Additional steam reactivation experiments on natural sorbent calcined/sintered under different conditions were also performed (Table S3). Very similar hydration of the samples is obtained under different conditions, but generally, the lowest degree of hydration occurred for samples produced under more drastic conditions (1100  $^\circ\text{C}$ , 24 h), as expected based on increased sintering with increasing temperature.

Samples obtained under different conditions were carbonated before and after reactivation. Figure 4 shows such carbonation curves for sorbent obtained at 1100  $^\circ\text{C}$ . Here curves have similar shapes as those for spent sorbent in multiple cycles (Figure 3), but the final values are noticeably lower in the case of sorbent obtained at high temperature. This shows reactivation of more sintered sorbent is also possible. This is important, because more intensive sintering and decrease of sorbent activity may be expected in real



**FIGURE 4.** Steam reactivation effect on sorbent activity during carbonation in the TGA—sorbent calcined/sintered at 1100 °C for 24 h and hydrated by steam.

**TABLE 3.** BET Surface Area ( $S_{\text{BET}}$ ) of Kelly Rock Samples Obtained under Following Conditions: Calcination (850 °C, 2 h,  $\text{N}_2$ ); Sulfation (850 °C, 2 h, 15%  $\text{CO}_2$ , 3%  $\text{O}_2$ , 1%  $\text{SO}_2$ ,  $\text{N}_2$  Balance);  $\text{CO}_2$  Capture (20 Cycles, Carbonation: 650 °C, 30 min, 20%  $\text{CO}_2$ ,  $\text{N}_2$  Balance; Calcination: 850 °C, 30 min,  $\text{N}_2$ ); Hydration (200 °C, 30 min, Saturated Steam)

sample	pretreatment	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )
KR06 (600–750 $\mu\text{m}$ )	calcination, 1100 °C, 24 h	2.28
KR09 (600–750 $\mu\text{m}$ )	calcination, 850 °C, 24 h	3.86
KR10 (75–150 $\mu\text{m}$ )	calcination	4.06
KR11 (300–425 $\mu\text{m}$ )	calcination	4.54
KR12 (600–750 $\mu\text{m}$ )	calcination	4.89
KR21 (600–750 $\mu\text{m}$ )	calcination + sulfation	1.85
KR24 (600–750 $\mu\text{m}$ )	calcination + sulfation + $\text{CO}_2$ capture + calcination	1.91
KR25 (75–150 $\mu\text{m}$ )	calcination + $\text{CO}_2$ capture + calcination	3.18
KR26 (300–425 $\mu\text{m}$ )	calcination + $\text{CO}_2$ capture + calcination	3.33
KR27 (600–750 $\mu\text{m}$ )	calcination + $\text{CO}_2$ capture + calcination	2.96
KR39 (600–750 $\mu\text{m}$ )	calcination + sulfation + $\text{CO}_2$ capture + hydration + calcination	5.17
KR40 (75–150 $\mu\text{m}$ )	calcination + $\text{CO}_2$ capture + hydration + calcination	6.89
KR41 (300–425 $\mu\text{m}$ )	calcination + $\text{CO}_2$ capture + hydration + calcination	7.36
KR42 (600–750 $\mu\text{m}$ )	calcination + $\text{CO}_2$ capture + hydration + calcination	8.46

reactors, e.g., if the calcination temperature needs to be increased with the aim of producing  $\text{CO}_2$  in higher concentration (>95%) or for the case of working under increased pressure (see eq 2).

Figure S5 also shows that hydrated sorbents have better properties than the original sorbent. This may also be seen from the parameters in Table 2.

It is generally accepted that solid activity in heterogeneous reactions such as sulfation and (cyclic) carbonation is affected by structural properties of the solid (e.g., pore structure). BET surface area measurements were made for samples of sorbent obtained in this study (Table 3). The specific pore surface area and pore volume distribution of sorbents were also analyzed using the BJH method. The results and conclusions are in agreement with BET data and are not presented here. BET surface areas are highest for sorbents shown to be most active in the TGA experiments—the unsulfated samples after hydration and calcination (KR40, KR41, and KR42: 6.89–8.46  $\text{m}^2/\text{g}$ )—which were significantly higher than in the case of spent sorbent (KR25, KR26, and KR27: 2.96–3.33  $\text{m}^2/\text{g}$ ), as well as in the case of original sorbent after calcination (KR10, KR11, and KR12: 4.06–4.89

$\text{m}^2/\text{g}$ ). This is in close agreement with the conclusion that steam hydration actually gives the sorbent better properties than the original untreated sorbent (see Figures S1 and S3). Moreover, in both cases, BET surface area increases with particle size, i.e., with decreasing impurity content, which indicates that impurities improve sintering.

Sulfation strongly influences both carbonation and hydration, resulting in lower BET surface area after hydration and calcination of partially sulfated samples (KR39: 5.17  $\text{m}^2/\text{g}$ ) in comparison with the corresponding unsulfated sample (KR42: 8.46  $\text{m}^2/\text{g}$ ). However, the BET surface area of reactivated sulfated sorbent (KR39: 5.17  $\text{m}^2/\text{g}$ ) is significantly higher than before reactivation (KR24: 1.91  $\text{m}^2/\text{g}$ ). The lowest pore surface area was determined in partially sulfated samples (KR21: 1.85  $\text{m}^2/\text{g}$ ). The value after cyclic carbonation was somewhat higher (KR24: 1.91  $\text{m}^2/\text{g}$ ), which indicates that no additional decrease of surface area occurred during  $\text{CO}_2$  cycles. Somewhat higher surface area observed after  $\text{CO}_2$  cycles may be linked to sorbent reactivation by  $\text{CO}_2$  with respect to sulfation, i.e.,  $\text{CO}_2$  enhances the ability of the sorbent to capture  $\text{SO}_2$  (10).

Surface areas of sorbent calcined/sintered under different conditions showed a strong influence of temperature, e.g., the small BET surface area value of the sample sintered at 1100 °C for 24 h (KR06: 2.28  $\text{m}^2/\text{g}$ ). However, a “deeply” sintered sorbent can be reactivated (Figures 4 and S5). The time was not critical for sorbent activity (Figures S1 and S4 and Tables 2 and S2), which was also confirmed by the BET surface area values for samples KR09 (3.86  $\text{m}^2/\text{g}$ ) and KR12 (4.89  $\text{m}^2/\text{g}$ ), which are relatively similar despite the very different calcination/sintering times (2 and 24 h).

To examine sorbent surface morphologies, SEM images of samples were obtained at different magnifications, from 20 $\times$  to 10000 $\times$ . A Hitachi S3400 SEM with 20 kV of accelerating voltage was used. Examination shows surface morphologies are in agreement with BET surface area determinations. Typical SEM images are given in Figure S6. It was found that sintered particle samples before reactivation (a, b) contain larger sub-grains than samples after reactivation (c, d), which directly correlates with higher surface area and better activity in the  $\text{CO}_2$  cycles.

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## Supporting Information Available

Tables and Figures showing TGA analysis of reactivated sorbent from  $\text{CO}_2$  capture cycles and reactivated “deeply” sintered sorbent; TGA results of multiple calcination/carbonation tests of natural sorbent (in typical and short-time multicycle carbonation tests), reactivated spent sorbent from calcination/carbonation cycles (partially sulfated and unsulfated) and reactivated “deeply” sintered sorbent; and SEM images of the sorbents. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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