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# CO<sub>2</sub> Looping Cycle Performance of a High-Purity Limestone after Thermal Activation/Doping

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The influence of thermal pretreatment on the performance of a high-purity limestone (La Blanca) during CO<sub>2</sub> capture cycles is investigated in this paper. This limestone was chosen for more detailed investigation because, in earlier research, it failed to show any favorable effect as a result of thermal pretreatment. Here, the original sample, with a particle size of 0.4–0.6 mm, and ground samples were thermally pretreated at 1000–1200 °C, for 6–24 h, and then subjected to several carbonation/calcination cycles in a thermogravimetric analyzer (TGA). This work shows that thermal pretreatment failed to produce a significant self-reactivation effect during CO<sub>2</sub> cycles, despite the use of a wide range of conditions during pretreatment (grinding, temperature, and pretreatment duration) as well as during cycling (CO<sub>2</sub> concentration and duration of the carbonation stage). Additional doping experiments showed that both high Na content and lack of Al in La Blanca limestone cause poor self-reactivation performance after thermal pretreatment. Scanning electron microscope–energy-dispersive X-ray (SEM–EDX) analyses also confirmed more pronounced sintering and loss of activity, which we believe are caused by the relatively high Na content. However, stabilization of sorbent particle morphology by Al can allow this limestone to show self-reactivation performance and higher conversions over a longer series of CO<sub>2</sub> cycles.

## Introduction

The separation of CO<sub>2</sub> from flue gas by CaO-based sorbents in fluidized bed combustion (FBC) systems is a new and intensively investigated technology for reduction of CO<sub>2</sub> emissions from fossil fuel power generation systems.<sup>1,2</sup> The process can produce a concentrated stream of CO<sub>2</sub>, ready for liquefaction. Sequestration of liquid CO<sub>2</sub> in a wide range of geological formations can help in the mitigation of climate change caused by greenhouse gases in the atmosphere.<sup>3,4</sup>

The CaO-based FBC CO<sub>2</sub> looping cycle process is based on the use of inexpensive and abundant limestone (or dolomite) that can easily be decomposed to lime (CaO). This sorbent has favorable thermodynamic properties in comparison to other metal oxides,<sup>5</sup> and its use in FBC systems allows the technology to be economically competitive with other options for producing

pure streams of CO<sub>2</sub>.<sup>6–8</sup> The amount of sorbent that must be used in a number of capture/regeneration (carbonation/calcination) cycles strongly depends upon its rate of loss of activity. A possible option for the system is sorbent regeneration, although the practicality of such an approach has still to be demonstrated. However, carbonation conversions normally decrease with increasing numbers of reaction cycles. The decay of activity is described qualitatively<sup>9,10</sup> and quantitatively<sup>11,12</sup> by simple models, which are based on the idea of sorbent sintering.<sup>9,13,14</sup> 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<sub>3</sub>) on the reacting CaO surface.<sup>15</sup> Thus, a very fast initial carbonation reaction stage finishes with a lower

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level of conversion (typically less than 10%) and then shifts into a very slow reaction stage, which is useless for a practical system and controlled by diffusion through the product layer of CaCO<sub>3</sub>.<sup>13,16</sup>

The improvement of sorbent activity for extended use in commercial plants is imperative because sorbent replacement costs strongly influence the overall cost of a Ca looping cycle process.<sup>8</sup> Reactivation by hydration currently appears to be a promising method for recovery of the sorbent activity as noted above.<sup>17–19</sup> Another approach is sorbent doping, but unfortunately to date, it does not appear to significantly improve sorbent activity during multiple carbonation cycles,<sup>20,21</sup> probably because of the fact that most doping agents enhance sintering, which interestingly is also enhanced by the presence of impurities in the sorbent.<sup>22,23</sup> An exception is doping by Al<sub>2</sub>O<sub>3</sub>, which shows fairly promising results.<sup>21,24–26</sup>

The thermal pretreatment of the sorbent at high temperatures showed beneficial effects in the case of a number of sorbents.<sup>10,22</sup> Here, thermal pretreatment typically causes lower conversions during the early cycles, but conversions in later cycles are higher than those for the original, untreated sorbents. Thus, the overall removal capacity over the lifetime of a given limestone is greater. This effect is more pronounced in the case of sorbents with small particles obtained by synthesis<sup>10</sup> or grinding.<sup>27</sup> Our recent study<sup>27</sup> showed that conversions of four Canadian limestones, after grinding and pretreatment at temperatures of 1000–1200 °C, increased along cycles, reaching ~50% in the 30th cycle. This phenomenon of increasing conversion with an increasing number of reaction cycles has been called self-reactivation. Developing sorbents with self-reactivation performance and their use for CO<sub>2</sub> capture would be of great interest because the economics and environmental advantages of the

**Table 1. Elemental Analysis of Limestone Samples Used**

compound	La Blanca	Kelly Rock
Al <sub>2</sub> O <sub>3</sub> (wt %)	<0.10	1.0
CaO (wt %)	54.39	51.61
Fe <sub>2</sub> O <sub>3</sub> (wt %)	<0.01	0.37
K <sub>2</sub> O (wt %)	<0.02	0.27
MgO (wt %)	0.11	0.52
Na <sub>2</sub> O (wt %)	1.07	<0.10
SiO <sub>2</sub> (wt %)	<0.10	3.70
TiO <sub>2</sub> (wt %)	<0.03	0.06
loss on fusion (wt %)	44.20	41.69
sum	99.77	99.32

process to a large extent depend upon the change in sorbent activity with an increasing number of cycles.<sup>6–8</sup>

However, it should be mentioned that there are sorbents that do not show enhanced performance after pretreatment at high temperatures, and La Blanca limestone is one example. In tests on La Blanca,<sup>28</sup> precalcination of limestones was aimed at CaO sorbents of lower initial pore surface area but more stable structure for subsequent carbonation/calcination cycles. However, the test failed with this high-purity limestone (with Na as the main impurity) with typical particle size ranges and carbonation/calcination reaction times. The present study is a detailed re-investigation of the behavior of La Blanca limestone after high-temperature pretreatment. The influence of different conditions during pretreatment and CO<sub>2</sub> looping cycles as well as the influence of impurities/additives were examined to discover the causes for the different behavior observed with this limestone in comparison to previously studied Canadian limestones.

## Experimental Section

La Blanca (LB) (particle size of 400–600 μm) and Kelly Rock (KR) (particle size of 300–425 μm) limestones were used for the experiments described here. The elemental analysis of LB and KR limestones used are given in Table 1. Interesting characteristics of LB limestone are its high purity and almost complete absence of Si and Al. For this limestone, the main impurity is Na, 1.07% Na<sub>2</sub>O (1.92% in the calcined limestone). The results obtained with these limestones have been compared under the same conditions to results obtained with pure CaO in powdered form, derived from the calcination of calcium acetate.

Sample pretreatments at different temperatures and under various CO<sub>2</sub> looping cycle conditions were performed in two thermogravimetric analyzers (TGAs). In a Perkin-Elmer TGA-7 thermogravimetric analyzer, the sample was suspended in a quartz tube (i.d. of 20 mm) on a platinum pan (i.d. of 5 mm). The gas flow rate, controlled by a flow meter, was 0.04 dm<sup>3</sup>/min. The temperature and gas used were controlled by Pyris software. The second TGA setup has been described elsewhere,<sup>29</sup> and it is very similar in dimensions and operating conditions. Data on sample mass during the experiments were collected, and the degree of carbonation was calculated on the basis of the mass change, assuming that the mass change occurs only because of formation/decomposition of CaCO<sub>3</sub>.

To investigate the influence of thermal pretreatment on CO<sub>2</sub> looping performance, samples were preheated at 1000–1200 °C, typically for 6 h (some pretreatments were for 24 h). The conditions for the benchmark looping tests were 800 °C (isothermally, both calcination and carbonation), 30 min of carbonation, and 10 min of calcination, with 100% N<sub>2</sub> for calcination and 50% CO<sub>2</sub> (N<sub>2</sub> balance) for carbonation; 30 mg samples were used. Influences of CO<sub>2</sub> concentration and duration of the carbonation stage were

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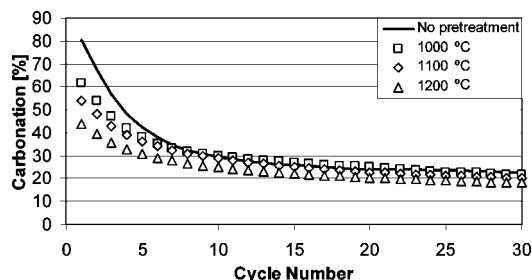
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**Figure 1.** Influence of the pretreatment of LB limestone at different temperatures for 6 h on sorbent capture capacities during CO<sub>2</sub> cycles.

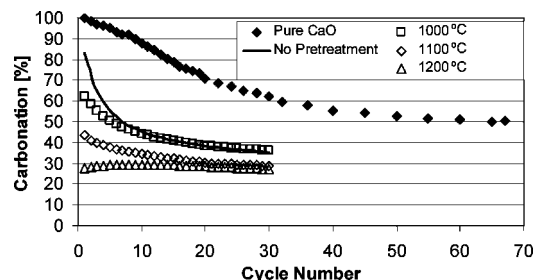
examined by variation of these parameters: 25–100% CO<sub>2</sub>, and 10–60 min carbonation. The important differences in behavior of pretreated LB and KR limestones were explored by sample doping prior to grinding and pretreatment. KR was doped with 10, 5, and 2.5 wt % Na<sub>2</sub>CO<sub>3</sub>, and LB was doped with 10, 5, and 2.5 wt %  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (1  $\mu$ m, BUEHLER). Benchmark experiments with CaO derived from calcium acetate did not include any doping.

The morphologies of the sample surfaces were examined by scanning electron microscopy (SEM) using a Hitachi S3400 microscope with 20 kV of accelerating voltage. SEM images were obtained at different magnifications, from 20 $\times$  to 10 000 $\times$ . The microscope was equipped with energy-dispersive X-ray (EDX) analyzers, which enabled us to examine the elemental composition of sample surfaces and correlate surface morphologies with elemental compositions. XRD data were collected on a Bruker D5000TT diffractometer over the angular range of 10–70° (2 $\theta$ ), in 0.02° steps and 20 s per step. The phases were identified, and quantitative analyses of the samples were performed using  $\alpha$ -alumina (Al<sub>2</sub>O<sub>3</sub>) as an internal spiking standard.

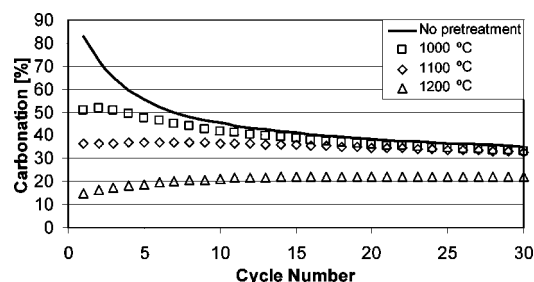
## Results and Discussion

The comparison of CO<sub>2</sub> capture capacity with increasing numbers of looping cycles for the “original” particle size (400–600  $\mu$ m) sample is given in Figure 1. Similar to a number of previously investigated limestones,<sup>29</sup> the original, nonground sorbent does not show self-reactivation behavior. Interestingly, the pretreated LB sorbent has a lower CO<sub>2</sub> capture capacity, even after 30 cycles, unlike our earlier results obtained for a number of Canadian limestones.<sup>22,27</sup> These earlier results suggested that suitably long thermal pretreatment at appropriate temperatures and durations could generate higher conversions after a longer series of cycles than those for original, untreated samples.

The next experiments were performed with powdered samples, because it has been qualitatively demonstrated that grinding helps in activation<sup>22,27</sup> and it can more clearly reveal intrinsic differences in performance during carbonation/calcination between the limestones (because of chemical composition differences). As a benchmark for these studies, the results obtained with pure (AR standard) CaO derived from powdered calcium acetate are also used in this discussion. The cycling results for powdered and pretreated samples of LB at high temperatures (Figure 2) are very different than those obtained with Canadian limestones. The powdered sample of LB did not show a significantly favorable influence of thermal pretreatment, and self-reactivation was obtained only at the highest temperature (1200 °C). However, the conversions beyond 15 cycles showed a slightly decreasing trend. These conversions are <30%, which is significantly lower than earlier results obtained for Canadian limestones (40–50%, after 30 cycles when they showed self-reactivation performance). On the other hand, the results in terms of conversion from pure CaO (calcined calcium acetate) show



**Figure 2.** Influence of the pretreatment of powdered LB limestone at different temperatures for 6 h on sorbent capture capacities during CO<sub>2</sub> cycles.



**Figure 3.** Influence of the pretreatment of powdered LB limestone at different temperatures for 24 h on sorbent capture capacities during CO<sub>2</sub> cycles.

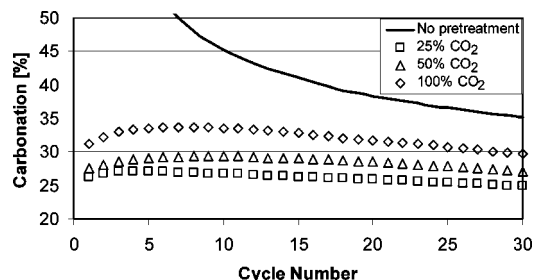
that it presents much better performance than natural limestones, in the range of 60% after 30 cycles and around 50% (stabilized) after 60 cycles. The importance of particle size and thus the importance of the type of grinding process in affecting the reversibility of the carbonation reaction should be mentioned here. Work by Barker<sup>30</sup> suggested that particles as small as 10 nm could display almost total reversibility in the carbonation reaction (for extended carbonation times and mild calcination conditions). It also needs to be stressed that the calcination conditions applied during the experiments carried out in this work helped to maintain particle conversion with the number of cycles and that powdered pure CaO is more sensitive to calcination temperature than natural limestones at typical grain size.<sup>31</sup>

Similar results (Figure 3) were obtained in the case of pretreatment for 24 h; however, the conversions of the sample pretreated at 1200 °C dropped to <20% showed a slight self-reactivation performance. This experiment demonstrated clearly that LB limestone has atypical properties with regard to behavior following thermal pretreatment and, in consequence, self-reactivation behavior. However, this is consistent with previously published research on LB limestone that showed an unfavorable influence of calcination at higher temperatures on CO<sub>2</sub> capture capacities.<sup>29</sup> Additionally, calcined and recarbonated samples of LB underwent a more detailed analysis of presintering effects (10 and 30 min calcination times in pure CO<sub>2</sub> at 960 °C) on sorbent performance following textural evolution, as well as on carbonation conversion, along the cyclic experiments.<sup>28</sup> In addition to the known mechanisms of deactivation because of grain growth and limited diffusion of CO<sub>2</sub> through the product layer, that work revealed that pore closure effects and pore size distributions with bottlenecks were also present in the samples (400–600  $\mu$ m), together with an overall

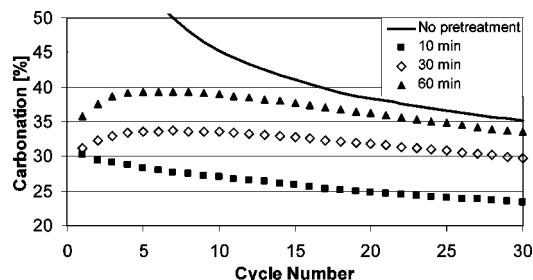
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**Figure 4.** Influence of the CO<sub>2</sub> concentration on carbonation conversions of powdered LB limestone pretreated at 1200 °C for 6 h.



**Figure 5.** Influence of carbonation durations on carbonation conversion of powdered LB limestone pretreated at 1200 °C for 6 h (the CO<sub>2</sub> concentration during carbonation was 100%).

shrinkage of the particles. The CaO presintering experiments with extended residence time (30 min) during the first calcination caused important changes in the pore network, with a pore-size distribution peaking at 189 nm, more than twice the size of the pores (85 nm) in the fresh CaO, calcined for 10 min.<sup>28</sup> However, despite these large initial differences in structure, the behavior of both systems rapidly converged, becoming virtually indistinguishable from each other after the 30th cycle, because the calcium carbonate formed during carbonation did not maintain a memory of its previous calcinations and recarbonations, with regard to its structural development.

Investigation of LB was continued in this work with powdered sample (to induce some activation obtained by grinding and to avoid pore effects at the particle level) to determine if this limestone has better behavior if one changes the (i) concentration of CO<sub>2</sub> and (ii) duration of carbonation stages. In Figure 4, one can see the slightly favorable influence of a higher CO<sub>2</sub> concentration on increased conversion in the initial cycles. It is also apparent that, during later cycles, conversions decrease in a more pronounced manner with higher CO<sub>2</sub> concentrations. Higher conversions (caused by higher CO<sub>2</sub> concentrations) result in a faster decrease of activity in later cycles, most likely as a result of the formation and decomposition of larger amounts of CaCO<sub>3</sub>, accelerating the loss of surface area and activity.

Figure 5 shows that increased carbonation duration slightly favors self-reactivation only during the initial cycles, here ~5 cycles (60 min carbonation) and during the first ~10 cycles (30 min carbonation). Beyond that, carbonation conversions decrease. This carbonation duration influence agrees with the

pore-skeleton model.<sup>10,27,28</sup> That model proposes the presence of a soft (more reactive) layer of sorbent at the surface of pores and a less reactive interior skeleton (responsible for the structural stability of the particle). With longer carbonation times at the beginning, higher conversions were obtained, which consequently increased the thickness of the soft layer and damaged the interior skeleton, leading to the loss of particle surface area and lower conversions in later cycles.

These results again demonstrate the very different behavior of LB limestone in comparison to four Canadian limestones that we have previously examined.<sup>27</sup> Thermal activation cannot generate self-reactivation behavior of LB in a longer series of cycles, despite the use of samples in powdered form, the variation of temperature and time for thermal pretreatment, and the variation of the CO<sub>2</sub> concentration. We expect that variation in calcination duration (which has not been examined for this limestone thus far but has been examined for Canadian limestones) will be equally ineffective.

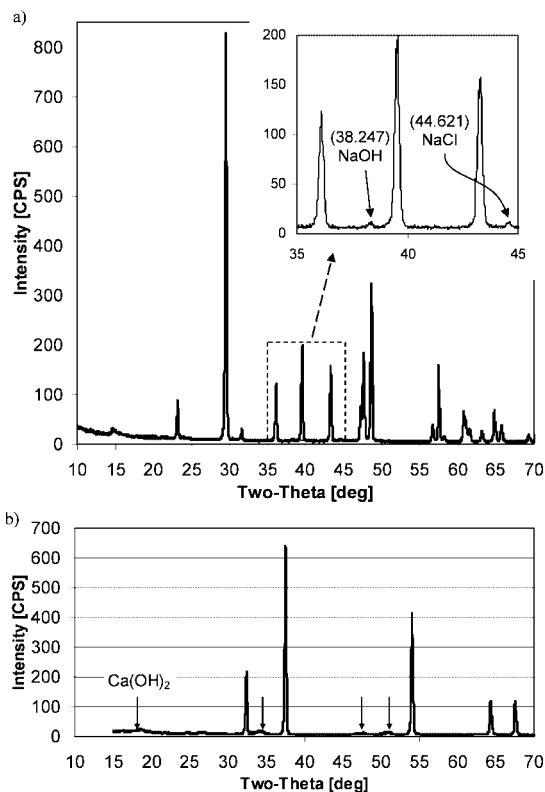
The examination was continued in an attempt to determine the causes for different properties displayed by LB limestone. In the elemental analysis of LB (Table 1), the somewhat higher Na<sub>2</sub>O content (1.07%) in comparison to that seen with our previously investigated limestones (<0.2%) was noted. Another potentially significant difference was the absence of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> in LB (0.0%) in comparison to analysis results for Canadian limestones (Al<sub>2</sub>O<sub>3</sub>, 0.33–1.44%; SiO<sub>2</sub>, 1.03–5.34%).<sup>17,18</sup>

When Si and Al are present, they may be combined with CaO in aluminosilicates, such as are found in clay minerals, common in limestone. The minerals can also contain Na as well as other elements. The fact that there was no Si or Al in LB suggests that in this limestone the Na is probably present in a different form. Thus, to determine how Na is present in LB, XRD analyses of the original limestone and a sample calcined at 1000 °C for 24 h (typically used for pretreatment) were performed and results are presented in Figure 6. An XRD spectrum of almost pure CaCO<sub>3</sub> can be seen in Figure 6a. Small peaks of NaO and NaCl are also present, and they are the only Na-containing impurities identified in the crystal phase. Their quantification showed that Na contained in them corresponds to the NaO content determined by elemental analysis (Table 1), which means that Na, most likely, is not present in a considerable amount in the CaCO<sub>3</sub> lattice structure or in any amorphous phase. However, after thermal pretreatment, Na-containing compounds were not identified (Figure 6b), which implies that, after decomposition of NaOH and NaCl, Na<sup>+</sup> ions are incorporated in the crystal structure of CaO. The XRD spectrum shows that the sample, apart from CaO, contains some Ca(OH)<sub>2</sub> that was formed during sample handling and preparation for the XRD test.

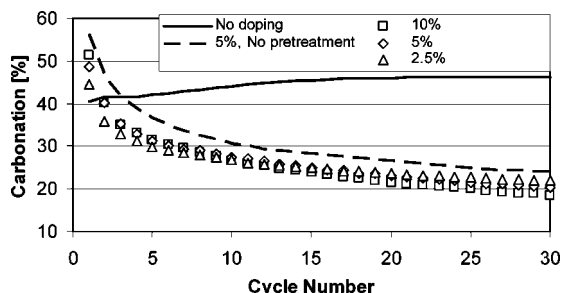
It is known that the presence of Na<sup>+</sup> ions in the crystal structure of CaO causes lattice defects, which enhance mass transfer and sintering,<sup>23</sup> that unfavorably reflect on CO<sub>2</sub> capture capacity.<sup>22</sup> Thus, the first idea was to check if and how doping of limestone by Na<sub>2</sub>CO<sub>3</sub> affects its capture capacity in a series

**Table 2.** Results of XRD Quantitative Analyses of KR Samples Doped with 5 wt % Na<sub>2</sub>CO<sub>3</sub> after Pretreatment/Cycles

chemical compound	KR plus 5% Na <sub>2</sub> CO <sub>3</sub> 1000 °C, 24 h		KR plus 5% Na <sub>2</sub> CO <sub>3</sub> 1000 °C, 24 h, 30 CO <sub>2</sub> cycles	
lime CaO (wt %)	74.4		77.8	
sodium calcium silicate Na <sub>2</sub> CaSiO <sub>4</sub> (wt %)	6.3	(2.2 wt % Na <sub>2</sub> O)	7.3	(2.5 wt % Na <sub>2</sub> O)
sodium aluminum silicon oxide Na <sub>1.95</sub> (Al <sub>1.95</sub> Si <sub>0.05</sub> O <sub>4</sub> ) (wt %)	3.2	(1.2 wt % Na <sub>2</sub> O)	3.6	(1.3 wt % Na <sub>2</sub> O)
sodium aluminum oxide NaAlO <sub>2</sub> (wt %)	1.5	(0.6 wt % Na <sub>2</sub> O)	0.8	(0.3 wt % Na <sub>2</sub> O)
larnite Ca <sub>2</sub> (SiO <sub>4</sub> ) (wt %)	11.6		7.4	
portlandite Ca(OH) <sub>2</sub> (wt %)	3.0		3.1	
sum	100.0	(4.0 wt % Na <sub>2</sub> O)	100.0	(4.1 wt % Na <sub>2</sub> O)



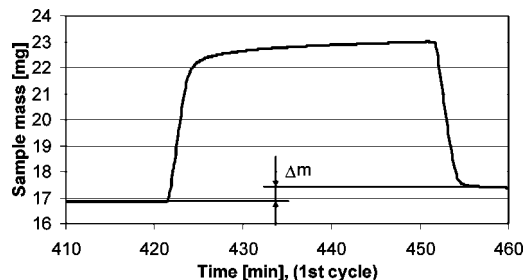
**Figure 6.** XRD spectra of LB samples: (a) original limestone and (b) lime after calcination at 1000 °C for 24 h.



**Figure 7.** Influence of doping of KR limestone by  $\text{Na}_2\text{CO}_3$  on its  $\text{CO}_2$  capture capacity after activation at 1000 °C for 6 h.

of  $\text{CO}_2$  looping cycles. KR limestone (300–425  $\mu\text{m}$ ) was chosen for these experiments. Measured masses of limestone were mixed with corresponding masses of  $\text{Na}_2\text{CO}_3$  to obtain mixtures with 10.0, 5.0, and 2.5 wt % of  $\text{Na}_2\text{CO}_3$  in the limestone. The mixtures were ground, and TGA runs were performed: pretreatment at 1000 °C (the temperature that gave the best self-reactivation result<sup>27</sup>) for 6 h followed by 30  $\text{CO}_2$  cycles (30 min/50%  $\text{CO}_2$  for carbonation and 10 min/100%  $\text{N}_2$  for calcination).

From Figure 7, it can be seen that KR, which with no doping displayed a pronounced self-reactivation effect, showed a drastic loss of activity with increasing cycles after doping, especially during the initial cycles. Moreover, pretreatment had a negative effect on capture capacity; i.e., conversions of pretreated samples were lower than those for an untreated sample. An interesting result is the increased conversions with increasing amount of doped  $\text{Na}_2\text{CO}_3$  during the first ~15 cycles and the opposite effect during the remaining cycles. This, we believe, is the result of two opposing effects of Na on CaO capture capacity. The first effect is a favorable increase of  $\text{Ca}^{2+}$  diffusion in CaO/ $\text{CaCO}_3$  in the presence of  $\text{Na}^+$  ions. This enhanced diffusion in the product layer in general can be expected to accelerate



**Figure 8.** KR sample (doped with 5 wt %  $\text{Na}_2\text{CO}_3$ ) mass changes during the first carbonation/calcination cycle after pretreatment at 1000 °C for 6 h.

gas–solid reactions at the reacting surface. For example, in sulfation, there is evidence that doping of the sorbent with  $\text{Na}_2\text{O}$  increases conversion.<sup>32</sup>

The second effect is enhancement of mass transfer in the presence of  $\text{Na}^+$  ions, which leads to more pronounced sintering.<sup>23</sup> This effect is cumulative with increasing numbers of cycles and, after ~15 cycles in the experiment explored here, becomes dominant. The sorbent surface is sintered to such an extent that conversion loss caused by it cannot be compensated by conversion growth because of enhanced diffusion in the product layer.

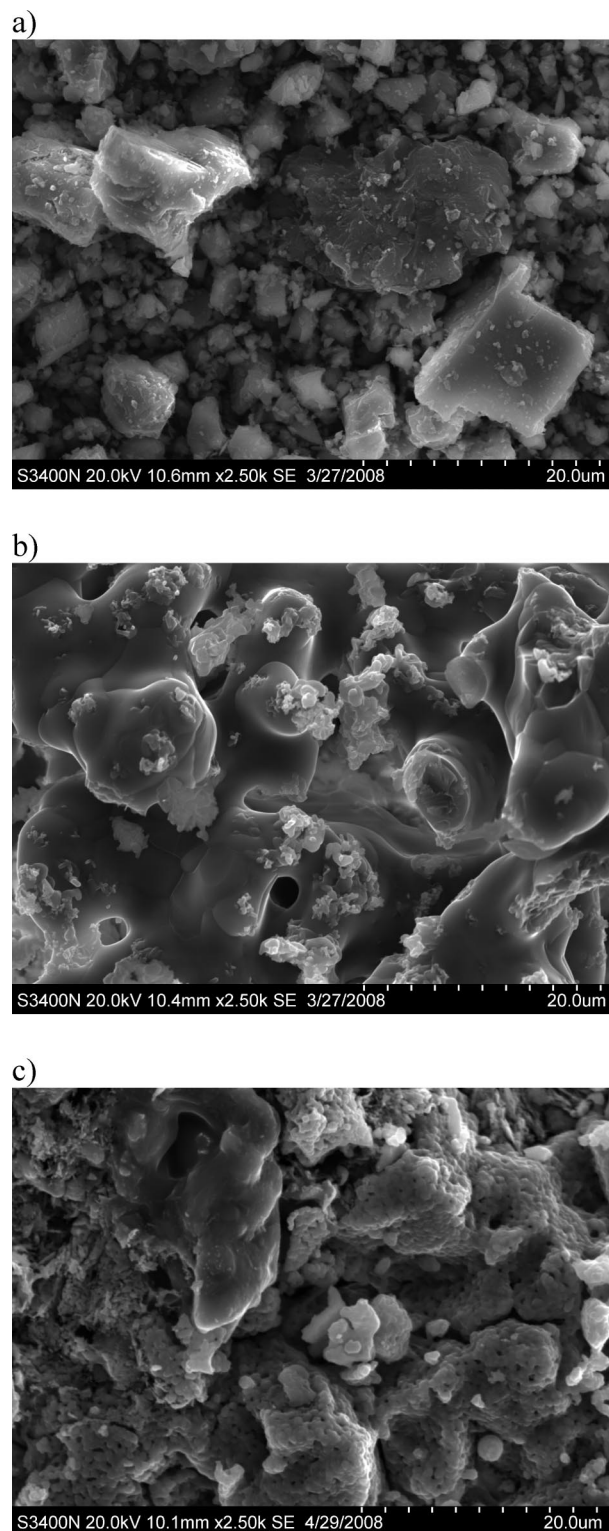
Additional effects that enhance sintering in CaO/ $\text{Na}_2\text{O}$ / $\text{CO}_2$  systems include the lower melting point/nonstability of  $\text{Na}_2\text{O}$  as well as the formation of other compounds ( $\text{Na}_2\text{Ca}(\text{CO}_3)_2/\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$ ) with lower melting points in comparison to that of CaO. The evidence for their formation can be seen in Figure 8, where mass changes during the first cycle are presented for a sample doped with 5%  $\text{Na}_2\text{CO}_3$  and pretreated at 1000 °C for 6 h. Sample mass after carbonation and decomposition is clearly higher than that before carbonation. This suggests that compound(s) containing  $\text{CO}_2$  must have been formed, and we have recently demonstrated a rather similar effect with  $\text{Na}_2\text{CO}_3$  and  $\text{CaSO}_4$ .<sup>33</sup>

The SEM images of KR powder doped with 5%  $\text{Na}_2\text{CO}_3$  before and after 30 cycles (no pretreatment) are presented in Figure 9. For comparison, a SEM image of an original (undoped) sample after 30  $\text{CO}_2$  cycles is also presented. These images very strongly suggest pronounced sintering and the loss of surface area as a result of the presence of Na in the CaO powder. The results presented in Figures 7–9 highlight the unfavorable influence of Na in CaO during a series of  $\text{CO}_2$  cycles, especially when considering pretreated samples. This is one possible explanation for the poorer performance of pretreated LB limestone in comparison to Canadian limestones.

However, it should be highlighted here that doping of KR by  $\text{Na}_2\text{O}$  may have different effects than those of the presence of Na in LB. With KR, at the temperatures used, the additive would give a surface melt, which enhances ion migration across phase boundaries; reactions with the natural impurities are also possible, confirmed by the results of XRD analyses of doped samples after pretreatment/cycles (Table 2 and Figure 10). It can be seen that Si- and Al-containing compounds were formed with the  $\text{Na}_2\text{O}$  dopant. The spectra of the two samples are very similar, with the same peaks only somewhat differing in the intensity, showing that most reactions already occurred during pretreatment at high temperature. The content of  $\text{Na}_2\text{O}$ , obtained

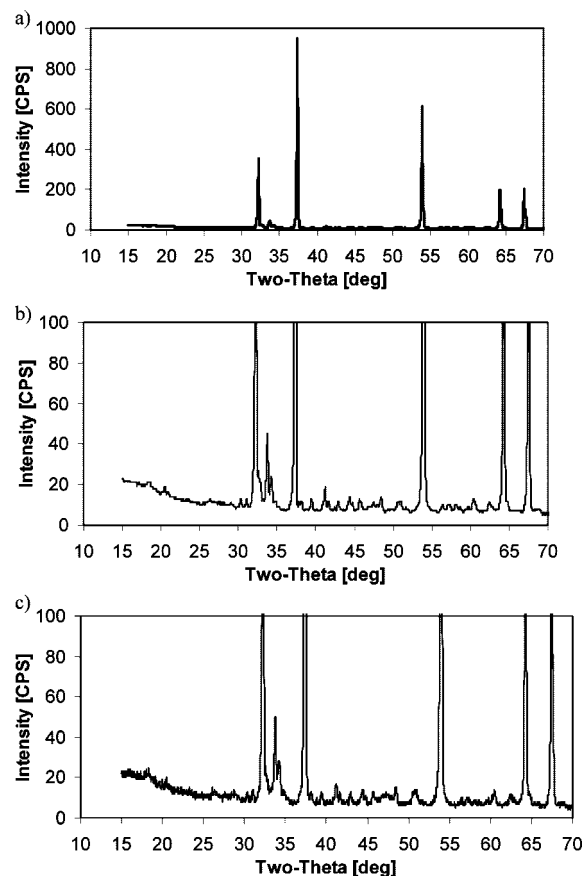
(32) Borgwardt, R. H.; Bruce, K. R.; Blake, J. An Investigation of Product-Layer Diffusivity for CaO Sulfation. *Ind. Eng. Chem. Res.* **1987**, *26*, 1993–1998.

(33) Wang, J.; Wu, Y.; Anthony, E. J. Reactions of Solid  $\text{CaSO}_4$  and  $\text{Na}_2\text{CO}_3$  and Formation of Sodium Carbonate Sulfate Double Salts. *Thermochim. Acta* **2007**, *459*, 121–124.

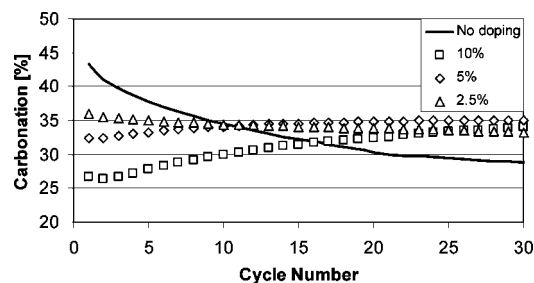


**Figure 9.** SEM images of (a) KR powder doped with 5% Na<sub>2</sub>CO<sub>3</sub>, (b) residue after 30 CO<sub>2</sub> cycles, and (c) original sample after 30 CO<sub>2</sub> cycles.

as the sum of Na<sub>2</sub>O contents in identified Na-containing compounds (about 4%), is somewhat lower than what should be as a result of sample doping (5%). This suggests that some Na may be in the amorphous phase as well as in the CaO lattice (because of similar Ca<sup>2+</sup> and Na<sup>+</sup> ionic radii). These CaO lattice defects enhance ion migration, i.e., mass transfer in CaO particles, leading to more pronounced loss of activity along CO<sub>2</sub> cycles. Here, it should also be mentioned that there is some evidence available in the literature,<sup>34</sup> indicating that doping with



**Figure 10.** XRD spectra of KR samples doped with 5 wt % Na<sub>2</sub>CO<sub>3</sub>: (a and b) after pretreatment at 1000 °C for 24 h and (c) after pretreatment at 1000 °C for 24 h and 30 CO<sub>2</sub> cycles.



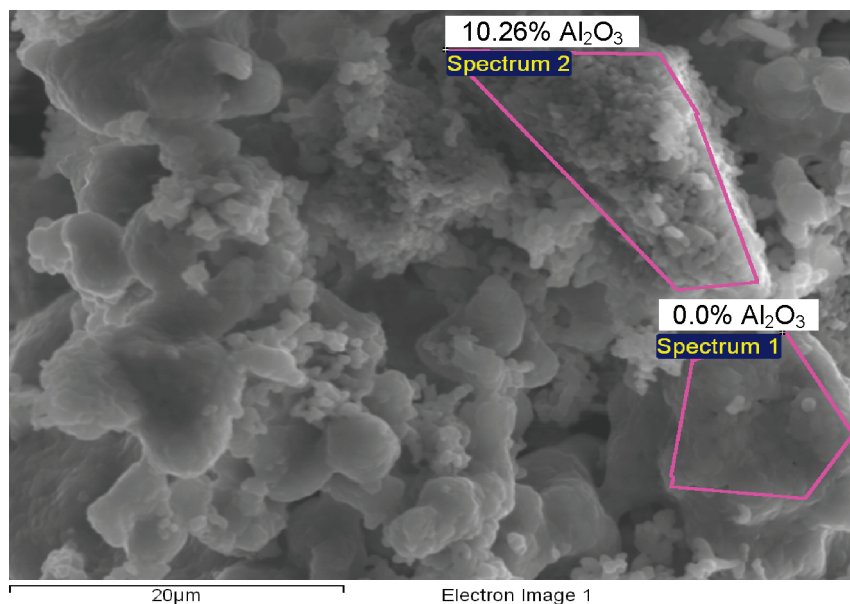
**Figure 11.** Influence of doping of LB limestone with Al<sub>2</sub>O<sub>3</sub> on its CO<sub>2</sub> capture capacity after activation at 1100 °C for 6 h.

very small amounts of Na<sub>2</sub>O (by washing with very dilute solutions of Na<sub>2</sub>CO<sub>3</sub>) might be favorable for long-term reactivity.

The absence of Si and Al in LB limestone may also lead to the poorer performance of pretreated samples, although the evidence for a favorable effect of Si is at best ambiguous. Thus, it is known that SiO<sub>2</sub> reacts with CaO, producing silicates with lower melting points than those of CaO, which suggests there would be an unfavorable influence of SiO<sub>2</sub>, and this has been recently experimentally confirmed.<sup>21</sup> By contrast, there is evidence that Al in CaO improves its thermal and CO<sub>2</sub> capture stability.<sup>24–26</sup> To demonstrate such an effect, LB was doped with Al<sub>2</sub>O<sub>3</sub> and ground and the sorbent was pretreated at 1100 °C for 6 h. The results for conversions during carbonation/calcination cycles are presented in Figure 11. Here, a clear influence of doping on carrying capacity of the sorbent can be

(34) Fennell, P. S.; Pacciani, R.; Dennis, J. S.; Davidson, J. F.; Hayhurst, A. N. The Effects of Repeated Cycles of Calcination and Carbonation on a Variety of Different Limestones, as Measured in a Hot Fluidized Bed of Sand. *Energy Fuels* **2007**, *21*, 2072–2081.





**Figure 12.** SEM–EDX analyses of  $\text{Al}_2\text{O}_3$  content at the surface of sample LB, doped with 5 wt %  $\text{Al}_2\text{O}_3$ , pretreated at 1100 °C for 6 h, and cycled (after 30  $\text{CO}_2$  cycles).

seen. It is apparent that, with increasing amounts of added  $\text{Al}_2\text{O}_3$ , the carrying capacity decreases in the first few cycles. We believe that this is most likely because of the formation of  $\text{CaO}-\text{Al}_2\text{O}_3$  compounds, whose existence we have previously demonstrated in FBC ashes, for example.<sup>35</sup> However, sorbent capacity in the following cycles increases for those samples doped with 10 and 5 wt %  $\text{Al}_2\text{O}_3$ ; the sample doped with 2.5 wt %  $\text{Al}_2\text{O}_3$  slowly loses activity with increasing numbers of cycles, but this sample also has significantly better performance than that of undoped LB.

These results clearly show the favorable effect of Al on sorbent performance. This means that, besides the negative effects of the high Na content of LB limestone, another probable cause for the absence of a self-reactivation effect is a deficiency of Al. The influence of Al on sorbent morphology, which is the determining factor for  $\text{CO}_2$  capture capacity, has been investigated by SEM–EDX analyses of the sorbent surfaces. The results presented in Figure 12 are typical for an  $\text{Al}_2\text{O}_3$ -doped sample analyzed after 30  $\text{CO}_2$  cycles. A quite different sample morphology, compared to those presented in Figure 9b (sample doped with  $\text{Na}_2\text{CO}_3$ ), is apparent. Moreover, different areas of surface morphology exist (Figure 12), depending upon the  $\text{Al}_2\text{O}_3$  content. The more sintered areas with larger grains have no  $\text{Al}_2\text{O}_3$  or only small concentrations. These analyses further highlight the favorable influence of Al, which behaves as a kind of “binder”, stabilizing the  $\text{CaO}$  structure and preventing sintering. The lack of Al in LB limestone appears to be another reason that this material showed very poor self-reactivation performance.

### Conclusions

Thermal pretreatment and self-reactivation of sorbent during  $\text{CO}_2$  looping cycles were re-investigated on a high-purity

limestone (La Blanca). This was performed to explore differences in the behavior of four Canadian limestones after pretreatment and that for LB limestone. Results presented here showed no significant improvement in performance for LB after pretreatment, despite grinding and wide time and temperature variation for the pretreatment. Self-reactivation behavior was noted after pretreatment at 1200 °C for 24 h, but the conversions obtained were low (<20%) and not of practical interest. Increased  $\text{CO}_2$  concentration and carbonation duration during cycles generated self-reactivation performance only during the initial cycles; after that, the drop in activity was more pronounced than that in the case of lower  $\text{CO}_2$  concentrations and shorter carbonation durations.

It appears that the chemical composition of sorbent plays a significant role in determining sorbent performance after thermal pretreatment. The influences of Na and Al were examined in more detail in this work. Doping of KR limestone (which previously showed self-reactivation) with  $\text{Na}_2\text{CO}_3$  was performed to produce Na levels in the calcined limestone similar to LB. This produced a drastic loss of activity with increasing cycles, despite pretreatment. This result can be correlated with the relatively high content of Na in LB and its loss of activity with increasing cycles, after pretreatment. Moreover, because LB originally does not contain significant Al, it is interesting that, after  $\text{Al}_2\text{O}_3$  doping, it showed increased activity with increasing reaction cycles. The absence of Al in the original LB sample is, therefore, suggested as another likely cause for poor performance after pretreatment. Thus, the final conclusion reached here for LB is that the failure of thermal pretreatment to produce self-reactivation during  $\text{CO}_2$  cycles is due to an unfavorable combination of relatively high Na content and the absence of significant Al.

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