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# Pilot-Scale Study of CO<sub>2</sub> Capture by CaO-Based Sorbents in the Presence of Steam and SO<sub>2</sub>

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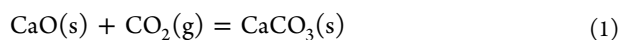
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**ABSTRACT:** Calcium looping cycles require an oxy-fired calciner burning coal for sorbent regeneration. Thus, in addition to O<sub>2</sub> and CO<sub>2</sub>, the flue gases will include both steam and SO<sub>2</sub>, and similarly, carbonation of real flue gases will occur in the presence of steam. However, to date, most research has been done without either of these two gaseous components present. Here, batch combustion experiments were performed in a pilot-scale fluidized-bed reactor to study the effects of steam and SO<sub>2</sub> addition on CO<sub>2</sub> capture by limestone-based sorbents calcined under oxygen-enriched air and oxy-fuel conditions. The initial fast kinetically controlled CO<sub>2</sub> capture stage was dramatically reduced when the sorbent was calcined at realistic temperatures in the presence of SO<sub>2</sub>. This is attributed to both greater sintering due to higher local calcination temperatures required by high CO<sub>2</sub> concentrations and CaSO<sub>4</sub> formation. By contrast, steam in the synthetic flue gas during carbonation extended the initial, high-efficiency CO<sub>2</sub> capture period compared with that observed during carbonation with dry synthetic flue gases. A comparison between pilot-scale fluidized-bed combustion (FBC) and thermogravimetric analysis (TGA) results showed that sorbent reactivity was considerably lower during pilot-scale FBC testing, as anticipated given the higher calcination temperatures employed in the FBC reactor and the presence of the other feed gases. The enhanced CO<sub>2</sub> capture efficiency in FBC reactors with steam present was also confirmed by TGA tests. These results are important because they demonstrate how sorbent deactivation effects seen in realistic FBC calcium-looping operation can be successfully reduced by the presence of steam in the carbonator.

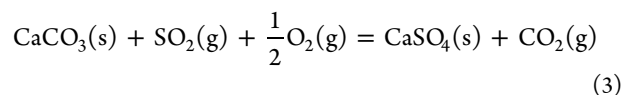
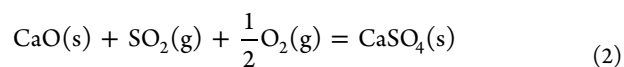
## 1. INTRODUCTION

CO<sub>2</sub> emissions from coal-fired power plants are believed to be a major contributor to global warming and climate change.<sup>1</sup> A promising solution to reduce such CO<sub>2</sub> emissions is postcombustion capture from flue gas, with subsequent compression, transportation, and sequestration in the deep oceans or in underground geological formations.<sup>2–4</sup> Of the many developing capture technologies, CO<sub>2</sub> absorption processes such as calcium looping appear to be promising. Calcium looping is considered to be technically feasible at an industrial scale, economically competitive,<sup>5,6</sup> and environmentally benign because of the relatively inert nature of the solid residues produced by the process. Moreover, the spent residues could also be used in cement manufacture, for example.<sup>7–9</sup>

Much research has demonstrated the potential of fluidized-bed combustion (FBC), as a technology to carry out Ca looping cycles.<sup>9</sup> Circulating fluidized-bed combustion (CFBC) systems are particularly suitable for processing large amounts of solids,<sup>10</sup> and reactions between gas and solid streams are significantly enhanced by superior mixing that maximizes mass and heat transfer along with reaction rates. Therefore, at appropriate temperatures and pressures, a flue gas stream can be decarbonized by being passed through a fluidized bed of calcined limestone to form CaCO<sub>3</sub> (carbonation, forward reaction of eq 1). This carbonated material can then be transferred to a second fluidized bed or calciner where, at higher temperatures and/or lower pressures, the calcination reaction occurs (reverse reaction of eq 1). The resulting gas stream is concentrated CO<sub>2</sub> (>90%), which is then suitable for liquefaction and ultimate sequestration.



FBC reactors are also used for SO<sub>2</sub> removal using calcium-based sorbents by either indirect (eq 2) or direct (eq 3) sulfation.<sup>11</sup>



Unfortunately, SO<sub>2</sub> in calcium looping systems decreases sorbent activity, as the SO<sub>2</sub> irreversibly forms CaSO<sub>4</sub>.<sup>12–15</sup> This requires the use of additional sorbent, which reduces the environmental and economic benefits of the calcium looping process.<sup>5,6</sup> One solution to this problem is to desulfurize the flue gases in a separate reactor.<sup>16</sup> However, there is evidence that partial sulfation reduces the loss of material due to elutriation from the FBC reactor,<sup>17</sup> and the use of a separate SO<sub>2</sub> removal step would increase both the complexity and the cost of a Ca looping system. TGA studies<sup>18,19</sup> and a study with a small bubbling FBC<sup>20</sup> showed that steam appears to enhance CO<sub>2</sub> capture performance during CO<sub>2</sub> capture cycles, but those tests did not include the deactivation effects due to the presence of SO<sub>2</sub>. Moreover, the effect of the simultaneous presence of SO<sub>2</sub> and steam has still not been explored in pilot-plant studies.<sup>21–24</sup> Therefore, the primary aim of this work was to examine the effect of steam on the CO<sub>2</sub> capture efficiency and utilization of sorbent calcined under more realistic

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Table 1. XRF Elemental Analyses of Cadomin and Piasek Wapieny Limestones

component	content (wt %)			
	Polish limestone	Cadomin limestone	component	Polish limestone
SiO <sub>2</sub>	0.85	1.30	MgO	0.89
Al <sub>2</sub> O <sub>3</sub>	0.24	0.40	SO <sub>3</sub>	<0.1
Fe <sub>2</sub> O <sub>3</sub>	0.09	0.11	Na <sub>2</sub> O	<0.2
TiO <sub>2</sub>	<0.03	0.04	K <sub>2</sub> O	0.06
P <sub>2</sub> O <sub>5</sub>	<0.03	<0.03	LOF	43.64
CaO	54.10	50.64		

operating conditions (higher temperatures and CO<sub>2</sub> concentrations) and with SO<sub>2</sub> present during calcination in a pilot-scale FBC reactor.

## 2. EXPERIMENTAL SECTION

**2.1. Pilot-Scale FBC Reactor.** The pilot-scale dual-fluidized-bed system is described in detail elsewhere.<sup>25</sup> The system comprises two separate FBC reactors (calciner and carbonator), but only one reactor was used for the batch experiments performed here, and it was operated in bubbling-bed mode during both calcination and carbonation. CO<sub>2</sub> capture cycles were achieved by altering both temperature and gas compositions. In addition, the reactor was designed to allow the introduction of superheated steam together with fluidization gas. The reactor's internal diameter is 0.1 m, and it is surrounded by three 4.5-kW electric heaters that provide supplemental heating during system startup/preheating. Instrumentation ports are situated at approximately 0.3-m intervals along the reactor's total length and are used for both temperature and pressure measurements. The gas analysis sampling port is located on top of the reactor cyclone, and during tests, data on gas outlet concentrations were continuously monitored. The system control and data acquisition were operated using Labview (National Instruments) through a FieldPoint instrument interface.

**2.2. Experimental Conditions.** **2.2.1. Sorbents.** Two natural limestones were used for experimental testing (Table 1), Cadomin (Canadian) and Piasek Wapieny (Polish), with purities of 90.0 and 95.6% and mean surface-to-volume diameters of 612 and 512  $\mu$ m, respectively. For convenience, the Piasek Wapieny limestone will be referred to hereafter as Polish limestone.

**2.2.2. Calcination Conditions.** Sorbents were calcined under two different sets of conditions, namely, oxygen-enriched air or oxy-fuel combustion, which in both cases implied elevated CO<sub>2</sub> concentrations compared with those used during air firing. Before each cyclic test of CO<sub>2</sub> capture, a fresh amount of sorbent (~6.0 kg) was loaded into the reactor at room temperature. The reactor was heated, and fluidization and feeding of biomass fuel were started at ~600 °C. The temperatures during oxy-fuel and oxygen-enriched combustion were approximately 910–920 °C and 860–870 °C, respectively. These temperatures are ~30 °C higher than those thermodynamically required under given CO<sub>2</sub> partial pressures,<sup>26</sup> and they were chosen to ensure a practical calcination rate.

The fuel used for calcination was low-ash biomass (wood pellets), and its proximate and ultimate analyses are listed in Table 2. The average flue gas compositions, fuel feed rates, and oxygen flow rates under the two sets of calcination conditions are detailed in Table 3. For experiments with SO<sub>2</sub> addition, inlet SO<sub>2</sub> concentrations were 2000 ppm, but only ~20 ppm

Table 2. Proximate and Ultimate Analyses of Biomass (Wood Pellets<sup>a</sup>) Used in Calciner

component	content (wt %)
Proximate Analysis	
moisture	7.81
ash	0.68
volatiles	75.54
Ultimate Analysis	
FC	15.97
C	45.80
H	5.52
N	<0.10
S	<0.05
O	40.04

<sup>a</sup>Pure fiber hardwood blend.

was measured during the entire calcination period in the outlet flue gas. The total calcination time was ~60 min, which also means that, in experiments with SO<sub>2</sub> present, the sorbent was sulfated for that period.

**2.2.3. Carbonation Conditions.** When calcination was finished, the reactor was cooled to ~600 °C, and gas flows were switched to enable carbonation. The amount of calcined material at the beginning of the carbonation step was ~3.5 kg. The gas flow rates and gas composition at the inlet in the reactor are listed in Table 4. The carbonation step was 70 min long, and during that period, the gas composition at the outlet was continuously measured. To observe the effect of steam on the performance of the limestone sorbents, carbonation was performed with and without steam added, and a heated line was used to introduce the steam to ensure that condensation did not occur. During several runs, after the CO<sub>2</sub> concentration in the outlet gas had increased rapidly, approaching the CO<sub>2</sub> inlet concentration (CO<sub>2</sub> breakthrough), the temperature was subsequently raised to ~700 °C, which resulted in a rapid decrease in CO<sub>2</sub> concentration. These tests showed that the sorbent performance (i.e., its capture efficiency) was very sensitive to temperature changes after CO<sub>2</sub> breakthrough (see Figure 1 below). Therefore, to compare the effects of steam on the CO<sub>2</sub> capture performances of different sorbents, calcined with or without SO<sub>2</sub>, only the results obtained during the initial period including CO<sub>2</sub> breakthrough are presented here.

**2.3. TGA Tests.** The effects of steam on the CO<sub>2</sub> capture efficiency by a sorbent partially sulfated during calcination were also compared by performing tests using a Perkin-Elmer TGA-7 thermogravimetric analyzer. The sorbent sample (~5 mg) was suspended in a quartz tube (20-mm i.d.) on a platinum pan (5-mm i.d.). The gas flow rate was controlled with a flowmeter, at 0.04 dm<sup>3</sup>/min. The temperature and gas used were controlled with Pyris software. Sample mass data during the experiments were monitored, and the degrees of both sulfation and

Table 3. Fuel Feed and Gas Flow Rates and Average Gas Composition at the FBC Reactor Outlet during Limestone Calcination

calcination conditions	temperature (°C)	feed/flow rate				outlet gas composition (dry basis)				
		fuel (kg/h)	oxygen (SLPM)	air (kg/h)	recycle (kg/h)	SO <sub>2</sub> (SLPM)	O <sub>2</sub> (vol %)	CO <sub>2</sub> (vol %)	CO (vol %)	SO <sub>2</sub> (ppm)
O <sub>2</sub> -enriched air	860	1.4	40	9.0	—	0.25	7.5	35	1.0	20
oxy-fuel	910	1.7	65	—	9.0	0.25	6.5	80	1.0	20

Table 4. Gas Flow Rates and Inlet Gas Composition during CO<sub>2</sub> Capture Steps

carbonation conditions	temperature (°C)	flow rate			inlet gas composition			
		air (SLPM)	CO <sub>2</sub> (SLPM)	steam (kg/h)	N <sub>2</sub> (vol %)	O <sub>2</sub> (vol %)	CO <sub>2</sub> (vol %)	steam (vol %)
no steam	600	65	5.7	0	72.7	19.3	8.0	0
steam present	600	56	5.7	0.48	59.3	15.7	8.0	17.0

carbonation were calculated on the basis of mass change, assuming that mass change occurred only as a result of the irreversible formation of CaSO<sub>4</sub> and the reversible formation/decomposition of CaCO<sub>3</sub>.

The samples were calcined in an atmosphere containing 50% CO<sub>2</sub> and 2250 ppm SO<sub>2</sub> (balance N<sub>2</sub>). The temperature program for the first calcination included heating to 870 °C, followed by an isothermal step at 870 °C for 10 min. At the beginning of the cooling step, the gas mixture was switched to N<sub>2</sub> to avoid sulfation and carbonation before the desired carbonation temperature was reached. A gas mixture containing 10% CO<sub>2</sub> in nitrogen was introduced when a temperature of 600 °C was reached, and carbonation was continued for 20 min isothermally at 600 °C. Here, 20% steam was introduced in the gas mixture for the tests of CO<sub>2</sub> capture in the presence of steam. Steam was produced using a syringe pump and steam generator. Feed lines containing both steam and the mixed gas were insulated and electrically heat-traced to ensure no steam condensation. Both heating and cooling rates were 50 °C/min. In all, five carbonation/calcination cycles were performed, and SO<sub>2</sub> was present during each calcination step, whereas steam was present only during carbonation tests exploring the effect of steam addition.

### 3. RESULTS AND DISCUSSION

**3.1. Effect of Calcination Conditions.** The calcination of sorbents was performed under both oxygen-enriched air and oxy-fuel conditions, with and without SO<sub>2</sub> present. Under such conditions, one must examine the effects of both high CO<sub>2</sub> concentrations and the presence of SO<sub>2</sub> during calcination on the effectiveness of subsequent CO<sub>2</sub> capture. That is, high CO<sub>2</sub> concentrations during calcination under realistic Ca looping conditions are required to produce concentrated CO<sub>2</sub> streams, and SO<sub>2</sub> is always present if solid fossil fuels are used to generate heat for sorbent regeneration in the calciner.

**3.1.1. Effect of CO<sub>2</sub> Partial Pressure and Temperature.** Figure 1 shows the carbonator outlet CO<sub>2</sub> concentration during the first cycle of CO<sub>2</sub> capture from simulated flue gas (8% CO<sub>2</sub>, balance air) for tests with both oxygen-enriched and oxy-fuel calcined Cadomin limestone. CO<sub>2</sub> capture by CaO-based sorbents takes place in two distinct stages:<sup>9</sup> a fast kinetically controlled stage, followed by a significantly slower diffusion-controlled stage. In practice, only the fast reaction stage is important for CO<sub>2</sub> capture in FBC reactors, and Figure 1 shows that, during the initial period of CO<sub>2</sub> capture, the CO<sub>2</sub> concentration was <0.5% and was mainly determined by the equilibrium CO<sub>2</sub> partial pressure. This means that the reaction is under the fast kinetically controlled stage. However, when the

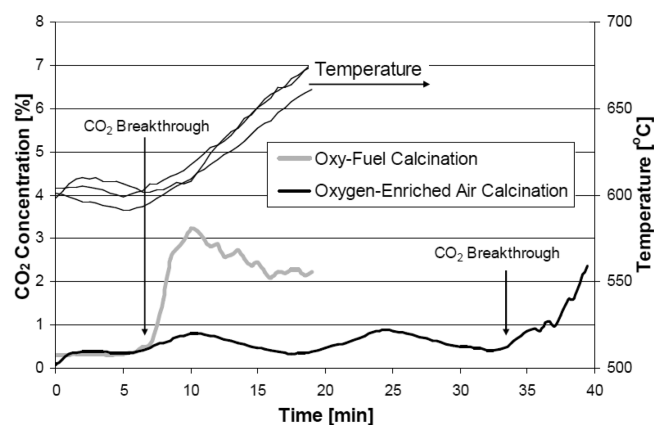


Figure 1. CO<sub>2</sub> concentration at the FBC carbonator outlet during CO<sub>2</sub> capture (batch test) from simulated flue gas (8 vol % CO<sub>2</sub>, balance air) at 600 °C by Cadomin limestone calcined at 860 °C under oxygen-enriched air and at 910 °C under oxy-fuel combustion conditions. Temperatures measured at three different positions in the bed are presented for the oxy-fuel calcination run.

level of sorbent carbonation reaches some critical value, the fast stage shifts to a slow diffusion-controlled stage, at which point the activity of the sorbent is insufficient to prevent CO<sub>2</sub> breakthrough, and the CO<sub>2</sub> concentration immediately increases at the carbonator outlet. The duration of the period before CO<sub>2</sub> breakthrough depends on the sorbent activity and is a useful parameter for comparing the activities of sorbents calcined here under different conditions, as well as evaluating the effects of steam addition.

The CO<sub>2</sub> concentration profiles in Figure 1 show that, for the sorbent calcined under oxygen-enriched air calcination conditions, the fast CO<sub>2</sub> capture period was ~35 min, or 7 times longer than for the sorbent calcined under oxy-fuel conditions. These results are similar to those reported earlier by Symonds et al.<sup>27</sup> and are explained by sorbent sintering,<sup>28</sup> which is more prominent during calcination under high CO<sub>2</sub> concentrations/temperatures.<sup>29,30</sup> Although not presented here for reasons of space, the same phenomenon was also observed for the Polish limestone.

These results show that the effect of high CO<sub>2</sub> concentrations is quite dramatic in comparison to that of previous work performed using a TGA reactor.<sup>18,31</sup> As an example, Table 5 lists the carbonation conversions over the first two cycles for Cadomin limestone for experiments performed in both a TGA reactor<sup>31</sup> and a pilot-scale FBC reactor (this work), at similar temperatures and carbonation conditions. As previously reported,<sup>31</sup> the addition of CO<sub>2</sub> during the first calcination

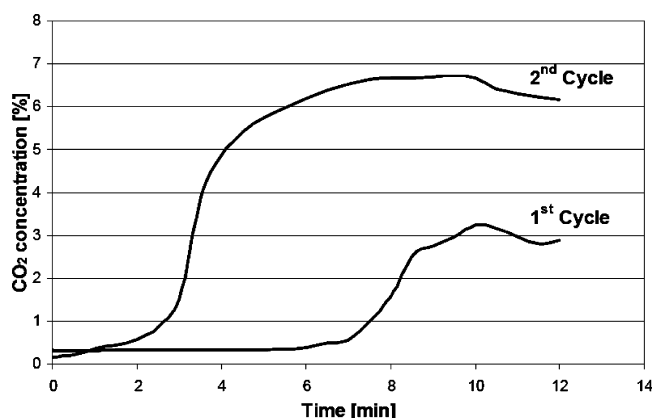


**Table 5.** Comparison of Carbonation Conversions in a TGA Reactor<sup>31</sup> and in a Pilot-Scale FBC Reactor (This Work) for Cadomin Limestone over Two Cycles

reactor	conditions		cycle	carbonation conversion
	carbonation	calcination		
TGA	15% CO <sub>2</sub> (balance N <sub>2</sub> ), 700 °C, 30 min	100% N <sub>2</sub> , 700 °C, 60 min	1	0.75
			2	0.68
		90% CO <sub>2</sub> (balance N <sub>2</sub> ), 925 °C, 30 min	1	0.54
			2	0.31
pilot-scale FBC	O <sub>2</sub> -enriched air		1	0.26
			2	0.24
	oxy-fuel		1	0.27
			2	0.11

caused a decrease in the subsequent carbonation conversion to a level typically achieved after 5–6 cycles for the same sorbent calcined in a pure N<sub>2</sub> atmosphere. However, in the case of the pilot-scale FBC tests presented here (Table 5), for calcination in a CO<sub>2</sub>-rich atmosphere, the carbonation conversion in the first cycle fell to levels typically seen after 15–20 cycles with calcinations in a pure N<sub>2</sub> atmosphere or after 5–6 cycles with calcinations in a high-CO<sub>2</sub> (90%) atmosphere when similar experiments were performed in a TGA reactor.

This significant decrease in sorbent activity over repeated cycles can also be explored in terms of CO<sub>2</sub> concentration at the outlet of the carbonator for the first two cycles (Figure 2).

**Figure 2.** CO<sub>2</sub> concentration at the FBC carbonator outlet during the first two CO<sub>2</sub> capture cycles (batch test) from simulated flue gas (8 vol % CO<sub>2</sub>, balance air) at 600 °C by Cadomin limestone calcined at 910 °C under oxy-fuel combustion conditions.

As expected, during the second cycle, the high-CO<sub>2</sub>-capture-efficiency period is shorter, and the CO<sub>2</sub> capture during the diffusion-limited period is reduced. These results agree with those of similar FBC tests, using simulated gasification syngas streams,<sup>27</sup> for both oxygen-enriched air and oxy-fuel calcination conditions.

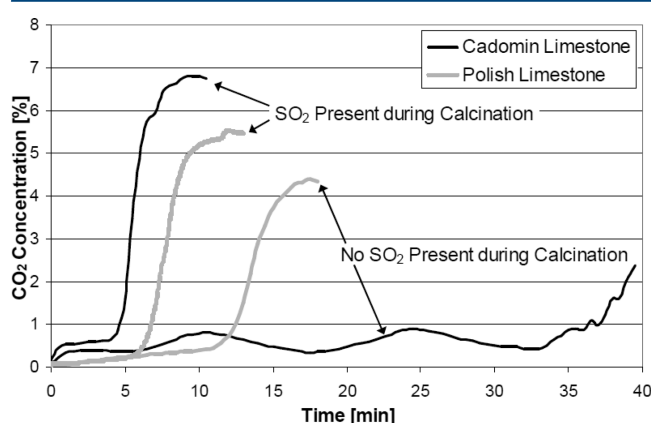
The large disparity in carbonation conversions obtained in TGA and pilot-scale experiments is believed to be related to pore sintering associated with the calcination process, which depends mainly on the gas composition, final calcination temperature, heating rate, and duration. First, an increase in temperature tends to increase pore sizes, which reduces the surface area.<sup>32,33</sup> Second, high CO<sub>2</sub> concentrations enhance sintering, and moreover, other gases such as steam (typically

present in a Ca looping operation) can also promote sintering.<sup>29</sup> Finally, it should also be pointed out that the combined effect of CO<sub>2</sub> and steam on sorbent sintering is believed to be even more severe.<sup>30</sup>

These factors that enhance sintering are simultaneously present and even more pronounced during pilot-scale FBC testing. In particular, it is reasonable to suppose that, during calcination in an FBC reactor, the CO<sub>2</sub> will be released to the emulsion phase, causing significantly higher CO<sub>2</sub> concentrations around the sorbent particles than in the bulk gas phase. In other words, the CO<sub>2</sub> concentrations measured at the calciner outlet are lower than those around calcining sorbent particles. Thus, to complete calcination, the temperatures required to achieve a practical calcination rate are appreciably higher than those predicted based on the measured CO<sub>2</sub> concentration at the outlet of the reactor. For example, based on the results in Table 3, the measured CO<sub>2</sub> concentration during calcination under oxy-fuel condition was approximately 80 vol %. The equilibrium temperature at this CO<sub>2</sub> partial pressure is approximately 880 °C, whereas the actual required temperature for reasonably rapid calcination was about 910 °C. This increased temperature enhanced the sintering observed during the pilot-scale testing presented in this work. Other important factors affecting sorbent sintering during pilot-scale FBC testing involve the effect of char particle temperatures, which are significantly higher during burning than the bulk temperature of the fluidized bed, and the presence of low-melting-point compounds in the ash from solid fuels. In particular, it has been shown that the average particle temperature of a series of coals and coal chars was 87–191 °C above the average bed temperature during combustion.<sup>34</sup> Moreover, during oxy-fuel or oxygen-enriched air combustion, even higher local temperatures due to burning particles can be expected, especially for more reactive fuels such as biomass (higher porosity and pore surface area of wood char), as confirmed by modeling studies of combustion with elevated O<sub>2</sub> concentrations.<sup>35</sup> These high char particle burning temperatures can cause local superheating of sorbent particles during any physical particle–particle contacts. Moreover, ash can build up on the surface of the sorbent particles, resulting in local melts on the sorbent particle surface, which additionally enhances sorbent sintering and deactivation.<sup>36</sup> Although the ash content in the feed fuel was relatively low (0.68 wt %), it still seems plausible that ash melts on the sorbent surface were a significant factor affecting sintering. Moreover, it should also be noted that, during each calcination, up to ~1% of the sorbent could be sulfated (under the conditions in this study), which could additionally contribute to the sintering. That is, there is potential for low-temperature eutectic melts with CaSO<sub>4</sub>,<sup>37</sup> which could promote sintering.

Another important difference between TGA and pilot-scale FBC experiments that can affect CO<sub>2</sub> capture efficiency is the presence of steam during calcination, as all fuels that might reasonably be used in the calciner contain moisture and hydrogen. In this particular case, the respective values are 7.91 and 5.52 wt %, (wood pellets, Table 2). Hence, the resulting presence of steam in the calciner must affect sorbent sintering during calcination and its subsequent performance during CO<sub>2</sub> capture. Also, as noted above, the simultaneous presence of both CO<sub>2</sub> and steam has a combined effect on sintering, and these results show that it is critical to include steam during the calcination of calcium-based sorbents in TGA experiments to accurately simulate pilot-scale FBC conditions.

**3.1.2. Effect of SO<sub>2</sub> Addition.** Figure 3 shows the CO<sub>2</sub> concentration at the outlet of the carbonator during the first



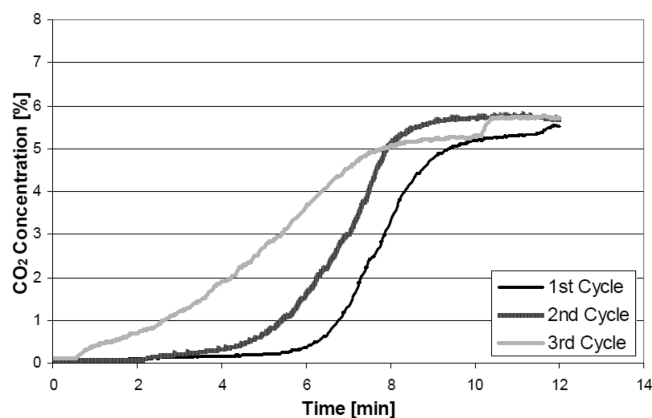
**Figure 3.** CO<sub>2</sub> concentration at the FBC carbonator outlet during CO<sub>2</sub> capture (batch test) from simulated flue gas (8 vol % CO<sub>2</sub>, balance air) at 600 °C for the two limestones tested, calcined at 860 °C under oxygen-enriched air combustion conditions with (2000 ppm) and without SO<sub>2</sub>.

cycle of CO<sub>2</sub> capture from a simulated flue gas (8% CO<sub>2</sub>, balance air), with both limestones calcined under oxygen-enriched air conditions in the presence and absence of SO<sub>2</sub>. It can be seen that the initial kinetically controlled CO<sub>2</sub> capture stage was dramatically reduced from ~35 to only ~4 min. Moreover, during the diffusion-controlled capture stage, the CO<sub>2</sub> outlet concentration was significantly higher than that seen without SO<sub>2</sub> addition during sorbent calcination. Similar, if less pronounced, effects were observed for the Polish limestone.

Based on these observations, it is plausible to argue that the surface of the particles partially sulfated during calcination is less porous, significantly increasing the diffusion resistance. Moreover, during carbonation remaining pores at the surface of sorbent particles are also plugged by the carbonation product (CaCO<sub>3</sub>). This phenomenon is consistent with the fact that a CaSO<sub>4</sub> shell at the particle surface is formed during sulfation of most limestones,<sup>38</sup> and this has also been recently demonstrated for the simultaneous sulfation and carbonation tests.<sup>39</sup>

Even greater sorbent deactivation can be expected over repeated CO<sub>2</sub> capture cycles because CaSO<sub>4</sub> is continually produced during each cycle. Figure 4 illustrates the CO<sub>2</sub> concentration at the outlet for the first three cycles of CO<sub>2</sub> capture by the Polish limestone. These results show that the high-CO<sub>2</sub>-capture-efficiency period decreased from ~6 min during the first cycle to <1 min during the third cycle. From this result, it appears that, after calcination in the presence of SO<sub>2</sub> over three cycles, the buildup of CaSO<sub>4</sub> on the particle surface is such that the only available CaO for carbonation is found in the interior of the partially sulfated sorbent particles. As the CaSO<sub>4</sub> does not decompose under calcium-looping-cycle conditions, the CaSO<sub>4</sub> product shell must gradually increase over repeated cycles, leading to greater diffusion resistance.<sup>11</sup> Finally, after only three cycles, the fast carbonation period has almost disappeared, and from the very beginning, the reaction is controlled by CO<sub>2</sub> diffusion through the sulfate shell.

These results suggest that CO<sub>2</sub> capture by calcium-based sorbents employing realistic calcination conditions poses significant challenges. The combination of higher calcination

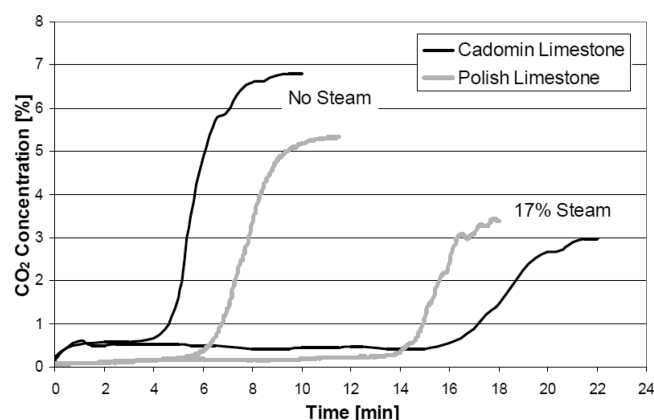


**Figure 4.** CO<sub>2</sub> concentration at the FBC carbonator outlet during the first three CO<sub>2</sub> capture cycles (batch test) from simulated flue gas (8 vol % CO<sub>2</sub>, balance air) at 600 °C by Polish limestone calcined at 860 °C under oxygen-enriched air combustion conditions in the presence of 2000 ppm SO<sub>2</sub>.

temperatures and CO<sub>2</sub> concentrations, along with the presence of steam and SO<sub>2</sub>, can be expected to lead to dramatically reduced sorbent performance and CO<sub>2</sub> capture efficiency. Thus, to avoid large amounts of fresh sorbent makeup, which negatively affect the overall economics of the calcium-looping-cycle process, other methods to improve sorbent activity should be considered if the use of makeup sorbent is to be kept to low levels.<sup>9,40</sup>

**3.2. Effect of Steam during Carbonation.** It is known that the presence of gaseous species such as steam significantly impacts solid-state diffusion.<sup>30</sup> Until recently, there was little evidence in the literature suggesting that the presence of steam in flue gas would enhance sulfation or carbonation. Therefore, experimentation performed by TGA typically did not include steam during sulfation/carbonation. However, steam is present in a real flue gas originating from both the moisture and hydrogen in coal or other carbonaceous feed stocks and could be added if it were desirable. A study by Symonds et al.<sup>41</sup> on CO<sub>2</sub> capture from syngas showed a significant improvement in the overall sorbent conversion with the addition of steam, which was also observed by Manovic and Anthony<sup>18</sup> over a larger temperature range (350–800 °C) for several different calcium-based sorbents. Recent studies by Wang et al.<sup>42</sup> and Stewart et al.<sup>43</sup> have also clearly shown a strong positive influence of steam on sulfation. Therefore, the effect of the presence of steam in flue gas during carbonation was examined to evaluate the performance of the sorbent (partially sulfated) when subjected to more realistic conditions.

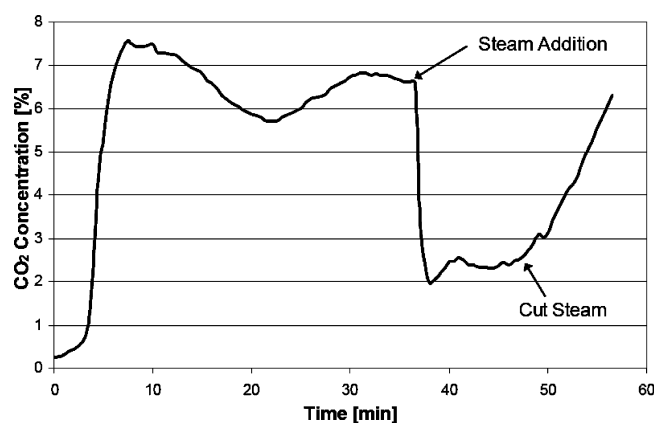
Figure 5 shows the effect of steam addition on the CO<sub>2</sub> concentration at the outlet of the carbonator during the CO<sub>2</sub> capture from synthetic flue gas (8% CO<sub>2</sub>, balance air) by limestones partially sulfated during calcination under oxygen-enriched air combustion conditions. It can be clearly observed that the CO<sub>2</sub> capture efficiency was superior in the presence of 17% steam; that is, the duration of the high-CO<sub>2</sub>-capture-efficiency period was considerably longer. The rapid kinetically controlled stage of CO<sub>2</sub> capture by the Polish limestone increased from ~5 to ~14 min, an increase of nearly 3 times, with an average CO<sub>2</sub> capture of 98% over this period. A similar but even better result can be seen for Cadomin limestone, for which the high-CO<sub>2</sub>-capture-efficiency period was even longer. These results are in agreement with the work of Manovic and Anthony,<sup>18</sup> which showed that steam addition reduces diffusion



**Figure 5.** Effect of the presence of steam in the FBC carbonator on  $\text{CO}_2$  concentration (dry basis) at the outlet during  $\text{CO}_2$  capture (batch test) from simulated flue gas (8 vol %  $\text{CO}_2$ , balance air) at  $600^\circ\text{C}$  by two tested limestones calcined at  $860^\circ\text{C}$  under oxygen-enriched air combustion conditions with 2000 ppm  $\text{SO}_2$ .

resistance during carbonation in a TGA reactor and that the onset of the diffusion-controlled stage is consequently delayed by the presence of steam.

The effect of steam on  $\text{CO}_2$  capture efficiency is further illustrated by the results presented in Figure 6. In this



**Figure 6.** Effect of steam addition/cut into the FBC carbonator on  $\text{CO}_2$  capture efficiency by Cadomin limestone during the second  $\text{CO}_2$  capture cycle (first carbonation presented in Figure 5).

experiment, Cadomin limestone, partially sulfated during calcination under FBC oxygen-enriched air-fired conditions in the presence of 2000 ppm  $\text{SO}_2$ , was employed for  $\text{CO}_2$  capture from a dry synthetic flue gas mixture. During the second capture cycle (presented in Figure 6), the carbonator outlet  $\text{CO}_2$  concentration rapidly increased after a few minutes and, despite some instability due to temperature fluctuations, stayed above 6 vol % for 35 min. When steam at 17 vol % was introduced with the flue gas into the carbonator, the outlet  $\text{CO}_2$  concentration instantly decreased to  $\sim 2.5\%$ . After  $\sim 12$  min of  $\text{CO}_2$  capture from the steam-containing gas mixture, steam was cut, causing the outlet  $\text{CO}_2$  concentration to increase sharply to a level seen for  $\text{CO}_2$  capture with no steam ( $>6$  vol %). These results support a hypothesis that steam enhances diffusion through the product layer/shell (in this case, both  $\text{CaCO}_3$  and  $\text{CaSO}_4$ ).

Table 6 summarizes the carbonation conversions for the two limestones partially sulfated during calcination. These con-

**Table 6.** Summary of Carbonation Conversion of Tested Limestones Calcined with  $\text{SO}_2$  Addition

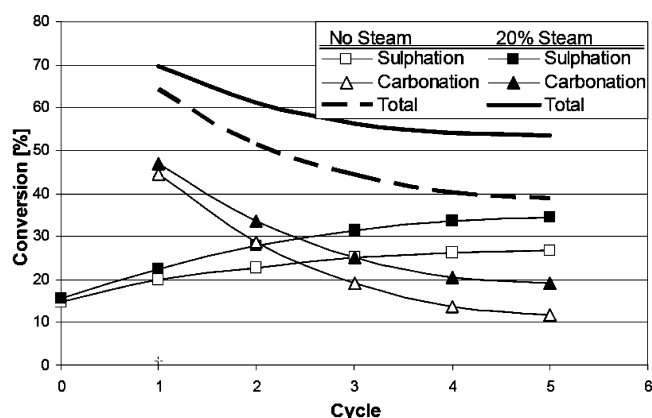
sorbent	calcination conditions	carbonation feed gas	cycle	carbonation conversion
Cadomin limestone	$\text{O}_2$ -enriched air	8% $\text{CO}_2$ , balance air	1	0.166
			2	0.168
		8% $\text{CO}_2$ , 17% $\text{H}_2\text{O}$ , balance air	1	0.359
			2	0.388
	oxy-fuel	8% $\text{CO}_2$ , balance air	1	0.131
			2	0.133
		8% $\text{CO}_2$ , 17% $\text{H}_2\text{O}$ , balance air	1	0.179
			2	0.156
			3	0.218
Polish limestone	$\text{O}_2$ -enriched air	8% $\text{CO}_2$ , balance air	1	0.222
			2	0.192
			3	0.178
		8% $\text{CO}_2$ , 17% $\text{H}_2\text{O}$ , balance air	1	0.315
			2	0.182
	oxy-fuel	8% $\text{CO}_2$ , balance air	1	0.143
			2	0.110
			3	0.100
		8% $\text{CO}_2$ , 17% $\text{H}_2\text{O}$ , balance air	1	0.312
			2	0.133
			3	0.126

versions were determined by heating samples in a muffle furnace. For tests performed with no steam addition during carbonation, there was a decrease in carbonation conversion of sorbents calcined under oxy-fired combustion conditions compared to that of oxygen-enriched air calcination, 21.0% and 40.5% for Cadomin and Polish limestone, respectively. In the case of the Cadomin limestone, the addition of steam during carbonation resulted in increased conversions of roughly 124% and 40% for oxygen-enriched air and oxy-fuel calcination conditions, respectively. Similar improvements were observed for the Polish limestone, with carbonation conversion increases of approximately 26% and 62% for oxygen-enriched air and oxy-fuel calcination conditions, respectively.

Although there are some differences in the behavior of the two limestones, in both cases, the presence of steam during carbonation significantly increased the carbonation conversion over repeated cycles. An important result from this work is that steam can reduce the effects of  $\text{SO}_2$  on sorbent performance during  $\text{CO}_2$  capture cycles, as was clearly confirmed by supporting TGA experiments. The results presented in Figure 7 show that, during the first calcination of Cadomin limestone,  $\sim 15\%$  of the sorbent was converted to  $\text{CaSO}_4$ . Moreover, sulfation conversion increased with subsequent  $\text{CO}_2$  capture cycles, and it was clearly greater when steam was present during carbonation. These results indicate that the presence of steam during carbonation changes sorbent morphology and that sulfation is enhanced during calcination regardless of the fact that steam was not present during this stage.

It is evident that carbonation is hindered by sulfation, resulting in only  $\sim 12\%$  carbonation conversion after five cycles. However, despite higher sulfation conversions with steam present during calcination, the subsequent carbonation conversions were also higher ( $\sim 19\%$  after five cycles). This encouraging finding supports the results obtained in the FBC reactor (Figures 5 and 6) and shows that the presence of steam during carbonation reduces the negative effects of  $\text{SO}_2$  on the  $\text{CO}_2$  capture activity of  $\text{CaO}$ -based sorbents.





**Figure 7.** Sulfation and carbonation conversions during CO<sub>2</sub> capture cycles in TGA by Cadomin limestone. Conditions: calcination in 50% CO<sub>2</sub> (balance N<sub>2</sub>) in the presence of 2250 ppm SO<sub>2</sub> at 870 °C for 10 min; carbonation in 10% CO<sub>2</sub> (balance N<sub>2</sub>) at 600 °C for 20 min.

#### 4. CONCLUSIONS

Calcium looping tests were performed using a pilot-scale FBC reactor, operated in batch mode, to explore the effect of high CO<sub>2</sub> concentrations and the presence of SO<sub>2</sub> during calcination on CO<sub>2</sub> capture efficiency. Under these conditions, the initial rapid kinetically controlled CO<sub>2</sub> capture stage was dramatically reduced. Moreover, CO<sub>2</sub> capture efficiency was substantially reduced during the diffusion-controlled stage. This was attributed to both enhanced sorbent sintering and the formation of a solid CaSO<sub>4</sub> layer/shell, which increases the diffusion resistance. With steam present in the feed gas during carbonation, the fast CO<sub>2</sub> capture period was significantly extended with enhanced CO<sub>2</sub> capture efficiency compared to carbonation with only CO<sub>2</sub> present. These findings were confirmed by TGA experiments which also included both SO<sub>2</sub> and steam addition. These results suggest that CO<sub>2</sub> capture cycles in TGA experiments should encompass as many of the factors present during FBC operation as possible (i.e., higher calcination temperatures/CO<sub>2</sub> concentrations, and the presence of steam and other gases such as SO<sub>2</sub>), to avoid somewhat misleading results and conclusions related to sorbent performance.

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##### Notes

The authors declare no competing financial interest.

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