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# The Effect of Steam on the Fast Carbonation Reaction Rates of CaO

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**ABSTRACT:** Postcombustion CO<sub>2</sub> capture using calcium looping (CaL) is a rapidly developing technology based on the reaction between CaO and CO<sub>2</sub>. The influence of the presence of steam in the flue gas on the carbonation reaction has been barely studied in the literature. Experiments using a thermogravimetric analyzer (TGA) were carried out to study the effect of steam over the very short reaction time where the carbonation reaction takes place under the kinetic-controlled regime. A simple reaction particle model is applied to interpret the results obtained and to derive reaction rate constants and support the quantitative discussion on steam effects. Results obtained in this work indicate that steam has no influence on the reaction rate constant.

## INTRODUCTION

CO<sub>2</sub> capture using calcium looping (CaL) is a rapidly developing technology for a range of postcombustion and precombustion applications.<sup>1,2</sup> An essential aspect of these systems is the fast reaction between CaO and CO<sub>2</sub> under carbonation conditions. It is well-known that carbonation is only fast for a limited interval of Ca conversion and that this maximum conversion decreases with the number of reaction cycles.<sup>3,4</sup> During this fast stage, reaction takes place on the free surface of CaO and the whole process is limited by the kinetics of the reaction between CaO and CO<sub>2</sub>. The end of the fast stage takes place when the growing CaCO<sub>3</sub> grains form a continuous layer over the unreacted CaO surfaces. From this point, the carbonation reaction can still continue as the CO<sub>2</sub> diffuses through the product layer. This second regime has a much lower reaction rate as the chemical reaction and the diffusion of CO<sub>2</sub> control the reaction rate.<sup>5</sup> CaL systems for postcombustion CO<sub>2</sub> capture operate at atmospheric pressure and typical inlet CO<sub>2</sub> concentrations before capturing between 10 and 15%. Under these conditions, recent experimental and modeling studies<sup>6–8</sup> related to the carbonator reactor have shown that the main parameters affecting the CO<sub>2</sub> capture efficiency in this reactor are the carbonation reaction rate constant during the fast carbonation stage ( $k_s$ ) and the maximum CO<sub>2</sub> carrying capacity of the mixed solids in the fluidized bed system ( $X_{ave}$ ). Here,  $X_{ave}$  represents the maximum CaO conversion to CaCO<sub>3</sub> that can be achieved for the sorbent at the end of the fast reaction stage, which is considered the only useful conversion period in postcombustion CO<sub>2</sub> capture Ca-looping processes.

Different experimental techniques can be used to determine these characteristics parameters. Typically, carbonation reaction rate constants have been determined by using thermogravimetric analyzers (TGA).<sup>9–12</sup> During these tests, it is important to carefully design the experimental setup to avoid any diffusion effect which may affect the determination of the intrinsic reaction parameters. The evolution of the maximum CO<sub>2</sub> carrying capacity of the CaO particles has also been studied widely at the laboratory scale using different experimental

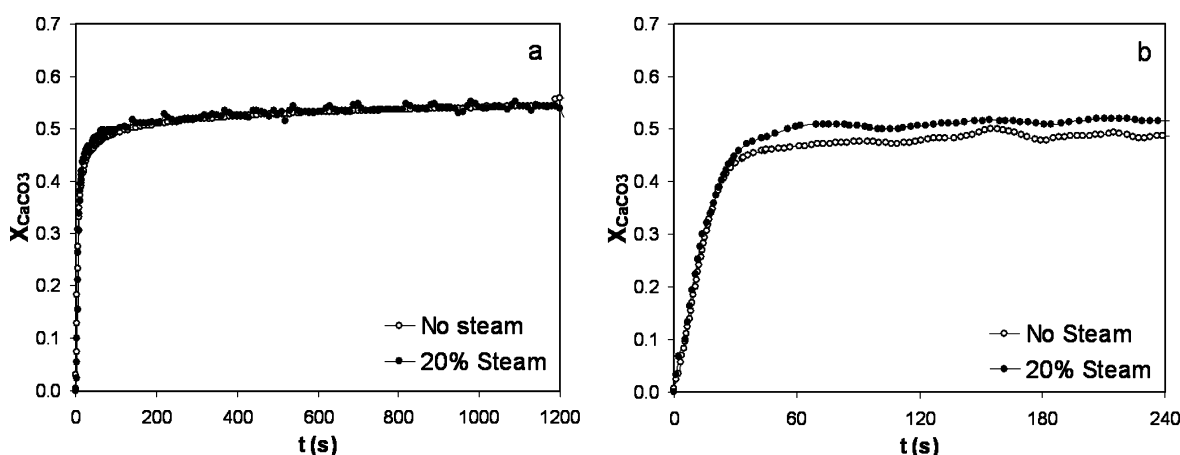
techniques such as TGA or small fluidized beds. Several studies have discussed in detail the effect of the carbonation conditions (i.e., carbonation temperature, CO<sub>2</sub> concentration, and reaction time) and how these modify the evolution of the sorbent deactivation curves during carbonation/calcination cycles.<sup>5,13–15</sup> However, as mentioned above, the impact of these variables is limited due to the narrow operating windows of CO<sub>2</sub> concentration and reaction times available in the carbonator reactors (carbonation temperature = 650 °C, CO<sub>2</sub> partial pressure < 15 kPa, H<sub>2</sub>O partial pressure < 20 kPa, and particle reaction times well below 5 min). The influence of SO<sub>2</sub> and its irreversible reaction with CaO is much stronger, and has been previously investigated for Ca-looping systems.<sup>16–18</sup> As indicated in an earlier work by Manovic and Anthony,<sup>19</sup> little attention has been paid to the influence of the presence of steam in the flue gas. Virtually, all the experimental work found in the Ca-looping literature has been carried out using synthetic flue gases composed of a mixture of N<sub>2</sub>/air and CO<sub>2</sub> (no steam). There are some previous studies<sup>19–25</sup> on the effect of steam on sorbent conversion, but these are focused on the precombustion application of Ca-looping thus using experimental conditions far from those expected in the postcombustion CO<sub>2</sub> capture carbonator (high H<sub>2</sub>O and CO<sub>2</sub> molar fraction, or high pressures). The early work of Dobner et al.,<sup>20</sup> looking at the effect of steam on carbonation of dolomites, notes that steam can “catalyze” the reaction between CO<sub>2</sub> and CaO especially at low temperatures (~550 °C). Yang and Siao<sup>21</sup> studied the effect of partial pressure of steam on the carbonation reaction of limestones up to pressures of 5 MPa between 550 and 650 °C. Under these experimental conditions, they have shown that steam greatly increases the sorbent carbonation conversion. In contrast, a recent study by Lindén et al.<sup>25</sup> looking at the influence of water vapor on carbonation of fresh calcined limestone in the temperature range of 450–550

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**Figure 1.**  $X_{\text{CaCO}_3}$  vs time for KR (a) and PS (b) limestones for  $N = 3$  (carbonation temperature = 650 °C;  $\text{H}_2\text{O}$  partial pressure = 20 kPa,  $\text{CO}_2$  partial pressure = 20 (a), 10 (b) kPa).

°C found that steam has negligible effect at temperatures above 500 °C.

Manovic and Anthony<sup>19</sup> recently reported the effect of steam on the carbonation of different fresh calcined limestones in a TGA under relevant conditions for postcombustion Ca looping. They found that steam has a positive effect on the sorbent conversion under conditions when the diffusion through the product layer becomes the limiting step. Donat<sup>22</sup> et al. reported that steam increases the carbonation reaction rate by lowering the diffusion resistance in experiments carried out in a mini-fluidized bed reactor. Symonds et al.<sup>23</sup> showed that the presence of steam increases the high  $\text{CO}_2$  capture efficiency period during experiments carried out in a bubbling bed carbonator. On the other hand, Sun et al.<sup>24</sup> showed no appreciable effect of steam on carbonation conversion during multicycle tests in a TGA.

The objective of this work is to study the influence of steam on CaO carbonation, by focusing only on the possible effects in the very short reaction time (typically less than 1 min) where the carbonation reaction is completely governed by kinetic control (the fast reaction regime). For this purpose, reaction rates have been measured in differential conditions in a thermobalance under typical carbonation conditions in postcombustion Ca-looping systems with and without steam. A simple reaction particle model has been used to interpret the results obtained and to derive reaction rate constants and support the quantitative discussion on steam effects.

## EXPERIMENTAL SECTION

Two different limestones were used for this study, KR limestone from Canada with a particle size less than 50  $\mu\text{m}$  and PS limestone from Poland with a particle size of 75–125  $\mu\text{m}$ . The calcination/carbonation cycling of the sorbents was studied experimentally using two different TG analyzers. Two different series of cycling tests have been done by carrying out the carbonation step with and without steam in the reacting gas mixture. In both types of tests, calcination was carried out without steam and  $\text{CO}_2$  in order to avoid the introduction of any additional variable that can affect the activity of the sorbent apart from the presence of steam during carbonation.

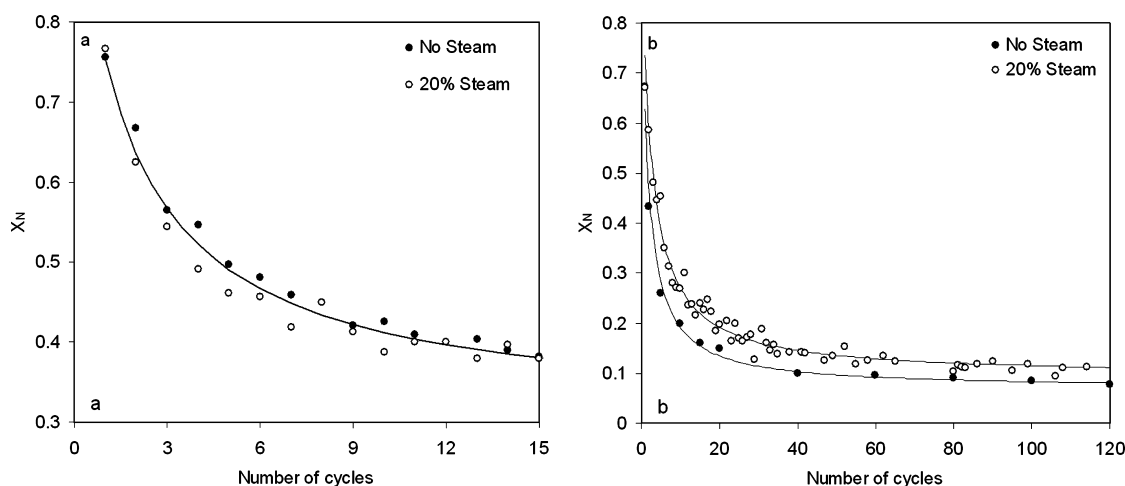
One of the TGA analyzers is a commercial device (Perkin-Elmer TGA-7). In this TGA, gas flow rates were controlled using flowmeters, and steam was generated by a syringe pump and a steam generator. The calcination step was carried out

under nitrogen at 800 °C for 10 min, and carbonation was carried out using a mixture of gases ( $p_{\text{CO}_2} = 20$  kPa,  $p_{\text{H}_2\text{O}} = 20$  kPa, nitrogen as balance) at 650 °C for 20 min. This TGA has been used to test KR limestone up to a maximum of 15 cycles. The second TGA equipment employed was specially design for multicycling tests and has been described elsewhere.<sup>26</sup> The reacting gas mixture was fed into the bottom of a quartz tube reactor placed into a furnace. The gas flow was regulated by mass flow controllers, and the steam was generated by external electric heating of the water flow set by a liquid mass flow controller. The temperature and sample weight were continuously recorded on a computer. The experimental routine consisted of calcination of the sample under air at 900 °C for 5 min, and carbonation using a mixture of gases ( $p_{\text{CO}_2} = 10$  kPa,  $p_{\text{H}_2\text{O}} = 20$  kPa, air as balance) at 650 °C for 5 min. PS has been tested in this experimental device using a maximum number of cycles of 120. In both experimental devices, initial tests were carried out to establish the experimental conditions needed to avoid external diffusion effects (sample mass below 3 mg and total gas flow above 120 mL/min).

## RESULTS AND DISCUSSION

Figure 1 shows an example of curves obtained during the carbonation step which represents the evolution  $\text{CaO}$  conversion ( $X_{\text{CaCO}_3}$ ) with time for both limestones. As can be seen, the curves show the typical shape, with an initial fast reaction stage where the overall process is controlled by the chemical reaction between  $\text{CaO}$  and  $\text{CO}_2$ . The end of this initial stage takes place quite suddenly and from this point, the diffusion of  $\text{CO}_2$  through the built-up layer of calcium carbonate limits the conversion capacity of the sorbent.<sup>5</sup>

As can be seen in Figure 1a and 1b, the reaction has almost stopped once the fast reaction stage is finished and the increase of conversion with time is negligible. This indicates the low diffusion rate of  $\text{CO}_2$  through the  $\text{CaCO}_3$  layer under these experimental conditions. Looking at the evolution of  $X_{\text{CaCO}_3}$  with time in the slow reaction regime, it can be seen that the presence of steam has little influence on  $\text{CO}_2$  diffusion. This was a surprising result when it was compared with those presented by Manovic and Anthony,<sup>19</sup> where they reported an important effect of steam on carbonation reaction of fresh calcined limestones during the diffusion-controlled regime. A



**Figure 2.** Evolution of sorbent conversion ( $X_N$ ) with the number of cycles for KR (a) and PS (b) limestones.

possible explanation for the different results may lie in the experimental setup used in that previous study. Much larger masses of sample (30 mg) and larger limestone particles ( $\sim 0.5$  mm) were used, and overall trends observed in the results did not indicate the need of differential conditions that should only be of concern for study of the fast reaction stage. Under these experimental conditions, the results were affected by the external diffusion effect in the small bed of solids in the reactor device and by internal diffusion in larger particles involved in  $\text{CO}_2$  sorption. The steam effects under these conditions are consistent with previous works referred above where the effect of steam on gas diffusivities has been also reported.<sup>20</sup>

In contrast, in the present work, special care was taken to focus on the fast reaction stage only and to avoid any external diffusion effect (bed of solids or around the basket of the TGA), by using a very low mass of solids ( $\sim 3$  mg) and high gas velocities (0.02–0.06 m/s at carbonation temperature) in the TG analyzers. Moreover, smaller sorbent particle-sized samples were used in this work to reduce intraparticle diffusion effects. As can be seen in Figure 1, under the conditions studied, no differences are observed in the evolution of CaO conversion to  $\text{CaCO}_3$  during the initial fast reaction stage during the experiments with and without steam when external diffusion resistances are removed. This is an important result as it supports the conclusions of previous CaO carbonation kinetic studies carried out with no steam on the reacting gas mixtures.

On the other hand, it is noticeable in Figure 1b, that the transition from the fast to the slow reaction regime for PS limestone takes place to a slightly higher sorbent conversion in the presence of steam. This can be due to the beneficial effect of steam on the diffusion controlled regimen reported by other authors<sup>19,20</sup> which can shift the transition between both stages to higher conversions. This results in a higher conversion at the end of the carbonation step.

Figure 2 shows the sorbent conversion at the end of the carbonation step ( $X_N$ ) with the number of cycles for both limestones tested with and without steam. Figure 2a shows the evolution of KR limestone conversion up to 15 cycles. As can be seen,  $X_N$  achieved under both experimental conditions (with and without steam) are almost identical, confirming the results shown in Figure 1a and indicating that steam has no effect on sorbent conversion on the whole carbonation step, including both reaction stages, for this powdered limestone sample ( $< 50$   $\mu\text{m}$ ).

In the case of PS limestone, a higher number of cycles has been used to check any potential positive effect of steam observed in Figure 1b for highly cycled particles. As can be seen in Figure 2b, the conversion of the sorbent is still higher when steam is present after a high number of cycles. These results indicate that depending on the limestone tested and its particle size, steam can have a slight positive influence by increasing the sorbent conversion at the end of the carbonation step which could be attributed to the positive influence of steam during the diffusion controlled stage.

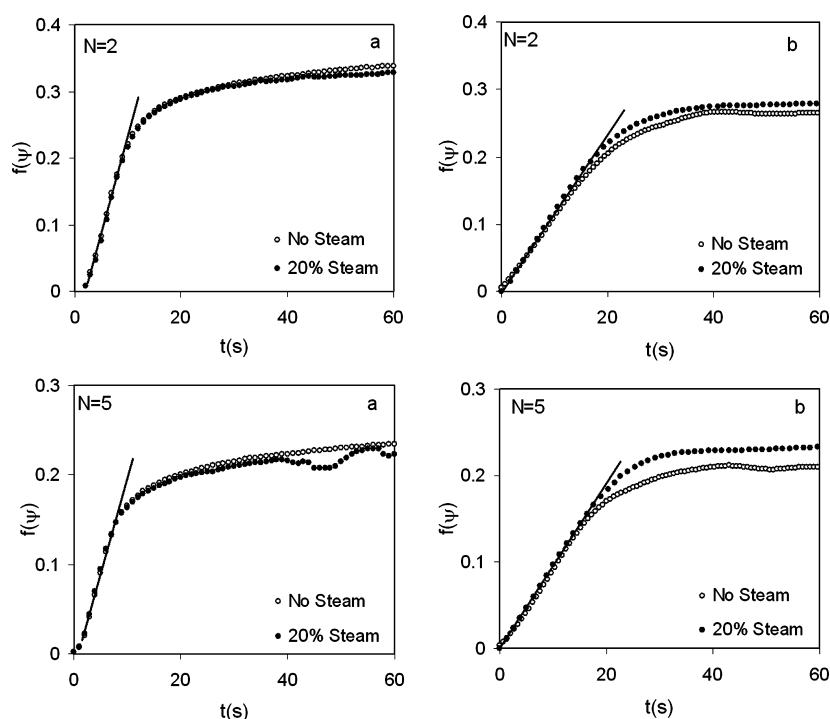
To discuss the effects of steam on reaction rates, we have fitted all obtained  $X$  vs  $t$  plots (like those presented in Figure 1) by a suitable model. In this manner, the rate parameters of the carbonation reaction during the initial fast reaction stage were derived. We have used the random pore model (RPM).<sup>9</sup> According to this model, the conversion rate of the sorbent under the chemical reaction-controlled stage can be calculated as

$$\frac{dX}{dt} = \frac{k_s S (C_{\text{CO}_2} - C_{\text{CO}_2\text{eq}})(1-X)\sqrt{1-\Psi \ln(1-X)}}{(1-\varepsilon)} \quad (1)$$

where  $k_s$  is the rate constant for the surface reaction,  $S$  is the reaction surface area per unit of volume,  $\varepsilon$  is the porosity of the particles and  $C$  is the  $\text{CO}_2$  concentration. In eq 1,  $\Psi$  is a structural parameter that takes into account the internal particle pore structure, which can be calculated as

$$\Psi = \frac{4\pi L(1-\varepsilon)}{S^2} \quad (2)$$

where  $L$  is the initial pore length in the porous system per unit of volume. This model has been recently applied successfully to study the carbonation conversions of multicycled CaO particles.<sup>12,15</sup> This was done by considering the changes of the structural parameters as they evolve during cycling toward more opened pore structures.<sup>27</sup> These parameters ( $S$ ,  $L$ , and  $\varepsilon$ ) can be determined from experimental measurements.<sup>28</sup> However, the evolution of these structural parameters during cycling presents difficulties for the application of the RPM. To avoid the experimental determination of these parameters in each cycle and to simplify the application of the RPM, Grasa et al.<sup>29</sup> proposed a methodology to estimate  $S_N$  and  $L_N$  for each cycle, from the initial values ( $S_0$  and  $L_0$ ) and the maximum  $\text{CO}_2$  carrying capacity of the sorbent ( $X_N$ ) (see reference 29 for



**Figure 3.** Representation of  $f(\psi)$  vs time for KR (a) and PS (b) limestones for different number of cycles (carbonation temperature = 650 °C;  $\text{H}_2\text{O}$  partial pressure = 20 kPa,  $\text{CO}_2$  partial pressure = 20 kPa (a), 10 kPa (b)).

more details). The initial reaction surface area ( $S_0$ ) of the fresh calcined limestones has been estimated from the maximum  $\text{CO}_2$  carrying capacity of the sorbent in the first cycle assuming the  $\text{CaCO}_3$  layer thickness at the end of the fast reaction regimen to be 49 nm.<sup>30</sup> We have assumed for both limestones initial values of  $3.40 \times 10^{14} \text{ m}^2/\text{m}^3$  and 0.46 for pore length ( $L_0$ ) and porosity ( $\epsilon$ ), respectively, using the values presented by Grasa et al.<sup>29</sup> According to the RPM, the particle conversion under the chemical reaction regime can be calculated as a function of time by the equation<sup>9</sup>

$$\frac{1}{\psi_N} [\sqrt{1 - \psi_N \ln(1 - X)} - 1] = \frac{k_s S_N (C_{\text{CO}_2} - C_{\text{CO}_2\text{eq}}) t}{(1 - \epsilon)} \quad (3)$$

The reaction rate constant ( $k_s$ ) can be calculated by plotting the left side of eq 3 against time from the slope in the fast reaction regime. Figure 3 shows an example of this representation for both limestones during the second and fifth cycles with and without steam.

Table 1 shows the mean reaction rate constants calculated for each cycle for the two limestones under both experimental

**Table 1.** Reaction Rate Constants ( $k_s$ ) ( $\text{m}^4/\text{mol s}$ ) at 650 °C Calculated Using the RPM Model for Both Limestones

limestone	no steam	20% steam
KR	$4.60 \pm 0.14 \times 10^{-10}$	$4.85 \pm 0.25 \times 10^{-10}$
PS	$2.23 \pm 0.28 \times 10^{-10}$	$2.30 \pm 0.25 \times 10^{-10}$

conditions tested (no steam and 20% steam). KR limestone is slightly more reactive than PS limestone as it has a higher reaction rate constant. As can be seen, the steam has no influence on the reaction rate constant and similar  $k_s$  values are

obtained when carbonation tests are carried out with and without steam for both limestones. Reaction rate constants obtained for both limestones are in agreement with those obtained by other researchers using reacting gas mixtures where no steam was present.<sup>9,12</sup>

## CONCLUSIONS

The effect of steam on carbonation kinetics has been studied using two different limestones under differential conditions. Reaction rates have been determined under typical carbonation conditions (650 °C and  $\text{CO}_2$  partial pressure around 15 kPa) with and without steam. It has been shown that steam has no influence on the reaction rate constant and similar values were calculated with and without the presence of steam (20%) in the reacting gas. Values obtained for each limestone are in agreement with those found previously in the literature in absence of steam.

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## NOTATION

$C_{\text{CO}_2}$  = concentration of  $\text{CO}_2$ ,  $\text{kmol}/\text{m}^3$ ; eq, equilibrium  
 $F_0$  = molar make up flow of CaO fed to the calcium looping,  $\text{mol}/\text{s}$   
 $F_{\text{CO}_2}$  = molar flow of  $\text{CO}_2$  fed to the carbonator,  $\text{mol}/\text{s}$   
 $k_s$  = rate constant for surface reaction,  $\text{m}^4/\text{kmol s}$   
 $L_N$  = total length of pore system,  $\text{m}/\text{m}^3$



$N$  = number of calcination/carbonation cycles  
 $S_N$  = reaction surface area per unit of volume after  $N$  cycles,  $\text{m}^2/\text{m}^3$   
 $X_{\text{CaCO}_3}$  = CaO molar conversion to  $\text{CaCO}_3$  with time  
 $X_N$  = CaO molar conversion to  $\text{CaCO}_3$  at the end of the carbonation step  
 $\varepsilon$  = porosity  
 $\psi_N = 4\pi L_N(1 - \varepsilon)/S_N^2$

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