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# Reactivity of CaO-based sorbent for Calcium Looping Technology in presence of steam

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## ABSTRACT

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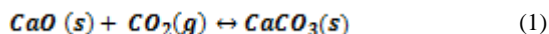
CO<sub>2</sub> Capture  
CaO looping cycle  
Steam  
Carbonation  
Reaction Rate

Calcium looping cycle is a post-combustion technology to capture CO<sub>2</sub> from power station flue gas using the reversible reaction between CaO and CO<sub>2</sub> to form CaCO<sub>3</sub>. The influence of the presence of steam in the flue gas on the carbonation reaction was studied using a thermogravimetric analyzer (TGA). Steam was found to enhance the diffusion-controlled stage of carbonation in thirty calcination/carbonation cycles experiments with limestone (Havelock and Purbeck) used as sorbent. An improvement in conversion and carrying capacity was noticed in Havelock with an achieved conversion of 17% after 30 cycles and a carrying capacity of 0.13gCO<sub>2</sub>/gCaO. On the other hand, Purbeck limestone showed no significant improvement in carbonation extent when steam was present. Reaction rate coefficients were determined using the Random Pore Model and a value of  $(4.33 \pm 1.50) \times 10^{-10} \text{m}^4 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  was obtained for experiments without steam whereas the steam experiments yielded a value of  $(2.47 \pm 1.01) \times 10^{-10} \text{m}^4 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ .

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## 1. Introduction

Carbon Capture and Storage refers to the set of techniques developed to capture CO<sub>2</sub> from the exhaust gases of power stations or from other industrial sources (named as stationary emissions sources). [1] CCS is recognized as an important piece for mitigating the risks of climate change, since the emissions of CO<sub>2</sub> and other greenhouse gases (GHG's) are continuously increasing due to the incessant reliance on fossil fuels. [2] This work focuses on Calcium Looping Cycle (CaL), a post-combustion CCS technology which is based on the reversible reaction between CaO and CO<sub>2</sub>, according to eq.1:



CaL is in the early demonstration stages [3], but governments are implementing strategies to accelerate commercial deployment. [4]. The key advantages of this technology when compared to others are: (1) use of cheap and abundant sorbent (limestone); (2) low energy penalty; (3) use of mature large-scale equipment (fluidized bed reactors); (4) synergy with cement industry. On the other hand, the main drawback is the sorbent rapid loss of reactivity after several cycles of CO<sub>2</sub> capture-and-release.[4]

The direct reaction of eq.1 is known as carbonation and it is responsible for the CO<sub>2</sub> absorption. Carbonation is an exothermic reaction ( $\Delta_r H_{298\text{K}} = -178 \text{ kJ} \cdot \text{mol}^{-1}$ ) and Bhatia and Perlmutter [5] described it as an incomplete first-order reaction. The extent of

the reaction comprises a first-stage where carbonation is rapid and chemically controlled and a second stage where the rate is diffusional controlled (diffusion through the CaCO<sub>3</sub> layer). The transition between the fast and slow regimes takes place suddenly at a given level of conversion, which is gradually lower with the increasing number of calcination/carbonation cycles.[6]. Alvarez et al. [7] found that the transition between stages occurs when a critical carbonated product layer of 50nm thickness is deposited at the particle surface.

Carbonation conversion is associated with the specific surface area of the sorbents which is therefore linked to the sorbent pore structure. [8] The sorbent exposure to extreme experimental conditions such as temperature and pressure causes changes in the sorbent initial morphology, responsible for the sorbent decay. Factors known to influence the sorbent reactivity include: (1) presence of sulfur species; (2) Sintering; (3) Pore blockage. Sintering of the sorbent cause grain growth or pore shrinkage and occurs predominantly during calcination reaction due to the higher temperatures present in this reaction (~900°C). [8] Pore blockage is caused by the deposition of CaCO<sub>3</sub> during carbonation reaction. This product layer fills up the superficial pores, and thus, the interior pore network is not available for further carbonations. [6] The sorbent decay processes are responsible for a reduction in the CaL cost efficiency. Thus, several studies focused on overcoming the reactivity loss of the natural sorbents. Research has been done in three main paths: (1) determination of optimal operating conditions; (2) development

of synthetic/supported sorbents; (3) study of sorbent enhancement techniques (hydration, thermal pre-treatment, sorbent doping). [9,10] Most of the experimental work has been carried out using synthetic flue gases composed of a mixture of  $N_2$ /air and  $CO_2$ . [11] However, the flue gas composition has a more extensive range of compounds. Steam is generally 5-10% of a combustion flue gas and so its influence during calcination/carbonation is relevant for determining the reactivity through multiple cycles. [4,12] It is of general agreement that the presence of steam increases the rate of sintering and the rate of calcination.[4] However, there is no consensus in the literature about the effect of steam on carbonation reaction. Symonds et al. [13] showed that the presence of steam increases the high  $CO_2$  capture efficiency period during experiments carried out in a bubbling bed reactor. Also, in a reactivity study of different types of limestone (samples with ~30mg and size fractions range between 250-500 $\mu$ m) in a TGA under post-combustion capture conditions (gas mixture with 20% $CO_2$  and 10-20% of steam), the carbonation conversion was more than doubled at 400 $^{\circ}C$ . [14] Manovic and Anthony [14] reported that this was associated to an enhancement of the solid-state diffusion in the product layer by the presence of steam. Similar results were obtained by Donat et al. [4] in experiments carried out in a mini-fluidized bed reactor. The effect of steam on sorbent reactivity was said to occur in two ways: (i) promoting sintering during calcinations that lead to larger pores in the sorbent (~50nm diameter), which appear to be more stable; (ii) reducing the diffusion resistance through the  $CaCO_3$  layer. In contrast, Sun et al. [15] showed no appreciable effect of steam on carbonation conversion during multi-cycle tests in a TGA. A later paper from Arias et al. [16] noticed only a little influence of steam on carbonation conversion in experiments performed in a TGA using limestone (particle sizes <50 $\mu$ m; mass <3 mg) in presence of post-combustion conditions during cycles. No influence on the diffusion of  $CO_2$  in the diffusion-controlled step was also found. [16] On the other hand, testing a wet flue gas (steam present) in a pilot-plant for calcium looping processes in Stuttgart [4,17] the  $CO_2$  capture efficiency showed to improve significantly (from 80% to 95% at 600 $^{\circ}C$ ) when compared to reactions performed under a dry gas.

Thereby, the purpose of the present work is to improve understanding about the steam influence on carbonation reaction and on its kinetics. Experiments of calcination/carbonation cycles were performed in a TGA under an atmosphere containing steam and compared to experiments performed with a gas mixture containing only  $N_2$  and  $CO_2$ . Carbonation, reaction rates and carrying capacities were calculated. SEM analysis was performed in order to understand the evolution of the sorbent morphology during cycles. The Random Pore Model was applied to the experimental results to derive reaction rate constants as well as diffusion parameters and therefore support the discussion on steam effects.

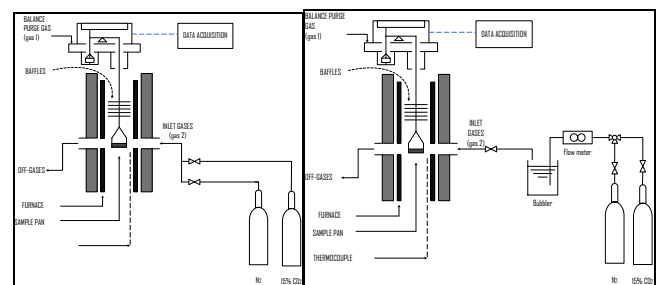
## 2. Experimental

In this work, all the experiments were performed in a thermogravimetric analyser (TA Q5000 IR), which was used to simulate the continuous operation by changing the temperature for calcination and carbonation reactions. Firstly, experiments were carried out in order to determine the optimum conditions to study the carbonation reaction kinetics. For the experimental set-up used, different flow rates (100,120,130,140,160,200ml/min),

weight of the sample (2mg, 2.5mg, 3mg, 4mg, 6mg), particle size (150-355 $\mu$ m; 355-500 $\mu$ m; 500-710 $\mu$ m) and carbonation temperature (600,650,700 $^{\circ}C$ ) were analyzed and the most suitable ones were selected. Thus, the experimental conditions used were: flow rate of 140ml/min; 3mg of sample mass; particle size in the range of 355-500 $\mu$ m. Experiments with an empty pan were also performed to check for possible disturbances in the weight readings done by the TGA. [61]

The experiments of calcination/carbonation cycles were divided in two different groups: experiments performed with and without steam present (Figure 1). Calcination reactions were performed at a constant temperature of 900 $^{\circ}C$  whereas the temperature of carbonation was 650 $^{\circ}C$ . Both reactions lasted only 5minutes. The heating and cooling rate were the same, 120 $^{\circ}C$ /min, with the particularity of performing the cooling down under a  $N_2$  atmosphere to assure that the carbonation reaction only started at the desired temperature (650 $^{\circ}C$ ). Thirty calcination/carbonation cycles were performed under 15%(v/v)  $CO_2$  balance in nitrogen. In the experiments performed with steam, gases were regulated by an external flow controller and directed to a saturator filled up with deionised water (100ml of volume) in order to leave saturated in water. Steam concentrations used during the experiments were ~1.5%. A humidity probe was displaced in the TGA outlet line to record the relative humidity and therefore to follow the steam concentration. Relative humidity was not higher than 60-70% in order to avoid water condensation. For calibration of the humidity measurements, five saturated salt solutions (magnesium chloride; magnesium nitrate; sodium chloride; potassium chloride; potassium nitrate) with known values of relative humidity were used.

The reactions were followed by monitoring the mass temporal evolution. Both temperature and sample weight were recorded using a software, *Universal Analysis 2000*. The temperature inside the saturator was measured using a K thermocouple and it was registered with the software *Agilent VEE Pro 7.0*.



**Figure 1.** Schematic diagram of the experimental apparatus necessary to perform the cycling experiments (left figure: no-steam experiments set-up; right figure: steam experiments set-up)

### 2.1. Materials

Two types of limestone were used in the experiments, Havelock and Purbeck. These two types of limestone were selected because of their relative purity in terms of  $CaCO_3$ . The elemental composition of the limestones was determined by X-ray fluorescence in a previous work and is summarized in Table 1. Gases (15% v/v  $CO_2$  balance in nitrogen and  $N_2$ ) were provided by BOC and no moisture was detected.

**Table 1.** Chemical composition (%wt) of Havelock and Purbeck limestones[18]

Compound	Havelock	Purbeck
Ca	97.64	97.67
Fe	0.20	0.49
Mg	0.27	0.61
Al	0.15	0.21
Si	1.20	0.65
Mn	0.43	0.14
K	0.04	0.09
S	0.00	0.11
Zr	0.00	0.05

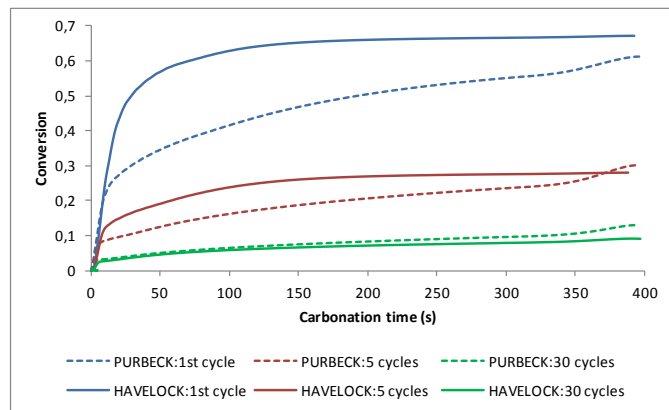
## 2.2 Characterization

The morphology of CaO samples after calcination/carbonation cycles was studied with a Hitachi TM-1000 scanning electron microscope (SEM) with a built in energy dispersive X-ray spectroscopy (EDX) analyser. Every particle was analysed in the calcine form (CaO). Before the observation, the samples were placed on alumina stubs and then coated with 30nm gold to avoid charging of the nonconductive CaO. The microscope magnification was limited to 10,000 times.

## 3. Results and Discussion

### 3.1. Thirty cycle experiments with Havelock and Purbeck limestones

Experiments without steam were performed to determine the reactivity of both Havelock and Purbeck limestones. Thirty calcination/carbonation cycles were carried out, because it is a reasonable approximation to be made of the conversion after many cycles. [3]

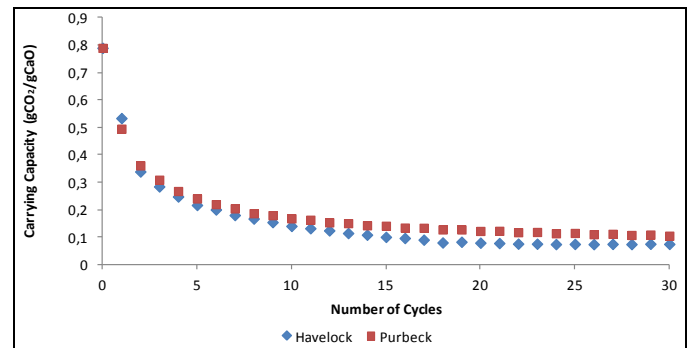


**Figure 2.** Conversions of Havelock and Purbeck limestones in the experiments performed without steam (cycles 1,5,30)

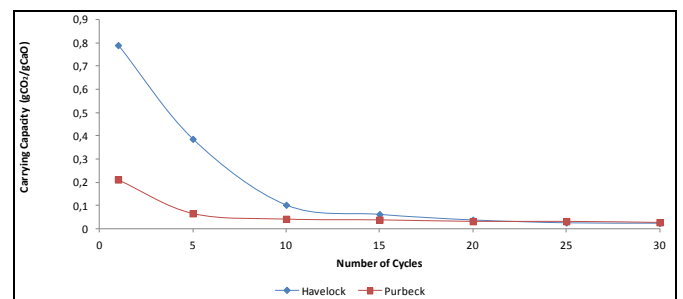
Figure 2 shows limestones' conversion determined for different number of cycles. As it was expected, conversion decreases with the number of calcination/carbonation cycles. After the first carbonation, Havelock limestone accomplished ~67% conversion while Purbeck achieved only 61%. However, in the end of the 5<sup>th</sup> cycle Purbeck achieved a 30% conversion, marginally higher than the carbonation conversion of Havelock and this tendency continued for the subsequent reactions. Both limestones achieved constant values of conversion in the last cycles, suggesting that the reactivity reached the decay asymptote before the end of cycle 30. Havelock reached a residual conversion of only 9.1% while Purbeck achieved 13%. These values are close to the residual conversion of 7-8% reported by

Grasa and Abanades [6] after many hundreds of cycles. A higher residual conversion allows the limestone to capture more CO<sub>2</sub>, and it will also reduce sorbent purge rates in a real system[19]. Despite the high conversion values obtained with Purbeck, it looks as if this limestone starts off with a lower initial rate, but ends up with a higher one (Figure 2).

Carbonation reaction rate is of a major importance concerning the CO<sub>2</sub> capture efficiency and so, it was calculated for both limestones. For the first carbonation Havelock achieved 0.0266 s<sup>-1</sup> of reaction rate and a value of 0.017 s<sup>-1</sup> was registered for Purbeck. These values were substantially higher than those reported by previous works.[9,19] Higher velocities of reaction were obtained by Havelock in the initial cycles, but around the 15<sup>th</sup> cycle Purbeck limestone started to exhibit faster rates. This high rate obtained by Purbeck in the last cycles, along with the acceleration in conversion in the end of the slow stage of carbonation when the temperature started to increase for the subsequent calcination step (Figure 2), shows that Purbeck limestone has a more important diffusion controlled regime.[20] Differences in texture and morphology of limestones are responsible for causing different behaviours.[21] The higher quantity of elements present in Purbeck's composition is thought to cause a inner morphological defect in the limestone that may enhance transport processes (improved diffusion controlled stage) [18]



**Figure 3.** Carrying capacity of Havelock and Purbeck through thirty calcination/carbonation cycles



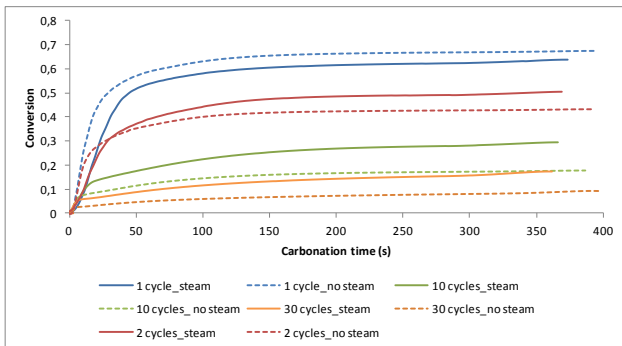
**Figure 4.** Carrying capacity of Havelock and Purbeck through thirty cycles for the fast carbonation stage only

In order to determine which sorbent can absorb a higher quantity of CO<sub>2</sub> the carrying capacity of each limestone was calculated. Figure 3 shows a fall in carrying capacity that is caused by pore blockage and sintering processes, which are responsible for a continuous loss of porosity and specific surface area of the sorbent. Around cycle 20, the carrying capacity of Havelock seems to stabilize for 0.075gCO<sub>2</sub>/gCaO (corresponding to 9.5% of conversion). On the other hand, Purbeck limestone achieved higher values of carrying capacity than those from Havelock, as it was observed in conversion results. Overall, Purbeck could absorb higher quantities of carbon dioxide.

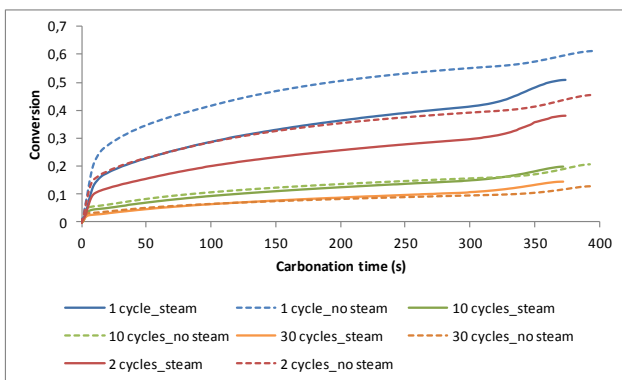
However, when excluding the diffusion controlled stage from carrying capacity (Figure 4) the results were substantially different. When only the fast carbonation stage is considered, Havelock limestone achieved better results until around the 20<sup>th</sup> cycle, where the diffusion controlled regime gains importance in the carbonation reaction. This result should be considered, because an extension of the carbonation reaction through the slow diffusion controlled stage will lead to an only little enhancement of CO<sub>2</sub> absorption, considering the extra time it would take and the size required for reactors. Thus, only the fast carbonation stage is of interest for large-scale industrial application. [18] However, when selecting the best limestone to apply in a real industrial unit, tests for the specific conditions present at the site have to be done.

### 3.2. Effect of Steam in CaO-sorbents performance

The second set of experiments comprised the performance of thirty cycle experiments with Havelock and Purbeck limestones, although with steam being also introduced in the TGA (atmosphere with CO<sub>2</sub>, N<sub>2</sub> and steam). Steam concentration was only ~1.5% , but it is expected to characterize well the effects caused by steam, since Donat et al. [4] found an asymptotic reactivity of the sorbents at around 1% steam.



**Figure 5.** Conversion of Havelock in the thirty cycle experiments performed with and without steam



**Figure 6.** Conversion of Purbeck in the thirty cycle experiments performed with and without steam

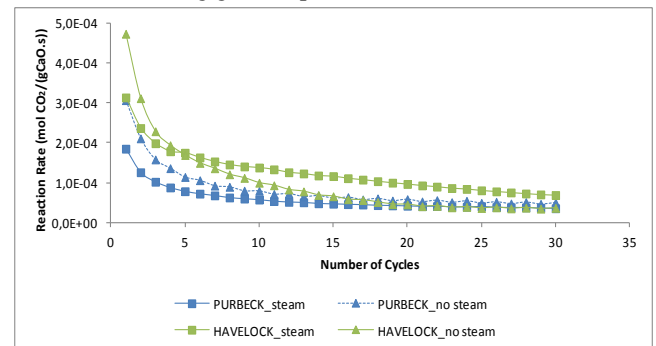
Figure 5 shows that Havelock experiments performed with steam achieved higher carbonation conversions, except in the first cycle, where a ~63.7% conversion was obtained. After this cycle, the enhancement by steam was noticeable and a 37% conversion was accomplished in the 5<sup>th</sup> cycle (around a 34% increase). In the end of the thirty cycles, the conversion was 17%, almost twice the value obtained in the experiments without steam. A very different behaviour was exhibited by Purbeck limestone (Figure 6). The value for the first carbonation was around ~50.9%, much lower than the conversion obtained

without steam. However, the results were gradually improved and a value of 14.4% conversion was achieved in the 30<sup>th</sup> cycle, slightly higher than the correspondent conversion in the experiments without steam. This gradual enhancement was also observed for Havelock. Considering this, it arises the idea that steam may improve the conversion by enhancing the diffusion controlled regime, since this regime becomes more relevant with increasing number of cycles. Since Purbeck limestone already has a more intense diffusion controlled stage, this could be the reason for its lower enhancement by steam.

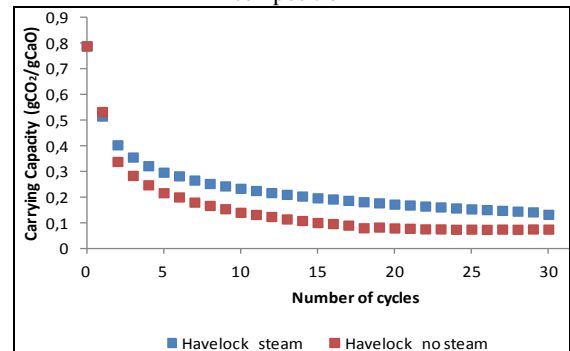
Overall, the presence of steam seems to result in an increased CaO conversion over cycles, as reported by previous researchers, e.g. Symonds et al.[13]. The reduced conversion obtained in the first cycle may be related with sintering effects, since steam also increases the rate of sintering during calcinations, leading to larger pores and less surface area.[18,13,22] Still, these larger pores appear to be more stable in the succeeding cycles. [18,13]

Figure 7 shows a comparison between the maximum reaction rate obtained for each cycle in experiments with Havelock and Purbeck. Such as in Donat [18], a prolonged and enhanced fast stage of carbonation was noticed due to the presence of steam, particularly for Havelock. This improvement in the fast stage was said to be due to a reduction in the CO<sub>2</sub> diffusion resistance. [18]

Considering all experiments done, the highest conversions and reaction rates were obtained for Havelock when steam was present in the reacting gas composition.



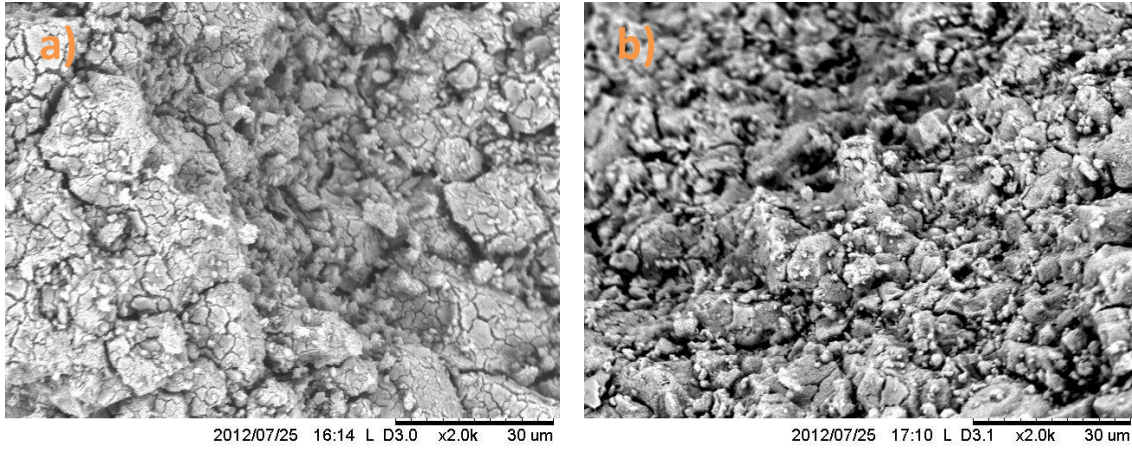
**Figure 7.** Maximum reaction rates of Purbeck and Havelock in experiments with and without 1.5% steam present in the gas composition



**Figure 8.** Carrying Capacity of Havelock in the thirty cycle experiments performed with and without steam

In terms of carrying capacity, the experiments performed with Havelock in presence of steam obtained again the highest values. (Figure 8). In presence of steam, this limestone seemed not to have achieved the decay asymptote during the thirty cycles. More 49% of CO<sub>2</sub> was absorbed and the carrying capacity after cycle 30 was 0.13gCO<sub>2</sub>/gCaO. Initially, Purbeck limestone achieved lower carrying capacities in the presence of steam, but after around the 10<sup>th</sup> cycle the performance started to be identical.





**Figure 9.** SEM images of Havelock particles after thirty calcination/carbonation cycles with a magnification of 2000x. (a) Particle cycled with no steam; b) Particle cycled in presence of steam)

### 3.3. Scanning electron microscopy (SEM)

Particles of Havelock were observed using a scanning electron microscope in order to visualize the changes in the particles' morphology when reacted under an atmosphere containing steam. The main aim was to try to understand the higher conversions and reaction rates obtained in the steam experiments. The surface morphology of a limestone changes greatly over the course of reaction.[23] After the first calcination, limestones are an extremely porous solid with pores of about 2-3µm at the particle surface. [24] After five and thirty calcination/carbonation cycles the limestone's surface was observed and compared. As expected, sintering effects increased from the 5<sup>th</sup> cycle to the 30<sup>th</sup> cycle. Figure 9 shows particles after subjected to thirty calcination/carbonation cycles and it is possible to see that particles cycled without steam suffered a more intense sintering process (smooth areas). Particles cycled with steam kept a higher porosity and therefore a higher surface area was available. As a result, higher conversions and reaction rates were obtained. [4]

### 3.4. Random Pore Model (RPM)

A simple reaction model was used in order to try to quantify the enhancement caused by the presence of steam during the calcination/carbonation cycles. The Random Pore Model (RPM) allows to derive reaction rate constants ( $k_s$ ) and to determine the diffusion parameter ( $D$ ).

According to this model the reaction rate of a gas-solid reaction in the presence of a product layer diffusion resistance is expressed by eq.2. [5] This expression accounts for the internal pore structure of the particle by using the parameter  $\psi$ .

$$\frac{dX}{dt} = \frac{k_s S_0 C(1-X) \sqrt{1-\psi \ln(1-X)}}{(1-\epsilon) \left[ 1 + \frac{\beta Z}{\psi} (\sqrt{1-\psi \ln(1-X)} - 1) \right]} \quad (2)$$

$$\psi = \frac{4\pi L_0(1-\epsilon)}{S_0^2} \quad (3)$$

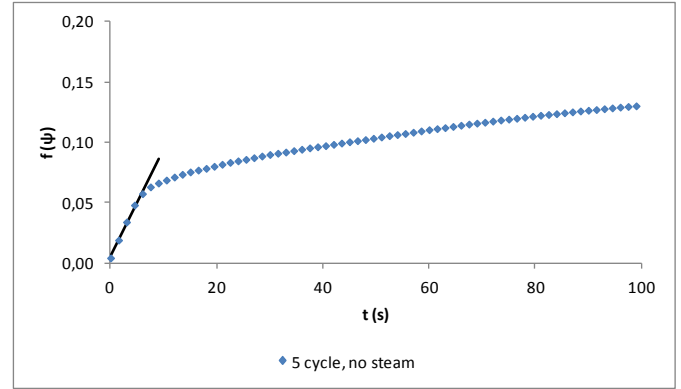
In these equations,  $k_s$  is the rate constant for the surface reaction,  $S$  is the reaction surface area per unit of volume,  $\epsilon$  is the porosity of the particle,  $C$  is the  $\text{CO}_2$  concentration and  $L_0$  represents the initial pore length per unit of volume. Due to the small quantities of sample allowed in the TGA, it was not possible to perform mercury porosimetry or gas adsorption analysis. Therefore, the initial textural parameters used,  $S_0$ ,  $L_0$

and  $\epsilon$ , were from similar experiences performed by other researchers ( $S_0=4.64 \times 10^7 \text{m}^2 \cdot \text{m}^{-3}$ ;  $L_0=4.75 \times 10^{14} \text{m} \cdot \text{m}^{-3}$ ;  $\epsilon=0.507$ ). [24,25]

For a reversible first-order system, eq.2 can be simplified and integrated in the regime of chemical reaction control (eq.4). [26].

$$f(\psi) = \frac{1}{\psi} \left[ \sqrt{1 - \psi \ln(1 - X)} - 1 \right] = \frac{k_s S_0 (C_b - C_e) t}{2(1 - \epsilon)} \quad (4)$$

The determination of the reaction rate constant ( $k_s$ ) is done by plotting the left side of eq.4,  $f(\psi)$ , against time. Adjusting a linear trend to the fast reaction regime,  $k_s$  can be determined by the slope. Figure 10 shows an example of this procedure.



**Figure 10.** Representation of  $f(\psi)$  vs. time for the 5<sup>th</sup> cycle of the experiments without steam

In order to estimate the evolution of the structural parameters, Grasa et al. [26] proposed a methodology to estimate the surface area and the pore length for the  $N^{\text{th}}$  cycle,  $S_N$  and  $L_N$ .

$$S_N = S_0 X_N \quad (5)$$

$$L_N = L_0 X_N \frac{r_{p0}}{r_{pN}} \quad (6)$$

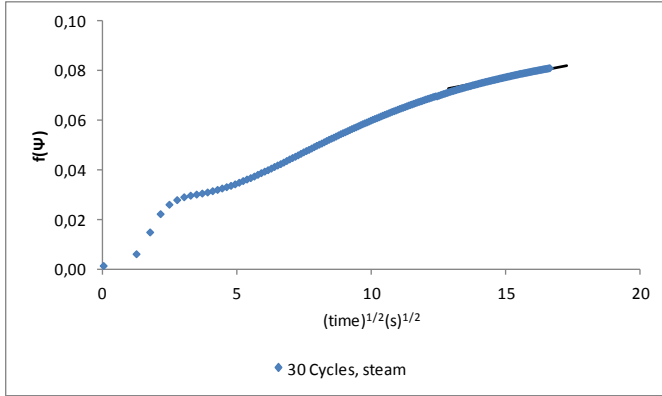
In eq.6, in order to determine the pore length it is assumed that  $r_{p0}/r_{pN}$  has a value of 0.1 for highly cycled particles. The maximum carbonation conversion ( $X_N$ ) is determined applying the Grasa Equation to the experimental conversion.[6]

The second slow stage of carbonation reaction is controlled by a product layer diffusion and so, the integration of eq.2 gives:

$$\frac{1}{\psi} \left[ \sqrt{1 - \psi \ln(1 - X)} - 1 \right] = \frac{S_0}{(1-\varepsilon)} \sqrt{\frac{D_p t}{2Z}} \quad (7)$$

The effective diffusivity of carbonation reaction can be determined from the linear slope when the left hand side of eq.7 is plotted against the square-root of time. The effective diffusivity is related to the apparent product layer diffusion,  $D_p$ , according to eq.8. An example of the diffusion coefficient determination is shown in Figure 11.

$$D_p = \frac{M_{CaO} D C_b}{\rho} \quad (8)$$



**Figure 11.** Representation of  $f(\psi)$  vs. the root of time used for the determination of  $D_p$ .

After the determination of  $k_s$  and  $D$  parameters, it is possible to calculate conversion using the model. The calculation of conversions is done differently for the two carbonation stages. The first stage, chemically controlled is determined using eq.9. [26,27] and the slow stage controlled by both chemical reaction and diffusion of  $CO_2$  through the product layer is determined by eq.11.

$$X = 1 - \exp\left(\frac{1 - \left(\frac{\tau}{2} + 1\right)^2}{\psi}\right) \quad (9)$$

$$\tau = \frac{k_s (C_b - C_\varepsilon) S_0 t}{(1-\varepsilon)} \quad (10)$$

$$X = X_{k-D} + \left( 1 - \exp\left(\frac{1}{\psi} - \frac{\left[\sqrt{1 + \beta Z \tau} - \left(1 - \frac{\beta Z}{\psi}\right)^2\right]^2 \psi}{\beta^2 Z^2}\right)\right) \quad (11)$$

$$\beta = \frac{2 \times k_s \times \rho_{CaO} \times (1-\varepsilon)}{M_{CaO} \times D \times S_0} \quad (12)$$

It is important to define a transition between regimes and it was assumed to happen when the reaction rate become less than 20% of the maximum reaction rate. [18] However, the transitory conversion ( $X_{k-D}$ ) was later adjust by a least-square fitting using the *Solver* function of *Excel* in order to improve the fitting exercise.

Figure 12 shows the experimental conversion plotted together with eqs.9 and 11. It can be seen that the RPM model overall predicted well the conversion, but the fitting was better to the initial cycles. For the last cycles the fitting was not so good given that the model seems not to characterize so well the diffusion controlled stage. The model also showed difficulty in representing the transition between the two regimes of carbonation reaction (strongly controlled by both mechanisms - chemical reaction and diffusion through the product layer). The textural parameters used as inputs in the RPM ( $\varepsilon$ ,

$S_0$  and  $L_0$ ) were not determined for our particles and this may affect the fitting of the model to the experimental results.

**Table 2.** Results obtained from the RPM application

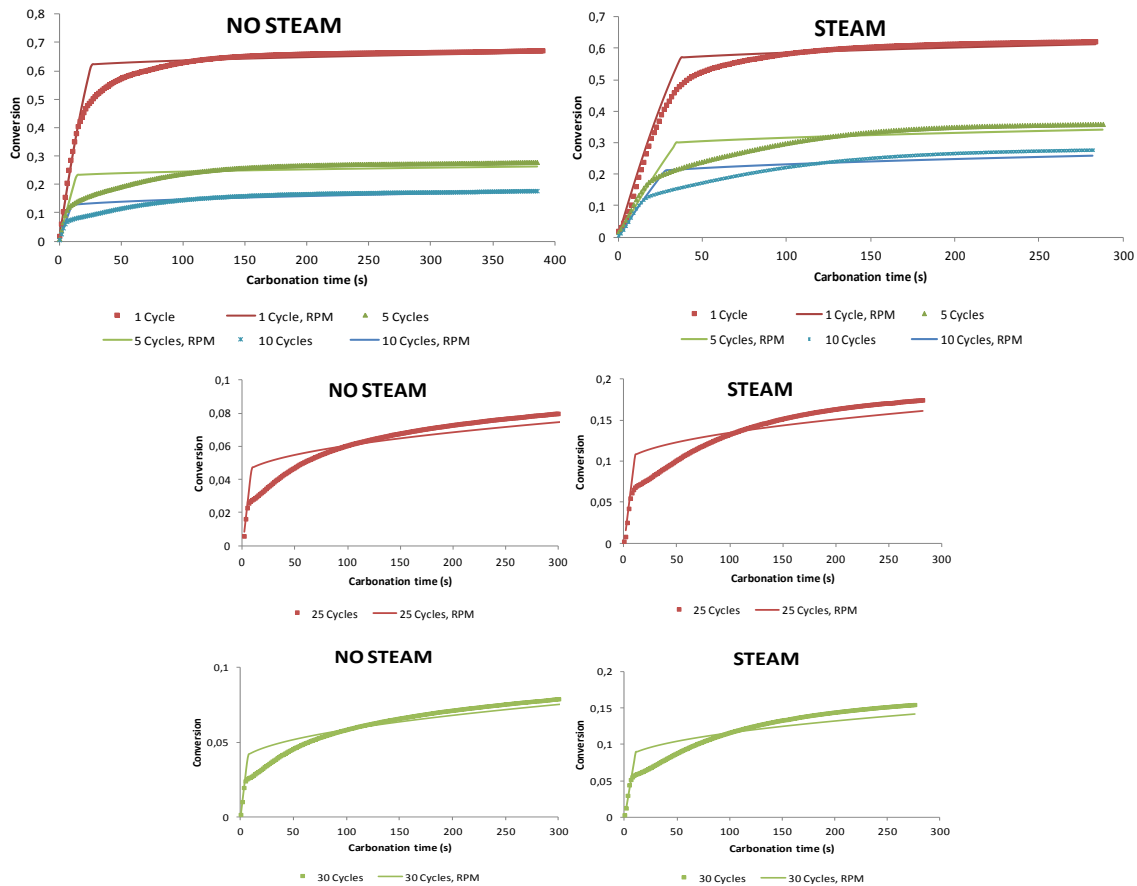
	NO STEAM	STEAM
$k_s$ ( $m^4 \cdot mol^{-1} \cdot s^{-1}$ )	$(4.37 \pm 1.50) \times 10^{-10}$	$(2.47 \pm 0.86) \times 10^{-10}$
$D$ ( $m^2 \cdot s^{-1}$ )	$(1.77 \pm 1.65) \times 10^{-15}$	$(1.45 \pm 1.02) \times 10^{-15}$

The reaction rate constants and the diffusion coefficients determined by the model are summarized in Table 2. The values obtained are in agreement with values registered in the literature. [4, 14,27] Particles cycled without steam showed to be slightly more reactive during the fast stage of carbonation, since higher values of  $k_s$  were obtained. Looking at these values one would say that steam has no influence on the reaction rate constant. However, this has to be verified again by applying the model with the correct parameters of  $S$ ,  $L$  and  $\varepsilon$ .

The mean effective diffusion obtained similar values for both experiments performed with and without steam. Nevertheless, it is important to note that the model did not fit very well the diffusion controlled stage so the accuracy of these values is not assured. Except for the first cycles, the positive influence of steam in the product layer diffusion was not very visible. However, the initial textural parameters used in the model belonged to Havelock particles cycled with a no steam atmosphere and it may have negatively influenced the results achieved in the steam experiments.

#### 4. Conclusions

The main focus of this work was to get a better understanding on how steam influences the CaO-sorbents performance, mainly how it affects the carbonation reaction and its kinetics. Experiments of calcination/carbonation cycles were performed under post-combustion conditions with Havelock and Purbeck sorbents with and without the presence of steam. Higher conversions were achieved by Havelock limestone in presence of 1.5% of steam. In the end of the 30th cycle a 91% improvement was registered in comparison to no experiments without steam. Carrying capacity was also enhanced by the presence of steam and a value of  $0.13 gCO_2/gCaO$  was obtained in the end of the thirty cycle experiments. Purbeck limestone had only a little enhancement of 12% in the last cycle conversion and no significant improvements were obtained in carrying capacities. Steam proved to enhance the diffusion controlled stage of carbonation and this was already reported in the literature, however different limestones may achieve different results. The RPM showed to fit properly to the experimental data, although with difficulty in characterizing the slow stage of carbonation. Values obtained with the model showed that particles cycled without steam were slightly more reactive.



**Figure 12.** Comparison between the experimental conversion and the conversion calculated using the random pore model for experiments with and without steam

## Notation

- $k_s$  – Rate constant for the surface reaction ( $\text{m}^4 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ )  
 $S$  – Reaction surface area per unit of volume ( $\text{m}^2 \cdot \text{m}^{-3}$ )  
 $\varepsilon$  – Porosity  
 $L$  – Pore length per unit of volume ( $\text{m}^2 \cdot \text{m}^{-3}$ )  
 $t$  – Time (s)  
 $D_p$  – Apparent product layer diffusion ( $\text{m}^2 \cdot \text{s}$ )  
 $D$  – Effective diffusion coefficient ( $\text{m}^2 \cdot \text{s}$ )  
 $X_{k-D}$  – Conversion ( $\text{gCaCO}_3/\text{gCO}_2$ )  
 $Z$  – Ration volume fraction  
 $\alpha$  – Molar volume ( $\text{m}^3 \cdot \text{mol}^{-1}$ )  
 $C$  – Molar concentration of  $\text{CO}_2$  ( $\text{mol} \cdot \text{m}^{-3}$ ); e- equilibrium; b - bulk  
 $M_{\text{CaO}}$  – Molar mass of calcium oxide ( $\text{kg} \cdot \text{mol}^{-1}$ )  
 $r_p$  – Porous radius (m)  
 $\rho_{\text{CaO}}$  – Density of calcium oxide ( $\text{kg} \cdot \text{m}^{-3}$ )

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