

# INVESTIGATION ON THE EFFECT OF STEAM ON THE SORBENT PERFORMANCE FOR THE CALCIUM LOOPING PROCESS

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## Abstract

In this work the performance of an Italian limestone was investigated to understand the effect of the presence of steam during the Calcium Looping (CaL) process. The investigation was carried out simulating CaL conditions in a lab-scale fluidized bed operated in batch mode alternatively as a calciner and as a carbonator. The operating conditions were 940°C with 70% of CO<sub>2</sub> (in volume) and 650°C with 15% of CO<sub>2</sub>, to simulate the calcination and the carbonation stages, respectively. The percentage of steam (when present) was 10%. The experimental campaign consisted of tests where steam was present only during the calcination stage, only during the carbonation stage, or in both; the results were compared with a dry base case where the steam was not present. During each step the CO<sub>2</sub> capture capacity was monitored and at the end of each test the exhaust sorbents were analyzed in terms of their porosimetric features. Finally, results were compared with those obtained in a previous investigation on a different (more reactive) German sorbent in order to correlate the sorbent performance with the microstructural features of the sample.

## Introduction

This research article deals with calcium looping (CaL) as a post-combustion technique for capture and storage of carbon dioxide [1–4]. This process is generally proposed to be carried out in dual interconnected fluidized bed (FB) systems, and it is based on alternated temperature-swing uptake of CO<sub>2</sub> followed by its concentrated release. CO<sub>2</sub> capture is achieved in a FB carbonator, fed with the combustion flue gas to be treated (ca. 15% CO<sub>2</sub>) and with a stream of cheap CaO-sorbent. The reactor is kept at temperatures of 650–700°C, and the reaction between CO<sub>2</sub> and CaO to give CaCO<sub>3</sub> is exothermic. The flue gas issuing from the carbonator is CO<sub>2</sub>-lean, while the carbonated sorbent is sent to a calciner. The latter is the FB reactor where the concentrated release of CO<sub>2</sub> takes place. Calcination of

CaCO<sub>3</sub> is carried out at around 900–950°C. A gaseous stream rich in CO<sub>2</sub>, ready for processing and storage (or utilization), is obtained. The solid product of calcination (CaO) is sent back to the carbonator for another CaL cycle. As calcination is endothermic, and as its temperature of operation is higher than that of the carbonator, the calciner is also typically fed with a supplementary fuel. This fuel is burnt in oxy-fuel mode (no inlet N<sub>2</sub>) to avoid dilution of the exit CO<sub>2</sub>. Other relevant aspects to be taken into consideration when designing CaL at the operational scale are the high-temperature sintering phenomena that lead to sorbent deactivation upon iterated looping and sorbent attrition that usually takes place in FB reactors [1,5,6]. The operating conditions of a CaL process most likely imply the presence of steam. It is usually present in the combustion flue gas to be treated in the carbonator, and also as a combustion product of the supplementary fuel in the calciner. The possible positive role of steam upon calcination/carbonation stages appears as one of the CaL aspects that deserve further investigation, to help providing important indications for the correct design of a CaL process [7–9].

This paper aims at giving a contribution on this topic. CaL experiments were carried out using a limestone-based Italian sorbent in a lab-scale FB reactor, in the absence or presence of steam (when present, during either carbonation or calcination, or both). The results were compared with those obtained in a previous investigation [9] on a different (more reactive) German sorbent based on limestone, with the aim of outlining a general picture about the interrelationships among the role of steam, sorbent porosity and capture capacity of CO<sub>2</sub>.

**Table 1.** Main operating conditions of the CaL tests.

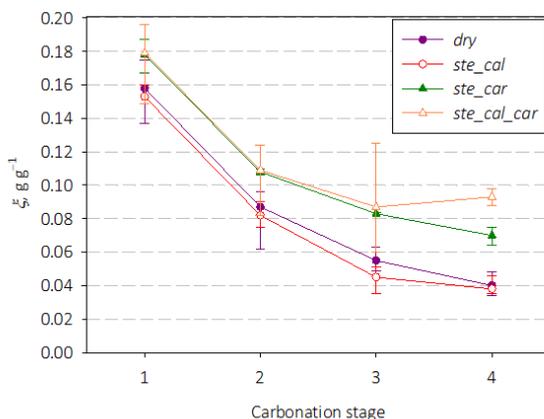
|   |                    | <b>Calcination</b>            | <b>Carbonation</b>            |
|---|--------------------|-------------------------------|-------------------------------|
| <b>Temperature</b>                          |                    | 940°C                         | 650°C                         |
| <b>Stage duration</b>                       |                    | 20min                         | 15min                         |
| <b>Fluidization velocity</b>                |                    | 0.7m/s                        | 0.6m/s                        |
| <b>Gas composition (vol.) (balance Air)</b> | <b>dry</b>         | 70% CO <sub>2</sub>           | 15% CO <sub>2</sub>           |
|   | <b>ste_cal</b>     | 10% Steam+70% CO <sub>2</sub> | 15% CO <sub>2</sub>           |
|   | <b>ste_car</b>     | 70% CO <sub>2</sub>           | 10% Steam+15% CO <sub>2</sub> |
|   | <b>ste_cal_car</b> | 10% Steam+70% CO <sub>2</sub> | 10% Steam+15% CO <sub>2</sub> |

## 2. Materials, equipment, methods, operating conditions and techniques

This study was focused on the behaviour of an Italian limestone (Massicci), initially sieved in the 0.4–0.6 mm particle size range and very rich (97.38%) in CaCO<sub>3</sub>. CaL tests were carried out in a lab-scale FB reactor (40 mm-ID) made of stainless steel and operated at atmospheric pressure. The system was equipped with filters that enabled the time-resolved collection of elutriated fines at the exhaust. The inert bed material consisted in 150 g silica sand, 0.9–1 mm size range. The analysis of flue gas was performed online. It is highlighted that the same FB reactor served as both calciner and carbonator. Each CaL experiment consisted in 4 complete calcination/carbonation cycles, plus a 5<sup>th</sup> calcination stage. A CaL experiment was started with the 1<sup>st</sup> calcination stage, where a defined mass of raw

sorbent ( $m_0=20$  g) was loaded into the reactor. At the end of each stage, the bed material was retrieved from the reactor. The reactor itself was brought to the operating conditions of the subsequent stage (for example: 1<sup>st</sup> carbonation after 1<sup>st</sup> calcination, and so on), and then the bed material fed back to it. Please refer to a previously-published work [1] for further details concerning the equipment and the operating methodology.

The main process conditions are listed in Table 1. The effect of steam was investigated by adding it during calcination stages only (“ste\_cal” tests, to indicate calcination runs carried out with steam), carbonation stages only (“ste\_car”) or during both (“ste\_cal\_car”). CaL experiments carried out without the presence of steam were referred to as “dry”. With all the other conditions left unchanged with respect to dry tests, steam was added to the fluidizing gas replacing the same amount of air in the volumetric percentage of 10% during either calcination or carbonation or both stages. For each carbonation stage, the CO<sub>2</sub> capture capacity ( $\xi$ ) was calculated on the basis of the analysis of flue gas. Selected sorbent samples were characterized by means of N<sub>2</sub> porosimetry carried out in a Quantachrome Autosorb instrument for the analysis of microporosity (pores <2 nm) and macroporosity (2–20 nm).

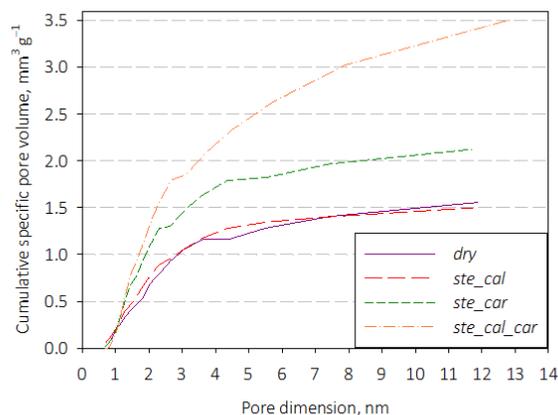


**Figure 1.** CO<sub>2</sub> capture capacity as a function of the carbonation stage for Massicci sorbent cycled under the four different operating conditions.

### 3. Results and discussion

The values for the CO<sub>2</sub> capture capacity ( $\xi$ ) obtained for the Italian sorbent with reference to the four carbonation stages and under the four different cases are reported in Figure 1. Capture capacities of CO<sub>2</sub> in the range (decreasing order): 0.179–0.093 (ste\_cal\_car), 0.178–0.070 (ste\_car), 0.158–0.040 (dry) and 0.153–0.038 (ste\_cal) g g<sup>-1</sup> were observed. The following can be highlighted: i)  $\xi$  decreases along with the number of carbonation stages in any case, due to the unavoidable sintering effects of the sorbent particles promoted by high

temperature; ii) the effect of steam is not relevant when added upon calcination stages only, but it is significant in enhancing the sorbent reactivity in the *ste\_car* and *ste\_cal\_car* cases. Namely, when steam is added during carbonation a 13% increase in  $\xi$  is observed after the 1st carbonation, a value that becomes as high as 75% (*ste\_car*) and 130% (*ste\_cal\_car*) after the 4th carbonation, with respect to the base-case (dry).



**Figure 2.** Cumulative pore undersize distribution for Massicci sorbent. Data are reported for materials after the 5<sup>th</sup> calcination, and for each operating condition.

Figure 2 illustrates the cumulative pore undersize distributions (values in specific pore volume) for the sorbents obtained at the end of the CaL experiment (5<sup>th</sup> calcination) for the four different cases. The values of the cumulative specific pore volume are correspondingly listed in Table 2. The sample cycled in presence of steam in both stages (*ste\_cal\_car*) was the only one showing  $V_{TOT} > 3 \text{ mm}^3 \text{ g}^{-1}$ . The sample cycled in presence of steam upon carbonation (*ste\_car*) was characterized by  $V_{TOT} = 2.1 \text{ mm}^3 \text{ g}^{-1}$ . The porosity for both *ste\_cal* and *dry* was lower. A similar trend was observed from the separate inspection of the micro- and mesoporosity contribution.

**Table 2.** Cumulative specific pore volume ( $V_{TOT}$ ) for the cases reported in Fig.2. Splitting of  $V_{TOT}$  into micropore and mesopore contribution is reported as well.

|                    | $V_{TOT} [\text{mm}^3 \text{ g}^{-1}]$    |
|--------------------|---|
| <b>dry</b>         | 1.6 (0.7 microporosity+0.9 mesoporosity)  |
| <b>ste_cal</b>     | 1.5 (0.8 microporosity +0.7 mesoporosity) |
| <b>ste_car</b>     | 2.1 (1.1 microporosity +1.0 mesoporosity) |
| <b>ste_cal_car</b> | 3.5 (1.3 microporosity +2.2 mesoporosity) |

The porosity developed in a sorbent particle after a calcination stage is influenced by the amount of  $\text{CO}_2$  captured during the previous carbonation stage. In fact, the

more the CO<sub>2</sub> captured, the larger the development of porosity related to the release of CO<sub>2</sub> upon subsequent calcination. With this premise, the porosimetric results can be explained by coming back to Figure 1: after the 4<sup>th</sup> carbonation, the most active material was ste\_cal\_car, then ste\_car and then the others. This reinforces the strict and mutual relationship among operating conditions, performance of CO<sub>2</sub> capture and sorbent structural changes.

The discussion is now broadened by considering the results obtained in a previous experimental campaign [9], where a German limestone (EnBW; ca. 100% CaCO<sub>3</sub>) was used as CaL sorbent. Operating conditions were the same as for Massicci. The German sorbent is intrinsically more reactive under each case. The higher reactivity for EnBW is related to its more favourable porous structure: cumulative specific pore volumes after the 5<sup>th</sup> calcination ranged from 7.9 to 11.7 mm<sup>3</sup> g<sup>-1</sup> (cf. Table 2 for Massicci). By taking into account all the experiments, the CO<sub>2</sub> capture capacity for EnBW increases by ca. 25% on average (values spanning from nearly 5% to 80%) with respect to Massicci. The positive effect of steam, in particular when it is added upon carbonation (ste\_cal\_car and ste\_car cases), has been observed for EnBW as well, with even higher enhancements with respect to the dry case than those observed for Massicci. For example, when steam is added upon carbonation a 22% increase in the CO<sub>2</sub> capture capacity (1<sup>st</sup> carbonation) was observed for EnBW, vs. 13% reported for Massicci. This gives again indications about the positive role of steam when present in the carbonator of a CaL cycle.

## Conclusions

With reference to an Italian limestone, the presence of steam during carbonation stages – through the improvement of CO<sub>2</sub> diffusion phenomena across the sorbent particle – is able to increase its capacity of CO<sub>2</sub> capture, so contrasting the unavoidable sintering effects that reduce this parameter as long as the number of calcium looping cycles increases. Taking as a baseline what was observed in the no-steam case, the experiments carried out in presence of steam upon carbonation determined an increase in the CO<sub>2</sub> capture capacity of 13% after the 1<sup>st</sup> carbonation stage and of 75% after the 4<sup>th</sup> carbonation stage. A direct correlation between sorbent capture capacity upon carbonation and development of porosity upon subsequent calcination was observed. The results were finally compared with those obtained in a parallel experimental campaign where a more porous and reactive material (a German limestone) was used. The positive effect of steam upon carbonation was confirmed: for example, after the 1<sup>st</sup> carbonation the CO<sub>2</sub> capture capacity increased by 22% (with respect to the no-steam case). To properly judge the effect of steam under the operational point of view and more in general to properly compare different materials, the combined interrelationships among operating conditions, sorbent nature and porosity, CO<sub>2</sub> capture capacity and possible presence of steam should be carefully considered.

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