# THE EFFECT OF STEAM ON CALCIUM LOOPING: PERFORMANCE OF AN ITALIAN LIMESTONE-BASED SORBENT

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**Abstract** – Calcium looping has been investigated in this work with a particular focus on the effect of the presence of steam during calcination and/or carbonation stages. The experiments were carried out using an Italian limestone in a lab-scale fluidized bed reactor. Calcium looping cycles were performed at temperatures of 940 and 650°C and in atmospheres containing 70 and 15% $CO_2$ for calcination and carbonation stages, respectively. When present, steam accounted for 10% in the fluidizing gas. The $CO_2$ concentration in the flue gas was continuously monitored and was used for the evaluation of the $CO_2$ capture capacity for each carbonation stage in the calcium looping experiments. During these stages and the corresponding calcination ones, the rate of fines generation by elutriation was measured through collection of the attrited fines in a filters system. Analysis of the particle size distribution of in-bed fragments of sorbent after each calcination and carbonation stage allowed measuring the extent of fragmentation. Porosimetric analyses on selected samples complemented the overall characterization. The results aimed at outlining a picture about the interrelationship among the role of steam, sorbent porosity, $CO_2$ capture capacity and attrition/fragmentation tendency.

## GENERAL OVERVIEW

This research article deals with calcium looping (CaL) as a post-combustion technique for capture and storage of carbon dioxide (Coppola et al., 2013; Zhao et al., 2013; Cormos, 2014; Ströhle et al., 2014; Li et al., 2016; Perejón et al., 2016). 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 $CO_2$ followed by its concentrated release. $CO_2$ capture is achieved in a FB carbonator, fed with the combustion flue gas to be treated (ca. 15% $CO_2$) and with a stream of cheap CaO-sorbent. The reactor is kept at temperatures of 650–700°C, and the reaction between $CO_2$ and CaO to give $CaCO_3$ is exothermal. The flue gas issuing from the carbonator is $CO_2$-lean, while the converted sorbent stream is sent to a calciner. The latter is the FB reactor where the concentrated release of $CO_2$ takes place. Calcination of $CaCO_3$ is carried out at around 900–950°C. A gaseous stream rich in $CO_2$, 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 endothermal, and as its temperature of operation is higher than that of the carbonator, the calciner is also fed with a supplementary fuel. This fuel is burnt in oxy-fuel mode (no inlet $N_2$) to avoid dilution of the exit $CO_2$. Part of the stream rich in carbon dioxide and exiting the calciner is recycled for safety reasons. Thus, the fluidizing atmosphere in the calciner is quite rich (ca. 70%) in $CO_2$, but the calcination of calcium carbonate into calcium oxide is anyway favoured owing to the high operating temperatures. Recent ideas to bypass the need of using the supplementary fuel (and the related oxy-fuel combustion mode) are being developed basing on the concept of "solar calcination reactor", cf. Tregambi et al. (2015, 2016) and references therein. 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, sorbent attrition/fragmentation that usually takes place in FB reactors (Coppola et al., 2013; Valverde and Quintanilla, 2013; Xiao et al., 2014), possible reactivation of the $CO_2$ capture capacity of sintered particles through intermediate hydration stages (Coppola et al., 2014a, 2014b; Materić et al., 2014; Blamey et al., 2015; Coppola et al., 2015) and means for reusing the purged streams rich in calcium in the industry of construction materials (Telesca et al., 2014, 2015). Operating conditions of a CaL process likely imply the presence of steam. It can be present in the combustion flue gas to be treated in the carbonator, and 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 investigation in the current

research period, to help providing important indications for the correct design of a CaL process (Champagne et al., 2013; Li et al., 2014; Yin et al., 2014; Duelli (Varela) et al., 2015; Champagne et al., 2016; Coppola et al., 2017). This paper aims at giving a contribution in this field. CaL experiments were carried out using a limestone-based Italian sorbent in a lab-scale FB reactor, in absence or presence of steam (when present, upon either carbonation or calcination, or both). The results aimed at outlining a picture about the interrelationship among the role of steam, sorbent porosity, capture capacity of $CO_2$ and tendency to attrition/fragmentation.

## EXPERIMENTAL

The results of this study were 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 $CaCO_3$. CaL tests were carried out in a lab-scale FB reactor (40 mm-ID) made of stainless steel and operated at atmospheric pressure. The reactor was electrically heated and fluidized with gas of pre-set composition. 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 5th calcination stage. A CaL experiment was started with the 1st 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 typical of the subsequent stage (for example: 1st carbonation after 1st calcination, and so on), and then the bed material fed back to it. Please refer to a previously-published work (Coppola et al., 2013) for further details concerning the equipment and the operating methodology. The main process conditions are listed in Table 1.

Table 1: Main operating conditions of the CaL tests.

| | calcination | carbonation |
|---|---|---|
| **dry** | | |
| Temperature | 940°C | 650°C |
| Test duration | 20 min | 15 min |
| Fluidization superficial velocity | 0.7 m s⁻¹ | 0.6 m s⁻¹ |
| Fluidizing gas composition (vol.) | 70% $CO_2$+30% air | 15% $CO_2$+85% air |
| **ste_cal** | | |
| Fluidizing gas composition (vol.) | 10% steam+70% $CO_2$+20% air | 15% $CO_2$+85% air |
| **ste_car** | | |
| Fluidizing gas composition (vol.) | 70% $CO_2$+30% air | 10% steam+15% $CO_2$+75% air |
| **ste_cal_car** | | |
| Fluidizing gas composition (vol.) | 10% steam+70% $CO_2$+20% air | 10% steam+15% $CO_2$+75% air |

CaL experiments carried out without the presence of steam were referred to as "*dry*". With reference to *dry* tests, the following conditions were adopted: for calcination, temperature=940°C, fluidizing atmosphere containing 70% $CO_2$, fluidization velocity=0.7 m s⁻¹; for carbonation, temperature=650°C, fluidizing atmosphere containing 15% $CO_2$, fluidization velocity=0.6 m s⁻¹. Fluidization velocities were set at 2–2.5 times the incipient fluidization velocity. Calcination and carbonation tests lasted 20 and 15 min, respectively, enough to bring the related chemical reactions to practical completion as verified by flue gas analyses. For each carbonation stage, the $CO_2$ capture capacity was calculated on the basis of the analysis of flue gas as the mass of $CO_2$ cumulatively captured in that carbonation stage divided by the mass of sorbent initially fed to the system:

$$\xi = \frac{\int_0^t \left[ W_{CO_2}^{inlet} - W_{CO_2}^{outlet}(t) \right] dt}{m_0} \tag{1}$$

where $W$ indicates mass flow rates. The rate of fines generation by elutriation ($E$) was measured as a function of time during each stage. It was defined as the mass of elutriated fines collected in a filter divided by the time interval for which that filter was in operation and by the initial mass of sorbent. Post-processing of elutriation data allowed to calculate $f_{LE}$, that is the fraction lost by elutriation, defined as the mass fraction of fines cumulatively elutriated during a stage with reference to the initial mass of sorbent. After each calcination and carbonation stage, and after having retrieved the bed material (sand+sorbent) from the bed,

the solid mixture was separated by mechanically sieving. This was possible taking into account the coarser size range of the sand particles and the negligible attrition phenomena for sand. The sorbent fraction obtained after separation was characterized by mechanical sieving using sieves of different size, to investigate its particle size distribution (PSD) as deriving from in-bed fragmentation phenomena. As previously written, after this analysis the sorbent was re-mixed with sand in the FB system for the subsequent stage. PSD was expressed in terms of cumulative values of $x(d_i)$, where $x$ is the absolute mass fraction of particles having mean size $d_i$. Two relevant parameters are defined. The fraction of fragments:

$$f_{FR} = \sum_{d_i < 0.4 \, mm} x(d_i) \tag{2}$$

takes into account the in-bed sorbent fragments finer than the lower limit of the feed size range. The fraction of fines:

$$f_{FI} = \sum_{d_i < 0.1 \, mm} x(d_i) \tag{3}$$

takes into account the subset of in-bed sorbent fragments finer than 0.1 mm. Selected sorbent samples were characterized by means of $N_2$ porosimetry carried out in a Quantachrome Autosorb instrument for the analysis of microporosity (pores <2 nm) and macroporosity (2–20 nm). 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*"). Water vapour was generated by a Bronkhorst Controlled Evaporator and Mixer (CEM) apparatus, yielding a superheated steam+air mixture at the temperature of 250°C ca. 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. To account for experimental errors, each single experimental test of CaL reported in this paper has been carried out in triplicate. When commenting the results, the mean values will be referred to.

## RESULTS AND DISCUSSION

The values for $\xi$ obtained for the Italian sorbent with reference to the four carbonation stages and under the four different cases are reported in Fig. 1. Capture capacities of $CO_2$ 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$^{-1}$ were observed. The following can be highlighted: i) $\xi$ decreases alongwith 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, not relevant when added upon calcination stages only, is significant in enhancing the sorbent reactivity in the *ste_car* and *ste_cal_car* cases. Namely, when steam is added at least upon carbonation a 13% increase in $\xi$ is observed after the 1$^{st}$ carbonation, a value that becomes as high as 75% (*ste_car*) and 130% (*ste_cal_car*) after the 4$^{th}$ carbonation, with respect to the base-case (*dry*).
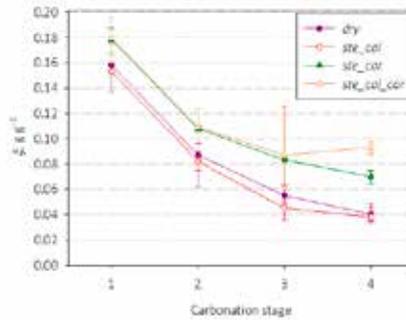


Fig. 1. $CO_2$ capture capacity as a function of the carbonation stage for Massicci sorbent cycled under the four different operating conditions.

The rates of fines generation for each case are reported in Fig. 2. The general $E$ versus time trend is decreasing, as usual in these cases (Coppola et al., 2013, 2014a, 2014b, 2015). It is also recalled that thermal shocks are mostly active at the beginning of each stage: sorbent particles are in fact retrieved from the FB at

the end of each stage and fed back to the FB at the beginning of the subsequent one. From the quantitative point of view, the average $f_{LE}$ values per stage were, in decreasing order: 0.85±0.50% (*ste_cal_car*), 0.76±0.49% (*ste_cal*), 0.65±0.39% (*dry*) and 0.32±0.22% (*ste_car*). This means that, with respect to the no-steam case: i) when added at least upon calcination, steam weakens the particle structure enhancing the sorbent tendency to undergo attrition/elutriation. It is reminded that the adopted fluidization velocity is such as the coarse sorbent particles cannot be elutriated by entrainment, so the material lost by elutriation is to be ascribed to the generation of fines by attrition; ii) as the addition of steam upon carbonation enhances the sorbent reactivity (see Fig. 1), this increases the sorbent resistance to surface wear. In fact, a higher degree of conversion of soft CaO into hard $CaCO_3$ makes the particle shell –subject to surface wear– harder.

The cumulative PSD obtained by analyzing in-bed sorbent fragments after the 1st, 3rd and 5th calcination stages are reported in Fig. 3 for each of the four operating conditions. The results can be more easily discussed by referring to the values for $f_{FR}$ and $f_{FI}$: i) the fraction of <0.4 mm-fragments increases as the process goes on. More in detail, $f_{FR}$ values (in decreasing order) from 15.2% to 35.2% (*ste_cal_car*), from 14.2% to 25.6% (*ste_cal*), from 12.4% to 27.8% (*dry*) and from 9.5% to 21.8% (*ste_car*). Namely, the same "ranking" as the one observed about elutriation rates is here obtained, reinforcing the comments about the effect of steam on the characteristics of the particle structure for this sorbent; ii) the trend of $f_{FI}$ is decreasing alongwith the number of cycles. This witnesses that the sorbent fines smaller than 0.1 mm are those prevailingly undergoing elutriation, and therefore constituting only a secondary part of the fragments retrieved from the FB after each stage. Substantially the same ranking as above was observed, with $f_{FI}$ decreasing from 2.4% to 1.2% (*ste_cal_car*), from 2.9% to 1.0% (*ste_cal*), from 2.6% to 1.0% (*dry*) and from 1.7% to 0.5% (*ste_car*).

Fig. 4 illustrates the cumulative pore undersize distributions (values in specific pore volume) for the sorbents obtained at the end of the CaL experiment (5th calcination) for the four different cases. The values of 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 $mm^3$ $g^{-1}$. The sample cycled in presence of steam upon carbonation (*ste_car*) was characterized by $V_{TOT}$=2.1 $mm^3$ $g^{-1}$. The porosity for *ste_cal* and *dry* was lower. A similar trend was observed from the separate inspection of the micro- and meso-porosity contribution. The porosity developed in a sorbent particle after a calcination stage is influenced by the amount of $CO_2$ captured during the previous carbonation stage. In fact, the more the $CO_2$ captured, the larger the development of porosity related to the release of $CO_2$ upon subsequent calcination. With this premise, the porosimetric results can be explained by coming back to Fig. 1: after the 4th 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 $CO_2$ capture and sorbent characteristics. The above considerations should not straightforwardly lead to the choice of *ste_cal_car* operating condition as the best one. One relevant parameter of exercise is in fact the amount of fragmented/elutriated material. In this respect, the presence of steam upon calcination has demonstrated –for this sorbent– to determine a mechanically weaker particle structure. Therefore, the best of the four cases for this sorbent is the one with steam upon carbonation only (*ste_car*), that entails a positive effect on the $CO_2$ capture (the presence of steam during the $CO_2$ capture facilitates the $CO_2$ diffusion across the particle) and a more resistant particle structure with respect to the no-steam (*dry*) case.

Table 2: Cumulative specific pore volume ($V_{TOT}$) for the cases reported in Fig. 4. Splitting of $V_{TOT}$ into micropore and mesopore contribution is reported as well.

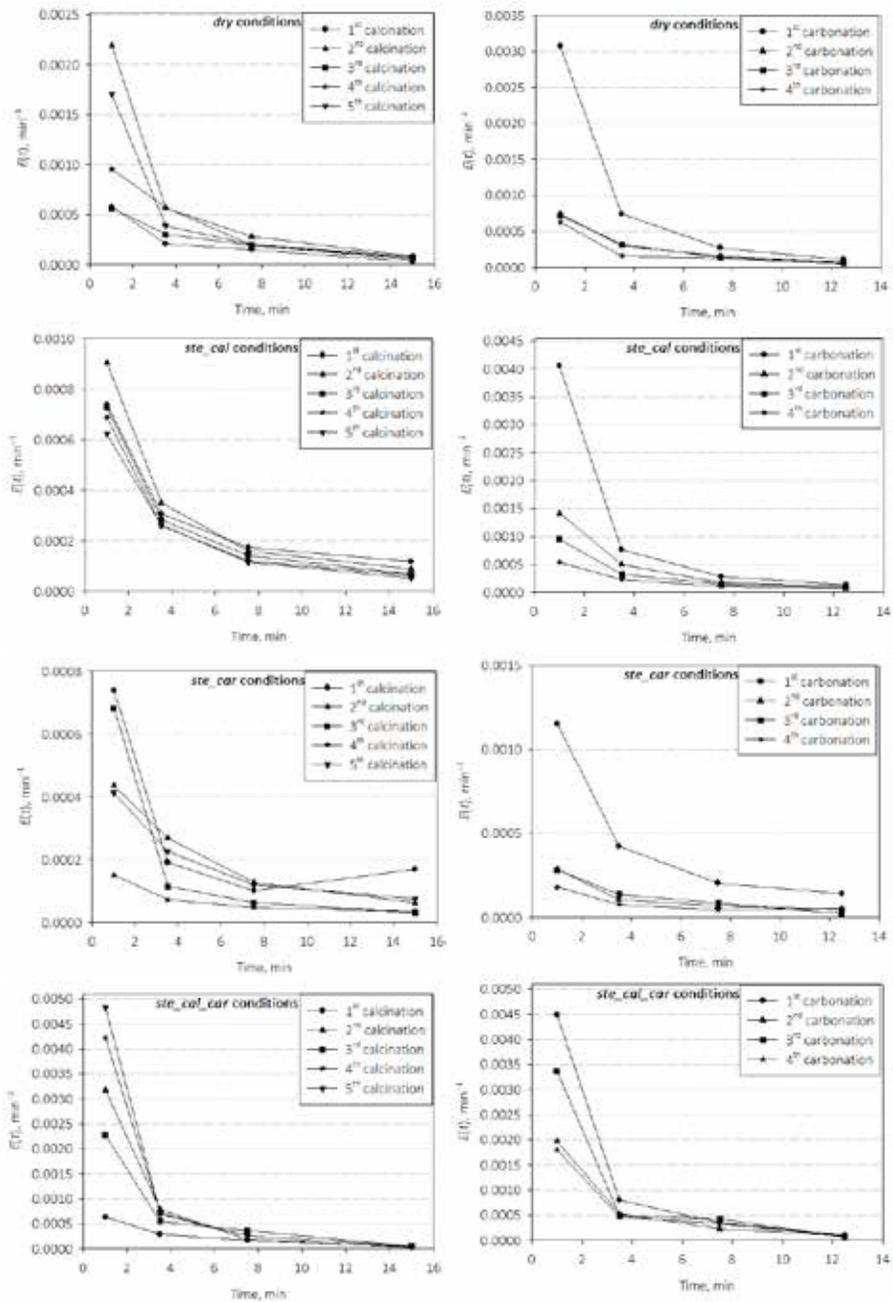| | $V_{TOT}$ [$mm^3$ $g^{-1}$] |
|---|---|
| *dry* | 1.6 (0.7 microporosity+0.9 mesoporosity) |
| *ste_cal* | 1.5 (0.8 microporosity +0.7 mesoporosity) |
| *ste_car* | 2.1 (1.1 microporosity +1.0 mesoporosity) |
| *ste_cal_car* | 3.5 (1.3 microporosity +2.2 mesoporosity) |

Fig. 2. Elutriation rate as a function of time for Massicci sorbent. Data are reported for each calcination and carbonation stage, and for each operating condition.
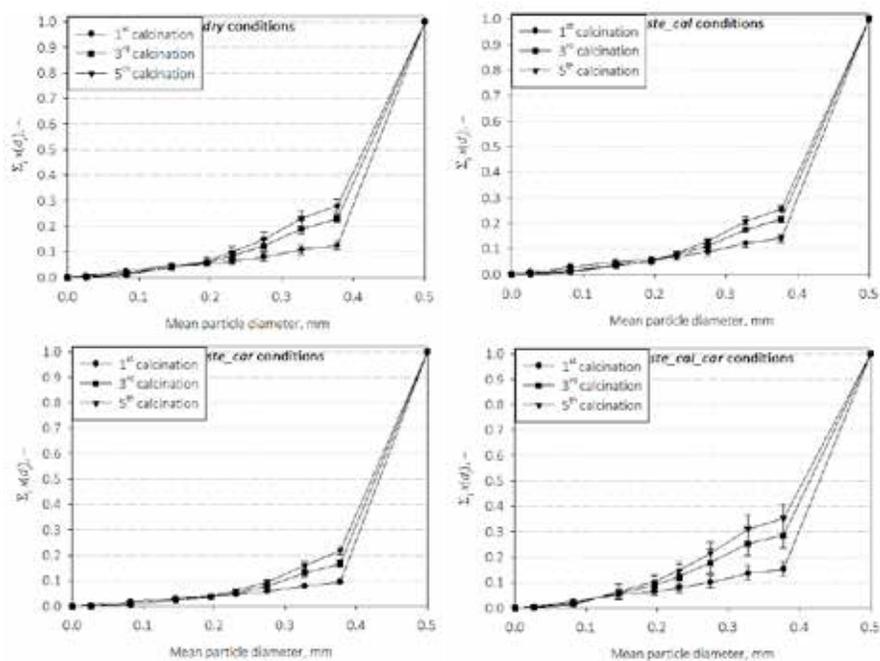
Fig. 3. Cumulative particle size distribution for in-bed fragments of Massicci sorbent. Data are reported for materials after the 1st, 3rd and 5th calcination, and for each operating condition.
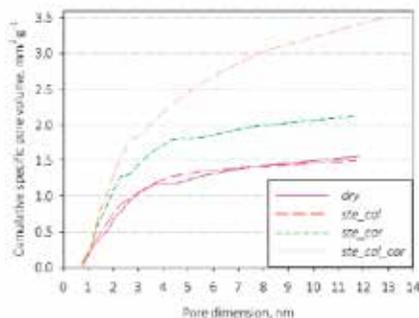


Fig. 4. Cumulative pore undersize distribution for Massicci sorbent. Data are reported for materials after the 5th calcination, and for each operating condition.

## CONCLUSIONS

With reference to an Italian limestone, the presence of steam during carbonation stages –through the improvement of $CO_2$ diffusion phenomena across the sorbent particle– is able to increase its capacity of $CO_2$ 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 $CO_2$ capture capacity of 13% after the 1st carbonation stage and of 75% after the 4th carbonation stage. The higher conversion of CaO into $CaCO_3$ in the case in which steam was present upon carbonation entails also a particle structure which is more resistant to attrition: the mass fraction of fines lost by elutriation per stage was in average 0.32%, against 0.65% observed for the no-steam case. Even larger were the values obtained in the case that steam was added upon calcination, a circumstance that determines a weaker particle structure.

The analysis of the size distributions of in-bed sorbent fragments confirmed the trend. A direct correlation between sorbent capture capacity upon carbonation and development of porosity upon subsequent calcination was observed. To properly judge the effect of steam under the operational point of view, the combined interrelationships among operating conditions, sorbent nature and porosity, $CO_2$ capture capacity, attrition/fragmentation tendency and possible presence of steam should be carefully considered.

## ACKNOWLEDGMENT

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