CHARACTERIZATION OF CALCIUM LOOPING SORBENTS WITH A NOVEL TWIN BED REACTOR

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Abstract – The experimental characterization of sorbents for Calcium Looping (Ca-L) processes is generally accomplished by thermogravimetric analysis or by using single fluidized bed bench scale reactors. Unfortunately, these methods present several limitations, the most significant being the poor ability to reproduce the thermal history that sorbent particles experience in a real Ca-L plant. This limitation may severely affect the correct evaluation of the sorbent behavior in terms of CO_2 capture capacity and attrition. In this study, a recently presented experimental apparatus is applied for Ca-based sorbent testing under conditions that simulate a realistic thermal history of the sorbent. The apparatus consists of two identical lab-scale bubbling beds (Twin Beds - TB) operated batchwise as the calciner and the carbonator, respectively. The reactors are connected to each other via a rapid solids pneumatic transfer line, designed so as to enable rapid and selective transfer of the sorbent from one reactor to the other at the end of each calcination/carbonation stage. The two beds consist mostly of coarse-grained silica sand, acting as a thermal ballast, to which sorbent samples to be characterized are added.

The TB apparatus has been used to investigate the effect of the thermal history on the performances of one German and one Italian limestones, in terms of CO_2 capture capacity and attrition tendency, upon multiple calcination/carbonation cycles under the typical operating conditions of the Ca-L process. The results have been also compared with those obtained for the same sorbents under similar operating conditions, for tests carried out in a single lab-scale fluidized bed reactor (SB). The comparison showed that the CO_2 capture capacity values in the TB system, for both sorbents, are higher than those found in SB tests. On the contrary, the absence of strong thermal shocks in the TB experiments leads in general to a decrease of the attrition tendency, with a reversal in terms of generated fines between calcination and carbonation stages. Indeed, the generation rate of fines measured in the TB tests during carbonation is lower than that measured in the corresponding calcination stage, which is opposite to what was found during the tests in the SB device. These findings seem to underline a non-negligible role of the sorbent thermal history on its CO_2 capture performance in Ca-L.

INTRODUCTION

In the framework of the CO_2 capture techniques the Calcium Looping process (Ca-L) is one of the most promising technologies for the post-combustion CO_2 capture since it uses natural and cheap Ca-based sorbents such as limestone and dolomite (Abanades, 2013). The process consists of two reactors: the carbonator where the calcium oxide, in the temperature range of 650-700°C, reacts with the CO_2 contained in the flue gas coming from a power plant, producing a CO_2-free flue gas and calcium carbonate; this latter is sent to the calciner where at higher temperatures (850-950°C) the calcination reaction takes place, yielding a pure CO_2 stream, ready for transportation and sequestration, while the produced calcium oxide can restart a new cycle into the carbonator. The recirculation of the sorbent between the two reactors is typically obtained by means of the utilization of two interconnected fluidized beds, which also ensures an intimate contact between gaseous and solid phases (Lisbona et al., 2013, Dieter et al., 2014).

The main drawback related to Ca-L is the decay of CO_2 capture capacity with the number of the cycles that is mainly related to the sintering of the material caused by the high temperature (especially during the calcination stage) and the reaction environment (presence of CO_2 and H_2O) (Coppola et al., 2012, 2013, Valverde et al., 2013, Materic et al., 2014). Furthermore, the utilization of fluidized beds implies that the sorbent particles are subject to attrition phenomena, which produce fines which can be elutriated together with the gas phase and change the particle size distribution of the bed material (Scala et al., 2013). However,

the particle breakage may have a positive effect because it can make further surface available for the CO_2 capture.

These aspects prove to be crucial for the correct design of a Ca-L system. In the last decade, many efforts have been carried out by the scientific community to evaluate the impact of these issues, and the typical lab-scale experimental devices employed are either thermogravimetric analyzers (TG) or single fluidized beds (SB) (Itskos et al., 2013). Despite these techniques are able to provide important information, they are affected by several constraints. Remarkably, experimental procedures for TG and SB do not permit to simulate the thermal history experienced by the sorbent in a real Ca-L plant. In these devices multiple cycles of calcination/carbonation are simulated by temperature ramp or, in SB systems, the sorbent is injected from ambient temperature in the hot reactor producing excessive thermal shock to the material (Coppola et al., 2015). In this way, particle sintering may result to be modified with a consequent alteration of the CO_2 capture capacity and of the attrition tendency. In addition, the intrinsic nature of fixed bed in TG does not allow evaluating attrition phenomena.

In this paper, an original experimental lab-scale apparatus is employed in order to overcome TG and SB limitations. The system, called twin beds (TB) apparatus, consists of two identical fluidized beds which can be operated separately as calciner and carbonator in batch mode. Its peculiarity is the presence of a duct, partially immersed in both reactors, which permits a fast transportation of the sorbent, at the end of each stage (calcination or carbonation), by a valve system. A complete description and characterization of the TB system is reported in the work of Coppola et al. (2016). It is worth to emphasize that the TB apparatus does not reproduce a continuous Ca-L process, but only recreates a sorbent particle thermal history as close as possible to reality. In particular, a German limestone (named EnBW) and an Italian limestone (named Massicci) have been tested under typical Ca-L conditions in the TB apparatus and the CO_2 capture capacity and the attrition tendency have been assessed. The results have been compared to similar tests performed in single SB apparatus on the same limestones. In general, the results denote the relevance of the sorbent thermal history on the CO_2 capture capacity and the attrition tendency.

EXPERIMENTAL

Figure 1 shows the TB system used for the experimental campaign: the reactor on the left (East bed – EB) is operated as Carbonator, while the right one (West bed – WB) as Calciner. A transport duct, with a diameter smaller than the reactor size, is lowered in both reactors and is partially immersed into the bed material. The valves system located on the duct and at the top gas exit of both reactors permit to transport the sorbent from the calciner to the carbonator and vice-versa. In particular, during a calcination (or carbonation) stage the valves on the duct are closed, while the valves on the top gas exit are open. When the calcination stage is over, the top gas exit valve of the calciner is closed and the duct valves are opened to permit the fast pneumatic transport of the material to the other reactor. In this way, the sorbent undergoes the typical thermal shock of a Ca-L system. At the top a gas exit duct leading to a two-exit head equipped with two compartments used for the housing of filters, whose filtration efficiency is >99% for >10 μm particles, for elutriated fines collection. A steel hopper for solid feeding to the bed is connected sideways to each reactor. The equipment is supplied with an additional vertical duct, located in the middle between the twin beds and connected with the transport duct by means of a 3-way valve. At the bottom of this duct a removable stainless steel container is placed. The aim of this duct is to carry out a fast discharge of the reactors and to collect the whole bed material into the container. All gases where fed to the reactors by high-precision mass flowmeters/controllers.

A German limestone (EnBW) and an Italian one (Massicci), both in the size range 400-600μm, were used as sorbent material, while silica sand (900-1000μm) in both reactors was used as a buffering material in order to avoid significant bed temperature variations due to chemical reactions and solid transportation. This size difference between sorbent and sand, coupled with the density different of the materials and specific fluidization velocities, determines a segregation of the smaller and lighter sorbent material to the top section of the bed and that of the larger and heavier sand material to the lower section (Olivieri et al., 2004, Tagliaferri et al., 2013). This segregation (intentionally induced) is an essential point for obtaining a preferential transport of the sorbent to the detriment of sand (Coppola et al., 2017).
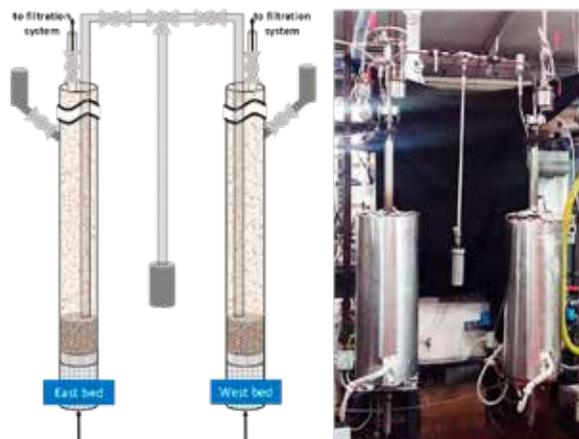
Figure 1. Twin fluidized bed apparatus.

Ca-L experiments, for the routinely characterization of the sorbent materials, have been carried out up to 15 calcination/carbonation cycles in less than 9 hours with the TB apparatus, a much shorter time if compared to those required for the tests operated in the SB systems (5 cycles in two-three days). Before heating up the system, ~150g and ~90g of silica sand were charged in the WB and the EB, respectively. The different amount of sand between the two reactors was necessary to compensate for the sand transported together with the sorbent material between the reactors, as explained before. An initial amount of 20 g of fresh limestone was injected into the WB by the hopper. Calcination was carried out at 940 °C for 20 min with a gas containing 70% CO_2 (balance air), to simulate a calcination under oxy-firing environment, while carbonation was carried out at 650 °C for 15 min with a gas containing 15% CO_2 (balance air) to simulate the CO_2 concentration in a typical flue gas. The fluidizing gas velocities were 0.50 m/s during each step. The operating conditions of the experiments are given in Table 1. During each step of calcination or carbonation, filters were used to collect fines elutriated with the outlet gas in order to evaluate the sorbent attrition. Specifically, four filters were used sequentially for determined time intervals. After this time, each filter was removed and when it was cooled, it was weighed. The weight difference of the filter before (empty) and after its use divided for the time interval returned the elutriation rate. The CO_2 capture capacity after each carbonation stage was evaluated by working out the CO_2 concentration profiles at the exhaust monitored by a continuous analyzer.

Table 1. Operating conditions for hot Ca-L tests.

	Calcination	Carbonation
Temperature, °C	940	650
CO_2 concentration, %vol	70 (rest air)	15 (rest air)
Time, min	20	15
v_f, m/s	0.5	

RESULTS

Figure 2 reports the CO_2 capture capacity, expressed as grams of captured CO_2 per grams of initial sorbent, as a function of the number of cycles for the two investigated limestones. As expected, the capture capacity decreases along the 15 cycles reaching asymptotic values approximately after the 10th cycle. Moreover, it can be noted that the CO_2 uptake for EnBW (red dots) remains higher than that for Massicci limestone (blue dots) for all cycles. This is due to a higher sintering resistance of the German sorbent with respect to the Italian competitor. This finding is completely consistent with that found by Coppola et al. (2013) for the same

sorbents, under similar conditions, in tests carried out in a single fluidized bed. Figure 3 shows the comparison of the CO_2 capture capacity as a function of the number of cycles in the TB system and the SB system for EnBW limestone (on the left) and for Massicci limestone (on the right) for 5 cycles. It is worthy to note that for both sorbents the capture capacity is higher in TB system with respect to the SB apparatus. Presumably, this is a consequence of the more limited thermal shock experienced by the sorbent particles in the present tests with respect to the tests performed in the single bed apparatus (where the sorbents are discharged to ambient temperature after each calcination/carbonation step) with a consequent slowing down of the sorbent sintering. These results suggest that the thermal history of the sorbent has a relevant influence on the CO_2 capture capacity.
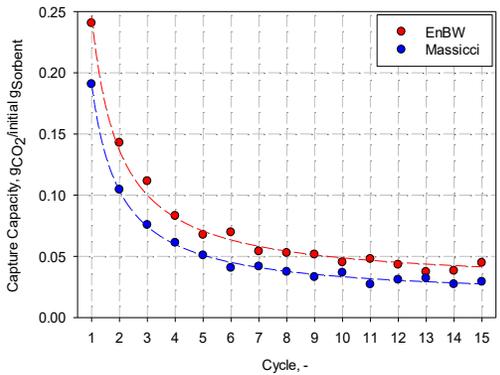

Figure 2. CO_2 capture capacity of the sorbent as a function of the number of cycles for the TB apparatus.
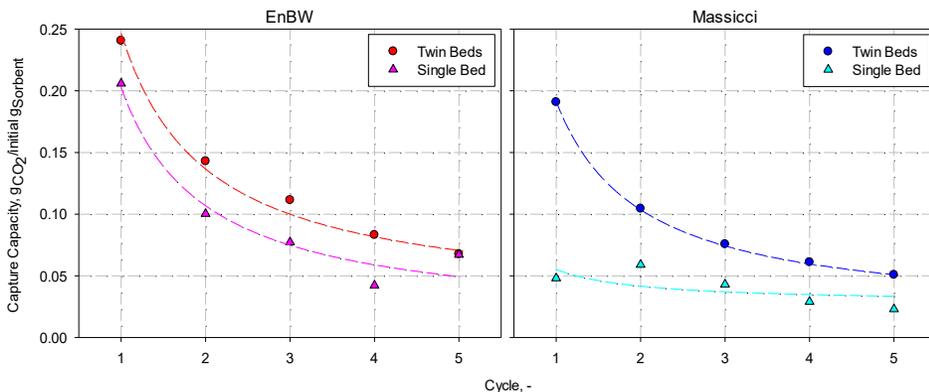

Figure 3. CO_2 capture capacity of the sorbent as a function of the number of cycles: TB vs SB.

Figure 4 reports the mean elutriation rate (expressed as the mass of elutriated fines per mass of initial sorbent per time of single stage of calcination or carbonation) for 10 cycles of calcination/carbonation. As expected, the elutriation rate decays with the cycle number and this behavior is strictly related to the particle hardening caused by sintering. In particular, it can be seen that the attrition tendency of Massicci limestone is higher than that of EnBW; again, these results are in agreement with those found by Coppola et al. (2013). In Fig. 5 a comparison of the elutriation rate between TB and SB systems for both sorbents is shown: in general, the attrition tendency of the sorbents results higher for the tests in the SB apparatus and this difference appears to be more accentuated during carbonation. Again, the thermal history seems to have a significant effect also for the attrition tendency. Moreover, it is interesting to remark that the attrition propensity seems to undergo a reversal between calcination and carbonation: indeed, in SB tests the amount of elutriated fines during carbonation is more elevated with respect to calcination, while the behavior was opposite in the TB tests. Probably, this is a combination of the different thermal shocks undergone by the sorbent in the two different

devices, the chemical composition and the sintering degree of the sorbent. Indeed, at the starting of the carbonation stage the sorbent is mainly composed by CaO and hence it is more porous and softer than $CaCO_3$. This, combined with the large thermal shock in the SB system, entails an elevated generation of fines by means of primary fragmentation. Conversely, in the TB system the thermal shock effect for the carbonation stage is totally absent, because the sorbent is directly transferred from the Calciner (940°C) to the Carbonator (650°C) (without any intermediate cooling).
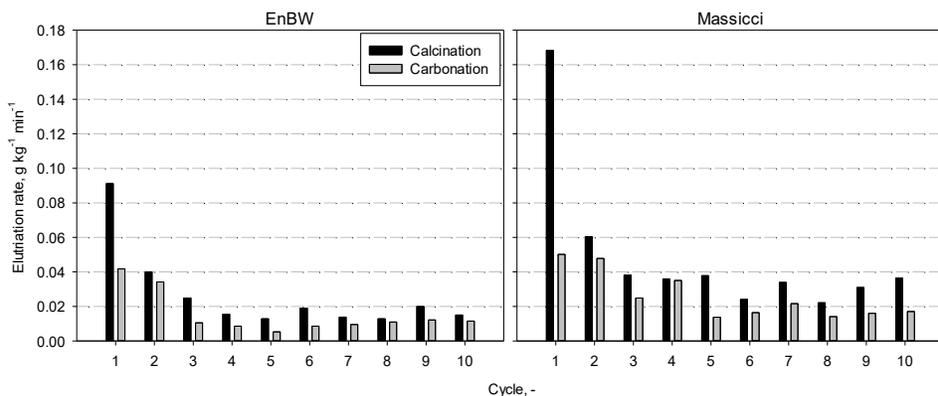

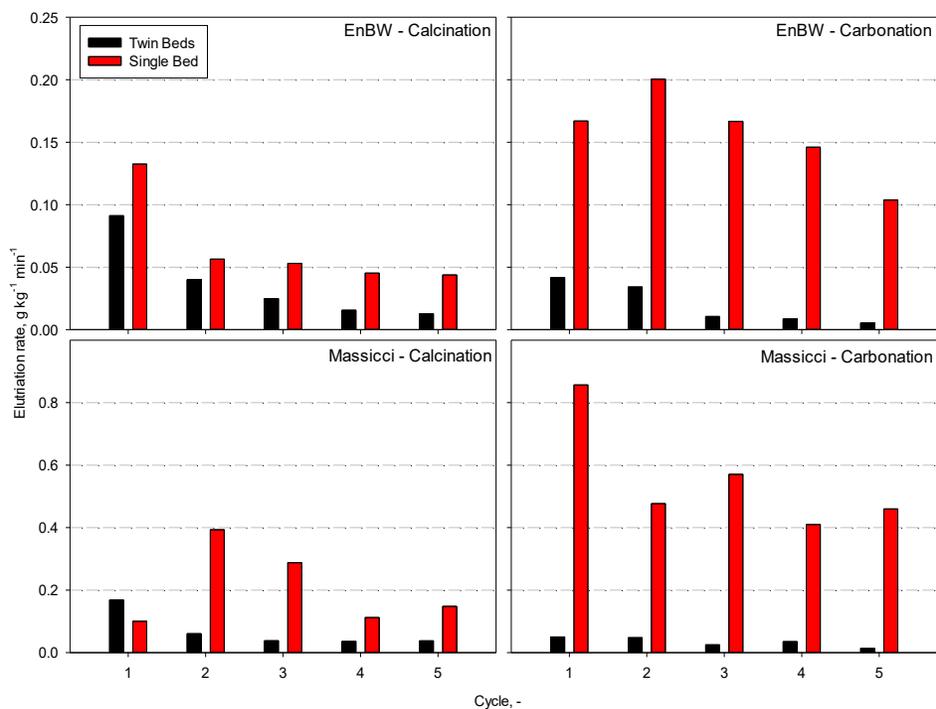Figure 4. Elutriation rate as a function of the number of cycles for the TB apparatus.

Figure 5. Elutriation rate as a function of the number of cycles: TB vs SB.

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CONCLUSIONS

An innovative TB apparatus was used to characterize Ca-L sorbents. The main feature of the system is represented by the possibility to overcome the typical limitations by which TG and SB techniques are affected. In particular, the system can recreate the thermal history experienced by a sorbent in a real Ca-L plant.

Tests at typical Ca-L temperatures were carried out to evaluate the effect of the thermal history on the CO_2 capture capacity and the attrition tendency. The performance of two different limestones was investigated. Interestingly, the comparison of these results with those previously obtained with the same limestone under comparable operating conditions in a SB apparatus pointed out that capture capacity and elutriation rate values were higher than those found in the single bed tests. In particular, the attrition tendency appears to be particularly dependent on the thermal history experienced by the sorbent. Indeed, the absence of thermal shock in the TB during the transportation from the calciner to the carbonator leads to a lower generation of fines during the carbonation stage with respect to calcination. This result is opposite to that found for the tests in SB. This finding seems to underline the relevant role of the sorbent thermal history on its performance in Ca-L systems.

In conclusion, the larger thermal shocks experienced by the sorbent in the single bed system tests appear to be detrimental in terms of CO_2 capture and attrition tendency. In the future additional tests will be carried out on different limestones to conclusively confirm this result and, furthermore, specific investigations through porosimetry and microscopic analyses will be conducted in order to understand how the thermal history affects the particle structure.

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