



## Research article

## Characterization of calcium looping sorbents with a novel twin bed reactor

Antonio Coppola<sup>a,\*</sup>, Fabrizio Scala<sup>a,b</sup>, Piero Salatino<sup>a,b</sup><sup>a</sup> Istituto di Ricerche sulla Combustione, Consiglio Nazionale delle Ricerche, Piazzale Vincenzo Tecchio 80, 80125 Napoli, Italy<sup>b</sup> Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, Piazzale Vincenzo Tecchio 80, 80125 Napoli, Italy

## ARTICLE INFO

## Keywords:

Calcium looping  
 Fluidized bed  
 Limestone  
 CO<sub>2</sub> capture  
 Attrition

## 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. These methods may present 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<sub>2</sub> capture capacity and attrition. In this study, a purposely developed 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 performance of two limestones, in terms of CO<sub>2</sub> capture capacity and attrition tendency, upon multiple calcination/carbonation cycles under the typical operating conditions of the Ca-L process. The results have been compared with those obtained for the same sorbents carried out in a single lab-scale fluidized bed reactor (SB) and under the same operating conditions. The comparison showed that the CO<sub>2</sub> capture capacity in the TB system is larger than that found in SB tests for both sorbents. 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 smaller than that measured in the corresponding calcination stage, which is opposite to what was found during the tests in the SB device. These findings indicate that the sorbent thermal history plays a non-negligible role on its CO<sub>2</sub> capture performance in Ca-L.

## 1. Introduction

In the framework of the CO<sub>2</sub> capture techniques, the Calcium Looping (Ca-L) process is one of the most promising ones [1–9]. The main advantage of this technology is the utilization of cheap, natural and non-toxic Ca-based sorbent materials (such as limestone or dolomite) which entail a competitive cost for CO<sub>2</sub> capture as compared to other proposed techniques. Moreover, Ca-L, being a post-combustion technology, could be used to retrofit existing power plants. The process consists of two reactors: the carbonator where the calcium oxide, in the temperature range of 650–700 °C, reacts with the CO<sub>2</sub> contained in the flue gas producing a CO<sub>2</sub>-depleted 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 CO<sub>2</sub>-rich

stream, ready for purification, transportation and sequestration, while the produced calcium oxide can restart a new cycle in the carbonator. The circulation of the sorbent between the two reactors is typically carried out by operating a dual interconnected fluidized beds system, which also ensures an intimate contact between gaseous and solid phases [10,11].

Since the calcination reaction is strongly endothermic Shimizu and coworkers [12,13] suggested to couple the Ca-L plant with an Air Separation Unit (ASU) in order to carry out an oxy-combustion of an auxiliary fuel, such as coal, to sustain the calcination reaction. Another possible option would be represented by the utilization of a Concentrated Solar Power (CSP) system integrated with the calciner [14]. This alternative would provide the heat required for calcination directly by solar energy [15].

\* Corresponding author.

E-mail address: [coppola@irc.cnr.it](mailto:coppola@irc.cnr.it) (A. Coppola).

The main drawback related to Ca-L is the decay of the CO<sub>2</sub> capture capacity with the number of cycles that is mainly related to sintering of the material caused by the high temperature (especially during the calcination stage) and the reaction environment (presence of CO<sub>2</sub> and H<sub>2</sub>O) [16–19]. Studies about reactivation of spent sorbents or utilization of alternative or synthetic/functionalized sorbents, in order to limit the impact of sintering, have been carried out by several research groups [20].

Another possible cause of CO<sub>2</sub> capture capacity decay is represented by the presence of SO<sub>2</sub> in the flue gas, and hence during the carbonation stage, since SO<sub>2</sub> reacts with CaO to form calcium sulphate. The occurrence of sulphation permanently hinders calcium oxide, due to the irreversibility of the sulphation reaction at the operating temperatures of Ca-L. Moreover, SO<sub>2</sub> could be present also into the calciner if coal is used to sustain the calcination reaction [16,17].

Furthermore, the utilization of fluidized beds implies that the sorbent particles are subject to attrition phenomena, which produce fines that can be elutriated together with the gas phase and change the particle size distribution of the bed material [21]. However, the particle breakage may have a positive effect because it can make further surface available for CO<sub>2</sub> 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) [22,23]. These techniques are very helpful experimental tools, but 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 ramps or, in SB systems, the sorbent is injected from ambient temperature in the hot reactor in each cycle producing an unrealistic thermal shock to the material [24]. In this way, particle sintering may be affected with a consequent alteration of the CO<sub>2</sub> capture capacity and of the attrition tendency. In addition, the intrinsic fixed bed nature of the sample in TG does not allow evaluating attrition phenomena. Obviously, the thermal history is correctly reproduced in continuous Ca-L bench-scale and pilot-scale facilities [25], but in these units is not possible to easily derive the effect of the number of cycles on the sorbent performance, due to the complex distribution of particle residence times.

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 the calciner and the carbonator, both 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 reference [26]. It is important to emphasize that the TB apparatus does not reproduce a continuous Ca-L process, but only recreates a sorbent particle thermal history approaching the real one. In particular, a German limestone (named EnBW) and an Italian limestone (named Massicci) have been extensively tested under typical Ca-L conditions in the TB apparatus and the CO<sub>2</sub> capture capacity and the attrition tendency have been assessed. The results have been compared to similar tests performed in a single SB apparatus on the same limestones. In general, the results denote the relevance of the sorbent thermal history on the CO<sub>2</sub> capture capacity and on the attrition tendency.

## 2. Experimental

Fig. 1 shows the TB system used for the experimental campaign: the reactor on the left (East bed – EB) is operated as the carbonator, while the right one (West bed – WB) as the calciner. Both reactors are

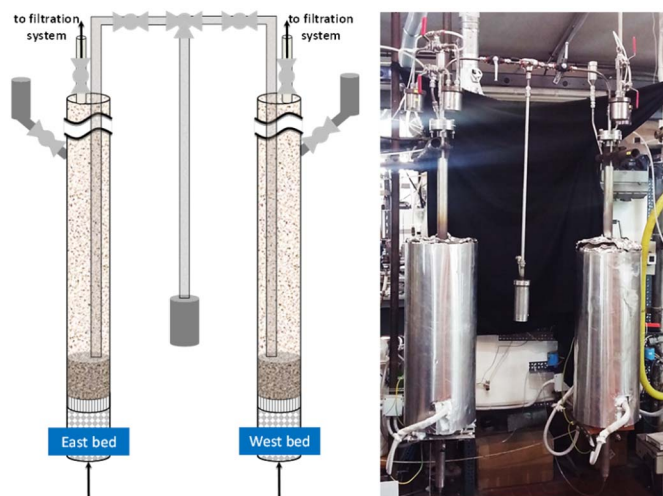


Fig. 1. Twin fluidized bed apparatus.

electrically heated by means of ovens and are operated in batch mode. A transport duct, with a diameter smaller than the reactor size, is located in both reactors and is partially immersed into the bed material. The valve system located on the duct and at the top gas exit of both reactors permits 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 valve on the top gas exit is 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 of the reactor a gas exit duct leads 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 were fed to the reactors by high-precision mass flowmeters/controllers.

A German limestone (EnBW, CaCO<sub>3</sub> content 99.2 wt%) and an Italian one (Massicci, CaCO<sub>3</sub> content 98.5 wt%), both in the size range 400–600 μm, were used as sorbent materials, while silica sand (900–1000 μm) 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 difference 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 [27,28]. This intentionally induced segregation is an essential point for obtaining selective transport which maximizes the sorbent transfer and limits the sand one [26].

Ca-L experiments, for the evaluation of the performance of the sorbent materials, have been carried out up to 20 calcination/carbonation cycles in about 10 h 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, ~150 g and ~90 g 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 loaded into the WB through the hopper. Calcination

Download English Version:

<https://daneshyari.com/en/article/6656464>

Download Persian Version:

<https://daneshyari.com/article/6656464>

[Daneshyari.com](https://daneshyari.com)