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Measuring attrition properties of calcium looping materials in a 30 kW pilot plant

Mónica Alonso [a,*], Borja Arias [a], José Ramón Fernández [a], Olivier Bughin [b], Carlos Abanades [a]

[a] *Instituto Nacional del Carbón, CSIC-INCAR, Francisco Pintado Fe, 26, 33011 Oviedo, Spain*
[b] *Carmeuse Research & Technology, Rue du Château 13A, 5300 Seilles, Belgium*

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ABSTRACT

The attrition of CaO-based solids operating in calcium looping (CaL) post-combustion CO_2 capture systems is an important factor to consider when limestones are selected as sorbent precursors. In this work, four commercial natural limestones with similar chemical compositions but with very different mechanical properties were tested in a 30kWth calcium looping pilot plant. The main attrition mechanisms that act upon the limestones (i.e. fragmentation, decrepitation and abrasion) were identified on the basis of the evolution of their particle size distributions during the start-up and the first calcination of each batch. Great differences in the performance of the selected limestones were observed, which confirms the suitability of the experimental procedure employed for sorbent screening purposes in these high-velocity, high-temperature pilot plants. Several attrition indexes reported in the literature were tested to conclude that the Total Particle Generated Index (TPGI) and the Maximum Diameter of Particles Generated (MDPG) indexes are the most useful for quantifying attrition phenomena and rank limestones.

1. Introduction

Calcium looping, CaL, is an emerging CO_2 capture technology in which particles of CaO are used to capture CO_2 from a flue gas, typically in a fluidized bed, giving rise to $CaCO_3$, which is subsequently decomposed in an oxy-fired fluidized bed combustor [1–7]. The calcium looping in fluidized beds for post-combustion applications has already been demonstrated in several test facilities of up to 1–2 MW_{th} scale [8–12]. The rapid development of the CaL technology is due to the use of reactor configurations and materials very similar to those typically employed in large-scale fluidized-bed combustion power plants.. In CaL systems, natural limestone is used as a source of CaO because of its low cost and suitable fluidisation properties. An important design parameter of the calcium looping processes is the consumption of limestone (i. e., the make-up flow) needed to sustain a certain level of activity of the CaO material for the capture of CO_2 and to compensate for the CaO loss in the cyclones located downstream of the interconnected carbonator and calciner reactors. Thus, to ensure the selection of the most appropriate sorbent the mechanical properties of the material circulating between the reactors must be taken into consideration.

Attrition, defined as the unwanted breakage of particles, results in the degradation of the solids and in a change in the size and number of particles. It is influenced by a large number of variables related to the design of the system the properties of the solids and the reacting environment [13]. In fluidized beds the most common attrition mechanisms are induced by mechanical motion and by temperature or pressure gradients inside the particles as they are subjected to fast changes in their environment [14, 15]. The main attrition mechanisms caused by mechanical motion are abrasion, when breakage takes place exclusively on the particle surface generating fines, and fragmentation, when the particles are broken into similar coarse fragments [13, 16]. Abrasion usually takes place due to the low velocity impacts between particles in the dense bed. There is an initial peak of fines generation which then decreases as the particles round off [17–19]. Fragmentation typically occurs due to high velocity impacts in the grid jets, cyclones and at the exit of the circulating fluidized bed reactors. The extent of particle fragmentation increases with the impact velocity, the multiplicity of impacts and it is also affected by the specific properties of the solids [20]. On the other hand, the main attrition mechanism induced by internal forces is decrepitation (or primary fragmentation), which generates both coarse and fine particles. This phenomenon is generally caused by thermal shock during rapid heating and/or by the fast release of gas from the solids [13].

There is substantial literature available on the attrition of limestone in fluidized bed combustors, where CaO is typically used as a SO_2 sorbent [21–26]. However, the knowledge acquired so far on this phenomenon for the specific conditions of post-combustion CaL systems is still scarce [7, 20, 27–34]. There is general agreement that CaO-based sorbents sinter and deactivate during the CO_2 capture process (i.e. their

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[*] Corresponding author.
E-mail address: mac@incar.csic.es (M. Alonso).

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CO_2 carrying capacity diminishes as the number of carbonation-calcination cycles increases) and they become progressively harder and rounder in shape [27, 28, 30–34]. The sulfation of CaO greatly reduces the generation of fines from abrasion, since the sulfate layer formed on the outer surface tends to improve the strength of the particles [35, 36]. Moreover, calcination and carbonation reactions also affect the extension and pattern of fragmentation. The particles of raw limestones and re carbonated sorbents are the most resistant to impact loading, whereas those of calcined sorbents are the weakest [20]. Decrepitation in limestones is mainly caused by the release of CO_2 during the first calcination, which changes the morphology of particles, rather than by thermal shock [35].

Despite the existing consensus on the qualitative attrition mechanisms noted above, there is a wide variety of tests and techniques that are used to quantify attrition and to rank materials in terms of attrition performance. Standard attrition tests available for other applications do not provide sufficient relevant information for each type of material and application. The great variability in attrition of natural limestones requires for highly empirical approaches to investigate these phenomena under specific process conditions. No feasible method to study the different attrition mechanisms separately is available as yet (unlike the study of chemical reaction phenomena). Hence the use of lump attrition parameters like the "attrition index" is the norm in quantitative attrition studies.

The attrition index proposed by Forsythe and Hertwig in 1949 for fluid cracking catalysts [37] is still considered to be a useful parameter for evaluating solids mechanical degradation during fluidization. In this methodology, an attrition rate is arbitrary defined considering the amount of material with a particle size of below 44 μm (325 mesh) produced per hour. This index is useful for the comparative testing of materials under similar and strictly controlled conditions [13]. Other attrition indexes reported in the literature are based on Gwyn's formulation [38]. Gwyn assumes that the amount of material elutriated corresponds to the attrited material, which can be fitted to a power-law time dependent function. However, this formulation is only valid when abrasion is the main attrition mechanism during the operation. Some authors consider that these definitions are not sufficiently accurate for describing the attrition process since they do not take into account the breaking of particles when fines are not produced [16] or the fact that not all the fines produced are elutriated [39]. Amblard et al. [39] recently defined another attrition index to overcome these limitations. This index is based on the evolution with time of the entire particle size distribution (PSD) of the solids during the test including the elutriated material (and not only the fines generated below 45 μm, as in the case of classical attrition indexes). The main limitation of this procedure is the greater experimental effort needed to obtain a detailed assessment of the particle size distributions under realistic conditions.

In the present work, the methodology developed by Amblard et al. [39],has been adapted to study the resistance to attrition of four limestones with similar chemical composition in a 30 kW fluidized-bed pilot plant operated under conditions similar to those of larger calcium looping systems (i.e., with high gas velocities and high temperatures). With this procedure, the dominant attrition mechanisms for each limestone are identified and the solids can be ranked according to the extent of particle attrition, which can facilitate the screening of sorbents in calcium looping applications.

2. Experimental

2.1. Limestones

Four commercial limestones, labelled A, B, C and D, were used for the purpose of this study. The materials were provided by Carmeuse from their extensive database of limestones with different mechanical properties and geological origin. The chemical compositions of these limestones were determined by means of an X-Ray Fluorescence Spectrometer (SRS 3000 Bruker) following the fused cast-bead method (PERLX'3 Philips). As can be seen in Table 1, from a chemical composition point of view, all the limestones are of a high purity, although it should be noted that limestone B has a higher SiO_2 content.

Carbonation-calcination tests were carried out in order to determine the CO_2 carrying capacity. The experiments were performed in a thermogravimetric analyser that has been described in detail elsewhere [40]. Fig. 1 shows the evolution of the maximum carbonation conversion (X_N) for the four sorbents with the number of carbonation-calcination cycles. It is generally accepted that the decay in the CO_2 carrying capacity for a variety of limes and reaction conditions can be expressed by Eq. 1, employing an average deactivation constant k of 0.52 and a residual molar conversion X_r of 0.075 [41].

$$X_N = \frac{1}{\frac{1}{(1-X_r)} + kN} + X_r \qquad (1)$$

As can be seen in Fig. 1, the deactivation curves of the four sorbents are very similar and follow the trend marked by Eq. (1).

Moreover, the Particle Size Distributions (PSDs) of the fresh limestones were obtained using a Beckman-Coulter LS 13320 laser diffraction particle size analyser in dry mode. Air was used to disperse the solids in the laser chamber. In accordance with the recommendations of the manufacturer, 1 wt% of fumed silica ($d_p = 7$ nm) was added to facilitate the dispersion of the samples.

As can be seen in Fig. 2, the fresh A-D limestones have similar PSDs and in all cases around 90 vol% of the distributions are between 100 and 400 μm. Therefore, the starting point for all the attrition test is a group of limestones with almost identical particle size distributions and chemical performance as CO_2 regenerable sorbents.

2.2. The 30 kW CaL pilot plant at INCAR-CSIC

Although the outline of the 30 kW plant has been explained in detail elsewhere [42–44], a brief description of the pilot plant is given below, including the modifications made for the attrition test. The test rig consists of two circulating fluidized bed reactors (see Fig. 3). Both reactors have an internal diameter of 0.1 m. The carbonator is 6.3 m in height, whereas the calciner has a height of 6.1 m. There are no air distributors in the reactors to facilitate the feed of solids directly to the risers. The solids are fed in by means of two screw-feeders located at the cold air entrances to the risers. The air is blown into the facility by a fan and the flowrates to the risers and loop-seals are independently controlled by means of mass flow controllers. The bottom 3 m of each riser is surrounded by independently controlled electrical ovens, while the rest of the primary loop is thermally insulated. Each riser is connected to a high-efficiency primary cyclone, where the solids and gas phases are separated with a efficiency of about 97–99%. There are also two secondary cyclones before the stacks to ensure that there is no significant loss of solids from the facility. Downstream of the primary cyclones, the solids fall into the loop-seals through the standpipes. The loop-

Table 1
XRF analysis of the limestones (in wt%).

Oxide	A	B	C	D
MgO	0.37	0.85	0.65	0.48
Al_2O_3	0.00	0.27	0.13	0.18
SiO_2	0.18	1.40	0.3	0.56
SrO	0.00	0.02	0.02	0.03
K_2O	0.00	0.05	0.00	0.03
CaO	55.92	54.14	55.64	55.21
Fe_2O_3	0.00	0.00	0.05	0.00
SO_3	0.07	0.21	0.00	0.10
LOI[a]	43.46	43.05	43.35	43.44
Total	100.00	99.99	100.14	100.03

[a] LOI: Lost On Ignition.