



Primary fragmentation of limestone under oxy-firing conditions in a bubbling fluidized bed

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ABSTRACT

Primary fragmentation of two limestones was studied in a lab-scale bubbling fluidized bed under simulated oxy-firing conditions and, for comparison, under traditional air-firing conditions. The influence of bed temperature, particle size and simultaneous occurrence of sulphation reaction was tested. Additional experiments in a heated strip apparatus were performed to determine if primary fragmentation occurred under high heating rate conditions, but in the absence of particle collisions.

Results of the experiments show that only limited fragmentation occurred to both limestones tested under all operating conditions. Under oxy-firing conditions primary fragmentation was significantly reduced with respect to air-fired operation, most likely because of the absence of limestone calcination under high CO₂ atmospheres. Thermal shock upon limestone injection in the hot bed appears not to be able to induce significant particle fragmentation by its own.

Particle size, bed temperature and simultaneous occurrence of sulphation reaction were found not to influence significantly the limestone primary fragmentation extent under both oxy-firing and air-firing conditions. On the contrary, the limestone type was found to be a more important variable with respect to the fragmentation tendency.

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1. Introduction

Oxy-firing (OF) is a combustion technology that allows to obtain a high CO₂ concentration at the exhaust which can be transported and stored, avoiding emission to the atmosphere. It is one of the options that has shown best potential for short-term implementation at the commercial scale [1–4]. Its main disadvantage is the energy consumption necessary to produce pure oxygen, in some cases up to 60% of the additional power consumption. The overall efficiency of the power plant is typically reduced by about 7–9 percentage points [4]. Most of the activity reported so far in the literature about oxy-firing was applied to pulverized burners [5–7], while only recently oxy-firing was studied in fluidized bed applications [8–13].

The combination of oxy-firing and fluidized bed technologies provides one of the most promising combustion options with CO₂ capture. In fact, the following additional advantages can be obtained: low NO_x emissions, in-situ desulphurization capability, and high fuel flexibility. In particular, as regards the SO₂ capture process in the combustor, limestone or dolomite particles can be directly fed in the combustion chamber as part of the bed. SO₂ capture by calcium-containing materials depends on several parameters: temperature,

particle size and its properties (age, porosity, and composition), total pressure and CO₂ partial pressure [14], but in general a high capture efficiency can be obtained. Under OF conditions, carbon dioxide partial pressures established in the reaction zone may be large to the point of preventing limestone calcination. Sulphur capture is accordingly affected, the main pathway being direct sulphation of the raw limestone [15].

During the residence time of the sorbent particles in bed, they suffer internal stresses, chemical reactions, and impacts with other particles and with the internals of the combustor. All these phenomena may produce particle fragmentation or attrition. On the one side, it is necessary to reduce attrition in order to avoid excessive elutriation and to increase particle residence time in the bed for a better calcium exploitation [16]. On the other side, particle fragmentation may improve calcium utilization by generating smaller particles that increase the available surface for SO₂ capture and by breaking the CaSO₄ shell around the particles. These contrasting effects imply the existence of an optimal particle size for the SO₂ sorbent [17,18].

Depending on the causes that produce fragmentation and attrition in the fluidized bed and on the characteristic particle size of the generated fragments, these phenomena can be divided in three groups [19]:

- Primary fragmentation: it is produced when limestone is introduced in the hot reactor due to thermal shock and/or to the release

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of gases during particle heating (calcination). As a result of this type of fragmentation, both coarse and elutriable particles may be generated.

- Secondary fragmentation: it is produced by mechanical stresses suffered by the particles due to high-energy collisions with other particles and internals of the reactor. During secondary fragmentation, mostly coarse particles are formed.
- Attrition by abrasion: the causes are similar as for the secondary fragmentation, but, in this case, low-energy collisions are involved, and fine and easily elutriable particles are generated.

Fluidized bed attrition and fragmentation of limestone under air-firing (AF) conditions have been extensively studied, with a focus on how calcination, sulphation and simultaneous calcination–sulphation influence these phenomena [16,20,21]. It was found that the initial particle attrition rate is high due to particle rounding off, but as time goes by, this value decreases until a steady value is reached [18]. The occurrence of sulphation further decreases the steady attrition rate by hardening the particle surface. A similar behaviour was observed under OF conditions, but the attrition rate was lower than under AF conditions, with a slightly increasing trend as sulphation reaction proceeded [22]. Secondary fragmentation by high-velocity impacts was also characterized under both AF and OF conditions [23,24], showing that the particle breakage is highly dependent on the impact velocity and on the occurrence of chemical reactions that change the particle morphology. With this respect impact fragmentation appears to be significantly hindered by the absence of calcination under OF conditions.

As regards primary fragmentation, this phenomenon has been characterized for different limestones under AF conditions [16,21], but a much more limited effort was reported under OF conditions. Hu and Scaroni [25] carried out experiments under high temperature conditions and found that limestone that did not suffer an important thermal shock, did not show a high fragmentation level after calcination. Saastamoinen et al. [26], developed a model that describes limestone fragmentation due to calcination and thermal shock that was validated for 18 kinds of limestones under AF conditions. The authors predicted a less pronounced primary fragmentation under calcination-hindered conditions. Yao et al. [27] analyzed the influence on primary fragmentation of several parameters as heating rate, particle size, the type of limestone and calcination/sulphation.

It is very important to well characterize primary fragmentation of limestone, since its extent strongly influences the particle size distribution of the sorbent that will take part in the desulphurization process in the fluidized bed. CO₂ release upon calcination is considered to be the main cause of primary fragmentation [16,21], thus a great difference in the limestone behaviour is expected between air-firing and oxy-firing conditions. In this paper we have thoroughly studied in a lab-scale fluidized bed the primary fragmentation suffered by two different limestones under different operating conditions and gaseous environments, with a focus on their behaviour under OF conditions.

2. Experimental

2.1. Fluidized bed apparatus

Primary fragmentation experiments were carried out in a lab-scale bubbling fluidized bed made of stainless steel, 1 m high and with an internal diameter of 4 cm. The reactor was electrically heated and its temperature was controlled by means of a chromel–alumel thermocouple located 0.4 m above the distributor plate and a high precision PID controller. The fluidizing gas was introduced at the bottom of the reactor through a perforated plate that acts as a distributor, with 55 holes of 0.5 mm diameter in a triangular pitch.

The fluidizing gas flow, composed by a mixture of air, CO₂ and/or N₂–SO₂ from cylinders, was measured by means of two high precision

mass flowmeters which were specifically calibrated for each gas used. The exhaust gases were continuously sampled for on-line concentration measurement by a series of NDIR gas analyzers (CO₂, CO and SO₂) and a paramagnetic one (O₂). Further details can be found in [16,22].

The inert bed was composed of 150 g of quartz sand in the size range 0.1–0.212 mm, with a minimum fluidization velocity $U_{mf} = 0.01$ m/s. In previous research activities [21] fragmentation was studied using coarser sand, in a size range larger than the limestone initial size. In this way, limestone fragments which remained in the bed and inert sand could be easily separated by sieving. In this work, however, the limestone initial particle size was too large (>0.9 mm) to use this technique. In addition, large sand particles require a high fluidization velocity that increases attrition by abrasion. This fact was undesirable for the aim of this work that was focused on primary fragmentation. The sand size range used in this work was well below the initial size of the limestone and sieving was still considered to be a good way to separate the two materials. The limestone fraction belonging to the 0.1–0.212 mm size range after the fragmentation tests was very limited and was assumed to be produced mostly by surface abrasion. Fluidization velocity was set at 0.15 m/s in all the experiments in order to reduce as much as possible the extent of attrition by abrasion.

2.2. Heated strip apparatus

This apparatus was used to check if any primary fragmentation occurred to the limestone particles by simulating the high heating rates typical of fluidized beds, but without the presence of particle collisions. In this way the simultaneous effect of secondary fragmentation and attrition by abrasion, unavoidable in the fluidized bed experiments, was hindered. The typical particle heating rates in a heated strip device are of the order of 10⁴ K/s, as opposed to the ~10³ K/s values relevant for a fluidized bed.

The heated strip apparatus is a special heated grid device, where the usual metal grid is replaced as the sample holder by a pyrolytic graphite foil thermally stabilized for use up to 2500 °C [28]. The apparatus is enclosed in a quartz vessel. The strip heats up by Joule effect reaching temperatures as high as 2000 °C in less than 0.2 s. The temperature of the grid is set by changing the value of the voltage at the two extremes of the strip. Due to the very high heating rate, the strip can be considered isothermal for the entire duration of the test.

A batch of limestone particles (0.4 g) was laid on the strip. In the case of mm-sized particles the surface of the particles in physical contact with the strip can be considered to stay at the strip temperature, but the upper part of the particles could be colder. Although convective cooling is modest, due to very small gas velocities inside the chamber and the short duration of the tests, heat is dispersed at the upper surface of the particles by radiation. The apparatus was therefore modified applying a curved mirror on top which reflects the radiation of the strip on the particle top surface. A two colour LAND Infrared pyrometer was used to monitor the strip temperature across the quartz vessel. A preliminary calibration of the IR camera was performed to take into account quartz absorption.

The heated strip tests were carried out under a pure nitrogen atmosphere. The sample was rapidly heated to either 850 or 1200 °C, and maintained at this temperature for up to 3 min. At the end of the test the sample was collected and weighed to check if complete calcination had occurred. The test was repeated for a number of times necessary to reach a total sample mass of ~2 g. The particles in the sample were then observed and compared with the initial ones to determine if primary fragmentation had occurred.

2.3. Limestones

Two types of limestone were chosen for the experimental tests. The first one was an Italian limestone called Massicci with a high Ca

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