

ENHANCED FLUIDIZED BED DESULFURIZATION BY PRE-TREATED LIMESTONE PARTICLES

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Abstract

In this work we have tested the fluidized bed desulfurization performance of lime particles obtained by means of a proprietary limestone slow calcination pre-treatment technique. This performance was compared with that of the parent untreated limestone particles. The occurrence of particle fragmentation and attrition during the fluidized bed operation was also investigated with a specific test protocol for both limestone and pre-treated lime sorbents. Two particle size ranges were tested under typical fluidized bed coal combustion conditions ($T = 850^{\circ}\text{C}$; $\text{SO}_2 = 1800$ ppm). The experiments were complemented by porosimetric and morphological (SEM) analyses of the sorbent. Results showed that limestone pre-treatment was able to preserve the high mechanical strength of the parent particles as opposed to the fast *in situ* calcination typically active in fluidized beds. In addition, a high calcium reactivity and final conversion were observed for the pre-treated lime particles, leading to a SO_2 capture capacity per unit mass of sorbent much higher than that obtained with the untreated limestone. Simple economic evaluations suggest that the use of the pre-treated lime in place of limestone can involve significant economies for fluidized bed coal combustor operators.

Introduction

Removal of sulfur oxides generated during fluidized bed (FB) combustion is typically accomplished by *in situ* injection of limestone or dolomite [1]. At atmospheric pressure, sorbent particle sulfation proceeds according to the following reactions:



i.e., the sorbent first calcines (reaction 1) to yield porous calcium oxide which, in turn, is able to remove SO_2 (reaction 2) producing calcium sulfate. Particle sulfation most typically conforms to a core-shell sulfation pattern: a sharp reaction front establishes in the sorbent particles between the porous unreacted CaO core and the compact CaSO_4 outer shell [2-6]. Extensive sulfation of the core is prevented by the onset of a strong diffusional resistance to SO_2 migration through the shell. Calcium conversion seldom exceeds 30-40%, so that over-stoichiometric sorbent feeding is required, resulting in increased production of solid waste.

The particle size distribution (PSD) of the bed material is an important factor in FB combustors, as it affects fluid-dynamics, heat transfer and pollutants formation. When the bed material contains an SO_2 sorbent, like limestone or dolomite, its PSD also affects the desulfurization efficiency in the boiler. If the sorbent particles are too fine, they rapidly

escape as fly ash, and calcium conversion decreases because of the insufficient residence time. On the contrary, if the sorbent particles are too coarse, conversion decreases because of limited penetration of sulfur into the particle. The PSD of the sorbent establishing at the steady state in the boiler is the result of the interplay of a number of processes. In particular, attrition and fragmentation phenomena can substantially affect the sorbent PSD and, in turn, the performance of the desulfurization process [7-9].

Attrition and fragmentation of limestone during FB combustion have been thoroughly characterized over the last decade [9-16]. Key phenomenological features and mechanistic pathways of sorbent attrition in FB combustors have been disclosed with the aid of a comprehensive test protocol consisting of different and mutually complementary test procedures [9,11,14,15]. In particular, sorbent attrition phenomena have been classified into: i) *primary fragmentation*, which occurs immediately after the injection of sorbent particles in the hot bed as a consequence of thermal stresses and internal overpressures due to CO₂ emission; ii) *attrition by abrasion*, related to the occurrence of surface wear as the FB emulsion phase is sheared by the passage of bubbles, generating mostly fine/quickly elutriable fragments; iii) *secondary fragmentation*, a result of high-velocity impacts of sorbent particles against targets (bed material, reactor walls/internals), occurring mostly in the jetting region of the FB and in the exit region of the riser and the cyclone of circulating FB reactors. The critical influence of the progress of calcination and sulfation on attrition of limestone in FB combustors has long been recognized [7,9,14]. These reactions bring about relevant modifications of the mechanical and morphological properties of the sorbent particles which significantly affect the mechanisms and extent of particle breakage. For example, the progress of sulfation decreases the attrition rate with respect to that of the native porous lime due to the formation of a more compact and tougher sulfate shell at the periphery of the particle [9].

The aim of this work was to explore the possibility to enhance the sulfur capture capacity of the sorbent during FB combustion, and at the same time to increase its mechanical resistance with respect to attrition and fragmentation phenomena. A proprietary limestone slow calcination pre-treatment technique was developed by Calcidrata S.p.A., which appears to be promising for the production of a relatively cheap desulfurization sorbent with suitable characteristics. An Italian limestone was pre-treated with this technique and then tested in a lab-scale FB reactor for its SO₂ capture performance and attrition/fragmentation behavior. The results were also compared with those obtained by using the same untreated raw limestone under the same operating conditions.

Experimental

Apparatus. The sorbent sulfation experiments were carried out in a stainless steel atmospheric bubbling fluidized bed reactor 40 mm ID and 1 m high (Fig. 1). The fluidization column was heated by two 2.2 kW electric furnaces. The temperature of the bed, measured by means of a chromel-alumel thermocouple, was kept constant by a PID controller. The distributor of fluidization gas was a perforated plate with 55 holes 0.5 mm in diameter disposed in a triangular pitch.

Batches of material could be fed to the reactor via a hopper connected sideways to the upper part of the freeboard. The latter was equipped with a three-way valve. By operating this valve it was possible to convey flue gases alternately to two removable filters of sintered brass (100% filtration efficiency for > 10 μm-particles). This device allowed time-resolved collection of elutriated fines.

The fluidizing gas flow, composed by a mixture of air and N₂-SO₂, was measured by means of two high precision mass flowmeters which were specifically calibrated for each gas used. Analysis of CO₂ and SO₂ concentrations in the flue gas was accomplished by means of two NDIR analyzers on line. Further details can be found in [9].

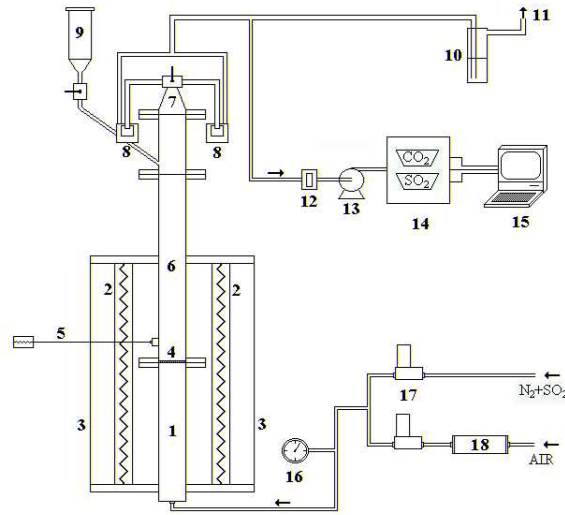


Figure 1. Experimental apparatus. (1) gas preheating/premixing section; (2) electrical furnaces; (3) ceramic insulator; (4) gas distributor; (5) thermocouple; (6) fluidization column; (7) two-exit head; (8) sintered brass filters; (9) hopper; (10) SO₂ scrubber; (11) stack; (12) cellulose filter; (13) membrane pump; (14) gas analyzer; (15) personal computer; (16) manometer; (17) mass flow meter/controller; (18) air dehumidifier (silica gel).

Procedures. The reactor was charged with a bed made of sand (150 g), and then heated to the temperature of 850°C prior to each experiment. The fluidizing gas superficial velocity was 0.75 m/s. Experiments were carried out by feeding a 20 g sorbent batch in the bed while keeping a flow of dry air containing sulfur dioxide (1800 ppm) and 8.5% by volume of oxygen. Under these conditions calcination and sulfation occurred at the same time.

The degree of calcium conversion during sulfation was calculated as a function of time by working out the SO₂ concentration at the exhaust according to:

$$X_{Ca}(t) = \frac{\int_0^t [F_{SO_2}^{in} - F_{SO_2}^{out}(t)] dt}{n_{Ca}} \quad (3)$$

where $F_{SO_2}^{in}$ and $F_{SO_2}^{out}(t)$ are, respectively, the molar rates of SO₂ fed to the reactor and in the exhaust gas, and n_{Ca} is the overall moles of calcium fed to the reactor. SO₂ oxidation to SO₃ inside the reactor was accounted for following the procedure detailed by Scala et al. [9].

Rates of fines generation by attrition of bed material were determined by measuring the amount of fines carried over by the fluidizing gas and elutriated from the reactor. The assumption underlying this procedure was that the residence time of elutriable fines in the reactor could be neglected and that elutriation rate could be assumed equal to the rate of fines generation by attrition at any time during limestone conversion. Elutriated fines were collected by means of the two-exit head by letting the flue gas flow alternately through sequences of filters (one was in use while the previous one was replaced) for definite periods of time. In order to prevent hydration and/or recarbonation of the collected material, each filter was readily put in a drier after being used where it was cooled down before it was weighed. The difference between the weights of the filters before and after operation, divided by the time interval during which the filter was in operation, gave the average fines generation rate relative to that interval. Attrition of sand could be neglected [9].

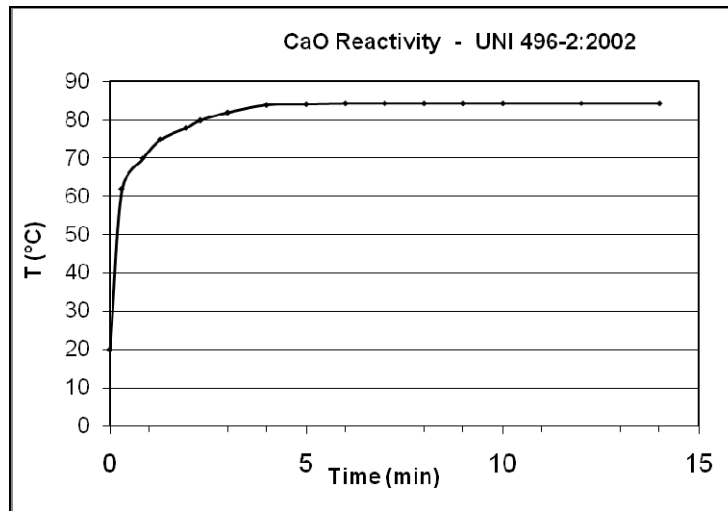


Figure 2. Slaking kinetics of pre-treated CaO (62°C at 25’).

Particle size distribution of bed sorbent at the end of the run was determined by retrieving the bed material from the reactor and subjecting it to particle size analysis. Retrieval of sorbent particles after sulfation could be easily accomplished by discharging the bed from the reactor and sieving the sorbent out of the sand. This operation was carried out gently in order to avoid further attrition of particles, but rapidly because of the propensity of calcined sorbent to absorb moisture when in contact with ambient air. The sorbent was eventually characterized from the standpoint of particle size distribution by sieving.

Materials. The bed material consisted of mixtures of sorbent and sand. Sand belonged to the nominal size range 900-1000 μm . Minimum fluidizing velocity was 0.4 m/s.

The sorbent used in this work was a high-calcium Italian limestone (*Boundstone* in Dunham’s classification) quarried from Mesozoic carbonate succession (Est Sardinia) and commonly named “*Biancone di Orosei*”. Chemical analysis of the raw limestone was carried out by a Philips PW 1400 XRF spectrometer, operating with a Rh tube at 30 kV and 60 mA, and gave a CaCO_3 content of 98,83% by weight.

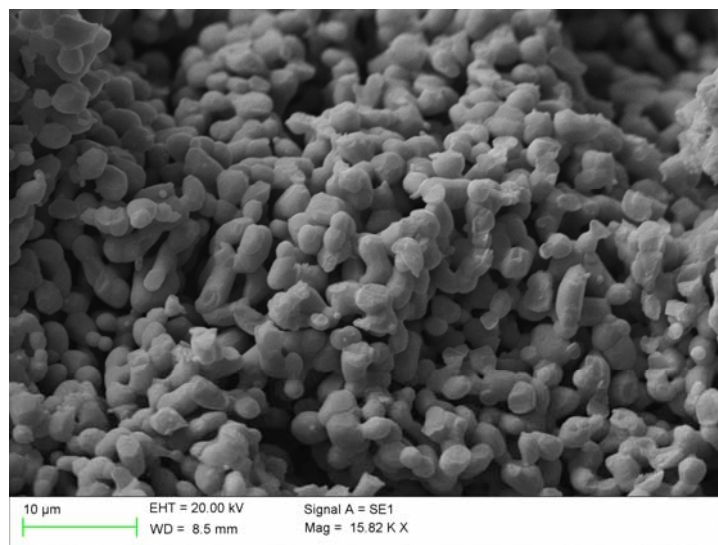


Figure 3. SEM micrograph (Secondary Electrons) of the surface of a pre-treated CaO particle.

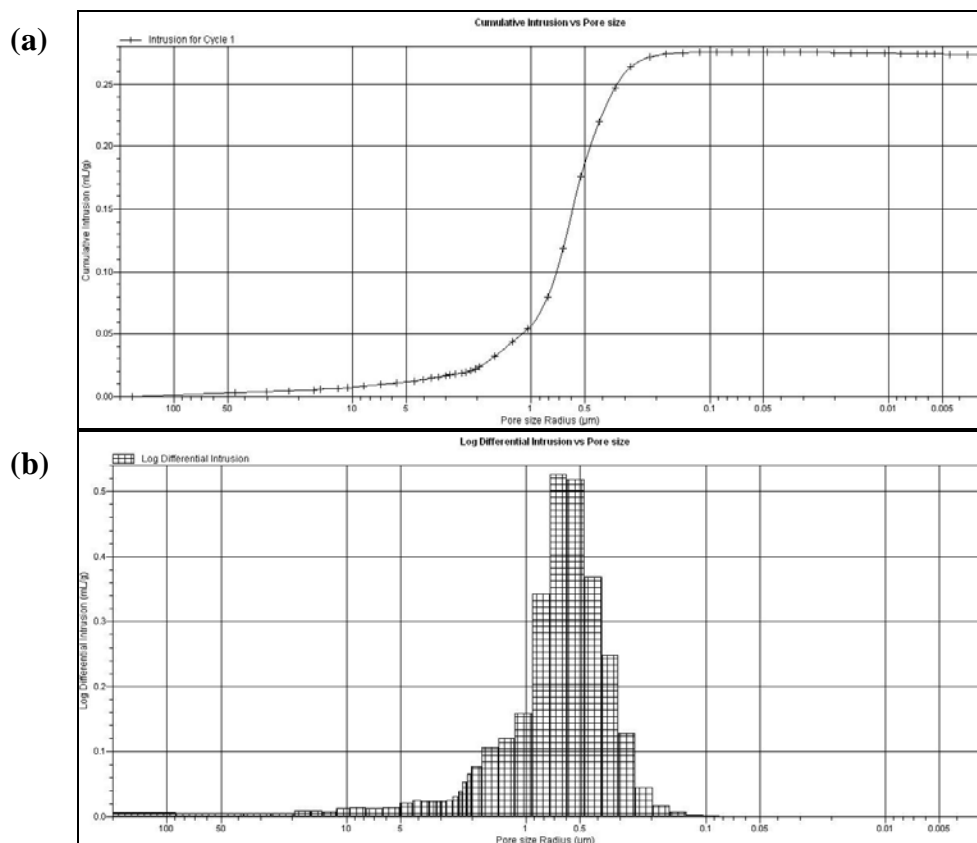


Figure 4. Porosimetric features of pre-treated CaO (MIP technique): (a) Cumulative Intrusion vs. Pore size radius, and (b) Log. Differential Intrusion vs. Pore size radius.

The sorbent was used either as received or after a proprietary pre-treatment process. This pre-treatment process consisted in the slow calcination of limestone at mild temperature and under controlled gaseous environment. After this pre-treatment, the sorbent consisted mostly of CaO (95.0%). Batches of both as received and pre-treated sorbent were sieved in the two nominal size ranges: 200-300 and 400-600 μm .

Microstructural-morphological SEM investigation of the CaO manufactured by Calcidrata S.p.A. were performed, on conductive samples, by a Zeiss Leo 50 XP apparatus operating with 20 kV of accelerating voltage and an electron source of LaB₆. Pore size distribution and total porosity of CaO were obtained by means MIP (mercury intrusion porosimetry) techniques using a Micromeritics Autopore IV porosimeter operating at 2000 bar. Slaking kinetics test of CaO was carried out in wet condition in a special dewar device (Fapa instrument) according to UNI EN 459-2:2002 standard.

Results

Pre-treated lime characterization. Quicklime manufactured by Calcidrata S.p.A. by means of the slow calcination treatment is very reactive as results from the slaking kinetics test (Fig. 2). In fact, after addition of water, the temperature of the lime sample rises up to 60 $^{\circ}\text{C}$ in few tens of seconds. SEM investigations (Fig. 3) indicate that the microstructure of the pre-treated lime is composed of equigranular CaO crystallites, of pseudocylindrical shape, with dimensions in the range 2-3 μm . MIP porosity is around 50%, with a unimodal dimensional distribution of pores (Fig. 4). Pore size radius classes are mostly concentrated in the interval 0.4-0.9 μm . The calculated specific surface area is over 15 m^2/g .

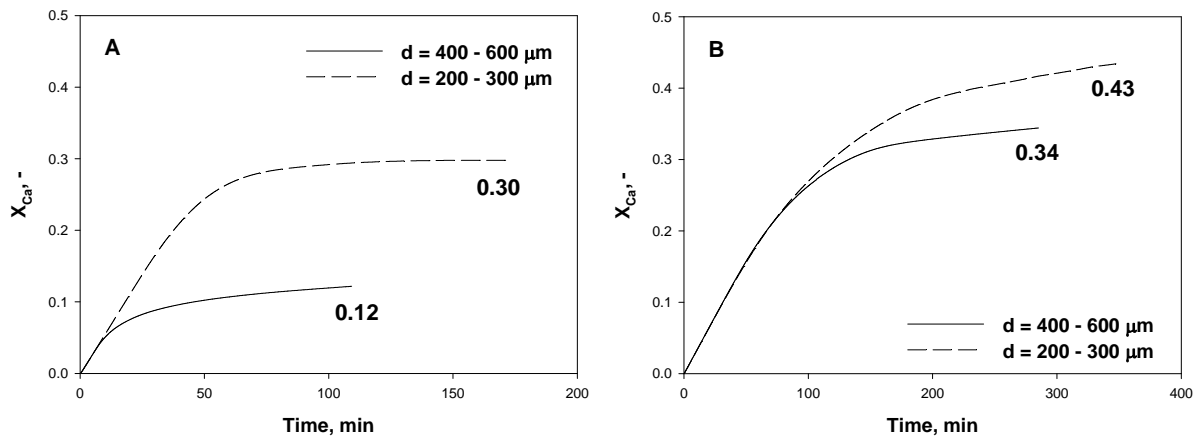


Figure 5. Conversion degree of calcium oxide into sulfate as a function of time for sorbent particles of different size sulfated batchwise in fluidized bed at 850°C and 1800 ppm SO₂. A) Raw limestone; B) Pre-treated CaO.

Desulfurization performance. Figure 5 reports the degree of calcium conversion X_{Ca} as a function of time during the FB sulfation of batches of either sorbent. Two particle sizes have been tested. For the raw limestone calcium conversion at the end of the test was relatively low, especially for the larger particle size. The pre-calcined sorbent performed better with a 34-43% calcium conversion after about 300-350 min, depending on the particle size. The increase of calcium conversion was particularly evident for the 400-600 μm particles.

In order to better compare the performance of the two sorbents, the sulfur capture data have been worked out to obtain the SO₂ capture capacity of the sorbents. This quantity represents the grams of SO₂ captured per gram of sorbent, and is a more practical way to rank the sorbent performance.

Figure 6 shows the SO₂ capture capacity as a function of time for the same experiments reported in Fig.5. Comparison of the results for the two sorbents highlights the much better performance of the pre-calcined lime.

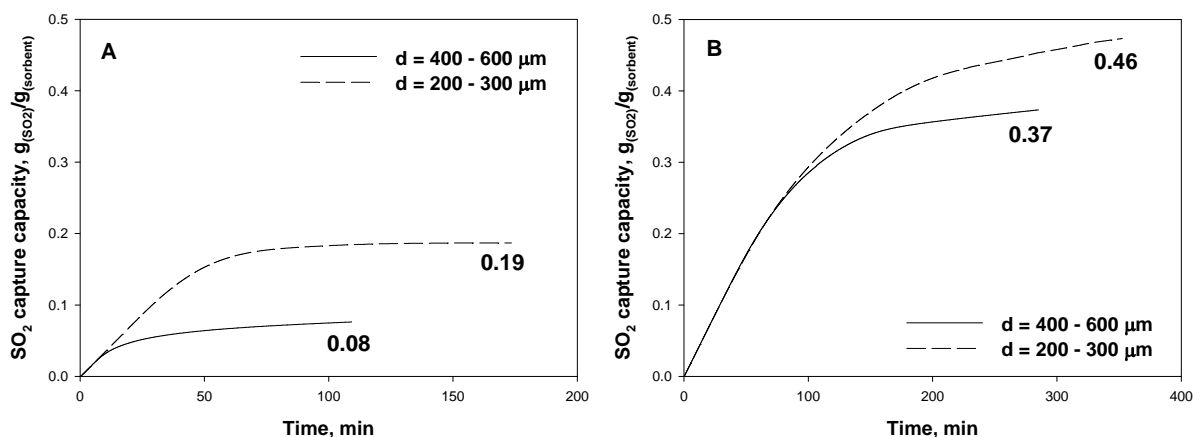


Figure 6. SO₂ capture capacity as a function of time for sorbent particles of different size sulfated batchwise in fluidized bed at 850°C and 1800 ppm SO₂. A) Raw limestone; B) Pre-treated CaO.

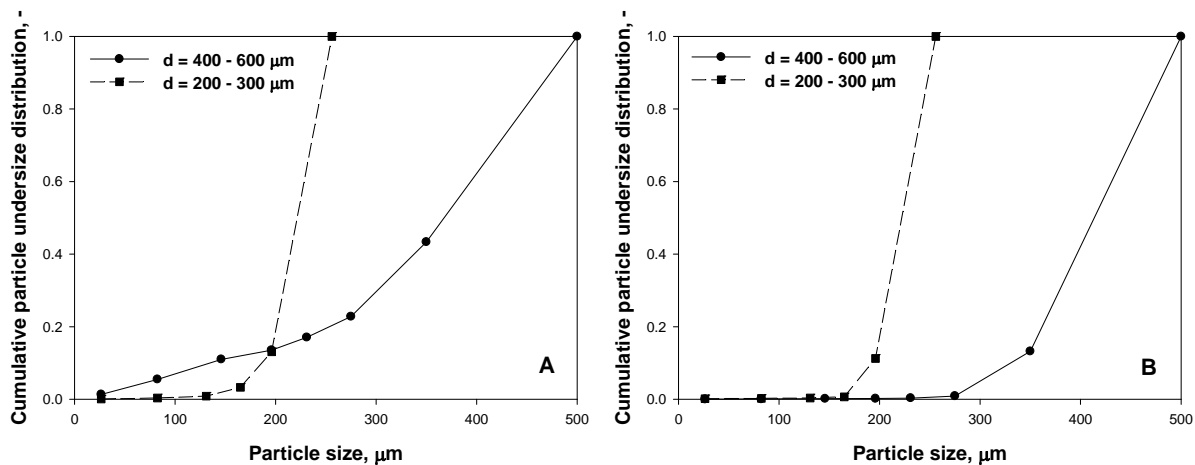


Figure 7. Cumulative particle undersize distribution of sorbent particles of different size sulfated batchwise in fluidized bed at 850°C and 1800 ppm SO₂.
A) Raw limestone; B) Pre-treated CaO.

Under similar operating conditions, 2-4 times less sorbent is needed to obtain the same SO₂ capture performance. The reason of this result relies on the combination of two effects: the better calcium exploitation of the pre-calcined sorbent (Fig.5), and the lower molecular weight of CaO with respect to CaCO₃. This last effects, of course, determines a larger number of moles of Ca available for reaction with SO₂ in the pre-calcined lime per unit mass of sorbent.

Attrition behavior. Figure 7 reports the cumulative particle size distribution of the sorbent samples discharged from the bed after FB sulfation, for both particle sizes tested. The raw limestone (Fig.7A) exhibits a moderate fragmentation for the 200-300 μm particles, and a significant fragmentation for the 400-600 μm particles. Limestone fragmentation is mostly caused by the rapid calcination of the particles upon feeding in the hot bed, which generates significant overpressures inside the particles during CO₂ release [9].

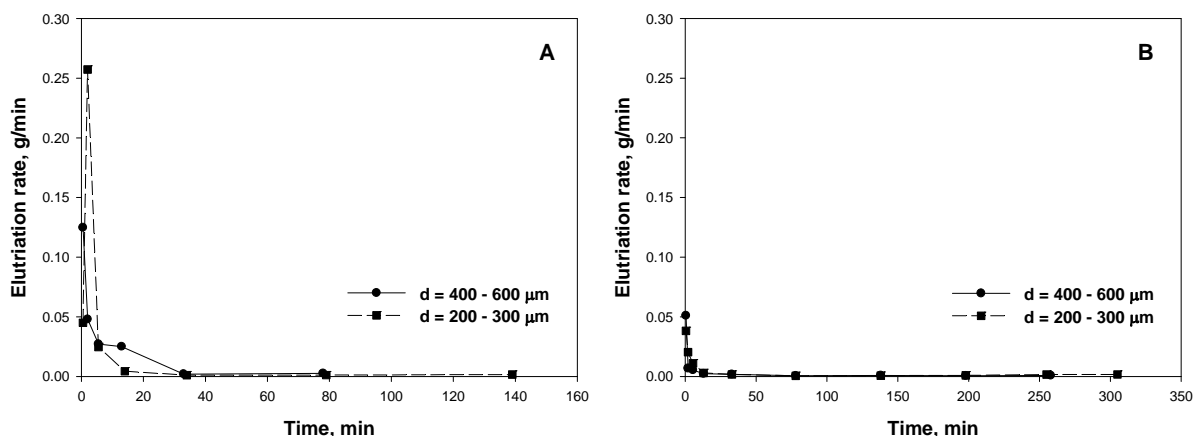


Figure 8. Fines elutriation rate as a function of time during batchwise sulfation of sorbent particles of different size in fluidized bed at 850°C and 1800 ppm SO₂.
A) Raw limestone; B) Pre-treated CaO.

Larger particles are related to higher internal overpressures, which determine a higher degree of fragmentation. The population of particles below the initial particle size range (fragments) accounts for 4 and 23% of the sample mass for the 200-300 and 400-600 μm particles, respectively. The pre-calcined sorbent exhibits a different behaviour (Fig.7B). Very limited fragmentation is evident at the end of the runs. For this sorbent the fragments account for less than 1% of the sample mass for both particle size ranges. This result is certainly caused by the absence of significant calcination in the fluidized bed for the pre-calcined lime, but also indicates that the slow calcination/treatment is effective in strengthening the sorbent structure.

Figure 8 shows the fines elutriation rate measured during FB sulfation experiments with the two sorbents. The fines elutriation rate shows an initial high peak due to particle rounding off. As sulfation proceeds, the fines elutriation rate decreases until a steady value is reached. This decay occurs over a time scale comparable with that over which calcium is sulfated, and should be related to the progress of reaction through the formation of a sulfate layer, harder than the oxide, on the particle surface [9,11]. A comparison between the two sorbents shows that the raw limestone generates more fines especially during the first 20 min. The total quantity of elutriated fines during the raw limestone experiments was 0.92 and 0.82 g for the 200-300 and 400-600 μm particles, respectively. For the pre-calcined lime the total quantity of elutriated fines was approximately halved, namely 0.49 and 0.34 g for the 200-300 and 400-600 μm particles, respectively. Again, this result further confirms that the sorbent pre-treatment is able to give a large mechanical resistance to the particles.

Economic analysis

A simple case study was carried out on the basis of the typical operating conditions of an Italian full-scale FB unit burning international low-sulfur coals and using a limestone similar to that used in this work. The analysis of the solid residues coming out from the plant (coal ash + spent sorbent) gave an average content of unused CaCO_3 and CaO of ~ 7 and $\sim 20\%$, respectively. Taking into account that the total quantity of solid residues is of the order of 160,000 tons per year, and that the raw limestone has an average cost of 30 € per ton, the following “penalties” associated with the inefficient use of traditional limestone in the plant can be estimated (yearly costs):

- a) the cost for unused CaCO_3 (336,000 €);
- b) the cost for unused CaO (1,714,560 €);
- c) the cost associated to the consumption of coal that is burned to generate the necessary heat to produce unused CaO by calcination (521,600 €) – this cost was calculated assuming an average cost of 100 € per ton of coal;
- d) the cost for CO_2 emissions deriving from limestone calcination in the FB and from the fraction of coal burning for unused CaO production (606,239 €) – this cost was calculated assuming an average cost of 15 € per ton of produced CO_2 ;
- e) the cost associated to landfilling of unused CaCO_3 and CaO and of ash from the fraction of coal burning for unused CaO production (1,958,085 €) – this cost was calculated assuming an average landfilling cost of 45 € per ton of residue.

Summing up these costs, the total penalty associated to the inefficient use of limestone for this plant is 5,136,484 €. From this simple estimation, it is clear that considerable economies can be obtained by the plant operator if these penalties can be minimized. With this respect, the use of the pre-treated sorbent developed by Calcidrata S.p.A. would be associated with a number of advantages. First, since the sorbent is pre-calcined, no unused CaCO_3 would be present in the process, no coal would be necessary for CaO production, and no CO_2 would be produced by sorbent calcination. This means that costs a), c) and d) would become zero. Second, the fraction of unused CaO would decrease because of the better calcium conversion

and lower sorbent attrition in the FB. As a consequence also the cost associated to landfilling of unused CaO would decrease. Thus, on the basis of these simple considerations the pre-treated sorbent appears to be promising for its use in FB coal-burning plants. It will be possible to carry out the detailed calculation of these economies once the cost per ton of the pre-treated sorbent will be available.

Finally, a further advantage for the sorbent supplier should be mentioned. Since the FB operator requires a well defined particle size distribution of the sorbent, after milling a significant fraction of undersize particles are typically produced. While this residue has practically no market for limestone, it is highly valuable for lime and can be used to produce slaked lime for the building market.

On the other side, it must be highlighted that since lime is hygroscopic and irritant, the storage and conveying devices should be sealed in order to avoid contact with moisture and with plant operators. This would of course add an initial cost to upgrade the storage and conveying devices of the plant.

Acknowledgements

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