



The influence of temperature on limestone sulfation and attrition under fluidized bed combustion conditions

Fabio Montagnaro^a, Piero Salatino^{b,c}, Fabrizio Scala^{b,*}

^a Dipartimento di Chimica – Università degli Studi di Napoli Federico II, Complesso Universitario del Monte di Sant'Angelo, 80126 Napoli, Italy

^b Istituto di Ricerche sulla Combustione – CNR, Piazzale Vincenzo Tecchio 80, 80125 Napoli, Italy

^c Dipartimento di Ingegneria Chimica – Università degli Studi di Napoli Federico II, Piazzale Vincenzo Tecchio 80, 80125 Napoli, Italy

ARTICLE INFO

Article history:

Received 14 October 2009

Accepted 16 October 2009

Keywords:

Fluidized bed combustion

Sulfation

Attrition

Elutriation

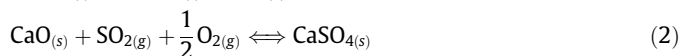
ABSTRACT

The influence of temperature on attrition of two limestones during desulfurization in a fluidized bed reactor was investigated. Differences in the microstructure of the two limestones were reflected by a different thickness of the sulfate shell formed upon sulfation and by a different value of the ultimate calcium conversion degree. Particle attrition and fragmentation were fairly small under moderately bubbling fluidization conditions for both limestones. An increase of temperature from 850 °C to 900 °C led to an increase of the attrition rate, most likely because of a particle weakening effect caused by a faster CO₂ evolution during calcination. This weakening effect, however, was not sufficiently strong to enhance particle fragmentation in the bed. The progress of sulfation, associated to the build-up of a hard sulfate shell around the particles, led in any case to a decrease of the extent of attrition. Sulfation at 900 °C was less effective than at 850 °C, and this was shown to be related to the porosimetric features of the different samples.

© 2009 Elsevier Inc. All rights reserved.

1. Introduction

Sulfur oxides generated during the Fluidized Bed (FB) combustion of solid fuels can be captured by means of the in situ injection of CaCO₃-based sorbents, such as limestones. Under overall oxidizing conditions and at atmospheric pressure, sorbent particle sulfation proceeds according to the following reactions:



and most typically conforms to the core–shell pattern, with a porous unreacted CaO inner core surrounded by a compact reacted CaSO₄ outer shell. This sulfate layer prevents the extensive sulfation of the core due to the strong SO₂ diffusional resistance offered by the shell itself; therefore, the degrees of calcium conversion seldom exceed 30–40% [1–6].

Substantial changes in the sorbents particle size distribution can be brought about by particle attrition and fragmentation in FB combustors [7–11]. Scala et al. [12–14] classified sorbent comminution phenomena in FB on the basis of the relevant breakage mechanism and size of generated fragments: *primary fragmentation* occurs immediately after the particles injection into the bed,

as a consequence of thermal stresses and of internal overpressure due to CO₂ emission, and results in the generation of either coarse or fine fragments; *attrition by abrasion* generates fine particles that are quickly elutriated, and is related to the occurrence of surface wear as the FB emulsion phase is sheared by the passage of bubbles; *secondary fragmentation* generates coarser fragments than attrition by abrasion, and is the result of high-velocity impacts among particles and targets such as bed material, reactor walls and internals in the grid region, or in the exit region of the riser and in the cyclone of a circulating bed.

The influence of FB operating temperature on the sorbent sulfur capture efficiency has been extensively studied and is somewhat complicated by the conflicting effects of surface reaction rate increase and available specific surface decrease (due to sintering phenomena) as reaction temperature increases [15–18]. Moreover, the influence of temperature on sulfur uptake should also be analyzed in the light of the competition between diffusional and kinetic resistances. However, an investigation on the effect of bed temperature on limestone attrition and fragmentation phenomena and their connection with the sulfation behavior and the microstructural properties is still lacking and appears of great practical interest. The aim of this work is to give a contribution in this direction, by investigating two limestones employed in an industrial-scale circulating FB boiler (termed Limestone A and Limestone B, respectively). The experimental campaign was carried out at 900 °C, with the aim of assessing the extent of primary fragmentation, attrition by abrasion and SO₂ uptake upon sorbent

* Corresponding author. Tel.: +39 081 7682969; fax: +39 081 5936936.
E-mail address: scala@irc.cnr.it (F. Scala).

Nomenclature

d	diameter (mm)
d_s	mean Sauter diameter (mm)
E	finer elutriation rate (g min^{-1})
F	molar rate (mol min^{-1})
n	moles fed to the reactor (mol)
t	time (min)
W_0	initial sorbent mass (g)
x	mass fraction (-)
X	degree of conversion (-)

Subscripts and superscripts

Ca, SO_2	relative to chemical species
i	relative to the i th interval

in, out relative to reactor inlet and outlet

Abbreviations

CC	computer controlled
EDX	energy dispersive X-ray
FB	fluidized bed
ID	internal diameter
NDIR	non-dispersive infra red
SEM	scanning electron microscope
XRD	X-ray diffraction

calcination/sulfation in a lab-scale FB reactor. The sorbents (both as-received and pre-processed) were also characterized from the standpoint of their chemical and microstructural features. These results were compared with those obtained in parallel and separate experiments carried out at 850 °C on the same two limestones and reported in a previous publication [19].

2. Experimental*2.1. Fluidized bed calcination and sulfation tests*

Calcination and sulfation tests were carried out in a stainless steel atmospheric bubbling FB reactor [12]. The reactor was an electrically-heated lab-scale facility, 40 mm ID and 1 m high. The gas distributor was a perforated plate with 50 holes of 0.5 mm ID in a triangular pitch. A two-exit brass head was mounted on top of the fluidization column, to convey flue gases through either of two cylindrical sintered brass filters (100% filtration efficiency for >10- μm particles). Alternated use of filters enabled time-resolved capture of elutriated fines at the exhaust. On-line analysis of SO_2 and CO_2 was accomplished by two NDIR analyzers.

The bed material consisted of mixtures of limestone and silica sand. The reactor was charged with a bed of 150 g of sand in the size range 0.85–1 mm and then heated to 900 °C prior to each experiment. The fluidizing gas superficial velocity was fixed at 0.8 m s^{-1} . It is worth recalling that tests conditions, corresponding to moderate bubbling, were such that sorbent particles were exposed to surface wear only (apart from primary fragmentation), while impact fragmentation could be ruled out.

During each FB calcination test a sample of fresh limestone (20 g sieved in the particle size range 0.4–0.6 mm) was loaded into the bed fluidized with air. The sample was calcined until complete conversion of CaCO_3 – CaO occurred (reaction (1)), as indicated by the CO_2 concentration in the flue gases. At the end of the test the limestone was easily sieved out of the bed material because of its smaller particle size, and particle size distribution determined by sieve analysis.

FB sulfation experiments were carried out by feeding a batch of fresh limestone of 20 g in the particle size range 0.4–0.6 mm in the bed fluidized with an SO_2 –oxygen–nitrogen mixture (1800 ppmv SO_2 , 8.5%v O_2 , balance N_2). Under these conditions calcination and sulfation occurred at the same time. At the end of the test the limestone was sieved out of the bed material and its particle size distribution characterized by sieving. The degree of calcium conversion during sulfation (reaction (2)) was calculated as a function of time by working out the SO_2 concentration at the exhaust according to:

$$X_{\text{Ca}}(t) = \frac{\int_0^t [F_{\text{SO}_2}^{\text{in}} - F_{\text{SO}_2}^{\text{out}}(t)] dt}{n_{\text{Ca}}} \quad (3)$$

where $F_{\text{SO}_2}^{\text{in}}$ and $F_{\text{SO}_2}^{\text{out}}(t)$ are, respectively, the molar rates of SO_2 fed to the reactor and in the exhaust gas, and n_{Ca} is the overall moles of calcium fed to the reactor. SO_2 oxidation to SO_3 inside the reactor was accounted for following the procedure detailed by Scala et al. [12]. $X_{\text{Ca}}(t)$ was reproducible within $X_{\text{Ca}}(t) \pm 1\%$.

During both kinds of experiments, rates of fines generation by attrition were determined by measuring the amount of fines carried over by the fluidizing gas and elutriated from the reactor. Elutriated fines were collected by means of the two-exit head previously described by letting the flue gas flow alternately through sequences of filters for definite periods of time. The difference between the weights of the filters after and before operation, divided by the time interval during which the filter was in operation, gave the average fines elutriation rate (E) relative to that interval.

2.2. Sorbents characterization

As-received, calcined and sulfated sorbent particles were characterized by: X-ray diffraction (XRD), carried out by means of a Philips PW1710 diffractometer, with a diffraction angle ranging from 5° to 60° 2θ $\text{CuK}\alpha$. XRD aimed at qualitative speciation of the main crystalline phases in the samples; mercury porosimetry, carried out by means of a Carlo Erba P2000 porosimeter operated at pressures ranging from 1 to 2000 bar (corresponding to pore radii in the range from 6800 to 4 nm). Porosimetric data were worked out in terms of cumulative pore undersize distributions; SEM–EDX analysis: particles cross sections of sulfated sorbent material (polished and embedded in epoxy resin) were analyzed by means of a Scanning Electron Microscope (SEM) – Philips XL30 – with a LaB_6 filament and equipped with an Energy Dispersive X-ray (EDX) probe – Edax DX-4 – for elemental mapping of sulfur and calcium throughout the particle cross section; Computer Controlled (CC) SEM–EDX analysis: an algorithm was set up for automated analysis of EDX elemental maps with the aim of obtaining semi-quantitative indicators of sulfur distribution throughout the particle cross section. This procedure generated probability density functions of pointwise sulfur contents that could be directly related to the sorbent particle sulfation pattern, and provided a reliable tool for semi-quantitative comparative analysis of samples of different nature [20,21].

3. Results and discussion*3.1. Fluidized bed calcination tests*

These tests were carried out to understand the influence of CO_2 evolution on particle attrition and fragmentation in the absence of a parallel sulfation reaction. Fig. 1a shows the cumulative particle

Download English Version:

<https://daneshyari.com/en/article/652579>

Download Persian Version:

<https://daneshyari.com/article/652579>

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