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Fluidized bed calcium looping cycles for CO_2 capture under oxy-firing calcination conditions: Part 1. Assessment of six limestones

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HIGHLIGHTS

- Six limestones were tested under realistic FB calcium looping conditions.
- Oxy-firing conditions during calcination severely depressed the CO_2 capture capacity.
- The presence of SO_2 further depressed the CO_2 capture capacity.
- The effect of SO_2 was strongly dependent on its concentration.
- Limestone attrition was limited under all experimental conditions.

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ABSTRACT

Six limestones were tested for CO_2 capture during calcium looping cycles in a lab-scale fluidized bed apparatus. Batch tests were carried out under alternating calcination–carbonation conditions representative of a process with calcination in an oxy-firing environment ($T = 940\,°C$, 70% CO_2). The effect of the presence of SO_2 was also studied at two concentration levels: 1500 ppm SO_2 during both carbonation and calcination, simulating CO_2 capture from uncontrolled flue gas and regeneration in an oxy-fired calciner burning high-sulfur coal; 75 ppm SO_2 during carbonation and 750 ppm SO_2 during calcination, simulating CO_2 capture from already desulfurized flue gas and regeneration in an oxy-fired calciner burning medium-sulfur coal. Limestone attrition processes were characterized during the tests by measuring the changes of the sorbent particle size distribution and the fines elutriation rate along conversion over repeated cycles.

Results showed that for all the limestones the CO_2 capture capacity decreased with the number of cycles reaching a very low asymptotic value. The combination of high bed temperature and high CO_2 concentration during the calcination stage significantly enhanced particle sintering. Moderate attrition rates were experienced by the sorbent particles mostly during the first cycle. In the subsequent cycles the attrition rate progressively declined, due to the concurrent chemical–thermal treatment making the sorbent surface increasingly hard. The presence of a high SO_2 concentration significantly depressed the sorbent CO_2 capture capacity, because of the buildup of a compact $CaSO_4$ layer on the particle surface. Under a lower SO_2 concentration level, the effect on CO_2 capture capacity was less important. In both conditions, limestone attrition was only influenced to a limited extent by SO_2. The slight variations of the sorbent particle size distribution indicated that very low particle fragmentation occurred over the repeated cycles.

1. Introduction

The increase of CO_2 concentration in the atmosphere is recognized as the main responsible for global warming [1]. Power plants firing fossil fuels represent the most important source of CO_2 emissions. A promising way for reducing such emissions is to separate CO_2 from flue gas to produce a concentrated CO_2 stream ready for sequestration (post-combustion capture). In such a process, CO_2 is separated from the flue gas by absorption with organic solvents such as ethanolamine or by reaction with solid particles such as lime [2]. The main advantage of a post-combustion process is the possibility to easily retrofit existing plants.

Recently, several experimental studies have been reported on CO_2 capture using Ca-based looping cycles in fluidized bed (FB)

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systems [3–5]. This process is based on the reversible exothermic calcium oxide carbonation reaction:

$$CaO(s) + CO_2(g) = CaCO_3(s) \quad (1)$$

Carbonation proceeds at a satisfactory rate at temperatures in the range 650–700 °C, while the reverse calcination reaction is carried out at 850–950 °C. The sorbent, typically calcium oxide derived from natural limestone or dolomite, is continuously cycled between two reactors. In the first reactor (the carbonator) CaO particles capture CO_2 from the flue gas. The carbonated sorbent particles are then circulated to the other reactor (the calciner) where CO_2 release takes place. The regenerated CaO particles are returned to the carbonator, leaving a concentrated stream of CO_2 ready for sequestration.

The typical reactor configuration for the calcium looping process consists of two interconnected fluidized beds. This configuration permits solids circulation between the reactors and ensures an intimate contact between the solid and gas phases. The fluidizing gas in the carbonator is the flue gas coming from the combustion process, while the fluidizing gas in the calciner must establish an oxy-firing environment either with recycled CO_2 or a CO_2/H_2O mixture that allows a lower temperature in the calciner.

In early work Barker [6] studied the effect of consecutive cycles of carbonation and calcination and found that the CO_2 capture capacity of limestone decreased with the number of cycles. This result has been more recently confirmed by other authors [7–9]. The main cause of this decrease has been identified in sorbent sintering and in the associated change of pore size, which primarily depends on the operating temperature and on the duration of the cycles. The CO_2 capture capacity of the fresh sorbent decreases quickly during the first cycles until an asymptotic value is reached, which then remains approximately constant over many cycles.

A further problem may be represented by the presence of SO_2 in the flue gas, which reacts with lime to form $CaSO_4$:

$$CaO(s) + SO_2(g) + \frac{1}{2}O_2(g) = CaSO_4(s) \quad (2)$$

The outer sulfated layer formed by reaction (2) may hinder the diffusion of CO_2 in the pores and affects the mechanical properties of the sorbent [3,8,10]. Unfortunately, reaction (2) is irreversible in the temperature range used for calcium looping, so that CaO reacted with SO_2 is permanently lost [11,12]. This reaction further reduces the sorbent CO_2 capture capacity.

In a FB reactor limestone particles are also subjected to attrition. Limestone attrition during FB calcination and sulfation has been extensively studied [13–16]. Three attrition mechanisms were identified: primary fragmentation, secondary fragmentation and attrition by abrasion. Primary fragmentation occurs upon injection of the sorbent particles in the hot reactor, as a consequence of thermal stresses due to fast heating of the particles, and of internal overpressures due to CO_2 release during calcination. Both coarse and fine fragments are generated during this process. On the other hand, secondary fragmentation and attrition by abrasion are caused by the mechanical stresses due to collisions among particles and with the FB internals. Secondary fragmentation generates coarser fragments, while attrition by abrasion generates finer ones. During the calcium looping process, particle attrition may determine both a change of the bed particle size distribution and a calcium loss from the circulating loop, as elutriable fines leaving the cyclone with the gas stream. This loss of material contributes together with sorbent deactivation to define the required make-up of fresh sorbent.

Blamey et al. [5] report that there is limited available literature addressing attrition of limestone upon carbonation and calcination cycling. Attrition of one limestone was recently studied during calcium looping cycles under relatively mild conditions [17,18]. The attrition rate of the sorbent was found to be larger during the first cycle declining during the subsequent cycles. Bed temperature and CO_2 concentration both influenced the sorbent behavior in the tests. The presence of SO_2 in the flue gas decreased the CO_2 capture capacity, but only moderately affected attrition.

In this work the CO_2 capture performance and the extent of particle attrition of limestones was studied in a bubbling FB by simulating the calcium looping process with consecutive calcination/carbonation cycles under more realistic oxy-firing conditions. Six limestones with similar chemical composition were selected to check if they behaved differently during the tests. The influence of the SO_2 concentration level on the CO_2 capture capacity and on particle attrition was also investigated. In a separate activity [19] the samples produced during these tests have been characterized by means of X-ray Diffraction (XRD) and Energy Dispersive X-ray Spectroscopy–Scanning Electron Microscopy (EDS–SEM), as well as N_2-porosimetry.

2. Experimental

2.1. Materials and experimental set-up

The six raw sorbents used in the tests were all high-calcium limestones (calcite >94% by weight) from different European countries. Table 1 shows their chemical composition, as obtained by means of X-ray Fluorescence (Instrument: SRS 3400, Bruker). Fused beads were prepared for the analysis. The SO_3 content of the sorbents was measured using wet chemical analysis according to EN 196-2. Gases used in the tests were mixtures of air, CO_2 and SO_2/N_2.

The tests were performed in a stainless steel bubbling FB reactor, 40 mm ID operated at atmospheric pressure (Fig. 1). The reactor consists of three sections: (a) the preheater/premixer of the fluidizing gas, 0.66 m high; (b) the fluidization column, 0.95 m high; and (c) the brass two-exit head placed on top of the reactor with a hopper to feed the solids in the reactor and connected with the exhaust line. The gas distributor is a perforated plate with 55 holes of 0.5 mm diameter in a triangular pitch. The reactor is electrically heated with two semi-cylindrical furnaces. A type-K thermocouple, located 40 mm above the gas distributor, allows measuring the reactor temperature and is connected with the PID temperature controller of the furnaces. The two-exit head is used to convey flue gases alternatively through one of two cylindrical sintered brass filters, whose filtration efficiency is 1 for >10 μm-

Table 1
Chemical composition of limestones (% by weight).

Sample	Origin	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	TiO_2	LOI	Sum
Massicci	Italy	1.11	0.37	0.14	54.53	0.44	0.06	0.02	0.00	0.02	43.13	99.82
Schwabian Alb	Germany	3.51	0.50	0.18	53.64	0.51	0.08	0.02	0.00	0.02	41.94	100.40
EnBW	Germany	0.30	0.13	0.08	56.01	0.26	0.00	0.02	0.00	0.01	43.50	100.31
Xirorema Sand	Greece	0.83	0.26	0.36	55.13	0.56	0.00	0.01	0.00	0.02	42.87	100.04
Tarnow Opolski	Poland	1.73	0.34	0.39	54.04	0.94	0.00	0.02	0.00	0.02	42.64	100.12
Czatkowice	Poland	3.91	0.39	0.31	52.88	0.99	0.00	0.02	0.00	0.03	41.43	99.96