

LIMESTONE ATTRITION DURING FLUIDIZED BED CALCIUM LOOPING CYCLES FOR CO₂ CAPTURE: THE EFFECT OF SO₂

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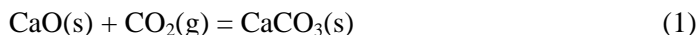
Abstract

Attrition of six different limestones was studied during calcium looping cycles for CO₂ capture in a lab-scale fluidized bed apparatus. The tests were carried out under realistic conditions representative of a process with calcination in an oxy-firing environment. The focus of the activity was to investigate the effect of the presence of SO₂ both in the calcination and in the carbonation stages. Experiments without SO₂ were also performed, for comparison. Attrition processes were characterized by following the modifications of bed sorbent particle size distribution and the elutriation rates of fines throughout conversion over repeated cycles.

Results showed that the presence of a high SO₂ concentration significantly depressed the sorbent CO₂ capture capacity, most likely because of the formation of an impervious CaSO₄ layer on the surface of the particles. The extent of limestone attrition was only slightly influenced by the presence of SO₂. The analysis of the particle size distribution of the bed material over repeated calcination/carbonation cycles indicated that particle fragmentation was limited.

Introduction

Several experimental studies have reported on CO₂ capture using Ca-based looping cycles in fluidized bed systems [1-3]. The process is based on the reversible exothermic carbonation reaction:



Carbonation proceeds with 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, is repeatedly cycled between two reactors. In one reactor (the carbonator) carbonation of CaO particles occurs, capturing CO₂ from the flue gas. The sorbent particles are then

circulated to another reactor (the calciner) where calcination takes place. The regenerated CaO particles are returned to the carbonator, leaving a concentrated stream of CO₂ 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 with either recycled CO₂ or a CO₂/H₂O mixture that enables a lower temperature in the calciner.

In early work Barker [4] studied the effect of repeated cycles of carbonation and calcination of limestone and found that the CO₂ capture capacity of the sorbent decreased with the number of cycles. This result has been more recently confirmed by other authors [5-7]. The main cause of this decrease has been identified in sorbent sintering and in the associated changes of pore size, which mostly depends on the process temperature and on the duration of the cycles.

Another problem is represented by the possible presence of SO₂ in the flue gas, which reacts with lime to form CaSO₄ according to the following reaction:



The outer sulfated layer formed by reaction (2) hinders the diffusion of CO₂ in the pores and affects the mechanical properties of the material [1,6,8]. Unfortunately, reaction (2) is irreversible in the temperature range of interest so that the lime reacted with SO₂ is permanently lost. This reaction further reduces the CO₂ capture capacity of the sorbent.

In a fluidized bed reactor limestone particles are also subjected to attrition phenomena. Several studies on limestone attrition during calcination and sulfation in fluidized beds have been reported in the literature [9-12]. In the context of the calcium looping process, particle attrition determines a net calcium loss from the circulating loop, as elutriable fines leaving the cyclone with the gas stream. This loss of material adds to sorbent deactivation and contributes to the required make-up of fresh sorbent.

Experimental

The six raw sorbents used in the tests were all high-calcium limestones (calcite > 94% by weight) from different European countries. Gases used in the tests were mixtures of air, CO₂ and SO₂/N₂.

The experiments were carried out in a stainless steel bubbling fluidized bed reactor, 40 mm ID operated at atmospheric pressure. 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; 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 placed around the upper part of the preheater/premixer and the lower part of the fluidization column. The two-exit head is used to convey flue gases through either of two cylindrical sintered brass filters, whose filtration efficiency is 1 for $> 10\text{ }\mu\text{m}$ -particles. Alternated use of the filters enables time-resolved capture of elutriated fines at the exhaust. Downstream of the two-exit head, a fraction of the exhaust gas is continuously sampled to measure CO_2 and SO_2 concentrations with a NDIR analyzer in order to monitor the progress of reactions.

Five calcination/carbonation cycles were carried out in all the experiments using an initial amount of 20 g of fresh limestone, sieved in the size range 0.4-0.6 mm. The bed consisted of 150 g of silica sand in the size range 0.85-1.0 mm and the fluidizing velocities were 0.7 and 0.6 m/s in the calcination and carbonation stages. Before each test the reactor was charged with the silica sand and heated up to the desired temperature (940°C). The bed was fluidized with a gas mixture containing 70% CO_2 . These conditions were selected to simulate calcination in an oxy-firing environment. When the set temperature was reached, the limestone particles were injected in the reactor through the hopper. The progress of calcination was followed during the run by measuring the CO_2 concentration at the exhaust. The run ended when calcination was complete (20 min). At this point the bed was rapidly discharged and cooled down. The sand was separated from the limestone by sieving and re-injected in the fluidized bed reactor. The temperature of the bed was then set to the carbonation temperature (650°C). When the new temperature was reached the carbonation reaction was started by fluidizing the bed with a mixture of air and CO_2 (15% v/v), and injecting the calcined sorbent particles. The progress of carbonation was followed during the run by measuring the CO_2 concentration at the exhaust. Again, the run ended when carbonation was practically complete (15 min). The bed was rapidly discharged and cooled down (in 100% CO_2 to avoid possible calcination). The procedure described before was then repeated in all the cycles.

During the experiments the rates of fines generation were determined by measuring the amount of fines carried over by the fluidizing gas and elutriated from the reactor. The Particle Size Distribution (PSD) of the sorbent was determined by sieving the bed material after each calcination and carbonation stage. The CO_2 capture capacity of the sorbent during the carbonation stage was evaluated from the CO_2 concentration profile at the exhaust. The total amount, by mass, of CO_2 uptaken during the experiment, divided by the initial amount of limestone (20 g), gave the sorbent capture capacity.

The effect of SO_2 on calcium looping was studied by injecting SO_2 in the inlet gas during both calcination and carbonation stages. Severe conditions were used (1500 ppm SO_2), simulating CO_2 capture from uncontrolled flue gas and regeneration in an oxy-fired calciner burning high-sulfur coal. Calcium conversion to sulfate during calcination/carbonation was evaluated from SO_2 concentration profiles at the exhaust.

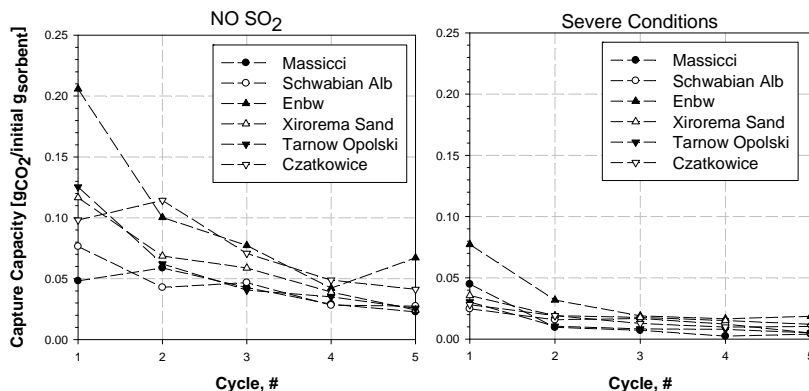


Figure 1. CO₂ capture capacity of the six limestones as a function of the number of cycles for experiments carried out without SO₂ (left) and with SO₂ (right).

Results

Figure 1 reports the sorbent CO₂ capture capacity as a function of the number of cycles for the six limestones tested. Results of tests with or without SO₂ are compared. As expected, the capture capacity decreases with the number of cycles for all the limestones reaching an asymptotic value already after the fourth cycle. This residual capture capacity is much lower than that typically found under milder conditions [3]. The explanation for this result lies in the combination of high temperature and high concentration of CO₂ during calcination that significantly enhances sintering [13].

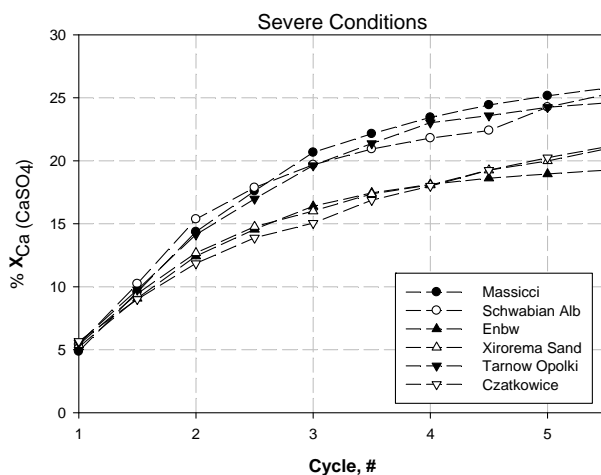


Figure 2. Calcium conversion degree to sulfate of the six limestones as a function of the number of cycles (each data point represents conversion after half cycle).

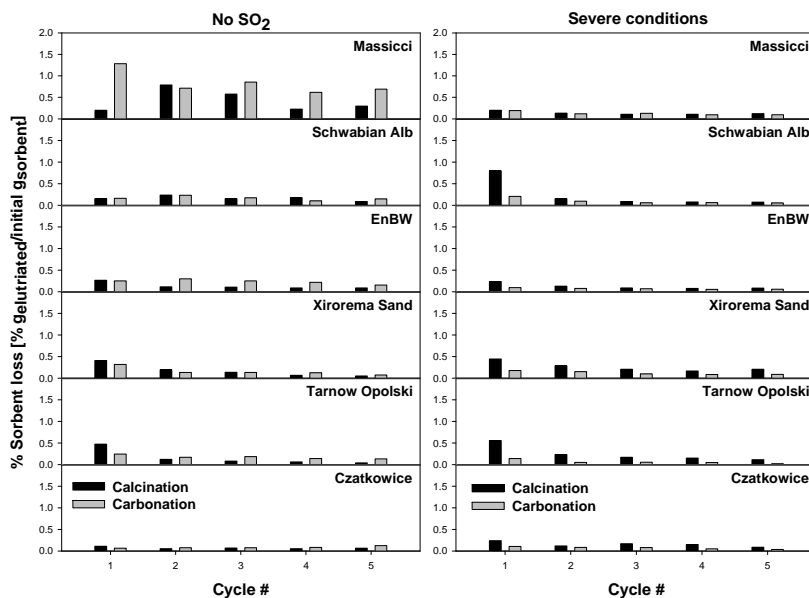


Figure 3. Percent mass of elutriated fines for the six limestones as a function of the number of cycles during experiments without SO_2 (left) and with SO_2 (right).

When a high SO_2 concentration is present in the gas flow a further decrease of the CO_2 capture capacity is found for all the limestones. This behavior can be explained by the progressive formation of a calcium sulfate shell around the particles that hinders intraparticle diffusion of CO_2 in the pores of the sorbent. It is interesting to note, however, that the relative ranking of the six limestones towards CO_2 capture is not altered by the presence of SO_2 . Figure 2 reports the calcium conversion degree to sulfate during the tests. The three best performing limestones (EnBW, Xirorema Sand and Czatkowice) are those sulfating to a lower extent.

The PSD was evaluated after every calcination and carbonation stage for each limestone. All the PSD curves had a similar shape, with only slight differences in the amount of produced fragments among the six limestones. The presence of SO_2 appeared to slightly reduce the extent of fragmentation for all the limestones. Altogether, analysis of the PSD curves indicated that particle fragmentation was limited, as witnessed by the small amount of particles with size $< 400 \mu\text{m}$.

Figure 3 reports the mass of elutriated fines (as % of the initial mass) collected during each calcination and carbonation stage as a function of the number of cycles, with or without the presence of SO_2 . As a general trend, it can be noted that for all the limestones the fines elutriation rate is relatively large only during the first cycle and decreases with the number of cycles. This suggests that hardening of the particle surface takes place over the cycles, which is consistent with the progressive sintering of the sorbent. The average fines elutriation rate is approximately the same during the calcination and the carbonation stages. This

indicates that sintering is able to harden the particles irrespective of the chemical composition (CaO or CaCO_3). Comparison of the results with and without SO_2 shows that when a high SO_2 concentration was used, the fines elutriation rate slightly decreased. It appears that a more compact calcium sulfate shell is formed increasing the hardness of the particles.

On the basis of the above results, an average limestone loss rate by elutriation from a dual fluidized bed system can be estimated in the range 0.3-0.5%/h under realistic conditions (a larger value of 1.3%/h was evaluated for Massicci). These values are lower than the 2%/h found by Charitos et al. [14] during continuous operation of a 10 kW_{th} dual fluidized bed facility. It must be underlined, however, that in this plant the calciner was operated as a high velocity riser (4-6 m/s), and that a limestone with a smaller particle size (0.2-0.4 mm) was used in the experiments. On the whole, as discussed by Charitos et al. [14], these figures would not represent a process limitation, since they are well below the expected sorbent make-up rate required to maintain sufficient sorbent activity.

Acknowledgements

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