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FLUIDIZED BED CALCIUM LOOPING CYCLES FOR CO₂ CAPTURE: A COMPARISON BETWEEN DOLOMITE AND LIMESTONE

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ABSTRACT

CO₂ capture and attrition behavior of a dolomite were studied during calcium looping cycles in a lab-scale fluidized bed. Results were compared to those obtained with six limestones in similar tests. The experiments were carried out under conditions representative of a process with calcination in an oxy-firing environment (T = 940°C, CO₂ = 70%_{v/v}), with or without the presence of SO₂. Results showed that the CO₂ capture capacity of the dolomite was larger than that of the limestones, in spite of the lower calcium content of the sorbent. The presence of SO₂ depressed the sorbent CO₂ capture capacity. Contrary to the limestones, the dolomite was subject to extensive attrition and fragmentation.

INTRODUCTION

The increase of CO₂ 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 CO₂ emissions. A promising way for reducing such emissions is to separate CO₂ from flue gas to produce a concentrated CO₂ stream ready for sequestration. In a post-combustion process, CO₂ 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 the post-combustion process is the possibility to easily retrofit existing plants.

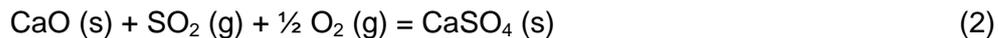
Recently, several experimental activities have been reported on CO₂ capture using Ca-based looping cycles in fluidized bed systems (3-5). The process is based on the reversible exothermic carbonation reaction:



Carbonation proceeds with a satisfactory rate at temperatures in the range 650–700°C, while the reverse calcination reaction is carried out at 900–950°C. The sorbent, typically CaO derived from natural limestone, is repeatedly cycled between two reactors. In one reactor carbonation of CaO particles occurs, capturing CO₂ from the flue gas. The sorbent is then circulated to another reactor 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 this 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.

Many authors found that the CO₂ capture capacity of Ca-based sorbents decreased with the number of cycles (6-9). The main reason was identified in sorbent sintering and in the associated change of pore size. 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 sulfation 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 (3,8,10). 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 (11-14). More recently the study has been extended to limestone attrition under calcium looping conditions (15-17). In the context of calcium looping, 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.

Most of the experimental work on calcium looping reported to date has been directed to characterize the performance of limestone, while only limited activity has been carried out with dolomite (18). The aim of this work was to study the CO₂ capture performance and the attrition propensity of a dolomite by simulating the calcium looping process with repeated calcination/carbonation cycles under realistic conditions in a lab-scale bubbling fluidized bed. The focus of this activity was to quantify the extent of particle attrition during the cycles and the effect of chemical reactions on the sorbent mechanical resistance. The effect of the presence of SO₂ in the gaseous environment on the CO₂ capture capacity and on the extent of particle attrition was also studied. The performance of the dolomite was compared to that of six limestones tested in similar conditions (17).

EXPERIMENTAL

Materials and experimental set-up

A Polish dolomite (Redziny) and six European high-calcium limestones (for comparison) were tested in this work, whose chemical analysis is reported in Table 1. 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 is electrically heated with two semi-cylindrical furnaces. A two-exit head is used to convey flue gases through either of two cylindrical sintered brass filters, whose filtration efficiency is 1 for > 10 μm-particles.

Table 1: Chemical composition of sorbents (% by weight).

Sample	Origin	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	TiO ₂	LOI
Massicci	Italy	1.11	0.37	0.14	54.53	0.44	0.06	0.02	0.00	0.02	43.13
Schwabian Alb	Germany	3.51	0.50	0.18	53.64	0.51	0.08	0.02	0.00	0.02	41.94
EnBW	Germany	0.30	0.13	0.08	56.01	0.26	0.00	0.02	0.00	0.01	43.50
Xirorema Sand	Greece	0.83	0.26	0.36	55.13	0.56	0.00	0.01	0.00	0.02	42.87
Tarnów Opolski	Poland	1.73	0.34	0.39	54.04	0.94	0.00	0.02	0.00	0.02	42.64
Czatkowice	Poland	3.91	0.39	0.31	52.88	0.99	0.00	0.02	0.00	0.03	41.43
Dol. Redziny	Poland	0.91	0.22	0.25	31.80	20.90	0.00	0.00	0.00	0.02	45.12

Alternated use of the filters enables time-resolved capture of elutriated fines at the exhaust. Downstream of the head, the exhaust gas is continuously sampled to measure CO₂ and SO₂ concentrations with a NDIR analyzer in order to monitor the progress of reactions. More details of the apparatus can be found in (11,17).

Procedures

Five calcination/carbonation cycles were carried out in all the experiments using an initial amount of 20 g of fresh sorbent, sieved in the range size 0.4-0.6 mm. The sorbent was diluted in a bed of sand to avoid excessive temperature variations during reactions. The bed consisted of 150 g of silica sand in the size range 0.85-1.0 mm and the gas velocities were 0.7 and 0.6 m/s in the calcination and in the carbonation stages, respectively. It is noted that the presence of sand may somewhat enhance sorbent attrition as discussed by Scala et al. (11).

Before each test the reactor was charged with the sand and heated up to the desired temperature (940°C). The bed was fluidized with a gas mixture containing 70% CO₂. These experimental conditions were selected to simulate calcination in an oxy-firing environment. In fact, it was found in preliminary tests that a bed temperature as high as 940°C was necessary to calcine the sorbent at reasonable rates at 70% CO₂. When the set temperature was reached, the limestone particles were injected in the reactor through the hopper. After injection, the sorbent underwent rapid heating from ambient temperature to the reactor temperature, resulting in a thermal shock. The run ended when calcination was complete. 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 CO₂ (15%), and by injecting the calcined sorbent through the hopper. Again, the run ended when carbonation was complete. The bed was rapidly discharged and cooled down (in 100% CO₂ to avoid possible calcination). This procedure was then repeated in all the cycles. The same duration of the first calcination stage (20 min) was used for the subsequent calcination stages, and the same criterion was applied for the duration of the carbonation stages (15 min).

During the tests, fines generation rate was determined by measuring the amount of fines elutriated from the reactor. The difference between the weight of filters after and before operation, divided by the time interval of filter operation, gave the average elutriation rate in that interval. The Particle Size Distribution (PSD) of the sorbent was determined by sieving the bed material after each stage. Sieving was carried out gently to avoid further particle attrition, but rapidly, because of the propensity of the calcined sorbent to absorb moisture in ambient air.

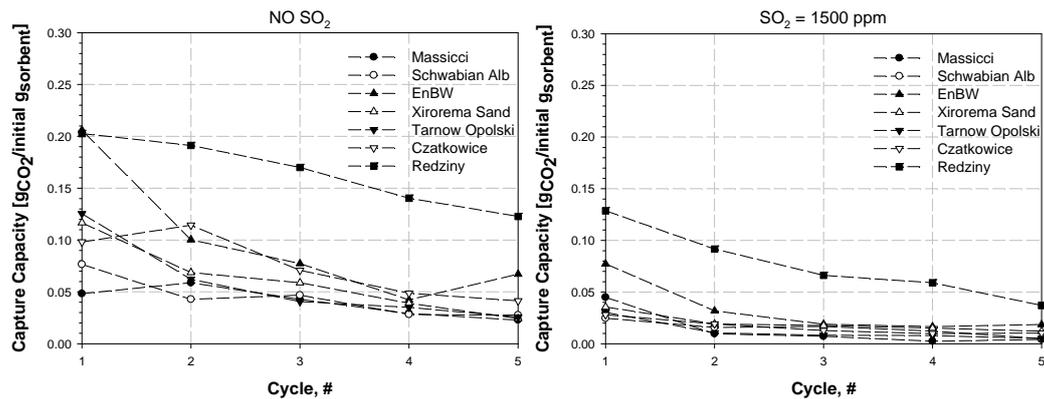


Figure 1: CO₂ capture capacity of the sorbents as a function of the number of cycles for experiments carried out without SO₂ (left) and with SO₂ (right).

Tests carried out to study the effect of sulfur dioxide were performed under the same conditions as those without SO₂, the only difference being the presence of 1500 ppm of SO₂ in the inlet gas, both during calcination and carbonation. This concentration was selected to simulate CO₂ capture from uncontrolled flue gas and regeneration in an oxy-fired calciner burning high-sulfur coal.

RESULTS

CO₂ capture capacity

Fig. 1 reports the sorbent capture capacity as a function of the number of cycles for the six limestones (17) and the dolomite (Redziny) tested under the same operating conditions. Results of tests with or without SO₂ (1500 ppm) are compared. As expected, the capture capacity decreased with the number of cycles for all the sorbents, typically reaching an asymptotic value already after the fourth cycle. This residual capture capacity of the limestones (0.02-0.07 g_{CO₂}/g_{sorbent} in the tests without SO₂) was much lower than that typically found under milder conditions (of the order of 0.1-0.2 g_{CO₂}/g_{sorbent} as reported by Blamey et al. (5)). The obvious explanation for this result lies in the experimental evidence that the combination of high temperature and high concentration of CO₂ during calcination significantly enhances sintering (19).

The CO₂ capture capacity of the dolomite was larger than that of the limestones and remained relatively large along the cycles in spite of the lower Ca content of the sorbent and of the high temperature and CO₂ concentration during calcination. The residual capture capacity after the 5th cycle for the dolomite was 0.12 g_{CO₂}/g_{sorbent}. This result highlights the positive effect of the large magnesium content of the dolomite in preserving Ca reactivity and reducing particle sintering.

When SO₂ was present a further decrease of the CO₂ capture capacity (of the order of 3-6 times) was found for all the sorbents. The residual capture capacity was 0.004-0.04 g_{CO₂}/g_{sorbent} in this case. This behavior can be explained by the progressive formation of a calcium sulfate shell around the particles (both during calcination and carbonation) that hinders intraparticle diffusion of CO₂ in the pores of the sorbent. Noteworthy, the CO₂ capture capacity of the dolomite remained larger than that of the limestones along the cycles.

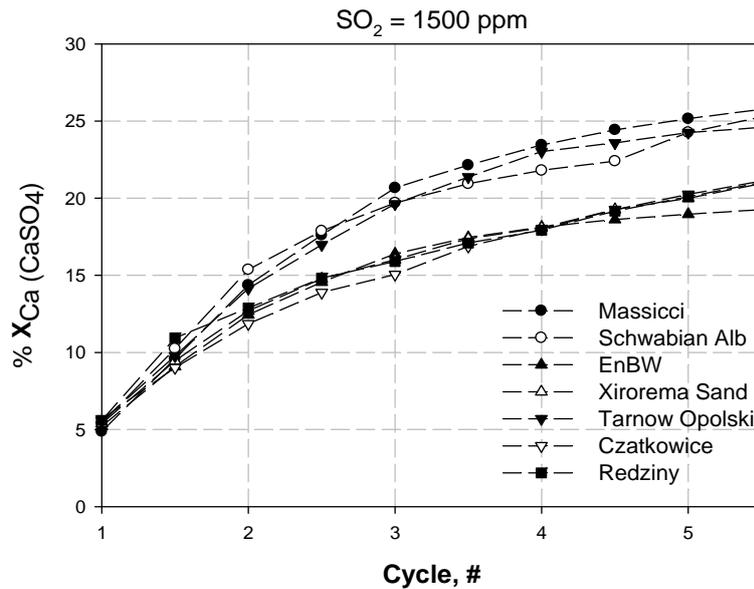


Figure 2: Calcium conversion degree of the sorbents to sulfate as a function of the number of cycles (each data point represents conversion after half cycle).

Fig. 2 reports the cumulative calcium conversion degree to sulfate during the tests, as calculated from the SO₂ concentration profiles at the exhaust. It appears that the best performing sorbents (Redziny dolomite, and EnBW, Xirorema Sand and Czatkowice limestones) were those sulfating to a lower extent.

Particle size distribution

Fig. 3 compares the measured particle size distributions (PSDs) of the six limestones and of the dolomite after the fifth carbonation stage in tests carried out with or without SO₂ (1500 ppm) in the fluidizing gas. The PSD was evaluated after every calcination and carbonation stage for each limestone. However, only the PSDs recorded after the fifth carbonation were plotted in the figures, for clarity, since all the other PSDs were very similar to each other.

It can be observed that for the six limestones all the PSD curves have a similar shape, with only slight differences in the amount of produced fragments. The presence of SO₂ appears to slightly reduce the extent of fragmentation for all the limestones. Altogether, analysis of the PSD curves indicates that particle fragmentation is limited, as witnessed by the small amount of retrieved particles with size < 400 μm.

As regards the dolomite sorbent, particle fragmentation was extensive. The mass fraction of fragments after the 5th cycle was about three times more than for the limestones. Particle fragmentation was mostly active upon the 1st calcination (not shown in the figure). The most likely reason for this result is that decomposition of magnesium carbonate only occurs during this stage, since magnesium does not contribute to the CO₂ capture process during the carbonation stages. Also for the dolomite the presence of SO₂ slightly reduced the extent of fragmentation.

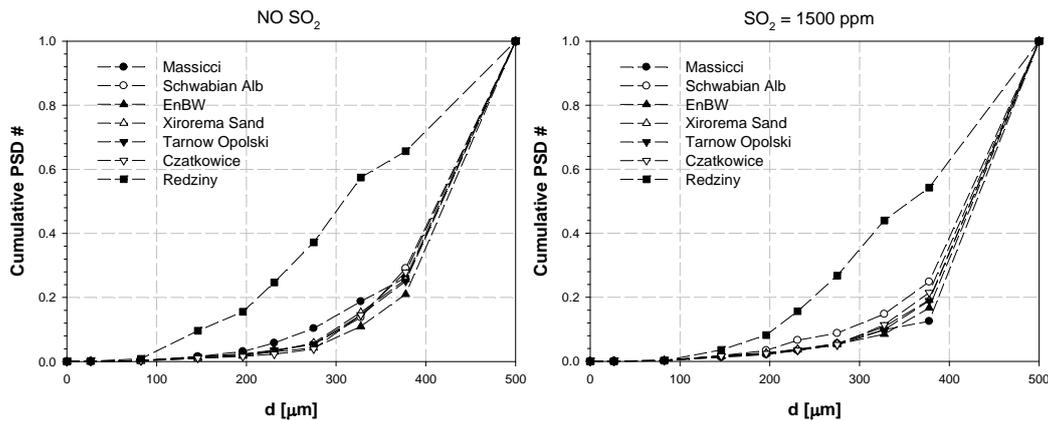


Figure 3: Cumulative particle undersize distribution of the sorbents after the 5th carbonation stage. Left: without SO₂. Right: with SO₂.

Elutriation rate

Fig. 4 reports the average elutriation loss of fines collected during each calcination and carbonation stage as a function of the number of cycles, in tests carried out with or without the presence of 1500 ppm SO₂. As a general trend, it can be noted that for all the sorbents fines elutriation was relatively large only during the first cycle and decreased with the number of cycles. This suggests that hardening of the particle surface took place over the cycles, which is consistent with the progressive sintering of the sorbent.

It can be noted that for the six limestones the average fines elutriation rate was approximately the same during the calcination and the carbonation stages (it was typically slightly larger during the carbonation stage in the tests without SO₂, the opposite in the tests with SO₂). This indicates that sintering was able to harden the particles irrespective of the chemical composition (CaO or CaCO₃). Comparison of the results with or without SO₂ indicates that the elutriation rates were similar, slightly lower (of the order of 1-2 times, except for Massicci where it is 5 times lower) when SO₂ was present in the gas. It appears that the effect of sintering prevails over the formation of a calcium sulfate shell in determining the surface hardness of the particles.

The attrition rate of the dolomite was larger than that of the limestones, and was not influenced significantly by the presence of SO₂. This result can be attributed to two concurring factors. On the one side, sintering appears to be reduced for this sorbent, making the particles softer. On the other side, the extensive particle fragmentation (Fig. 3) increased the sorbent surface area subject to attrition in the bed.

On the basis of the above results, an average sorbent loss rate by elutriation from a dual fluidized bed system can be estimated of the order of 0.5%/h for limestone and of the order of 2.0%/h for dolomite, under realistic conditions. On the whole, as discussed by Charitos et al. (20), 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.

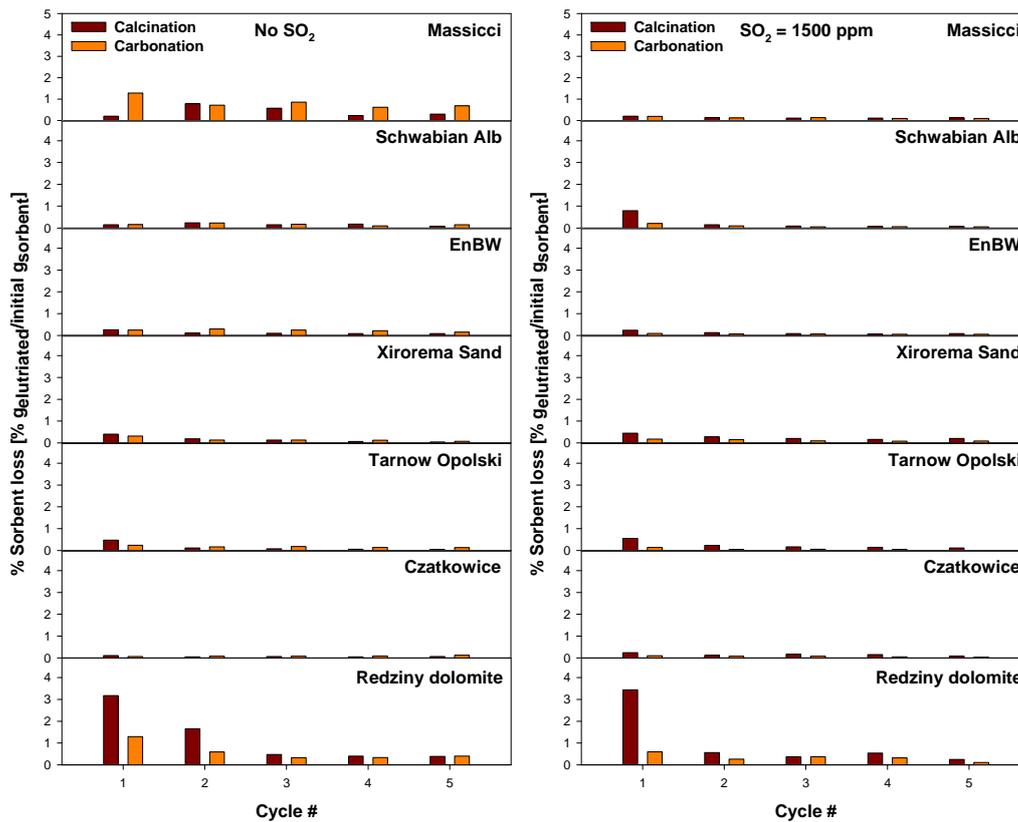


Figure 4: Average fines elutriation loss as a function of the number of cycles for experiments carried out without SO₂ (left) and with SO₂ (right).

CONCLUSIONS

The CO₂ capture capacity and the attrition propensity of a dolomite were assessed during multiple calcination/carbonation cycles in a lab-scale fluidized bed reactor under conditions representative of a process with calcination in an oxy-firing environment. In addition, the effect of the presence of SO₂ in the flue gas was investigated. The performance of the dolomite was compared with that of six high-calcium limestones tested under the same operating conditions.

Results showed that the CO₂ capture capacity decreased with the cycles, as expected. The presence of a high CO₂ concentration during calcination (70%) and a high calcination temperature (940°C) determined a significant decrease of the CO₂ capacity for all the limestones, due to the enhancement of particle sintering. This effect, however, was less important for the dolomite. The CO₂ capture capacity of the dolomite was always larger than that of the limestones, and remained relatively large along the cycles in spite of the lower calcium content of the sorbent. This result highlights the positive effect of the large magnesium content of the dolomite in reducing the particle sintering effect.

The analysis of the particle size distribution (PSD) of bed material over repeated calcination/carbonation cycles indicated that particle fragmentation was limited for all the limestones. The fines elutriation rate was relatively large only during the first cycle and decreased with the number of cycles, since the combined chemical-thermal treatment affected the particle structure making it increasingly

hard. On the contrary, the dolomite sorbent was subject to extensive attrition and fragmentation. The PSD of the dolomite significantly changed along the cycles.

The presence of SO₂ further depressed the CO₂ capture capacity for all the sorbents, most likely because of the formation of an impervious CaSO₄ layer on the surface of the particles. Conversely, attrition was only slightly affected by the presence of SO₂.

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