PERFORMANCE COMPARISON BETWEEN DOLOMITE AND LIMESTONE IN FLUIDIZED BED Ca-LOOPING CYCLES FOR CO₂ CAPTURE

A. Coppola*, F. Montagnaro**, P. Salatino***, F. Scala*

a.coppola@irc.cnr.it

*Istituto di Ricerche sulla Combustione, Consiglio Nazionale delle Ricerche
Piazzale Vincenzo Tecchio 80, 80125 Napoli, Italy

**Dipartimento di Scienze Chimiche, Università degli Studi di Napoli Federico II
Complesso Universitario di Monte Sant’Angelo, 80126 Napoli, Italy

***Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale,
Università degli Studi di Napoli Federico II
Piazzale Vincenzo Tecchio 80, 80125 Napoli, Italy

Abstract
The CO₂ capture capacity and the 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 limestone, the dolomite was subject to extensive attrition and fragmentation.

Introduction
Ca-based looping cycles represent a promising post-combustion technology to remove CO₂ from flue gas. The main advantages of this technology are the use of cheap Ca-based sorbents and the possibility to easily retrofit existing plants [1]. Recently, several experimental activities have been reported in the literature on CO₂ capture using calcium looping in fluidized bed systems [2]. The process is based on the reversible exothermic carbonation reaction:

\[ \text{CaO}_{(s)} + \text{CO}_2{(g)} = \text{CaCO}_3{(s)} \] (1)

The Ca-based sorbent (typically derived from natural limestone) is continuously cycled between two reactors. In one reactor (the carbonator, 650-700°C) carbonation of CaO particles occurs, capturing CO₂ from the flue gas. The sorbent particles are then sent to another reactor (the calciner, 900-950°C) 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. On the other hand, the use of fluidized beds promotes attrition phenomena which determine a net calcium loss from the circulating loop [3,4], as elutriable fines leaving the cyclone with the gas stream.

Many authors found that the CO₂ capture capacity of Ca-based sorbents decreased with the number of cycles [5]. 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 (reducing the CO₂ capture capacity of the sorbent) according to the following sulfation reaction:

\[ \text{CaO}(s) + \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) = \text{CaSO}_4(s) \] (2)

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

Most of the experimental work on calcium looping reported to date has been directed to characterize of the performance of limestone, while only limited activity has considered dolomite as a possible sorbent [7]. The aim of this work was to quantify the CO₂ capture performance and the attrition propensity of a dolomite, compared to those relative to six limestones tested in similar conditions [4], under simulated realistic calcium looping process conditions. 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.

Experimental

Materials and experimental set-up. A Polish dolomite (Redziny) was used in this work, whose chemical analysis was: CaO = 31.80%; MgO = 20.90%; SiO₂ = 0.91%; Fe₂O₃ = 0.25%; Al₂O₃ = 0.22%; TiO₂ = 0.02%; LOI = 45.12%. The six limestones tested for comparison were all high-calcium limestones (calcite > 94% by weight) from different European countries, whose composition is reported in [4]. 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. Further details of the apparatus are reported elsewhere [4,8].

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 silica sand (150 g, 0.85-1.0 mm) to avoid excessive temperature variations during calcination and carbonation reactions. More details of the procedures can be found in [4]. The main operating conditions of the experiments are reported in Table 1.

During the experiments fines generation rates were determined by measuring the amount of fines elutriated from the reactor collected by means of filters. The
Particle Size Distribution (PSD) of the sorbent was determined by sieving the bed material after each calcination and carbonation stage.

**Table 3.** FB tests experimental conditions.

<table>
<thead>
<tr>
<th>Calcination/Carbonation</th>
<th>Without SO₂</th>
<th>With SO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration [min]</td>
<td>20/15</td>
<td>20/15</td>
</tr>
<tr>
<td>Temperature [°C]</td>
<td>940/650</td>
<td>940/650</td>
</tr>
<tr>
<td>Inlet CO₂ [% v/v]</td>
<td>70/15</td>
<td>70/15</td>
</tr>
<tr>
<td>Inlet SO₂ [ppm]</td>
<td>0/0</td>
<td>1500/1500</td>
</tr>
</tbody>
</table>

Tests carried out to study the effect of SO₂ on calcium looping were performed under the same conditions as those without SO₂, the only difference being the presence of 1500 ppm of sulfur dioxide in the inlet gas flow, both under calcination and carbonation stages. This concentration was selected to simulate typical values of SO₂ in uncontrolled flue gas.

**Results**

*CO₂ capture capacity.* Fig. 1 reports the sorbent capture capacity as a function of the number of cycles for the six limestones [4] 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 4th cycle. The residual capture capacity of the limestones (0.02-0.07 g CO₂/g sorbent in the tests without SO₂) was much lower than that found for the dolomite (0.12 g CO₂/g sorbent), in spite of the lower calcium content. This result highlights the positive effect of the large magnesium content of the dolomite in reducing particle sintering.

![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).](image)

When SO₂ was present in the gas flow 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 $0.004 - 0.04 \text{ g}_{\text{CO}_2}/\text{g}_{\text{sorbent}}$ in this case. 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. Noteworthy, the CO$_2$ capture capacity of the dolomite remained larger than that of the limestones along the cycles.

**Figure 2.** Cumulative particle undersize distribution of the sorbents after the 5$^{th}$ carbonation stage. Left: without SO$_2$. Right: with SO$_2$.

**Particle size distribution.** Fig. 2 compares the measured particle size distributions (PSDs) of the six limestones and of the dolomite after the 5$^{th}$ carbonation stage in tests carried out with or without SO$_2$ (1500 ppm) in the fluidizing gas. 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 SO$_2$ appears to slightly reduce the extent of fragmentation for all the limestones. As regards the dolomite sorbent, particle fragmentation was extensive. The mass fraction of fragments after the 5$^{th}$ cycle was about three times more than for the limestones. Particle fragmentation was mostly active upon the 1$^{st}$ 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 CO$_2$ capture process during the carbonation stages. Also for the dolomite the presence of SO$_2$ slightly reduced the extent of fragmentation.

**Elutriation rate.** Fig. 3 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 SO$_2$. As a general trend, it can be noted that for all the sorbents fines elutriation 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 SO$_2$, the opposite in the tests with SO$_2$). This indicates that sintering was able to harden the particles irrespective of the chemical composition (CaO or CaCO$_3$). Comparison of
the results with or without SO$_2$ indicates that the elutriation rates were similar, slightly lower when SO$_2$ 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.

![Figure 3](image)

**Figure 3.** Average fines elutriation loss as a function of the number of cycles for experiments carried out without SO$_2$ (top) and with SO$_2$ (bottom). ‘Limestones’ (left) refers to the average values of the six limestones.

The attrition rate of the dolomite was larger than that of the limestones, and was not influenced significantly by the presence of SO$_2$. 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 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. [9], 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.

**Conclusions**

Results showed that the CO$_2$ capture capacity decreased with the cycles, as expected. The presence of a high CO$_2$ concentration during calcination (70%) and a high calcination temperature (940°C) determined a significant decrease of the CO$_2$ capacity for all the limestones, due to the enhancement of particle sintering. On the contrary, the CO$_2$ 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. On the contrary, the dolomite sorbent was subject to extensive attrition and fragmentation.

The presence of SO$_2$ further depressed the CO$_2$ capture capacity for all the sorbents, most likely because of the formation of an impervious CaSO$_4$ layer on the surface of the particles. Conversely, attrition was only slightly affected by the presence of SO$_2$.

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**References**


