Sulfation and Reactivation of Three Limestones in a Dry Desulfurization Process

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INTRODUCTION

Dry desulfurization by direct injection of sorbents into a fossil-fuel boiler or a coal-fired burner offers a potential cost-effective alternative to more expensive SO₂ removal technologies, such as semidry or wet flue gas desulfurization. To achieve compliance with environmental quality standards on sulfur emissions, this simple technology typically uses commercial limestone as dry powdered sorbent, which reacts at high temperature (800-900°C) with the flue gas. It is a widespread opinion that, in the high temperature region, the sulfur capture by limestone is accomplished by two reaction steps: (1) fast calcination (decomposition) of CaCO₃ to produce high surface area and high porosity calcium oxide and (2) sulfation of the obtained CaO, in the presence of O₂, to form both CaSO₄ and CaSO₃ [1].

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]  
\[ \text{CaO} + \text{SO}_2 \rightarrow \text{CaSO}_3 \]  
\[ \text{CaO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{CaSO}_4 \]

Despite several studies [2-3] related to the system limestone/SO₂ have been proposed, it is still difficult to predict the behavior of these sorbents in sulfur dioxide removal processes, not only in real-size applications but also in laboratory-scale tests. Therefore, the first aim of this work has been to evaluate the sulfur adsorption efficiency of three different commercial limestones in a laboratory-scale equipment. Moreover, the solid CaCO₃ usually exhibits a partial conversion to calcium sulfate and sulfite [4]. Since a large amount of the sorbent goes unreacted through the process, a regeneration treatment to restore the spent sorbent reactivity has been also investigated.

EXPERIMENTAL APPARATUS

Experimental tests were carried out in a well-mixed recycle reactor, located in an electrical tubular oven. As shown in figure 1, the cylindrical quartz-made reactor was constituted by two sections: the pre-heating zone (A), 900 mm height and 32 mm i.d., partially filled with alumina pellets in order to heat quickly the reactants up to the reaction temperature, and the reaction section (B), 400 mm height and 27 mm i.d., provided by a porous sample holder and an internal cooling jacket. During the experiments, the upper part of the reactor was kept inside the oven, while the reaction section was rapidly inserted into the pre-heating tube when the gaseous stream reached stationary conditions at 850°C. The limestone amount (size-fraction: 0.4-0.6 mm) for the experiments was approximately 0.7 g; it was set on the sample holder prior to insert the reaction section inside the oven. This test procedure allows to simulate the direct limestone injection that occurs in real-size applications, studying also the initial simultaneous sorbent calcination and sulfation of the
obtained CaO. Before leaving the reactor the flue gas was quickly quenched by contacting it with the internal cooling jacket.

The reactor was provided by an alumina pipe, used in the reactivation stage for feeding water inside the pre-heating zone to produce steam, and by an external recycle loop, with a gas recirculation pump, in order to obtain high linear velocities in the reactor, thus reducing the mass transfer resistance toward the sorbent particles.

The laboratory equipment was fed with a synthetic flue gas, containing SO₂, CO₂, air and N₂. The total flow rate of the pre-mixed gas has been set to 2.15 NL/min with a partial pressure of 1300 ppm SO₂, while a flow rate in the range 45-55 NL/min has been measured downstream the recirculation pump. Gas sampling and analysis has been performed through a continuous gas analyzer (Horiba PG-250), provided by IR detector, to monitor the outlet gas concentrations; moreover, after each experimental run, the inlet SO₂ concentration in the flue gas has been measured by-passing the reactor for a few minutes.

Consequently, the on-line results were obtained in the form of outlet SO₂ and CO₂ concentrations as a function of time, allowing the determination of the characteristic sulfation and calcination curves. The typical trends evidenced experimentally are shown, for the sake of example, in figures 2-a for SO₂ and 2-b for CO₂. The sulfur fixed on the sorbent, as well as the amount of CO₂ produced by CaCO₃ decomposition, were evaluated from these data by integration with respect to time of the area bounded between the curves obtained with and without limestone inside the reactor. Sorbent conversion (S/Ca) is computed as follows:

$$\frac{S}{Ca} = \frac{SO_2 \text{ moles adsorbed}}{\text{initial moles of Ca(OH)}_2}$$  (3)
Fig. 2  Examples of the experimental curves: a) SO$_2$ measured trends with (○) and without (♦) limestone; b) CO$_2$ desorption curves with (□) and without (▲) limestone.

The calcium utilization has been also evaluated by means of chemical analyses performed with inductively coupled plasma - optical emission spectrometry (ICP-OES, Perkin-Elmer Optima 2000 DV) on the spent sorbents. ICP analyses provide informations about the unreacted CaO, theoretically available for a new desulfurization test, and an independent way to measure the overall (CaSO$_3$ + CaSO$_4$) sulfur amount fixed on limestone.

RESULTS AND DISCUSSION

Several preliminary desulfurization tests were performed with ground marble (high purity CaCO$_3$) to verify the reliability of the experimental procedure, which has been found to be satisfactory; the measured conversion values were all in the range 21-26%. Then, it was investigated the influence of three different commercial limestones on SO$_2$ removal; in particular, the degree of sulfation of the three samples was calculated to be 25-28% for Limestone A, 24-29% for B and 26-30% for C. These S/Ca values are very close to each other, showing that the three sorbents had similar SO$_2$ removal efficiency. These results underlined that the main problem of the process is related to the partial conversion of the solid CaCO$_3$, with consequent high disposal costs.

As reported in figures 2-a and 2-b, the process initially involves simultaneous calcination and sulfation, then only sulfation of the calcinated sorbent was observed. As mentioned before, the decomposition of CaCO$_3$ at high temperature, through a reduction of the solid volume, produces a porous CaO, which begins to quickly react with SO$_2$ to form calcium sulfate and sulfite. Sulfation products are usually formed close to the surface of the sorbent particles and its larger molar volume causes pores plugging, which reduces the diffusion of SO$_2$ through the product layer, preventing full calcium utilization.

Reactivation of the partially utilized limestone by steam hydration [5-6] has been performed, foreseeing the possibility to recycle back the hydrated products to a new desulfurization stage, so as to enhance the overall sulfur uptake of the sorbent.

In situ steam reactivation were carried out at 250°C for 30 minutes, by pumping 0.4 ml/min of water inside the pre-heating zone of the reactor; the reactor was also flushed with nitrogen, 1.5 Nl/min, to improve the contact between steam and the spent sorbents. Steam hydration leads to the formation of Ca(OH)$_2$, which has a molar volume larger than the unreacted CaO; therefore, the reactivation breaks the sulfate/sulfite shell formed during the desulfurization step allowing, respectively, the exposure of fresh material for a further sulfation run and a better diffusion of SO$_2$ toward the solid sorbent. As reported in table I, all the samples were restorable with steam and it was possible to reach an high sorbent conversion resulfating the hydrated products.
<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Run Number</th>
<th></th>
<th></th>
<th></th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
<td>II</td>
<td>III</td>
<td>IV</td>
<td>V</td>
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<tr>
<td>Limestone A</td>
<td>28%</td>
<td>11%</td>
<td>18%</td>
<td>7%</td>
<td>6%</td>
</tr>
<tr>
<td>Limestone B</td>
<td>24%</td>
<td>21%</td>
<td>11%</td>
<td>6%</td>
<td>5%</td>
</tr>
<tr>
<td>Limestone C</td>
<td>30%</td>
<td>24%</td>
<td>18%</td>
<td>7%</td>
<td>8%</td>
</tr>
</tbody>
</table>

Tab. I  Limestones utilization in a cycle of sulfation and reactivation tests.

![Graph showing overall conversion over run number](image)

Fig. 3  Effect of sequencing reactivations on the overall sorbent conversion: 10.7% CO₂; 3.8% O₂; 1300 ppm SO₂; (♦) Limestone A; (∆) Limestone B; (•) Limestone C.

One of the investigated sorbents, Limestone C, was more reactive than other ones, while Limestones A and B had a similar behavior (figure 3). Moreover, experimental outcomes have shown that spent sorbents could be reused in several cycles of sulfation and reactivation increasing the total sorbent utilization up to 87%. After a sequence of desulfurization tests, a uniform sulfation has been reached inside the sorbent particles; the degree of sulfation decreases after each test and, in particular, it has been found a negligible increase after four experimental runs.

It should be noted that the overall solid utilization has been greatly increased since the reactivation can be carried out several times on the same sorbents; a good recovery in the spent sorbents reactivity it was observed mainly in second and third reactivation step.

REFERENCES