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Sulfation and Carbonation Competition in the Treatment of Flue Gas from a Coal-Based Power Plant by Calcium Hydroxide

Abstract: In this work, a gas containing CO_2 and SO_2 at the usual concentrations on the coal combustion flue gas reacted with calcium hydroxide to evaluate and quantify the influence of SO_2 on the CO_2 capture and vice versa. This influence was quantified with a continuous gas analyzer and by thermogravimetry (TG). Results show that the CO_2 retained increases in general as its concentration does and decreases as the SO_2 concentration increases. A similar behavior was found for the SO_2 retention at different CO_2 concentrations being more relevant the influence of the presence of SO_2 on the CO_2 capture than the opposite one. Results suggest that for a high CO_2 capture, SO_2 should be eliminated previously. With respect to the reaction process it was found that the desulfurization product clearly identified was $CaSO_3 \cdot \frac{1}{2}H_2O$; in the reaction between $Ca(OH)_2$ and CO_2, $CaCO_3$ is mainly obtained, the complex $CaO \cdot CO_2$ being another possible product synthesized in low amount. Gas analyzer shows that SO_2 and CO_2 react simultaneously and that a part of the $CaCO_3$ reacts with the SO_2 and releases CO_2. Sulfation values calculated by TG and from the gas analyzer are very similar but the amount of CO_2 captured is not possible to know clearly by TG due to the synthesis and decomposition of $CaCO_3$ during the process. The study of the evolution of the sorbent porosity in the process reveals that the presence of both acid gases produces a lower blockage of the pores than when only one gas is present probably due to the generation of new pores in the reaction of $CaCO_3$ and SO_2.

Keywords: CO_2 and SO_2 capture, low temperature, flue gas, calcium hydroxide

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1 Introduction

Coal combustion is one of the energy sources for electricity generation. Coal produced about 18% of Spanish electricity and recently, as Spain depends on coal industry for employment, the government, according to the European Community, approved to maintain subsidies for domestic coal used to generate energy up to 2014 [1]. The flue gas generated from coal combustion power plant contains CO_2 (about 12%) and SO_2 at concentrations depending on the coal sulfur content, as well as NO_x, H_2O, O_2 and N_2.

There are three main approaches to capture the CO_2 generated from a primary fossil fuel or biomass, classified as post-combustion (capture from the flue gas), pre-combustion separations (capture in the gasification process, before the combustion step) and oxy-fuel firing, use of oxygen instead of air as comburent gas [2, 3, 4]. Developed post-combustion technology consists in the flue gas absorption in an aqueous solution with amines, mainly in the form of gas–liquid absorption columns. This technology is commonly used in various industries faced with the task of removing CO_2 from gas mixtures containing a wide range of species in different concentrations [5, 6]. Adsorption at low temperatures (up to 423 K) is considered one potential alternative with the added advantage that solids are easy to handle [7]. Carter, L.D [8] proposed the combined capture and storage of CO_2 and SO_2 or H_2S for conventional power plants to reduce cost in power production. The relevance of CaO, $Ca(OH)_2$ or calcium-based sorbents on the removal of acid gases, like SO_2, NO_x, HCl or CO_2, justifies the great number of works focused on the preparation of efficient calcium-based sorbents. Arias et al. [9] studied the sulfation behavior of cycled CaO particles in Ca-looping CO_2 capture system. Sun et al. [10] and Manovic and Anthony [11] found that SO_2 impedes the cyclic CO_2 capture by limestone or calcium aluminate pellets, because of the blockage by sulfation products, suggesting that desulfurization of flue gas before CO_2 capture is essential for CO_2 cyclic capture at high temperature. Several works have studied the process of simultaneous CO_2 and SO_2 retention by

CaO or Ca(OH)$_2$ at medium or low temperature and at the usual CO$_2$ and SO$_2$ concentration in the flue gas of a coal-based power station. Kramer et al. [12] stated the main reactions implied in the desulfurization process with Ca(OH)$_2$ when CO$_2$ was present. Guang et al. [13], working with Ca(OH)$_2$, injected in the flue gas, at temperatures about 500°C, SO$_2$ concentrations of 3,000 or 1,500 ppm and CO$_2$ concentrations of 14% found that the carbonation of the sorbent hinders the SO$_2$ capture even though slight alterations in CO$_2$ concentrations did not have significant effects on the SO$_2$ removal. Ho et al. [14] proved that when O$_2$, CO$_2$ and SO$_2$ were present in the flue gas, the sulfation and carbonation reactions took place simultaneously and the carbonate formed further reacted with SO$_2$ to form sulfite. Liu et al. [15], working at the conditions similar to those in the bag filters of dry or semi-dry flue gas desulfurization (FGD) systems, found when CO$_2$ and SO$_2$ are present that the final carbonate amount was lower than when only CO$_2$ is present because the CaCO$_3$ reacts with SO$_2$. For a constant CO$_2$ concentration of 12.6%, the SO$_2$ capture after 1 h of reaction was nearly independent on the SO$_2$ concentration from 1,000 to 50 ppm of SO$_2$ and this capture was insensitive to the presence of CO$_2$.

In a previous work [16], experiments of chemisorption of CO$_2$ at 50°C were performed with a dry flue gas (10% CO$_2$ in He), commercial Ca(OH)$_2$ and with this hydroxide supported on mesoporous materials to investigate the possibility of a cyclic CO$_2$ capture at low temperature. In that work, it was found that CO$_2$ was retained as a CaO·CO$_2$ complex and also as CaCO$_3$ in higher amounts. Even when the amount of CO$_2$ retained as CaO·CO$_2$ was low, the sorbents could be regenerated at 550°C and used cyclically without appreciable loss in activity.

In the present work, the influence of the presence of SO$_2$ and CO$_2$, at the usual concentrations in a coal combustion flue gas, on the co-capture of both gases by calcium hydroxide at low temperature is studied. The objectives were to know the reaction process and the products synthesized to explain the modification of the sorbent porosity and the influence of the presence of one gas on the capture of the other one, quantifying with two different techniques, this influence. All of this information will be used to predict the influence of the presence of SO$_2$ on the cyclic CO$_2$ capture by Ca(OH)$_2$ at low temperature.

2 Experimental section

A commercial Ca(OH)$_2$, supplied by Calcinor, was used as sorbent.

A Camsizer XT from Retsch with the dry dispersion module was used to obtain the particle size distribution of the sorbent. The isotherm of the commercial calcium hydroxide before and after the reaction was obtained by using a Micromeritics ASAP-2010 apparatus by N$_2$ adsorption. The specific surface area was calculated using the BET (Brunauer, Emmett, Teller) method and the pore size distribution from the desorption branch of the isotherm following the BJH (Barreto, Joyner & Halenda) procedure. A Setaram thermal analyzer model SETSYS-1700 was used for the thermogravimetric (TG) curve determination.

2.1 Reaction of the sorbent with CO$_2$ and SO$_2$

In the laboratory experimental setup, shown in Figure 1, a flue gas containing CO$_2$ and SO$_2$, at the usual concentrations in the exhausted gas of a coal combustion power station, is conducted through commercial Ca(OH)$_2$, used as sorbent. The concentration of SO$_2$ and CO$_2$ after the reaction was continuously monitored in an Emerson MLT-1 NGA 2000 gas analyzer and data were compiled with a personal computer equipped with NGA win control software. The breakthrough curves of both gases were plotted
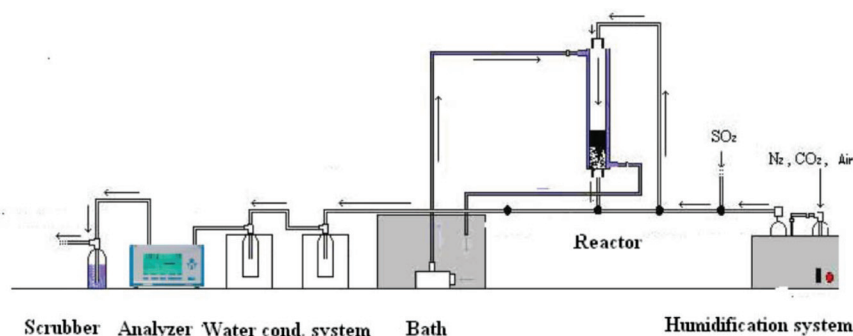

Figure 1 Experimental setup of the reaction process

with the analyzer data and the calcium utilization of the sorbent in the reaction with CO_2 and SO_2 and the total calcium utilization were obtained from the area above the curve. One gram of the sorbent, commercial calcium hydroxide, dispersed in 30 g of inert silica sand was placed in a 3.6 cm diameter glass-made jacketed fixed bed reactor at 55% of relative humidity and at temperature of 58°C. The composition of the gas stream was 12% or 6% or 0% CO_2; 9.5% synthetic air; 5,000, 2,500, 1,000 or 0 ppm SO_2 and balanced N_2, being 1,000 ml/min the flue gas rate.

Table 1 shows the concentrations of the acid gases essayed. Three runs were performed for each condition. When the reaction time was over, 1 h approximately, (controlled by the breakthrough curves), the reacted sorbent was sieved to separate it from the sand. Some of the reacted sorbents were submitted to TG analysis.

2.1.1 Determination of the calcium utilization or calcium conversion in the reaction with CO_2 or SO_2 and of the total calcium utilization

The calcium utilization or the calcium conversion in the reaction of $Ca(OH)_2$ with CO_2 or SO_2 in percentage is defined as:

$$\frac{\text{moles of } CO_2 \text{ captured} / \text{grams of sorbent}}{\text{moles of calcium} / \text{grams of sorbent}} \times 100 \quad \text{or}$$

$$\frac{\text{moles of } SO_2 \text{ captured} / \text{grams of sorbent}}{\text{moles of calcium} / \text{grams of sorbent}} \times 100 \quad (1)$$

The sum of these two terms will be the total calcium utilization. The moles of CO_2 and SO_2 captured, at any time and after 1 h of reaction, were calculated from the area above the breakthrough curves. For sorbents

submitted to TG analysis, the amounts of CO_2 or SO_2 were also obtained from TG data. The moles of calcium in the sorbent were calculated considering the commercial calcium hydroxide composition. To calculate the calcium utilization in the reaction with CO_2 by TG it must be considered that the $CaCO_3$ present in the reacted sorbent is mainly due to the $CaCO_3$ present in the commercial $Ca(OH)_2$, the $CaCO_3$ synthesized with the CO_2 captured and the $CaCO_3$ disappeared by reaction with SO_2.

3 Results and discussion

Particle size distribution of the commercial $Ca(OH)_2$ obtained with the Camsizer shows that 100% of the sample is lower than 200 μm, being 90% lower than 80 μm and 10% lower than 10 μm. The purity of the commercial $Ca(OH)_2$ determined by TG analysis using N_2 as purge gas was 82.7% being 9% the $CaCO_3$ content. The specific surface area of the commercial $Ca(OH)_2$ calculated following the BET method was 13 m^2/g.

3.1 Reaction process and products identification

Breakthrough curves of CO_2 and SO_2 were discussed in a previous work [17], showing that both gases react simultaneously with the calcium hydroxide according to Ho et al. [14]. Furthermore, the CO_2 breakthrough curve shows at about 600 s, a gas concentration higher than the initial one due to the reaction of SO_2 with $CaCO_3$ that releases CO_2. From the area above the breakthrough curves and applying eq. (1), conversion values at any time and after 1 h of reaction are calculated. Results are shown in Table 2.

Table 1 Concentrations of SO_2 and CO_2 at different runs

SO_2 conc. (ppm)	0	1,000	2,500	5,000	1,000	2,500	5,000	1,000	2,500	5,000
CO_2 conc. (%)	12	12	12	12	6	6	6	0	0	0

Table 2 Mean values (of three runs) $\pm$ standard deviation of calcium conversion in the reaction with SO_2 or/and CO_2 for different experimental conditions

CO_2 conc. (%)	12	12	12	12	6	6	6	0	0
SO_2 conc. (ppm)	5,000	2,500	1,000	0	5,000	2,500	1,000	5,000	2,500
$Ca(OH)_2$ conv. to $CaSO_3$ (%)	14.8 $\pm$ 0.5	11 $\pm$ 1	10.7 $\pm$ 0.6		15.1 $\pm$ 0.9	13 $\pm$ 2	10 $\pm$ 1	20 $\pm$ 2	17.6 $\pm$ 0.9
$Ca(OH)_2$ conv. to $CaCO_3$ (%)	14 $\pm$ 1	16 $\pm$ 1	20 $\pm$ 2	27.0 $\pm$ 0.6	11 $\pm$ 1	10.4 $\pm$ 0.8	10.2 $\pm$ 0.7		
Total $Ca(OH)_2$ conversion (%)	29 $\pm$ 2	27 $\pm$ 2	31 $\pm$ 3		26 $\pm$ 2	23 $\pm$ 3	20 $\pm$ 2		

In that previous work, the calcium conversion in the reaction with SO_2 or CO_2 versus time showed different shapes mainly at the beginning of the process, principally due to the great differences in SO_2 and CO_2 concentration in the gas mixture (Table 1) and in consequence a great difference in their reaction rates. The calcium conversions with time in the reaction with CO_2 showed a first step in which the reaction of $Ca(OH)_2$ with CO_2 was very fast, in a chemically controlled process; this step was followed by a period diffusional controlled with a slow CO_2 capture or even with no appreciable capture. The calcium conversions with time in reaction with SO_2 showed that the SO_2 capture increased at any time with its concentration for a CO_2 constant concentration, being the highest SO_2 capture when CO_2 was not present.

A great difference in the CO_2 capture depending on the presence of SO_2 in the flue gas was also found (27% without SO_2 and 14% with 5,000 ppm of SO_2 and 12% of CO_2, after 1 h of reaction, as Table 2 shows). Liu et al. [15], working at similar temperature, relative humidity and CO_2 concentration, found a CO_2 capture, after 1 h of reaction, very similar to that found in this work, when SO_2 was not present.

In all runs performed with both gases, except in experiments with 12%, CO_2 and 1,000 ppm SO_2, there is a time period, at about 600 s, with values of CO_2 concentrations higher than the initial one, revealing a net CO_2 production. The $CaCO_3$ present in the sorbent or produced in the reaction of $Ca(OH)_2$ and CO_2 reacts with SO_2, a stronger acid than CO_2, and releases CO_2. Although this reaction occurs all the time, only when the amount of CO_2 captured is lower than the amount of this gas released, a net CO_2 emission is detected. In the experiment performed without CO_2 and 5,000 ppm of SO_2, CO_2 emissions were also detected, meaning that the $CaCO_3$ present in the commercial $Ca(OH)_2$ also reacts with SO_2. These results obtained from analyzer data were confirmed by mass spectrometry (MS) analysis [17].

TG, differential scanning calorimetry (DSC) and MS results of the sorbent before and after the reaction allowed us in a previous work [17] to explain and discuss the analyzer data, the reactions that occur in the process and the conversion results obtained. $CaSO_3 \cdot \frac{1}{2}H_2O$ was the unique desulfurization product clearly identified. $CaSO_4$ was not identified by TG–MS as MS peaks of SO_3 were not found, probably due to the decomposition of the calcium sulfate at elevated temperatures to form CaO, SO_2 and O_2 according to bibliography [18]. $CaCO_3$ is the main product of CO_2 capture and $CaO \cdot CO_2$, another product. DSC and MS data allowed distinguishing the calcination of the $CaCO_3$ formed from the CO_2 capture than that present in the initial sorbent.

Table 3 $Ca(OH)_2$ conversion values obtained from gas analyzer data and from TG data

CO_2 (%)/SO_2 (ppm) concentrations	$Ca(OH)_2$ conversion to $CaCO_3$ (%) gas analyzer/ TG	$Ca(OH)_2$ conversion to $CaSO_3$ (%) gas analyzer/TG
12/5,000	14.3/24.0	14.7/14.2
	13.6/13.0	15.6/15.2
12/2,500	14.6/4.4	10.1/12.4
12/1,000	20.0/13.1	9.5/9.4
12/0	27/10.3	
0/5,000		18.8/19.0

According to the objectives of the work, Table 3 shows conversion values obtained after 1 h of reaction with two different techniques, from gas analyzer and from TG data of the reacted sorbent. Results show that the calcium conversion values in the reaction with SO_2 are very similar independently of the experimental procedure used to calculate it, but there is no concordance in the results of calcium conversion in the reaction with CO_2. In the calculation of conversion to $CaCO_3$ from gas analyzer data, the moles of CO_2 are the net amount of this gas captured. Conversion values from TG data are calculated from the final $CaCO_3$ remaining in the sorbent after 1 h of reaction that, as has been explained, depends on three different processes: the $CaCO_3$ present in the commercial $Ca(OH)_2$, the $CaCO_3$ synthesized with the CO_2 captured and the $CaCO_3$ disappeared by reaction with SO_2. Because of that, TG technique is not a good tool to quantify the real amount of CO_2 captured and it is better to use the gas analyzer data.

Table 2 shows the mean values (obtained from three runs for each condition) of calcium conversion in the reaction with SO_2 or CO_2 obtained from gas analyzer data after 1 h of reaction and values of total $Ca(OH)_2$ conversion. As values show, the capture of SO_2 increases with SO_2 concentration for a constant CO_2 concentration and also increases as CO_2 concentration decreases though this influence is nearly inappreciable at the conditions essayed. The CO_2 capture increases with CO_2 concentration for a constant SO_2 concentration and decreases as SO_2 concentration increases for a constant 12% concentration of CO_2. For a CO_2 concentration of 6% there is almost no variation on CO_2 capture at different SO_2 concentrations. Results obtained at the usual SO_2 and CO_2 concentrations in the flue gas of 2,500 ppm and 12% confirm that both acid gases compete to react with the base. But results of Table 2 and previous work also show that at these usual concentrations, the presence of SO_2 has a higher influence on the CO_2 capture ($Ca(OH)_2$

conversion values to $CaCO_3$ varied from 15.6% to 27.0% as the SO_2 concentration goes from 2,500 to 0 ppm) than the presence of CO_2 on the SO_2 capture (conversion to $CaSO_3$ varied from 11.9% to 17.6% as the CO_2 concentrations diminishes from 12% to 0%). Guan et al. [13] found that slight alterations in CO_2 concentrations did not have significant effects on the SO_2 removal and Liu et al. [15] also found little variation on the SO_2 capture when CO_2 at 12.6% of concentration was or was not present. Although the rapid reaction of CO_2 with $Ca(OH)_2$ at the beginning of the process to form $CaCO_3$ blocks the pore holes and hinders the diffusion of SO_2, the desulfurant properties of the salt and the lower acidity of CO_2 explain that the real influence of CO_2 on the SO_2 capture is less relevant than vice versa. The same considerations can be used to explain that despite the great difference in the concentrations of both gases, the moles of SO_2 and CO_2 captured are very similar.

When both gases are present, total conversion of calcium hydroxide is the highest, the base is more efficiently used; but if the aim of the process is to retain CO_2, considering the great influence of the SO_2 on its capture, it would be more convenient, as it has been proposed, to desulfurize previously the gas [15]. If the co-capture is the option, conversion results obtained quantify the CO_2 capture reduction, related to the presence of SO_2 at the conditions essayed in this work.

In a previous work [19], the variation of the specific surface area of calcium hydroxide before and after its reaction with CO_2 and/or SO_2 at the concentration of 12% and 5,000 ppm, respectively, was studied. Results indicate that after the reaction with both gases the specific surface area of the sorbent is slightly higher than after the reaction with each gas alone. Figure 2 shows the pore size distribution of $Ca(OH)_2$ before and after the

reaction at the same conditions used in that previous work. This figure shows a high pore blockage after the reaction due to the solid products, mainly $CaCO_3$ and $CaSO_3 \cdot \frac{1}{2}H_2O$. Within the reacted sorbents, the highest remaining porosity corresponds to the sorbent after the reaction with both gases. This result can be explained, at least in part, considering that when both gases are present, the $CaCO_3$ reacts with SO_2 releasing CO_2 and generating new pores. That means that when calcium hydroxide is used to retain CO_2 in the presence of SO_2, at low temperature, the reversible adsorption of CO_2 as $CaO.CO_2$, found in the previous work [16] could be higher than without SO_2, due to the higher porosity available.

4 Conclusions

The study of the reaction of CO_2 and SO_2 with commercial calcium hydroxide at low temperature in a continuous gas analyzer proves and quantifies the simultaneous reaction of the sorbent with both gases and the CO_2 release in the reaction of $CaCO_3$ with SO_2.

According to previous TG–DSC–MS results, the main reaction product of calcium hydroxide and SO_2 at this low temperature is $CaSO_3 \cdot \frac{1}{2}H_2O$. The main product of the reaction of CO_2 and $Ca(OH)_2$ is $CaCO_3$. The detection by MS of little amounts of CO_2 released within 425–525°C and the difference between the $Ca(OH)_2$ reacted and the $CaCO_3$ formed when SO_2 is not present suggest the possible formation of a $CaO \cdot CO_2$ complex, postulated in a previous work.

Only data of the gas analyzer allow determining the CO_2 captured, while the SO_2 captured can also be determined from TG data. Results of calcium conversion show that both acid gases compete to react with the base but it
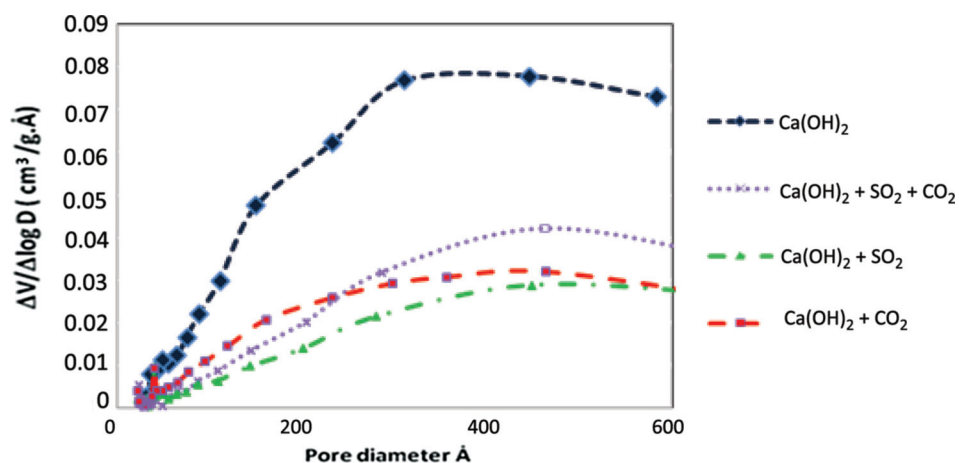

Figure 2 Pore size distribution of $Ca(OH)_2$ before and after the reactions

is higher than the influence of SO_2 on the CO_2 capture than the influence of CO_2 on the SO_2 retention. That result can be explained considering that CO_2 is a weaker acid than SO_2 and that $CaCO_3$ acts as desulfurant.

Despite the higher CO_2 concentrations with respect to SO_2, in all the conditions tested (12% or 6% CO_2 versus maximum 5,000 ppm SO_2), the strongest acidity of SO_2 makes that the moles of the base that react with both gases are of similar order of magnitude. When both gases are present the base is more efficiently used (total calcium conversion is higher than the conversion with one gas).

According to these conclusions obtained working at low temperature, if the purpose of the process is mainly to retain CO_2, it is convenient to desulfurize previously the flue gas. If the aim is to co-capture, this work shows the reduction on the retention of each gas when both gases are present. Nevertheless, as the porosity reduction after the reaction with both gases is lower than the reduction with one gas, it is predictable that the reversible adsorption of CO_2 as $CaO \cdot CO_2$ could be higher than without SO_2.

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