

Use of TG-DSC-MS and Gas Analyzer Data to Investigate the Reaction of CO₂ and SO₂ with Ca(OH)₂ at Low Temperature

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To investigate the reaction of calcium hydroxide with CO₂ and SO₂ simultaneously, a gas containing both gases reacted with the calcium base at 58 °C and a relative humidity of 55 %. Different CO₂ and SO₂ concentrations were performed being the composition of the gas stream 12, 6 or 0 % CO₂; 5000, 2500, 1000 or 0 ppm SO₂, 9.5 % synthetic air and balanced N₂, with a flue gas rate of 1000 mL/minute. A continuous gas analyzer controlled the CO₂ and SO₂ concentrations in the effluent gas and the breakthrough curves of both gases were obtained. The gas analyzer data show that SO₂ and CO₂ compete to react with the base reacting simultaneously. By using thermogravimetry (TG), differential scanning calorimetry (DSC) and mass spectrometry (MS) techniques, calcium sulphite hemihydrate, CaSO₃·1/2H₂O, was identified as the unique desulfurization product detected. CaSO₄ was not identified although O₂ was present in the gas mixture. CaCO₃ was the main product of the reaction of calcium hydroxide and CO₂ being the complex CaO·CO₂ another possible product synthesized in low amounts. From analyzer data it was proved that a part of the CaCO₃ present in the sorbent or synthesized in the process reacts with the SO₂ and release CO₂. Results of this work show that the combination of continuous gas analyzer data and TG-DSC-MS techniques, not used before to study this reaction, is a good and easy way to clarify the process and the products of reaction.

1. Introduction

Coal combustion is one of the energy sources for electricity generation supplying the 12 % of Spanish electricity. The flue gas generated from the coal combustion power plant contains CO₂ (about 12%) and SO₂ at concentrations depending on the coal sulphur content, as well as NO_x, H₂O, O₂ and N₂. Within the post combustion technologies developed to capture the SO₂ after the combustion, adsorption at low temperatures (up to 423 K) is considered one alternative with the added advantage that solids are easy to handle. In previous works different calcium hydroxide based sorbents have been prepared, analysed and used at low temperature, Renedo et al. (2006) and Renedo et al. (2012). To reduce cost in power production, Carter (2010) proposed the combined capture and storage of CO₂ and SO₂ or H₂S for conventional power plants. Kramer et al. (1997) stated the main reactions implied in the desulfurization process with Ca(OH)₂ when CO₂ was present and Li et al. (2000) working with Ca(OH)₂ injected in the flue gas, at temperatures about 500 °C, SO₂ concentrations of 3000 or 1500 ppm and CO₂ concentrations of 14 % found that the carbonation of the sorbent hinders the SO₂ capture even though slight alterations in CO₂ concentrations did not have significant effects on the SO₂ removal. Ho et al. (1996) proved that when O₂, CO₂ and SO₂ were present in the flue gas, the sulfation and carbonation reactions took place simultaneously and the carbonate formed, further reacted with SO₂ to form sulphite. Liu et al. (2010), working at the conditions similar to those in the bag filters of dry or semi dry Flue Gas Desulfurization (FGD) system, founded that when CO₂ and SO₂ were present, the final carbonate amount was lower than when only CO₂ is present because the CaCO₃ reacts with SO₂.

In a previous work, Fernández et al. (2010) found that CO_2 was mainly retained as CaCO_3 but also, in low amounts, as a $\text{CaO}\cdot\text{CO}_2$ complex. These results were obtained in experiments of chemisorption of CO_2 at $50\text{ }^\circ\text{C}$ that were performed with a dry flue gas (10% CO_2 in He), commercial $\text{Ca}(\text{OH})_2$ and with calcium hydroxide supported on mesoporous materials.

In the present work, the process of simultaneous SO_2 and CO_2 capture, at their usual concentrations in a coal combustion flue gas by calcium hydroxide at low temperature is studied. The objectives were to know the reaction process and the products synthesized based on the CO_2 and SO_2 continuous analyzer data and on the results found analyzing the reacted sorbent by thermogravimetry (TG), differential scanning calorimetry (DSC) and mass spectrometry (MS) techniques.

2. Experimental procedure

A commercial $\text{Ca}(\text{OH})_2$, supplied by Calciner S.A., was used as sorbent and the desulfurization reaction was performed in the laboratory experimental set-up, shown in Figure 1. The gas stream without SO_2 passed through the humidification system. After humidification, the gas mixture with SO_2 flowed through the reactor that contained one gram of the sorbent dispersed in 30 g of inert silica sand at 55 % of relative humidity and at temperature of $58\text{ }^\circ\text{C}$. The composition of the gas stream was: 12, 6 or 0 % CO_2 ; 9.5 % synthetic air; 5000, 2500, 1000 or 0 ppm SO_2 and balanced N_2 being 1000 mL/minute the flue gas rate.

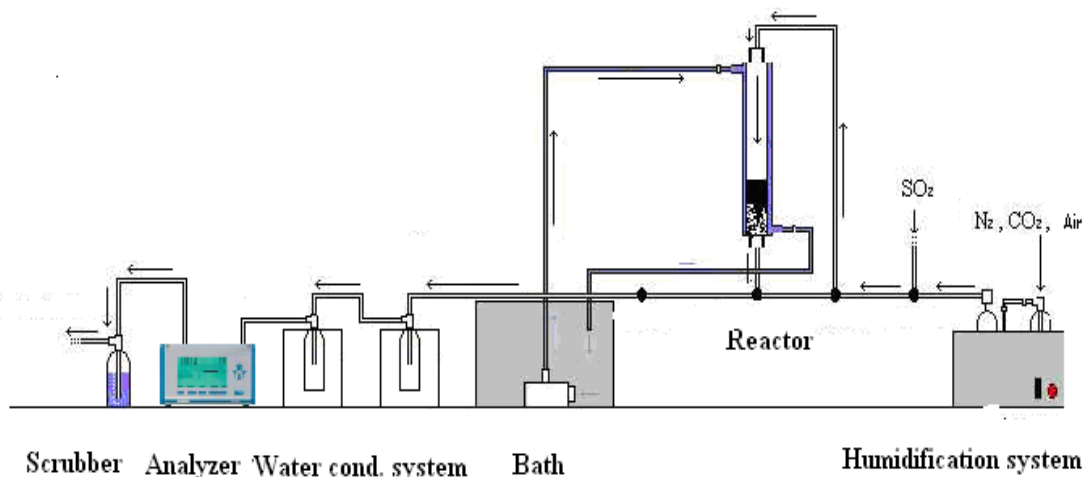


Figure 1: Experimental set up of the reaction process

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 a NGA win control software. The breakthrough curves of both gases were plotted with the analyzer data. When the reaction time was over, 1 hour 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, DSC and MS analysis. A Setaram thermal analyzer model SETSYS-1700 was used for the TG and DSC curves determination. This TG instrument was coupled to a Balzers Thermostar/Omnistro mass spectrometer (Pfeiffer vacuum) for evolved gas analysis. The carrier gas used was N_2 at a flue rate of 100 mL/min and the temperature was increased from room temperature to $1350\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C}/\text{min}$. The number of m/z signals selected corresponds to H_2O (18), SO_2 (64), SO_3 (80) and CO_2 (44).

3. Results and Discussion

3.1 Reaction process

Before starting the desulfurization reaction, there is an initial stabilization period in which the gas mixture does not pass through the reactor. After this period, the gas leaving the reactor passes through two ice traps to condense the water content before getting the analyser. Figure 2 shows the breakthrough curves of CO_2 and SO_2 for a run with about 12 % of CO_2 and 5000 ppm of SO_2 . The first horizontal zone corresponds to the gases concentration stabilization.

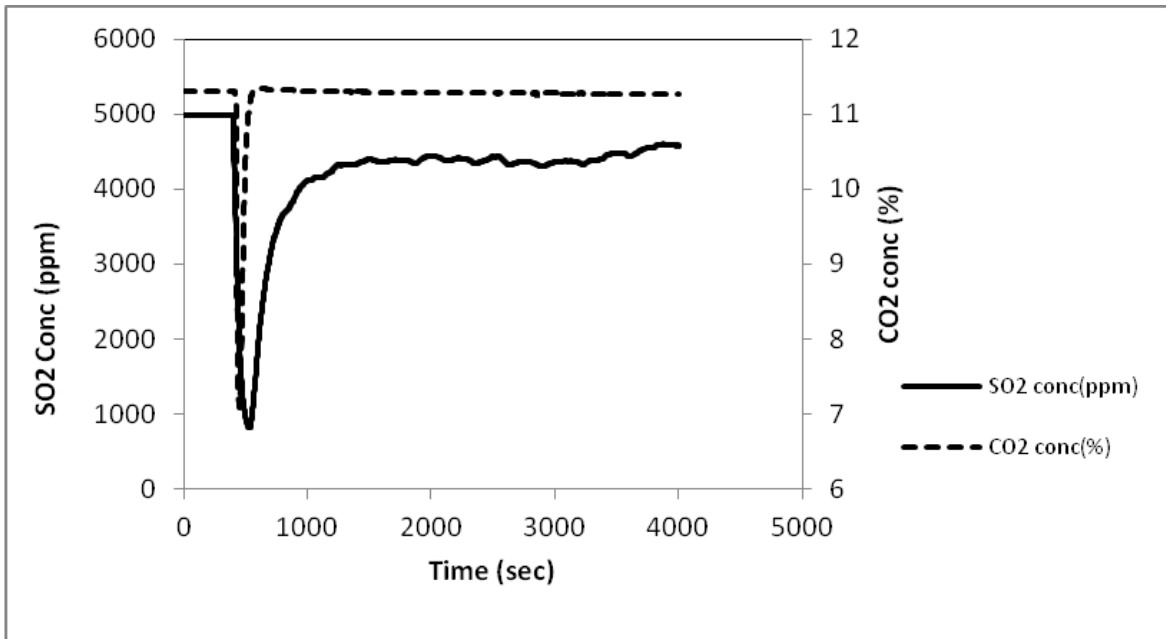


Figure 2: Breakthrough curves of SO_2 and CO_2 for one experiment with a flue gas containing 12 % of CO_2 and 5000 ppm of SO_2

Figure 2 shows that both gases react simultaneously with the calcium hydroxide according to Ho et al. (1996). Furthermore, the CO_2 breakthrough curve shows at about 600 s of reaction, a gas concentration higher than the initial one due to the reaction of SO_2 with CaCO_3 that release CO_2 .

From analyzer data, curves of mol SO_2 or mol of CO_2 captured versus time were drawn. Figures 3 and 4 show both curves.

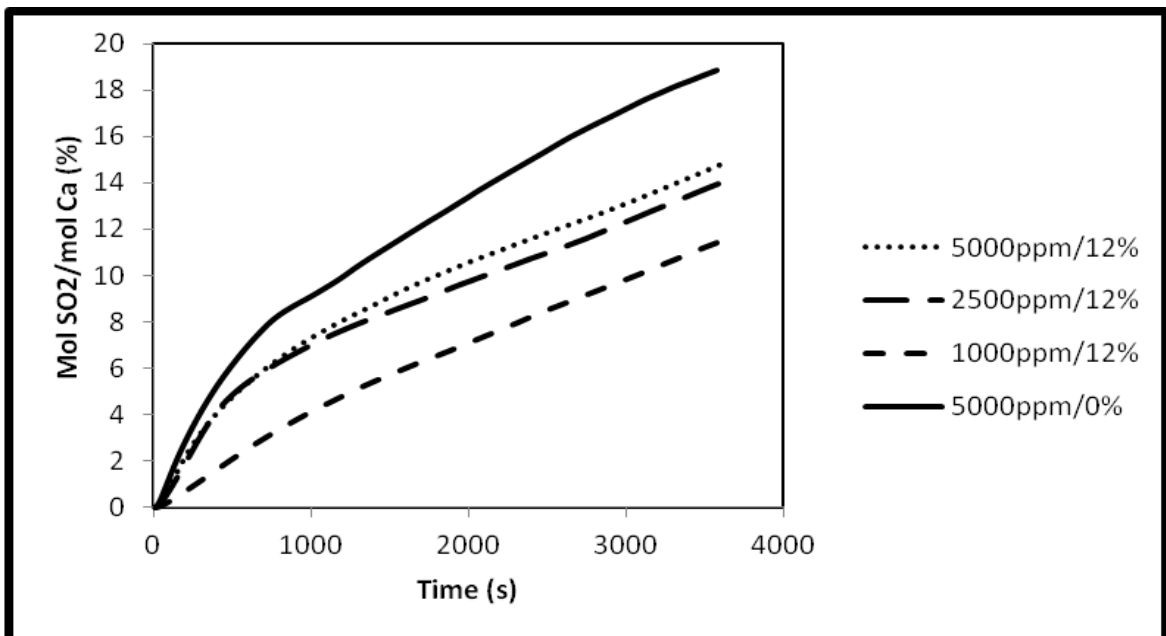


Figure 3: Mol of SO_2 captured for a CO_2 concentration of 12 % and a SO_2 concentrations of 5,000, 2,500 or 1,000 ppm and 0 % of CO_2 with 5000 ppm of SO_2

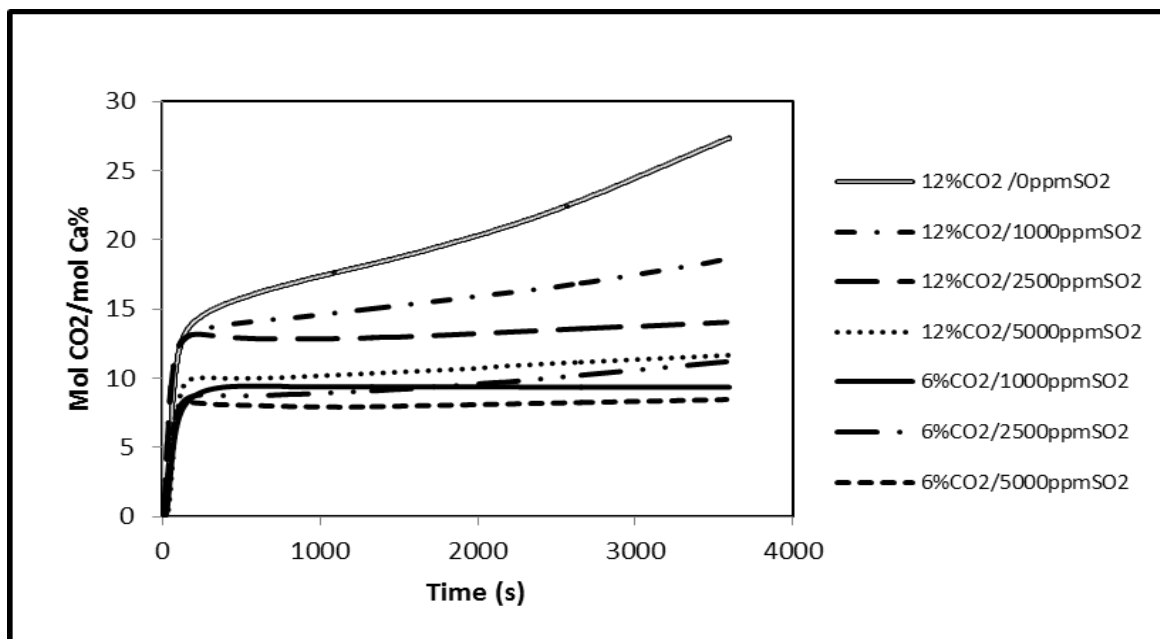


Figure 4: Moles of CO₂ captured in the reaction with CO₂ at different experimental conditions

Comparing Figures 3 and 4, different shapes mainly at the beginning of the process are found. These different shapes are principally due to the great differences in SO₂ and CO₂ concentration in the gas mixture and in consequence to a great difference in their reaction rates. Figure 4 shows a first step in which the reaction of Ca(OH)₂ with CO₂ is very fast, in a process chemically controlled; this step is followed by a period diffusionally controlled with a slow CO₂ capture or even with no appreciable capture. In all runs performed with both gases, except in experiments with 12 % CO₂ and 1,000 ppm SO₂, there is a time period, at about 600 seconds, with values of CO₂ concentrations higher than the initial one. These results only can be explained considering a net CO₂ production. The CaCO₃ present in the sorbent or produced in the reaction of Ca(OH)₂ and CO₂, reacts with SO₂, a stronger acid than CO₂, and release CO₂. Although this reaction occurs all the time, only when the amount of CO₂ captured is lower than the amount of this gas released, a net CO₂ emission is detected. These results obtained from analyzer data are confirmed by MS analysis. Figures 3 and 4 also show the competence between both acid gases to react with the base as the highest SO₂ or CO₂ captures are obtained when only one gas is present in the process: experiments with (5000 ppm SO₂ / 0 % CO₂ and 12 % CO₂ and 0 ppm of SO₂).

3.2 Products of the Reaction

TG, DSC and MS results of the sorbent allow us to complete the study of the reaction process and to know the products of the reaction. Figure 5 shows the TG curve corresponding to the Ca (OH)₂ after the reaction with CO₂ (12 %) and SO₂ (5,000 ppm) as well as DSC and MS curves for this run. (The rest of the TG curves are omitted).

TG curve shows a first mass loss (near 125 °C) due to the loss of humidity, followed by other two dehydration processes: the water of the product CaSO₃.1/2 H₂O (at about 360 °C) and the Ca(OH)₂ dehydration at the temperature range of 370-465 °C. These water losses were confirmed by three endothermic peaks in the DSC curve and three signals of water emission (m/z = 18) in the MS curve.

At the temperature range of 554-850 °C, TG curve shows a mass loss due to the CaCO₃ calcination and DSC curve presents two endothermic peaks and MS curve shows two overlapped signals of CO₂ emission (m/z = 44) that can be attributed to the calcination of the CaCO₃ present in the sorbent and of that synthesized in the process.

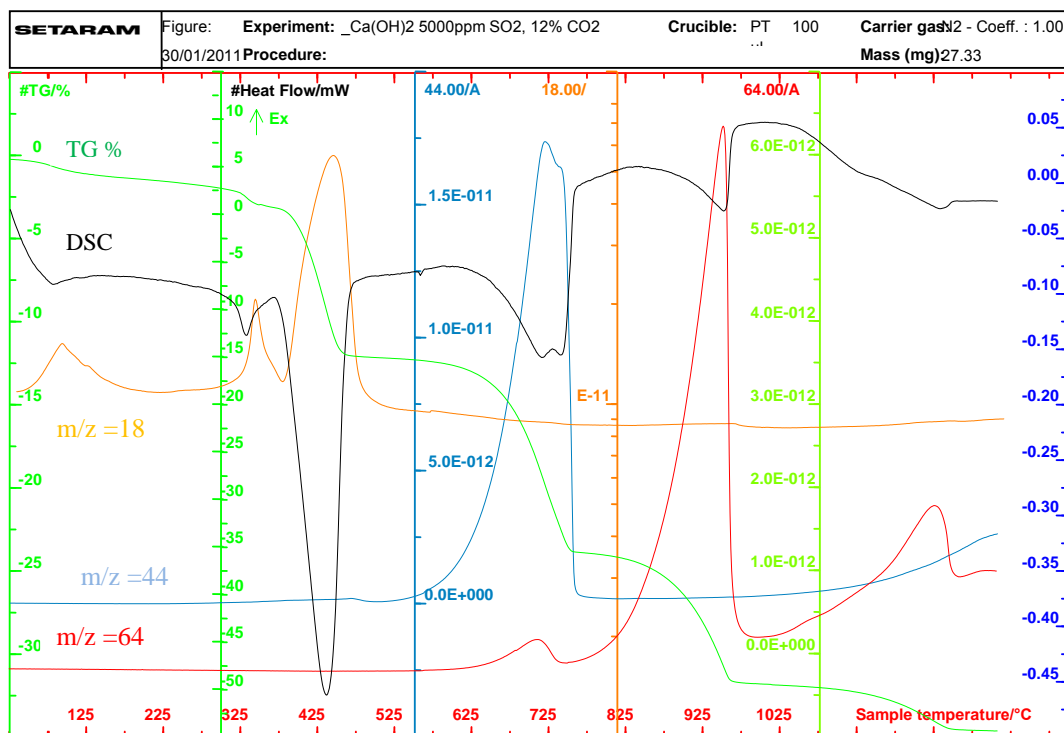


Figure 5: TG, DSC and MS curves of sorbent after reaction with SO₂ (5,000 ppm) and CO₂ (12 %) being N₂ the carrier gas at 100 mL/min.

A small peak of CO₂, within 425-525 °C is attributed to the decomposition of the CaO.CO₂ complex identified in a previous work by Fernández et al. (2010). The low intensity of this peak is due to the CO₂ scale with an intense CO₂ emission peak in the range of the calcination temperature. The synthesis of this complex is also suggested considering the TG mass losses of the sorbent after the reaction with CO₂ alone (experiment 0 ppm SO₂ /12 % CO₂). This TG is not shown. In this run, the moles of Ca(OH)₂ reacted should be equal to the moles of CaCO₃ formed, but that amount, calculated from the TG mass loss, was higher than the CaCO₃ formed suggesting that another product of the reaction between CO₂ and Ca(OH)₂ must be synthesized.

Three peaks of molecular weight 64, at about 725, 1,000 and 1,250 °C were identified by MS. Last one is probably due to the decomposition of a sulphur compound present in the commercial calcium hydroxide as this peak also appears in the TG of this calcium hydroxide. Commercial calcium hydroxide contains as impurity compounds of sulphur at 0.067 % and 0.168 % of SO₃. The peak at about 1000 °C corresponds to the CaSO₃ synthesized in the reaction and the first one detected within 725 and 875 °C, not present in the initial calcium hydroxide, was also found after the reaction with a gas without SO₂ and hence cannot correspond to SO₂.

From mass loss values at about 360 °C and in the range 875-1,025 °C it can be deduced that CaSO₃.1/2 H₂O is the desulfurization product synthesized. The presence of SO₃ with a molecular weight of 80, corresponding to the CaSO₄ decomposition, was also investigated but it was not detected showing that this product has not been synthesized though O₂ is present in the flue gas.

As a summary of TG, DSC and MS results it can be stated that CaSO₄ is not a product of desulfurization reaction at low temperature, being CaSO₃.1/2 H₂O the unique desulfurization product. CaCO₃ is the main product of CO₂ capture and CaO.CO₂ another one. DSC and MS data allows distinguishing the calcination of the CaCO₃ formed from the CO₂ captured than that present in the initial sorbent.

4. Conclusions

The study of the reaction of CO₂ and SO₂ 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 CO₂ release in the reaction of CaCO₃ with SO₂.

According to TG-DSC-MS results, the unique reaction product of calcium hydroxide and SO₂ at this low temperature, despite the presence of O₂, is CaSO₃.1/2 H₂O. The main product of the reaction of CO₂ 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 $\text{CaO}\cdot\text{CO}_2$ complex, postulated in a previous work.

Data of the gas analyzer and TG-DSC-MS techniques allows discussing the evolution of the CaCO_3 present in the sorbent, synthesized in the reaction with CO_2 or disappeared by reaction with SO_2 .

According to the results of the present study, in future works, the use of calcium hydroxide or of sorbents based on this compound at higher temperature will be investigated.

Acknowledgement

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