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Flue gas desulphurization at low temperatures. Thermogravimetric characterization of the reaction product

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Abstract

The chemical behaviour of calcium hydroxide, used as sorbent in the dry desulphurization process at low temperatures has been evaluated by means of thermochemical analysis. The final solid of the desurphurization reaction at low temperatures under conditions simulating exhausting flue gas from coal fired plants has been identified as a mixture of calcium sulphite monohydrate, calcium carbonate and unreacted calcium hydroxide. The influence of the flue-gas composition and the solid conversion in the chemical composition of the final solid has been studied. Results allow the main characteristics of the dry desulphurization reaction at low temperatures using calcium based sorbents to be established by means of thermochemical analysis.

INTRODUCTION

Acid rain and the acidification of the environment has emerged as a serious global problem during recent decades. By far the most dominant air pollutants contributing to acid rain are nitric oxides and sulphur dioxide. World wide, emission of nitric oxides is about 500 tons NO per year; only about 10% of this is manmade. The global annual manmade emissions of sulphur are currently about 75 to 100 million tons; about 70% of this originates from combustion of fossil fuels. The natural emission of sulphur, mainly from the sea and swamp areas, is believed to be of the same magnitude [1]. In clearly defined areas, however, the manmade emissions undoubtedly predominate.

Consequently, regulations are now in effect in many countries to restrict emissions of sulphur and nitrogen oxides and particulate matter generated

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by utilities and industry. The three primary approaches to reducing emissions available today are (1) change the fuel, (2) modify or change the combustion process, or (3) reduce the emissions with a post-combustion treatment system.

The first option (fuel switching), although it would appear simple enough, has several drawbacks related to the availability of raw materials. Changing the combustion process also can prove untenable. If a new installation were being planned, then installation of an advanced combustion system would be a viable option for reduction of sulphur dioxide emissions. However, in the event that this construction was due to the forced shutdown of an existing, not fully depreciated, installation or was being retrofitted onto an operational power plant, then the economics might prove unattractive.

Where an existing installation cannot be shut down, post combustion treatment may prove the only viable emissions-reduction option. Dry scrubbing appears to offer some advantages in comparison with conventional "wet" scrubbing with lime or limestone. These advantages involve capital cost, retrofit capability and ease of waste disposal [2].

In-duct dry sorbent injection is an important new alternative among the dry processes [3]. The technology involves the injection of a dry sorbent, typically hydrated lime, in conjunction with the gas conditioning by water spraying in the ductwork downstream of the air preheater, but ahead of the particulate collection utility in a coal-fired boiler system [4].

A first step in order to describe the desulphurization process is to identify the product of the reaction between $Ca(OH)_2$ and SO_2 at low temperatures. In the literature several authors have proposed different product formulations (calcium sulphite or sulphate), but there is no specific work to clear the notorious disagreement of the literature.

Glasson and O'Neill [5] indicate that the reaction product is $CaSO_3$ at temperatures below 300°C and $CaSO_4$ between 300 and 1000°C. At low temperatures these authors formulate the predominating desulphurization product as $CaSO_3 \cdot 0.5H_2O$.

In the same way Ruiz-Alsop [6], Diffenbach et al. [7] and Moyeda et al. [8] suggest the following sulphation reaction at low temperatures:

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 \cdot 0.5H_2O + 0.5H_2O$$

In contrast, Rice and Bond [9] and Lindbauer [10] suggest $CaSO_4$ as the final reaction product because of oxidation in the presence of oxygen in the gas effluent.

Klingspor et al. [11] do not formule the final product of the reaction, working under similar conditions to Seeker et al. [12,13], but suggest a reaction mechanism with calcium sulphite as sulphation product. However these authors establish the possibility of obtaining calcium sulphate by the oxidation of intermediate species, $H_2O \cdot SO_2$ or HSO_3^-, neglecting the oxidation as being impossible after the formation of calcium sulphite.

Finally, Seeker et al. [12,13] carrying out their experiments at a fixed bed with air and 2200 ppm of SO_2 at temperatures between 63°C and 138°C and water vapour partial pressures between 0.23 and 0.40 atm, analyze the presence of $CaSO_3$ and $CaSO_4$ in the reaction product. Results show that the main amount of sulphur is found as sulphite, in the range between 96% and 69%. These authors indicate that higher bed temperatures increase the appearance of sulphate. However, direct formation of sulphate has been shown to be very slow at these temperatures [14]. Therefore, the oxidation of calcium sulphite to calcium sulphate will proceed at low temperatures, this being the source of the observed sulphate.

Except for Seeker et al. [12,13], the rest of the authors do not analyze the reaction product, and establish the formulation of the dry desulphurization product at low temperatures from the literature.

Taking into account the practical relevance of the reaction between SO_2 and calcitic sorbents at low temperatures, and the disagreement on the identification of the reaction product, in this work the latter has been identified at several reaction conditions using the following analytical techniques: ion chromatography to obtain the degree of the solid conversion and thermogravimetry to obtain the solid decomposition pattern before and after the desulphurization reaction has been performed in a laboratory fixed bed reactor.

By means of the interpretation of these results, the reaction product has been formulated chemically, pointing out the possibility of the product oxidation by the presence of oxygen in the flue gas and the degree of the product hydration.

EXPERIMENTAL

Materials

The sorbent used in this investigation was calcium hydroxide (hydrate) obtained under controlled conditions (isothermal, 100°C; large L/S ratios; CaO available from Dolomitas del Norte S.A.). The physical properties of the sorbent are shown in Table 1.

TABLE 1

Physical properties of the hydrate

Specific surface ($m^2\ g^{-1}$ BET)	17.5
Pore volume ($cm^3\ g^{-1}$)	1.283
Porosity	0.716
Particle diameter (μm)	< 60
Pore diameter (mean) (μm)	0.707
Skeletal density ($g\ cm^{-3}$)	1.964

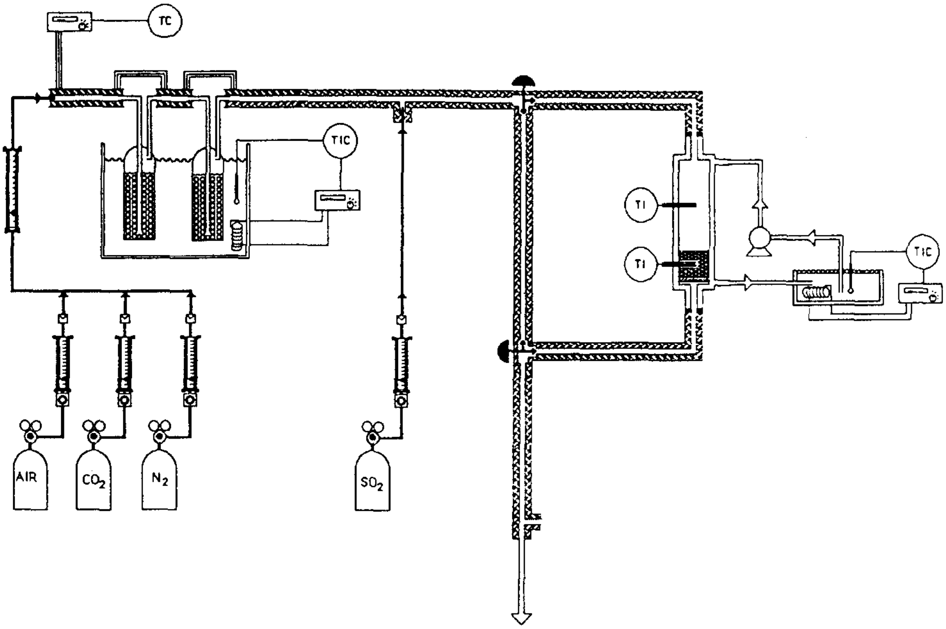


Fig. 1. Experimental set-up.

High purity sulphur dioxide, nitrogen, carbon dioxide and synthetic air were employed, and the desired gas mixtures were obtained by fitting the appropriate flow rates using precalibrated rotameters.

Apparatus and procedures

The reaction was carried out in a jacketed fixed bed reactor made of glass, under isothermal conditions, where the sorbent is dispersed in an inert silica sand. The entire bed is supported on a 3.6 cm diameter fritted glass plate contained in the glass cylinder.

Prior to the addition of SO_2 to the gas mixture, it is passed through the humidification system where the gas is in contact with water vapour produced at a steady rate in two absorbers each of 250 ml. Both flasks contain small glass spheres in order to improve the contact between gas and liquid phases and are submerged in a water bath at maintained constant temperature by means of a controller.

After water saturation and addition of the corresponding amount of SO_2 the gas is conducted to the reactor through a system of preheated pipes. The reactor is maintained at the reaction temperature by means of the hot water passing through the jacket. A schematic diagram of the experimental set-up is shown in Fig. 1.

The wet bulb temperature was measured just downstream of the reactor using a wetted wick thermometer. The difference between dry and wet bulb temperatures is the "approach to saturation", which together with the pressure measurement (U tube manometer) establishes the relative humidity under the test conditions.

After 1 h of reaction the experiment was concluded and the entire bed brought out from the reactor. All the experiments were carried out twice in order to obtain two groups of reacted samples at the same conditions.

One of these samples is sieved to separate the reacted sorbent ($D_p < 60$ μm) from the inert silica sand ($D_p = 200–250$ μm) using a Retsch Vibro type sieving unit. The sorbent without inert sand is analysed using the thermogravimetric technique, in a Perkin-Elmer TGA-7 unit with a PE 7500 microprocessor and a TAC-7 thermal analysis controller. Synthetic air was used as carrier gas (30 ml min^{-1}) in order to oxidize the $CaSO_3$ formed in the desulphurization reaction to $CaSO_4$ and in this way measure the mass increase of the oxidation. In all TG analysis the sample mass was between 5 and 20 mg. The temperature program was

$$30°\text{C} \xrightarrow{20°\text{C min}^{-1}} 600°\text{C (20 min)} \xrightarrow{20°\text{C min}^{-1}} 850°\text{C}$$

The other reacted sample is used to calculate the solid conversion: the sorbent and the silica sand are mixed with 20 ml of 1 M HCl and deionized water in order to solubilize the sorbent and separate it from the inert silica by filtration. The resulting solution is treated with a bichromate solution to oxidize the sulphite anion to sulphate. This solution is analysed with a Dionex Series 2000 i ion chromatograph, with conductivity detector and HPIC-CS5 column.

This analysis allows the quantitative evaluation of the amount of SO_2 that has reacted in the bed as SO_4^{2-}. Therefore, knowing the number of calcium moles in the bed (by means of TG analysis of the sorbent before the reaction) the solid conversion is presented as mol SO_2 per mol calcium and with the mass balance in the bed, the composition of the latter can be obtained as mol of each component per mol of calcium.

RESULTS AND DISCUSSION

The influence of the flue gas without SO_2 in the solid composition has been studied. In Table 2 the reaction conditions are shown. Two experiments without SO_2 each of 1 h duration have been performed with two different compositions of the gas phase: (A) nitrogen, 100%; (B) oxygen, 2%; carbon dioxide, 12%; nitrogen, 86% (dry composition by volume).

The thermal curve of the humidified hydrate in (B) conditions (Fig. 2), indicates that the conversion of $Ca(OH)_2$ into CaO occurs between 420 and 550°C, with an additional mass loss between 600 and 850°C. This mass loss is due to the decomposition of $CaCO_3$, originally in the solid and formed in the carbonation reaction.

TABLE 2

Reaction conditions

Reaction temperature (°C)	52
Relative humidity	0.916
Sorbent	Hydrate
Inert	Silica
Sorbent/inert ratio	1/30
Gas flow rate (cm^3 min^{-1})	1500
Linear velocity (cm s^{-1})	2.5
Sorbent mass (g)	1

In Table 3 the composition of the fresh hydrate and humidified in (A) and (B) conditions, obtained by means of thermal analysis, are shown in mol per mol calcium.

These results indicate that $Ca(OH)_2$ is slightly carbonated in the absence of CO_2 due to the hydrate manipulation after the reaction (A conditions). Calcium hydroxide reacts with carbon dioxide in the flue gas (B conditions) to form $CaCO_3$ that is decomposed in the same temperature range as the calcium carbonate originally in the solid.

In order to evaluate the influence of the gas composition on the desulphurization product, a set of experiments has been carried out. In Table 4 the flue gas composition of the experiments is shown.

The resulting compositions of solids obtained by thermogravimetric and ion chromatography analyses are shown in Table 5.

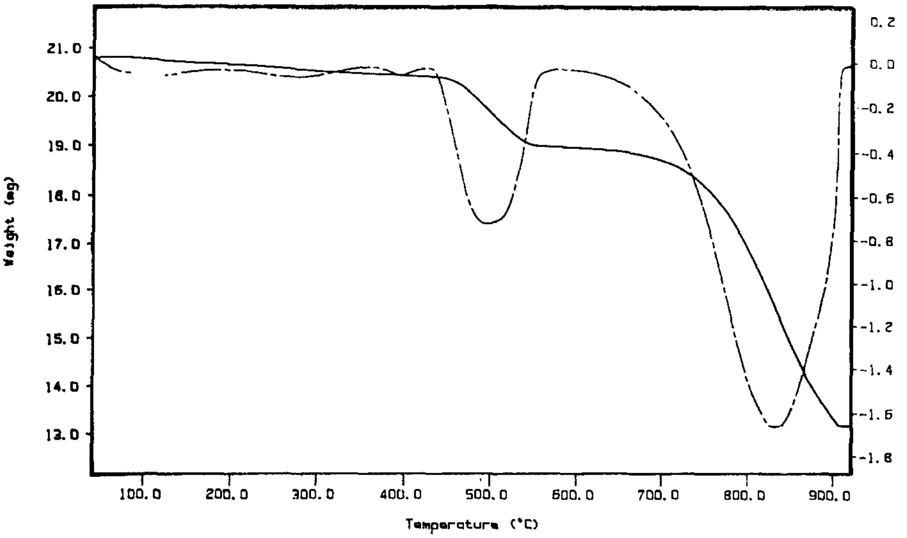


Fig. 2. Thermal curve of the humidified hydrate under (B) conditions.

TABLE 3

Solid composition (mol per mol calcium)

	Hydrate	Humidified in (A)	Humidified in (B)
H_2O of humidity	0.050	0.060	0.108
$Ca(OH)_2$	0.856	0.755	0.397
$CaCO_3$	0.144	0.245	0.602

In Fig. 3 the TG diagrams, mass against time, for the experiments carried out with 1.0% of SO_2 and N_2 (R2) and with 0.01% of SO_2 and N_2 (R4) are shown. The first mass loss, between 30 and 200°C, is due to the humidity of the solid; the second one, between 200 and 375°C is due to the dehydration of the reaction product; the next, between 400 and 460°C, to the dehydration of calcium hydroxide; and the final mass loss, between 600 and 850°C, is due to the decomposition of calcium carbonate. The mass increase between 460 and 600°C is due to the oxidation reaction of the desulphurization product.

Product hydration grade

By means of the mass loss produced between 200 and 375°C, it is possible to calculate the water-of-hydration/product molar ratio. In Table 6 this ratio is shown for each reaction.

This ratio average between hydration water and product indicates that the desulphurization product has one hydration water molecule independent of the flue gas composition and sorbent conversion.

Product oxidation grade

By means of ion chromatography the sorbent solid conversion is obtained as sulphate, so it is impossible to determine the sulphite and sulphate percentage present in the solid. The mass increase in TG analysis due to the oxidation reaction of calcium sulphite

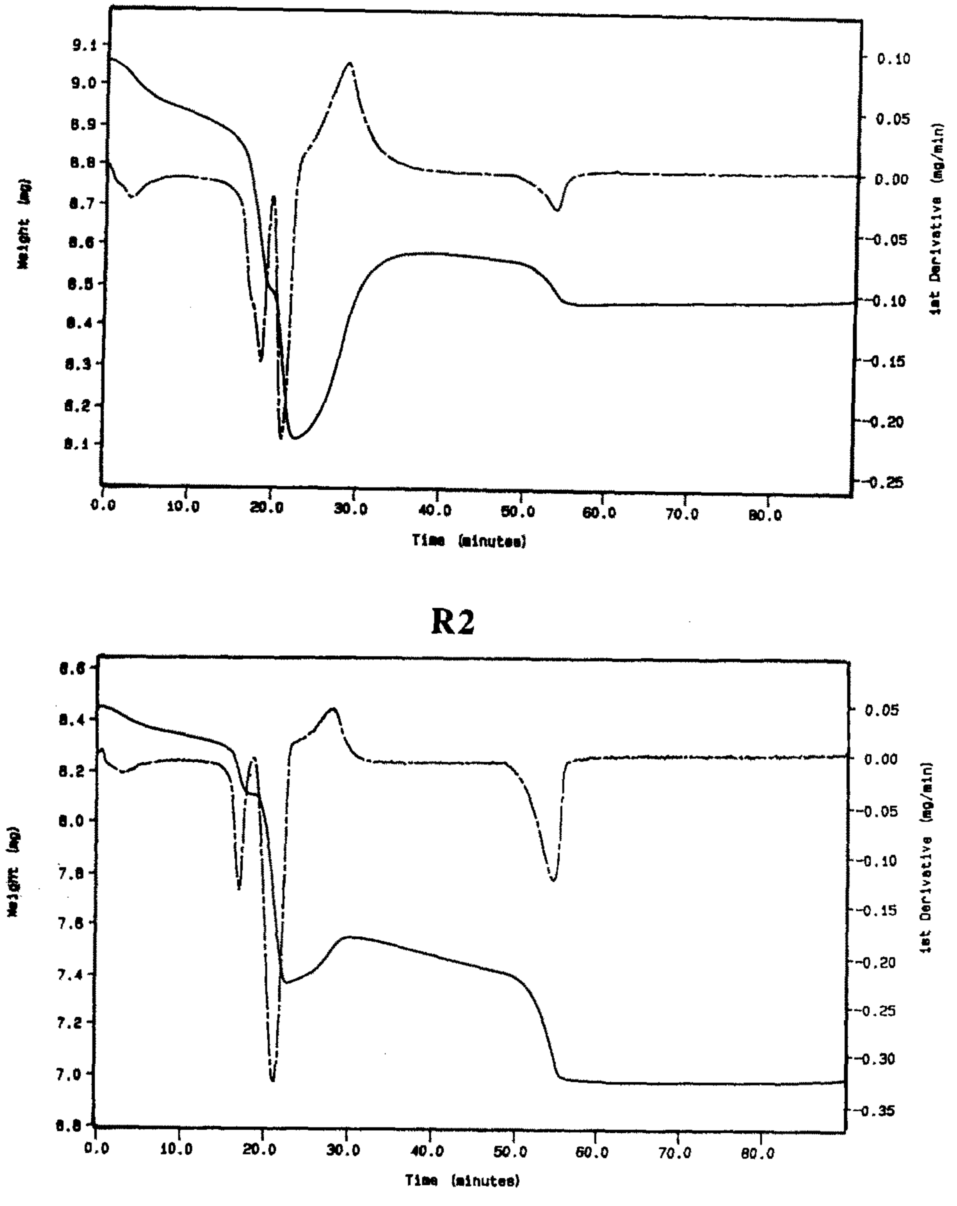
$$CaSO_3 + 0.5O_2 \rightarrow CaSO_4$$

TABLE 4

Flue gas composition

Reaction	Concentration (vol.%)		
	SO_2	CO_2	O_2
R1	100.0	0.0	0.0
R2	1.0	0.0	0.0
R3	1.0	12.0	2.0
R4	0.01	0.0	0.0
R5	0.01	12.0	2.0

carried out in the thermobalance with air as carrier gas, allows us to calculate the number of moles of oxygen consumed by the reacted solid sample. In Table 7 the oxygen consumed to product mole ratio is presented for all reactions.



R2

R4

Fig. 3. Thermal curves for the experiments carried out with 1.0% SO_2 and N_2 (R2) and with 0.01% SO_2 and N_2 (R4).

TABLE 5

Desulphurization product composition (mol per mol calcium)

	R1	R2	R3	R4	R5
H_2O of humidity	0.182	0.147	0.184	0.073	0.109
H_2O of product	0.616	0.503	0.512	0.181	0.153
$Ca(OH)_2$	0.380	0.429	0.435	0.636	0.392
O_2 of oxidation	0.351	0.306	0.271	0.085	0.078
$CaCO_3$	–	0.060	0.055	0.184	0.444
Product	0.620 [a]	0.510 [a]	0.510 [a]	0.180 [a]	0.165 [a]

[a] Obtained by ion chromatography.

This molar ratio average indicates that each mol of product needs 0.53 mol of oxygen to be oxidized. As the stoichiometric ratio is 0.50, the total product is $CaSO_3$, independent of the oxygen present in the flue gas. Therefore the dry desulphurization product at low temperatures using calcium based sorbents is calcium sulphite monohydrate $CaSO_3 \cdot H_2O$.

Apart from this main conclusion a number of others can be reached after reviewing the data of Table 5.

In the reactions carried out with high SO_2 concentrations (R1, R2 and R3) the calcium carbonate originally in the sorbent (0.144 mol $CaCO_3$ per mol calcium) reacts totally (R1) and partially (R2, 0.060 mol $CaCO_3$ per mol calcium; R3, 0.055 mol $CaCO_3$ per mol calcium) with the SO_2, unreacted $Ca(OH)_2$ remaining in the solid.

The reactions with CO_2 (R3 and R5) and without CO_2 (R2 and R4) reach the same solid conversion at the same SO_2 concentrations. This indicates that the $CaCO_3$ produced during the carbonation of the $Ca(OH)_2$ has the same behaviour with the SO_2 as the reactive calcium hydroxide, and both compounds, $CaCO_3$ and $Ca(OH)_2$, lead to the same desulphurization product $CaSO_3 \cdot H_2O$. Therefore the CO_2 in the flue gas has no influence on the final solid conversion of the adsorbent, in spite of reacting with $Ca(OH)_2$ to form $CaCO_3$.

TABLE 6

Water-of-hydration/product molar ratio

R1	0.99
R2	0.99
R3	1.00
R4	1.00
R5	0.93
Average	0.98

TABLE 7

O_2 of oxidation/product molar ratio

R1	0.57
R2	0.60
R3	0.53
R4	0.47
R5	0.47
Average	0.53

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