INFLUENCE OF THE TEMPERATURE ON CALCIUM SULFITE CONTENT OF THE REACTION OF SO₂ WITH CaO

K. M. ALLAL, M. ABBESSI and M. ZERDAOUI

Institut de Chimie industrielle, Universite de Annaba, B.P. 12, El hadjar, Algeria
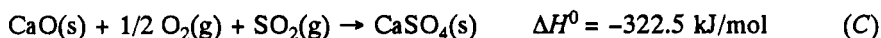
The purification of the gases containing sulfur oxides such as SO_2 and SO_3 can be realized by reacting with dry alkaline substances like calcium oxide. At relatively low temperatures (<500 °C) calcium sulfite ($CaSO_3$), an unstable product of the reaction can be formed and may react reversibly to give back SO_2. It is therefore important that the reaction be controlled. The influence of the temperature on the amount of calcium sulfite formed has been studied experimentally by means of a thermobalance. The formation of $CaSO_3$ can be avoided if the temperature is higher than 650 °C.

Flue gases containing sulfur dioxide and sulfur trioxide are released by many industries into the atmosphere. It is therefore necessary to purify the flue gases in order to minimize the effect of air pollution. One way to reduce the content of these acid gases is through reactions with dry and fine alkaline sorbents such as CaO, $CaCO_3$ and $Ca(OH)_2$ in fixed or fluidized bed reactors[1-3].

During the last twenty years, a number of investigations have been made on the kinetics of the reaction of SO_2 with limestones in the dry desulfurization process. Two major directions have been emphasized in these investigations:

1. the study of the effect of various process variables on the reaction rate[4-6] and
2. the identification of the reaction mechanism with the help of a suitable model[7,8].

The sorption of SO_2 by limestones or calcium hydroxide involves two consecutive reaction steps as shown below.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \qquad \Delta H^0 = 178.9 \text{ kJ/mol} \qquad (A)$$

$$Ca(OH)_2(s) \rightarrow CaO(s) + H_2O(g) \qquad \Delta H^0 = 109.5 \text{ kJ/mol} \qquad (B)$$

$$CaO(s) + 1/2\,O_2(g) + SO_2(g) \rightarrow CaSO_4(s) \qquad \Delta H^0 = -322.5 \text{ kJ/mol} \qquad (C)$$

A study on the effect of temperature on dissociation of $CaCO_3$ and $Ca(OH)_2$ showed that maximum surface area (as measured by BET method) was obtained at temperatures

of 800 °C for a 10 μm particle diameter of $CaCO_3$ and at 650 °C for a 6 μm particle diameter of $Ca(OH)_2$ (Fig. 1). This agrees with the fact that high conversion rates of CaO to $CaSO_4$ are reached at these temperatures[9,10].

The rate of sulfation (reaction (C)) is the important step in all pollution control processes. Calcium oxide formed from reaction (A) or (B) can react with SO_2, in the presence of oxygen, to give calcium sulfate according to the reaction (C), and in the absence of oxygen at relatively low temperatures to produce calcium sulfite according to reaction (D).

$$CaO(s) + SO_2(g) \rightarrow CaSO_3(s) \qquad \Delta H^0 = -240 \text{ kJ/mol} \qquad (D)$$

Because $CaSO_3$ may be formed during the process and since it can react reversibly to produce SO_2, it is consequently essential that the effect of the temperature of the reaction on the amount of sulfite formed is studied. In this paper the experiments have been carried out by means of a thermogravimetric method. The temperature range at which the adsorption should be realized in order to avoid the formation of $CaSO_3$ is consequently defined.

The objective of the present work is to determine the amount of calcium sulfite formed through reaction (D), and the optimum temperature at which one should carry out the experiment to get the lowest amount of sulfite, hence a better conversion rate of CaO to $CaSO_4$.

EXPERIMENTAL

A thermobalance (type STA 429 from Netzch) has been used as a differential reactor for the experimental determination of the sulfite content. The apparatus shown in Fig. 2 can register the weight increase of the solid sample during the reaction. To obtain differential measurements, the use of small masses of sorbents and relatively high flow rates of gases are necessary[9]. During the experiment, the sample must be placed on a inert carrier made of ceramic fibers. The sample is heated with a defined heating rate. From the top through L1 nitrogen was introduced (Fig. 2). This is done to evacuate CO_2 and H_2O formed during
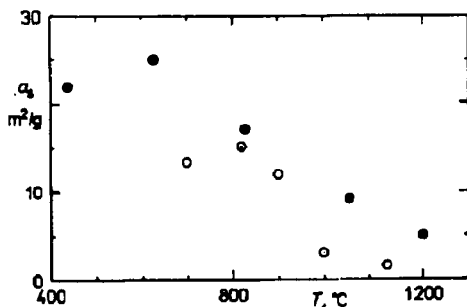

Fig. 1
Influence of the temperature of dissociation on the specific area (a_s) of CaO. O $CaCO_3$ (10 μm), ● $Ca(OH)_2$ (6 μm)

reactions (*A*) and (*B*) through L3. Once the temperature of the reaction is reached, with the weight of the sample being constant, sulfation reaction can be started. The sulfated products are heated afterwards under an inert atmosphere of nitrogen and, an UV spectrometer was installed in order to detect the SO_2 content in the flue gas.

A series of 8 mg samples of $CaCO_3$, having a particle diameter equal to 10 μm, were first calcinated at 800 °C. The sulfation reaction was carried out, with SO_2 at a concentration equal to 1 000 ppm, at different temperatures between 300 °C and 650 °C in a thermobalance.

RESULTS AND DISCUSSION

The heating under a inert atmosphere (N_2) of the sulfated products brings about a first decrease in weight at a temperature of about 600 °C, followed by a second one at a temperature of 1 050 °C. Figure 3 represents a typical experimental data set using a thermobalance. The dash-doted curves *1, 2, 3* and *4* represent the temperature change during the experiment. The dark curve shows the change in weight of the sample as a function of time. The first part of the curve shows an increase of the weight due to the adsorption of the sulfur oxide molecules by the sorbent at a constant temperature of 400 °C according to reactions (*C*) and (*D*). The second part, corresponding to the heating process, represents two alternative increases and decreases in weight of the sample. These are presumably caused by the buoyancy effect (for the increases) and the dissociation of $CaSO_3$ and $CaSO_4$ (for the decreases). Measurements realized by means of the UV spectrometer show a first peak of SO_2 corresponding to the dissociation of $CaCO_3$ according to the following reaction:
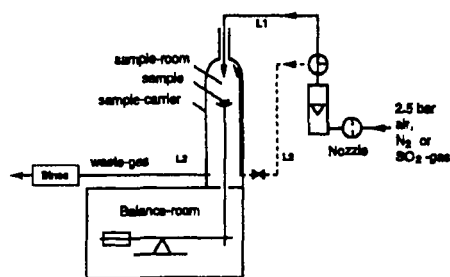
$$CaSO_3(s) \rightarrow CaO(s) + SO_2(g) \qquad (E)$$
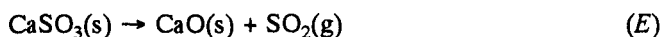

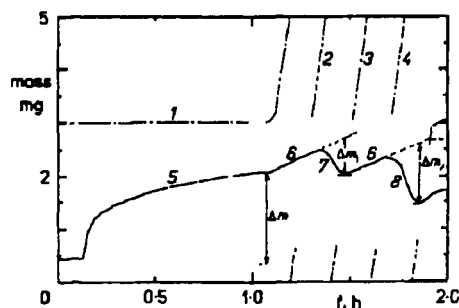FIG. 2

Experimental set up

FIG. 3

Sulfation at 400 °C. Curves *1 – 4*: temperature change during the experiment. *5* Sulfation reaction, *6* heating process, *7* dissociation of $CaCO_3$, *8* dissociation of $CaSO_4$. Temperature change during the experiment *1* 500 °C, *3* 1 000 °C

reaching a maximum concentration of 130 ppm as shown in Fig. 4. Proceeding further in the heating process leads to the appearance of a second peak of SO_2 due presumably to the dissociation of $CaSO_4$ according to the below reaction:

$$CaSO_4(s) \rightarrow CaO(s) + SO_2(g) + 1/2\, O_2(g) \qquad (F)$$
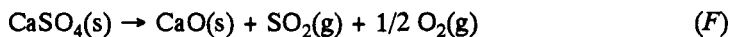
The increase in weight due to the buoyancy effect has been determined as a function of the temperature, and taken into consideration in the calculations.

The sulfite content is therefore given by the following relation:

$$\text{mole \% of } CaSO_3 = \frac{\Delta m_1}{M_{SO_2}} \left(\frac{\Delta m_1}{M_{SO_2}} + \frac{\Delta m_2}{M_{SO_3}} \right)^{-1} 100, \qquad (1)$$

where Δm_1 is mass of SO_2 produced from reaction (E), Δm_2 is mass of SO_3 produced from reaction (F), M_{SO_2} is molecular weight of SO_2, and M_{SO_3} molecular weight of SO_3.

According to the mass balance,

$$\Delta m_1 + \Delta m_2 = \Delta m, \qquad (2)$$

where Δm corresponds to the mass of sulfur oxides that reacted through reactions (C) and (D).

The amount of sulfite formed is represented in Fig. 5 as a function of the temperature of the reaction, reaching a maximum at a temperature of 400 °C. The $CaSO_3$ content is
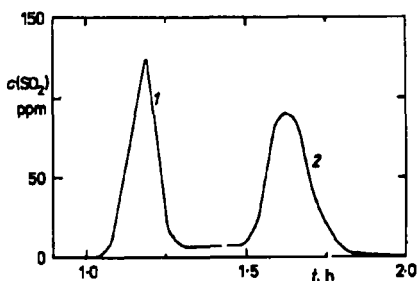

FIG. 4
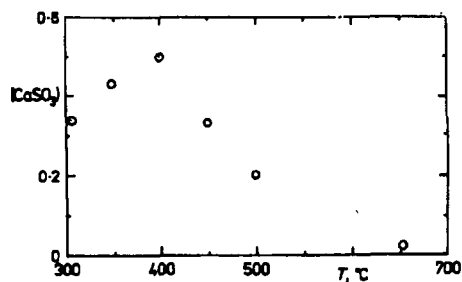Heating in nitrogen atmosphere. *1* Dissociation of $CaSO_3$, *2* dissociation of $CaSO_4$

FIG. 5
Influence of the temperature on the $CaSO_4$ mole fraction (x). Sorbent $CaCO_3$ (10 μm), SO_2 concentration 1 000 ppm, $T = 800$ °C

negligable at temperatures higher than 650 °C. It is therefore advised, for industrial applications, to operate in this range in order to avoid the formation of $CaSO_3$.

A part from this, at temperatures higher than 600 °C, disproportion of calcium sulfite to calcium sulfide and calcium sulfate may happen according to the following reaction:

$$4\,CaSO_3(s) \rightarrow CaS(s) + 3\,CaSO_4(s) \qquad \Delta H^0 = -75.2\ kJ/mol\,, \qquad (G)$$

where a maximum amount of sulfide is reached at a temperature of 800 °C. Because this reaction is not related to any change in weight, it is impossible to evaluate the amount of CaS formed by means of a thermobalance. However, the amount of sulfide formed can be neglected since sulfation reactions have been carried out at temperatures lower than 650 °C.

Another way to measure the amount of sulfite formed is through the oxidation of $CaSO_3$ according to the reaction:

$$CaSO_3(s) + 1/2\,O_2(g) \rightarrow CaSO_4(s)\,. \qquad (H)$$

An increase in weight corresponding to the amount of oxygen that reacted is to be expected in a thermobalance, as shown in Fig. 6. The amount of calcium sulfite is therefore deduced from the stoichiometry of the above reaction assuming a 100% conversion. The effect of the buoyancy must be taken into account when measuring the amount of oxygen reacted.

To confirm the amount of sulfite calculated from Eq. (1), the oxidation of $CaSO_3$ method should be carried out quantitatively.
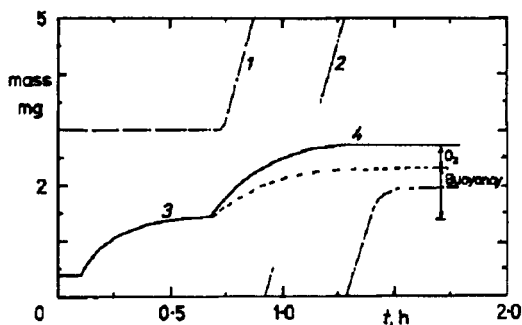
FIG. 6
Experimental recording on a thermo-balance during the oxidation of $CaSO_3$ ($T = 400$ °C). Temperature change during the experiment 1 500 °C, 2 750 °C; 3 sulfation reaction, 4 oxidation of $CaSO_3$

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