Absorption of Sulfur Dioxide by Limestone in a High Temperature Fluidized Bed

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The importance of the limestone desulphurization process for the control of sulfur dioxide pollution has been emphasized.   Details of the experimental set-up for such a process along with the necessary analytical procedures have been described.   Factors influencing the sulfation reaction have been critically discussed.

NOTATIONS

d = particle diameter, μm

T = reaction temperature, °K

t = reaction time, hr

V = fluidizing velocity, m^3/hr

V_{mf} = minimum fluidizing velocity, m^3/hr

W_s = sulphur amount as calcium sulphate, %

r = additive ratio, $\dfrac{(CaCO_3) \text{ actual}}{(CaCO_3) \text{ theoretical}}$

INTRODUCTION

Rapid industrialization has been the principal cause for the" growing problem of atmospheric pollution by sulfur dioxide emission.   Statistics indicate that the discharge of sulfur dioxide to the atmosphere in the USA amounted to about 34 Mt in 1970 which is likely •to double by 1990 with the continuation of the present practices for SO_2 control[1].   Coal and oil-based power plants; ore smelters and crude processing refineries are the major sulfur dioxide emission sources. • Various schemes have been proposed for its removal from waste gases and a comparative description of these is available in.literature[2,3].

The'four major desulphurization processes available

T   ' '

1. Catalytic process (oxidation of SO_2 to H_aSO_4 or reduction of SO_2 to elemental sulphur).

2. Absorption of SO_a on activated carbon (Reinluft process),3. Alkali-aluminium oxide process and

4; Lime-limestone process.

Of these the lime-limestone process has been widely accepted in view of its inherent advantages such as simplicity of the process, low capital investment and ready availability of the material at low cost.   Though the process can either be dry or wet type, the former is more widely adopted.   Two' serious drawbacks of this process are the low desulphurization efficiency and the poor additive utilization.   The salient points of different investigations relating to the two main aspects of dry limestone desulphurization process, namely, the reactivity parameters of lime with respect to SO_2 and the mechanism of lime sulfation reaction have been reviewed by the authors.   The objective of the investigations reported in this paper was to study the influence of various reaction parameters on the limestone sulfation reaction in a high temperature fluidized bed.

EXPERIMENT

Fig 1 shows the essential features of the experimental set-up used.   The most important part of the unit is the resistance-heated tubular fluidized bed reactor (Fig 2) consisting of three concentric graphite tubes of 14,19.8 and 27 cms inside diameter.   The outermost tube is
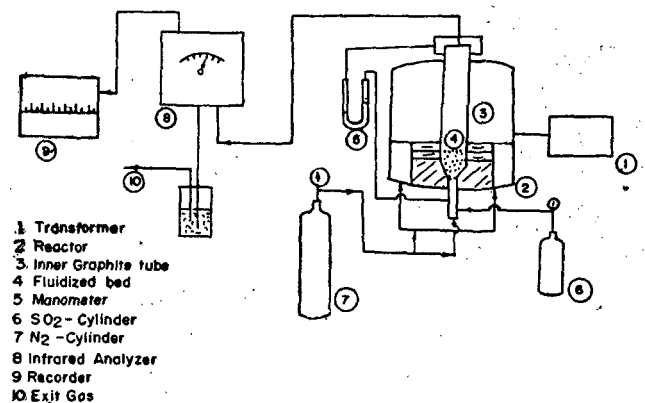

1 Transformer
2 Reactor
3 Inner Graphite tube
4 Fluidized bed
5 Manometer
6 SO2 - Cylinder
7 N2 - Cylinder
8 Infrared Analyzer
9 Recorder
10 Exit Gas

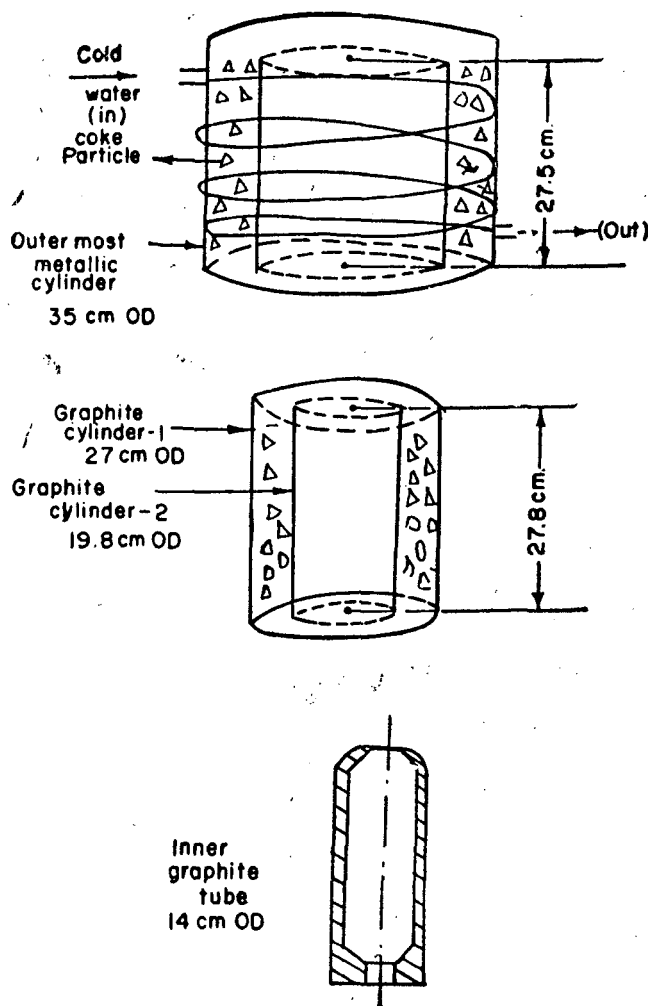Fig 1 *Schematic diagram of the experimental set-up.*

Fig 2 Details of the reactor

of cast iron with 35 cm inside diameter and has eight cooling coils. Nitrogen was used as the fluidizing gas and sulfur dioxide in definite proportion was injected into the nitrogen stream. The quantity of the gases was measured by calibrated rotameters. Pressure drop across the fluidized bed reactor was measured with a manometer. Limestone particles were charged into the innermost graphite tube. A copper sieve of 75 micron size was fixed to the bottom of this tube to support the fluidized bed.

The minimum fluidization velocities for the different particle sizes were determined by separate experiments. While taking a run, a definite amount of limestone was charged into the reactor and heating was continued in a nitrogen atmosphere, till the desired reaction temperature was reached. The velocity of the fluidizing gas was maintained higher than the minimum to ensure fluidized conditions of the reacting limestone particles. Sulfur dioxide was then introduced in definite proportion into the nitrogen stream and the reaction proceeded for a fixed time. The reacted material was then analyzed gravimetrically for its sulfur content after conversion of the sulfur compound formed to the corresponding sulphate with the help of an oxidizing agent. The inlet and outlet compositions of sulfur dioxide with respect to the reactor was continuously recorded with the help of an on-line infrared analyser. The distribution of sulfur in the reacted ljmestone particle was obtained with the help of a scanning electron microscope.

The experiments were conducted for particle size (d) ranges 500-700, 800-1000 and 1000-1300 pm; at reaction temperatures (T) 1170, 1220, 1270 and 1370°K; for reaction times (t) 0.5, 1.0 and 2.0 hr; with relative gas fluidizing velocities (Vj/V_{mf}) 1.4, 1.8, 2.2 and 2.6; for additive ratios (r) 2.0, 3.0 and **4.0**

RESULTS AND DISCUSSION

INFLUENCE OF REACTION TEMPERATURE •

Temperature dependency of the sulfation reaction can be seen from the chemical analysis of the reacted particles (Table 1). From thermodynamics and also
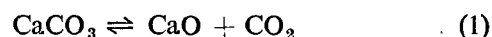
TABLE 1 SULPHUR CONTENT OF REACTED PARTICLES*

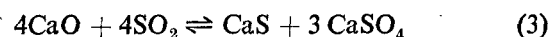| T,°K	Ws, %
1 170	50.70
1 220	57.42
1 270	60.54
1 370	5.81

*at t = 0.5 hr, d = 500-700 μm and r = 2.0

from the previous investigations, 1 300°K has been found to be the optimum reaction temperature. Above this temperature, the absorption capacity of limestone is low. The reason for this' can be explained from, the following reactions which take place in a non-oxidizing atmosphere.

Calcination

$$CaCO_3 \rightleftharpoons CaO + CO_2 \qquad (1)$$

Sulfation

$$CaO + SO_2 \rightleftharpoons CaSO_3 \qquad (2)$$

$$4CaO + 4SO_2 \rightleftharpoons CaS + 3CaSO_4 \qquad (3)$$

Calcination at high temperature produces dead burnt lime, which has lower sulfur dioxide absorption capacity than the normal lime[4]. Further at temperatures much above 1 300°K, the backward reactions (2) and (3) become prominent as is evident from Fig 3.

INFLUENCE OF REACTION TIME

The sulfate content of the reacted limestone particles increases with increase in reaction time (Fig 4). • For each particle size and reaction temperature, there exists a definite reaction time after which further sulfation does not take place. It can also be concluded that the sulfation reaction proceeded rapidly in its early stages but slowed down as the time of exposure continued. This finding is in conformity with that of Hartman and Coughlin[5]. • •

INFLUENCE OF THE AMOUNT OF CALCIUM CARBONATE

In view of the low additive utilization, the amount of limestone used in all the above investigations was twice the stoichiometric amount. To study the effect of the
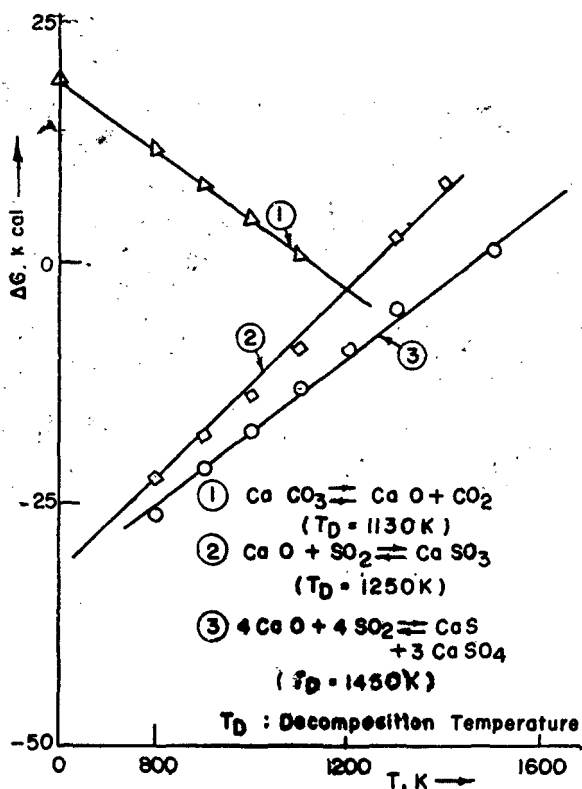
Fig 3 Heats of formation (ΔG) for calcination and sulfation reaction as function of temperature
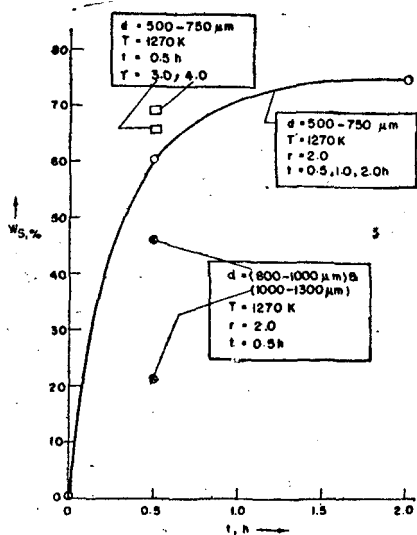
Figure labels:
(1) Ca CO$_3$ ⇌ Ca O + CO$_2$
   (T$_D$ = 1130 K)
(2) Ca O + SO$_2$ ⇌ Ca SO$_3$
   (T$_D$ = 1250 K)
(3) 4 Ca O + 4 SO$_2$ ⇌ CaS
   + 3 Ca SO$_4$
   (T$_D$ = 1450 K)
T$_D$: Decomposition Temperature

Fig 4 Effect of other reaction variables (r, f. d.) on sulfation reaction

amount of calcium carbonate on the absorption capacity, three and four times the stoichiometric amounts were used for reaction. Maximum sulfate conversion Was obtained when the limestone used was four times the theoretical amount as is evident from Fig 4.

INFLUENCE OF PARTICLE SIZE

Three different particle sizes were used for the sulfation reaction. The conversion was inversely proportional to particle size (Fig 4).

INFLUENCE OF PRECALCINATION -

Calcination of limestone before sulfation increases the reactivity of the particles. For a comparison,

three samples of limestone were precalcined at 1 270°K and were then reacted with sulfur dioxide. The sulphate contents were found to be higher in each case than the corresponding uncalcined sample (Fig 5).
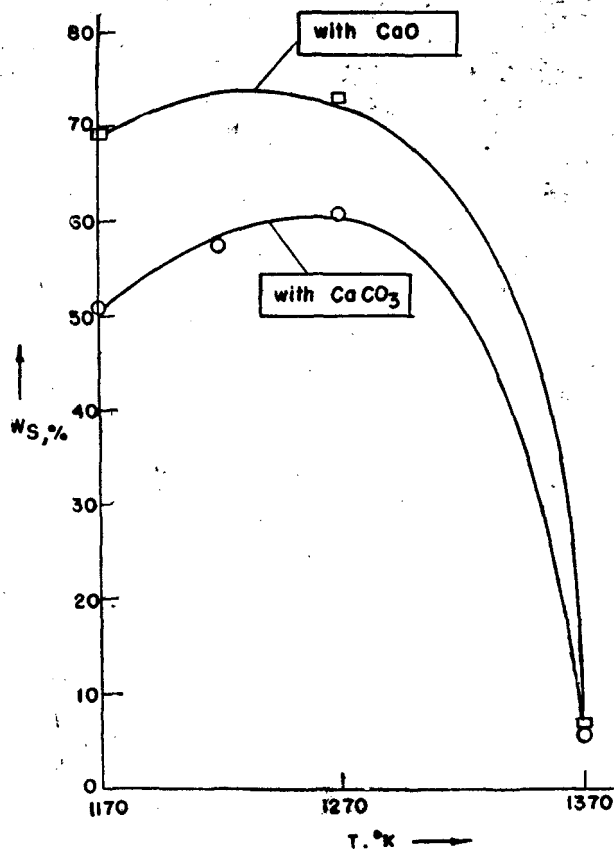

Fig 5 Effect of reaction temperature and pre-calcination on sulfation reaction

The activation energy calculated with the help of Arrhenius equation for the four runs (Table-1) was found to be 120 kj/mole.

ACKNOWLEDGEMENT

REFERENCES

1. J M. Ludwig and P. W. Spaite. Control of Sulfur Oxide Pollution'. Chemical Engineering Progress, vol 63, no 6,1967, p 82.

2. BR Hubble, SSiegel and P T Cunningham. On the Feasibility of the CaSO$_4$—CaS Reaction for Regeneration of Sulfated Dolomite or Limestone in Sulfur Dioxide Pollution Control Processes'. Journal of the Air Pollution Control Association, vol 25, no 12,1975, p 1256.

3. C G Cortelyou. 'Commercial Processes for SO$_2$ Removal'. Chemical Engineering Progress, vol 65, no 9,1969, p 69.

4. G K Roy and W Weisweiler. Kinetics of Lime-Limestone Sulfation. High Tempercturescind High Pressures, vol 31, 1981, p333.

5. D C Drehmel.'Test tc Evaluate Reactivity of Boiler—Calcined Limestone used in Air Pollution Control'. Proceedings of American Power Conference, vol 50, no 8, 1971, p 666.

6. M Hartmann and R W Coughlin. 'Reaction of Sulfur dioxide with Limestone and the Grain Model'. American Institute of Chemical Engineers Journal, vol 22, no 3, 1976, p 4S0.

DISCUSSION

S K Mukherjee

What is the bed temperature ? What is the 1ype of membrane used? Does attrition due to fluidization scrub off reaction product and expose new reactive surface?.

Author

Bed temperature varied from 1 170 to 1 370°K. The membrane used was a grid of copper. Yes, particle attrition exposes new reactive surface; but in the present work this aspect was not studied quantitatively.

Dr P Dakshinamurthy

What is the efficiency of absorption?

Author

The efficiency of absorption is defined in terms of calcium sulfate formed after absorption reaction and its numerical value varies from 5% to 60 % depending on particle size, reaction time and temperature, and pre-calcination.