

Absorption Mechanism of Sulphur dioxide Pollutant in a High Temperature Fluidized Bed of Limestone

Dr G K Roy, Associate Member

Dr W Weisweiler, Non-member

The limitations of the limestone desulphurization process as an abatement measure for sulphur dioxide pollution have been outlined. A quantitative approach to the absorption of sulphur dioxide on limestone in terms of various reaction variables has been attempted. The mechanism of limestone sulphation reaction has been postulated. A correlation for the diffusion coefficient of sulphur dioxide in limestone has been suggested.

NOTATIONS

- d = particle diameter, μm
 D = diffusion coefficient, cm^2/sec
 t = reaction time, hr
 T = reaction temperature, $^\circ\text{K}$
 r = additive (sorbent) ratio, $\frac{(\text{CaCO}_3)_{\text{actual}}}{(\text{CaCO}_3)_{\text{theoretical}}}$
 W_s = sulphur amount as calcium sulphate, %

INTRODUCTION

In recent years pollution due to sulphur dioxide emission from power plants consuming sulphur-laden fuel, ore smelters and various sulphur or sulphuric acid based chemical industries has created increasing awareness all over the world. Among the various schemes proposed to abate the pollution^{1,3} one economic proposition of wide applicability has been the use of limestone and dolomite as sorbents in processes for SO_2 removal from flue gas wherein the contact between the sorbent material and the gas is readily obtained either by dry injection of material into the boiler combustion chamber or by passing combustion gases through a bed of limestone.

Although much information is available on the role of chemical composition, physical properties and pretreatments of sorbents of varied geologic origin on sorbent capacity, kinetic information available on limestone sulphation reaction is comparatively scanty. An exhaustive review⁴ has been made by the authors on limestone sulphation reaction kinetics. It has been observed by

earlier investigations that there are two major limitations of the dry limestone desulphurization process: (1) poor additive utilization and (2) low desulphurization efficiency. As a first step of refinement the authors have conducted several absorption experiments in a high temperature fluidized bed and obtained encouraging results. Reactivity of calcium oxide (the decomposition product of limestone) reported to have ceased at low sulphate conversion was found to be appreciably enhanced in a fluidized bed⁵.

EXPERIMENTAL

The essential features of the experimental set-up has been given elsewhere⁵. Absorption of sulphur dioxide from a $\text{N}_2\text{-SO}_2$ mixture was achieved in a high temperature fluidized bed of limestone. The reacted material was analysed for its sulphur content gravimetrically. The distribution of sulphur in the reacted limestone particles was obtained with the help of a scanning electron microscope. The experiments were conducted for particle size (d) ranges 400-500, 500-750, 800-1 000, 900-1 100 and 1 000-1 300 μm ; at reaction temperatures (T) 1 070, 1 170, 1 220, 1 270, 1 370 and 1 470 $^\circ\text{K}$; for reaction times (t) 0.5, 1.0, 1.5, 2.0 and 3.0 hr, and for additive ratios (r) 1.5, 2.0, 3.0, 4.0 and 5.0.

RESULTS AND DISCUSSION

QUANTITATIVE APPROACH TO SULPHUR DIOXIDE ABSORPTION ON LIMESTONE IN TERMS OF REACTION PARAMETERS

The dependency of sulphation reaction on various reaction parameters, namely, the reaction temperature and the time, the particle size and the amount of the

Dr G K Roy is with Regional Engineering College, Rourkela, and Dr W Weisweiler is with Institute für Chemische Technik, Universität Karlsruhe, West Germany.

This paper was received on October 9, 1982. Written discussion on this paper will be received until April 30, 1983.

sorbent has been established. Amount of sulphur dioxide absorption reported as conversion of the sorbent to calcium sulphate was found to be directly proportional to the reaction temperature upto the optimum value. Also the conversion is directly proportional to reaction time and sorbent (additive) amount and indirectly proportional to the particle size of the additive material within the ranges of experiments conducted.

Correlation

The amount of conversion can be expressed as a function of the reaction parameters as

$$W_s = A(T)^{a_1}(t)^{a_2}(r)^{a_3}(d)^{a_4} \quad (1)$$

where A is a constant and a_1, a_2, a_3, a_4 are the exponents of the reaction variables. The effect of the individual variable can be seen from Table 1. By plotting the

TABLE 1 EFFECT OF VARIOUS REACTION PARAMETERS ON CONVERSION

REACTION TEMPERATURE		
Operating Parameter, T, °K	% Conversion, W_s	Constant Parameters
1 000	39.00	t = 0.5 hr r = 2.0 d = 500 - 750 μm ($d_{\text{av}} = 625 \mu\text{m}$)
1 170	50.70	
1 220	57.42	
1 270	60.54	
REACTION TIME		
Operating Parameter, t, hr	% Conversion, W_s	Constant Parameters
0.5	60.54	T = 1 270°K r = 2.0 d = 500 - 750 μm ($d_{\text{av}} = 625 \mu\text{m}$)
1.0	68.00	
1.5	71.00	
2.0	75.00	
ADDITIVE AMOUNT		
Operating Parameter, r	% Conversion, W_s	Constant Parameters
1.5	56.00	T = 1 270°K t = 0.5 hr d = 500-750 μm ($d_{\text{av}} = 625 \mu\text{m}$)
2.0	60.54	
3.0	65.90	
4.0	68.94	
5.0	72.00	
PARTICLE SIZE		
Operating Parameter, $d_{\text{av}}, \mu\text{m}$	% Conversion, W_s	Constant Parameters
450	92.00	T = 1 270 °K r = 2.0 t = 0.5 hr
625	60.54	
900	45.94	
1 000	30.00	
1 150	21.20	

Conversion against each of the reaction variables on log-log co-ordinates, the exponents of equation (1) are evaluated. After substitution of these exponents, equation (1) becomes

$$W_s = A [(T)^{1.67} (t)^{0.23} (d)^{-1.29} (r)^{0.37}]^B \quad (2)$$

where B is the exponent of the overall product.

The products have been calculated and plotted against conversion. The data fits well into a straight line by the least square method (Fig 1) and the equation for the line is given by

$$W_s = 1.49 (T)^{1.64} (t)^{0.23} (d)^{-1.26} (r)^{0.36} \quad (3)$$

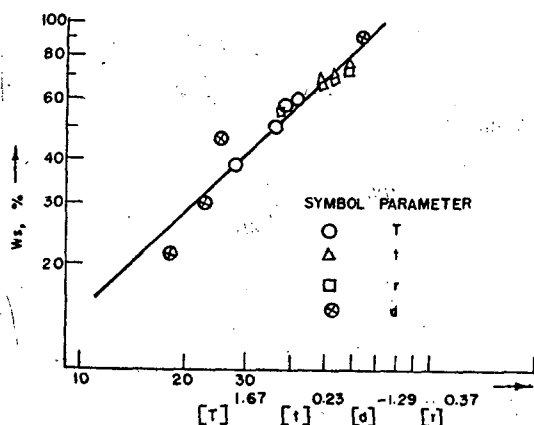


Fig 1 Relationship between conversion and system variables

The values of the conversion calculated by using the above equation have been compared with the experimental values in Table 2. The calculated values differ from the experimental by $\pm 17\%$ for most of the cases and the mean and standard deviations have been found to be 7.6 and 10.5, respectively.

TABLE 2 COMPARISON OF CONVERSION VALUES

T, °K	t, hr	$d_{\text{av}}, \mu\text{m}$	r	$W_s, \%$ (EXPERIMENTAL)	$W_s, \%$ (CALCULATED)	% DEVIATION
1 000	0.5	625	2.0	39.00	40.69	+4.33
1 170	0.5	625	2.0	50.70	52.64	+3.83
1 220	0.5	625	2.0	57.42	56.38	-1.81
1 270	0.5	625	2.0	60.54	60.22	-0.53
1 270	1.0	625	2.0	68.00	70.63	+3.87
1 270	1.5	625	2.0	71.00	77.53	+9.20
1 270	2.0	625	2.0	75.00	82.83	+10.44
1 270	0.5	625	1.5	56.00	54.29	-3.05
1 270	0.5	625	3.0	65.90	69.69	+5.75
1 270	0.5	625	4.0	68.94	77.29	+12.11
1 270	0.5	625	5.0	72.00	83.75	+16.32
1 270	0.5	450	2.0	92.00	91.098	-0.98
1 270	0.5	900	2.0	45.94	38.03	-17.22
1 270	0.5	1 000	2.0	30.00	33.31	+11.03
1 270	0.5	1 150	2.0	21.20	27.93	+31.75

POSTULATION OF REACTION MECHANISM

About ten reacted particles from each of the runs have been analyzed for the distribution of sulphur in a scanning electron microscope. Two distinct phenomena are observed from the electro-micrographs obtained.

For most of the cases the concentration of sulphur has been found to decrease along the diameter and reach almost to zero value towards the centre of the particles (Fig 2). This suggests diffusion to be the rate-limiting step in the reaction of sulphur dioxide with limestone. For very small particles, sulphur concentration has been found to decrease along the diameter upto a certain distance after which it remains almost unaltered indicating thereby the combined influence of diffusion and chemical reaction. However, in general, the non-catalytic reaction of sulphur dioxide with limestone can be assumed to be diffusion-controlling, which is in conformity with the observations of earlier investigators¹⁻³. The diffusion coefficients for a few cases have been calculated.

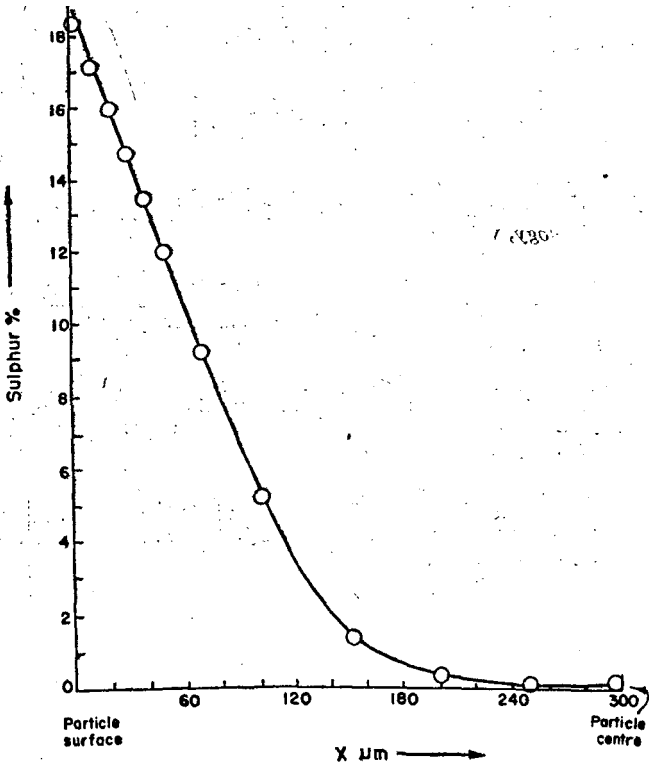


Fig 2 Distribution of sulphur along the diameter of a reacted particle

It is observed that the rate of reaction or, consequently the rate of diffusion is inversely proportional to particle size and reaction time and directly proportional to reaction temperature (up to the optimum value of temperature). Sorbent particles of different sizes present pore structures of varying characteristics which influence the rate of diffusion. Further the pore size distribution of the ultimate reacting particles, (the calcined limestone) is considerably affected by the calcination temperature. Beyond the optimum temperature, dead burnt lime with poor pore structure is formed which reduces the diffusion rate of sulphur dioxide. The rate of diffusion decreases with time owing to pore mouth closure and formation of a calcium sulphate layer on the calcium oxide surfaces.

Correlation

The diffusion coefficient for the non-catalytic SO₂-CaCO₃ reaction can be expressed as

$$D = B(T)^{b_1} (d)^{b_2} (t)^{b_3} \quad (4)$$

where B is a constant and b_1, b_2, b_3 are the exponents of the reaction variables. The effect of individual variable can be seen from Table 3. By plotting the conversion against each of the reaction variables on log-log co-ordinates, the exponents of equation (4) are evaluated. After substitution of the exponents, equation (4) becomes,

$$D = B [(T)^{1.20} (t)^{-0.29} (d)^{-0.43}]^C \quad (5)$$

where B is the coefficient and C is the exponent of the overall product. The values of B and C are evaluated from the straight line relationship obtained by plotting diffusivity against the products in Fig 3. The final correlation is

$$D = 8.56 \times 10^{-44} (T)^{11.77} (t)^{-0.28} (d)^{-0.42} \quad (6)$$

TABLE 3 EFFECT OF VARIOUS REACTION PARAMETERS ON DIFFUSIVITY

REACTION TEMPERATURE		
Operating Parameter, T, °K	Diffusivity, cm ² /s D × 10 ⁸	Constant Parameters
1 170	0.84	t = 0.5 hr d _{av} = 1 150 μm
1 270	1.77	
1 370	4.50	
1 470	11.60	
REACTION TIME		
Operating Parameter, t, hr	Diffusivity, cm ² /s D × 10 ⁸	Constant Parameters
0.5	2.35	T = 1 270 °K d _{av} = 625 μm
1.0	1.98	
2.0	1.60	
3.0	1.44	
PARTICLE SIZE		
Operating Parameter, d _{av} , μm	Diffusivity, cm ² /s D × 10 ⁸	Constant Parameters
1 150	1.77	T = 1 270 °K t = 0.5 hr
625	2.35	
450	2.75	

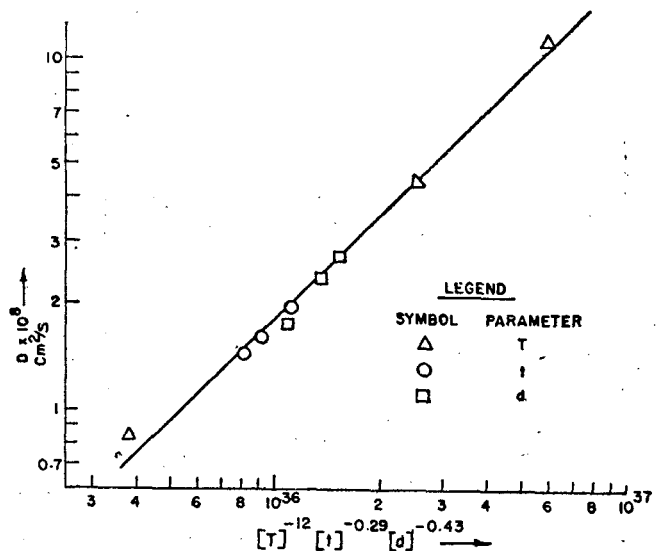


Fig 3 Relationship between diffusivity and system variables

Diffusion coefficients calculated by equation (6) have been compared with the experimental values in Table 4. The mean and standard deviations have been found to be 4.9 and 6.2, respectively

TABLE 4 COMPARISON OF DIFFUSIVITY VALUES

T°K	t, hr	d _{av} , μm	D × 10 ⁸ EXPERI- MENTAL	D × 10 ⁸ CALCU- LATED	% DEVI- ATION
1 170	0.5	1 150	0.84	0.70	-16.67
1 370	0.5	1 150	4.50	4.47	-0.67
1 470	0.5	1 150	11.60	10.25	-11.64
1 270	1.0	625	1.98	1.95	-1.52
1 270	2.0	625	1.60	1.61	+0.63
1 270	3.0	625	1.44	1.43	-0.69
1 270	0.5	450	2.75	2.72	-1.09
1 270	0.5	625	2.35	2.37	+0.85
1 270	0.5	1 150	1.77	1.83	+3.39

CONCLUSION

A maiden attempt has been made in this paper to quantify the amount and the mode of conversion of limestone in a dry lime-resulphurization process—the well established sulphur dioxide pollution abatement measure practised over the last two decades. The correlations were found to be valid within the ranges of the experimental investigations. However, more investigations can be conducted with limestone and dolomite samples of various geologic origin in order to make the correlations of wider applicability.

ACKNOWLEDGMENT

The financial assistance received from the Ministry of

Education and Social Welfare, Government of India for conducting some experiments and final processing of the above communication is gratefully acknowledged by Dr G K Roy.

REFERENCES

1. KC Biswal and G K Roy. 'Sulphur dioxide Pollution Control by Wet Scrubbing Methods'. *Journal of the Institution of Engineers (India)*, vol 62, Pt EN 3, June 1982, p 120.
2. C Syamala Rao. 'Sulphur dioxide Pollution Control'. *Chemical Engineering World*, vol 14, no 6, 1979, p 47.
3. T D Venkatesan and G Yayathi. 'SO₂—Emission Control'. *Chemical Age of India*, vol 31, no 7, 1980, p 741.
4. W Weisweiler and G K Roy. 'Kinetics of lime-limestone Sulphation: Review of Lime Reactivity and Sulphation Kinetics in the Dry Limestone Desulphurization Processes'. *High Temperatures—High Pressures*, vol 13, 1981, p 333-
5. G K Roy and W Weisweiler. 'Absorption of Sulphur dioxide by Limestone in a High Temperature Fluidized Bed'. *Journal of the Institution of Engineers (India)*, vol 62, pt CH 2, February 1982, P 33.
6. C Y Wen and M Ishida. 'Reaction Rate of Sulphur dioxide with Particles Containing Calcium oxide'. *Environmental Science & Technology*, vol 7, no 8, 1973, p 703.
7. R L Pigford and G Sliger. 'Rate of Diffusion—controlled Reaction between A Gas and A Porous Solid Sphere'. *Industrial Engineering Chemistry (Process Design and Development)*, vol 12, no 1, 1973, p 85.
8. M Hartman and R W Coughlin. 'Reaction of Sulphur dioxide with Limestone and the Influence of Pore Structure'. *Industrial Engineering Chemistry (Process Design and Development)*, vol 13, no 3, 1974, p 248.
9. Timor Dogu. 'The Importance of Pore Structure and Diffusion in the Kinetics of Gas-solid Non-Catalytic Reactions : Reactions of Calcined Limestone with SO₂'. *Chemical Engineering Journal*, vol 21, 1981, D 213.