

- W = residual weight of fixed carbon in coal char at reaction temperature T of temperature-programed run [kg]
- W_0 = initial weight of fixed carbon in coal char sample [kg]
- θ = reaction time [min]
- ϕ = heating-up speed of temperature-programed run, $dT/d\theta$ [$K \cdot min^{-1}$]
- <Subscript>
- ϕ = non-isothermal, temperature-programed run

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SULPHUR DIOXIDE RETENTION BY CALCINED LIMESTONE UNDER OXYGEN LEAN CONDITIONS

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Key Words: Fluidized Bed Combustor, Sulphur Dioxide, Calcined Limestone, Oxygen Concentration, Kinetics

A kinetic study of sulphur dioxide capture by calcined limestone at 1123 K was conducted by thermogravimetric analysis over a relatively wide range of diameter of limestone particles and concentrations of oxygen as well as sulphur dioxide. The experimental conditions were chosen by taking into consideration the practical operating conditions of a fluidized-bed coal combustor. Results are reported in particular on the effects of oxygen concentration on the rate of sulphur dioxide retention; these effects are of practical importance for staged air firing operation of the bed. A formula which took into account the oxygen and sulphur dioxide concentrations could predict the rate of sulphur dioxide retention at various degree of utilization of sulphur sorbent by defining an approximate maximum utilization level as solid reactivity. This parameter could be expressed by a linearly and monotonously decreasing function of the rate. Detailed effects of particle size on the expression were investigated.

Introduction

Stack emissions from coal-fired boilers are considered to be a major sources of both nitrogen oxides and sulphur dioxide emissions. However, the employment of flue-gas treatment facilities increases construction costs as well as operating costs of power plants and also reduces thermal efficiency.⁴⁾

Thus the fluidized-bed combustion technique is being developed as a prospective alternative to conventional combustion systems. Sulphur dioxide released by combustion can be removed within the bed by limestone fed to the combustor. The combustion temperature is determined to be about the optimum for retention of sulphur dioxide by limestone. The maximum emission level of nitrogen oxides from a fluidized-bed combustor must be reduced to the level projected for the conventional combustion system at the time when fluidized-bed combustion becomes

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commercially available. For this purpose, staged air firing is considered to be necessary for meeting the stringent regulations. In this operation, the air used for combustion is separated into a primary air stream supplied from the plenum chamber and a secondary air stream injected above the bed surface into the freeboard. Since all fuels are injected in the primary stage, the bed is operated under a deficiency of oxygen. Extensive investigations concerning the control of nitrogen oxides have concluded that the optimum stoichiometric ratio of the primary air to the air required for complete combustion range from 0.9 to about unity. Since the oxygen used for combustion is transferred from the bubble phase to the emulsion phase where combustion predominantly takes place, the concentration of oxygen under staged air firing will be markedly lower than that in the conventional operation. Operational experience with pilot plants indicates that improved emission control of nitrogen oxide by staged air firing resulted in the reduction of sulphur retention efficiency.¹⁰⁾

A number of investigations have been published on the kinetics of sulphur dioxide capture by calcined limestone under oxygen-rich conditions.^{2,3,6)} The significant conclusions widely accepted are (1) the reduction of sulphation rate with time, (2) the existence of a maximum sorbent utilization determined by rate and particle size, (3) an initial reaction rate proportional to sulphur dioxide concentration, and (4) progressive divergence from the volume reaction model with increase in sulphation. In contrast to these extensive investigations concerning sulphur dioxide capture under oxygen-rich conditions, quantitative information under oxygen-lean conditions is insufficient.

Several studies have been conducted to investigate sulphur retention by taking account of the structural changes in the pores, and detailed mathematical formulas of sulphur retention have been derived on the basis of pore or grain models^{1,2,5,6)} where the intrinsic reaction rate is assumed to be proportional to sulphur dioxide concentration.⁷⁾ When applying the above detailed models to the fluidized-bed combustor, some computational difficulties arise. Therefore, simplified overall equations which are first-order reactions of sulphur dioxide, have been employed for the analysis.^{3,8)} However, the effect of oxygen concentration on the rate was not taken into consideration in the analysis.^{3,8)}

On the basis of the above discussion, there are clearly defined requirements for carrying out an investigation into the sulphur retention rate under oxygen-lean conditions at various levels of sorbent utilization and for obtaining a simple formula of the rate.

1. Experiment

1.1 Apparatus

An isothermal thermogravimetric analysis was conducted at atmospheric pressure to investigate the reaction kinetics of the sulphation reaction of calcined limestone particles. The thermogravimetric analyzer employed was a conventional electrobalance, the Shimadzu TG-31. The samples were heated by an external heater controlled by a conventional PID controller to attain a constant heating rate as well as to keep the reaction temperature constant. The reactor was a quartz tube with a 38 mm internal diameter. The sample holder (20 mm in internal diameter and 15 mm in height) was a basket-shaped skeleton of quartz wires in which a single layer of the sample material was sandwiched by quartz wool layers so that the effect of mass transfer around the particles could be ignored. The maximum gas velocity (300 cm³/min) which did not disturb the measurement of weight change was employed. The temperature of the samples was measured by a chromel-alumel thermocouple placed 5 mm below the skeleton, and was recorded continuously. The sample holder and the top of the thermocouple were located in the middle part of an electric furnace so that the temperature difference between the sample and the thermocouple could be ignored.

1.2 Materials

Japanese limestone (Iwato), the analysis of which is given in **Table 1**, was used as the sorbent. The diameter of particles employed for most of the experiments was from 0.297 mm to 0.59 mm (average 0.34 mm). Samples of different sizes (0.085, 0.097, 0.118, 0.14, 0.27, 0.34, 0.51 mm) were used to evaluate the effect of particle size on the rate. The weight of the samples used for the thermogravimetry ranged from 7 to 30 mg, of which less than 15% was moisture.

The pore size distribution measured by a mercury penetration porosimeter (Micrometric Instrument Co., type 900-910) is shown in **Fig. 1**. The properties of the calcined limestone used are given in **Table 2**. The samples of limestone used for the measurements of physical properties was calcined under a nitrogen atmosphere at a constant heating rate of 20 K/min and was kept for more than ten minutes at 1123 K.

The concentrations of sulphur dioxide and oxygen ranged respectively from 380 cm³/m³ to 5.7 × 10³ cm³/m³ and from 140 cm³/m³ to 2.4 × 10⁴ cm³/m³.

1.3 Procedure

The sample of limestone placed in the sample holder was heated in the nitrogen stream at a constant heating rate (20 K/min) to the chosen reaction temperature (1123 K). After the desired temperature was attained, the sample was maintained at that temperature for more than ten minutes to confirm the com-

Table 1. Analysis of Iwato limestone

(weight percent)				
CaO	MgO	SiO ₂	Al ₂ O ₃ and Fe ₂ O ₃	Weight loss after calcination
55.28	0.36	0.57	0.23	43.44

Table 2. Physical and structural properties of calcined limestone

Pore volume ¹⁾	0.284 cm ³ /g
Specific surface ²⁾	23.7 m ² /g
Apparent density ³⁾	1.53 g/cm ³
Porosity ⁴⁾	0.553

1) Calculated from Fig. 1
2) BET method (Shimadzu Sorptgraph ADS-1B)
3) Pycnometer
4) Calculated from apparent density of limestone and true density of CaO

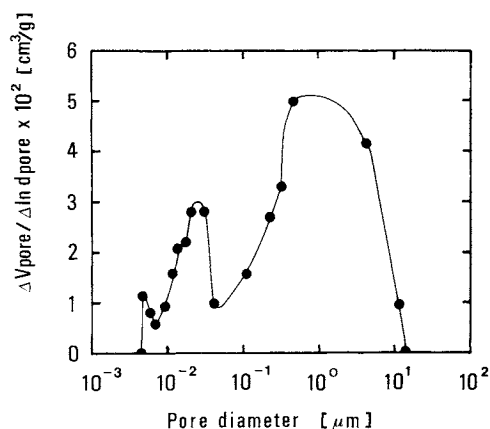


Fig. 1. Pore size distribution of calcined limestone.

pletion of calcination by visual observation of the recorded weight change. During the calcination, no breaking of particles was observed. Then the reactant gas mixture was introduced and the increase in weight due to sulphation was recorded continuously until no further increase in weight was detected. Then oxygen diluted by nitrogen (10–20%) was introduced. No appreciable change in weight was detected. In several experimental runs, it was also confirmed that no appreciable weight change was detected when the gas was switched to diluted oxygen without sulphur dioxide in the course of the sulphation reaction. This indicates that CaS or CaSO₃ did not exist.

2. Result

2.1 Analysis of experimental results

A typical weight change curve for limestone during calcination and sulphation is shown schematically in Fig. 2. Hardly any reduction in limestone weight was detected up to 873 K. The significant reduction in

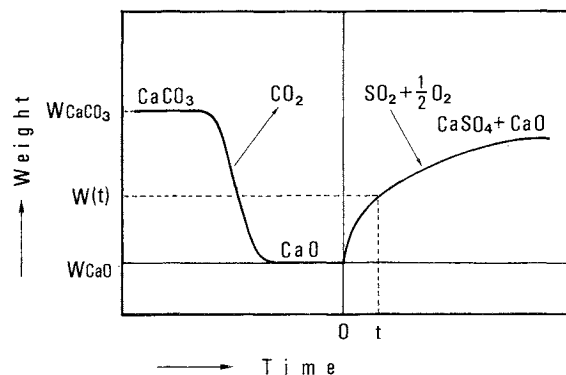


Fig. 2. Schematic description of weight change of limestone samples during calcination and sulphation.

weight due to calcination started from about 923 K, and the weight tended toward a certain saturated value. The weight loss after 873 K could be attributed to the removal of the carbon dioxide by calcination, assuming the original limestone was calcium carbonate. Thus the completion of calcination could be determined by the above procedure. When introducing the reactant gas mixture, a progressive increase in weight was observed. It was assumed that the sulphation of calcined limestone was taking place by the following reaction.



The preliminary experimental results shown in procedure section suggest that no species other than CaSO₄ were formed and that the decomposition of calcium sulphate by the reversal of Eq. (1) can be ignored. Further, the order of the equilibrium constant $(1/[\text{SO}_2][\text{O}_2]^{1/2})$ in Eq. (1) is around 0.78 (cm³/m³)^{-3/2} at 1123 K, a value more than 10⁴ times that of $1/[\text{SO}_2][\text{O}_2]^{1/2}$ chosen for the present experimental conditions.

The maximum increase in weight by complete sulphation of the calcined limestone can be expressed as

$$W_{\text{CaSO}_4} - W_{\text{CaO}} = \frac{M_{\text{CaSO}_4} - M_{\text{CaO}}}{M_{\text{CaCO}_3} - M_{\text{CaO}}} (W_{\text{CaCO}_3} - W_{\text{CaO}}) \quad (2)$$

Thus the conversion can be

$$X(t) = \frac{W(t) - W_{\text{CaO}}}{W_{\text{CaSO}_4} - W_{\text{CaO}}} \quad (3)$$

During the initial period of the experiment, the intrinsic desulphurization rate could not be obtained due to mechanical vibration of the balance caused by introducing the reactant gas. All data employed in the following analysis were obtained after the initial period, and the consumptions of sulphur dioxide and oxygen within the reacting section were respectively less than 7% in this analysis.

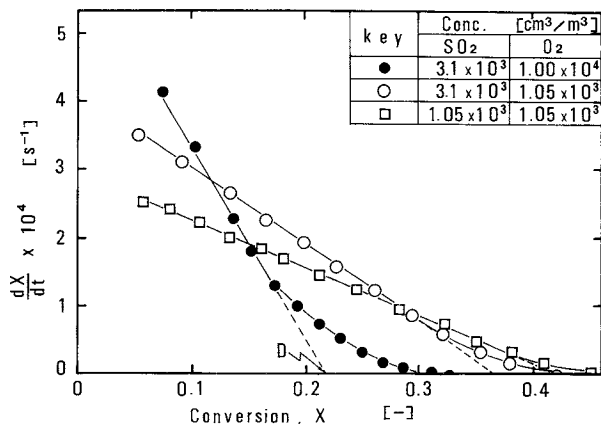


Fig. 3. Typical examples of conversion rate vs. conversion curve of sulphur capture and definition of maximum utilization by straight-line approximation ($d_p=0.34$ mm).

2.2 Determination of rate constant and introduction of maximum sorbent utilization by straight-line approximation

The conversion rate (the time derivative of conversion) was evaluated as a function of conversion by graphic differentiation of the conversion vs. exposure time curve. No significant effects of gas flow rate or amount of samples on the conversion rate were observed in this analysis. Therefore, it was concluded that the effect of mass transfer around the particles could be ignored. Further, the data obtained under the condition where the consumption of the reactants did not exceed 7% were used for the analysis, so the reactor could be regarded as a differential one. Typical examples are shown in Fig. 3. The data represent the effects of sulphur dioxide and oxygen concentration on the conversion rate as a function of conversion. For a slower initial rate, namely lower oxygen or sulphur dioxide concentration, a linear relationship between conversion rate and conversion could be observed over a relatively wide range of sulphation. The range of conversion in which the conversion rate is linear to the conversion becomes narrower as the reaction rate increases. There is a progressive deviation from the straight line with increase in sulphation. By ignoring this deviation, the conversion rate can be expressed as

$$dX/dt = K(D - X) \quad (4)$$

where D corresponds to the intercept of the straight line at abscissa and D may be defined as the maximum utilization by straight-line approximation of the sorbent. K corresponding to the slope of the straight line is considered to be the reaction rate parameter which can be expressed as a function of the concentrations of both reactants.

2.3 Effects of the concentrations of reactants on the rate parameters

Figure 4 represents the rate parameters evaluated at

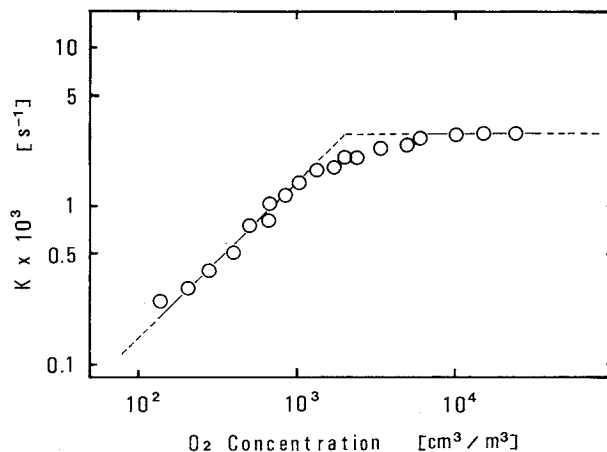


Fig. 4. Dependence of reaction rate parameter K on oxygen concentration ($[SO_2]=3.1 \times 10^3$ cm³/m³, $d_p=0.34$ mm).

various levels of oxygen concentration while keeping the concentration of sulphur dioxide constant (3.1×10^3 cm³/m³). As observed from this figure, the dependency of the rate parameter is divided into two regions. The rate corresponding to the lower oxygen concentration range is linearly proportional to the oxygen concentration. Thus the rate can be described as first-order dependent on oxygen concentration. However, the rate parameter remains constant over the range of higher oxygen concentration. Thus this portion of the data can be interpreted as zero-order dependent on oxygen concentration.

Data were also obtained at various levels of concentration of sulphur dioxide while keeping the level of oxygen concentration constant (1.05×10^3 and 2.4×10^4 cm³/m³). In the case of lower oxygen concentration, a concentration dependence similar to the data shown in Fig. 4 was found. However, in the case of higher oxygen concentration the rate appears to be proportional to sulphur dioxide concentration throughout the entire range, which is less than 4.4×10^3 cm³/m³. This indicates that the rate under an oxygen-rich concentration can be expressed as a first-order reaction with respect to sulphur dioxide throughout the entire region investigated, and this tendency coincided with previous findings.²⁾ The transition points between the zero-order reaction and the first-order reaction are around $[SO_2]/[O_2]=1.5$. To summarize all the data obtained for $d_p=0.34$ mm, the rate parameter can be expressed as

$$K = k_1[SO_2] \quad \text{for } [SO_2]/[O_2] \ll 1.5 \quad (5)$$

$$K = k_2[O_2] \quad \text{for } [SO_2]/[O_2] \gg 1.5 \quad (6)$$

By combining Eqs. (5) and (6), the rate can be described as

$$K = 1/(1/k_1[SO_2] + 1/k_2[O_2]) \quad (7)$$

All the data including those obtained under other

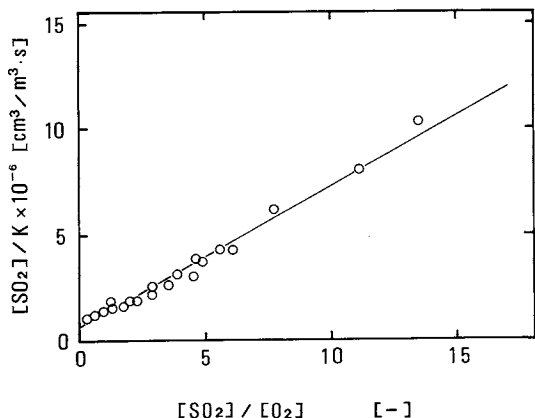


Fig. 5. Determination of rate constants k_1 and k_2 ($d_p = 0.34$ mm).

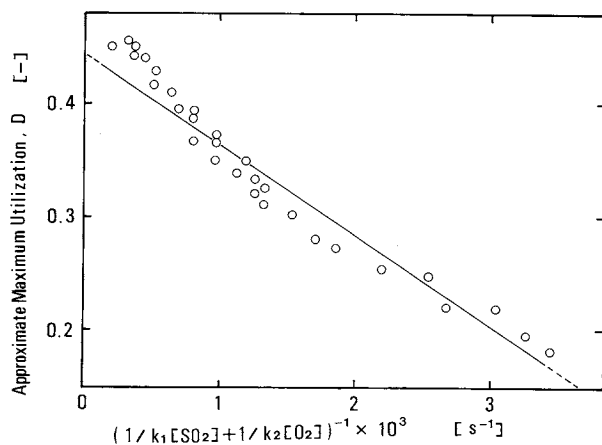


Fig. 6. Determination of maximum utilization by straight-line approximation as a function of reaction rate parameter, K ($d_p = 0.34$ mm).

conditions not specified in this section are plotted in Fig. 5. Since the ratio of sulphur dioxide concentration to the rate parameter is linearly proportional to that of sulphur dioxide to oxygen concentration, k_1 and k_2 can be determined from respective intercepts on the ordinate and slope. The values obtained for k_1 and k_2 are

$$k_1 = 0.99 \times 10^{-6} (\text{cm}^3/\text{m}^3)^{-1} \text{s}^{-1}$$

$$k_2 = 1.5 \times 10^{-6} (\text{cm}^3/\text{m}^3)^{-1} \text{s}^{-1}$$

2.4 Dependence of maximum utilization by straight-line approximation on rate parameter

It was shown in Fig. 3 that the maximum utilization by straight-line approximation, D , appears to be significantly dependent on the rate parameter, K , namely the concentrations of both reactants at constant temperature. The experimentally observed values of this parameter are plotted against calculated values of the rate parameter, K , in Fig. 6. A fairly good linear relationship between the above two parameters is observed. Thus the following equation can be obtained.

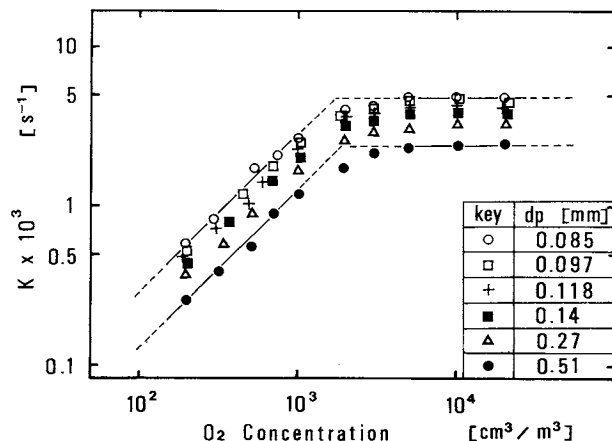


Fig. 7. Effects of particle size on the rate under constant sulphur dioxide concentration, $3.1 \times 10^3 \text{ cm}^3/\text{m}^3$.

$$D = a - bK = a - b/(1/k_1[\text{SO}_2] + 1/k_2[\text{O}_2]) \quad (8)$$

The experimentally determined a and b are respectively 0.44 and 80 s.

2.5 Effects of particle size

The experiments described above were repeated to evaluate the effects of particle size on the rate constants (k_1, k_2) and the approximate maximum utilization of sorbents. The dependence of the rate parameter K on oxygen concentration measured at a constant concentration of sulphur dioxide ($3.1 \times 10^3 \text{ cm}^3/\text{m}^3$) is shown in Fig. 7. Similar effects of particle size were measured by keeping the oxygen concentration constant but by changing the sulphur dioxide concentration. From these results the reaction rates (k_1, k_2) were found to increase with decreasing particle size. However, it is evident that the functional relationship expressed by Eq. (7) can be applied to samples of different sizes by modifying the rate constants (k_1, k_2). It should be pointed out that the transition points from the first-order reaction scheme to the zero-order reaction scheme appeared to remain the same as mentioned previously ($k_2/k_1 = 1.4\text{--}1.7$) over the whole range of particle size investigated. For each particle diameter the values of the ratio of sulphur dioxide concentration to rate parameter were calculated and plotted against the ratio of sulphur dioxide to oxygen concentration in the same way as in Fig. 5. The values obtained for each rate constant k_1 , k_2 , and the ratio of k_2 to k_1 are plotted against particle diameter on abscissa in Fig. 8. The values of k_1 and k_2 at 1123 K are expressed as functions of the particle diameter as

$$k_1 = 0.62 \times 10^{-6} d_p^{-0.44} \quad (9)$$

$$k_2 = 0.95 \times 10^{-6} d_p^{-0.44} \quad (10)$$

The values of a and b were also obtained in the same way as in Fig. 6 and the values are plotted

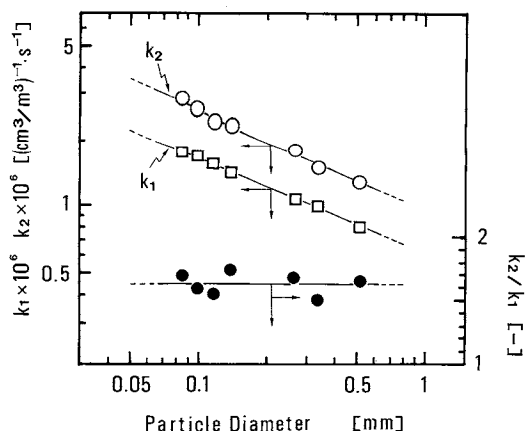


Fig. 8. Dependence of rate constants, k_1 and k_2 , on particle size.

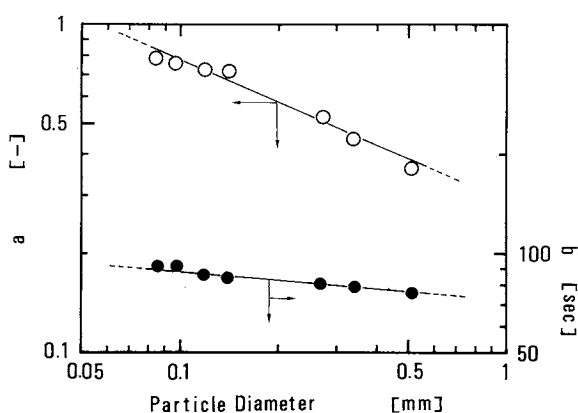


Fig. 9. Dependence of approximate maximum utilization constants a and b on particle size.

against particle diameter on abscissa in Fig. 9. The values of a and b at 1123 K are also expressed as functions of the particle diameter as

$$a = 0.28d_p^{-0.44} \quad (11)$$

$$b = 71d_p^{-0.1} \quad (12)$$

Since the initial conversion rate of sulphur retention can be approximated to KD , the initial rate is proportional to -0.88 power of the particle diameter. This indicates that the initial rate is significantly controlled by mass transfer. Furthermore, the conversion rate is reduced rapidly with increasing conversion, namely the sulphur retention, and this reduction of conversion rate with conversion is enhanced by increased particle size. This phenomenon may be attributed to the progressive reduction in pore volume caused by the deposit of sulphate within the pores.

3. Discussion

Another straight line approximation which was derived from a wider range of conversion rate vs.

conversion curve using the least square method was successfully employed to evaluate the sulphur retention of fluidized-bed combustors.³⁾ However, the application of this formulation was restricted to combustors operated under conventional single-stage combustion. The applicability of the present straight-line approximation, which is extended to a wider range of concentration of both sulphur dioxide and oxygen, was verified experimentally by use of a fluidized-bed combustor in which the same limestone as employed in the present study was used under a staged air firing. The results have been published elsewhere.⁹⁾

The present straight-line approximation is characterized by an increasing deviation from the experimentally observed conversion rate vs. conversion curve with an increase in sulphation. However, no significant error will be committed. This is explained as follows. The maximum concentration of sulphur dioxide in the emulsion phase is estimated to be $1000 \text{ cm}^3/\text{m}^3$ for a coal whose sulphur content is 1%, assuming that the formation rate of sulphur dioxide in the emulsion phase is proportional to the rate of combustion and also that the maximum concentration of carbon dioxide is approximately $2.1 \times 10^5 \text{ cm}^3/\text{m}^3$ (21%).

Furthermore, operational experience has demonstrated that loss of limestone attributable to either initial erosion due to thermal shock and release of carbon dioxide by calcination or a steady erosion caused by the intensive motion of solids is significant. Limestone is therefore required not only as sorbent but also as bed material to maintain the bed level. Thus, the conversion of limestone in the bed is relatively low ($X=0.2-0.35$). The deviation of the present approximation from the conversion rate vs. conversion curves was significant only over a higher range of conversion ($X>0.4$) when the concentration of either sulphur dioxide or oxygen was lower than $1000 \text{ cm}^3/\text{m}^3$. Thus the conversion rate vs. conversion curve can be well approximated to a single straight line under operating conditions of fluidized-bed combustors.

The effect of particle diameter on the maximum utilization estimated by the straight-line approximation is consistent with the results obtained by the previous investigators.^{1,8)} Equation (8) indicated that the maximum utilization is a function of the reaction rate parameter, K . This indicated that the dynamic change of the conversion rate is dependent on the time history of the concentrations surrounding the particles as well as the diameter of particles. The detailed mechanism of this phenomenon has not yet been elucidated.

Conclusion

Empirical rate equations of sulphur dioxide capture by calcined limestone particles were developed at 1123 K by means of thermogravimetric analysis over a wide range of particle diameter (0.085–0.51 mm), oxygen concentration ($140\text{--}2.4 \times 10^4 \text{ cm}^3/\text{m}^3$) and sulphur dioxide concentration ($380\text{--}5.7 \times 10^3 \text{ cm}^3/\text{m}^3$). The obtained rate expression indicated below was not only a function of the concentration of sulphur dioxide, as was known previously, but also a function of the concentration of oxygen.

$$dX/dt = k(D - X)$$

$$K = 1/(1/k_1[\text{SO}_2] + 1/k_2[\text{O}_2])$$

$$D = a - bK$$

This formula takes account of the effect of particle size in the reaction rate parameter (K) and can predict the rate at various degrees of solid utilization by introducing a parameter termed maximum utilization by straight-line approximation (D). The effects of the reduction of porosity induced by the increase in conversion on the reduced rate were thus taken into consideration.

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Nomenclature

a	= constant defined by Eq. (8)	[—]
b	= constant defined by Eq. (8)	[s]
d_p	= average diameter of limestone particles	[mm]
d_{pore}	= pore diameter of calcined limestone	[μm]
D	= maximum utilization by straight-line approximation	[—]
k_1	= reaction rate constant defined by Eq. (5)	$[(\text{cm}^3/\text{m}^3)^{-1} \text{s}^{-1}]$

k_2	= reaction rate constant defined by Eq. (6)	$[(\text{cm}^3/\text{m}^3)^{-1} \text{s}^{-1}]$
K	= reaction rate parameter defined by Eq. (4)	$[\text{s}^{-1}]$
M_{CaCO_3}	= molecular weight of CaCO_3	[—]
M_{CaO}	= molecular weight of CaO	[—]
M_{CaSO_4}	= molecular weight of CaSO_4	[—]
$[\text{O}_2]$	= oxygen concentration	$[\text{cm}^3/\text{m}^3]$
$[\text{SO}_2]$	= sulphur dioxide concentration	$[\text{cm}^3/\text{m}^3]$
t	= time	[s]
V_{pore}	= cumulative pore volume of CaO	$[\text{cm}^3/\text{g}]$
W_{CaCO_3}	= initial weight of limestone particles	[g]
W_{CaO}	= weight of calcined limestone	[g]
W_{CaSO_4}	= weight defined by Eq. (2)	[g]
$X(t)$	= conversion defined by Eq. (3)	[—]

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