

Effect of Nitrogen Dioxide on the Measurement of Sulfur Dioxide Concentration with the Lead Peroxide Method

Yoshishige HAYASHI

ABSTRACT

For the precise evaluation of SO₂ concentration measured with the lead peroxide method, the effect of nitrogen dioxide on the method is studied experimentally. The experiment has been carried out with a cylindrical PbO₂ pellet and SO₂-NO₂-N₂ gas mixture. The selectivity to produce the solid product and the transfer mechanism for gaseous reactant in the porous solid are discussed according to the data obtained in this experiment.

Key words: PbO₂ method, Effect of NO₂ gas on reaction, Selectivity, PbO₂-NO₂-SO₂ reaction system, Unreacted-core model.

Introduction

In general, it is recognized that SO₂ concentration measured with the lead peroxide method is affected not only by weather conditions but also by several gaseous substances coexisting with SO₂. As a basic research to evaluate precisely the values measured with the lead peroxide method, the effects of wind velocity, atmospheric temperature and humidity were discussed in a previous paper.¹⁾ Recently the air pollution by NO_x from an automobile exhaust gas and so on has been developing into a serious problem, and so a strict regulation for NO₂ concentration has been set forth. In fact, NO_x is coexisting with SO_x in the atmosphere and the effect of NO_x on the measurement of SO₂ concentration is also very important to the precise evaluation of the measured SO₂ concentration.

In this paper, the effect of NO₂ on the measurement of SO₂ concentration with the lead peroxide method was studied. The reaction equation for NO₂-PbO₂ system is as follows; 2NO₂ (gas) + 2PbO₂ (solid) → Pb(NO₂)₂PbO (solid) + 0.5 O₂ (gas). The experiment was carried out under the conditions of 500~1500 ppm (v/v) SO₂-N₂ and/or 300~1500 ppm (v/v) NO₂-N₂ gas mixtures with the cylindrical PbO₂ pellet. The ends of the PbO₂ pellet were sealed.

1. Theoretical analysis

The unreacted-core model was used to estimate k_f and \mathcal{D}_e because this model had a good representation to the transfer mechanism for PbO₂-SO₂ reaction system.¹⁾ The assumptions used to reduce the complexity of the mathematical treatment were the same as those in the previous paper.¹⁾ Furthermore, the following assumptions were made for PbO₂-SO₂-NO₂ reaction system;

(1) The reaction between SO₂ and NO₂ is negligible.²⁾ Furthermore the interaction between both gases is negligible at the diffusion process in porous solid because of both concentrations are relatively low.

(2) The products of this reaction such as sulfate and nitrate do not react with the gaseous reactants.

(3) The reaction interface for SO₂ is identical to that for NO₂.

In this case, the basic equation, boundary and initial conditions are the same as those in the previous paper¹⁾ and the following relations are obtained by disregarding the chemical reaction resistance.

For reaction time of gaseous reactant i ,

$$t_i = \frac{Ra_i C_{S0}}{2C_{i0}} \frac{1}{k_{fi}} f_i + \frac{R^2 a_i C_{S0}}{4C_{i0}} \frac{1}{\mathcal{D}_{ei}} \times \{f_i + (1-f_i) \ln(1-f_i)\} \quad (i=A, B) \quad (1)$$

For amount of solid product of gaseous reactant i ,

$$W_i = \pi R^2 L C_{S0} f_i \quad (i=A, B) \quad (2)$$

The overall fractional conversion is

$$f_i = f_A + f_B \quad (3)$$

On the other hand, the selectivity for this reaction is defined as

$$\Psi_A = f_A/f_i, \quad \Psi_B = 1 - \Psi_A \quad (4)$$

and the relationship between W_i and f_i is

$$W_i = \pi R^2 L C_{S0} f_i / \Psi_i \quad (i=A, B) \quad (5)$$

2. Experimental equipment and procedures

An equipment and analytical procedures used here were almost the same as those in the previous paper¹⁾ and in this paper, only the different points are described. Nitrogen oxide is likely to cause the photochemical reaction and the teflon tube between the holder and the reaction chamber was covered with black vinyl tape and further, the homogenizing and reaction chambers were put into a darkroom.

Analysis of the nitrate produced by PbO₂-NO₂ reaction was done by the zinc reduction naphthyl-ethylene diamine method. The gas velocity was 0.16 cm/s and the relative humidity was about

Table 1. Operating conditions

Run	u [m/s] $\times 10^2$	C_{A0} [ppm]	C_{B0} [ppm]	T [K]
1	0.200	500	0	287
2	0.200	1000	0	288
3	0.200	1500	0	287
4	0.200	0	300	287
5	0.200	0	600	287
6	0.200	0	900	287
7	0.200	0	1200	288
8	0.200	0	1500	289
9	0.200	500	300	287
10	0.200	500	600	287
11	0.200	500	900	287
12	0.200	1000	300	287
13	0.200	1000	600	288
14	0.200	1000	900	287
15	0.200	1500	300	287
16	0.200	1500	600	288
17	0.200	1500	900	287

Table 2. Calculated properties for SO₂-PbO₂ reaction

C_{A0} [ppm]	$k_{fA} \times 10^2$ [m/s]	$\mathcal{D}_{eA} \times 10^4$ [m ² /s]
500	0.3952	0.007879
1000	0.5045	0.003946
1500	0.5547	0.003948

Table 3. Calculated properties for NO₂-PbO₂ reaction

C_{B0} [ppm]	$k_{fB} \times 10^2$ [m/s]	$\mathcal{D}_{eB} \times 10^4$ [m ² /s]
300	3.6523	0.001269
600	0.7478	0.001316
900	0.3655	0.002297
1200	0.3289	0.003188
1500	0.4345	0.002645

60%. In Table 1, the operating conditions are summarized.

3. Experimental results and discussions

Tables 2 and 3 show the values of k_{fi} and \mathcal{D}_{ei} for PbO₂-SO₂ and PbO₂-NO₂ reactions estimated by Eq. (1), respectively.

In Fig. 1, the results of PbO₂-SO₂ and PbO₂-NO₂ reaction systems are shown as a plot of $f_{i, \text{pure}}$ vs. t . When the fractional conversions for both reaction systems are compared at the same concentration of gaseous reactants, it is found that the difference in fractional conversion is slight under the relatively low concentration and clear under the high concentration. In general, the fractional conversion for SO₂ is larger than that for NO₂ under the same operating conditions.

Figure 2 shows the effect of NO₂ on the PbO₂-SO₂ reaction. The effect increases with decreasing the SO₂ concentration.

In Fig. 3, as a typical example to discuss on the selectivity, f_i and f_j are plotted against t for the case of 1000 ppm SO₂-600 ppm NO₂-PbO₂ reaction system. The selectivity defined by Eq. (4)

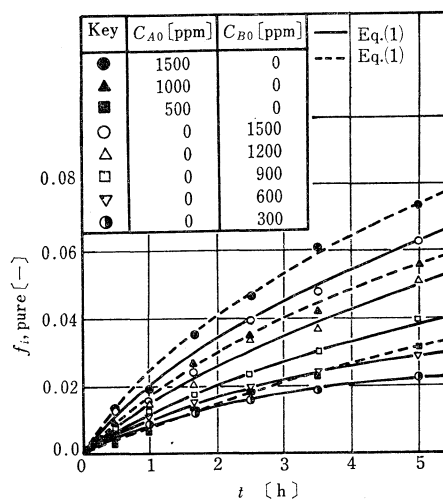


Fig. 1. Effect of SO₂ and NO₂ concentrations on total amount of solid product

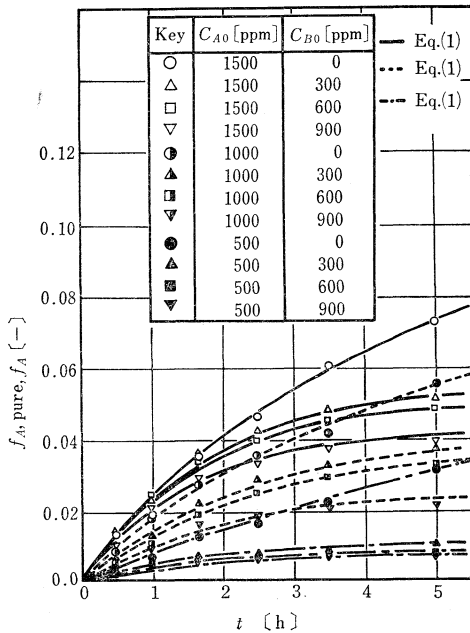


Fig. 2. Effect of NO_2 concentration on $\text{PbO}_2\text{-SO}_2$ reaction system

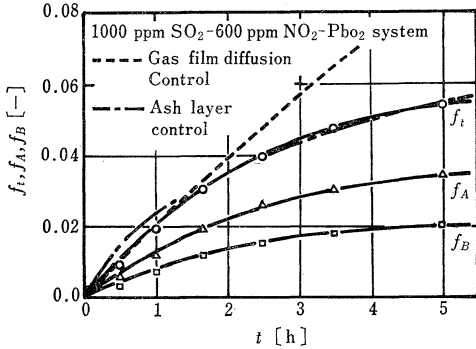


Fig. 3. f_i and f_i vs. t for the case of 1000 ppm SO_2 -600 ppm NO_2 - PbO_2 reaction system

can be estimated from the results in this figure by separating the individual curves into gas film diffusion controlling region and ash layer controlling region. The results are shown in Fig. 4 as a plot of Ψ and $C_{B0}/(C_{B0}+C_{A0})$. As is evident from this figure, there is a strong correlation between Ψ and $C_{B0}/(C_{A0}+C_{B0})$, and the degree of the effect of NO_2 on the $\text{PbO}_2\text{-SO}_2$ reaction at the gas film diffusion controlling region is almost the same as that at the ash layer controlling region. That is, the results show that it depends on the ratio of NO_2 occupied in the total amount of gaseous reactants and the selectivity is constant regardless of the reaction time at the same operat-

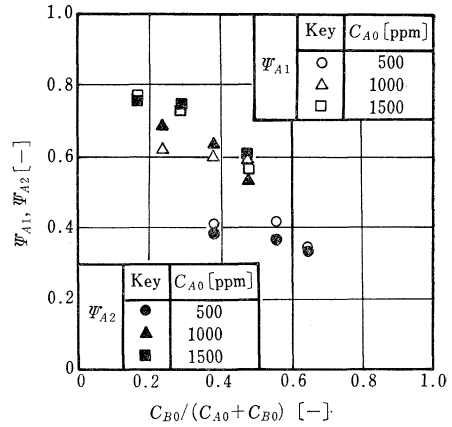


Fig. 4. Relationship between Ψ_{A1} , Ψ_{A2} and $C_{B0}/(C_{A0}+C_{B0})$

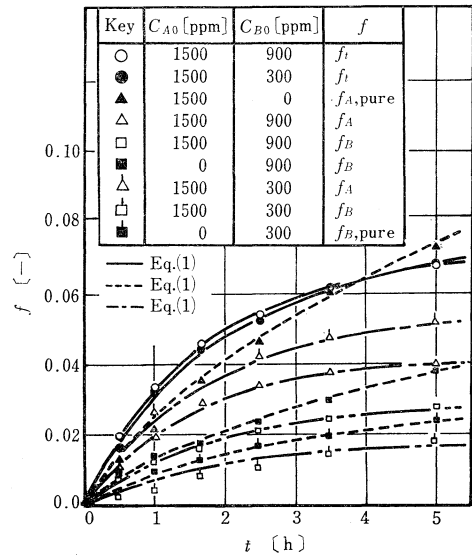


Fig. 5. Comparison of fractional conversions for SO_2 and NO_2 - PbO_2 reactions and those for SO_2 - NO_2 - PbO_2 reaction

ing conditions. It will then be concluded that its effect is not evaluated only from the absolute value for NO_2 concentration and increases with decreasing the SO_2 concentration at a constant NO_2 concentration.

Figure 5 shows the comparison of fractional conversions for one-component gaseous reactant-solid reaction and those for two-component one. As is evident from Fig. 5, the slope of f_i curves for the latter reaction decreases with proceeding the contact time in comparison with the results for the former, $f_{A,pure}$. When the overall fractional conversion f_i is compared with $f_{A,pure}$, the

difference in both fractional conversions shows the greatest value at about 2 hour from the start of reaction and at about 4 hour, it is reversed and further, the overall fractional conversion f_t has not very much change according to the NO_2 concentration at a constant SO_2 concentration although the change of the individual fractional conversion, f_A and f_B with NO_2 concentrations is recognized remarkably.

On the other hand, the reaction rate constants were estimated by the Arrhenius plot. The results showed that the rate constant for $\text{PbO}_2\text{-SO}_2$ reaction was about $1.8 \times 10^{-3} \text{ sec}^{-1}$ and that for $\text{PbO}_2\text{-NO}_2$ reaction was about $1.5 \times 10^{-7} \text{ sec}^{-1}$ at atmospheric temperature. When the reaction rate constants for both reactions are compared, it is found that the former is at least 10^4 times large as the latter at atmospheric temperature. In this case, the gas film mass transfer coefficients for both reactions are almost the same as those in Tables 2 and 3. For the $\text{PbO}_2\text{-SO}_2\text{-NO}_2$ reaction system, then, the structure of pore in the ash layer seems to be very complicated by the simultaneous reaction of SO_2 and NO_2 in PbO_2 compared to the case of individual reaction systems and in addition, it can be considered that the reaction interfaces in the pellet for SO_2 and NO_2 are almost the same.

Conclusion

To estimate the degree of the effect of NO_2 on the SO_2 concentration measured with the lead peroxide method, the experiment for $\text{PbO}_2\text{-SO}_2\text{-NO}_2$ reaction system was performed by using the cylindrical PbO_2 pellet and the reaction rate constants for $\text{PbO}_2\text{-SO}_2$ and $\text{PbO}_2\text{-NO}_2$ reactions were estimated. The following results were obtained;

(1) The fractional conversion of SO_2 for the $\text{PbO}_2\text{-SO}_2\text{-NO}_2$ reaction system is smaller than that for $\text{PbO}_2\text{-SO}_2$ reaction system at constant SO_2 concentration.

(2) The selectivity to produce the lead sulfate on the $\text{PbO}_2\text{-SO}_2\text{-NO}_2$ reaction system has a very strong correlation with the ratio of NO_2 occupied in the total amount of gaseous reactants.

(3) The selectivity is held constant regardless of the reaction time at the same operating conditions.

(4) The reaction rate constant for $\text{PbO}_2\text{-SO}_2$ reaction is at least 10^4 times large as that for $\text{PbO}_2\text{-NO}_2$ reaction at atmospheric temperature.

(5) The moving velocity for the reaction interface is relatively slow compared to the chem-

ical reaction rate.

(6) The reaction interfaces in a pellet for both SO_2 and NO_2 are almost the same.

Acknowledgment

The author would like to thank Dr. H. Hirai for his helpful advice, The author is also grateful to Messrs. H. Nishimura and Y. Ohota for his help in the experiment.

REFERENCES

- 1) Hayashi, Y.: The study on mass transfer mechanism for $\text{PbO}_2\text{-SO}_2$ reaction system, *J. Japan Soc. Air Pollut.*, **16**(5), 285(1981)
- 2) Liu, M. K., M. A. Yocke and P. Mundkur: Numerical solution of reactive plumes, *AIChE Symp. Ser.*, **73**, 66 (1977)

Nomenclature

a_i	=stoichiometric coefficient of gaseous reactant i	[—]
C_{i0}	=concentration of gaseous reactant i in solid	[mol/m ³]
C_{S0}	=initial concentration of solid reactant	[mol/m ³]
\mathcal{D}_{ei}	=effective diffusivity of gaseous reactant i in porous solid	[mol/m ³]
f_i	=fractional conversion of gaseous reactant i	[—]
f_t	=overall fractional conversion	[—]
k_{fi}	=gas film mass transfer coefficient of gaseous reactant i	[m/s]
L	=height of cylindrical pellet	[m]
R	=radius of cylindrical pellet	[m]
T	=temperature of gas	[K]
t_i	=contact time of gaseous reactant i [s], [h]	
u	=mean gas velocity	[m/s]
W_i	=amount of solid product of gaseous reactant i	[mol]
W_t	=total amount of solid product	[mol]
Ψ_i	=selectivity of gaseous reactant i defined by Eq. (4)	[—]
subscripts		
1	=gas film diffusion controlling region	
2	=ash layer diffusion controlling region	
A	= SO_2	
B	= NO_2	
pure	= $\text{SO}_2\text{-PbO}_2$ system or $\text{NO}_2\text{-PbO}_2$ system	

二酸化鉛法による亜硫酸ガス濃度測定に及ぼす二酸化窒素ガスの影響

林 良 茂

金沢大学工学部化学工学科
920 金沢市小立野2-40-20

二酸化鉛法によって測定された亜硫酸ガス濃度を精度良く評価するために、二酸化鉛法による亜硫酸ガス濃度測定に及ぼす NO_2 の影響を実験的に調べた。実験は円柱状の PbO_2 ペレットと SO_2 - NO_2 - N_2 系の混合ガスを

用いて行った。生成した反応物に対する選択率と固体内での反応ガスの移動機構を、本実験で得られたデータに基づいて検討した。

(昭和56年6月8日受付)