Removal of Atmospheric Pollutants

(6) Absorption of Lean NO in Aqueous Slurries of $Ca(OH)_2$ with $NaClO_2$ or $Mg(OH)_2$ with $NaClO_2$

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大気汚染物質除去に関する研究

(6) $Ca(OH)_2$,$NaCl_2$と$Mg(OH)_2$,$NaClO_2$スラリーによる希薄NOの吸収

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The absorption of lean NO in an aqueous slurry of $Ca(OH)_2$ or $Mg(OH)_2$ with $NaClO_2$ was carried out using a stirred tank absorber with a plane gas-liquid interface at 25℃ and 1 atm. The rates of absorption of NO and the accompanying desorption of NO_2 for the $Ca(OH)_2$ slurry were in clese agreement with those for the aqueous mixed solution of $NaClO_2$ and NaOH with higher OH^- concentration, whereas for the $Mg(OH)_2$ slurry, the absorptin rate of NO noticeably exceeded that for the former systems. Furthermore, the ratio of the NO_2 desorption rate to the NO absorption rate considerably exceeded the theoretical perediction for gas absorption with the consecutive reaction (maximum deviation attainned 117 %) . Also, chlorine dioxide was detected in the gas phase. It was deduced from these experimental evidences that there occur both desorption of the decomposition product ClO_2 and gas-phase oxidation of NO with ClO_2 to produce NO_2.

INTRODUCTION

In the previous work [1,2] , the absorption of lean No in aqueous mixed solutions of $NaClO_2$ and NaOH was carried out using a stirred vessel with a plane gas-liguid interface, and the chemical absorption kinetics was analyzed. As a result, the following information was derived. In the high NO concentration region greater than 2000 ppm, the order of reaction with respet to NO was estimated as 2, whereas for the NO concentration less than several hundred ppm, the reaction order varied from 2 to 1 with decreasing the NO concentration. The order of reaction of ,$NaClO_2$ was determined as unity only for the $NaClO_2$ concentration greater than 0.8 molar. For the concentration less than 0.8 molar, the dependence on the concentration becomes markedly and a simple relationship was not extracted. when the concentration of $NaClO_2$ exceeds 0.8 molar and the partial pressure of NO exceeds 0.002 atm, the reaction between NO and $NaClO_2$ in an aqueous solution can be regarded as second—order in NO and first—order in $NaClO_2$. The effect of the NaOH concentration on the third—order rate constant k was expressed by $k=3.80\times10^{12}\exp(-3.73\ [NaOH])$ in the range of $0.5<[NaOH]<0.5$ molar. In considering this result, the rate of the reaction increases with decreasing the NaOH concentratiom, but too low concentration of OH^- results in decomposition of $NaClO_2$. Then a decomposition product ClO_2 is evolved in the gas phase and the gasphase oxidation of NO takes place. Hence in order to suppress the decomposition of $NaClO_2$ and give the absorbent a stable oxidation ability, it is necessary to keep the OH^- concentration to a value. However, if a depletion of OH^- due to the reaction can be prevented, then the decomposition of $NaClO_2$ may be suppressed even when the concentration of OH^- is kept low. Such a situation is established by using sparingly soluble alkaline—earth hydroxide as an alkali source. An aqueous slurry of $Ca(OH)_2$ or $Mg(OH)_2$ has low concentration of OH^- but high alkaline capacity. Thus, in the present work, the absorption rate of NO by an aqueous slurry of $Ca(OH)_2$ with $NaClO_2$ or $Mg(OH)_2$ with $NaClO_2$ in a

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stirred vessel was measured and the absorption mechanism was analyzed in terms of the chemical absorption theory.

EXPERIMENTAL

All the absorption runs were made using a stirred tank absorber with a plane gas—liquid interface at 25 ℃ and 1 atm . The absorber used (I.D.=80 mm, Liquid volume=500 cm^3) is the same as in the previous work [1,2] . The absorber was operated centinuously with respect to the gas phase and batchwise with respect to the liquid phase. Two stirrers driven by two separate motors were used to agitate the gas and liquid phases. The stirring speeds of the liquid phase and gas phase stirrers were maintained at 162 and 500 rpm, respectively. The concentration of NO in the feed stream was varied from 50 to 800 ppm.The concentrations of NO and NO_2 in the gas phase were determined by UV derivative spectrophotometer (Yanaco UO-1). Absorption rates of NO were calculated from the difference between inlet and outlet concentrations of NO and the total gas flow rate. Also, desorption rate of NO_2 were calculated from the outlet concentration of NO_2 and the total gas flow rate.

EXPERIMENTAL RESULTS AND DISCUSSION

1. Absorption of NO in an aqueous slurry of $Ca(OH)_2$ with $NaClO_2$

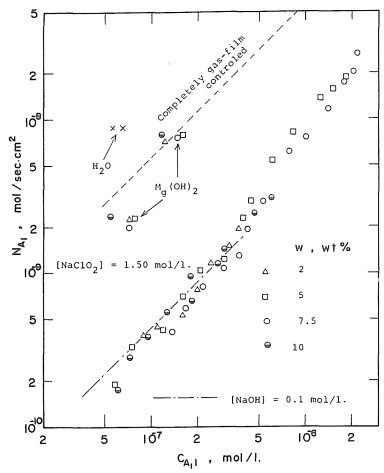

Fig. 1. Absorption rates of NO for the $NaClO_2/Ca(OH)_2$ slurry system.

Figure l shows absorption rates of NO in aqueous slurries of $Ca(OH)_2$ with $NaClO_2$under various NO concentrations. The liquid phase contains 2,5,7.5 and 10 wt% of fine $Ca(OH)_2$ particles in an aqueous $NaClO_2$ solution. The OH^- concentration in the agueous solution saturated with $Ca(OH)_2$ amounts to 0.046 g—ion/l. It is apparent that experimental absorption rates are not influenced by the solid concentration. The dot-dash line represents the absorption rate of NO by an aqueons mixed solution of 1.5 molar $NaClO_2$ and 0.1 molar NaOH [2] . In the range of $C_{Ail} < 5\times10^{-7}$ mol/1, the slope of the dot-dash line approximately equals unity,which implies that the reaction between NO and $NaClO_2$ in an alkaline solution can be expressed by first-order with respect to NO. When using $Ca(OH)_2$ as an alkaline sources, the OH^- concentration in a slurry (0.046 g—ion/1) corresponds to about half the value for the dot-dash line. These, the reaction rate constant for the slurry solution is increased by c.a. 22 percent, but the absorption rate increases only by c.a.11 percent. In this way, experimental absorption rates fall closely on the dot-dash line within the experimental error. The experimental result that the absorption rate is not influenced by the slurry concentration may be expected from the theoretical prediction that the absorption process lies under the fast-reaction regime.

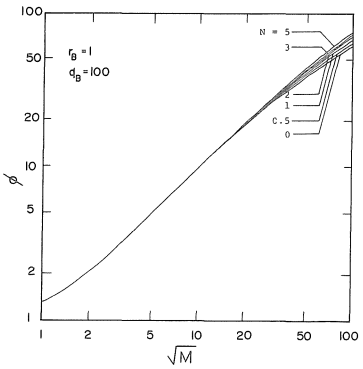

Fig. 2. Dependence of the parameter N on the enhancement factor for the slurry system.

Figure 2 indicates the relationship between enhancement factor and reaction-diffusion modulus as a parameter of N for gas absorption with a second -order reaction in slurry (A(g)→AB(aq), B(s)→(aq), A(aq)+νB(aq)→products). The parameter N is defined by $k_S A_P z^2_L / D_B$, where A_P is equal to $6w/pd_P$, and hence is proportional to solid concentration w. This figure clearly shows that the relatinn of Φ vs $\sqrt{M}$ is almost independent of N or w in a fast-reaction regime. The rates of NO absorption in a slurry of $Ca(OH)_2$ with $NaClO_2$ may be expected from the previous work [2] , and it is deduced that $NaClO_2$ in absorbent is not excessively decomposed.

2. Absorption of NO in an aqueous slurry of $Mg(OH)_2$ with $NaClO_2$

In an aqueous solution saturated with $Mg(OH)_2$, the OH^- concentration is equal ot 0.00092 g-ion/1.

As the absorption of NO proceeds, the pH of the absorbent near the gas-liquid interface may shift above 7, because reaction products through reaction (iii) described later, HNO_3 and HNO_2, are accumulated. In an acidic solution, the absorbent $NaClO_2$ decomposes to form ClO_2:

$$4ClO_3^- + 2H^+ \rightarrow 2ClO_2 + ClO_3^- + Cl^-$$

The absorption spectra of the chlorine dioxide evolved from an aqueous solution of $NaClO_2$ with 1.

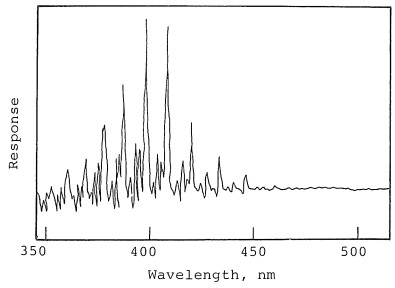

Fig. 3. Absorption spectra of ClO_2evoled from aqueous $NaClO_2$ solution by adding H_2SO_4.

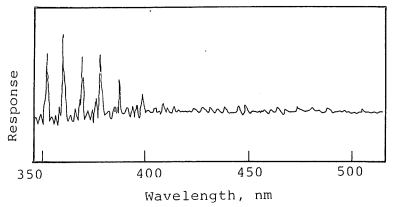

Fig. 4. Absorption spectra of effluent gas.

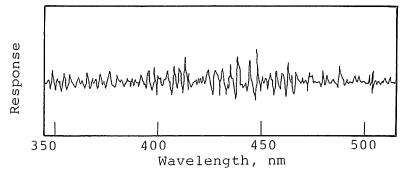

Fig. 5. Absorption spectra of NO_2 diluted with N_2.

5 molar by adding small amount of H_2SO_4 are shown in Fig. 3. The absorption spectra here are the second-order derivative of the direct (conventional) absorption spectra. A series of characteristic peaks identifying ClO_2 appears in the range of wave length of 350 nm-450nm. Figure 4 indicates the measurements of absorption spectra of the effluent gas during the NO absorption, whereas Figure 5 shows the absorption spectra of NO_2 only diluted with N_2.Judging from comparison of absorption spectra depicted in Figs. 3 through 5, there exists ClO_2 in the effluent gas during the NO absorption. That is, the form of absorption spectra in the range of 350-400nm in wave length in Fig. 4 suggests the presence of ClO_2. On the other hand, it is considered that the absorption spectra for chlorine overlap on those for nitrogen dioxide, but chlorine could not be detected because the molecular extinction coefficient for chlorine is much lower than that for nitrogen dioxide. (Thus,in the analyzer used, the lowed, limit of detection for chlorine was about 5000 ppm.)

Figure 6 shows a typical example of variation of the absorption rate (N_{A1}) and the degree of removal of NO with the process time. The time required to reach the steady-state in the absorption process, is increasing with an increase in solid concentration, but the absorption rate at steady-state is independent of the solid concentration. The steady-state absorption rate, which is plotted against the interfacial concentration in Fig. 1, is enough high not to be expected from the results for the aqueous slurry of $Ca(OH)_2$ with $NaClO_2$ as well as the aqueous mixed solution of $NaClO_2$ and NaOH. It is reduced from detected components in the effiuent gas that such high absorption rates are attributed to the existence of the gas-phase oxidation of NO with ClO_2. In Fig. 6 is also shown the variation of the

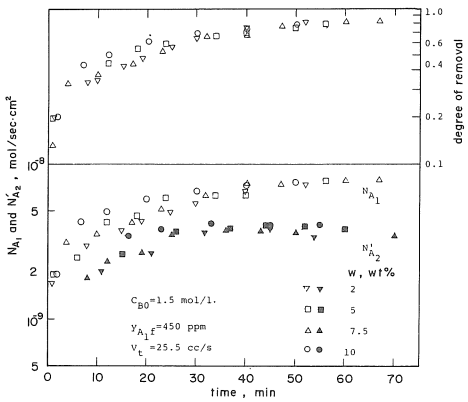

Fig. 6. Absorption rate of NO and desorption rate of NO_2 for the $NaClO_2/Mg(OH)_2$ slurry system. Effect of solid concentration.

desorption rate of NO_2(including the production rate of NO_2 due to the gas-phase oxidation of NO with ClO_2) with the process time. From the figure, the ratio N'_{A2}/N_{A1} at steady-state attains 0.43～0.52. Also, for $y_{A1f}=215$ ppm, N'_{A2}/N_{A1} attained 0.28～0.41. For the $NaClO_2/Ca(OH)_2$ slurry system, on the other hand, the ratio for y_{A1f} = 205 ppm reduced to 0.16～0.19. This magnitude can be predicted from the simulation of gas absorption with the consecutive reaction whose mechanism and kinetics are well defined in the previous work [1,2]

Figure 7 shows the effect of $NaClO_2$ concentration on the rate of NO absorption N_{A1} and the rate of NO_2 desorption (including gas-phase production) N'_{A2}.The $NaClO_2$ concentration has negligible effect

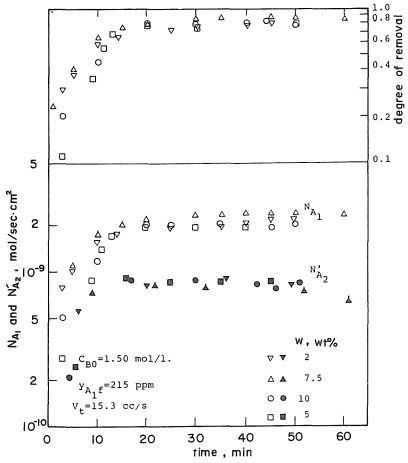

Fig. 7. Absorption rate of NO and desorption rate of NO_2. Effect of $NaClO_2$ concentration.

on the variation of N_{A1} and N'_{A2} with time. This fact favorably supports the speculation that there considerably exists a conversion of NO to NO_2 in the gas phase.

3. Simulation of the processes of the NO absorption and the accompanying NO_2 desorption

Dissolved NO reacts with ClO^-_2 in an alkaline solution of $NaClO_2$ to produce NO_2 by

$$2NO+ClO^-_3 \rightarrow 2NO_2+Cl^- \qquad (i)$$

Some of NO_2 produced is consumed by the liquid-phase reactions:

$$4NO_2+ClO^-_3+4OH^- \rightarrow 4NO^-_3+Cl^-+2H_2O \qquad (ii)$$

and

$$2NO_2+H_2O \rightarrow HNO_3+HNO_2 \qquad (iii)$$

Some evolves into the gas phase without undergoing any chemical reaction. In the following, the processes of the NO absorption and the accompanying NO_2 desorption are formulatde on the basis of the film model, and the magnitude of the ratio of NO_2 desorption rate to NO absorption rate will be estimated.

The reactions relevant to NO and NO_2 can be described by the following relations:

$$A_1+\nu B \rightarrow A_2+P_1 \qquad (\nu_1=1/2) \qquad (I)$$

$$A_2+\nu_2 B \rightarrow P_2 \qquad (\nu_2=1/4) \qquad (II)$$

$$A_2 \longrightarrow P_3 \qquad (III)$$

First, the problem will be considered for the absorption of NO in an aqueous mixed solution of 1.5 molar $NaClO_2$ and 0.2 molar NaOH. The gas-phase concentration of NO is put 1250 ppm ($C_{A1i}=2\times10^{-6}$ mol/l), where the reaction rate expression is well established [1]. Under such a high concentration region, reaction (I) can be expressed by second-order in NO (A_1) and first-order in $NaClO_2$ (B) and its rate constant at 25 ℃ is estimated as 1.8×10^{12} (1/mol)²/sec [1]. Reaction (II) is found to be second-order in NO_2 (A_2) and first-order in $NaClO_2$ (B) and the third-order reaction rate constant at 25 ℃ is derived to be 7.32×10^8 (1/mol)²/sec [2]. Reaction (III) (hydrolysis of NO_2) can be also expressed by second-order in NO_2 and its rate censtant at 25 ℃ is derived as 3.09×10^8 1/mol sec [2]

When Reactions (I), (II) and (III) are taking palce in the liquid phase, mass balance equations for components A_1, A_2 and B can be written as follows:

$$D_{A_1}\frac{d^2C_{A_1}}{dz^2}=k_I C^2_{A_1} C_B \qquad (1)$$

$$D_{A_2}\frac{d^2C_{A_2}}{dz^2}=k_{II} C^2_{A_2} C_B+k_{hyd} C^2_{A_2}-k_I C^2_{A_1} C_B \qquad (2)$$

$$D_B\frac{d^2C_B}{dz^2}=\nu_1 k_I C^2_{A_1} C_B+\nu_2 k_{II} C^2_{A_2} C_B \qquad (3)$$

The boundary conditions are given by

$$\text{at} \quad z=0; \quad C_{A_1}=C_{A_1 i}, \quad D_{A_2}\frac{dC_{A_2}}{dz}=k_{GA_2}(C_{A_2 i}-C_{A_2 g}), \quad \frac{dC_B}{dz}=0 \qquad (4)$$

$$\text{at} \quad z=z_L; \quad C_{A_1}=C_{A_2}=0, \quad C_B=C_{BO} \qquad (5)$$

The mass balance equations and boundary conditions may be put into the following dimensionless form:

$$\frac{d^2Y_{A_1}}{dx^2}=M_1 Y^2_{A_1} Y_B \qquad (6)$$

$$\frac{d^2Y_{A_2}}{dx^2}=\left(\frac{M_1 s r_2}{r_1}\right)Y^2_{A_2} Y_B+\left(\frac{M_1 s' r_2}{r_1}\right)Y^2_{A_2}-\left(\frac{M_1 r_2}{r_1}\right)Y^2_{A_1} Y_B \qquad (7)$$

$$\frac{d^2Y_B}{dx^2}=\left(\frac{M_1}{r_1 q_1}\right)Y^2_{A_1} Y_B+\left(\frac{M_1 s}{r_1 q_2}\right)Y^2_{A_2} Y_B \qquad (8)$$

$$\text{at} \quad x=0; \quad Y_{A_1}=1, \quad \frac{dY_{A_2}}{dx}=B_I(Y_{A_2 i}-Y_{A_2 g}), \quad \frac{dY_B}{dx}=0 \qquad (9)$$

$$\text{at} \quad x=1; \quad Y_{A_1}=Y_{A_2}=0, \quad Y_B=1 \qquad (10)$$

The parameters included in Eqs. (6) to (10) take following quantities for the conditions developed here:

$$s=\frac{k_{II}}{k_I}=4.07\times10^{-4} \qquad s'=\frac{k_{hyd}}{k_I C_{BO}}=1.14\times10^{-4}$$

$$q_1=\frac{C_{BO}}{\nu_1 C_{A_1 i}}=1.5\times10^5 \qquad q_2=\frac{C_{BO}}{\nu_2 C_{A_1 i}}=3\times10^6$$

$$M_1=3.12\times10^7 \quad r_1=0.745 \quad r_2=1.35$$

The Biot number B_I takes 730 under the present experimental conditions and Y_{A2g} is assumed to be zero.

The above ordinary differential equations, Eqs. (6) to (8), are nonlinear:therfore analytical solutions are not expected. Then, a set of differential equations were approximated by the time-centered implicit finite difference equations. These implicit equations were simplified by linearinzing the reaction terms. A set of resultant simultaneous linear equations was solved by the method of tridiagonal equations. Numerical results were expressed in terms of enhancement factor ϕ_{A1} and ratio N'_{A2}/N_{A1} defined by

$$\phi_{A_1}=-\left(\frac{dY_{A_1}}{dx}\right)_{x=0} \tag{11}$$

and

$$\frac{N'_{A_2}}{N_{A_1}}=\left(\frac{r_1}{r_2\phi_{A_1}}\right)\left(\frac{dY_{A_2}}{dx}\right)_{x=0} \tag{12}$$

as a function of reaction-diffusion modulus $\sqrt{M_1}$

In the course of computation, scales of q_1 and q_2 were reduced by 10^3 because of rapid convergence. Thereby M_1 decreases by a factor 10^{-3}, whereas s' increases by a factor 10^3. Numerical results are shown in fig. 8. N'_{A2}/N_{A1} is calculated as 0.29 when

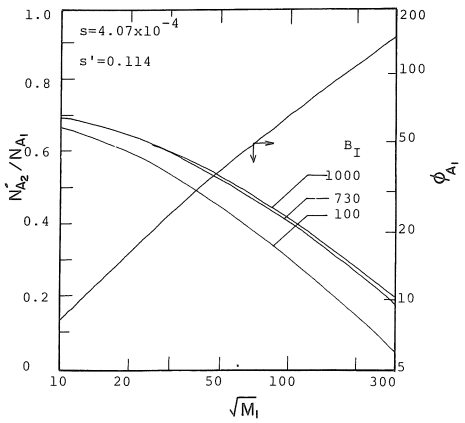

Fig. 8. Theoretical relation of N'_{A_2}/N_{A_1} vs $\sqrt{M_1}$ and ϕ_{A_1} vs $\sqrt{M_1}$ for the NO-$NaClO_2$/NaOH system.

$\sqrt{M_1}=177$ and $B_1=730$.

For the $NaClO_2/Ca(OH)_2$ slurry system, OH^- concentration is evaluated 0.046 g-ion/l: thereby $k_l=3.20\times10^{12}$ (1/mol)²/sec and s'=0.0644. The s value is assumed to be equal to that for the previous case ($s=4.07\times10^{-4}$). In this case, q_1 and q_2 are also reduced by a factor 10^3. Figure 9 shows computational result as a plot of N'_{A2}/N_{A1} vs $\sqrt{M_1}$, where N'_{A2}/N_{A1} is obtained

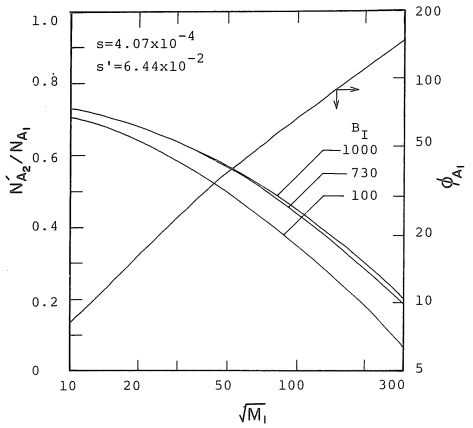

Fig. 9. Theoretical relation of N'_{A_2}/N_{A_1} vs $\sqrt{M_1}$ and ϕ_{A_1} vs $\sqrt{M_1}$ for the NO-$NaClO_2/Ca(OH)_2$ system.

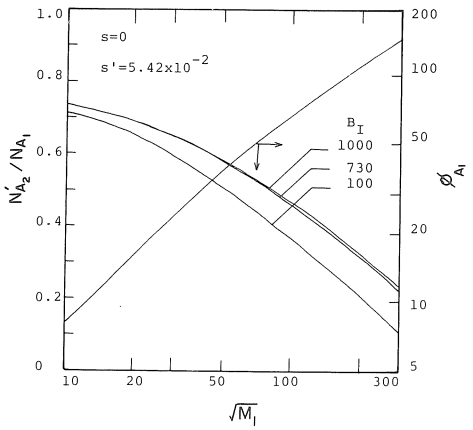

Fig. 10. Theoretical relation of N'_{A_2}/N_{A_1} vs $\sqrt{M_1}$ and ϕ_{A_1} vs $\sqrt{M_1}$ for the NO-$NaClO_2/Mg(OH)_2$ system.

as 0.24 when $\sqrt{M_1}=235$. and $B_l=730$. This prediction a bit exceeds experimental results (0.16 to 0.19).

For the $NaClO_2/Mg(OH)_2$ system, the OH^- concentration is negligibly small and there appears no contribution is negligibly small and there appears no contribution of reaction (II). Therefore s=0. The s' value reduces to 0.0542 ($k_l=3.80\times10^{12}$ (1/mol)²/sec). Numerical results are shown in Fig. 10. N'_{A2}/N_{A1} is calculated as 0.24 when $\sqrt{M_1}=284$ and $B_l=730$. On the other hand, experimental values of N'_{A2}/N_{A1} ranged from 0.43 ot 0.52 for $y_{A1f}=450$ ppm as shown in Fig. 6 and from 0.28 to 0.41 for $y_{A1f}=215$ ppm. It also suggests that there significantly occur both desorption of the decomposition product ClO_2 into the gas phase and gas-phase oxidation of NO with ClO_2 to produce NO_2.

CONCLUSION

The rates of absorption of NO and the accompanying desorption of NO_2 the $NaClO_2/Ca(OH)_2$ slurry system, were satisfactorily expected from the previous observation in the aqueous mixed solution of $NaClO_2$ and NaOH with higher OH^- concentration, whereas for the $NaClO_2/Mg(OH)_2$ slurry system, the absorption rate of NO noticeably exceeded that for the former systems and the ratio of the NO_2 desorption rate to the NO absorption rate considerably exceeded the theoretical prediction for gas absorption with the consecutive reaction. The maximum deviation between two factors has attained 117 %. Also, chlorine dioxide was detected in the gas phase. It was deduced from these experimental evidences that there significantly occur both desorption of the decomposition product ClO_2 into the gas phase and gas-phase oxidation of NO with ClO_2 to produce NO_2.

Acknowledgements—The authors wish to express their thanks to Japan Securities Scholarship Foundation for its finan-cial support.

NOTATION

A_P surface area of solid particles $=6w/\rho d_P$, cm^2/cm^3-dispersion

B_l Biot number $=k_{GA2}/\overset{\circ}{k}_{LA2}$

C concentration in liquid phase, mol/cm^3 or mol/l

D biffusivity in liquid phase, cm^2/sec

d_P average diameter of solid particles, cm

k_{II} rate constant of reaction (II), $(1/mol^2)/sec$

k_L mass transfer coefficiet in liquid phase, cm/sec

M_l reaction-diffusion modulus $=k_l C_{Ali} C_{BO}/(\overset{\circ}{k}_{LAl})^2$

V_t total gas flow rate, cm^3/sec

W concentration of solid, g/cm^3-dispersion of wt%

$*$ relative to that in the bulk of liguid or at solid surface

ρ density of solid, g/cm^3

$\circ$ without chemical reaction

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