

SO₂ — REMOVAL USING AMMONIA SOLUTION IN A PACKED COLUMN

Kyung Ho Row and Won Kook Lee*

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology

Seoul 131, Korea

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Abstract—The effect of variables on efficiency of SO₂ removal from a simulated waste gas by use of ammonia solution was studied. The variables were gas, feed solution and recirculation flow rate, SO₂ concentration in the gas phase, NH₃ concentration in the ammonia solution, and pH in scrubber effluent solutions.

The scrubber was 3" —OD methyl metacrylate column packed with 1" —plastic Rasching rings in 90 cm packed height.

Solution analysis was performed by Palmrose method and pH meter.

The following empirical equations were obtained by regression analysis;

$$EFF = 33.52 G^{0.0552} F^{0.118} R^{0.772}$$

$$EFF = 64.10 S^{0.143} N^{0.0153}$$

$$k_G = 3.51 \times 10^{-6} G^{1.160} L^{0.647}$$

INTRODUCTION

Sulfur dioxide is emitted from various sources such as the burning of coal, the combustion of petroleum, the smelting of ores containing sulfur, and many others. Among the many alternatives to prevent SO₂ mission, FGD (Flue Gas Desulfurization) systems are most promising. A major classification of the FGD systems is; (1) recovery of SO₂ in a useful form, and (2) formation of a product intended for discard as a solid waste. Although it is desirable to recover a useful product, all the recovery processes developed so far are higher cost than the throwaway type. The throwaway methods have a major disadvantage, however, that the pollution problem is not completely solved. Removal of SO₂ from gas streams by ammonia has been investigated by many workers for many years [1].

The original objective was not control of SO₂ emission but rather production of ammonium sulfate. A pilot plant work was done beginning in 1953, on adapting ammonia scrubbing in power plants for burning high-sulfur coal.[10]

There has been a rapid expansion of work on applying ammonia scrubbing to the power plant in the period of 1960-1970. The scrubbing continues to offer the promise of high solution capacity, low absorbent cost, and salability of the sulfate produced. If phenomena in the scrubber is fully understood and a more economical

regeneration method is developed, the process will be more attractive than other methods for sulfur dioxide recovery.

THEORETICAL BACKGROUND

(1) Vapor pressure and pH in NH₃-H₂O-SO₂ system

The vapor pressure of sulfur dioxide over ammonium sulfite bisulfite is a highly important consideration in ammonia scrubbing

The vapor pressures were determined by the method of Johnstone[2] over the pH range of 4.71-5.96.

The results were expressed by the following equations;

$$P_{SO_2} = M \frac{(2S-C)^2}{C-S} \quad (1)$$

$$P_{NH_3} = N \frac{C(C-S)}{2S-C} \quad (2)$$

The constants were;

$$\log M = 5.865 - \frac{2369}{T}$$

$$\log N = 13.680 - \frac{4987}{T}$$

For the practical scrubbing system, in which sulfate is present, the partial pressures are;

$$P_{SO_2} = M \frac{(2S-C+2A)^2}{C-S-2A} \quad (3)$$

* To whom correspondence should be directed.

$$P_{\text{NH}_3} = N \frac{C(C - S - 2A)}{2S - C + 2A} \quad (4)$$

Chertkov[3] also determined the vapor pressure of sulfur dioxide in presence of sulfate from the following equation;

$$P_{\text{SO}_2}(\text{true}) = P_{\text{SO}_2}(\text{cal.}) \frac{C + A}{C} \quad (5)$$

$P_{\text{SO}_2}(\text{cal.})$ is the calculated value by Eq. (1) without presence of the sulfate.

The vapor pressures of sulfur dioxide determined by Johnstone and Chertkov are basic data in $\text{NH}_3\text{-SO}_2\text{-H}_2\text{O}$ system and can be used to predict mass transfer coefficient.

The relationships between (S/C) and pH were proposed by Johnstone [2]

$$\text{pH}_J = -4.62(S/C) + 9.2, 0.7 < S/C < 0.9 \quad (6)$$

and Chertkov [10],

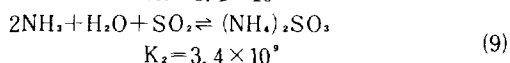
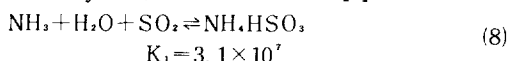
$$\text{pH}_C = -4.0(S/C) + 8.88, 0.5 < S/C < 0.95 \quad (7)$$

From above relationships, composition of $\text{NH}_4\text{HSO}_3\text{-(NH}_4)_2\text{SO}_3$ solution can be obtained only by the information of pH in the solution. Outside this range, however, the relationship was not linear.

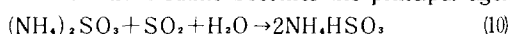
The pH reported for pure ammonium sulfite solution was 8.0; values for bisulfite were 3.0 for 5% solution and 2.7 for 45% solution [10].

(2) Gas-phase Mass Transfer Coefficient

When ammonia solution is introduced into the scrubber system, it reacts as follows [4];



In either case, the reaction does not continue long until ammonium sulfite becomes the principal agent.



Due to high value of K_1 , K_2 , chemical absorption in $\text{NH}_3\text{-H}_2\text{O-SO}_2$ system may be assumed to be fast reaction. Since sulfur dioxide is quite soluble in ammonia solution, it would be expected that the liquid film resistance to sulfur dioxide would be low.

Assuming that the mole fraction of sulfur dioxide in the scrubber is much less than unity, then [5]

$$G \, dm = R_{av} \, a \, dh \quad (11)$$

$$R_{av} = k_G P \, m \quad (12)$$

, where P is the total pressure

From Eq. (11) and Eq. (12),

$$k_G a = \frac{G}{H P} \ln \frac{m_B}{m_T} \quad (13)$$

Therefore, $k_G a$ can be calculated by a measurement of the mole fractions of sulfur dioxide at the top

and bottom of the absorption column with packed height H .

EXPERIMENT

(1) Experimental Apparatus

A schematic diagram of experimental apparatus is shown in Fig.1. Absorption column (D) was made of ID-6.5cm methyl metacrylate cylinder to be observed inside of it easily. The column was packed with 0.64cm plastic Raschig rings and the packed height was 90cm.

The gas mixer (E) was made of ID-2.54cm P.V.C. pipe packed with 0.64cm plastic Raschig rings to mix the air and the sulfur dioxide uniformly. The air scrubber and humidifier (F) was for eliminating CO_2 from the air, and for saturating the air with water vapor.

It was packed with 0.95cm plastic Raschig rings about a half of its height, and 0.5N solution of sodium-hydroxide was filled.

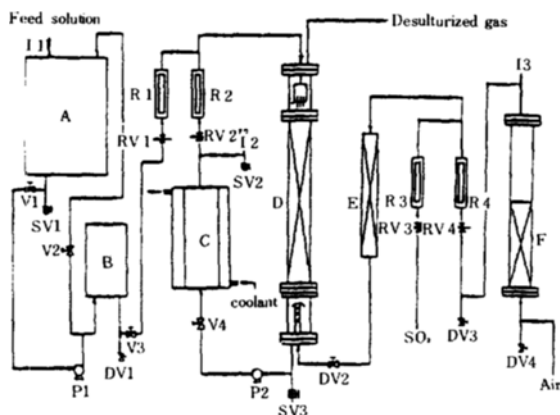
(2) Experimental Procedure

The ammonia solution was put through I_1 into the feed tank (A) with valve V_1 closed, and through I_2 , cooler (C) was also filled with the ammonia solution with valve V_4 closed. Flow rates of the feed solution was controlled by V_1 and V_2 . 0.5N solution of sodium-hydroxide was frequently put into the air scrubber and humidifier (F) through I_3 to keep the absorbing capacity. SO_2 -contained solution was put into the absorption column (D), and then entered to the inlet of recirculation pump (P_2), and the recirculation flow rate was adjusted by RV_2 . SO_2 -contained ammonia solution was changed into yellow as it absorbed SO_2 .

Samples were obtained through SV_2 and SV_3 , and pH of the samples were measured and recorded at a regular interval. The operation was continued until these two pH values were same and kept constant at 6.9. Experiment was continued by changing gas velocities, feed solution and recirculation flow rates, and concentrations of sulfur dioxide in the gas-phase and ammonia in the feed solution. The operating conditions of this study were shown in the Table 1.

Table 1. Operating Conditions.

Superficial gas velocity	12.6—27.6 cm/sec
Ammonia solution flow rate	0.25—0.75 cm ³ /sec
recirculation flow rate	10.33—13.33 cm ³ /sec
packed height	90 cm
SO_2 concentration in the gas-phase	1.9—6.0 % (by volume)
NH_3 concentration in the ammonia solution	2.0—9.5 % (by volume)
pH of scrubber effluent	6.9



- A : Feed solution tank
 B : Surge tank for feed solution
 C : Cooler and surge tank for recirculating liquid
 D : Absorption column
 E : Gas (air+SO₂) mixer
 F : Air scrubber and humidifier
 I1 - I3 : Inlets of solutions
 P1 : Feed solution pump
 P2 : Recirculation pump
 R1 - R4 : Rotameters
 V1 - V4 : Valves
 DV1 - DV4 : Valves for drain
 RV1 - RV4 : Valves for rotameters
 SV1 - SV3 : Sampling valves

Fig. 1. Schematic Diagram of Experimental Apparatus.

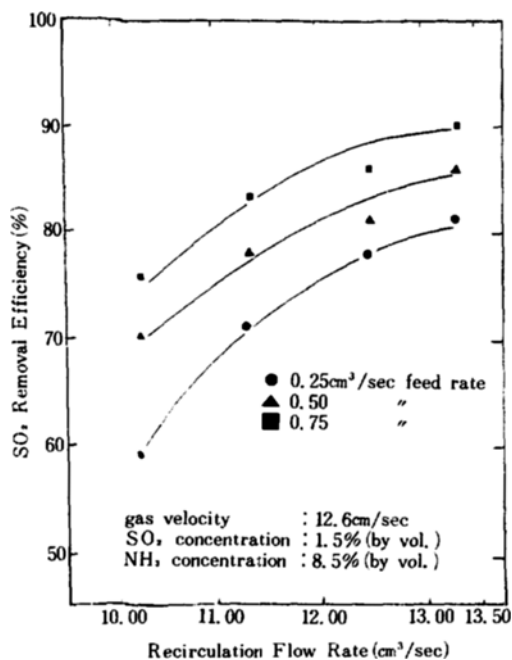


Fig. 2. The Effect of Ammonia Solution, Recirculation Flow Rates on SO₂ Removal Efficiency at Constant Gas Velocity.

RESULTS AND DISCUSSIONS

(1) Effect of Gas, Feed Solution, and Recirculation Flow Rates on SO₂ Removal Efficiency

When the flow rate of feed solution was more than the recirculation flow rate, it took a long time to reach the steady state. It followed that pH of scrubber effluent (feed solution and recirculation liquid) dropped very slowly. To overcome the difficulty, the feed solution flow rate was set much less than the recirculation flow rate. The feed solution flow rate was set at 0.25, 0.50, 0.75 cm³/sec and the recirculation flow rate at 10.33, 11.33, 12.50, 13.33 cm³/sec in this study. As shown in Fig. 2, SO₂ removal efficiency increased with increasing the feed solution and the recirculation flow rate at constant gas velocity of 12.6 cm/sec.

The reason is that the absorptive capacity of the feed solution and the recirculation liquid increases with their higher flow rates at constant gas velocity. Fig. 2 also shows that rate of increase in SO₂ removal efficiency is retarded at higher recirculation flow rates. Comparing Fig. 2 with Fig. 3, it can be seen that the SO₂ removal efficiency at the gas velocity of 27.6 cm/sec was slightly higher than that at 12.6 cm/sec. The results show that the effect of the gas velocity on the SO₂ removal efficiency was smaller at constant liquid flow rates.

In packed column, interfacial area was strongly affected by liquid flow rates and negligibly affected by gas

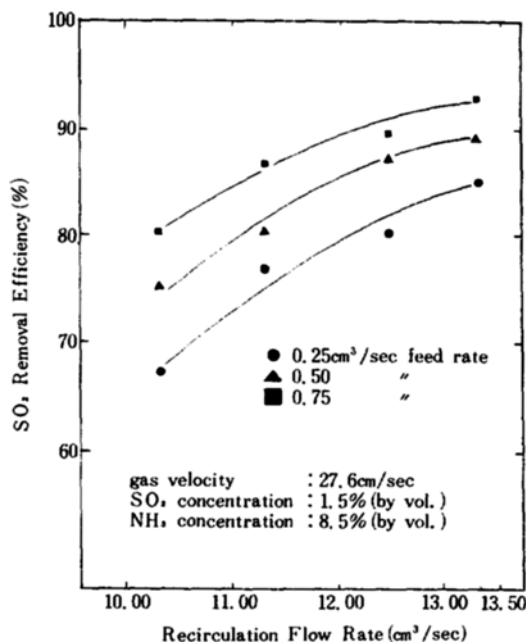


Fig. 3. The Effect of Ammonia Solution, Recirculation Flow Rates on SO₂ Removal Efficiency at constant Gas Velocity.

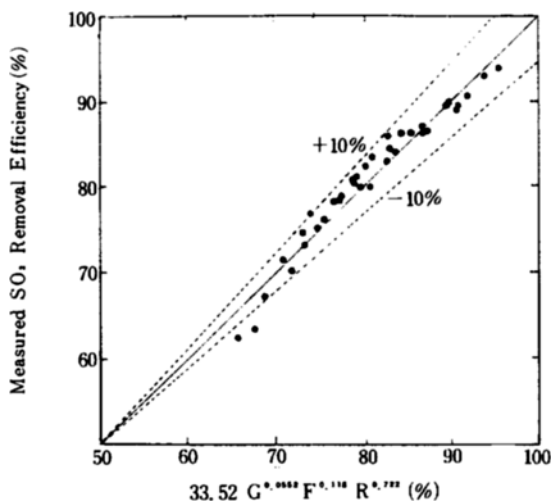


Fig. 4. Correlation of SO_2 Removal Efficiency with respect to Gas, Feed Solution and Recirculation Flow Rates.

flow rates [6]. But Chertkov [7] pointed out that high gas velocity was desirable because the benefit from higher mass transfer more offsetted than the cost of the higher pressure drop. Fig. 4 shows the plot of the measured SO_2 removal efficiency and that calculated from the following empirical correlation.

$$\text{EFF} = 33.52 G^{0.0552} F^{0.118} R^{0.772} \quad (14)$$

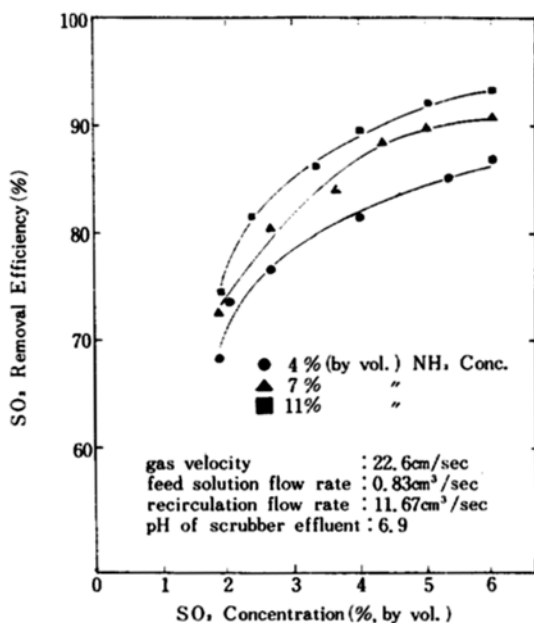


Fig. 5. The Effect of SO_2 Concentration in the Gas-phase on SO_2 Removal Efficiency.

(2) Effect of Concentrations of SO_2 and NH_3 and pH of scrubber effluent on SO_2 removal efficiency

As shown in Fig. 5, the SO_2 removal efficiency increased with the SO_2 concentration in the gas-phase. That was due to increasing driving force in the interface between gas and liquid in case of increasing SO_2 concentration in the gas phase. Thus the more SO_2 was absorbed into the ammonia solution.

Moreover, in such case, temperature of scrubber effluent rised because of the exothermic reaction in the absorption column, and that accelerated the reaction rate in the liquid-phase and increased the diffusivity. From Fig. 6, the SO_2 removal efficiency also increased with the NH_3 concentration in the feed solution, and this was due to increasing NH_4^+ concentration in the solution, which accelerated the reaction with SO_2 in the gas-phase. Therefore, more ammount of ammonium sulfite and ammonium bisulfite were produced.

In such case the higher NH_3 concentration in the feed solution, the more absorptive capacity of the solution in the absorption column.

According to Hikita [8], the reaction factor increased with the concentration of ammonia solution. It means that the SO_2 removal efficiency was improved in the case of higher concentration of ammonia solution. Moreover, increases in the effective interfacial area in packed column contribute to higher SO_2 removal efficiency in the case of higher concentration of ammonia solution. According to Puranik [9] et al., all effective interfacial area consisted of dynamic area and static area.

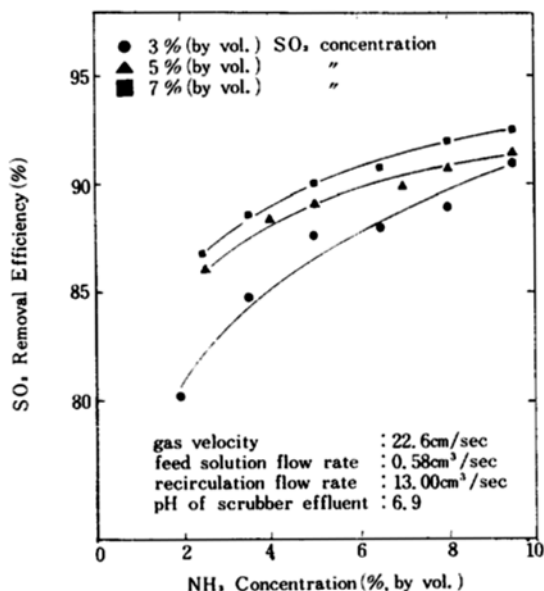


Fig. 6. The Effect of NH_3 Concentration in the Feed Solution on SO_2 Removal Efficiency.

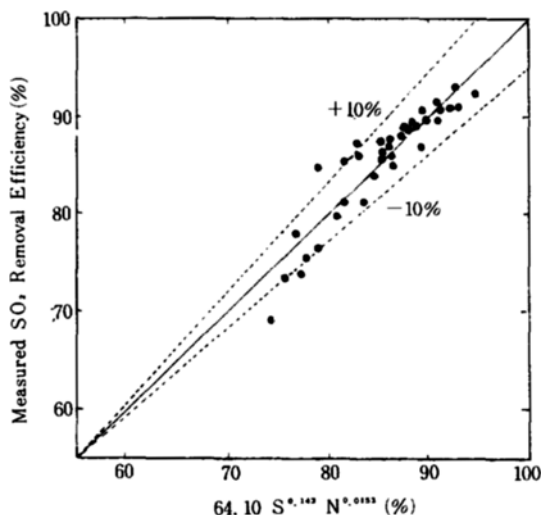


Fig. 7. Correlation of SO₂ Removal Efficiency with respect to Concentrations of SO₂ in the Gas-phase and NH₃ in the Feed Solution.

But in the physical absorption, effective interfacial area was mainly dynamic area, because the semistagnant pockets tended to be saturated in short time and ineffective for mass transfer, and in the chemical absorption, when solute was absorbed in water or a infinitely dilute solution, the effective interfacial area would be the section of moving liquid and gas through packing materials in a packed column. As the concentration of the solvent was increased more, the semistagnant liquid would be as the effective interfacial area. Therefore higher concentration of the solvent contributed more to effective interfacial area. Though it is difficult to know the portion of static area, it may be part of effective interfacial area in higher solvent concentration. Fig. 7 shows the measured SO₂ removal efficiency and that from the following empirical correlation,

$$\text{EFF} = 64.10 S^{0.143} N^{0.0153} \quad (15)$$

From Eq. (15), it can be easily seen that the effect of SO₂ concentration in the gas-phase on SO₂ removal efficiency was higher than that of NH₃ concentration in the ammonia solution. Fig. 8 shows the variation of pH in scrubber effluent. In pH > 6.5, the effect of pH on SO₂ removal efficiency is better and pH of 6.9 is used for other experiment.

(3) Effect of Gas and Liquid Flow Rates on Gas Film Mass Transfer Coefficient

The mass transfer coefficients published in the literatures are difficult to compare one another because of the different experimental conditions, such as type of scrubbers, gas velocity, solution composition and concentration, and temperature. The ammonia solution

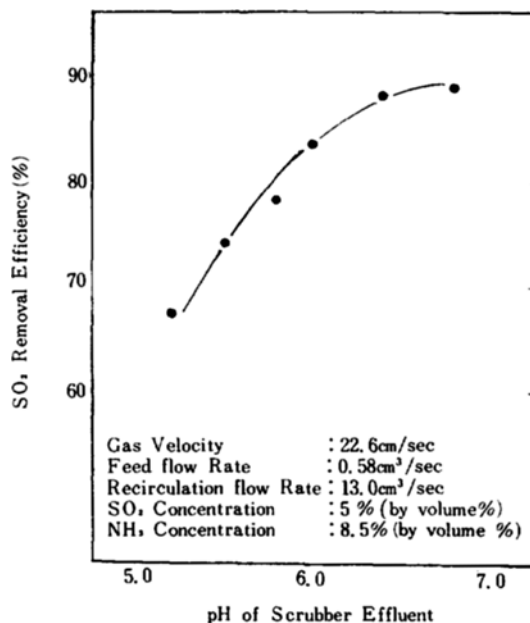


Fig. 8. The Effect of pH of Scrubber Effluent on SO₂ Removal Efficiency.

process for absorption of SO₂ from flue gases with formation of ammonium sulfite-bisulfite solution has long been used in a chemical technology. However, few correlations have been made of available data on the rate of mass transfer in the system [10]. Fig. 9 shows volumetric gas-phase mass transfer coefficient, $k_G a$,

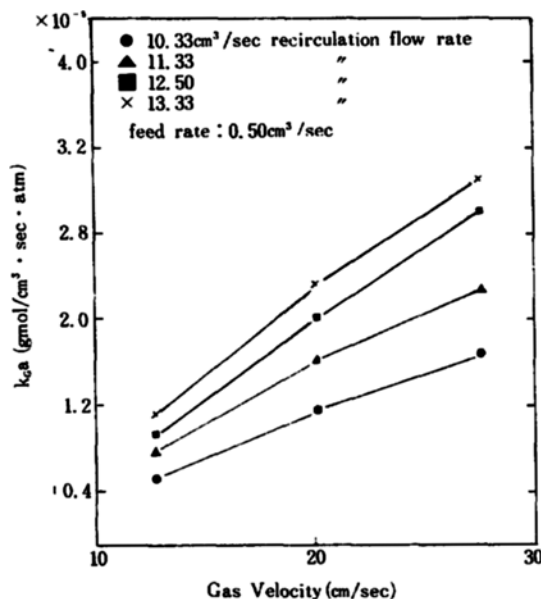


Fig. 9. The Effect of Gas Velocity on Volumetric Gas Phase Mass Transfer Coefficient, $k_G a$.

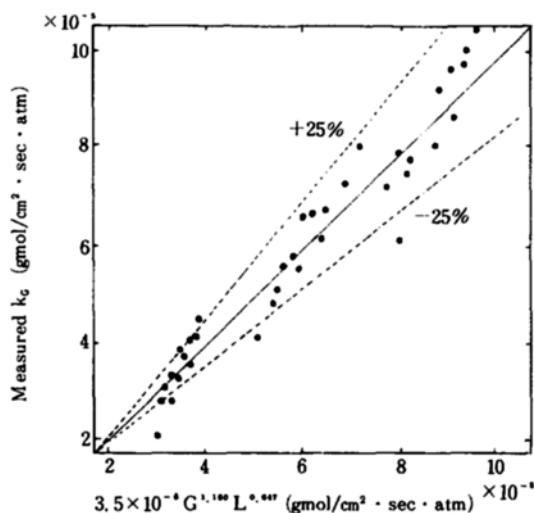


Fig. 10. Correlation of Gas Film Mass Transfer Coefficient with respect to Gas and Liquid Flow Rates.

with gas velocity. The $k_G a$ can be obtained by Eq. (13). As discussed in the section of IV-(1), the effect of gas velocity on the SO_2 removal efficiency was considerably small. That was, at constant feed solution and recirculation flow rates, the SO_2 removal efficiency at higher gas velocity was almost small as that at lower gas velocity. It means that the absorption rate of SO_2 into the ammonia solution at higher gas velocity was more than that at lower gas velocity. Therefore, volumetric gas-phase mass transfer coefficient, $k_G a$, increased with increasing gas velocity, and the following correlation was obtained.

$$k_G a = 7.61 \times 10^{-6} G^{1.26} F^{0.312} R^{1.50} \quad (16)$$

In Eq. (16), power of gas velocity was smaller than that of liquid flow rates. The dependence of the interfacial area on the liquid flow rate and size of packings was found to be as follows [6];

$$a = 1.474 L^{0.380} D^{-0.754} \quad (17)$$

The packed tower used above was 4''-OD methylmethacrylate cylinder packed with 1/2'', 3/8'', 1/4'' plastic Rischig rings in 80 cm packed height. In constant size of packings, effective interfacial area can be correlated only by liquid flow rate. The introduction of above correlation is to show the effect of gas film mass transfer coefficient without effective interfacial area on various flow rates.

Therefore, gas-film mass transfer coefficient, k_G , could be obtained substituting Eq. (17) to Eq. (16). The feed solution and the recirculation flow rates were replaced by the liquid flow rates so the following correlation of gas-film mass transfer coefficient with respect to gas and liquid flow rates was obtained;

$$k_G = 3.51 \times 10^{-6} G^{1.160} L^{0.647} \quad (18)$$

Fig. 10 shows the plot of measured and calculated gas-

film mass transfer coefficient from Eq. (18).

Comparing the power of the gas flow rate to that of liquid flow rate, the gas film resistance dominated in the system. If absorption of a gas in a liquid was followed by a rapid and irreversible chemical reaction, the effect of the liquid film could be minimized, and it might be possible to choose conditions that a true gas film mass transfer coefficient could be obtained [11].

CONCLUSIONS

1. The effect of gas velocity on the SO_2 removal efficiency was considerably smaller than that of the feed solution and the recirculation flow rates, and the following empirical correlation was obtained.

$$\text{EFF} = 33.52 G^{0.0552} F^{0.118} R^{0.772}$$

2. The relation of the SO_2 removal efficiency to concentrations of SO_2 in the gas phase and of NH_3 in the feed solution was expressed by the following empirical correlation.

$$\text{EFF} = 64.10 S^{0.143} N^{0.0153}$$

3. From the following empirical correlation, gas-film resistance dominated in this $\text{NH}_3\text{-H}_2\text{O-SO}_2$ system.

$$k_G = 3.51 \times 10^{-6} G^{1.160} L^{0.647}$$

NOMENCLATURE

A :	concentration of sulfate, moles of sulfate/100 moles of water
a :	interfacial area per unit packed column, cm^2/cm^3
C :	concentration of ammonia, moles of ammonia/100 moles of water
D_p :	(total surface area of Rasching ring/ π) $^{1/2}$, cm
EFF :	SO_2 removal efficiency ($= 1 - \frac{m_r}{m_b}$), %
F :	feed solution flow rate, $\text{cm}^3/\text{cm}^2 \cdot \text{sec}$
G :	superficial gas (air + SO_2) velocity, cm/sec ; molar flow rate of insoluble gas in Eq. (11), $\text{g mol}/\text{cm}^2 \cdot \text{sec}$
H :	packed height, cm
h :	distance from top of packing, cm
K :	equilibrium constant
K_1, K_2 :	rate constant, sec^{-1}
k_G :	gas-film mass transfer coefficient, $\text{g mol}/\text{cm}^2 \cdot \text{sec} \cdot \text{atm}$
$k_G a$:	volumetric gas-phase mass transfer coefficient, $\text{g mol}/\text{cm}^2 \cdot \text{sec} \cdot \text{atm}$
L :	liquid flow rate, $\text{cm}^3/\text{cm}^2 \cdot \text{sec}$
m_b, m_r :	mole fraction of SO_2 ; of bottom of packed column; of top of packed column
N :	concentration of ammonia, % (by volume)
P :	total pressure, atm