Simultaneous Removal of SO$_2$ and NO by Sodium Chlorite Solution in Wetted-Wall Column

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Abstract─The effect of feeding rate of NaClO$_2$ solution, inlet SO$_2$ and NO concentration, [NaClO$_2$]/[SO$_2$+NO] molar ratio (η), L/G ratio and, solution pH on the simultaneous removal of SO$_x$/NO$_x$ has been investigated in a wetted-wall column. Both SO$_x$ and NO$_x$ removal efficiencies are enhanced with the increasing feeding rate of NaClO$_2$ solution and attain a steady state. NO$_x$ removal efficiency increases with increasing SO$_2$ concentration, but SO$_x$ removal remains unaffected with increasing NO concentration. In an acidic medium, DeSO$_x$ and DeNO$_x$ efficiency increased with increasing [NaClO$_2$]/[SO$_2$+NO$_x$] molar ratio and attained a steady state. NO$_x$ removal starts only after the complete removal of SO$_x$. The excess of NaClO$_2$ does not enhance NO$_x$ removal efficiency. Solution pH does not affect the DeSO$_x$ and DeNO$_x$ efficiency. The maximum SO$_x$ and NO$_x$ removal efficiencies achieved at the typical operating conditions of commercialized FGD processes are about 100 and 67%, respectively.

Key words: NaClO$_2$, Wetted Wall Column, Removal Efficiency, DeSO$_x$, DeNO$_x$

INTRODUCTION

Sulfur oxides (SO$_x$) and nitrogen oxides (NO$_x$) are the major air pollutants which are emitted from stationary sources such as power plants, incinerators and combustors. The most effective technology for SO$_2$ removal is flue gas desulphurization (FGD). Commercial processes for the removal of SO$_2$ use limestone slurry as a scrubbing solution. These wet FGD processes have been widely accepted because of lower cost, simple operation and higher SO$_x$ removal efficiency compared to other processes [Cooper and Alley, 1994].

Technologies for the NO$_x$ removal can be divided into combustion control and post-combustion treatment. Combustion control aims at reducing the NO$_x$ formation during the combustion of fossil fuel. Post-combustion methods include a variety of techniques such as selective non-catalytic reduction (SNCR), selective catalytic reduction (SCR), thermal DeNO$_x$ and scrubbing etc. SNCR approaches require higher reaction temperature (about 900-1,000 °C) with an elaborate temperature control to avoid ammonia breakthrough or effective NO$_x$ emission control [Lyon, 1987]. Catalytic reduction methods can remove the NO$_x$ with an efficiency of 80 to 95%. Recent developments in SCR include the use of activated carbon and zeolites (CuZSM-5 and FeZSM-5) [Heck and Farrauto, 1995; Feng and Hall, 1996]. However, SCR processes require the higher operating cost and additional space. Catalytic poisoning due to SO$_2$ laden flue gas is another major drawback of SCR processes, which reduces the life of catalyst and makes the process inconsistent. Among these technologies, scrubbing methods are economically most competitive and have the advantage of controlling other acid gases and particulates at the same time [Yang et al., 1996].

In spite of successful commercial operation of individual desulfurization and denitrification processes, considerable attention has been focused on the simultaneous removal of SO$_2$ and NO$_x$ in a single reactor considering the capital investment, operating cost, and the space for equipment. The FGD process is being quite efficiently used in incinerators and boilers, so if minor adjustment in it may work for simultaneous removal of SO$_2$ and NO$_x$ then it will prove a more compact and cost effective technology for the future.

Interest has been focused on the additives to oxidize insoluble NO to soluble NO$_2$ which can be absorbed into alkaline solution. Various oxidants such as H$_2$O$_2$ [de Pavia and Kachan, 1998], KMnO$_4$ [Brogren et al., 1997; Chu et al., 2001], organic hydroperoxides [Perlmutter et al., 1993], peracids [Littlejohn and Chang, 1990], NaClO$_2$ [Brogren et al., 1998; Sada et al., 1978; Hsu et al., 1998], and ferrous-chelating agents [Shi et al., 1997; Harriott et al., 1993] have been investigated, and NaClO$_2$ has been found the most promising chemical for NO oxidation. Simultaneous removal of NO and SO$_2$ using NaClO$_2$ solution has also been reported by several researchers [Yang and Shaw, 1988, Adewuyi et al., 1999; Chien and Chu, 2000]. Most of the work done till now has concentrated more or less on batchwise experimentation. Combined DeSO$_x$ and DeNO$_x$ results from the continuous operation of gas-liquid contactors may be helpful for successful application of wet DeNO$_x$ process combined with wet FGD processes. Thus, the present study is aimed at investigating the effect of various operating variables on the simultaneous removal of SO$_2$ and NO from flue gas in the wetted wall column using sodium chlorite solution.

EXPERIMENTAL

1. Experimental Apparatus

A schematic diagram of the experimental system is shown in Fig. 1. This system consists of a simulated flue gas supply unit, co-current wetted wall column, gas analyzing system, and data acquisition system. The solution pH was continuously controlled by pH controller (KFC-MK-250) interfaced with personal computer using NaOH

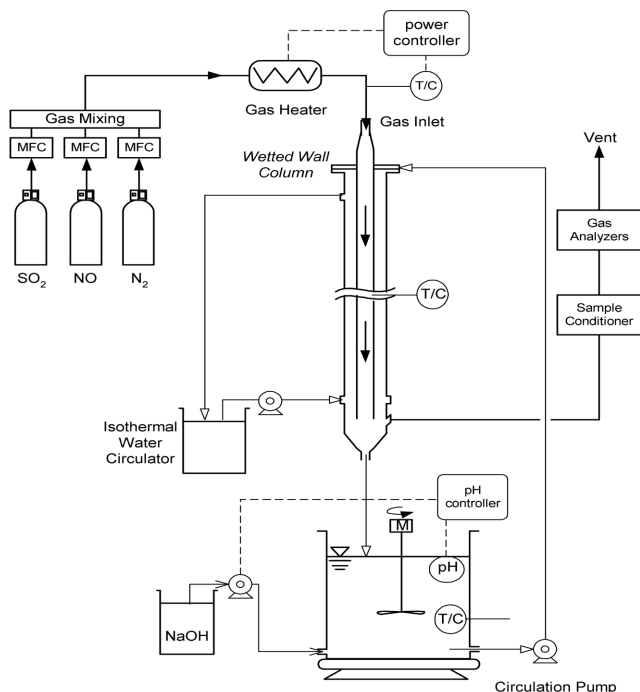[†]To whom correspondence should be addressed.
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Fig. 1. Schematic diagram of experimental system.

solution. The simulated flue gas was obtained by controlled mixing of SO_2 (Anjun Gas, purity 99%), NO (Matheson, purity 99.5%), N_2 and O_2 using mass flow controllers (MFC, Sierra Ins.). Temperature of the gas mixture was controlled by electric heater. The wetted wall column is made of five Pyrex tubes (each having ID= 0.015 m, Height=1.0 m). A water jacket, which is made of acryl tube (ID=0.050 m), was mounted at the outer surface of the Pyrex tube.

2. Experimental Procedure

A scrubbing solution containing 0.1 M $NaClO_2$ was introduced to the top of the reactor with a circulating pump (Fluid Metering Inc., Model QB). Temperature of wetted wall column was maintained at 30 °C by circulating the water from thermostat. After attaining stability of system, simulated flue gas was injected to the top of reactor column. Temperature of flue gas was maintained at 30 °C using the gas heater. Inlet and outlet concentration of SO_2 and NO_x were measured by SO_2 analyzer (Model 43C, Pulsed Fluorescent type, Thermo Environment Inc.) and NO_x analyzer (Model 42C,

Table 1. Experimental conditions for the wetted wall column system

Variables	Range*
Solution pH	2.0-6.0 (4.5)
Reaction temperature (°C)	30
SO_2 input concentration (ppm)	0-1800 (680)
NO input concentration (ppm)	0-860 (340)
$NaClO_2$ feeding rate (ml/min)	0-50 (20)
Gas flow rate (L/min)	45
Slurry flow rate (L/min)	0.15-0.65 (0.35)
Solid contents (wt%)	2.0

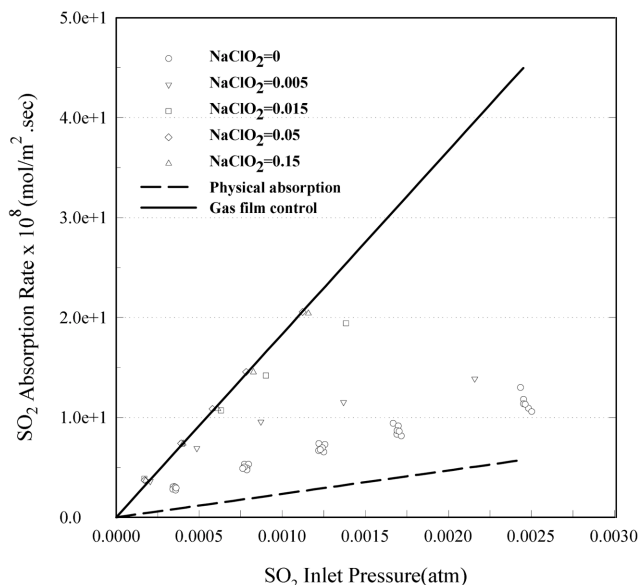*The value in the parenthesis is the base line condition.

Fig. 2. Effect of SO_2 inlet pressure on SO_2 absorption rate at different $NaClO_2$ concentrations.

Chemiluminiscent Type, Thermo Environment Inc.), respectively. The solution pH was controlled by addition of 0.1 M NaOH solution using auto pH controller. The detailed experimental conditions are summarized in Table 1.

RESULTS AND DISCUSSION

The effect of SO_2 concentration on SO_2 absorption rate using $NaClO_2$ solution is shown in Fig. 2 along with the theoretical absorption lines. Gas film control line without liquid film resistance and physical absorption line in Fig. 2 can be described by Eqs. (1) and (2), respectively [Lancia et al., 1997].

$$r_{SO_2} = k_g a \cdot P_{SO_2} \tag{1}$$

$$r_{SO_2} = \left(\frac{1}{k_g a} + \frac{H_{SO_2}}{\Phi k_l^0 a} \right)^{-1} (p_{(SO_2)av} - H_{(SO_2)} C_{(SO_2)aq}) \tag{2}$$

Where all the terms have the same significance as discussed earlier [Lancia et al., 1997]. Fig. 2 shows that SO_2 absorption rate increases linearly with increasing the SO_2 partial pressure and $NaClO_2$ concentration. It is also noteworthy that the rate determining step is shifted to the gas film control region from the physical absorption region as the concentration of $NaClO_2$ increases. This means that SO_2 species at the gas-liquid interface is rapidly depleted by the following chemical reactions with $NaClO_2$.

$$2SO_2 + NaClO_2 + 2H_2O \rightarrow NaCl + 2H_2SO_4 \tag{3}$$

In the acidic solution formed by SO_2 absorption, $NaClO_2$ also decomposes to produce ClO_2 as follows [Kieffer and Gordon, 1968; Deshwal et al., 2003]:

$$5ClO_2^- + 4H^+ \rightarrow 4ClO_2 + Cl^- + 2H_2O \tag{4}$$
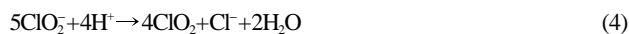
Since chlorine dioxide is also a very strong oxidant, and fairly soluble in water, it can also oxidize SO_2 gas yielding H_2SO_4 as below:
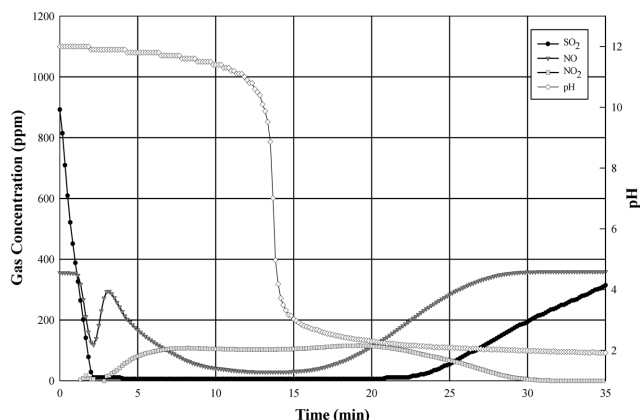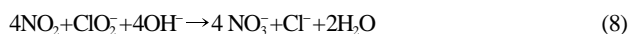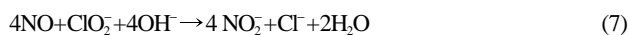
Fig. 3. Variation of pH, NO, NO$_2$ and SO$_2$ concentration as a function of reaction time in wetted wall column (NaClO$_2$=0.01 M, input NO=350 ppm, input SO$_2$=1,200 ppm, T=30 °C).

$$5SO_2+2ClO_2^-+6H_2O \rightarrow 5H_2SO_4+2HCl \tag{5}$$

The variation of NO, NO$_2$, SO$_2$, and solution pH as a function of reaction time in the wetted wall column is demonstrated in Fig. 3. The outlet concentration of SO$_2$ decreased rapidly to zero within 3 min and 100% removal of SO$_2$ was maintained until NaClO$_2$ was consumed completely. The outlet concentration of NO also showed a similar trend as that of SO$_2$. Sodium chlorite can oxidize NO into NO$_2$, NO$_2^-$ or NO$_3^-$ species as follows:

$$NO+ClO_2^- \rightarrow 2NO_2+Cl^- \tag{6}$$

$$4NO+ClO_2^-+4OH^- \rightarrow 4 NO_2^-+Cl^-+2H_2O \tag{7}$$

$$4NO_2+ClO_2^-+4OH^- \rightarrow 4 NO_3^-+Cl^-+2H_2O \tag{8}$$

Which one of the above is the dominating reaction depends on the pH of solution and the chlorite concentration. In an acidic medium [Brogen et al., 1998], NaClO$_2$ is a powerful oxidant and converts only NO into NO$_2$ as shown in Eq. (6); however, in alkaline solution it behaves as good absorbing medium leading to formation of NO$_3^-$. The pH of the reaction solution decreased from 12 to 2 in the course of reaction due to absorption of SO$_2$ and NO. In an acidic condition, NaClO$_2$ decomposes into ClO$_2$ gas which can further oxidize NO as follows:

$$5NO+3ClO_2+4H_2O \rightarrow 5HNO_3+3HCl \tag{8}$$

The effect of feeding rate of NaClO$_2$ solution on SO$_2$/NO removal efficiency at pH of 4.5 with initial SO$_2$ and NO concentration of 640 and 850 ppm, respectively, is presented in Fig. 4. In the absence of NaClO$_2$, removal efficiency of SO$_2$ is around 72% and there is no sign of NO$_x$ removal. It is certainly due to the higher solubility of SO$_2$ compared to that of NO. Small addition of NaClO$_2$ did not affect the NO$_x$ removal efficiency, whereas DeSO$_x$ efficiency increased continuously. NO removal starts only after achieving 100% SO$_2$ removal efficiency. Further increase in the feeding rate of NaClO$_2$ solution enhanced the removal efficiency of NO$_x$. The maximum DeNO$_x$ efficiency achieved was approx. 70%. Though NO was completely oxidized to NO$_2$ but complete absorption of NO$_2$ has not been achieved. It is because of a sharp decrease in pH of solution due to absorption of SO$_2$ and NO, which decreased the absorbing
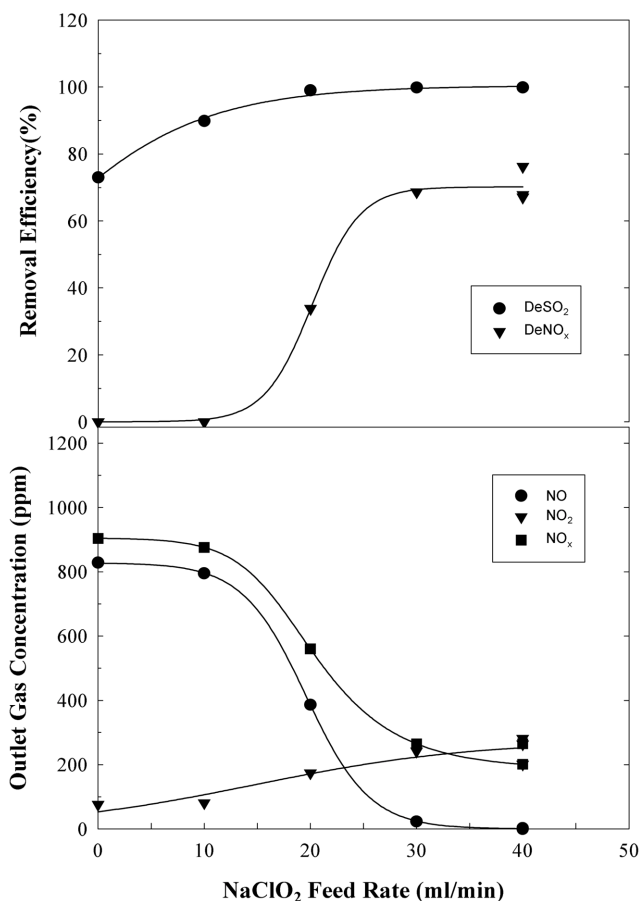
Fig. 4. Effect of feeding rate of NaClO$_2$ solution on SO$_x$/NO$_x$ removal efficiency at pH of 4.5, input SO$_2$ and NO concentration of 640 and 850 ppm, respectively.

capability of NaClO$_2$ [Brogen et al., 1998]. It confirms that the oxidation rate of SO$_2$ is faster than that of NO in acidic medium, and that it is inexpedient to use NaClO$_2$ solution for scrubbing flue gas having very high content of SO$_2$ compared to NO.

The effect of SO$_2$ concentration on SO$_2$/NO removal efficiency and outlet concentration of NO, NO$_2$, and SO$_2$ at pH of 4.5, NaClO$_2$ feeding rate of 40 ml/min and input NO concentration of 340 ppm is shown in Fig. 5. SO$_2$ removal efficiency showed a constant value of about 100% and NO$_x$ removal efficiency increased from 52 to 65% on increasing inlet SO$_2$ concentration from 380 to 1,800 ppm. As shown in Fig. 5, NO output concentration remained almost zero, implying that the complete oxidation of NO occurs on the addition of 40 ml/min NaClO$_2$ solution. Sada et al. [1978a] reported that the presence of SO$_2$ during the absorption of NO in the NaClO$_2$ solution reduces the pH rapidly at the gas-liquid interface and low pH leads to the formation of ClO$_2$ gas by acidic decomposition of NaClO$_2$. Therefore, the complete removal of NO might be caused by ClO$_2$ gas collected in the solution as suggested in Eq. (8). As can be seen in Fig. 5, NO$_2$ concentration also decreases with increasing the SO$_2$ concentration, indicating the enhancement in NO$_2$ absorption rate. Increasing SO$_2$ concentration in the scrubbing solution enhances the concentration of HSO$_3^-$ and SO$_3^{-2}$ ions which are supposed to promote the NO$_2$ absorption rate [Shen and Rochelle, 1998; Littlejohn et al., 1993; Takeuchi et al., 1978a, b].
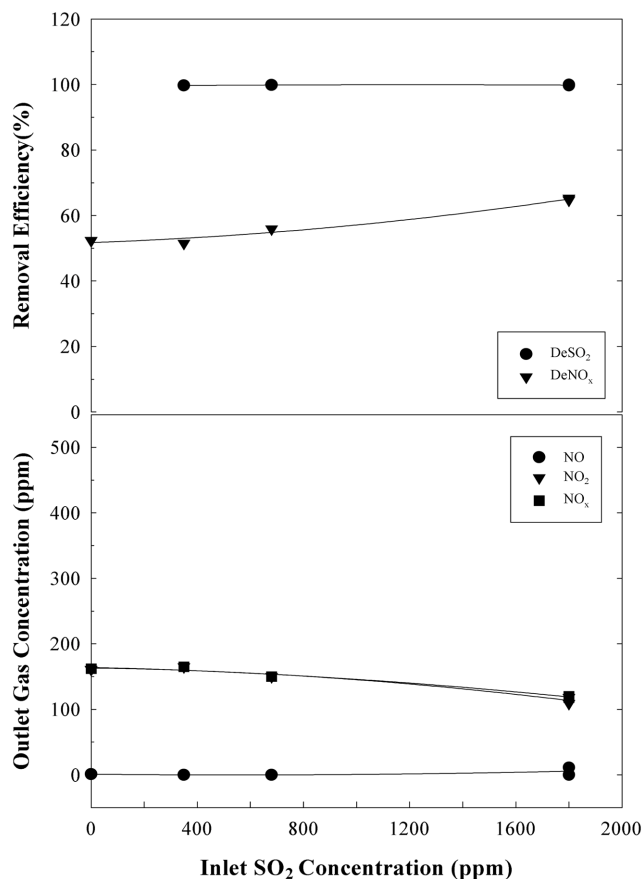
Fig. 5. Effect of inlet SO₂ concentration on SO$_x$/NO$_x$ removal efficiency at pH of 4.5, NaClO₂ feeding rate of 40 ml/min and input NO concentration of 340 ppm at 30 °C.
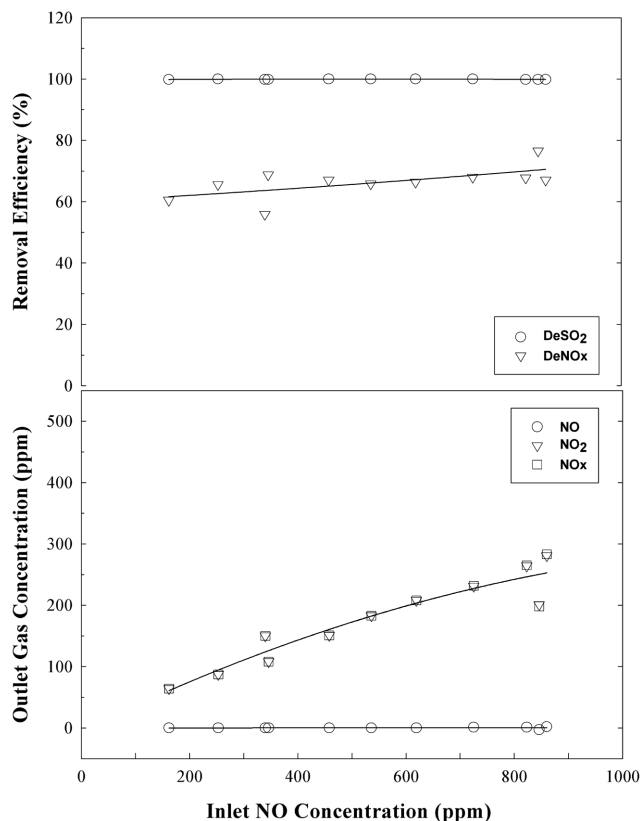

Fig. 6. Effect of inlet NO concentration on SO$_x$/NO$_x$ removal efficiency at pH of 4.5, NaClO₂ feeding rate of 40 ml/min and input SO₂ concentration of 680 ppm at 30 °C.
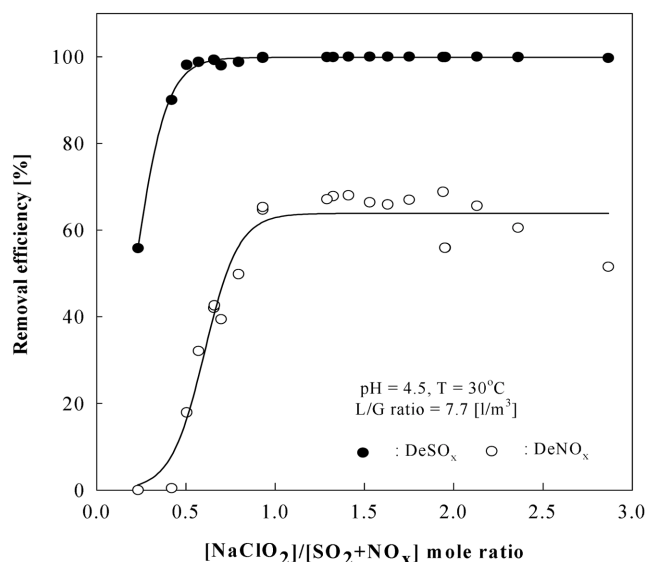

Fig. 7. Effect of [NaClO₂]/[SO₂+NO$_x$] mole ratio on the SO$_x$/NO$_x$ removal efficiency.

The effect of inlet NO concentration on SO$_2$/NO removal efficiency at pH of 4.5, temperature 30 °C, inlet SO$_2$ concentration of 680 ppm and NaClO$_2$ feeding rate of 40 ml/min is presented in Fig. 6. As can be seen, SO$_2$ removal efficiency is about 100% and NO$_x$ removal efficiency ranges from 65 to 70%. NO concentration was increased from 160 to 860 ppm, but there was occurred no significant increase in NO$_x$ removal efficiency. It is clear from results that though NO is completely oxidized into NO$_2$ by NaClO$_2$, further absorption of NO$_2$ into NO$_3^-$ is incomplete due to lower pH.

The effect of [NaClO$_2$]/[SO$_2$+NO] molar ratio (η) on the SO$_x$/NO$_x$ removal efficiency is reported in Fig. 7. SO$_2$ removal efficiency increases sharply with increasing the [NaClO$_2$]/[SO$_2$+NO] molar ratio, and 100% SO$_2$ removal is achieved at molar ratio of 0.5. Whereas, NO$_x$ removal efficiency started increasing only above η value of 0.5 and attained a steady state thereafter. No further improvement in NO removal has been noticed on increasing [NaClO$_2$]/[SO$_2$+NO] molar ratio beyond one.

Effects of L/G ratio on the SO$_x$/NO$_x$ removal efficiency are presented in Fig. 8. SO$_2$ removal efficiency shows a constant value of about 100% and NO$_x$ removal efficiency increases slightly with increasing the L/G ratio. The slight increase in the k$_g$a value with increasing the L/G ratio in a wetted wall column may be responsible for the increase in NO$_x$ removal efficiency.

The effect of solution pH on SO$_x$/NO$_x$ removal efficiency at two

different [NaClO$_2$]/[SO$_2$+NO] molar ratios (i.e., η=0.66 and 0.93) with the NaClO$_2$ feeding rate of 40 ml/min and initial SO$_2$ and NO gas concentration of 1,800 and 340 ppm, respectively, is shown in Fig. 9. As can be seen in this figure, SO$_2$ and NO$_x$ removal efficiency remained unaffected by the change of solution pH in the acidic me-
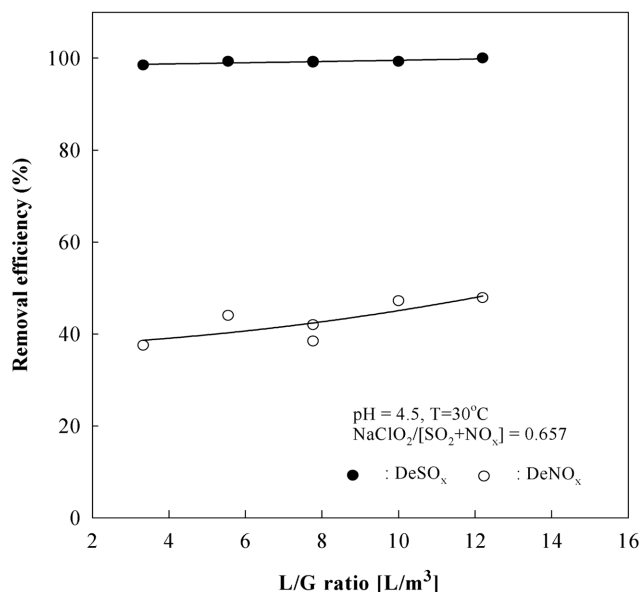
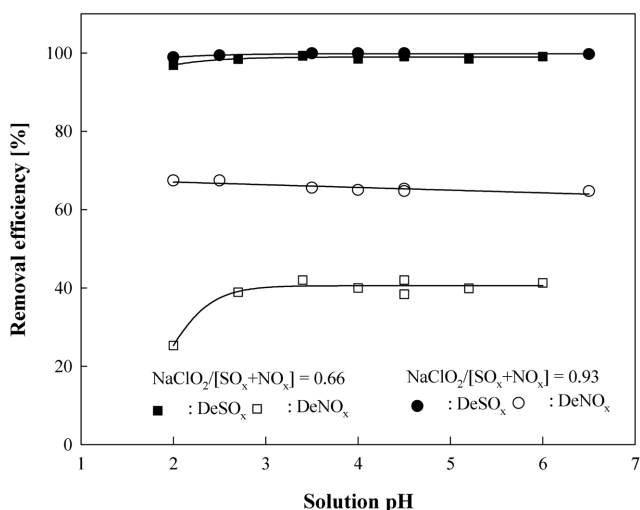**Fig. 8. Effect of L/G ratio on the SO$_x$/NO$_x$ removal efficiency.**

Fig. 9. Effect of solution pH on the SO$_x$/NO$_x$ removal efficiency at two different [NaClO$_2$]/[SO$_2$+NO] molar ratios.

dium.

CONCLUSIONS

A study on the simultaneous removal of SO$_2$ and NO$_x$ using Na ClO$_2$ solution has been carried out in a wetted wall column. Absorption of SO$_2$ is mainly advanced at a lower value of [NaClO$_2$]/ [SO$_2$+NO] molar ratio because the absorption rate of SO$_2$ is faster than that of NO$_x$. Excess of NaClO$_2$ solution does not enhance the SO$_2$/NO$_x$ removal efficiency in acidic medium, because the NO is completely oxidized to NO$_2$ above the [NaClO$_2$]/[SO$_2$+NO] mole ratio of 1.0. The maximum DeSO$_2$ and DeNO$_x$ efficiency achieved is 100% and 67%, respectively, in the wetted-wall column absorber. Keeping in mind the cost of NaClO$_2$ solution, simultaneous removal of SO$_x$/NO$_x$ using NaClO$_2$ solution seems to be more reasonable for the flue gas containing higher NO$_x$ and lower SO$_2$ concentra-

tion.

NOMENCLATURE

C_{SO_2} : concentration of SO$_2$ aqueous phase [mol·L^{-1}]
$C_{SO_2}^{i}$: concentration of SO$_2$ at the interface [mol·L^{-1}]
H_{SO_2} : Henry's constant [atm·L·mol^{-1}]
$k_g a$: volumetric gas-side mass transfer coefficient [mol·cm^{-3}· s^{-1}·atm^{-1}]
$k_l a$: liquid-phase mass transfer coefficient [s^{-1}]
p_{SO_2} : partial pressure of SO$_2$ in the bulk gas phase [atm]
$p_{(SO_2)av}$: logarithmic average of inlet and outlet SO$_2$ partial pressure [atm]
$p_{SO_2}^{i}$: partial pressure of SO$_2$ at the interface [atm]
$p_{(SO_2)in}$: inlet SO$_2$ partial pressure [atm]
$p_{(SO_2)out}$: outlet SO$_2$ partial pressure [atm]
$r_{(SO_2)}$: SO$_2$ absorption rate [mol·cm^{-3}·s^{-1}]
T   : operation temperature [K]

Greek Letter
Φ : enhancement factor

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