

Simultaneous Removal of SO₂ and NO by Sodium Chlorite Solution in Wetted-Wall Column

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Abstract—The effect of feeding rate of NaClO₂ solution, inlet SO₂ and NO concentration, [NaClO₂]/[SO₂+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 NaClO₂ solution and attain a steady state. NO_x removal efficiency increases with increasing SO₂ concentration, but SO_x removal remains unaffected with increasing NO concentration. In an acidic medium, DeSO_x and DeNO_x efficiency increased with increasing [NaClO₂]/[SO₂+NO] molar ratio and attained a steady state. NO_x removal starts only after the complete removal of SO_x. The excess of NaClO₂ 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: NaClO₂, 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 SO₂ removal is flue gas desulphurization (FGD). Commercial processes for the removal of SO₂ 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 SO₂ 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 SO₂ 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 SO₂ 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 NO₂ which can be absorbed into alkaline solution. Various oxidants such as H₂O₂ [de Pavia and Kachan, 1998], KMnO₄ [Brogren et al., 1997; Chu et al., 2001], organic hydroperoxides [Perlmutter et al., 1993], peracids [Littlejohn and Chang, 1990], NaClO₂ [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 NaClO₂ has been found the most promising chemical for NO oxidation. Simultaneous removal of NO and SO₂ using NaClO₂ 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 SO₂ 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

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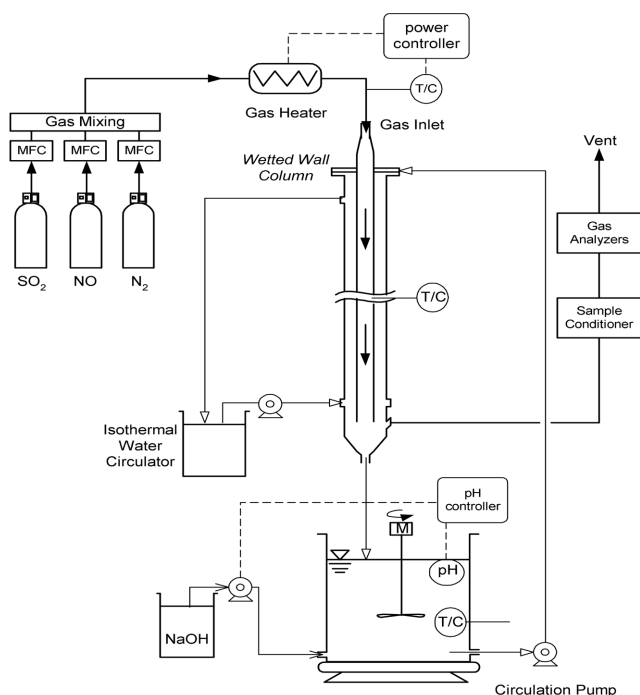


Fig. 1. Schematic diagram of experimental system.

solution. The simulated flue gas was obtained by controlled mixing of SO₂ (Anjun Gas, purity 99%), NO (Matheson, purity 99.5%), N₂ and O₂ 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 NaClO₂ 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 SO₂ and NO_x were measured by SO₂ 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.

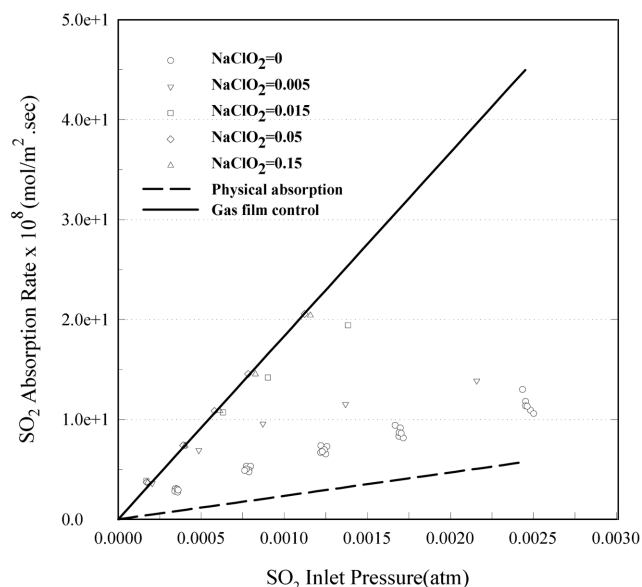


Fig. 2. Effect of SO₂ inlet pressure on SO₂ absorption rate at different NaClO₂ concentrations.

Chemiluminescent 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 SO₂ concentration on SO₂ absorption rate using NaClO₂ 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].

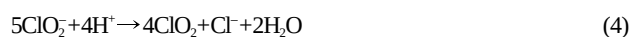
$$r_{\text{SO}_2} = k_g a \cdot P_{\text{SO}_2} \quad (1)$$

$$r_{\text{SO}_2} = \left(\frac{1}{k_{g,a}} + \frac{H_{\text{SO}_2}}{\phi k_{l,a}^0} \right)^{-1} (p_{(\text{SO}_2)\text{av}} - H_{(\text{SO}_2)} C_{(\text{SO}_2)\text{aq}}) \quad (2)$$

Where all the terms have the same significance as discussed earlier [Lancia et al., 1997]. Fig. 2 shows that SO₂ absorption rate increases linearly with increasing the SO₂ partial pressure and NaClO₂ 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 NaClO₂ increases. This means that SO₂ species at the gas-liquid interface is rapidly depleted by the following chemical reactions with NaClO₂.



In the acidic solution formed by SO₂ absorption, NaClO₂ also decomposes to produce ClO₂ as follows [Kieffer and Gordon, 1968; Deshwal et al., 2003]:



Since chlorine dioxide is also a very strong oxidant, and fairly soluble in water, it can also oxidize SO₂ gas yielding H₂SO₄ as below:

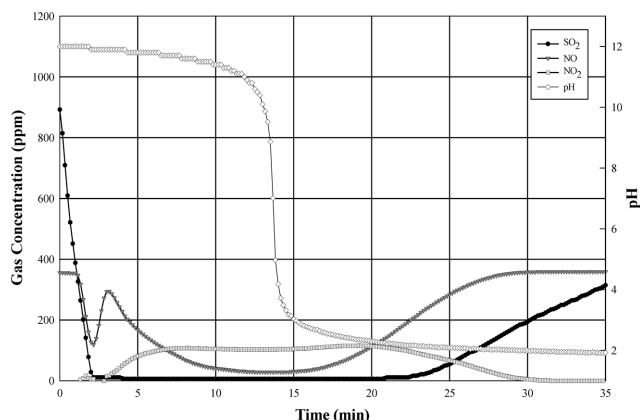
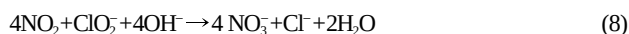
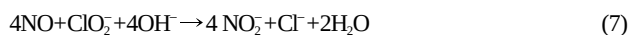


Fig. 3. Variation of pH, NO, NO₂ and SO₂ concentration as a function of reaction time in wetted wall column (NaClO₂=0.01 M, input NO=350 ppm, input SO₂=1,200 ppm, T=30 °C).



The variation of NO, NO₂, SO₂, and solution pH as a function of reaction time in the wetted wall column is demonstrated in Fig. 3. The outlet concentration of SO₂ decreased rapidly to zero within 3 min and 100% removal of SO₂ was maintained until NaClO₂ was consumed completely. The outlet concentration of NO also showed a similar trend as that of SO₂. Sodium chlorite can oxidize NO into NO₂, NO₂ or NO₃ species as follows:



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], NaClO₂ is a powerful oxidant and converts only NO into NO₂ as shown in Eq. (6); however, in alkaline solution it behaves as good absorbing medium leading to formation of NO₃⁻. The pH of the reaction solution decreased from 12 to 2 in the course of reaction due to absorption of SO₂ and NO. In an acidic condition, NaClO₂ decomposes into ClO₂ gas which can further oxidize NO as follows:



The effect of feeding rate of NaClO₂ solution on SO₂/NO removal efficiency at pH of 4.5 with initial SO₂ and NO concentration of 640 and 850 ppm, respectively, is presented in Fig. 4. In the absence of NaClO₂, removal efficiency of SO₂ is around 72% and there is no sign of NO_x removal. It is certainly due to the higher solubility of SO₂ compared to that of NO. Small addition of NaClO₂ did not affect the NO_x removal efficiency, whereas DeSO_x efficiency increased continuously. NO removal starts only after achieving 100% SO₂ removal efficiency. Further increase in the feeding rate of NaClO₂ solution enhanced the removal efficiency of NO_x. The maximum DeNO_x efficiency achieved was approx. 70%. Though NO was completely oxidized to NO₂ but complete absorption of NO₂ has not been achieved. It is because of a sharp decrease in pH of solution due to absorption of SO₂ and NO, which decreased the absorbing

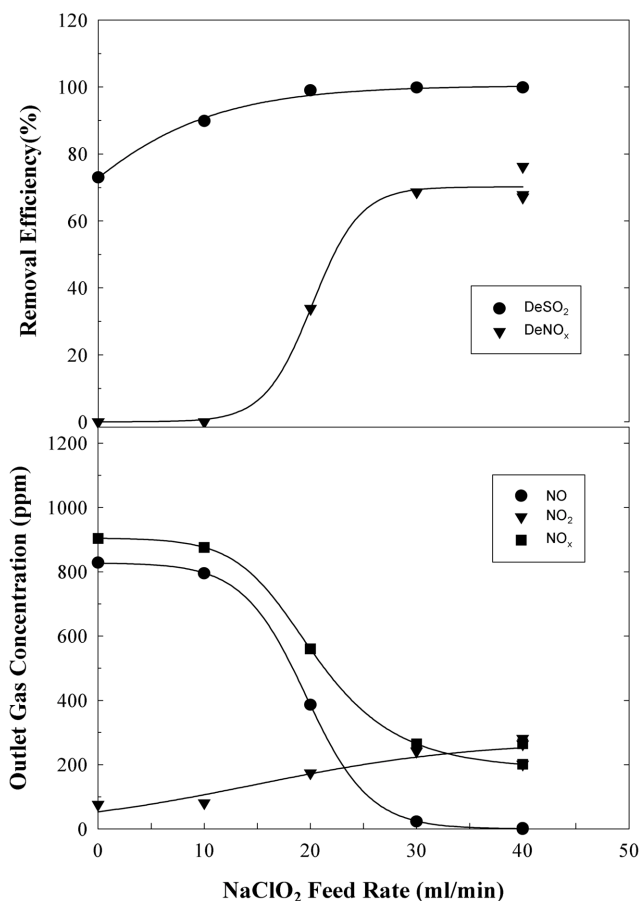


Fig. 4. Effect of feeding rate of NaClO₂ solution on SO_x/NO_x removal efficiency at pH of 4.5, input SO₂ and NO concentration of 640 and 850 ppm, respectively.

capability of NaClO₂ [Brogen et al., 1998]. It confirms that the oxidation rate of SO₂ is faster than that of NO in acidic medium, and that it is inexpedient to use NaClO₂ solution for scrubbing flue gas having very high content of SO₂ compared to NO.

The effect of SO₂ concentration on SO₂/NO removal efficiency and outlet concentration of NO, NO₂, and SO₂ at pH of 4.5, NaClO₂ feeding rate of 40 ml/min and input NO concentration of 340 ppm is shown in Fig. 5. SO₂ removal efficiency showed a constant value of about 100% and NO_x removal efficiency increased from 52 to 65% on increasing inlet SO₂ 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 NaClO₂ solution. Sada et al. [1978a] reported that the presence of SO₂ during the absorption of NO in the NaClO₂ solution reduces the pH rapidly at the gas-liquid interface and low pH leads to the formation of ClO₂ gas by acidic decomposition of NaClO₂. Therefore, the complete removal of NO might be caused by ClO₂ gas collected in the solution as suggested in Eq. (8). As can be seen in Fig. 5, NO₂ concentration also decreases with increasing the SO₂ concentration, indicating the enhancement in NO₂ absorption rate. Increasing SO₂ concentration in the scrubbing solution enhances the concentration of HSO₃⁻ and SO₃²⁻ ions which are supposed to promote the NO₂ absorption rate [Shen and Rochelle, 1998; Littlejohn et al., 1993; Takeuchi et al., 1978a, b].

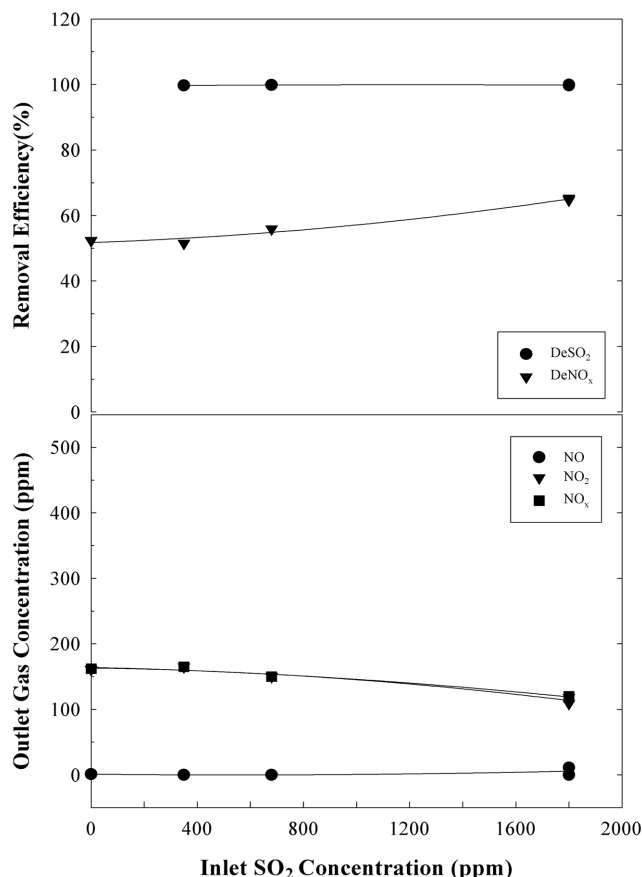


Fig. 5. Effect of inlet SO₂ concentration on SO_x/NO_x removal efficiency at pH of 4.5, NaClO₂ feeding rate of 40 ml/min and input NO concentration of 340 ppm at 30 °C.

The effect of inlet NO concentration on SO₂/NO removal efficiency at pH of 4.5, temperature 30 °C, inlet SO₂ concentration of 680 ppm and NaClO₂ feeding rate of 40 ml/min is presented in Fig. 6. As can be seen, SO₂ 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 NO₂ by NaClO₂, further absorption of NO₂ into NO₃⁻ is incomplete due to lower pH.

The effect of [NaClO₂]/[SO₂+NO] molar ratio (η) on the SO_x/NO_x removal efficiency is reported in Fig. 7. SO₂ removal efficiency increases sharply with increasing the [NaClO₂]/[SO₂+NO] molar ratio, and 100% SO₂ 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 [NaClO₂]/[SO₂+NO] molar ratio beyond one.

Effects of L/G ratio on the SO_x/NO_x removal efficiency are presented in Fig. 8. SO₂ 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_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

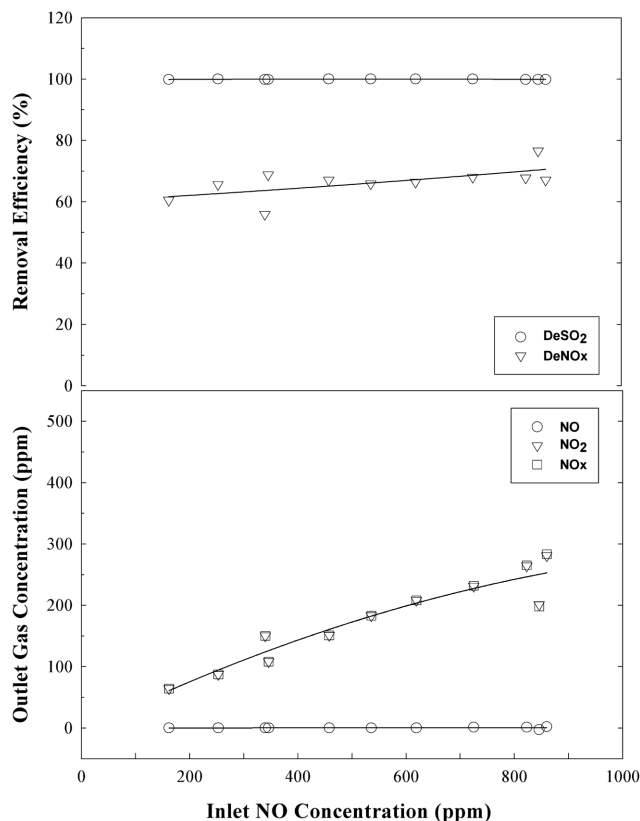


Fig. 6. Effect of inlet NO concentration on SO_x/NO_x removal efficiency at pH of 4.5, NaClO₂ feeding rate of 40 ml/min and input SO₂ concentration of 680 ppm at 30 °C.

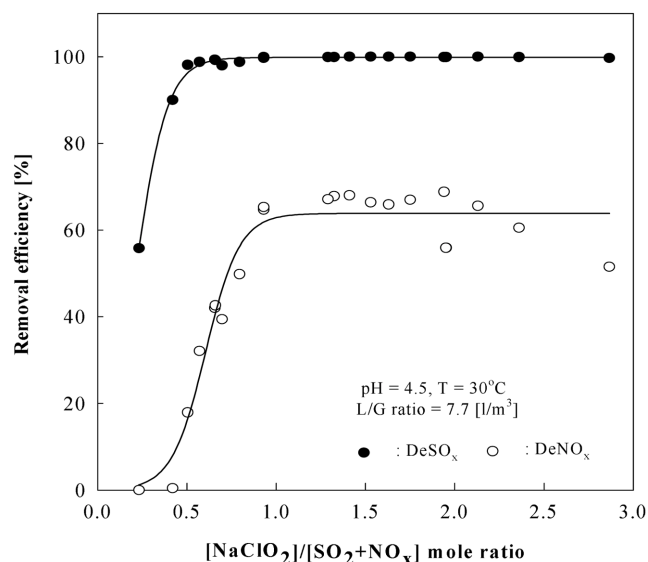


Fig. 7. Effect of [NaClO₂]/[SO₂+NO_x] mole ratio on the SO_x/NO_x removal efficiency.

different [NaClO₂]/[SO₂+NO] molar ratios (i.e., η =0.66 and 0.93) with the NaClO₂ feeding rate of 40 ml/min and initial SO₂ and NO gas concentration of 1,800 and 340 ppm, respectively, is shown in Fig. 9. As can be seen in this figure, SO₂ and NO_x removal efficiency remained unaffected by the change of solution pH in the acidic me-

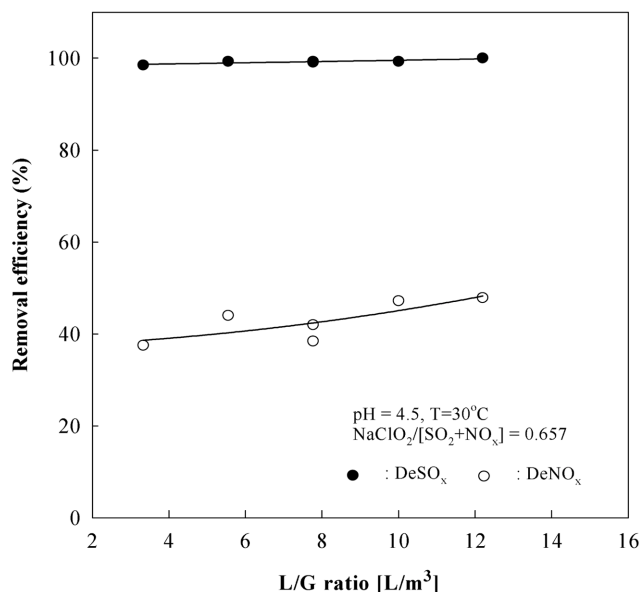


Fig. 8. Effect of L/G ratio on the SO_x/NO_x removal efficiency.

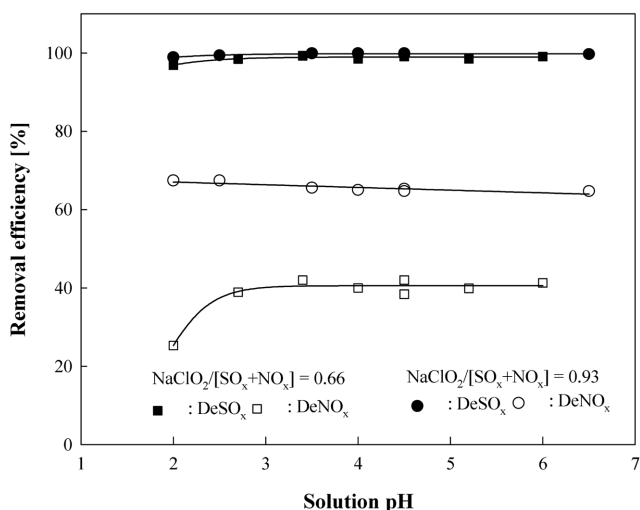


Fig. 9. Effect of solution pH on the SO_x/NO_x removal efficiency at two different [NaClO₂]/[SO₂+NO] molar ratios.

dium.

CONCLUSIONS

A study on the simultaneous removal of SO₂ and NO_x using NaClO₂ solution has been carried out in a wetted wall column. Absorption of SO₂ is mainly advanced at a lower value of [NaClO₂]/[SO₂+NO] molar ratio because the absorption rate of SO₂ is faster than that of NO_x. Excess of NaClO₂ solution does not enhance the SO₂/NO_x removal efficiency in acidic medium, because the NO is completely oxidized to NO₂ above the [NaClO₂]/[SO₂+NO] mole ratio of 1.0. The maximum DeSO₂ and DeNO_x efficiency achieved is 100% and 67%, respectively, in the wetted-wall column absorber. Keeping in mind the cost of NaClO₂ solution, simultaneous removal of SO_x/NO_x using NaClO₂ solution seems to be more reasonable for the flue gas containing higher NO_x and lower SO₂ concentra-

tion.

NOMENCLATURE

- C_{SO_2} : concentration of SO₂ aqueous phase [mol·L⁻¹]
 $C_{SO_2}^i$: concentration of SO₂ at the interface [mol·L⁻¹]
 H_{SO_2} : Henry's constant [atm·L·mol⁻¹]
 k_{ga} : volumetric gas-side mass transfer coefficient [mol·cm⁻³·s⁻¹·atm⁻¹]
 k_a : liquid-phase mass transfer coefficient [s⁻¹]
 p_{SO_2} : partial pressure of SO₂ in the bulk gas phase [atm]
 $p_{(SO_2)av}$: logarithmic average of inlet and outlet SO₂ partial pressure [atm]
 $p_{SO_2}^i$: partial pressure of SO₂ at the interface [atm]
 $p_{(SO_2)in}$: inlet SO₂ partial pressure [atm]
 $p_{(SO_2)out}$: outlet SO₂ partial pressure [atm]
 $r_{(SO_2)}$: SO₂ absorption rate [mol·cm⁻³·s⁻¹]
 T : operation temperature [K]

Greek Letter

- Φ : enhancement factor

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