Removal of SO_2 and NO from flue gas by wet scrubbing using an aqueous $NaClO_2$ solution

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Abstract

This study used a $NaClO_2$/NaOH solution as the additive/absorbent to determine the extent of NO_x removal in a wet scrubbing system. A combined SO_x/NO_x removal system was also tested. The experiments were performed in a bench-scale spraying sieve tray wet scrubber in a continuous mode. The operating variables included NO and SO_2 concentrations, L/G ratio, molar ratio, and initial pH.

The results of the individual $DeNO_x$ experiments show that the maximum $DeNO_x$ efficiencies ranged from 3.1 to 12.6%. The results of the combined $DeSO_x$/$DeNO_x$ experiments show that the maximum $DeNO_x$ and $DeSO_x$ efficiencies ranged from 36.6 to 71.9% and from 89.4 to 100.0%, respectively. The major parameters affecting NO_x removal efficiencies are the L/G ratio and the dosage of additive. The major parameter influencing $DeSO_x$ efficiencies is the L/G ratio. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Wet scrubber; Absorption; Sodium chlorite; Nitric oxide; Flue gas; Wet scrubbing

1. Introduction

Acid precipitation is a current air pollution problem caused mainly by SO_2 and NO_x. Conventionally, engineers use wet scrubbing SO_2; the most widely used process is flue gas desulfurization (FGD) process. Although the wet FGD system has experienced high SO_2 removal efficiencies, that is not so for NO_x. The reason for this process failure is that NO, which accounts for more than 90% of NO_x in the flue gas, is quite insoluble in water. Since the wet scrubbing system currently dominates the FGD market, a minor adjustment of the system may work for the combined SO_x/NO_x removal system and should be cost-effective. The $DeSO_x$ wet scrubbing SO_x removal system is not new to us. It has, however, many

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unknowns if it is to be used as a $DeNO_x$ system. In general, additives have to be added to the scrubbing system to convert relatively water insoluble NO to soluble NO_2 which can then be removed by alkaline absorbents.

Possible NO oxidants are ClO_2 or O_3 [1,2]. However, these additives are quite expensive as well as very dangerous in equipment operating in the gas phase. Therefore, chemical reagents added to the liquid phase have been widely used lately. There are many reagents such as $FeSO_4/H_2SO_4$, Fe(II) EDTA, $KMnO_4/NaOH$, $NaClO_2/NaOH$, $Na_2S/NaOH$, $Na_2S_2O_4/NaOH$, H_2O_2, Na_2SO_3, $FeSO_4/Na_2SO_3$, $CO(NH_2)_2$, NaOH, Na_2CO_3 and P_4 (yellow phosphorus) that have been tested for NO_x absorption [3–6]. Of this group, $NaClO_2$ was the most effective reagent [7–15].

The absorption of NO_x in $NaClO_2$ solution was studied by Teramoto et al. [7] and Sada et al. [8–10] in the late seventies. Teramoto et al. investigated the effect of various operating conditions on the absorption rates in mixed aqueous solutions of $NaClO_2$ and NaOH, using a semi-batch agitated vessel with a flat gas–liquid interface. They found that the absorption of NO proceeded in the region of the fast pseudo *m*th order reaction and the absorption rate was not affected by liquid-phase mass transfer coefficient. The NO concentration dependence of the absorption rate was more pronounced in the higher concentration range than that in the lower concentration range. The absorption rate increased greatly with $NaClO_2$. However, the absorption rate decreased markedly with an increase in NaOH. The effect of temperature on the absorption rate was found to be much greater in the lower concentration range on NO.

Sada et al. [8] also performed a series of kinetic studies using $NaClO_2$ as the additive in a stirred tank absorber. The concentration of NO in the gas stream ranged from 0.8 to 15%. The rate of reaction was found to be second order in NO and first order in $NaClO_2$. They also did some work on the absorption of dilute NO concentrations (<1%) with the same $NaClO_2$ concentrations as above. The results showed that the order of reaction in NO varied from 2 to 1 because of the lower interfacial concentration of NO [9]. In both cases, they claimed that the oxidation power of $NaClO_2$ increased with a decrease in pH value of the solution. However, the reaction product, NO_2, may desorb from the solution in the case with less OH^-. Therefore, the addition of OH^- to the solution is required in order to fix NO_2 as NO_3^-. That suggested that the reaction proceeds as follows:

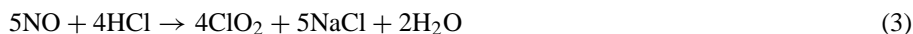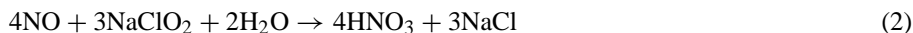$$4NO + 3ClO_2^- + 4OH^- \rightarrow 4NO_3^- + 3Cl^- + 2H_2O \tag{1}$$

In addition to the above kinetic studies, some researchers published their performance investigations on the absorption of NO_x. The experimental equipment, operating conditions and results of these studies [11–15] are summarized in Table 1. Chan [11] found that the liquid and gas flow rates had little effect on NO_x removal, while increasing liquid chlorite concentrations enhanced NO_x absorption. Absorption of NO_x tended to be totally gas-film controlled at all NO_x input levels. The experimental results of Yang and co-workers [12,13] showed that NO can be quantitatively oxidized by $NaClO_2$ in an aqueous solution. During scrubbing, NO was oxidized to NO_3^- and ClO_2^- was converted to Cl^-. Due to the production of HNO_3, the pH value decreased sharply from 10 to 3 within minutes of operation. Low concentrations of NaOH increased the effectiveness of NO absorption in the $NaClO_2$ aqueous scrubbing solution by 7%, while higher NaOH concentrations decreased

Table 1
Experimental setup, operating conditions and results of related investigations

Reference	Reactor type	[NaClO$_2$] (M); [NaOH] (M)	p_{NO_x} (ppm)	pH	Gas–liquid contact time (s)	NO$_x$ removal efficiency (%)	Temperature (°C)
[11]	Packed	0.05–0.67; –	200–900	–	9–18.5	<70	Room temperature
[12]	Bubble	0.008–0.08; –	2000	10–14	60	<100	Room temperature
[13]	Spray packed	0.037–0.15; 0.008–0.08	300–2000	6.5–12.9	–	<95	Room temperature
[14]	Packed	0–0.6; –	290	8–12	11.8	51–84	Room temperature
[15]	Packed	0.05–0.2; 0–1.0	200–1000	4.5–9.5	1.1	15.9–61.5	Room temperature
This work	Sieve tray	0.0008–0.0035; –	200–800	4–6	1	36.6–71.9[a]	25[a]

[a] For combined DeSO$_x$ and DeNO$_x$ tests.

or inhibited the absorption. They also suggested that the reactions proceed under acidic condition as follows:

$$4NO + 3NaClO_2 + 2H_2O \rightarrow 4HNO_3 + 3NaCl \tag{2}$$

$$5NO + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O \tag{3}$$

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

Brogren et al. [14] found that the pH value of the absorbing liquid had a significant impact on the absorption efficiency. The major fraction of the nitrogen oxides was absorbed via the hydrolysis of N_2O_3 and N_2O_4. Hsu et al. [15] performed the NO absorption study using a packed column. Their results indicated that the NO oxidation efficiency and removal efficiency could reach 98.8 and 61.5%, respectively.

So far, no one has attempted to determine the removal efficiencies of NO and SO_2 simultaneously by using a $NaClO_2$ solution in a spraying sieve tray wet scrubbing system. In this work, we used a low concentration $NaClO_2$ solution under acidic condition in a bench-scale spraying sieve tray column to investigate the effect of various parameters on SO_2 and NO_x absorption efficiency.

2. Experimental work

2.1. Experimental setup

The experimental system used in this work included a simulated flue gas production system, a scrubber, and a sampling and analysis system as shown in Fig. 1.

2.1.1. Flue gas simulation system

The flue gas simulation system was composed of an air compressor (Swan, 1/4 hp), a pure SO_2 cylinder (99%, San Fu), a pure NO cylinder (99.7%, IWATANI), a pure N_2 cylinder (99.9%, San Fu), four mass flow controllers (Teledyne Hasting-Raydist HFC-202), two plug-flow mixers (Omega, FMX-7103 & FMX-7106), and a custom-made electric temperature controlled heater. Flow rates of NO, SO_2 and N_2 were controlled by three mass flow controllers. Before adding compressed air, NO and SO_2 were diluted with N_2 in a plug flow mixer in order to avoid the production of a huge amount of NO_2. The diluted NO and SO_2 mixture was further diluted, in another plug flow mixer by adding compressed air, to the desired concentrations. The simulated flue gas was then introduced into the scrubber. All pipes, valves, regulators, and fittings were made up of SS-316 or Teflon.

2.1.2. Bench-scale scrubber

The scrubber used for preliminary tests was a custom-made Lucite spray sieve tray absorber. The length of the reaction zone from the point at gas inlet to the spray-nozzle is 20 cm. The internal diameter of the absorber is 3 cm. Two sieve trays, with a 7 cm span, were located at the center of the reaction zone. There were 19 holes, 4 mm in diameter each,
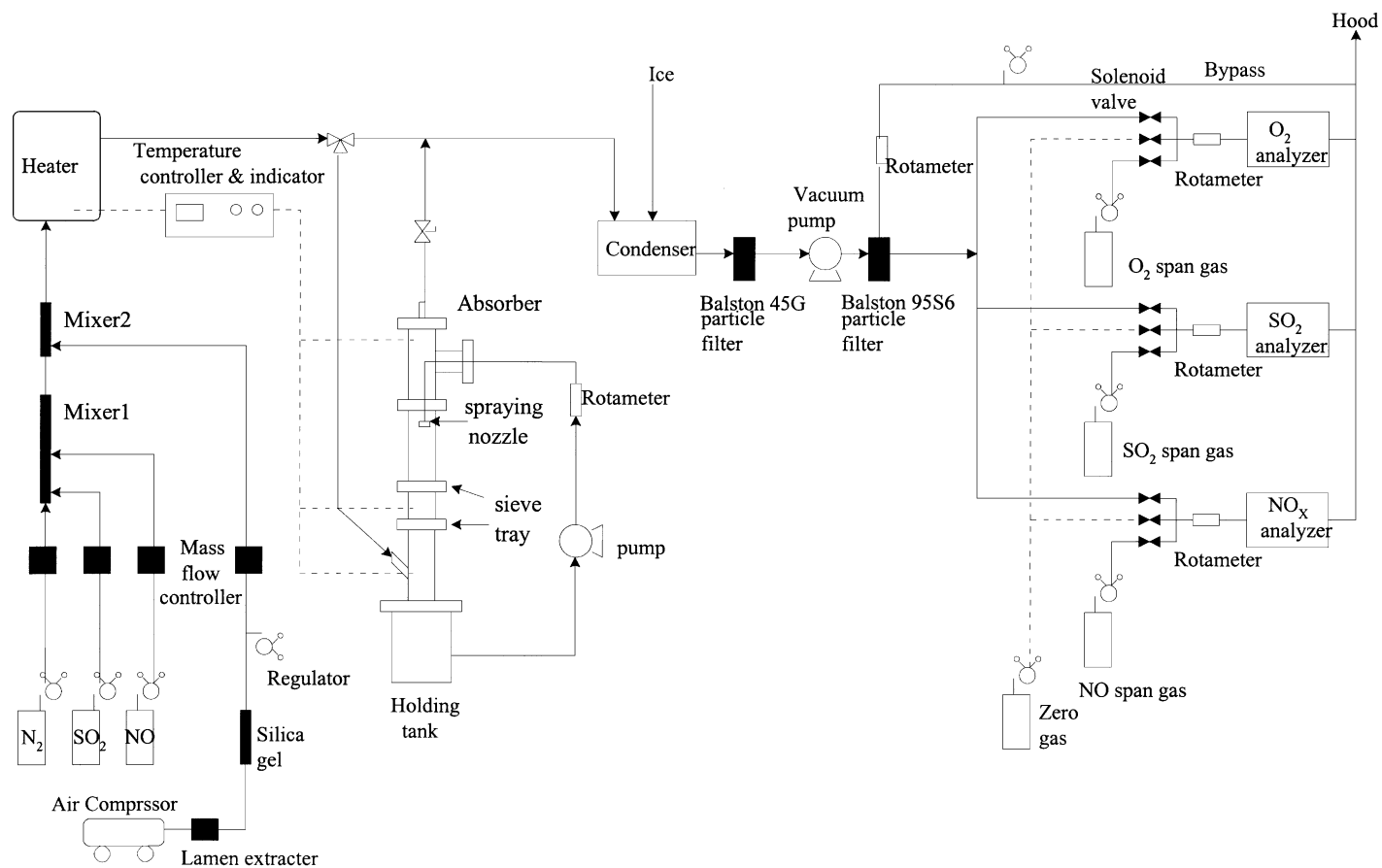
Fig. 1. Schematic diagram of a bench-scale wet scrubber for combined removal of SO_2 and NO from simulated flue gas.

on each tray. The ratio of total hole opening area to the cross-sectional area of the absorber for each tray was 32%. The size of scrubber used for simultaneous removal study was the same as that used in preliminary tests, but it was made up of SS-316. The spray-nozzle was a Unijet 1/4TT-SS+TG-SS0.4+W6051SS-100 (System Spraying Co.). The feed pump was a Micropump magnet pump (model 201). A rotameter was used to control the flow of the spray solution.

2.1.3. Sampling and analysis system

The scrubbed gas, which was saturated with water, might have contained particulates. Therefore, an ice box impingement condenser (Pyrex) was installed between the sampling port and various gas analyzers. This arrangement was designed to avoid damage to the vacuum pump and analyzers by the condensed water and particles and to assure the precision and accuracy of SO_2 analysis because SO_2 is very soluble in water. Four rotameters were installed before the O_2 analyzer (Signal Model 8000 magneto dynamic type), SO_2 analyzer (Milton Roy ZRF NDIR SO_2 analyzer), NO_x analyzer (Analysis Automation Limited Model 441 chemiluminescent type), and bypass exit, respectively.

The specific surface area of spray droplets was measured using a Malvern series 2600 laser analyzer.

2.2. Experimental procedures

Initially, we performed two sets of preliminary semi-batch tests at 65°C. The range of operating conditions is given in Tables 2 and 3. For the semi-batch studies, the simulated flue gas flowed continuously and the absorbing liquid was added batchwise.

For the continuous wet scrubbing $DeSO_x/DeNO_x$ studies, the range of operating conditions is listed in Tables 4 and 5. Both of gas flow and liquid flow were continuous and non-recirculated. The operating temperature in continuous studies was kept at room temperature. The calculated flue gas residence time of the flue gas between gas inlet and spraying nozzle was 1.0 s. For corresponding L/G ratio condition, the gas flow rate and liquid flow rate were kept constant and adjusted, respectively. The O_2 concentration of simulated flue gas was 6%. The initial pH value of the spray solution was adjusted to the desired value by adding H_2SO_4.

Table 2
Operating conditions of the NO_x removal efficiency in the first set of preliminary $DeNO_x$ tests[a]

Run no.	NO_x concentration (ppm)	O_2 concentration (%)	L/G ratio (l/m³)	$NaClO_2/NO$	NO_x removal efficiency (%)
P-A1	300	6	10	0.66	80.7
P-A2	800	2	10	1.0	91.8
P-A3	800	6	30	1.0	87.1
P-A4	800	12	30	0.66	87.5

[a] The operating temperature was 65°C. The initial pH value of spray solution was 7.0. The spray solution was recirculated and no makeup fresh abosrbent was added. The length of each run was 1 h. Based on this run time, if the average $NaClO_2/NO$ molar ratio was 1.0, the $NaClO_2/NO$ molar ratio would be 60 in the first minute.

Table 3
Operating conditions of the SO_x/NO_x removal efficiency in the second set of preliminary tests[a]

Run no.	NO concentration (ppm)	O_2 concentration (%)	L/G ratio (l/m^3)	NO_x removal efficiency (%)	SO_x removal efficiency (%)
P-B1	300	2	5	46.7	59.8
P-B2	300	6	5	44.0	60.8
P-B3	300	2	10	80.1	77.1
P-B4	300	6	10	88.8	91.6
P-B5	800	2	5	80.7	94.0
P-B6	800	6	5	76.0	96.0
P-B7	800	2	10	95.8	100.0
P-B8	800	6	10	96.8	99.0

[a] The operating temperature was 65°C. The initial pH value of spray solution was 7.0. The spray solution was recirculated and no makeup fresh abosrbent was added. The SO_2 concentration was 1000 ppm. The average $NaClO_2/NO$ molar ratio was 1.0.

3. Results and discussion

3.1. Measurement of spray droplet size and specific surface area

By using laser droplet size distribution analyzer (Malvern 2600) to analyze the size of the sprayed droplets and the specific surface area, the mean droplet size was determined to range from 595 to 1085 μm at an L/G ratio of 4–10 l/m^3. As shown in Fig. 2, the higher the L/G ratios were, the greater the gas–liquid contacting surface area was.

3.2. Preliminary tests

The results of preliminary tests are shown in Figs. 3 and 4, and Tables 2 and 3. It was found that the NO_x removal efficiency was satisfactory at an L/G ratio$=10 l/m^3$ in the first preliminary test set. Therefore, we lowered the experimental range of the L/G ratio to 5–10 l/m^3 in the second preliminary test set. The effect of $NaClO_2$ concentration was found

Table 4
Operating conditions of the individual NO_x removal efficiency for the continuous $DeNO_x$ system

Run no.	NO concentration (ppm)	L/G ratio (l/m^3)	$NaClO_2/NO$ (molar ratio)	Initial pH value
0[a]	400	7	0.0	5
1	400	7	1.0	5
2	200	7	1.0	5
3	800	7	1.0	5
4	400	5	1.0	5
5	400	10	1.0	5
6	400	7	0.5	5
7	400	7	1.5	5
8	400	7	1.0	4
9	400	7	1.0	6

[a] The absorbing liquid of run no. 0 was deionized water.

Table 5
Operating conditions and the combined SO_x/NO_x removal efficiency of the continuous $DeSO_x/DeNO_x$ system

Run no.	SO_2 concentration (ppm)	NO concentration (ppm)	L/G ratio (l/m^3)	$NaClO_2/(SO_2+NO)$ (molar ratio)	Initial pH value
0[a]	1000	400	7	0	5
1	1000	400	7	1.0	5
2	500	400	7	1.0	5
3	2000	400	7	1.0	5
4	1000	200	7	1.0	5
5	1000	800	7	1.0	5
6	1000	400	5	1.0	5
7	1000	400	10	1.0	5
8	1000	400	7	1.0	5
9	1000	400	7	0.8	5
10	1000	400	7	1.2	4
11	1000	400	7	1.0	6

[a] The absorbing liquid of run no. 0 was deionized water.

not to be significant in the range used because its effect may be suppressed by the high L/G ratio. Since the affect of O_2 concentration in the range of 6–12% was not significant either, we also lowered the experimental range of the O_2 concentration to 2–6% in the second preliminary test set.
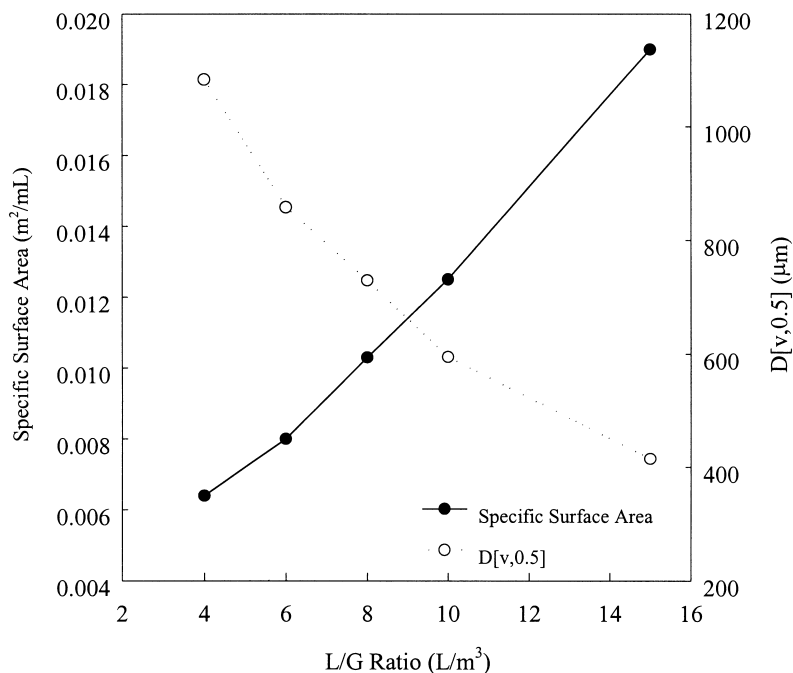
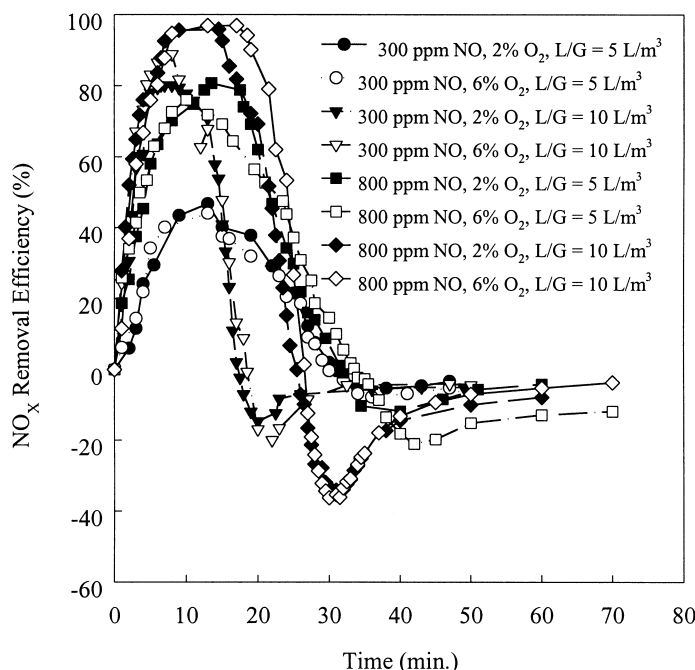Fig. 2. Relationship between specific surface area and L/G ratio.

Fig. 3. NO_x removal efficiency for the second set of preliminary tests.

As shown in Fig. 3, a higher NO_x concentration (800 ppm) and a correspondingly higher $NaClO_2$ concentration helped to achieve higher $DeSO_x$ efficiency that was sustained longer than at a lower NO concentration test (300 ppm). This result might be attributed to the reaction of SO_2 with NaOH and ClO_2 produced by the residual $NaClO_2$ since the SO_2 concentrations were the same for both higher and lower NO concentration tests. The L/G ratio was also found a significant factor affecting the $DeSO_x$ efficiency. A higher L/G ratio ($10 \, l/m^3$) helped to achieve a higher $DeSO_x$ efficiency but resulted in a shorter reaction period than the lower L/G ratio ($5 \, l/m^3$) for the lower NO concentration tests. However, the affect of L/G ratio was suppressed by the affect of the NO concentration for the higher NO concentration tests. The affect of the O_2 concentration in the range of 2–6% was not significant for all tests.

Using Fig. 3, the period of the reactions in the second preliminary test set was determined to be shorter than that of the first preliminary test set because of the larger $NaClO_2$ consumption by SO_2. Higher NO concentrations helped to achieve higher $DeNO_x$ efficiencies and sustained longer reaction period than the lower NO concentration tests. The reason for this affect was the same for the $DeSO_x$ efficiency affect described above. The affects of the L/G ratio and O_2 concentration for the $DeNO_x$ efficiency were also the same as in the case of the $DeSO_x$ efficiency described above. However, a very interesting phenomenon was found here. This phenomenon has to be interpreted in conjunction with Fig. 4. Fig. 4 showed the variation of pH value with time for the wet scrubbing combined SO_x/NO_x removal system.
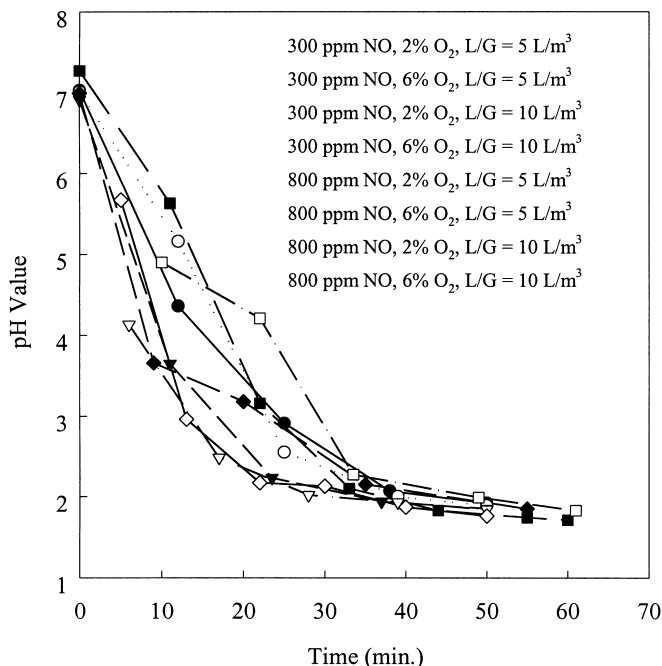
Fig. 4. Variation of the pH value with time for the second set of preliminary tests.

The pH decreased from its initial value of 7.0 to 1.85 at the end. The higher the L/G ratio was, the faster the maximum NO_x removal efficiency could be reached. At the same time, a larger amount of NO_2 desorbed previously absorbed faster too. That affect is why the NO_x removal efficiencies became negative near the end of the absorption. In order to avoid this phenomenon, the proper operating pH range should be in the 4–5.5 range, which is compatible with conventional FGD systems.

3.3. Individual DeNO$_x$ tests

The results for the continuous study of the individual DeNO$_x$ system are shown in Figs. 5–8. One can see that the NO$_x$ removal efficiency was not good. Comparing these results with the result of the preliminary test, the maximum DeNO$_x$ efficiency of the semi-batch study is seven times greater than that of the continuous study. This result may be attributed to a reduction of the operating temperature from 65 to 25°C and a lesser concentration of NaClO$_2$ in the absorbing solution. Teramoto et al. [7] indicated that the absorption rate doubled as the operating temperature changed from 25 to 50°C [7]. These data reveal that in the absence of oxidants, the DeNO$_x$ efficiency of conventional FGD process is not acceptable.

Fig. 5 indicates that the higher the NO$_x$ concentrations are, the higher the DeNO$_x$ efficiencies are. This results suggest that the removal of NO$_x$ may be kinetically controlled in
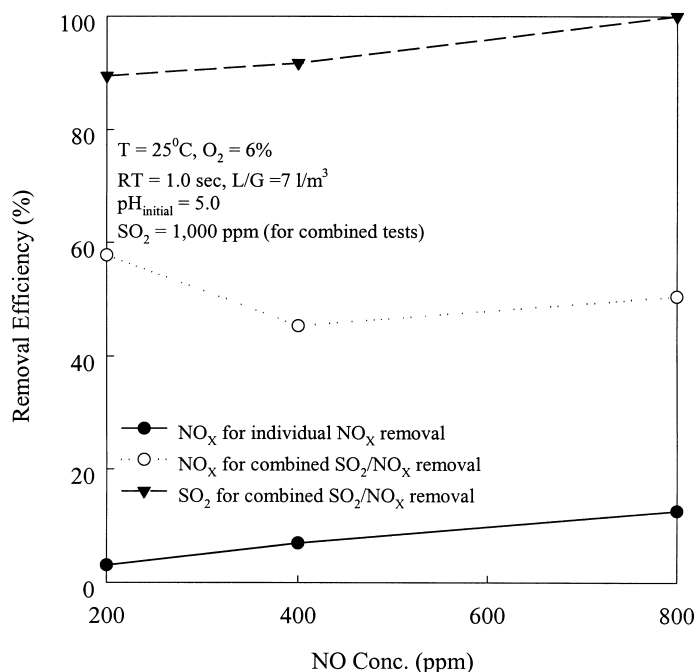
Fig. 5. Effect of NO concentration on SO_x/NO_x removal efficiencies for the continuous removal system.

the range of 200–800 ppm. Chan [11] and Hsu et al. [15] observed similar results to this work. The same tendency is found for the effect of the L/G ratio as shown in Fig. 6. The higher the L/G ratios are, the higher the $DeNO_x$ efficiencies are. This result is due to higher L/G ratios increasing the gas–liquid contacting surface area and mass transfer. Yang and Shaw [13] found the same trend. From Fig. 7, one can see the $DeNO_x$ efficiency is markedly affected by the molar ratio of $NaClO_2$ to NO. The initial pH value of the $NaClO_2$ solution in the range of this study is not a significant factor for the NO_x removal efficiencies as shown in Fig. 8.

3.4. Combined $DeNO_x$ and $DeSO_x$ tests

The results for the continuous study of combined $DeSO_x/DeNO_x$ system are shown in Figs. 5–9. The NO_x and SO_2 removal efficiencies are in the range of 36–72 and 88–100%, respectively. When compared to the individual $DeNO_x$ system, one may speculate that the improvement of $DeNO_x$ efficiency may result from the increased addition of $NaClO_2$ to the solution as well as the presence of SO_2. The final pH of solution decreased from 5.0 to 2.0–2.5. From Eqs. (3) and (4), we could conclude that NO is oxidized by the Cl_2 and ClO_2 under acidic conditions and NO_2 is formed. Takeuchi et al. [16] indicated that the SO_3^{2-} ion could improve the $DeNO_x$ efficiency. As shown in Fig. 5, there is no defined trend for the $DeNO_x$ efficiencies, and therefore we need more tests before coming to a conclusion.
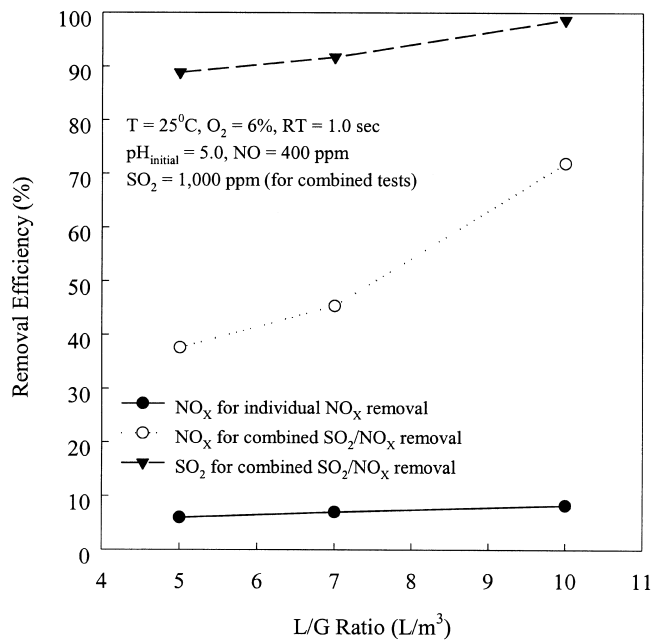
Fig. 6. Effect of L/G ratio on SO_x/NO_x removal efficiencies for the continuous removal system.
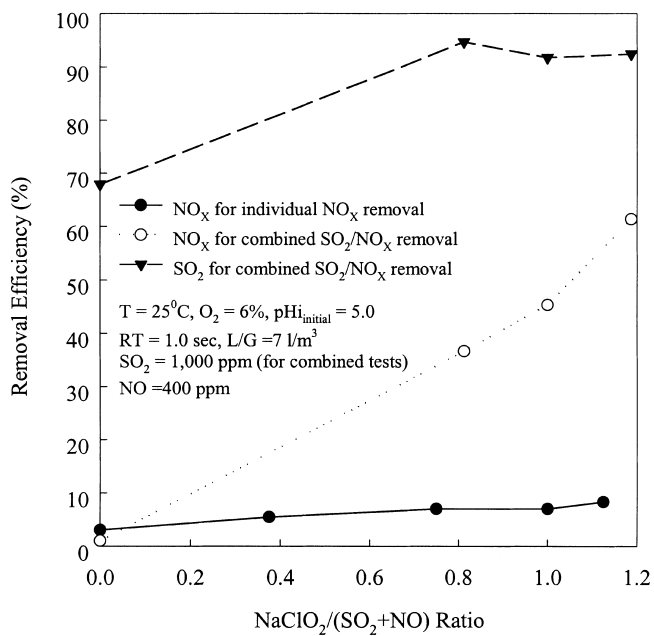

Fig. 7. Affect of molar ratio of $NaClO_2/(SO_2+NO)$ on SO_x/NO_x removal efficiencies for the continuous removal system.
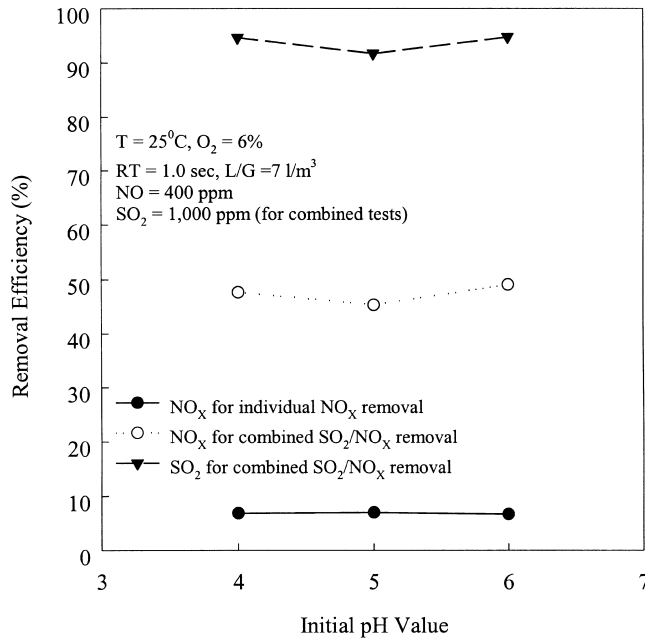
Fig. 8. Affect of initial pH value on SO_x/NO_x removal efficiencies for the continuous removal system.
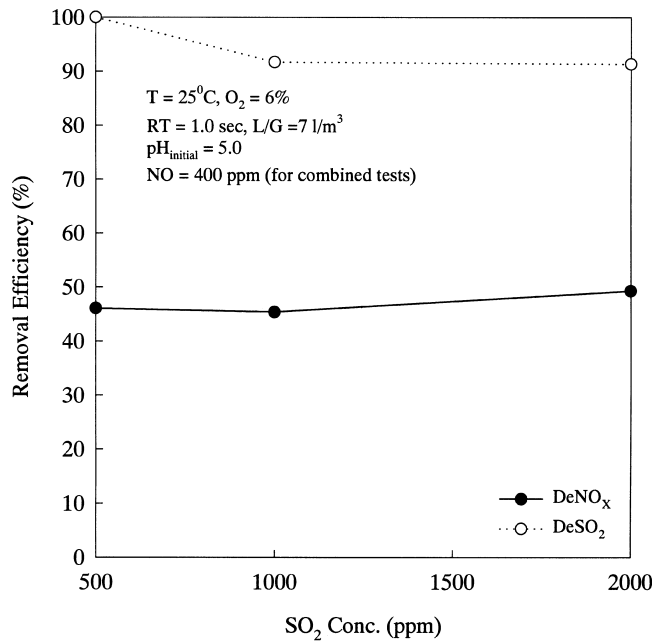

Fig. 9. Affect of SO_2 concentration on SO_x/NO_x removal efficiencies for the continuous combined SO_2/NO_x removal system.

From Fig. 5, one can see that the higher the L/G ratios are, the higher the $DeNO_x$ and $DeSO_x$ efficiencies are. In the range of this study, the $DeNO_x$ efficiency is highly influenced by the molar ratio of $NaClO_2$ to (SO_2+NO) as shown in Fig. 7. On the other hand, the molar ratio is not a significant factor for the $DeSO_x$ efficiencies. The initial pH value of the $NaClO_2$ solution is not a significant factor for the SO_x/NO_x removal efficiencies in the range from 4 to 6 as shown in Fig. 7. From Fig. 8, one can see that concentration is not a significant factor for the $DeNO_x$ and $DeSO_x$ efficiencies of the combined SO_2/NO_x removal system.

The comparison of NO_x removal efficiencies between this work and the cited literatures is shown in Table 1. Although the removal efficiencies of this work are lower than that of others, this result may due to that the gas–liquid contact time is shorter and the concentration of $NaClO_2$ is lower than the other studies.

4. Conclusions

For the combined SO_x/NO_x removal system employed in this study, the maximum NO_x and SO_2 removal efficiencies are in the range of 36–72 and 88–100%, respectively. These results indicate that this process could be utilized for as FGD system as well as being developed for the simultaneous removal of SO_2 and NO_x from flue gas. The $DeNO_x$ efficiency is mainly affected by the L/G ratio and the concentration of $NaClO_2$ in the solution.

Further work needs to be done on the kinetics of absorption of lean SO_2 and NO_x in aqueous mixed solutions of $NaClO_2$ and NaOH. The variation of the ions in the liquid phase measured by ion chromatography will also be a major focus in the next experimental series.

Acknowledgements

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