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The simultaneous removal of sulfur dioxide and nitrogen dioxide by the limestone slurry with addition of organic acid additives

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Abstract−This study investigates the effects of organic acid on the simultaneous absorption of SO_2 and NO_2 in the packed column. Organic acids, i.e., formic acid, acetic acid, and propionic acid, were used as additives. In the case of the absence of additives, when SO_2 and NO_2 were simultaneously absorbed into the limestone slurry, both SO_2 and NO_2 contributed to increasing the mutual absorption efficiency. In the simultaneous absorption of SO_2 and NO_2 with addition of additives, the SO_2 removal efficiency appeared in the order of formic acid<no addition<propionic acid<acetic acid. Acetic acid has a superior buffer capacity and intermediate hydrophobic interaction, resulting in the highest SO_2 absorption efficiency. In the slurry with the addition of acetic acid and propionic acid, the reactions of absorbed SO_2 and NO_2 predominantly took place; thus, the SO_4^{2-}/SO_3^{2-} ratio was greater than 1. In terms of formic acid, the slurry pH was maintained at approximately 4.0, which departs from the appropriate range, attributed to the small pKa value, showing a negative effect on SO_2 and NO_2 removal. In the slurry with formic acid added, the SO_2 predominantly reacted with formic acid; hence, the SO_4^{2-}/SO_3^{2-} ratio was less than 1.

Keywords: Absorption, Desulfurization, Denitrification, Simultaneous Removal, Organic Acid Additive

INTRODUCTION

The nitrogen oxide and sulfur dioxide in the atmosphere are reported to generate PM 2.5 through a photochemical reaction [1,2]. Large amounts of these materials are emitted from the flue gas of coal-fired power plants and their emissions are expected to increase as energy consumption increases, driven by continuous economic growth [3]. In preparation for this, the South Korean government is enforcing environmental regulations on the pollutant emissions of power plant flue gas. Moreover, it is propelling the temporary operation break and closure of the coal-fired power plants and increase of power generation ratio by combined cycle power plant with low pollutants henceforward. However, considering the construction cost, fuel cost, and facility maintenance cost of combined cycle power plants, a coal fired power plant is superior in economic terms. Therefore, if only pollutants from coal fired power plants can be reduced, the availability of existing coal-fired power plants can be increased [4]. For this, advanced treatment of NO_x and SO_2 near the combined cycle plant emission level is required in the flue gas of coal fired power plants. The most widely known techniques for the removal of nitrogen oxide and sulfur dioxide of coal-fired power plant flue gas are selective catalytic reduction (SCR) and wet flue-gas desulfurization (FGD), respectively. Although the NO_x removal efficiency of SCR is 80%-90%, improvement of the current technique is required for emissions to satisfy the reinforcing regulation standards. Approximately 95% of NO_x among flue gas is present as NO with low solubility and reactivity. If the NO can be oxidized to NO_2 with high solubility before the FGD process, the simultaneous absorption of SO_2 and NO_x in the FGD can be enabled, and the finally-emitted NO_x concentration can also be reduced. The NO oxidation process includes the use of chemical oxidants, such as ozone and hydrogen peroxide, selective catalytic oxidation, and photocatalyst oxidation [5-7]. Among them, ozone oxidation is more reactive to NO than SO_2, has higher oxidation efficiency, and has no decomposition by-products [1,8,9]. Meanwhile, due to the quality deterioration of coal and limestone along with the reinforcement of emission regulations, research on the improvement of desulfurization efficiency of the FGD process is being conducted. There is a method of using additives with pH buffer capacity at the interface between gas-liquid and solid-liquid to increase the desulfurization efficiency [10,11]. Additives are classified into alkali additives and organic acid additives. Alkali additives are dissolved in water in a form of salt and provide basicity, improving the SO_2 mass transfer [12,13]. Organic acid additives have pH buffer capacity in the limestone slurry, decrease sedimentation rate of slurry particles, and reduce the scaling risk to the desulfurization system [10,14]. These additives should have a suitable solubility in the slurry, have a low vapor pressure, be chemically stable and non-toxic [14,15].

Although previous investigators have studied NO_2 absorption with sodium hydroxide, sodium sulfite, sulfuric acid, and calcium sulfite, these studies were usually performed under conditions far from that of FGD process based on limestone slurry in south Korea [7,16]. To the best of our knowledge, organic acids have been usually studied to improve desulfurization, so studies on the simultaneous absorption of SO_2 and NO_2 with organic acid are lacking. In this study, we investigated the characteristics of simultaneous absorp-

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tion of SO_2 and NO_2 in the limestone slurry with organic acid additives. We selected three organic acids, such as formic acid, acetic acid, and propionic acid, which are monobasic acids with a simple structure. The desulfurization and denitrification efficiencies with different initial SO_2 and NO_2 concentrations, types of additives, and slurry pH in the packed column were studied and the chemical behavior of the SO_2 and NO_2 absorption process in the limestone slurry in the presence of organic acid was investigated.

EXPERIMENTAL

1. Material

The limestone used in this study was obtained from Yeongheung Power Station. It was ground and sieved to prepare a sample of 325 mesh or less. The chemical composition of limestone was characterized by XRF (Rigaku, ZSX Primus), the results of which are displayed in Table 1. Formic acid (AR, ≥85.0%), acetic acid (AR, ≥99.5%), and propionic acid (AR, ≥99.0%) supplied by Daejung Chemicals (Siheung, Korea) were used as organic acid additives.

2. Experimental Procedure

A schematic diagram of the experimental equipment is presented in Fig. 1. As shown, the experimental equipment is composed of a packed column reactor, a gas supply system, a slurry storage and injection system, and analytical equipment. The packed column reactor made of glass material was manufactured to have an inner diameter of 50 mm and a height of 650 mm, and Teflon tube packings of 4 mm×10 mm were randomly placed in the glass reactor. The glass reactor was manufactured to be a double jacket, and its reaction temperature was maintained at 25 °C. The gas flow of gases used in the tests, i.e., SO_2, NO_2, O_2, and N_2, was controlled using a gas flowmeter (Mass Flow Controller, Brook-MFC, 5850E), and each gas was mixed and injected into the bottom of the reactor. The reaction gas emitted to the top of the reactor passed through the cold trap to remove the moisture and was injected into the analytical equipment for the prevention of analytical equipment damage from moisture. The limestone slurry was stirred in the storage tank at 400 rpm and injected to the upper part at a fixed amount

Table 1. Chemical composition of limestone (wt%)

CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	Others
95.80	1.12	0.10	0.82	0.62	1.54

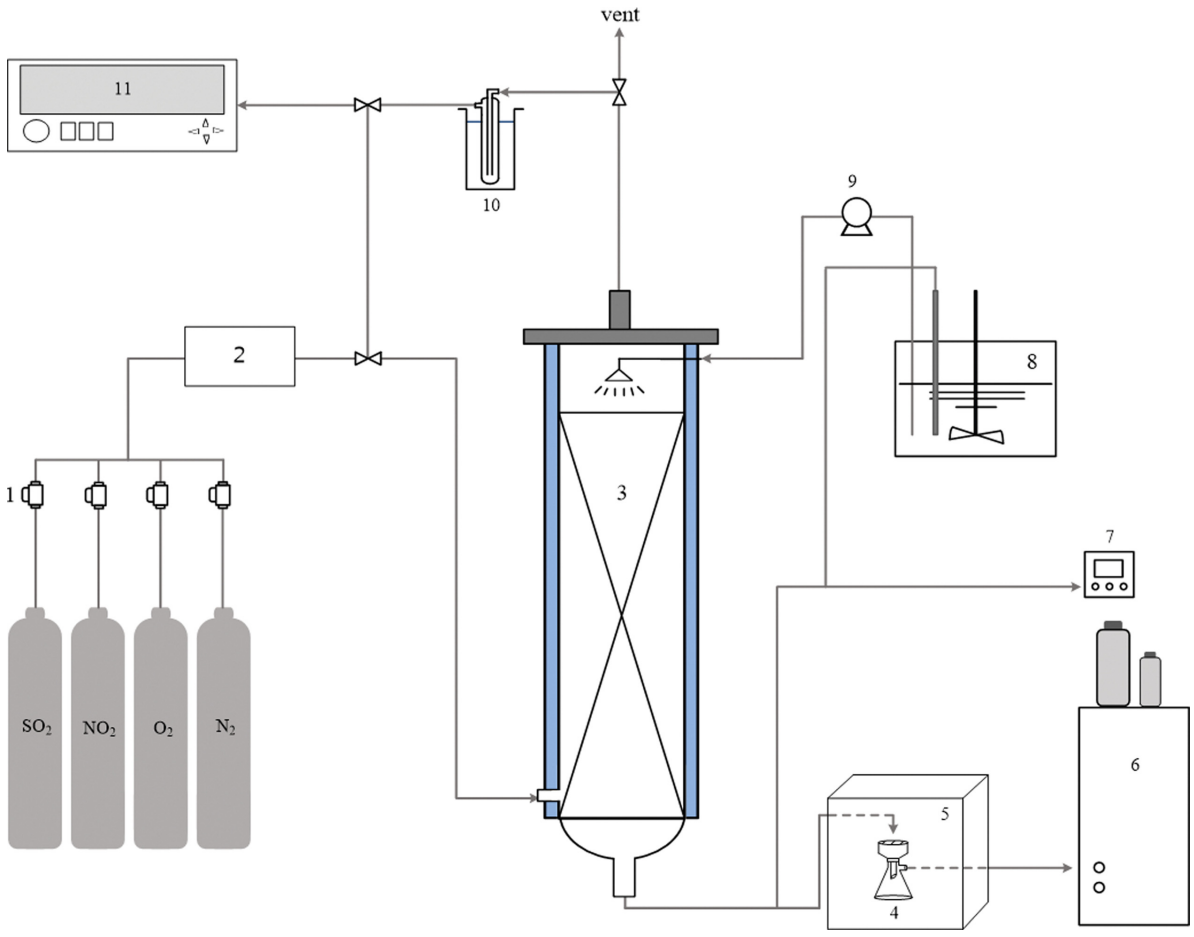

Fig. 1. Schematic diagram of the experimental setup.

1. Mass flow controller
2. Gas mixing chamber
3. Packed bed reactor
4. Filter
5. N_2 Box
6. Ion chromatography
7. pH meter
8. Slurry storage tank
9. Pump
10. Cold trap
11. NO_x analyzer, SO_2/CO_2 analyzer

Table 2. Experimental conditions

Prameter		Value
Inlet gas concentration	SO_2	200-1,000 ppm
	NO_2	200-500 ppm
	O_2	3%
	N_2	balance
Inlet gas flow rate		4 L/min
Limestone slurry concentration		0.1%
Liquid flow rate		36 ml/min
Organic acid concentration		15 mM
Temperature		25 °C

using a peristaltic tubing pump (Longer Precision Pump Co., YZ1515x). For the experiments designed to investigate the effects of organic acid additives, the limestone slurry and organic acid were mixed for 1 h in the storage tank and injected into the top of packed column reactor. To measure the pH change of the limestone slurry, a pH meter (PH 340i, WTW, Germany) was used. The experimental operating conditions of all tests are listed in Table 2.

The NO_2 concentration of reactant gas emitted to the top of the reactor was analyzed with an NO/NO_2 analyzer (Eco Physics, CLD 60), and an SO_2/CO_2 gas analyzer (Horiba, VS-3000) was utilized for the measurement of SO_2 and CO_2 concentrations. The reaction slurry emitted to the bottom of the reactor was subjected to vacuum filtration using a membrane filter (HYUNDAI Micro Co., CA045047A). The filtration was conducted under a nitrogen atmosphere to prevent the oxidation of sulfite ions and nitrite ions. Ion chromatography (Metrohm, Eco IC) was used for the ion analysis of the filtrate; in addition, the concentration of sulfite ion was measured using the iodometric titration method. The limestone slurry with moisture removed through the vacuum filter was dried at 60 °C for 12 h and its characteristic analysis was carried out using XRD (MiniFlex 600, Rigaku). The removal efficiency of SO_2 and NO_2 among the reaction gases was calculated as follows:

$$\text{Removal efficiency}\ (\%) = \frac{C_{in} - C_{out}}{C_{in}} \times 100\%$$

where C_{in} is the initial concentration of SO_2 or NO_2 before the injection to the reactor, and C_{out} is the concentration emitted from the reactor top. In the final absorption efficiency, C_{out} is the average value of the concentration emitted from the reactor top at between 60 min and 70 min after the reaction, and the pH value is the average at between 60 min and 70 min after the reaction.

RESULTS AND DISCUSSION

1. Absorption Test of Sulfur Dioxide into Limestone Slurry

The absorption test of SO_2 into the limestone slurry and water was conducted using the packed column; the results are shown in Fig. 2. When 1,000 ppm of SO_2 was introduced in the limestone slurry, approximately 850 ppm of SO_2 was absorbed and approximately 580 ppm of CO_2 gas was produced. When 200 ppm of SO_2 was introduced, approximately 97% (194 ppm) of SO_2 was absorbed and approximately 133 ppm of CO_2 gas was produced. The inorganic carbon concentration in the limestone slurry obtained after the reaction was analyzed with a TOC analyzer and was found to be a few ppm. The major reactions of SO_2 absorbed into the limestone slurry are given below [12,17-19].

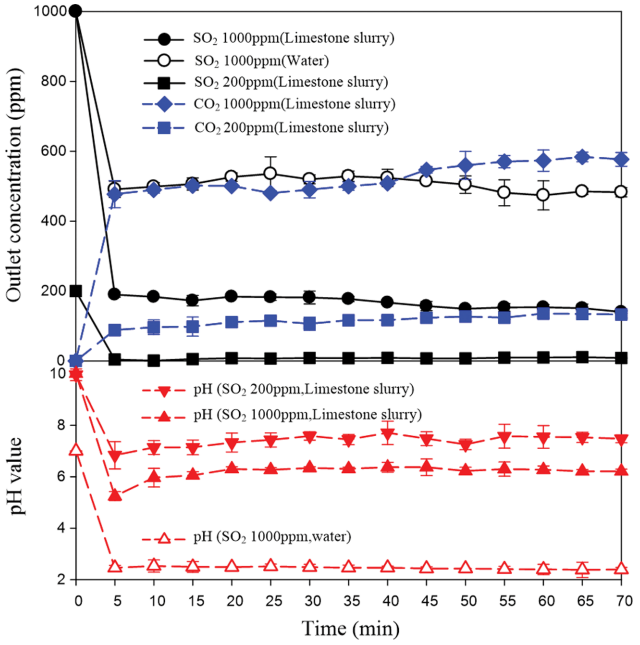

Fig. 2. Comparison of outlet concentration of SO_2 and CO_2 and pH value on limestone slurry or water (inlet SO_2 concentration= 1,000 ppm, 200 ppm).

$$SO_2 \rightleftharpoons SO_{2(aq)} \quad (1)$$

$$SO_{2(aq)} + H_2O \rightleftharpoons H_2SO_{3(aq)} \quad (2)$$

$$H_2SO_{3(aq)} \rightleftharpoons H^+ + HSO_3^- \quad (3)$$

$$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-} \quad (4)$$

$$CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^- \quad (5)$$

$$HCO_3^- + H^+ \rightleftharpoons CO_{2(aq)} + H_2O \quad (6)$$

$$CO_{2(aq)} \rightleftharpoons CO_2 \quad (7)$$

$$CaCO_3 + SO_2 \rightleftharpoons Ca^{2+} + SO_3^{2-} + CO_2 \quad (8)$$

$$Ca^{2+} + SO_3^{2-} + \tfrac{1}{2}H_2O \rightarrow CaSO_3 \cdot \tfrac{1}{2}H_2O_{(s)}\ \text{(hannerbachite)} \quad (9)$$

$$SO_3^{2-} + \tfrac{1}{2}O_{2(aq)} \rightleftharpoons SO_4^{2-} \quad (10)$$

$$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O_{(s)}\ \text{(gypsum)} \quad (11)$$

When 1,000 ppm of SO_2 was introduced into the water, 50% (500 ppm) of SO_2 was absorbed and the slurry pH was 2.4. These results are attributed to the fact that SO_2 hydrolyzed and hydrogen ion was created, as presented in reactions (1)-(4). As shown in Fig. 2, the concentration of the generated CO_2 gas was always approximately 70% of the absorbed SO_2 concentration regardless of the SO_2 inlet concentration; these results suggest that SO_2 hydrolysis and reaction with limestone occurred simultaneously. When the SO_2 inlet concentration was 1,000 ppm and 200 ppm, the slurry pH was 6.2 and 7.5, respectively. The slurry pH in the wet lime-

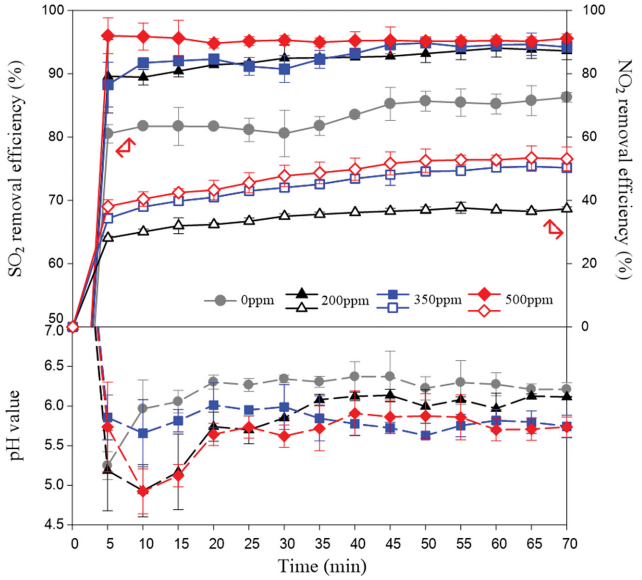

Fig. 3. Effect of inlet NO_2 concentration on SO_2 removal efficiency and pH value (inlet SO_2 concentration=1,000 ppm).

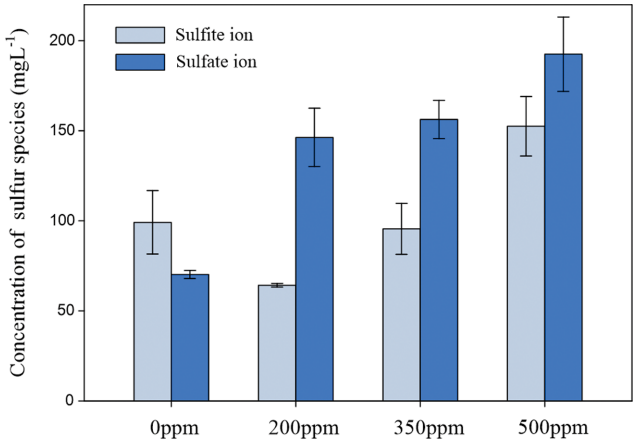

Fig. 4. Effect of inlet NO_2 concentration on sulfite and sulfate ion concentration in the $CaCO_3$ slurry (inlet SO_2 concentration= 1,000 ppm).

stone scrubbing is usually designed to be in the range of 5.0-6.0 [3,12]. While the SO_2 dissolution rate increases at high slurry pH, the limestone dissolution rate increases at low slurry pH [10]. Reaction (8) is the overall reaction of reactions (1)-(7). The slurry dried at 60 °C after the reaction was confirmed by XRD analysis. Gypsum transformed from limestone was observed as presented in reaction (11), but hannerbachite was not observed.

2. Effect of Inlet Concentration of NO_2 on the Simultaneous Removal of SO_2 and NO_2

A simultaneous absorption test of SO_2 and NO_2 in the limestone slurry with changing NO_2 inlet concentration was carried out and the results are presented in Figs. 3 and 4. When SO_2 and NO_2 are simultaneously absorbed, the NO_2 inlet concentration affects the SO_2 absorption efficiency. As shown in Fig. 3, the SO_2 removal efficiency in the absence of NO_2 was approximately 85%, but when NO_2 was introduced, the SO_2 removal efficiency increased to approximately 94%, 95%, and 96%, depending on the increase of NO_2 inlet concentration. These results suggest that NO_2 plays a role in improving the SO_2 absorption efficiency. The reactions that take place when SO_2 and NO_2 are simultaneously absorbed are presented below [5,6].

$$NO_2 \rightleftharpoons NO_{2(aq)} \quad (12)$$

$$2NO_2 + H_2O \rightarrow HNO_{2(aq)} + HNO_{3(aq)} \quad (13)$$

$$HNO_{2(aq)} \rightleftharpoons H^+ + NO_2^- \quad (14)$$

$$HNO_{3(aq)} \rightleftharpoons H^+ + NO_3^- \quad (15)$$

$$2NO_{2(aq)} + SO_3^{2-} + H_2O \rightleftharpoons 2H^+ + 2NO_2^- + SO_4^{2-} \quad (16)$$

Reactions (12)-(15) show the absorption, hydrolysis, and dissociation of NO_2 in water. Reaction (16) is the reaction occurring when SO_2 and NO_2 are simultaneously absorbed, and the sulfite ion generated from reactions (3) and (4) reacts with absorbed NO_2 and oxidizes to sulfate ion [20]. If reaction (16) is expedited, the consumption of sulfite ion in the slurry increases; thus, reactions (1)-(4) are expedited to the forward direction and the SO_2 absorption efficiency also increases. In the reaction (16), the $NO_{2(aq)}/SO_3^{2-}$ mole ratio is 2. As presented in Fig. 3, when the NO_2 inlet concentration is 200, 350, and 500 ppm, the NO_2 removal efficiency is only 37%, 50%, and 53%, respectively; hence, the $NO_{2(aq)}/SO_3^{2-}$ mole ratio is 0.08, 0.18, and 0.28, respectively, which are much lower than 2. For this reason, the difference in SO_2 removal efficiency with different NO_2 inlet concentration was not significant, as shown in Fig. 3. On the contrary, as the NO_2 inlet concentration increases, the NO_2 absorption efficiency also increases, and thus the slurry pH decreases. Fig. 3 shows that increasing the NO_2 inlet concentration from 0 to 200, 350, and 500 ppm results in a decrease in slurry pH from approximately 6.2 to 6.1, 5.7, and 5.7, respectively.

Fig. 4 shows the concentrations of sulfite ion and sulfate ion generated in the slurry after the reaction. As shown in Fig. 4, the increase in NO_2 inlet concentration increases the total concentration of sulfite ion and sulfate ion in the slurry, which is in agreement with the results presented in Fig. 3. In contrast, the SO_4^{2-}/SO_3^{2-} mole ratio in the slurry was less than 1 with the absence of NO_2, but the SO_4^{2-}/SO_3^{2-} mole ratio was higher than 1 with the presence of NO_2. This can be explained by the fact that when NO_2 is introduced, the sulfate ion is generated through reaction (10) along with reaction (16).

3. Effect of Inlet Concentration of SO_2 on the Simultaneous Removal of SO_2 and NO_2

The effect of SO_2 inlet concentration on the NO_2 absorption in the case of simultaneous absorption of SO_2 and NO_2 was investigated. As can be seen in Fig. 5, the NO_2 removal efficiency in the presence of SO_2 increased compared to the case with the absence of SO_2, and it was 37%-39% regardless of the SO_2 inlet concentration. As the SO_2 inlet concentration increased from 0 to 200, 500, 800, and 1,000 ppm, the slurry pH decreased from 9.6 to 7.3, 6.7, 6.5, and 6.1, respectively. Zheng et al. [6] reported that the products of SO_2 hydrolysis enhance the absorption efficiency of nitrogen oxide. Reaction (16) indicates that SO_2 and NO_2 enhance the absorption efficiency of NO_2 and SO_2, respectively. Fig. 5 also shows

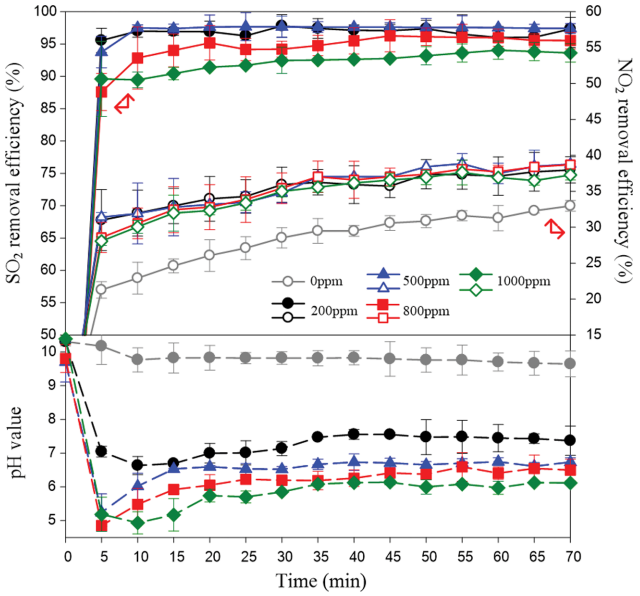

Fig. 5. Effect of inlet SO_2 concentration on SO_2 (closed symbols) and NO_2 (open symbols) removal efficiency and pH value (inlet NO_2 concentration=200 ppm).

that the SO_2 removal efficiency for different SO_2 concentrations is 94%-98%. Because the $SO_3^{2-}/NO_{2(aq)}$ mole ratio in reaction (16) is 0.5, the introduced SO_2 at a concentration of over 200 ppm is a sufficient concentration to increase the absorption efficiency of 200 ppm NO_2. Therefore, it is understandable that the NO_2 removal efficiency appeared to be similar, regardless of the SO_2 inlet concentration. If the absorption efficiency of SO_2 and NO_2 is the same, the contribution of SO_2 is more significant than that of NO_2.

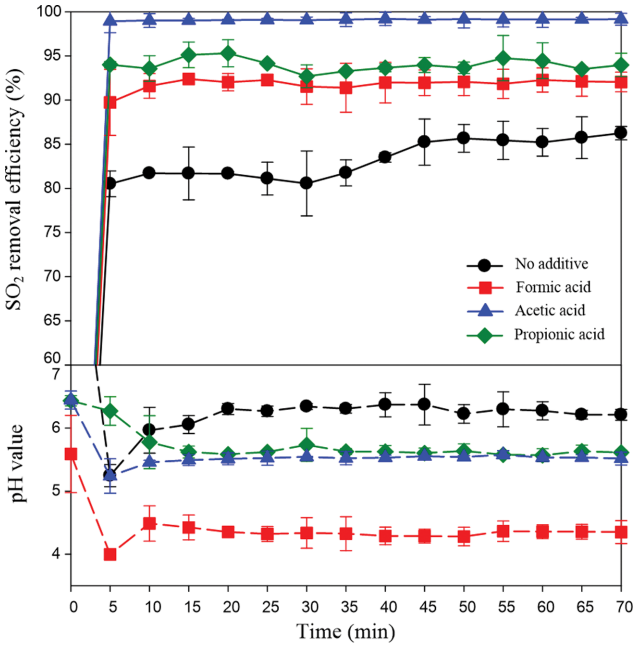

Fig. 6. Effect of organic acid on SO_2 removal efficiency and pH value (inlet SO_2 concentration=1,000 ppm).

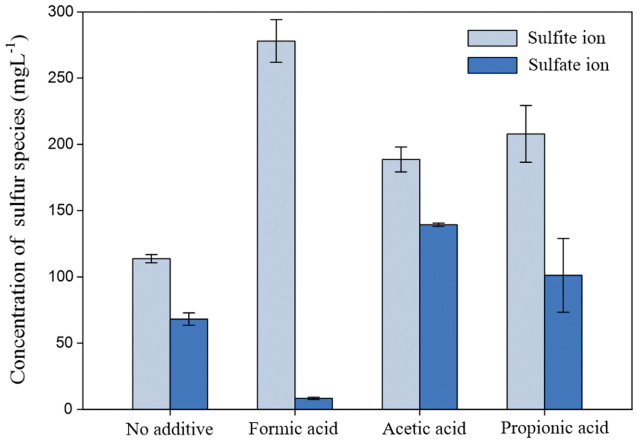

Fig. 7. Effect of organic acid on sulfite and sulfate ion concentration in the $CaCO_3$ slurry.

4. Effect of Organic Acid on Removal of SO_2

Slurry pH is one of the factors affecting the SO_2 absorption efficiency. Ideal desulfurization additives reduce the mass transfer resistance at the gas-liquid interface while stably maintaining the slurry pH [10]. Organic acids are known to improve the desulfurization efficiency and utilization efficiency of limestone [14]. SO_2 absorption experiments on the limestone slurry with the addition of three monobasic organic acids were conducted, the results of which are presented in Figs. 6 and 7. As shown in Fig. 6, in the case of no addition of organic acid into the slurry, the SO_2 removal efficiency was approximately 85%; however, when propionic acid and formic acid were added to the slurry, the SO_2 removal rate increased to approximately 94% and 91%, respectively. When acetic acid was added to the slurry, an SO_2 removal efficiency of approximately 99% was obtained. If the organic acid is added to the limestone slurry, the following reactions are considered [15,21].

$$HA_{(aq)} \rightleftharpoons H^+ + A^- \quad (17)$$

$$SO_{2(aq)} + A^- + H_2O \rightleftharpoons HSO_3^- + HA_{(aq)} \quad (18)$$

In reactions (17) and (18), A^- is a conjugate base of acid HA. In the experiments where the organic acid is added, the limestone slurry and organic acid were stirred for 1 h in the slurry storage tank before the experiments. During this process, part of the organic acid dissociates into hydrogen ion and A^- ion, as outlined in reaction (17), producing CO_2. The hydrogen ion generated from the acid HA dissociation participates in reaction (5) and generates bicarbonate ion from the limestone, consequently increasing the dissolution rate and utilization efficiency of limestone. Subsequently, the absorbed SO_2, as shown in reaction (18), reacts with A^- ion, generating bisulfite ion and regenerating HA. Therefore, the SO_2 absorption increases as reaction (18) is expedited.

As can be seen in Fig. 7, the sulfite ion increases in the slurry with the addition of organic acid regardless of the type of organic acid; the total concentration of sulfite ion and sulfate ion also increases. This result suggests that reaction (18) took place in the slurry with the organic acid added, and the SO_2 absorption increased. In the slurry with the addition of organic acid, the SO_4^{2-}/SO_3^{2-} mole

ratio was in the order of formic acid (≈0.03)<propionic acid (≈0.49)<acetic acid (≈0.74). It has been reported that when the pK_a value of organic acid is in the range of 4.5-5, it buffers the pH of the limestone slurry [14,20]. The pK_a values of acetic acid and propionic acid are 4.75 and 4.88, respectively, whereas the pK_a value of formic acid is 3.75 [22]. Because of the high acidity of the formic acid, the slurry pH with the addition of formic acid was approximately 4.3 (Fig. 6). Because the oxidizing power of the dissolved oxygen becomes weaker at lower pH [23], it is expected that the oxidation of sulfite ion was suppressed in the slurry with the addition of formic acid, and thus a very low SO_4^{2-}/SO_3^{2-} mole ratio was obtained.

On the contrary, as shown in Fig. 6, the slurry pH with the addition of acetic acid and propionic acid was kept constant at 5.5 and 5.6, respectively; however, the SO_2 removal efficiency in the slurry with propionic acid added was lower than that in the slurry with acetic acid added. In the FGD system, the SO_2 absorption is hindered if the slurry pH is below 4.5 [24]. The slurry pH with the addition of formic acid is very low at approximately 4.3, but the SO_2 removal efficiency in the slurry with the addition of formic acid was slightly lower than that in the slurry with the addition of propionic acid. These results can be explained by the hydrophobic interaction of organic acids. Because the solid-liquid mass transfer resistance increases in the limestone slurry due to the hydrophobic interaction, the dissolution rate of limestone decreases [17]. The decrease in the dissolution rate of limestone leads to an increase in sulfite ions and consequently a reduction in SO_2 absorption. It is speculated that among the three organic acids, the carbon chain length of propionic acid is the longest; thus, the hydrophobic interaction appeared to be relatively the most significant in the slurry with the addition of propionic acid, while the hydrophobic interaction was found to be the smallest in the slurry with the addition of formic acid.

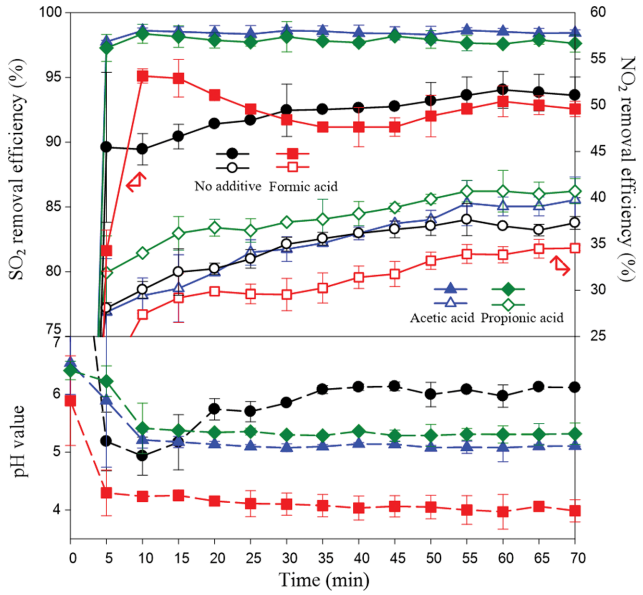

Fig. 8. Effect of organic acid and SO_2 (closed symbols) and NO_2 (open symbols) removal efficiency and pH value (inlet SO_2 concentration=1,000 ppm, NO_2 concentration=200 ppm).

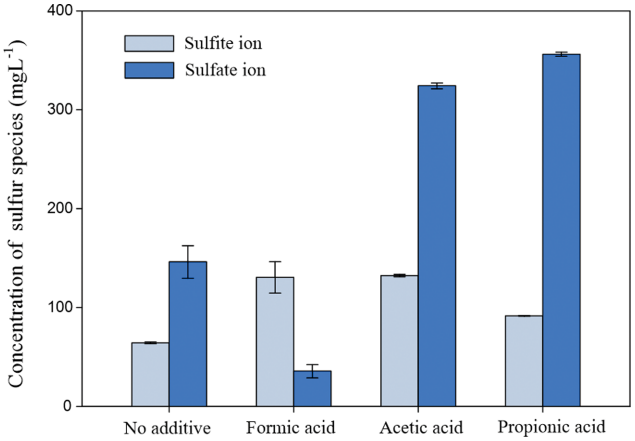

Fig. 9. Effect of organic acid on sulfite and sulfate ion concentration in the $CaCO_3$ slurry (inlet SO_2 concentration=1,000 ppm, NO_2 concentration=200 ppm).

5. Effect of Organic Acid on the Simultaneous Removal of SO_2 and NO_2

Simultaneous absorption tests of SO_2 and NO_2 in the limestone slurry with the addition of three organic acids were carried out, and the results are shown in Figs. 8, 9, and 10. If the organic acid is added into the wet limestone scrubbing, the simultaneous absorption reaction of SO_2 and NO_2 becomes very complicated. As shown in Fig. 8, the SO_2 removal efficiency in the slurry with acetic acid and propionic acid added is 99% and 98%, respectively, and the slurry pH is maintained at 5.1 and 5.3, respectively. These results are attributed to the fact that acetic acid or propionic acid contributes to the improvement of the SO_2 absorption efficiency along with NO_2, similar to the results of sections 2 and 4. However, the SO_2 removal efficiency in the slurry with the addition of formic acid was lower than for the case of slurry with no addition of organic acid, and the slurry pH was kept constant at approximately 4.0.

As presented in Fig. 9, the total concentration of sulfite ion and sulfate ion in the slurry with the addition of acetic acid and propionic acid increased compared with the case with no addition of organic acid, and the SO_4^{2-}/SO_3^{2-} mole ratio was also higher than 1. These results suggest that reaction (16) predominantly takes place over reaction (18) during the simultaneous absorption of SO_2 and NO_2, indicating that the NO_2 absorption has a more significant effect on the SO_2 absorption compared to the addition of acetic acid or propionic acid. In contrast, the total concentration of sulfite ion and sulfate ion in the slurry with the addition of formic acid did not increase and, above all, the SO_4^{2-}/SO_3^{2-} ratio was below 1. These results indicate that the SO_2 absorption was suppressed due to the low slurry pH with the formic acid added, and reaction (18) predominantly occurred over reaction (16). Fig. 8 shows that if formic acid is added to the slurry, the NO_2 removal efficiency becomes lower than for the case with no addition of organic acid. This result suggests that reaction (16) was inhibited at low slurry pH; thus, the NO_2 absorption efficiency decreased.

Fig. 10 presents the concentrations of nitrate ion and nitrate ion generated in the slurry after the reaction. Regardless of the addition of organic acid, the nitrate ion accounts for most of the ions

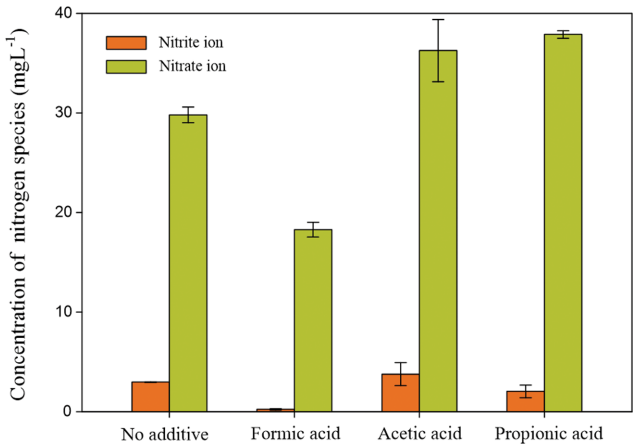

Fig. 10. Effect of organic acid on nitrite and nitrate ion concentration in the $CaCO_3$ slurry (inlet SO_2 concentration=1,000 ppm, NO_2 concentration=200 ppm).

in the slurry. This result is attributed to the oxidation of nitrite ion due to the dissolved oxygen outlined in reaction (19) for the case where the slurry pH is maintained in the range of 5.0-6.0 [6,25].

$$2NO_2^- + O_{2(aq)} \rightarrow 2NO_3^- \quad (19)$$

$$NO_{2(aq)} + A^- + H_2O \rightleftharpoons H^+ + NO_3^- + HA_{(aq)} \quad (20)$$

Reaction (19) shows that if the formation of nitrate ion is inhibited, the NO_2 absorption declines. In reaction (19), the dissolved oxygen participates in the NO_2 absorption; hence, to improve the NO_2 removal rate, not only the concentration of dissolved oxygen but also the oxygen inflow concentration could be an important factor. However, as shown in Fig. 10, the nitrite ion in the slurry with the addition of formic acid is very low and the slurry pH is very low at 4.0. For these reasons, reaction (20) can be proposed. Because reaction (20) is the reaction between the absorbed NO_2 and the organic acid, it does not affect the SO_2 absorption.

CONCLUSIONS

When SO_2 and NO_2 are simultaneously absorbed in the limestone slurry, both SO_2 and NO_2 contribute to increasing the mutual absorption efficiency. Because the reaction ratio between sulfite ion and NO_2 absorbed in the slurry is 1 : 2, if the absorption efficiency of SO_2 and NO_2 is the same, the contribution of SO_2 is expected to be more significant than that of NO_2 for the increase in the absorption efficiency of each other. Because of this reaction, the SO_4^{2-}/SO_3^{2-} ratio in the slurry appeared to be greater than 1.

When three types of monobasic organic acid, i.e., formic acid, acetic acid, and propionic acid, were added to the limestone slurry, in the case of NO_2 absence, the SO_2 absorption efficiency appeared in the order of no addition<formic acid<propionic acid<acetic acid. The highest effect of acetic acid on the enhancement of the SO_2 absorption efficiency can be related to its superior buffer capacity and modest hydrophobic interaction. Although formic acid has a small hydrophobic interaction, its low buffer capacity resulted in the lowest SO_2 absorption efficiency. Because bisulfite is formed through the reaction between absorbed SO_2 and organic acid in the limestone slurry with the addition of organic acid, the SO_4^{2-}/SO_3^{2-} ratio appeared to be below 1.

When SO_2 and NO_2 were simultaneously absorbed in the limestone slurry with the addition of three types of monobasic organic acids, namely, formic acid, acetic acid, and propionic acid, the effect of improving the absorption efficiencies of SO_2 was found to be in the order of formic acid<no addition<propionic acid<acetic acid. In case of NO_2 absorption efficiency, it was found to be in order of formic acid<no addition<acetic acid<propionic acid. The negative effect of formic acid on the enhancement of the SO_2 absorption efficiency is attributed to the restraint of SO_2 absorption because the slurry pH is kept constant at 4.0, departing from the range of 5.0-6.0. SO_2 absorbed into the slurry with the addition of acetic acid and propionic acid participating in the reaction with absorbed NO_2 more predominantly compared with the reaction with organic acid; therefore, the SO_4^{2-}/SO_3^{2-} ratio was above 1. SO_2 absorbed into the slurry with the addition of formic acid participated in the reaction with formic acid more predominantly compared with the reaction with absorbed NO_2; thus, the SO_4^{2-}/SO_3^{2-} ratio was below 1. The NO_3^-/NO_2^- ratio was found to be much higher than 1 in the limestone slurry with the addition of monobasic organic acid. These results are attributed to the oxidation of nitrite ion by dissolved oxygen and the reaction between absorbed NO_2 and added organic acid.

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