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Absorption–reduction technique assisted by ozone injection and sodium sulfide for NO_x removal from exhaust gas

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Abstract

A two-stage process consisting of an ozonizing chamber and an absorber containing a reducing agent solution was proposed to remove nitrogen oxides (NO_x) from exhaust gas. In the ozonizing chamber where the exhaust gas is treated by ozone, NO (the main component of NO_x) was oxidized to NO_2, and in the next step, NO_2 was reduced to N_2 by sodium sulfide (Na_2S) used as the reducing agent. The NO_x removal efficiency obtained by this two-stage process was higher than 95%. It was found that about three fourth of sodium sulfide was consumed without reacting with NO_x, and accordingly the amount of sodium sulfide required should be four times that of NO_x to be removed. The problem regarding the emission of H_2S from Na_2S was deeply related to the pH of the reducing agent solution, which could be solved by adjusting the pH using a basic reagent (NaOH). The concentrations of NO_2^- and NO_3^- in the reducing agent solution after processing were analyzed, which showed that about 25% of the NO_x removed from the exhaust gas was simply dissolved in the reducing agent solution, i.e., about 75% of the NO_x removed was reduced to N_2.

Keywords: Ozone; Sodium sulfide; Reducing agent; Nitrogen oxides

1. Introduction

The great concern over the emission of nitrogen oxides (NO_x) and sulfur dioxide (SO_2) from fossil fuel combustion has led to the development of various technologies to remove them. Several wet desulphurization technologies including calcium–gypsum process, magnesium oxide scrubbing, and double alkali process have been applied to the removal of SO_2 [1,2]. For NO_x control, catalytic, absorption and adsorption processes have been developed [2–5], among which selective catalytic reduction (SCR) is regarded as the best available technology. When SO_2 and NO_x are treated separately by these technologies, it leads to increasing the investment and operating costs. To overcome this problem, there have been many attempts such as nonthermal plasma technology, electron beam irradiation technology and adsorption technology to remove SO_2 and NO_x at the same time, but only few commercial applications are reported [6–8].

The main component of NO_x (NO plus NO_2) in most practical exhaust gases is NO. Unlike NO having low solubility, NO_2 is highly soluble in water. Thus, if NO is converted into NO_2, it can be further treated by a wet method. The desirable mode of NO_x removal from exhaust gases by a wet method may be the reduction to N_2. One feasible method to reduce NO_x to N_2 is to use a reducing agent such as sodium sulfide (Na_2S) [9]. Sodium sulfide can reduce NO_2 to N_2 while it is converted into sodium sulfate (Na_2SO_4) that is a nontoxic compound. Sodium sulfide can also remove SO_2 effectively, which makes it possible to treat NO_x and SO_2, simultaneously. In order to take advantage of this wet reduction technique, NO in the exhaust gas should be converted into NO_2, prior to contacting with the reducing agent solution. An easily available means to convert NO into NO_2 may be the injection of ozone into the exhaust gas.

Ozone can be efficiently produced by dielectric barrier discharge (DBD) [10]. In the previous study [11], it has been found that the ozone injected into the exhaust gas reacts fast with NO in a wide range of temperature before getting decomposed into O_2 and O. Moreover, it has been shown that the ozone injection method is more energy-efficient for the oxidation of NO to NO_2 than typical nonthermal plasma process directly applied to the exhaust gas. Thus, the combination of the ozone injection method with the wet reduction technique may be a potential way to remove NO_x effectively.

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In this work, the removal of NO_x by using the ozone injection method and the reducing agent was investigated. For the present system, a DBD device using ac high voltage was employed as the ozone generator. The performance of the combined process (ozone injection method plus wet reduction technique) for the removal of NO_x was evaluated using a simulated exhaust gas. It was also a matter of concern how much the removed NO_x is reduced to N_2, which was estimated by measuring the concentration of total nitrogen species in the reducing agent solution after processing. Besides, the reducing agent (Na_2S) can form hydrogen sulfide (H_2S), depending on the pH of the reducing agent solution. To prevent the emission of H_2S by adjusting the pH, sodium hydroxide (NaOH) was used together with the reducing agent in some experiments.

2. Experimental

The schematic diagram of the semi-batch type experimental apparatus consisting of a DBD device to generate ozone, an ozonizing chamber to mix the exhaust gas and ozone, and an absorber is shown in Fig. 1. Ozone produced in the DBD device was continuously fed to the ozonizing chamber to convert NO into NO_2, and then the exhaust gas modified in the ozonizing chamber was directed to the absorber containing an aqueous sodium sulfide solution where NO_2 was reduced to N_2. A cylindrical glass tube whose inner diameter and length are 2.5 cm and 50 cm was used as the ozonizing chamber. The effective volume of the ozonizing chamber was calculated to be 245 cm^3. The DBD device employed as the ozone generator was described in detail in the preceding study [11]. The voltage applied to the DBD device was varied from 15 to 26 kV (peak value) to change the amount of ozone generated. The DBD device was operated at room temperature. The feed gas to generate ozone molecules in the DBD device was air.

The simulated exhaust gas was prepared by mixing air and small amount of concentrated NO gas (5.0% (v/v) balanced with N_2). The flow rate of the concentrated NO gas was controlled by a mass flow controller (MFC, Model 1179A, MKS Instruments Inc., USA). In the simulated exhaust gas, a small portion (about 4–6%) of NO was naturally oxidized to NO_2 due to the presence of oxygen. The inlet concentrations of NO_x ($NO + NO_2$) was adjusted to 300 ppm (parts per million, volumetric; 1 ppm corresponds to 4.1×10^{-5} mol/m^3 at 25 °C and 1.0 atm). The flow rate of the simulated exhaust gas prepared as mentioned above was 8.33×10^{-5} m^3/s (5 L/min) on the basis of room temperature. The residence time of the exhaust gas in the ozonizing chamber was 2.9 s.

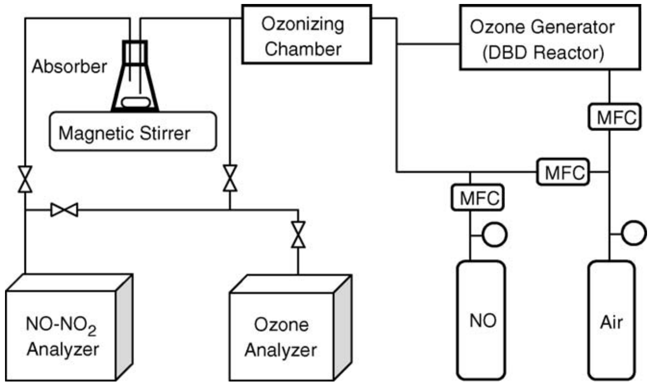

Fig. 1. Schematic diagram of the experimental apparatus.

The amount of NO converted into NO_2 was changed by the amount of ozone produced in the DBD device, i.e., the higher ac voltage applied to the DBD device was, the more ozone was produced, thereby converting more NO into NO_2 in the ozonizing chamber placed before the absorber. Sodium sulfide was purchased from Mallinckrodt Laboratory Chemicals (USA) in a hydrated form ($Na_2S{\cdot}9H_2O$). The products of the reaction between the reducing agent and NO_2 are N_2 and sodium sulfate (Na_2SO_4). Sodium sulfate is a nontoxic water-soluble compound. The reducing agent was dissolved in 600 mL distilled water, and the aqueous reducing agent solution prepared was poured into the absorber. The initial concentration of the reducing agent in the absorber was 0.6% (w/w). When the simulated exhaust gas was passing through the absorber, the reducing agent solution was well mixed by a magnetic stirrer. So as to estimate the distribution ratio of the amount of NO_x reduced to N_2 to that simply dissolved, the concentrations of NO_2^- and NO_3^- in the reducing agent solution were analyzed.

The NO and NO_2 concentrations were analyzed by a chemiluminescence NO–NO_2–NO_x analyzer (Model 42C, Thermo Environmental Instruments Inc., USA). For the measurement of the concentration of ozone, a portable gas analyzer (Porta Sens II, Analytical Technology Inc., USA) was used. The concentration of hydrogen sulfide was measured by a chemical detector (Product number 4HM, Gastec Co., Japan). The concentrations of NO_2^- and NO_3^- in the reducing agent solution after processing were analyzed by brucine colorimetric method and diazotization colorimetric method, respectively [12].

3. Results and discussion

3.1.1. Oxidation of NO by ozone

The experiments on the oxidation of NO to NO_2 were conducted using the ozone injection method. In most practical exhaust gases, NO forms the majority of NO_x. When ozone is injected into the ozonizing chamber, NO in the exhaust gas is oxidized to NO_2 by the following reaction:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

Fig. 2 shows the concentrations of NO and NO_2 obtained by varying the concentration of ozone added to the exhaust gas. The solid lines in Fig. 2 are the concentrations of NO and NO_2 calculated by the mathematical model developed in the preceding study [11]. The oxidation of NO to NO_2 is chiefly dependent on the amount of ozone added to the exhaust gas. As can be seen, the concentration of NO decreased in proportion to the increase in the concentration of ozone added, producing NO_2. The results in Fig. 2 strongly suggest that the present ozonizing method can successfully be used for the oxidation of NO to NO_2.

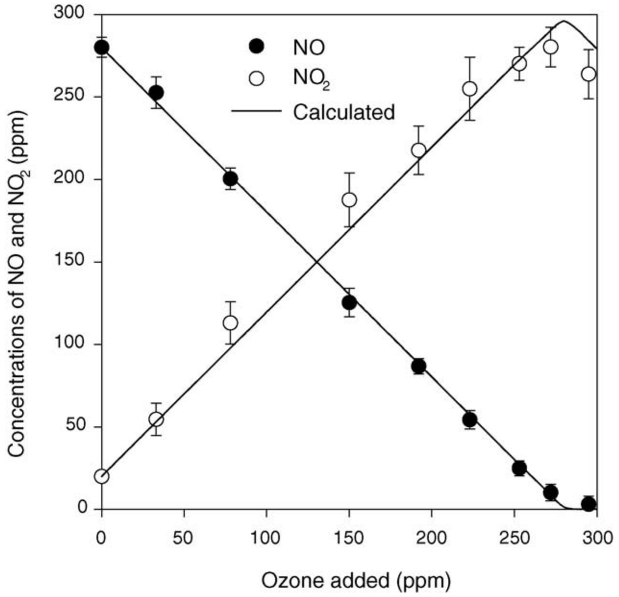

Fig. 2. Concentrations of NO and NO_2 obtained by varying the amount of ozone added to the exhaust gas.

3.2. Removal of NO_x

The simulated exhaust gas was first treated in the ozonizing chamber to produce NO_2, as described above, and then the modified exhaust gas (NO_2-rich exhaust gas) was directed to the absorber containing reducing agent. At the inlet of the absorber (at the outlet of the ozonizing chamber), the concentrations of NO and NO_2 were 10 ± 5 and 290 ± 10 ppm, respectively.

The reducing agent in the absorber to reduce NO_2 to N_2 was 0.6% (w/w) sodium sulfide nonahydrate ($Na_2S{\cdot}9H_2O$). The reaction between NO_2 and Na_2S is as follows:

$$2NO_2 + Na_2S \rightarrow N_2 + Na_2SO_4 \tag{2}$$

According to reaction (2), the reducing agent Na_2S can take four oxygen atoms from NO_2, being converted into Na_2SO_4 that is a nontoxic compound. In the preliminary experiment, the NO_x removal efficiency without the injection of ozone was found to be less than 10%, indicating that NO should be converted into NO_2 for effective removal.

The concentration profiles of NO and NO_2 at the outlet of the absorber are presented in Fig. 3. As observed, the concentration of NO_2 as well as NO was kept low in the early stage because it was effectively removed by reaction (2). However, at about 120 min, the concentration of NO abruptly increased, and the emission of H_2S was observed. At this time, the pH of the reducing agent solution decreased to below 10. This result can be attributed to the increase in the concentration of inorganic acids. When the concentration of remaining Na_2S is sufficiently high, NO_2 is mostly reduced to N_2 by reaction (2). But, as the reducing agent is consumed, NO_2 dissolved in the aqueous solution can form HNO_2 and HNO_3, instead of being reduced toN_2:

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3 \tag{3}$$

$$HNO_2 \rightarrow H^+ + NO_2{}^- \tag{4}$$

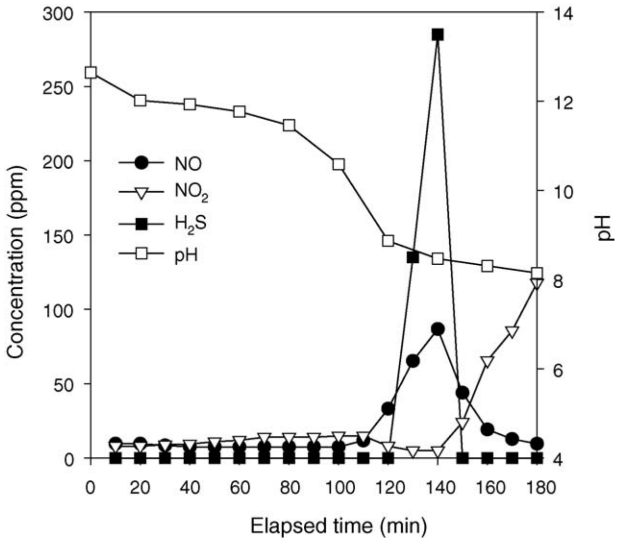

Fig. 3. Concentrations of NO, NO_2 and H_2S at the outlet of the absorber, and pH variation of the reducing agent solution ($Na_2S{\cdot}9H_2O$: 0.6% (w/w)).

$$HNO_3 \rightarrow H^+ + NO_3{}^- \tag{5}$$

The proton relieved from the acids reacts with the reducing agent to form hydrogen sulfide as below

$$Na_2S + 2H^+ \rightarrow H_2S + 2Na^+ \tag{6}$$

In addition, the reaction between Na_2S and nitric acid can produce NO as follows:

$$3Na_2S + 8HNO_3 \rightarrow 6NaNO_3 + 3S + 2NO + 4H_2O \tag{7}$$

Reactions (3)–(7) may explain why NO and H_2S increased after a lapse of 120 min, despite the fixed concentrations of NO and NO_2 at the inlet of the absorber. In this context, it is important to maintain the concentration of the acids as low as possible.

The equilibria of sodium sulfide system can be expressed in terms of its stepwise protolysis [13]:

$$S^{2-} + H^+ \rightarrow HS^-, \quad K_1 = \frac{[H^+][S^{2-}]}{[HS^-]} = 1.3 \times 10^{-13} \tag{8}$$

$$HS^- + H^+ \rightarrow H_2S, \quad K_2 = \frac{[H^+][HS^-]}{[H_2S]} = 1.0 \times 10^{-7} \tag{9}$$

From Eqs. (8) and (9), the fractional compositions of H_2S, HS^- and S^{2-} can be written as

$$\frac{[H_2S]}{F} = \frac{[H^+]^2}{[H^+]^2 + K_2[H^+] + K_1K_2} \tag{10}$$

$$\frac{[HS^-]}{F} = \frac{K_2[H^+]}{[H^+]^2 + K_2[H^+] + K_1K_2} \tag{11}$$

$$\frac{[H_2S]}{F} = \frac{K_1K_2}{[H^+]^2 + K_2[H^+] + K_1K_2} \tag{12}$$

where F is $[H_2S] + [HS^-] + [S^{2-}]$. In Fig. 4, the fractional composition of each component calculated using Eqs. (10)–(12) is shown as a function of pH. As can be seen, the fraction of H_2S increases as pH decreases. At pH below 5.0, H_2S is

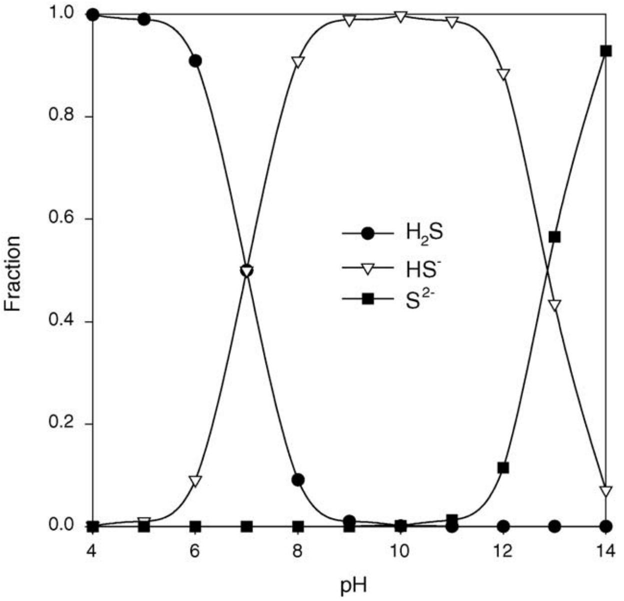

Fig. 4. Fractional compositions of H_2S, HS^- and S^{2-} as a function of pH.

predominant while no H_2S is present at pH higher than 10. From Fig. 4, it is evident that H_2S will not form, provided that pH is kept sufficiently high. In this context, it is important to maintain pH to above 10 during the treatment. One simple method to keep the alkalinity of the reducing agent solution is to use a basic reagent such as NaOH, together with the reducing agent.

Fig. 5 shows the concentration profiles of NO and NO_2 when 0.3% (w/w) NaOH was used together with the reducing agent. In this case, the concentration of NO did not increase during the experiment, and the formation of H_2S was not observed. This result is obviously due to the suppression of reactions (6) and (7) by NaOH. The increase in the concentration of NO_2 after 140 min resulted from the depletion of the reducing agent. As can be seen, the pH of the reducing agent solution was around 12 throughout the experiment.

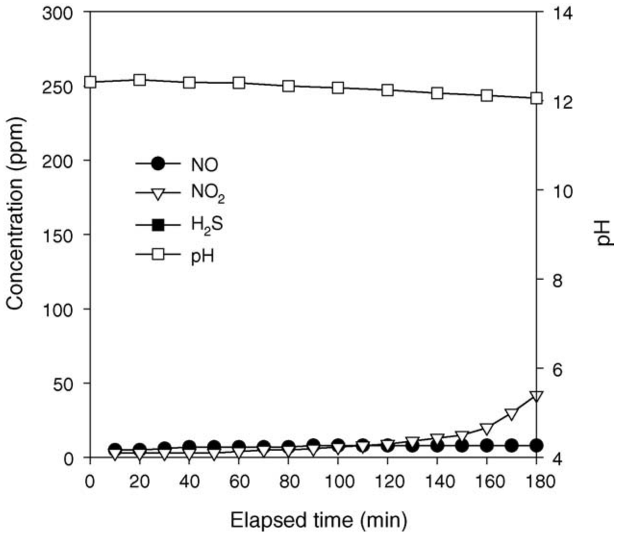

Fig. 5. Concentrations of NO, NO_2 and H_2S at the outlet of the absorber, and pH variation of the reducing agent solution ($Na_2S{\cdot}9H_2O$: 0.6% (w/w); NaOH: 0.3% (w/w)).

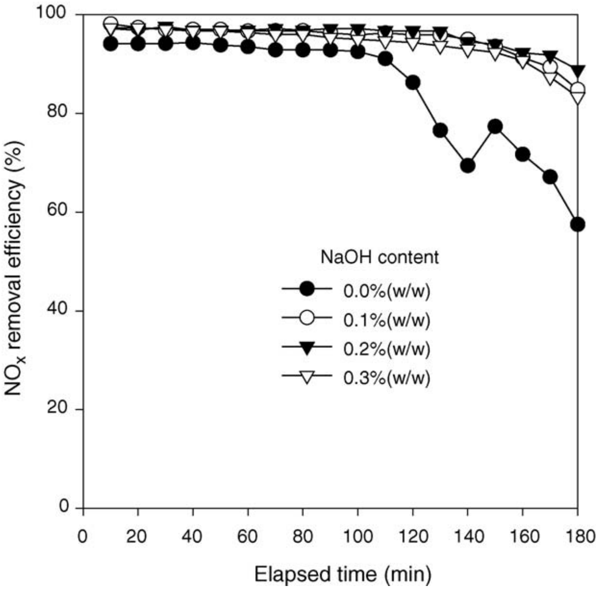

Fig. 6. Effect of NaOH concentration on the NO_x removal efficiency ($Na_2S{\cdot}9H_2O$: 0.6% (w/w)).

The effect of NaOH concentration on the NO_x removal efficiency is given in Fig. 6. The concentration of sodium sulfide nonahydrate was fixed at 0.6% (w/w), and the concentration of NaOH was varied up to 0.3% (w/w). In the absence of NaOH, the NO_x removal efficiency abruptly decreased at about 120 min, and increased again. This result is related to the formation of NO by reaction (7) (see also Fig. 3). On the other hand, in the presence of NaOH, abrupt decrease in the NO_x removal efficiency was not observed because the alkalinity of the reducing agent solution during the treatment was kept sufficiently high. Besides, in the range of 0.1–0.3% (w/w), the NO_x removal efficiency was not dependent on the concentration of NaOH. The decrease in the NO_x removal efficiency after 140 min in the presence of NaOH was due to the increase in the concentration of NO_2, resulting from the depletion of the reducing agent.

In Fig. 7, the concentrations of $NO_2{}^-$, $NO_3{}^-$ and total nitrogen (TN:$NO_2{}^- + NO_3{}^-$) in the reducing agent solution are given as a function of time elapsed. Before 120 min, $NO_2{}^-$ was kept very low and $NO_3{}^-$ was around 30 mg/L. On the other hand, at 120 min, the concentration of $NO_2{}^-$ and also the concentration of total nitrogen rapidly increased, implying that sodium sulfide to reduce NO_2 to N_2 was almost depleted. As can be seen in Fig. 3, NO and H_2S started to be formed at about 120 min, which almost coincided with this result. According to the stoichiometric calculation using reaction (2), the depletion of the reducing agent should take place four times later than this result. The reason for the faster depletion of the reducing agent is due to the presence of oxygen in the simulated exhaust gas. Sodium sulfide reacts with oxygen as follows:

$$Na_2S + 2O_2 \rightarrow Na_2SO_4 \qquad (13)$$

Putting all data together, the amount of sodium sulfide required should be about four times the value calculated

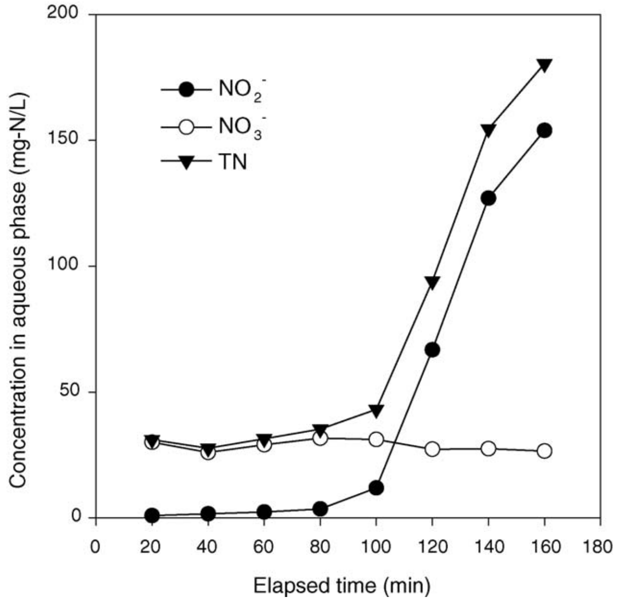

Fig. 7. Concentrations of nitrite and nitrate in the reducing agent solution with the elapsed time ($Na_2S{\cdot}9H_2O$: 0.6% (w/w); NaOH: 0.1% (w/w)).

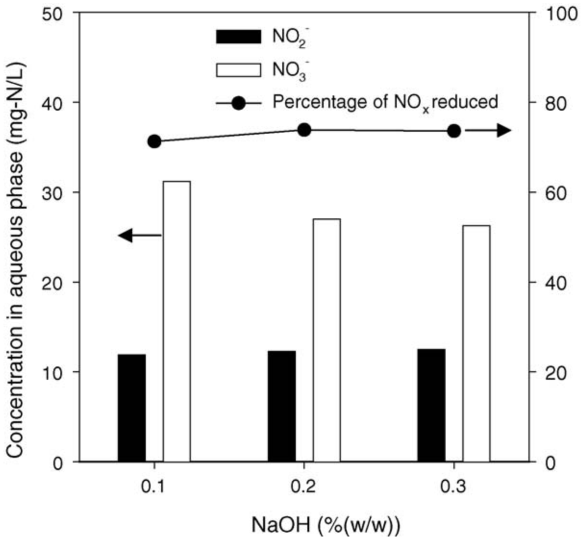

Fig. 8. Concentrations of nitrite and nitrate in the reducing agent solution after 100 min, and percentage of the removed NO_x reduced to N_2 at different NaOH concentrations ($Na_2S{\cdot}9H_2O$: 0.6% (w/w)).

by reaction (2), i.e., about three fourth of sodium sulfide is consumed through the reaction with oxygen.

As shown above, the present ozone injection and wet reduction technique was very effective for the treatment of NO_x, showing high removal efficiency more than 95%. But, it was not clear how much the removed NO_x was reduced to N_2, which can be estimated by measuring the concentration of the total nitrogen species dissolved in the reducing agent solution. Fig. 8 presents the concentrations of NO_2^- and NO_3^- in the reducing agent solution after an elapsed time of 100 min. In this figure, the percentage of the removed NO_x that was reduced to N_2 is also given, which was calculated by a material balance, i.e., total molecules of NO_x removed from the exhaust gas minus those of nitrogen species ($NO_2^-+NO_3^-$) is equal to the amount of NO_x reduced to N_2. As can bee seen, it was found that about 75% of the removed NO_x was reduced to N_2 regardless of the concentration of NaOH.

4. Conclusions

Dielectric barrier discharge is an easily available method to produce ozone that is a strong oxidant. When ozone was injected into the exhaust gas, NO, which is the main component of nitrogen oxides (NO_x), was rapidly oxidized to NO_2. In the next step, the NO_2 formed was reduced to N_2 by sodium sulfide used as the reducing agent. The two-stage process proposed in this study was very effective for the removal of NO_x. When the exhaust gas passed through the ozonizing chamber and the absorber containing the reducing agent sequentially, more than 95% NO_x removal efficiency was obtained. The rate of depletion of the reducing agent during the treatment of the exhaust gas was much faster than that expected by reaction stoichiometry, obviously due to the oxygen in the exhaust gas. The amount of sodium sulfide required was found to be about four times the amount of NO_x removed. The formation of H_2S from Na_2S was able to be avoided by adjusting the pH of the reducing agent solution using NaOH. The analysis of the concentrations of NO_2^- and NO_3^- in the reducing agent solution after processing showed that about 75% of the NO_x removed from the exhaust gas was reduced to N_2.

Acknowledgment

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