Study on the removal of NO_x from simulated flue gas using acidic $NaClO_2$ solution

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Abstract

The study on the removal of NO_x from simulated flue gas has been carried out in a lab-scale bubbling reactor using acidic solutions of sodium chlorite. Experiments were performed at various pH values and inlet NO concentrations in the absence or presence of SO_2 gas at 45°C. The effect of SO_2 on NO oxidation and NO_2 absorption was critically examined. The oxidative ability of sodium chlorite was investigated at different pH values and it was found to be a better oxidant at a pH less than 4. In acidic medium, sodium chlorite decomposed into ClO_2 gas, which is believed to participate in NO oxidation as well as in NO_2 absorption. A plausible NO_x removal mechanism using acidic sodium chlorite solution has been postulated. A maximum NO_x removal efficiency of about 81% has been achieved.

Key words: bubbling reactor; acidic sodium chlorite; flue gas; NO_x removal

Introduction

The combustion of fossil fuels in the stationary sources such as power plants, incinerators, and boilers, leads to the emission of sulfur oxides (SO_x) and nitrogen oxides (NO_x), which are the most pervasive air pollutants. The emission of SO_x and NO_x is a major environmental concern because of their hazardous effects on human health and the ecosystems. NO_x are particularly responsible for atmospheric ozone depletion (Karlsson, 1997), smog and visibility problems. Therefore, an efficient technology for the reduction of NO_x emissions from both stationary and mobile sources is highly desirable.

The most effective technology for the SO_2 removal is flue gas desulphurization (FGD) process. Although the wet FGD process has attained high SO_2 removal efficiency, yet it is not much effective for NO_x removal. Technologies for the NO_x removal can be divided into combustion control and flue gas cleansing processes. Combustion control aims at reducing the NO_x formation during combustion of fossil fuel. Flue gas treatment includes selective non-catalytic reduction (SNCR), selective catalytic reduction (SCR), wet scrubbing, adsorption and electron beam irradiation and so on. Among these technologies, scrubbing methods are economically the most competitive and have advantage of controlling other acid gases and particulates at the same time (Yang et al., 1996).

Wet scrubbing process for the removal of SO_2 currently dominates the market so a minor adjustment in it for the simultaneous removal of SO_2 and NO_x will prove more compact and cost effective technology for the future. NO_x removal in the wet scrubbing is quite complicated due to numerous parallel and consecutive reactions occurring in the solution phase. NO accounts for more than 90% of NO_x in the flue gas. The inert nature of NO has posed a persistent problem for industry. The solubility of NO decreases with increasing temperature and is independent of pH over a wide range. The low solubility of NO in aqueous solution appreciably increases the liquid phase resistance to mass transfer. In general, additives are added into wet scrubber to first convert the relatively water insoluble NO to fairly soluble NO_2 which can be further removed by alkaline absorbents.

Aqueous solutions of numerous oxidants such as hydrogen peroxide (Baveja et al., 1979), metal chelates (Chang and Littlejohn, 1983), $KMnO_4$ (Sada et al., 1977; Brogen et al., 1997; Chu et al., 1998), chlorine dioxide (Jin et al., 2006) and sodium chlorite (Sada et al., 1978a, b, 1979a, b; Brogen et al., 1998; Yang and Shaw, 1998; Hsu et al., 1998; Adewuyi et al., 1999; Chien and Chu, 2000; Chu et al., 2001; Lee et al., 2005) have been investigated to determine their effectiveness in the removal of NO_x. Sodium chlorite has proved the most efficient oxidant among them. A great deal of efforts has been made on NO oxidation and NO_x removal using sodium chlorite
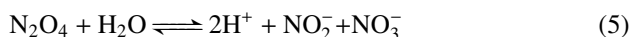
in the alkaline medium. Literature survey reveals that the studies on NO_x removal using acidic sodium chlorite solution are lacking. Sodium chlorite has poor oxidative ability in alkaline medium; therefore it may not be as effective oxidant for NO oxidation in alkaline medium as in acidic medium. With this view, we attempted to investigate the effect of various operating variables on NO_x removal efficiency using acidic $NaClO_2$ solution in a lab-scale bubbling reactor.

1 Experiments and methods

1.1 Solution chemistry involved in the NO_x removal

The mechanism of NO_x removal in the wet scrubbing involves numerous parallel and consecutive reactions. In acidic medium, it is assumed that sodium chlorite mainly works as an agent to oxidize NO into NO_2 (Brogen *et al*., 1998). Further absorption of NO_2 is believed to takes place via hydrolysis of N_2O_3 or N_2O_4 (Decanini *et al*., 2000; Thomas and Vanderschuren *et al*., 2000). The stoichiometry of various reactions involved in the NO_x removal can be expressed as:

$$2NO + ClO_2^- \longrightarrow 2NO_2 + Cl^- \tag{1}$$

$$NO + NO_2 \rightleftharpoons N_2O_3 \tag{2}$$

$$2NO_2 \rightleftharpoons N_2O_4 \tag{3}$$

$$N_2O_3 + H_2O \rightleftharpoons 2H^+ + 2NO_2^- \tag{4}$$

$$N_2O_4 + H_2O \rightleftharpoons 2H^+ + NO_2^- + NO_3^- \tag{5}$$

1.2 Experimental

The experimental set up used for the removal of NO_x is shown in Fig.1. It is composed of simulated flue gas supply system, bubbling reactor, pH control system, ClO_2 absorber, data acquisition system, and sampling cum analysis system.

The simulated flue gas was obtained by controlled mixing of SO_2, NO and N_2 gas using mass flow controllers (MFC). Reactor (internal volume = 8 L) was made up of acrylic material. The diameter and height of the reactor were 15 and 45 cm, respectively. Continuous stirring was provided by mechanical agitator with a speed of 250 r/min. Temperature of the reaction vessel was controlled within 45 ± 0.1°C. The pH of reaction solution was controlled by using an auto-pH control system (KFC-MK-250, S. Korea) by continuous addition of H_2SO_4 or NaOH solution with the help of peristalsis pump (Cole Parmer Co., USA). The chlorine-dioxide absorber (2 L vessel) consisted of 2% carbonate buffered potassium iodide solution (1.5 L). The detailed experimental conditions for the present study are given in Table 1.

Table 1   Experimental conditions for system

Variable	Range
Volume of reactor (L)	5
pH of solution	2.5–7.5
Reaction temperature (°C)	45
SO_2 input concentration (ppmv)	360–1400
NO input concentration (ppmv)	360–760
$NaClO_2$ concentration (mol/L)	0.05–0.2
Flue gas flow rate (L/min)	45
Forced air flow rate (L/min)	5

1.2.1 Materials

Standard gases included N_2 (99%), SO_2 span gas (99%) and NO span gas (99.9%). N_2 and SO_2 were the products of Anjeon Gas Co., Korea and NO was the product of Mathieson, Co., Germany. Sodium chlorite (98%, Junsei
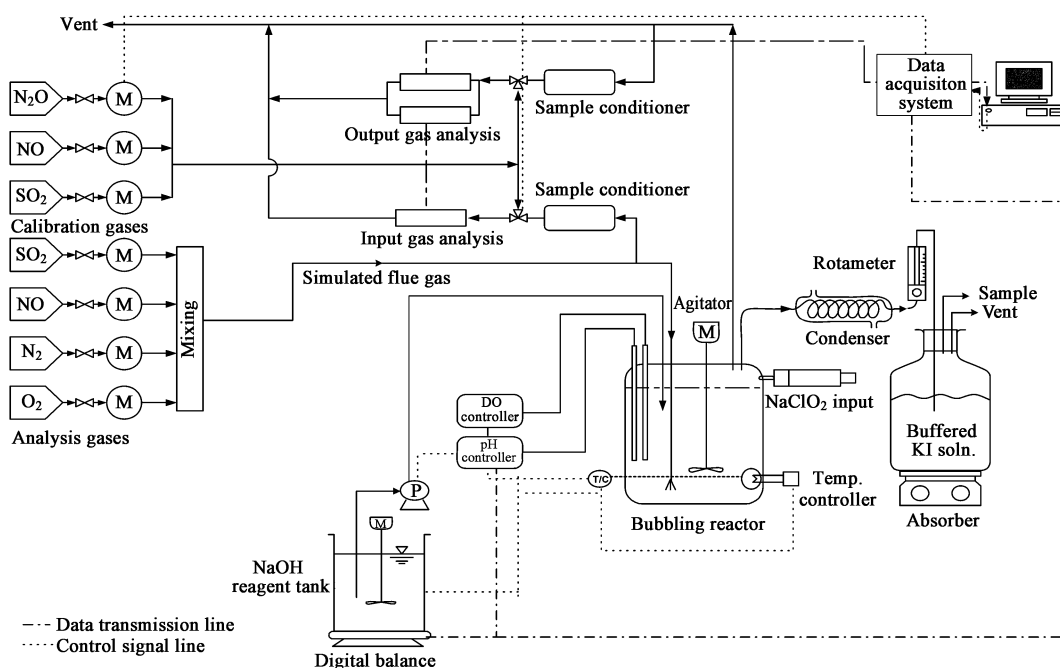

Fig. 1   A schematic diagram for removal of NO_x from the simulated flue gas.

Chemical Co. Ltd., Japan), sulfuric acid (98%, PFP, Osaka, Japan), potassium iodide (99.5%, Samchun Pure Chem. Co. Ltd., Korea) and sodium thiosulfate (99%, Shinyo Pure Chem. Co. Ltd., Osaka, Japan) were the analytical grade reagents used in the present study.

1.2.2 Analysis of gases, reaction solution and absorber solution

The inlet and outlet gas concentrations were analyzed after removing its moisture in the sample conditioner by the NO analyzer (Model-42C, Chemiluminescent type, Thermo Environmental Instruments Inc., USA) and SO$_2$ analyzer (Model-Ultramat 23, IR type, Siemens, Germany). O$_2$ concentrations were analyzed with help of dissolved oxygen (DO) meter (835A, Thermo Orion, USA). Chlorine-dioxide formed as a result of decomposition of sodium chlorite is carried out by nitrogen gas and is absorbed in carbonate buffered 2% KI solution. Samples from the bubbling reactor were analyzed by ion chromatograph (IC). Samples from chlorine dioxide absorber were titrated iodometrically against standard NTS solution using auto-titrator (Metrohm-Swiss). The potentiometric titration system included a 670 titroprocessor, 730 sample changer, 665 dosimat and Pt electrode.

2 Results and discussion

A series of experiments were carried out to investigate the NO$_x$ removal from simulated flue gas in presence/absence of SO$_2$ using acidic sodium chlorite solution in the lab scale bubbling reactor. The reactivity of the oxidative absorbent, NaClO$_2$, was examined at various pH values by measuring the inlet and outlet NO and NO$_2$ concentrations. The effect of various operating variables has been investigated on the NO oxidation and NO$_2$ absorption.

2.1 Removal of NO$_x$ in the absence of SO$_2$ using acidic sodium chlorite solution

Five liter solution of 0.05 mol/L NaClO$_2$ was taken in the reactor. Sufficient amount of acid was injected into reactor to achieve the desired initial pH. Experiments were
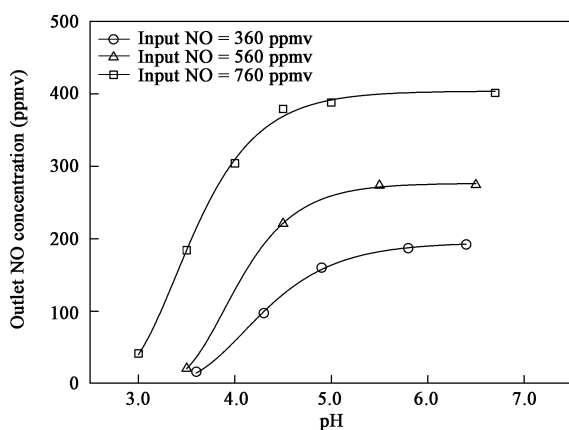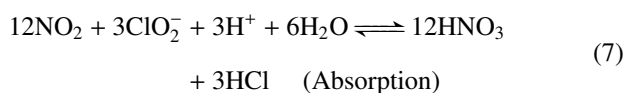
performed at various input NO concentrations (360, 560 and 760 ppmv) in the absence of SO$_2$ gas to investigate the oxidative power of NaClO$_2$ at different pH values. The concentration profile of outlet NO gas is presented in Fig.2. Outlet NO concentration increased with increasing pH. Almost 100% oxidation of NO occurred at a pH $\leqslant$ 3.5. It suggests that sodium chlorite has high oxidative ability at lower pH values.

Figure 3 depicts the variation in NO$_x$ removal efficiency with pHs at different input NO concentrations. NO$_x$ removal is about 50% at a pH $\leqslant$ 3.5 and it decreased on increasing pH. Authors (Brogen *et al.*, 1998) reported that chlorite is mainly consumed to oxidize NO into NO$_2$ and most of the nitrogen oxides are absorbed via hydrolysis of N$_2$O$_3$ and N$_2$O$_4$. Therefore it is suggested that pH of the reaction solution should be low enough to give chlorite high ability to oxidize, but high enough to allow the absorption via hydrolysis of N$_2$O$_3$ and N$_2$O$_4$. The pH of reaction solution is thus considered a crucial parameter. Although the hydrolysis of N$_2$O$_3$ and N$_2$O$_4$ (Eqs.(4) and (5)) is supposed to produce nitrite and nitrate ions, when the samples from the bubbling reactor were analyzed before and after the experiment using IC, it only confirmed the formation of nitrate and chloride ion, but showed no sign of formation of nitrite ion.

NaClO$_2$ has high oxidative ability in acidic medium. The absence of nitrite ions in the reaction solution in this study indicates that NO is completely oxidized into nitrate by acidic sodium chlorite solution. The NO$_x$ removal mechanism in acidic sodium chlorite solution thus is slightly different from that proposed for alkaline NaClO$_2$ solution and seems to involve following steps:

$$2NO + ClO_2^- + H^+ \rightleftharpoons 2NO_2 + HCl \quad \text{(Oxidation)} \quad (6)$$

$$12NO_2 + 3ClO_2^- + 3H^+ + 6H_2O \rightleftharpoons 12HNO_3 \\ + 3HCl \quad \text{(Absorption)} \quad (7)$$

The overall reaction obtained by combining above equations may be written as:

$$12NO + 9ClO_2^- + 9H^+ + 6H_2O \rightleftharpoons 12HNO_3 + 9HCl \quad (8)$$

Fig. 2 Outlet NO concentration at different pH values in the absence of SO$_2$ when NaClO$_2$ concentration was 0.05 mol/L, and temperature was 45°C.
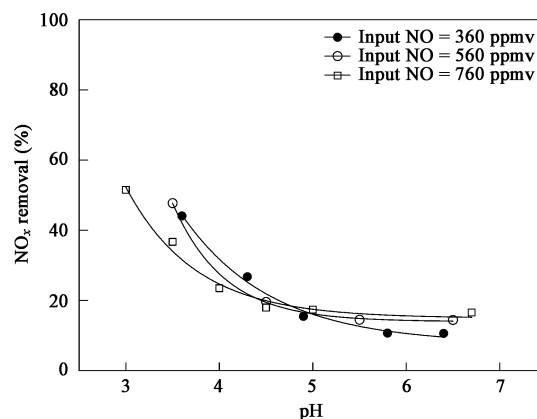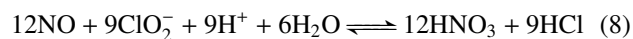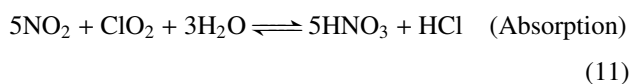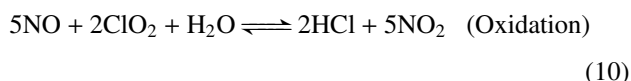

Fig. 3 NO$_x$ removal at different pHs in the absence of SO$_2$. Condition: NaClO$_2$ conc. 0.05 mol/L; temp 45°C.

Further, sodium chlorite has quite fast reaction kinetics in the acidic medium. It decomposes in the acidic medium producing chlorine-dioxide. The yellowish green color appeared in the reaction solution during the course of experiment indicating the formation of ClO_2. The decomposition of chlorite in acidic medium takes place as the literature (Deshwal *et al.*, 2004; Deshwal and Lee, 2005):

$$5ClO_2^- + 4H^+ \rightleftharpoons 4ClO_2 + Cl^- + 2H_2O \quad (Decomposition)$$

$$(9)$$
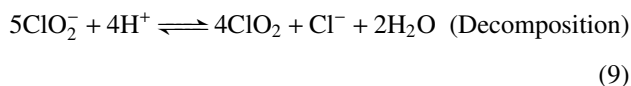
Chlorine-dioxide gas formed by decomposition of chlorite is a very strong oxidant. It is believed to oxidize NO into NO_2, which is subsequently absorbed in the form of nitrate as follows (Jin *et al.*, 2006; Deshwal *et al.*, 2007):

$$5NO + 2ClO_2 + H_2O \rightleftharpoons 2HCl + 5NO_2 \quad (Oxidation)$$

$$(10)$$

$$5NO_2 + ClO_2 + 3H_2O \rightleftharpoons 5HNO_3 + HCl \quad (Absorption)$$

$$(11)$$

The overall reaction obtained by combining Eqs.(10) and (11) may be written as:

$$5NO + 3ClO_2 + 4H_2O \rightleftharpoons 5HNO_3 + 3HCl \quad (12)$$
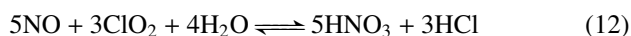
The NO_x removal using acidic sodium chlorite thus involves a complex combination of reactions wherein both chlorite as well as chlorine-dioxide acts as oxidative absorbents.

Although a major part of ClO_2 is used in oxidizing NO into nitrate, yet a part of it may escape away causing secondary pollution. Therefore, outlet gas stream was passed through an absorber containing 2% KI solution to analyze ClO_2 quantitatively. It was found that ClO_2 concentration in the outlet gas was negligible. It may be due to quite high solubility of ClO_2 gas in the aqueous solution. It helped us in deciding the optimum conditions to minimize the emanation of ClO_2 so that the rational utilization of the sodium chlorite can be made.

2.2 Removal of NO_x in the presence of SO_2 using acidic sodium chlorite solution

NO_x removal was performed at various input NO concentrations (350, 550 and 750 ppmv) and $NaClO_2$ concentration of 0.05 mol/L in presence/absence of SO_2. NO oxidation was about 94%–96% in the absence of SO_2 at a pH of 3.5. When NO_x removal was performed in presence of 360 ppmv of SO_2, 100% complete oxidation of NO occurred. The NO_2 absorption also increased about 5%–8% in the presence of SO_2 as shown in Fig.4. The 100% oxidation of NO may be attributed either to the catalytic effect of SO_2 (Littlejohn *et al.*, 1993) or to the formation of H_2SO_4 which consequently decreased the solution pH during the course of reaction and helped in relatively rapid decomposition of chlorite into chlorine dioxide. ClO_2 is well known strong oxidant (Jin *et al.*, 2006) and it not only supported oxidation of NO into NO_2 but also helped in absorption of NO_2 as suggested earlier in Eqs.(10) and (11).
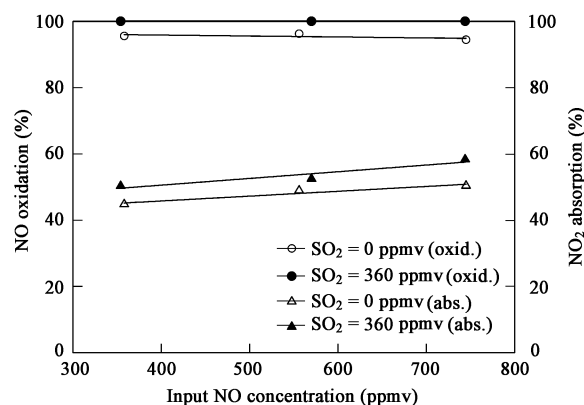

Fig. 4 NO oxidation and NO_2 absorption in the presence/absence of SO_2 at different input NO concentrations. Condition: $NaClO_2$ conc. 0.05 mol/L; Temp. 45°C; pH 3.5.

2.3 Effect of inlet SO_2 concentration on NO_x removal

To confirm the catalytic effect of SO_2 on the NO_x removal, some more experiments were performed at input NO concentration of 760 ppmv, $NaClO_2$ concentration of 0.2 mol/L, and pH of 4.0 at 45°C by varying the inlet SO_2 concentration. It was found that 100% oxidation of NO occurred after minimal loading of SO_2 as can be seen in Fig.5. NO_2 absorption also increased slowly (ca. 8%) with increasing SO_2 concentrations. It implies that SO_2 not only helped in oxidation of NO but also demonstrated marginal effect on NO_2 absorption. The enhanced NO oxidation seems to be due to the formation of acid, thereby lowering the pH. Sodium chlorite has higher oxidative ability at lower pHs, so it oxidized NO almost completely. The increased NO_2 absorption is probably due to the formation of intermediate sulfite ion, which promoted the NO_2 absorption via free radical mechanism proposed elsewhere (Littlejohn *et al.*, 1993). However, the strong oxidants (chlorite and chlorine dioxide) may have oxidized sulfite into sulfate and that is why NO_2 absorption did not improve much.
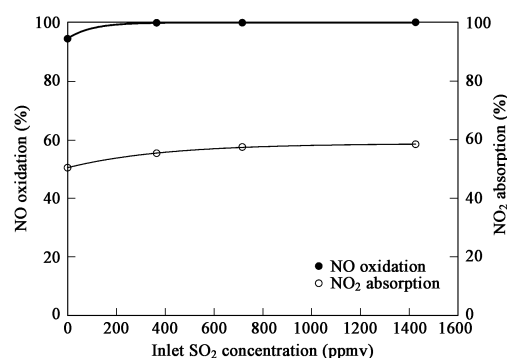

Fig. 5 Effect of inlet SO_2 concentration on NO_x removal efficiency. Condition: input NO 760 ppmv, $NaClO_2$ conc. 0.2 mol/L; temp. 45°C; pH 4.0.

2.4 Effect of pH on NO_x removal using acidic sodium chlorite solution

The oxidative power of sodium chlorite was critically examined by performing some experiments in the presence
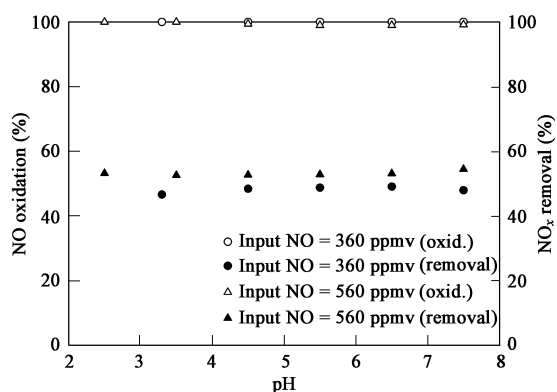
Fig. 6 NO oxidation and NO$_x$ removal at different pHs in presence of SO$_2$. Condition: NaClO$_2$ conc. 0.05 mol/L; temp. 45°C.

of SO$_2$ at different pH values at inlet NO concentration of 360 and 560 ppmv and inlet SO$_2$ concentration of 350 ppmv. NO was oxidized into NO$_2$ completely as shown in Fig.6. However, NO$_x$ removal did not improve with increasing pH as expected from higher absorption power of chlorite at higher pH values. It is attributed to the fact that absorption of NO$_2$ is markedly affected by sodium chlorite at higher pH values but is largely affected by chlorine dioxide at lower pH values. Therefore NO$_x$ removal remained more or less unaffected in the large range of pH as seen in Fig.6.

2.5 Role of chlorine dioxide in NO$_x$ removal

Experiments were carried out at input NO and SO$_2$ concentration of 350 and 360 ppmv respectively using relatively concentrated (0.2 mol/L) NaClO$_2$ solution. Sufficient amount of acid was injected into reactor to achieve the initial pH of 3.5. Fig.7 displays the outlet concentration of NO and NO$_2$ and the NO$_x$ removal efficiency with the passage of time.
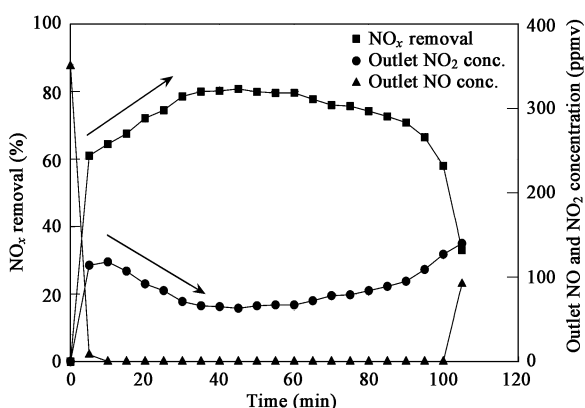

Fig. 7 NO$_x$ removal and concentration profile of NO, NO$_2$ with time. Condition: NaClO$_2$ conc. 0.2 mol/L; input NO 350 ppmv; input SO$_2$ 360 ppmv; temp. 45°C.

In the present study, initial pH is very low (3.5), therefore complete oxidation of NO into NO$_2$ is not unexpected as sodium chlorite has quite high oxidative ability at low pH value. However, absorption of NO$_2$ is favored by higher pH as suggested by earlier workers (Brogen *et al.*, 1998), therefore NO$_2$ absorption as well as NO$_x$ removal should

not be much high at the experimental pH of 3.5. On the contrary, NO$_x$ removal and the profile of outlet NO$_2$ concentration in Fig.7 reflected very interesting results. Even though concentrations of chlorite decreased with time due to its acidic decomposition into chlorine dioxide yet NO$_x$ removal increased in the beginning and attained a quite high NO$_2$ absorption efficiency of 81%. This initial increase in the NO$_x$ removal and decrease in outlet NO$_2$ concentration clearly demonstrates the role of ClO$_2$ in the NO$_2$ absorption at lower pH value.

3 Conclusions

The present study deals with the NO$_x$ removal from simulated flue gas using acidic sodium chlorite solution in the lab-scale bubbling reactor. The oxidative ability of sodium chlorite has been examined at various pH values in the absence or presence of SO$_2$ gas. SO$_2$ demonstrated catalytic effect on NO oxidation but it showed negligible effect on NO$_2$ absorption. In acidic medium, NaClO$_2$ mainly oxidized NO into NO$_2$. The presence of chlorine dioxide in acidic medium facilitated NO oxidation as well as NO$_2$ absorption. A plausible mechanism of NO removal using acidic sodium chlorite has been proposed, which involves several oxidation reactions.

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