Simultaneous removal of SO$_2$ and NO by wet scrubbing using aqueous chlorine dioxide solution

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Abstract

The present study attempts to generate chlorine dioxide (ClO$_2$) gas continuously by chlorate–chloride process and to utilize it further to clean up SO$_2$ and NO$_x$ gases simultaneously from the flue gas in the lab-scale bubbling reactor. Experiments were carried out to examine the effect of various operating parameters like input SO$_2$ concentration, input NO concentration, pH of the reaction medium, and ClO$_2$ feeding rate on the SO$_2$ and NO$_x$ removal efficiencies at 45 °C. Complete oxidation of NO into NO$_2$ occurred on passing sufficient ClO$_2$ gas into the scrubbing solution. SO$_2$ removal efficiency of about 100% and NO$_x$ removal efficiency of 66–72% were achieved under optimized conditions. NO$_x$ removal efficiency decreased slightly with increasing pH and NO concentration. Input SO$_2$ concentration had marginal catalytic effect on NO$_2$ absorption. No improvement in the NO$_x$ removal efficiency was observed on passing excess of chlorine dioxide in the scrubbing solution.
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1. Introduction

Fossil fuels, viz. coal, petroleum, and natural gas are the major sources of the energy. According to a statistical survey of Korea Energy Management Corporation (2002), petroleum, coal, and natural gas contributed 49.1, 23.5, and 11.1%, respectively, to the total energy generated by the various sources in Korea. Combustion of fossil fuels in the stationary sources such as power plants, incinerators, and boilers results into emission of SO$_2$ and NO$_x$. Though the flue gases from these sources mainly contain NO and NO$_2$ but the major component of NO$_x$ is NO (ca. 90%). Flue gas desulfurization (FGD) is the most widely used process that can remove SO$_2$ efficiently. However, NO cannot be as easily removed as SO$_2$. Technologies for NO$_x$ removal include combustion control and post-combustion treatment. Combustion control aims at reducing the NO$_x$ formation during combustion of fossil fuels. Post-combustion methods include selective non-catalytic reduction (SNCR), selective catalytic reduction (SCR), scrubbing, etc. Among these technologies, scrubbing methods are economically the most competitive and have advantage of controlling other acid gases and particulates at the same time [1].

In general, additives are added into scrubbing system first to convert relatively inert NO into NO$_2$, which can be removed by alkaline absorbents. Aqueous solutions of numerous oxidants have been investigated to determine their effectiveness in the removal of NO$_x$ [2–20], and sodium chlorite [7–17] has proved the most efficient oxidant among them. However, the drawback with sodium chlorite is that it has good oxidizing ability at lower pHs while the absorbing capability is good at higher pHs. Therefore, pH is a crucial parameter to oxidize NO into NO$_2$ and to absorb NO$_2$ thereafter. Secondly, it is relatively unstable and quite expensive chemical. It is produced itself by reduction of chlorine dioxide as follows:

$$2ClO_2 + H_2O_2 + 2NaOH \rightarrow 2NaClO_2 + O_2 + 2H_2O \qquad (1)$$
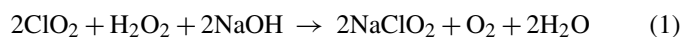
In the recent years, chlorine dioxide, a novel neutral oxy-chlorine species has attracted significant commercial attention not only due to environmental concern but also for its wide applications in the fields of bleaching, oxidation, and disinfection. It is commercially used in textile, paper, fat, and pulp bleaching, waste water treatment, water purification, removal of iron, manganese, H$_2$S,

and phenols from industrial wastes, medical treatment, sanitation, food processing, fumigation, deodorization, aquaculture, etc. The chlorine dioxide based bleaching process; the so-called ECF technology [21] has become quite popular in the production of bleached chemical pulps.

Chlorine dioxide is always generated on-site because of its unstable nature and risk of rapid decomposition. It can be produced from acid solutions of either sodium chlorite [22–27] or sodium chlorate [28–35]. Most of the small-scale generators use sodium chlorite as the precursor material. Other applications where large quantities of chlorine dioxide are needed, utilize sodium chlorate. Though the conditions for the production of ClO_2 from sodium chlorite can be controlled better than from sodium chlorate but chlorite is more expensive and chemically unstable. Therefore, from industrial point of view, sodium chlorate is more suitable raw material for ClO_2 generation.

Chlorine dioxide can be produced by reduction of chlorate with a wide variety of reducing agents in a relatively concentrated acidic media as follows:

$$ClO_3^- + 2H^+ + e^- \rightarrow ClO_2 + H_2O \qquad (2)$$
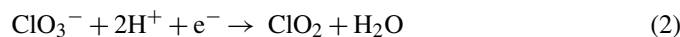
The choice of reducing agent is very important depending on the optimum reaction conditions, by-products, and the economics of the process. In all chlorate-based processes, chloride ion plays a crucial role. No chlorine dioxide is formed if chloride is not present in the reaction medium. With this view, we selected chlorate–chloride process to generate ClO_2 gas and further used this gas for the removal of SO_2 and NO from the flue gas. The general stoichiometry of chlorate–chloride process may be expressed as [31–35]:

$$4H^+ + 2ClO_3^- + 2Cl^- \rightarrow 2ClO_2 + Cl_2 + 2H_2O \qquad (3)$$

In our earlier work [32], we studied the kinetics and mechanism of the above process. This process is extremely simple to operate, responds immediately, and gives highest yield of ClO_2 at the lowest cost among all other commercial processes.

In the present study, ClO_2 has been utilized directly to oxidize NO. It not only reduced the cost but also solved the problem of pH adjustment. Chlorine dioxide, however, has been extensively used for oxidation, disinfection, and bleaching, but no reference is cited on its use in the simultaneous removal of SO_2 and NO. There is no doubt about the oxidizing capability of ClO_2. Standard oxidation potential of chlorine dioxide in gas and solution phase is -0.95 and -1.27 V, respectively [36]. It has the potential to oxidize NO into NO_2. Therefore with this aim, chlorine dioxide has been chosen to clean up NO_x and SO_2 simultaneously from the flue gas.

2. Experimental

The experimental system is divided into two parts, i.e., chlorine dioxide generation unit and flue gas treatment unit. A schematic diagram of the experimental system is shown in Fig. 1.
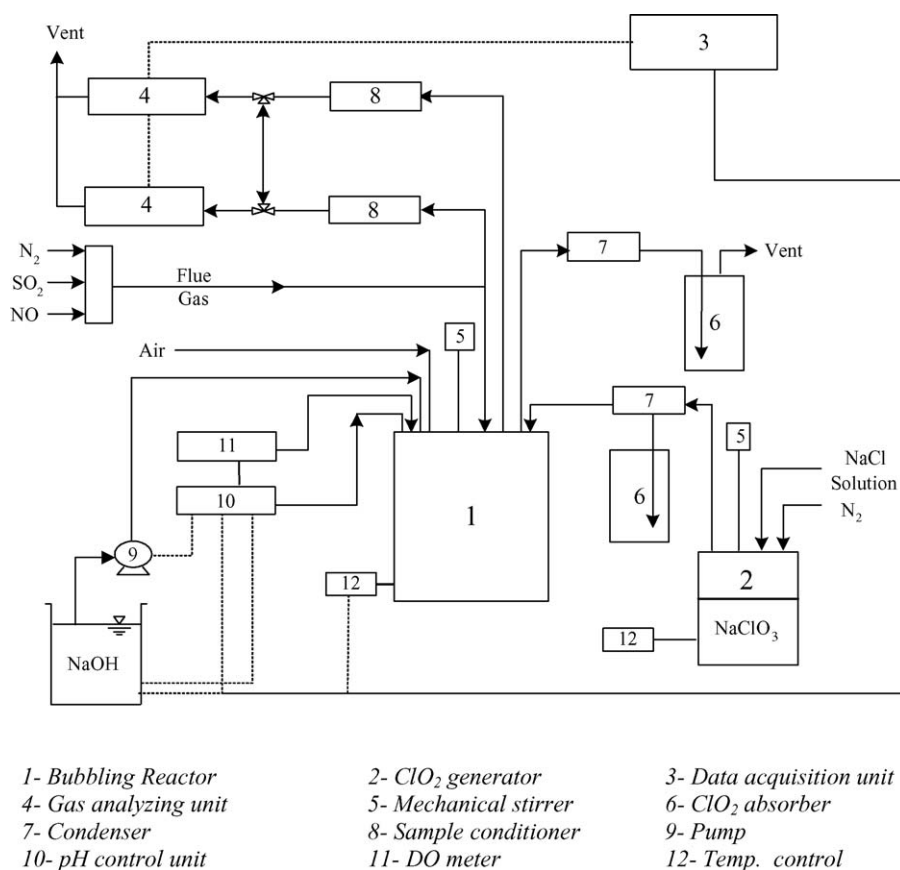

1- Bubbling Reactor
4- Gas analyzing unit
7- Condenser
10- pH control unit
2- ClO_2 generator
5- Mechanical stirrer
8- Sample conditioner
11- DO meter
3- Data acquisition unit
6- ClO_2 absorber
9- Pump
12- Temp. control

Fig. 1. A schematic diagram of lab-scale bubbling reactor for simultaneous removal of SO_2 and NO_x from simulated flue gas.

2.1. Chlorine dioxide generation unit

This unit composed of a reactor, which is well-stirred sealed vessel having total volume of 2.5 L. Concentrated sodium chloride solution (1–2 M) was continuously injected into reactor at a suitable flow rate (0.5–1.5 mL/min) by a syringe pump (Model-200, KDS Scientific Inc., USA). The reactor was filled with 1.5 L solution of sodium chlorate (0.2–0.4 M) in a relatively concentrated sulfuric acid (11–12N). Continuous stirring was provided by a mechanical agitator. Temperature of the reaction vessel was controlled within $45 \pm 0.1\,°C$ by water thermostat (WBC-1506D, JEIO TECH, Korea). The reactor was wrapped with an aluminium foil to avoid any photo-dissociation of chlorine dioxide. Nitrogen gas was purged through the reaction mixture using a bubbling device at a flow rate of 2 L/min. Chlorine dioxide carried by N_2 gas was further introduced into bubbling reactor.

2.2. Flue gas treatment unit

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 bubbling reactor is a well-stirred sealed vessel (ID, 15 cm; height, 45 cm) having internal volume of 8 L. The simulated flue gas was obtained by controlled mixing of SO_2, NO, and N_2 using mass flow controllers (MFC). Air was introduced into reactor using air pump to maintain the dissolved O_2 concentrations about 30–40% of the saturated O_2 concentrations. Continuous stirring was provided by a mechanical agitator (4 blades disc, turbine type impeller) with a speed of 250 rpm. Temperature of the reaction vessel was controlled within $45 \pm 0.1\,°C$. The pH of reaction solution was controlled by using an auto-pH control system (KFC-MK-250, Korea) by continuous addition of NaOH (0.2 M) solution with the help of peristalsis pump (Cole-Palmer Co., USA). The chlorine dioxide absorbers (2 L vessel) consisted of ca. 2% carbonate buffered potassium iodide solution (1.5 L). Samples from reactor and absorbers were analyzed either by ion chromatograph (IC) or by iodometric titration using auto-titrator (Metrohm-Swiss). The inlet and outlet gas concentrations were analyzed after removing its moisture in the sample conditioner by the SO_2 analyzer (Model-Ultramat 23, IR type, Siemens, Germany), NO_x analyzer (Model-42C, Chemiluminescent type, Thermo Environmental Instruments Inc., USA), and DO meter (835A, Thermo Orion, USA).

2.3. 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. Sodium chlorate (98%, Junsei Chemical Co. Ltd., Japan), sodium chloride (99.5%, Aldrich Chem. Co. Inc., USA), sulfuric acid (98%, PFP, Japan), potassium iodide (99.5%, Samchun Pure Chem. Co. Ltd., Korea), and sodium thiosulfate (99%, Shinyo Pure Chem. Co. Ltd., Japan) were the analytical grade reagents used in the present study.
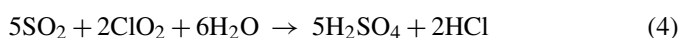
3. Results and discussion

The experiments for the simultaneous removal of SO_2 and NO were conducted by passing chlorine dioxide gas into the scrubbing solution. Effects of various parameters, viz. input NO and SO_2 concentration, ClO_2 feeding rate, and pH of reaction medium were investigated in a lab-scale bubbling reactor at 45 °C.

3.1. Simultaneous removal of sulfur dioxide and nitric oxide

Simultaneous removal of SO_2 and NO was studied at 45 °C, pH 3.5, and input SO_2 and NO concentration of 500 and 350 ppm, respectively. SO_2 and NO_x removal efficiencies and concentration profiles of various ions with the passage of time are presented in Fig. 2. It was observed that ClO_2 cleaned up both SO_2 and NO quite efficiently. ClO_2 oxidized NO into NO_2 completely and a consistent and reproducible NO_2 absorption efficiency of about 70% was observed. The $DeSO_x$ efficiency obtained at an optimum ClO_2 feeding rate of 0.82 mmol/min was almost 100%.

In the acidic medium, NO and SO_2 removal by chlorine dioxide is considered to follow the following mechanism [12,13]:

$$5SO_2 + 2ClO_2 + 6H_2O \rightarrow 5H_2SO_4 + 2HCl \tag{4}$$

$$5NO + 2ClO_2 + H_2O \rightarrow 5NO_2 + 2HCl \quad \text{(oxidation)} \tag{5}$$

$$5NO_2 + ClO_2 + 3H_2O \rightarrow 5HNO_3 + HCl \quad \text{(absorption)} \tag{6}$$

The overall reaction for the NO_x removal can be written as [12,13]:

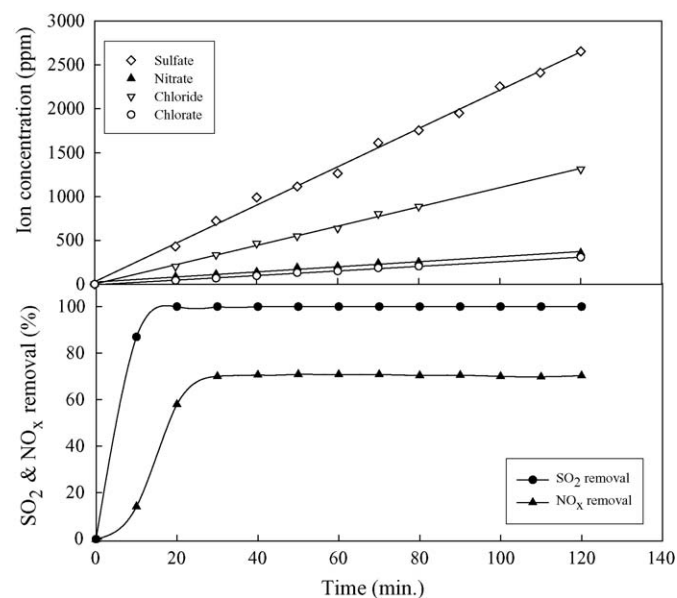$$5NO + 3ClO_2 + 4H_2O \rightarrow 5HNO_3 + 3HCl \tag{7}$$

Fig. 2. Simultaneous removal SO_2 and NO_x with time using ClO_2 at 45 °C, pH 3.5, ClO_2 feeding rate of 0.82 mmol/min, and input NO and SO_2 concentration of 350 and 500 ppm, respectively, also shown are the concentrations of various ions formed.
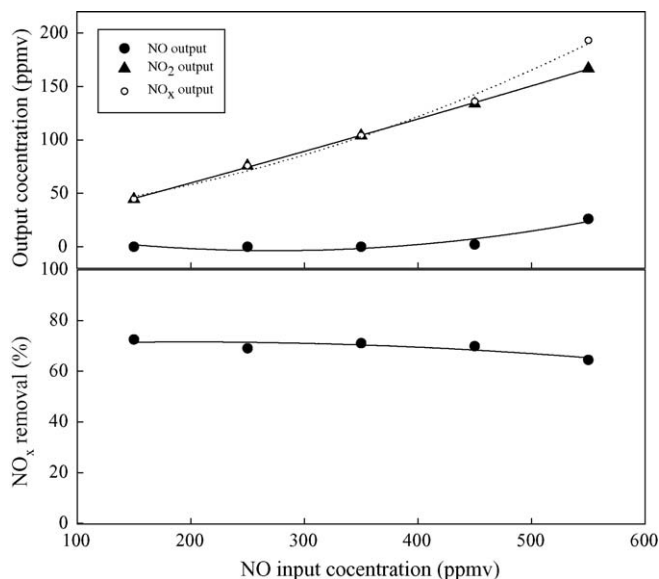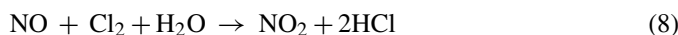
Fig. 3. Effect of input NO concentration on NO_x removal at 45 °C, pH 3.5, input SO_2 concentration of 500 ppm, and ClO_2 feeding rate of 1.11 mmol/min.

Chlorine gas produced along with chlorine dioxide as suggested in Eq. (3) is again a strong oxidant. Yang et al. [1] reported that chlorine is capable of oxidizing NO into NO_2 and nitrate. The stoichiometry of reaction between chlorine with NO can be expressed as [1]:

$$NO + Cl_2 + H_2O \rightarrow NO_2 + 2HCl \qquad (8)$$

$$2NO + 3Cl_2 + 4H_2O \rightarrow 2HNO_3 + 6HCl \qquad (9)$$

Formation of sulfate, nitrate, and chloride as suggested above was confirmed by analyzing the samples from bubbling reactor using an ion chromatograph.

3.2. Effect of input NO concentration

Effect of input NO concentration on the simultaneous removal of SO_2 and NO_x at 45 °C was investigated at input SO_2 concentration of 500 ppm, ClO_2 feeding rate of about 1.11 mmol/min, and pH 3.5. Fig. 3 displays the NO_x removal efficiency at various input NO concentrations. It was found that NO_x removal efficiency remained almost constant at around 70% when input NO concentration was increased from 150 to 550 ppm. The slight decrease in the end was due to insufficient ClO_2 feeding rate as reflected in the increase in output NO concentration.

3.3. Effect of input SO_2 concentration

Experiments were also carried out at 45 °C, pH 3.5, and input NO concentration of 350 ppm to investigate the effect of input SO_2 concentration on NO_x removal efficiency. As can be seen in Fig. 4, NO_x removal was around 66% in the absence of input SO_2. At input SO_2 concentration of 250 and 500 ppm, NO_x removal increased from 66 to about 70%. This enhancement in
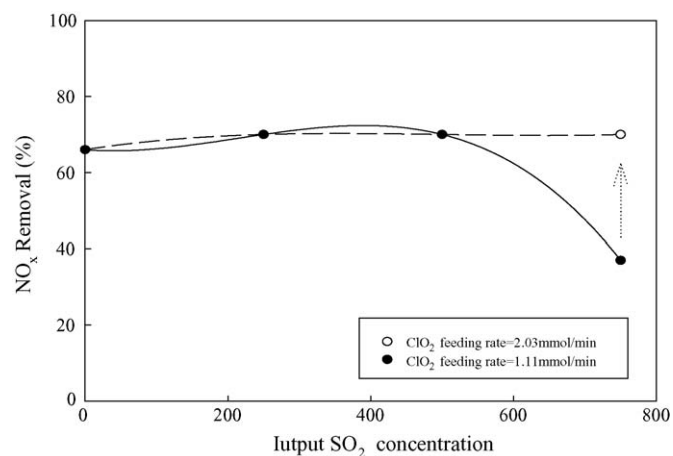

Fig. 4. Effect of input SO_2 concentration on NO_x removal at 45 °C, pH 3.5 and input NO concentration of 350 ppm.

NO_x removal is believed due to reaction of S(IV) species with nitrogen dioxide, consequently increasing the NO_2 absorption [37].

3.4. Effect of ClO_2 feeding rate

Some experiments were also performed to investigate the effect of ClO_2 feeding rate on SO_2/NO_x removal efficiency at 45 °C, pH 3.5, and input NO and SO_2 concentration of 350 and 500 ppm, respectively. It is clear from Fig. 5 that NO_x removal started only after achieving complete removal of SO_2. NO_x removal started above ClO_2 feeding rate of 0.55 mmol/min and thereafter increased sharply and attained a steady state. Complete oxidation of NO into NO_2 occurred on passing sufficient chlorine dioxide gas into scrubbing solution and the maximum $DeNO_x$ efficiency obtained was around 71%.
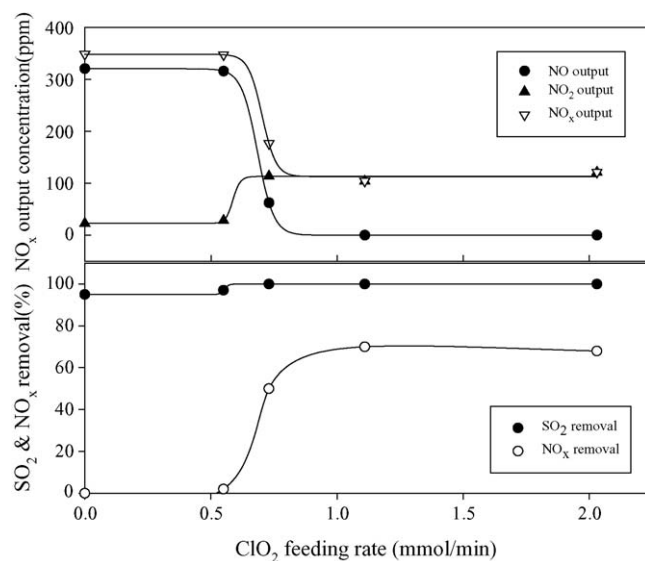

Fig. 5. Effect of ClO_2 feeding rate on SO_2/NO_x removal at 45 °C, pH 3.5, and input NO and SO_2 concentration of 350 and 500 ppm, respectively.
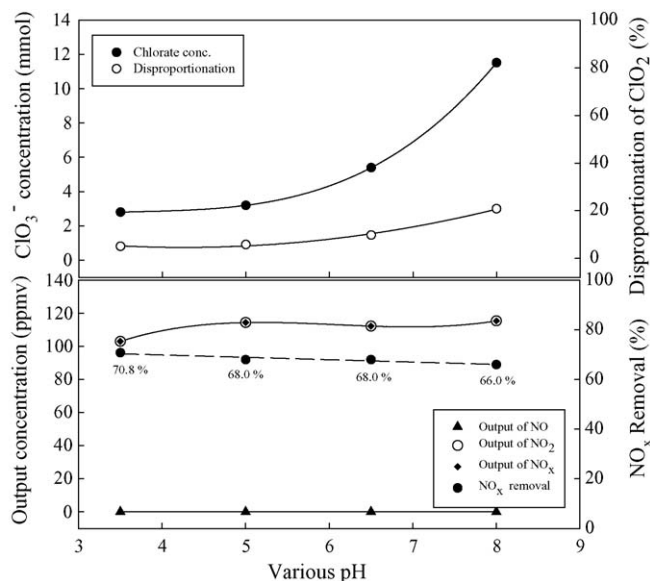
Fig. 6. Effect of pH on NO_x removal at $45\,^\circ C$, ClO_2 feeding rate of 1.11 mmol/min, input NO and SO_2 concentration of 350 and 250 ppm, respectively, also shown are the chlorate formed by the disproportionation of ClO_2.

3.5. Effect of pH

The pH of reaction medium is a crucial parameter when the NO_x removal is done using sodium chlorite solution. In the present study, pH of reaction medium was varied from 3.5 to 8 at constant input NO and SO_2 concentration of 350 and 250 ppm, respectively at $45\,^\circ C$ and its effect on NO_x removal, output NO, and NO_2 concentration is reported in Fig. 6. At constant ClO_2 feeding rate of about 1.11 mmol/min, the NO_x removal efficiency was found 70.8% at pH of 3.5 and it decreased slightly with increasing pH. It may be attributed due to disproportionation of ClO_2 at higher pH. When pH reaches neutrality, the disproportionation of chlorine dioxide [22,24,27] starts and it leads to formation of chlorite and chlorate as follows:

$$2ClO_2 + 2NaOH \rightarrow NaClO_2 + NaClO_3 + H_2O \qquad (10)$$
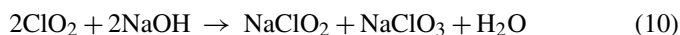
The chlorate formed is quite stable under these conditions but chlorite is again a strong oxidant and absorbent for NO and NO_2, respectively. Thus, the $NaClO_2$ produced in Eq. (10), is in situ utilized in the removal the NO from flue gas as follows:

$$4NO + 3NaClO_2 + 4NaOH$$
$$\rightarrow 4NaNO_3 + 3NaCl + 2H_2O \qquad (11)$$
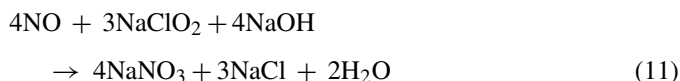
The mechanism of above reaction has been discussed earlier [7,11–14,17]. The chlorate concentration and percent disproportionation of ClO_2 at various pHs is shown in Fig. 6.

4. Conclusion

Chlorine dioxide proved quite promising additives for the simultaneous removal of SO_2 and NO. It exhibited almost 100% SO_2 removal, 100% NO oxidation, and 66–72% NO_x

removal efficiency. Input NO concentration has negligible effect on NO_x removal. NO_x removal efficiency increased marginally with increasing input SO_2 concentration but decreased with increasing pH. The excess supply of ClO_2 did not improve the NO_x removal efficiency. In conclusion, it is reasonable to say that chlorine dioxide is a suitable additive for the simultaneous removal of SO_2 and NO from the flue gas. It is quite effective in a wide pH range and does not require any tight pH control. It is cheaper too when compared with other additives.

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