Reaction mechanism in the Sulfur dioxide and Nitric oxide Removal using Euchlorine Gas

Dong-Seop Jin, Bo-Reong Park, Hang-Dae Cho, Won-Kil Choi, Bal Raj Deshwal\(^1\), Young-Seong Park\(^2\), and Hyung-Keun Lee\(^*\)
Clean Energy Research Department, Korea Institute of Energy Research,\(^1\)
Department of Chemistry, A. I. J. H. M. College, India,\(^1\)
Department of Environmental Engineering, Daejeon University\(^2\)(hklee@kier.re.kr\(^*\))

1. Introduction
Combustion of fossil fuel results in emission of SO\(_2\) and NO\(_x\). Among various technologies conventionally used for removal of SO\(_2\) and NO, scrubbing methods are economically most competitive and have advantage of controlling other acid gases and particulates at the same time [Yang et al., 1996]. No efforts ever have been made to utilize ClO\(_2\) gas in the removal of SO\(_2\) and NO from the flue gas. This has promoted us to clean up NO\(_x\) and SO\(_2\) simultaneously from flue gas by passing chlorine dioxide gas into the scrubbing solution.

Chlorine dioxide is powerful oxidant and disinfectant. In the recent years, it has attracted significant commercial attention not only due to environmental concern but also due to its wide applications in the fields of bleaching, oxidation and disinfection. Chlorine-dioxide can be formed by reduction of chlorate with a wide variety of reducing agents in a relatively concentrated acid solution as follows:

\[
\text{ClO}_3^- + 2H^+ + e^- \rightarrow \text{ClO}_2 + H_2O \tag{1}
\]

The choice of reducing agent has a great bearing 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 ion is not present in the reaction medium. With this view, we selected chlorate-chloride process to generate ClO\(_2\) gas for further use in removing SO\(_2\) and NO from the flue gas. The general stoichiometry of chloride-chlorate process [Deshwal and Lee, 2004, Hong et al., 1967] can be expressed as:

\[
4H^+ + 2\text{ClO}_3^- + 2\text{Cl}^- \rightarrow 2\text{ClO}_2 + \text{Cl}_2 + 2H_2O \tag{2}
\]

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.

2. Experimental Section
The experimental system as shown in Figure 1 is divided into two parts i.e. chlorine dioxide generation unit and flue gas treatment unit. Chlorine dioxide generation unit is composed of a reactor which is a well stirred sealed vessel having total volume of 2.5L. Concentrated sodium chloride solution (2M) was continuously injected into reactor at a suitable flow rate by syringe pump. The reacter was filled with 1.5L solution of sodium chlorate (0.4M) in a relatively concentrated sulfuric acid (~12N). Continuous stirring was provided by a mechanical agitator. Temperature of the reaction vessel was controlled within 45±0.1°C by water thermostat. 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 2L/min. Chlorine-dioxide carried by N2 gas was further introduced into bubbling reactor.

Flue gas cleansing unit composed of simulated flue gas supply system, bubbling reactor, pH control system, ClO2 absorber, data acquisition system, and sampling cum analysis system. The simulated flue gas was obtained by controlled mixing of SO2, NO, N2 and O2 using mass flow controllers. Continuous stirring was provided by mechanical agitator with a speed of 250rpm. 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 by continuous addition of NaOH (0.2M) solution with the help of peristalsis pump. The chloride dioxide absorber (2L vessel) consisted of ca. 2% carbonate buffered potassium iodide solution (1.5L). Samples from reactor and absorber were analyzed using either ion chromatograph (IC) or iodometrically with the help of auto-titrator (Metrohm-Swiss). The SO2 and NOx concentrations of inflow gas were analyzed using the gas analyzers (Ultramat 23, Siemens, Germany and Model: 42C, Thermo Environmental Instruments Inc., USA) after removing the moisture in the sample conditioner.

3. Results and discussion

There is no doubt about the oxidizing capability of ClO2. It can oxidize NO into NO2; therefore it may prove useful for removal of NO from the flue gas. With this view, experiments for removal of NO and simultaneous removal of SO2 and NO have been conducted using chlorine dioxide. A plausible mechanism has also been proposed.

3.1. Removal of Nitric oxide

Experiments were carried out at pH of 3.5 and input NO concentration of 500ppm in absence of input SO2 at 45°C to investigate the NOx removal using chlorine-dioxide. NOx removal efficiency and ion concentration measured by ion chromatograph are plotted versus time in Figure 2. It was observed that ClO2 can oxidize NO into NO2 completely and a consistent and reproducible NO2 absorption efficiency of about 60% is maintained.

3.2. Simultaneous removal of sulfur dioxide and nitric oxide

Simultaneous removal of SO2 and NO was also studied at input SO2 and NO concentration of 500 and 350ppm respectively at pH of 3.5 at 45°C. SO2 and NOx removal efficiencies are presented in Figure 3. It is observed that ClO2 can clean up both SO2 and NO quite efficiently. The maximum DeSOx and DeNOx efficiency obtained at an optimum NaCl (2M) feeding rate of 0.5ml/min are about 100 and 60% respectively.

3.3. Mechanism Involved in the removal of SO2 and NO using chlorine-dioxide

In the acidic medium:

\[
5\text{SO}_2 + 2\text{ClO}_2 + 6\text{H}_2\text{O} \rightarrow 5\text{H}_2\text{SO}_4 + 2\text{HCl} \quad (3)
\]

\[
5\text{NO} + 2\text{ClO}_2 + \text{H}_2\text{O} \rightarrow 5\text{NO}_2 + 2\text{HCl} \quad \text{(oxidation)} \quad (4)
\]

\[
5\text{NO}_2 + \text{ClO}_2 + 3\text{H}_2\text{O} \rightarrow 5\text{HNO}_3 + \text{HCl} \quad \text{(absorption)} \quad (5)
\]

The overall reaction for NOx removal can be written as:

\[
5\text{NO} + 3\text{ClO}_2 + 4\text{H}_2\text{O} \rightarrow 5\text{HNO}_3 + 3\text{HCl} \quad (6)
\]

Chlorine gas produced along with chlorine dioxide as suggested in Eq. (2) is also a strong oxidant. Yang et al. [1996] reported that chlorine is capable of oxidizing NO into NO2 and nitrate. Stoichiometry of reaction of chlorine with NO can be expressed as:

\[
\text{NO} + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{NO}_2 + 2\text{HCl} \quad (7)
\]

\[
2\text{NO} + 3\text{Cl}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + 6\text{HCl} \quad (8)
\]

Formation of sulfate, nitrate and chloride as suggested above is confirmed by analyzing the sample from bubbling reactor using ion chromatograph and variation of ion concentration with time is presented in Figure 2 and 4.
3.4. Effect of pH:

The pH of reaction medium is a crucial parameter in the removal of SO₂ and NO. In the present study, pH of reaction medium was varied from 3.5 to 11 at constant input NO concentration of 500ppm in absence of SO₂ at 45°C and its effect on NO₃ removal is reported in Figure 5. At constant NaCl(2M) feeding rate of 0.5ml/min, there occurred no change in the NOₓ removal efficiency when pH is increased from 3 to 6 but thereafter removal efficiency decreased until pH 8 and again increased up to pH 9 and attained a steady state. It may be attributed due to different mechanism involved in NOₓ removal at different pH. When pH reaches neutrality, the disproportionation [White et al., 1942] of chlorine dioxide starts and it leads to formation of chlorite and chlorate as follows:

\[ 2\text{ClO}_2 + 2\text{NaOH} \rightarrow \text{NaClO}_2 + \text{NaClO}_3 + \text{H}_2\text{O} \]  \hspace{1cm} (9)

So 50% of ClO₂ is converted into chlorite which is again a strong oxidant and absorbent for NO and NO₂ respectively. NOₓ removal mechanism changes when medium of solution changes from acidic (pH < 7) to alkaline (pH > 7). The decrease in NOₓ removal efficiency at pH around 7 or above is believed due to insufficient chlorite in reaction solution. The NOₓ removal mechanism in alkaline medium can be summarized as:

**In Alkaline Medium:**

\[ 2\text{NO} + \text{NaClO}_2 \rightarrow 2\text{NO}_2 + \text{NaCl} \text{ (oxidation)} \] \hspace{1cm} (10)

\[ 4\text{NO}_2 + \text{NaClO}_2 + 4\text{NaOH} \rightarrow 4\text{NaNO}_3 + \text{NaCl} + 2\text{H}_2\text{O} \text{ (absorption)} \] \hspace{1cm} (11)

The overall reaction can be written as:

\[ 4\text{NO} + 3\text{NaClO}_2 + 4\text{NaOH} \rightarrow 4\text{NaNO}_3 + 3\text{NaCl} + 2\text{H}_2\text{O} \] \hspace{1cm} (12)

The above mechanism has been discussed in detail by several workers [Sada et al., 1979, Brogen et al., 1998] To confirm the belief that NOₓ removal mechanism changes in the alkaline medium, the NaCl feeding rate was enhanced so that more chlorite is formed by disproportionation of unused dissolved ClO₂ and it was found that NOₓ removal attained a steady state at higher NaCl feeding rate due to formation of sufficient chlorite. At NaCl(2M) feeding rate of 1.5ml/min, constant NOₓ removal efficiency of around 60% was achieved in the wide pH range of 3 to 11.

4. Conclusions

**Merits of using ClO₂ in SO₂ and NOₓ removal**

Chlorine dioxide has proved most promising chemical for simultaneous removal of SO₂ and NO. The merits of chlorine dioxide can be summarized as:

- 100% SO₂ removal efficiency, 100% NO oxidation and ~60% NOₓ removal efficiency.
- Low capital cost,
- pH needs no tight control. It is as effective at low pH as at high pH.
- Operation of the system is comparatively easier.
- Easy to handle the waste water

References


Fig. 1. A schematic diagram of the experimental apparatus.

Fig. 2. NOx removal and ion concentration with passage of time using chlorine dioxide.

Fig. 3. Simultaneous removal SO2 and NOx with time using chlorine dioxide.

Fig. 4. Variation in ion concentration with time on passing chlorine dioxide in simultaneous removal SO2 and NOx.

Fig. 5. Effect of pH on NOx removal at constant NO input concentration of 500ppm at 45°C.