

ClO₂를 이용한 SO₂와 NO_x 제거 반응 메커니즘

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

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1. Introduction

Combustion of fossil fuel results in emission of SO₂ and NO_x. Among various technologies conventionally used for removal of SO₂ 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 ClO₂ gas in the removal of SO₂ and NO from the flue gas. This has promoted us to clean up NO_x and SO₂ 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:



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 ClO₂ gas for further use in removing SO₂ 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:



This process is extremely simple to operate, responds immediately and gives highest yield of ClO₂ 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 reactor 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 chlorine 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 NO_x 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 NO_x removal using chlorine-dioxide. NO_x 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.

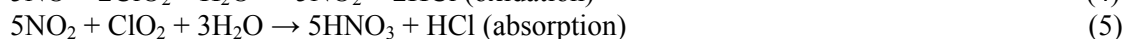
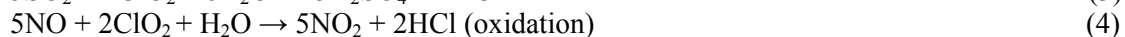
3.2. Simultaneous removal of sulfur dioxide and nitric oxide

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 NO_x removal efficiencies are presented in Figure 3. It is observed that ClO₂ can clean up both SO₂ and NO quite efficiently. The maximum DeSO_x and DeNO_x 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:

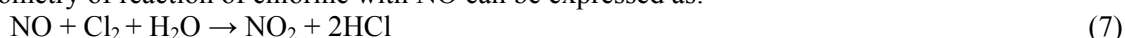
NO and SO₂ removal by chlorine-dioxide is considered to follow the following mechanism:



The overall reaction for NO_x removal can be written as:



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:



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.

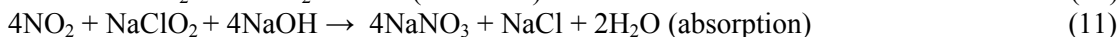
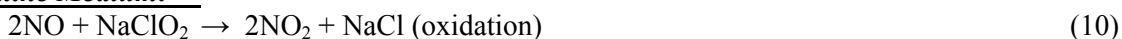
3.4. Effect of pH:

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 NO_x removal is reported in Figure 5. At constant NaCl(2M) feeding rate of 0.5ml/min, there occurred no change in the NO_x 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 NO_x 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:



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

In Alkaline Medium:-



The overall reaction can be written as:



The above mechanism has been discussed in detail by several workers [Sada et al., 1979, Brogen et al., 1998] To confirm the belief that NO_x 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 NO_x 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 NO_x 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 NO_x 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% NO_x 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

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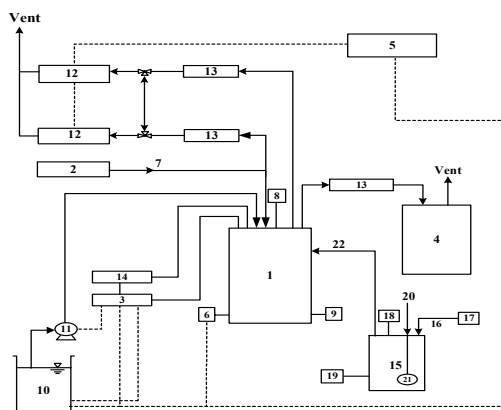


Fig. 1. A schematic diagram of the experimental apparatus.

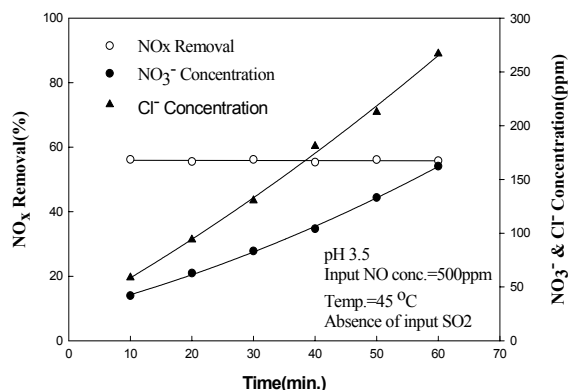


Fig.2. NO_x removal and ion concentration with passage of time using chlorine dioxide.

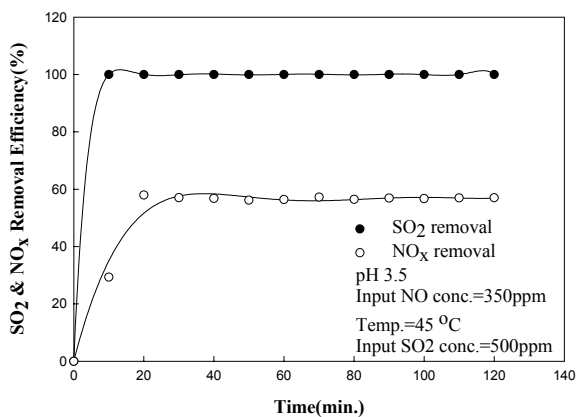


Fig. 3. Simultaneous removal SO₂ and NO_x with time using chlorine dioxide.

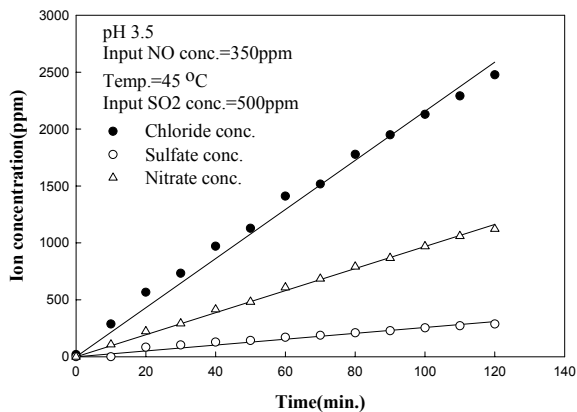


Fig. 4. Variation in ion concentration with time on passing chlorine dioxide in simultaneous removal SO₂ and NO_x.

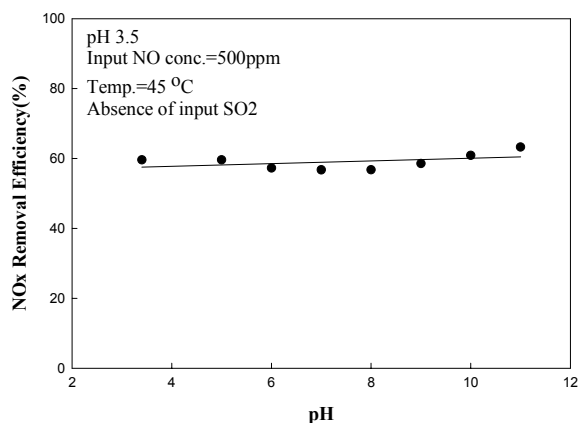


Fig. 5. Effect of pH on NO_x removal at constant NO input concentration of 500ppm at 45°C