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# 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.

*Keywords:* Removal; Sulfur dioxide; Nitric oxide; Bubbling reactor; Chlorine dioxide

## 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, $H_2S$,

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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:

$$ClO_3^- + 2H^+ + e^- \rightarrow ClO_2 + H_2O \tag{2}$$

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]:

$$4H^+ + 2ClO_3^- + 2Cl^- \rightarrow 2ClO_2 + Cl_2 + 2H_2O \tag{3}$$

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.

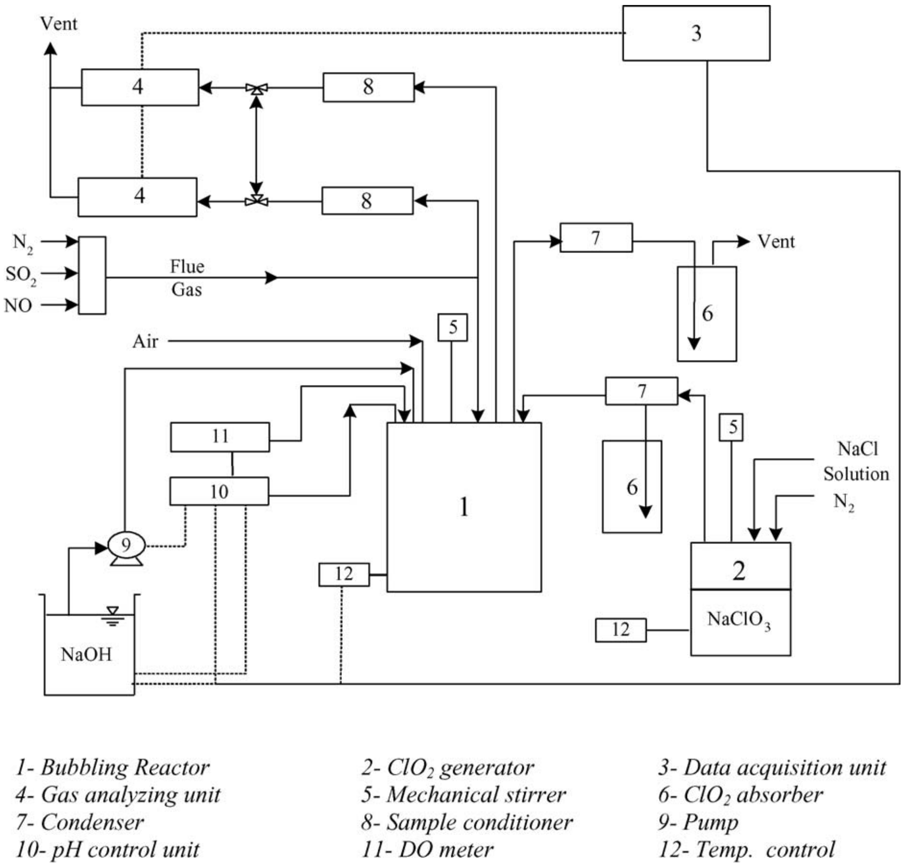

Fig. 1. A schematic diagram of lab-scale bubbling reactor for simultaneous removal of $SO_2$ and $NO_x$ from simulated flue gas.