



Application of Gaseous ClO₂ on Disinfection and Air Pollution Control: A Mini Review

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ABSTRACT

During the severe pandemic of coronavirus, the development and deployment of efficient disinfection technology have attracted hospitals' attention. Chlorine dioxide (ClO₂) gas has been validated as an efficient disinfectant and air pollution control due to its high oxidation ability. This article reviewed the principles and application of ClO₂ gas on disinfection, sterilization and air pollutants abatement. The principles of ClO₂ gas production, chemistry and related generator issues were discussed. We also review some case studies of the application of ClO₂ gas in the medical field and food industry as a sterilizer. Oxidation of nitrogen oxide (NO_x), sulfur oxide (SO_x), mercury (Hg), and volatile organic compounds (VOCs) using ClO₂ gas has been investigated. The process chemistry and demonstration of applying ClO₂ gas for air pollutants oxidation and absorption have also been provided. In conclusion, we suggest the future priority research direction of ClO₂ gas application are included the development of smart and robust ClO₂ gas release system, the integration of an innovative robotic technology in ClO₂ sterilization for epidemic prevention, and the evaluation of ClO₂ emissions impact on indoor air quality in hospitals.

Keywords: ClO₂; Disinfection; Sterilization; Oxidation; COVID-19.

INTRODUCTION

The international emergency of the coronavirus disease 2019 (COVID-19) pandemic has raised health and sanitation concerns for human society. Precautionary principles should be taken into account to overcome severe outbreak (Hsiao *et al.*, 2020). To efficiently prevent infection from human to human, physical capture and biological disinfection items have been utilized (Chen *et al.*, 2017). Significant capture of over 97% by the physical filters such as the N95FFR has been observed in a wide particle size range (Ratnesar-Shumate *et al.*, 2008). In hospital care, the Centers for Disease Control and Prevention (CDC) estimated that hospital-associated infection (HAI) reaches approximately 1.7 million patients per year in the U.S., resulting in the additional healthcare cost of \$4.5 to \$6.5 billion each year (Klevens *et al.*, 2007). Disease outbreak and cleaning assignment related to the reduction of bacterial and viral organism transmission have received considerable attention (Aygun *et al.*, 2002). Alternatives for

disinfection in hospital rooms including fumigation agents and ultraviolet (UV) light technologies have been deployed. Typical fumigation agents such as ozone (O₃) and hydrogen peroxide (H₂O₂) vapor and UV technologies have been utilized in clinics (Umezawa *et al.*, 2012). In addition, three fumigants for room decontamination in the intensive care units (ICU) are formaldehyde gas, hydrogen peroxide vapor, and chlorine dioxide (ClO₂) gas. In the U.S., large numbers of animal and neonatal ICUs have been contaminated when using fumigants to avoid the infection of multiple patients.

ClO₂ gas is a U.S. EPA recognized sterilizer that has been applied for decontamination in the federal buildings. ClO₂ gas has a green-yellowish color and irritating odor and is a volatile and strong molecule. This type of gas is unstable and when photo-oxidized by sunlight it generates the chloride (Cl⁻), chlorite (ClO⁻) and chlorate (ClO₃⁻). In 1814, ClO₂ was discovered by Sir Humphrey Davy, who produced the gas from the reaction between sulfuric acid (H₂SO₄) and potassium chlorate (KClO₃), followed by replacing the H₂SO₄ with hypochlorous acid (HOCl) and the KClO₃ with sodium chlorate (NaClO₃) (Kastner and Das, 2005). ClO₂ gas has been used for small spaces in patient care rooms due to its penetrating ability. However, some research has argued that gaseous or aqueous ClO₂ performed non-efficient decontamination in the healthcare environment because

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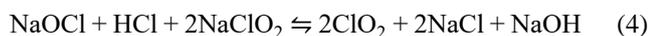
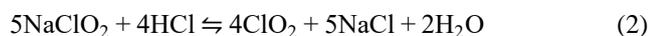
ClO₂ would break down under ambient conditions to limit its penetrating ability (Canter *et al.*, 2005). ClO₂ can also be applied for the disinfection of drinking water by controlling the chemical reaction. The concerning organisms in drinking water are disease causing viruses and pathogens. Bacterial spores (e.g., *Bacillus*) in drinking water treatment processes have been investigated using ClO₂ for disinfection (Young, 2016). The generated ClO₂ gas is dissolved into the drinking water for further treatment with the desired dose of chemical agent by adjusting the gas flow rate. Haas (2011) found that the application of ClO₂ shows superior inactivation of microorganisms as compared to chlorine (Cl₂), especially in the disinfection of drinking water. The target waterborne pathogens could be eliminated via oxidation of ClO₂.

This article reviewed the chemistry, principles and application of ClO₂. We firstly scrutinized the principles of gaseous ClO₂ generation and its generators. Application of ClO₂ gas for disinfection and sterilization in terms of medical biocide, the food industry and industrial odor control were further depicted. We also reviewed the recent literature of application of gaseous ClO₂ for air pollution control, especially nitrogen oxide (NO_x), sulfur oxide (SO_x), mercury (Hg), and volatile organic compounds (VOCs) oxidation and its mechanisms.

Gaseous Chlorine Dioxide Generation

Principles

ClO₂ gas is difficult to store and transport. Due to its explosive and unstable characteristics then, it needs to be manufactured on site. ClO₂ gas or Cl₂ gas are usually produced from sodium chlorite (NaClO₂), or sodium chlorate (NaClO₃) with peroxydisulfate (H₂S₂O₈) or hydrochloric acid (HCl). The series of chemical reactions is presented in Eqs. (1) to (3). The reactions between NaClO₂ and Cl₂ gas, or HCl or H₂S₂O₈ can generate the desired ClO₂ gas with sodium chloride or sodium sulfate. In some case, ClO₂ gas can also be made from the reaction of sodium hypochlorite (NaOCl) with NaClO₂ and HCl (Eq. (4)).



ClO₂ gas as an alternative for chemical sterilization or as an oxidative gas works offers bactericidal, virucidal and sporicidal properties like chlorine and processes efficiently at temperatures from 25°C to 30°C, which do not lead to the formation of trihalomethanes or chloramines and is not mutagenic or carcinogenic for humans (Kowalski and Morrissey, 2004). Stevens (1982) demonstrated the organic halogen formation with ClO₂ dosages of 5, 10, and 20 mg L⁻¹ with the temperatures of 4 to 36°C. He concluded the non-significant effect of temperatures on organic halogen formation when applying the ClO₂ disinfection. ClO₂ gas is commonly used for decontaminating spaces, surfaces and

equipment with concentrations between 10 and 30 mg L⁻¹. Lerouge (2012) applied ClO₂ gas for the sterilization of medical products through rapid spread for a duration of 1.5–3 hr. without post-sterilization.

However, the problem is that ClO₂ gas is explosive. The solution containing ClO₂ can escape from the liquid when people use it for disinfection. Jin *et al.* (2008) investigated that limiting the concentration to lower than 9.5% to 10% in the air is suggested to avoid explosion. Exposure to chlorine from ClO₂ could cause irritation and burns. The chain reaction related to ClO₂ gas explosion were listed in Eqs. (5) and (6). The content of Cl₂O₃ product could determine the explosive level.



Eye exposure can also result in irritation, watering eyes and blurry sight. They concluded that the induction time (i.e., the time interval from sparking to explosion) was 2195 ms and 8 ms at 10% and 90% of ClO₂ gas, respectively. The maximum explosion pressure was increased from 0.024 MPa to 0.641 MPa as ClO₂ concentration was enhanced from 10% to 90%. When ClO₂ gas is decomposed due to explosion, the stable intermediate (Cl₂O₃) is formed. ClO₂ gas can spontaneously decay depending on the temperature, humidity and light intensity. Although no previous research has mentioned that ClO₂ can react with building materials or contents, it has been reported that O₃ gas can react with indoor carpet. Therefore, to ensure the adequate and safe application of ClO₂ gas for space decontamination, the appropriate dose, sufficient diffusion time and non-explosive concentration should be provided. In addition, ClO₂ can be absorbed by the skin, which can damage tissue and blood cells. When people inhale ClO₂ it can cause many symptoms including coughing, sore throat, severe headaches, lung oedema and bronchio spasma and lung exposure of ClO₂ can cause bronchitis. Thus, the health standard of 0.1 ppm for ClO₂ exposure has been suggested (WHO, 2002).

ClO₂ Gas Generators

The main challenge of ClO₂ gas application is the difficulty of storage due to its unstable characteristics. As a result, ClO₂ gas needs to be manufactured on-site. Development of ClO₂ generators has been investigated since the early 1990s. Jeng and Woodworth (1990) found that 3% to 5% gaseous ClO₂ was generated with air mixture by vaporization of a chlorine solution using 500 g of sodium chlorite chips in a ta column container. Eylath *et al.* (2003) proposed a prototype ClO₂ gas generator that produces 2% ClO₂ gas with 98% nitrogen in small plastic cartridges carrying solid NaCl. When they set the target of ClO₂ gas concentration to 5 mg L⁻¹ for use in spatial sterilization, the exposure time was 20 minutes. This prototype generator had a maximal volume of 8,000 L of ClO₂ gas with 100 mg L⁻¹ concentration under an atmospheric pressure of 50 Pascals. In addition, Cl₂ gas formation should be avoided during production of ClO₂ gas. Huang and Chen (2017) used the iodometric method to

analyze the exhausted gas from a ClO₂ generator which contained Cl₂ gas and ClO₂ gas. The absorbance value of ClO₂ occurred at the wavelength of about 280–470 nm. They developed a large-scale ClO₂ generator which is also a gas flow spectrophotometer to real-time analyze ClO₂ gas concentration. The ClO₂ gas stripped from the reacted solution can achieve the yield ratio of 91.21% and the concentration of 3.5%. Some researchers proposed that ClO₂ gas can be stripped out from the high purity of ClO₂ solution using an advanced gas-liquid contactor (Huang and Chen, 2017). By using nitrogen as the stripping gas and passing it through a contactor, ClO₂ gas could be released. The gas flow rate and temperature are the key operating parameters for ClO₂ gas stripping from an aqueous ClO₂ solution with a known concentration. The temperature of 30°C to 40°C was maintained by a water bath and a constant concentration of ClO₂ solution was consecutively circulated to strip the ClO₂ gas (Hultén *et al.*, 2017).

Currently, several commercialized ClO₂ gas generators have been deployed in different fields. OxyChem corporation invented a ClO₂ gas chemical feeder. Three basic designs include a vacuum feed system that pulls stream into the generator, and a pressure feed system that pushes the steam back into the generator. The liquid chemicals (e.g., HCl and NaOCl) are mixed with the precursor chemical with a required residence time of 15 minutes to generate the ClO₂ gas. A CA-300 type ClO₂ gas generator was developed by PurgoFarm, Korea. The design uses aqueous NaClO₂ which flows through the multi-porous membrane electrode assembly under an acid condition to strip out highly pure ClO₂ gas via an electrochemical driving force (Gates, 1988). Recent developments of ClO₂ generators focus on robust control and sustained release technology to produce smaller, more precise amounts of doses, thereby increasing the practical feasibility.

Chlorine Dioxide Gas Used in Disinfection and Sterilization

Medical Biocide

To control indoor bio-aerosols and viruses in hospitals and for medical equipment, many aerobiological technologies (i.e., ventilation, filtration, ultraviolet germicidal irradiation, photocatalytic oxidation, ionization and thermal sterilization) and medical biocides such as disinfectors have been developed (Yoosook *et al.*, 2009). O₃ gas has been used for disinfection due to its high oxidization and germicidal efficacy. Huang *et al.* (2012) demonstrated 90% germicidal efficacy for *E. coli*, *C. famata*, and spores of *P. citrinum* using gaseous O₃ that has substantially higher activity than ClO₂. Apart from ozonation, gaseous ClO₂ is another option that is used as an oxidizer or disinfectant in the medical area. ClO₂ can be used in liquid or gas form and is applied effectively against pathogenic microorganisms such as fungi, bacteria, viruses, spore-forming bacteria and bio film. As follows, we review some case studies of the application of ClO₂ gas decontamination in hospitals.

Luftman *et al.* (2006) evaluated the ClO₂ gas used to decontaminate a 4800 m³ facility with a total ClO₂ dosage of 400 ppm per hr in a single evening. This trial test proved

ClO₂ gas to provide effective disinfection in a normal hospital room. Liou *et al.* (2007) investigated the sterilization effect of indoor air of laboratories, hospitals and conference rooms using 200–1000 ppm ClO₂ gas. They mixed 3.35% NaClO₂ solution and 85% H₂PO₄ at a 10:1 volume ratio to generate the ClO₂ gas. At the end concentration of 625 ppm, the disinfection efficacy of 90% was achieved in 30 minutes. Lorcheim (2011) confirmed that ClO₂ gas can be used to treat beta-lactam manufacturing in a pharmaceutical plant. With various concentrations of ClO₂ gas and exposure times, the pharmaceutical manufacturer asked for 3-log (99.9%) reduction of eight different beta-lactams on various surfaces. Lowe *et al.* (2013) exposed ClO₂ gas at 10 sites in a hospital room to evaluate the germicidal efficacy of 385 ppm ClO₂ gas for health-associated diseases and pathogens such as *Acinetobacter baumannii*, *E. coli*, *Enterococcus faecalis*, *Mycobacterium smegmatis*, and *Staphylococcus aureus*. They verified that 7 to 10-log reductions of viable organisms could be achieved. Sealing of the doors of each room was implemented to prevent gas leakage. Shirasaki *et al.* (2016) applied ClO₂ gas as a sterilizer in a hospital room (87 m³) with concentrations from 0.8 ppm to 40.8 ppm for 2 h to 3 h. They were no differences in concentration between 0.1 m to 2.5 m above the floor. Under 80% relative humidity, the colony formation of both *Staphylococcus aureus* and *E. coli* was inhibited with 3 ppm exposure of ClO₂ gas. In addition, in situ generated ClO₂ gas has been considered for halogen-based biocides. ClO₂ is 4–7 times more powerful than Cl₂, even though it is less stable under acid condition. ClO₂ gas is easily decomposed under sun light so there is little tendency to form organochlorine by-products (Karsa, 2007).

Food Industry

Foodborne disease, which originates from contaminated food or drinking water, is a major concern of food safety. The presences of foodborne disease outbreaks due to global warming-related pathogenic bacteria has increased (Hall *et al.*, 2002; Choi *et al.*, 2015). The disinfection of drinking water is mainly used in the food and beverage industry. Gaseous ClO₂ has been shown to be an effective disinfectant for decreasing microbial loads on various fruits and vegetables (Gómez-López *et al.*, 2009). Research of application of ClO₂ gas for the reduction of microbial populations in water has been less common. Although aqueous ClO₂ use in drinking or washing water for fruits and vegetables has been approved by the U.S. Food and Drug Administration (FDA), gaseous ClO₂ has not been authorized for use in food processing (Smith *et al.*, 2014). This is because ClO₂ gas can generate chlorine residues on food products during decontamination. However, recent researchers have argued that low concentrations of Cl residues on the food are not toxic. ClO₂ gas has higher penetration capacity than in the aqueous form and is more effective for oxidizing contamination without the formation of trihalomethane. ClO₂ gas has been commonly used to reduce the microbiological problem on green peppers, roma tomatoes, tomatoes, and frozen blueberries (Ahmed *et al.*, 2017). Thus, case studies of ClO₂ gas treatment for food processing are reviewed in the following paragraph.

Golden *et al.* (2019) demonstrated that ClO₂ gas releasing

sachets can be utilized in small food processors of spices as a post-lethality treatment alternative. In the spice industry, *Salmonella enterica* is a major concern for food security. The application of slow-releasing ClO₂ gas of 100, 200, or 500 mg ClO₂ per kg-spice from sachets has been employed and the performance of *Salmonella* decontamination of black pepper, cumin, and sesame seed after 1, 10, and 30 days post-treatment has been evaluated. The trial tests indicated that the *Salmonella* of black pepper, cumin, and sesame seed decreased from 0.81 to 2.74 log CFU g⁻¹ via ClO₂ disinfection. Kim and Song (2017) integrated ClO₂ gas with ultraviolet-C (UV-C) light, and fumaric acid to inactivate *Listeria monocytogenes* and *E. coli* O157:H7 on plums. With ClO₂ gas of 30 ppm for 20 min, fumaric acid of 0.5%, and UV-C of 10 kJ m⁻², the populations of *L. monocytogenes* and *E. coli* O157:H7 were decreased by 6.26 and 5.48 log CFU g⁻¹, respectively. Kim *et al.* (2016) evaluated the antimicrobial effect of *Salmonella* inoculation onto eggshells using ClO₂ gas under various concentrations, contact times, humidity levels, and percentages of organic matter. The inactivation of *Salmonella* was more effective with ClO₂ gas treatment under high moisture conditions. A 4 log reduction in the population of *Salmonella* was achieved after 30 min of ClO₂ exposure at 20 ppm, 40 ppm, and 80 ppm. They suggested using ClO₂ gas as a sterilizer for controlling *Salmonella* in the egg industry. In addition, ClO₂ gas can also be applied for disinfection in cafeterias. Hsu and Huang (2013) tested two different approaches of gaseous ClO₂ releasing by an aerosol device in disinfecting a student cafeteria. One was a one-off treatment and the other was a twice-daily treatment. The bioaerosol levels of bacteria and fungi were measured. The air quality before and after disinfection was evaluated. They measured that the average levels of bacteria and fungi decreased 65% and 30% from 972.5 ± 623.6 and 1534.1 ± 631.8 colony-forming units (CFU) m⁻³, respectively, in the one-off treatment. The twice-daily ClO₂ treatment enhanced the reduction levels of bacterial and fungal concentrations by 74% and 38%, respectively.

Chlorine Dioxide Gas Used as an Oxidizer for Gaseous Pollutants

Principles

The research related to chlorine oxide chemistry has been investigated in a wide variety of fields. Atmospheric interactions of chlorine species were the main focus of early research. The application of ClO₂ as an oxidizer agent also drawn attention for air pollution control, especially NO_x control. The simultaneous removal of NO_x and SO_x using ClO₂ oxidation has gained interest in flue gas cleaning. Traditional NO_x and SO_x control faces the challenges of high operation cost and energy demand, thus the simultaneous removal of multi-air pollutants (i.e., including gas and particulates matters) has been investigated in recent years (Chen *et al.*, 2020). This idea involves the treatment of air pollutants in the same unit process, thereby reducing the process units and land area. The oxidation combining absorption process for NO_x and SO_x reduction is a practical approach because the chemical interactions of sulfur and nitrogen species in the liquid phase promote wet scrubbing as

an available option (Ajdari *et al.*, 2015). NO can be converted to NO₂ with O₂ under atmospheric conditions, though the reaction rate is too slow to affect the NO oxidation from boiler to stack. Therefore, the introduction of oxidative agents such as O₃, H₂O₂, and ClO₂ can significantly improve the NO oxidation (Jin *et al.*, 2006).

Apart from using the O₃ and H₂O₂ as an oxidizer for NO_x, the application of ClO₂ gas to NO_x removal has been investigated in recent years. It is cheaper than O₃ only if the ClO₂ generator can be successfully on-line operation. The use of H₂O₂ has the higher explosive risk. The chemical interactions between NO, SO₂, and ClO₂ have been investigated. Although the SO_x species have high water solubility that can be absorbed easier than NO, the chemistry of ClO₂ on SO₂ oxidation can affect the NO_x species oxidation. Fig. 1 shows an overview of the process chemistry of NO_x-SO_x-ClO₂ in the gas and liquid phase. The ClO decomposed from ClO₂ and NO oxidation can further oxidize the SO₂ to create SO₃ and Cl. The absorption of SO₂ and SO₃ on the liquid side can contribute to the formation of sulfuric acid (H₂SO₄) and sulfurous acid (H₂SO₃). Some nitrogen-sulfur complexes can be formed as well. The dissociation of H₂SO₄ and H₂SO₃ can lead to acid pH in the solution. These chain reactions are highly dependent on pH. When the pH of solution is below 2, the formation of N₂O, a kind of greenhouse gas, happens. When the pH value is around 4, the predominant reaction pathway is the formation of hydroxylamine disulfonate acid (HADS) (Haunstetter and Weinhart, 2015). Therefore, the pH control should be considered in the oxidation-absorption of NO-SO₂-ClO₂ treatment, which could not only increase the de-NO_x and de-SO_x but also avoid strong greenhouse gas emissions (i.e., N₂O).

The reaction between H₂O₂ and NO_x usually occurs in the aqueous condition, where the high gas-liquid mass transfer barrier should be overcome. The reaction of ClO₂ gas with NO has been reported. Table 1 shows the reaction kinetic between NO and ClO₂ in the gas phase and its related dissociation in the liquid phase. It can be seen that all the reaction constants in the gas phase are larger up to 7 to 15 power of 10. The oxidation of NO to NO₂ in reactions 1 and 2 occurs under ambient conditions. When the vapors and liquid of ClO₂ exist, the hydrolysis of chlorine occurs to form HCl, as shown in reactions 5 and 6. The strong acid formation can contribute to a low pH condition. The stoichiometric ratio for NO to ClO₂ is 0.5. When the Cl is consumed to generate the HCl and ClO (reaction 3), the molar ratio decreases to approximately 0.4. The overall oxidation-absorption reaction of NO and ClO₂ is 5NO + 3ClO₂ + 4H₂O → 5HNO₃ + 3HCl. In reactions 7 to 9, the oxidation of NO and NO₂ convert to higher valence NO_x species such as N₂O₃ and N₂O₄, which can easily dissolve into water (Johansson *et al.*, 2018). Although some studies have debated whether gaseous HNO₃ can be formed from NO₂ and vapors (England and Corcoran, 1974), gaseous nitric (HNO₃) and nitrous acid (HNO₂) are quickly transferred in aqueous condition when the vapors present. Table 2 shows the reaction kinetic between NO and SO₂. Reactions 1 to 3 are the main reaction of ClO₂ oxidizing SO₂. The other

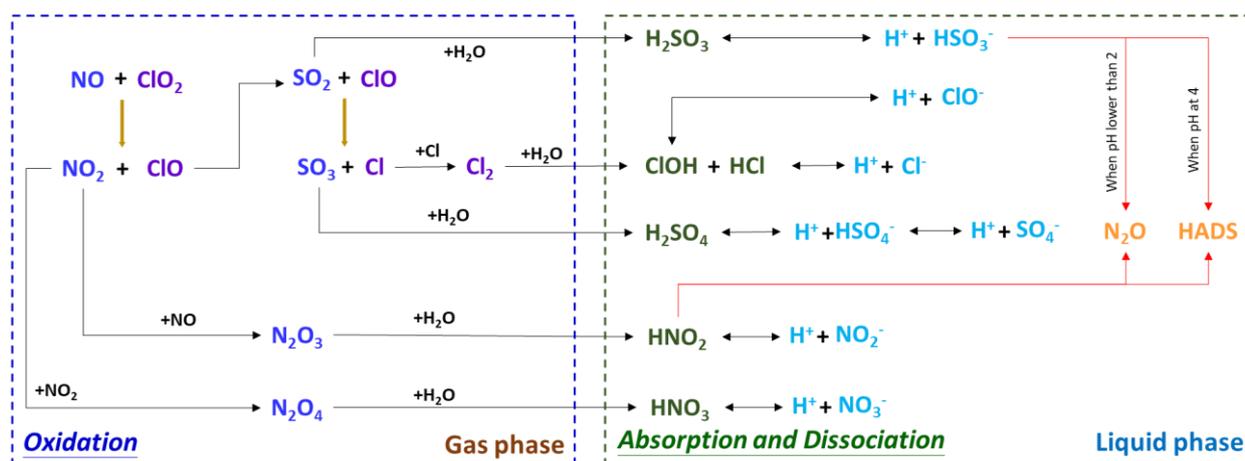


Fig. 1. Process chemistry of NO_x and SO_x oxidized by ClO_2 . Adapted from (Haunstetter and Weinhart, 2015).

Table 1. Reaction kinetic between NO and ClO_2 in the gas phase and its related dissociation in the liquid phase.

No.	Reaction	Reaction constant (k) ($\text{m}^3 \text{ kmole}^{-1} \text{ s}^{-1}$)	Activity energy (E) (J mol^{-1}) ^a	References
Gas oxidation				
1	$\text{NO} + \text{ClO}_2 \rightarrow \text{NO}_2 + \text{ClO}$	6.62×10^7	-2910	(Leu and Demore, 1978)
2	$\text{NO} + \text{ClO} \rightarrow \text{NO}_2 + \text{Cl}$	3.73×10^9	-2450	(Li et al., 2002)
3	$\text{Cl} + \text{ClO}_2 \rightarrow 2\text{ClO}$	1.93×10^{10}	-1413	(Atkinson et al., 2007)
4	$2\text{ClO} \rightarrow \text{ClO}_2 + \text{Cl}$	2.11×10^8	11330	(Atkinson et al., 2007)
5	$\text{NO} + \text{HCl} \rightarrow \text{HNO} + \text{Cl}$	1.58×10^{10}	210000	(Higashihara et al., 1978)
6	$\text{NO}_2 + \text{HCl} \rightarrow \text{HNO}_2 + \text{Cl}$	3.9×10^8	98110	(Rosser and Wise, 1960)
7	$\text{NO} + \text{NO}_2 \rightarrow \text{N}_2\text{O}_3$	-	-	(Kaczur, 1996)
8	$2\text{NO}_2 \rightarrow \text{N}_2\text{O}_4$	5×10^8	-	(Borrell et al., 1988)
9	$\text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2$	7.83×10^{15}	53120	(Atkinson et al., 1997)
Absorption and dissociation				
1	$2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3$	1×10^8	-	(Lee and Schwartz, 1981)
2	$\text{HNO}_2 \rightarrow \text{NO} + \text{NO}_2 + \text{H}_2\text{O}$	13.4	-	(Park and Lee, 1988)
3	$\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_2$	1.58×10^8	-	(Park and Lee, 1988)

Table 2 Reaction kinetic between SO_x and ClO_2 in the gas phase and its related dissociation in the liquid phase.

Gas oxidation				
No.	Reaction	Reaction constant (k) ($\text{m}^3 \text{ kmole}^{-1} \text{ s}^{-1}$)	Activity energy (E) (J mol^{-1}) ^a	References
1	$\text{SO}_2 + \text{ClO}_2 \rightarrow \text{SO}_3 + \text{Cl}$	2409	-	(Eibling and Kaufman, 1983)
2	$\text{SO}_2 + \text{NO}_2 \rightarrow \text{SO}_3 + \text{NO}$	6.31×10^9	27000	(Armitage and Cullis, 1971)
3	$4\text{SO}_2 + 2\text{ClO}_2 \rightarrow 4\text{SO}_3 + \text{Cl}_2$	-	-	(Kaczur, 1996)
4	$\text{SO}_2 + \text{HOCl} \rightarrow \text{SO}_3 + \text{HCl}$	-	-	(Kaczur, 1996)
5	$\text{SO}_2 + 2\text{HNO}_2 \rightarrow \text{HNO} + \text{Cl}$	-	-	(Kaczur, 1996)
6	$\text{SO}_2 + \text{OH} \rightarrow \text{HOSO}_2$	7.89×10^8	-	(Atkinson et al., 2004)
7	$\text{HOSO}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{SO}_3$	7.89×10^8	2740	(Atkinson et al., 2004)

chain reactions would be occurred in the same time based on the temperature and pressure condition. In addition, Table 3 presents the reaction kinetic of Cl species in NO_x - SO_x - ClO_2 system. As the Cl atom generated from ClO_2 decomposition, it can be synthesized to Cl_2 followed by dissolving into the vapor to form HCl. In reactions 4 and 5, NO_2 and HNO_3 can also react with Cl or ClO to form the high active chlorine nitrate (ClNO_3) that could be decomposed into NO_2 and ClO with high activity energy (reaction 6).

NO_x - SO_x -Hg Control

ClO_2 gas application offers additional possibilities other than the use of aqueous ClO_2 solution, which depends on the production method. Gaseous ClO_2 can convert the NO to NO_2 , thereby increasing the feasibility of the downstream scrubbing process for simultaneous removal of NO_x and SO_x . Even though gaseous ClO_2 has hazardous and unstable characteristics, the proper management of manufacturing of ClO_2 production can decrease the accident risk. The research

Table 3. Reaction kinetic of Cl species in NO_x-SO_x-ClO₂ system.

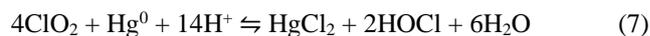
Gas oxidation				
No.	Reaction	Reaction constant (k) (m ³ kmole ⁻¹ s ⁻¹)	Activity energy (E) (J mol ⁻¹) ^a	References
1	2Cl → Cl ₂	5.802 × 10 ⁸	-6690	(Widman and DeGraff, 1973)
2	Cl ₂ + H ₂ O → HOCl + HCl	-	-	(Kaczur, 1996)
3	H ₂ O + Cl → HCl + OH	1.17 × 10 ⁸	63850	(Bryukov <i>et al.</i> , 2006)
4	HNO ₃ + Cl → NO ₃ + HCl	9.03 × 10 ⁹	36420	(Poulet <i>et al.</i> , 1978)
5	NO ₂ + ClO → ClNO ₃	5.94 × 10 ¹⁰	-	(Atkinson <i>et al.</i> , 2007)
6	ClNO ₃ → NO ₂ + ClO	1.66 × 10 ¹⁵	94780	(Anderson and Fahey, 1990)
7	ClNO ₃ + Cl → Cl ₂ + NO ₃	3.79 × 10 ⁹	-1210	(Atkinson <i>et al.</i> , 2007)

related to the simultaneous removal of NO_x and SO_x via enhanced oxidation by ClO₂ from flue gas based on technical-scale experiments and simulations was initiated five years ago.

Li *et al.* (2015) used ClO₂ gas to oxidize NO with the oxidation efficiency of 82% at the ClO₂/NO molar ratio of 0.8. They found the oxidation selectivity of NO with ClO₂ was higher than that of SO₂ oxidation, which was observed until NO became completely oxidized. The other critical factor influencing NO oxidation efficiency was temperature. When the temperature ranged from 70°C to 290°C, NO oxidation efficiency decreased with the rising temperature. However, they also found that the NO oxidation efficiency slightly decreases with rising SO₂ concentration, which represents minor competition between NO and SO₂. In addition, the mercury (Hg) gas can be efficiently oxidized to Hg²⁺ by ClO₂ with an oxidation efficiency of 86% at the ClO₂/NO molar ratio of 0.3. Hultén *et al.* (2017) found that higher oxidation efficiency of NO was gained when more ClO₂ gas was added. The presence of SO₂ with NO can lead to nitrogen-sulphur interactions in the liquid phase. A ClO₂/NO molar ratio of 0.6 can contribute to the NO removal efficiency of 79%, and it could be further enhanced to 94% with an absorption solution of Na₂CO₃ and Na₂SO₄. They also balance the nitrogen in the system, playing a major part as NO is converted to HNO₃ in the condensate liquor and HNO₂ in the absorption solution. Johansson *et al.* (2018) focused on NO_x and SO_x removal chemistry from combustion-derived flue gases using gaseous ClO₂. The simulated NO and SO₂ flue gas concentrations were 250 ppm and 1000 ppm, respectively. Under the temperature range of 100°C to 180°C, vapors in the range of 0% to 25%, and ClO₂/NO molar ratios in the range of 0.2 to 0.6, they observed that the water concentration has no effect on ClO₂ oxidation. The temperature should be limited to under 200°C to avoid lower oxidation of NO with ClO₂. Gaseous HNO₃ formed with the ClO₂/NO molar ratio of 0.6. Furthermore, Johansson *et al.* (2019) used ClO₂ gas treatment for flue gases from a 100 kW gas-fired furnace. The integration of a wet-scrubber and ClO₂ oxidation in the gas phase achieved NO and SO₂ removal efficiency of up to 90% and 99%, respectively. Afterward, the absorption ratio of NO₂ in the liquid phase using Na₂SO₃ and Na₂CO₃ reached up to an estimated 82%.

The U.S. EPA proposed Mercury and Air Toxics Standards to regulate the mercury emission from power plants due to 91% coal-combustion basis mercury emission (U.S. EPA,

2011). During the coal combustion, mercury would be released major as Hg⁰ form. When mercury reacts with different acid gas, the three different forms including Hg⁰, Hg²⁺ (e.g., HgCl₂), and particulate Hg (Hg_p) could be presence (Hutson, 2007). Because of the low water solubility of mercury, the use of oxidizer for mercury either in gas phase or in liquid phase can significantly enhance the absorption efficiency of mercury. Therefore, the application of ClO₂ gas or solution in the existing scrubber technology can decrease the mercury emissions (Krzyzyska and Hutson, 2012). The chemical reaction between ClO₂ and Hg⁰ in the acid condition is shown in Eq. (7):



Zhao *et al.* (2008) reported finding mercury(II)-chlorine ion (HgClO₂²⁺) could be reacted with ClO₂ under acidic conditions and form Hg²⁺ and ClO₃⁻ in an acidic solution of sodium chlorite as shown in Eq. (8):



Volatile Organic Compounds (VOCs) Control

The necessitates of a wide range of volatile organic compound (VOC) emissions remediation in industries is also a kind of odor resource (Sironi *et al.*, 2007). VOC treatment and odor control can be conducted using ClO₂ in wet scrubbers. The “Odor Control Rules” promulgated by the U.S. EPA have raised public concerns about non-attainment zones, which are areas with poor air quality that cannot meet the national standard. A few studies of the kinetics of ClO₂ reaction with VOCs have discussed process design and optimization. Table 4 shows the current cases of VOCs treatment using ClO₂ gas. Kastner *et al.* (2003a) provided kinetic analysis showing that ClO₂ could not be reacted with aldehyde types of VOCs such as hexanal and 2-methylbutanal, considering the pH and temperature effects. The main removal pathway of aldehyde removal was via mass transfer in the wet scrubber (Kastner and Das, 2005). Methanethiol, Ethanethiol, dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) can efficiently react with ClO₂. The overall reaction of ClO₂ on ethanethiol, DMS or DMDS is a second and third order reaction, thus the reaction rate depends on the pH. For example, the reaction rate of ethanethiol and DMDS could be increased from 25 to 4200 L mol⁻¹ s⁻¹ and 1.4 × 10⁶ L mol⁻¹ s⁻¹ from pH of 3.6 to 5.1 and pH of 9.

Table 4 The current cases of VOCs treatment using ClO₂ gas in a wet scrubber system.

VOCs types	Operation conditions	References
Hexanal and 2-methylbutanal	pH: 3.6–5.1 Temperatures: 23–40°C	(Kastner et al., 2003a)
Aldehyde	Temperatures: 50–65°C	(Kastner and Das, 2005)
Ethanethiol	pH: 5.1	(Kastner et al., 2003b)
Dimethyl disulfide	pH: 9	(Kastner et al., 2003b)
Formaldehyde	Dosages of ClO ₂ were set as 5, 25, 50 and 100 mg m ⁻³	(Wu et al., 2015)

These odor-causing compounds can be controlled in a wet scrubber in a small range of pH. Moreover, Kastner et al. (2003b) also suggested that incorporating oxidation kinetics into a wet scrubber system can appropriately predict the removal efficiency and reaction rate with increasing pH, but practical trials are still needed for industrial scale scrubbers. Wu et al. (2015) applied ClO₂ gas for 1.0 mg m⁻³ formaldehyde (CH₂O) decomposition under different reaction of 5, 10, 20, 30, 45, 60 min and the dosages of ClO₂ were set as 5, 25, 50 and 100 mg m⁻³. They found that the removal rate of CH₂O was increased by ClO₂ dosage and contacting time. The favorable ClO₂ gas concentration and reaction time for 1.0 mg m⁻³ CH₂O treatment were concluded to 30 mg m⁻³ and 30 min, respectively. The removal ratio of CH₂O was increased from 10% to 60% at exposure time of 60 min and ClO₂ dosage of 25 mg m⁻³. The highest removal ratio of CH₂O was up to 90% with dosage of ClO₂ of 100 mg m⁻³. When ClO₂ gas dissolved into aqueous solution, the reactivity of ClO₂ with organic compounds is predominant in the gas phase because the existence of organic compounds in water generally in low concentration. Ganiev et al. (2005) summarized the reaction kinetic reactivity on ClO₂ with organic compounds, in terms of hydrocarbons, alcohol, ketones, aldehydes, carboxylic acids, amines, thiols and phenols.

CONCLUSIONS

Gaseous ClO₂ has been implemented as a disinfectant, sterilizer and oxidizer in different fields. The principle of ClO₂ gas production is the reaction between sodium chlorite and hydrochloric acid. Due to the unstable and easy to decompose characteristics of ClO₂ gas, in-situ production technology needs to be developed. ClO₂ gas can be used for antimicrobial decontamination in the medical area, food processing and odor mitigation because of its high penetration and oxidation ability. In addition, the oxidation of air pollutants such as NO_x, SO_x, Hg, and VOCs using ClO₂ gas has been successfully demonstrated in recent research. Consequently, this mini review provided an overall introduction of ClO₂ gas application. To enhance the ClO₂ processing and treatment efficiency, future priority research directions include development of substantial and reliable ClO₂ gas release systems, combination of for innovative robotic technology for ClO₂ sterilization of epidemic prevention, and evaluation of the effects of ClO₂ dosages on indoor air quality in hospital.

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