# The Effect of Temperature and Humidity on the Decomposition Rate of Chlorine Dioxide

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Abstract— Chlorine dioxide (ClO<sub>2</sub>) is commonly utilized for virus elimination, sanitization, deodorization, and anti-fungal purposes. When improving indoor air quality using chlorine dioxide, it is necessary to distribute it indoors at appropriate concentrations. However, ClO<sub>2</sub> decomposes in space and absorbs the wall surface. The purpose of this paper is to clarify the effect of temperature and humidity on the decomposition rate of ClO<sub>2</sub>. We conducted decomposition experiments in the chamber and analyzed the concentration of ClO<sub>2</sub> using ion chromatography. The results indicate that humidity has a much greater impact than temperature on the decomposition rate of ClO<sub>2</sub>. We proposed a two-variable function of temperature and humidity for the decomposition rate of ClO<sub>2</sub> that represents the experimental results. Although the Arrhenius equation would explain the effect of temperature, the reaction mechanism between chlorine dioxide and water vapor is still unclear.

*Keywords*—chlorine dioxide, decompositon rate, chamber experiment, effect of temperature and humidity

### I. INTRODUCTION

Chlorine dioxide (ClO<sub>2</sub>) has a pungent odor similar to chlorine and is an orange-to-yellow gas heavier than air at room temperature. ClO<sub>2</sub> is a type of radical, and its strong oxidizing power is known to have virus removal, sanitizing, deodorizing, and anti-fungal properties [1]. Al-Otoum *et al.* reported that replacing chlorine in the water distribution system with ClO<sub>2</sub> reduces trihalomethane concentrations by about 80% [2]. Moreover, due to its solubility in water, ClO<sub>2</sub> can be used in the form of dissolved gas as well as in its gaseous state. With various combinations of usage forms and generation methods, ranging from large-scale production using reaction tanks to simple methods involving the placement of tablets in water, ClO<sub>2</sub> is a versatile substance that allows for efficient utilization depending on the quantity and application.

There is some evidence of health risks from  $ClO_2$  [3]. Concerning rats, pulmonary edema and emphysema were observed after single exposures, and in some cases, deaths were observed. The number of occurrences was also concentration-dependent. The human eye and respiratory tract irritation were also observed at high concentrations [3]. In terms of workplace safety, the United States Occupational Safety and Health Administration (U.S. OSHA) has set the 8hour time-weighted average permissible exposure limit (PEL-TWA) for ClO<sub>2</sub> inhalation at 0.1 ppm [4]. The Japan Chlorine Dioxide Industry Association has set an "indoor concentration guideline" of 0.01 ppm, which level is considered safe for humans even if they are exposed to it for their entire lifetime [1]. Regarding the solution of dissolved  $ClO_2$  gas, The Water Supply Law in Japan mandates a maximum  $ClO_2$  level of 0.6 mg/L in tap water [5]. The Food Safety Commission of Japan has established a tolerable daily intake (TDI) of 0.0029 mg/kg bw/day (as chlorite ion) for  $ClO_2$  in soft drinks [6]. The Japan Chlorine Dioxide Industry Association has established a provisional tolerable daily intake (TDI) of 0.029 mg/kg bw/day (as chlorite ion) for  $ClO_2$  (solvent) [1].

Currently, ClO<sub>2</sub> is approved for use as a disinfectant in drinking water, bleaching of pulp paper, disinfection of pool water, and wheat flour treatment in both Japan and the United States [7–9]. Japan has not approved it as a disinfectant for foods other than wheat, medical and quasi-drug products [8]. In China, however, its use as a disinfectant against COVID-19 was approved for disinfection of water (drinking water and hospital sewage), object surfaces, kitchen utensils, food processing tools and equipment, fruits and vegetables, medical instruments (including endoscopes), and air [10]. Experiments in Taiwan have reported the reduction of bacteria and mold counts when ClO<sub>2</sub> is used for disinfecting student cafeterias, libraries, or carrels [11, 12]. Using ClO<sub>2</sub> for fruit disinfection has been shown to reduce Salmonella, enterohemorrhagic E. coli O157:H17, Listeria monocytogenes on the surfaces of strawberries and blueberries, as well as significantly reduce tebuconazole residues on peaches, nectarines, and apricots after harvest [13, 14]. It was also reported that ClO<sub>2</sub> activated with citric acid can remove Ulva prolifera, which causes green tide [15]. Buenavista et al. also showed that using ClO<sub>2</sub> instead of fumigants could eliminate the pest without adversely affecting wheat [16]. The use of ClO<sub>2</sub> as a disinfection method during the cultivation of mushroom Hypsizygus ulmarius was reported to prevent substrate contamination by harmful microorganisms and to shorten the cultivation cycle [17]. In addition, replacing chlorine with  $ClO_2$  for treating biological fouling before reverse osmosis processing has been shown to significantly extend the half-life of aromatic polyamide membranes and effectively control cartridge filter clogging at concentrations approximately 1/100 of what would be required when using chlorine [18, 19]. Imaeda et al. conducted a comparative study on the loss of vitamins when ClO<sub>2</sub> was used as a water disinfectant because chlorine, which is conventionally used for disinfection of tap water, causes the destruction of vitamins as well as disinfection, and reported that there was less vitamin loss [20].

When improving indoor air quality using  $ClO_2$ , it is necessary to distribute it indoors at appropriate concentrations. However,  $ClO_2$  is easily soluble in water, and photolysis, thermal decomposition, or adsorption to walls and other surfaces in a space are possible [21–25]. Therefore, when determining the appropriate quantity of  $ClO_2$  for spraying, we should understand the decrease in concentration due to decomposition and adsorption. This study aimed to clarify the effect of temperature and humidity on the decomposition rate of  $ClO_2$  gas by decomposition experiments using a chamber.

# II. MATERIALS AND METHODS

### A. Experiment Overview

The equipment used in this study is shown in Table 1. A set of experiments was conducted to measure the decomposition rate of ClO<sub>2</sub> in a chamber with controlled temperature and humidity. An overview of the experiment is shown in Fig. 1. The chamber with a volume of  $1.8 \text{ m} \times 1.8$  $m \times 3.0$  m is connected with tubes for ClO<sub>2</sub> supply and air sampling. ClO<sub>2</sub> is supplied to the chamber from a ClO<sub>2</sub> generator outside the chamber. A circulator was installed inside the chamber to agitate the supplied ClO<sub>2</sub>. It was confirmed by the pilot experiment that the air in the chamber was sufficiently agitated and that leakage from the chamber and wall absorption were negligible. In this experiment, ClO2 was collected from the chamber's center using a pump. Two impingers and a pump were connected in series with tubing and aspirated at 0.5 L/min for 20 minutes. The samples were collected and analyzed by ion chromatography. Note that ClO<sub>2</sub> is known to photolyze [21–25], so the chamber was light-shielded.

Table 1. Details of equipment used in this experiment			
Equipment	Product name (Maker)		
Chamber	Growth chamber TGC-3 (ESPEC MIC CORP.)		
Temperature and humidity	Wireless Thermo Recorder RTR-503		
measuring instrument	(T&D Corporation)		
Circulator	YAR-FKW15(WH)		
	(YAMAZEN)		
Sampling pump	SP208-1000Dual		
	(GL Sciences Inc.)		
ClO <sub>2</sub> generator	Cleverin Generator LISPASS S-II		
	(Taiko Pharmaceutical Co., Ltd.)		
Ion chromatography	Dionex ICS-1000		
	(Thermo Fisher SCIENTIFIC)		
Autosampler	AS50		
	(Thermo Fisher SCIENTIFIC)		
Column	IonPac AG12A/AS12A		
	(Thermo Fisher SCIENTIFIC)		
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In the experiment, we first increased the  $ClO_2$  concentration inside the chamber to approximately 1–2 ppm by supplying  $ClO_2$  from the  $ClO_2$  generator. Subsequently, we started to measure after we stopped the  $ClO_2$  supply. The air in the chamber was collected at regular intervals and its concentration was measured by ion chromatography analysis.

The rate of decrease of  $ClO_2$  concentration in the chamber was assumed to be proportional to the concentration. The rate of decrease is expressed by the Eq. (1).

$$\frac{dC}{dt} = -kC \leftrightarrow C = C_0 e^{-kt} \tag{1}$$

where C is the ClO<sub>2</sub> concentration (ppm),  $C_0$  is the initial ClO<sub>2</sub> concentration (ppm), t is time (h), and k is the

proportionality constant (1/h).

The proportionality constant k represents the sum of the amount of leakage from the chamber, decomposition, and wall adsorption. The amount of leakage and wall absorption was sufficiently small compared to that of decomposition in the pilot experiment. Therefore, in this study, we examined the dependence of the decomposition rate on temperature and humidity.



Fig. 1. Experiment overview.

## B. Emission of ClO<sub>2</sub>

 $ClO_2$  was supplied to the chamber at about 120 mg/h for 15 or 30 minutes using a  $ClO_2$  generator. The initial concentration in the air in the chamber was about 1 ppm or 2 ppm. The initial concentration of 2 ppm was used for cases where the decomposition rate was so high that it would be difficult to measure the concentration. The time was set as 0 min when the supply of  $ClO_2$  was finished, and the concentration was measured five times at 0 min, 60 min, 120 min, 180 min, and 240 min to obtain the decomposition rate.

The experiment was repeated under different temperature and humidity conditions to determine the effect of temperature and humidity on the decomposition rate.

# *C.* Sampling of ClO<sub>2</sub> from the Chamber

ClO<sub>2</sub> supplied to the chamber is aspirated by a pump and collected in the adsorbent that consists of potassium iodide (KI), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), and sodium bicarbonate (NaHCO<sub>3</sub>) at 1.2 mM, 1.5 mM, and 1.5 mM, respectively. Since ClO<sub>2</sub> exists as chlorite ions (ClO<sub>2</sub><sup>-</sup>) in the collection solution, the concentration of chlorite ions is measured by ion chromatography and converted to ClO<sub>2</sub> gas concentration.

#### D. Analysis of Samples

To obtain the decomposition rate of  $ClO_2$  in this study, ion chromatography was used to measure the concentration. The analytical conditions of ion chromatography are shown in Table 2.

Table 2. Ion chromatography analysis conditions			
Parameter	Condition		
Eluent	4.5 mM Na <sub>2</sub> CO <sub>3</sub> , 0.5 mM NaHCO <sub>3</sub>		
Eluent flow rate	1.5 mL/min		
Column temperature	35 deg.C		
Detector	Conductivity detection		
Current value	21 mA		
Sample introduction amount	25 µL		

Calibration curves were prepared using the absolute calibration curve method at five concentration levels: 0.01 mg/L, 0.05 mg/L, 0.1 mg/L, 0.5 mg/L, and 1 mg/L. Chlorite ion standard solution 998 mg/L (Fujifilm Wako Pure

Chemicals Co., Ltd.) was used as the reagent after dilution. The calibration curves were obtained two times and they showed good consistency.

### III. RESULT AND DISCUSSION

A well-presented results section coupled with a convincing discussion will definitely prove the novelty and importance of your study. It should provide a concise and precise description of the experimental results, their interpretation, as well as the experimental conclusions that can be drawn.

# A. ClO<sub>2</sub> Decomposition Experiment

The concentration changes of ClO<sub>2</sub> gas over time are shown in Fig. 2. The details of experimental conditions (temperature and humidity) and estimated decomposition rate for each case number are shown in Table 3. Temperatures in the chamber are maintained and the standard deviations are less than 1 deg. C during each experiment. The leakage of water vapor from the chamber is negligible then absolute humidity did not vary. As shown in Fig. 2, the concentration decreases in the first-order reaction, so the hypothesis of Eq. (1) is appropriate. In cases 1, 2, 3, 4, and 5, where the decomposition rate is higher, the ClO<sub>2</sub> concentration after 4 hours is below the detection limit and is therefore absent. The determination coefficient of concentration changes is over 0.999 in all the cases, uncertainty of this experiment is small enough to neglect. Using these results, the relationship between the decomposition rate of ClO<sub>2</sub> and absolute temperature and humidity is examined.



Fig. 2. The concentration changes of ClO<sub>2</sub> gas over time on varied conditions.

Table 3. Experiment conditions (temperature and humidity) and estimated decomposition rate of ClO<sub>2</sub>

Case	Temperature (deg.C)	Relative humidity (%)	Absolute humidity (g/m <sup>3</sup> )	K (1/h)
1	33.8	81.9	30.5	1.4110
2	32.0	87.5	29.6	1.5840
3	27.3	96.1	25.2	1.0570
4	28.0	90.2	24.6	1.2200
5	27.3	91.8	24.1	1.1200
6	26.5	90.3	22.6	0.7317
7	30.1	68.0	20.8	0.4513
8	28.7	60.0	17.0	0.2578
9	27.7	59.4	15.9	0.2069
10	26.2	64.0	15.8	0.2155
11	32.3	44.4	15.3	0.2572
12	33.2	39.1	14.1	0.2390
13	26.5	53.0	13.3	0.2122
14	25.6	46.0	11.0	0.2153

As shown in Fig. 2, the decomposition rate of  $ClO_2$  varies greatly depending on temperature and humidity conditions.

The Arrhenius equation in Eq. (2) shows the relationship between decomposition rate and absolute temperature.

$$k = A \exp\left(-\frac{E}{RT}\right) \leftrightarrow \ln k = \ln A - \frac{E}{RT}$$
 (2)

where *k* is the reaction rate (1/h), *A* is the frequency constant (1/h), *R* is the gas constant (J/(mol·K)), and *E* is the activation energy (J/mol). From Eq. (2), the logarithm of the decomposition rate (ln*k*) is linear with respect to the inverse of the absolute temperature  $(\frac{1}{T})$ . A scatter plot of ln*k* versus  $\frac{1}{T}$  is shown in Fig. 3. The decomposition rate tends to increase with increasing temperature to be consistent with Eq. (2), but the coefficient of determination is not large (R<sup>2</sup> = 0.0578). This result indicates absolute temperature is not a dominant factor in the decomposition rate of ClO<sub>2</sub> gas.



Fig. 3. Relationship between the inverse of absolute temperature and decomposition rate.

A scatter plot of decomposition rate versus absolute humidity is shown in Fig. 4. The higher the absolute humidity, the greater the decomposition rate ( $R^2 = 0.9281$ ). The decomposition rate increased in proportion to the 2.5 power of absolute humidity.

These results suggest that the decomposition rate of  $ClO_2$ in air is more affected by humidity than temperature. Samples plotted upwards from the estimated relationship between the inverse of absolute temperature and decomposition rate (cases 1–6) are high humidity conditions, and others are low in Fig. 3. Eq. (2) does not conclude the effect of humidity. That's why the coefficient of determination is not large. Therefore, humidity in the room is a large impact on decomposition rate of  $ClO_2$  and we should spray  $ClO_2$  to the room with measuring humidity. The direct effect of absolute temperature on the decomposition rate is considered to be small. However, it would be necessary to consider the indirect effect of temperature since there is an increase in humidity due to the increase in saturated water vapor content as the temperature rises.



Fig. 4. Relationship between absolute humidity and decomposition rate.

# *B.* Discussion on the Decomposition Rate Equation of ClO<sub>2</sub>

From the result shown in Fig. 3, 4, *E* and *A* can be evaluated under the known gas constant. In this study, *E* was  $5.41 \times 10^4$  J/mol and *A* was  $1.96 \times 10^9$  1/h. Based on the results of this experiment, the equation for the decomposition rate of ClO<sub>2</sub> gas is as follows:

$$k = 5.88 \times 10^5 \times H^{2.46} \exp\left(-6505.9 \times \frac{1}{T}\right)$$
(3)

where *H* is the absolute humidity  $(g/m^3)$ .

A scatter plot of calculated and measured decomposition rates according to Eq. (3) is shown in Fig. 5. The coefficient of determination is as high as  $R^2 = 0.7915$ , which is considered sufficient to express the decomposition rate of ClO<sub>2</sub>.



Fig. 5. Comparison of calculated and measured decomposition rates.

#### IV. CONCLUSION

In this study, the relationship between the decomposition rate of ClO<sub>2</sub> and temperature and humidity was investigated by measuring the concentration of ClO<sub>2</sub> every 60 minutes using a chamber. The amount of change in the decomposition rate due to changes in absolute temperature was small, and the direct effect of absolute temperature on the decomposition rate can be considered negligible in the range of 298 to 307 K covered in this study. On the other hand, the decomposition rate of ClO<sub>2</sub> was found to be significantly affected by absolute humidity. In the range of 11 to 31 g/m<sup>3</sup> covered in this study, the coefficient of proportionality was 2.5. Therefore, when controlling indoor ClO<sub>2</sub> concentrations, it is crucial to consider the variation in decomposition rate due to absolute humidity. The experimental results suggest that the presence of water vapor accelerated the decomposition of ClO<sub>2</sub>, but the mechanism is unclear. Therefore, further studies on the reaction process and rate are needed.

#### CONFLICT OF INTEREST

The authors declare no conflict of interest.

# AUTHOR CONTRIBUTIONS

Matsuo and Kondo made the research plan; Fukuma conducted experiments; Fukuma, Matsuo, Miura, Shimadera, and Kondo conducted data analysis; all authors had approved the final version.

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#### REFERENCES

- [1] Japan Chlorine Dioxide Industry Association, (2014), *Evaluation to set voluntary management standards of Chlorine Dioxide*. (in Japanese). [Online]. Available: http://chlorinedioxide.or.jp/clo2
- [2] F. A. Otoum, M. A. A-Ghouti, T. A. Ahmed, M. A-Dieyeh, and M. Ali, "Disinfection by-products of chlorine dioxide (chlorite, chlorate, and trihalomethanes): Occurrence in drinking water in Qatar," *Chemosphere*, vol. 164, pp. 649–56, December 2016.
- [3] IPCS UNEP//ILO//WHO. (2002). Concise International Chemical Assessment Document, No.37 Chlorine Dioxide (Gas). [Online]. Available: chromeextension://efaidnbmnnnibpcajpcglclefindmkaj/https://www.nihs.go. jp/hse/cicad/full/no37/full37.pdf
- [4] U.S. Department of Labor Occupational Safety and Health Administration, (1978). Occupational Health Guideline for Chlorine Dioxide. [Online]. Available: https://www.osha.gov/chemicaldata/16
- [5] Ministry of Health, Labor and Welfare, "Ministerial ordinance for technical standard of Water Supply" (in Japanese), 2000.
- [6] Food safety commission of Japan, 2008, Chemical Substance / Pollution Substance Expert Committee, Evaluation report of soft drink, Chlorine Dioxide (2008) (in Japanese).
- US Code of Federal Regulations. Title 21 CFR. https://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/CFRSearch .cfm. Accessed Octorber 11, 2023.
- [8] U.S. Environment Protection Agency (EPA), National Primary Drinking Water Regulations.
- [9] Ministry of Health of Japan, Standards for foods, additives by Ministry of Health of Japan, Notification No. 370 (in Japanese).
- [10] Supervision Letter of the National Health Commission Office, Notice issued by Office of National Health Commission on printing and distributing the guidelines for using disinfectants. No. 147, Guideline for using Disinfectants February 2020 (in Chinese).
- [11] C. S. Hsu, M. C. Lu, and D. J. Huang, "Effect of gaseous chlorine dioxide on student cafeteria bioaerosols," *Clean Soil Air Water*, vol. 42, no. 1, pp. 12–19, May 2013.
- [12] M. C. Lu, C. S. Hsu, D. J. Huang, C. K. Liang, and J. W. Huang, "Statistical evaluation of disinfection performance of chlorine dioxide and WAHW in improving indoor air quality of university library," *Journal of Aerosol Science*, vol. 115, pp. 113–120, January 2018.
- [13] P. Luu, V. S. Chhetri, M. E. Janes, J. M. King, and A. Adhikari, "Efficacy of gaseous chlorine dioxide in reducing Salmonella enterica, E. coli O157:H7, and Listeria monocytogenes on strawberries and blueberries," *LWT*, vol. 79, no. 10, pp. 1673–79, April 2021.
- [14] H. Calvo, D. Redondo, S. Remon, M. E. Venturini, and E. Arias, "Efficacy of electrolyzed water, chlorine dioxide and photocatalysis for disinfection and removal of pesticide residues from stone fruit," *Postharvest Biology and Technology*, vol. 148, pp. 22–31, February 2019.
- [15] R. He, Y. Zeng, S. Zhao, J. Zhang, P. He, and J. Liu, "Use of citric acid-activated chlorine dioxide to control Ulva prolifera," *Marine Pollution Bulletin*, vol. 194(B), 115357, September 2023.
- [16] R. M. Buenavista, E. Xinyi, B. Subramanyam, J. L. Rivera, M. Casada, and K. Siliveru, "Evaluation of wheat kernel and flour quality as influenced by chlorine dioxide gas treatment," *Journal of Stored Products Research*, vol. 102, 102127, May 2023.
- [17] F. Atila, "Possibility of safe, easy and lower cost substrate disinfection with chlorine dioxide in Hypsizygus ulmarius cultivation," *Scientia Horticulturae*, vol. 318, 112139, August 2023.
- [18] A. Wang, S. Huo, J. P. Croue, and C. Liu, "Reaction of polyamide membrane model monomers with chlorine dioxide: Kinetics, pathways, and implications," *Water Research*, vol. 241, 120159, August 2023.
- [19] M. Song, S. J. Im, D. Jeong, and A. Jang, "Reduction of biofouling potential in cartridge filter by using chlorine dioxide for enhancing anti–biofouling of seawater reverse osmosis membrane," *Environmental Research*, vol. 180, 108866, January 2020.
- [20] K. Imaeda, T. Watanabe, S. M. Chen, C. Q. Lin, Y. Yoshimura, K. Uchiyama, K. Ohsawa, Y. Ohtani, and K. Tamura, *The Pharmaceutical Society of Japan*, vol. 37, no. 3, pp.191–196, 1991.
- [21] Y. Lee, G. Burgess, M. Rubino, and R. Auras, "Reaction and diffusion of chlorine dioxide gas under dark and light conditions at different temperatures," *Journal of Food Engineering*, vol. 144, pp. 20–28, January 2015.
- [22] T. Ogawa, Japan Tappi, vol. 10, no. 65, pp. 378-87, 1956.
- [23] M. A. Brusa, L. J. Perissinotti, M. S. Churio, and A. J. Colussi, "Mechanism of chlorine dioxide photodissociation in condensed media," *Journal of Photochemistry and Photobiology*, vol. 101, no. 2–3, pp. 105–11, December 1996.

- [24] T. Yang, M. Zhu, L. An, G. Zeng, C. Fan, J. Li, J. Jiang, and J. Ma, "Photolysis of chlorite by solar light: An overlooked mitigation pathway for chlorite and micropollutants," *Water Research*, vol. 233, 119809, April 2023.
- [25] S. Zheng, H. Ji, W. Qin, C. Chen, Z. Wu, K. Guo, W. Wei, W. Guo, and J. Fang, "Production of reactive species during UV photolysis of chlorite for the transformation of micropollutants in simulated

drinking water," Chemical Engineering Journal, vol. 470, 144076, August 2023.

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