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Formation of Chlorite and Chlorate from Chlorine Dioxide with Han River Water

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Abstract−This study was designed to elucidate the behavior of chlorine dioxide in drinking water systems. Furthermore, the factors that influence the formation of chlorite, chlorate in terms of reaction time, concentration of chlorine dioxide, pH, temperature and UV irradiation were experimentally reviewed. At 20 °C, pH 7, 70-80% of chlorine dioxide injected was converted to chlorite and 0-10% of that was transformed into chlorate within 120 min with 2.91 mg/L of DOC. The amount of chlorite formed also increased when pH and temperature increased. As DOC content increased, the residual chlorine dioxide decreased but the amount of chlorite and chlorate were increased. These experiments revealed that chlorate was a dominant by-product under UV irradiation. The models that were obtained by the regression analysis for the formation of chlorite and chlorate from chlorine dioxide with Han River water are as follows: Chlorite (mg/L)$=10^{-2.20}[ClO_2]^{0.45}[pH]^{0.90}[temp]^{0.27}[TOC]^{1.04}[time]^{0.20}$, Chlorate (mg/L)$=10^{-2.61}[ClO_2]^{1.27}[pH]^{-0.50}[temp]^{1.28}[TOC]^{0.31}[time]^{0.12}$

Key words: Chlorine Dioxide, Chlorite, Chlorate, Disinfection, Factors

INTRODUCTION

Chlorine is one of the most common disinfectants used in drinking water treatment because it is very economical and has good germicidal ability. But it is reported that it reacts with organic material and bears THMs (trihalomethanes) that are classified as suspicious cancer-causing material. So, many concerns are focused on alternative disinfectants such as chlorine dioxide, ozone, UV and etc. [Geo, 1992; Kong et al., 2003].

In particular, the use of chlorine dioxide was listed as one of the most suitable treatment technologies for control of THMs [Karen and Philip, 1987]. As an example of typical results, Ohio River water was dosed with various combinations of chlorine dioxide and chlorine. It is significant to note that even small amounts of chlorine dioxide are sufficient to inhibit the formation of THMs by as much as 20% [Miltner, 1976]. And there is increased interest in using chlorine dioxide to treat drinking water for taste, odor control and oxidation of iron and manganese [Robert et al., 1990].

Chlorine dioxide can be decomposed to chlorite and chlorate in water [Gates and Harrington, 1995], both of which have negative effects on health [Johanna et al., 1993]. That is why standards for concentration of chlorine dioxide and its by-products are established in many countries [Aieta and James, 1986]. WHO recommends that the concentration of chlorite should not exceed 0.2 mg/L in drinking water. In 1996, the Safe Drinking Water Amendments were established to control disinfectant residuals and chlorite by USEPA. The maximum contaminant level (MCL) and the maximum residual disinfectant level (MRDL) were established at 1.0 mg/L for chlorite and 0.8 mg/L for chlorine dioxide, respectively [Richard and Frederick, 1991]. In Korea, the limit for chlorine dioxide in potable water is 0.5 mg/L [Ministry of Environment, the Republic of Korea, 1995]. The toxicity of chlorine dioxide, chlorite and chlorate is considered to be the same because chlorine dioxide and chlorate can be rapidly converted to chlorite in the human body [Lyman, 1986].

The objective of this study is to evaluate the consumption rate of chlorine dioxide and the formation rates of chlorite and chlorate in the water treatments using chlorine dioxide. A further objective is to investigate the factors that influence the formation of chlorite and chlorate, such as reaction time, concentration of chlorine dioxide dosed, pH, temperature, UV irradiation and so on and develop models for the formation of chlorite and chlorate from chlorine dioxide in water treatment.

MATERIALS AND METHODS

1. Generation of Chlorine Dioxide

Chlorine dioxide was produced with a laboratory scale generator by acid activation of sodium chlorite as seen in Fig. 1. The chlorine dioxide gas formed was driven off by sparging with air and carried through three traps in series before it was absorbed into distilled water cooled in an ice bath. The impurities in the initial solution were not detected significantly in every blank test.

The stock solutions were standardized by a UV spectrophotometer (UV-1601, Shimadzu, Japan) since the absorption of chlorine dioxide is just proportioned to its concentration at 360 nm. The bottles which contained chlorine dioxide were covered tightly by aluminum foil to minimize the decomposition of chlorine dioxide when they were exposed to UV light. The mother solution of chlorine dioxide was kept in a refrigerator. Its concentration was determined at the beginning of each experiment.

2. Sample Collection

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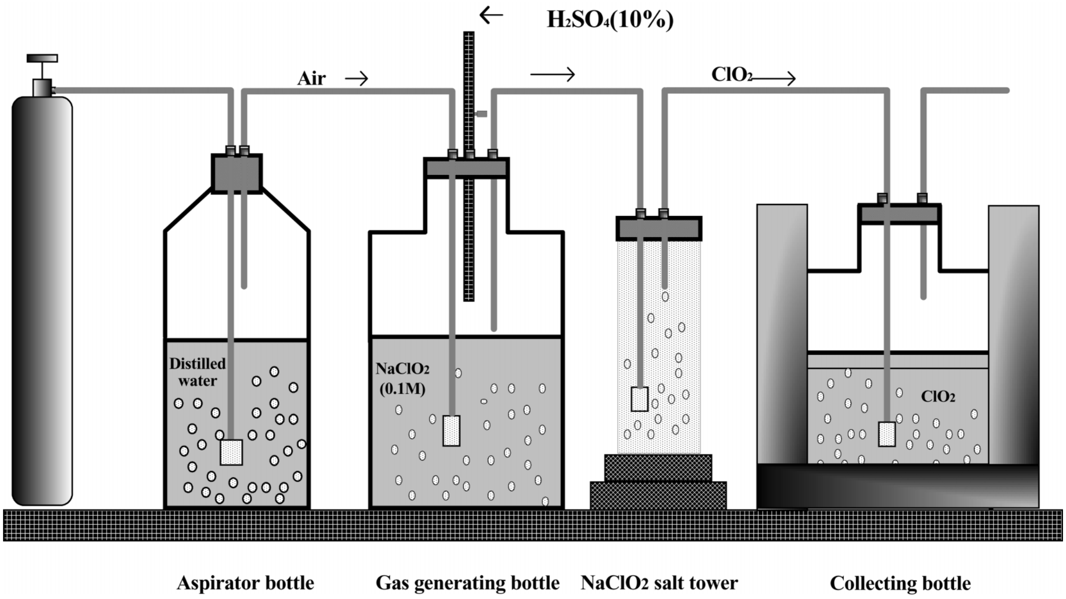

Fig. 1. Chlorine dioxide generation system.

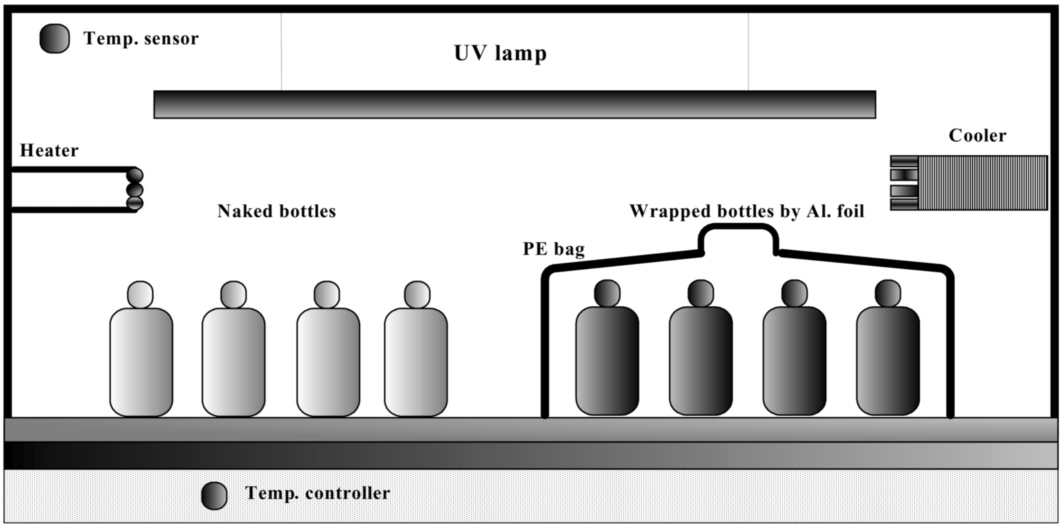

Fig. 2. Schematic diagram of apparatus for reaction of chlorine dioxide.

Water samples were collected from three points of the Han River by grab sampling and stored in a dark and cool cabinet. Artificial DOC (Dissolved Organic Carbon) was not added on purpose. They were filtrated by a 0.2 μm membrane filter before chlorine dioxide was injected.

3. Experimental Apparatus

The schematic diagram of experimental equipment is shown in Fig. 2. In order to set initial pH in reaction, a 1% solution of phosphoric acid and caustic soda was used. The samples in which chlorine dioxide was mixed together were poured into 500 mL glass bottles until they overflowed to avoid the head space and capped. The samples were left under a UV lamp in an incubator. The UV lamp was a low-pressure mercury lamp that had a 30 cm arc length with 365 nm wavelength. The distance between the UV lamp and the samples was 25 cm. The intensity of UV irradiation was 3.8 mW/cm^2 according to the information from the lamp manufacturer. Some samples that needed to be kept in the dark were shielded by wrapping with aluminum foil and black PE film, respectively. To compare the formability of chlorite and chlorate from the chlorine dioxide under sunlight with them under UV irradiation and in the dark, some samples were exposed to sunlight directly. For reference, the average intensity of midday sunlight is 11.6 mW/cm^2 in UV range and 41.6 mW/cm^2 in visible range [Kim, 1998]. The total reaction time was set at 120 min since the same contact time is usually required in water treatment plants.

4. Analytical Method

Concentrations of chlorite and chlorate were determined by ion chromatography. The operating conditions of the chromatograph (DX-300, Dionex, USA) are given in Table 1.

Because chlorine dioxide and other anions can cause some interference with the measurement, a spurge with nitrogen gas was needed [Jeong et al., 1993]. Also, $NaNO_2$ was added to enlarge the in-

Table 1. Operating conditions of ion chromatograph

Item	Analyzing condition
Separate column	Ionpac AS9-HC
Guard column	Ionpac AG9-HC
Eluent	9.0 mM Na_2CO_3
Eluent flow rate	1.0 mL/min
Suppressor	ASRS-with external water mode
Injection loop	150 μL
Pump	DXP pump
Detector	Suppressed conductivity
Storage solution	9.0 mM Na_2CO_3

jection loop for determining concentration by ppb (μg/L) level.

The standard solutions of chlorite and chlorate were prepared by dilution of the ultra pure reagents. Concentration was measured in every 10 injections. The limits of detection were 0.010 mg/L for chlorite and 0.012 mg/L for chlorate.

Total Organic Carbon (TOC) was measured in acidified, unfiltered samples by injection into a Shimadzu TOC-5000 analyzer [Kim et al., 2002].

RESULTS AND DISCUSSION

1. Effect of Initial Chlorine Dioxide

Fig. 3 illustrates the variation of residual chlorine dioxide depending on its initial concentration at 20 °C. Chlorine dioxide reacted violently with organic substances in water in the first 15 min and it was decomposed continuously to 120 min.

When the initial concentrations of chlorine dioxide were 0.5, 1 and 3 mg/L, the concentrations of chlorine dioxide remaining were 0.01, 0.16 and 1.89 mg/L after 120 min. The ratios of residual chlorine dioxide to initial chlorine dioxide were 2.0, 16.3 and 63.1%.

Fig. 4 shows the variation of chlorite and chlorate depending on initial concentration of chlorine dioxide. The formation of chlorite within 15 min was very dominant as consumption of chlorine dioxide was also very prominent. Concentration of chlorite formed increased more rapidly when chlorine dioxide was dosed in high concentration, but the transformation rate decreased more slowly.

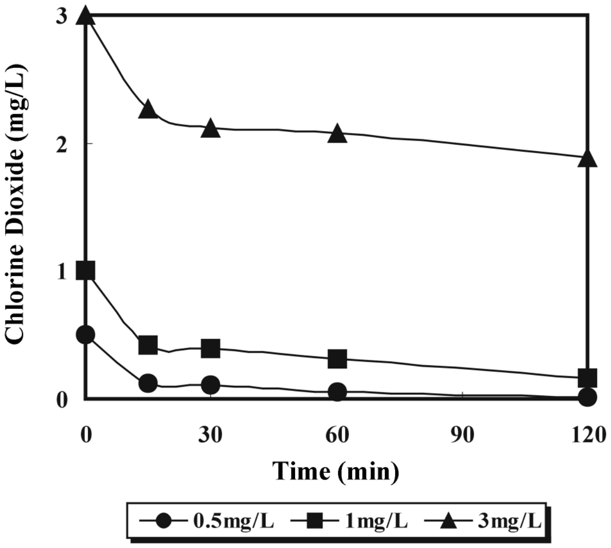

Fig. 3. Variation of residual chlorine dioxide depending on initial chlorine dioxide.

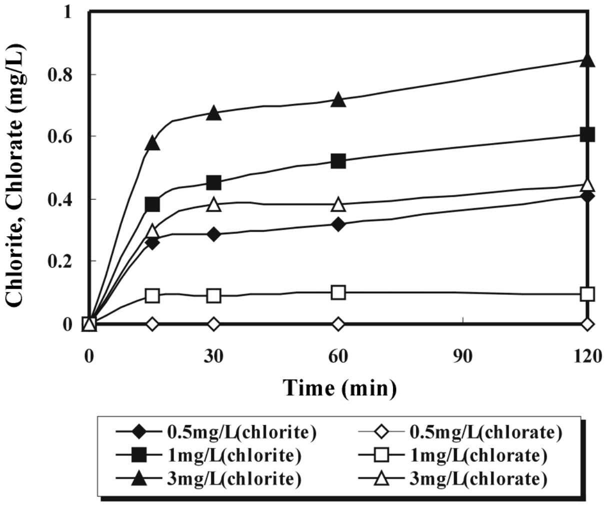

Fig. 4. Variations of chlorite, chlorate depending on initial chlorine dioxide.

Within 120 min, the ratios of chlorite formed from chlorine dioxide were 84.0, 72.3 and 76.4% when initial chlorine dioxide was 0.5, 1 and 3 mg/L, respectively. It is evident that a great proportion of chlorine dioxide was converted to chlorite.

The concentration of chlorate formed was also higher when the initial concentration of chlorine dioxide was higher. However, when chlorine dioxide was 0.5 mg/L, chlorate was not found. But when chlorine dioxide was 1 and 3 mg/L, the ratios of chlorate transformed from chlorine dioxide were 1.0 and 14.9%.

To not exceed the MCLs (Maximum contaminant levels) for chlorine dioxide and chlorite recommended by USEPA, it appeared that chlorine dioxide dose should not exceed 1.64 mg/L in the case of this sample (DOC=2.91 mg/L).

2. Effect of pH

Fig. 5 illustrates the variation of residual chlorine dioxide and Fig.

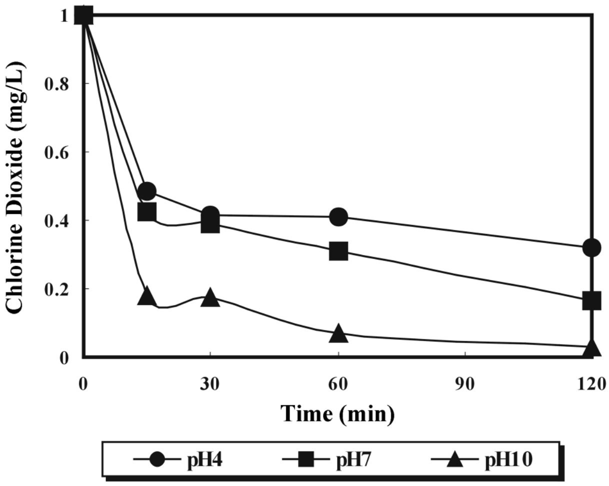

Fig. 5. Variation of residual chlorine dioxide depending on pH.

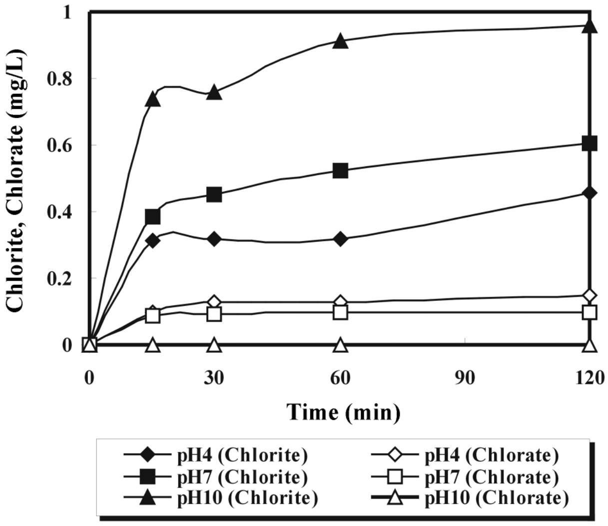

Fig. 6. Variations of chlorite, chlorate formed depending on pH.

6 shows the variation of chlorite and chlorate formed depending on the pH when chlorine dioxide was injected at 1 mg/L at 20 °C.

The oxidation-reduction reaction of chlorine dioxide in water resulted in the formation of chlorite ion as follows:

$$ClO_2+e \rightarrow ClO_2^-$$

In alkaline solution, as the conversion ratio to by-products was higher, chlorine dioxide was decomposed relatively faster. Especially when pH was 10, chlorine dioxide reacted with the reductants in water continuously and was converted to by-products most greatly compared to other pH range. This may have been caused by the disproportionate reaction of chlorine dioxide under basic conditions:

$$2ClO_2+2OH^- \rightarrow ClO_2^-+ClO_3^-+H_2O$$

As the results show in Fig. 5 and Fig. 6, it was coincident with the fact that the activity of chlorine dioxide depends on pH. It is known that pH controls the number of electrons [Narkis et al., 1990]. When pH was 4, 7 and 10 after 120 min, the ratios of chlorite formed from chlorine dioxide were 45.0, 61.0 and 96.0%. This means that chlorite was formed in larger proportions when pH was higher.

On the other hand, the concentration of chlorate formed was higher when pH was lower. At pH 7, chlorate was transformed to about 10% from chlorine dioxide. Meanwhile at pH 4, chlorate was transformed to about 15% from chlorine dioxide. By the way, at pH 10, chlorate was not formed at all.

In condition of low pH, chlorine dioxide converts to chlorate. This can be understood by means of the following steps [Rav-Acha et al., 1984]:

$$4ClO_2+4H^++4e \rightarrow 4HClO_2$$
$$4HClO_2 \rightarrow 2ClO_2+ClO_3^-+Cl^-+2H^++H_2O$$

3. Effect of Temperature

Fig. 7 illustrates the variation of residual chlorine dioxide and Fig. 8 shows variation of chlorite and chlorate as formed depending on temperature when chlorine dioxide was injected at 1 mg/L at 20 °C.

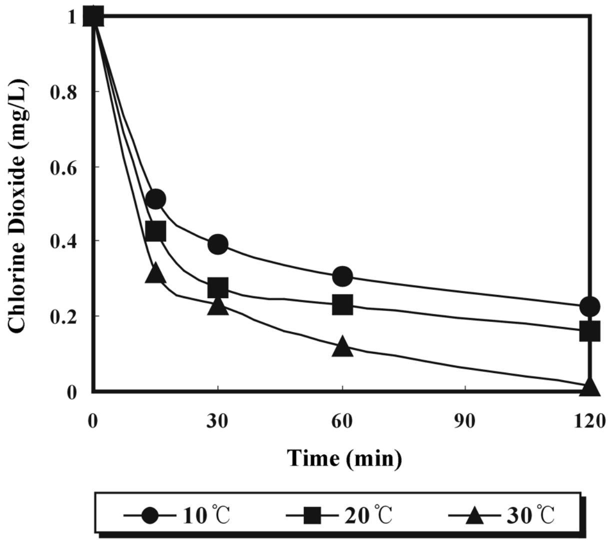

Fig. 7. Variation of residual chlorine dioxide depending on temperature.

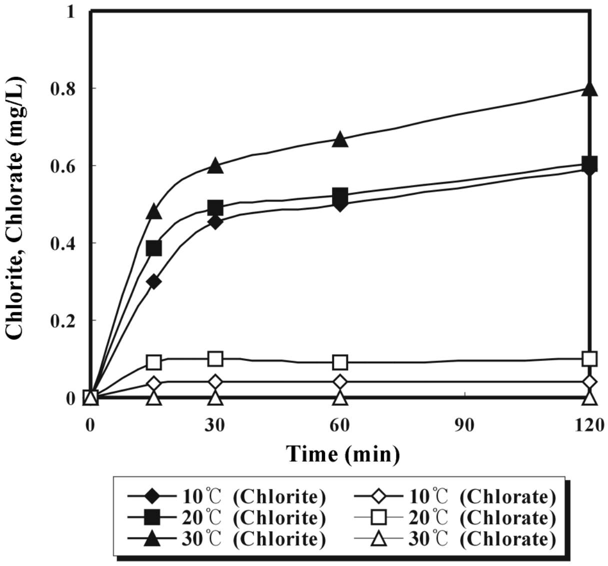

Fig. 8. Variations of chlorite, chlorate formed depending on temperature.

As temperature affects the rate of reaction, chlorine dioxide consumption increased with temperature. The ratios of chlorine dioxide consumed to chlorine dioxide dosed were 77.2, 83.7 and 98.6% after 120 min at 10, 20 and 30 °C.

The formation of chlorite was considerably active at lower temperature. The percentage of chlorite transformed from chlorine dioxide was 59.0 and 60.5% at 10 and 20 °C, respectively, but it reached even 80.2% at 30 °C.

As in the Arrhenius equation, the rate of a chemical reaction is seriously affected by reaction temperature. Thus, the rate of every reaction at a 10 °C higher temperature can be expected to be twice as fast as that at a primary temperature. According to the results of this study, chlorite production at 120 min was approximately 1.33 times higher at 30 °C than at 20 °C. Meanwhile, the formation of chlorite at 20 °C was only 1.03 times higher on the average than

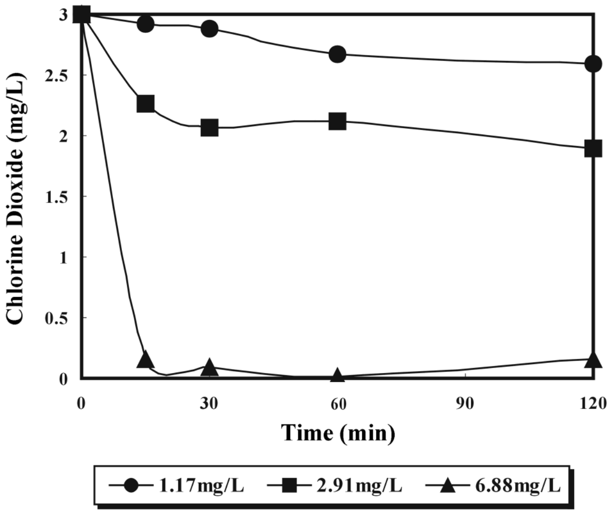

Fig. 9. Variation of residual chlorine dioxide depending on DOC.

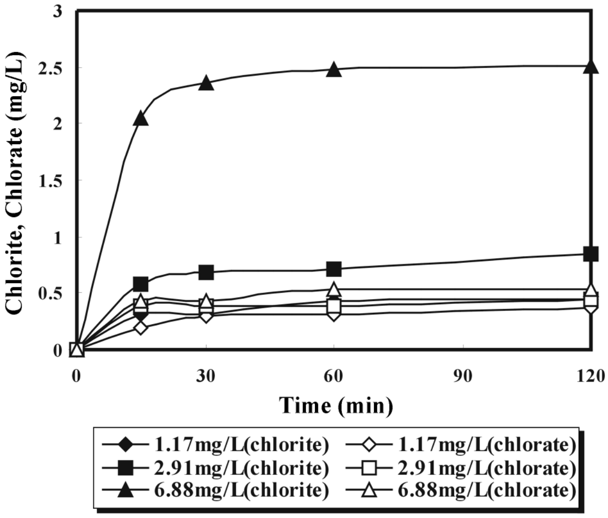

Fig. 10. Variations of chlorite, chlorate formed depending on DOC.

that at 10 °C. It means that chlorite can be produced relatively well even in the winter season.

In a wide range of temperature, chlorate was formed within 10% of dosed chlorine dioxide. The ratios of chlorate formed from chlorine dioxide were 5.4 and 10.0% at 10 and 20 °C after 120 min. At 30 °C, No chlorate was formed.

4. Effect of DOC

Fig. 9 illustrates the variation of residual chlorine dioxide and Fig. 10 shows variation of chlorite and chlorate depending on DOC when chlorine dioxide was injected at 3 mg/L.

As concentration of DOC in water increased, chlorine dioxide decreased. After 120 min, chlorine dioxide consumption was 0.40 1.11, 2.83 mg/L when DOC was 1.17, 2.91 and 6.88 mg/L. The consumption ratios of chlorine dioxide to DOC were 34, 38 and 41% when DOC was 1.17, 2.91 and 6.88 mg/L. Therefore, nearly 0.40 mg/L of chlorine dioxide was consumed by increasing DOC by 1 mg/L after 120 min contact time.

The ratios of chlorite transformed from chlorine dioxide were to 15.0, 28.2 and 83.8% when DOC was 1.17, 2.91 and 6.88 mg/L. In other words, chlorite transformation increased as DOC increased. The formation of chlorate showed the same trend as that of chlorite. The ratios of chlorate formed from chlorine dioxide were 12.2, 14.9 and 16.0% when DOC was 1.17, 2.91 and 6.88 mg/L. This result was contrary to a study by Jeong et al. [1993] that showed that the formation of chlorate was not related to concentration of DOC. However, the ratios of chlorite to DOC injected in every case were not so much different: 38.5, 29.1 and 36.5%.

5. Effect of UV

When samples reacted with chlorine dioxide under UV irradiation and in the dark, respectively, at pH 7, 20 °C and concentration of chlorine dioxide injected was 3 mg/L, the results are shown in Fig. 11 and Fig. 12. Chlorine dioxide under UV and sunlight irradiation was consumed more than that in the dark.

In these experiments, under sunlight irradiation, chlorite was formed only in a small amount, approximately 0.01 mg/L. Therefore, it seems that the predominant species in the reaction of chlorine dioxide under sunlight is not chlorite but other by-products. Under sunlight, the concentration of chlorate transformed was 56%

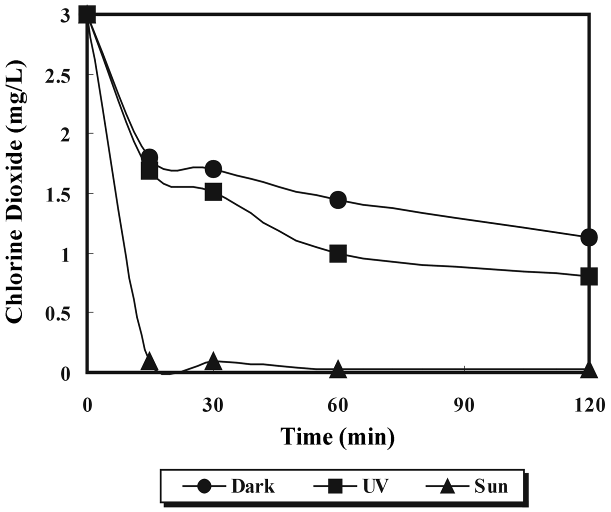

Fig. 11. Variation of residual chlorine dioxide depending on UV.

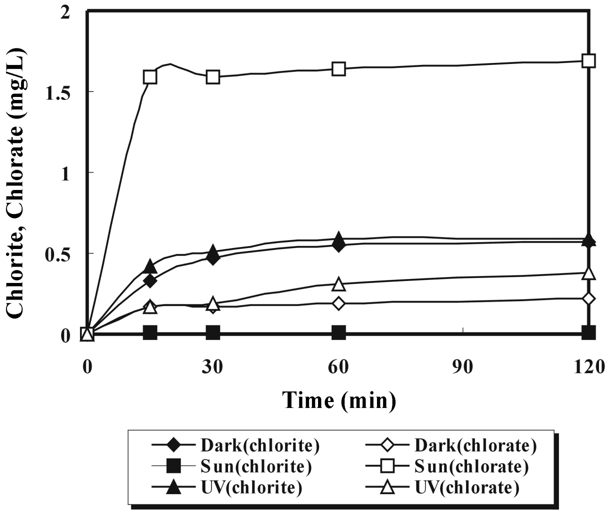

Fig. 12. Variations of chlorite, chlorate formed depending on UV.

from chlorine dioxide after 120 min. Also, the concentration of chlorate formed under sunlight was 9.9 and 4.5 times higher than the concentration in the dark and under UV irradiation, respectively.

Consequently, it appears that the predominant species in the reaction of chlorine dioxide under UV is chlorate and its formation progresses rapidly. This result is also explained by the equation that was designed by Masschelein et al. [1979]:

$$2ClO_2+hv+H_2O=HClO_3+HCl+2O\cdot$$

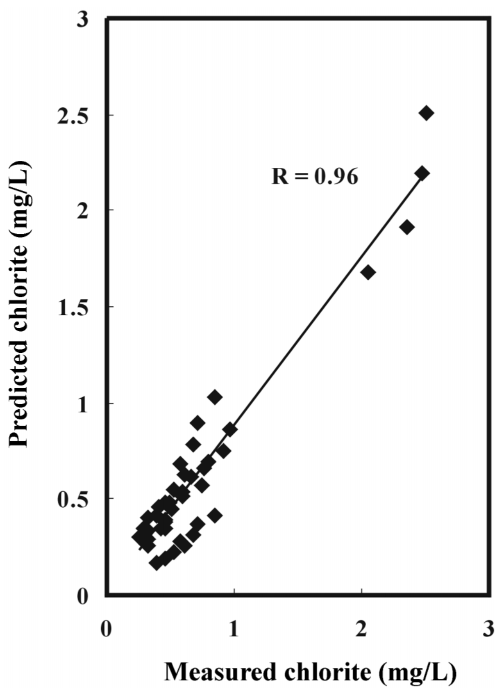

Fig. 13. Predicted chlorite and measured chlorite by internal data simulation via this study.

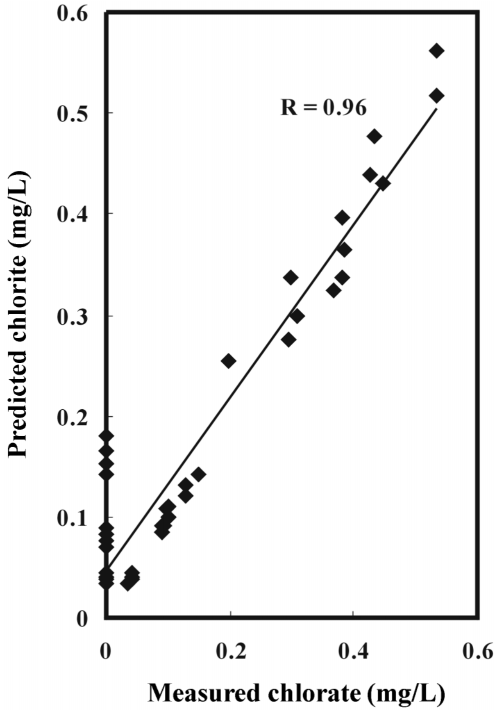

Fig. 14. Predicted chlorate and measured chlorate by internal data simulation in this tudy.

6. Models for Formation of Chlorite and Chlorate

In this study, the models for the formation chlorite and chlorate in the reaction of sample with chlorine dioxide were obtained by the regression analysis of SAS. The models are as follows:

$$\text{Chlorite (mg/L)}=10^{-2.20}[ClO_2]^{0.45}[pH]^{0.90}[temp]^{0.27}[TOC]^{1.04}[time]^{0.20}$$
$$\text{Chlorate (mg/L)}=10^{-2.61}[ClO_2]^{1.27}[pH]^{-0.50}[temp]^{1.28}[TOC]^{0.31}[time]^{0.12}$$

In these models, the order of contribution in the formation of chlorite and chlorate from chlorine dioxide can be readily seen.

A comparison of concentration between predicted by-products and measured by-products via the models developed in this study is displayed in Fig. 13. R values of regression line in both cases were 0.96.

CONCLUSIONS

The objective of this study was to better understand the behavior of chlorine dioxide and its by-products, chlorite and chlorate in drinking water. This study placed particular emphasis on the factors that influence the formation of DBPs such as reaction time, concentration of chlorine dioxide, pH, temperature and UV irradiation. Based on the data collected in this study, the following can be concluded:

Within 120 min, 70-80% and 0-10% of chlorine dioxide injected was converted to chlorite and chlorate, respectively. The formation of chlorite showed a tendency to increase with pH and temperature.

The consumption ratio of chlorine dioxide was 0.34-0.41 when DOC was in the range of 1.17-6.88 mg/L. In addition, the consumption rate of chlorine dioxide increased with higher concentration of the organic pollutants. As DOC content was higher, residual chlorine dioxide was lower but formation of chlorite and chlorate increased. The ratios of chlorite and chlorate formed from chlorine dioxide were 15.0-83.8 and 12.2-17.8%, respectively.

Chlorate was the dominant by-product under UV irradiation. It was generated 9.9 and 4.5 times more under sunlight than in the dark and under UV irradiation, respectively.

The models that were obtained by the regression analysis for the formation of chlorite and chlorate from chlorine dioxide are as follows:

$$\text{Chlorite (mg/L)}=10^{-2.20}[ClO_2]^{0.45}[pH]^{0.90}[temp]^{0.27}[TOC]^{1.04}[time]^{0.20}$$
$$\text{Chlorate (mg/L)}=10^{-2.61}[ClO_2]^{1.27}[pH]^{-0.50}[temp]^{1.28}[TOC]^{0.31}[time]^{0.12}$$

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