Optimization of the ozone dosage at the drinking water treatment plant of Kluizen
Jan Cromphout, Stefanie Goethals and Liesbeth Verdickt

ABSTRACT
De Watergroep, a Flemish drinking water utility, aims to optimize the ozonation process at the Kluizen surface waterworks in order to obtain sufficient inactivation of pathogenic micro-organisms while minimizing the formation of bromate. In literature, the inactivation of micro-organisms is described as a first order process in ozone exposure (ozone concentration multiplied by exposure time or CT value). In the full-scale plant, the ozone exposure was determined at different temperatures and ozone doses, and an empirical relation between ozone exposure, ozone dose and temperature was derived. Based on the results, the optimum ozone dose required to obtain a Log 2 removal of viruses and a Log 1 removal of Giardia was determined as a function of temperature. Bromate formation was found to be dependent on the ozone dose rather than on the CT value. Therefore, an empirical relation between bromate formation, ozone dose and temperature was established. Bromate formation was found to be far below the legal standard of 10 μg/L when the optimum ozone dose, required to achieve the disinfection goals for viruses and Giardia, is applied.

INTRODUCTION
De Watergroep, a Flemish drinking water utility, operates a 60,000 m³/day surface waterworks in Kluizen, situated near Ghent (Belgium). The raw water is captured from lowlands and stored in reservoirs with an overall storage capacity of 11 Mm³ prior to treatment. The raw water quality at the intake point to the reservoirs is monitored, and if necessary from a quality perspective, intake of water into the reservoirs can be interrupted. The water is treated by clarification, partly in sludge blanket clarifiers and partly by flotation, followed by filtration on hydroanthracite and sand, oxidation with ozone, two-stage granular activated carbon (GAC) filtration (BGAC-GAC; contact time two times 15 min) and disinfection with chlorine. A treatment scheme of the plant is provided in Figure 1. The ozonation was implemented in 2003 for oxidation and disinfection purposes, in replacement of an intermediate chlorination step ahead of filtration. The ozonation has some major benefits. Firstly, the earthy-musty taste and odour compound methyl isoborneol which caused customer complaints in the past, is oxidized in the ozonation step. Furthermore, organic matter removal and biostability of the finished water improved considerably, as ozone enhances the biodegradability of natural organic matter on the activated carbon. Finally, replacing the intermediate chlorination by ozonation resulted in a substantial decrease in trihalomethane levels (Cromphout et al. 2005; Cromphout & Vanhoucke 2008).

Several control strategies can be applied to the ozonation process. The easiest strategy is to apply a constant ozone dose, however, this does not account for changes in water quality. A more advanced control strategy is applied by Vivaqua at the waterworks of Tailfer (Belgium), where a constant residual ozone concentration in the last compartment of the contact chambers is aimed at (Courtois 2005). After modelling the ozonation process, Waternet (the Netherlands) changed its control strategy from applying a constant dosing set point (although different during winter and summer) to a dosage giving rise to a constant inactivation of Giardia (Van der Helm et al. 2009).

In the literature, the inactivation of micro-organisms by means of ozonation is often described using the
Chick-Watson model:

\[ \log \left( \frac{N}{N_0} \right) = -K_t (C^n \times T) \]

with \( N_0 \) and \( N \) being the numbers of a particular organism before and after disinfection; \( K_t \), the rate constant for its inactivation, dependent on temperature; \( C \), the ozone concentration (mg/L); \( n \), a constant known as the coefficient of dilution; \( T \), the reaction time (min).

In most cases, the dilution coefficient is approximately 1 and the inactivation is a first-order process in the \( CT \) value (Crittenden et al. 2005). For the temperature range of 3–22 °C, relevant with respect to surface water treatment in Belgium, the effect of temperature on the rate constant \( K_t \) can be described by the following equation:

\[ K_t = K e^{kt} \]

with \( t \), temperature in °C; \( k \), a constant.

By combining this equation with the Chick-Watson model, the following inactivation equation is obtained:

\[ K e^{kt} (CT) = \log \left( \frac{N_0}{N} \right) \quad (1) \]

Table 1 presents an overview of rate constants and their temperature coefficients for disinfection with ozone found in the literature.

Bromate is a harmful by-product of ozonation. From data obtained at different locations, Sohn and co-workers (Sohn et al. 2004) developed a multiple regression model to predict bromate formation as a function of total organic carbon (TOC) and bromide concentration of the water, pH, temperature and ozone dose:

\[ [\text{BrO}_3^-] = 1.55 \times 10^{-6} \times [\text{TOC}]^{1.26} \times [\text{pH}]^{5.82} \times [\text{O}_3]^{1.57} \times [\text{Br}]^{0.73} \times T^{0.28} \times (1.035)^{t - 20} \]

with [\text{BrO}_3^-], bromate concentration in μg/L; [TOC], total organic carbon concentration in mg C/L; [O_3], the applied ozone dose in mg/L; [Br], bromide concentration in μg/L; \( T \), residence time in minutes; \( t \), temperature in °C.

Von Gunten et al. (2001) observed that bromate formation consists of an initial fast increase proportional to the ozone dose, after which the bromate concentration increases linearly with the \( CT \) value.
Van der Helm (2007), on the other hand, concluded that the total amount of bromate formed after ozonation shows a linear relationship with the total CT value.

In this paper, an ozonation control strategy is elaborated for the waterworks in Kluizen, with the aim of maintaining a Log 2 removal of viruses and a Log 1 removal of Giardia while bromate formation is kept at a minimum. Empirical relationships describing ozone exposure and bromate formation as a function of temperature and ozone dose were derived from measurements in the full-scale plant at different temperatures and ozone doses. Then, the ozone dose required to achieve the disinfection goals was calculated as a function of temperature, based on a combination of the empirical relationship between ozone exposure, ozone dose and temperature with literature data on the inactivation of viruses and Giardia as a function of ozone exposure and temperature. Finally, the empirical relationship between bromate formation, ozone dose and temperature was used to evaluate bromate formation at the ozone dose required for disinfection.

**MATERIAL AND METHODS**

**Full scale ozonation**

The ozonation system consists of two Wedeco EFFIZON® ozone generation units, each with a production capacity of 4,000 g/h. A gaseous mixture of ozone and oxygen is introduced to a side stream (50 m³/h) of the feed to the pressurized activated carbon filters by means of a Venturi injector. Subsequently, this side stream is re-introduced into the main water flow just in front of a static mixer (Figure 2). The ozone dose can be adjusted by changing the gas flow rate and/or the concentration of ozone in the gas flow (Cromphout & Vanhoucke 2008; Audenaert et al. 2010). The applied ozone dose depends on the water flow, the gas flow and the ozone concentration in the gas mixture, which are continuously monitored. To monitor the ozone demand of the water, UV₂₅⁴₅nm absorbance is measured on-line before and after ozonation.

**Ozonation experiments**

Over a period of more than six months, covering a temperature range from 2.2 to 22.5 °C, 12 full scale ozonation experiments were conducted. In each experiment, different ozone doses, ranging from 0.8 to 3.0 mg O₃/L, were applied. For each ozone dose applied, a 1 L sample of ozonated water was taken from the main stream, straight after the static mixer (see Figure 2), and the ozone concentration of this sample was measured every minute until the ozone concentration dropped below the detection limit. The residence time of the water between the ozone injection point and the sampling point, equal to 18–23 s depending on the water flow rate, was neglected in the calculations of ozone exposure.

Ozone was analysed on the spot by the indigo method using Accu Vac Ampuls and a HACH® DR/890 portable colorimeter. UV₂₅⁴₅nm absorbance, TOC, pH and bromate were measured in the laboratory. Bromate was analysed by ion chromatography with post column reaction and photometric detection, with a sensitivity of 0.5 μg/L.

**RESULTS AND DISCUSSION**

**Ozone exposure CT**

For two of the 12 full scale ozonation experiments, the results are presented in Table 2 and Figure 3. The first one was conducted in February at a water temperature of 3.4 °C, the other one in July at 22.5 °C. Although the ozone decay is a first order process (Langlais et al. 1991), the experimental results could be approximated reasonably well by a linear relationship (see Figure 3):

\[ C = C_0 - bT \]
Only the results of the experiments resulting in values greater than 0.95, 0.8 and 0.65 for the linear least squares regression coefficient $R^2$ when respectively three, four and five data points were available, were considered in the following derivation of an overall empirical relationship between ozone exposure, ozone dose and temperature. These $R^2$-values correspond to a confidence interval of 90%.

The total ozone exposure $CT$, expressed in mg.min/L, was estimated by integrating the linear relationship established above:

$$CT = \int_0^T (C_0 - bT) \, dT = \frac{C_0^2}{2b}$$

with $C_0$, the ozone concentration at time zero according to the linear approximation; $b$, the slope of the decay line.

As such, the ozone exposure ($CT$) at different temperatures and doses was calculated. No correction for the deviation from plug flow is used because the minimum contact time in the carbon filters above the carbon bed is 12 min, and in most cases the ozone disappeared after a reaction time of less than 5 min. Figure 4 shows the $C_0$ and $CT$ values as a function of the ozone dose. The instantaneous ozone demand, and thus $C_0$, are proportional to the ozone dose and almost independent of temperature. The instantaneous ozone consumption is mainly due to the reaction of ozone with natural organic matter (NOM) resulting in a decrease of the UV$_{254\text{nm}}$ absorbance ($\text{Van der Helm et al.} 2007$). Hence, the instantaneous ozone consumption can be derived from measurements of UV$_{254\text{nm}}$ absorbance before and immediately after ozonation. It was expected that the instantaneous ozone consumption would be higher in the summer due to the impact of higher temperature on the reaction kinetics. However, the percentage decrease in UV$_{254\text{nm}}$ absorbance was found to be almost linear with the ozone dose ($R^2 = 0.88$), showing only a very low temperature dependency. A possible explanation is that in the summer, the components that have the highest degradability by ozone are already oxidized by the UV radiation of the sun, compensating for the effect of temperature on the ozonation kinetics.

The slope $b$ is strongly dependent on temperature. As a result, $CT$ is also dependent on temperature, as shown in

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<th>Temp (°C)</th>
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<th>UV$_{254\text{nm}}$ (m)</th>
<th>TOC (mgC/L)</th>
<th>Ozone dose (mg/L)</th>
<th>UV$_{254\text{nm}}$ after ozonation (m)</th>
<th>BrO$_3$ formation (μg/L)</th>
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<th>Ozone concentrations in mg/L after different time intervals</th>
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The following relationship between $CT$, temperature and ozone dose was derived on an empirical basis:

$$CT \text{e}^{xt} = y \text{e}^{zD}$$

with $D$, the ozone dose in mg/L; $t$, the temperature in degrees Celsius; $x$, $y$, $z$, calibration coefficients.

For different values of $x$, $CT \text{e}^{xt}$ was plotted as a function of $D$ and values for $y$ and $z$ were determined using least squares regression. The best fit ($R^2 = 0.86, n = 30$) was obtained for $x = 0.05$, $y = 0.08$ and $z = 1.3$ (see Figure 5).

Thus:

$$CT \text{e}^{0.05t} = 0.08 \text{e}^{1.3D}$$

(2)

**Disinfection capacity**

The calculated ozone exposures are more than adequate for a total elimination of *E. coli*, but even the highest values are totally insufficient to obtain a significant removal of *Cryptosporidium*. For a Log 2 and a Log 1 inactivation of viruses and *Giardia* oocysts, respectively, using the $K$ and $k$ values listed in Table 1, Equation (1) becomes:

$$CT \cong 0.96 \text{e}^{-0.07t}$$

(3)

Combining Equations (2) and (3) results in the following relationship between the optimum ozone dose and

Figure 4.
temperature:

\[0.96e^{-0.07t} = 0.08e^{1.3D - 0.05t}\]

The optimum ozone dose in mg/L then becomes:

\[D_{	ext{opt}} = 1.9 - 0.015t\]

The effect of higher disinfection kinetics at higher temperatures is partially compensated by an increase of the ozone decay. The overall effect is that the ozone dose can be lowered by only 0.15 mg/L for an increase of the temperature by 10°C in order to maintain a constant level of inactivation for viruses and Giardia.

**Formation of bromate**

Because TOC, bromide concentrations (110 ± 14 μg/L) and pH varied between narrow ranges, the influence of these parameters on the bromate formation could not be established. Bromate formation appeared to be dependent on the ozone dosage \((R^2 = 0.86)\). The influence of the \(CT\) value, on the other hand, is rather limited \((R^2 = 0.35)\), indicating that most of the oxidation of bromide occurs at the start of the ozonation process. A good fit \((R^2 = 0.93)\) between bromate formation (in μg/L), ozone dose and temperature is given by the following empirical relationship, plotted in Figure 6:

\[\text{BrO}_3 = 2De^{0.014t} - 1.4\]
Additional research revealed that up to one-third of the bromate is already formed in the side stream (Figure 2). A typical dissolved ozone concentration in this side stream is 20 mg/L, and residence time is 20 s, resulting in a bromate concentration in the side stream of 20 μg/L. In the near future the ozone generation units will be retrofitted, on this occasion the residence time in the side stream will be limited by placing the Venturi injectors as close as possible to the main water pipe.

Control strategy for the ozonation process

Based on the empirical correlations presented above, a new control strategy for the ozonation plant was introduced. The ozone dosage applied is the dosage required to obtain a 2 Log inactivation of viruses and 1 Log inactivation of Giardia oocysts, whereas previously, a constant dose of 2.5 mg/L was used. The dosage required to obtain the desired inactivation of viruses and Giardia is presented as a function of temperature in Figure 7, together with the corresponding bromate formation. Clearly, applying the new control strategy restricts bromate formation to values below 3 μg/L.

CONCLUSIONS

Water quality control no longer focusses only on product quality control but also includes more and more a control of the treatment processes. In this study, a control strategy for the ozonation process in the Kluizen drinking water treatment plant was developed based on field measurements and empirical correlations between ozone dose, temperature, ozone exposure (CT) and bromate formation. Although simple models, with a limited number of calibration parameters, were used, a good correlation between the data and the model was obtained. With the new control strategy, a constant inactivation of Giardia and viruses is achieved, while the bromate formation is kept far below the legal standard of 10 μg/L.

REFERENCES


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