Ozone oxidation can provide multiple benefits for drinking water utilities, including disinfection of Cryptosporidium, Giardia, and coliform bacteria and oxidation of contaminants such as methylisoborneol, geosmin, cyanotoxins, pharmaceuticals, and personal care products (von Sonntag & von Gunten 2012). In the early 1990s, many utilities implemented ozone to provide a barrier to Cryptosporidium. The US Environmental Protection Agency (USEPA) published guidance in the Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) regarding the use of ozone for Cryptosporidium inactivation (USEPA 2010). Since then, several methods of determining ozone exposure—i.e., concentration times time \((C \times T)\)—have been evaluated, including the \(T_{10}\) method (i.e., effluent \(C \times T_{10}\)), continuously stirred tank reactor (CSTR) method, extended \(T_{10}\) method, extended CSTR method, and extended-integrated \(C \times T_{10}\) (USEPA 2010, Najm et al. 2009, Rakness et al. 2005). Maximizing \(C \times T\) credit can be essential to compliance with the disinfectant/disinfection byproduct regulations while minimizing operating costs. These approaches have focused on measuring ozone exposure \((C \times T)\) in the contactor following ozone dissolution from gas to liquid phase. However, the dissolution zone is often overlooked and unaccounted for when evaluating the overall \(C \times T\) and disinfection byproduct (i.e., bromate) formation.

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**BACKGROUND**

**Ozone dissolution.** Ozone systems have five primary components: feed gas supply, ozone generator, ozone contactor, and ozone destruction system (Rakness 2005). In this study, focus was placed on the ozone dissolution system to transfer ozone from the gas phase to the liquid phase. Ozone dissolution can occur through either fine bubble diffusion (FBD) or sidestream addition (SSA).

**FBD.** Before 2000, FBD was considered state of the art, and the majority of ozone plants constructed used this method of ozone dissolution. During an FBD application, ozone gas is transferred into water via stone or ceramic diffusers, often located in the bottom of the first contact chamber, followed by a series of baffled compartments providing contact time for microbial inactivation (dissolved ozone residual exposure) as shown in Figure 1, part A. Diffuser depth is considered optimized between

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Pilot-scale data were generated to improve operational guidance for fine bubble diffusion (FBD) and sidestream addition (SSA) systems with respect to unaccounted-for ozone exposure—i.e., concentration times time \((C \times T)\), and bromate formation during ozone dissolution. In FBD systems, results showed significant ozone dissolution \(C \times T\) (0.31–2.85 mg-min/L) and bromate formation (0.8–9.1 µg/L) occurring in the bubble column, which is not included in regulatory compliance \(C \times T\) calculations. Utilities may consider taking contactors out of service to minimize contact time and corresponding bromate formation in the dissolution zone. In SSA systems, ozone dosages (7.2–18.6 mg/L) were transferred to approximately 20% of the overall plant flow for ~5 s, which produced bromate (2.6–5.7 µg/L). As the contact time exceeded the design guidance in the sidestream flow (>30 s), bromate formation became far more significant (40–140 µg/L). When the sidestream flow is operated with short contact times (~5 s), bromate formation can be minimized.
18 and 22 ft, resulting in a hydrostatic pressure of around 10 psi (Rakness 2005). Maximum transfer efficiency is approximately 85% for air-fed (1–2% ozone by weight) systems and 95% for oxygen-fed (8–10% ozone by weight) systems (Rakness 2005). Following ozone dissolution, dissolved ozone residual is measured in the various downstream compartments of the contactor using on-line analyzers to calculate ozone $C \times T$.

Although simple to use, FBD can become problematic because of operation and maintenance concerns (e.g., accessibility to diffusers, confined-space entry). These types of ozone contactors are often designed for a contact

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**FIGURE 1** Simplified pilot-scale process schematics of ozone dissolution system and ozone contactor regions identified as dissolution $C \times T$ and compliance $C \times T$

- **A** FBD system
- **B** SSA$_{\text{w-dg}}$
- **C** SSA$_{\text{w-o-dg}}$

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$C \times T$—concentration times time, CSTR—continuously stirred tank reactor, FBD—fine bubble diffusion, SSA$_{\text{w-dg}}$—sidestream addition with degas, SSA$_{\text{w-o-dg}}$—sidestream addition without degas

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time of 1–3 min per contact chamber compartment at the maximum flow rate. In practice, seasonal or diurnal plant flow rate changes can occur, increasing or decreasing the contact time in the dissolution column and in the downstream compartments of the contactor. The flow dynamics can result in changes in the extent of dissolved ozone residual decay and bromate formation occurring in the bubble column. This formation is significant from a regulatory perspective, since the disinfection zone where $C \times T$ is accrued begins immediately after the bubble column when determining the ozone exposure for regulatory credit.

**SSA.** Over the past decade, SSA has emerged as an alternative method of ozone dissolution because of advancements in ozone generation technology. Medium-frequency ozone generators can produce high-concentration ozone gas (10–12% ozone by weight) that reduces the operating gas flow rate and corresponding pumping costs to achieve the desired (lower) gas-to-liquid ratios (Rakness 2005). During an SSA application, approximately 20% of the plant flow is routed through a sidestream, where ozone gas is added to the water flow via a Venturi device (Figure 1, parts B and C). The Venturi may act as either an injector or eductor, depending on the pressure of the ozone feed gas supply entering the Venturi. In SSA applications with degas (SSA$_{\text{w-dg}}$), a degas separator follows the injection of ozone gas to remove coalesced ozone gas bubbles from the sidestream flow (Jackson et al. 2007). During sidestream addition without degas (SSA$_{\text{wo-dg}}$), a high concentration of dissolved ozone plus undissolved oxygen/ozone gas remains in the sidestream liquid flow until it blends with the bulk liquid flow. Downstream mixing is typically achieved by using nozzle injection, static mixers, or both. Although the dissolved ozone contact time may be only a few seconds in the sidestream flow, the reactions involved in this initial phase of ozone decomposition (time <20 s) are not very well understood (Buffle et al. 2006). This initial phase of ozonation is typically regarded as an advanced oxidation process with significant hydroxyl radical production.

**Bromate formation during ozone dissolution.** The reactions taking place within the sidestream flow and FBD are relevant when considering the amount of bromate production during ozone dissolution (Rakness et al. 2012). Bromate is regulated at a maximum contaminant level (MCL) of 10 µg/L by USEPA (1998). Many factors contribute to the production of bromate in drinking water, including bromide concentration, ozone exposure ($C \times T$), hydroxyl radical exposure, pH, temperature, alkalinity, and natural organic matter (Hofmann & Andrews 2006, Siddiqui et al. 1995, Krasner et al. 1993).

Bromate formation occurs from the oxidation of bromide by ozone and hydroxyl radicals through three different pathways (von Gunten 2003, von Gunten & Oliveras 1998, von Gunten & Hoigné 1994, Haag & Hoigné 1983). During the direct pathway, ozone oxidizes hypobromite ($\text{OBr}^-$) to bromite and then bromate. During the direct–indirect and indirect–direct pathways, both hydroxyl radicals and ozone participate in intermediate oxidation reactions resulting in bromate formation. The hypobromous acid (HOBr)/OBr$^-$ equilibrium ($pK_a = 8.8$) is a key factor affecting each of these bromate formation pathways.

These observations regarding HOBr/OBr$^-$ equilibrium have led to two commonly used chemical mitigation techniques: pH depression and ammonia (NH$_3$-N) addition (von Gunten 2003, Pinkernell & von Gunten 2001, Ozekin et al. 1998, von Gunten & Oliveras 1998, Siddiqui et al. 1995). Reducing the pH to 6.0 shifts the HOBr/OBr$^-$ equilibrium toward HOBr, thereby limiting bromate formation via the direct pathway, and reduces hydroxyl radical exposure, thereby limiting bromate formation by 60–75% via the direct–indirect and indirect–direct pathways (Pinkernell & von Gunten 2001). NH$_3$-N addition ($\leq 0.2$ mg/L) in the presence of HOBr/OBr$^-$ results in the formation of bromamine, which is slowly oxidized to nitrate by ozone (Haag et al. 1984). Preoxidation with chlorine dioxide (1 mg/L) has also shown to minimize bromate formation by 75% (Newkirk et al. 2006, Zhou & Neemann 2004). Chloramine-based pretreatment (0.1–0.5 mg/L) has been proved to reduce bromate by 65–95% through bromamine formation and reduced hydroxyl radical exposure (Benotti et al. 2011, Wert et al. 2007, Buffle et al. 2004, von Gunten 2003).

**Study objective.** The objective of this study was to quantify ozone exposure and bromate formation during ozone dissolution using either FBD or SSA (with and without degas) as part of a project funded by the Water Research Foundation (Wert et al. 2016). As noted previously, if FBD systems are operated below the design flow rate, the contact time in the dissolution zone may increase and subsequently increase ozone exposure and bromate formation in the initial chamber. In SSA systems, the high dose of ozone in the sidestream creates concern among utilities with water quality conditions favorable for bromate formation (e.g., high bromide concentration, high pH). Pilot-scale experiments were performed to understand the significance of ozone exposure and bromate formation during ozone dissolution in FBD, SSA$_{\text{w-dg}}$, and SSA$_{\text{wo-dg}}$ systems.

**DEFINITION OF DISSOLUTION $C \times T$ AND COMPLIANCE $C \times T$**

Disinfection guidelines for the use of ozone have been established for viruses, *Giardia*, and *Cryptosporidium* by USEPA in the Surface Water Treatment Rule (SWTR) and LT2ESWTR (USEPA 2006, 1989). To comply with these regulations, guidance manuals are available that explain how disinfection credit is to be determined using ozone (USEPA 2010, 1991). Guidance is provided regarding contactor configurations, tracer studies, and determination of ozone exposure ($C \times T$). Ozone $C \times T$ is calculated
from the dissolved ozone residual concentration (C) and contact time (T). The typical contactor configuration used in the guidance manuals involves gas–liquid mass transfer in the first dissolution chamber of an FBD contactor, followed by C × T determination in subsequent chambers (disinfection zone).

Compliance C × T calculations are used to determine the log inactivation credit for viruses, *Giardia*, and *Cryptosporidium*. However, significant ozone exposure (i.e., C × T) may occur in the dissolution zone of these ozone contactors that is not included in regulatory C × T determinations. This dissolution C × T is important in that it affects initial residuals, ozone demand, overall ozone exposure, and bromate formation. Dissolution C × T can be calculated in the first chamber of FBD systems (Figure 1, part A), which can be greatly influenced by flow rate fluctuations. When the operating flow is below the design flow rate, the contact time in the first chamber increases, along with ozone exposure and bromate formation. Compliance C × T begins downstream of the bubble diffusion column, typically using on-line dissolved ozone analyzers. The overall exposure C × T is the sum of dissolution C × T and compliance C × T. The guidance manuals outline the amount of disinfection credit given for the first dissolution chamber (Table 1) for virus, *Giardia*, and *Cryptosporidium*. In the SWTR (part 0.3.3.1), direct virus and *Giardia* inactivation credit is given (no C × T credit), provided that the measured residual exceeds indicated values (USEPA 1991). In the LT2ESWTR, there is no direct credit or C × T credit given for *Cryptosporidium* inactivation in the first dissolution chamber (USEPA 2010).

While the guidance for C × T credit was illustrated with FBD systems, a similar framework can be applied to sidestream ozone contactors. In SSAw-dg systems, bubbles are present for a short duration and then removed via the degas vessel (Figure 1, part B). Therefore, there is no additional gas–liquid mass transfer in the sidestream or combined liquid flow. The dissolution zone C × T applies only to the percentage of flow in the sidestream. The compliance C × T zone is considered to begin at the point where the sidestream flow is blended with the bulk flow. The exposure C × T may be useful when evaluating the overall bromate formation and can be calculated as dissolution C × T times the dilution factor plus compliance C × T.

In SSAwo-dg systems, dissolution C × T exposure occurs in the sidestream flow and in the blended flow before entering the first chamber of the ozone contactor (Figure 1, part C). This can result in bromate formation before the zone where compliance C × T is measured. Since a dissolved ozone residual exists in the bulk flow as it enters the upflow or cocurrent chamber of the contactor, this chamber is considered to be equivalent to the cocurrent second chamber of the FBD contactor (as discussed previously) and can be used to calculate C × T credit for compliance purposes.
entered the bottom of the column and rose to the top. At design flow (25 gpm), the contact time in the column was approximately 2 min. A ceramic diffuser\(^1\) with a rated pore size of 15 µm was located in the bottom of the column to transfer ozone gas into the water. Ten sample ports were located vertically along the column every 10 in. to facilitate column profiling. Ozone gas was generated using an oxygen-fed generator.\(^2\) The gas flow rate was typically 2 slm (standard liters per minute) and was controlled using a mass flow controller.\(^3\) Gas-phase ozone concentrations were continuously monitored in the feed gas\(^5\) and off-gas leaving the FBD column.\(^5\)

Testing was conducted in the FBD column using flow rates of 25, 10, and 6 gpm, which correspond to hydraulic detention times of 2, 5, and 8.5 min, respectively. The transferred dose (2.5 mg/L) was held constant throughout the testing, which was conducted in triplicate. Dissolved ozone residuals and bromate were monitored at each sampling port along the entire depth of the contactor column. Dissolved ozone residuals at each port were collected in triplicate in order to minimize the amount of variability in the measurements. The dissolved ozone residual concentration was multiplied by the respective theoretical contact time in each parcel of water between the sampling ports assuming ideal plug flow (chamber volume divided by flow rate). The calculated \(C \times T\) values for each parcel of water between the sampling ports were summed to create a cumulative ozone exposure for the column, referred to as the dissolution \(C \times T\).

**SSA pilot-plant description and experimental plan.** A 25 gpm pilot plant was used to conduct the SSA ozone testing, again using Colorado River water from Lake Mead. The sidestream piping was constructed of clear polyvinyl chloride (PVC) to observe bubble coalescence following gas injection. The SSA process included two parallel sidestream systems operated with (SSA\(_{\text{w-dg}}\)) or without (SSA\(_{\text{wo-dg}}\)) degas separation. During SSA\(_{\text{w-dg}}\), the 25 gpm flow rate was split, with 6.5 gpm directed through the sidestream followed by a pressure indicator (Figure 1, part B). Ozone gas was generated using an oxygen-fed generator\(^2\) with concentrations ranging from 6 to 12%, depending on the test condition. Ozone gas was added to the sidestream using a Venturi device\(^6\) followed by a pressure indicator (0–60 psig) and degas separator.\(^7\) Depending on flow and pressure conditions, the Venturi acted as either an injector (positive pressure) or eductor (negative pressure). The contact time during SSA\(_{\text{w-dg}}\) was approximately 25 s. Following degasification, the off-gas from the degas separator was sent to an ozone destruct unit.\(^8\) During SSA\(_{\text{wo-dg}}\), the 25 gpm flow rate was split, with 4.0 gpm directed through the sidestream, followed by a pressure indicator (Figure 1, part C). Ozone gas was again added to the sidestream using a Venturi device,\(^9\) followed by a pressure indicator (0–60 psig). The contact time during SSA\(_{\text{wo-dg}}\) was approximately 2.5 s. For both SSA\(_{\text{w-dg}}\) and SSA\(_{\text{wo-dg}}\), the sidestream flow was blended with the bulk flow via a pipeline flash reactor using opposite-facing nozzles.

Following gas–liquid mass transfer via SSA and blending, the 25 gpm flow was split, with 6 gpm proceeding to a pilot-scale ozone contactor and the remaining flow (~19 gpm) quenched with calcium thiosulfate and discharged to waste. The pilot-scale ozone contactor (6 gpm) consisted of 12 PVC chambers, each providing 2 min of contact time for a total contact time of 24 min. Sampling ports were located at the top, middle, and bottom of each chamber to facilitate contactor profiling. Dissolved ozone residuals were continuously measured at chambers 3, 5, and 7,\(^10\) Off-gas was collected into a central manifold at the top of each column, connected to the off-gas leaving the 25 gpm FBD column, and subsequently measured using the off-gas analyzer described previously. All on-line instrumentation was interfaced into a programmable logic controller, allowing computer software to calculate and log ozone operating parameters.

During SSA, a relatively high ozone dose may be applied to achieve the desired blended ozone dose in the bulk flow. The high ozone dose in the sidestream also brings the perception of high bromate formation. However, bromate formation is a function of dissolved ozone and hydroxyl radical exposure (\(C \times T\)) with time being a key variable when evaluating bromate production in SSA systems. As noted previously, SSA systems are typically designed with only a few seconds of exposure time in the sidestream flow before blending with the bulk water flow. The objective of this phase of the study was to investigate typical SSA conditions in which the sidestream ozone dose (and corresponding dissolved ozone residual) is variable and the contact time is constant.

In order to evaluate different SSA operating scenarios, a number of gas-to-liquid ratios were tested, ranging from 0.04 to 0.12 during SSA\(_{\text{w-dg}}\) and 0.07 to 0.18 during SSA\(_{\text{wo-dg}}\), while targeting a constant transferred ozone dose of 2.5 mg/L in the blended flow. The corresponding transferred ozone dosages in the sidestream flow varied from 4.1 to 10.1 mg/L during SSA\(_{\text{w-dg}}\) and 7.2 to 18.6 mg/L during SSA\(_{\text{wo-dg}}\). In order to achieve these operating conditions, the flow rate remained constant in the sidestream flow during SSA\(_{\text{w-dg}}\) or SSA\(_{\text{wo-dg}}\), but the total flow rate was varied. These operating scenarios resulted in different dilution factors being applied.

**Analytical methods.** Dissolved ozone residuals were measured after steady-state operation had been achieved using method 4500-O3, Ozone by Indigo Colorimetric Method (Rakness et al. 2010, *Standard Methods* 1999). Bromate concentrations were measured using liquid chromatography with tandem mass spectrometry (Snyder et al. 2005). The minimum reporting limit was determined to be 0.1 µg/L. Samples were quenched and preserved with ethylenediamine.
RESULTS AND DISCUSSION

Effect of variable flow conditions on FBD. During countercurrent operation of the bubble column, the dissolution $C \times T$ increased as the water approached the diffuser (as shown in Figure 3, part A). Results showed minimal overall dissolution $C \times T$ (0.3 mg-min/L) at the design flow rate of 25 gpm and dissolution time (i.e., contact time for ozone gas–liquid mass transfer) of 2 min. When the flow rate was decreased to 10 and 6 gpm, the dissolution time in the bubble column increased to 5 and 8.5 min, respectively. The profiles of dissolved ozone residual concentration increased from the top of the column to the bottom (near the diffuser), and the corresponding overall dissolution $C \times T$ also increased to 1.5 and 2.9 mg-min/L, respectively. These dissolution $C \times T$ values can be significant if bromate formation is a concern. As mentioned previously, the dissolution $C \times T$ occurring in the bubble column is not included when determining $C \times T$ for regulatory compliance. As a result, bromate formation can occur in the dissolution chamber (Figure 3, part B). When the operating flow rates were 25 gpm (dissolution time = 2 min), 10 gpm (dissolution time = 5 min), and 6 gpm (dissolution time = 8.5 min), the bromate concentration leaving the bubble column was 0.8, 5.6, and 9.1 µg/L, respectively.

During cocurrent operation, the dissolution $C \times T$ increased as water and gas flowed from the bottom of the bubble column to the top, as shown in Figure 4, part A. Results showed slightly greater dissolution $C \times T$ (1.1 mg-min/L) than for countercurrent operation at the design flow of 25 gpm (dissolution time = 2 min). When the flow rate was decreased to 10 gpm (dissolution time = 5 min) and 6 gpm (dissolution time = 8.5 min), the dissolution $C \times T$ again increased to 2.5 and 3.5 mg-min/L, respectively. Again, these ozone exposures can contribute significantly to bromate formation (Figure 4, part B). Results showed that the ozone exposure at 25, 10, and 6 gpm resulted in 2.5, 4.9, and 11 µg/L, respectively, of bromate leaving the bubble column for cocurrent operation.

Whether operating under countercurrent or cocurrent flow conditions, FBD systems can experience significant dissolution $C \times T$ and bromate formation, as shown by the results in Figures 3 and 4. The observed $C \times T$ values can be used to calculate respective log inactivation credits for Cryptosporidium, Giardia, and viruses according to the equations (11-1, 11-2, and 11-3, respectively) published in the LT2ESWTR Toolbox Guidance Manual (USEPA 2010). Table 2 shows the unaccounted-for disinfection credit occurring within the dissolution zone for the pilot conditions tested. Under low-flow conditions (dissolution time = 8.5 min), nearly 0.5 log of Cryptosporidium inactivation credit is occurring in the dissolution zone of an FBD chamber that is not accounted for when determining regulatory compliance. The current USEPA framework for determining log inactivation credit does not allow Cryptosporidium inactivation credit for the initial bubble diffusion chamber.

![Figure 3](image-url)
Under normal operating conditions, drinking water treatment plants often operate at flow rates well below the design condition. For example, the Alfred Merritt Smith Water Treatment Facility operated by the Southern Nevada Water Authority (Las Vegas) is designed to treat a maximum daily flow of 600 mgd. However, the plant operates with instantaneous flows ranging from 100 to 550 mgd, with average daily flows around 200 mgd in winter and 400 mgd in summer. The ozone process includes eight 12-chamber contactors operated in parallel. During periods of low flow, contactors are taken out of service in order to improve the response time of dissolved ozone analyzers, minimize contact time in the dissolution chamber, improve ozone process control and stability, and as shown by the current study, reduce bromate formation.

Since continuous characterization of dissolved ozone residuals in bubble contact chambers may not be practical as performed at pilot scale in this study, other treatment

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**FIGURE 4** Profile results in the FBD column for dissolution $C \times T$ (A) and bromate formation (B) during cocurrent operation

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**TABLE 2** Calculated *Cryptosporidium*, *Giardia*, and virus log inactivation credit for observed dissolution $C \times T$ in a bubble contactor

<table>
<thead>
<tr>
<th>Flow Regime</th>
<th>Flow Rate gpm</th>
<th>Dissolution Time* min</th>
<th>Dissolution $C \times T$ mg-min/L</th>
<th>Inactivation Credit log</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cryptosporidium</td>
</tr>
<tr>
<td>Countercurrent</td>
<td>25</td>
<td>2</td>
<td>0.3</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>5</td>
<td>1.5</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>8.5</td>
<td>2.9</td>
<td>0.50</td>
</tr>
<tr>
<td>Cocurrent</td>
<td>25</td>
<td>2</td>
<td>1.1</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>5</td>
<td>2.5</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>8.5</td>
<td>3.5</td>
<td>0.62</td>
</tr>
</tbody>
</table>

* Dissolution time is defined as the contact time for ozone gas–liquid mass transfer.

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$C \times T$—concentration times time, FBD—fine bubble diffusion

Dissolution time is defined as the contact time for ozone gas–liquid mass transfer.

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$C \times T$—concentration times time

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Temperature = 16°C
process alternatives may be needed to minimize ozone exposure and bromate formation in the bubble diffusion chamber. With the bromate MCL established at 10 µg/L, utilities should consider taking contactors out of service if bromate formation becomes problematic. This would help minimize the amount of contact time in the dissolution zone and corresponding bromate formation. Alternatively, if taking some contactors out of service is not an option, then a chemical control strategy as discussed previously may be needed to minimize bromate formation.

Effect of sidestream ozone dose on bromate formation. In the case of SSAw-dg, dissolved ozone residuals in the sidestream flow varied from 4.0 to 8.7 mg/L after 2.5 s under the transferred ozone conditions specified previously. The ozone exposure resulted in dissolution $C \times T$ values in the sidestream flow between 1.7 and 3.6 mg-min/L and bromate formation between 2.0 and 9.7 µg/L (Figure 5). However, blending the sidestream flow (20–60%) with the bulk flow (40–80%) dilutes both the dissolution $C \times T$ and bromate concentration. In the blended flow, the bromate contribution from the diluted sidestream flow was calculated to be between 1.1 and 1.9 µg/L, which corresponded well with the measured bromate concentrations between 1.5 and 3.0 µg/L in the blended flow.

In the case of SSAwo-dg, dissolved ozone residuals in the sidestream flow varied from 5.4 to 13.2 mg/L after 2.5 s under the transferred ozone conditions specified previously. The ozone exposure resulted in dissolution $C \times T$ values in the sidestream flow between 0.23 and 0.55 mg-min/L and bromate formation between 2.6 and 5.7 µg/L (Figure 6). However, blending the sidestream flow (11–34%) with the full process flow (66–89%) again dilutes both the dissolution $C \times T$ and bromate concentration. In the blended flow, the bromate contribution from the diluted sidestream flow was calculated to be between 0.75 and 0.87 µg/L, which corresponded well with the measured bromate concentrations between 0.9 and 1.6 µg/L in the blended flow. Future research may provide further clarification regarding the relative contributions of ozone and hydroxyl radical exposure on bromate formation in the sidestream flow.

The results illustrated the importance of low contact times when high dosages of ozone are applied in SSA systems with water quality conditions favorable for bromate formation. Under the conditions studied, the contribution of bromate formation from ozone dissolution was minimal (≤3.0 µg/L during either SSAw-dg or SSAwo-dg). If greater bromate production is observed, a chemical bromate mitigation strategy may be required for the sidestream flow. Unlike with FBD, only a portion of the total flow is treated by sidestream ozonation. Therefore, calculating disinfection credit for Cryptosporidium, Giardia, or viruses is not appropriate since the total flow has not been treated with ozone. Compared with FBD systems, however, the hydraulics of a sidestream system are less susceptible to flow rate variations.

Importance of minimizing sidestream contact time. The objective for this portion of the study was to investigate SSAw-dg conditions in which first, the sidestream ozone dose is constant, and second, the time is variable and exceeds the design guidance for SSA systems. During testing, SSAw-dg was operated to achieve a transferred ozone dose of 11.1 mg/L (gas-to-liquid ratio = 0.10). Following the degas separator, the sidestream flow was collected into a batch reactor, and dissolved ozone residuals and bromate were analyzed over time to simulate the impact of longer contact times in the sidestream ($t > 30$ s). Results are shown in Figure 7 in terms of contact time and ozone $C \times T$. At greater contact times and ozone exposures, bromate formation can be significant (40–140 µg/L).

![FIGURE 5](image-url) Bromate formation in the sidestream flow (SSA_w-dg, contact time = 25 s) and blended flow at various sidestream transferred ozone doses

![FIGURE 6](image-url) Bromate formation in the sidestream flow (SSA_w-dg, contact time = 25 s) and blended bulk water flow at various sidestream transferred ozone doses
At greater ozone dosages, increased hydroxyl radical formation may be expected, resulting in accelerated ozone decomposition and increased bromate formation. Again, it was not the intention of these experiments to differentiate between bromate formation mechanisms (ozone and/or hydroxyl radicals) but rather to illustrate the importance of minimizing time within the sidestream under high ozone dose conditions, which inherently restricts these reactions and the extent and rate of ozone decomposition.

**Bromate formation following blending of the sidestream and bulk flow.** The contribution of bromate from the sidestream flow was measured and discussed in the previous section.

The objective for this portion of the study was to investigate bromate formation after blending the sidestream flow with the bulk flow via nozzle injection at the pipeline flash reactor under background raw water conditions (70 µg/L) and after addition of a bromide spike (170 µg/L) to the raw water. Dissolved ozone residual and bromate samples were collected immediately after blending—i.e., the start of the disinfection zone for sidestream applications (Figure 1, parts B and C). Results showed a linear relationship between bromate formation and compliance C × T in the ozone contactor whether either SSAwo-dg or SSAw-dg was used for ozone dissolution (Figure 8). On entering the disinfection zone, the bromate formation was <3 µg/L and then increased linearly with ozone exposure (compliance C × T). On the basis of decades of research on bromate formation, this relationship was expected, and it emphasizes the need to control bromate formation in the compliance zone of the contactor. However, a comparison of the amount of bromate formation in the disinfection zone (18 µg/L) in Figure 8 and the bromate formation in the sidestream flow (~50 µg/L) in Figure 7 under similar ozone C × T conditions (~5 mg-min/L) and background bromide conditions (70 µg/L) shows interesting differences. The differences illustrate the likely significance and contribution of hydroxyl radical exposure in the sidestream flow, whereas ozone C × T is likely more significant at lower ozone exposures following blending of the sidestream and full process flow. Under elevated bromide conditions (170 µg/L), bromate formation increased up to 36 µg/L with a compliance C × T value of 5.2 mg-min/L. With elevated bromide conditions, a bromate mitigation strategy (as discussed previously) is often needed to minimize bromate formation.

**CONCLUSION**

Ozone systems commonly use either FBD or SSA for gas–liquid mass transfer into water. In FBD systems, the dissolution zone may include significant dissolution C × T that is not included in regulatory compliance C × T calculations. This dissolution C × T is accompanied by bromate formation. FBD systems are typically designed so that the first contact chamber has 1–3 min of contact time, which minimizes dissolution C × T and bromate formation in the dissolution zone. However, full-scale plants are rarely operated at design flow, which can increase contact time and corresponding bromate formation in the dissolution zone. In this study, when flow rates were decreased 60–75%, the increased contact time resulted in greater dissolution C × T (1.5–2.9 mg-min/L) and bromate formation (5.6–9.1 µg/L) before the compliance zone for disinfection began. Therefore, FBD systems should consider taking parallel contactors out of service to minimize contact time in the dissolution zone when operating at reduced flow.

In SSA systems, consideration should also be given to the contact time in the sidestream flow in order to minimize ozone exposure and bromate formation. During pilot-scale
testing, ozone dosages between 4.1 and 18.6 mg/L were applied to the sidestream flow. With less than 25 s of contact time in the sidestream, bromate formation remained <10 µg/L. Following blending, the sidestream flow contributed <2 µg/L in the combined flow entering the ozone contactor. When sidestream contact times of up to 10 min were evaluated, bromate formation became significant in the sidestream flow (140 µg/L). Therefore, SSA systems should operate the sidestream flow near the design criterion (typically <5–6 s) in order to minimize dissolution C × T and corresponding bromate formation.

DEDICATION

This article is dedicated to coauthor Kerwin L. Rakness, who passed away on June 9, 2016. Throughout his career, Kerwin exemplified outstanding technical engineering skill, brilliant diplomatic talent, and constructive leadership within the water industry. He gracefully taught numerous professionals, including utility managers, operators, technicians, consultants, academics, manufacturers, and regulators, how to effectively use ozone technology to protect human health for millions of people around the world. Many of his experiences were shared in his AWWA book Ozone in Drinking Water Treatment: Process Design, Operation, and Optimization, which is a key reference for anyone working in the municipal ozone field. Kerwin was also passionate about sharing his experiences and knowledge through the International Ozone Association.

ACKNOWLEDGMENT

The Water Research Foundation (WRF) provided financial support for this project (4588). The WRF project manager Kenan Ozekin and WRF project advisory committee members, including Chandra Mysore (Jacobs Engineering Group, Pasadena, Calif.), James Muri (Massachusetts Water Resources Authority, Boston, Mass.), and Benito Mariñas (University of Illinois at Urbana) provided advice and constructive comments regarding the project approach. The authors also thank three anonymous reviewers for providing valuable feedback regarding the manuscript.

Many members of the Southern Nevada Water Authority in Las Vegas were responsible for the completion of this project. Greg Bock assisted with the pilot-plant testing. Dave Rexing and Jennifer Fuel provided administrative support for the project. Oscar Quinones, Janie Zeigler-Holady, and Brett Vanderford provided assistance with sample preparation and bromate analysis. Robert Devaney provided insight regarding full-scale plant operation and turnaround production.

Other members of the project team provided valuable insight regarding ozone design and operation, including Jeff Neemann (Black & Veatch, Irvine, Calif.), Chris Schulz (CDMSmith, Denver, Colo.), and Glenn Hunter (Process Applications Inc., Fort Collins, Colo.). Bill Mundy (Regional Municipality of Halton, Ont.) provided case study information regarding the full-scale performance of three treatment plants utilizing different mass transfer systems. Craig Thompson (West Yost Associates, San Francisco, Calif.) and Joe Drago and Jean Debroux (Kennedy/Jenks, San Francisco, Calif.) provided access to the ozone utility database. Jim Jackson (Mazzei Injector Company, Bakersfield, Calif.) provided insight into the design and operation of the pilot-scale sidestream injection system and pipeline flash reactor.

ENDNOTES

1Refraction Technologies Corp., Newark, N.J.
2GM-1, Primozone, Loddekopinge, Sweden
3Smart Track 100, Sierra Controls, Carson City, Nev.
4HI-X, IN USA Inc., Needham, Mass.
5H-1 LR, IN USA Inc., Needham, Mass.
6584, Mazzei Injector Co., Bakersfield, Calif.
7DS-150 PVDF with N4 nozzle, Mazzei Injector Co., Bakersfield, Calif.
8D212, Pacific Ozone, Bencina, Calif.
9484, Mazzei Injector Co., Bakersfield, Calif.
10Rosemount Analytical, Tempe, Ariz.

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https://doi.org/10.5942/jawwa.2017.109.0048

PEER REVIEW

Date of submission: 10/19/2016
Date of acceptance: 01/03/2017

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