

Impact of Chlorine Dioxide Pre-Oxidation of Ozone in Preventing Bromate Formation

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Abstract

The USEPA will require increased disinfection capability and lower disinfection byproduct levels when the proposed Long Term 2 Enhanced Surface Treatment Rule (LT2ESWTR) is promulgated. With increased disinfection, it is more difficult for ozone plants with bromide source water to comply with the 10 ppb bromate maximum contaminant level (MCL). In 2005, it was demonstrated through a laboratory and plant study at the El Paso's 60 MGD Jonathan Rogers Water Plant that chlorine dioxide pre-oxidation of ozone reduces bromates by 78% at 1.5 mg/L dose, which was similar to the AWWARF study results at Contra Costa California in 2002. Linear regression equations were developed for the laboratory and plant studies in determining the effects of ozone concentration, chlorine dioxide dose, and ozone contact time on bromate formation.

Key words: Ozone; bromates; chlorine dioxide;

Introduction

The USEPA will require increased disinfection capability and lower disinfection byproduct levels when the proposed Long Term 2 Enhanced Surface Treatment Rule (LT2ESWTR) is promulgated. The future target pathogen will be *Cryptosporidium sp.*, which is 16 times more resistant to inactivation than the current target protozoan, *Giardia sp.*, according to the USEPA proposed CT tables for ozone and chlorine dioxide. While disinfection requirements will increase, the disinfection byproduct levels will decrease to 80 ppb for TTHMs and 60 ppb for HAAs based on the highest location running annual average (LRAA) level. Since increased disinfection will be required, it is more difficult for ozone plants with bromide source water to comply with the bromate maximum contaminant level (MCL) of 10 ppb.

There are three treatment options available for lowering bromates. They are:

1. chlorine dioxide pre-oxidation of ozone,
2. ammonia addition, and
3. pH control.

These treatment methods were evaluated in the 2002 AWWARF study performed in Contra Costa California. The highlights of the Contra Costa study demonstrated that:

1. 1.0 mg/L of chlorine dioxide and pH 6.0 substantially reduced the bromate formation,
2. chlorine dioxide had similar coagulant doses as ozone,
3. chlorine dioxide did not adversely affect filter operation,
4. modest energy reduction resulted,
5. chlorite byproduct played a role in bromate reduction,
6. ammonia addition was less effective than chlorine dioxide and pH adjustment.

Based on the Contra Costa Study results and a proposal presentation to the El Paso Water Utilities management team, they authorized laboratory and plant studies at the 60 MGD Jonathan Rogers Water Plant in El Paso, Texas for evaluating the capability of chlorine dioxide to lower bromates. Eka Chemicals, Inc., division of Akzo Nobel, was selected to supply the chlorine dioxide generator and chemicals during the study.

Objectives

There were six study objectives in the bromate prevention study. The study results were to:

1. determine the effect of ozone residual and contact time on bromate formation,
2. determine the effect of chlorine dioxide in reducing bromates,
3. determine the effect of ozone on chlorite and chlorate levels,
4. develop predictive least squares linear regression equations for ozone alone and the combined effect of ozone and chlorine dioxide on bromates,
5. maintain chlorite level at less than 0.1 mg/L in the finish water,
6. increase disinfection capability of the ozone while lowering bromate levels.

Initial Assumptions

There were three major assumptions made based on the literature review and previous experiences in other studies. They were that:

1. bromate formation is primarily due to the ozone concentration (residual) and contact time,
2. peroxone treatment prevents additional bromate formation after the first cell treatment with ozone alone for disinfection credit,
3. chlorine dioxide prevents bromate formation as a pre-oxidant to ozone (Ferguson et al. 1991; Finch et al. 1997; Langlais and Brink 1991; Zhou and Neemann 2004; Tarquin and Rittmann, 2001).

Jonathan Rogers Water Plant Treatment Process

The 60 MGD Jonathan Rogers Water Plant (Figure 1) treats Rio Grande River Water during the months of March through October. The raw water is lifted into 5 storage ponds by three screw conveyor pumps. After initial settling of turbidity in the storage pond, the settled water pumps lift the water into the plant treatment trains where a small dose of ozone is added to reduce some taste and odors and reduce coagulant dosages by micro-flocculation action. Bromates are not formed at this point due to the low ozone dosage. The ferric chloride coagulant is then added to reduce the turbidity and TOC levels through mixing and sedimentation processes.

The original plant design specified excess lime treatment with the ferric chloride followed by re-carbonation at the end of sedimentation to lower the pH level. However, since excess lime and re-carbonation are no longer needed, the re-carbonation chamber is an ideal location for chlorine

dioxide addition because the detention time permits complete decay of the chlorine dioxide species prior to entering the first ozone cell contactor. Since the Contra Costa Study showed that the chlorite residual was the significant species in preventing bromate formation, it may be also important to minimize chlorate formation by reducing the chlorine dioxide species level prior to entering the ozone contactor and only forming chlorates from the reaction of ozone with the chlorite by-product. Previous studies on the Rio Grande River showed each mg/L of chlorine dioxide formed about 0.67 mg/L of chlorite byproduct (Rittmann 1999). Therefore, it was expected that about 0.67 mg/L of chlorates would be in the effluent from a 1 mg/L chlorine dioxide dose.

After chlorine dioxide addition, ozone is added to the first cell of the Pre-Filtration Ozone Contactor to obtain disinfection credit based on the ozone residual times the contact time (CT). The pH of the water entering the ozone contactor is about 7.3. As the water passes from the first cell into the second cell, then, about 1 mg/L of hydrogen peroxide is added to react with the ozone residual forming peroxone which reduces taste and odors from geosmin, MIB, and pyrazine and prevents additional bromate formation. The Plant Operators set the ozone dose to at least 0.3 mg/L ozone residual in the first cell for inactivation of *Giardia sp.* However, the bromates are also formed from the reaction of bromide with the ozone. After peroxone treatment, the water passes through biological granular activated carbon (GAC) filters, where turbidity is reduced to less than 0.1 ntu and more total organic carbon (TOC) is removed. After filtration, chlorine and phosphate chemicals are added to further disinfect the water and prevent corrosion, respectfully, within the distribution system.

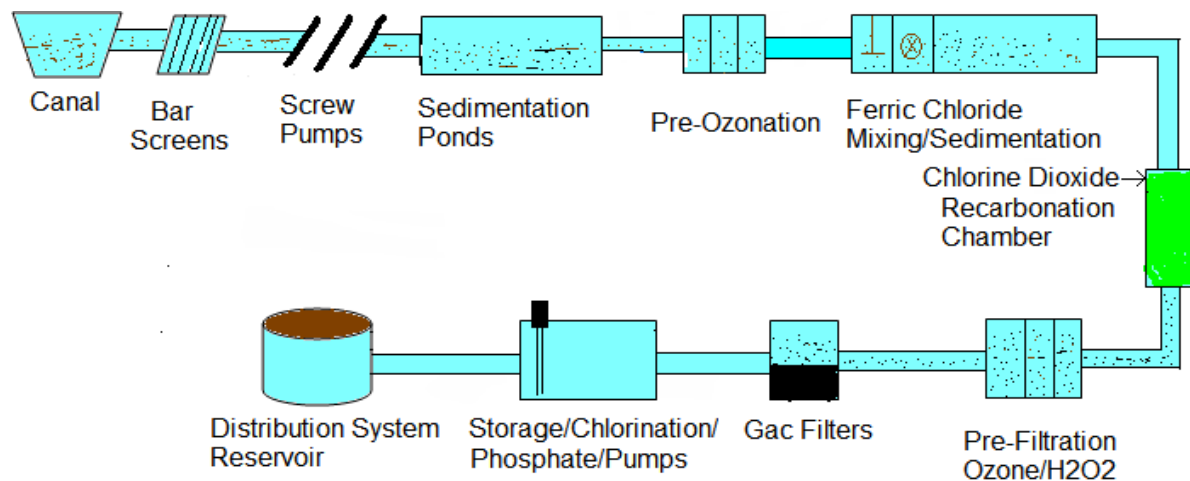


Figure 1. Jonathan Rogers Water Treatment Plant Flow Schematic

Disinfection Synergy from Combined Oxidants

Since 1995, researchers (Ferguson et al. 1991; Finch et al. 1997) have determined that combining disinfectants such as ozone or chlorine dioxide with chlorine increased disinfection inactivation of *Cryptosporidium sp.* greater than the sum of each oxidant's capability (Figures 2 and 3). While chlorine alone will not inactivate *Cryptosporidium sp.* at practical doses, it can enhance the capability of ozone or chlorine dioxide by a synergistic effect. Although this USEPA emerging technology, currently, has not determined the precise mechanism for the synergism,

the research studies have observed this phenomenon many times. It is foreseeable additional disinfection credit could be granted by regulatory agencies for combined disinfectants based on demonstration projects. However, at the present, disinfection credit can be taken for the sum of the disinfectants used in the plant process.

Figure 2 shows an example of the effect of chlorine dioxide alone to inactivate *Cryptosporidium sp.* at the 0.5 log level with CT equal to 45 and chlorine increasing the inactivation to 2.5 log at higher chlorine dosages even though chlorine alone cannot inactivate *Cryptosporidium sp.* Figure 3 depicts a lesser synergy effect from ozone and chlorine on inactivation of *Cryptosporidium sp.* but has higher capability than chlorine dioxide alone. However, the combined effect from chlorine dioxide, ozone, and chlorine should indeed provide superior *Cryptosporidium sp.* inactivation capability while minimizing bromate formation.

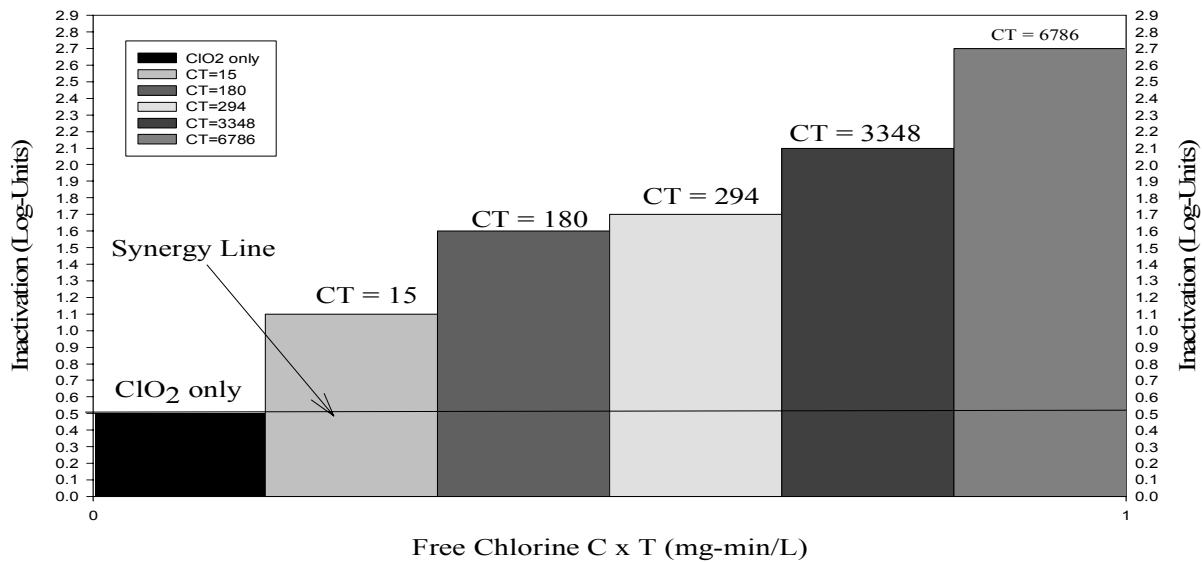


Figure 2. *Cryptosporidium* Log-Kill by Synergism of Cl₂ after 1.0 mg/l of ClO₂ for 45 minutes

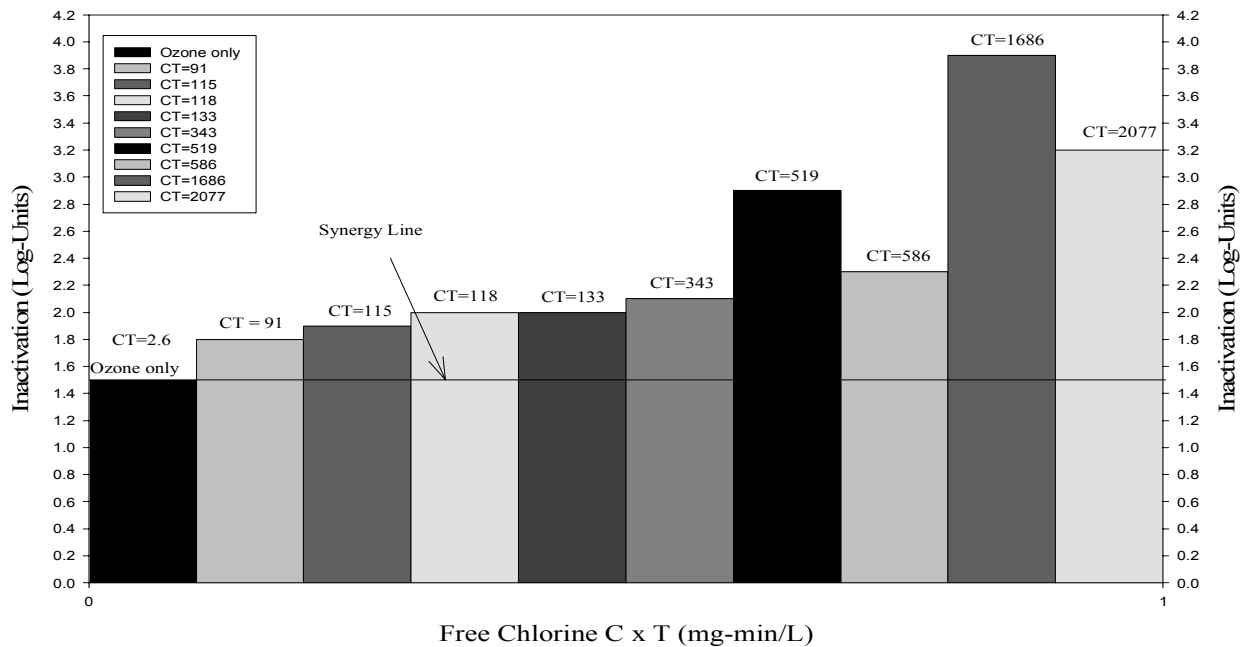


Figure 3. Inactivation of *C. parvum* oocysts by O₃ and Cl₂ at pH 6 and 22^o C

2002 Laboratory and Plant Ozone Studies at Jonathan Rogers Water Plant

In 2002, laboratory and plant studies were performed at the Jonathan Rogers Water Plant with the goal of minimizing bromate formation by having better control of the ozone dose. Two regression curves were developed from the laboratory and plant studies. Based on the plant regression curve, the operators could have better control of the bromates at less than 10 ug/L levels using ozone residuals and plant flows as independent variables (Tarquin and Rittmann 2002). However, the operators continued to have difficulty in controlling bromates at lower production levels especially at ozone residuals of 0.3 mg/L. Since the ozone residuals at 0.3 mg/L or higher were needed to provide reliable disinfection credit, the plant flow rate would have to operate at near full capacity. The plant operators needed a way to lower bromate formation at a minimum of 0.3 mg/L ozone residual for a wider production range. Therefore, chlorine dioxide was selected for evaluation to lower bromates at lower production rates for ozone residuals greater than 0.3 mg/L, especially, if increased disinfection capability is needed to meet future requirements.

Experimental

Materials and Methods

The 2005 laboratory study used equipment and procedures necessary for developing accurate and reproducible results with the following specifications:

1. The sample size was 1 liter,
2. The ozone transfer efficiency should be equal or higher than the plant's ozone transfer efficiency,

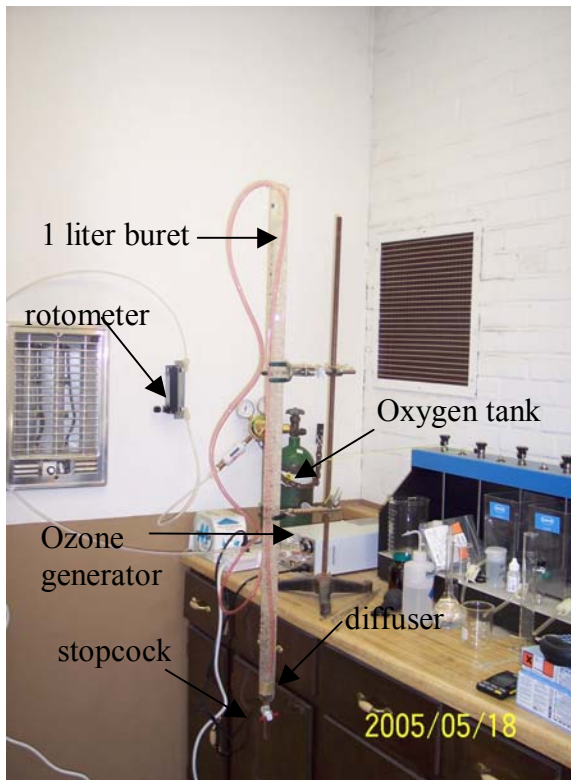
3. The analysis was done at the precise contact times of the ozone contactor based on the plant's production rates,
4. The lab ozone generator had sufficient ozone generator capacity with variable dosage capability,
5. The bromate formation potential in the lab study should be equal or higher than the Plant study results,
6. The ozone residual analyses was based on the same analytical method used by the plant operators,
7. The laboratory test procedures would mimic the plant operation as much as possible.

A one-liter buret was used for testing each sample. The buret's stopcock at the bottom of the buret made it easy to remove ozonated samples at precise time periods. The four-foot length and narrow diameter of the buret also facilitated excellent ozone transfer efficiency by placing the fine bubble aerator stone above the stopcock (picture 1). Three – 100 mL bromate samples for 3 different contact periods were sampled from each one-liter sample. Pure oxygen gas passes through a rotometer set at 2- liters per minute rate into the ozone generator where the ozone gas exits through a hose to the diffuser on top of the stopcock in the buret. Picture #2 shows a close-up view of the Ozone Solutions Model AC-500 generator. Picture #3 shows the Hach 890 analyzer for ozone residual, which is the same analyzer used by the operators. The chlorine dioxide species analyses were performed by the laboratory and plant operators (APHA, AWWA and WEF 1999).

Laboratory Bromate Model for Ozone Only

After setup of the laboratory equipment, the first step of the laboratory study was to determine the optimum ozone dose for ozone residuals in the range of 0.01 to 0.75 mg/L at contact times corresponding to the Jonathan Rogers Water Plant production rates of 5 MGD to 10 MGD per ozone contactor. There are six contactors designed for two plants with each contactor rated at a maximum of 10 MGD. Plant #1 has four-10 MGD treatment trains while Plant #2 has two–10 MGD treatment trains for a total production of 60 MGD. Three contact periods of 3, 4, and 5 minutes per first contactor cell corresponds approximately to the range of 5 to 10 MGD per contactor.

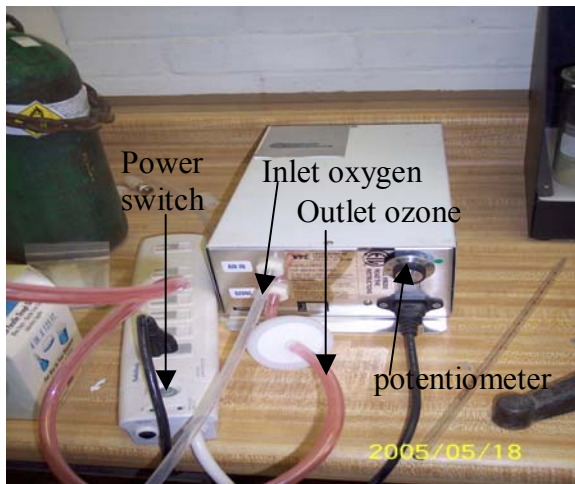
Initial ozone doses, at the maximum potentiometer setting of 10, had ozone residuals exceeding 0.75 mg/L within 30 s. With several trials and errors, the ideal potentiometer setting was 3 for ozone residuals in the range of 0.3 to 0.75 mg/L at the 3 to 5 min contact periods. With the experimental parameters determined, the next step was to begin testing samples for bromates compared to ozone residuals at the three contact periods using ozone and hydrogen peroxide. Samples were collected at the re-carbonation chamber and a 50% hydrogen peroxide solution was taken from the plant tank in order to dose at 1 mg/L as hydrogen peroxide for converting the ozone residual to peroxone.



Picture #1. Laboratory Equipment



Picture #3. HACH 890



Picture #2. Closeup of Ozone Generator



Picture 4. BrO₃ & O₃ Residual Samples

The actual bromates versus predicted bromates for ozone residuals and contact times are shown in Figure 6 below. Twenty-seven samples were analyzed with an R square of 0.89. The ozone residuals were from 0.35 to 0.73 mg/L and the contact times were 3, 4, and 5 min. Actual bromates were from 8.1 to 16.6 $\mu\text{g/L}$ with a mean of 11.4 $\mu\text{g/L}$ while the range of residuals (actual – predicted bromates) were -1.2 to $+ 1.1$ $\mu\text{g/L}$ (Table 1). The bromide levels were 170 to 220 $\mu\text{g/L}$. The predictive equation was:

[1] Bromates, $\mu\text{g/L} = -3.49 + (2.94 \times \text{O}_3 \text{ time, minutes} + (6.7 \times \text{O}_3 \text{ residual, mg/L}))$.

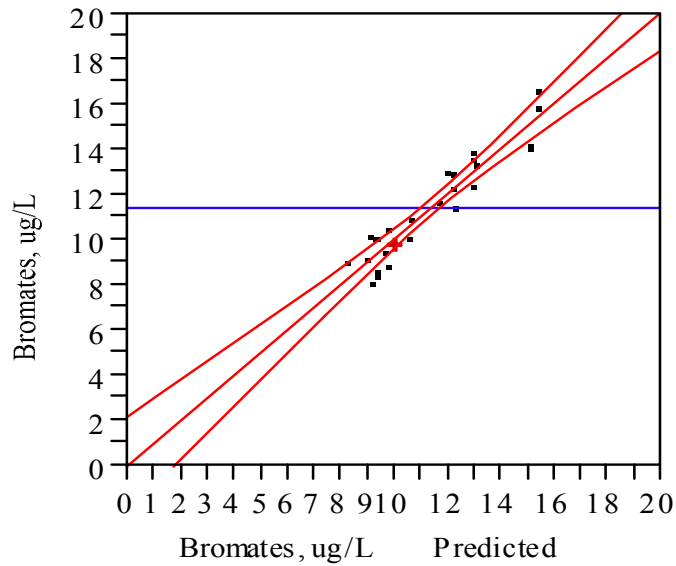


Figure 6. Actual versus Predicted Bromates Model for Ozone Only

Table 1. Data of Actual versus Predicted Bromates based on Ozone Model Equation

No.	Contact Time, minutes	O ₃ Residual, mg/L	Actual BrO ₃ , μ g/L	Predicted BrO ₃ , μ g/L	Actual – Predicted BrO ₃ , μ g/L
1	4	0.73	13.3	13.1	0.2
2	4	0.72	13.6	13.1	0.5
3	4	0.53	11.7	11.8	-0.1
4	3	0.44	9	8.3	0.7
5	3	0.67	8.8	9.8	-1
6	4	0.35	10.1	10.6	-0.5
7	3	0.57	10.2	9.1	1.1
8	4	0.71	13.9	13	0.9
9	3	0.61	8.4	9.4	-1
10	4	0.37	10.9	10.7	0.2
11	3	0.71	9.9	10.1	-0.2
12	4	0.71	12.4	13	-0.6
13	3	0.56	9.1	9.1	0
14	3	0.66	9.4	9.7	-0.3
15	3	0.67	10.5	9.8	0.7
16	4	0.62	11.4	12.4	-1
17	5	0.6	14.2	15.2	-1
18	3	0.6	10.1	9.3	0.8
19	4	0.6	12.3	12.3	0
20	5	0.6	14.1	15.2	-1.1
21	3	0.59	8.1	9.3	-1.2
22	3	0.62	8.6	9.5	-0.9
23	4	0.6	12.9	12.3	0.6
24	5	0.64	15.9	15.5	0.4
25	3	0.61	10.1	9.4	0.7
26	4	0.57	13	12.1	0.9
27	5	0.64	16.6	15.5	1.1
Min.	3	0.35	8.1	8.3	-1.2
Max.	5	0.73	16.6	15.5	+1.1

In the 2005 lab study, the JMP SPSS software determined the leverage effect from each independent variable as shown in Figures 7 and 8. The Prob > F value is the observed significance probability (P-value) of obtaining a greater F value by chance alone if the specified model fits no better than the overall response mean. Observed significance probabilities of .05 or less are often considered evidence of a regression effect. Also, at the 10 μ g/L bromate level in Figure 7, the bromate MCL will be exceeded when the contact times are greater than 3.2 minutes, which means that the ozone contactor production should be at least 10 MGD rate. Figure 8 predicts the maximum ozone residual of 0.41 mg/L at 10 μ g/L bromates. Therefore, at 10 MGD production per contactor with ozone residuals greater than 0.41 mg/L, it is probable that the bromate MCL will be exceeded. On the other hand, at ozone residuals less than 0.41

mg/L for contact times at 3.25 min (10 MGD production) or less, then the MCL will not be exceeded.

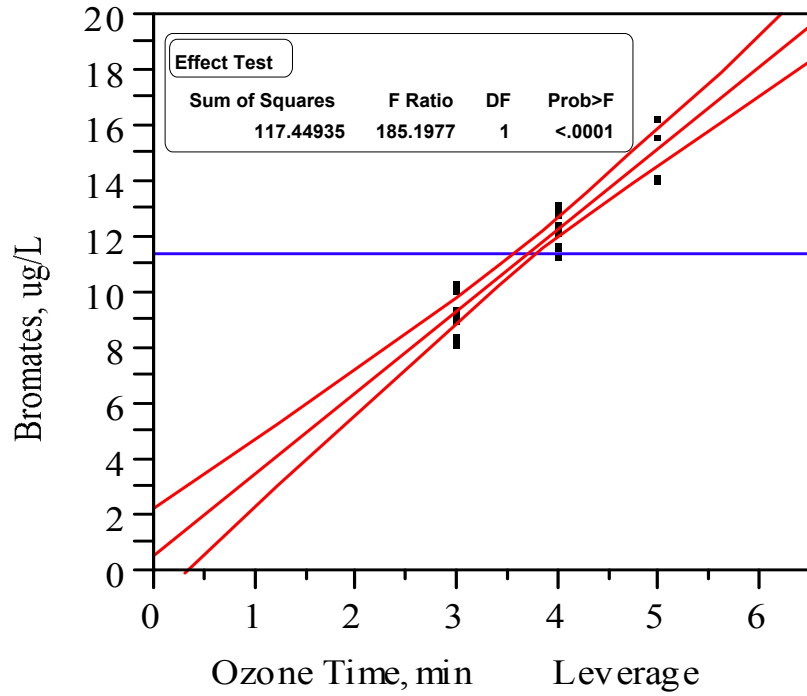


Figure 7. Bromate, $\mu\text{g/L}$ versus Ozone Time, Minutes Leverage Effect

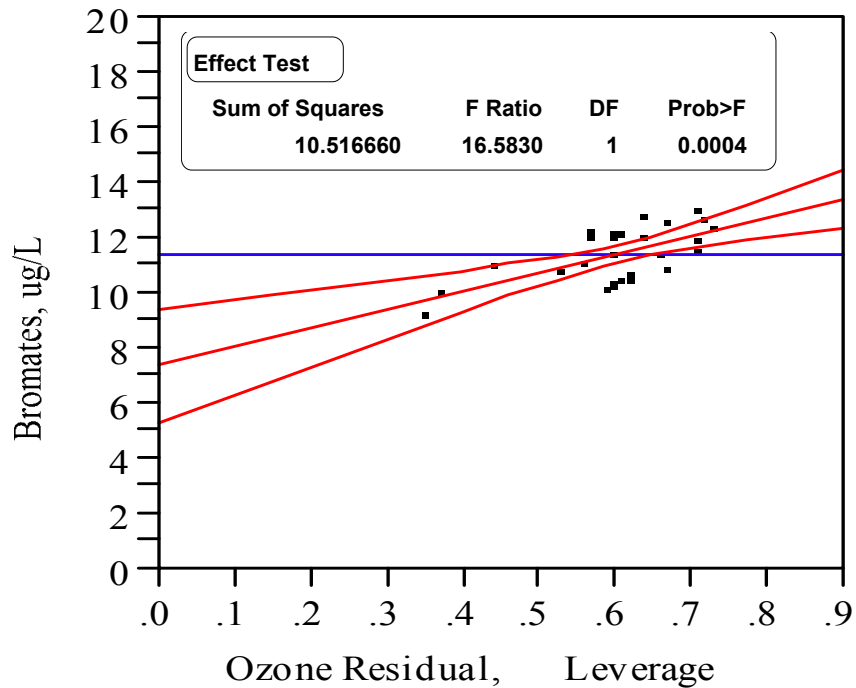


Figure 8. Bromates, $\mu\text{g/L}$ versus Ozone Residual, mg/L Leverage Effect

Laboratory Bromate Model for Ozone and Chlorine Dioxide

After completing the bromate model with ozone alone, the procedure for the chlorine dioxide effect was done similarly. Again, ozone was added at the same dose setting and contact times but with the chlorine dioxide doses added at 0.5, 1.0, and 1.5 mg/L prior to the ozone. The contact time for the chlorine dioxide was from 1 to 2 minutes to simulate the contact times in the re-carbonation chamber. One mg/L of hydrogen peroxide was added at the end of each ozonation period to simulate the plant condition. All bromate samples were preserved with EDA as recommended in Standard Methods.

The predicted versus actual bromate model using ozone and chlorine dioxide had 29 observations with an R-square of 0.90 and a mean of 7.0 $\mu\text{g/L}$ (Figure 9). The range of actual bromates was 2.9 to 13.6 $\mu\text{g/L}$. Table 3 shows the residuals were -1.4 to $+1.6$ $\mu\text{g/L}$. The bromide levels were also 170 $\mu\text{g/L}$ to 220 $\mu\text{g/L}$. The ozone residuals were 0.01 to 0.74 mg/L at contact times of 3, 4, and 5 minutes. The predictive equation is as follows:

$$[2] \quad \text{Bromates, } \mu\text{g/L} = 0.40 + (2.87 \times \text{O}_3 \text{ time, minutes}) + (3.23 \times \text{O}_3 \text{ Residual, mg/L}) + (-6.09 \times \text{ClO}_2 \text{ Dose, mg/L}).$$

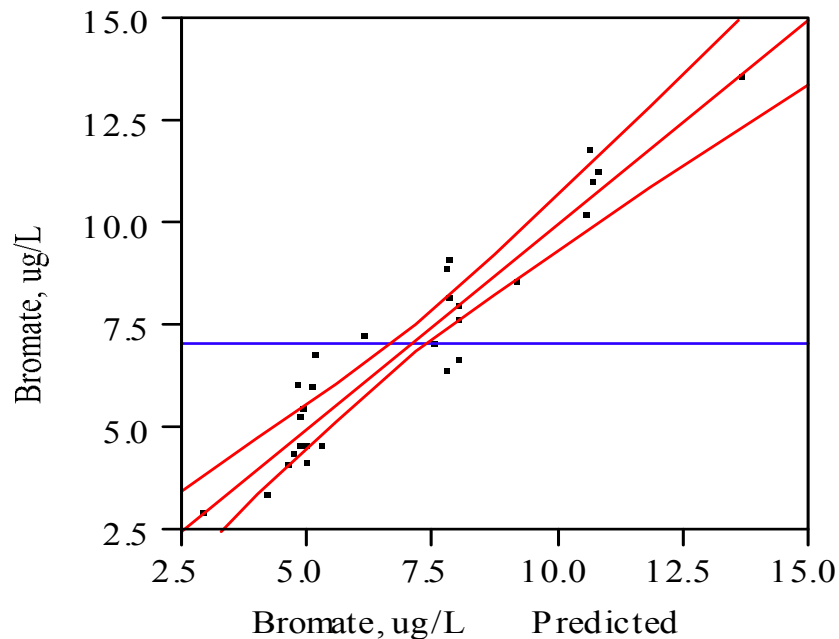


Figure 9. Predicted versus Actual Bromates for Ozone and Chlorine Dioxide

Table 3. Actual versus Predicted Bromates Model Data for O₃ & ClO₂

Number of Sample	Time, minutes	Ozone Residual, mg/L	Actual Bromates, $\mu\text{g/L}$	Predicted Bromates, $\mu\text{g/L}$	Residuals, $\mu\text{g/L}$	Chlorine Dioxide Dose, mg/L
1	4	0.55	7.1	7.6	-0.5	1
2	4	0.6	4.1	4.7	-0.6	1.5
3	4	0.66	4.6	4.9	-0.3	1.5
4	4	0.12	8.6	9.2	-0.6	0.5
5	4	0.12	7.3	6.2	1.1	1
6	4	0.65	6.1	4.8	1.3	1.5
7	4	0.67	5.3	4.9	0.4	1.5
8	3	0.58	4.4	4.8	-0.4	1
9	4	0.71	6.7	8.1	-1.4	1
10	3	0.01	2.9	2.9	0	1
11	3	0.4	3.4	4.2	-0.8	1
12	3	0.74	4.6	5.3	-0.7	1
13	4	0.71	7.7	8.1	-0.4	1
14	3	0.65	4.2	5	-0.8	1
15	4	0.63	6.4	7.8	-1.4	1
16	3	0.65	4.6	5	-0.4	1
17	4	0.62	6.4	7.8	-1.4	1
18	3	0.64	5.5	5	0.5	1
19	4	0.64	8.2	7.9	0.3	1
20	5	0.65	11	10.8	0.2	1
21	3	0.71	6.8	5.2	1.6	1
22	4	0.65	9.1	7.9	1.2	1
23	5	0.63	11.8	10.7	1.1	1
24	3	0.58	8.9	7.8	1.1	0.5
25	4	0.63	11.3	10.9	0.4	0.5
26	5	0.61	13.6	13.7	-0.1	0.5
27	3	0.68	6	5.1	0.9	1
28	4	0.71	8	8.1	-0.1	1
29	5	0.6	10.2	10.6	-0.4	1
Min	3	0.01	2.9	2.9	-1.4	1
Max	5	0.74	13.6	13.7	+1.6	1.5

Ozone Residuals leverage on Bromates with Chlorine Dioxide

Figure 10 shows the effect of ozone residual leverage on bromate formation when chlorine dioxide doses are 0.5, 1.0, and 1.5 mg/L. With chlorine dioxide, the ozone residual does not intercept the 10 $\mu\text{g/L}$ bromate MCL line on the graph. This implies that the maximum ozone residual of 0.75 mg/L could be utilized in the plant operation as compared to the 0.4 mg/L maximum residual for ozone alone. The Probability >F analysis is also less than 0.05 at the 0.0024 value, which indicates significant regression effect.

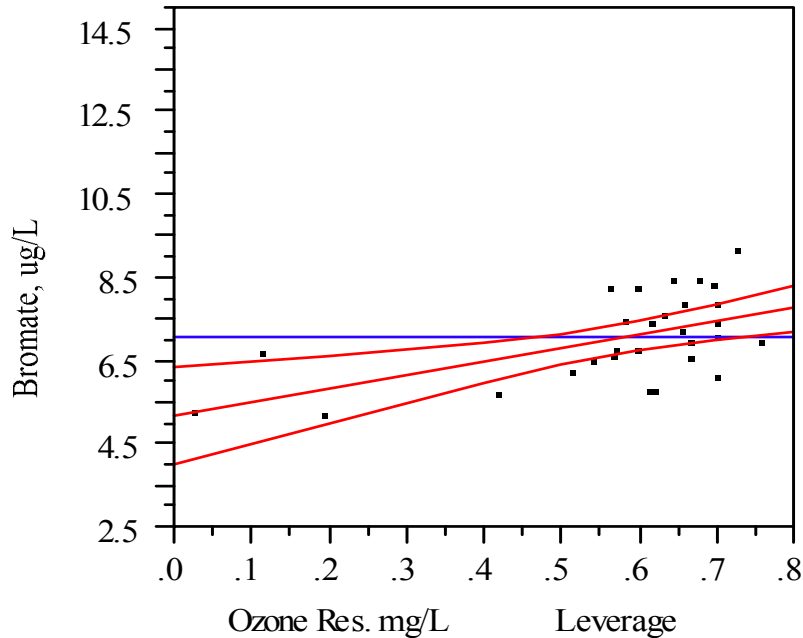


Figure 10. Ozone Residuals leverage on Bromates with Chlorine Dioxide

Bromates versus Ozone Contact Time with Chlorine Dioxide

Figure 11 shows the effect of ozone contact time on bromates with chlorine dioxide dosages from 0.5 to 1.5 mg/L. At the 10 $\mu\text{g/L}$ bromate level, the contact time is 4.8 minutes or 6.8 MGD per contactor as compared to 3.2 minutes or 10 MGD per contactor without chlorine dioxide. When both leverage graphs are considered together, the maximum ozone residual of 0.75 mg/l will permit a minimum of 6.8 MGD per contactor without exceeding the 10 $\mu\text{g/L}$ bromate level. At 0.3 mg/L ozone residual and 1.5 mg/L chlorine dioxide dose, then 5.0 MGD per contactor would comply with the 10 $\mu\text{g/L}$ MCL level. The Probability >F analysis is also less than 0.05 at the 0.0001 value, which indicates significant regression effect. The lower Probability > F analysis value of 0.0001 for the contact time compared to the ozone residual graph value of 0.0024 indicates more significance in its regression effect as also shown by the steeper angle of the graph across the horizontal line. If the graph was horizontal, then the Probability > F analysis value would exceed 0.05 indicating no significant regression effect.

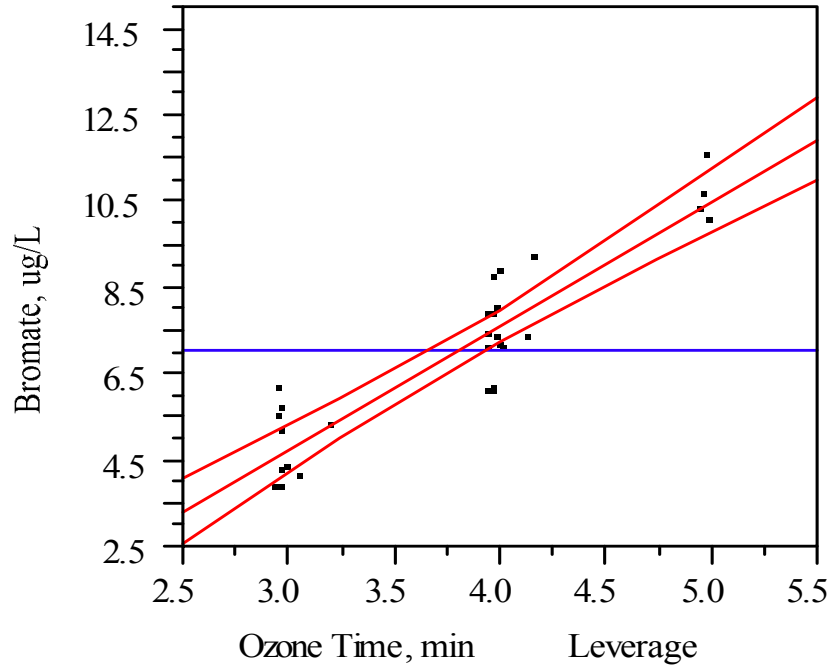


Figure 11. Bromates versus Ozone Contact Time with Chlorine Dioxide

Bromates versus Chlorine Dioxide Doses of 0.5 to 1.5 mg/L

Figure 12 depict the leverage effect of chlorine dioxide doses from 0.5 to 1.5 mg/L in reducing bromate levels at the rate of 6 $\mu\text{g/L}$ per mg/L of chlorine dioxide dose. Also, the graph indicates the 0.5 mg/L dose is not sufficient to lower bromates below the 10 $\mu\text{g/L}$ MCL for bromates. At the 1.0 mg/L chlorine dose, the bromate levels were below the MCL while the 1.5 mg/L dose can comply with the 5 $\mu\text{g/L}$ bromate level. Again, the Probability >F analysis is also less than 0.05 at the 0.0001 value, which indicates significant regression effect.

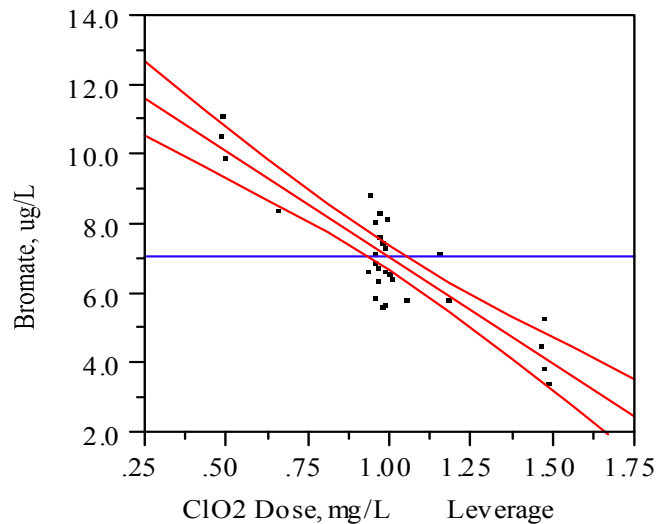


Figure 12. Bromates versus Chlorine Dioxide Doses of 0.5 to 1.5 mg/L

Summary Comparison of Bromate Levels in Laboratory Study

Table 4 summarizes the effect on bromates from ozone dose only and 3 chlorine dioxide doses at flow rates from 5 MGD to 10 MGD per contactor based on the 2005 Laboratory Study. When ozone alone is used, then, flows greater than 8.0 MGD per contactor at 0.3 mg/L ozone residual is recommended in order to meet the bromate MCL. At a flow of 7.0 MGD per contactor or greater, then a minimum dose of 0.5 mg/L of chlorine dioxide is required. The 1.0 mg/L chlorine dioxide dose can be used at flows of 6.0 MGD per contactor or greater. At the lowest flow of 5.0 MGD per contactor, then 1.5 mg/L of chlorine dioxide is required to meet the bromate MCL of 10 $\mu\text{g/L}$. The laboratory study showed an average 65% reduction of bromates at 1.5 mg/L chlorine dioxide dose for contact times of 3.25 minutes (10 MGD rate per contactor) to 6.5 minutes (5.0 MGD rate per contactor).

Table 4. Comparison of Bromate Levels from Laboratory Data in 2005 Study

MGD per contactor	Contact Minutes	Ozone Residual, mg/L	1.5 mg/L Chlorine Dioxide Dose	1.0 mg/L Chlorine Dioxide Dose	0.5 mg/L Chlorine Dioxide Dose	Ozone Only	% Reduction Range
5.0	6.5	0.3	10.0	13.1	16.2	17.6	8 to 42
6.0	5.4	0.3	7.0	9.9	13.4	14.4	7 to 51
7.0	4.64	0.3	5.2	7.8	10.8	12.2	11 to 57
8.0	4.06	0.3	3.1	6.1	9.2	10.5	12 to 70
9.0	3.61	0.3	1.8	4.8	7.9	9.1	13 to 80
10.0	3.25	0.3	<1.0	3.8	6.9	8.1	15 to 91

2005 Plant Study Results of Bromate Formation from Ozone and Contact Time

Figure 13 and Table 5 show the results from the 2005 plant study of ozone and contact time effects on bromates at Jonathan Rogers Water Plant. Figure 13 depicts the predicted versus actual bromate least squares model for ozone and contact time which had 18 observations with an R-square of 0.94 and a mean of 5.3 $\mu\text{g/L}$. The range of actual bromates was 3.0 to 19 $\mu\text{g/L}$. In Table 5, the actual minus predicted residuals were -1.4 to + 1.2 $\mu\text{g/L}$. The ozone residuals were 0.24 to 0.47 mg/L at contact times of 3.26 to 5.50 min. The bromide levels were also 170 to 220 $\mu\text{g/L}$. The predictive equation is as follows:

[3] Bromates, $\mu\text{g/L} = -43.75 + (68.60 \times \text{Ozone Residual, mg/L}) + (7.46 \times \text{Contact time, minutes}),$

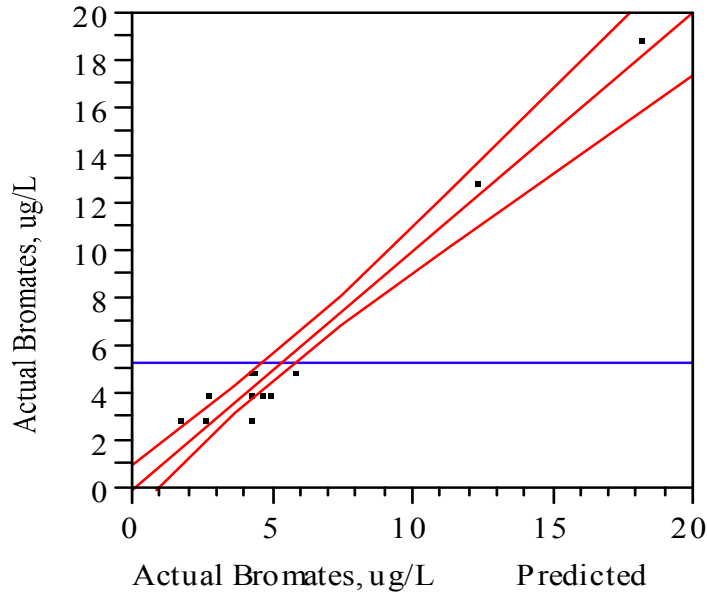


Figure 13. 2005 Plant Study of Predicted versus Actual Bromates from Ozone and Contact Time

During the period of June 14 to July 19, chlorine dioxide was not added in order to obtain baseline plant data prior to adding chlorine dioxide during the rest of the treatment season through October. However, during two days in early September, the chlorine dioxide generator was found unexpectedly off due to a power surge from an electrical storm. This caused high bromate levels in samples #17 and #18 from the high ozone residuals and long contact times at low flow rates. Therefore, these sample results were included with the data in Table 5 when no chlorine dioxide was added.

To assure reliable chlorine dioxide feed, a tri-colored light alarm system was installed the next week to alert the operator when the chlorine dioxide generator shuts down. The normal operation prior to chlorine dioxide addition was to operate with high flow rates and low ozone residuals through the ozone contactors in order to minimize the bromate levels. This was exemplified in the data for sample numbers 1 through 16, which had bromates at the 3 to 5 $\mu\text{g/L}$ level.

Figure 14 depicts the effect of ozone residual leverage on bromate formation based on the whole model equation. The Probability >F analysis value of 0.0001 indicates significant regression effect. Although ozone residual is important in controlling bromates, the contact time is more significant in its impact on bromate formation according to the model equation.

Table 5. 2005 Plant Study Results of Ozone and Contact Time Effects on Bromates

#	Flow, MGD	Ozone Res., mg/L	Time, minute	ClO ₂ , mg/L	Actual BrO ₃ μg/L	Predicted BrO ₃ , μg/L	Actual – Predicted, μg/L
1	10.03	0.35	3.24	0	5	4.4	0.6
2	10.07	0.35	3.22	0	5	4.3	0.7
3	9.05	0.32	3.59	0	4	5.0	-1.0
4	9.05	0.32	3.59	0	4	5.0	-1.0
5	8.33	0.3	3.90	0	5	5.9	-0.9
6	8.33	0.3	3.90	0	5	5.9	-0.9
7	10.06	0.35	3.23	0	4	4.4	-0.4
8	10.06	0.35	3.23	0	3	4.4	-1.4
9	10.06	0.35	3.23	0	3	4.4	-1.4
10	10.06	0.35	3.23	0	4	4.4	-0.4
11	9.9	0.35	3.28	0	4	4.7	-0.7
12	9.9	0.32	3.28	0	3	2.7	0.3
13	10.15	0.33	3.20	0	4	2.8	1.2
14	10.15	0.33	3.20	0	4	2.8	1.2
15	9.98	0.31	3.25	0	3	1.8	1.2
16	9.98	0.31	3.25	0	3	1.8	1.2
17	8.14	0.47	3.99	0	19	18.3	0.7
18	5.91	0.22	5.50	0	13	12.4	0.6

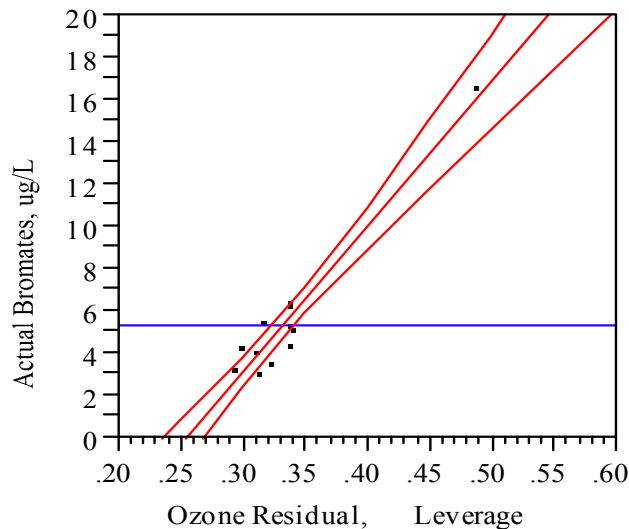


Figure 14. 2005 Plant Study Results of Ozone Residual Leverage on Actual Bromate Levels

Figure 15 depicts the effect of contact time in minutes leverage on actual bromate formation. The Probability >F analysis value of 0.0001 also indicates significant regression effect. The graph shows that <3.9 minutes (>8 MGD flow rate) contact time is necessary to maintain bromates less than 10 μg/L. Therefore, the maximum ozone residual should not exceed 0.35 mg/L in order to

meet the bromates MCL at 10 $\mu\text{g/L}$ based on the whole model equation. Since the recommended minimum ozone residual is 0.3 mg/L for *Giardia sp.* inactivation credit, the plant flow rate would have to exceed 8.0 MGD resulting in a narrow operational range of ozone residuals. In a practical sense, it is not possible to achieve consistent compliance from ozone dose alone. Since the bromate limit has been established, the plant operators have generally operated at lower ozone residuals to prevent excessive bromate formation and relied upon the CT from chlorine for achieving compliance of *Giardia sp.* inactivation credit.

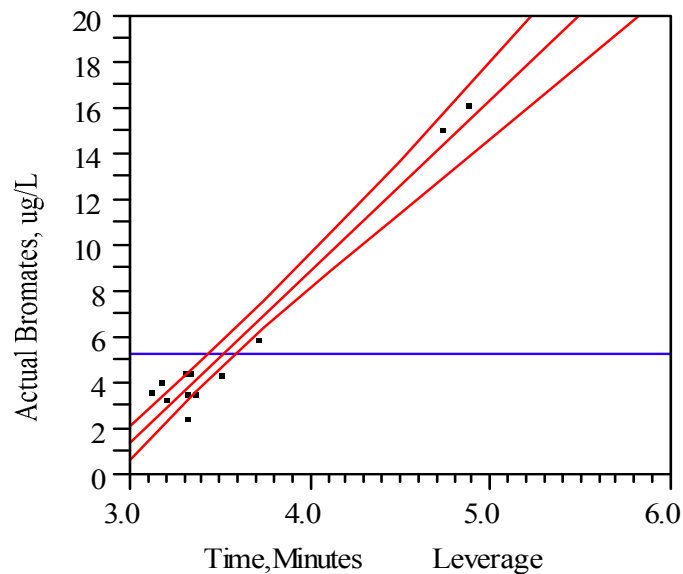


Figure 15. 2005 Plant Study Results of Contact Time Leverage on Actual Bromate Levels

2005 Plant Study of Ozone and Chlorine Dioxide Dose Effects on Bromates

Figure 16 and Table 6 show the results of the 2005 Plant Study of ozone and chlorine dioxide effects on bromate formation. The predictive equation for the plant study is as follows.

$$[4] \quad \text{Bromates, } \mu\text{g/L} = -1.95 + (4.01 \times \text{ozone residual, mg/L}) + (2.98 \times \text{time, minutes}) + (-6.35 \times \text{Chlorine Dioxide, mg/L}), \text{ R square} = 0.92.$$

Figure 16 depict the results of 41 observations listed in Table 6 with a mean of response of 2.9 $\mu\text{g/L}$. The range of bromate levels were 1 to 13 $\mu\text{g/L}$. The actual minus predictive values were equal to -1.4 to +1.6 $\mu\text{g/L}$. The range of contact times were 3.26 min (10.14 MGD rate) to 5.63 minutes (5.825 MGD rate). The range of the ozone residuals were 0.2 to 0.65 mg/L. The highest bromate level of 13 $\mu\text{g/L}$ exceeded the MCL because of insufficient chlorine dioxide dose of 0.44 mg/L while the second highest bromate level of 10 $\mu\text{g/L}$ had an insufficient chlorine dioxide dose of 0.73 mg/L for the contact time of 5.0 minutes (6.55 MGD rate). The longest contact time of 5.63 minutes (5.825 MGD) and highest ozone residual of 0.65 mg/L with a high chlorine dioxide dose of 1.4 mg/L exemplified the best capability of the chlorine dioxide at a 9.0 $\mu\text{g/L}$ bromate level.

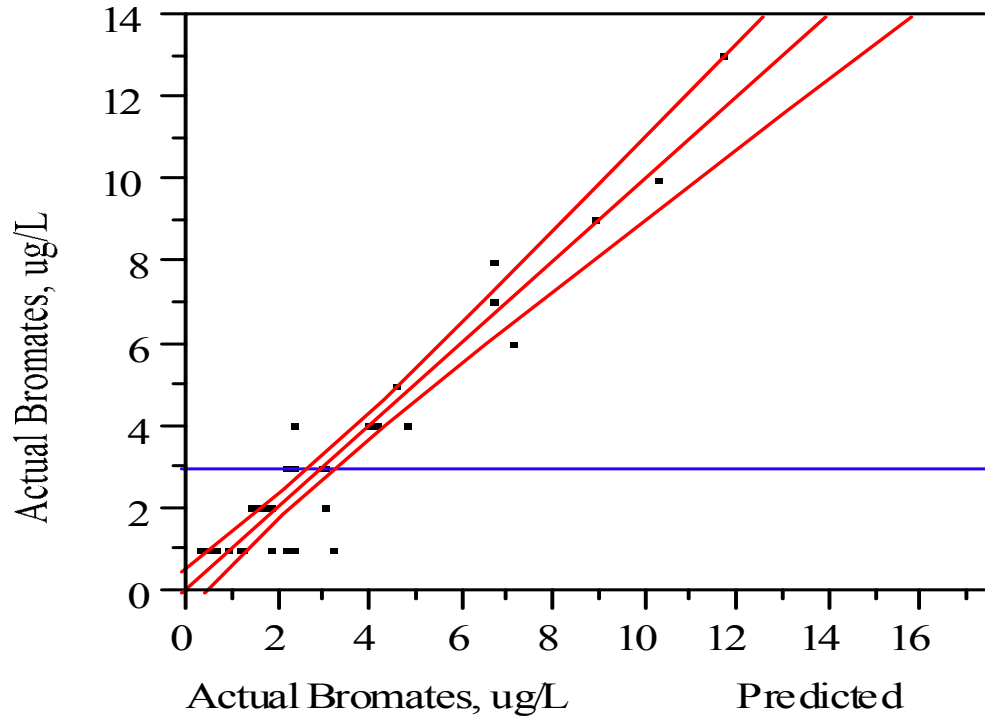


Figure 16. 2005 Plant Study of Ozone and Chlorine Dioxide Effects on Bromate Formation

Table 6. 2005 Plant Study of Chlorine Dioxide and Ozone Effects on Bromates

#	Flow, MGD	O ₃ Res, mg/L	Time, min.	ClO ₂ , mg/L	Actual BrO ₃ , μg/L	Pred BrO ₃ , μg/L	Actual – Predict
1	9.91	0.23	3.30	1.28	1.0	0.5	+0.5
2	9.91	0.23	3.30	1.28	1.0	0.5	+0.5
3	9.05	0.27	3.55	1.40	1.0	0.7	+0.3
4	10.04	0.2	3.28	1.26	1.0	0.4	+0.6
5	10.04	0.2	3.28	1.26	1.0	0.4	+0.6
6	9.95	0.28	3.29	1.23	1.0	1.0	0.0
7	9.33	0.31	3.45	1.31	1.0	1.2	-0.2
8	9.33	0.31	3.45	1.31	1.0	1.2	-0.2
9	9.72	0.26	3.35	1.33	1.0	0.5	+0.5
10	9.72	0.26	3.35	1.33	1.0	0.5	+0.5
11	7.29	0.36	4.46	1.67	3.0	2.3	+0.7
12	7.29	0.36	4.46	1.67	1.0	2.3	-1.3
13	7.27	0.38	4.47	1.67	1.0	2.4	-1.4
14	7.27	0.38	4.47	1.67	1.0	2.4	-1.4
15	7.3	0.45	4.45	1.74	3.0	2.3	+0.7
16	7.3	0.45	4.45	1.74	3.0	2.3	+0.7
17	8.4	0.485	3.82	0.73	8.0	6.7	+1.3
18	8.4	0.485	3.82	0.73	7.0	6.7	+0.3
19	8.13	0.31	3.95	1.09	4.0	4.0	0.0
20	8.13	0.275	3.95	1.23	3.0	3.0	0.0
21	9.135	0.385	3.52	1.10	2.0	3.1	-1.1
22	9.135	0.385	3.52	1.10	3.0	3.1	-0.1
23	6.54	0.41	5.01	1.67	4.0	4.2	-0.2
24	6.54	0.41	5.01	0.44	13.0	11.7	+1.3
25	6.55	0.485	5.00	0.73	10.0	10.3	-0.3
26	8.14	0.5	3.95	0.73	6.0	7.2	-1.2
27	8.33	0.305	3.85	1.45	2.0	1.5	+0.5
28	8.33	0.305	3.85	0.94	5.0	4.6	+0.4
29	7.98	0.365	4.03	1.53	2.0	1.9	+0.1
30	7.98	0.365	4.03	1.53	2.0	1.9	+0.1
31	8.785	0.405	3.65	1.40	2.0	1.7	+0.3
32	8.785	0.405	3.65	1.40	2.0	1.7	+0.3
33	8.23	0.325	3.90	1.44	2.0	1.8	+0.2
34	8.23	0.325	3.90	1.44	2.0	1.8	+0.2
35	8.19	0.15	3.92	0.80	4.0	4.9	-0.9
36	8.19	0.32	3.92	1.53	1.0	1.3	-0.2
37	7.41	0.255	4.38	1.53	4.0	2.4	+1.6
38	7.41	0.255	4.38	1.53	3.0	2.4	+0.6
39	7.67	0.345	4.21	1.60	1.0	1.9	-0.9
40	7.67	0.345	4.21	1.60	1.0	1.9	-0.9
41	5.825	0.65	5.63	1.40	9.0	8.9	+0.1

Summary Table Results of 2005 Plant Study based on Predictive Equations for Ozone and Chlorine Dioxide Effects on Bromate Formation

Tables 7 and 8 show the bromate levels for 3.25 minutes to 6.5 minutes (5 to 10 MGD rates) at ozone residuals of 0.3 mg/L and 0.4 mg/L with three chlorine dioxide doses compared to ozone alone. Equation [3], Bromates, $\mu\text{g/L} = -43.75 + (68.60 \times \text{Ozone Residual, mg/L}) + (7.46 \times \text{Contact time, minutes})$, was used for the ozone only calculations, while Equation [4] Bromates, $\mu\text{g/L} = -1.95 + (4.01 \times \text{ozone residual, mg/L}) + (2.98 \times \text{time, minutes}) + (-6.35 \times \text{Chlorine Dioxide, mg/L})$, was used to perform the calculations for the chlorine dioxide doses.

Table 7 shows that the 0.5 mg/L chlorine dioxide dose with 0.3 mg/L ozone residual was insufficient to reduce bromates at contact times less than 4.06 minutes (>8.0 MGD flow) while longer contact times and higher chlorine dioxide doses were effective. The 1.0 mg/L chlorine dioxide dose was similarly ineffective at the contact time of 3.61 minutes (>9.0 MGD) or less but was effective at reducing bromates at longer contact periods. Only the 1.5 mg/L chlorine dioxide dose was consistently capable of lowering bromates at 5.0 to 9.0 MGD flow rates by an average of 73 per cent. Therefore, the chlorine dioxide is needed only for flow rates from 5.0 MGD to 9.0 MGD when the ozone residual is 0.3 mg/L

Table 7. Bromate Formation for 3 Chlorine Dioxide Doses and Ozone only at 0.3 Ozone Residual in Plant Study

Flow, MGD	Time, minutes	Ozone Residual, mg/L	1.5 mg/L ClO ₂ Dose, mg/L	1.0 mg/L ClO ₂ dose, mg/L	0.5 mg/L ClO ₂ dose, Mg/L	Ozone only	% Reduction Range
5.0	6.5	0.3	9.1	12.3	15.4	25.3	39 to 64
6.0	5.4	0.3	5.8	9.0	12.2	17.1	29 to 79
7.0	4.64	0.3	3.6	6.7	9.9	11.4	13 to 68
8.0	4.06	0.3	1.8	5.0	8.2	7.1	0 to 75
9.0	3.61	0.3	<1.0	3.7	6.8	3.8	0 to ~80
10.0	3.25	0.3	<1.0	2.6	5.8	<1.0	0

On the other hand, Table 8 shows all chlorine dioxide doses are effective at all flow rates in reducing bromates when the ozone residual is 0.4 mg/L. The 1.5 mg/l chlorine dioxide met the 10 $\mu\text{g/L}$ bromate MCL at all flow rates while the 1.0 mg/L chlorine dioxide dose complied at flows greater than 6.0 MGD per contactor and the 0.5 mg/L dose is only effective at flows greater than 8.0 MGD per contactor. At 1.5 mg/L dose, the average reduction of bromates is 82% with only a very slight increase in bromates of about 0.4 $\mu\text{g/L}$ when the ozone residual is increased from 0.3 mg/L to 0.4 mg/L. Therefore, the optimum ozone residual is 0.4 mg/L with a 1.5 mg/L chlorine dioxide dose. Since the plant can now operate at the higher ozone residual level, the plant should have consistent disinfection credit capability and increased TOC removal which should lower TTHM levels in the distribution system. The average bromate reduction for ozone residuals from 0.3 to 0.4 mg/L should be 78% at 1.5 mg/L chlorine dioxide dose. However, the Contra Costa study showed 78% reduction with 1.0 mg/L chlorine dioxide dose but had a lower TOC level of 2.0 mg/L compared to El Paso's 3.0 mg/L level.

Table 8. Bromate Formation for 3 Chlorine Dioxide Doses and Ozone Only at 0.4 mg/L Ozone Residual in Plant Study

Flow, MGD	Time, minutes	Ozone Residual, mg/L	1.5 mg/L ClO ₂ Dose, mg/L	1.0 mg/L ClO ₂ dose, mg/L	0.5 mg/L ClO ₂ dose	Ozone only	% Reduction Range
5.0	6.5	0.4	9.5	12.7	15.8	32.2	51 to 70
6.0	5.4	0.4	6.2	9.4	12.6	24.0	48 to 74
7.0	4.64	0.4	4.0	7.1	10.3	18.3	44 to 78
8.0	4.06	0.4	2.2	5.3	8.6	14.0	39 to 84
9.0	3.61	0.4	<1.0	4.0	7.2	10.6	32 to 91
10.0	3.25	0.4	<1.0	2.9	6.1	7.9	23 to ~94

Ozonation effect on Chlorine Dioxide and Chlorite levels in Laboratory Study

Table 9 shows the effect of ozone on chlorine dioxide and chlorite levels from laboratory data. Twelve samples were taken of chlorine dioxide dosages at 1.0 & 0.5 mg/L. The results show all chlorite levels were less than 0.1 mg/L with chlorates formed from the reaction of ozone with chlorine dioxide and/or chlorite. The % total chlorates formed of the applied chlorine dioxide dose were from 56.8% to 73.4% with an average of 67.6%, typical of chlorite levels in previous chlorine dioxide studies on the Rio Grande River. The 0.5 mg/L chlorine dioxide dose showed lower chlorate formation as a percentage of the applied dose because the higher chlorine dioxide doses may have some low levels of the chlorine dioxide species entering the ozone contact chamber. However, the total percentage range of byproducts was within expectations as compared to experiences in other plants. Chlorates are not regulated as an adverse health concern in drinking water by USEPA.

Table 9. Ozone Effect on Chlorine Dioxide and Chlorite Levels

Sample ID	*ClO ₂ Dose, mg/L	ClO ₂ ⁻ , mg/L	ClO ₃ ⁻ , mg/L	% Total Oxidants of ClO ₂ dose
1	1.0	<0.1	0.731	73.1
2	1.0	<0.1	0.731	73.1
3	1.0	<0.1	0.734	73.4
4	1.0	<0.1	0.691	69.1
5	1.0	<0.1	0.671	67.1
6	1.0	<0.1	0.664	66.4
7	0.5	<0.1	0.293	58.6
8	0.5	<0.1	0.284	56.8
9	0.5	<0.1	0.293	58.6
10	1.0	<0.1	0.716	71.6
11	1.0	<0.1	0.718	71.8
12	1.0	<0.1	0.720	72.0
Average	0.875	<0.1	0.60	67.6
Maximum	1.0	<0.1	0.734	73.4
Minimum	0.5	<0.1	0.284	56.8

Ozone effect on Chlorite and Chlorate levels in Plant Study

Table 10 shows the results of 38 samples from the ozone effect on chlorite and chlorate levels during the plant study period of July 21 to October 12. The chlorite levels were <0.01 mg/L except on 10/4 when it was 0.149 with a chlorine dioxide dose of 0.95 mg/L. The average % total oxidants of the chlorine dioxide dosages were 62%, lower than the laboratory study at 67%. As in the Contra Costa study, the chlorine dioxide and chlorite levels were converted to chlorates by the ozone. Based on previous chlorine dioxide studies in the late 1990s, the chlorine dioxide's initial demand (<1 min) for the Rio Grande River water was about 1.5 mg/L (Rittmann, 1999). Since the maximum detention time is about 2 minutes before the chlorine dioxide treated water enters the ozone contactor, the ozone should react only with the chlorite species. The plant chlorine dioxide dosages were converted to mg/L from PPM (gals/MG) by multiplying the plant PPM dosages by 1.377, the specific gravity of Purate™ chemical. This was necessary because lab results for chlorate and chlorite are based on mg/L. However, the plant operators could continue to calculate dosages based on PPM but when comparing lab results to plant chlorate levels, then the conversion of the data is necessary.

Table 10. Ozone Effect on Chlorite and Chlorate Levels in Plant Study

No.	Sample Date	*ClO ₂ Dose, mg/L	Chlorite, mg/L	Chlorate, mg/L	% Total Oxidants of ClO ₂ Dose
1	7/28	1.93	<0.01	1.12	58
2	7/29	1.93	<0.01	1.04	54
3	8/1	1.81	<0.01	0.98	54
4	8/2	1.74	<0.01	1.05	60
5	8/3	1.78	<0.01	1.07	60
6	8/4	1.70	<0.01	1.10	65
7	8/5	1.72	<0.01	1.06	62
8	8/8	1.82	<0.01	1.18	65
9	8/9	1.81	<0.01	1.11	61
10	8/10	1.81	<0.01	1.10	61
11	8/15	2.34	<0.01	1.20	51
12	8/18	2.32	<0.01	1.20	52
13	8/19	2.29	<0.01	1.06	46
14	8/22	2.52	<0.01	1.06	42
15	8/23	2.44	<0.01	1.44	59
16	8/24	2.43	<0.01	1.40	58
17	8/29	2.30	<0.01	1.15	50
18	8/30	2.19	<0.01	1.16	53
19	8/31	1.95	<0.01	1.09	56
20	9/1	1.51	<0.01	1.05	70
21	9/6	2.3	<0.01	1.14	50
22	9/12	0.0	<0.01	0.100	0
23	9/14	2.0	<0.01	1.42	71

Table 10 (cont.)

24	9/21	1.99	<0.01	1.39	70
25	9/23	1.96	<0.01	1.31	67
26	9/26	2.03	<0.01	1.34	66
27	9/27	1.98	<0.01	1.38	70
28	9/28	1.11	<0.01	0.917	83
29	9/29	1.12	<0.01	0.893	80
30	9/30	1.12	<0.01	0.874	78
31	10/3	1.06	<0.01	0.909	86
32	10/4	2.08	0.149	0.270	20
33	10/5	2.06	<0.01	1.03	50
34	10/6	2.20	<0.01	1.28	58
35	10/7	2.32	<0.01	1.37	59
36	10/10	1.92	<0.01	1.59	83
37	10/11	1.94	<0.01	1.41	73
38	10/12	1.86	<0.01	1.77	95
AVG		1.88	<0.01	1.16	62

*The plant chlorine dioxide dosages were converted to mg/L from PPM by multiplying the plant PPM dosages by 1.377, the specific gravity of Purate™, Eka Chemical, Inc.

Conclusions

The following conclusions from the 2005 Laboratory and Plant Studies, can be made with reasonable certainty:

1. The lab and plant studies predict accurately the effect of ozone residual, contact time, and chlorine dioxide dose on bromate formation.
2. Bromates were reduced by 6.1 and 6.34 $\mu\text{g/L}$ per mg/L of chlorine dioxide dose in the lab and the plant studies respectively.
3. Chlorite residuals were consistently less than 0.01 mg/L after ozonation with chlorine dioxide doses of 0.5 mg/L to 1.5 mg/L in the lab and plant studies.
4. Chlorate levels were 67% and 62% of the applied chlorine dioxide dose in the lab and plant studies, respectively.
5. Ozone alone can comply with the 10 $\mu\text{g/L}$ bromate MCL at contact times of 4.06 minutes or less (>8.0 MGD rate per contactor) with 0.3 mg/L ozone residual but at the 0.4 mg/L ozone residual level, the contact time of 3.61 min or less (>9.0 MGD rate per contactor) is necessary to comply with the bromate MCL.
6. The 0.5 mg/L chlorine dioxide dose with 0.3 mg/L ozone residual was insufficient to reduce bromates at contact times less than 4.06 min (>8.0 MGD flow) while longer contact times and higher chlorine dioxide doses were effective.
7. Chlorine dioxide doses of 0.5 to 1.5 mg/L are effective at contact times of 6.5 min (5 MGD flow) to 3.25 min (10 MGD flow) in reducing bromates when the ozone residual is 0.4 mg/L.
8. The average bromate reduction for ozone residuals from 0.3 to 0.4 mg/L should be 78% at 1.5 mg/L chlorine dioxide dose. However, the Contra Costa study showed 78%

reduction with 1.0 mg/L chlorine dioxide dose but had a lower total organic carbon treatment level of 2.0 mg/L compared to El Paso's 3.0 mg/L level.

9. Since the plant can now operate at the higher ozone residual level of 0.4 mg/L, the plant should have consistent disinfection credit capability for *Giardia sp* inactivation while increasing TOC removal and resulting in lower TTHM levels in the distribution system.
10. Based on these results, the plant could further reduce the bromates by lowering the current pH level of 7.3 prior to ozone and chlorine dioxide treatment in order to obtain *Cryptosporidium sp* inactivation credit.

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