TECHNICAL BULLETIN

Impact of Chlorine Dioxide Pre-Oxidation of Ozone in Preventing Bromates

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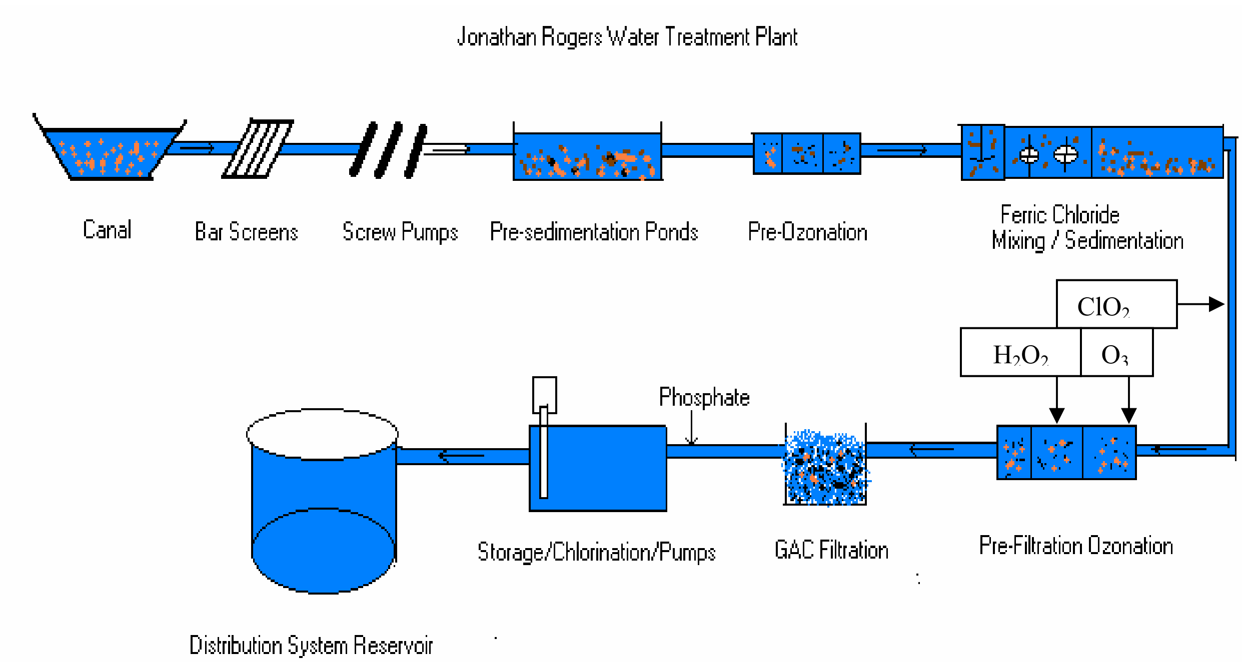
Background

The USEPA will require increased disinfection capability and lower disinfection byproduct levels when the proposed Long Term 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). Laboratory and plant studies at Contra Costa California in 2002 and at El Paso Texas in 2005 showed that chlorine dioxide pre-oxidation of ozone prevented bromate formation very effectively. In addition, combined oxidants have a synergistic effect on the inactivation of *Cryptosporidium sp.* The three treatment options available for lowering bromates are: 1. Chlorine dioxide pre-oxidation of ozone. 2. Ammonia addition, or 3. PH control. These treatment methods were evaluated in the AWWARF study performed in Contra Costa California in 2002. The highlights of the Contra Costa study demonstrated that 1. Chlorine dioxide or water adjusted to pH 6.0 substantially reduced 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. In 2005, El Paso's Jonathan Rogers Water Plant (Figure 1) also demonstrated through lab and plant studies the effectiveness of chlorine dioxide pre-oxidation of ozone in reducing bromate formation.

Figure 1 – Jonathan Rogers Water Treatment Plant Flow Schematic



El Paso Study Objectives

The El Paso study objectives were to: 1. determine the effect of ozone residual and contact time on bromate formation, 2. determine effect of chlorine dioxide on reducing bromates, 3. determine the effect of ozone on chlorite and chlorate levels.

Initial Assumptions

Initial assumptions 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 for disinfection credit, 3. Chlorine dioxide prevents bromate formation.

2005 Laboratory Study Procedures

The laboratory procedures were based on simulating the Jonathan Rogers Plant operation by evaluating the effects from two independent variables (ozone residual and production rate) under the plant operator's control. Although the independent variables of pH, temperature, bromide level, and TOC affect bromate formation too, these variables were not included in the evaluation. The intent of the experimental design was to develop predictable bromate formation equations based on ozone residual levels and contact times (production rates) at constant temperature in the laboratory compared to plant conditions. The lab procedure was intentionally designed to have more efficient ozone transfer to solution to cause higher bromate formation as compared to the plant process in order to provide a safety factor for the plant study, especially, when chlorine dioxide is not used.

The major laboratory equipment included: 1). Ozone Solutions Model AC-500 Ozone Generator with pure oxygen carrier gas and 10 position switch; 2). 1.5 L Buret with stopcock; 3). Hach 890 Analyzer with Accuvac vials; 4). Oxygen Gas Rotometer; 5). Fine bubble diffuser.
One-liter samples were treated with chlorine dioxide dosages from 0.5 mg/L to 1.5 mg/L for a maximum of two minutes contact time and then were transferred to the 1.5-liter buret. Fine bubble ozone gas was passed through each sample at 3, 4, and 5 minutes time periods, which simulated the production range at the Jonathan Rogers Water Plant. After each time interval, about 100 ml of sample was withdrawn from the stopcock at the bottom of the buret. Accuvac vials were used for ozone residual measurement. The remainder of the sample was treated with 1 ppm of hydrogen peroxide and then preserved with ethylenediamine (EDA) before transporting the samples to the laboratory for bromate analysis. The ozone dose setting was determined by trial and error measurement of ozone residuals in the range of 0.01 mg/L to 0.75 mg/L at the 3,4, and 5-minute contact periods. This procedure simulated the Jonathan Rogers Water Plant process, except the lab procedure had better ozone transfer capability.

Bromate Model with Chlorine Dioxide Pre-oxidation

The model developed by JMP Statistical Software for the predicted versus actual bromate levels using ozone and chlorine dioxide had 29 observations with a R^2 of 0.90 and a mean of 7.0 ug/L.

The range of actual bromate levels was 2.9 ug/L to 13.6 ug/L. The range of bromate residuals was –1.4 ug/L to +1.6 ug/L. The bromide levels were 170 to 220 ug/L. The ozone residuals were from 0.01 mg/L to 0.74 mg/L at contact times of 3,4, and 5 minutes. The predictive equation is: Bromates, ug/L = 0.40 + (2.87 X O_3 time, minutes) + (3.23 X O_3 Residual, mg/L) + (-6.09 X ClO_2 Dose, mg/L).

Table 1 summarizes the effect on bromates from ozone doses (residuals) and three chlorine dioxide doses at flow rates from 6 mgd to 10 mgd per contactor. According to the bromate predictive equation, about 91% of bromate formation is caused by the contact time at 0.3 mg/L ozone residual. Therefore, bromate reduction without chlorine dioxide treatment will depend primarily on reducing the contact time or increasing the production rate. Since the shortest contact time of 3.25 minutes or 10 mgd per contactor flow rate exceeds the MCL for bromates, then, chlorine dioxide treatment is necessary to reduce the bromates based on the laboratory study.

At chlorine dioxide doses between 1.0 mg/L and 1.5 mg/L, the bromate levels were less than the MCL at flow rates from 6.0 to 10 MGD per contactor. The range of % bromate reduction was 18% to 85% for chlorine dioxide doses from 0.5 mg/L to 1.5 mg/L.

Table 1- Comparison of Bromate Levels from Laboratory Data

MGD per contactor	Contact Minutes	Ozone Residual, mg/L	1.5 mg/L ClO_2	1.0 mg/L ClO_2	0.5 mg/L ClO_2	Ozone only, ug/L	% Reduction Range with ClO_2
6.0	5.4	0.3	7.8	10.8	13.8	16.9	18 to 53
7.0	4.64	0.3	5.6	8.6	11.6	14.7	21 to 62
8.0	4.06	0.3	3.9	6.9	10.0	13.0	23 to 70
9/0	3.61	0.3	2.6	5.6	8.7	11.7	26 to 78
10.0	3.25	0.3	1.6	4.6	7.7	10.7	28 to 85

Table 2 depicts the effect of ozone and chlorine dioxide on bromates in the plant study. The predictive equation for the plant study is: Bromates, ug/L = 5.8258X +(-6.09 X ClO_2, mg/L), where X = CT, ozone Concentration, mg/L times the Time, minutes with a R^2 of 0.95. At flow rates of 5.0 MGD per contactor and ozone residuals of 0.3 mg/L or greater, the MCL is exceeded without chlorine dioxide treatment. If the bromate MCL is reduced to 5.0 ug/L or the disinfection requirements increase with LT2ESWTR, then, additional bromate reduction may be necessary. Using chlorine dioxide will reduce bromates while permitting higher ozone dosages to comply with increased disinfection requirements. In addition, there may be more disinfection credit available in future regulations for the synergistic effect from the combination of ozone and chlorine dioxide oxidants, which would not be available from lower pH level treatment or ammonia addition. The El Paso plant study showed an average 75% reduction of bromates at 1.0 mg/L chlorine dioxide dose compared to 78% for the Contra Costa study.

Table 2 – Comparison of Bromate levels from Plant Data

MGD per contactor	Contact Minutes	Ozone Residual, mg/L	1.5 mg/L ClO_2	1.0 mg/L ClO_2	0.5 mg/L ClO_2	Ozone only	% Red. Range with ClO_2
5.0	6.5	0.3	2.3	5.3	8.4	11.4	26 to 80
6.0	5.4	0.3	<1.0	3.3	6.4	9.4	32 to >90
7.0	4.64	0.3	<1.0	2.0	5.1	8.1	37 to >90
8.0	4.06	0.3	<1.0	1.0	4.1	7.1	42 to >90
9.0	3.61	0.3	<1.0	<1.0	3.3	6.3	48 to >90
10.0	3.25	0.3	<1.0	<1.0	2.7	5.7	53 to >90

Table 3 shows the effect of ozone on chlorine dioxide and chlorite levels from laboratory data. The results indicate that all chlorite levels were less than 0.1 mg/L and chlorates were formed from the reaction with ozone. 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 previous studies. The plant study results showed an average of 62% total oxidants (chlorates only) of the applied dose. Chlorates are not regulated as an adverse health concern in drinking water.

Table 3 – Ozone Effect on Chlorine Dioxide and Chlorite Levels

Sample ID	ClO_2 Dose, mg/L	$ClO2^-$, mg/L	ClO_3^-, mg/L	% Total Oxidants of ClO_2 Dose
137	1.0	<0.1	0.731	73.1
138	1.0	<0.1	0.731	73.1
139	1.0	<0.1	0.734	73.4
140	1.0	<0.1	0.691	69.1
141	1.0	<0.1	0.671	67.1
142	1.0	<0.1	0.664	66.4
143	0.5	<0.1	0.293	58.6
144	0.5	<0.1	0.284	56.8
145	0.5	<0.1	0.293	58.6
156	1.0	<0.1	0.716	71.6
157	1.0	<0.1	0.718	71.8
158	1.0	<0.1	0.729	72.9
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**

Conclusions

The following conclusions can be made with reasonable certainty:

1. Bromates were reduced by 6.1 ug/L per mg/L of chlorine dioxide dose.

2. Chlorite residuals were <0.1 mg/L after ozonation with chlorine dioxide doses from 0.5 mg/L to 1.5 mg/L in the lab and plant studies.

3. Ozone alone can comply with the 10-ug/L bromate limit at flow rates greater than 6.0 MGD per contactor (5.4 minutes) with a 0.3 mg/L ozone residual or less in El Paso.

4. Chlorine dioxide doses from 1.0 to 1.5 mg/L had bromates less than 5 ug/L at flow rates greater than 5.0 mgd per contactor (6.5 minutes) with a 0.3 mg/L ozone residual.

5. Chlorine dioxide pretreatment will allow higher ozone dosages (residuals) without exceeding the bromate MCL, which increases the disinfection capability of the plant process.

6. The combined oxidant's effect from chlorine dioxide and ozone should permit additional disinfection credit for the inactivation of C*ryptosporidium sp.* from regulatory agencies.

7. The El Paso plant study showed an average 75% reduction of bromates at 1.0 mg/L chlorine dioxide dose compared to 78% for the Contra Costa study.

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