Comparison of Chlorite and Chlorate based Chlorine Dioxide Generation on the Reduction of THMs Formation

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Abstract

In 1997, Eka Chemicals introduced the SVP-Pure® chlorate-based, chlorine dioxide generator for the municipal and industrial markets. The generator utilizes a chlorine-free chemistry, which does not produce chlorite or chlorine with the chlorine dioxide in the generator solution. By comparison, the chlorite-based generators of chlorine dioxide often contain some un-reacted chlorite and chlorine in the generator solution. Although both systems are capable of 95+% conversion of their precursor chemicals to chlorine dioxide, it is important to compare their capability in actual operation. Is there a difference in performance between chlorine dioxide generated from sodium chlorite and sodium chlorate? To answer that question, a two-year laboratory and plant study was performed in El Paso Texas to determine the effect of the two chlorine dioxide generation methods on the reduction of THMs formation potential in drinking water. Three conditions were evaluated: 1. Chlorine doses effect on raw river water; 2. Rio Linda best trim settings (5-10% excess chlorine) generator solutions effect on raw river water; 3. Eka Chemicals SVP-Pure® generator solutions effect on raw river water.
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Laboratory Studies

The raw water source for the studies was the Rio Grande River, which was available for treatment during the period of March through September in El Paso, Texas. The raw water samples were dosed with chlorine dioxide solutions obtained from the existing Rio Linda chlorine dioxide generators utilizing sodium chlorite/chlorine gas and the Eka Chemicals SVP-Pure® chlorine dioxide generator utilizing a sodium chlorate/hydrogen peroxide/sulfuric acid system. In chlorite-based systems for generating chlorine dioxide, chlorine is normally overfed by 5% to 10% to ensure high efficiency conversion of the chlorite to chlorine dioxide. A comparison of these results was made to samples similarly dosed from the Eka Chemicals SVP-Pure® chlorine dioxide generator, which does not contain chlorine or chlorite but utilizes 40% sodium chlorate and 10% hydrogen peroxide solution with a 78% sulfuric acid solution.

Rio Grande settled water samples were dosed with chlorine dioxide from each generator at various dosages of chlorine dioxide and chlorine solutions. Contact times were 1-hour and 24-hours. The raw water pH was 8.3 but samples were also pH adjusted in the range of 5 to 9 before adding oxidants. Raw TOC levels were about 3 to 5 mg/L. After adding chlorine dioxide at various dosages, the samples were placed in a dark closed container for 1-hour and then were chlorinated at various dosages for 1 hour or 24-hour periods, after which they were de-chlorinated and analyzed for THMs.

Rio Linda Chlorite Based Chlorine Dioxide Generator Results

The Rio Linda chlorine dioxide generator results predicted THMs based on 3 to 7.5 mg/L chlorine dioxide dosages and followed by chlorine dosages of 2 to 7 mg/L at contact times of 1 hour and 24 hours for pH levels from 5 to 9 and TOC concentrations ranging from 2.8 to 4.9 mg/L. Nineteen samples were analyzed and the results reported in Table 1 below. The model equation depicted in Figure 1 below predicted the THMs range from 0 to 134 ppb as compared to the actual THMs from 2.8 ppb to 141 ppb based on the whole model equation of Predicted THMs = -95.0 + (-9.0* ClO_2, mg/L) + (2.9 * Cl_2, mg/L) + (3.9 * Time, hours) + (-5.9 * TOC, mg/L) + (18.5 * pH). The R square was excellent at 0.95 with a mean of response of 55.9 ppb THMs.

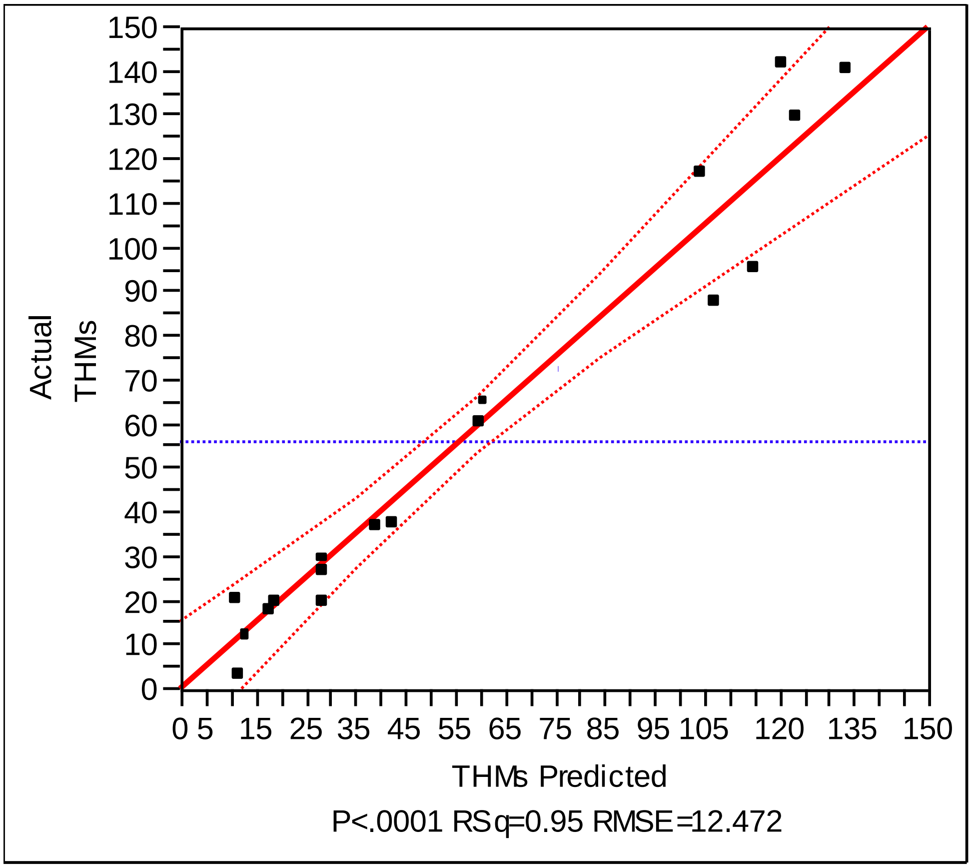

Figure 1 – Rio Linda Chlorine Dioxide Generator THM Data from Table 1

Table 1- THMs Using Rio Linda Chlorine Dioxide Generator

Item #	Sample ID	ClO_2 Dose, mg/L	Cl_2 Dose, mg/L	Time, Hours	TOC, mg/L	pH	Actual THMs	Predicted THMs
1	53	3	7	1	4.6	8.3	19.2	28.6
2	43	5	2	1	4.1	9	2.8	11.7
3	54	4	7	1	4.9	8.3	17.4	17.8
4	55	5	7	1	4.1	8.3	11.7	13.4
5	56	7.5	7	1	3.4	8.3	11.8	0
6	103	5	7	24	3.5	8.3	87	107.4
7	162	3	7	1	4.6	8.3	28.9	28.6
8	223	3	7	24	4.3	8.3	141	120.8
9	225	3	7	24	4.3	5	60	59.9
10	229	3	7	1	2.8	8.3	36	39.1
11	230	4	7	1	3	8.3	26.2	28.9
12	231	5	7	1	3.1	8.3	19.3	19.3
13	249	3	7	24	3.8	8.3	129	123.7
14	250	5	7	24	4	8.3	116	104.5
15	259	3	7	24	4.3	9	140	133.7
16	260	5	7	24	4.4	9	95	115.0
17	275	3	7	24	4.1	5	64	61.1
18	46	5	2	1	4.2	9	20	11.1
19	276	5	7	24	4.1	5	37	43.0

Eka SVP-Pure Chlorate Based Chlorine Dioxide Generator Results

The Eka SVP-Pure Chlorine Dioxide generator predicted THM results based on 3 to 7.5 mg/L chlorine dioxide dosages in combination with chlorine dosages of 2 to 7 mg/L at contact times of 1 hour and 24 hours for pH levels from 5 to 9 and TOC concentrations ranging from 2.8 to 5.3 mg/L. Seventeen samples were analyzed and the results reported in Table 2 below. The model equation depicted in Figure 2 below predicted the THMs range from 5.1 to 156 ppb as compared to the actual THMs from 0 ppb to 141 ppb. The whole model equation was as follows: Predicted THMs = -89.4 + (-11.2* ClO_2, mg/L) + (4.1 * Cl_2, mg/L) + (3.8 * Time, hours) + (-11.4 * TOC, mg/L) + (21.8 * pH). The R square was excellent at 0.94 with a mean of response of 60.5 ppb THMs. The factors for chlorine dioxide dose and TOC of -11.2 ppb and -11.4 ppb per mg/L, respectively, shows the oxidation potential of chlorine dioxide in reducing THM precursors, the humic and fulvic acids. In this experimental design, the THMs were not removed by coagulation or filtration because each raw sample was dosed only with the oxidants.

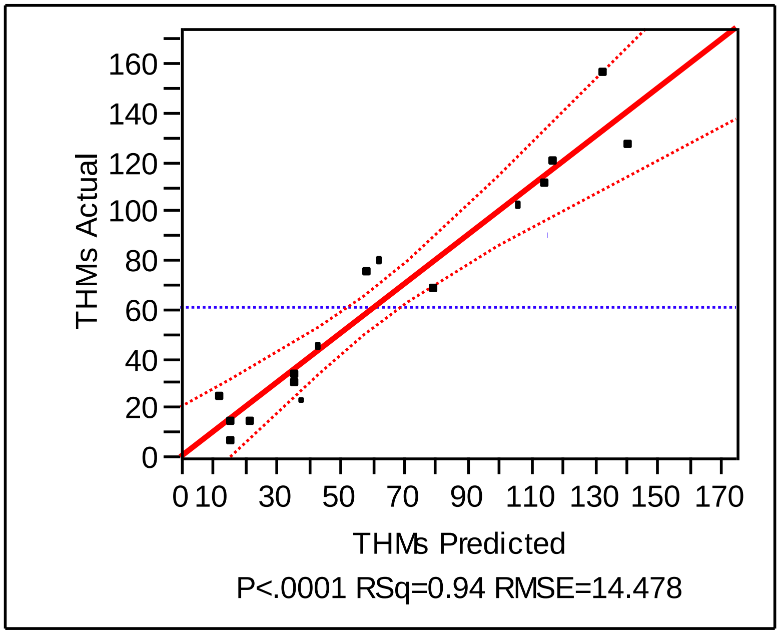

Figure 2 – Eka SVP-Pure Chlorine Dioxide Generator THM Data from Table 2

Table 2- THMs Using Eka SVP-Pure Chlorine Dioxide Generator

Item #	Sample ID	ClO_2 Dose, mg/L	Cl_2 Dose, mg/L	Time, hours	TOC, mg/L	pH	Actual THMs, ppb	Predicted THMs, ppb
1	45	5	2	1	4.1	9	5.1	15.9
2	65	3	7	1	4.6	8.3	21.4	38.1
3	66	4	7	1	5	8.3	14	22.3
4	67	5	7	1	4.6	8.3	13.6	15.6
5	234	3	7	1	2.8	8.3	74.6	58.6
6	235	4	7	1	3.1	8.3	43.5	43.9
7	236	5	7	1	2.8	8.3	32.3	36.1
8	253	3	7	24	3.3	8.3	126	140.8
9	254	5	7	24	3.4	8.3	120	117.2
10	263	3	7	24	5.3	9	156	133.3
11	264	5	7	24	5	9	111	114.2
12	272	5	7	24	4.2	7	67.8	79.7
13	279	3	7	24	3.8	5	79.2	63.2
14	280	5	7	24	4.2	5	29.6	36.2
15	340	5	7	24	4.7	8.49	101.4	106.5
16	48	5	2	1	4.4	9	23.2	12.4
17	68	7.5	7	1	4.4	8.49	9.1	-6.1

THMs generated by Chlorine without Chlorine Dioxide Effects

In a third set of 1-hour and 24-hour samples, a wide-range of chlorine dosages was added to 27 samples (Table 3), de-chlorinated, and then analyzed for THMs. The 1-hour contact period was chosen because it approximates the detention period in the primary sedimentation tanks (where chlorine dioxide is applied) at a 20-mgd flow rate. The 24-hour period was chosen to calibrate the THM results to the average detention time in the distribution system from the Water Treatment Plant. In this set of experiments, the chlorine dose was extended from 7 mg/L to a maximum of 100 mg/L while the other independent variables of contact time, TOC and pH, were about the same levels as used in the chlorine dioxide experiments. The model equation depicted in Figure 3 predicted the THMs range from 55 to 252 ppb as compared to the actual THMs from 26 ppb to 274 ppb based on the whole model equation of: Predicted THMs = -180.1 + (0.88 * Cl_2, mg/L) + (4.84 * Time, hours) + (-0.32 * TOC, mg/L) + (27.7 * pH). The R square was also excellent at 0.94 with a mean of response of 128 ppb THMs. In other studies, only about 10% to 15% of TOC contain humic and fulvic acids, which have been identified as the precursors for THM formation. Therefore, the low factor for TOC of –0.32 in this model equation likely shows the insignificance of chlorine compared to chlorine dioxide in terms of oxidation of THMs.

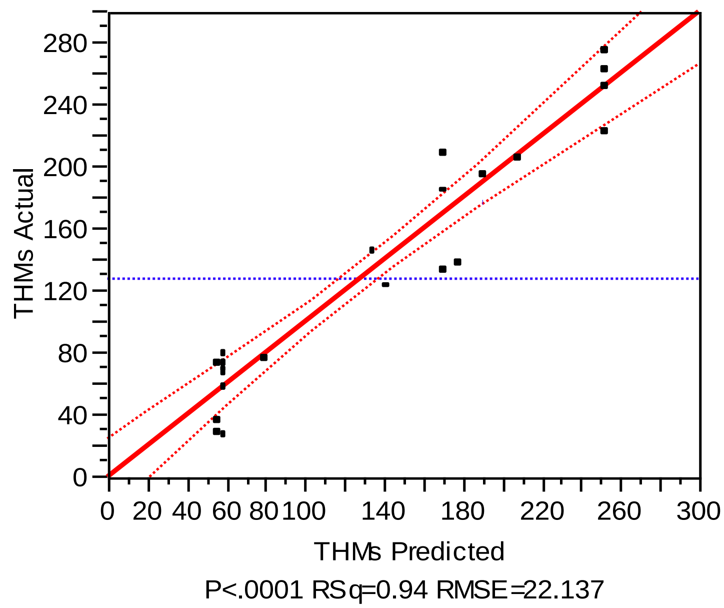

Figure 3 – Chlorine Generated THM Data from Table 3

Table 3 – THMs using Chlorine Only

Item #	Sample ID	Cl_2 Dose, mg/L	Time, hours	TOC, mg/L	pH	Actual THMs, ppb	Predicted THMs, ppb
1	2	7	1	4.5	8.3	73	59
2	3	7	1	4.1	8.3	68	59
3	30	2	1	4.1	8.3	73	55
4	49	2	1	4.3	8.3	35	55
5	1	7	1	4.1	8.3	73	59
6	50	2	1	4.1	8.3	27	55
7	69	7	1	5.9	8.3	26	59
8	70	7	1	4.8	8.3	57	59
9	71	7	1	3.6	8.3	57	59
10	85	7	24	4.2	8.3	133	171
11	86	15	24	3.8	8.3	137	178
12	87	50	24	3.9	8.3	204	208
13	88	100	24	3.8	8.3	222	252
14	91	7	1	5.8	8.3	68	59
15	93	100	24	5.4	8.3	274	252
16	113	100	24	4.9	8.3	262	252
17	133	7	1	4.6	8.3	66	59
18	134	7	24	5.2	8.3	183	170
19	135	100	1	5.1	8.3	122	141
20	136	100	24	4.5	8.3	274	252
21	171	100	24	5.2	8.3	251	252
22	255	7	1	2.8	8.3	79	60
23	281	7	24	3.9	8.3	207	171
24	291	7	24	4.7	9	194	190
25	292	7	24	5.1	7	145	134
26	293	7	24	4.3	5	76	79
27	336	7	1	4.1	8.3	73	59

Comparison of Chlorine Dioxide Model Equations

When comparing the model equations for the chlorite based generator results to the chlorate based, it showed that the Eka chlorate based generator has greater effect on lowering THMs from the chlorine dioxide dose, TOC concentration and contact time. On the other hand, the chlorite based generator results showed greater effect on lowering THMs from chlorine dose, pH and the intercept value. Depending upon the particular raw water quality parameters, the difference in the THMFP calculation for the chlorine dioxide model equations would likely be within the experimental error of THM analysis. The Appendix A shows the calculated predicted THMs for the chlorate and chlorite systems based on their model equations. The parameters used were as follows: 3 to 7 mg/L chlorine dioxide doses, 7 mg/L chlorine dose, 24 hours contact time, 3 to 5 mg/L TOC range, and 6 to 8 pH range. The average THM prediction for the chlorate and chlorite systems was the same at 81 ppb.

Calculation of Chlorine Dioxide effect on THM reduction

Since the average THM formation is 81 ppb for both chlorine dioxide models, then the chlorine effect alone can also be determined by using the same parameter conditions. Appendix B shows the predicted THMs for chlorine doses of 3 to 7 mg/l, 24 hours contact time, 3 to 5 mg/L TOC, and 6 to 8 pH. The average THM level was 133 ppb. By subtracting the chlorine dioxide models average THM level from the chlorine alone THM average divided by the average chlorine dioxide dose of 5 mg/L, one can determine the amount of the chlorine dioxide effect on reducing THMs per mg/L of chlorine dioxide. Therefore, the amount of THMs reduced by each mg/L of chlorine dioxide is equal to 133 – 81/5 = 10.4 ppb. All samples were kept at 23 ºC. In laboratory testing performed 10 years previously on Rio Grande water, the dose response studies showed an average of 10 ppb THM reduction per mg/L of chlorine dioxide over a wider range of chlorine dioxide dosages (1 to 10 mg/L) using optimum Rio Linda generator settings at pH 8.3 with similar TOC levels. The results of this study are consistent with the earlier work.

Plant Studies

There are two 20 MGD surface water treatment plants in El Paso, Texas, which treat Rio Grande River water during the months of March through September. The plants use a physical-chemical treatment process involving screening, silt and mud removal, chlorine dioxide addition to raw water, pre-sedimentation, ferrous chloride addition (chlorite reduction), coagulation/flocculation, secondary sedimentation, granular activated carbon filtration, chlorination and poly/orthophosphate chemical addition for corrosion protection. Since the two plants are similar in design and operation, the conditions for a comparative evaluation of the two chlorine dioxide treatment technologies are ideal.

The plant studies were conducted to verify the laboratory results. Samples were taken from the raw water (Canal), primary effluent (1 hour after chlorine dioxide addition), from the secondary effluent immediately prior to chlorination, and from the product water (filter effluent). The samples were subjected to the same analyses as identified above.

The raw water samples averaged 67 µg/L THMFP at 1-hour contact time with 7 mg/L chlorine addition. After adding 2.5-mg/L chlorine dioxide dose at the raw in each plant from the Rio Linda and Eka Chemicals generators, the THMFP was 44 µg/L and 41 µg/L, respectively at the secondary effluent in each plant. Therefore, the THM potential reduction was 23 µg/L and 26 µg/L, respectively, or 9.2 and 10.4 µg/L per mg/L of chlorine dioxide showing about the same results as the lab study. [1,2,3.]

Conclusions

Based on the laboratory and plant studies, the following conclusions can be made with reasonable certainty:

1. The Eka Chemicals SVP-Pure Chlorine Dioxide Generator and Rio Linda Chlorine Dioxide Generator reduced THMs by 10 ppb per mg/L of chlorine dioxide in the chlorine dioxide dosage range of 3 to 7 mg/L, pH range of 6 to 8, and TOC levels from 3 to 5 mg/L.
2. Chlorine dioxide from the Eka Chemicals SVP-Pure chlorate-based chlorine dioxide generator and the Rio Linda chlorite-based chlorine dioxide generator performed equally. within the experimental error of THM analyses on Rio Grande River water.
3. The laboratory model equations' negative factors for chlorine dioxide dose and TOC show the oxidation potential of chlorine dioxide in reducing THM precursors, the humic and fulvic acids, because coagulation and filtration was not part of the experimental design.
4. The low factor of -0.3 for TOC in the model equation for chlorine alone shows the lack of effectiveness of chlorine without chlorine dioxide to oxidize THM precursors even at high chlorine dosages of 100 mg/L.
5. In the plant studies, the THMFP reduction was 23 µg/L and 26 µg/L, respectively, or 9.2 and 10.4 µg/L per mg/L of chlorine dioxide showing about the same results as the lab study.

References

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1. Rittmann, D., *Can You Have Your Cake and Eat It Too With Chlorine Dioxide*, J. Water Engineering and Management, April 1997.

2. Rittmann, D. & A. Tarquin, *Impact of Mixing Chlorine with Chlorine Dioxide on TTHMs Formation in Drinking Water,* Journal of Water Engineering and Management, August & September 2002.

3. Rittmann, D., Impact of Cl_2 In The Generation of ClO_2 On DBPs In Drinking Water, Doctoral Dissertation, University of Texas at El Paso, El Paso, Texas, July, 1999.

About the Author

Dr. Douglas Rittmann has a PhD in Environmental Science and Engineering from the University of Texas at El Paso and he is a registered professional engineer in Texas. He has more than 35 years experience in water and wastewater utility operations. In 1993, he developed the first plant use of ferrous chloride to reduce excessive chlorite levels at El Paso Texas.

Appendix A

ClO2 Dose	Cl2 Dose	Time	TOC	pH	Pred. Chlorate	Pred. Chlorite
3	7	24	3	6	94	86
3	7	24	4	6	82	80
3	7	24	5	6	71	74
3	7	24	3	7	115	104
3	7	24	4	7	104	99
3	7	24	5	7	93	93
3	7	24	3	8	137	123
3	7	24	4	8	126	117
3	7	24	5	8	114	111
4	7	24	3	6	82	77
4	7	24	4	6	71	71
4	7	24	5	6	60	65
4	7	24	3	7	104	95
4	7	24	4	7	93	90
4	7	24	5	7	81	84
4	7	24	3	8	126	114
4	7	24	4	8	114	108
4	7	24	5	8	103	102
5	7	24	3	6	71	68
5	7	24	4	6	60	62
5	7	24	5	6	48	56
5	7	24	3	7	93	86
5	7	24	4	7	81	80
5	7	24	5	7	70	75
5	7	24	3	8	114	105
5	7	24	4	8	103	99
5	7	24	5	8	92	93
6	7	24	3	6	60	59
6	7	24	4	6	48	53
6	7	24	5	6	37	47
6	7	24	3	7	81	77
6	7	24	4	7	70	71
6	7	24	5	7	59	66
6	7	24	3	8	103	96
6	7	24	4	8	92	90
6	7	24	5	8	80	84
7	7	24	3	6	48	50
7	7	24	4	6	37	44
7	7	24	5	6	25	38
7	7	24	3	7	70	68
7	7	24	4	7	59	62
7	7	24	5	7	47	57
7	7	24	3	8	92	87
7	7	24	4	8	80	81
7	7	24	5	8	69	75
				Average	81	81

Appendix B

Cl2 Dose	Time, hours	TOC, mg/L	pH	Pred THMs
3	24	3	6	104
3	24	4	6	104
3	24	5	6	103
3	24	3	7	132
3	24	4	7	131
3	24	5	7	131
3	24	3	8	159
3	24	4	8	159
3	24	5	8	159
4	24	3	6	105
4	24	4	6	104
4	24	5	6	104
4	24	3	7	132
4	24	4	7	132
4	24	5	7	132
4	24	3	8	160
4	24	4	8	160
4	24	5	8	159
5	24	3	6	106
5	24	4	6	105
5	24	5	6	105
5	24	3	7	133
5	24	4	7	133
5	24	5	7	133
5	24	3	8	161
5	24	4	8	161
5	24	5	8	160
6	24	3	6	107
6	24	4	6	106
6	24	5	6	106
6	24	3	7	134
6	24	4	7	134
6	24	5	7	134
6	24	3	8	162
6	24	4	8	162
6	24	5	8	161
7	24	3	6	107
7	24	4	6	107
7	24	5	6	107
7	24	3	7	135
7	24	4	7	135
7	24	5	7	134
7	24	3	8	163
7	24	4	8	162
7	24	5	8	162
			Average=	133