# TROUBLESHOOTING CHLORINE DIOXIDE GENERATORS: CORRECTIVE ACTIONS FOR AN ESTABLISHED GENERATION FACILITY IN WICHITA FALLS

**By**

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## ABSTRACT

The City of Wichita Falls, Texas (the City) adds chlorine dioxide ($ClO_2$) to the pipelines that convey raw water to two of their water treatment facilities. Beginning in October 2004, maintenance of $ClO_2$ residual throughout the entire length of the raw water pipes became increasingly difficult. This situation caused serious concern because $ClO_2$ is the primary disinfectant used during the winter months of operation.

Four possible reasons for the low $ClO_2$ residuals were investigated, including (1) flawed analytical procedures possibly producing erroneous $ClO_2$ concentrations, (2) raw-water $ClO_2$ demands being higher than those historically observed, (3) poor $ClO_2$ generator performance, and (4) accumulation of organic matter, including biofilm,) in the raw-water lines. Results of this investigation showed that the problem was mostly likely caused by improper $ClO_2$ generator performance, and once that problem was corrected, $ClO_2$ residuals in the raw-water pipelines returned to former levels.

## KEYWORDS

Chlorine dioxide, decay, generator, analysis.

## 1.0 BACKGROUND AND OBJECTIVE

The City of Wichita Falls, Texas (the City) adds chlorine dioxide ($ClO_2$) to the pipelines that convey raw water to two of their water treatment facilities (WTFs), Cypress and Jasper. Beginning in December 2004, maintenance of $ClO_2$ residual throughout the entire length of the raw water pipes became increasingly difficult. For unknown reasons, $ClO_2$ residuals were seldom detected at the most-distant sampling points and were either low or non-detectable at intermediate sites as well as those nearest the $ClO_2$ injection points in both raw water mains serving the Cypress and Jasper WTFs. This situation caused serious concern because $ClO_2$ is the primary disinfectant during the winter months of operation. This paper presents an overview of the troubleshooting approaches taken to identify and correct the problem and discusses lessons learned from the investigation itself.

## 2.0 FACILITY OVERVIEW

The City's Cypress WTF and Jasper WTF obtain their raw water from a 110 million-gallon Secondary Reservoir. The Secondary Reservoir contains a mixture of varying amounts of water from two large lakes, Lake Arrowhead and Lake Kickapoo. Therefore, the raw water quality in the Secondary Reservoir at any given time varies with the water quality in the two lakes and the relative amounts of each that are blended. Neither lake thermally stratifies during the summer because each has an artificial circulation system that continually circulates the water from surface to bottom. **Figure 1** is a condensed diagram of the Wichita Falls water system. As shown in this figure, raw water is conveyed to each WTF by two separate pipelines. The diameter of the Cypress raw-water line is 42 inches and it is approximately 1 mile long; the diameter of the Jasper raw-water line is 48 inches, and it is about 5 miles long.

Chlorine dioxide is added to water from the Secondary Reservoir shortly after it enters the raw water pipelines. Three $ClO_2$ sampling points (D1, D2, and D3) are situated on each raw water pipeline (**Figure 1**). Samples are routinely collected at these points and at the WTFs and analyzed for $ClO_2$. Generator effluents are typically analyzed only weekly for $ClO_2$, chlorite ion ($ClO_2^-$) and chlorine. From these data, generator efficiencies (yields) are calculated as a check on proper generator performance.

The City owns three Rio Linda $ClO_2$ generators, each rated at 250 pounds per day (PPD). Two generators provide $ClO_2$ for each of the WTFs, and the third is a backup. These generators use 25% sodium chlorite ($NaClO_2$) solution and gaseous chlorine as the two reactants used in producing $ClO_2$. Two pounds of $ClO_2$ are produced for each pound of chlorine added. Routine generator maintenance was outsourced by the City to the company that provides the $NaClO_2$ solution.

## 3.0 TROUBLESHOOTING APPROACH

An investigation for the reason $ClO_2$ concentrations could not be consistently and reliably maintained in the raw-water pipelines was begun in November 2005. The team consisted of City of Wichita Falls Water Utilities management, laboratory and field staff with the support of Black & Veatch Corporation staff and Dr. Donald Gates, an independent consultant who is recognized internationally as a specialist in $ClO_2$ chemistry, generator performance, and chemical analysis. The investigation included evaluations of the $ClO_2$ generators, review of the $ClO_2$ analytical procedures in the field and laboratory, and examination of raw-water quality data.

Chlorine dioxide concentrations were determined during the investigation by amperometric titration, which is routinely used by the City because it is an approved method for compliance monitoring of $ClO_2$, and by a variation of the lissamine green B (LGB) method with a commercial hand-held LGB analyzer (Palintest USA Chlordiox Pocket Analyzer). One advantage of the LGB method is that neither chlorine nor chlorite ion interferes and, while the Palintest analyzer is not approved for compliance monitoring, it did prove to be an excellent alternative to amperometric titration for rapidly determining $ClO_2$ residuals at the three raw-water sampling sites and during $ClO_2$-demand studies in the laboratory.

The investigation included an evaluation of four potential explanations for the City's sudden inability to maintain an adequate $ClO_2$ residual in the raw-water pipelines: (1) flawed analytical procedures were possibly producing erroneous $ClO_2$ concentration data, (2) raw-water $ClO_2$ demands were greater than those that had been historically observed, (3) the $ClO_2$ generators were performing poorly, and (4) organic matter accumulations, including biofilm in the raw water lines, were creating an additional $ClO_2$ over and above the demand in the raw water itself. Evaluation of each factor is presented in the following sections.

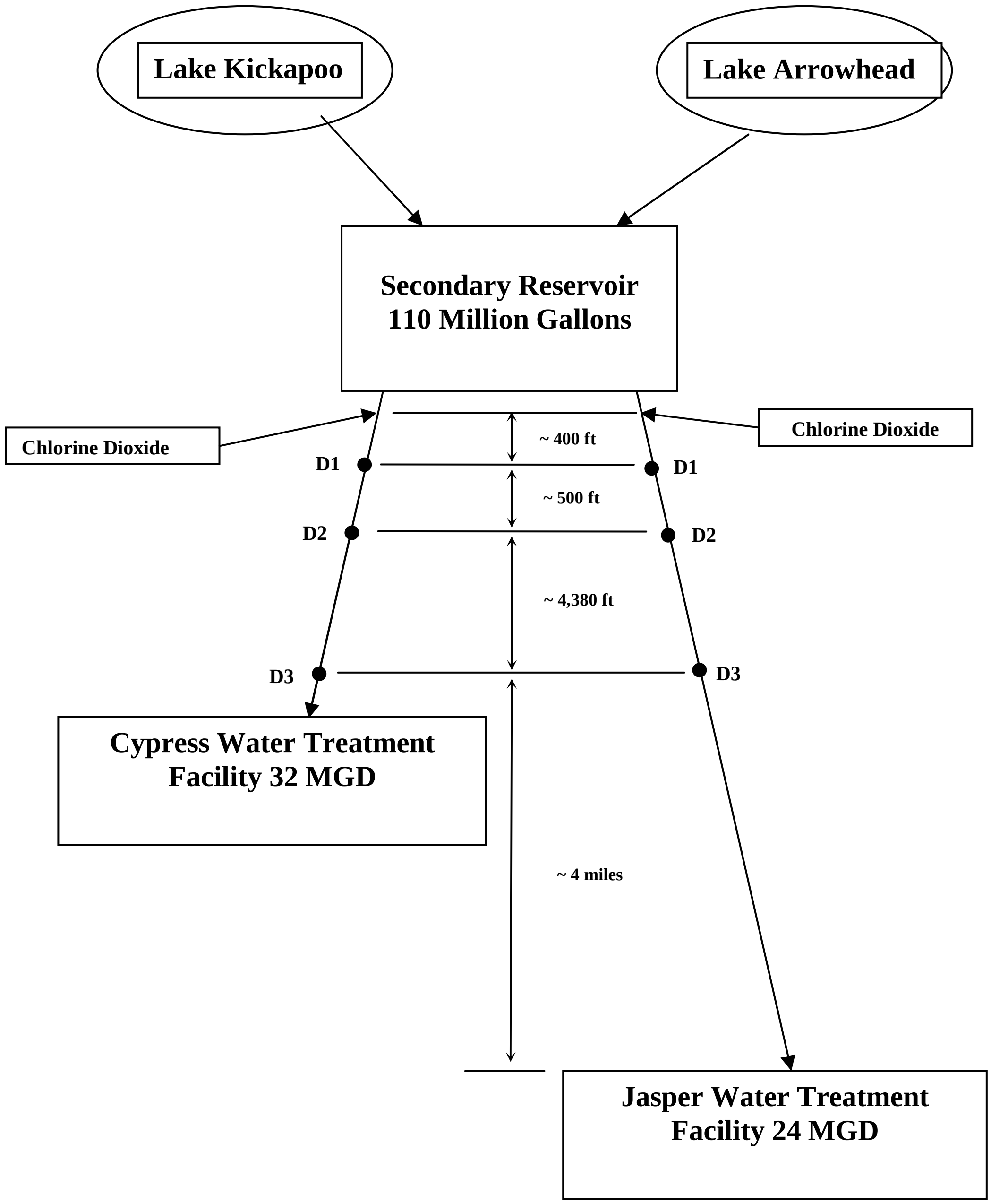


**Figure 1. City of Wichita Falls Drinking Water Treatment Process Flow Diagram.**

## 4.0 EVALUATION OF LABORATORY PROCEDURES

Chlorine dioxide, chlorite ion, and chlorine are routinely analyzed by WTF laboratory personnel and plant operators with KEM auto-titrators, which are computer-controlled. The method used for the $ClO_2$ analyses is Method 4500-$ClO_2$ E Amperometric Method II described in *Standard Methods the Analysis of Water and Wastewater*[1]. The titrant was 0.00564 Normal (N) phenylarsene oxide (PAO). Samples collected at the various sampling points in the raw water lines are analyzed without dilution, but generator effluent analyses typically involve titrating only 2 mL of the effluent added directly to 200 mL water in the titration vessel.

After working with the City's laboratory staff, the conclusion was reached that the analytical results obtained with the automatic titrator were adequate for purposes of this investigation and the methods used by the laboratory staff could be ruled out as the cause of the observed low $ClO_2$ concentrations in the raw-water pipelines. Field $ClO_2$ concentrations determined with the LGB Pocket Analyzer at the various sampling points in the raw-water lines correlated well with those obtained by amperometric titration, thus confirming the previous conclusion.

## 5.0 CHLORINE DIOXIDE DEMAND INVESTIGATION.

The $ClO_2$ demands of water from Lake Kickapoo and Lake Arrowhead were evaluated separately in order to determine their relative contributions to the overall $ClO_2$ demand of the blended water in the Secondary Reservoir. The demand studies involved dosing either a single large volume of raw water with $ClO_2$ and withdrawing aliquots at intervals for analysis or dosing several smaller volumes of water that are "sacrificed" at intervals for analysis. The latter approach eliminates several potential errors associated with mixing during the contact period and withdrawing samples for analysis. Raw water samples were dosed with $ClO_2$ at concentration of 1.0 mg/L.

One of the challenges that had to be overcome in order to determine the raw-water $ClO_2$ demand was the preparation of an adequate $ClO_2$ stock solution that could be used for dosing the raw water. The $ClO_2$ stock solutions used initially for the demand studies were samples of generator effluent that were standardized by analyzing them through spectrophotometric analysis at 360 nanometers (nm) and calculating the $ClO_2$ concentration according to the Beer-Lambert Law[2]. However, the generator effluent contains not only $ClO_2$ but also chlorine and chlorite ion, each

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[1] Standard Method 4500-ClO2 E Amperometric Method II uses the following calculations:

$ClO_2$ (mg/L) = 1.25 x (B-D) x 0.00564 x 13,490 / 200
Chlorite (mg/L) = D x 0.00564 x 16,863 / 200
Chlorine (mg/L) = [A – (B – D) / 4] x 0.00564 x 35,453 / 200,

where Titration A titrates the chlorine and one-fifth of the available chlorine dioxide, Titration B titrates four-fifths of the chlorine dioxide and chlorite, Titration C titrates the non-volatilized chlorine (nitrogen gas purges the sample of the chlorine dioxide), but.is not used in any calculation, and Titration D titrates the chlorite.

[2] The Beer-Lambert law (or Beer's law) is the linear relationship between absorbance and concentration of an absorbing species. When working in concentration units of molarity, the Beer-Lambert law is written as $a = \epsilon b c$, where a = measured absorbance at 360nm, b = the cell path in cm, c = the $ClO_2$ concentration in mol/L, and $\epsilon$ = the $ClO_2$ molar absorptivity at 360nm (1,225 $M^{-1}$ $cm^{-1}$). To find the mg/L concentration of a pure $ClO_2$ solution, the following equation is used:

$ClO_2$ (mg/L) = [a x 67.45 g/L x M x 1,000 mg/g] / [1cm x (1,225 x M)/cm] of which absorbs UV radiation at 360 nm. Thus, the resulting absorbance reading was too high and led to an over-estimation of the $ClO_2$ concentration. After this error was discovered, a laboratory-scale $ClO_2$ generator was constructed according to procedures described in *Standard Methods for the Examination of Water and Wastewater* (except that vacuum was used to purge $ClO_2$), and pure $ClO_2$ (at a concentration of up to 300 mg/L) was generated by reacting sulfuric acid and $NaClO_2$. Later in the study, a more highly concentrated, pure $ClO_2$ solution (~3,000 mg/L $ClO_2$) was prepared by CDG Technology, Inc. with their patented gaseous chlorine/solid sodium chlorite generator and shipped by express mail to the City's laboratory. This solution was used in subsequent $ClO_2$ demand studies. Standardization of this highly concentrated solution required dilution in distilled and deionized (DI) water to reduce the UV absorbance to < 1.5.

The LGB method was used for the first few $ClO_2$ demand studies because concentrations could be determined more quickly by this method than by amperometric titration, especially within the first 5 minutes of the demand studies. **Figure 2** shows the results of replicate $ClO_2$ demand studies with Secondary Reservoir water in comparison to a "field demand curve" constructed from $ClO_2$ concentrations observed by LGB analysis at sites D1, D2, and D3 in the Cypress raw-water line when the $ClO_2$ dose based on a mass balance calculation of the generator stream was less than 1.0 mg/L. For reasons that cannot be explained, the $ClO_2$ residuals determined during the laboratory studies declined much more rapidly than those observed in the raw-water line. One possible explanation is that $ClO_2$ was lost to the atmosphere while the lab-tested samples were being mixed.

**Figure 3** compares the $ClO_2$ demands of water from Lake Kickapoo, Lake Arrowhead, and the Secondary Reservoir on November 9, 2005. Lake Kickapoo water showed a significantly faster $ClO_2$ decay rate during the initial 2 minutes than in Lake Arrowhead and Secondary Reservoir waters despite the fact that the Lake Kickapoo TOC concentration was the lowest of the three. The reason for this difference is unknown, but it may indicate some differences in the nature of the organic matter in the two source lakes.

Several other $ClO_2$ demand studies of Lake Kickapoo and Lake Arrowhead water were conducted during November 2005 and the results were similar to those presented in **Figure 3**. The overall conclusion from these studies is that with few exceptions most of the $ClO_2$ demand occurs during the first five minutes after $ClO_2$ is added, and no consistent relationship exists between the demand and TOC or DOC concentrations. However, the observed decay rates alone cannot the rapid loss of $ClO_2$ observed in the raw-water lines. More studies would be needed before one could determine if different blends of Lake Kickapoo and Lake Arrowhead in the Secondary Reservoir affect the rates of the $ClO_2$ demand, but it seems safe to conclude that this is a minor consideration. The specific ultraviolet absorbances (SUVA) of water in the lakes are both less than 3, though the SUVA of Lake Kickapoo was greater than the SUVA of Lake Arrowhead. This difference may account for the greater $ClO_2$ demand in Lake Arrowhead water.

## 6.0 CHLORINE DIOXIDE GENERATOR PERFORMANCE

Beginning November 8, 2005, the generator PLC readings and $ClO_2$ concentrations determined by the LGB method at the sampling sites in the raw water lines to both WTFs were recorded.

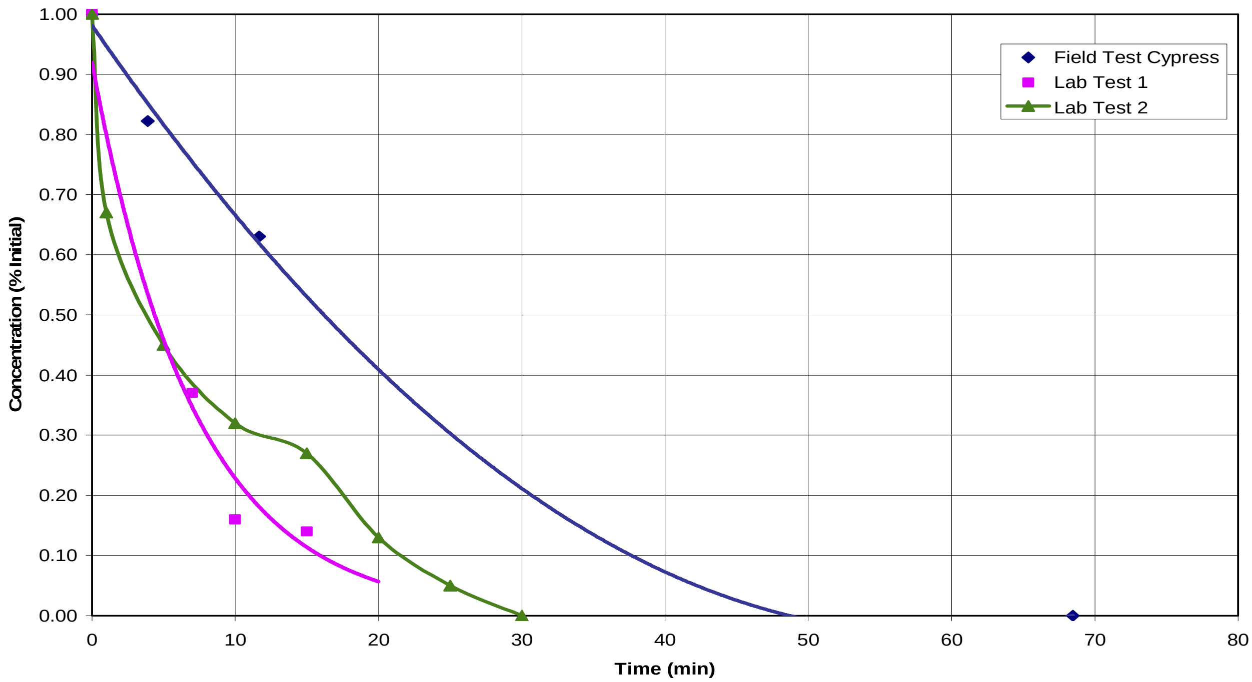


**Figure 2.** **Chlorine dioxide demand curves, November 8, 2005. Field data were collected at sites D1, D2, and D3 in the raw-water line to the Cypress Water Treatment Facility. The $ClO_2$ dose to the raw-water line was 1.0 mg/L.**

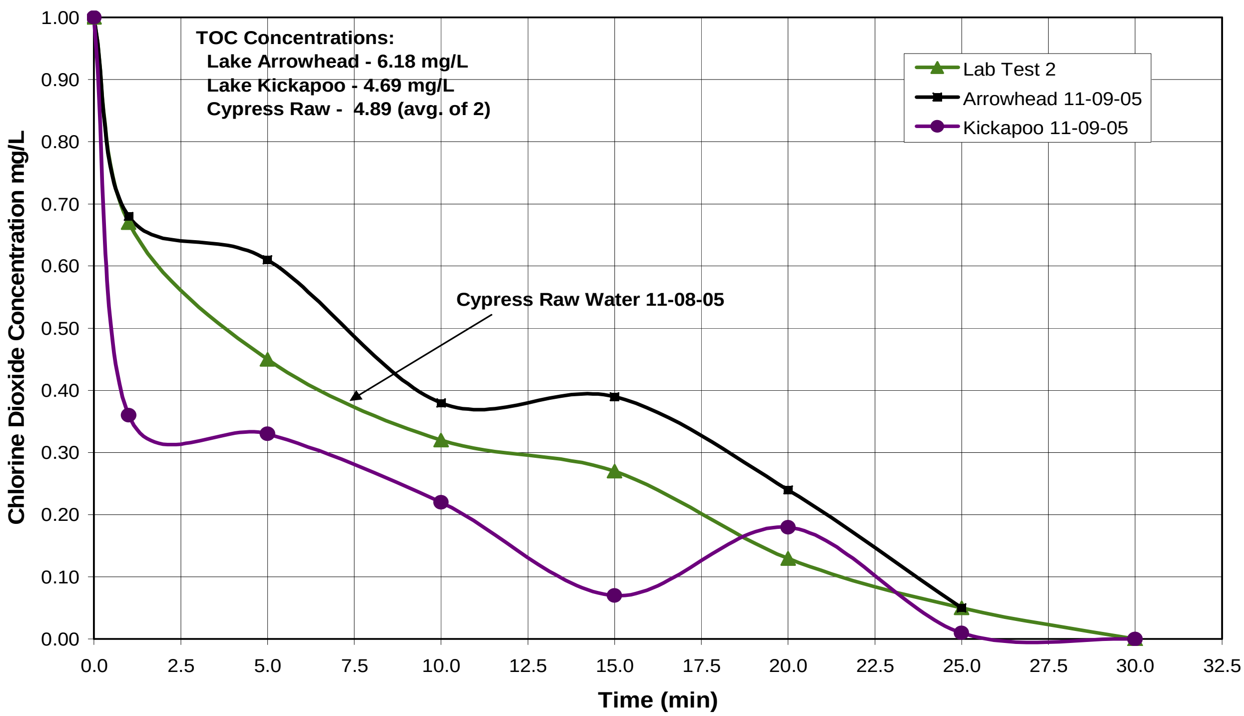


**Figure 3.** **Chlorine dioxide demand curves: Lake Arrowhead and Lake Kickapoo, November 9, 2005 shown in comparison to Cypress WTF raw water from the Secondary Reservoir.**

**Table 1** shows the observed PLC data. At that time, the $ClO_2$ set points on Generators 1 and 3 were 1.0 mg/L and 1.1 mg/L $ClO_2$, respectively. In some instances the PLC readings varied erratically. The $ClO_2$ dosages indicated by the PLC were compared against dosages calculated by performing a mass balance of the generator effluent and the raw water flow. This mass balance used the following equation:

$$C = Cg \times Qg / (Q + Qg), \text{ where}$$

C = Resulting $ClO_2$ raw water concentration, in mg/L or ppm.
Cg = Analyzed ClO2 concentration in generator effluent, in mg/L or ppm.
Q = Raw water flow rate, in gpm
Qg = Generator effluent flow rate, in gpm

**Table 1. PLC data recorded November 7-9, 2005.**

| Date, 2005 | WTF[1] | Gene-rator | PLC Readings, lb/day | | | Generator Flow, gpm | WTF Flow, mgd | Generator Effluent $ClO_2$, mg/L | Raw Water $ClO_2$, mg/L * | Raw Water $ClO_2$, mg/L ** |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $Cl_2$ | $NaClO_2$ | $ClO_2$ | | | | | |
| 11/7 | C | No. 1 | 64.5 | 171.0 | 124.0 | 8.50 | 14.00 | 993 | 0.9 | 1.1 |
| | J | No. 3 | 31.0 | 68.0 | 48.0 | 9.00 | 5.00 | 617 | 1.6 | 1.2 |
| 11/8 | C | No. 1 | 38.5 | 98.4 | 69.9 | 8.50 | 8.00 | 451 | 0.7 | 1.0 |
| | J | No. 3 | | | | 8.75 | 6.00 | 480 | 1.0 | -- |
| 11/9 | J | No. 3 | 181.8 | 5.0 | 57.4 | 8.75 | 5.98 | 447 | 0.9 | 1.2 |

[1] C = Cypress WTF, J = Jasper WTF
* Based on mass balance of generator effluent and raw water flow
** Based on PLC data

The calculated raw water $ClO_2$ concentrations are also shown in **Table 1**. Additionally, generator yields and purities[1] were calculated on the basis of the generator effluent analyses as shown in **Table 2**.

Analysis of data presented in **Tables 1 and 2** and field-verification of the $NaClO_2$ feed rate led to the conclusion that the $ClO_2$ generators were not performing properly due to the following observations:

- The product stream (effluent) contained high concentrations of chlorine. As a consequence, the pH was generally less than pH 2.5-3. Over-feeding chlorine and low pH ensure that most all of the $NaClO_2$ will be converted to $ClO_2$, but in this operational mode, the generators are not operating as they are designed to operate. The original Rio Linda generators were designed to react gaseous chlorine and vaporized $NaClO_2$ in the reaction chamber to produce gaseous $ClO_2$, thus guaranteeing yields in excess of 95 percent. If operated properly, the generators would produce effluent streams that would contain only minimal amounts of chlorite ion and chlorine. In addition to generator yields, effluent purity

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[1] % Yield = Chlorine Dioxide (mg/L) x 100 / [Chlorine Dioxide (mg/L) + Chlorite (mg/L)]

% Purity = Chlorine Dioxide (mg/L) x 100 / [Chlorine Dioxide (mg/L) + Chlorine (mg/L) + Chlorite (mg/L)]*

* True purity would also use the chlorate value in the calculation. Since most laboratories do not perform the fifth titration for chlorate and it is very difficult to perform and get accurate results, it is not included here.

should be considered as a criterion for evaluating generator performance. Purity calculations take into account excess chlorine concentrations, whereas yield calculations do not. As shown in **Table 2**, purities fell at times to 70 percent or less (in events not reported in the table) even when the yields exceeded 95 percent.

**Table 2. Generator Effluent Analyses, Yields, and Purities, November 7 through November 30, 2005**

| Date, 2005 | Generator | WTF | Time Collected | Concentrations, mg/L | | | Yield, % | Purity, % |
|---|---|---|---|---|---|---|---|---|
| | | | | $ClO_2$ | Chlorite | Chlorine | | |
| 11/7 | No. 1 | Cypress | 10:50 a.m. | 1163 | 1.75 | 135.0 | 99.85 | 89.5 |
| 11/7 | No. 1 | Cypress | 1:12 p.m. | 993 | 4.76 | 141.1 | 98.2 | 86.2 |
| 11/7 | No. 3 | Jasper | 1:12 p.m. | 617.0 | 0.48 | 192.1 | 99.9 | 76.2 |
| 11/8 | No. 1 | Cypress | 9:50 a.m. | 452.0 | 23.7 | 22.4 | 95.0 | 90.7 |
| 11/8 | No. 3 | Jasper | 9:50 a.m. | 480.4 | 16.9 | 176.0 | 96.8 | 71.4 |
| 11/9 | No. 3 | Jasper | 8:55 a.m. | 446.8 | 5.0 | 181.8 | 98.9 | 70.5 |
| 11/11 | No. 3 | Jasper | 3:50 p.m. | 304.3 | 4.5 | 110.0 | 97.0 | 72.7 |
| 11/15 | No. 2 | Cypress | 8:48 a.m. | 1793.0 | 4.8 | 57.5 | 98.3 | 95.0 |
| 11/15 | No. 2 | Cypress | 9:48 a.m. | 1560.0 | 0.0 | 254.4 | 99.9 | 84.2 |
| 11/18 | No. 2 | Cypress | 2:15 p.m. | 1047.4 | 16.6 | 118.6 | 98.4 | 88.6 |
| 11/18 | No. 2 | Cypress | 4:30 p.m. | 1318.0 | 10.1 | 55.1 | 99.2 | 95.3 |
| 11/18 | No. 2 | Cypress | 2:55 p.m. | 1047.4 | 16.6 | 118.6 | 98.4 | 88.6 |
| 11/21 | No. 2 | Cypress | 3:42 p.m. | 1468.9 | 30.9 | 54.2 | 97.9 | 94.5 |
| 11/21 | No. 2 | Cypress | 5:00 p.m. | 1459.4 | 14.7 | 2.8 | 99.0 | 98.8 |
| 11/29 | No. 2 | Cypress | 9:30 a.m. | 1433 | 4.28 | 33.6 | 99.7 | 97.4 |
| 11/29 | No. 2 | Cypress | 4:15 p.m. | 1407 | 41 | 0 | 97.2 | 97.2 |
| 11/30 | No. 2 | Cypress | 9:30 a.m. | 1219 | 52 | 17 | 95.9 | 94.6 |
| 11/30 | No. 2 | Cypress | 10:55 a.m. | 1208 | 55.2 | 10 | 95.9 | 95.1 |
| 11/30 | No. 2 | Cypress | 2:15 p.m. | 1260 | 38 | 12 | 97.1 | 96.2 |

- A check of the $NaClO_2$ feed rate with a graduated cylinder revealed that $NaClO_2$ was being substantially underfed. The reason for this problem was found to be that the $NaClO_2$ tank elevation was lower relative to the elevation of the reaction column than was normally recommended by the manufacturer (at least 3 feet above the reaction column) to allow adequate control of the chlorine gas by vacuum. After the $NaClO_2$ day tank was raised on November 18, the feed rate was again checked with a graduated cylinder and found to be in accordance with the rate suggested by Rio Linda in 1992.

Once the problem with the $NaClO_2$ feed rate was corrected, the chlorine feed rate was adjusted to match stoichiometry (i.e., 50 pounds of chlorine per 100 pounds of $ClO_2$ produced). Once these adjustments were made, both the generator yields and purities exceeded 95 percent. In addition, $ClO_2$ concentrations at the sampling points increased significantly, although they were still somewhat below levels observed prior to October 2004.

Analysis of the data presented in **Table 2** shows that it is very important to calculate purity in addition to yield. As seen in this table, it is possible to have a yield of 95% or greater and have a purity that is 70% or less. This would indicate that the generation process is inefficient and excess chlorine, chlorite, or both are being produced. When the generator effluent yield and purity are above 95% and 90%, respectively, effluent $ClO_2$ levels are relatively high and chlorite levels are relatively low.

In addition to the above issues, observation of generator performance showed erratic and unstable PLC readings with alarms frequently going off. A detailed inspection of generator instrumentation and controls identified a number of issues including, among others, calibration problems with the chlorine flow-control valves, a return stream that was being added to the raw water was unaccounted for in the WTF raw water flow signal sent to the generator PLC, and erroneous controller update and reset times.

Once these problems were corrected, the generators feed settings closely matched the amounts dictated by stoichiometry and generator effluent analyses showed high yields and purities. Shortly thereafter, the $ClO_2$ concentrations in the raw water returned to expected levels.

## 7.0 CHLORINE DIOXIDE DEMAND IN THE RAW WATER LINES

Chlorine dioxide concentrations in the raw water lines determined by LGB at sampling sites D1, D2, and D3 are shown in **Table 3** in comparison to $ClO_2$ concentrations at similar contact times during laboratory demand studies. It was hypothesized that if field demands in the pipelines were significantly lower than demands indicated by laboratory studies, perhaps accumulations of organic matter in the pipelines were responsible. Limited laboratory demand studies and PLC data did not always support that hypothesis however, and, in fact, the “field demands” indicated in **Table 3** were sometimes lower, not higher, than would have been predicted from the laboratory studies. Nevertheless, steps were taken to address this fourth potential reason for the observed $ClO_2$ losses that had been a problem for over a year, namely that either biofilms on the pipe walls or other organic deposits within the pipelines were creating additional $ClO_2$ demands. To address this possibility, a decision was made to “burn” the pipelines with a high concentration of $ClO_2$ and thereby reduce or eliminate the additional demands.

On November 28, the $ClO_2$ fed to the Cypress raw-water line was turned off and chlorite ion was monitored at the WTF until it could no longer be detected. Then, enough $ClO_2$ was added to the raw-water line to create a residual that would last several hours. Afterwards, concentrations at D3 were statistically higher than before the burn, averaging 0.149 mg/L. The conclusion was that the $ClO_2$ demand in the pipe lines was reduced by the “burn” treatment, but the improvement t was not large enough to fully explain the low $ClO_2$ residuals that had been observed since October 2004.

## 8.0 CONCLUSIONS AND RECOMMENDATIONS

The results of the investigation showed that improper ClO2 generator performance was the most likely reason for the low ClO2 concentrations observed in the raw water lines beginning in

October, 2004. A variety of factors were involved, including improper functioning of the PLCs, incorrect calibration of the chorine control valves, overfeeding of chlorine, and inadequate elevation of the sodium chlorite day tank with respect to the reaction column. After the problems were corrected, the generators began to perform properly, and $ClO_2$ residuals once again were detected at all the raw-water sampling points, thus allowing the City to better meet their Ct requirements for the winter months. While most problems with the generators were resolved, the existing units have surpassed the normal generator life of 10 to 15 years. Therefore, a recommendation was made to consider replacement of the existing generators with new units when feasible. Generator operational checks recommended for ensuring adequate performance follow:

**Table 3 – Raw Water Field versus Lab Demand Test Results**

| Point | Pipe L [a], ft | Plant Flow, mgd | Travel Time [a], minutes | LGB $ClO_2$ Field, mg/L | LGB $ClO_2$ Lab, mg/L |
|---|---|---|---|---|---|
| **Cypress 11/08/05** | | | | | |
| D1 | 400 | 8 | 5.2 | 0.82 [b] | 0.49 [b] |
| D2 | 900 | 8 | 11.7 | 0.63 [b] | 0.39 [b] |
| D3 | 5280 | 8 | 68.4 | 0 [b] | 0 [b] |
| **Cypress 11/09/05** | | | | | |
| D1 | 400 | 11.9 | 3.5 | 0.37 | Not determined |
| D2 | 900 | 11.9 | 7.9 | Not determined | Not determined |
| D3 | 5280 | 11.9 | 46.0 | Not determined | Not determined |
| **Jasper 11/09/05** | | | | | |
| D1 | 400 | 5.98 | 9.1 | 0.08 | 0.26 after 10 min |
| D2 | 900 | 5.98 | 20.4 | 0.04 | 0.10 after 10 min |
| D3 | 5280 | 5.98 | 119.5 | 0 | 0 after 25 min. |

[a] From point of injection to indicated sample point
[b] As shown on **Figure 2**

1. It is very important to calculate purity of the generator effluent in addition to yield. As seen in this study, when the generation process is inefficient and excess chlorine, chlorite, or both are being produced, it is possible to have relatively high yields (e.g., 95% or greater) but relatively low purities (e.g. 70% or less) at the same time. In order to ensure that generator effluent $ClO_2$ levels are high and chlorine and chlorite levels are low, the generator effluent yield and purity need to be above 95% and 90%, respectively. Furthermore, since excess chlorine and chlorite in the generator effluent can produce chlorate, efficient generator effluent yields and purities are necessary to ensure that chlorate levels will stay relatively low.

2. As a generator performance check, the theoretical raw water $ClO_2$ concentration calculated through a mass balance of the generator effluent and the raw water streams should be compared to the raw water $ClO_2$ concentration reported by the generator PLC. If the two values are not similar, then the generator may not be functioning properly.

Organic matter accumulation in the Cypress raw-water line may have contributed to the lower-than-normal $ClO_2$ residuals in the pipeline beginning in October 2004, but it was most likely a minor contributor to the overall problem. "Burning" the line by dosing with a high concentration of $ClO_2$ appeared to increase $ClO_2$ concentrations at D3, but the increase was not nearly as great as that brought about by improvements in generator performance.

The $ClO_2$ demands of water from Lake Kickapoo and Lake Arrowhead that were determined in laboratory studies did not differ greatly despite the fact that Lake Kickapoo TOC and SUVA were somewhat greater than the TOC and SUVA of Lake Arrowhead water. Typically, more than 60 percent of the $ClO_2$ added to samples from each lake was consumed within first five minutes after dosing. Once this high initial demand was met, the $ClO_2$ concentration declined slowly over the next 20-30 minutes. The conclusion from these studies was that, despite some differences, the water quality in the two lakes can be ruled out as a major reason for the observed losses of $ClO_2$ in the raw-water pipe lines beginning in late 2004.

Finally, the low $ClO_2$ residuals in the raw-water line did not appear to be the result of improper laboratory analysis techniques. However, purchase of a manual Fischer-Porter titrator was recommended so that results of $ClO_2$ analyses obtained with it to could be compared to those obtained with the current automatic titrators. Lessons regarding analytical procedures that were learned from this investigation are applicable anywhere $ClO_2$ is used. They include the following:

1. Before using glassware for $ClO_2$ analyses, it should be soaked in a 50% solution of nitric acid for 24 hours and then rinsed with deionized water.

2. Generator effluents to be used for laboratory $ClO_2$ demand studies should not be standardized by the spectrophotometric procedure described in this paper unless they contain high $ClO_2$ concentrations (>500-600 mg/L) and low chlorine and chlorite ion concentrations;

3. If dilution is required before generator effluents can be analyzed spectrophometrically, the $ClO_2$ demand of the dilution water should be evaluated. If it is high, the $ClO_2$ concentration determined by the spectrophotometric analysis will be reduced;

4. The end-point of the amperometric titration procedure should be the midpoint of the inflection curve when the potential drop is first detected, not when movement of the ammeter needle ceases;

5. Results obtained with automatic titrators should be compared with results obtained with results obtained with manual titrators if at all possible.

6. If $ClO_2$ is being analyzed by amperometric titration for Ct requirements, collect 2 samples for analyses. Use 250mL glass amber bottles and clearly mark one bottle for titrations A and B, and one bottle for titrations C and D. Add 2g of granular potassium iodide (KI) to the bottle for titrations A and B. This in essence will "preserve" the $ClO_2$ in the sample. This is especially important if the sample-collection location is relatively far from the laboratory because the $ClO_2$ demand continues to be exerted while the sample is in transit.

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