Technical Memorandum

To: Ron Ponte (Tata & Howard Engineers)

From: Dean Gregory (CDG Environmental LLC)

CC: Dave Morris (CDG)

Date: December 29, 2009

Re: CDG Chlorine Dioxide Pilot Project at the Town of Canton

1.0 Background

In order to obtain New Technology Approval from the MA DEP, CDG Environmental LLC conducted a 5-day pilot study at a groundwater pumping station in the Town of Canton. A full-scale CDG Gas:Solid™ chlorine dioxide generator was installed at the pump station and the system was operated from November 19 – 23, 2009. **The primary objective of the piloting was to demonstrate that the CDG system delivers accurate chlorine dioxide dosing over a wide range of settings.** Because the chlorine dioxide (ClO_2) demand in the Canton raw water was very high (i.e. there was no residual to measure), the only means of gauging the accuracy of the dosing was by measuring chlorite ion residuals for different applied doses. Chlorite ion (ClO_2^-) is a direct byproduct of the reaction between chlorine dioxide and reducing compounds and its concentration should be proportional to the applied dose. Additionally, given the USEPA MCL of 1.0 mg/L, characterizing the chlorite ion residuals resulting from a range of typical water treatment doses was another objective of this project.

2.0 Experimental Methods

Chlorine dioxide generator. The CDG Gas:Solid generator that was operated at the Canton facility is shown in Figure 1. The system shown is capable of producing 8 ppd of chlorine dioxide (GS-8). The MA DEP visited the site on Nov. 2, 2009 and observed the system in normal operation. A detailed explanation of the system's operational features was provided at that time by a CDG representative.

ClO_2 dosing and ClO_2^- sampling. The experimental matrix completed for this project is provided in Table 1. The target doses were 0.5, 1.0, and 1.5 mg/L. The chlorite results indicate that actual doses were slightly higher. The small discrepancy between the target and actual doses was due to the fact that the chlorine gas was fed through a manually-controlled

rototmeter that offered limited resolution, i.e. there was a significant difference between using the top or the middle of the floating ball to set the chlorine flow. In this project the middle of the ball was consistently used but it appears that using the top of the float would have been more accurate.

Figure 1 CDG Gas:Solid chlorine dioxide generator at the Canton pump station. The Saf-T-Chlor drum (white) is shown in lower right.

Table 1 Experimental matrix for Canton chlorine dioxide pilot.

Operating Day	Run Time	Flow Rate	Target ClO_2 Dose[1]	Scale Reading
	hours	gpm	mg/L	lbs
1	8	340	1.5	279
2	10	340	1.5/1.0	278
3	10	340	1.0	278
4	10	340	0.5	277
5	4	340	0.5	276

[1] Actual applied doses were slightly higher.

The system was operated at each dose for approximately 1.5 working days. The system was shut down at the end of each day and started up again the following morning. Chlorine dioxide gas was fed under vacuum into an injector that was supplied by a side-stream (approximately 10 gpm) diverted from the main water line (Figure 2). The total raw water flow was 340 gpm. Chlorite samples were collected at the end of each day and just before a dose change was made, thereby providing two samples per dose, collected on different days. The samples were analyzed using ion chromatography (EPA method 300.0) at a certified laboratory selected by Canton personnel.

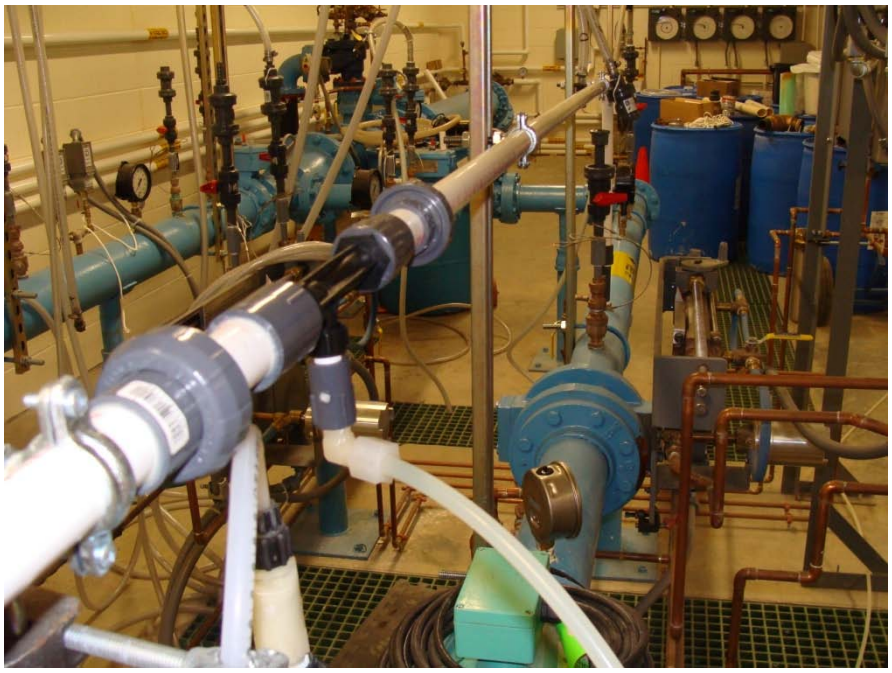

Figure 2. Chlorine dioxide gas feed line and injector system. The water supply for the injector was a sidestream diverted from the main transmission line.

Water quality. Although historical water quality data were not available for the well used in this pilot project (other than very basic parameters such as pH and temperature), it was known that the source contained a relatively high level of dissolved Mn^{2+} and, to a lesser extent, dissolved iron (Fe^{2+}). Indeed, observations from the project indicated that the stoichiometric requirement for complete Mn oxidation exceeded even the highest applied ClO_2 dose of 1.5 mg/L Given that the required stoichiometry of the reaction is 2.45 mg ClO_2/mg Mn^{2+}, it appears that the Mn^{2+} concentration was at least 0.6 – 0.7 mg/L. The impact of the 1.5 mg/L dose on the appearance of the Canton raw water is shown in Figure 3. The color change is due to dissolved manganese, Mn^{2+}, being oxidized to $MnO_{2\,(s)}$, which is a gold-brown precipitate.

3.0 Results

Chlorite ion formation. The results of the 6 chlorite samples are provided in Table 2. Overall, the chlorite ion residuals correlated well with the applied chlorine dioxide doses and were consistent from one day to the next, i.e. after the system had been shut down and re-started. As discussed above in Experimental Methods, the applied doses were slightly higher than the target doses.

The one exception in the data is the chlorite value of 0.65 mg/L for sample #3 (dose = 1.0 mg/L). The other result at that applied dose was 1.10 mg/L. Whether it was due to a sample collection error or a possible oversight at the analytical laboratory is not known, but the 0.65 mg/L result for sample #3 is inconsistent with the other data and appears to be inaccurate. In

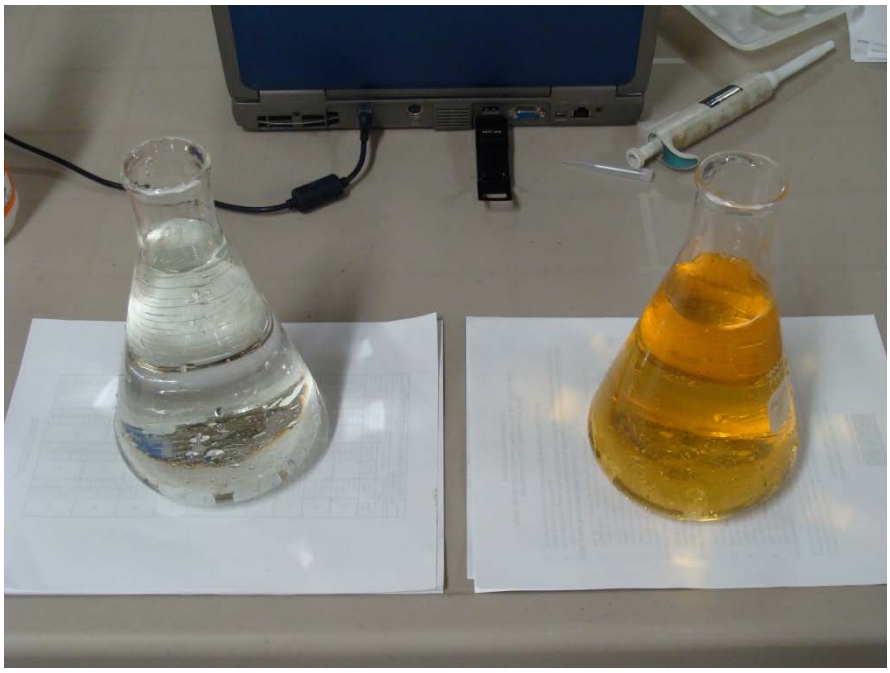

Figure 3. Impact of oxidation by chlorine dioxide on dissolved Mn in Canton raw water. Applied chlorine dioxide dose = 1.5 mg/L, pH = 7.4. Raw water Mn concentration not known.

fact, that value correlates well with samples 5 and 6 (dose = 0.5 mg/L), which may indicate that the laboratory analyzed one of those samples twice.

Table 2 Chlorite results.

Sample ID	Collection Date	Target ClO_2 Dose[1]	Chlorite Resdiual
		mg/L	mg/L
1	11-19	1.5	1.60
2	11-20	1.5	1.50
3	11-20	1.0	0.65[2]
4	11-21	1.0	1.10
5	11-22	0.5	0.71
6	11-23	0.5	0.61

[1] Actual applied doses were slightly higher.

[2] This value is abnormally low and appears to be inaccurate.

The correlation of the chlorite ion residuals with the applied chlorine dioxide dose is shown in Figure 4 (the anomalous result from sample 3 was not used for this plot). One noteworthy aspect of Figure 4 is that the chlorite ion residuals appear to be approximately 100 percent of the applied chlorine dioxide dose. These results were due to the high Mn^{2+} concentration in

the raw water. The ClO_2 molecule is only transformed to ClO_2^- upon reaction with Mn^{2+}. In other reactions, such as those with natural organic matter, some chlorite is further reduced to chloride ion (Cl^-). However, given that the vast majority of the ClO_2 demand in this water was due to Mn^{2+} and samples were collected immediately downstream of the ClO_2 injection point, before the chlorite had a chance to react further or be removed by conventional water treatment processes, it was anticipated that the chlorite ion residuals would be relatively high. Typically, in full-scale water treatment facilities the chlorite ion concentration in finished water is 50 – 60 percent of the applied chlorine dioxide dose.

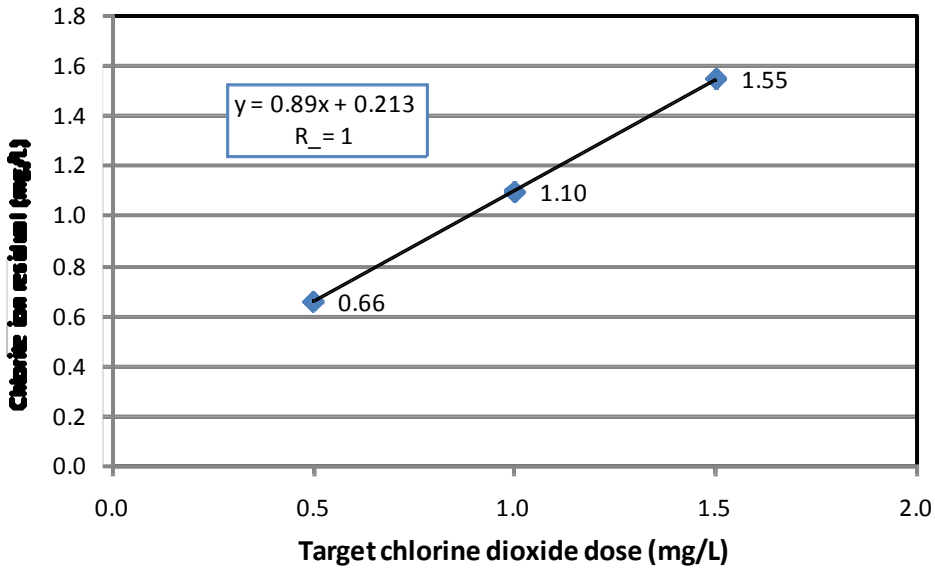

Figure 4. Target chlorine dioxide doses vs. chlorite ion residual at Canton pilot plant. Sample 3 data was not used in this plot. Actual doses were slightly higher than targeted doses. For the 0.5 and 1.5 mg/L doses, values shown are the average from two samples.