Dialing Down Disinfection Byproducts With Chlorine Dioxide Pre-Oxidation

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Initial Considerations

Today, the most commonly used disinfectants for potable water are chlorine and chloramine. The use of chlorine is increasingly subject to criticism due to its numerous reactions with organics and the respective regulations. Chlorine represents both safety- and health-related risks and effects and reacts quickly with organic matter to form disinfection byproducts (DBPs). Such effects can be mitigated by applying a disinfectant with different characteristics.

As a potential alternative, chlorine dioxide (ClO_2) is a strong and selective oxidizer and offers several advantages in treatment and distribution of drinking water. The ClO_2 forms fewer halogenated DBPs and can be used at lower concentrations with shorter contact times to achieve equivalent disinfection than the concentrations and contact time required for chlorine and chloramine disinfection. It's also less reactive to changes in pH than chlorine and has been proven more effective over a broader range of pH than free chlorine [1].

Since the 1970s, ClO_2 has been implemented in distribution systems after the discovery of total trihalomethanes (TTHMs) and other DBPs that are still being discovered to date. It has been utilized in Europe and in the United States as both the primary disinfectant and pre-oxidant, with around 1,200 plants currently implementing its disinfection [1]. The selective reactivity enables ClO_2 to control waterborne pathogens without reacting with organic DPB precursors. Unlike chlorine, ClO_2 reactions in water do not result in the formation of TTHMs and haloacetic acids (HAA5) because "when ClO_2 oxidizes organic material it's reduced to chlorite, but does not chlorinate the resulting organics" [2]. It can be applied for a variety of water quality issues, including DBP formation control, taste and odor issues, or nitrification in the distribution system, especially in distribution systems where water age with long dead-end mains are a concern [2].

The use of ClO_2 can be tailored to a specific facility's need, and can be used for the primary disinfectant or as a preliminary oxidant, followed by chlorine or chloramines. It has been shown to have five times stronger oxidation potential and disinfection efficacy than chlorine [3]. Realizing the impact of ClO_2 on the regulatory challenges faced today, its applicability becomes very broad with potable water treatment and other means of disinfection.

Recent studies have identified results indicating that ClO_2 has significant potential to provide preliminary oxidation of organics prior to sodium hypochlorite disinfection, which has shown to reduce DBPs formed in the potable water distribution system. The ClO_2 disinfection is an acceptable method of treatment within U.S. Environmental Protection Agency (EPA) regulations, as well as the Florida Administrative Code (F.A.C.), pursuant to the following: "All suppliers of water shall maintain a minimum free chlorine residual of 0.2 milligrams per liter, or a minimum combined chlorine residual of 0.6 milligrams per liter, or an equivalent ClO_2 residual throughout their drinking water distribution system at all times."

Regulatory guidelines identify ClO_2 as an acceptable method of inactivating viruses and bacteria to achieve 4-log virus inactivation and residual disinfection. The EPA regulates ClO_2 as a primary disinfectant with a maximum residual disinfectant level (MRDL) of 0.8 mg/L. When dosed, ClO_2 dissociates in water to form chlorite, which has a maximum contaminant level (MCL) of 1 mg/L. Controlling chlorite levels to comply with the MCL is one of the keys to successfully implementing ClO_2.

Chlorine Dioxide Generation Overview

There are multiple ways to produce ClO_2. Traditionally, it's generated from the reaction of chlorine gas with sodium chlorite. Chlorine gas is not common to most municipalities due to the extensive safety risks associated with operation and storage. Accordingly, chlorine gas-based ClO_2 generation is not applicable due to the aversion to the chlorine gas operational and safety concerns. Recently, alternative methods of generation have hit the market for ClO_2 through the reaction of sodium chlorite with sodium hypochlorite and an acid, such as hydrochloric or sulfuric acid. The primary methods of ClO_2 production are through a vacuum eduction generator, or through combining powder components to generate batch solutions, which contain stabilizers to minimize off-gassing of ClO_2 while stored. Regardless of the production method, ClO_2 should be produced within a 0.1-0.5 percent solution, to reduce risk of an exothermic reaction. The ClO_2 used in the pilot study was produced from vacuum eduction of three liquid components (sodium hypochlorite, hydrochloric acid, and sodium chlorite) through an onsite generator in a side-stream of water forming a 0.2-0.3 percent ClO_2 solution. The equipment provided by this pilot testing application was supplied by Evoqua.

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Pilot Study

Pilot Overview

Utilities Inc. of Florida (UIF) currently owns and operates the Lake Groves Water Treatment Plant (Lake Groves WTP) in the LUSI South service area in South Lake County. With the onset of the Stage 2 Disinfectant/Disinfectant Byproducts (D/DBP) Rule, UIF has made efforts to maintain compliance with DBPs through well blending, which places better-quality wells in service with high-organic wells to offset or minimize the DBP impact when the poorer quality wells are in service. This strategy lowered the TTHM levels, but the system has still periodically exceeded the regulatory limit of 80 parts per bil (ppb). The UIF currently utilizes sodium hypochlorite as the sole disinfectant for its storage and distribution system; as a result, the sodium hypochlorite reacts with the naturally occurring organics that produce TTHMs and HAA5. As such, UIF has sought alternative methods of treatment, as well as disinfectants to achieve compliance with the Stage 2 D/DBP Rule.

Utilizing the results from the laboratory testing to establish dosing parameters, UIF proceeded with 10 weeks of pilot testing at Lake Groves WTP utilizing ClO_2 as a pre-oxidant within the water treatment process to achieve reduction of TTHMs formed in the distribution system. The results of this piloting effort confirm the overall reduction of TTHMs, as well as the system's ability to maintain chlorite levels below the MCLs. During the full-scale pilot testing, laboratory data were collected for development of this report and subsequent verification for permit approval of the full-scale pilot testing implementation.

The next step in the process was to demonstrate the laboratory effects on the full-scale utility system. A pilot testing approval package was completed and submitted to the Florida Department of Environmental Protection (FDEP). While the chemical has been used in the utility industry, a small number of utilities throughout the U.S. have used ClO_2 for color, odor, and taste removal, with only a handful of utilities using it as a primary disinfectant. Accordingly, several questions and comments were discussed with FDEP prior to garnering the approval to proceed with the pilot. Following approval from FDEP, the full-scale pilot test was implemented at Lake Groves WTP.

The overarching goals of the full-scale pilot study included a dosing of ClO_2 and a gradual increase in concentration to determine the general range of effectiveness and vigorous field and laboratory testing of the treatment process, both during the pre-oxidant dosage and after, to ensure public safety, as well as compliance with the regulations. The utility and onsite staff completed routine efforts to operate, adjust dosages, and use the field work to obtain all the required samples. The staff's thorough analysis and consideration of the results proved very helpful in concluding the effect of each process adjustment.

Upon approval from FDEP, the pilot was initiated at the Lake Groves facility for 10 weeks of testing and monitoring. The duration was selected to determine the optimum dosing rate to reliably maintain TTHMs and HAA5 below regulatory limits. The ClO_2 was used in conjunction with sodium hypochlorite, which served as the primary and residual disinfectant within the utility distribution system. The sampling period allowed for a biweekly adjustment in dosing rate to determine the optimal dosage of ClO_2 for each location. At the end of the pilot testing, the data were analyzed to confirm that the anticipated TTHM and HAA5 reduction in the distribution system was recognized, including the impacts of a varied dosage.

Pilot Setup and Equipment

The full-scale pilot injected ClO_2 into the clearwell immediately following the forced draft aerators, and a parallel sodium hypochlorite injection was dosed within the same clearwell. The water was then pumped to the ground storage tanks (GST) where approximately 20 hours of storage resides under normal operational conditions. From the GST, finished water is pumped into the distribution system via the high-service pumps. Prior to the point of entry (POE), the water is continuously sampled for ClO_2 residual and chlorite. The pilot program included the physical components to generate and inject ClO_2 oxidant into the process stream. The physical equipment required to complete this pilot test includes the components as follows for the Lake Groves WTP site:

- *ClO_2 Generation System* – A ClO_2 generation system rated for a maximum of 50 lb of ClO_2 produced/hour was utilized for ClO_2 production and injection. The generator system educts three chemical components into a potable water stream for safe and continuous ClO_2 production. The generator was equipped with a control panel to adjust and monitor the dosage rate and was located in an enclosed area. The ClO_2 is formed within the generator and was injected as a dilute solution. The ClO_2 generation system was mounted on a stainless steel skid and consists of the following major components:
  - Water booster pump with downstream pressure regulating valve and water rotameter to control the input water flow.
  - Three chemical feeds for sodium hypochlorite, sodium chlorite, and hydrochloric acid, each with rotameter for flow control. Chemical feed tubes were directly attached to chemical storage totes for vacuum suction.
  - Liquid jet venturi pump inductor (*in situ*).
  - Control panel to adjust and monitor dosage rate.
- *ClO_2 Chemical Precursors* – 25 percent sodium chlorite, 12.5 percent sodium hypochlorite, and 15 percent hydrochloric acid were the three chemical precursors, which were vacuum-fed to the generation system to safely control the reaction and prevent unwanted byproduct formation. Sodium hypochlorite was already stored and used onsite. The sodium chlorite and hydrochloric acid were delivered in 265-gal chemical totes, which were attached to the generator feed by tubing inserted into the chemical tote.
- *Sampling Stations* – Several sampling taps located within the process stream were identified to pull grab samples of the treated water.
- *Grab Sample Analyzer* – One handheld analyzer for routine monitoring of ClO_2 residual and chlorite (Palin-Test Analyzer was utilized for daily samples, as well as to confirm the online analyzer readings).
- *Online Chlorite Sample Analyzer* – One analyzer for continuous monitoring of chlorite levels at the POE to the distribution system.

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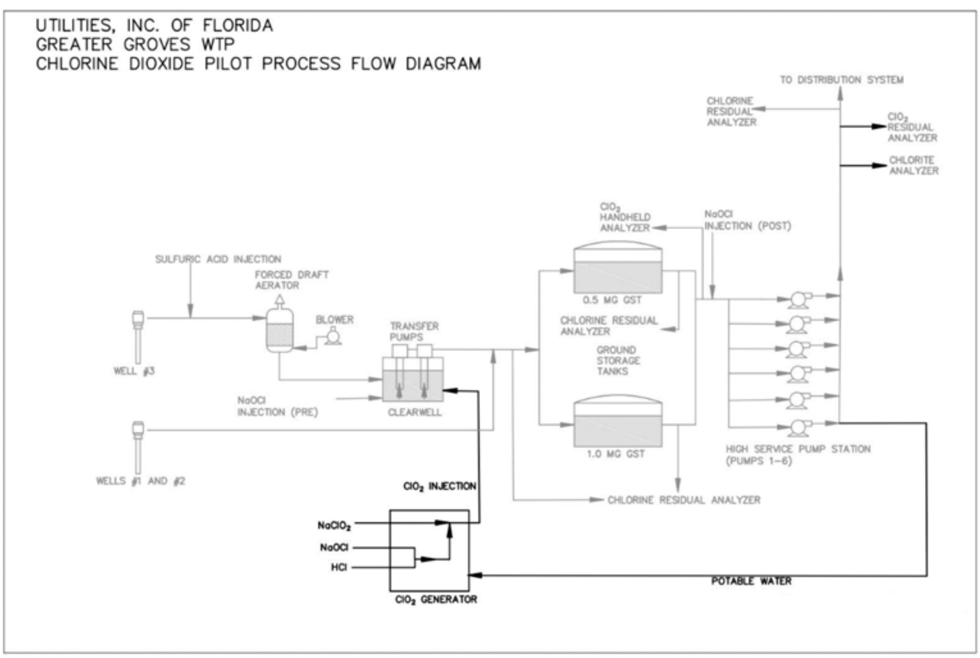

Figure 1. Chlorine Dioxide Pilot Test Schematic

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- *Online ClO_2 Residual Sample Analyzer* – One analyzer for continuous monitoring of ClO_2 residual at POE.
- *Online ClO_2 Monitoring and Control System* – One control panel capable of receiving the analog signals from the online analyzers, pump controls, and operator interface with the control system

The dosage of ClO_2 was initiated at 0.8 parts per mil (ppm) dosing rate for the distribution system to achieve the desired TTHM and HAA5 reduction; it was then decreased to 0.6 ppm for two weeks and tested for the final four weeks at 1.0 ppm. Downstream of the injection point, both before and after storage, the ClO_2 residual was monitored using a handheld ClO_2 analyzer. Further monitoring in the distribution system included the POE, the average water age within the distribution system, and the extents of the distribution system. The ClO_2 generation system started and stopped in conjunction with Well #3, which has a 3,000-gal-per-minute (gpm) capacity and is the primary source of TTHM formation in the water from the Lake Groves WTP. Since the well pumping rate is fixed, the chemical dosing was paced on the constant flow rate and initiated directly with the well run times.

The ClO_2 levels were monitored a minimum of once per day within the eight hours of staffed operation of the treatment plant. The handheld probe identified the ClO_2 levels that were used to confirm/regulate the feed rate of the ClO_2. The online ClO_2 residual analyzer, which sampled from the POE and was tied into the Lake Groves supervisory control and data acquisition (SCADA) system, had a predetermined maximum alarm set point of 0.6 ppm of ClO_2 residual to ensure that the MRDL of 0.8 ppm was not exceeded. If the residual ppm level reached 0.6 ppm of ClO_2 residual, its generation system was programmed to turn off until manually reset by the operations staff. Due to the low initial dosage rate ClO_2 residual at POE, it did not reach the 0.6 ppm maximum level. Figure 1 displays the pilot study process flow diagram for the Lake Groves WTP highlighting the chemical dosing and sample points within the treatment process.

While the pilot operations were ongoing, it was imperative to monitor the performance, as well as any concerning parameters within the treatment plant and throughout the distribution system. A monitoring and sampling plan was implemented throughout to study to ensure that the performance could be quantified and public health protected.

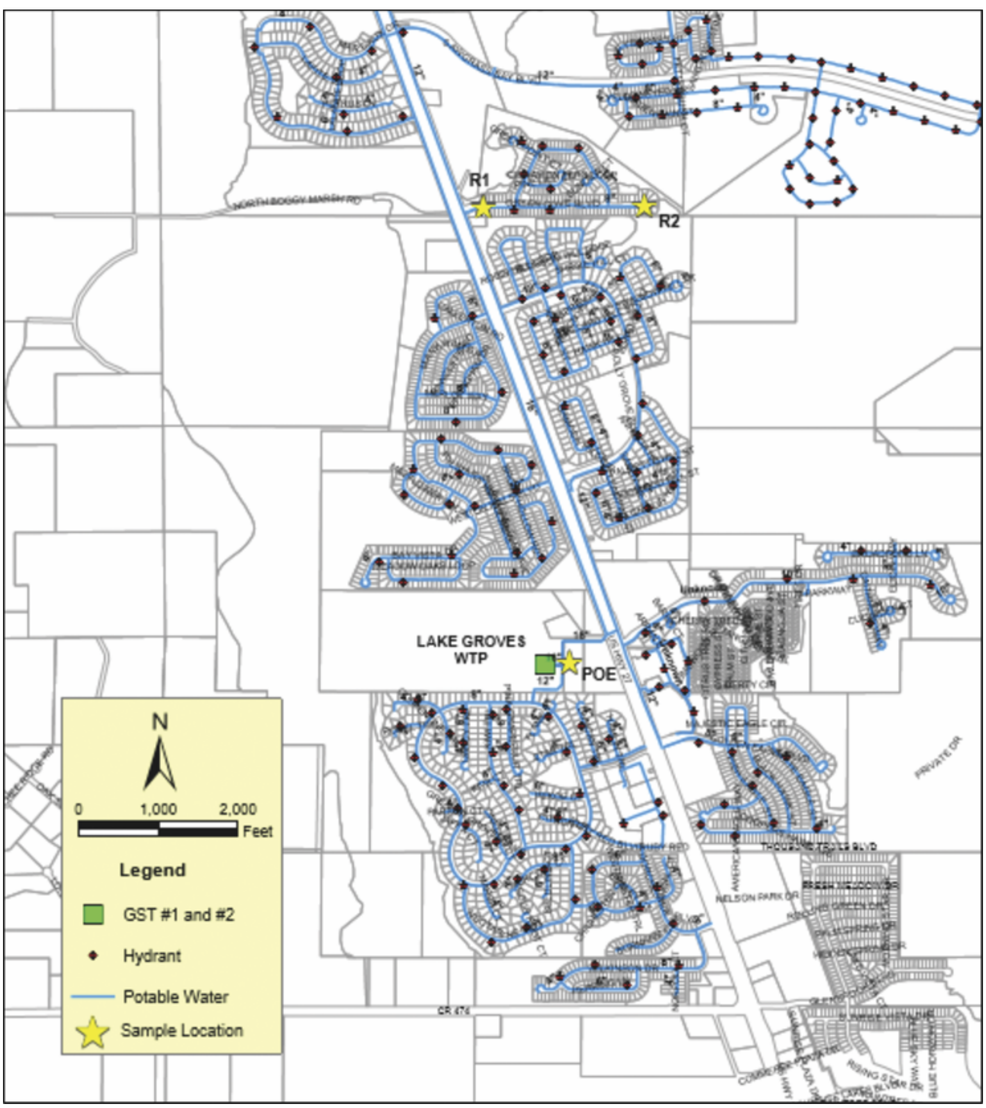

Figure 2. Sample Location Map

Distribution System Sampling

Distribution system samples were conducted weekly throughout the pilot study and were analyzed in the Orlando Utilities Commission (OUC) Water Quality Laboratory for TTHM and HAA5 concentrations. The distribution system DBP samples are imperative to the pilot study because they measured the ability of ClO_2 to delay/eliminate DBP formation. The distribution system locations were selected to provide a DBP formation curve demonstrating the beginning to the extents of the distribution system. The average water age of each location was used to compare the distribution system results to the baseline chlorinated TTHM formation curve. Water age was determined from performing an analysis in the distribution system hydraulic model during existing average daily demand (ADD) conditions. The following sampling locations were utilized for the TTHM and HAA5 distribution system analysis:

- *POE* – Represents the point that the disinfected and treated water enters the distribution system. (Approximate water age = 1 day/24 hours)
- *Residual Site 1 (R1)* – Represents the average residence time location, and was taken off a potable water sample tap at the entrance to the Savannas neighborhood, north of the Lake Groves WTP. (Approximate water age = 1.7 days/40 hours)
- *Residual Site 2 (R2)* – Represents the maximum residence time location, and is one of the FDEP Stage 2 D/DBP Rule compliance locations. (Approximate water age = 2.25 days/54 hours)
- *Lake Louisa WTP (Connected Consecutive Water System)* – Represents the point where the water from Lake Groves WTP enters the LUSI North service area by feeding into the

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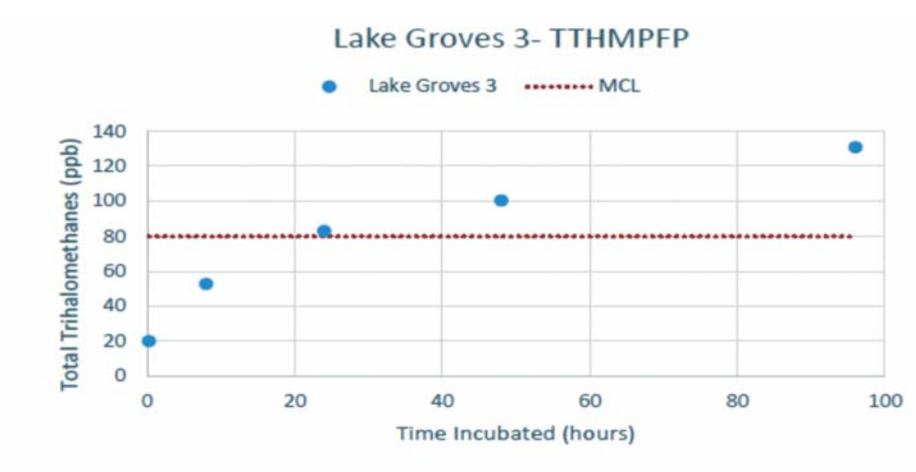

Figure 3. Well #3 Raw Total Trihalomethane Formation Potential

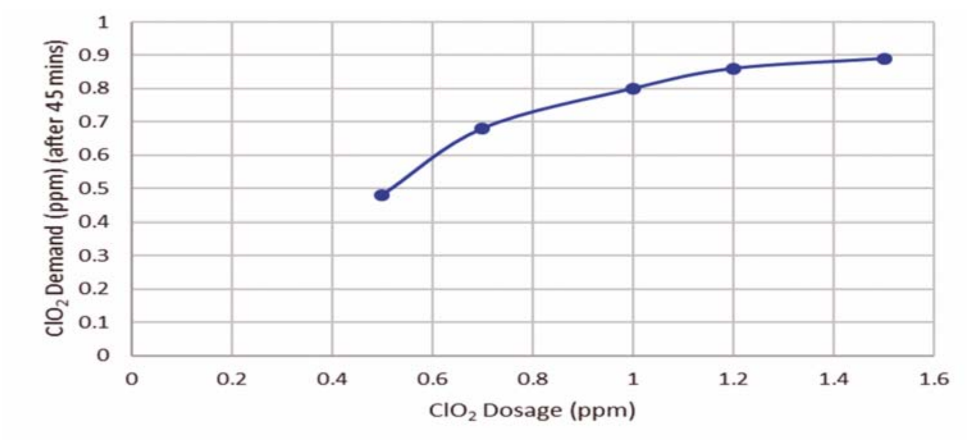

Figure 4. Chlorine Dioxide Dosage Versus Demand Curve

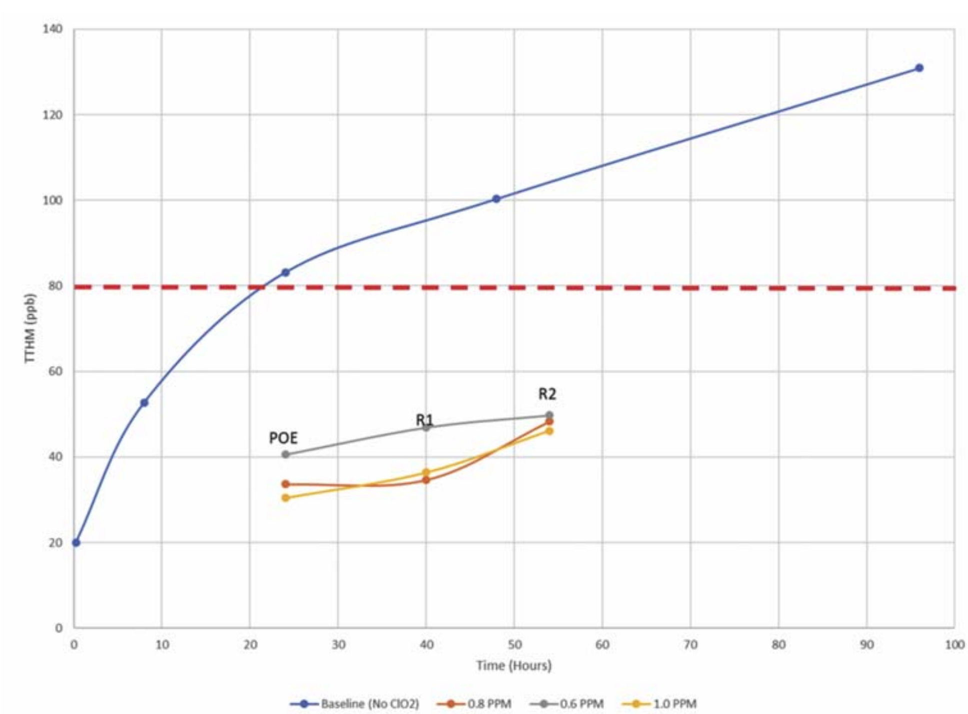

Figure 5. Total Trihalomethane Results

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Lake Louisa GST. (Approximate water age = 2 days/48 hours)

The distribution system analysis sample locations are displayed in Figure 2.

Results and Observations

Baseline Formation Potential

The University of Central Florida (UCF) Environmental Systems Engineering Institute (ESEI) conducted an evaluation in April 2016 of the byproduct formation for all the wells supplying the LUSI North and South service area. From the testing, a sample was pulled from Well #3, which identified it as the biggest contributor to the facility's water quality challenges; specifically, Well #3 testing revealed high TTHM formation potential, as shown in Figure 3. The Well #3 TTHM concentrations reached 130 ppb at a disinfection contact time of 96 hours (~4 days), which is expected to be above the Stage 2 D/DBP Rule limit set when blended with the other wells supplying this facility. The 80-ppb MCL is exceeded at a low water age of approximately one day. The ESEI also reported an HAA5 concentration of 50.95 ppb at a disinfection contact time of 96 hours. The Well #3 formation curve serves as a baseline for comparison with the delayed formation when utilizing ClO_2 pre-oxidation within the pilot testing.

Chlorine Dioxide Demand Testing

Preliminary onsite testing was completed to determine the ClO_2 demand on the aerated raw water on June 21, 2017. Since ClO_2 was planned to be injected downstream of the packed tower aerators during full-scale pilot testing, the preliminary sample was aerated in the laboratory before demand testing was conducted. The sample was divided and dosed with five different concentrations of ClO_2, ranging from 0.5 to 1.5 ppm. The samples were stored in a dark container to prevent ultraviolet degradation for 45 minutes. The ClO_2 demand (calculated from subtracting the ClO_2 residual after 45 minutes from the initial dosage rate) leveled off at approximately 0.86 ppm at an initial dosage of 1.2 ppm. The demand versus dosage curve that resulted from the ClO_2 demand testing is shown in Figure 4. This set the standard for the pilot testing to begin at an initial dosage of about 0.8 ppm.

Disinfection Byproduct Reduction

The full-scale pilot TTHM concentrations are compared to the chlorinated formation potential (containing no ClO_2) in Figure 5. At a time of approximately 24 hours, the POE ranged from 24-40 ppb, as compared to the formation curve that did not contain ClO_2, which had already exceeded the 80 ppb limit. The 40-hour time was represented in the distribution system by site R1, and ranged between 27-50 ppb. The results at site R2 ranged from 37–52 ppb, a 50 percent reduction from the baseline formation curve. These data confirm the effectiveness of using ClO_2 as a preliminary oxidant to deter the formation of TTHMs. At the minimum 0.6 ppm dosage tested during the pilot, the TTHM concentrations were approximately 10 percent lower than the maximum dosage of 1.0 ppm, showing a small difference in formation for the minimum and maximum dosing rates.

The HAA5 distribution system results, displayed in Figure 6, showed a range of 12-22 ppb at the POE, 14-22 ppb at the average residence time location, and 21-30 ppb at the maximum residence time location. The HAA5 remained at least 50 percent below the 60 ppb limit through the duration of the pilot. The HAA5 concentrations were approximately 40 percent lower than the baseline comparison value of 50.95 ppb reported by ESEI.

Regulatory Compliance Sampling

Throughout the pilot study, the ClO_2 residual at the POE remained at 0.06 mg/L and less, as shown in Figure 7, which is near zero and significantly below the MRDL of 0.8 mg/L. Many ClO_2 residual readings were recorded at 0.01 mg/L, which is the lower detection limit of the online analyzer. These results confirm the hypothesis that a majority of the ClO_2 was consumed prior to reaching the entrance of the distribution system. Minimal ClO_2 residual is expected with pre-oxidation due to the small initial dosage needed and the relatively high organics found in the raw water.

The chlorite levels, displayed in Figure 8, were maintained at less than 0.25 mg/L, well below the 1.0 mg/L MCL. Since chlorite is formed from the aqueous dissolution of ClO_2, the chlorite concentration increases as ClO_2 demand is consumed. The POE samples tested were the maximum amount of chlorite recorded within the testing analysis.

Conclusions

Based on the full-scale pilot study, the following improvements are recommended:

- Install pre-oxidation ClO_2 generation system to reduce TTHM and HAA5 concentrations in conjunction with the current disinfectant used.

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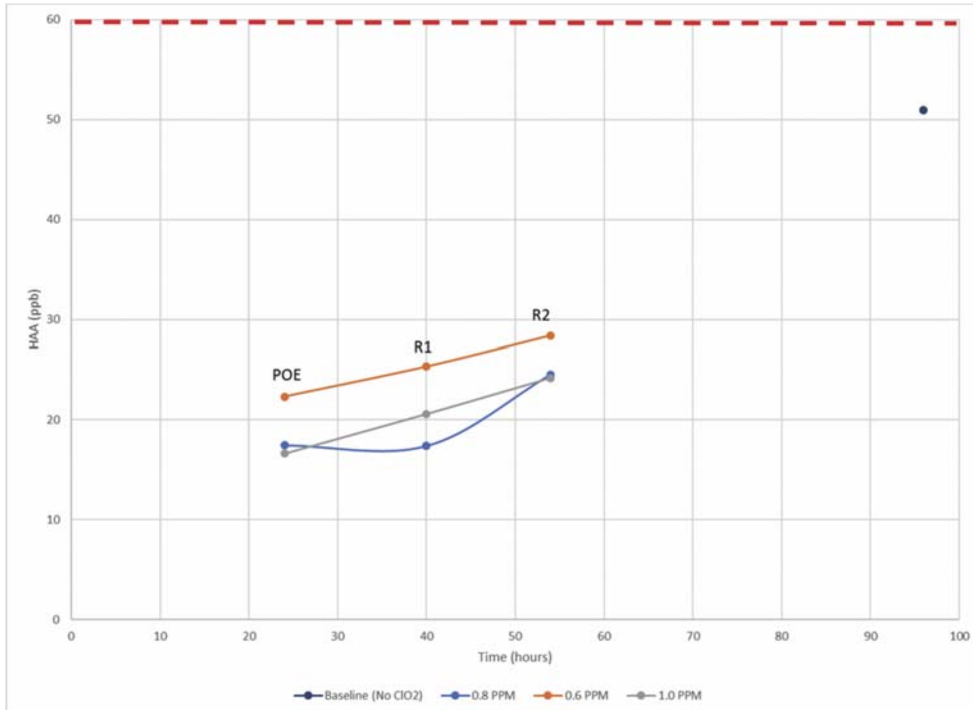

Figure 6. Haloacetic Acids Results

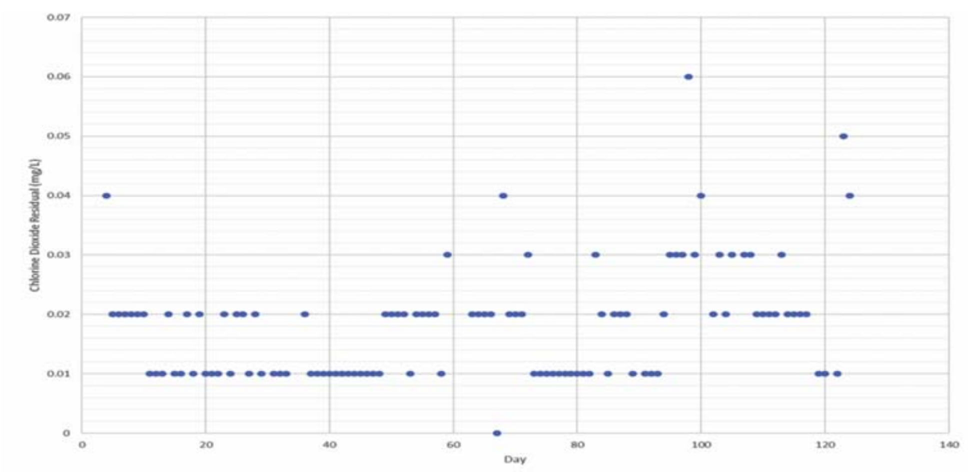

Figure 7. Chlorine Dioxide Residual at Point of Entry

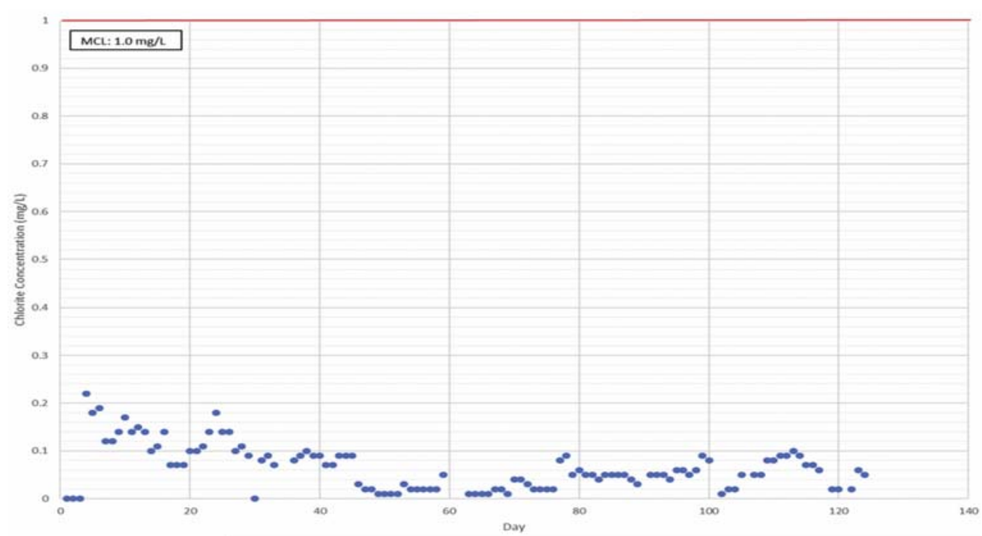

Figure 8. Chlorite at Point of Entry

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- Initiate the ClO_2 generation system at a design dosage of 0.8 ppm (26.67 lb/day).
- The generator for permanent installation can be wall-mounted in the existing sodium hypochlorite building, with the hydrochloric acid and sodium chlorite bulk storage tanks stored outside of the building under a covered structure.

The following timeline is recommended for full-scale installation:

- May – June 2018: Construction permit application and approval
- June – December 2018: Construction
- January 2019 – Stage 2 D/DBP Rule compliance with all production wells

The estimated capital cost for construction of a permanent system is approximately $200,000. The yearly operating costs include three chemical generation components: sodium hypochlorite, hydrochloric acid, and sodium chlorite. The estimated annual cost of a permanent ClO_2 generation system is approximately $66,000 per year if the system were to run constantly at the 4.32-mil-gal-per-day (mgd) or 3,000-gpm well capacity, which equates to an annual operating cost of $15,600 per mgd, or $0.0428/1,000 gal of water produced.

Table 1 compares the approximate cost of a ClO_2 system to three other DBP precursor removal methods: granular activated carbon (GAC), ion exchange, and reverse osmosis (RO) membranes. The costs for the three additional options are consistent with the information presented in the 2016 "Lake Groves Disinfection Reduction Report." An average daily flow (ADF) of 3 mgd based on planned demands for the service area was used for annual cost projections; the capital cost differential for ClO_2 versus the treatment identified is significantly less. In addition, ClO_2 operating costs are also approximately 25 percent of the cost for RO membranes, which is the next cost-effective option.

The cost projections over a 20-year period are shown in Figure 9. The long-term cost of ClO_2 is $12 million less than the next lowest option; furthermore, the system only requires Well #3 for operation, and Wells #1 and #2 can return to backup operation.

Table 1. Chlorine Dioxide System Cost Comparison

Treatment Alternative	Capital Cost ($)	Estimated Annual Operating Cost ($/ 3 MGD)	Estimated Annual Operating Cost ($/ mgd)	20-Year Net Present Value (NPV): Capital and Operating Cost ($/3 mgd)
Ion Exchange	$11,650,000	$328,500	$109,500	$18,121,191
GAC	$7,000,000	$1,029,300	$343,100	$27,307,913
Membranes	$9,890,000	$208,050	$69,350	$13,985,262
ClO_2	$200,000	$46,800	$15,600	$1,282,188

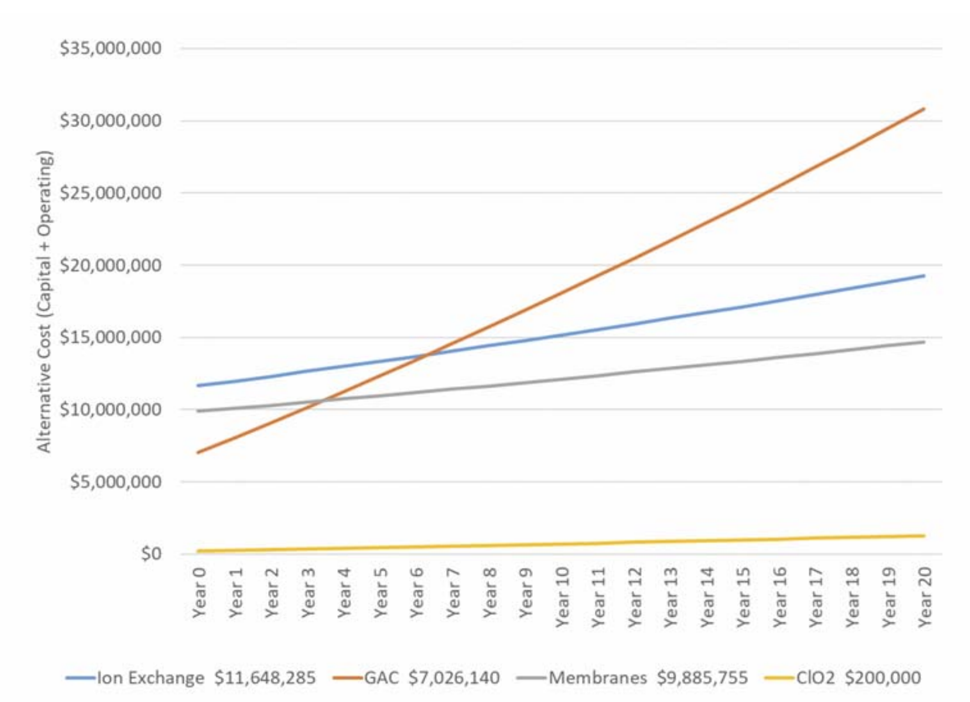

Figure 9. Capital and Operational Cost Comparison

Recommendations

The ClO_2 proved to be highly effective at minimizing DBP formation, while saving capital costs compared to other treatment upgrades; however, ClO_2 is sparsely used for potable water applications, so it's imperative to fully understand the process before investigating its use. The following recommendations are based on lessons learned from the pilot study and extensive efforts of ClO_2 testing at other facilities prior to this full-scale study.

- The ClO_2 is proven to be an effective tool to maintain compliance with the Stage 2 D/DBP Rule, but it's still recommended to perform field and laboratory testing to verify the compatibility with the water characteristics. A full- or pilot-scale study is recommended prior to installation of a permanent ClO_2 system to evaluate the effects within the distribution system. The goals of the pilot study would be to reveal the effects of ClO_2 on a system's specific water quality and identify optimal ClO_2 dosing for maximum cost savings.
- It's important to gain understanding and consensus from state and local regulators and to remain in compliance with all water quality regulations while performing a ClO_2 pilot study. Chlorite levels in the distribution must be monitored regularly and maintained below the MCL. It's recommended to ensure that the ClO_2 and chlorite samples are being accurately assessed from either a laboratory or a handheld sample analyzer. Inaccurate test results and wrongly reported concentrations can affect regulatory compliance and cause unnecessary public concern.
- It's recommended that the available options for ClO_2 generation be reviewed and understood. Several factors are important when understanding generation options, including operator training and availability, goal usage of ClO_2, redundancy needs, and chemical safety. Moreover, the aspects of each generation system need to be compatible with the process application and utility production conditions. Generators often produce ClO_2 on demand; however, ClO_2 storage is not often recommended for these *in situ* generation units.
- Proactive and direct public communication is recommended before ClO_2 is used in treatment processes. If utilizing ClO_2 as a disinfectant, proper notification is required, similar to the transition from chloramine to

chlorine disinfection. Although ClO_2 technology is not "new," the public may be concerned hearing about the use of an unfamiliar chemical. It's important to emphasize the benefits of ClO_2 and compare its safety to typical disinfectants.

Final Considerations

All in all, careful consideration should be given to the implementation of ClO_2 within a water production or distribution facility. While the chemical is effective in maintaining disinfectant residuals, as well as improving aesthetics in distribution system water quality, the appropriate process addition may be as a pre-oxidant, rather than as the primary disinfectant.

The use of ClO_2 has shown promise as a strong disinfectant chemical for other utilities aspiring to reduce DBPs without incurring significant capital cost associated with high-end treatment or the routine distribution system maintenance challenges associated with chloramines. As a viable pre-oxidant or alternative disinfectant, it should be considered when these DBP or distribution system challenges are present.

Acknowledgments

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