Chlorine Dioxide Treatment for Disinfection Byproduct Reduction

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One of the largest issues facing Florida utilities today is the reduction of disinfection byproducts (DBPs) to comply with the Stage 2 Disinfection Byproducts Rule. Current treatment methods of DBP precursor reduction, such as membrane treatment, ion exchange, and granular activated carbon treatment, can incur significant capital and operational expenses. Many utilities have turned to chloramine disinfection to minimize DBP formation, which offers minimal capital expense, but chloramine disinfection brings its own routine challenges to maintaining distribution systems.

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Background

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 disadvantages and hazards. Chlorine represents both safety- and health-related risks and effects and reacts quickly with organic matter to form DBPs, but 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 and shorter contact times to achieve disinfection than is required for chlorine and chloramine disinfection. It is 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].

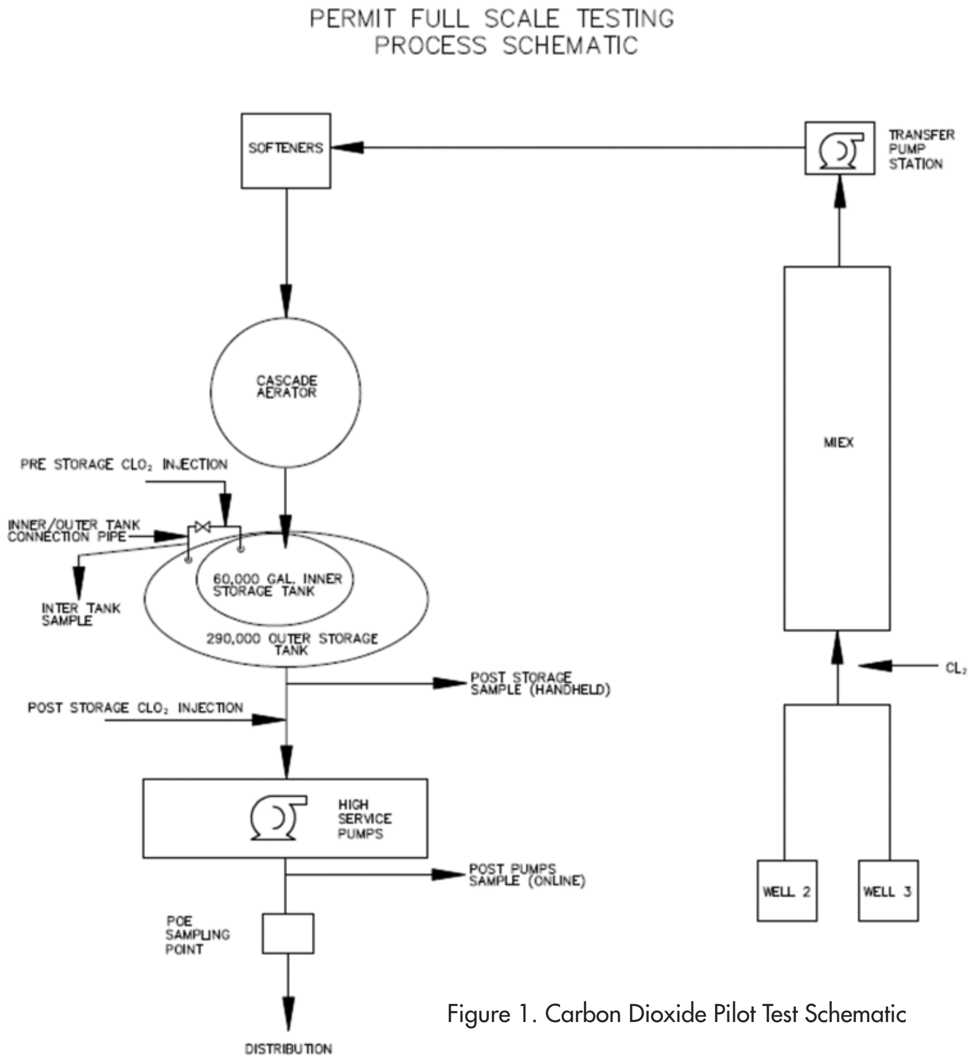

Figure 1. Carbon Dioxide Pilot Test Schematic

The use of ClO_2 has been implemented in distribution systems since the 1970s after the discovery of total trihalomethanes (TTHMs) and other DBPs, which are still being discovered to date. It has been utilized in Europe and the United States as both a primary disinfectant and preoxidant, with around 1,200 plants currently implementing its disinfection [1]. The selective reactivity enables ClO_2 to control waterborne pathogens without reacting with organic DBP precursors. Unlike chlorine, ClO_2 reactions in water do not result in the formation of TTHMs and haloacetic acids (HAA_5) because “when ClO_2 oxidizes organic material, it is reduced to chlorite, but does not chlorinate the resulting organics” [2].

The ClO_2 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 within long dead-end mains is a concern [2]. The use of ClO_2 can be tailored to a specific facility’s need; it can be used for the primary disinfectant or as a preliminary oxidant, followed by chlorine or chloramines, and has been shown to have five times stronger oxidation potential and disinfection efficacy than chlorine [3].

Regulatory guidelines, such as Florida Administrative Code (FAC) 62-555, identify ClO_2 as an acceptable method of inactivating viruses and bacteria to achieve 4-log virus inactivation. The U.S. Environmental Protection Agency (EPA) regulates ClO_2 as a primary disinfectant, with a maximum residual disinfectant level (MRDL) of 0.8 mg/L. When injected, 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 chlorine dioxide.

Chlorine Dioxide Generation Overview

There are multiple ways to produce ClO_2. Traditionally, chlorine dioxide was generated from the reaction of chlorine gas with sodium hypochlorite. Chlorine gas-based ClO_2 generation is not recommended, due to operational difficulty and safety concerns of handling chlorine gas. Recently, it has become increasingly common to produce chlorine dioxide through reaction of sodium chlorite with an acid, such as hydrochloric or sulfuric acid.

The primary methods of ClO_2 production are through an injection/eduction generator, or through combining powder components that contain stabilizers to minimize off-gassing of ClO_2 while stored. Regardless of the production method, ClO_2 should be produced within a 0.2-0.5 percent solution, to reduce risk of an exothermic reaction. The ClO_2 used in the pilot study (to be discussed) was produced from mixing two powder components, as supplied by Twin Oxide-USA LLC, with water forming a 0.3 percent ClO_2 solution.

Pilot Study

Preliminary Analysis of Need

Pluris Utility currently owns and operates the Wedgefield Potable Water and Wastewater Utility (utility). With the onset of the Stage 2 Disinfectants/Disinfection Byproducts Rule (D/DBPR), the utility attempted to maintain compliance with the DBPs through the MIEX® ion exchange treatment system to remove organics before disinfection. In recent quarters, the TTHM samples exceeded 80 parts per bil (ppb), increasing the rolling annual average of the sample sites to encroach upon the regulatory limit of 80 ppb. Prior to the study, the utility utilized sodium hypochlorite (chlorine) as the sole disinfectant for its storage and distribution system. Despite the utility's efforts to streamline the chlorine dosage and reduce the residual concentration, it was unable to achieve TTHMs below 80 ppb in the distribution system. Even at the lower concentrations, this disinfectant's reaction with the naturally occurring organics was producing a high level of TTHMs. As such, the utility sought alternative methods of treatment, as well as disinfectants to achieve compliance with the Stage 2 D/DBPR. Having experienced the maintenance-intensive operation efforts of chloramines and water quality concerns, the utility opted not to consider chloramine disinfection for this application.

Through field testing and laboratory evaluation of ClO_2 products, the utility decided to implement a full-scale pilot test within the distribution system. Field testing efforts included demand analysis testing at the water treatment plant, with onsite residual analyzers and demand curve identification. Further investigation included laboratory testing of chlorine dioxide injection, incubation, and sodium hypochlorite injection to simulate using chlorine dioxide as a preoxidant to chlorine disinfection. This testing was completed by the University of Central Florida (UCF) Environmental Systems Engineering Institute (ESEI) team and it revealed that this application was not suitable for the utility. After reviewing the results from this testing, additional laboratory testing was conducted to simulate chlorine dioxide being injected as the primary disinfectant, followed by incubation over a five-day water-age analysis. The results from this laboratory testing proved positive for the utility in support of a full transition to chlorine dioxide and the significant potential to reduce TTHMs within its distribution system.

The ClO_2 solution laboratory testing results revealed the apparent advantages of full disinfection without the negative DBP formation effects associated with chlorine. Full-scale pilot testing was predicted to have similar results, provided that the residual maintenance was achievable for the distribution system. A close watch on regulatory parameters was necessary to ensure compliance with the regulatory limits of chlorite MCL and chlorine dioxide MRDL.

The next step in the process was to demonstrate the laboratory effects on the full-scale utility system, and 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, only a select few utilities have used chlorine dioxide 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 Wedgefield's water treatment plant (WTP).

The overarching goals of the full-scale pilot study included a gradual transition from chlorine disinfection to chlorine dioxide, vigorous field and laboratory testing of the treatment process during the transition (and after) to ensure public safety, and compliance with the regulations. The utility and onsite staff completed extensive efforts to obtain all the required samples, and their thorough analysis and consideration of the results proved very helpful in concluding the effect of each process adjustment.

At the beginning of the pilot study, ClO_2 was injected into the ground storage tank in parallel with the current chlorine disinfectant dose. The ClO_2 residual in the distribution system was monitored to identify the attainment of the desired residual. Once the 0.2 parts per mil (ppm) ClO_2 residual was attained, chlorine dosage was trimmed slowly to perform the gradual disinfection transition. As chlorine was reduced, continuous monitoring of the ClO_2 residuals ensured the required 0.2 ppm minimum per FDEP's approval.

To assess the regulatory water quality compliance parameters, including the Stage 2 D/DBPR, multiple sample locations were identified within the distribution system; the utility's two compliance locations identified for HAA_5 and TTHMs were also included. Each sample location was monitored routinely for chlorine residual, ClO_2 residual, and chlorite concentration. The first formal location was chosen to be as close to the first customer as possible (20429 Mansfield St., Orlando, Fla.). The second formal location represents the average distribution system water age (20305 Majestic St., Orlando, Fla.). A third formal location was chosen to represent the maximum distribution system water age (19520 Glen Elm Way, Orlando, Fla.).

The pilot study sampling recorded the ClO_2

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residual at the point of entry (POE), averaging 0.43 mg/L, which is below the MRDL of 0.8 mg/L. The ClO_2 residual was at or above the minimum of 0.2 mg/L, in compliance with Florida Administrative Code (FAC) 62-555. The chlorite concentration in the distribution system ranged from 0.02 mg/L to 0.98 mg/L, resulting in an average concentration of 0.69 mg/L throughout the pilot study; the chlorite data is below EPA's MCL goal for chlorite of 1 mg/L. The MIEX system remained functional throughout the pilot study and will continue to be used to maintain low levels of organics and effective removal of hydrogen sulfide.

Overview of Pilot Setup and Equipment

The Wedgefield WTP includes two raw water wells feeding directly into the MIEX system, with a minor dose of sodium hypochlorite to mitigate biological growth within the contactor basins. The MIEX system removes approximately 60 percent of the total organic compounds and offers the additional benefit of approximately 95 percent removal of hydrogen sulfide. The MIEX-treated water flows to a clearwell and is then partially pumped through a softening system prior to combining for tray aeration and storage in the onsite ground storage tank. The ground storage tank consists of concentric tanks and is divided into an inner tank (approximately 60,000 gal) and an outer tank (approximately 290,000 gal). Produced water flows from the aerator to the inner tank and then through a single 12-in. pipe connection using a static differential between the inner and outer tanks. High-service pumps pull finished water from the outer storage tank to meet the potable demand. The treated water was disinfected using sodium hypochlorite immediately following the tray aerators, as the water collects in the inner storage tank.

The pilot study was designed to inject a premixed 0.3 percent ClO_2 solution downstream of the tray aerators and between the inner and outer ground storage tank to allow for backwashing of the onsite softeners from the inner tank, and prior to ClO_2 injection. The location was selected to utilize the hydrogen sulfide removal currently being achieved through the MIEX system and downstream of the softeners to prevent any oxidation of the softening media. As the water is transferred from the inner to the outer tank, chlorine dioxide is injected to achieve the primary disinfection for the finished water. See Figure 1 for a plant process schematic.

The dosage of ClO_2 was initiated at 1 ppm. Following injection, the ClO_2 residual was monitored using the handheld ClO_2 analyzer from the sample port installed on the pipeline connecting the inner and outer tank. After storage, ClO_2 was monitored via a handheld, as well as an online, analyzer for continuous readings as the water enters the distribution system. Additional monitoring in the distribution system was completed using the handheld analyzer.

The pilot program included the physical components to mix, store, inject, and monitor the ClO_2 disinfectant in the process stream. Given the powder supply chosen for chlorine dioxide generation, the pilot system was implemented to complete this pilot test. The specific components included the following equipment:

- *Product Mixing Tank.* A single 300-gal tank for mixing the two-component ClO_2 product and solution water.
- *Product Transfer Pump.* A single pump to transfer the fully mixed, 0.3 percent ClO_2 solution from the mixing tank to the storage tank.
- *Product Storage Tank.* Dual 600-gal tanks for storing the mixed ClO_2 product to supply the chemical metering pumps.
- *Inter-Storage Chemical Metering Pump.* A chemical metering pump dosing system, with flow-paced control (and residual alarm), to draw from the ClO_2 product storage tanks and dose the ClO_2 through one injector located at the pipe connecting the storage tank's inner and outer tank.
- *Post-Storage Chemical Metering Pump.* A chemical metering pump dosing system, with flow-paced control (and residual alarm), to draw from the ClO_2 product storage tanks and dose the ClO_2 through one injector located in the suction piping to the high-service pumps.
- *Sampling Stations.* Sampling taps located within the process to pull grab samples of the treated water immediately after injection and after storage in the outer tank.
- *Grab Sample Analyzer.* One Palintest handheld analyzer for routine monitoring of ClO_2 residual and chlorite at each of the sampling locations identified.
- *Online Chlorite Sample Analyzer.* One analyzer for continuous monitoring of chlorite levels at the POE to the distribution system.
- *Online ClO_2 Residual Sample Analyzer.* One analyzer for continuous monitoring of ClO_2 residual at the POE to the distribution system.
- *Online ClO_2 Monitoring and Control System.* One control panel capable of receiving the analog signals from the online analyzers, tank level monitoring, pump controls, and operator interface with the control system.

These physical components were inspected a minimum of two to four times per day as the operations staff completed its sampling efforts, as well as during the routine operation and maintenance of the existing treatment plant. Continuous operator monitoring and control was available through the internet-based supervisory control and data acquisition (SCADA) application for this system.

Optimization Plan

While starting up the chemical system, the utility staff closely monitored the residuals as the transition to ClO_2 extended through the distribution system. The ClO_2 chemical dosage was

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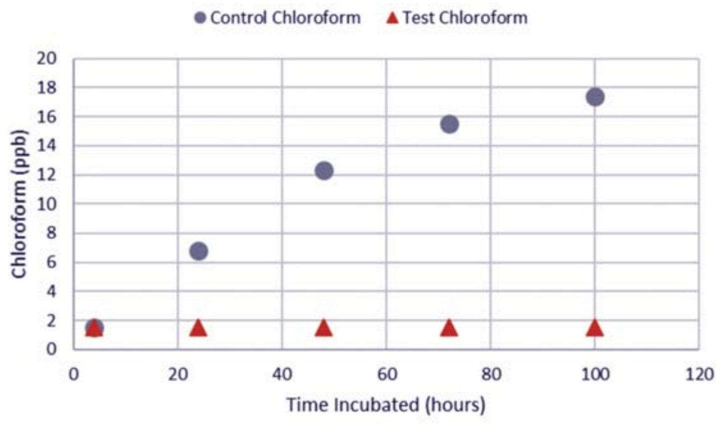

Figure 2. Chloroform Formation Potential

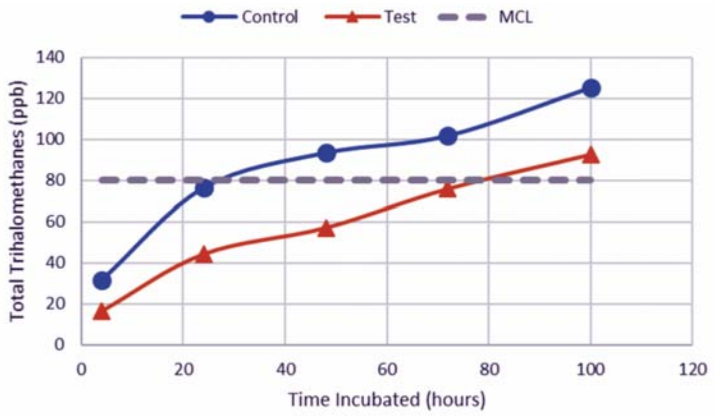

Figure 3. Total Trihalomethane Formation Potential