

GLENN W. HOLDEN

Chlorine Dioxide Preoxidation for DBP Reduction

USING CHLORINE DIOXIDE
FOR PREOXIDATION IS
HELPING WATER
TREATMENT PLANTS MEET
THE STAGE 2 DISINFECTANTS
AND DISINFECTION
BYPRODUCTS RULE.

Use of chlorine dioxide (ClO_2) in surface water treatment plants has grown significantly as regulations addressing disinfection byproduct (DBP) formation have become increasingly stringent over the last two decades. For example, the US Environmental Protection Agency's (USEPA's) Stage 2 Disinfectants and Disinfection Byproducts Rule (DBPR) requires systems to identify locations within their distribution systems with high levels of DBPs to serve as sampling sites. Water systems must meet the maximum contaminant levels (MCLs) for total trihalomethanes at 0.08 mg/L and the sum of five haloacetic acids at 0.06 mg/L, taken as an average at each monitoring location (a locational running annual average) instead of as a system-wide average as allowed under the Stage 1 DBPR.

To comply with more stringent DBP regulations, many surface water treatment plants needed to change their DBP control strategies, including preoxidation with ClO_2 . Because of its selective reactivity, in comparison with chlorine and other oxidizing agents, ClO_2 is effective in controlling waterborne pathogens while minimizing halogenated DBPs. ClO_2 is a broad-spectrum microbiocide; as effective as chlorine against viruses, bacteria, and fungi; and more effective than chlorine for the inactivation of the encysted parasites *Giardia* and *Cryptosporidium parvum* (Chauret et al. 2001). ClO_2 is also an effective control strategy for taste, odor, color, iron, and manganese removal (Stevens 1982, Mounsey & Hagar 1946).

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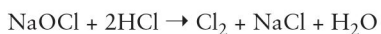
OXIDIZING TRIHALOMETHANE PRECURSORS

In contrast to chlorine and bromine, the reactions of ClO_2 with humic substances, which act as DBP precursors, do not result in the formation of trihalomethanes (THMs) and haloacetic acids (HAAs) because when ClO_2 oxidizes organic material, it is reduced to chlorite but does not chlorinate the resulting organics (Aieta & Berg 1986). Oxidized THM precursors are then removed during coagulation, settling, and filtration before final chlorination, resulting in significantly decreased levels of THMs in the finished water. Pretreatment with ClO_2 also has an inhibiting effect on THM formation when chlorine is used subsequently for disinfection (Yang et al. 2013). HAA levels are unaffected by pre-oxidation with ClO_2 (Harris 2001).

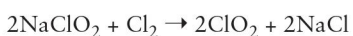
When used for pre-oxidation and disinfection, ClO_2 provides several other site-specific advantages, including iron and manganese and taste and odor control, as well as nitrification control in outlying areas of distribution systems (McGuire et al. 1999). The following case studies describe how three water utilities have adopted ClO_2 to meet system-specific objectives.

ONSITE ClO_2 GENERATION

All three water utilities highlighted in this article operate ClO_2 generator systems that produce ClO_2 in a two-stage reaction process under vacuum conditions. In the first stage, molecular chlorine gas is generated in situ by the reaction of 15% solution of sodium hypochlorite (NaOCl) with a 15% solution of hydrochloric acid (HCl):



In the second stage, the chlorine gas reacts under vacuum with 25% sodium chlorite (NaClO_2) solution to produce high-purity ClO_2 in milliseconds with a minimum yield and conversion efficiency averaging from 95 to 99%:



The 15 mgd South Water Treatment Plant in Lubbock, Tex., came on line in 2012. Photo courtesy of the City of Lubbock, Tex.

LUBBOCK, TEX.

The 15 mgd South Water Treatment Plant (see the photographs on this page), which came on line in 2012, includes microfiltration in its treatment train. The plant is supplied by Lake Allen Henry, which is approximately 60 mi away. Total organic carbon (TOC) levels of reservoir water are in the range of 5–6 mg/L. A 250 mil gal terminal storage reservoir built next to the plant provides a certain degree of settling before treatment, and although the influent turbidity is fairly consistent (0.5–2.0 ntu), the plant's designers understood that effective pretreatment would be critical to effective membrane performance.

To achieve this, upstream treatment ahead of the plant includes ClO_2 oxidation to reduce formation of THMs and improve flocculation and

sedimentation. ClO_2 is injected at the outlet of the reservoir at concentrations in the range of 0.8–1.0 mg/L. From the reservoir outlet, flows enter a 48 in. raw water pipeline that allows for appropriate contact time (CT) before the plant's rapid mix, from which grab samples are collected to confirm ClO_2 and chlorite levels.

“Following membrane filtration, there is a chlorine contactor area right before the clearwell where we add a minimal dosage (0.5–0.6 mg/L) of free chlorine to meet our disinfection CT—to actually prove it out,” said the plant superintendent, Mike Lowe. “Because the water has already been disinfected with our chlorine dioxide pretreatment, we use only a minimal amount of free chlorine to meet our prescribed disinfection credits, and then immediately tie it up with ammonia on the inlet side of the



The South Water Treatment Plant has six individual microfiltration skids, each with a 2.5 mgd filtration capacity. Photo courtesy of the City of Lubbock, Tex.



The West Clearwell serves San Diego's 34 mgd Otay Water Treatment Plant. Photo by Jim McVeigh, City of San Diego, Calif.

clearwell storage. With that, we go into the clearwell with 1.0 to 1.5 mg/L of monochloramine. Then, on the discharge of the high service pumps, we add another 2.5 to 3 mg/L of preformed monochloramine. Our goal is for water to leave the facility with 3.5 mg/L of monochloramine.”

Plant operators perform daily titrations for ClO_2 and chlorite as well as all other duties for ClO_2 use required by the Texas Commission of Environmental Quality (TCEQ). The plant does not currently claim ClO_2 as its primary disinfectant for regulatory purposes, although the plant could meet its disinfection credit using it. Lowe says the plant plans to claim ClO_2 to meet its disinfection credit in the near future.

“We don’t want to inject any more free chlorine than we absolutely have to because of the TOC levels in our raw water. Whenever we have lake turnover or an upset that raises organic levels coming into the plant, TOC levels could increase to 8 to 10 mg/L,

and then it’s going to be even more critical,” he said. They plan to meet their disinfection credit using ClO_2 and discontinue use of free chlorine as their primary disinfectant. According to Lowe, “We will still blend with ammonia to form monochloramines for our distribution system, but the water will never be exposed to free chlorine for any length of time.”

Chlorite, which is a byproduct of ClO_2 reduction, is maintained at 0.4–0.5 mg/L in the distribution system and benefits the system by inhibiting the formation of ammonia-oxidizing bacteria, nitrogen-oxidizing bacteria, and biofilms. “We only lose about a half of a milligram per liter of our chloramines out in our distribution system, thanks to the chlorite ion-reducing nitrification. We typically measure a 2.9–3.1 mg/L residual at the far stretches of our system, areas that had previously been problematic for us.”

Over the next couple of years, Lubbock also plans to convert its

other surface water plant, the 75 mgd North Water Treatment Plant, from free chlorine to ClO_2 disinfection. The plant, built in the 1960s, is a conventional sand filtration plant that currently uses powdered activated carbon (PAC) for odor control.

“This plant runs very well, but its PAC system needs to be replaced. The new chlorine dioxide system will be replacing our old PAC system, saving the city significant capital costs. Our taste and odor issues there are solely of an organic nature, so the chlorine dioxide will handle those as well as oxidize the DBP precursors coming into the plant,” Lowe said.

Unlike its South Water Treatment Plant, which feeds from reservoirs owned by the city, Lubbock’s North Water Treatment Plant receives raw water purchased from the Canadian River Municipal Water Authority (CRMWA). CRMWA provides the city with raw water that is typically a blend of two sources: a large groundwater field located in Roberts County, Tex., and surface water from Lake Meredith, approximately 160 mi away.

Because of a long-term drought in the Texas Panhandle, Lake Meredith suffered declining levels, and Lubbock’s North Water Treatment Plant received 100% groundwater for approximately three years. Recently, however, sufficient rainfall has raised water levels in the lake so that it can again be blended with groundwater sent to the plant.

“The lake was so low for so long, all of its vegetation is now submerged and beginning to decay, driving the TOC levels up in our flows to the plant,” Lowe said. “The city has no control over the blend ratio that the authority sells us. Our concern is that, using only free chlorine, and without the use of chlorine dioxide, there’s a much greater potential to exceed our MCLs for DBPs. So, we’ve determined that using ClO_2 as our primary disinfectant is our safest strategy.”

Until ClO_2 generation is installed, Lubbock’s North Water Treatment Plant has gained TCEQ approval to inject 25% NaOCl following rapid

mix to maintain 0.4–0.5 mg/L chlorite ion in the city’s distribution system.

“Our distribution system has some relatively long, dead-end mains where water age is a big concern,” Lowe said. “The chlorite ion reduces the risk of nitrification from biofilm in our system.”

SAN DIEGO, CALIF.

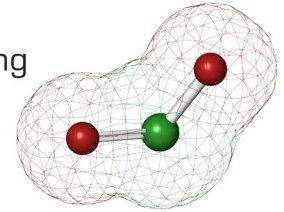
San Diego’s 34 mgd Otay Water Treatment Plant (see the photograph on page 38) is the smallest of the city’s three water treatment facilities and serves a population of approximately 200,000. It is a conventional treatment plant that uses coagulation, flocculation, sedimentation, filtration, and disinfection. The plant receives raw water from two sources—imported water from the Colorado River and local runoff collected in three reservoirs totaling approximately 150,000 acre-ft. In 2011, the plant completed an expansion and upgrade that included conversion from chlorine (injected just prior to filtration) to ClO₂ disinfection to control the formation of THMs to meet the requirements of the Stage 2 DBPR.

“Because water is very valuable here, we intentionally manage our reservoirs not to overflow,” said Jim McVeigh, senior water operations superintendent for San Diego’s Otay Water Treatment Plant. “If we’re

running our plant to 20 mgd and can use our own lake water instead of imported water from the Colorado River, that’s about \$40,000 a day in reduced purchased-water costs. As a result, our local water is rarely

was concern of bromate formation. We also looked at UV [ultraviolet], but UV doesn’t do a whole lot on the front end of a water plant,” he said. “For UV to be effective, you have to have fairly clear water. And although

Pretreatment with ClO₂ also has an inhibiting effect on THM formation when chlorine is used subsequently for disinfection.



released from the dam; rather, it’s essentially evaporating and concentrating prior to use. It’s relatively warm water, typically no cooler than 15°C, so there’s biological activity going on all year in the lake.”

The TOC levels in these reservoirs ranges from 6 to 8 mg/L, which creates a high potential for elevated DBPs in the city’s distribution system. Although the system was compliant under the Stage 1 DBPR when sampling could be averaged over sampling sites, the utility realized it needed to change its primary disinfection agent to comply with the Stage 2 DBPR.

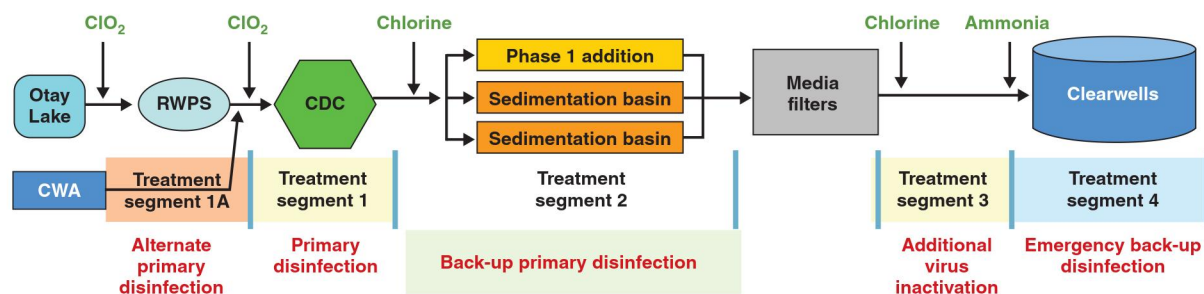
“We looked at several options,” McVeigh said. “The city’s two other treatment plants converted to ozone as the alternative disinfectant. But because of the bromide levels in lake water serving the Otay plant, there

UV is an effective disinfectant, it does nothing to oxidize constituents in the water.”

The utility ultimately selected ClO₂ as the alternative to chlorine for primary disinfection because of its relatively low cost and the fact that it does not form significant concentrations of regulated halogenated organic compounds. The utility designed a ClO₂ system (automatic flow-paced batch system generators using chlorine gas and sodium chlorite), which was put into operation in fall 2010.

ClO₂ is applied to the raw water as it leaves the outlet tower of the reservoir. From the tower, the water is pumped approximately 1,700 ft to the plant (Figure 1.) At the front end of the plant, ClO₂ levels are continuously monitored while the plant’s supervisory control and data

FIGURE 1 Otay Water Treatment Plant disinfection strategy^a



CDC—chlorine dioxide contacting effluent, ClO₂—chlorine dioxide, CWA—San Diego County Water Authority, DBPR—Disinfectants and Disinfection Byproducts Rule, RWPS—raw water pump station, THMs—trihalomethanes

^aImplemented February 2011, the strategy included converting from chlorine to ClO₂ disinfection to control the formation of THMs to meet the Stage 2 DBPR.

acquisition (SCADA) system performs a real-time computational analysis of *Giardia* disinfection to optimize the ClO₂ dosage to provide

good oxidation just prior to coagulation, we see better treatment with chlorine dioxide, especially with the harder-to-treat lake water. We get

bed anthracite filter media was replaced with 30 in. of granular activated carbon (GAC). The city made this change primarily for taste and odor control; however, GAC is also a very effective barrier to chlorite (Świetlik et al. 2002).

Using ClO₂ ahead of the treatment plant has reduced the DBP formation potential of the water.

a 1.2 log disinfection rate, which is approximately twice that required by regulation.

“Chlorine dioxide allows us to have disinfection and oxidation in the front end of the treatment process without formation of THMs,” McVeigh said (Figure 2). “With

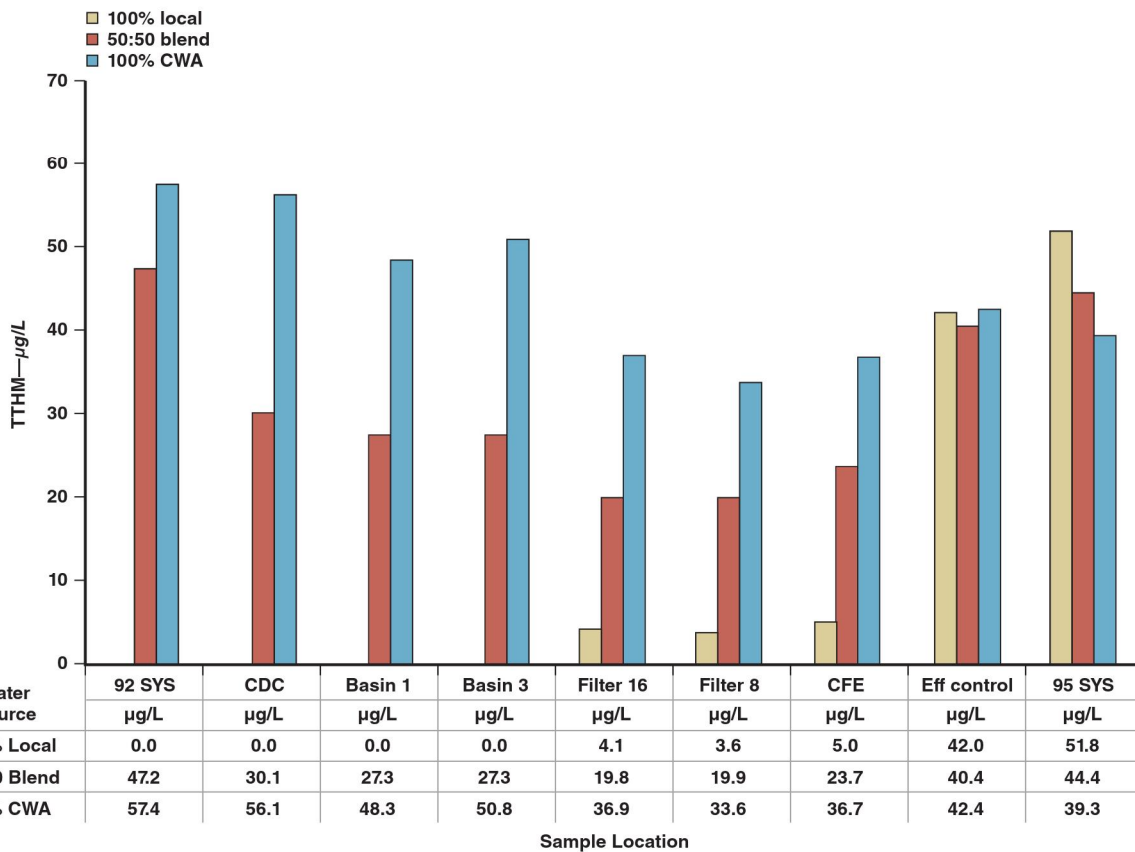
better coagulation in general, better particle removal, because the oxidative power of chlorine dioxide is materially affecting the particle contaminants in the water and making them coagulate better.”

At the same time the ClO₂ system was installed, the plant’s 30 in.-deep

The small amount of chlorite ion remaining after filtration aids in reducing nitrification in San Diego’s distribution system. On average, between 0.2 and 0.3 mg/L of chlorite (20–30% of the MCL) is delivered to the distribution system from the Otay facility.

“Since we began feeding chlorine dioxide, there have been no major nitrification issues in the part of the city’s distribution system served by

FIGURE 2 Otay Water Treatment Plant TTHM profile study^a



92 SYS—combined raw water influent prior to any treatment; 95 SYS—clearwell outlet, Otay point-of-entry, chloramines; Basin 1 and Basin 3—effluent water from settling basins; CDC—chlorine dioxide contactor (effluent compliance sample for chlorine dioxide contact time); CFE—combined filter effluent (prior to chlorine and caustic addition); CWA—San Diego County Water Authority; eff control—effluent control structure (combined filter effluent with free chlorine); Filter 8 and Filter 16—individual filter effluent; THM—trihalomethanes; TTHM—total trihalomethanes

^aThe study used samples taken from representative locations along the treatment process and designed to track THM formation as the water moved through the plant.

the Otay Plant,” McVeigh said. “Previously, we had to do a lot of flushing, but since our chlorine dioxide system has been up and running we haven’t had a speck of problems with nitrification.”

Using ClO_2 ahead of the treatment plant has reduced the DBP formation potential of the water. “THM levels measured in the city’s distribution system from the Otay Plant are equal to or less than those from the city’s other two plants that use ozone when treating the same water source,” McVeigh said. “We’re well into compliance even on our lake water. In 2015, when we were on lake water the entire year, even in the warmest water months (our worst THM season) our THMs were in the 60s (ppb). In a comparable year without chlorine dioxide it would have been between 120 and 150 ppb. The switch to chlorine dioxide has been what has allowed us to comply with the Stage 2 DBPR.”

The next stage for the Otay Plant at the time this article was written was to modify its existing three-chemical ClO_2 generation system to accept the use of electrolytic-generated 0.8% bleach as a starting raw material, thereby eliminating the need to store and handle chlorine gas cylinders onsite (see the photograph on this page).

“The only real trick is this system will be making 800 lb/d of electrolytic-generated bleach instead of the typical 8 lb,” McVeigh said. The plans for the plant also include using the electrolytically generated bleach to treat its distribution system residual disinfectant.

LITTLE ROCK, ARK.

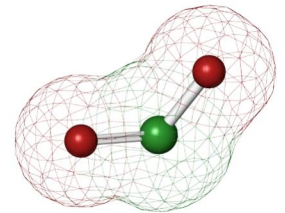
As with San Diego’s Otay Plant, Central Arkansas Water management considered several options before deciding on ClO_2 to help its two surface water treatment plants comply with the Stage 2 DBPR. Central Arkansas Water is a metropolitan water system that serves a population of approximately 400,000 with 137,000 residential,

commercial, industrial, and master-metered customers in three counties.

“We looked at ozone, chlorine dioxide, and various ion exchange

sedimentation, and filtration. Fluoride, zinc polyphosphate, lime, and sodium hypochlorite are added before the water enters the clearwell and

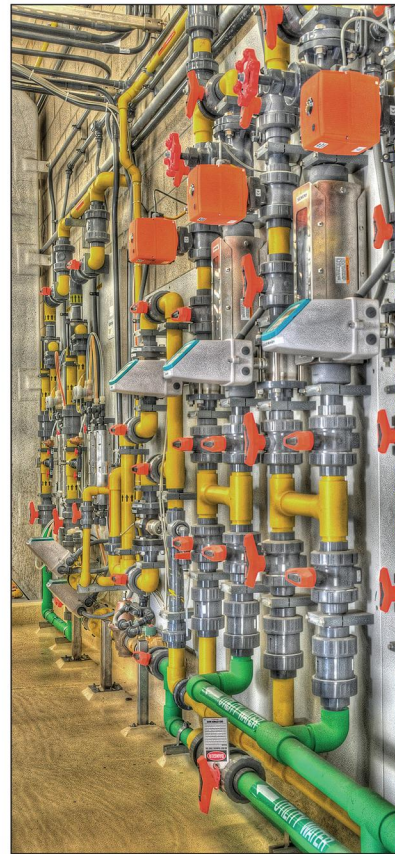
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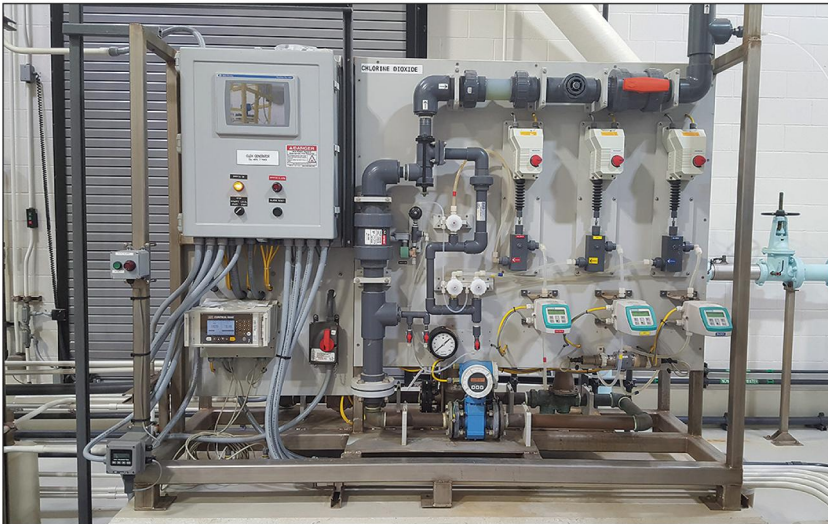
technologies,” said Doug Graham, assistant director of water production. “The main inorganic byproduct of chlorine dioxide, chlorite, looked far more manageable to us than that of ozone’s oxidative effects on bromide to create bromate (MCL 10 ppb). And chlorine dioxide seemed much easier to deal with than the resin beads, the regeneration steps, and managing the brine streams of the various ion exchange systems.”

Central Arkansas Water’s Jack H. Wilson Treatment Plant (see the photographs on page 42) has a maximum treatment capacity of 133 mgd and its main source of raw water is Lake Maumelle. The utility’s other plant, the Ozark Point Treatment Plant (see the photograph on page 42) has a rated capacity of 24 mgd, and its main raw water source is Lake Winona (its other source is Lake Maumelle). The utility has a regulating reservoir that both lakes’ waters can go into and be drawn from by either plant, separately or simultaneously when needed. If one of the plants is treating less than its main source is providing, it goes into the regulating reservoir. Conversely, if more water is needed than what is being supplied, the plants can draw from the reservoir. ClO_2 is typically fed for preoxidation at a 1.0 mg/L dosage rate at the Ozark Point Treatment Plant and at 0.5–0.6 mg/L at the Jack H. Wilson Plant (see the photograph on page 42). At both plants, the chlorine dioxide is applied to the raw water approximately 300 ft before entering a rapid mix stage where aluminum sulfate and lime are added before flocculation,

ultimately moves into the distribution system. The major difference in treatment schemes between the two plants is that the Jack H. Wilson Plant uses conventional anthracite filters, while the Ozark Point facility uses biologically active carbon (BAC) filters.



The San Diego Otay Water Treatment Plant’s automatic flow-paced batch system ClO_2 generators using chlorine gas and sodium chlorite are currently in the final stages of modification to three chemical systems to accept the use of electrolytic-generated 0.8% bleach. Photo by Jim McVeigh, City of San Diego, Calif.



Top: Central Arkansas Water's Jack H. Wilson Treatment Plant has a maximum treatment capacity of 133 mgd. Middle: Central Arkansas Water's Ozark Point Treatment Plant has a rated capacity of 24 mgd. Bottom: The two Central Arkansas plants use three chemical chlorine dioxide generators. The self-tuning, automatic generators produce chlorine dioxide in a two-stage reaction process under vacuum conditions (bottom). *Photos courtesy of Central Arkansas Water.*

“At the Ozark Plant, we have different organic loadings coming in from Lake Winona,” Graham said. “That lake water has a much higher formation potential for THMs, so we’re using both the chlorine dioxide and the biologically active carbon filters to help reduce as much of the THM precursors and TOC as possible. Chlorine dioxide doesn’t remove the TOC, but it oxidizes and changes its molecular structure, and then we let coagulation and the filters remove as much of it as possible. This combination has been quite effective for us.”

“We also receive additional benefits from using chlorine dioxide,” Graham added. Specifically, ClO_2 reacts rapidly with soluble forms of iron and manganese to form precipitates that can be removed through coagulation, sedimentation, and filtration. “In the fall, our lakes roll over and we get elevated amounts of inorganics coming in off the bottoms as well as taste and odor compounds,” he said. “By using chlorine dioxide at the front end of our plants, we don’t have to feed another oxidizer or anything additional. Feeding just the one chemical takes care of three things: DBP precursors at the front end of the plants, oxidation of inorganics (like manganese and iron), and taste and odors.”

Graham added, “Before we used chlorine dioxide, we fed potassium permanganate out at the different iron and manganese sources, miles away from our treatment plants, so there would be plenty of time for it to react before it reached the plants. Now, we simply bump up the chlorine dioxide dose a very small amount, if necessary.”

PRACTICAL RECOMMENDATIONS

Graham recommends that utilities run a comprehensive pilot study before deciding to use ClO_2 . “You want to be sure it’s right for your water because all waters are different,” he said. “A pilot study will tell you how chlorine dioxide is going to affect the chemistry of your water,

which is important because you want to try to minimize any impacts or unintended consequences of feeding a new chemical. Then after pilot testing, if you decide to go with chlorine dioxide, I recommend looking very closely at the different generation and feed equipment, the support you can get, and the track record of the equipment providers.”

McVeigh relayed that “because ClO₂ results in some inorganic byproduct chlorite ion (the latter having a USEPA MCL limit of 1 mg/L entering the distribution system), the potential exists to add an acute regulated contaminant to our water. I think the smartest thing for us was our decision to add GAC in our filters because it controls the chlorite ion very efficiently. You can use a chemical addition, such as ferrous chloride or ferrous sulfate, to deal with the chlorite, but I would recommend GAC if you can afford it. In the long run, operationally, it’s a much better approach.”

Lowe says it’s important to have a high level of technical competence to operate and monitor equipment, chemicals, and residuals. “Operators of these systems need to be well trained,” he said. “It’s extremely important, especially if the plant is utilizing chlorine dioxide to meet its disinfection credit, that operators know how to do it right, because disinfection is a serious public health issue. Chlorine dioxide use is probably not for everybody,” he said. “For example, it may not be a good fit for real small systems with one part-time operator.”

Lowe recommends that potential users become fully aware of all that is involved in generating and using ClO₂, not just with the operations and maintenance of the system, but also the safety and analytical aspects of it. “Many in our industry understand the benefits of chlorine dioxide, but many need to better understand that these systems need to be operated and maintained at optimal levels,” he said. “I prefer the lease agreement situation we have with

our technology provider where a technician comes to our plant on a monthly basis, runs an efficiency test on our generator and equipment, and makes sure everything is the way it needs to be to stay in good operating condition. Plus, if there’s ever a problem, they have to respond promptly within a set time period.”

ABOUT THE AUTHOR



Glenn W. Holden currently serves as a business development and corporate accounts manager of chlorine dioxide and disinfection products with the Municipal Services Division of Evoqua Water Technologies, 181 Thorn Hill Rd., Warrendale, PA 15086 USA; glenn.holden@evoqua.com. He has also served as a global product manager of chlorine dioxide products with Evoqua & Siemens. He has more than 35 years of experience in the industry, having served in various domestic and international roles in both the municipal and industrial water treatment fields for companies such as Evoqua WT, Siemens WT, Altivia, Pureline Treatment Systems, Betz Dearborn, and Vulcan Chemical Technologies. He holds a BS degree in chemistry with extensive chemical engineering experience, and he is a recipient of several chlorine-dioxide-based process and applications patents. Holden is an active member of AWWA and the American Chemistry Council’s Chlorine Dioxide Industry Panel.

<https://doi.org/10.5942/jawwa.2017.109.0089>

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