Chlorine Dioxide Requires Reliable Monitoring Protocols

Disinfecting drinking water with chlorine dioxide is becoming more common as utilities seek to reduce disinfection by-product formation in finished water and enhance coagulation, but monitoring can be tricky.

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ADVANCED REAGENTLESS monitoring technology—combined with key operations and maintenance (O&M) protocols—is helping water treatment facilities accurately detect and analyze chlorine dioxide (ClO_2) as low as 0.01 mg/L, even in treatment stages with wide variances in pH, turbidity, flow, pressure, and temperature. The technology is helping the Wemlinger Water Treatment Plant in Aurora, Colo., meet its ClO_2 monitoring needs.

Listed in the US Environmental Protection Agency's Long-Term 2 Enhanced Surface Water Treatment Rule as a microbiological disinfection tool to inactivate *Giardia* cysts and *Cryptosporidium* oocysts, ClO_2 forms significantly fewer halogenated disinfection by-products (DBPs) than free chlorine generates and doesn't react with ammonia to form less-active chloramines. However, ClO_2 does form chlorite (ClO_2^-), a regulated by-product, and chlorate.

In using ClO_2 for disinfection credit, underdosing can lead to inadequate disinfection, and overdosing can also have negative impacts, including formation of unacceptable chlorite and chlorate ions. Accurate and responsive ClO_2 monitoring and control is critical to avoid negatively affecting the treatment process and finished water quality.

MONITORING METHODS

Accurately measuring ClO_2 residual as a process control parameter can be difficult because of changes in sample pH and interference from chlorine and other oxidizing disinfectants. Historically, error may have been introduced by a standard method of analysis that provides a ClO_2 detection limit of 0.1 mg/L. The detection limit should be lower, because the ideal range of ClO_2 is 0.02–0.08 mg/L in finished water. Because of this and other difficulties, traditional methods may not provide an appropriate accuracy below 0.1 mg/L ClO_2. One alternative is to measure ClO_2 by a reagentless electrochemical method, which uses a stable membrane that is resistant to most interference and independent of changes in sample pH.

The membrane provides electrochemical specificity for the passage of ClO_2 molecules. The diffusion of ClO_2 across this membrane is rapid, and the sensor uses an amperometric technique for detection (Figure 1). Once diffused across the membrane, ClO_2 undergoes an electrochemical reaction in the electrolyte solution, where ClO_2 is reduced to chloride ions and water. Each chloride ion reacts with silver (I) from a reference electrode to form silver chloride and subsequently releases one electron. Five electrons are generated in this reaction. The current generated through the electron release is measured and is directly proportional to the concentration of ClO_2 in the sample.

The rate of diffusion across this membrane is temperature sensitive, and the result requires temperature compensation.

Figure 1. ClO_2 Probe Operation

Molecules in a sample diffuse through a porous membrane to a narrow region between the membrane and a cathode that contains the electrolyte.

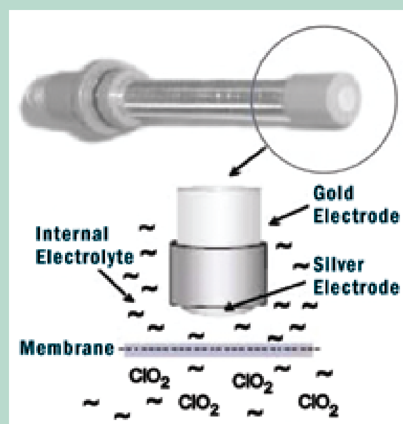
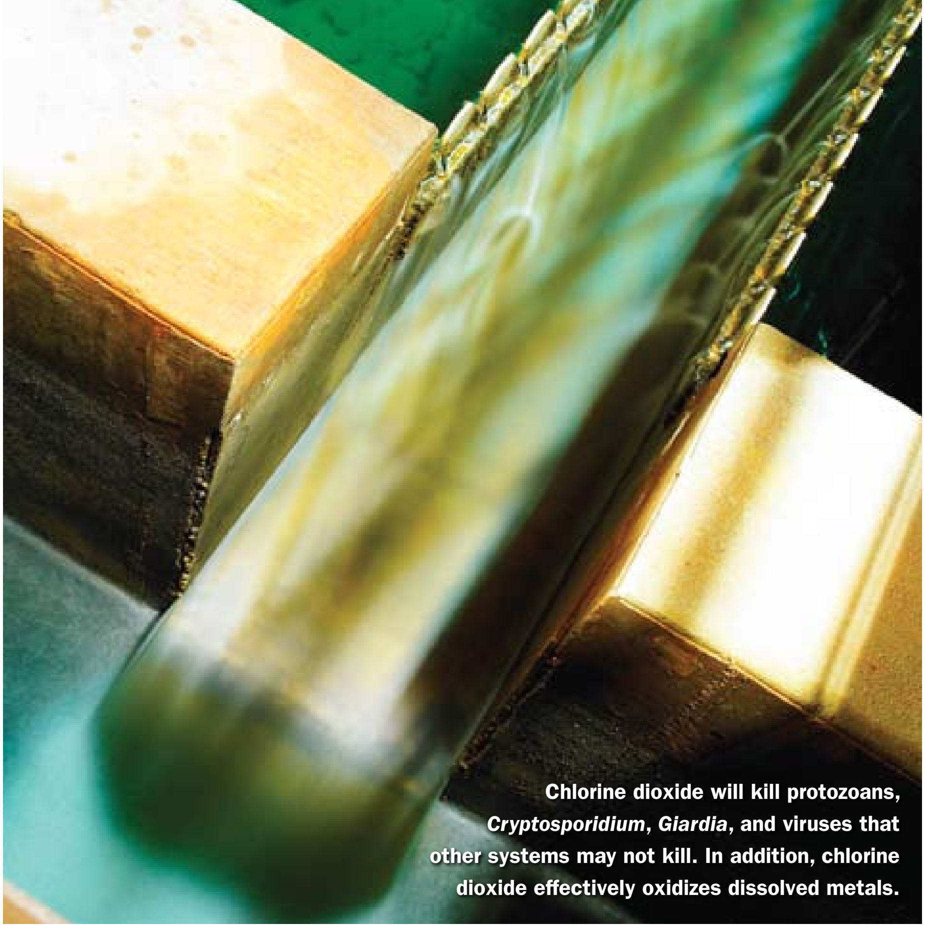


FIGURE AND PHOTOGRAPHS: HACH, USA



Chlorine dioxide will kill protozoans, *Cryptosporidium*, *Giardia*, and viruses that other systems may not kill. In addition, chlorine dioxide effectively oxidizes dissolved metals.

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This new technology incorporates temperature correction algorithms that are applied to the raw measurement value to produce an accurate ClO_2 measurement in the sample stream. The technology can routinely deliver an accurate value in the μg/L range.

FIELD USE

The reagentless sensor is used to successfully monitor ClO_2 at various stages of treatment within the 80-mgd Wemlinger Water Treatment Plant, which uses ClO_2 as its primary disinfectant. The facility is a direct filtration plant, with 15 filters that receive chemically dosed water from six flocculation basins. The facility treats surface water of widely ranging raw-water quality. In the past, the Wemlinger plant struggled with using process ClO_2 meters and their performance at different sampling points. Several instrument designs were tested, including reagentless meters, all of which resulted in unsatisfactory performance because of various factors, including plugged sample lines and flow blocks, rapidly fouled membranes, sample-flow and pressure changes, and poor temperature compensation. Requiring excessive daily maintenance and inspection, the instruments fell short of the plant's performance requirements.

Many process analytical methods demonstrate high performance in highly treated or filtered waters. When ClO_2 is injected in prefiltered waters for contact time (CT) credit, the disinfectant must be monitored in raw and settled water immediately prior to filtration, because the ClO_2 concentration may decrease across the filters. In these applications, the analyses may be subject to wide variances in pH, turbidity, flow, pressure, and temperature, any of which can affect accurate measurement.

MONITORING REQUIREMENTS

While evaluating reagentless ClO_2 monitoring technology, the plant achieved overall success because its O&M staff worked closely with the sensor manufacturer to develop and implement the protocols required to achieve accurate, reliable monitoring. The first ClO_2 monitoring point is located immediately before flocculation, after raw water is injected with chlorine, ClO_2, aluminum sulfate (alum), and cationic polymer, and then flash mixed. This is the most challenging point for analysis because of concerns about turbidity, large debris, and the potential for coagulated solids to plug the flow block housing the ClO_2 sensor (Figure 2, page 20).

To address these concerns, a large 40-mesh screening filter was placed upstream from the instrument flow block to ensure flow to the sensor could be maintained within the specified range. At this injection point, ClO_2 residual is expected to be at its highest value—between 70 percent and 80 percent of the initial dose—by the time it reaches this first sampling point. If a deviation from this range is observed, an operator inspects the ClO_2 feed system and, if the feed system is operating correctly, adjusts the dosage accordingly.

The second ClO_2 monitoring point is located immediately before filtration, where the water has a higher concentration of coagulated solids that could plug sample lines and foul the sensor membrane. The plant uses this value to determine ClO_2 decay rate, which affects CT calculation, as ClO_2 progresses through this phase of treatment.

The third and final monitoring point is in the combined filter effluent prior to adding chlorine and ammonia. Here the goal is for ClO_2 concentration to be less than 0.1 mg/L. Sampling at three locations is required to meet part of the plant's established CT requirements and to maintain chlorine throughout the treatment process for 3-log inactivation of *Giardia*. The Surface Water Treatment Rule also requires a 0.01 mg/L ClO_2 detection limit for CT calculations.

OPERATION AND MAINTENANCE PROTOCOLS

The trial demonstrated that accurate ClO_2 analysis was possible with appropriate sampling, maintenance, and calibration procedures at the three sampling locations. Several steps ensure the desired level of performance.

Step 1—Correct Sampling Points. The plant continuously monitors and confirms that the initial presence of ClO_2 after chemical addition to raw water is followed by subsequent decay as it proceeds downstream through treatment.

Step 2—Membrane Replacement. Although the manufacturer recommended a semiannual change, the plant staff

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instituted a monthly membrane replacement protocol. Membrane replacement cost is nominal and ensures decreased fouling. Such maintenance is minimal from a time and labor perspective.

Step 3—Adequate Sample Flow. The performance of membrane-based analytical systems is subject to flow changes. The plant carefully follows manufacturer requirements regarding minimum–maximum sample flow rates to protect against plugging. Drain lines must also be installed with adequate grade to effectively remove the volume of sample as it leaves the flow block.

Step 4—Proper Temperature Calibration. ClO_2 measurement is temperature sensitive. The reagentless ClO_2 monitor has a temperature compensation function, which works best when the temperature sensor is properly calibrated. During calibration, the sample temperature should be measured from where the sample flows through the flow block and is entered into the instrument controller prior to calibrating ClO_2 concentration.

Step 5—ClO_2 Calibration. Calibration is accomplished through comparison with a bench analysis of a grab sample, which should be taken when the sample exits the flow block. The bench method should have the range and sensitivity that matches the application range of the process instrument, and the analysis should be conducted without delays because of the analyte's volatility.

The Wemlinger plant calibrates the ClO_2 analyzer according to Standard Methods 4500-ClO_2-D. However, the plant staff has changed one test methodology, which has been approved by the local regulatory agency. Technicians add more glycine reagent when the sample temperature drops below 10°C. The basic method requires a stated reagent quantity to be added for a temperature of 25°C; however, because of decreased water temperature, the additional reagent allows colorimetric reaction for ClO_2 to proceed but suppresses interfering reactions.

Figure 2. ClO_2 Sensor Housing

A large screening filter is placed upstream from the instrument flow block to ensure flow to the sensor is maintained within a specified range.

Two alternative bench methods that specifically monitor levels below 0.1 mg/L can be used as the calibration reference: the Chlorophenol Red method, which is appropriate for a range of 0–1 mg/L ClO_2, and the Amaranth method, which has a better sensitivity and lower detection limit.

Step 6—Inspection and Maintenance Protocols. Wemlinger plant personnel have found this step to be one of the most important to accurately, reliably, and continuously measure ClO_2 in process water samples. Maintenance protocols are based on the location of each sensor. Key protocols involve routine inspections for sample flow, sample draining, and plugged lines. To avoid sensor membrane fouling, membranes and the electrolyte solution are replaced monthly.

MEETING MONITORING NEEDS

When ClO_2 was adopted as the primary disinfectant, the Wemlinger Water Treatment Plant was required to find a process analytical method that could be used reliably at various points throughout the treatment process. Successful monitoring involved using a reagentless analyzer coupled with appropriate sampling and maintenance protocols. Success in evaluating the technology and establishing and implementing proper O&M protocols are helping the plant meet its ClO_2 monitoring needs.

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