

Treatment of Industrial Plant Water with Chlorine Dioxide

Chlorine dioxide (ClO₂) is effective as both a disinfectant and an oxidant in water treatment. Chlorine dioxide is a broad-spectrum microbiocide effective over a wide pH range. Unlike chlorine, chlorine dioxide does not react with organic materials to form trihalomethanes. Chlorine dioxide is also non-reactive with ammonia-nitrogen and with most treatment chemicals (corrosion and scale inhibitors) present in process water systems.

Application Description

Bacteria present in plant influent water cause fouling in cooling system exchangers, cooling tower film fill, ion exchange media, and creates health hazards in water used for drinking. Treatment of plant influent water provides a clean, relatively bacteria-free water source for the plant processes.

Microbiological control is a major problem not just in the plant cooling water system but also in ion exchange media. The bacteria that get through the treatment process are small enough to get inside the resin bead or the reverse osmosis (RO) membrane. A bacterial community is established which continues to grow and is relatively impervious to normal methods of control. As the bacterial community flourishes, it restricts movement of fluids through the membrane or resin increasing the back pressure, which results in a decrease in run lengths and a reduction in system performance. Thus, control of microbiological activity is essential to maintaining long-term performance in these systems.

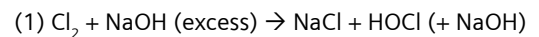
Treatment Alternatives

Gaseous chlorine has been used historically because it is relatively inexpensive and is a very effective microbiocide. Recent trends away from the use of gaseous chlorine have led many plants to consider alternatives. Such alternatives include sodium hypochlorite (bleach), ozone, bromine and chlorine dioxide.

Bleach

Bleach is a common replacement for chlorine gas.

Bleach is essentially chlorine gas reacted with an excess of free caustic as shown below:



For every molecule of HOCl required to meet the demand of the water, one sodium ion and one chloride ion is also added from the balanced chemical equation (1).

The active component of bleach is hypochlorous acid, and therefore bleach follows the same reaction chemistry as chlorine gas dissolved in water. The pH and the degree of organic contamination present in the water will have direct impact on the feed rate of bleach required to adequately disinfect the influent water. At high pH's (>9) such as those found in lime softened makeup water, hypochlorous acid is essentially completely dissociated to hypochlorite ion, which is relatively ineffective as a microbiocide. The presence of free ammonia or organic contamination will result in an additional bleach demand that will have to be overcome to maintain a free chlorine residual.

Bleach programs are often more expensive on a total program cost basis in contaminated systems than alternatives such as chlorine dioxide because of the many side reactions and limited stability.

Application Note

Chlorine Dioxide

Chlorine dioxide is effective in the control of microbiological growths in industrial process waters under conditions unfavorable to chlorine or chlorine alternatives.

Chlorine dioxide does not significantly hydrolyze in water retaining its biocidal activity over a broad pH range. It is a very selective oxidizer and will not react with many of the compounds with which chlorine reacts. It is particularly effective in systems having a high pH, ammonia-nitrogen contamination, persistent slime problems, or where the microbial contamination is aggravated by contamination with vegetable or mineral oils, phenols or other high chlorine-demand producing compounds.

In general, chlorine dioxide can be used for pretreatment of demineralizer resins. However, some RO membrane types are very sensitive to oxidizers. Before attempting to use chlorine dioxide for RO re-treatment, check with the membrane or resin manufacturer and your Wallace & Tiernan Representative for compatibility.

Advantages of Chlorine Dioxide

Chlorine dioxide has unique performance characteristics that make it the ideal choice for microbiological control in many cases.

- Chlorine dioxide is effective over a broad pH range.
- Chlorine dioxide may extend demineralizer run length times.
- Chlorine dioxide does not react with organics to form THMs.
- Chlorine dioxide does not react with ammonia-nitrogen.
- Chlorine dioxide is effective at low dose rates in contaminated systems compared to alternative biocides.
- Chlorine dioxide does not react with triazole corrosion inhibitors.
- Chlorine dioxide is very effective for biofilm and algae control.
- Chlorine dioxide may reduce the requirement for microbiological control chemicals in the cooling water.

Feed Requirements

The required dosages will vary with water conditions, the severity of contamination and the degree of control desired.

The required chlorine dioxide residual concentrations range between 0.1 and 5.0 mg/L. Chlorine dioxide may be applied either continuously or intermittently. The typical chlorine dioxide residual concentration range is 0.1 - 1.0 mg/L for continuous doses, and 0.1 - 5.0 mg/L for intermittent doses.

The minimum acceptable residual concentration of chlorine dioxide is 0.1 mg/L for a minimum one-minute contact time.

For more information on dosage requirements specific to your application, contact your Siemens Representative.

Method of Feed

Chlorine dioxide is a gas produced by activating sodium chlorite with an oxidizing agent or an acid source. Sodium chlorite is converted to chlorine dioxide through a chlorine dioxide generator and applied as a dilute solution. Chlorine dioxide solutions should be applied to the processing system at a point and in a manner which permits adequate mixing and uniform distribution. The feed point should be well below the water level to prevent volatilization of the chlorine dioxide. Avoid co-incident feeding of chlorine dioxide with lime or powdered activated carbon.

Chlorine Dioxide Analysis

Residual chlorine dioxide concentrations must be determined by substantiated methods which are specific for chlorine dioxide. Two suitable methods are published in *Standard Methods for the Examination of Water and Wastewater*¹:

4500-ClO ₂ D	DPD-Glycine Method
4500-ClO ₂ E	Amperometric Method II

References

1. *Standard Methods for the Examination of Water and Wastewater*, APHA, AWWA and WEF, Washington, D.C. (20th Ed., 1998).

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