CONTROL OF THMs WITH CHLORINE DIOXIDE

Chlorine dioxide (ClO_2) is effective as both a disinfectant and an oxidant in water and wastewater treatment. Its selective reactivity makes chlorine dioxide a powerful oxidizing agent useful in many water treating applications for which chlorine and other oxidizing agents are unsuitable. Unlike chlorine, chlorine dioxide does not react with naturally occurring organic materials to form trihalomethanes (THMs). Chlorine dioxide aids in reducing the formation of TTHMs and haloacetic acids (HAA) by oxidizing precursors, and by allowing the point of chlorination to be moved farther downstream in the plant after coagulation, sedimentation, and filtration have reduced the quality of natural organic material (NOM)[1].

Application Description

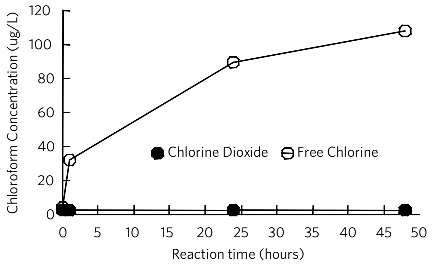
THMs are produced when free chlorine or bromine reacts with natural organic matter in the water. The identification of THMs in chlorinated water supplies led to concerns over their potential health effects including reproductive effects and the classification of chloroform, bromodichloromethane and certain other disinfection by-products (DBPs) as carcinogens.

The final Disinfectants and Disinfection Byproducts Rule[2] (DBPR) set a maximum contaminant level (MCL) of 0.08 mg/L for total trihalomethanes (TTHM) in drinking water, and extended the MCL to all size systems. In addition, a new MCL of 0.06 mg/L was established for haloacetic acids (HAA5).

In contrast with chlorine, the reactions of chlorine dioxide with humic substances (the precursors of trihalomethanes) do not result in the formation of THMs. Three well-documented case histories: Evansville, Indiana[3], Hamilton Ohio[4], and Galveston, Texas[5] demonstrate the versatility and effectiveness of chlorine dioxide for THM control in municipal water treatment systems.

Figure 1

Chloroform production in water containing 5 mg humic acid dosed with chlorine dioxide or free chlorine



Many treatment methods have been developed to remove THMs once they have been formed by chlorine treatment. However, chlorine dioxide treatment method is superior in preventing or substantially reducing their initial formation. Figure 1 compares the effect on chloroform formation when water containing humic acid is treated with chlorine dioxide and chlorine.

Chlorine dioxide prevents THM formation by disinfecting without chlorinating organic materials and by oxidizing the organic THM precursors. This means that pretreatment with chlorine dioxide has an inhibiting effect on THM formation when chlorine is subsequently used for treatment.

Chlorine dioxide is not only economical, but is also effective in preoxidation and disinfection as a replacement for prechlorination. Pretreatment with chlorine dioxide oxidizes the THM precursors, which are removed during coagulation, settling, and filtration before final chlorination. This modification of standard chlorination practices can result in a 50-70% decrease in TTHMs in the finished water. For this reason, the EPA has identified chlorine dioxide as an alternative or supplemental oxidant-disinfectant that is one of the most suitable for TTHM treatment and control[1].

Feed Requirements

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

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. Do not apply sodium chlorite directly to potable water. Avoid co-incident feeding of chlorine dioxide with lime or powdered activated carbon.

Chlorine Dioxide Analysis

In addition to other monitoring requirements, the USEPA also requires that water systems using chlorine dioxide for disinfection or oxidation must monitor their system for chlorine dioxide and chlorite.

Chlorine Dioxide: For compliance monitoring for residuals of chlorine dioxide, one of the two approved methods specified in 40 CFR §141.131(c) must be used:

DPD Method, 4500-ClO_2 D, and
Amperometric Method II, 4500-ClO_2 E.[6]

Where approved by the state, systems may also measure residual disinfectant concentrations of chlorine dioxide by using DPD colorimetric test kits.

Sodium Chlorite: For compliance monitoring for chlorite, water systems must use one of three approved methods specified in 40 CFR §141.131(b):

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

Amperometric Method II, 4500-ClO_2 E
Ion Chromatography, EPA Method 300.0[7], or
Ion Chromatography, EPA Method 300.1[8].

The regulations further specify that Amperometric Titration may be used for routine daily monitoring of chlorite at the entrance to the distribution system, but that Ion Chromatography must be used for routine monthly monitoring of chlorite and for additional monitoring of chlorite in the distribution system.

References

[1] USEPA, "Alternative Disinfectants and Oxidants Guidance Manual," EPA/815/R-99/014, (April 1999).

[2] Federal Register, National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts, 63 FR 69389 (December 16, 1998).

[3] Lykins, B.W., Jr. and Griese, M.H., "Using Chlorine Dioxide for Trihalomethane Control," JAWWA, 78, 88 (1986).

[4] Augenstein, H.W., "Use of Chlorine Dioxide to Disinfect Water Supplies," JAWWA, 66, 716 (1974).

[5] Myers, G.L., et al., "Control of Trihalomethanes and Taste and Odor at Galveston County Water Authority," Proc. Annual Meeting, AWWA, at Denver, CO, 1667-1675 (1986).

[6] Standard Methods for the Examination of Water and Wastewater, APHA, AWWA and WEF, Washington, D.C. (20th Ed. l998).

[7] Methods for the Determination of Inorganic Substances in Environmental Samples. USEPA. 1993. EPA/600/R-93/100

[8] USEPA Method 300.1, Determination of Inorganic Anions in Drinking Water by Ion Chromatography, Revision 1.0. USEPA. 1997. EPA/600/R-98/118.

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