

# Iron and Manganese Removal with Chlorine Dioxide

Chlorine dioxide (ClO<sub>2</sub>) 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. Chlorine dioxide reacts rapidly with soluble forms of iron and manganese to form precipitates that can be removed through sedimentation and filtration. Preoxidation with chlorine dioxide is effective for iron and manganese removal and improves coagulation and settling, resulting in better filter-run times<sup>1</sup>.

## Application Description

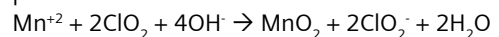
Iron and manganese problems affect far more water systems than almost any other water quality concern. Iron (Fe) and manganese (Mn) exceed recommended secondary maximum concentration levels in roughly 40% of the public water supplies in the United States. These recommended levels of 0.3 mg/L Fe and 0.05 mg/L Mn correspond to approximate concentrations at which iron and manganese will cause aesthetic problems such as colored water, turbidity, staining, and taste.

Iron and manganese may also accelerate biological growths in the distribution system, further exacerbating taste, odor, and color problems. A common preventive treatment is the oxidation of relatively soluble Fe (II) and Mn (II) to insoluble Fe (III) and Mn (III, IV) and the oxidation of any organic-complexing agents. This is followed by removal of the Fe (III) and Mn (III, IV) precipitates by filtration, sometimes preceded by sedimentation. Unoxidized Fe (II) and Mn (II) can be adsorbed by hydrous ferric and manganic coatings on the filter media where the reduced forms are subsequently oxidized to Fe (III) and Mn, (III,IV).

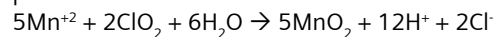
## Manganese

Manganese present in water supplies at concentrations in excess of 0.05 mg/L can cause discoloration in laundered goods, "black" water, water main incrustation, deposits on industrial equipment such as paper machines, debris at water customers' taps and may negatively impact taste in drinking water and beverages. Though chlorine can be used to control these problems, it reacts so slowly that manganese ions may still be in the water distribution system after 24 hours. Chlorine dioxide reacts much more rapidly with manganese, oxidizing it to manganese dioxide (1). Manganese dioxide is insoluble in water and can be filtered out before it leaves the treatment plant. Above pH 7 an average of 2.45 mg/L of chlorine dioxide is required to remove 1 mg/L of manganese. Best results are obtained when the pH is greater than 7.

pH>7



pH<7



Chlorine dioxide has also been reported to oxidize organically bound manganese<sup>2</sup>.

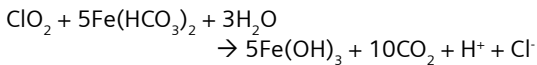


## Application Note

## Iron

Iron from acid waters cannot be tolerated in certain industrial wet processes commonly used in the textile, pulp and paper, and beverage industries. Iron can be a problem, either from the effects of its presence in the water alone, or because iron-bearing water has promoted the growth of iron bacteria.

Chlorine dioxide rapidly oxidizes iron (II) to iron (III), which precipitates as iron hydroxides. Above pH 5, an average of 1.2 mg/L of chlorine dioxide is required to remove 1.0 mg/L of iron. The reaction is favored at neutral-to-alkaline pHs. Above pH 5, the resulting ferric form of iron is 99% removable by a 0.45 micron filter after five minutes.



Chlorine dioxide has also been reported to oxidize organically bound iron<sup>2</sup>. Chlorine dioxide has been used in situations in which iron removal was not the primary concern, but where iron-bearing waters had promoted the growth of iron bacteria in the distribution system. In one particular case, the iron bacteria could not be controlled with excess free chlorine residuals (>5 mg/L), presumably because the organically bound iron was unreactive with the chlorine and yet remained bio-available to the bacteria protected in the attached biofilms. Chlorine dioxide has been used to control these biofilms. It removes the attached bacteria and exposes them to the disinfectant while the iron is being oxidized.

## Feed Requirements

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

## 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<sub>2</sub> D, and  
Amperometric Method II, 4500-ClO<sub>2</sub> E<sup>3</sup>.

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 Wallace & Tiernan Representative.

Amperometric Method II, 4500-ClO<sub>2</sub> E  
Ion Chromatography, EPA Method 300.0<sup>4</sup>, or  
Ion Chromatography, EPA Method 300.1<sup>5</sup>.

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. Stevens, A.A., "Reaction of Chlorine Dioxide", *Environ. Health Perspect.* 46; 101 (1982).
2. Masschelein, W.J., *Chlorine Dioxide: Chemistry and Environmental Impact of Oxychlorine Compounds*, Ann Arbor Sci. Publ., Ann Arbor, MI (1979).
3. *Standard Methods for the Examination of Water and Wastewater*, APHA, AWWA and WEF, Washington, D.C. (20th Ed. 1998).
4. *Methods for the Determination of Inorganic Substances in Environmental Samples*. USEPA. 1993. EPA/600/R-93/100.
5. 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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