



Purate[®] Product Bulletin

**Impact of Chlorine Dioxide and
Chlorite Byproduct on Iron and
Manganese Reduction**

By

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Introduction

Chlorine dioxide is more effective as a disinfectant and oxidant in water treatment compared to chlorine, chloramines or potassium permanganate. In addition, chlorine dioxide and the chlorite byproduct can more effectively reduce natural iron and manganese in source waters because they can oxidize organically bound iron and manganese at lower dosages than other oxidants. Chloramines are unable to oxidize iron or manganese. The chlorine dioxide chemistry has a “one-two punch” in reducing iron and manganese levels in drinking water. The first reaction with soluble iron and manganese occurs with the powerful chlorine dioxide species. After this initial reaction, the chlorite byproduct species is formed which further reacts with the soluble iron and manganese. From these two reactions, the iron and manganese is completely oxidized to an insoluble form, within seconds, where it can be removed by sedimentation or filtration processes (1-7).

Chemistry of Chlorine Dioxide

Chlorine dioxide gas is readily soluble in water and remains in solution as dissolved gas in the pH range of 2 to 10. It does not hydrolyze to any appreciable extent like chlorine, which is weaker as a disinfectant and oxidant especially with increasing pH levels. About 50 to 70 percent of the chlorine dioxide gas reacted in water treatment will result initially in chlorite formation by the following reduction half-reaction (1):



Aieta and Berg (2) showed that oxidizable material such as iron and manganese reduce the ClO_2^- formed in Equation 1 by the following reaction:



Chemistry of Iron Oxidation

Chlorine dioxide and the chlorite byproduct rapidly oxidize Fe (II) to Fe (III), which precipitates in sedimentation or is removed by filtration. After the initial reaction by the chlorine dioxide gas per Equation 1, the chlorite by product (above pH 6.5) continues to convert the soluble Fe (II) to Fe (III) by the following reaction based on Equation 2 (2):



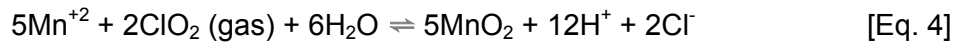
In typical applications of chlorine dioxide to water streams containing iron, manganese, and other oxidizables, about 50-70% of the chlorine dioxide is initially converted to chlorite while simultaneously oxidizing some iron and manganese (Eq. 1). The chlorite formed is capable of continuing to oxidize iron according to Equation 3 where 1 mg of soluble ferrous iron will be converted to 1 mg of ferric iron by 0.3 mg/L of chlorite.



The reactivity of chlorite and the ferrous ion is well known, as it is common practice to use ferrous chloride or ferrous sulfate to reduce or eliminate chlorite in drinking water treated with chlorine dioxide. Dosage rates of 1.0 mg ferrous were demonstrated to remove 0.3 mg chlorite at full-plant scale in El Paso Texas (7). If manganese is available in the source water, then additional chlorine dioxide may be needed to oxidize it from the soluble Mn⁺² form to the precipitated Mn⁺⁴ form.

Chemistry of Manganese Oxidation

As in iron oxidation, chlorine dioxide and chlorite react rapidly with soluble manganese by oxidizing it to manganese dioxide based on the following equation.



Equation 4 indicates about 0.5 mg of chlorine dioxide is required to oxidize 1 mg of soluble manganese to the precipitated form of manganese dioxide, based on the complete reaction of chlorine dioxide and chlorite to chloride. For example, a chlorine dioxide dose of 1.4 mg/L with 1.0 mg/L chlorite residual may oxidize up to 2 mg/L of soluble manganese to the precipitated manganese dioxide state. In the United States, about 40% of raw water supplies exceed 0.3 mg/L iron and 0.05 mg/L manganese. Often, source waters contain both iron and manganese. In these waters, the sum of each parameter should be determined for the total amount of chlorine dioxide and chlorite byproduct required for complete oxidation (1-7).

Chlorine Dioxide Compared to Other Oxidants

Table 1 depicts the superior effectiveness of chlorine dioxide and chlorite as compared to other oxidants in the oxidation of iron and manganese (3).

Table 1. Oxidant Doses Required for Oxidation of Iron and Manganese

Oxidant	Iron (II) (mg/mg Fe)	Manganese (II) (mg/mg Mn)
*Chlorine Dioxide including Chlorite	0.3	0.5
Chlorine	0.62	0.77
Ozone	0.43	0.88
Potassium Permanganate	0.94	1.92

* Chlorine Dioxide alone requires 1.2 mg/mg Fe & 2.45 mg/mg Mn. It is recommended that a bench-scale evaluation be performed to verify the above theoretical oxidant doses required for oxidation of iron and manganese because source water qualities vary widely and may cause different results.



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Application of Chlorine Dioxide

Chlorine dioxide is produced on site from two chemicals (Purate® and 78% Sulfuric Acid) using an Eka Chemicals Inc. SVP-Pure® Generator. The chlorine dioxide solution should be applied at a point in the water treatment process where uniform mixing is possible. It is recommended that the feed point should be well below the water level or at a point where volatilization of the chlorine dioxide gas is prevented. Also, chlorine dioxide should not be fed with lime or powdered activated carbon at the same location.



SVP-Pure® ClO₂ Generator



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About the Author

Dr. Douglas Rittmann has a PhD in Environmental Science and Engineering from the University of Texas at El Paso and he is a registered professional engineer in Texas. He has more than 35 years experience in water and wastewater utility operations. In 1993, he developed the first full-plant use of ferrous chloride to reduce excessive chlorite levels in El Paso Texas.

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