The Chemical Reaction

As an oxidizer chlorine dioxide is very selective. It has this ability due to unique one-electron exchange mechanisms. Chlorine dioxide attacks the electron-rich centers of organic molecules. One electron is transferred and chlorine dioxide is reduced to chlorite (CLO2-).

Chlorine dioxide is more selective as an oxidizer than chlorine. While dosing the same concentrations, the residual concentration of chlorine dioxide is much higher with heavy pollution than the residual concentration of chlorine.

By comparing the oxidation strength and oxidation capacity of different disinfectants, one can conclude that chlorine dioxide is effective at low concentrations. Chlorine dioxide is not as reactive as ozone or chlorine and it only reacts with sulfuric substances, amines and some other reactive organic substances.

In comparison to chlorine and ozone, less chlorine dioxide is required to obtain an active residual disinfectant. It can also be used when a large amount of organic matter is present.

The oxidation strength describes how strongly an oxidizer reacts with an oxidizable substance. Ozone has the highest oxidation strength and reacts with every substance that can be oxidized. Chlorine dioxide is weak, it has a lower potential than hypochlorous acid or hypobromous acid.

The oxidation capacity shows how many electrons are transferred at an oxidation or reduction reaction. The chlorine atom in chlorine dioxide has an oxidation number of +4. For this reason chlorine dioxide accepts 5 electrons when it is reduced to chloride.

Oxidant	Chem Name	Oxidation Strength	Oxidation Capacity
Ozone	O_3	2.07	2 e-
Hydrogen Peroxide	H_2O_2	1.78	2 e-
Hypoclorus Acid	HOCL	1.49	2 e-
Hypobromus Acid	HOBr	1.33	2 e-
Chlorine Dioxide	CLO_2	0.95	5 e-

The following comparisons show what happens when chlorine dioxide reacts.

First, chlorine dioxide takes up an electron and reduces to chlorite: CLO2 + e- ® CLO2-

The chlorite ion is oxidized and becomes a chloride ion: CLO2- + 4H+ + 4e- ® Cl- + 2H2O

These comparisons suggest that chlorine dioxide is reduced to chloride, and that during this reaction it accepts 5 electrons.

The chlorine atom remains, until stable chloride is formed.

This explains why no chlorinated substances are formed. When chlorine reacts it does not only accept electrons; it also takes part in addition and substitution reactions. During these reactions, one or more chlorine atoms are added to the foreign substance (chlorination).

Does chlorine dioxide oxidize in the same way as chlorine? Contrary to chlorine, chlorine dioxide does not react with ammonia nitrogen (NH3) and hardly reacts with elementary amines. It does oxidize nitrite (N02) to nitrate (NO3). It does not react by breaking carbon connections. No mineralization of organic substances takes place. At neutral pH or at high pH values, sulfuric acid (H2SO3) reduces chlorine dioxide to chlorite ions (CLO2-). Under alkalic circumstances chlorine dioxide is broken down to chlorite and chlorate (ClO3-) :

2 CLO2 + 2OH- = H2O + ClO3- + CLO2-

This reaction is catalyzed by hydrogen (H+) ions. The half life of watery solutions of chlorine dioxide decreases at increasing pH values. At low pH, chlorine dioxide is reduced to chloride ions (Cl-).

When bacteria are eliminated, the cell wall is penetrated by chlorine dioxide. Organic substances within cells and on the surface of cell membranes react with chlorine dioxide, causing cell metabolism to be disrupted. Chlorine dioxide also reacts directly with amino acids and the RNA in the cell. This reaction is not dependent on reaction time or concentration. Unlike non-oxidizing disinfectants, chlorine dioxide kills microorganisms even when they are inactive. Microorganisms are unable to build up resistance to chlorine dioxide.