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## Disinfectants Chlorine Dioxide

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### Chlorine dioxide

Chlorine dioxide is mainly used as a bleach. As a disinfectant it is effective even at low concentrations, because of its unique qualities.



Figure 1: sir Humphrey Davy discovered chlorine dioxide in 1814.

#### When was chlorine dioxide discovered?

Chlorine dioxide was discovered in 1814 by Sir Humphrey Davy. He produced the gas by pouring sulphuric acid (H<sub>2</sub>SO<sub>3</sub>) on [potassium chlorate](#) (KClO<sub>3</sub>). Then he replaced sulphuric acid by hypochlorous acid (HOCl). In the last few years this reaction has also been used to produce large quantities of chlorine dioxide. [Sodium chlorate](#) (NaClO<sub>3</sub>) was used instead of potassium chlorate.

$$2\text{NaClO}_3 + 4\text{HCl} \rightarrow 2\text{ClO}_2 + \text{Cl}_2 + 2\text{NaCl} + 2\text{H}_2\text{O}$$

#### What are the characteristics of chlorine dioxide ?

Chlorine dioxide (ClO<sub>2</sub>) is a synthetic, green-yellowish gas with a chlorine-like, irritating odor. Chlorine dioxide is a neutral [chlorine](#) compound. Chlorine dioxide is very different from elementary chlorine, both in its chemical structure as in its behavior. Chlorine dioxide is a small, volatile and very strong molecule. In diluted, watery solutions chlorine dioxide is a free radical. At high concentrations it reacts strongly with reducing agents. Chlorine dioxide is an unstable gas that dissociates into chlorine gas (Cl<sub>2</sub>), [oxygen](#) gas (O<sub>2</sub>) and heat. When chlorine dioxide is photo-oxidized by sunlight, it falls apart. The end-products of chlorine dioxide reactions are chloride (Cl<sup>-</sup>), chlorite (ClO<sup>-</sup>) and chlorate (ClO<sub>3</sub><sup>-</sup>).

At -59°C, solid chlorine dioxide becomes a reddish liquid. At 11°C chlorine dioxide turns into gas. Chlorine dioxide is 2,4 times denser than air. As a liquid chlorine dioxide has a bigger density than water.

#### Can chlorine dioxide be dissolved in water?

One of the most important qualities of chlorine dioxide is its high water solubility, especially in cold water. Chlorine dioxide does not hydrolyze when it enters water; it remains a dissolved gas in solution. Chlorine dioxide is approximately 10 times more soluble in water than chlorine. Chlorine dioxide can be removed by aeration or carbon dioxide.

Table 1: the solubility of chlorine dioxide in water

temperature (°C)	pressure (mm Hg)	solubility (g/L)
25		3.01
25	34,5	1,82
25	22,1	1,13
25	13,4	0,69
40	8,4	2,63
40	56,2	1,60
40	18,8	0,83
40	9,9	0,47
60	106,9	2,65
60	53,7	1,18
60	21,3	0,58
60	12,0	0,26

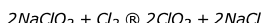
#### How can chlorine dioxide be stored?

The best way to store chlorine dioxide is as a liquid at 4 °C. At this state it is fairly stable. Chlorine dioxide cannot be stored for too long, because it slowly dissociates into [chlorine](#) and [oxygen](#). It is rarely stored as a gas, because it is explosive under pressure. When concentrations are higher than 10% chlorine dioxide in air, there is an explosion hazard. In a watery solution, chlorine dioxide remain stable and soluble. Watery solutions containing approximately 1% ClO<sub>2</sub> (10 g/L) can safely be stored, under the condition that they are protected from light and heat interference. Chlorine dioxide is rarely transported, because of its explosiveness and instability. It is usually manufactured on site.

#### How is chlorine dioxide produced?

Chlorine dioxide is explosive under pressure. It is difficult to transport and is usually manufactured on site. Chlorine dioxide is usually produced as a watery solution or gas. It is produced in acidic solutions of sodium chlorite (NaClO<sub>2</sub>), or sodium chlorate (NaClO<sub>3</sub>). For large installations sodium chlorite, chlorine gas (Cl<sub>2</sub>), sodium hydrogen chlorite (NaHClO<sub>2</sub>) and sulphuric or hydrogen acid are used for the production of chlorine dioxide on site. To produce chlorine dioxide gas, hydrochloric acid (HCl) or chlorine is brought together with sodium chlorite.

The to main reactions are:



Chlorine dioxide as a disinfectant

$2NaOCl + Cl_2 \rightarrow 2ClO_2 + 2NaCl$   
 (Acidified hypochlorite can also be used as an alternative source for chlorine.)

And:  
 $5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O$   
 (One disadvantage of this method is that it is rather hazardous.)

An alternative is:  
 $2NaClO_2 + Na_2S_2O_8 \rightarrow 2ClO_2 + 2Na_2SO_4$

Chlorine dioxide can also be produced by the reaction of sodium hypochlorite with hydrochloric acid:  
 $HCl + NaOCl + 2NaClO_2 \rightarrow 2ClO_2 + 2NaCl + NaOH$

The amount chlorine dioxide that is produced varies between 0 and 50 g/L.

**What are the applications of chlorine dioxide?**

Chlorine dioxide has many applications. It is used in the electronics industry to clean circuit boards, in the oil industry to treat sulfides and to bleach textile and candles. In World War II, chlorine became scarce and chlorine dioxide was used as a bleach. Nowadays chlorine dioxide is used most often to bleach paper. It produces a clearer and stronger fiber than chlorine does. Chlorine dioxide has the advantage that it produces less harmful byproducts than chlorine. Chlorine dioxide gas is used to sterilize medical and laboratory equipment, surfaces, rooms and tools. Chlorine dioxide can be used as oxidizer or disinfectant. It is a very strong oxidizer and it effectively kills pathogenic microorganisms such as fungi, bacteria and viruses. It also prevents and removes bio film. As a disinfectant and pesticide it is mainly used in liquid form. Chlorine dioxide can also be used against anthrax, because it is effective against spore-forming bacteria.

**Chlorine dioxide as an oxidizer**

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 ( $ClO_2^-$ ).

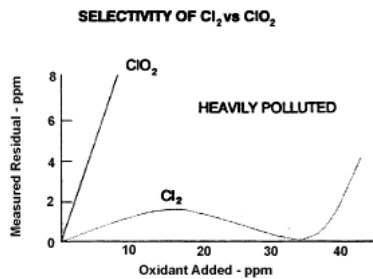


Figure 2: chlorine dioxide is more selective as an oxidizer than chlorine. While dosing the same concentrations, the residual concentration of chlorine dioxide is much higher with heavy pollution than the residual concentration of chlorine.

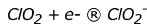
By comparing the oxidation strength and oxidation capacity of different disinfectants, one can conclude that chlorine dioxide is effective at low concentrations. Chlorine dioxide is not as reactive as ozone or chlorine and it only reacts with sulphuric substances, amines and some other reactive organic 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. When we look at the molecular weight, chlorine dioxide contains 263 % 'available chlorine'; this is more than 2,5 times the oxidation capacity of chlorine.

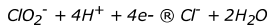
Table 2: the oxidation potentials of various oxidants.

oxidant	oxidation strength	oxidation capacity
ozone (O <sub>3</sub> )	2,07	2 e-
hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	1,78	2 e-
hypochlorous acid (HOCl)	1,49	2 e-
hypobromous acid (HOBr)	1,33	2 e-
chlorine dioxide (ClO <sub>2</sub> )	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:



The chlorite ion is oxidized and becomes a chloride ion:



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.

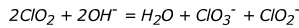
Table 3: the availability of chlorine per mol weight

agent	available chlorine (%)
chlorine (Cl <sub>2</sub> )	100
bleaching powder	35-37
calcium hypochlorite (Ca(OCl) <sub>2</sub> )	99,2
commercial calcium hypochlorite	70-74
sodium hypochlorite (NaOCl)	95,2
industrial bleach	12-15
house hold bleach	3-5
chlorine dioxide	263,0
monochloramine	137,9
dichloramine	165,0

<a href="#">Trichloramine</a>	176,7
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#### **Does chlorine dioxide oxidize in the same way as chlorine?**

Contrary to chlorine, chlorine dioxide does not react with ammonia nitrogen (NH<sub>3</sub>) and hardly reacts with elementary amines. It does oxidize nitrite (NO<sub>2</sub>) to nitrate (NO<sub>3</sub>). It does not react by breaking [carbon](#) connections. No mineralization of organic substances takes place. At neutral pH or at high pH values, sulphuric acid (H<sub>2</sub>SO<sub>3</sub>) reduces chlorine dioxide to chlorite ions (ClO<sub>2</sub><sup>-</sup>). Under alkaline circumstances chlorine dioxide is broken down to chlorite and chlorate (ClO<sub>3</sub><sup>-</sup>) :



This reaction is catalyzed by hydrogen (H<sup>+</sup>) 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<sup>-</sup>).

#### **Does chlorine dioxide produce byproducts?**

Pure chlorine dioxide gas that is applied to water produces less disinfection byproducts than oxidators, such as chlorine. Contrary to ozone (O<sub>3</sub>), pure chlorine dioxide does not produce bromide ([Br<sup>-</sup>](#)) ions into bromate ions (BrO<sub>3</sub><sup>-</sup>), unless it undergoes photolysis. Additionally chlorine dioxide does not produce large amounts of aldehydes, ketones, ketone acids or other disinfection byproducts that originate from the ozonisation of organic substances.

#### **What are the disinfection applications of chlorine dioxide?**

Drinking water treatment is the main application of disinfection by chlorine dioxide. Thanks to its adequate biocidal abilities, chlorine dioxide is also used in other branches of industry today. Example are sewage water disinfection, industrial process water treatment, cooling tower water disinfection, industrial air treatment, mussel control, foodstuffs production and treatment, industrial waste oxidation and gas sterilization of medical equipment.

#### **How does chlorine dioxide disinfect?**

Chlorine dioxide disinfects through oxidation. It is the only biocide that is a molecular free radical. It has 19 electrons and has a preference for substances that give off or take up an electron. Chlorine dioxide only reacts with substances that give off an electron. Chlorine, oppositely, adds a chlorine atom to or substitutes a chlorine atom from the substance it reacts with.

#### **How does disinfection by chlorine dioxide work?**

Substances of organic nature in bacterial cells react with chlorine dioxide, causing several cellular processes to be interrupted. Chlorine dioxide reacts directly with amino acids and the RNA in the cell. It is not clear whether chlorine dioxide attacks the cell structure or the acids inside the cell. The production of proteins is prevented. Chlorine dioxide affects the cell membrane by changing membrane proteins and fats and by prevention of inhalation. When bacteria are eliminated, the cell wall is penetrated by chlorine dioxide. Viruses are eliminated in a different way; chlorine dioxide reacts with peptone, a water-soluble substance that originates from hydrolysis of proteins to amino acids. Chlorine dioxide kills viruses by prevention of protein formation. Chlorine dioxide is more effective against viruses than chlorine or [ozone](#).

#### *Can chlorine dioxide be used against protozoan parasites?*

Chlorine dioxide is one of a number of disinfectants that are effective against Giardia Lambia and Cryptosporidium parasites, which are found in drinking water and induce diseases called 'giardiasis' and 'cryptosporidiosis'. The best protection against protozoan parasites such as these is disinfection by a combination of ozone and chlorine dioxide.

#### *Can microorganisms become resistant against chlorine dioxide?*

Chlorine dioxide as a disinfectant has the advantage that it directly reacts with the cell wall of microorganisms. This reaction is not dependent on reaction time or concentration. In contrast to non-oxidizing disinfectants, chlorine dioxide kills microorganisms even when they are inactive. Therefore the chlorine dioxide concentration needed to effectively kill microorganisms is lower than non-oxidizing disinfectant concentrations. Microorganisms cannot build up any resistance against chlorine dioxide.

#### *Can chlorine dioxide be used against bio film?*

Chlorine dioxide remains gaseous in solution. The chlorine dioxide molecule is powerful and has the ability to go through the entire system. Chlorine dioxide can penetrate the slime layers of bacteria, because chlorine dioxide easily dissolves, even in hydrocarbons and emulsions. Chlorine dioxide oxidizes the polysaccharide matrix that keeps the [bio film](#) together. During this reaction chlorine dioxide is reduced to chlorite ions. These are divided up into pieces of bio film that remain steady. When the bio film starts to grow again, an acid environment is formed and the chlorite ions are transformed into chlorine dioxide. This chlorine dioxide removes the remaining bio film.

#### *What are the disinfection byproducts of chlorine dioxide?*

The reaction process of chlorine dioxide with bacteria and other substances takes place in two steps. During this process disinfection byproducts are formed that remain in the water. In the first stage the chlorine dioxide molecule accepts an electron and chlorite is formed (ClO<sub>2</sub><sup>-</sup>). In the second stage chlorine dioxide accepts 4 electrons and forms chloride (Cl<sup>-</sup>). In the water some chlorate (ClO<sub>3</sub><sup>-</sup>), which is formed by the production of chlorine dioxide, can also be found. Both chlorate and chlorite are oxidizing agents. Chlorine dioxide, chlorate and chlorite dissociate into [sodium](#) chloride (NaCl).

#### **Can chlorine dioxide be used to disinfect drinking water?**

In the 1950's the biocidal capability of chlorine dioxide, especially at high pH values, was known. For drinking water treatment it was primary used to remove inorganic components, for example [manganese](#) and [iron](#), to remove tastes and odors and to reduce chlorine related disinfection byproducts.

For drinking water treatment chlorine dioxide can be used both as a disinfectant and as an oxidizing agent. It can be used for both pre-oxidation and post-oxidation steps. By adding chlorine dioxide in the pre-oxidation stage of surface water treatment, the growth of algae and bacteria can be prevented in the following stages. Chlorine dioxide oxidizes floating particles and aids the [coagulation](#) process and the removal of turbidity from water.

Chlorine dioxide is a powerful disinfectant for bacteria and viruses. The byproduct, chlorite (ClO<sub>2</sub><sup>-</sup>), is a weak bactericidal agent. In water chlorine dioxide is active as a biocide for at least 48 hours, its activity probably outranges that of chlorine. Chlorine dioxide prevents the growth of bacteria in the drinking water distribution network. It is also active against the formation of bio film in the distribution network. Bio film is usually hard to defeat. It forms a protective layer over pathogenic microorganisms. Most disinfectants cannot reach those protected pathogens. However, chlorine dioxide removes bio films and kills pathogenic microorganisms. Chlorine dioxide also prevents bio film formation, because it remains active in the system for a long time.

#### *How much chlorine dioxide should be dosed?*

For the pre-oxidation and reduction of organic substances between 0,5 and 2 mg/L of chlorine dioxide is required at a contact time between 15 and 30 minutes. Water quality determines the required contact time. For post-disinfection, concentrations between 0,2 and 0,4 mg/L are applied. The residual byproduct concentration of chlorite is very low and there are no risks for human health.

#### **Can chlorine dioxide be used to disinfect swimming pools?**

For swimming pool disinfection the combination of chlorine (Cl<sub>2</sub>) and chlorine dioxide (ClO<sub>2</sub>) can be applied. Chlorine dioxide is added to the water. Chlorine is already present in the water as hypochlorous acid (HOCl) and hypochlorite ions (OCl<sup>-</sup>). Chlorine dioxide breaks down substances, such as phenols. The advantages of chlorine dioxide are that it can be used at low concentrations to disinfect water, that it hardly reacts with organic matter, and that little disinfection byproducts are formed.

#### *How much chlorine dioxide should be dosed?*

The amount of disinfectant required needs to be determined first. This amount can be determined by adding disinfectant to the water and measuring the amount that remains after a defined contact time. The amount of chlorine dioxide that is dosed depends upon the contact time, the pH, the temperature and the amount of pollution that is present in the water.

**Can chlorine dioxide be used to disinfect cooling towers?**

Chlorine dioxide is used to disinfect the water that flows through cooling towers. It also removes bio films and prevents bio film formation in cooling towers. The removal of bio film prevents damage to and corrosion of equipment and piping and causes the pumping efficiency to be improved. Chlorine dioxide is also effective in removing [Legionella](#) bacteria. The circumstances in cooling towers are ideal for the growth of Legionella bacteria. Chlorine dioxide has the advantage that it is effective at a pH between 5 and 10 and that no acids are required to adjust the pH.

**What are the advantages of the use of chlorine dioxide?***Advantages*

The interest in the use of chlorine dioxide as an alternative for or addition to chlorine for the disinfection of water has increased in the last few years. Chlorine dioxide is a very effective bacterial disinfectant and it is even more effective than chlorine for the disinfection of water that contains viruses. Chlorine dioxide has regained attention because it is effectively deactivates the chlorine-resistant pathogens Giardia and Cryptosporidium. Chlorine dioxide removes and prevents bio film. Disinfection with chlorine dioxide does not cause odor nuisance. It destroys phenols, which can cause odor and taste problems. Chlorine dioxide is more effective for the removal of iron and manganese than chlorine, especially when these are found in complex substances.

*Does chlorine dioxide form chlorinated disinfection byproducts?*

The use of chlorine dioxide instead of chlorine prevents the formation of harmful halogenated disinfection byproducts, for example trihalomethanes and halogenated acidic acids. Chlorine dioxide does not react with ammonia nitrogen, amines or other oxidizable organic matter. Chlorine dioxide removes substances that can form trihalomethanes and improves coagulation. It does not oxidize bromide into bromine. When bromide containing water is treated with chlorine or ozone, bromide is oxidized into bromine and hypobromous acid. After that these react with organic material to form brominated disinfection byproducts, for example bromoform.

*Is the chlorine dioxide concentration needed for sufficient disinfection high?*

The use of chlorine dioxide reduces the health risk of microbial pollutions in water and at the same time decreases the risk of chemical pollutions and byproducts. Chlorine dioxide is a more effective disinfectant than chlorine, causing the required concentration to kill microorganisms to be much lower. The required contact time is also very low.

*Does the pH value influence chlorine dioxide efficiency?*

Contrary to chlorine, chlorine dioxide is effective at a pH of between 5 and 10. The efficiency increases at high pH values, while the active forms of chlorine are greatly influenced by pH. Under normal circumstances chlorine dioxide does not hydrolyze. This is why the oxidation potential is high and the disinfection capacity is not influenced by pH. Both temperature and alkalinity of the water do not influence the efficiency. At the concentrations required for disinfection, chlorine dioxide is not corrosive. Chlorine dioxide is more water-soluble than chlorine. In the last few years better and safer methods for chlorine dioxide production have been developed.

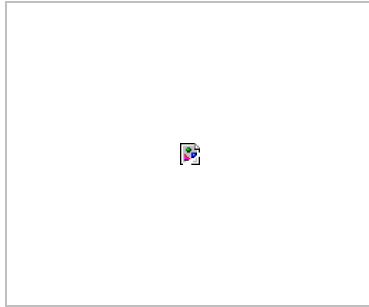


Figure 3: the influence of pH on efficiency is larger for chlorine than for chlorine dioxide

*Can chlorine dioxide be used combined with other disinfectants?*

Chlorine dioxide can be used to reduce the amount of trihalomethanes and halogenated acidic acids, formed by the reaction of chlorine with organic matter in water. Before the water is chlorinated, chlorine dioxide is added. The amount of ammonium in the water decreases. The chlorine that is added afterwards, oxidizes chlorite into chlorine dioxide or chlorate. Ozone can also be used to oxidize chlorite ions into chlorate ions. By the use of chloramines, nitrification can take place in the distribution network. To regulate this, chlorine dioxide is added.

Byproducts control by chlorine dioxide can take place in combination with adequate disinfection, especially the reduction of bromine containing trihalomethanes and halogenated acidic acids that originate from the reaction of bromine containing water with natural organic matter. Chlorine dioxide itself combined with bromine does not form hypobromous acid or bromate, while chlorine and ozone do. Chlorine dioxide has excellent anti-microbiological qualities without the non-specific oxidation of ozone.

**What are the disadvantages of the use of chlorine dioxide?***Is chlorine dioxide explosive?*

When producing chlorine dioxide with sodium chlorite and chlorine gas, safety measures must be taken with regard to the transport and use of chlorine gas. Sufficient ventilation and gas masks are required. Chlorine dioxide gas is explosive. Chlorine dioxide is a very unstable substance; when it comes in contact with sunlight, it decomposes. During chlorine dioxide production processes, large amounts of chlorine are formed. This is a disadvantage. Free chlorine reacts with organic matter to form halogenated disinfection byproducts.

*Does chlorine dioxide form byproducts?*

Chlorine dioxide and its disinfection byproducts chlorite and chlorate can create problems for dialysis patients.

*Is chlorine dioxide effective?*

Chlorine dioxide is generally effective for the deactivation of pathogenic microorganisms. It is less effective for the deactivation of rotaviruses and E. coli bacteria.

*What are the costs of chlorine dioxide use?*

Chlorine dioxide is about 5 to 10 times more expensive than chlorine. Chlorine dioxide is usually made on site. The costs of chlorine dioxide depend upon the price of the chemicals that are used to produce chlorine dioxide. Chlorine dioxide is less expensive than other disinfection methods, such as ozone.

**What are the health effects of chlorine dioxide?***Chlorine dioxide gas*

While using chlorine dioxide as a disinfectant, one has to keep in mind that chlorine dioxide gas can escape from a watery solution containing chlorine dioxide. Especially when disinfection takes place in a sealed space, this can be dangerous. When chlorine dioxide concentrations reach 10% or more in air, chlorine dioxide becomes explosive. Acute exposure of the skin to chlorine that originates from the decomposition of chlorine dioxide, causes irritations and burns. Eye exposure eyes to chlorine dioxide causes irritations, watering eyes and a blurry sight. Chlorine dioxide gas can be absorbed by the skin, where it damages tissue and blood cells. Inhalation of chlorine dioxide gas causes coughing, a sore throat, severe headaches, lung oedema and bronchio spasma. The symptoms can begin to show long after the exposure has taken place and can remain for a long time. Chronic exposure to chlorine dioxide causes bronchitis. The health standard for chlorine dioxide is 0,1 ppm.

*Development and reproduction*

Chlorine dioxide is thought to have effects on reproduction and development. However, there is too little evidence to ground this thesis. Further research is required.

*Mutagenity*

The Ames test is used to determine the mutagenity of a substance. The Ames test uses Salmonella bacteria that are genetically modified. No bacterial colonies are formed, unless they come in contact with a mutagenic substance that alters genetic material. Tests show that the presence of 5-15 mg/L ClO<sub>2</sub> increases the mutagenity of water. It is difficult to prove the mutagenity of chlorine dioxide and chlorine dioxide byproducts, because the substances are biocides. Biocides usually kill the indicator organisms that are used to determine mutagenity.

Check here for more information about [chlorine in freshwater ecosystems](#)

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