ERCOPure™

International Dioxcide
A division of ERCO Worldwide

BENEFITS OF CHLORINE DIOXIDE – INDUSTRIAL COOLING WATER

Product Information

Chlorine dioxide (ClO_2) is uniquely suited for use as a biocide for industrial cooling water systems (both open recirculating and once-through). It is an oxidizing biocide that is effective against all macroorganisms, microorganisms (including Legionella), and algae. As an oxidizing biocide, organisms cannot develop immunity to it. There are several major advantages involved in the use of ClO_2:

- It is much more effective against biofilms than traditional biocides used today.
- It is highly effective against Legionella.
- It produces lower system corrosion rates.
- It is compatible with other cooling water treatment chemistries.
- It is a “green” biocide.

General Description

- ClO_2 is a greenish-yellow gas with an odor similar to chlorine (Cl_2).
- Its solubility in water is approximately ten times greater than that of Cl_2.
- ClO_2 is generated and fed as an aqueous solution.
- It is effective across a wide pH range (5.0-10.0).

Elimination of Biofilms

Biofilms cause numerous problems in cooling water systems. These include:

- Loss of heat transfer – Biofilm is the most insulating compound found in cooling water systems, much more so than mineral scales. A few millimeters can cause loss of 20+% of heat exchange.
- Increased corrosion rates.
  - Differential cell corrosion
  - Pitting due to metabolic by-products of acid producing anaerobic bacteria (APBs).
  - Inability of corrosion inhibitors to contact and passivate metal surfaces
- Provide the environment for the growth of Legionella bacteria.
- Increase scaling potential. The negative surface charge of biofilms tends to concentrate scaling ions (e.g., Ca, Mg, etc.), such that they exceed solubility in the local area and precipitate.

Chlorine dioxide is much more effective for removal of biofilms than other alternatives for the reasons shown in the following figures. Once eliminated, the biofilms take up to several days to re-establish themselves. Thus, a system treated with ClO_2 will typically exhibit improved heat transfer and lower corrosion rates (typically 25-50% lower).

Figure 1: Biofilms have a negative surface charge. Chlorine and bromine hydrolyze to negatively charged hypochlorous acid or hypobromous acid in water, which are then repelled by the biofilm surface. Thus, the neutral ClO_2 molecule will penetrate the sessile bacteria (biomass), while the other compounds are repelled by the negative surface charge.

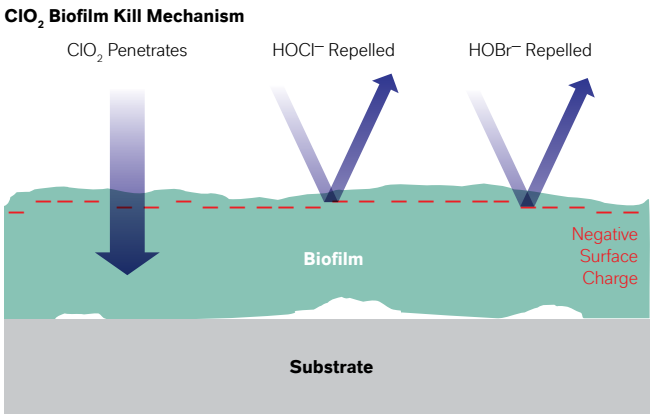


Figure 2: 50-70% of the ClO_2 reverts to chlorite (ClO_2^-) after reacting in the biofilm.

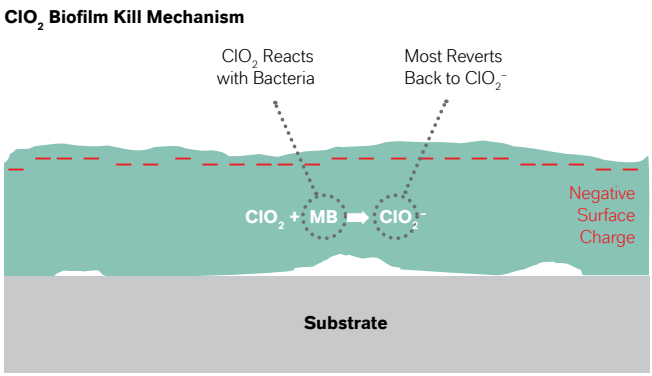
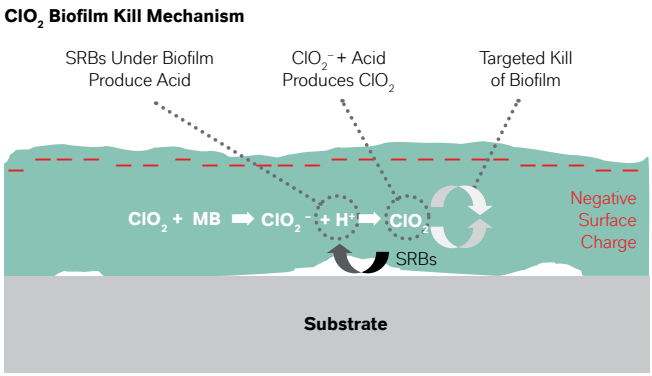


Figure 3: Under the aerobic biofilm, anaerobic bacteria will grow. Acid producing anaerobic bacteria (APBs) produce acid as a metabolic by-product. When the chlorite ion contacts the acid, it produces ClO_2, by the chlorite/acid reaction described on p. 3.



Counterflow cooling towers have a weak point with their high efficiency fill. This serves as an ideal bacterial growth location. It is wetted, saturated with oxygen, and has a high food loading through atmospheric scrubbing and any process leaks that are present. ClO_2 is the only biocide that has shown the ability to clean fouled, high efficiency fill online.

Legionella

Research has shown that Legionella requires higher life forms (i.e., amoeba, flagellates, etc.) as a host for reproduction. Thus, they flourish in a bacterial biofilm, where these organisms are found. By eliminating biofilms from

cooling systems, the potential for Legionella can be virtually eliminated. The Association of Water Technologies has published recommended treatment protocols for Legionella for numerous biocides, including chlorine, bleach, bromine, and nonoxidizing biocides. While all of the other programs feature “hyper” dosage treatment levels, the recommended program using ClO_2 is the same as our normal intermittent cooling water treatment program. This is a clear indicator that ClO_2 is highly effective at controlling Legionella without using extraordinary measures.

Lower System Corrosion Rates

As mentioned earlier, the largest influence on system corrosion rates are biofilms. They increase corrosion by several methods:

- The “patchy” or nonuniform coverage of metal surfaces establishes differential oxygen cell corrosion.
- APB species that are present under the aerobic biofilm are the primary source of pitting corrosion.
- Biofilms prevent corrosion inhibitors from successfully contacting and passivating system metal surfaces.

In addition, other oxidizing biocides typically encountered (e.g., chlorine, bleach, bromine) are fed continuously. They are also stronger oxidizers. This results in increased corrosion from their continuous presence. To make matters worse, when process leaks occur, feed rates of these compounds are normally increased substantially in an attempt to maintain a residual sufficient to control microbial growth. This further increases corrosion.

In contrast, ClO_2 is a weaker oxidant that, although counterintuitive, is an advantage:

- It does not react with organics (such as hydrocarbons), and, thus, results in little increase in dosage during process leaks.
- It is fed intermittently, typically only 2-4 hour per day, and, thus, is in the system only a small percentage of the total time.
- As a weaker oxidant, it is less corrosive.

The net result is that by using ClO_2 (a weaker oxidant), eliminating biofilm while feeding intermittently, and providing clean surfaces for corrosion inhibitors to effectively passivate, corrosion rates are significantly lower.

Compatible with Other Cooling Water Chemicals

Industrial cooling water treatment programs typically employ some combination of orthophosphate, polyphosphate, organic phosphates, tolyltriazole (TTA), scale inhibitors, and dispersants. Various researchers have performed work that shows ClO_2 will have no detrimental effect on these chemistries. This is logically consistent with the fact that as a weaker oxidant, ClO_2 would be expected to have no effect on chemistries that are routinely used with chlorine and bromine, which are stronger oxidants.

As an added benefit, chlorine and bleach are known to react with TTA, which is used as a copper alloy corrosion inhibitor in most cooling water treatment programs. ClO_2 does not react with it and can result in a measurable decrease in the required TTA dosage.

Environmental

As a weaker oxidizing compound, ClO_2 will not form chlorinated organics (as will chlorine, bleach, and bromine). This means that in the presence of hydrocarbons or other organic compounds, no objectionable organic compounds will be formed (such as chloroform — a carcinogen). Thus, there will be no potential discharge water permit violations due to the microbiological control program.

By eliminating the need for nonoxidizing compounds, the potential release of these long half-life poisons is prevented. As well, the potential of these poisons affecting the biological waste water treatment plant via the cooling tower blowdown is prevented.

The ultimate decay product of ClO_2 is chloride, which is totally unobjectionable at the feed rates used (<5 ppm).

All of these factors combine to make ClO_2 a “green” biocide.

Methods of ClO_2 Production

Chlorine dioxide must be produced at the point of use. Physical characteristics prevent its being produced off-site and transported. There are three potential methods of producing ClO_2 for industrial scale applications. The basic precursor required for all of them is sodium chlorite.

Chlorite + Hydrochloric Acid

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + H_2O$$

Chlorite + Chlorine Gas

$$2NaClO_2 + 2Cl_2 \rightarrow 2ClO_2 + 2NaCl$$

Chlorite + Sodium Hypochlorite + Hydrochloric Acid

$$2NaClO_2 + NaOCl + HCl \rightarrow 2ClO_2 + 3NaCl + H_2O$$

The chlorite/acid method produces a maximum of only 80% conversion of chlorite to ClO_2; thus, it is more expensive to produce ClO_2 with this process. For this reason, it is typically used for small applications only. The preferred methods are either the chlorite/chlorine gas or chlorite/bleach/acid generation methods. Our ClO_2 generators are capable of achieving conversions of 95+% of chlorite to ClO_2.

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Application to Cooling Water Systems

As a gas in aqueous solution, the preferred injection location is the suction of the circulating water pumps in the cooling system. Upon return to the cooling tower, most of it will be stripped from the water. To what degree it is removed depends largely upon the type of fill the cooling tower has. High efficiency fill allows more of the ClO_2 to return to the tower basin (up to ~50%), while splash bar type fill results in higher losses (~90%).

Cooling water systems treated with ClO_2 will require the following steps be taken to transition from other microbiological control programs.

- **Establish Baseline** performance. Monitor the existing program for a minimum of 30 days to establish microbiological growth rates, corrosion rates, etc.
- An initial **Cleanup Phase**
  - Usually 3-7 days in duration.
  - Feed at approximately 0.5-0.7 ppm residual at the circulating pump discharge for 8 hours per day.
- An **Optimization Phase** – Dosages and feed duration are adjusted based on microbiological testing to obtain minimum chemical consumption.
- **Intermittent Maintenance** dosage application.

Please contact International Dioxcide for dosage and cost calculations, as well as additional information on this product and its other uses.

Information Available

International Dioxcide, a division of ERCO Worldwide, has specialized in chlorine dioxide technologies for over 70 years, and is a leading supplier of sodium chlorite solutions and generator technology for a wide variety of markets. For additional information please contact the sales office at 1-800-477-6071 or online at idiclo2.com

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