

# Treatment of Biofilms with Chlorine Dioxide

Chlorine dioxide ( $\text{ClO}_2$ ) is effective as both a disinfectant and an oxidant in water treatment. Chlorine dioxide is a broad-spectrum microbiocide effective over a wide pH range. Unlike chlorine, chlorine dioxide does not react with organic materials to form trihalomethanes (THMs). Chlorine dioxide is also non-reactive with ammonia-nitrogen and with most treatment chemicals (corrosion and scale inhibitors) present in cooling water systems.

Chlorine dioxide is effective in the control of microbiological growths in industrial cooling waters under conditions unfavorable to chlorine. It is particularly effective in systems having a high pH, ammonia-nitrogen contamination, persistent slime problems, or where the microbial contamination is aggravated by contamination with vegetable or mineral oils, phenols or other high chlorine-demand producing compounds.



## Application Note

## Application Description

Three main types of organisms are found in cooling systems: bacteria, algae and fungi. While fungi are more complex, bacteria and algae share a common structure, which is shown in Figure 1.

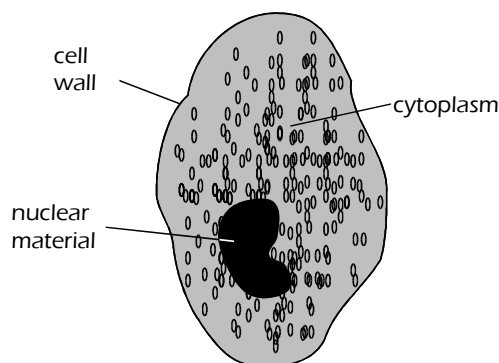


Figure 1 - Organism Cell Structure

The major components of all cells are the cell wall, the cytoplasm and the nuclear material. To survive and grow, microorganisms must keep their cellular material together, obtain food and excrete wastes, process food into energy and cellular material, and reproduce. For the simplest cells the cell wall serves the dual purpose of keeping the cellular material together and energy synthesis. While both cytoplasm and nuclear materials have a role in the conversion of food to cellular matter, only the nuclear matter is involved in reproduction.

Biocides kill microorganisms by attacking cellular sites and inhibiting necessary cellular functions. Two visual measures of poor microbiological control are the presence of algae and biofilm in the system.

Biofilm is the extracellular polymeric substances produced by bacteria along with the bacteria that produce it. The formation of biofilm, the nature of biofilm and the difficulty in inactivating biofilm bacteria is well known<sup>1</sup>. Bacterial biofilm, or slime as it is more commonly called, causes a number of problems in cooling systems. Losses in heat transfer translate to losses in production or increased energy costs. Increases in corrosion result from biofilm directly or indirectly through the promotion of anaerobic bacteria, *Desulfovibrio desulfuricans*. Bacterial biofilm may also harbor pathogenic organisms such as *Legionella*.

## Treatment Alternatives

The rate of biofilm production, which is dependent on a number of factors including available bacterial nutrient, will have a direct impact on the efficacy of any biocide program.

In general, the following relationships hold true for control and removal of bacterial biofilm and algae. These relationships may change slightly with increasing pH.

## Biofilm

$\text{ClO}_2 \gg \text{HOCl} \geq \text{HOBr} > \text{non-oxidizing biocides}$

## Algae

$\text{ClO}_2 > \text{certain non-oxidizing biocides} > \text{HOCl} > \text{HOBr}$

## Chlorine

Chlorine is known to be relatively ineffective at controlling slime<sup>2,3</sup>. It does not penetrate the slime layer, but only works on the surface, burning off layer after layer. A continuous feed of chlorine is common in large industrial cooling towers. Chlorine is ineffective if there is sufficient bacterial nutrient so that the rate of bacterial production is higher than the rate of biofilm removal by chlorine. This has been observed in numerous heavy industrial accounts<sup>4,5</sup>. In fairly clean cooling towers, continuous feed of chlorine is sufficient to provide excellent control of bacterial biofilm.

A continuous chlorine level can keep algae in control, although many towers with continuous chlorine levels have substantial algae growth. Again, the level of control achieved is a function of available nutrient present in the water and sunlight.

## Bromine

Bromine has been shown to penetrate and inactivate biofilm better than chlorine (i.e., it appears to be less reactive with biofilm constituents). However, in systems with high loading of bacterial nutrient, bromine appears to be a poor choice<sup>6,7</sup>.

Bromine is also less effective for control of algae than chlorine.

## Chlorine Dioxide

Chlorine dioxide has been shown to remove biofilm in very difficult to treat towers when applied intermittently at 0.6 – 1.0 mg/L based on recirculation rate<sup>8</sup>. When chlorine dioxide is applied correctly, it has been shown to control biofilm under a variety of conditions<sup>9</sup>. Because it is relatively non-reactive with the majority of biofilm constituents, it penetrates the biofilm and effectively inactivates biofilm bacteria.

Chlorine dioxide is also very effective for algae control<sup>10</sup>.

## Advantages of Chlorine Dioxide

- Unlike chlorine and bromine, chlorine dioxide is effective over a broad pH range.
- Chlorine dioxide does not react with ammonia-nitrogen or organics.
- Chlorine dioxide is effective at a lower dose rate than chlorine or bromine.
- Chlorine dioxide is more effective than chlorine or bromine for biofilm and algae control.

## Feed Requirements

For control of bacterial slime and algae in industrial recirculating and one-pass cooling systems, the required dosages will vary depending on the exact application and the degree of contamination present. The required chlorine dioxide residual concentrations range between 0.1 and 5.0 mg/L. Chlorine dioxide may be applied either continuously or intermittently. The typical chlorine dioxide residual concentration range is 0.1-1.0 mg/L for continuous doses, and 0.1-5.0 mg/L for intermittent doses. The minimum acceptable residual concentration of chlorine dioxide is 0.1 mg/L for a minimum one-minute contact time.

For more information on dosage requirements specific to your application, contact your Siemens Representative.

## 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.

## Chlorine Dioxide Analysis

Residual chlorine dioxide concentrations must be determined by substantiated methods, which are specific for chlorine dioxide. Two suitable methods are published in *Standard Methods for the Examination of Water and Wastewater*<sup>11</sup>:

4500-ClO <sub>2</sub> D	DPD-Glycine Method
4500-ClO <sub>2</sub> E	Amperometric Method II

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