

## TECHNIFAX

## Cooling Water Chlorination

Any comprehensive cooling water treatment program will include a biocide for the control of biological contamination. Oxidizing biocides, such as chlorine and bromine, and nonoxidizing biocides may be used. Although the use of chlorine has decreased over the past several years due to safety concerns, its use is still very widespread. In cooling water systems, the effective application of chlorine minimizes the presence of microorganisms that can cause biological fouling, contribute to corrosion, and reduce heat transfer.

The amount of chlorine required to maintain microbiological control in a cooling water system will vary depending on the chemical and physical environment of the water system.

## REACTIONS IN WATER

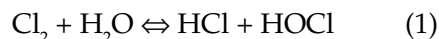
When chlorine is added to cooling water, a variety of reactions occur. The reactions depend on the components present in the cooling water and the system water characteristics.

Chlorination of cooling water may be accomplished with the use of a variety of materials. However, the most widely used and cost-effective form of chlorine is gaseous chlorine.

Other chlorination methods include use of materials such as sodium hypochlorite, calcium hypochlorite, chlorinated isocyanurate, and chlorinated hydantoin. Once in solution, all these compounds react in water to form hypochlorous acid and hypochlorite ion, which serve as disinfectants to control microbiological growth.

## CHLORINE CHEMISTRY

In discussing chlorination chemistry, it is necessary to first consider chlorine reactions in pure water. When added as a gas, chlorine rapidly hydrolyzes to form hydrochloric acid and hypochlorous acid.



The hypochlorous acid then partly dissociates to give hydrogen and hypochlorite ions.



The three forms of chlorine involved in these reactions, molecular chlorine ( $\text{Cl}_2$ ), un-ionized hypochlorous acid ( $\text{HOCl}$ ), and the hypochlorite ion ( $\text{OCl}^-$ ), exist together in equilibrium. Their relative proportions are determined by pH value (Figure 1), temperature, and dissolved solids.

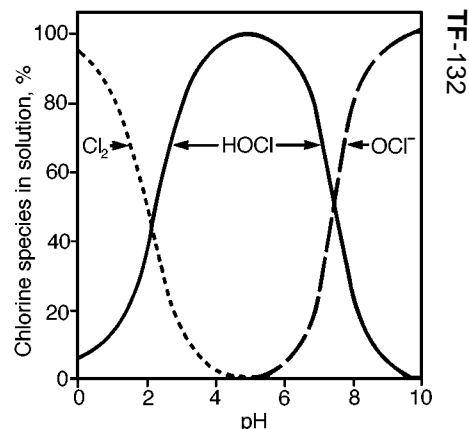
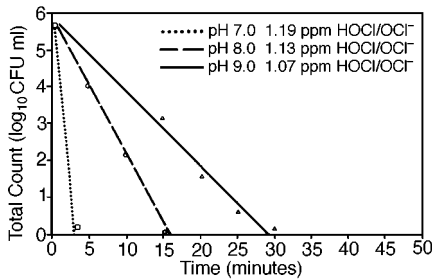


Figure 1 — Relative concentrations of chlorine compounds vs. pH

Chlorine present in water as  $\text{Cl}_2$ ,  $\text{HOCl}$  or  $\text{OCl}^-$ , or in any mixture of these, is defined as *free available chlorine*. This free available chlorine is the most biocidally active constituent of chlorine. Clearly, at the pH values encountered in water chlorination, free chlorine consists of a mixture of  $\text{HOCl}$  and  $\text{OCl}^-$ .

As a bactericide,  $\text{HOCl}$  is a much more rapid acting biocide than  $\text{OCl}^-$  (Figure 2). This is due to  $\text{HOCl}$  being uncharged and thus more easily diffusible through the cell wall. Consequently, in free residual chlorination, the higher the pH value, the slower the rate of kill because of a lower proportion of  $\text{HOCl}$ . This is particularly important in once-through cooling systems and in cooling systems practicing slug chlorination. These systems have limited contact time (minutes-hours) for

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**Figure 2** — Effect of HOCl/OCl<sup>-</sup> on *Pseudomonas*

chlorine (HOCl or OCl<sup>-</sup>) to work as a biocide, hence rate of kill is an important consideration.

In distilled water, all chlorine present will be free available chlorine because there is nothing present that will react with or consume the free chlorine. Industrial cooling water, on the other hand, has microorganisms present as well as other compounds that combine with and reduce the concentration of free available chlorine. These microorganisms and compounds together make up the *chlorine demand* of the water.

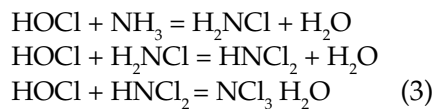
In addition to chlorine reacting with various constituents in water, large quantities of chlorine (30 to 40%) can be lost from a cooling system due to mechanical stripping, i.e., the escape of dissolved HOCl from water into the atmosphere. Chlorine in a system can also be degraded due to ultraviolet light from the sun. Free available chlorine in a cooling tower may disappear in less than one hour on a bright day, but remain two to four hours in the dark.

Free available chlorine = chlorine added to system — chlorine demand — chlorine stripped — chlorine degraded due to sunlight.

## CHLORINE REACTANTS

### Ammonia

Ammonia is one compound that reacts with chlorine; the reaction products are called chloramines (see the following reactions). Chloramines are referred to as *combined chlorine*. Free available chlorine and combined chlorine added together make up *total residual chlorine*.



Chloramines are much less effective bactericides than free HOCl or OCl<sup>-</sup>. The reactions between chlorine and ammonia to form chloramines are frequently overcome by the technique of *breakpoint chlorination*. In this method, chlorine is added until the free ammonia is used up; additional chlorine is subsequently added to maintain a residual of free available chlorine.

The quantity of chlorine required to achieve breakpoint, then, is based on the amount of ammonia present in the system. For every 1 ppm of ammonia present, up to 10 ppm of chlorine may be required to establish free available chlorine. A preferred alternative to the practice of breakpoint chlorination for the presence of ammonia is bromine chemistry. Bromamines, in contrast to chloramines, are excellent biocides and are almost as biocidal as free available bromine.

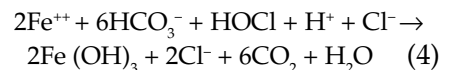
### Organic Nitrogen

Reactions with organic nitrogen are very complex and slow, particularly with some of the proteins and nucleic acids of microorganisms. The slowness of the reaction is probably due to steric hindrance. The slow reaction rate means that a long time (up to several days) can be required to reach a stable free residual chlorine level.

### Inorganics

Chlorine will oxidize certain inorganic molecules. It can readily oxidize ferrous iron (Fe<sup>++</sup>), manganous (Mn<sup>++</sup>), nitrite (NO<sub>2</sub><sup>-</sup>), and H<sub>2</sub>S. The presence of these inorganic constituents significantly increases the chlorine demand of the water, and consequently, the quantity of chlorine required for microbiological control. The chlorine which reacts is converted to chloride ions, which are not biocidal. Examples of oxidizing reactions involving inorganic molecules and chlorine are:

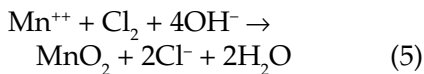
*Iron* — Free chlorine will oxidize ferrous ion as follows:



The oxidation of soluble iron is partially dependent on the concentration of HCO<sub>3</sub><sup>-</sup> (bicarbonate), and as a result, the reaction is very rapid above pH 7.0, where bicarbonate in natural waters is usually present in higher concentrations. Because alkalinity is lost in this reaction, the pH may be significantly lowered. The amount of pH reduction will depend on the alkalinity level of the water.

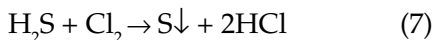
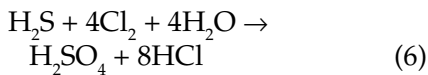
Each ppm of iron oxidized requires 0.64 ppm of chlorine.

*Manganese* — Manganese is oxidized by free available chlorine while chloramines have little effect on manganous compounds. Manganous oxidation by chlorine results in the precipitation of manganese dioxide:



The oxidation of manganese by chlorine is more rapid above pH 7.0 because the reaction depends on hydroxyl ions.

*Sulfur* — Chlorine will react rapidly with hydrogen sulfide gas to form dilute sulfuric acid and elemental sulfur. The ratio is pH dependent. At a pH of 7.0 with a weight ratio of 8:1  $\text{Cl}_2/\text{H}_2\text{S}$ , about 70% is oxidized to sulfate; at pH 9.0 about 50% is converted to sulfate and 50% to elemental sulfur.



Below the 8:1 ratio, Equation 7 is predominant.

Some elemental sulfur is nearly always present in systems where chlorine and hydrogen sulfide are in contact regardless of the ratio of chlorine to hydrogen sulfide.

### Oxidizable Organics

Non-microbiological organic materials present in cooling water may also be oxidized by chlorine. Oil, grease, leaves, pollen, process chemicals, lignin, tannin, and food products can significantly contribute to the chlorine demand in a system. A process leak of an

organic material may necessitate an increase in chlorination rate to overcome the added chlorine demand and to obtain a free residual to maintain microbiological control.

Most organic compounds react slowly with chlorine. However, the rates are dependent on pH and chlorine concentration. The overall water quality and other chemical species present play a significant role in the formation of chloroorganics. If HOCl is the main chlorinating agent, the formation of chlorinated organics will be proportional to the HOCl concentration. However, in the presence of high ammonia concentrations, a lower level of chlorinated organics will be formed because of the more rapid reaction of HOCl with  $\text{NH}_3$  to form chloramines.

## FORMS OF CHLORINE

### Gaseous Chlorine

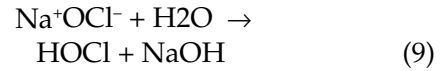
Because of the potential dangers associated with handling gaseous chlorine, this form of chlorine is being used less and less. When gaseous chlorine is added to water, it reacts as follows:



As discussed earlier, HOCl dissociates to form  $\text{OCl}^-$ . The amount of each is dependent upon pH. HCl is a very strong acid. When added to water, gaseous chlorine will reduce M alkalinity by 0.7 ppm (as  $\text{CaCO}_3$ ) for every 1 ppm of chlorine added to the water.

### Sodium Hypochlorite

Addition of sodium hypochlorite ( $\text{NaOCl}$ ) solution (bleach) to water also results in hypochlorous acid formation:

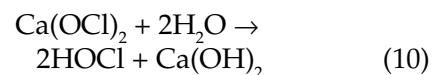


Adding bleach to water will affect the pH and alkalinity. About 1 ppm of M alkalinity (as  $\text{CaCO}_3$ ) is added for every ppm of  $\text{NaOCl}$  added. Some excess NaOH is present in the bleach solution to keep the pH above 11 for storage stability. However, when bleach is added to water, this excess NaOH has a minimal effect on alkalinity.

The pH effect of adding bleach to water depends on the original pH of the water. In low pH waters, the pH may increase significantly due to the additions of  $\text{NaOCl}$  and the resulting formation of NaOH (Equation 9). However, in higher pH waters where the  $\text{OCl}^-$  species is predominant, NaOH is not readily formed, and the pH increase is negligible.

### Calcium Hypochlorite

Calcium hypochlorite,  $\text{Ca}(\text{OCl})_2$ , dissociates in water to form hypochlorous acid and calcium hydroxide.



One mole of calcium is added for every two moles of hypochlorous acid. Note that calcium hardness is added.

## BIOLOGICAL ACTIVITY

A number of theories have been postulated to explain the effective biocidal activity of chlorine. The major biocidal activity is attributed to HOCl and OCl<sup>-</sup>. The active chlorine species kill the microorganisms by destroying cell enzymes and membranes. A free chlorine residual (HOCl, OCl<sup>-</sup>) will provide the best microbiological control. Free chlorine species are present in an equilibrium; the ratio of HOCl to OCl<sup>-</sup> is dependent on the pH.

As HOCl is utilized in killing microorganisms, more HOCl is produced immediately because of the redistribution from the more stable OCl<sup>-</sup> to provide continued biocidal activity.

The efficiency and disinfection performance of chlorine can vary depending on the concentration, contact time, and target organism. Each microorganism has a "specific sensitivity" to a certain chlorine level. Therefore, sufficient contact time and concentration will kill any microorganism. Microorganisms cannot develop a resistance to chlorine regardless of the number of times that they are exposed to chlorine because all organisms are composed of oxidizable organic matter.

*Contact time* is extremely important. By increasing the contact time, effective chlorination can be achieved at lower free chlorine residuals. In other words, longer contact times permit smaller residuals while shorter contact times (minutes) require high residuals to give equal microbiological kill. Widely published laboratory data have shown that

in *short contact time disinfection experiments*, the HOCl species is required to give fast kill. However, other laboratory experiments as well as practical industrial water treatment experience have shown that *continuous chlorination which allows a very long contact time is effective* in cooling water systems having pH's from 5.0 up to 9.5 (where OCl<sup>-</sup> is predominant).

## FREE CHLORINE — COMMON TEST METHODS

A variety of test methods are available for determining free chlorine (HOCl and OCl<sup>-</sup>) in water. However, regardless of the test method used, chlorine determinations should be started immediately after sampling. The chlorine content will decrease rapidly in water solutions, particularly if the samples are stored, agitated, or exposed to strong light. These conditions should be avoided to prevent false-low test results.

The most common and best methods for free chlorine determination in cooling water are amperometric titration, the FACTS (syringaldazine) method, and the DPD (diethyl-p-phenylene diamine) test method.

*Amperometric titration* is a particularly accurate method and is compatible with virtually every cooling water treatment including chromate. This method utilizes a small automatic titrator. With this instrument, the concentration of chlorine is determined by observing meter-indicated decreases in applied electric

current flowing through the test water sample. The decrease in current occurs when free chlorine is reduced to chloride by the addition of a phenyl arsine oxide titrant. In addition to free chlorine, the titrator can accurately determine both monochloramine and dichloramine (combined chlorine) residuals.

The *FACTS (syringaldazine) method* can be used in chromate-treated systems. In this test, the syringaldazine reagent is oxidized by free chlorine to give a pink-red color.

The *DPD (diethyl-p-phenylene diamine) test* is an accurate method for use in non-chromate treated cooling water systems. In the presence of chromate, the DPD test will give a false-positive test result. In this test, the free chlorine reacts instantly with the DPD indicator to produce a red-pink color when reacted with chlorine. The color should be read immediately for a true free chlorine reading.

## SUMMARY

The use of chlorine is a common method to control microorganisms in cooling water systems. Factors such as pH, temperature, and sunlight are important in the effective use of chlorine. Organic or inorganic water contaminants can react with chlorine and thus significantly increase the chlorine demand of the water. Contact time and concentration of chlorine are important factors affecting chlorine's performance for controlling microbiological growth in cooling water systems.