Industrial cooling-water systems are critical to the success of many chemical process industries (CPI) operations. Proper operation of cooling-water systems supports the financial drivers of energy efficiency, asset preservation and water savings, while optimizing overall process performance. When maintained properly, industrial cooling-water systems help enable processes to run seamlessly. Selecting the appropriate water-treatment solution for an industrial cooling-water system is critical, and typically includes consideration of mechanical, operational and chemical components of the system (Figure 1).

Among the important aspects of cooling-water treatment is the control of microbes. Biological control in an industrial water system is important for maintaining optimal performance in three areas: scale prevention, corrosion inhibition and fouling control. Failure to effectively control microbes in cooling water can cause the system to suffer from diminished operational efficiency, premature equipment failure, deteriorated product quality and increased health-related risks associated with waterborne pathogens.

Sources of microbial contamination in industrial water systems are numerous and may include, but are not limited to, airborne contamination, water make-up, process leaks and improperly cleaned equipment. These microorganisms can establish microbial communities on any wet or semi-wet surface of the water system. Additionally, biofilms formed by growing microbe communities have strong insulative properties, which drive up energy usage if not managed properly. It is therefore important that microbial biofilms and other fouling conditions be controlled or reduced to the greatest extent possible to minimize operational concerns and health-related risks associated with waterborne pathogens.

There are many biological control strategies available to the CPI today, including three chlorine-based oxidizing biocides: bleach (sodium hypochlorite; NaOCl), chlorine gas (Cl2) and chlorine dioxide (ClO2). Bleach is easily accessible and well accepted, and is used in most industries. Chlorine gas is common in ammonia and municipal water industries, while chlorine dioxide is often used in food-and-beverage, institutional and power industries. Important drivers in all these industries include safety, performance, water quality, compliance, convenience, reliability and sustainability. This article evaluates the three main chlorine-based biological control strategies for each of the seven drivers.

**Chlorine-based biological control**

The following paragraphs discuss bleach, chlorine gas and chlorine dioxide in the context of the seven drivers mentioned above.
Safety. A core tenet for major industrial operations is safety. The biological control strategy selected impacts safety in a variety of ways, including risk of exposure, environmental releases and sensitization of operators. Chlorine gas is highly toxic, making it a powerful disinfectant for water, but hazardous to humans, who must handle it in its gaseous form. As a result, operators require intense use of personal protective equipment for chlorine gas. For containment, chlorine gas requires high-pressure cylinders that come with an inherent risk of potentially large releases. It is important to note that safety and security legislation in many areas is expected to eventually force chlorine gas users to switch to a less hazardous program.

Utilizing bleach for microbial control requires a steady stream of bleach deliveries, each of which carries a risk of spills and worker exposure. Both bleach and chlorine gas add significant amounts of chloride ions to cooling water, increasing the risk of operator sensitization when exposed to cooling water.

In contrast, chlorine dioxide adds very little free chloride. For the same level of antimicrobial effectiveness, bleach requires a greater volume than chlorine dioxide. This may be a factor in reducing handling and exposure risks. Chlorine dioxide is generated on-site, as needed, so there is a need for a ClO₂-generation system, but no need for chlorine gas storage. This can be a factor in lowering the risk of a large-scale release. On-site generation equipment for chlorine dioxide requires integrated safety devices to monitor system parameters to ensure safe production of the chemical.

Performance. After safety, process performance is the next key area for which the choice of microbial control program has an impact. In many cases, the three biocidal programs being compared for biocidal efficacy are dictated by system conditions and the particular requirements will determine the antimicrobial program. In low-demand systems with near-neutral pH, bleach and chlorine gas are effective biocides. Chlorine dioxide is especially effective in challenged water systems. Chlorine dioxide is well known to control and remove biofilms from industrial water systems as the compound migrates, via molecular diffusion, from the bulk water into the biofilm, where it deactivates microbes that form the biofilm.

In addition to microbial control, the impact of the water-treatment strategy on scale prevention, corrosion inhibition, and fouling reduction also must be considered. Bleach and chlorine gas both increase chloride and hypochlorite ions in the cooling water system. This can increase the rate of corrosion within the system, leading to shorter-than-expected asset lifetimes. Chlorine dioxide is not aggressive toward other cooling water chemicals that may be present in the system, such as azoles for corrosion inhibition and polymeric scale inhibitors.

Finally, due to the broad spectrum of chlorine activity, chlorine gas and bleach can create taste concerns, which can be especially troublesome in process applications in the food, beverage and healthcare industries.

Water quality. Incoming water quality is important to understand, because the pH range of the water system will determine the activity rate of the microbial control program. Bleach is most effective at a pH range of 5.5–7.5, and it tends to increase the pH of a system over time. When working with bleach, some operators will treat with acid to maintain the optimal pH range. This works, but also introduces additional hazardous chemistries (acid) into the plant. Chlorine dioxide is effective at a broader pH range (pH 5–11) and requires less intervention to maintain a consistent pH (Figures 2 and 3). The effects of pH are discussed further in the next section.

Compliance. Regulatory compliance is a strong consideration when determining the best path forward for microbial control. In
the U.S., all biocides must be used in accordance with the U.S. Environmental Protection Agency and state environmental agency guidelines. Certain industries also have U.S. Food and Drug Administration (FDA) and NSF International (Ann Arbor, Mich.; www.nsf.org) considerations to address. Discharge limits frequently regulate the amount of eco-toxic disinfection byproducts, such as trihalomethanes (THM), haloacetic acids (HAA), or adsorbable organic halides (AOX), that can be present in discharged water. The formation of these byproducts is significantly higher with bleach and chlorine gas than with the use of chlorine dioxide. In cases where the byproduct discharge limits are extremely tight, chlorine dioxide may be a strong candidate for microbial control.

**Convenience.** Ongoing maintenance is required for all biological control strategies. For chlorine gas, that means regular monitoring of the high-pressure system and hazard analysis on a routine basis. Bleach requires tank and line monitoring for impacts from corrosion. Chlorine dioxide requires regular maintenance of the on-site generation equipment. When selecting a program, consider the level of involvement that your staff is able to address. Preventive maintenance schedules that are managed by the supplier can provide assurance that technical experts have recently inspected the equipment and that it is in good working order. Operator training delivered by those same experts can ensure that as your workforce changes, knowledge of the cooling water system operation stays consistent.

Another option that delivers convenience is remote 24-h per day, 7-d per week continuous digital monitoring of critical parameters with alerts to notify operators when the system requires attention. **Reliability.** In today’s world, the pressure to do more with less falls on everyone’s shoulders, so having a reliable solution and the additional expertise available to support process operations are more critical than ever. Bleach is a common microbial control chemistry and is effective with constant and consistent delivery. This requires a continuous supply of bleach moving around your facility to the appropriate application points. Bleach has a relatively short shelf life, especially under hot conditions, which adds to the need for frequent deliveries. Suppliers of bleach and chlorine gas tend to be commodity chemical suppliers who do not focus on unique situations or custom applications that arise frequently in cooling water systems.

On the other hand, chlorine dioxide requires on-site generation equipment that must be properly maintained to consistently and reliably deliver chemistry to water systems. Established chlorine dioxide suppliers have the expertise necessary to evaluate your application in order to survey, size and select the appropriate generation equipment for the needs of a particular process, and to apply the chemistry under the appropriate dosage scheme. The onsite generation of chlorine dioxide also enables the optimization of production throughput, as the system can accommodate fluctuations in production levels that may require variable production of chlorine dioxide.

**Sustainability.** All biocidal programs impact the sustainability of your operation. Energy-use and chemical-use cost savings are possible with bleach, but are greater with chlorine gas, and most significant with chlorine dioxide. This is mostly due to the reduction of biofilms, which greatly impact the efficiency of heat exchangers. In addition, there will be a decrease in energy consumption by cooling water pumps, as flow restrictions due to clogging are removed. Water savings are greatest for cooling water systems when the cycles of concentration can be maximized. Chlorine dioxide is superior for this driver due to the limited production of chloride ions.
Specific considerations
Assembled here are five additional considerations for use of chlorine-based microbial-control strategies in industrial cooling water applications.

**pH.** At a pH of 6.0–7.0, bleach has similar efficacy to chlorine dioxide, and is often used as a microbial control chemistry. Less chlorine dioxide is required to effectively reduce bacteria counts when compared to other chlorine-based programs at higher pH. Chlorine dioxide is effective across a broader pH range compared to chlorine gas and bleach. Figures 2 and 3 compare the equivalent dosage of ClO₂ per 100 pounds of NaOCl required to treat water at different pH ranges with the greatest benefit being seen at the upper end of the pH range.

**Contaminant effects.** Chlorine dioxide is less affected by pH and contaminants that create demand, such as oil, grease and ammonia. In addition to an overall lower rate of use, this means that the pH impact is minimized, thereby maximizing the microbial impact of the solution.

Figure 4 shows the effect of organic demand and pH on the free oxidant available for microbial control. The volume of bleach needed to maintain a similar level of free or available oxidant compared to chlorine dioxide, is much greater.

**Impact of biofilms.** As a dissolved gas, chlorine dioxide penetrates biofilm and removes slime. After the initial sloughing off of biofilm buildup in the system, this helps to restore heat transfer performance and energy efficiency. Figure 5 shows the impact of biofilm on flow, turbulence and pressure.

**Corrosion.** Corrosion rates affect the lifetimes of your assets. Corrosion rates and corrosion pit depth is reduced with chlorine dioxide. Figure 6 compares corrosion severity across two industrial water systems for chlorine gas, bleach and chlorine dioxide.

**Concluding remarks**
Biological control in an industrial water system is a key consideration in maintaining optimum performance. While there are many biological control strategies available in the marketplace, it is important to understand the differences between each and how they affect the drivers important to your site. Now that the key areas have been reviewed for chlorine-based treatments, you can evaluate each solution to determine which one best meets the drivers for your site. Safety, performance, water quality, compliance, convenience, reliability and sustainability are all important aspects of a robust solution and an optimal water-treatment program should also address mechanical, operational and chemical aspects of the system.

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