A Focus on Chlorine Dioxide: The "Ideal" Biocide

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ABSTRACT

The use of gaseous chlorine as a microbiocide for industrial cooling systems is declining because of safety, environmental and community impact considerations. Various alternatives have been explored, including bleach, bleach with bromide, bromo-chlorodimethyl hydantoin (BCDMH), non-oxidizing biocides, ozone, and chlorine dioxide, among others. Chlorine dioxide offers some unique advantages, due to its selectivity, effectiveness over a wide pH range, and speed of kill. Safety and cost issues have restricted its use as a viable replacement. This paper reviews the chemistry of chlorine dioxide and its use in cooling systems. Comparisons are made with chlorine, bromine and ozone. A novel approach to its use in a safe and effective way is described.

Keywords: chlorine dioxide, chlorine, ozone, bromine, oxidizer, biocide, review article

INTRODUCTION

The discovery of chlorine dioxide is generally credited to Sir Humphrey Davy, who reported the results of the reaction of potassium chlorate with sulfuric acid in the early 1800's.[1] Chlorine dioxide today is generated for smaller applications by the reaction of sodium chlorite with chlorine, via either gaseous chlorination (Equation 1) or the reaction of sodium hypochlorite with hydrochloric acid (Equation 2).

$Cl_2 + 2NaClO_2 \rightarrow 2ClO_2 + 2NaCl$ (1)

$HCl + NaOCl + 2NaClO_2 \rightarrow 2ClO_2 + 2NaCl + NaOH$ (2)

This chemistry was due to the pioneering efforts of J. F. Synan, J. D. MacMahon, and J. P. Vincent,[2] of Mathieson Chemical Company, now Olin Corporation. In 1944, the generation of chlorine dioxide to control taste and odor problems at a potable water facility at Niagara Falls, N.Y., was reported.

This first successful application led to its use in other municipal potable water treatment facilities which had similar problems.[3-6] Over the next 25 years researchers compared the disinfection efficiency of chlorine dioxide to that of the industry standard, chlorine.[7-15]

In the mid to late 70's, researchers linked chlorination of potable water to increased cancer mortality rates.[16-20] This increase in cancer mortality was tied to the production of trihalomethanes, THM's.[21,22] The USEPA established 0.1 ppm as the maximum THM containment level for drinking water. Research in the area of THM reduction in potable water [23-27] led to the EPA in 1983 suggesting the use of chlorine dioxide as an effective means of controlling THM's.

In 1986, there were an estimated 200 - 300 chlorine dioxide applications for potable water treatment in the USA, and applications in Europe numbered in the thousands.[28]

Chlorine dioxide is being used increasingly to control microbiological growth in a number of different industries, including the dairy industry,[29-31] the beverage industry,[32] the pulp and paper industries,[33-37] the fruit and vegetable processing industries,[38-41] various canning plants,[42,43] the poultry industry,[44-53] the beef processing industry,[54] and miscellaneous food processing applications.[55-59] It is seeing increased use in municipal potable water treatment facilities[61-65] and in industrial waste treatment facilities,[75-80] because of its selectivity towards specific environmentally-objectionable waste materials, including phenols, sulfides, cyanides, thiosulfates, and mercaptans.[81] It is being used in the oil and gas industry for downhole applications as a well stimulation enhancement additive.[82] Today, domestic industrial applications number in the thousands.[83]

Despite the many advantages of chlorine dioxide, relatively few heavy industrial plants have made the switch to this superior microbicide for cooling systems.[66-74] Historically, unless there was significant performance or cost advantages, there was no impetus to consider chlorine dioxide as a replacement for gaseous chlorine. In those instances where chlorine is not effective at microbiological control, such as a cooling tower with a high level of organics, ammonia, or amines, chlorine dioxide has been called on to bring control to these heavily fouled systems.

With the recent trend towards elimination of gaseous chlorine from the industrial plant site, there are increasing interests in exploring all the various alternatives to gaseous chlorine. This review compares four oxiding microbicides: HOCl, HOBr, ClO_2, and O_3, in light of the characteristics of an ideal microbicide.

Criteria for Ideal Biocide

What criteria would be expected for an 'Ideal Biocide'? Meitz[84] discussed several criteria of an ideal biocide; these criteria are summarized into four basic categories:

Performance	It must exhibit rapid kill of target organisms, with a high LC_{50} toward non-target organisms. It must be able to keep systems clean of biofilm; ideally it should be able to clean up already fouled systems. It should not be consumed by materials commonly encountered in cooling systems, e.g., hydrocarbons, wood, plastic, or other treatment chemicals. Finally, it must be effective over a wide range of operating conditions.
Environment	Side or by-product reactions should be minimized and reaction products should be environmentally friendly; neither it, its by-products, nor its reaction products should persist in the environment.
Safety	It must be safe and easy to handle.
Economics	It must be affordable.

These characteristics are discussed in the following pages. A comparison between chlorine dioxide and chlorine is made; hypobromous acid and ozone are included.

Disinfection Efficiency and pH

Many studies have been made comparing the disinfection efficiency of chlorine dioxide to chlorine. In one such study, varying dosages of chlorine dioxide or chlorine were added to solutions containing 15,000 viable cells/ml of E. coli at pH's of 6.5 and 8.5. The abscissa is the time in seconds required to kill 99% of the viable bacterial cells. The ordinate is the initial dosage of oxidant. The results are shown in Figure [1.8]

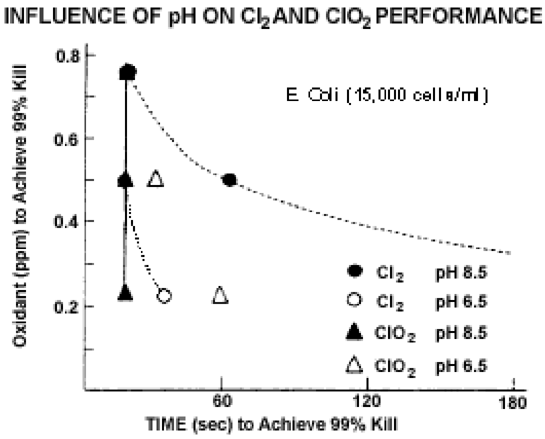

Fig. 1. Comparison of the Disinfection Efficiencies of ClO_2 with Cl_2 at pHs of 6.5 and 8.5

These results clearly shows the decreasing effectiveness of chlorine as the pH increases. This is to be expected because chlorine resets with water rapidly to form hypochlorous and hydrochloric acids. Hypochlorous acid, the primary biocide, dissociates as a function of pH, forming the hypochlorite ion. Hypochlorite is reported to be from 1/20 to 1/300 as effective at microbiological control as hypochlorous acid.[85,86]

Unlike chlorine, chlorine dioxide remains a true gas dissolved in solution. The lack of any significant reaction of chlorine dioxide with water is partly responsible for its retaining its biocidal effectiveness over a wide pH range. This property makes it a logical choice for cooling systems operated in the alkaline pH range, or cooling systems with poor pH control.

Hypobromous acid also dissociates with pH. The dissociation curve is essentially equivalent to that of chlorine; its curve is offset by about 1 pH unit toward the alkaline range from that of hypochlorous acid. For example, the pH of 50% dissociation of the hypohalous acid to the hypohalite anion is about 7.5 and 8.7 for chlorine and bromine, respectively.

The disinfection efficiency of ozone, like that of chlorine dioxide, is relatively pH independent.[87] However, as the pH increases above about 8.5, the half life decreases due to the rapid formation of significant amounts of hydroxyl radicals. These hydroxyl radicals are much more reactive than ozone and have a half-life of microseconds. The net effect is that at high pH's neither disinfection nor oxidation will occur.[105]

Kinetics of Disinfection

Figure 2 shows a comparison of dosages of several commonly used biocides used as hard surface sanitizers, i.e., for hospitals, food applications, dental offices, etc. Comparisons are made for dosages required to achieve a five-log reduction in bacterial populations for several strains of bacteria with a 60 second contact time.[88] It is clear from this figure that chlorine dioxide reacts very rapidly, achieving a 99.999% reduction in viable bacterial cells in one minute.

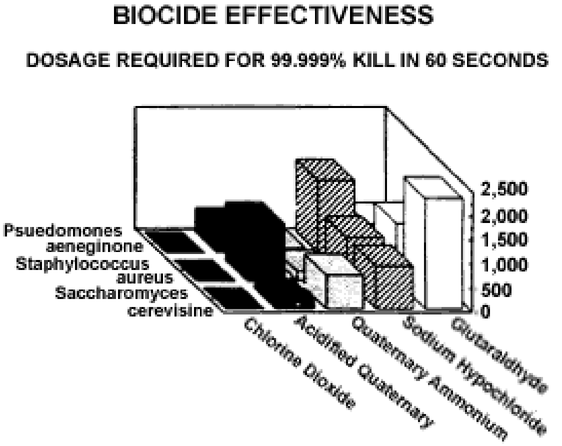

Fig. 2. Comparison of the Dosage Required to Achieve a 5-Log Reduction in Viable Bacteria at 60-Second Contact Time.

These results confirm those shown in Figure 1 along with those of earlier workers, who demonstrated the very rapid kill of bacterial populations by chlorine dioxide at times much less than the 30 minute period normally used in disinfection studies.[7,9,89,98]

The speed of disinfection of bromine is subject to some controversy. Many early researchers indicated that HOBr kills bacteria significantly faster than chlorine alone,[86,91] while others indicate it is slower at disinfection than chlorine.[92] Most probably, this discrepancy is due to work done on different strains of bacteria, as other researchers have noted the difficulty of establishing a clear criteria of which disinfectant is most effective for the same reason.[94] More work is needed here to establish clearly the relative biocidal efficiency of bromine as compared to that of chlorine.

It is generally agreed that ozone is the most rapid disinfectant.[93,94] This rapid reaction in 'dirty' systems results in a short half life of ozone in disinfection applications, e.g., from 10 - 20 minutes, at a pH < 8.5.

Selectivity

In potable and waste treatment applications, a number of researchers have commented on the significantly lower demand of the water for chlorine dioxide than for chlorine.[11,13,98] An example is shown in Figure 3.[11]

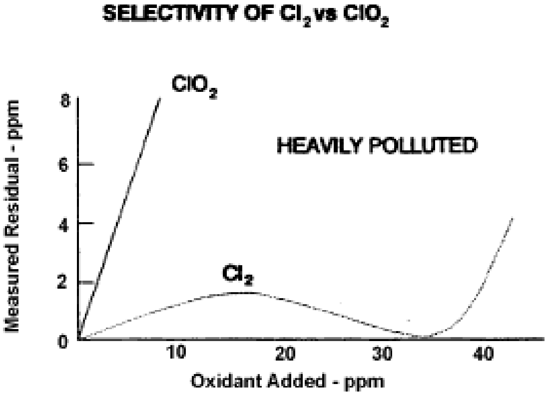

Fig. 3. Comparison of the Measured Residual vs. Dosage of ClO_2 with Cl_2 for a Heavily Contaminated Water.

Equivalent amounts of chlorine dioxide and chlorine were added to water streams with various levels of contamination. This figure shows the results for a highly polluted water stream. Residuals were measured after 30 minutes of contact, and the results were plotted against the initial dosage. The chlorine was largely consumed, regardless of how much was added. Chlorine dioxide, after some initial consumption, remained mostly unreacted. This characteristic is indicative of the much greater selectivity of chlorine dioxide than chlorine.

Chlorine is known to react with a wide variety of compounds.[95-97] It reacts primarily through oxidation, although it can react by both substitution and addition reactions.

There are many reports of the limited reaction of chlorine dioxide with organics.[11,67,77,81,98-100] This indicates that much more of the chlorine dioxide added to a system is available as a biocidal agent, and is not consumed to the degree that chlorine would be under the same circumstances.

In addition, chlorine will react with ammonia or any amine, while chlorine dioxide reacts very slowly with secondary amines, and not at all with primary amines or ammonia.

Bromine has a lower oxidation potential than chlorine, and thus would be expected to react predominantly by substitution, and not oxidation reactions. There is some controversy as to whether bromine acts more as an oxidizer or halogenator. Bromine is thought to oxidize faster than chlorine by some, producing fewer halogenated hydrocarbons than chlorine.[101] Other researchers have demonstrated in the laboratory that bromine tends to halogenate organics, while chlorine predominantly oxidizes, when chlorine and bromine react in combination.[155] The brominated organics which are formed are suspected to be more harmful than their chlorinated counterparts.[85]

Bromine also reacts with amines and ammonia. Unlike chlorine, bromamines largely retain their biocidal effectiveness, being almost as effective as hypobromous acid.[102] In addition, the bromamines formed have relatively short half-lives, thus eliminating the need for dechlorination in some plants.[103]

Ozone is the strongest oxidant which is used in disinfection. The products formed during reactions with organics are smaller organics which are more easily metabolized by bacteria than those formed from other oxidants.[104,105] This may create a problem in potable water systems where ozone is used as the sole disinfectant, as the rapid loss of a residual may result in a resurgence of microbiological growth downstream in the distribution system.[104] It may also be a problem in cooling water applications where the time to turn over the system is greater than the half life of ozone, because the residual does not persist.[106]

Compared to other oxidizers, ozone is relatively non selective, as it will react with many substances.[107] It reacts with ammonia at most cooling tower pH's, i.e., < 8.0.[105]

Bacterial Recovery after Disinfection

The phenomenon of rapid regrowth of bacteria in a highly organically loaded system after high chlorination is well established.[l08-110,112] How rapidly a bacterial population re-establishes itself after sterilization is an interesting phenomenon and is called bacterial recovery. This phenomenon has been the subject of some research. The results of one investigation is demonstrated in Figure 4. This figure, after Roberts, et. al., shows that after sterilization of a waste water stream with chlorine, the bacterial population re-establishes itself relatively rapidly.[111] For the same stream sterilized with chlorine dioxide bacterial recovery is somewhat slower.

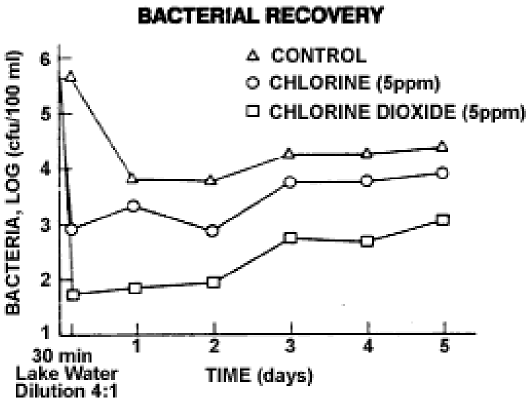

Fig. 4. Recovery of Bacterial Activity After Shock Dosage with ClO_2 and Cl_2.

A similar phenomenon was observed by McGuire and Dishinger.[70] In a cooling tower used for phenol destruction, one critical exchanger experienced fouling problems. Chlorine dioxide was fed just prior to this exchanger, keeping the exchanger clean. Even one week after the chlorine dioxide feed was stopped, the process outlet temperature had not reached the level it was prior to the introduction of the chlorine dioxide.

Relatively little information on bacterial recovery after disinfection with bromine was found. However, it is likely that recovery after disinfection with bromine would be comparable to that with chlorine.
For ozone, due to the rapid oxidation of organics into smaller, more easily metabolized fragments, rapid regrowth of bacteria is expected if the ozone residual is lost.[105]

Effectiveness on Biofilm Control/Removal
The disinfection requirements of an open recirculating industrial cooling system are markedly different from those of a potable water treatment facility. The disinfection goal of potable water facilities is the sterilization of water as measured by specific water borne pathogens. The goal of disinfection for industrial cooling systems is the removal or minimization of any biofilm, which retards heat transfer, causes biofouling, provides a place of agglomeration for marginally soluble or insoluble salts, and provides a place which nurtures and promotes the growth of highly corrosive anaerobic bacteria.[112]

One possible reason for the relatively slow re-growth of bacteria after sterilization by chlorine dioxide (Figure 4) lies in its superior ability to penetrate and disperse a biomass. By effectively killing and stripping off any biofilm, bacteria are much slower to re-establish than when the biofilm is left intact.[112]

Many researchers have cited the excellent biofilm removing properties of chlorine dioxide.[34-37,41,43,66,67,69-74,113] In at least one previously reported case history,[69] the introduction of chlorine dioxide into a heavily fouled cooling system resulted in an increase in both turbidity and calcium. These were explained by a dispersing of the biofilm which both increased turbidity and released small calcium carbonate particulates which had been trapped in the biofilm.

Other industries have made use of the excellent biofilm removal properties of chlorine dioxide, particularly the food industry.[41,43] Small cooling towers, frequently contaminated by food products or by-products, have tremendous slime forming potential. Chlorine dioxide has achieved widespread usage in such systems, due to its excellent biofilm dispersing/bacterial disinfecting properties.

Bromine has been shown to be significantly better than chlorine with regard to biofilm control by some researchers,[114] while others have found there to be little difference between chlorine and bromine.[86,115]

There is some controversy surrounding the effectiveness of ozone on biofilms. Some have reported that ozone can effectively control or remove biofilms[116,117], while other reports indicate that ozone is relatively ineffective on biofilms.[118,121]

Effects of System Contamination

Chlorine dioxide has a history of working exceptionally well in systems which are contaminated with ammonia.[69,122] It has also been very effective in cooling systems with a high level of organic contamination.[67,69,72,74]

A number of case histories were analyzed.[67,69,123-125] Figure 5 shows a rough relationship between oxidant demand and increasing system contamination. It is clear from this figure that as system contamination increases HOCl/NaBr becomes more economical than chlorine. As contamination continues to increase, chlorine dioxide becomes economically favored.

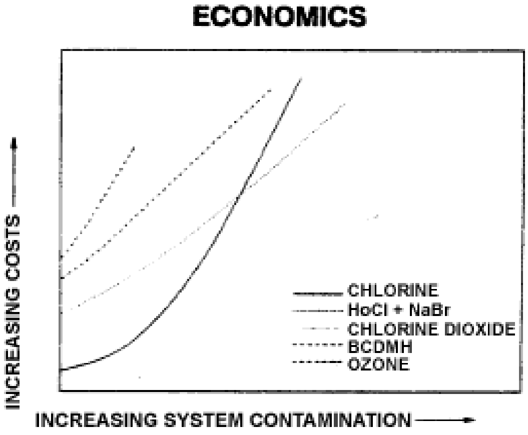

Fig. 5. General Overview of Relation Economics of Several Oxidants with Increasing System Contamination.

The problems with use of bromine, particularly the hydantoin-based material, becomes apparent in 'stressed' systems, such as in one Gulf Coast refinery, where rain water and other runoff water is collected in ponds, and used as supplemental cooling makeup water.[128] In this refinery, one 40,000 gpm recirculating cooling tower has a chlorine demand of 2000 lbs/day. In an attempt to move away from gaseous chlorine, bleach was used. A delivery was required every few days, creating unacceptable risks and inconvenience. From bleach, the plant moved to a hydantoin-type bromine material. In this high demand system, costs went up by a factor of eight, and this was limited only by the inability to dissolve more hydantoin. These costs did not including the tremendous increase in the feed rate of non-oxidizing biocides. Despite these efforts, the plant did not achieve or maintain adequate microbiological control. The plant has since moved back to gaseous chlorine on this cooling system.

In addition to this example, others have agreed that bromine is not recommended for use in hydrocarbon contaminated systems.[129]

Ozone works well in systems that are clean. As the demand for oxidant increases, required feed rates for ozone dramatically increase. For example, studies on the effectiveness of ozone for virus destruction has shown ozone to be very effective, in clean systems.[93] Other work, on contaminated systems with virus incorporated into bacterial cells, have indicated that ozone, probably because of its lack of selectivity, is relatively ineffective, even at high feed rates.[86,94]

In summary, for 'stressed' systems, e.g., systems which are contaminated with hydrocarbons or other contaminants, there is generally much less of a demand increase for chlorine dioxide than for other oxidizing biocides which may be used for microbiological control.

Disinfection Effectiveness Comparison:
The question has arisen as to how chlorine dioxide can be so effective at such low dosages. Figure 6 shows an overview of oxidizing biocides used as disinfectants in cooling systems. The left most column, labeled Oxidizing Strength, is the oxidation potential in volts. This parameter describes how strongly the oxidant reacts with an oxidizable substance. Thus ozone, which is the strongest agent listed, has a higher oxidation potential and will react strongly with everything that is oxidizable.[105,106] Hypochlorous acid, the active biocidal agent which is formed from the reaction of water and chlorine gas, is weaker than ozone, but stronger than hypobromous acid and chlorine dioxide. Finally, chlorine dioxide is the weakest agent shown. Hypochlorite and hypobromite are shown for comparison, but since these are in equilibrium with their counterparts, these should not be considered as separate entities.

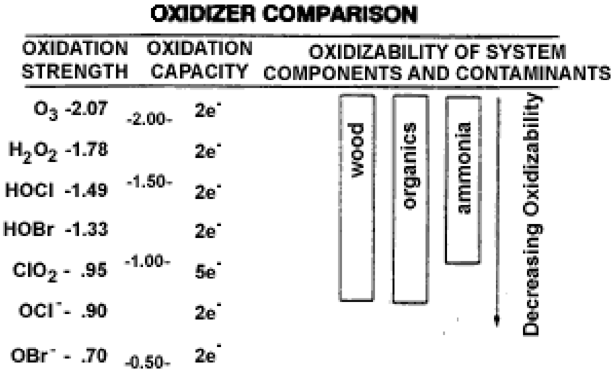

Fig. 6. Comparison of Oxidation Potential and Oxidation Capacity of Several Oxidants Along with Relative Oxidation of Materials Commonly Found in Cooling Water.

Column 2 shows the Oxidation Capacity of the various oxidizing biocides. That is, how many electrons are transferred during an oxidation reduction reaction. Because the chlorine atom in chlorine dioxide has an oxidation number of +4, chlorine dioxide can accept 5 electrons in an oxidation-reduction reaction, if it is reduced to chloride. Accounting for molecular weights, chlorine dioxide has 263% 'available chlorine', or slightly more than 2.5 times the oxidizing capacity of chlorine.

Finally, column 3 shows a subjective overview of the "oxidizability" of certain materials commonly encountered in cooling systems, or in other words, how easily these materials are oxidized. As one goes down this table, the materials shown are less easily oxidized. For example, ammonia, known to be oxidized by ozone and hypochlorous acid, reacts reversibility, with bromine and does not react with chlorine dioxide at all.

Wood is another material commonly found in cooling systems which is attacked by ozone and chlorine. Delignification is a well known phenomenon which occurs by chlorine attack at relatively high pH's. Chlorine dioxide will react with only the phenolic-type compounds in wood. In other words, chlorine and ozone react with far more of the compounds in wood than does chlorine dioxide.

In summary, Figure 6 shows that of the materials commonly found in open recirculating cooling systems, chlorine dioxide reacts with much fewer than chlorine or ozone, i.e., it is a much more 'selective' oxidant than either chlorine or ozone. Thus when added to a cooling system, far more of the chlorine dioxide is available to react with the intended target, e.g., bacteria and bacterial slimes than either chlorine or ozone.

Figure 6 shows oxidation reactions only. For chlorine and bromine, both addition and substitution reactions can also occur, producing organic halides. In addition, this figure is based on thermodynamic considerations. But kinetics also plays a very important part. For example, although ozone has the potential to react with many organics, some of these reactions are notably very slow.

ENVIRONMENTAL

Formation of Trihalomethanes

In the mid to late 70's researchers linked the chlorination of potable water to increased cancer mortality rates.[16-20] This increase in cancer mortality was related to increased levels of trihalomethanes, THM's, primarily chloroform.[21,22] Researchers found that chlorine reacted with certain naturally occurring organics to produce chloroform. As a result of this work, the USEPA set 0.1 ppm as the maximum THM containment level for drinking water. Subsequently, research in the area of THM reduction in potable water[23-27] led to the EPA in 1983 citing chlorine dioxide as an effective means of controlling THM's. Practical application has shown a significant reduction or absence of THM's in systems treated with chlorine dioxide.[28,61,64,89,98] And although THM production has been considered predominantly in the drinking water industry, the production of chloroform is seeing increased pressure from environmental regulators in industrial plants. In Colorado recently, one industrial plant which used gaseous chlorine made the switch to chlorine dioxide because the effluent limit for chloroform was reduced to 6 ppb, and the plant could not meet effluent guidelines while utilizing chlorine as the primary cooling tower microbicide.[130]

Bromine reacts with naturally occurring organics much like chlorine, producing THM's. As mentioned earlier, the mutagenicity of brominated organics is thought to be worse than its chlorinated counterparts.

Ozone does not directly produce THM's. However, in waters with significant bromide levels, the formation of bromoform has been observed.[126,127]

Formation of Haloorganics

It is a commonly held belief that for every organic molecule which exists there are one or more bacteria which can metabolize part or all of it.[131] However, research has shown that some molecules, particularly halogenated hydrocarbons, are at best very slowly metabolized if at all by bacteria.[132,133] This can result in a buildup of these chlorinated hydrocarbons in the environment. Currently held theories of bacterial evolution suggest that synthetic halogenated molecules will be degraded only if they bear a structural resemblance to those which occur in nature. Besides being quite resistant to biodegradation, many of these chlorinated hydrocarbons have been shown to be toxic for various life forms.[59,134] These factors have resulted in more than one environmental group becoming alarmed because of the use of halocarbons, e.g., chlorinated solvents.

A significant amount of halogenated hydrocarbons results from the reaction of chlorine or bromine-based microbicides, including gaseous chlorine, with organics in cooling towers.[131,135] These organics are present because of process leaks from petroleum refineries or petrochemical plants, airborne contamination, or as naturally occurring organics present in the makeup water.

In addition to the lack of THMs, the amount of total organic halides, TOX, found in systems treated with chlorine dioxide is extremely low or nonexistent.[136-138]

As mentioned earlier, bromine can react by substitution and addition reactions as well as by oxidation. The brominated hydrocarbons formed are more toxic than those produced by chlorine.

Ozone does not produce halogenated organics, except in waters where a significant bromide level is found. In such cases several brominated organic species have been found.[126,127]

Toxicity to Aquatic Organisms

In discussing relative toxicities, four aspects must be considered: the relative toxicity of the disinfecting agent, the half-life of the disinfecting agent, the relative toxicity of its by-products, and the relative toxicity of the reaction products. Free residual chlorine, along with its by-products are toxic to aquatic organisms.[139-142] Chloramines are also very toxic to aquatic organisms. In addition, the chlorinated organics are known to be toxic.

There is some controversy surrounding the toxicity of chlorine dioxide to aquatic organisms. Some researchers report that chlorine dioxide is two to three times more toxic than chlorine.[142] A number of others have reported that chlorine dioxide is several orders of magnitude less toxic than chlorine or its residual by-products.[86,113,143,144] It is likely that some of these studies have not separated the toxicities of the chlorine dioxide from that of the chlorite formed in the generation of chlorine dioxide.

Chlorite, the predominant oxidation by-product of chlorine dioxide, has been shown to produce signs of hemolytic stress when fed to animals, at levels as low as 50 ppm. The concern over individuals susceptible to oxidative stress has led to the limit for total chlorine dioxide, chlorite, and chlorate in drinking water being set at 1.0 ppm. However, in several studies performed on human subjects, no effect was observed.[145-148]

The toxicity of bromine residual is similar and in some cases not as severe as that of chlorine.[144] Bromamines do not appear to be as toxic as chloramines, primarily due to the relatively short half-life. Brominated hydrocarbons are thought to be significantly more toxic than chlorinated hydrocarbons.

Ozone is very toxic to aquatic life.[150] Its short half-life in most cases results in the dissipation of the ozone well before discharge to effluent. In systems with relatively short residence times, the toxicity of ozone will be a significant consideration. Ozone reacts with naturally occurring organics which are present in surface water to produce peroxides and epoxides which are known to be carcinogenic.[151-154]

SAFETY

The safety surrounding the use, storage, and handling of gaseous chlorine is an increasing concern. The safety aspects of chlorine are well established and have been reviewed elsewhere.[86] The safety considerations involved with the use of chlorine dioxide are three-fold.

First, there is the consideration of chlorine dioxide as a gas. Due to its instability, it must be generated on site. The generator chosen must be designed in such a way that gaseous chlorine dioxide cannot accumulate. Most generation systems are designed with safety features which will automatically shut the system down if catastrophic failures occur, such as the loss of dilution water.

The construction of a chlorine dioxide generator is not difficult. Commercially available ones are relatively simple, with pumps to move the precursors. For these types of systems, the safety aspects of the design have to be built in. That is, various controls are installed which are designed to work in case of a problem.

More elegant designs are those systems which are eductor driven. Such systems are inherently safe. Loss of dilution water leads to loss of vacuum and the generation of ClO_2 is interrupted. These systems rely on simple check valves to prevent the backflow of precursors. The system should be designed so that nowhere in the system does the concentration of chlorine dioxide exceed its solubility limit.

The second aspect is the storage of the precursors on site. For those plants desiring to eliminate gaseous chlorine storage, a three chemical feed approach would be appropriate (equation 2). Storage of precursors can be done safely. However, of all the incidents which have arisen out of the use of chlorine dioxide, by far the largest number have been because of improper storage or handling of the sodium chlorite solution. Attention to proper equipment selection and installation will solve these problems.

The third safety aspect is the operation of equipment by plant operators. Although modern generators can be made with proper safeguards, some knowledge of the generation process is required. An operator who operates the generator part time, and then only intermittently with shift work, will not be as alert to problems as one who operates the unit as his primary responsibility.

BCDMH in small quantities, requires attention and frequent refilling of brominators. Problems with control of such a feed system are notable. The generation of dust by the BCDMH is one significant disadvantage to using small quantities of the material.

The use of chlorine and sodium bromide adds another degree of complexity to the use of gaseous chlorine. The use of bleach and sodium bromide is perhaps the safest of all the alternatives discussed here.

Ozone equipment is reported to be maintenance intensive and expensive. Destruction of the excess ozone which is produced (and vents the system to atmosphere) is a requirement for systems used to treat potable water, swimming pools, and other applications.

In addition, there are concerns about human contact with water treated with ozone, as both ozone and the hydroxyl free radical which are formed are very strong oxidizing free radicals; some medical research has suggested a free radical mechanism for the initiation of cancer.

ECONOMICS

Although the properties discussed previously make chlorine dioxide an ideal choice as a microbicide for industrial cooling towers, its use as a chlorine replacement has been limited. One reason is the issue of costs. The use cost of chlorine dioxide can be several times that of gaseous chlorine. With the pressure to eliminate gaseous chlorine, chlorine dioxide costs become favorable to many of the conventional chlorine replacements. In fact, for heavily contaminated systems, the use cost of chlorine dioxide can rival that of chlorine.[66] The relative costs for common chlorine alternatives is similar to that reported previously, with some notable exceptions.

For clean systems:

pH 6.8-8.0

$Cl_2 < NaOCl < HOCl + NaBr < ClO_2 < BCDMH < ozone$

pH 8.0 - 9.3

$HOCl + NaBr < ClO_2 < BCDMH < Cl_2 < NaOCl < ozone$

For systems with high organic loading:

pH 6.8 - 9.3

$ClO_2 < HOCl + NaBr < BCDMH < Cl_2 < NaOCl < ozone$

For systems with ammonia contamination

pH 6.8 - 9.3
$ClO_2 < HOCl + NaBr < BCDMH < Cl_2 < NaOCl < ozone$

A NOVEL APPROACH

Unichem International has adopted an approach which minimizes the impact of the three considerations described above. An eductor driven generator and the three precursors required for most efficient generation have been mounted on a truck. The precursors are in individual double containment compartments, each precursor having its own catch basin in case of a leak. DOT approved containers allow transport on public highways, and the roll protection and compartmentalization insure safe transportation, even in case of an accident. Minimal quantities of the precursors are carried on each truck, i.e., just enough precursor is carried for that day's generation. Trucks are equipped with appropriate safety equipment. Deactivating solutions for the precursors and the chlorine dioxide solution are carried on the vehicle.

Unichem Generation Engineers are dedicated to the vehicle. Their job is to generate chlorine dioxide safely and efficiently. They locate the vehicle near the cooling tower of interest and then attach short, chemically resistant flexible hoses from the inlet and outlet of the generator to a specially designed piping arrangement. The pipe which provides motive water comes from the discharge of the cooling tower recirculation pumps. This water is piped to the site of the generator hookup. Generated dilute aqueous chlorine dioxide is returned normally to the pump sump through pipes to a header. Dilute aqueous chlorine dioxide is generated and introduced into the pump sump. The quantity, frequency, and duration have been previously determined during an initial two phase trial period which included system cleaning followed by feedrate optimization. While attending the generator during the generation process, the generation engineer performs some routine tests.

This mobile approach allows the cost of such a process to be spread over several cooling systems. The intermittent treatment approach and the performance characteristics of chlorine dioxide make such a system ideal for most cooling systems. Of course there will be those systems which require a treatment more than once every 1 to 3 days. For such systems, or for those systems which experience severe hydrocarbon leaks which create substantial increases in demand, and for periods where the truck is undergoing maintenance, a trailer mounted unit is used. For isolated systems, an on-site fixed generation system can be employed. The on-site fixed system does not answer all of the items listed above, however, the performance characteristics may outweigh other considerations in choosing a chlorine replacement.

The areas which have limited the use of chlorine dioxide in many industrial plants are the Safe to Use/Easy to Handle areas. These areas are addressed by the introduction of the mobile concept. Mobile generation systems have been used successfully in the oilfield for several years. The mobile system brings the following benefits:

- No storage of hazardous chemicals on-site.
- Minimal chemicals brought on site.
- No plant handling of hazardous chemicals.
- Economics which are comparable to BCDMH.
- No capital investment.
- Safety.

SUMMARY

The properties of an ideal microbicide have been described. The commonly used oxidizing biocides, chlorine, bromine, chlorine dioxide and ozone have been reviewed in the light of these properties. The results are summarized in Figure 7.

COMPARISON OF OXIDIZING BIOCIDES IN LIGHT OF THE CRITERIA OF AN 'IDEAL' BIOCIDE
Report Card

	HOCl	HOBr	ClO_2	O_3
PERFORMANCE				
High pH	C	B	A	A
Kinetics	B	B	A	A
Selectivity	C	B	A	D
Biofilm	B	B	A	C
System Contamination	C	C	A	D
Bacterial Recovery	B	B	A	C
ENVIRONMENTAL				
THM	C	C	B	A
TOX	C	C	B	A
Toxicity				
of primary oxidant	B	A	A	C
of oxidation by-products	B	B	C	A
of oxidation reaction products	B	C	A	D
residual life (short life best)	C	B	C	A
SAFETY				
Easy to Use	B	B	C	B
Safe to Handle	B	B	C	B
ECONOMICS				
Clean System	A	B	B	C
Contaminated System	C	C	A	C
Cumulative GPA	2.6	2.8	3.3	2.7

Fig. 7. Relative Rankings for Chlorine Bromine, Chlorine Dioxide in View of Characteristics of an Ideal Biocide.

Although these relative rankings are somewhat subjective, the rankings are based on data from the literature. Grades have been assigned to each category, and a cumulative grade point average has been computed.

It should be clear from this that although each of the oxidizers listed excel in one or more areas, when reviewed as a whole, chlorine dioxide comes closer to achieving the status of 'Ideal' biocide than any of the others.

CONCLUSIONS

The short term driving force for the move away from gaseous chlorine to the various alternatives is predominantly the health and safety issues relating to the handling, storage and integrity of one-ton cylinders. If the recent trend continues, the long term force driving the move away from gaseous chlorine will be the reaction products between chlorine and organics, and the impact that these chemicals have on the environment.

We have seen a move into bromine chemistry, although this will be undoubtedly a relatively short term measure for the same reason if the trend continues. Not much work environmentally has been done with brominated organics, although they are expected to be more harmful than structurally similar chlorinated organics.

Ozone as a viable long term replacement for chlorine is being explored, due to its excellent biocidal activity. However, ozone does suffer from several serious drawbacks. Because of its strong oxidizing ability, it will not differentiate between the target organisms and the corrosion inhibitor packages used with it to control scale and corrosion.[107] Its effectiveness on biofilm control is questionable.

If the industry trend continues, the useful life of hypohalous acid-based oxidizing biocides will be limited. With the additional factors of increasing water reuse, i.e., increasing system contamination, and regulatory requirements of non-oxidizing biocide re-registrations, i.e., decreasing availability of non-oxidizing biocides, the need for a high performance chlorine replacement is becoming increasingly apparent. The superior performance characteristics of chlorine dioxide coupled with the mobile feed system makes chlorine dioxide the 'Ideal' biocide.

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