ABSOLUTE OZONE®

Ozone in Cooling Water Treatment

By Mario C. Uy, World Environmental Technologies, Inc.

When commercial ozone generators were first introduced for cooling water treatment, they were marketed as a stand-alone treatment, a cure-all or panacea. We now know this is not the case. Because there have been many misconceptions regarding ozone, this article is intended to review the basics of ozone, its true capabilities and limitations, and its potential benefits in cooling water treatment applications.

What is Ozone?

Ozone (O_3) is formed by combining three atoms of oxygen. The air we breathe contains two atoms of oxygen (O) in the molecular form of O_2. When sufficient energy is applied to the molecular O_2, such as the discharge of electricity during a thunderstorm or strong UV radiation from the sun, some of the molecular O_2 will split into two individual oxygen atoms. When the individual oxygen atoms merge with other oxygen molecules (O_2), they form O_3. Ozone is a very unstable molecule and will readily revert O_2.

Capabilities

Ozone is a very powerful oxidizing biocide, viricide, fungicide, sporicide, disinfectant and sterilizer. It kills microorganisms on contact by cellular lysis and cytoplasmic dispersion - it directly ruptures the cell walls of the microorganisms, which results in an instantaneous death. By comparison, chlorine kills bacteria by diffusing through the cell wall and then oxidizing the enzymes within the cell.

Ozone kills microorganisms including *E. Coli, Legionella, Pneumophilia, Streptococcus Facalis Bacillus, Clostridium, amoebae cysts, Giardia, Cryptosporidium, Pseudomonas,* etc. It also eradicates fungi, mold and yeast. In addition, ozone:

- Oxidizes and mitigates pollutants from water and wastewater.
- Breaks down volatile organic compounds (VOC) such as, phenols, benzene, pesticides and other aromatic hydrocarbons.
- Breaks down inorganic compounds such as cyanides, sulfides, nitrites.
- Removes color.
- Bleaches.
- Removes taste and odor.
- Removes soluble iron and manganese indirectly by converting them to filterable insoluble solids.

Ozone is very friendly to the environment. The extra atom of oxygen makes ozone very unstable. While it has a half-life of about 20 minutes in clean water, its half-life in dirty water is even shorter as it is consumed by the microorganisms, VOCs and other compounds. Because ozone breaks down to oxygen, ozone does not leave any toxic or carcinogenic by-products. It does not impart any taste, odor, color or solids.

By comparison, chlorine forms carcinogenic by-products, such as trihalomethanes (THM) and other halogenated compounds. When added to water, chlorine hydrolyzes to hypochlorous acid, which further hydrolyzes to hypochlorite ion, both of which can linger and adversely affect our hydrological system.

Since ozone reverts rapidly to oxygen, it cannot be packaged and stored. Thus, it must be generated on-site. In turn, this on-site generation eliminates any hazards associated with transportation, storing and handling.

Table of Oxidizing Chemicals

Oxidizing agent	Oxidation potential(volts)	Power relative to chlorine
Fluorine (F_2)	3.6	2.25
Ozone (O_3)	2.07	1.52
Hydrogen Peroxide (H_2O_2)	1.77	1.30
Potassium Permanganate ($KMnO_4$)	1.67	1.23
Chlorine (Cl_2)	1.36	1.00
Chlorine Dioxide (ClO_2)	1.27	0.93
Bromine (Br_2)	1.09	0.80

Table is courtesy of CEC the Ozone Company

What is the Significance of Ozone?

Ozone is a very powerful oxidant, even more powerful than chlorine. Shown in Table 1 is a comparison of the oxidizing potential of ozone to other oxidizing agents.

Commercial Production

Ozone is produced commercially in the same way it is formed naturally by lightning or UV radiation from the sun. The commercial lightning method is called corona discharge. Dried air or oxygen is passed through an electrified field (corona) generated by a high voltage between positive and negative grids. The high voltage splits the molecular oxygen into atomic oxygen. Some of the atomic oxygen merges with molecular oxygen to form ozone, while other oxygen atoms simply recombine to form O_2. A fraction of oxygen in the air is transformed into ozone.

When ambient air is used as a feed gas, the amount of ozone generated is between 1 and 2 percent by weight in air. When oxygen is used as a feed gas, the ozone generated is between 6 and 12 percent by weight.

Natural UV radiation is simulated commercially by UV lamps. Air is passed through a chamber between the UV lamp and a shield. UV light can create or destroy ozone depending on the UV wavelength. Wavelengths of 185 nanometers (nm) are required for the generation of ozone and 254 nm for the destruction of ozone. This method produces a very low level of ozone and is usually suitable for small applications. In addition to these methods, ozone may also be made through electrolytic and chemical reactions.

How is Ozone Injected?

Ozone is typically injected into water via a venturi. A side stream water pump is typically used to create the vacuum on the venturi with a static mixer installed after it to ensure adequate mixing, distribution and proper contact between the ozone and water. Another less popular alternative is the diffuser method, where ozone is injected under pressure through diffusers creating bubble columns - much like air diffusers in aquariums.

Destroying Ozone

Ozone can be destroyed by catalytic conversion units, activated carbon filters, thermal destructors or by ultraviolet radiation.

Catalytic conversion is the most popular method of ozone destruction. Activated carbon filtration decomposes ozone but carbon is also consumed in the process. There is also a risk of fire as carbon could ignite under high exothermic condition. In thermal destruction, ozone is destroyed by heating it in excess of 300 degrees Celsius. Ultraviolet radiation decomposes ozone at the wavelength of 254 nanometers.

Early Misconceptions

In cooling water applications the most common problems encountered are scale, deposition, corrosion, fouling and microbiological (bacteria, algae, or fungi) growth. Today, there is an even greater threat – the emergence of pathogenic bacteria like *Legionella Pneumophila*. Microbiological growth is a concern because it contributes to and amplifies deposition, corrosion and fouling by acting as a nucleation point or catalyst for these problems. The effect of microbiological growth on scale, deposition and fouling is one of the early misconceptions of ozone.

Early applications showed that ozone also removed mineral deposits. Later, it was found that this removal was only true where the deposits were held in a bio-matrix. It is like the steel structure of a building that holds up all the bricks. By destroying the steel structure at strategic points, the whole building implodes.

Comparing this analogy to the bio-induced deposits, the bio-matrix held the deposits together, acting like glue. When the ozone destroyed the bio-matrix, the attached crystals became dispersed. Not understanding this phenomenon fully, some ozone manufacturers began marketing their equipment as a scale inhibitor. Needless to say, ozone failed to prevent mineral deposits under other conditions, such as supersaturation, excessive hardness, and alkalinity.

Because microorganism also induces other problems such as corrosion and fouling, ozone was also marketed early on as a corrosion and fouling inhibitor, under similar biological pretext. Likewise, ozone failed to prevent these problems under non-biological conditions.

Traditionally, non-oxidizing biocides and oxidizing biocides are used to control microbiological growth. Typical non-oxidizing biocides are organo-sulfur compounds (carbamate based, thiocyanate), organotin, isothiazolone, organobromine (dibromonitrilopropionamide), organic thiocyano-azole (benzothiazole), glutaraldehyde and quaternary ammonia.

Typical oxidizing biocides are chlorine, bromine and chlorine dioxide. Most of the biocides have a long-term negative impact on the environment. As such, there is a growing pressure to reduce or restrict these biocides in the blowdown water, especially if the water is being discharged to a waterway. In addition to the discharge burden, these biocides have to be stored, transported and handled, which increases potential health and injury risks to personnel.

Limitations

Because of its short half-life, ozone levels drop off rapidly as time progresses, and as the ozone moves away from the injection point, its disinfecting efficacy decreases. In systems with long piping runs, ozone may not travel far enough, leaving the farthest areas vulnerable to microbiological growth. This situation may be remedied by injecting ozone at various strategic points throughout the water system. A bio-dispersant can be added to penetrate and disperse the sessile bacteria (growing on surfaces) so that they can become planktonic (floating in water), thus enabling the bacteria to be transported to the ozone injection point for destruction

Increasing the ozone level at the injection point to raise residual level downstream is not recommended. The higher ozone concentration may destroy the water treatment chemicals, increase corrosion near the injection area and destroy seals, gaskets, or other components in the system.

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Ozone is limited in penetrating biofilm. It may burn the surface of the biofilm, protecting the microorganisms underneath from further destruction. Therefore, they will survive and will likely continue to cause localized corrosion. This situation may be remedied by adding a good bio-dispersant to penetrate and disperse the biofilm, including the bacteria living under the biofilm.

Ozone does not discriminate in terms of what it oxidizes. If ozone is used as a disinfectant in water loaded with other non-biological organic matters, they will also consume ozone. As such, there may not be enough ozone residual to accomplish the intended disinfection. The remedy is to generate more ozone to supply the total ozone demand. However, this increases costs in both operating and capital. As such, ozone may not be cost effective for these types of applications.

Potential Health Hazards

According to the EPA, "the same chemical properties that allow high concentration of ozone to react with organic material outside the body give it the ability to react with similar organic material that makes up the body. When inhaled, ozone can damage the lungs. Relatively low amounts can cause chest pain, coughing, shortness of breath, and throat irritation. Ozone may worsen chronic respiratory diseases such as asthma and compromise the ability of the body to fight respiratory infections."

EPA makes a distinction between ozone in the upper and lower atmosphere. Ozone in the upper atmosphere, referred to as stratospheric ozone, helps filter out damaging ultraviolet radiation from the sun. Conversely, ozone in the lower atmosphere, – the air we breathe – can be harmful to the respiratory system.

OSHA has issued a threshold limit value (TLV) on ozone exposure to 0.1 mg/L over eight hours per day and five days per week, or 0.3 mg/L for a 15-minute continuous exposure. Because of the potential health hazards, it is crucial to destroy any excess ozone in a safe way.

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ABSOLUTE OZONE®

On-Site Chlorine Dioxide: A Review of Uses, Safety and New Processes – Part II

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In part I, the author provided an introduction to chlorine dioxide, including nomenclature, differences between residual and demand, and what is meant by free, total and available chlorine dioxide. Part II discusses chlorine dioxide generation. In Part III, the author will present various delivery equipment, the handling of chlorine dioxide precursors, and application chemistry and performance.

The ideal approach in the measurement of efficiency would be to perform a steady state mass balance on a piece of equipment and calculate the percentage of conversion that is occurring based on the stoichiometric equations (5) through (9). Here is the first area for potential confusion. Equation 5 has a lower stoichiometric ratio of chlorine dioxide to sodium chlorite than equations 5 and 8. Thus, the chosen reaction would affect the calculated efficiency for a given mass balance. Indeed for the reaction in equation 5 the term activation, rather than efficiency, is often used as the percentage of conversion compared to the stoichiometric equation. Thus, in order to compare equipment utilizing different chemistries, it is prudent to compare the number of moles of chlorine dioxide output for the number of moles of sodium chlorite, or sodium chlorate input.

The mass balance approach has another weakness. It could be calculated by comparing the measured input of sodium chlorite, or sodium chlorate, with the measured output of chlorine dioxide. A simple uncertainty analysis indicates that such a mass balance is severely flawed, given that the concentration of sodium chlorite solution is much greater than that of the chlorine dioxide solution, 25 % (w/w) compared to typically 3,000 mg/L. An accurate mass balance would require a calculation involving errors from the actual molar concentration of the sodium chlorite, or chlorate, from a nominal weight percent solution, the flow rate of sodium chlorite or chlorate, typically measured by a rotameter which might be accurate to ± 5 % of full scale, or by cumbersome drawdown on a metering pump feed. The chlorine dioxide concentration could be measured relatively accurately, but again the flow rate would typically be measured with a rotameter accurate to ± 5 % of full scale with a flow two orders of magnitude larger than the precursor flow.

One approach that has been useful in the field has been to analyze the output of the generator and calculate the efficiency as defined in the following equation:

Equation (1)

$$Efficiency(\%) = \frac{[ClO_2]}{[ClO_2] + [ClO_2^-]} x100$$

Where:

$[ClO_2]$ = chlorine dioxide concentration in mg/L and $[ClO_2^-$
$]$ = chlorite ion concentration in mg/L.

For systems utilizing sodium chlorate the chlorate ion concentration can be substituted for the chlorite ion concentration.

This approach is routinely used for equipment in the municipal drinking water market. It does not rely on any flow rate measurements, but does require either a 4-step colorimetric or amperometric titration. Alternatively, the use of a spectrophotometer and a 2-step titration can be considered. These techniques are somewhat cumbersome and time consuming, but are routinely carried out in the field.

Yield

Yet another approach in measuring equipment performance is the yield. This term has the advantage of not being dependent on the chemistry involved or the use of inaccurate flow measurements. It has also been defined in an EPA Guidance Manual [i] and thus can be considered to be independent of any particular equipment manufacturer. *Yield* is defined in the following equation:

Equation (2)

$$Yield(\%) = \frac{[ClO_2]}{[ClO_2] + [ClO_2^-] + (\frac{67.45}{83.45})[ClO_3^-]} x100$$

Where

$[ClO_3^-]$ = chlorate ion concentration, mg/L and
(67.45/83.45) = molecular weight ratio of ClO_2^- to ClO_3^-.

Yield, however, requires the measurement of chlorate ion, which is presently not practical with a field test and typically requires the use of a lab based ion chromatographic technique. Thus, yield is of limited use in the field.

Excess chlorine is of concern in equipment utilized in the municipal drinking market. In general terms, it is the amount of chlorine in the effluent over that required for complete reaction. The same EPA guidance manual defines it as:

Equation (3)

$$Excess\_Chlorine(\%) = \frac{[Cl_2]}{[ClO_2]+[ClO_2^-]+(\frac{67.45}{83.45})[ClO_3^-] \times \frac{70.91}{2x67.45}} x100$$

Where
(70.91/(2x67.45)) = stoichiometric and molecular weight ratio of Cl_2 to ClO_2^-.

Excess chlorine is only of concern with methods that use chlorine or hypochlorite as a precursor.

Purity – Finally, purity is a term that is also used when considering equipment performance that is a somewhat more simple equation that is independent of equipment and chemistry and considers chlorine contaminated chlorine dioxide, it is also defined in the same EPA guidance manual:

Equation (4)

$$Purity(\%) = \frac{[ClO_2]}{[ClO_2]+[FAC]+[ClO_2^-]+[ClO_3^-]} x100$$

Where
[FAC] = free available chlorine concentration as chlorine, mg/L.

Like yield, purity requires measurement of the chlorate ion concentration and cannot be measured practically in the field. It should be noted that efficiency, yield, and purity are all instantaneously measured parameters – and that a good quality item of chlorine dioxide generating equipment should produce acceptable results consistently throughout its use.

Measuring Equipment Performance

The problems raised by the terms conversion, efficiency, yield and purity are of more concern with the potable water market than in the treatment cooling water systems, where the economic and regulatory impact of the different numbers obtained by the use of equations 1, 2 or 4 are not likely to be significant. It would seem prudent to ensure that any specification involving performance criteria on a chlorine dioxide generator is not only explicitly defined, but that the measurement techniques to be involved should also be defined. An even more prudent route might be to avoid any confusion by writing a specification that does not involve these terms, but, for example, requires performance criteria on the system being treated or considers the cost basis of chlorine dioxide itself, rather than the precursors themselves.

Chlorine Dioxide: Formation Chemistry and Delivery Equipment

There are a number of methods in which chlorine dioxide is generated on-site for the treatment of cooling waters. Although these choices may add complexity to the design of a chlorine dioxide system, their variety provides flexibility that allows selection of the method best suited for a particular installation. One potential problem is that vendors may have a favored method, or access to a limited selection that is not always best suited to every customer's needs; a good vendor will clearly explain the benefits to the specific customer of their choice.

Sodium Chlorite Based Generation - There are three main routes for generating chlorine dioxide from sodium chlorite.

Chlorite/Acid Reaction - (Also known as acid catalyzed chlorite ion auto-oxidation, acid activation or activation). Hydrochloric acid is typically used; the reaction is usually presented as:

$$5\mathrm{NaClO_2} + 4\ \mathrm{HCl} \rightarrow 4\mathrm{ClO_2} + 5\mathrm{NaCl} + 2\mathrm{H_2O} \qquad (5)$$

This chemistry has the advantage of requiring only two precursor chemicals, also since no chlorine species are used, there are very little chlorine species in the generator effluent, although chlorate ion can be present in significant quantities.

However, the stoichiometric ratio of chlorine dioxide to sodium chlorite is only 0.8. Additionally, most commercially available generators only achieve 90% of this yield, thus only about 70% of the sodium chlorite is converted to chlorine dioxide. This typically makes the economics unattractive except for small-scale systems.

Typically about 250% excess hydrochloric acid is used and this can result in high chloride concentrations and a very low pH, which has led to corrosivity concerns in certain systems. Additionally, because the reaction is relatively slow, a high concentration of precursors is required which requires an instrumented system to assure safe operation.

Delivery systems typically involve both an eductor and either solenoid driven or motor driven metering pumps to meter the precursor chemicals. Larger pump based systems typically include a third metering pump to provide dilution water to the reaction zone.

Chlorite Ion Oxidation with Chlorine - Chlorine gas is one of the most economical generation methods available when only the cost of precursors is considered. This is referred to as “2-part generation.” Recently a combination of sodium hypochlorite and acid has become more favored as plants try to minimize or eliminate the use of gaseous chlorine. This is referred to as “3-part generation.” The reactions are presented as:

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + NaCl \tag{6}$$

$$2NaClO_2 + NaOCl + 2HCl \rightarrow 2ClO_2 + 3NaCl + H_2O \tag{7}$$

The stoichiometric ratio of chlorine dioxide to sodium chlorite is 1. Typically commercial generators obtain over 90% of this conversion. Given that the sodium chlorite is by far the most costly of the precursors, these chemistries are often more attractive than chlorite/acid reaction. These groups of chemistries are the predominant methods used in the US potable water market and are thus relatively well understood.

Delivery systems utilizing chlorine gas are in essence modified chlorinators: the fundamental components are a water driven eductor (also known as a venturi or ejector) with two rotameters (also known as variable area flow meters) for each of the two precursor chemicals. The eductor loses vacuum with no water flow and this is an inherently safe way of limiting the precursor flows with a loss of dilution water.

Operation of this type of equipment is not complex, once the similarity between this type of system and a typical gas, or sodium hypochlorite, chlorinator is understood.

Delivery systems utilizing sodium hypochlorite and an acid may be eductor based, or alternatively either solenoid driven or motor driven metering pumps are used. For systems utilizing metering pumps an instrumented safety system must be used to ensure that the metering pumps do not operate in the event of loss of dilution water, as this would lead to the potential for an unstable chlorine dioxide concentration.

Manufacturers of both eductor and metering pump delivery systems for both gas and hypochlorite chemistries utilize one of two different reaction techniques. The first allows the reaction of the precursor chemicals undiluted under vacuum. The second dilutes the precursors before reaction with each other. Each method has its own advantages. The first allows a reaction that does not require such a low pH to be maintained as is required with the second. The second eliminates problems caused by salt clogging of the reaction zone resulting from a high concentration of reagents and avoids any location in the equipment with a potentially unstable chlorine dioxide concentration.

Eductor based systems have a given dilution water flow rate for a given inlet water pressure and eductor size. There is a limited concentration range in which they operate; the turndown that they offer in terms of chlorine dioxide production rate is limited without replacement of the installed eductor size, and possibly precursor rotameters. The turndown offered by metering pump systems is limited by the turndown of the metering pumps themselves. The metering pumps will also limit the maximum capacity of such a system, whereas selection of a larger eductor, within the limits of the hydraulics of the system piping can increase the capacity of an eductor-based system. Thus, manufacturers who offer eductor based systems often offer far fewer models than those who offer metering pump systems and this can be advantageous because a particular eductor based system can be utilized to treat different systems with very different capacity requirements.

Eductor based systems, especially those utilizing chlorine gas, are limited by the hydraulic performance of the eductor. One limitation is the acceptable backpressure seen by the eductor. However, the pressures seen in the vast majority of cooling systems do not cause problems.

Because chlorine is required for this generation chemistry there will be chlorine species in the generator effluent. This is not so much a concern in the treatment of cooling waters as in the treatment of potable waters. In potable water systems, chlorine dioxide is often used as a substitute for chlorine because chlorine species are responsible for the formation of chlorinated disinfection byproducts such as trihalomethanes (THMs) and haloacetic acids (HAAs). The concentrations of these byproducts are regulated in the US and elsewhere in many potable water systems.

There are other much less commonly used delivery systems available utilizing this chemistry. One utilizes the reaction of gaseous chlorine with a solid sodium chlorite product. This delivery system generates a gaseous chlorine dioxide stream with no chlorite ion, chlorate ion or molecular chlorine species in the chlorine dioxide. These benefits must be compared with the, often, unfavorable economics associated with producing special dilute chlorine formulations, or gaseous chlorine from a pressurized cylinder, or the handling of dry sodium chlorite and management of the spent waste material.

One recent development in chlorine dioxide delivery systems is a chlorine dioxide dosing system utilizing a hydraulically driven metering pump. This system has been proven in a variety of applications including the treatment of a cooling system at an oil refinery in California.

It is limited to the reaction of sodium chlorite, sodium hypochlorite and an acid. The novel aspect of this technology is the use of a hydraulically driven metering pump with three precursor chemical metering heads that simultaneously inject the precursors downstream of the hydraulic motor into the water stream that drives hydraulic motor coupled to the three metering heads.

This arrangement has some of the advantages of an eductor-based system such as the inherently safe function whereby a loss of motive water causes a loss of feed of precursors. It also has very high efficiency, yield and purity.

Electrochemical Oxidation of chlorite ion - This one electron anodic reaction is represented as:

$$ClO_2^- \rightarrow ClO_2 + e^- \qquad (8)$$

This method has the significant advantage of requiring only one precursor chemical.

Commercially available equipment has fallen into two categories. The first system utilizes a single pass of the precursor chemical through an electrochemical cell to generate chlorine dioxide. These systems do not fully convert chlorite ion to chlorine dioxide and have had a very limited capacity, which means they are suitable only for smaller cooling systems. They have a fixed chlorine dioxide generation rate.

The second type of electrochemical generator utilizes a chlorine dioxide selective membrane, which produces essentially pure chlorine dioxide and recycles the unreacted chlorite through the electrochemical cell, allowing almost full conversion. This type of system has a much larger capacity than the first type of system. It has been targeted at the potable water market and involves a large capital expenditure for complex equipment.

This method of generating chlorine dioxide presents the best opportunity for a dramatic step change in the generation of chlorine dioxide, but at present the commercial offerings are very limited.

Sodium Chlorate Based Generation - This method is represented by the following reaction:

$$NaClO_3 + 1/2\ H_2O_2 + 1/2\ H_2SO_4 \rightarrow 1/2O_2 + Na_2SO_4 + H_2O \qquad (9)$$

The sodium chlorate and hydrogen peroxide are available blended as a proprietary solution, thus only two liquid precursors may be required. The sulfuric acid may have to be of a specific concentration and low iron grade and the resulting chorine dioxide solution has a very low pH. However, in many cooling systems where acid is added for other reasons this may not be a problem. This reaction requires a high concentration of precursor chemicals and this requires an instrumented system to ensure safe operation.

Selection of Chemistry - Each of the methods, and indeed generating equipment used, will produce chlorine dioxide solutions with slightly different characteristics. These differences are expected to impact the treatment of very few cooling water systems. Thus the different formation chemistries available allow a selection of the most appropriate, safe, user friendly and economical method for a particular system. Therefore a comparison based on the cost of chlorine dioxide produced rather than of the precursor chemicals themselves can clarify the optimal chemistry. The diversity and flexibility in chemistries are actually an advantage that will allow more widespread use of chlorine dioxide in cooling systems.

Selection of Delivery Equipment – Most chlorine dioxide equipment is either based on the use of metering pumps or an eductor. Both these technologies are very commonly used in the dosing of cooling water and other systems with treatment chemicals and both have excellent reliability records when utilized correctly. Thus the reliability of chlorine dioxide delivery equipment is based upon good engineering practices and design practicality in addition to the selection of the auxiliary equipment options associated with the core dosing equipment.

All reputable manufacturers of chlorine dioxide equipment have refined equipment design and reliability over many years and can provide reliable equipment, if applied correctly. If there are stringent requirements on uptime, which is often not the case with the treatment of cooling waters, redundant delivery systems are often used.

It is interesting to note that one paper presented to this conference in 1999[ii] describes four years' operating experience at a power utility on multiple cooling towers using secondary waste water treated with chlorine dioxide. This paper describes no problems with the chlorine dioxide equipment, but significant failures of the acid and polymer dosing systems.

One aspect of consideration may become prominent as chlorine dioxide is utilized more for the treatment of smaller cooling systems. Often in these cases limitations in the minimum capacity of some chlorine dioxide systems has led to the use of chlorine dioxide solution, or batch tanks. Experience has shown that the use of such tanks can often be avoided and is difficult to design and maintain and as Trevor Kletz wisely opines "What you don't have can't leak."

Manufacturers offer equipment with a selection of levels of instrumentation and controls for safe operation and routine monitoring and control. Systems range from manual systems with a manually adjustable production rate and no indication of improper function other than physical observation to flow-pacing systems that automatically adjust chlorine dioxide production rate and will alarm in the event any process parameter has deviated from normal limits. Cooling systems do not typically require such sophistication, but very often will include timer and ORP operation. Specific requirements can often be achieved with chlorine dioxide equipment. As an example experience has been gained with the use of a chlorine dioxide dosing system in a Class 1, Division 2, Group C and D Hazardous Location at an Agricultural Chemicals plant in Alabama.

Safety of Chlorine Dioxide Use

Unfortunately there is little hard statistical analysis on the safety of the use of chlorine dioxide. One possible reason for this is that recently the number of incidents has not prompted significant enough interest to initiate detailed investigation.

There is, however, no doubt that there is concern within the industry about the safety of the use of chlorine dioxide. This probably stems from early experience where chlorine dioxide generation and use were not fully understood and it was misapplied.

By their very nature, biocides present risks in storage, handling and use. Chlorine dioxide is no exception. Due care must be taken with all of these biocides to ensure safe operation.

One report[iii] presented the results of a literature search over a 20-year period, combined with incidents detailed in private communications to the author. It found that the vast majority of incidents involved the improper storage or handling of the precursor chemicals. The second largest number of incidents involved misapplication or the intentional application of chlorine dioxide for a specific purpose that resulted in a problem. There were very few incidents involving the delivery system itself. Each of these three categories will be presented in turn with simple guidelines that can ensure safe use of chlorine dioxide.

Improper Storage and Handling of Precursors – Good practices that will ensure safe chlorine dioxide precursor chemical storage and handling are similar to those used for many hazardous chemicals. These include appropriate storage facilities, materials of construction, labeling and location. Handling can be safely carried out with appropriate training, the use of appropriate personal protective equipment (PPE), and proper handling equipment.

The properties of chlorine dioxide precursor chemicals require special attention and the relatively uncommon use may lead to misperceptions.

Aqueous sodium chlorite solutions have potential health effects:

Eye contact may cause severe irritation and may cause burns
Skin Contact may cause irritation and may cause burns
Inhalation may cause respiratory tract and mucous membrane irritation with sore throat, coughing and difficulty breathing
Ingestion may be harmful and may cause gastrointestinal irritation
Sodium chlorite is not listed by IARC, NTP, OSHA or ACGIH as a carcinogen.

These health effects mean that a safety shower and eyewash facilities must be immediately accessible when handling sodium chlorite solutions. Appropriate PPE, which is typically identified on the precursor product label, include coveralls chemical splash goggles, a face shield and impervious gloves and other clothing.

Sodium chlorite solutions are available in bulk delivery, in IBCs (totes), drums and pails. The appropriate container should be selected to minimize the risks associated with handling. It is often possible to draw out of the top of these containers and this will minimize any handling requirements.

Sodium chlorite solutions in contact with acids, organic materials, reducing agents or chlorine donors will produce chlorine dioxide gas. This can be avoided by storing sodium chlorite solutions away from such materials, using segregated secondary containment to keep any spills from such materials, clear labeling and signage, training and proper unloading procedures. Particular care should be taken with bulk unloading to ensure that a material other than sodium chlorite is not unloaded into a sodium chlorite bulk storage facility. Sensible precautions involve clear labeling, color coding of the connectors and a lock on the connector used to fill the bulk tank, so that an operator or the sodium chlorite supplier must be present and aware during a fill.

Additionally, care should be taken that sodium chlorite is not put into containers that contain, or have contained, incompatible materials. Empty sodium chlorite containers should be triple rinsed, marked as such, and disposed of in a proper manner.

Sodium chlorite in the dry form is a strong oxidizing agent, and if allowed to dry can be easily ignited by heat or friction. Care should be taken so those containers with a residual of sodium chlorite are not allowed to evaporate to dryness. The same is true of sodium chlorite spills. They should not be diked with absorbent pigs or allowed to dry.

If allowed to dry on cloth, wood or other combustible material sodium chlorite and sodium chlorate can create a fire hazard. This has caused an incident in which a worker handling sodium chlorite got a small amount of sodium chlorite of his cotton gloves that later ignited. Sodium chlorite and sodium chlorate should be stored and handled away from combustible materials, PPE should be impervious and workers trained in the hazards presented by sodium chlorite.

Bulk storage tanks and facilities for sodium chlorite require careful design. A tank manufacturer and sodium chlorite supplier typically should be involved in such a design.

Misapplication of Chlorine Dioxide – There have been incidents where chlorine dioxide has been used without a good understanding of the chemistry and properties of chlorine dioxide. Many of these have occurred in oil production and involve the reaction of chlorine dioxide with an organic material or sulfide. Any new application of chlorine dioxide should be thoroughly reviewed by a group familiar its properties and chemistries. A formal Process Hazard Analysis (PHA) should be used to ensure that adverse incidents will not occur.

One area of concern can be personnel exposure to chlorine dioxide gas. Chlorine dioxide should not be dosed into an enclosed space without careful monitoring and controls. Chlorine dioxide should be added to a system that has good ventilation where the potential exists for exposure to personnel. The OSHA 8-hour Time Weighted Average Permissible Exposure Limit is 0.1 mg/L, which is similar to the odor threshold.

Chlorine dioxide generation is not as uncommon as some people believe, indeed it is estimated that about 10 % of the US population receive drinking water that has been treated with chlorine dioxide. Its use has become common in potable water plants. As more operators have first hand experience with chlorine dioxide rather than unflattering perceptions, the perception that it can be used safely has become predominant in that industry.

Chlorine dioxide has been successfully used in the treatment of cooling waters for about three decades. Thus a great deal of experience has been obtained in the safe use of chlorine dioxide in such systems. A typical open recirculating cooling system consisting of a cooling tower and heat exchangers is a perfect system for the safe use of chlorine dioxide. Chlorine dioxide is typically dosed at levels that leave a residual that does not present the potential for unacceptable personnel exposure. A cooling tower by its very nature provides ventilation that prevents the occurrence of an unacceptably high concentration of chlorine dioxide in the atmosphere.

Certain precaution should be taken in treating typical cooling systems. A method should be used to ensure that chlorine dioxide is only dosed into a system that is in operation. This can be achieved by using a flow switch, an auxiliary contact on the recirculation pump, or where necessary, procedures for operator intervention. The chlorine dioxide dosage must be controlled to an amount that will not result in unacceptable overdosing. This can be achieved by allowing only a maximum production rate from the delivery system and routine monitoring of the chlorine dioxide residual in the system. One approach that is often used to optimize treatment that will prevent over treatment is the use of ORP (Oxidation Reduction Potential) monitoring. An ORP probe is used at some point in the process, typically the cold well, and the delivery system is run during a certain time period until the ORP reaches a predetermined level.

Delivery Systems – The extensive experience gained by delivery system manufacturers has led to many designs that allow safe and reliable operation. Some of the types of delivery systems were described in more detail in a previous section.

A delivery system should have undergone a rigorous Process Hazards Analysis (PHA) to ensure that it will operate safely. In assessing the delivery system, consideration should be given not only to the chemical reaction itself, but also maintenance and operational issues. A good delivery system will be designed to have sufficient valving and fittings to allow the purging and isolation of components for replacements and repairs. The delivery system should include an Emergency Stop Button to allow rapid shut down. It should have sufficient control flexibility to allow operation only with external interlocks and dose signals being used and provide a remote signal of alarm status. Eductor systems that operate on vacuum may be preferred since leaks in fittings will result in a leak of air into the precursor chemical lines, rather than a leak of precursors out of the lines.

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REFERENCES

1. Anonymous, Alternative Disinfectants and Oxidants Guidance Manual. United States Environmental Protection Agency, Office of Water, EPA 815-R-99-014, (1999)
2. Debenedetto. T *et al.,* IWC-99-42 (1999)
3. Simpson, G.D. *et al.,* Biocides: The safe and Effective Use of Chlorine Dioxide. Industrial Water Treatment, September/October (1995)

An Overview of FIFRA: Regulating the Manufacturing, Sales, and Application of Biocides

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The Federal Insecticide Fungicide and Rodenticide Act (FIFRA) is a far-reaching and intricate law. The U.S. Environmental Protection Agency (EPA) and trade associations hold three-day workshops to cover some of the more routine registration information and processes. And law firms hold one to two day sessions on individual issues, such as data compensation. This article is an introduction to some aspects of the FIFRA which are important to the industrial water treatment business.

Active Ingredient

Biocide businesses that innovate and introduce new products into the marketplace have invested considerable time and money into obtaining registrations. The EPA requires significant amounts of information on the active ingredient.

The active ingredient is any substance that is considered by the registrant to be the ingredient that acts on the target pest. Without this substance, the product would not function as a pesticide. The cost to develop the studies supporting a new industrial water treatment biocide active ingredient is close to $1 million.

End-Use Product Registration

End-use registration is a product containing an active ingredient(s) and other "inert" ingredients. It is the product applied at a use site and it includes directions for use to control the pest(s). The EPA data requirements for these products can also be significant.

For the bare minimum of test to support the chemistry and toxicity of a product, the cost is approximately $100,000.

There are two types of end-use products:

1. Public health use products (other than drugs as regulated by FDA) that are intended to control microorganisms infectious to man. These products require submission of efficacy data to the EPA to support registration.
2. Public health pesticides that are hard surface disinfectants claiming to kill organisms such as E. coli, pseudomonas or viruses such as HIV, and influenza.

Non-public health use products provide an economic or aesthetic benefit such as controlling odor, spoilage, deterioration, and fouling. Efficacy studies are generally not required to be submitted, but evidence of performance should be maintained in company files. Industrial water treatment products are non-public health products.

Supplemental Registrations

A supplemental registration allows fast entry to market without generating and submitting data, then waiting for EPA to review and accept the data. Supplemental registrations may also be called a sub-registration. A distributor, with the cooperation of the primary registrant, can sell a private labeled product within a very short period of time. The distributor is considered an agent of the registrant for all intents and purposes under the Act, and both the registrant and the distributor may be held liable for violations pertaining to the distributor product.

The typical interaction between a primary registrant and a supplemental registrant is as follows: A private label company (or "distributor" as EPA calls them) locates a product that fills a need and wants their company name on the label. The distributor then contacts the primary registrant. The primary registrant sends a supplemental registration package to the customer with instructions on how to use the product. The package should include the EPA label and EPA form. It may also include confidentiality, distributor, or other agreements. The customer then returns the completed package with a proposed label and signed documents to the primary registrant for review. The primary registrant reviews the label for conformance to the registered label. Only a few changes are allowed on the label. The primary registrant either signs documents or returns the label for correction. This cycle is continued until the label is perfect. The primary registrant returns a copy of the document to the distributor and mails the form to the EPA.

Product Label and Advertising Claim

The registered product label is important for a variety of reasons. The EPA stamped "accepted" label is a key element in regulating and evaluating EPA registered products. Manufacturers cannot sell or distribute a product with pesticide claims until they receive an accepted label from the EPA.

The label is written, printed, or graphic matter attached to the pesticide or any of its containers or wrappers. All other written, printed, or graphic matter that accompany the pesticide at any time, including an MSDS, technical data sheets, and internet or electronic media, could all be considered labeling and must not contradict the label.

Product advertising is an easily recognizable item in ads, newsletters, and brochures. The general guidance of each product is that the labels are legal, enforceable documents. Any false claims or misleading statements contained in these documents may bring fines and/or other actions by the EPA. Under the FIFRA, it is illegal to sell or distribute a registered pesticide with claims about the product that substantially differ from claims accepted as a part of its registration with EPA

The labels must meet the following criteria:

- Comply with EPA's regulatory requirements for text size, and text must be clear and legible.
- Be clear and understandable to the user under normal conditions.
- Provide accurate precautions and directions.
- Contain no false or misleading statements or implied federal government endorsements.

The EPA is very concerned about what claims are made on a label and other documents used in the sale of a registered product. They have issued several Public Relations Notices to registrants to clarify what are acceptable and unacceptable claims. EPA has addressed three types of label claims:

- General claims that can be unrelated to the pesticidal properties of the product (non-FIFRA claims, e.g., non-foaming or non-staining).
- Acceptable claims associated with the product name (e.g., Killz-All-Brom is not acceptable).
- Efficacy related claims, (e.g., bacteriostatic is acceptable, where as super-strength is unacceptable).

State Registration
State registrations require all pesticides sold in a state to be registered within that state. The registration requirements differ significantly for the various states. Most states request a copy of the label, MSDS, a complete application form, and a fee. The annual cost for one pesticide registered in all 50 states is over $7,000. Every year the product must go through a renewal process.

By law, California has the ability to assess a millage tax on each sale of pesticide in their state. The mill assessment rate per dollar of pesticide sales is currently at 17.50 mills for all pesticides. Agriculture pesticides pay an additional 0.75 mills.

Adverse Effect Reports
The distributor must either report adverse effect to the primary registrant or directly to the EPA. As mentioned previously, a supplemental registrant is considered to be an agent for the primary registrant. Usually the primary registrant will request that they do all reporting.

The types of information to be reported include human or domestic animal exposures. Reporting requirements change according to the severity of the incident. Information on adverse effects should be relayed to the primary registrant as quickly as possible. An adverse effect report includes unexpected results from a toxicity test, but also includes incident reports when a person or pet is exposed and have symptoms such as rash or burn.

Production Facilities

The requirement to register production facilities that produce pesticides or devices must have a registered establishment number assigned by the EPA. Production includes manufacturing, mixing, repackaging, and re-labeling. After an establishment has been registered, an annual pesticide production report must be submitted to EPA, due by March 1 of each year. Failure to report may result in fines and cancellation of the EPA Establishment Number.

The EPA Establishment Number of the final establishment in which it was produced or relabeled must appear on the label or immediate container of each pesticide product released for shipment from the producing establishment.

The producers and distributors of pesticide products must maintain records of production, inventory, shipping, and distribution, and must allow inspection of their records by EPA and state officials at reasonable times.

FIFRA Violations

The FIFRA vests substantial enforcement authority in EPA. When a violation is believed to exist, the EPA is authorized to order the person in violation to stop selling or using the pesticide, and may in certain cases seize the pesticide. Civil and criminal penalties may be imposed against violators. The FIFRA provides a long list of punishable acts. Some types of violations are unregistered pesticides sales, label misbranding, adulteration of a product, and failure to report adverse effects.

If these violations exist, the EPA will stop its sale and use through a Removal Order. This is the most effective remedy to prevent illegal sales. The EPA can impose a monetary penalty based on the Enforcement Response Policy of $5,500 for each offence. The formula to compute the penalty includes business size, gravity of violation, ability to pay, voluntary disclosure, and good faith adjustments. Prosecuting individuals in the criminal court may impose criminal penalties. This occurs when persons knowingly (willfully) violate the FIFRA.

An example of EPA enforcement occurred on October 2002 when the EPA issued a stop sale order for two companies making claims that their products were effective against Anthrax. Both companies were marketing and advertising their products over the Internet. In the press release EPA states: "The EPA continues to inspect advertisements on the Internet and other marketing venues to identify unregistered pesticides being illegally sold to the public. SARS and toxic mold are also items being monitored by the EPA."

In May 2003 a person was arrested for selling counterfeit, misbranded, adulterated, and mislabeled pesticides to numerous municipalities in Alabama and Georgia. The EPA's

Criminal Investigation Division and the FBI investigated the case. The individual who lived in Michigan pled guilty of selling unregistered pesticides and violating a Stop Sale and Use Order (SSUO). In this case, the plea agreement called for the defendant to spend up to nine months in jail and place advertisements in trade journals notifying customers that he violated the SSUO and stating that he will no longer sell the pesticide.

It is important to follow the guidelines set by the EPA for the manufacture, distribution, sale, and application of pesticides. Severe consequences can occur in terms of monetary fines or criminal prosecution for violating the FIFRA.

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