

## CHLORINE DISINFECTANTS AND ORP CONTROL

**Douglas G. Kelley, Ph. D.**

Technical Director, Inland Environmental Resources, Inc.  
P.O. Box 594, Loon Lake, WA 99148

### INTRODUCTION

The science of water disinfection is still a relatively new field for the tree fruit industry, as the widespread use of water disinfectants in this marketplace has only been occurring over the past couple of decades. In comparison, industrial water systems such as open recirculating cooling systems and evaporative condensers have been receiving chemical treatment for over five decades, and drinking water has been disinfected for over a century.

The initiation of drinking water treatment around 1900 was a major contributor to the dramatic increase in average life expectancy, from 47.3 years in 1900 to 69.7 years in 1960 (Ref. 1). Likewise, the initiation of the use of chlorine in apple and pear dump tanks about 20 years ago resulted in a dramatic reduction in fruit decay.

In this new millennium all water treatment applications are being challenged with new guidelines and changing markets. For instance, new U.S. Environmental Protection Agency (EPA) regulations have reduced the acceptable level of chlorinated disinfection by-products, such as chloroform, that can be present in drinking water (Ref. 2). Such guidelines encourage the use of lower doses of chlorine in drinking water. However, at the same time, another new regulation requires drinking water facilities to maintain their water systems free from harmful pathogens such as *cryptosporidium* (Ref. 3). In order to minimize the risk of pathogenic microorganisms in drinking water, this new regulation encourages the use of higher levels of chlorine. Finally, watch-dog environmental groups are taking legal action against municipal wastewater treatment plants that are out of compliance with chlorine residuals and high levels of chlorinated-organic by-products present in the discharge water. These new drinking water and wastewater regulations and legal pressures are already beginning to impact the fruit industry. In the midst of these regulatory changes at home, the industry is facing strong international marketing competition from countries that were much smaller players just a decade ago.

Fortunately for the tree fruit industry, many lessons can be rapidly assimilated from the more established water treatment applications. This paper attempts to provide two primary lessons that may aid in minimizing the impact of new regulations and new marketing pressures. The lessons involve optimization of disinfectant dosage, using on-line oxidation-reduction potential (ORP) technology, and minimization of disinfectant chemistry, using salt-free chlorine dioxide technology.

### OPTIMIZATION OF DISINFECTANT DOSAGE USING ORP CONTROL

ORP or “Oxidation Reduction Potential” has been discussed previously in this forum by Trevor Suslow of UC-Davis, as well as in a number of his articles (Ref. 4). Dr. Suslow has done an excellent job of explaining how water disinfection can be optimized through the use of an on-line ORP probe and controller that activates a chemical metering pump for “on-demand” delivery of an oxidizing disinfectant (such as chlorine). The continuous measurement of ORP values

provides a trend that can be related to the oxidant residual in the water system. ORP is a measure of the “oxidizing potential” or “reducing potential” of the water in millivolts. Most well waters possess an “oxidizing potential” that relates to an ORP reading in the range of 100 to 150 mV. When an oxidant like sodium hypochlorite (NaOCl, also called bleach) is added to a water system, the ORP millivolt (mV) reading increases with the increasing dosage. There is a direct correlation between oxidant residual, “oxidizing potential” of the water, and the ORP mV reading. Likewise, when a dechlorinating agent like sodium bisulfite (a reducing agent) is added to the water the ORP reading will drop back down to a low mV level.

Through the use of an on-line ORP probe and controller wired to turn on and off a chemical metering pump, a constant residual of an effective dose of disinfectant can be maintained in a tree fruit water system, regardless of how “dirty” the water may become. The practice of automated dosage control allows for optimized disinfection with the use of a minimal amount of chemical. The industrial standard practice of periodically slug-feeding 100 ppm chlorine into a dump tank is a far worse method, both for microbial minimization and for the risk of causing fruit quality defects.

Under certain water chemistry conditions, an ORP reading will change even though the concentration of the free chlorine in the water remains unchanged. Suslow has reported data using a Pulse Instruments ORP probe in which the ORP values in a water solution dosed with 3 ppm NaOCl were ~750 mV at pH 6.5 and ~610 mV at pH 8.5. This inverse correlation of ORP with pH is a unique attribute of the chemistry of chlorine in water.

### **EFFECT OF pH ON THE ORP READING OF CHLORINE**

Chlorine is typically applied into a tree fruit water system in the form of 12.5% NaOCl. When NaOCl dissolves in water it dissociates into caustic soda (NaOH) and hypochlorous acid (HOCl), equation 1.



The addition of NaOH into the water drives the pH to more alkaline levels. If the natural pH of the water is nearly neutral, then bleach addition will increase the pH to 8 or 9.

Hypochlorous acid, the most important form of chlorine in water, is also called “free chlorine” and is the primary agent responsible for killing microorganisms. However, HOCl is a weak acid in water, meaning that it partially dissociates into the hypochlorite anion ( $\text{OCl}^-$ ), equation 2. Unlike HOCl,  $\text{OCl}^-$  is a very poor biocide.



Hypochlorous acid is both a strong oxidant (1.49 V) and an effective biocide;  $\text{OCl}^-$  is a weaker oxidant (0.94 V) and very poor biocide. There is always an active equilibrium going on in water as chlorine switches back and forth from the HOCl form to the  $\text{OCl}^-$  form.

In equation 2, we can see that  $\text{H}^+$ , the chemical symbol for acid, plays an important role in determining the nature of chlorine in water. If the pH of the water is below 7 (acidic), the  $\text{H}^+$

concentration will be high. This will cause the  $H^+$  and  $OCl^-$  to combine, to form more HOCl, the biocidal form of chlorine.

Conversely, if the pH of the water is above 7 (alkaline or basic), the  $H^+$  concentration will be low. This will shift the equilibrium of equation 2 and cause the HOCl in the water to dissociate into  $H^+$  and  $OCl^-$ , the non-biocidal form of chlorine.

At a pH of 7.5, 50% of the chlorine in the water will be in the HOCl form and 50% will be in the  $OCl^-$  form.

Let's consider the practice of periodically slug-feeding 100 ppm of bleach into a dump tank water system. What will happen? There will be an initial increase in pH as the NaOH produced in equation 1 is introduced into the water. This increased pH will cause the HOCl/ $OCl^-$  equilibrium to shift to the  $OCl^-$  side. If the water at pH 7.5 before the bleach addition rose to pH 8.0 after the addition, then only ~25 ppm of the total 100 ppm dose of chlorine would actually provide any biocidal benefit. In this case, 75 ppm of the added bleach would be wasted. This is a lot of chemical (and salt) to add to the water for very little "bang-for-the-buck".

On the other hand, if an acid is used to maintain the pH of the water at pH 6.5, then ~95% of the bleach addition would remain in the HOCl (effective biocide) form.

When the chemical components in bleach have completely reacted, sodium chloride (NaCl) remains behind. With each subsequent dose of NaOCl into a water system, the NaCl concentration and total dissolved solids (TDS) level in the water climbs. If a dump tank water system receives either continuous or slug-doses of bleach for an entire week, the resulting TDS level at discharge will be very high. What effect does this increasing TDS level have on fruit quality?

### MINIMIZE CHEMISTRY AND OPTIMIZE DISINFECTION

One alternative to bleach is chlorine dioxide ( $ClO_2$ ). Chlorine dioxide was first used to replace chlorine as a pulp bleaching aid, because of the formation of toxic chlorinated by-products from chlorine use (equation 3a). Chlorine dioxide does not chlorinate organic molecules, but instead oxidizes them (equation 3b).



As an example of this important chemical difference, Table 1 provides the biocidal efficacy and trihalomethane (THM) formation of HOCl and  $ClO_2$  in a side-by-side pear dump tank study. There are two primary points to learn from this study. First,  $ClO_2$  at 1/10th the dose of chlorine gives better performance for minimization of *penicillium* and yeast populations in the dump tank water. Three part per million of  $ClO_2$  outperformed 30 ppm of NaOCl. This is consistent with numerous studies in drinking water and cooling water industries, showing that  $ClO_2$  is less consumed than chlorine by the organic debris in the water. An excellent resource for comparative disinfection data is the EPA Alternative Disinfectants and Oxidants Guidance Manual (Ref. 5).

Secondly, the THM level in the chlorinated dump tank was 2549 ppb, of which 2540 ppb was in the form of chloroform (a hazardous chlorinated organic by-product). The THM level in the ClO<sub>2</sub>-treated dump tank was 154 ppb. It is likely that the only 154 ppb THM level was a result of residual chlorine in the water used to fill and maintain the level in the dump tank.

**Table 1.** Chlorine dioxide is less affected by organics than chlorine and does not form chlorinated organics.

<b>Five-Day Study in Side-by-Side Floatless Pear Dump Tanks</b>		
	<b>Chlorine Dioxide Tank</b>	<b>Bleach Tank</b>
Oxidant concentration	3.15 ppm ClO <sub>2</sub> (0.19 to 5.7 ppm)	32 ppm TRO (0 to 120 ppm)
Penicillium (cfu/mL)	5.83	45.83
Yeast (cfu/mL)	0	101.0
<b>Trihalomethanes (ppb)</b>	<b>154</b>	<b>2549 (2540 ppb as HCCl<sub>3</sub>)</b>

Some of the biggest concerns with ClO<sub>2</sub> relate to its gaseous nature in water. However, when properly understood, this attribute can provide the industry with numerous benefits. As a dissolved gas in water, ClO<sub>2</sub> does not take part in the acid-base chemistry that dictates the effectiveness of chlorine. Instead, ClO<sub>2</sub> will provide the same degree of antimicrobial efficacy regardless of the pH. This allows ClO<sub>2</sub> to be used in very low pH dump tanks to de-scale apples, under conditions where chlorine cannot be used due to “gassing off” of toxic Cl<sub>2</sub> gas.

The biggest challenge with the use of ClO<sub>2</sub> is that it cannot be purchased in a drum like bleach—it must be generated on-site. Most traditional ClO<sub>2</sub> generation systems produce a mixture of ClO<sub>2</sub> and sodium chlorite, the starting material that is not completely converted to ClO<sub>2</sub> by the generator. Using this method, both ClO<sub>2</sub> and the salt precursor are added to the water system. However, new generation systems are coming into the market that produce a pure, salt-free form of ClO<sub>2</sub>, allowing for maximum disinfection, minimal chemical and salt addition to the water, and minimal formation of potentially hazardous by-products.

## **SAFETY ISSUES RELATED TO THE USE OF CHLORINE AND CHLORINE DIOXIDE**

There have been numerous instances of misapplication of chlorine and chlorine dioxide in the tree fruit industry that have resulted in “gassing off” of the oxidants, where a cloud of noxious gas rapidly fills an entire packing house room. Most of the issues with “gassing off” pertain to water temperature, pH, and oxidant dosage.

The most common occurrence of “gassing-off” with chlorine or bleach is when the pH of a dump tank water system is rapidly reduced with acid in order to use the tank for de-scaling hardness from the surface of apples. Recall from equation 2 that when the acidity is increased, the chemical equilibrium shifts to the formation of HOCl. Equation 4 shows another reaction that occurs at low pH—the release of chlorine gas, Cl<sub>2</sub>, from solution.



As the pH drops, Cl<sub>2</sub> gas can form, escape from solution, and result in the release of strong noxious chlorine odors into the packing house. In addition, a majority of the chlorine added to a dirty dump tank is transformed into chloramine (equation 5) through reactions with natural amine-containing organic molecules in the water.



Chloramines are much more volatile than chlorine, and are readily “gassed off” at reduced pH.

Being a dissolved gas in water, chlorine dioxide is much more volatile than chlorine or chloramines. In addition, gas-phase ClO<sub>2</sub> is comparably hazardous and noxious as chlorine. For this reason, the primary mechanisms for ClO<sub>2</sub> to “gas off” must be well understood in order to maintain a safe and effective ClO<sub>2</sub> application.

First, ClO<sub>2</sub> should never be applied to a heated water system, such as an apple dump tank that is being maintained at >80 °F. As a dissolved gas in water, ClO<sub>2</sub> is rapidly released from solution with increasing temperature. For effective microbial control, any biocide must be maintained at a sufficient residual. At dump tank water temperatures >80 °F, ClO<sub>2</sub> cannot be maintained at a sufficient residual in the water system. Attempts to do so will result in “gassing off” of the majority of the ClO<sub>2</sub> and a release of noxious gas into the packing house. Chlorine dioxide residuals of 0.5 to 1.0 ppm can be safely maintained at 70 °F, while ClO<sub>2</sub> residuals of 3 to 5 ppm can be safely maintained in 50 °F water.

Secondly, chlorine dioxide will “gas off” from a water system if the concentration in the water gets too high. A situation that can cause a high ClO<sub>2</sub> concentration is when a neutral pH dump tank is rapidly acidified for the purpose of de-scaling apples. The mechanism of “gassing off” is different than that discussed previously for chlorine. As was stated before, ClO<sub>2</sub> is stable in water regardless of the pH. However, ClO<sub>2</sub> can be regenerated within the acidic dump tank water through catalytic reactions (equations 6a and 6b).



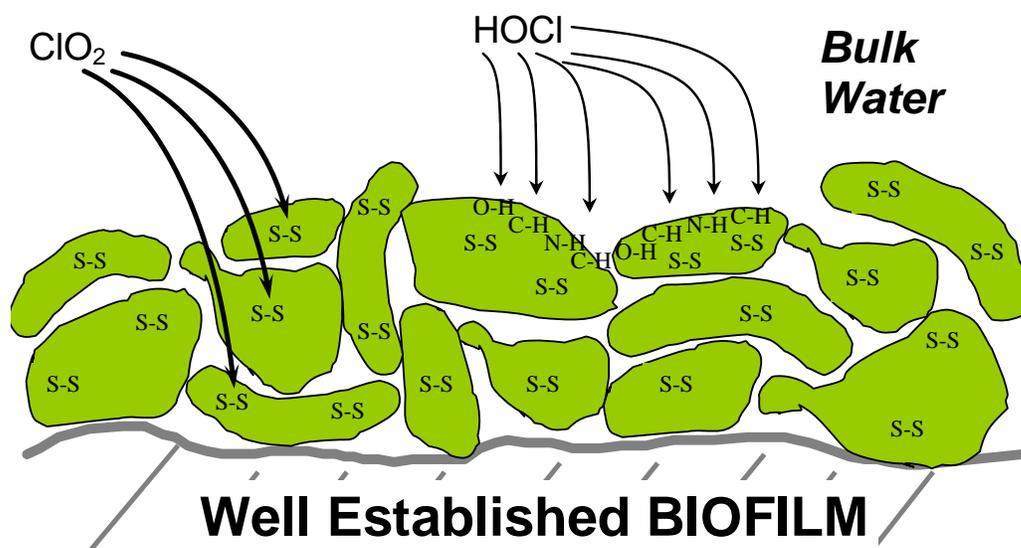
When ClO<sub>2</sub> reacts in water the majority of it is converted into the chlorite anion (ClO<sub>2</sub><sup>-</sup>), equation 6a. Over time the water system builds up a chlorite residual. Upon acidification of the dump tank, the residual chlorite reacts with acid to regenerate ClO<sub>2</sub> within the dump tank (equation 6b). If the chlorite residual was high and if the pH was rapidly dropped from 7 to 2, then the reaction in equation 6b will increase the ClO<sub>2</sub> concentration that may result in a “gassing off” situation. Because the rate of reaction 6b is slow, ClO<sub>2</sub> may continue to “gas off” for hours or days, depending on the chlorite residual in the water.

In order to avoid this, the pH of a ClO<sub>2</sub>-treated dump tank should be decreased gradually in accordance with on-line ORP monitoring. As acid is added, more ClO<sub>2</sub> is regenerated in the water, which will increase the on-line ORP value. After a few minutes the ClO<sub>2</sub> concentration will decrease again, due to reaction 6a, and more acid can be added to bring the ORP reading back up. Small intermittent additions of acid in unison with the resulting ORP readings will allow for a safe transition of the dump tank from neutral to acidic. Once the desired acidic pH is

reached,  $\text{ClO}_2$  can be used without concerns of “gassing off” despite the low pH condition. In fact, a reduced feed rate of  $\text{ClO}_2$  can be used under low pH conditions, due to the catalytic nature of reactions 6a and 6b.

Finally, unlike chlorine,  $\text{ClO}_2$  is excellent at removing biofilms, the microorganism populations living on the walls of all water systems. Typically, >99% of all microorganisms live on wetted surfaces and not in the bulk water. Chlorine is consumed by indiscriminant chemical reactions on the surfaces of biofilms, with most of those reactions having nothing to do with killing microorganisms. Most reactions of chlorine are with the polysaccharide protective coating that covers and protects biofilms. This is why it takes such a high dose of chlorine to provide effective microbial control, and why such high concentrations of chlorinated organics are formed during chlorination of “dirty water” systems. Because chlorine cannot effectively penetrate biofilms, a chlorine residual can be maintained in a “dirty water” system despite the presence of a healthy biofilm hiding beneath its slimy polysaccharide surface.

On the other hand,  $\text{ClO}_2$  is much more selective in the chemical reactions it undertakes, giving it the ability to penetrate biofilms in search of certain chemical functional groups. In a very simplistic view, Figure 2 shows how  $\text{ClO}_2$  can penetrate a biofilm to attack microorganisms with targeted reactions on sulfide-containing amino acids or protein disulfide linkages. These targeted reactions allow for effective biofilm destruction at very low  $\text{ClO}_2$  doses. Since  $\text{ClO}_2$  is so effective at reacting with and removing biofilms, it may require a long time and a high dosage of  $\text{ClO}_2$  to completely remove an existing biofilm and to achieve a  $\text{ClO}_2$  residual. Therefore, another mechanism of how  $\text{ClO}_2$  may “gas-off” from a dump tank water system involves setting a  $\text{ClO}_2$  dosing rate that for the first few hours of a day does not provide a residual, despite a constant  $\text{ClO}_2$  feed. Once the biofilm has been significantly removed, suddenly the  $\text{ClO}_2$  concentration will rapidly increase in accordance with the feed rate. Through the use of on-line ORP monitoring, this “gassing off” mechanism will be negated. ORP monitoring will detect the rapid increase in  $\text{ClO}_2$  concentration and turn off the metering pump before an unsafe  $\text{ClO}_2$  concentration can build.



**Figure 1.** Effect of chlorine and chlorine dioxide at biofilm penetration.

Armed with this knowledge, the use of ClO<sub>2</sub> into cold water systems, such as apple pre-size water systems, pear dump tanks, and cherry hydrocoolers can provide much improved microbial control compared to that achievable with sodium hypochlorite. In addition, selection of a technology that delivers pure, salt-free ClO<sub>2</sub> into the water system will greatly minimize the amount of chemicals that can potentially interact in a negative way with the development of good fruit quality.

## CONCLUSION

The primary goal in food process water disinfection must always be to impart the greatest killing impact to the microorganism population in the water and on the produce, while minimizing to the greatest extent possible any effects of the disinfectant on the food product itself. The primary focus of this article has been to more fully describe the differences in water chemistry of chlorine and ClO<sub>2</sub>, and how through this improved understanding the industry can better optimize its disinfection practices and minimize fruit quality concerns. The discussion in this article involved optimization of disinfectant dosage, through the use of on-line ORP technology, and minimization of disinfectant chemistry, through the expanded use of pure, salt-free chlorine dioxide technology. The application of on-line ORP monitoring provides the tree fruit industry with “demand-based” control that will result in improved safety, reliability, and effectiveness of decay management performance.

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