BIOFILM REMEDIATION IN HOT AND COLD WATER DISTRIBUTION SYSTEMS:

CHEMISTRY OVERVIEW AND ADVANTAGES GAINED THROUGH THE USE OF CHLORINE DIOXIDE

A PURELINE WHITE PAPER

OCTOBER, 2010

EXECUTIVE OVERVIEW

Legionella bacteria infect and cause hundreds cases of sickness and death each year, typically in buildings that house people with weakened immune systems such as the elderly, ill and very young. Common sites include healthcare facilities and hospitals, hotel complexes, resorts, really anywhere there is a location where water is supplied by an extensive distribution system. Common routes of infection include showers, sinks, fountains and cooling towers which can aerosolize water, allowing it to be inhaled into the lungs.

"Gas stripped" chlorine dioxide provides overall best-in-class, non-corrosive biocidal protection

The latest developments in small-scale production of gas stripped chlorine dioxide make it possible to inexpensively dose non-corrosive PureClO2 chlorine dioxide into water distribution systems and cooling towers.

With a long history of use in municipal water treatment and food processing, ***chlorine dioxide*** is well known as a powerful biocide which is also safe and environmentally friendly.

THE PROBLEM

Any water distribution system more than a few years old will likely have some contamination by anaerobic organisms and their associated biofilms. These organisms are highly adaptive and resistant to various stressors in their environment and deserve a degree of respect as they are very persistent. These mostly anaerobic organisms are almost always found beneath a polysaccharide/ slime coating they create to protect themselves from the stresses of temperature, biocides, other organisms and the like. Traditional oxidizing biocides are mostly ineffective; they can't penetrate this film to where the bacteria live, as they are diluted and degraded in the upper levels of the biofilm. ***These biocides just cannot penetrate to that base level of anaerobes that are creating the bulk of the problem.***

Where do Legionella bacteria live?

Problems are compounded by the fact that at the lowest levels of the biofilm, these organisms are creating hydrogen sulfide (H2S) and hydrochloric acid which causes corrosion of the pipe surface. This creates tubercles (small blisters in the surface of the metal) that become the ***incubation sites for Legionella bacteria*** which when inhaled (after being aerosolized from a shower or cooling tower) causes a pneumonia-like condition that is often fatal. Lastly, this corrosion now invites penetration of the metal and pinhole creation by sulfate and iron reducing organisms, the last microbes ClO_2 will encounter on this journey. These pinholes are often the first external sign that there is something very, very wrong going on inside the distribution piping.

THE CHALLENGE: IS THERE A BIOCIDE THAT IS EFFECTIVE WITH THE FOLLOWING PROPERTIES

- Is a broad spectrum biocide, that kills aerobic and anaerobic bacteria equally well
- Excellent penetration ability to attack the bacteria typically protected by the biofilm
- Non corrosive due to the soft metals used in water distribution systems
- Works well at the alkaline pH levels found in cooling towers
- Inexpensive; many treatment programs are labor and cost intensive

WHY CHLORINE DIOXIDE IS THE SOLUTION

Fortunately ClO_2 has some singular characteristics working to its advantage that the other oxidizing and non-oxidizing biocides don't, these include:

The ClO_2 molecule is very small, allowing it to penetrate to where these organisms live

- The small molecular size of ClO_2 allows it to penetrate deeper into the biofilm than other biocides. In most cases, one of the first things biocides do when they are diluted in water is hydrolyze with water and form a larger molecule; this is especially true with chlorine, as depending on the pH of the water it could hydrolyze to form either chlorine gas, hypochlorous acid or hypochlorite, all larger molecules than the original forms and >**10 times larger than a ClO_2 molecule**. The gaseous form of chlorine is corrosive and poisonous, the form created at moderate pH is highly corrosive and the alkaline hypochlorite has little effect on bacteria.
- **ClO_2 does not hydrolyze with water**, and remains a true gas in solution, reacting or degrading in the presence of only a few compounds and conditions; these include:
    - Iron
    - Manganese
    - Organic matter to varying degrees
    - Air agitation

ClO_2 actually "seeks out" organisms

- **The ClO_2 molecule actually seeks out organisms** as it has an affinity for the disulfide linkages found in the amino acids of cell walls. Once it finds these organisms, it penetrates the cell wall through cellular respiration and once inside, ClO_2 disrupts RNA replication, which is the heart of cellular metabolism… the cell quickly dies. This is a completely different and more effective mode of death compared to typical biocides.
- Organisms cannot develop any resistance or tolerance for the ClO_2 molecule, so the rotating of biocides to ensure efficacy is no longer necessary.
- ClO_2 is effective throughout the pH range with similar efficacy at a pH 2 through pH 10. All other oxidizing biocides lose much of their effectiveness at a pH >8, this is important when treating cooling towers as the water typically has an elevated pH.

A green biocide, degrading into very small quantities of two salts

When ClO_2 degrades it will form two salts, chlorite or chlorate. Given enough time and in the presence of sodium these will eventually form sodium chloride but in the presence of the acidic/ hydrochloric acid based environment deep in the biofilm, some of the chlorite will find a new electron to become positively charged again, **forming a new chlorine dioxide molecule, *inside the biofilm***. This will continue until the ClO_2 reaches the base layer of anaerobic bacteria that are seeding this process; they are killed, which then causes the biofilm to lose it's attachment to the surface and it will then be sloughed off by the water flow.

With the biofilm removed, the ClO_2 can now penetrate the pinholes in search of the **sulfate and iron reducing bacteria**. Once these organisms have been dispatched, ClO_2 will complete the oxidation of the damaged iron, converting ferrous iron to ferric and from soluble to insoluble, which will cause the damaged or dissolved iron to become a larger molecule slough off the surface or drop out of solution. **ClO_2 will complete the oxidation of the damaged, rusted surfaces of the pipe interior but not harm the undamaged iron**, ridding both the planktonic water and the pipes of iron corrosion. Note; filtration may be required for systems that have moderate or heavier corrosion. Continued treatment with ClO_2 will ensure remaining or newly introduced anaerobic bacteria cannot achieve the numbers required to become a problem again.

PureClO2 has significant advantages vs. the typical ClO_2 molecule

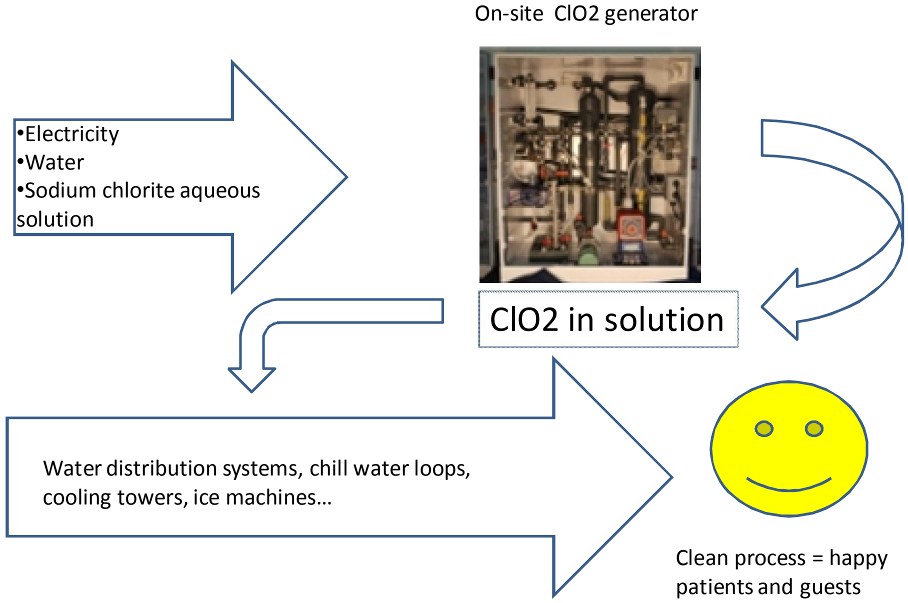
Pureline's patented gas stripping system is different than every other ClO2 generator in existence and makes a chlorine dioxide molecule that has no peer. Pureline creates a ClO2 molecule that is 99.5% pure ClO_2 at a pH of 7… pure, non-corrosive ClO2 at a neutral pH. This **highly effective, non corrosive** molecule has the characteristics to deliver what we are looking for!

Competing ClO_2 generators each create a chlorine dioxide solution that has at least some negative characteristics including:

- Acid; some generators use sulfuric, hydrochloric or citric acid as a precursor, these solutions will contribute to the corrosion of the distribution system
- Chlorine; many generators use chlorine bleach or gas as a precursor. The resulting solutions will be corrosive with the added hazard should the chlorine and acid react poisonous chlorine gas will be formed!

Illustration 1: Schematic overview of onsite ClO_2 production

PureClO2 requires only one precursor along with water and a small amount of electricity



As illustrated above, the new generation of onsite chlorine dioxide production takes place in a containerized production unit with just three inputs: feed water, sodium chlorite liquid and electricity.

Feed water quality is not critical, as the unit includes particle filters and a reverse osmosis purifier. Sodium chlorite is delivered in containers as small as 5 gallons. The electrical requirement for the one lb. unit is 120v with a daily cost for electricity of less than $2.00/day.

These onsite units produce chlorine dioxide in concentrations ranging from 500 to 3000 ppm. This chlorine dioxide solution is then added to fresh water at concentrations varying from <1 to 5 ppm depending on the application.

CHLORINE DIOXIDE IN BRIEF

In concentrated form, ClO_2 cannot be transported and is thus always generated on site

Chlorine dioxide (ClO_2) is a gas that is well known as powerful disinfectant in municipal water treatment facilities and in food processing industries. It is also used industrially for bleaching wood pulp and flour.

The chlorine dioxide molecule is relatively small, volatile, and very energetic. It is stable in dilute solution, but unstable in concentrated form. Thus, chlorine dioxide is almost always used as a dissolved gas in water in concentrations that range from 0.5 to 5 grams per liter. Because transportation of concentrated chlorine dioxide is not safe, chlorine dioxide is almost always produced on site.

A safe biocide with a broad range of applications

ClO_2 very effective in a water distribution system

ClO_2 is a highly effective biocide that kills bacteria, viruses, algae, fungi and protozoa.

Used properly, ClO_2has little or no effect on human, animal or fish cells and is safe to use. For example, ClO_2 has been approved for use in the processing of USDA organic and kosher foodstuffs.

ClO_2 is unsurpassed in disinfecting throughout a water system – also in "dead end" areas. For this reason, ClO_2 is often used to disinfect large and small chill water applications, municipal water systems and water systems in hospitals, where bacteria such as Legionella can prove to be stubbornly resistant to other biocides, chlorine in particular.

Furthermore, chlorine dioxide does not affect taste or form toxic chloramines or haloforms (THM). This is a characteristic that makes ClO_2 ideal for flavor sensitive applications such as wine and brewing.

In conclusion…

This should give you an idea of the potential risks that exist, mostly unseen and unnoticed until they are manifested by illness or a failure in hot and cold water distribution systems. These organisms cannot be effectively tested as they don't move around in the water; they are attached to the sides of the piping. It is advisable to review your treatment program and inspect piping during maintenance to determine whether potential risk exists as distribution pipe failure and guest/ patient illness have both proven to be very expensive lessons to many operations. For more information, don't hesitate to contact your Pureline representative or water treatment professional.

For additional information, please contact Steve Eberhard with Pureline at 503-519-5100 or at steve.eberhard@pureline.com

---

This white paper draws on information from:

PureLine R&D staff

EPA Guidance Manual, Alternative Disinfectants and Oxidants