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CHLORAMINES

OVERVIEW

Surface water sources (like water from streams, rivers and lakes) is full of leaves, decaying vegetation, fish and animals, algae, and other forms of plant life. When this matter decays in water it becomes dissolved organic matter. When chlorine is added to water that contains dissolved organic matter, the formation of “disinfection by-products” (DBP’s) occurs. These include “trihalogenated methanes” or trihalomethanes (THM's) and “haloacetic acids” (HAA’s.)

Contrary to what water suppliers have attempted to say about the subject for many years, it is now apparent that these compounds are potent carcinogens. This realization forced the EPA to drastically lower the amount of these dangerous disinfection by-products it will permit in domestic drinking water supplies with a new regulation called the Stage 1 Disinfection Byproduct Rule. You may find the text of this rule at: http://www.epa.gov/OGWDW/mdbp/dbp1.html

This new regulation requires water producers to limit the running average to THMs to 80 part per billion in the distribution system. Large surface water systems were required to comply by January 2002. Ground water systems and small surface water systems were required to comply by January 2004.

Compliance is a difficult issue. The best way to resolve the problem is also very expensive. It involves installing huge filtration systems that rely on expensive forms of carbon that must be backwashed and replenished regularly. To install this equipment would require an investment in infrastructure that most water utility companies are unwilling or unable to make.

That is why most water suppliers are electing to comply with these new Stage 1 requirements by converting their disinfection method from chlorination to chloramination. While these chemical compounds sound similar, they are very different.

Chlorination is usually accomplished by adding chlorine gas or a liquid chlorine compound similar to common household bleach into the water. While these are effective disinfection agents, the problem is that these forms of chlorine dissipate rapidly from the water supply through the mechanism of evaporation. If you put bleach in a bucket of water and leave it out, 98% of the chlorine will have escaped into the air within a few hours.

Chloramine however is different. It is the result of mixing chlorine with ammonia. Have you ever read the label on a bottle of bleach or ammonia? The directions carry a prominent warning not to mix these two chemicals together. The result is a dangerous chemical called monochloramine that is a form of nerve gas, and besides being toxic, is very irritating to the skin and mucous membranes.

So if monochloramine is so dangerous, why is it added to drinking water? One reason is that it is added in very small amounts. While it is not as effective as chlorination, the chemical DOES NOT dissipate from water. Because there is less chlorine present, chloramines have a lower potential to form carcinogenic by-products – or so we were told.

Unfortunately, it appears that chloramines have their own sets of potential health problems including gastrointestinal irritation, and exacerbation of skin problems, not to mention the possibility of creating other disinfection by-products known as Nitrosodimethylamines (NDMA's) that may be more carcinogenic than their predecessors.

This article summarizes what chloramines are, their chemical and biocidal characteristics, and what is known about removing them from water supplies.

WHY REVIEW?

The effects of chloramines on water chemistry and the equipment/methods used to "treat" chloraminated streams should be understood by water treatment professionals as well as health care providers because we will encounter this constituent with more frequency. This memo should give you the basics necessary to discuss how LivingWaters™ Products handle chloramines. The newness of this aspect of water treatment does not, unfortunately, allow all questions to be fully addressed. Indeed, if any conclusion can be drawn it is that too little has been done on how to remove chloramines once they are there (I found only one good article in the volumes of literature I reviewed on the subject, and the experts I contacted knew less than I did!)

WHAT ARE THEY?

Chloramines are biocides. Like Cl2 they are oxidants and kill bacteria by penetrating their cell walls and disrupting their metabolism. Chloramines are, however, much slower to "react". Unlike chlorine they do not evaporate from water. Neither are they removed by typical water treatment techniques. As with chlorine, municipalities aim for I to 2 mg/l (ppm) chloramine residual in the potable water supply.

Several disinfectants ranked by their "biocidal efficiency" and "stability" are noted below. (Biocidal efficiency was considered as the effectiveness of the disinfectant against a-number of viruses and bacteria in the pH range of 6 to 9. Stability reflects a lack of reactivity with constituents other than microorganisms and is a measure of persistence in the treated system)

BIOCIDAL EFFICIENCY (BEST TO WORST)

ozone > chlorine dioxide > free chlorine > chloramines

STABILITY (BEST TO WORST)

chloramines > chlorine dioxide > free chlorine > ozone

THEIR CHEMISTRY

Chloramines are typically generated on-site by the addition of ammonia (NH^3) to water containing free Cl^2 (HOCl or OCl depending upon the pH of the water). The optimum reaction pH is on the alkaline side, pH 8.4 (i.e., NH^3 (aq) + HOCI NH^2Cl + H^2O) Three forms of chloramine can result as well as undesirable but unavoidable interference reactions (#4 below).

Form

Name

Molecular Weight

Predominant

pH

Biocidal

Activity

1) NH 2Cl

Monochloramine

52

>7

best

2) NHCl 2
Dichloramine
85
4 to7
some

3) NCl 3
Trichloramine
119
1 to 3
mediocre

4) RNHCl
Organic Chloramine
Varies
Unk
Insignificant

Organic chloramines cannot be distinguished from the other forms of chloramines with standard methods of chloramine analysis.

Chloramines are not highly disassociated (in other words only minimally ionic). That fact and their low molecular weight make them difficult to remove via RO (discussed in more detail below). The monochloramine form is the best biocide, and as is noted, is the dominant specie at pH 7 and greater. Since slightly alkaline waters are less corrosive, municipalities in many cases maintain the monochloramine form and reduce corrosion potential at the same time. Note that at these alkaline pH's, chlorine exists as the hypochlorite ion (OCl) which has a higher oxidative potential than hypochlorous acid (HOCl), but is 80 to 100 times less effective as a disinfectant.

WHY REMOVE CHLORAMINES?

WATER TREATMENT CONCERNS

Like any other molecule, chloramines contribute to the overall total dissolved solids content of the water and like chlorine, are selectively reactive, thus may have deleterious effects on downstream processes. In equilibrium with chloramines are trace amounts of ammonia and/or hypochlorite ions. Their (NH^3 and HOCl) presence must also be recognized when one is designing an ultrapure treatment system to remove chloramines.

HEALTH ISSUES

By far the biggest health concern is that no long term, and very few short-term studies have been performed that can clarify the effect of chloramines on human metabolism.

What we know for sure about chloramines demonstrates that they are both reactive and persistent — not only in water, but also in human tissue. One study demonstrated that after 5 days, over 95% of a single dose of chloramine administered to laboratory rats was still concentrated in tissues including plasma, blood, skin, packed cells, kidney, nerves, testes, thymus gland, spleen, liver, muscle tissue, bone marrow, etc. Notwithstanding this information, utility companies around the country routinely misinform their customers, telling them that chloramines are effectively neutralized by stomach acids before they can reach the blood.

It is also known that chloramines cause DNA damage and are potential carcinogens. They are extremely dangerous to all forms of fresh and salt-water fish because they are absorbed directly from the gills and transported directly into the blood causing death in a short period of time.

In one study, doses at the levels used by municipalities to treat water resulted in a significant reduction of water consumption by rats vs. controls, along with significant decreases in glood glutathione levels in rats. Other studies demonstrated changes in the organ weights of rat spleens, livers, and kidneys. Other studies show that chloramine ingestion may be toxic to the organs that comprise the immune system.

The EPA admits that in their review of studies available, not much has been done to research the effect of oxidant stress on blood or tissues, nor is the long term effect of chloromine ingestion on plasma cholesterol metabolism.

Clinical reports of the effects of chloramines on humans show that some people suffer allergic contact dermatitis when exposed. Chloramines are also irritants to mucous membranes including those that line the nose, throat, and gastrointestinal system.

Remarkably, based on very few poorly designed studies, and virtually no long term studies, public utility companies routinely declare that the EPA has determined that the addition of chloramine to drinking water is absolutely safe!

METHODS OF TREATMENT

Distillation or evaporation does not effectively remove chloramines. During distillation the chloramines would be volatilized and carried over to the product water (distillate). This is especially important to keep in mind in the pharmaceutical, power and laboratory markets due to their heavy use of distillation technology (boilers in the power industry produce steam via evaporation). The effects of reactive chlorinated materials on their products are of special concern.

Neither is chloramine removal by reverse osmosis particularly effective. RO membranes will not reject significant percentages of the monochloramine form. Much like chlorine, it will pass through to the permeate side and become concentrated on the product water side. Due to tighter pore structure, TFC membranes would be expected to reject a slightly higher percentage of chloramines than cellulosic membranes but the amount rejected is not significant.

IX resin has a certain affinity for cations and anions. The more highly ionized species (such as sulphates, chlorides, etc.) are preferentially adsorbed to the resin over less strongly charged molecules such as chloramines. With RO as pretreatment, competition for exchange sites would be practically absent. Hence, some chloramines would be removed by "fresh" strong base IX resin, but this is not a reliable mode of treatment. Another portion of chloramines may decompose via oxidation in an IX system to the chloride ion as happens with Cl. Again, this is not a reliable reaction. Feed water quality and resin characteristics are likely to provide unique performance for each application.

Some degradation via oxidation of the cation resin could also expected. Though not nearly as severe as with free chlorine, life of the resin would be reduced a slight degree. While IX effect some chloramine removal, it has limitations

Catalytic Activated Carbon (CAC) is proven to reduce chloramine presence from 1 to 2 ppm to less than 0.1 ppm (a USP WFI requirement). The mode is similar to free aqueous chlorine destruction, however, with chloramines one encounters "by-products" of ammonia, chloride and nitrogen gas. Remember that AC does not adsorb C1 2or NH 2Cl like organics. Bear with me as I present the generally accepted reactions:

1. $NH_2Cl + H_2O + C^* \Rightarrow NH_3 + Cl^- + H^+ + CO^*$

2. $2NH_2Cl + CO^* \Rightarrow N_2(g) + H_2O + 2H^+ + 2Cl + C^*$

(C^* and CO^* represent carbon and carbon oxide surface (of catalytic activated carbon) respectively)

Note that in the reduction of free aqueous chlorine by AC only H^+ and Cl ions are generated:

3. $C^* + HOCl \Rightarrow CO^* + H^+ + Cl$

4. $C^* + OCl \Rightarrow CO^* + Cl$

For USP WFI requirements, ammonia nitrogen must also be less than 0.1 ppm in the product water. AC will not remove NH_3. At pH 7.5 or lower, both cellulosic and noncellulosic RO membranes would reduce the NH_3 and Cl concentrations to less than 0.1 ppm from AC feed waters up to 2 ppm NH_2Cl.

It appears that Catalytic Activated Carbon is one of the best methods to reduce chloramines. The literature notes some important facts in designing CAC beds for chloramine removal:

1. Chloramine reacts more rapidly with finer GAC particle sizes (CECA brand 12 x 40 mesh was found significantly better compared to Darco 12 x 40 and Witco 12 x 30 mesh).
2. Two gpm per square foot and 4 foot deep for an empty bed contact time of 15 minutes provides over one year run time with 1-2 ppm chloramine feed with effluent of less than 0.1 ppm.
3. The removal efficiency of GAC is much greater for free chlorine than for chloramines. Therefore, if one can first oxidize chloramines to free chlorine and N_2 the GAC bed can be sized smaller because GAC can handle Cl_2 much quicker.

SUMMARY

While the effect on public health by not disinfecting drinking water supplies would be far worse than the alternative, advising the public that either chlorination or chloramination are completely non-toxic methods is ill-advised. We now know that chlorination has contributed greatly to heart disease, cancer, and other serious health issues in our human population. There is no reason to believe that chloramination will prove to be less troublesome. In fact, just the opposite is likely.

Consumers interested in home appliances capable of solving this problem will be disappointed to learn that most popular treatment technologies are completely unable to handle chloramines without modification. These include most cartridge-based systems using ceramic or carbon media, reverse-osmosis systems, and distillation.

For systems designed to accept post-filters, Catalytic Activated Carbon filters can replace typical carbon filters in RO and distillation systems. Those interested in purchasing new systems are well-advised to consider purchasing a 6-stage LivingWaters™ Water Treatment System that is capable of removing not only chloramine, but also chlorine, their disinfection by-products, fluoride, heavy metals, organic compounds that cause tastes and odors, as well as render product water completely sterile, all without the need for power or high water pressure. If your need is for demineralized water, consider the LivingWaters™ 5 stage manifold RO system with catalytic carbon/KDF™55 pre-filtration media.

Those who have questions or updated information on chloramine ingestion are encouraged to call Conscious Living Systems, Inc. at our toll-free number 888-524-8627.