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Chloramines: Methods of Prevention and Elimination

Key Words: aquatic therapy, hydrotherapy, infection control, rehabilitation,

INTRODUCTION

Swedish pharmacist, Carl Wilhelm Scheele, discovered chlorine in 1774. Scheele was performing an experiment mixing and heating manganese dioxide and "marine acid" (hydrochloric acid). The yellow-green gas that resulted was chlorine. However, it wasn't until 1810 that English chemist, Sir Humphrey David, proved that chlorine was a separate element.

In 1895, Olin Corporation (then known as the Mathieson Alkali Company) opened the first chlorine plant to manufacture calcium hypochlorite. In 1909, the Niagara Alkali Company discovered a way to make chlorine into a liquid form by cooling and pressurizing gas chlorine. Then in 1927, Olin Corporation began manufacturing the HTH brand of calcium hypochlorite for swimming pool disinfection.

Chlorine Facts

Chlorine is the 17th atomic element and a member of the halogen family of elements. Chlorine gas is about 2.5 times heavier than air, and liquid

chlorine is 1.5 times heavier than water. Chlorine is slightly soluble in water, has a distinctive odor, and is greenish-yellow in color. Chlorine is neither flammable nor explosive, but it is combustible if it reacts with other materials. Because it is highly reactive, chlorine is found in nature only in combination with other products.

Today, chlorine is made by passing an electrical current through a salt-water solution. Sodium hydroxide (caustic soda or lye) and hydrogen gas are produced as by-products of chlorine formation.

Use in Pools

Chlorine is used as an infection control product in order to prevent the spread of communicable disease through pool and spa water. Chlorine is added to pool water for two primary purposes—sanitation and oxidation. Sanitation is the process of destroying pathogenic, disease-causing organisms such as bacteria, protozoa, and viruses. Oxidation is the process of chemically removing organic debris from the water. Organic contaminants include bather waste products such as perspira-

tion, saliva, urine, fecal matter, dead skin, body oils, and wastes. In addition, cosmetics, hair care products, deodorants, suntan oils and sunscreen products inadvertently brought into the pool on a bather's body, and other particulate matter such as dirt, pollen, plant matter, algae, and airborne pollutants which enter the pool build up in the water, and place a demand on chlorine. More chlorine consumed for oxidation leaves less chlorine available for sanitation. If the sanitizer demand is not satisfied, pathogens will begin to multiply, algae (a higher organism which may harbor bacteria) will grow, and the water may cloud or discolor. The demand for sanitizer must be met before residual chlorine levels can be established.

Other Uses

Although the general public primarily associates chlorine with swimming pool water disinfectant, it is interesting to note that less than 1 % of chlorine produced in the form of elemental gas chlorine and chlorinated compounds is used for pool water treatment.

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In addition to pool water treatment, chlorine has thousands of other uses. Chlorine is used to treat drinking water to make it safe for human consumption. It was first used as a water treatment in Lincoln, England in 1904 to stop the typhoid epidemic that had been plaguing the city. Chlorine was first used in the United States in 1908, to treat the municipal water supply in Jersey City, NJ. Today, more than 98% of the U.S. drinking water supply is treated with chlorine. Without chlorine, cholera, typhoid fever, dysentery and other water borne diseases would be rampant. The lifespan of the average American would be shortened.

One of the initial uses of chlorine was as a bleaching agent to whiten clothes. The French were whitening and brightening their clothing with chlorine as early as 1790. The Germans in World War I used chlorine as a chemical weapon. Today chlorine is used in the manufacture of explosives. Inhalation of diluted chlorine was popular as a treatment for the common cold during the 1920's.

Today, chlorine is used for cleaning and disinfecting, bleaching paper, food preparation, sewage treatment, and in the manufacture of thousands of medical, industrial and common household products including solvents, gasoline, transmission fluid, rocket fuel, pesticides and herbicides, cosmetics, perfumes, and deodorants, and pharmaceuticals. Vinyl plastics, from food wrap and home siding materials, to PVC pipe and vinyl liners all require the use of chlorine.

Environmental and Health Concerns

Chlorine is a respiratory irritant. Death can result from lengthy exposure to high concentrations (greater than 50 ppm) of chlorine in air or exposure to 300 -400 ppm for 30 minutes—Immediately Dangerous Life or Health Concentrations (IDLH) of 10 ppm. Researchers at the National Cancer Institute and the National Institutes of Health continue to study exposure to chloroform and carcinogenic by-products such as MX (a compound produced when chlorine reacts with organic material in water).

Chlorine is hazardous to aquatic plants and fish and can certainly damage vegetation, but some environmental groups' campaigns to ban chlorine are over broad. Environmental concerns over spills, disposal of chlorinated pool water, and the release of chlorine into the environment have introduced secondary containment requirements and neutralization tank installment to the pool industry.

Over 10 million tons of chlorine are used annually in North America. A ban on the use of chlorine would have an economic impact in the trillions of dollars. Supplemental and alternative products for pool water treatment continue to be introduced, but currently no single, stand alone product or chemical, works as well as chlorine for both sanitizing and oxidizing recreational pool water.

Specific Information – Use of Chlorine for Aquatic Treatment

Six chlorinated products are commonly used for pool water treatment: elemental gas chlorine, sodium, calcium and lithium

hypochlorite; and two isocyanurate products (sodium dichloro-s-triazinetrione and trichloro-s-triazinetrione). Since hand-feeding of chemicals into commercial pools is not permitted, chlorine is introduced with chemical feed pumps. Various types of feed pumps are used depending on the form of chlorine. These include gas chlorinators, diaphragm, piston, or peristaltic type positive displacement pumps; or erosion or erosion-soaker feeders.

When chlorine (Cl) is added to water (H₂O), hypochlorous acid (HOCl) and hydrochloric acid (HCl) result. HOCl, the active sanitizing ingredient, then partially dissociates to a hydrogen ion (H⁺) and a hypochlorite ion (OCl⁻). The OCl⁻ ions have a tendency to combine with nitrogen and ammoniated impurities in the water. Free chlorine consists of a mixture of both HOCl and OCl⁻ ions. The proportion of HOCl to OCl⁻ is both pH and temperature dependent.

More than the demand for chlorine is met when introducing chlorine so that a residual remains in the water. The chlorine residual, often referred to as the total available chlorine (TAC), is composed of both the free available chlorine (FAC) and combined available chlorine (CAC). Chlorine residual is often measured in parts per million (ppm). Parts per million is a quantitative indicator of residual, where chlorine weight is compared to the weight of water in the pool. Contact times time (CT) values should be used to determine whether ppm levels are adequate.

CAC, also referred to as chloramines or ammoniated chlorine compounds, should not be allowed to exceed 0.2 ppm.

Chloramines cause eye and mucous membrane irritation and emit the unpleasant "chlorine" odor often associated with poorly ventilated indoor pools. Chloramines are ineffective as sanitizers and oxidizers because they are too stable. They are 60 to 100 times slower than FAC at destroying unwanted products in the water. Furthermore, airborne chloramines can be very corrosive to metal fixtures and components in the natatorium.

Oxidation reduction potential (ORP), also known as Redox, or HRR, is a qualitative indicator of chlorine effectiveness. The ORP is a measure of water conductivity and indicates the potential generated for oxidation or work potential. Minimum, and occasionally maximum, levels of free available chlorine measured by weight in parts per million may be specified by code. However, chlorine should be added as needed to maintain an ORP between 750 and 900 millivolts.

Bacteriological water analysis is also used to confirm chlorine effectiveness. Presence-absence test, multiple tube fermentation, and membrane filtration tests are commonly utilized. The absence or presence at acceptable levels of coliform, pseudomonas aeruginosa, or other indicator bacteria confirms the adequacy of the chlorine sanitizer and oxidizer.

Breakpoint Chlorination

Chlorine is also used to "shock" or superchlorinate pool water to remove unwanted organic compounds, destroy impurities and dissolved waste products and algae, and break apart the chemical bond holding chlorine, ammonia and nitrogen together. The point at

which this chemical bond is broken is called "breakpoint." Breakpoint chlorination eliminates chloramines and other reductants that cause an increased chlorine demand.

In order to achieve breakpoint, a quantity of 7.6 molecules of free chlorine is used to break apart each molecule of combined chlorine. Several chemical reactions take place. Chlorine reacts with ammonia (NH_3) to form monochloramines (NH_2Cl). Free chlorine reacts with NH_2Cl to form dichloramines (NHCl_2). Free chlorine reacts with NHCl_2 to form trichloramines or nitrogen trichloride (NCl_3) and nitrates before the breakpoint is achieved. NCl_3 forms when the HOCl:Nitrogen molecular weight ratio is 12:1, and oily, insoluble, colloidal particles appear, cloud the water, migrate toward the water surface. These particles may be released into the ambient air further contaminating the natatorium environment.

Reaching the breakpoint is an all-or-none reaction. If breakpoint is not reached, the problem will be worse. When the chemical bond with ammonia is broken, free chlorine, nitrogen, water and inorganic chloride (salt) remain. Superchlorination of pool water should be done periodically, as needed, when the level of chloramines present in the water is greater than 0.2 ppm. Products used for superchlorination include chlorine in any form. However, stabilized chlorine products or isocyanurates (trichlor or dichlor) should not be used for superchlorination as excess cyanuric acid would be added to the water solution concurrently.

Before attempting breakpoint chlorination, lower the pH to 7.2 to

7.4 to increase the percentage of HOCl that forms and assure chemical balance of the water. Shocking a pool with unbalanced water, particularly with a high (basic) pH or high total alkalinity, will result in the formation of a white carbonate precipitate, which will cloud the water. However, some operators prefer to raise the pH when using acidic chlorine products like elemental gas chlorine for superchlorination since more offensive forms of chloramines develop rapidly at a very low pH.

To calculate breakpoint for superchlorination, use a DPD (N,N-diethyl-p-phenylenediamine) or FAS (ferrous ammonium sulfate) test kit to determine the FAC and TAC levels. Subtract the FAC from the TAC to find the CAC level. Multiply the CAC by a factor of 10, although a minimum factor of 7.6 is needed, to find the dose of chlorine necessary to reach the breakpoint. The factor of ten is used because most pool operators are uncertain of the precise amount of water in their pools, or of the exact percentage of available chlorine in the chlorine compound used. Thus, using the factor of ten allows error on the side of caution ensuring adequate chlorine left after breakpoint to satisfy chlorine demand with an adequate residual.

Determine the number of gallons of pool water to be treated and the percentage of available chlorine in the product that will be used to superchlorinate the pool. Calculate the amount of chlorine needed by weight, or refer to a standard chart or a chart provided by the chlorine manufacturer. see Table).

For example: If FAC = 1.0 ppm and TAC = 2.5 ppm, the

difference (CAC) = 1.5 ppm. Multiply 1.5 by 10 to determine that 15 ppm of chlorine must be added to the water in order to reach breakpoint. You know that the pool in question contains 360,000 gallons of water, and you plan to superchlorinate using 10% available sodium hypochlorite. By following the chart and inserting the appropriate numbers into the formula, you can determine that 50.6 gallons of 10% sodium hypochlorite must be added to a 360,000-gallon pool, to eliminate 1.5 ppm of combined chlorine.

(1.5 cups) (1 ppm) (10,000 gallons)

**(1.5 cups) (15 ppm) (36) =
810 cups/16 = 50.6 gallons**

Some health department regulations may prohibit swimmers from using the pool when chlorine concentrations are elevated. It is best to superchlorinate in the evening or during hours of pool non-operation to avoid causing respiratory irritation in users, as a result of off-gassing during the superchlorination process, and to allow chlorine levels to return to normal levels. The speed at which

breakpoint is reached depends on several factors, including: pH, pool water temperature, the FAC:CAC ratio, and the concentration of ammonia/nitrogen and organic nitrogen compounds imposing a chlorine demand. If the chemical reaction takes place and breakpoint is reached, the large amounts of chlorine added to the water will be consumed. Free chlorine will return to normal operating levels, and the combined chlorines will be eliminated.

Problems Reaching Breakpoint

Many pools operators have a great deal of difficulty ridding their indoor pools of chloramines. This is rarely a problem in outdoor pools since sunlight destroys chloramines and objectionable odors blow away. Unfortunately, HOCl also reacts with UV light (sunlight) and becomes an inactive chloride ion (Cl⁻) or salt.

Some pools have enormously high bather load:water volume ratios, resulting in heavy organic loading, and high levels of ammoniated impurities in the water. Spray features at amusement parks, health club spas, therapy pools,

swim school pools, and children's wading depth pools with interactive play features often have chlorine levels unfathomable to operators of more traditional swimming pools. It is not surprising to find that an 18,000 gallon swim school pool maintained at 94° Fahrenheit having a bather load of 300 pre-school aged children per day, will have a continuing problem with chloramines. Ten-thousand-gallon wading pools at successful commercial waterparks may have bather loads exceeding 2,000 children per day. It is not unusual to find amusement park water spray features with interactive fountains that have more users coming into contact with the water than number of gallons of water in the water feature. These same pools often have problems reaching breakpoint or keeping chloramines within acceptable levels.

If a chloramine residual persists in a pool in spite of the operator following proper breakpoint chlorination techniques, and continues to be a chronic nuisance, some of the following suggestions should be tried:

Amount	% Available Chlorine	Chlorine Product
1.5 cups	10%	Sodium hypochlorite
1.3 cups	12%	Sodium hypochlorite
1 cup	15%	Sodium hypochlorite
2.25 oz	60%	Sodium dichloro-s-triazinetrione
2 oz	65%	Calcium hypochlorite
1.5 oz	85%	Trichloro-s-triazinetrione
1.3 oz	100%	Elemental gas chlorine

Table. Amount of available chlorine necessary to raise the chlorine level 1 ppm per 10,000 gallons of pool water

Regular Dilution

Drain and replace with 30 liters (approximately 8 gallons) of fresh water per user per day, as recommended in the German DIN (Deutsch Industrie Normen) Standard 19,643: "Treatment & Disinfection of Swimming & Bathing Pool Water." The DIN Standard has been adopted by the European Community, and the International Federation of Swimming (FINA) requires water standards compatible with the DIN standard during international swimming competition.

Increase Exposure Time and Chlorine Concentration

You may be successful in reaching breakpoint by superchlorinating for longer periods of time with higher levels of chlorine.

Draw Water from the Pool Surface

Chloramines are concentrated near the surface of the water, as are most organic contaminants. During breakpoint chlorination, turn off the valve, which draws water from the main drains, and direct all the water through the perimeter overflow system. By circulating only through the skimmers or gutters, you will speed up the process by removing the water where chloramines are concentrated first.

GAC Filtration

Install secondary granulated activated carbon (GAC) filters and remove ammonia through filtration. GAC filters can be used to treat a slip-stream of water continually drawn off the main effluent line, or to treat source water prior to its being added to the pool. Many

pools in areas of the country where municipal water utilities are adding ammonia to the source water to prevent trihalomethane formation in drinking water are installing GAG filters to pre-treat fill water to keep ammonia levels below 0.02 ppm. Chloramination has become a common practice by water utilities in order to comply with U.S. EPA water quality standards for drinking water to prevent formation of chloroform, a known carcinogen. Since chloramines do not react with raw water organic precursors, which form when vegetation decays, monochloramines are commonly being used to treat water that has been stored in reservoirs. This practice is causing havoc in swimming pools,

Non Chlorine Oxidizers

Potassium peroxymonosulfate (AKA: monopersulfate), can be used instead of chlorine to shock, or oxidize chloramines and other organic contaminants from the water. The product is a buffered chemical compound which utilizes oxygen to prevent or destroy the eye irritation and odor qualities of pool water by reacting with ammonia to produce chloride and nitrogen. Sold under various trade or brand names, the product has been successfully marketed to homeowners, and is beginning to make inroads into the commercial pool market. Unlike chlorine, which must reach a "breakpoint", any amount of potassium peroxymonosulfate added to water will oxidize some material. Normally, 5 ounces - 1 pound/10,000 gallons of water is added weekly to pools and daily to spas. Non-chlorine oxidizers are totally soluble, do not raise chlorine

levels, do not cause bleaching, and do not affect water balance or pH.

Monopersulfates are especially recommended for pools or spas with high bather load to water volume ratios where total dissolved solids and ammonia normally build-up as a rapid pace. The pool owner should be cautioned however, that regular use of non chlorine oxidizers may irritate bathers causing them to itch. Also, potassium peroxymonosulfate has a known effect on liquid and tablet DPD reagents causing water samples to turn dark red and potentially causing false high FAC readings. DPD reagent #3 is oxidized by monopersulfate so the test actually reads the monopersulfate residual. This prevents an accurate reading distinguishing between FAC and TAC. Some test kit manufacturers sell FAS-DPD reagents that eliminate monopersulfate interference.

Some pools maintain a residual of monopersulfate to help eliminate bather waste and the build-up of organic contaminants, as a preventative rather than corrective treatment. One manufacturer (U.S. Filter) has patented a continuous breakpoint halogenation and peroxygenation system. Potassium peroxymonosulfate doesn't react with chlorine, but rather oxidizes contaminants and reduces the demand on the sanitizer. It should be noted though that not all products sold as non chlorine oxidizers contain the active ingredient potassium monopersulfate. For example, sodium percarbonate (AKA: sodium carbonate peroxyhydrate) releases or produced hydrogen peroxide, and reacts with chlorine.

Eliminate the Chlorine to Eliminate the Chloramines

Hydrogen peroxide (H_2O_2) or sodium thiosulfate can be added to the pool to drop the chlorine level to zero. This eliminates the free chlorine residual by converting chlorine to chlorine salt. When chlorine is eliminated from the water, chloramines are also eliminated. However, when chlorine is reintroduced, it will combine with ammonia present in the water and form chloramines. However, it is hoped that this process will be more gradual resulting in a less objectionable monochloramine rather than nitrogen trichloride.

Caution: Avoid adding excessive amounts of H_2O_2 or sodium thiosulfate to the water or a chlorine demand will be created. As a result, it will be difficult to reestablish a chlorine residual. Also, avoid adding products containing H_2O_2 to a pool with diatomaceous earth (DE) filters as H_2O_2 dissolves DE.

Zeolites

Zeolites with a high (at least 80%) percentage of clinoptilolite can be used as a filter media instead of #20 silica sand in sand filters. Zeolites are a family of granular, extremely porous volcanic minerals capable of removing ammonia from the water as well as particles as small as 5 microns in size, equivalent to the filtering capabilities of a DE filter. Zeolites for swimming pool filtration are marketed under various trade names such as Neptune Benson (Clinopure 80), British Zeolite Co. (Zeoclere-30), Innovative Water Science (Zeo-Pure 90), and Eco Smarte (Hydroxite #2). When a layer of 10% sodium chloride or table salt is added to the filter bed,

an ionic reaction causes the absorption and removal of ammonia as the water passes through the filter, thereby reducing chloramine formation. The pool operator must regenerate filter media every 6 months by backwashing, shocking with a salt solution, allowing the bed to reactivate for 24 hours, agitating the media and backwashing. Zeolites supplied by a reputable distributor should have a life expectancy 5 to 7 years.

Corona Discharge Ozone Systems

Organic contaminants are slightly reactive with ozone, but after partial oxidation, microflocculation allows their removal by filtration. Inorganic contaminants such as ammonia react significantly with ozone when the pH is maintained below 9.0. Ozone constantly oxidizes monochloramines to form chloride and nitrate ions. Unfortunately, ozone also destroys free chlorine residuals in the process of chloramine destruction, so chlorine lost in the process must be constantly replaced.

Ultraviolet (UV) Light

UV light from natural sunlight or UV light sanitation systems can be used to destroy chloramines and aerosolized chlorine compounds. If natural sunlight cannot be brought into the natatorium, UV light sanitation systems can be installed to provide supplemental sanitation and chloramine destruction.

UV light systems are installed in-line with either hydrogen peroxide or chlorine, which provides a residual sanitizer and oxidizer in the pool water. The system consists of a treatment chamber in-

stalled on the filter effluent line, control box and power supply. Photolytic liners are permanently attached to the internal surfaces of the treatment chamber. Water flows through the clear, quartz glass or TeflonÆ tubes, through the treatment chamber, by the UV lamps (arc tubes) and pathogens are destroyed. UV kills microorganisms by destroying the DNA in the cells. There is no change in water color, temperature, taste, pH, or chemical composition. However, turbid water will absorb UV light and make UV less effective as a disinfectant.

Disinfectant level is related to light intensity and exposure time. UV dosage is measured in either microwatt seconds per square centimeter (MWS/cm²). Intensity and exposure time may also be expressed in millijoules per square centimeter (mJ/cm²). Six thousand to 10,000 MWS/cm² or a minimum of 60 mJ/cm² is needed to destroy pathogenic organisms.

There are two types of UV lamps: low pressure (with an electromagnetic spectrum between 185 and 254 nanometers), and—more commonly used today—medium pressure, high-intensity lamps that have a wider electromagnetic spectrum between 180 and 400 nanometers and are unaffected by water temperature. UV is most germicidal in wavelengths between 240 and 280 nanometers. Organic compounds are best photo-oxidized by hydroxyl radicals in wavelengths below 230 nanometers. The bond between chlorine and nitrogen is broken, and chloramine destruction is most effective in the range of 245 and 340 nanometers, making low

pressure bulbs a poor choice for chloramine destruction.

Increase Airflow Over the Water Surface

It is not possible to superchlorinate below a pool blanket or inside an enclosed pipe. By definition, oxygen is necessary for oxidation and off-gassing to occur. If sufficient oxygen is lacking over the pool, breakpoint will not be achieved. Using a fire as an example, if the fuel is present but oxygen is lacking, combustion will not occur. Any mechanism should be employed to move large volumes of air over the pool including opening windows and doors and turning on exhaust fans. Unfortunately, chloramines removed from the water are released into the air in the natatorium. In an indoor pool, the wind is not available to blow away odors and irritants. Thus, the air handling system must be designed to take the place of nature. At least 8 complete air exchanges are required per hour. Air dampers should be opened to permit 100% fresh air to be brought in especially during breakpoint chlorination. During regular operation, as little as 15% fresh air may be permitted by code, but 40-100% is recommended depending on usage patterns, natatorium design, and equipment installed. For instance, pools that have water features installed that agitate water or aerosolize water vapor, particulates, or pathogenic organisms should exchange more air. The location and placement of supply registers and return/exhaust ducts should ensure low air supply, movement of air across the water surface at a velocity less than 25

feet per minute, and high air exhaust. This allows movement of the heavier gasses concentrated directly over the pool to be expelled near the ceiling level. Pollutants travel from positive to negative pressure areas, so natatoriums should be positively pressured in relation to outside and negatively pressured in relation to surrounding occupied spaces. The air handling system installed should be capable of providing thermal environmental temperatures acceptable to 80% or more of the primary/priority facility users, averting sick building syndrome problems, and preventing discernible odors, without evident drafts, stratification of air, thermoclines or temperature gradients.

Suggested Reading

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