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Chlorine & Chlorinated Compounds

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Interestingly, although the general public primarily associates chlorine with swimming pool water disinfection, less than 1% of chlorine produced, in the form of elemental gas chlorine and chlorinated compounds, is used for pool water treatment.

History

Chlorine was discovered in 1774 by Swedish pharmacist Carl Wilhelm Scheele. Scheele was performing an experiment which involved the mixing and heating of manganese dioxide and "marine acid" (hydrochloric acid). The yellow-green gas that resulted was chlorine. But, 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 its 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.

Chlorine is made today by passing an electrical current through a solution of salt water. As by-products of chlorine formation, sodium hydroxide (caustic soda or lye) and hydrogen gas are also produced.

Other Uses

In addition to pool water treatment, chlorine has thousands of other uses. Chlorine is used to treat drinking water to make is safe for human consumption. It was first used for this purpose in 1904 in Lincoln, England 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.

One of chlorine's initial uses was as a bleaching agent to whiten clothes. The French were whitening and brightening their clothing with chlorine as early as 1790.

Chlorine was used as a chemical weapon by the Germans in World War I. Today chlorine is used in the manufacture of explosives.

Inhalation of diluted chlorine was popular as a treatment for the common cold during the 1920s.

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.

Sanitation & Oxidation of Pool 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, that are harmful to human health. Chlorine is used as an infection control product in order to prevent the spread of communicable disease through pool and spa water. Oxidation is the process of chemically removing organic debris such as perspiration, saliva, urine, body oils and wastes, and other particulate matter from the water.

Six different chlorinated products are 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.

[Insert comparison charts]

Since hand feeding of chemicals into commercial pools is not permitted, chlorine is introduced, depending of the product form, with chemical feed pumps which include gas chlorinators, diaphragm, piston, or peristaltic type positive displacement pumps; or erosion or erosion-soaker feeders.

When chlorine (Cl_2) is added to water (H_2O), hypochlorous acid (HOCl) and hydrochloric acid (HCl) result. Hypochlorous acid, the active sanitizing ingredient, then partially dissociates to hydrogen ion (H) plus a hypochlorite ion (OCl^-). Hypochlorite ions have a tendency to combine with nitrogen and ammoniated impurities in the water. Free chlorine consists of a mixture of both hypochlorous acid and hypochlorite 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).

Minimum and occasionally maximum levels of free available chlorine, measured by weight in parts per million, may be specified by code. But, chlorine should be added as needed to maintain and oxidation reduction potential between 750 and 900 millivolts.

Combined available chlorine, also referred to as chloramines, CAC, or ammoniated chlorine compounds, should not be allowed to exceed 0.2 ppm. Chloramines cause eye and mucous membrane irritation, give off the unpleasant “chlorine” odor often associated with poorly ventilated indoor pools. Chloramines are ineffective as a sanitizer and oxidizer because they are too stable. They are 60 to 100 times slower than FAC at destroying unwanted products in the water.

Breakpoint Chlorination

Chlorine is also used to shock or superchlorinate pool water in order to remove unwanted organic compounds from the water, destroy impurities and dissolved waste products and algae, and break apart the chemical bond that holds chlorine and ammonia together. The point at which this chemical bond is broken is called “breakpoint”. Breakpoint chlorination eliminates chloramines which cause an increased chlorine demand.

In order to achieve breakpoint, a quantity of 7.6 molecules of free chlorine are used to break apart each 1 molecule of combined chlorine. Several chemical reactions take place and monochloramines, dichloramines and trichloramines form before the breakpoint is achieved. Reaching the breakpoint is an all-or-nothing reaction. If breakpoint is not reached, the problem will be worse. When the chemical bond with ammonia is broken, free chlorine, nitrogen, water and 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, and commercial brand non-chlorine oxidizing agents. Stabilized chlorine products, isocyanurates, should not be used for superchlorination.

To calculate breakpoint in order to superchlorinate, use a DPD test kit to find both the free and total available chlorine levels. Subtract the free available chlorine (FAC) from the total available chlorine (TAC) to find the combined available chlorine (CAC) level. Multiply the CAC by the factor 10, although only 7.6 is actually needed, to find the dose of chlorine you must introduce into the pool in order to reach the breakpoint. 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.

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

For example:

If free available chlorine is 1.0 ppm and total available chlorine is 2.5 ppm, the difference (combined available chlorine) is 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

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 the pool is not in operation to avoid respiratory irritation to users from off gassing during the superchlorination process, and to allow chlorine levels to drop back to normal levels. If the chemical reaction takes place and breakpoint is reached, the large amounts of chlorine added to the water will be used up in the process. Free chlorine will return to normal operating levels, and the combined chlorines will be eliminated.

Measuring Chlorine Effectiveness

Chlorine residual is often measured in parts per million (ppm). Parts per million is a quantitative indicator of residual, where weight of chlorine is compared to weight of water in the pool. CT values (contact over time) should be used to determine whether ppm levels are adequate.

Oxidation reduction potential (ORP), also known as Redox, or HRR, is a qualitative indicator of chlorine effectiveness. ORP measures conductivity of water and indicates the potential generated for oxidation or work potential.

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 Coliforms, Pseudomonas aeruginosa, or other indicator bacteria confirms the adequacy of the chlorine sanitizer and oxidizer.

Environmental and Health Concerns

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

Chlorine is hazardous to aquatic plants and fish, and can certainly damage vegetation, but Greenpeace's "Chlorine Kills" campaign is 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.

Future Without Chlorine?

Without chlorine, cholera, typhoid fever, dysentery and other water borne diseases would be rampant. The lifespan of the average American would be shortened.

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.

Chlorine & Chlorinated Compounds

Product	**Elemental gas chlorine**
Common name	Gas
Appearance	• Greenish gas • Delivered under pressure in 150 pound cylinders or 1 ton steel tanks
% available chlorine	100%
Produced by	Separating salt into its elemental products: chlorine, hydrogen gas and sodium hydroxide
To raise chlorine level 1 ppm per 10,000 gallons	1.3 ounces
pH	1.0 or less
Organic/Inorganic	Inorganic
Injection equipment	Chlorinator, scale, booster pump
Advantages	• Inexpensive to purchase • 100% chlorine • No additives or inert ingredients
Disadvantages	• Expensive to dispense • Extremely dangerous if handled improperly -- toxic to humans, animals and plant life • Use of chlorine gas for pool water treatment is prohibited in some states • Lowers pH significantly
Special precautions	• Store indoors, at or above ground level, in a separate, well ventilated room • Install an exhaust fan capable of 60 air exchanges per hour which draws from floor level • Tanks must be individually chained to the wall in an upright position • Install both audio and visual alarms to warn of leaks or high concentrations • Do not work alone in a gas chlorine room -- use the buddy system • Employees must be trained to use and must wear U.S. Bureau of Mines (USBM) or National Institute for Occupational Safety (NIOSH) approved gas masks with a dated fresh canister, or self contained breathing apparatus (SCBA) while exchanging tanks • Gas mask or SCBA must be stored immediately outside the chlorine room • Ammonium hydroxide (commercial strength ammonia) must be available to test for leaks • Spare tanks must be capped • A wrench must be kept on the tank stem to shut off the valve if leaks develop (turn clockwise to close) • Only individuals trained in proper safety procedures should be permitted to handle gas chlorine equipment. Licensing is required in some states. After the initial training, refresher training is required at least once every 6 months. • Tank exchanges should only be made when the pool is closed to the public • Replace gaskets when changing tanks to help avoid leaks • Post all required signage • Emergency pool evacuation procedures must be posted • Evacuation drills must be rehearsed on a regular basis • Keep pool emergency exit doors unlocked • Inject chlorine under vacuum, not under pressure

Product	**Sodium hypochlorite**
Common name	Liquid chlorine, bleach
Appearance	Yellowish-green clear liquid
% available chlorine	10 - 15%
Produced by	Bubbling gas chlorine through a solution of sodium hydroxide
To raise chlorine level 1 ppm per 10,000 gallons	1.0 - 1.5 cups
pH	13
Organic/Inorganic	Inorganic
Injection equipment	Peristaltic, diaphragm, or piston type chemical metering pumps
Advantages	• Relatively safe to handle unless splashed or swallowed • Nonflammable
Disadvantages	• Storage space: bulky • Short half life: Loses its effectiveness rapidly in heat and sunlight • Significantly raises pH • Approximately 1 quart of muriatic acid is needed to counter the effect of each 1 gallon of sodium hypochlorite used • Rapid build-up of TDS • Sodium dissolved in the water will eventually give the water a salty taste
Special precautions	• Secondary containment required • Personal protective gear required includes: goggles or a full face shield, neoprene glove and a splash guard apron • Store covered in a dark, cool location • Sodium hypochlorite test kit should be used to test product strength

Product	**Calcium hypochlorite**
Common name	Cal hypo, HTH
Appearance	• White granule • White tablet
% available chlorine	65 - 75%
Produced by	Passing chlorine gas over sodium hydroxide (lime)
To raise chlorine level 1 ppm per 10,000 gallons	2 ounces
pH	11.8
Organic/Inorganic	Inorganic
Injection equipment	• Often improperly added by broadcasting directly over pool • Made into a liquid then injected using a peristaltic, diaphragm, or piston type chemical metering pump • Erosion or erosion-soaker feeder
Advantages	• High percentage of available chlorine • Convenient and easy to use in tablet form
Disadvantages	• Flammable and combustible -- unsafe if improperly stored, allowed to get wet or contaminated with a foreign product • Raises pH • Partially insoluble • May cloud water, damage pool surfaces or cause chemical burns if added directly to the pool or in too great a quantity in too short a period of time • Dispose of residue -- only the dissolved liquid should be pumped into the pool return lines • May contribute to scale formation and calcification problems
Special precautions	• Store in its original container is a cool, dry place • Open containers outdoors in a well ventilated location • Personal protective gear including respiratory protection should be worn while handling • Do not dispose of spilled chemical in the trash or in a dumpster -- fire may result • Do not re use storage containers -- rinse, crush and destroy prior to disposal

Product	**Lithium hypochlorite**
Common name	Lithium
Appearance	White powder
% available chlorine	35%
Produced by	Bubbling gas chlorine through lithium, sodium and potassium sulfates, then drying
To raise chlorine level 1 ppm per 10,000 gallons	10.5 ounces
pH	10.7
Organic/Inorganic	Inorganic
Injection equipment	• Pre dissolve then injected using a peristaltic, diaphragm, or piston type chemical metering pump
Advantages	• Totally soluble -- no residue • Nonflammable, non combustible • Dust free • Long shelf life
Disadvantages	• High cost • Raises pH
Special precautions	Do not try to introduce through an erosion feeder -- dissolves much to rapidly

Product	**Sodium dichloro-s-triazinetrione**
Common name	Dichlor
Appearance	White granule
% available chlorine	56 or 62%
Produced by	Adding sodium bicarbonate and cyanuric acid to trichlor
To raise chlorine level 1 ppm per 10,000 gallons	2.25 ounces
pH	6.9
Organic/Inorganic	Organic (contains cyanuric acid)
Injection equipment	Dichlor feeder
Advantages	• Stabilized • Instantly soluble -- no residue or cloudiness • Neutral pH
Disadvantages	• Cyanuric acid build-up • Ties up chlorine and reduces ORP -- higher minimum chlorine residuals may be required by code • More frequent draining and refilling of pool
Special precautions	• Never place dichlor in a trichlor feeder -- rapid dissolving may result in a pressure build-up and explosion • Do not use in indoor pools

Product	**Trichloro-s-triazinetrione**
Common name	Trichlor
Appearance	• Solid white tablets or sticks • Granular form sold as a algaecide
% available chlorine	90%
Produced by	Drying cyanuric acid in the presence of gas chlorine
To raise chlorine level 1 ppm per 10,000 gallons	1.5 ounces
pH	2.9
Organic/Inorganic	Organic (contains cyanuric acid)
Injection equipment	• Erosion feeder (in-line) • Floating feeders (residential pools only)
Advantages	• Easy to store and use • Long shelf life -- can be purchased and delivered in quantity
Disadvantages	• Cyanuric acid build-up • Ties up chlorine and reduces ORP -- higher minimum chlorine residuals may be required by code • More frequent draining and refilling of pool • Significantly lowers pH • 4 ounces of sodium carbonate is needed for each 1 pound of trichlor added to the pool
Special precautions	• Never place tablets directly in the pool -- children may try to eat the tabs and be poisoned, and tablets will damage the pool surface • Do not place trichlor tabs in skimmer baskets • Do not use floating trichlor feeders in commercial pools • Do not use in indoor pools