Health Issues: Chlorinated Swimming Pools

The Need for Disinfection

Swimmers entering a pool immediately start to contaminate the water with a rich mixture of organic compounds and nitrogen containing products. Perspiration, saliva, urine, skin scales, hair, dirt, fecal matter, cosmetics, hair sprays, body oils, body parasites and microbes including bacteria and fungi are all added to the water. Absent a suitable means of filtration and disinfection, the pool water would quickly become a severe health risk, exposing people to a wide array of harmful chemicals and germs. The germs most commonly encountered in incidences of sickness from swimming pool waters are E. coli, Cryptosporidium, Giardia and Shigella. All these organisms cause intestinal problems and diarrhea.

Many of the larger solid contaminants are removed from the pool water by a process of filtration, but most of the chemical contaminants present, and many of the germs, are able to pass through the filtration media. Thus we can appreciate the need to use disinfectants or sanitizing agents. One very popular type of sanitizing agent used in the U.S. is chlorine. Other, less common agents used are bromine, ozone, iodine, silver or copper products added by electrolytic cells, or ultraviolet light. However, by far the most common product is chlorine, and for this reason this data sheet focuses on the chlorination process and its reaction with the organic carbon and nitrogen components that are the major chemical contaminants in swimming pool waters.

Chlorination of Pool Waters

There are diverse ways of introducing chlorine into pool waters. Chlorine can be stored under pressure as a gas and this can be piped directly into the water. However, chlorine gas is a very hazardous chemical and it needs extremely careful handling. Thus, most users opt for a far safer form of chlorine, available from compounds known as hypochlorites of common elements such as calcium, sodium or lithium, hence the names, calcium hypochlorite, sodium hypochlorite or lithium hypochlorite. When added to water these “chlorine salts” dissolve and release so-called chloride ions into the water. Their rate of dissolution, and first cost, usually determines which particular salt the a pool manager uses. The calcium hypochlorite is a dry powder, or granules, that dissolves slowly and leave a chalky residue that adds to the load on the pool’s filtration system. Lithium hypochlorite is the most expensive but it dissolves completely and is usually the salt of choice for hot tubs and spas, where the higher temperatures cause a high rate of chlorine loss that must constantly be topped-up with the addition of more salts. The cheapest form are the sodium hypochlorites, hence they are the most common salts used. Sodium hypochlorite is widely available as common household bleach such as Chlorox™; this is a 5% solution of sodium hypochlorite in water. Chemical supply companies also provide pool owners with more concentrated forms of sodium hypochlorite, usually as 10%, or 12%, aqueous solutions.

When we add chlorine, or chlorine ions, into the pool the chlorine reacts very quickly with the water to form two acids, hydrochloric acid and hypochlorous acid, according to this equation:

$$\underset{\text{Chlorine}}{Cl_2} + \underset{\text{Water}}{H_2O} = \underset{\text{Hydrochloric acid}}{HCl} + \underset{\text{Hypochlorous acid}}{HOCl} \qquad \text{(Eq.1)}$$

It is the hypochlorous acid that performs the bulk of the disinfection process. This acid is a strong oxidant, it is very reactive and hence is constantly being consumed and thus needs to be frequently topped up. Molecules of hypochlorous acid easily pass into the cell membrane of germs or microbes and start oxidizing the cell contents, thereby destroying them.

One problem is that the hypochlorous acid itself reacts with water to form ions according to this equation:

$$H_2O + HOCl \leftrightarrow H_3O^+ + OCl^- \qquad \text{(Eq. 2)}$$

Chlorine, present in water as HOCl or OCl^-, is defined as "free available chlorine". However, the hypochlorite ion (OCl^-) formed in this reaction has a negative charge attached to it, that interrupts its passage through cell membranes – the cells repel the negative ions, thus this form of "chlorine" is not nearly as effective a disinfectant as chlorine in the form of hypochlorous acid (HOCl). Fortunately, we now recognize that equation (Eq.2) is very dependent on the pH of the water. At a pH under 6, virtually all the chlorine ions are converted to HOCl. At pHs of 9 or above, virtually all the HOCl is converted to hypochlorite ions. The ideal goal is to maintain the pool water's pH in the range of 7.2 to 7.6, in this range approximately 50 to 75% of the chlorine present is in the form of the desirable hypochlorous acid (HOCl).

Acidity & Alkalinity or pH of Pool Waters

The acidity or alkalinity of pool waters is very important:

- The pH of a human body is slightly alkaline at about 7.2 – 7.8 pH. By maintaining the pool water around this level prevents burning of the skin from either too acid conditions or too caustic, or so-called, high alkaline conditions.
- The slightly alkaline conditions ensure that some of the sodium present in the chemical additives reacts with the hydrochloric acid formed in (Eq.1), to remove this very corrosive acid to form a relatively harmless common salt, sodium chloride.
- By keeping the pH in the range of 7.2 to 7.6 we help maintain the chlorine in the form of hypochlorous acid, the most beneficial form as far as germ disinfection is concerned.
- Most of the tile grouting in pools is composed of calcium sulfate, which in the presence of even mild acids will decompose, causing a steady breakdown in the pool's infrastructure.

Unfortunately, solutions of sodium hypochlorite are fairly strong alkalis (have a high pH) so when we add sodium hypochlorite solutions to the water the pH of the water increases. Thus it is often necessary to add an acidic chemical, such as acetic acid or dilute sulfuric acid to neutralize the excess alkalinity in the pool.

Since the maintenance of a narrow range of pH is of such importance, most regulatory authorities mandate a frequent check of pool pH and more chemicals, termed "buffers" are frequently added to pool waters to ensure that the pH is kept in the desired range. Typical buffers include sodium bicarbonate, which is common baking soda, to lower pH. Other pH adjusters used by pool owners include sodium bisulfate and many pool owners use carbon dioxide gas to lower pH, or sodium carbonate to raise it.

Other Chlorine Reactions

Chlorine, hypochlorous acid or hypochlorite ions, not only react with microbes, but also with other chemicals present in the water. Among the most common are those containing nitrogen or carbon atoms, such as are present in urine, perspiration and other body contaminants. Two distinct classes of chlorinated compounds are readily formed:

- Chloramines - from nitrogen containing compounds
- Trihalomethanes – from carbon containing compounds

Chloramines

Ammonia (NH_3) or compounds containing nitrogen and hydrogen linked atoms, such as proteins, are readily attached by chlorine, and depending on the severity of the attach, either one, two or all three of the hydrogen atoms of the ammonia molecule are substituted with chlorine atoms. Thus we have three different chloramines formed:

- NH_2Cl Monochloramine
- $NHCL_2$ Dichloramine
- NCL_3 Trichloramine, also called nitrogen trichloride

All three chloramines have some germicidal value, but are not nearly as effective as hypochlorous acid or even the hypochlorite ions. However, one well-known characteristic of these chloramines is that they evaporate easily from the pool water into the air. This is especially true of the trichloramine, which is a gas that is not very soluble in water. These chloramines have a very strong chlorine odor and when swimmers notice strong chlorine odors in the vicinity of the swimming pool, it is almost certainly chloramines that they are detecting, and not chlorine itself. The fact is that at the preferred residual chlorine concentration of a swimming pool of 1.0 to 1.5 ppm of chlorine, virtually all the chlorine is dissolved in water, and the odor in the air above the pool is hardly detectable.

Ironically, when swimmers complain of too much chlorine in the pool area, the real problem is one of <u>too little free chlorine in the water.</u> Too much of the chlorine has been converted to chloramines. Usually, the best corrective action is to add more chlorine to the water. In fact, "super-chlorination" or "shock-chlorination" of the water, where for a short period of time, up to ten times the usual dose of chlorine is added to the water, is a recommended cure when chloramines concentrations are too high (generally when the combined chlorine concentration exceeds 0.2 ppm). This is to ensure that adequate free chlorine levels reach all areas of the pool to effect disinfection.

Chloramines are irritants to the eyes and mucous membranes, and recent research completed in 2002, by doctors in Heartlands Hospital in Birmingham, England[i] and at the Catholic University of Louvain[ii], Belgium, have identified trichloramine, as the probable cause of respiratory problems and occupational asthma in swimmers and pool attendants, at indoor swimming pools. This observation may also help explain why an abnormal number of competitive swimmers experience asthma. Long hours of exposure to trichloramines, which will be at their highest concentration immediately above the water level in the pool, is the probable cause of this undesirable condition. Indeed the Birmingham study identified, in laboratory challenge tests, that nitrogen trichloride levels of 0.5 mg/m^3 were sufficient to trigger asthma type reactions in exposed persons. These levels are often exceeded in the air above indoor swimming pools.

For these reasons, every care should be taken to minimize chloramine formation in, and above, the swimming pools, by having swimmers wash thoroughly before entering the water, by treating the water to control chloramines, by maintaining adequate water exchange rates, and by constant dilution of the air above the indoor pools via good ventilation practices.

Apart from the “super-chlorination” treatment, or “chlorine shock treatment” of the pool to reduce chloramines, other chemical treatments are available, namely, the addition to the water of:

a) **Sodium thiosulfate:** This reacts with the chloramines to convert them back to ammonia and hypochlorous acid, as per this formula:

$$Na_2S_2O_3 + NHCL_2 + H_2O \longleftrightarrow NH_3 + HOCl + 2Na_2SO_4$$

(sodium thiosulfate + dichloramine + water) (ammonia+hypochlorous acid +sodium sulfate)

b) **Potassium Monopersulfate:** An efficient strategy to reduce chloramines in swimming pools and spas is to add potassium monopersufate (a Dupont product). This is a strong oxidizer with no chlorine content. It eliminates organic contamination and blocks chloramines production and enhances the efficiency of the existing chlorination. This is an easy product to use and causes minimum downtime of the pool, bathers can return within minutes of treatment, and avoids some of the corrosive risks inherent in using very high chlorine levels.

Trihalomethanes (THMs)

Methane (CH_4), a natural product of our bodies, contains carbon and hydrogen atoms linked together. Such links may be attacked by halogens, such as chlorine and bromine. The product of the attack is the substitution of the hydrogen atoms with the halogen atoms of chlorine or bromine. In the case of methane, the most common products are the so-called trihalomethanes, these being:

- $CHCl_3$ Chloroform, or trichloromethane.
- $CHBr_3$ Bromoform
- $CHCl_2Br$ Bromodichloromethane
- $CHClBr_2$ Dibromochloromethane

The rate of THM production is a function of the number of swimmers, the total organic carbon content of the water, the pH and the water temperature. The most important of the THMs is chloroform, this is a volatile gas that escapes from the water, it adds to the "chlorine-like" odor and more pertinently, chloroform as well as dibromochloromethane, are suspected human carcinogens. It is reported that elevated chloroform concentrations, immediately above the water of indoor swimming pools, is not uncommon. The recommended OSHA Permissible Exposure Limit (PEL) for chloroform is 50 ppm (equivalent to 240 mg/m^3), for an 8-hour Time Weighted Average (8-hr. TWA). But, the National Institute for Occupational Safety and Health (NIOSH) recommends a far tighter standard of 2 ppm (9.78 mg/m^3) as a 60-minute ceiling limit. This is likely to be exceeded in pools where poor water treatment protocols are practiced.

Swimming pools are considered to be the prime source of the public's exposure to chloroform and chloroform concentrations can be measured in the blood plasma of regular swimmers. The most significant factor in determining the rate of chloroform absorption by swimmers is the chloroform concentration in the air immediately above the water. Again, as is the case with the trichloramine, it is essential to maximize the use of ventilation to remove these potentially harmful contaminants from the air of indoor pools.

Indoor Swimming Pool Ventilation

The American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) defines ventilation rates for buildings, and these rates form the basis of virtually all building codes. In the case of swimming pools the major objective of the ventilation system is to balance the indoor relative humidity levels with energy consumption, whilst ensuring that airborne pollutants are effectively removed by a process of dilution. The preferred relative humidity level of the air in an indoor swimming pool is between 50 to 60%. Permitting the air to hold more moisture than the suggested 60% causes excessive condensation, which usually accelerates corrosive attacks on materials, and encourages the growth of molds and fungi.

The ventilation rate for an indoor swimming pool, as set by ASHRAE, is designed to provide acceptable indoor air quality for the average pool using chlorine as its primary disinfection process. The rate is also designed for average conditions. In the case of high occupancy public pools, the rate is liable to be somewhat inadequate.

ASHRAE stipulates that pools with no spectator areas should be ventilated at the rate of between 4 to 6 air changes per hour. Spectator areas should be ventilated at a rate of between 6 to 8 air changes per hour. The exhaust air from the pool is potentially rich in moisture and in chloramines and trihalomethanes. For this reason it is sensible not to use this as a source of return air for showers and locker rooms. Ideally the pool area should be operated under a negative air pressure of 0.05 to 0.15 inches of water, relative to the adjacent areas. Also, the exhaust grilles should be located as closely as is possible to the warmest water in the building, especially if there are whirlpools installed.

[i] Occupational asthma caused by chloramines in indoor swimming-pool air. By Thickett, McCoach, Gerber, Sadra & Burge (Eur Respir. J. 2002 May; 19(5): 827-32).

[ii] Lung hyper permeability and asthma prevalence in schoolchildren: unexpected associations with the attendance at indoor chlorinated swimming pools A Bernard, S Carbonnelle, O Michel, S Higuet, C de Burbure, J-P Buchet, C Hermans, X Dumont and I Doyle. Occupational and Environmental Medicine 2003;60:385-394