WATER TREATMENT OF SWIMMING POOLS, SPAS, AND HOT TUBS

The swimming pool market has grown at an average of ~2.2%/year over the last 11 years. The total number of pools in 2002 was ~7.6×10^6 in the United States (1). Residential pools represent ~90% of the total. About 55% are inground and ~45% aboveground. Inground pools are growing at a faster rate. The majority of inground pools are in Florida and California. Hundreds of cities operate public pools, and many schools, clubs, and camps have outdoor and indoor pools. Most motels and many hotels, condominiums, apartment complexes, and retirement communities also have pools on their premises. Although commercial pools account for only ~10% of the total, they represent about one-half of the treated water. The number of spas and hot tubs has grown at ~7% annually since 1991, with an estimated 5.6×10^6 spas and hot tubs in 2002 in the United States. About 17% of spas/hot tubs are attached to pools. California has the greatest number of spas and hot tubs.

1. Swimming Pools

Most swimming pools are of the recirculating type. Through filtration, chemical treatment, filter backwashing, and dilution with rain and makeup water, the water can be reused without draining and refilling. The only time that pools need to be drained and refilled is for repair or in cases of contamination, severe scaling or algae infestation. Some health codes require partial replacement of pool water (based on bather load) to maintain water quality in public swimming pools.

Sanitizing chemicals must be added regularly to oxidize pool contaminants and kill and control disease-carrying bacteria and other organisms introduced by swimmers and dirt entering the water. It also is necessary to destroy algae whose spores are carried into the water by wind and rain. Unchecked algal growth results in discolored water, unsightly growth on pool surfaces, clogging of filters, and provides breeding ground for bacteria.

The pH of pool water must be maintained within a desirable range for swimmer comfort and optimal effectiveness of chlorine sanitizers. In order to control the corrosive or scaling tendencies of pool water, it also is necessary to maintain a proper balance among pH, carbonate alkalinity, and calcium hardness.

Undesirable trace metals such as iron, manganese, or copper are sometimes found in source water or formed by corrosion of pool equipment. Unless removed, these metals discolor pool water and cause stains, especially damaging to plaster pool surfaces.

Filtration of pool water is necessary for removal of suspended solids that otherwise cloud water and interfere with the disinfection process. Periodic backwashing of the filter displaces the collected residue and debris.

The National Swimming Pool Foundation trains personnel as operators for public and private pools and spas through the Certified Pool/Spa Operator program (2).

1.1. Construction. New residential inground pool construction consists of concrete/gunite 63%, vinyl liner 33%, and fiberglass and other 4% (1). The pools vary in size from $\geq 4.6 \times 9.1$ m ($<15 \times 30$ ft) to $>6.1 \times 12.2$ m ($>20 \times 40$ ft) and have an average volume of ~ 109.8 m^3 (29,000 gal). Aboveground pools vary in diameter from ≤ 3.7 m (≤ 12 ft) to >7.3 m (>24 ft), have an average volume of 56.8 m^3 (15,000 gal), and typically have vinyl liners. The average size of commercial pools is 363.4 m^3 (96,000 gal).

1.2. Design. The basic recirculation loop of a swimming pool consists of strainers (for removing hair and lint), skimmers (in outdoor pools for removing large floating debris such as leaves, twigs, and insects), a pump, a filter, and in some cases, a chemical feeder and heater (typically gas).

The National Sanitation Foundation (NSF) sets standards and provides testing for circulation system components for pools, spas, and hot tubs (3).

Inground pools can have bottom drains allowing removal of some debris that settles to the bottom of the pool. Many pools also have automatic vacuums or systems for cleaning pool surfaces. Large pools require multiple inlets especially in the deep end to ensure adequate circulation and elimination of dead spots. Large municipal pools typically have balancing tanks to hold water displaced by bathers and are equipped with instrumentation for automatic measurement and control of available chlorine and pH via sanitizer and chemical feeders.

1.3. Chlorine-Based Sanitizers. Chlorine compounds are the most commonly used swimming pool sanitizers and include: calcium hypochlorite, lithium hypochlorite, sodium hypochlorite solution, chlorine gas, trichloroisocyanuric acid (Trichlor), and sodium dichloroisocyanurate (Dichlor) (Table 1) (see DISINFECTION). Sanitizer usage varies geographically (4), eg, in the Sun Belt overall consumption varies as follows: chloroisocyanurates > calcium hypochlorite > sodium hypochlorite, whereas, in the Snow Belt consumption generally varies in the order: calcium hypochlorite > chloroisocyanurates > sodium hypochlorite. However, in the Midwest, chloroisocyanurates predominate. Calcium hypochlorite usage is highest on the East Coast and lowest on the West Coast. Chloroisocyanurate users also use significant amounts of hypochlorites (typically calcium hypochlorite) for superchlorination or shock treatment since chloroisocyanurates are not recommended for this purpose.

Chlorine. Chlorine gas is used as a sanitizer mainly in large commercial pools requiring a high feed rate to maintain the desired residual. However, a small number of pool service companies also use chlorine gas for treatment of residential pools. Some state and local health codes specify chlorine gas as the required or preferred disinfectant for public pools above a certain size. Calcium and sodium hypochlorite are finding increased use in municipal and public pools because of the health and safety hazards of chlorine gas (see CHLORINE).

When chlorine dissolves in water, it hydrolyzes to produce hypochlorous and hydrochloric acids (5):

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl \qquad K^{25^\circ C} = 3.94 \times 10^{-4}\ M$$

Dissociation of hypochlorous acid produces hydrogen and hypochlorite ions:

$$HOCl \rightleftharpoons H^+ + ClO^- \qquad K_a^{25^\circ C} = 2.90 \times 10^{-8} M$$

The dissociation of hypochlorous acid depends on pH and, to a much lesser extent, temperature (6). At 25°C, it is ~0% at pH 5, ~50% at pH 7.5, and ~100% at pH 10; see Figure 1. Because of the acidity formed by chlorine gas, addition of soda ash (Na_2CO_3) or sodium sesquicarbonate ($Na_2CO_3 \cdot NaHCO_3$) is necessary to maintain proper pH and replenish alkalinity.

Chlorine is supplied as a liquefied gas under pressure in steel cylinders of 45–68-kg capacity. It requires special metering and feeding equipment and experienced supervision. Because of its toxicity, elaborate precautions against leakage are needed. Although Cl_2 gas is not expensive, initial equipment costs, cylinder demurrage, and potential hazards make this automatic disinfection system impractical for all but very large, heavily used pools. By contrast, some pool service companies treating residential pools simply use a small portable chlorine cylinder of ~9 kg net wt with flexible tubing and a chlorine diffuser. However, this method of pool treatment is risky because of the low pH region generated during rapid chlorine dissolution that can extend to the pool walls and bottom resulting in etching of plaster or tile grout pools surfaces or bleaching of vinyl liners.

Small electrolytic chlorine generators are available that are based on electrolysis of aqueous NaCl. The gaseous chlorine formed in the anode compartment is dissolved in the recirculating pool water and the sodium hydroxide formed in the cathode compartment can be used for adjusting the pH of the pool.

Calcium Hypochlorite. This chemical, marketed since 1928, is one of the most widely used swimming pool water sanitizers. Calcium hypochlorite, a crystalline solid, is a convenient source of available chlorine and is sold in granular or tablet form for use in home, semiprivate, and commercial pools. It contains small amounts of stabilizing $Ca(OH)_2$, which has a very small effect on pool pH (7). Calcium hypochlorite has superior storage stability and much higher available Cl_2 concentration than liquid bleach, which reduces storage requirements and purchasing frequency.When dissolved in water, $Ca(OCl)_2$ forms hypochlorite ions and hypochlorous acid (see DICHLORINE MONOXIDE, HYPOCHLOROUS ACID, AND HYPOCHLORITES).

$$Ca(OCl)_2 \longrightarrow Ca^{2+} + 2\ ClO^-$$
$$2\ ClO^- + 2\ H^+ \rightleftharpoons 2\ HOCl$$

Lithium Hypochlorite. Similar in action to other hypochlorites, this chemical is used to a small extent. It is more expensive than sodium or calcium hypochlorite.

Sodium Hypochlorite Solution. Sodium hypochlorite (liquid bleach) is usually bottled as a 10–15% available Cl_2 solution, containing 0.65–0.83%

NaOH for stability which has only a small effect on pool pH. It is a commonly used sanitizer for swimming pools. In pool water, it produces hypochlorite ions and hypochlorous acid similar to calcium hypochlorite.

Sodium hypochlorite is widely used in California and Florida, the two states with the largest number of inground pools, where it is a popular sanitizer with the home-pool owner because of low cost per unit package. It also is widely used for small public pools and for semicommercial pools such as at motels and camps. Disadvantages of sodium hypochlorite solution are low storage stability and bulkiness that requires a large storage area near large pools.

Small single-chamber electrochemical generators available for producing NaOCl (from electrogeneration of chlorine gas and sodium hydroxide) are based on electrolysis of pool water containing ~3000 ppm NaCl.

Chlorinated Isocyanurates. The cyanuric acid-based sanitizers, introduced for pool use in 1958, are stable crystalline compounds with moderate-to-high available Cl_2. Sodium dichloroisocyanurate, sold in granular form, dissolves rapidly, whereas trichloroisocyanuric acid dissolves very slowly and is widely used in the form of tablets in feeders, floating devices, or in the pool skimmer. Chloroisocyanurates are used primarily in residential pools and spas.

1.4. Other Sanitizers and Treatment Systems. Other sanitizers and swimming pool treatment systems used to a limited extent are bromine, quats, ozone, Cu-Ag ionizers, Cu-Ag and Zn-Ag cartridges, ultraviolet (uv), and uv-H_2O_2.

Bromine. Unlike chlorine, although bromine is commercially available, it is not used to sanitize pools. Bromine for swimming pool sanitation is supplied primarily by 3-bromo-1-chloro-5,5-dimethylhydantoin (BCDMH). A dibromo version was introduced in 2002 by Albemarle Corp. BCDMH is sold in tablet form (~95% assay) and has an av Cl_2 of ~28% and an av Br_2 of ~63% (total equivalent av Cl_2 ~59%). Because of low solubility, BCDMH requires larger feeders than used with Trichlor tablets.

Hydrolysis provides hypobromous acid for disinfection. The N–Cl bond hydrolyzes to a much smaller extent than the N–Br bond, forming HOCl, which reacts rapidly with residual bromide ion in the water forming more HOBr ($HOCl + Br^- \longrightarrow HOBr + Cl^-$). Hypochlorite sanitizers are typically used for shock treatment. The hydantoin ring can be cleaved by hypochlorite ion forming *N*-chloroisopropylamine, NCl_3, and CO_2 (8).

Bromine also can be generated *in situ* from bromide ion and an oxidizing agent, eg, dosing the pool with sodium bromide combined with routine addition of potassium peroxymonosulfate generates HOBr ($HSO_5^- + Br^- \longrightarrow BrO^- + HSO_4^-, BrO^- + H_2O \rightleftharpoons HOBr + OH^-$). Other oxidizing agents such as hypochlorites, chloroisocyanurates, and ozone also can be used as well as electrochemical oxidation. Recommended bromine concentrations are given in Table 2.

Like chlorine, unstabilized bromine is ~90% decomposed by sunlight in ~3 h. Polarographic studies show that cyanuric acid (CA) reacts with free bromine (ie, HOBr and BrO^-) forming bromoisocyanurates, which improves stability at sufficiently high CA concentrations, but not as effectively as stabilization of chlorine (9). Dimethylhydantoin, the parent compound of BCDMH, provides better stability, but still not equivalent to stabilzation of chlorine by CA (9).

Quats. The polymeric quaternary poly(hexamethylenebiguanide), PHMB, is a bacteriostat that requires routine addition of a quaternary ammonium-based algicide (alkyldimethylbenzylammonium chloride) (9). This sytem also employs an enzyme-based filter cleaner and a trace metal chelator. Since chlorine sanitizers cannot be used for shock treatment, H_2O_2 is used as the oxidant. However, H_2O_2 is a poor oxidizing agent for ammonium ion, urea and organic matter whose concentrations can increase with time and can result in development of PHMB-resistant bacteria (10). Excessive use of PHMB, algicide, and enzyme can cause foaming. PHMB and the quat-based algicide also can be removed by filter media, affecting filtration that necessitate peroiodic cleaning. Other problems with this system have been reported including off taste, staining, cloudiness, and biological growths (eg, slime mold and pink algae). This three-part system is not compatible with chlorine or bromine, copper-based algicides, persulfate oxidizers, or ozone.

Ozone. Ozone generators are based on uv or cd (so-called corona discharge; sometimes referred to as silent discharge). Although uv ozone generators are marketed, they are not effective for treating swimming pools because of the very low ozone concentrations produced (40–400 ppm in air) (11). Some cd ozonators producing marginally higher ozone concentrations also are not very effective. NSF certification requires that these uv and cd ozonators be used in connection with NSF certified feeders delivering 2 ppm chlorine and 4 ppm bromine (3).

By contrast with uv and very low output cd ozonators, cd ozone generators producing 1–2 wt % ozone in air can provide significant aqueous concentrations and are used extensively in Europe, primarily in large public or commercial pools (see OZONE). Although ozone is an effective biocide, it cannot be used as a primary disinfectant because of its instability, volatility, and toxicity. Thus, it is used primarily to provide supplemental oxidation of swimming pool contaminants. Ozone ($\sim$1 ppm) is added to the water in the external recycle loop, and after about a 2-min reaction time in a contactor, it is largely destroyed by filtration through granular activated carbon (11). Chlorine ($\sim$0.5 ppm) is then added to the water for disinfection. This system, which also employs flocculation, sand filtration, and a water purge, increases oxidation of bather contaminants by $\sim$20% compared to chlorination-flocculation-filtration. Due to the high capital costs, it can take as long as 8 years to break even.

By contrast with European standards, typical U.S. practice varies according to the type of installation (ie, new or retrofit) and can employ variations such as prefilter ozone injection combined with single mixed-media filtration and postfilter ozone injection and side stream ozonation (12). The use of partial flow side stream ozonation (typically 10–50%) will result in significantly lower contaminant removal than in European practice reducing cost effectiveness.

In smaller European public and semipublic pools, ozone is used in combination with NaBr to generate hypobromite ion, which hydrolyzes to hypobromous acid for disinfection ($O_3 + Br^- \longrightarrow BrO^- + O_2, BrO^- + H^+ \rightleftarrows HOBr$).

Ionizers. Ionizers generate small concentrations of copper ($\leq$0.3 ppm) and silver ($\leq$0.03 ppm) ions by electrochemical dissolution of a copper–silver electrode. They are not cost effective because they are expensive, require periodic replacement of expensive electrodes, have only a small effect on disinfection

(9,13), and chlorine sanitizers (preferably at NSPI recommended concentrations) are still necessary not only for effective disinfection but also for oxidation of swimming pool contaminants. In addition, since all of the copper and silver ions introduced into the water eventually precipitate forming colored insoluble matter, they can cause staining and discoloration. In bromine pools, the small silver concentration provided by ionizers is further reduced by precipitation of highly insoluble silver bromide.

Cartridges. Silver-containing ceramic cartridges (so-called candles) have been known since the 1930s. Their bactericidal effectiveness gradually decreased due to build up of organic slimes, necessitating periodic cleaning (14). Silver is a poor bactericide (15) because it is slow acting and was shown to be unsatisfactory for swimming pool disinfection (16).

Nevertheless, over the past decade, flow through cartridges containing chemically treated ceramic pellets have been marketed that introduce very small concentrations of copper and silver ($\sim$0.01–0.06 ppm) into the pool, much lower than ionizers. Flow through cartirdges delivering low concentrations of zinc and silver also have been marketed. The claim of contact disinfection, even if true, would only work when the pump was running. For example, in one minute the Cu-Ag cartridge treats only $\sim$0.3% of the water (at uncertain efficiency) while chlorine disinfects the entire pool. They are expensive, need cartridge element replacement every 6 months, and require a chlorine sanitizer (preferably at NSPI recommended concentrations) for effective disinfection and oxidation of swimming pool contaminants (9). Silver-based cartridges are not compatible with bromine sanitizers because of the insolubility of silver bromide.

Uv and uv-H_2O_2. The disadvantages of these systems are (*1*) uv provides little to no oxidation of pool contaminants; (*2*) bacteria are capable of repairing damage by uv light, reducing the inactivation rate; (*3*) both uv and uv-H_2O_2 do not supply a disinfectant residual in the pool, providing only localized disinfection whose rate is affected by turbidity and pool contaminants; and (*4*) although uv-H_2O_2 provides some localized oxidation of contaminants via transient hydroxyl radicals, H_2O_2 itself is a poor oxidant.

1.5. Sanitizer and Chemical Feeders. Feeders dispense chemicals in gaseous, liquid, and solid (both granular and compacted) forms. Many health departments require that public pools have approved feeding devices for the daily application of all chemicals, including sanitizers. A slurry feeder for diatomaceous earth (DE) on diatomite filter installations also may be required.

Gas Feeders. Chlorine gas is usually fed from a chlorine cylinder equipped with a pressure gauge, reducing valve, regulating valve, feed-rate indicator, and aspirator-type injector for dissolving the chlorine gas in water. The feeder can be manually, or more desirably automatically, controlled utilizing continuous amperometric or potentiometric measurement of the free chlorine residual. The chlorine solution is normally introduced into the return line to the filter.

Liquid Feeders. Liquid feeders employ positive-displacement metering pumps for adding aqueous solutions of sodium or calcium hypochlorite. The feed solutions are typically stored in polyethylene tanks of various capacities up to about 189 L (50 gal).

Solid Feeders. Feeders are available for feeding solid chemicals such as soda ash, diatomaceous earth, and sanitizers. Erosion-type feeders installed in the pool return line are commonly used for solid sanitizers in compacted form; typically tablets of calcium hypochlorite or trichloroisocyanuric acid. Off-line installation is used when it is impractical to install the feeder in the pool return line. Some feeders have an integral body with a chamber for holding tablets (17), whereas others employ a removable cartridge filled with tablets. The dissolving rate of the sanitizer is controlled by the depth of immersion of the tablets and varying the flow rate of water by means of a valve.

A feeder for $Ca(OCl)_2$ tablets or briquettes, used extensively in commercial pools, utilizes pulse feeding, ie, a slow water fill into the tablet dissolving chamber followed by a fairly rapid siphoning of the resultant concentrated solution into the pool return line. The feed rate is controlled by the depth of immersion of the tablets and the filling–draining frequency. Scaling is prevented by using an antiscalant (18).

Another type of feeding technique involves addition of tablets or sticks of sanitizing agent (calcium hypochlorite or trichloroisocyanuric acid) to the skimmer basket located in the filter return line. If bare calcium hypochlorite tablets are added to the skimmer, the filter pump must remain on until complete dissolution to avoid excessively high local concentrations of available chlorine which could cause corrosion. Partial encapsulation can significantly reduce or eliminate this problem. For example, slow dissolving cylindrical tablets of calcium hypochlorite ($\sim$200 g) for use in the skimmer are encased in a plastic wrap containing a small opening at either end for contact with water (19). Another skimmer device for continuous feeding of $Ca(OCl)_2$ uses tablets or briquettes in a plastic cylindrical container with a variable opening in the top.

A different type of feeder consists of a cartridge containing tablets or sticks, which is inserted to a variable depth into a hollow plastic flotation ring. Several units may be used which float freely around the pool continuously dispensing sanitizer. Feeders that dispense granular sanitizing agents such as calcium hypochlorite also are available.

pH Control Feeders. Feeders for controlling pH when using chlorine gas sanitation are typically based on pumping a solution of soda ash. Dry chemical feeders also can be used, eg, adding granular soda ash from a hopper by means of a reciprocating screw feeder to a solution chamber fed by pool water with the overflow mixing with the recirculating pool water. Liquid feeders for controlling pH when using hypochlorites typically pump muriatic acid. Gaseous carbon dioxide also can be used for pH adjustment.

1.6. Water Quality Maintenance. In addition to controlling algae and microorganisms such as bacteria, proper swimming pool maintenance requires control of free and combined available chlorine (FAC and CAC), pH, alkalinity, hardness, and saturation index. Recommended ranges for various swimming pool parameters are shown in Table 2 (20).

Disinfection. The bactericidal properties of chlorine (21), bromine (22), and ozone (21) have been reviewed. The biocidal properties of chlorine and bromine are due principally to the formation of hypochlorous and hypobromous acids which kill bacteria, algae, and other microorganisms. Chlorine is a more effective sanitizer than bromine on a ppm basis against bacterial spores (23), bacteria (22,24), and viruses (25). Disinfection with bromine is less sensitive to pH than with chlorine. Although, bromamines are better disinfectants than chloramines, they are less stable.

Disinfection with chlorine and bromine is primarily a function of the free available halogen concentration, the type of organism (ie, bacteria, viruses, protozoa, etc), contact time, pH, and temperature. In the case of chlorine, the cyanuric acid concentration exerts a significant effect on disinfection (see discussion under stabilizer). Dimethylhydantoin also can affect disinfection by bromine. In addition, turbidity, ammonia, and organic matter can adversely affect disinfection (26).

For a given organism at constant temperature, the rate of disinfection is expressed mathematically by the Chick-Watson law: $\log (N/N_0) = -kC^n t$, where N and N_0 are the concentrations of organism at times t and 0, k is a constant, C is the disinfectant concentration, and n is a constant (ca. -1 for disinfection of *Escherichia coli* by HOCl).

The constant k varies with temperature according to the following relationship: $\ln (k_2/k_1) = (-E/R)(1/T_1 - 1/T_2)$, where: k_1 and k_2 are the value of k at temperatures T_1 and T_2 (in kelvins), E is the activation energy ($\sim$31.4 kJ mol^{-1} for disinfection of *E. coli* by HOCl at pH 7.5), and the ideal gas constant $R = 1.987$ $J\,K^{-1}\,mol^{-1}$.

Halogens inactivate bacteria by diffusion of hypohalous acid through the cell membrane followed by disruption of cell metabolism (26). By contrast, ozone and quats such as PHMB inactivate bacteria by damaging the cell membrane but by different mechanisms, and metallic ions such as silver disrupt cellular enzymatic reactions by binding to sulfhydryl groups of cellular proteins (13). The effectiveness of metal ions varies in the following order: $Ag > Cu > Zn$ and correlates with the insolubility of the corresponding sulfides. The efficiency of disinfection is determined bacteriologically by the standard plate-count (SPC) technique and by examination for fecal coliform bacteria (27).

Maintenance Available Chlorine. Chlorine sanitizers are a source of available chlorine, which is a measure of the oxidizing power of the electropositive chlorine in a compound expressed in terms of elemental chlorine. In an unstabilized pool without combined available chlorine (CAC, ie, chloramines), the avialable chlorine is due to $HOCl + ClO^-$ and is called free (ie, FAC). However, in a cyanuric acid stabilized pool, $\sim$99% of the available chlorine is in the form of chloroisocyanurates. Although chloroisocyanurates analyze as FAC via DPD, they only represent potential FAC because they only form HOCl and ClO^- upon hydrolysis.

Because it is difficult to maintain a stable residual in unstabilized outdoor pools due to rapid photochemical decomposition ($\sim$90% in 3 h), virtually all such pools are stabilized with cyanuric acid. In stabilized pools, the recommended ideal free available chlorine concentration is 2–4 ppm (20). Unstabilized indoor pools can be effectively sanitized with $\sim$0.5 ppm free av Cl_2.

The free av Cl_2 can be maintained by the following: periodic broadcasting of granular sanitizers (typically calcium hypochlorite), manual or mechanical addition of liquid sodium hypochlorite or chlorine gas, or by means of tableted sanitizers (calcium hypochlorite or trichloroisocyanuric acid) placed in the skimmer, in floaters, or in-line or off-line feeders. FAC and CAC in swimming-pool water are determined colorimetrically by the Palin DPD test using *N*,*N*-diethyl-*p*-phenylenediamine (27).

Superchlorination–Shock Treatment. Superchlorination or shock treatment of pool water is necessary since organic matter, nitrogen compounds, and algae consume free available chlorine and can impede disinfection. Reaction of chlorine with constituents of urine or perspiration (primarily $NH_4{}^+$, amino acids, creatinine, uric acid, etc) produces chloramines (N–Cl compounds), which do not hydrolyze significantly to HOCl because they strongly bind chlorine (28), and therefore are poor disinfectants. For example, monochloramine (NH_2Cl) is only 1/280 as effective as HOCl against *E. coli* (29). By contrast with other nitrogenous compounds, urea the main bather contaminant, does not form significant amounts of combined chlorine (30), consequently, it does not affect disinfection (31). Nevertheless, it must be destroyed because it is a nutrient for bacteria and algae.

Ammonium ion is introduced into pool water by sweat and urine and by decomposition of chlorinated organo N compounds such as chloroamino acids. It reacts rapidly with chlorine forming monochloramine, which can persist in the absence of sunlight and sufficient free chlorine.

$$2\ NH_4^+ + 2\ HOCl \rightarrow 2\ NH_2Cl + 2\ H^+ + 2\ H_2O$$

The presence of sufficient free chlorine via normal maintenance dosing or during superchlorination or shock treatment results in formation of unstable dichloramine which decomposes to N_2 thereby causing a reduction in CAC (30,32). A small amount of nitrate ion also is formed.

$$\begin{array}{ll} & 2\ NH_2Cl + 2\ HOCl \rightarrow 2NHCl_2 + 2\ H_2O \rightarrow N_2 + HOCl + 3\ HCl + H_2O \\ \text{Overall}: & 2\ NH_4^+ + 3\ HOCl \rightarrow 2\ N_2 + 3\ HCl + 2\ H^+ + 3\ H_2O \end{array}$$

The above chemistry, known as breakpoint chlorination, is in reality much more complex and has been modeled by computer (33). Cyanuric acid does not interfere (34).

Urea (30,35), amino acids (36), and creatinine (37) also are decomposed during superchlorination or shock treatment forming transient ammonia chloramines. However, the process is slower than with ammonium ion (see N-HALAMINES). Decomposition of chloroisocyanurates by av Cl_2 also forms transient chloramines.

Ammonia chloramines (mono-, di-, and trichloramine) also are decomposed by sunlight, consequently they tend not to pose a significant problem in all but the most heavily used outdoor pools. Monochloramine decomposes as follows (38):

$$3\ NH_2Cl + 3h\nu \rightarrow N_2 + NH_4^+ + 2\ H^+ + 3\ Cl^-$$

Dichloramine and trichloramine are expected to be even less stable in sunlight because they are much stronger absorbers of uv light.

Superchlorination typically refers to adding FAC equal to 10 × ppm CAC, whereas shock treatment generally involves addition of 1 lb of 65% $Ca(OCl)_2$/10,000 gal (37,850 L) of water, which is equivalent to ~8 ppm FAC. The frequency of superchlorination or shock treatment depends on bather load and temperature. Calcium hypochlorite, because of its convenience, is widely used for superchlorination and shock treatment. Sodium hypochlorite, LiOCl, or chlorine gas also can be used. Chloroisocyanurates are not recommended since their use would result in excessive cyanuric acid concentrations.

pH Control. The optimal range for bather comfort and efficiency of disinfection of chlorine sanitizers is pH 7.2–7.8 where the biocidal agent HOCl represents 69–35% of FAC. This percentage increases at lower pH, but increased eye irritation and corrosion may occur. At higher pH, the HOCl fraction decreases (eg, to 26% at pH 8.0) and the ClO^- fraction correspondingly increases leading to greater photochemical decomposition and reduced rate of disinfection. Hypochlorite ion is only 1/80 as effective as HOCl against *E. coli* (26).

The pH of swimming pool water is largely a function of the following equilibria (39):

$$\begin{aligned}
&\mathrm{CO_2(aq) + H_2O \rightleftharpoons H_2CO_3} \qquad K^{25^\circ\mathrm{C}} = 1.54 \times 10^{-3}\\
&\mathrm{H_2CO_3 \rightleftharpoons H^+ + HCO_3^-} \qquad K^{25^\circ\mathrm{C}}_{\mathrm{H_2CO_3}} =\sim 2.9 \times 10^{-4} M\\
&\mathrm{H_2CO_3^* = CO_2(aq) + H_2CO_3}\\
&\mathrm{H_2CO_3^* \rightleftharpoons H^* + HCO_3^-} \qquad K_1^{25^\circ\mathrm{C}} = K_{\mathrm{H_2CO_3}}/(K+1) = 4.45 \times 10^{-7} M\\
&\mathrm{HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}} \qquad K_2^{25^\circ\mathrm{C}} = 4.69 \times 10^{-11} M
\end{aligned}$$

Where the K values are thermodynamic equilibrium constants at infinite dilution. The concentration of true carbonic acid (H_2CO_3) is negligible in comparison to dissolved carbon dioxide, eg, only 0.15% of the latter is hydrated to carbonic acid at 25°C. The hypothetical species $H_2CO_3{}^*$ is introduced because it is difficult to distinguish between CO_2(aq) and H_2CO_3 by acid–base titration. As shown above, the ionization constant K_1 is a composite constant representing both the CO_2 hydration reaction and ionization of true H_2CO_3. Temperature-dependent equations for K_1 and K_2 are (40):

$$\begin{aligned}
K_1 &= -356.3094 - 0.060920T + 21834.37T^{-1} - 1684915T^{-2} + 126.8339 \log T\\
K_2 &= -107.8871 - 0.032528T + 5151.79T^{-1} - 563713.9T^{-2} + 38.92561 \log T
\end{aligned}$$

where T is in kelvin.

The total concentration of species C_T (mol/L) is given by

$$C_\mathrm{T} = [\mathrm{H_2CO_3^*}] + [\mathrm{HCO_3^-}] + [\mathrm{CO_3^{2-}}]$$

The concentrations (mol/L) of individual species are represented by

$$[\mathrm{H_2CO_3^*}] = C_\mathrm{T}\alpha_0 \quad [\mathrm{HCO_3^-}] = C_\mathrm{T}\alpha_1 \quad [\mathrm{CO_3^{2-}}] = C_\mathrm{T}\alpha_2$$

where α_0, α_1, and α_2 are the ionization fractions, ie, the mol fraction of $[H_2CO_3{}^*]$, $[HCO_3{}^-]$, and $[CO_3{}^{2-}]$, respectively. The ionization fractions can be expressed in terms of the hydrogen ion concentration ($[H^+]=10-^{pH}/\gamma H+$ where $\gamma H+$ is the activity coefficient of hydrogen ion) and applicable equilibrium constants.

$$\alpha_0 = (1 + K_1^c/[H^+] + K_1^c K_2^c/[H^+]^2)^{-1}$$
$$\alpha_1 = \left([H^+]/K_1^c + 1 + K_2^c/[H^+]\right)^{-1}$$
$$\alpha_2 = ([H^+]/(K_1^c K_2^c) + [H^+]/K_2^c + 1)^{-1}$$

where $K_1{}^c$ and $K_2{}^c$ are concentration equilibrium constants and are given by: $K_1{}^c=K_1\gamma H_2CO_3^*/(\gamma H+\gamma HCO_3{}^-)$ and $K_2{}^c=K_2\gamma HCO_3{}^-/(\gamma H+\gamma CO_3{}^{2-})$. A plot of ionization fractions for $[H_2CO_3{}^*]$, $[HCO_3{}^-]$, and $[CO_3{}^{2-}]$ as a function of pH at 25°C is shown in Figure 2.

In stabilized pools, the following equilibrium also is important (41):

$$H_3Cy \rightleftharpoons H_2Cy^- + H^+ \qquad K^{25^\circ C}_{H_3Cy} = 1.32 \times 10^{-7} M$$

Although cyanuric acid is a tribasic acid, only the first ionization is important at normal swimming pool pHs. The concentration of cyanurate ion is given by $[H_2Cy^-] = C'_T\alpha'_1$, where Cy represents the tri-isocyanurate anion, C'_T is the total concentration of cyanuric acid and cyanurate ion and α'_1 is the mol fraction of cyanurate ion which is given by $\alpha'_1 = \left([H^+]/K_{H_3Cy} + 1\right)^{-1}$, where K_{H_3cy} is the first ionization constant of cyanuric acid whose temperature dependence is expressed by (42):

$$\log K_{H_3Cy} = -31.08 + 0.154T - 2.441 \times 10^{-4} T^2$$

where T is in kelvin. A plot of ionization fractions for the cyanuric acid system at 25°C is shown in Fig. 3.

Total alkalinity (Alk_T mol/L) is expressed by

$$Alk_T = [HCO_3^-] + 2[CO_3^{2-}] + [H_2Cy^-] + [OH^-] - [H^+] = C_T(\alpha_1 + 2\alpha_2) + C'_T\alpha'_1 + [OH^-] - [H^+]$$

Multiplication by 5×10^4 gives the total alkalinity in ppm calcium carbonate. At typical pool pH, the concentration of hydroxyl and hydrogen ions can be neglected. In addition to cyanurate, other alkaline substances (eg, borate) that may be present in significant concentrations in pool water also can contribute to total alkalinity (43). Alkalinity provides buffering, ie, resistance to pH change (44).

The buffer intensity (β) of pool water is a function of alkalinity and pH. It is proportional to the slope of the titration curve at a given point and is defined as the amount of acid or base required to change pH by one unit. For stabilized swimming pool water, β (meq/L/pH unit) is expressed numerically by

$$\beta = 2.3\{C_T[\alpha_1(\alpha_0 + \alpha_2) + 4\ \alpha_0\alpha_2] + C'_T\alpha'_0\alpha'_1 + [OH^-] + [H^+]\}$$

where α'_0 is the mol fraction of cyanuric acid. Alternatively, β can be defined as the change in alkalinity per pH unit, ie, $\beta = \Delta\text{Alk}/\Delta\text{pH}$. Multiplying β by 5×10^4 converts it to ppm alkalinity/pH unit. The buffer intensity decreases with increasing pH over the typical pH range (7.2–7.8) of pool water.

Although swimming pools are open to the atmosphere they are not in equilibrium with atmospheric carbon dioxide (45). Because of periodic acid addition for pH adjustment, swimming pools are maintained in a supersaturated state with respect to dissolved carbon dioxide. Thus, swimming pools continuously evolve carbon dioxide causing the pH to increase with time, the rate increasing with increasing carbonate alkalinity, turnover rate (R_t), surface-to-volume ratio (R_{sv}), and temperature (T is in kelvin) (46), but decreasing with increasing cyanuric acid concentration for given values of the other variables. The rate constant for CO_2 loss is given by:

$$k = k'AB \exp\,(-2,516.4/T)\ (\text{ppm day})^{-1}$$

where $k' = 0.0341 + 0.009R_t + 0.016R_t^{\,2}$ is the rate constant for a given value of R_t at 27.8°C (82°F) and $R_{sv} = 0.28$ (R_{sv} is the reciprocal of the average pool depth), $A = (R_{sv}/0.28)$ is the correction for different surface-to-volume ratios, and $B = 4296.4$ is the preexponential factor. A computer program has been used to calculate CO_2 loss rates under different pool conditions.

The upward pH drift is modified according to the acidity or basicity of the sanitizer. Hypochlorites raise pH to a small extent, whereas acidic sanitizers lower it (7). The weekly pH changes (at pH 7.5, 100 ppm CA, 100 ppm carbonate alkalinity, and 1000 ppm TDS) due to recommended maintenance doses are: Cl_2 −0.22, Trichlor −0.14, Dichlor −0.09, NaOCl +0.02, and $Ca(OCl)_2$ +0.01 (7). The actual pH changes will depend on actual sanitizer usage. A weekly shock treatment dose will raise pH by 0.02. These are the pH changes that result after decomposition of the added av Cl_2. In the case of chlorine gas, or in cases of heavy Trichlor usage, the effect of CO_2 loss can be completely offset causing the pH to drift downward.

The pH is measured colorimetrically with phenol red indicator. High FAC causes lower pH readings due to bleaching of the indicator and resultant HCl formation. The pH of pool water is readily controlled with inexpensive chemicals. Hydrochloric or sulfuric acids or sodium bisulfate lower it, whereas sodium carbonate raises it. Since acid addition neutralizes a portion of the alkalinity, this must be replenished if the alkalinity drops below the minimum. By contrast, pH adjustment with carbon dioxide does not affect alkalinity. Tables and equations for determining chemical additions for adjusting pH, alkalinity, hardness, and cyanuric acid are given in Ref. 47.

Alkalinity. In swimming-pool water at its normal pH range, the so-called carbonate alkalinity is due primarily to bicarbonate with a very small contribution from carbonate. Alkalinity is expressed in terms of ppm of equivalent $CaCO_3$. Because of its buffering intensity, alkalinity resists changes in pH when sanitizing chemicals are added to pool water. Since cyanuric acid is largely neutralized at pool pH, cyanurate ion also contributes to alkalinity. Consequently, in stabilized pools the alkalinity determination is corrected for ~0.33 × ppm cyanuric acid in the normal pH range (7.2–7.8) (43).

Sodium bicarbonate ($NaHCO_3$) is generally added to increase alkalinity and muriatic acid (HCl), sulfuric acid (H_2SO_4), or sodium bisulfate ($NaHSO_4$) to reduce it. In general, with acidic sanitizers such as chlorine gas or trichloroisocyanuric acid, ideal total alkalinity should be in the 100–120 ppm range, whereas, with alkaline products such as calcium, lithium, or sodium hypochlorite, a lower ideal total alkalinity of 80–100 ppm is recommended (20).

Alkalinity is determined by titration with standard sulfuric acid using a mixed bromcresol green–methyl red indicator after dechlorination of the sample with thiosulfate. Dechlorination with thiosulfate causes higher readings due to formation of hydroxyl ion (43):

$$\mathrm{HOCl} + 2\ \mathrm{S_2O_3^{2-}} \rightarrow \mathrm{Cl^-} + \mathrm{S_4O_6^{2-}} + \mathrm{HO^-}$$

$$\mathrm{ClO^-} + 2\ \mathrm{S_2O_3^{2-}} \rightarrow \mathrm{Cl^-} + \mathrm{S_4O_6^{2-}} + 2\ \mathrm{HO^-}$$

The error is approximately equal to the FAC at pH 7.2–7.8. However, it is significant only at high FAC, eg, during superchlorination or shock treatment.

Hardness. Water hardness is caused by certain polyvalent metals and is expressed in terms of ppm of equivalent $CaCO_3$. In swimming pool water, hardness is caused primarily by calcium ions and to a lesser extent magnesium ions. To ensure proper water balance calcium hardness should be at or near the $CaCO_3$ saturation value. At 25°C, pH 7.5, 1000 ppm total dissolved solids, 100 ppm total alkalinity, 50 ppm cyanuric acid, the calculated saturation Ca hardness is ~301 ppm, which is within the NSPI recommended ideal range of 200–400. Values at other pool conditions can be calculated using the saturation index formula. Calcium hardness is determined by titration with ethylenediaminetetraacetic acid (EDTA) at pH 12–13 using Eriochrome Blue Black R, Eriochrome Black T, calmagite, hydroxynaphthol blue, or other suitable indicator. Hardness is raised with $CaCl_2$ and is lowered by draining some of the pool water and adding water of lower hardness.

Saturation Index. Materials of construction used in pools are subject to the corrosive effects of water, eg, iron and copper equipment can corrode whereas concrete and plaster can undergo dissolution, ie, etching. The corrosion rate of metallic surfaces has been shown to be a function of the concentrations of Cl^-, SO_4^{2-}, dissolved O_2, alkalinity, and Ca hardness as well as buffer intensity, time, and the calcium carbonate saturation index (48). Deposition of a protective layer of crystalline $CaCO_3$ has been proposed for protection of metallic surfaces against corrosion by using the natural calcium and alkalinity in water (49).

A significant concern in swimming pools is prevention of etching or scaling (ie, precipitation of $CaCO_3$), which can be controlled by maintenance of a proper degree of saturation with respect to calcium carbonate. The calcium carbonate dissolution–precipitation equilibrium (where the γ terms are activity coefficients) is represented by

$$\mathrm{CaCO_3(s)} \rightleftharpoons \mathrm{Ca^{2+}} + \mathrm{CO_3^{2-}} \qquad [\mathrm{Ca^{2+}}]\gamma_{\mathrm{Ca^{2+}}}[\mathrm{CO_3^{2-}}]\gamma_{\mathrm{CO_3^{2-}}} = K_\mathrm{s}$$

$$\mathrm{CO_3^{2-}} + \mathrm{H^+} \rightleftharpoons \mathrm{HCO_3^-} \qquad [\mathrm{HCO_3^-}]\gamma_{\mathrm{HCO_3^-}}/([\mathrm{CO_3^{2-}}]\gamma_{\mathrm{CO_3^{2-}}}[\mathrm{H^+}]\gamma_{\mathrm{H^+}}) = 1/K_2$$

$$\text{Overall}: \qquad \mathrm{CaCO_3(s)} + \mathrm{H^+} \rightarrow \mathrm{Ca^{2+}} + \mathrm{HCO_3^-}$$

$$[\mathrm{Ca^{2+}}]\gamma_{\mathrm{Ca^{2+}}}[\mathrm{HCO_3^-}]\gamma_{\mathrm{HCO_3^-}}/([\mathrm{H^+}]\gamma_{\mathrm{H^+}}) = K_s/K_2$$

The temperature dependent equation for the solubility product constant K_s is (40):

$$\mathrm{Log}\ K_\mathrm{s} = -171.9065 - 0.077993T + 2839.319T^{-1} + 71.595\ \log\ T$$

where T is the temperature in kelvin. The tendency of a water to precipitate or dissolve calcium carbonate can be determined by the calcium carbonate saturation index (*SI*).

The *SI* is the common logarithm of the degree of $\mathrm{CaCO_3}$ saturation, ie, $[\mathrm{Ca^{2+}}]\gamma_{\mathrm{Ca^{2+}}}[\mathrm{CO_3^{2-}}]\gamma_{\mathrm{CO_3^{2+}}}/K_\mathrm{S} = [\mathrm{Ca^{2+}}]\gamma_{\mathrm{Ca^{2+}}}[\mathrm{HCO_3^-}]\gamma_{\mathrm{HCO_3^-}}K_2/([\mathrm{H^+}]\gamma_{\mathrm{H^+}}K_\mathrm{S})$, where the terms in brackets represent molar concentrations. The original version of the saturation index (49) has been updated for more recent data on K_s and revised by substitution of [*Hard*] (calcium hardness) and [*Alk*] (alkalinity) in ppm $\mathrm{CaCO_3}$, for $[\mathrm{Ca^{2+}}]$ and $[\mathrm{HCO_3}^-]$, respectively, resulting in the following equation (50):

$$SI = \mathrm{pH} + \log\ [Alk] + \log\ [Hard] + TC + C$$

Where: $\mathrm{TC} = 0.0155T_\mathrm{c}$ is a temperature correction term that adjusts log (K_2/K_s) from its value at 0°C (−2.25) to higher temperatures T_c (°C); $C = A + B - 9.7$; $A = \log\ (K_2/K_\mathrm{s})$; $B = \log \gamma_{\mathrm{HCO_3^-}} + \log \gamma_{\mathrm{Ca^{2+}}}$, $\gamma_{\mathrm{HCO_3^-}}$ and $\gamma_{\mathrm{Ca^{2+}}}$ are the activity coefficients of bicarbonate and calcium ions; and 9.7 is a logarithmic factor that converts units of hardness and alkalinity from mol/L to ppm.

Activity coeficients are calculated using the Davies approximation, $\log \gamma = -0.5z^2[\sqrt{\mu}/(1 + \sqrt{\mu}) - 0.3\mu]$ where z is the ionic charge and μ is the ionic strength. The ionic strength can be calculated by $\mu = 0.5\Sigma c_i z_i^2 = 2.5 \times 10^{-5} \times TDS = 1.6 \times 10^{-5} \times \kappa$, where c_i is the concentration of an individual ion and z_i its ionic charge, *TDS* is ppm total dissolved solids, and κ is the conductivity in micro Siemens/cm. At 1000 ppm *TDS*, $C = 12.29$.

SI also is equal to $\mathrm{pH}_a - \mathrm{pH}_s$, where pH_a is the actual or measured pH, and pH_s is the pH that the water should have to be at $\mathrm{CaCO_3}$ saturation (ie, water that does not deposit or dissolve $\mathrm{CaCO_3}$), ie, $\mathrm{pH}_s = \mathrm{pH}_a - SI$. Ion pair formation typically has a small effect on *SI* (51).

The saturation index is rooted in thermodynamics (52). It is a scaling index and not a corrosion index. The numerical value of *SI* for a given water determines its departure from equilibrium, ie, >0 = oversaturated, 0 = saturated, and <0 = undersaturated. The higher the positive value of the index ($SI > 0$), the greater the tendency for $\mathrm{CaCO_3}$ precipitation or scaling and the lower the negative value ($SI < 0$), the greater the tendency for etching. Water with a sufficiently negative index will not only etch concrete, plaster, and tile grout but it also can dissolve an existing protective film of $CaCO_3$.

Clear water with moderate to high positive values of *SI* does not undergo spontaneous homogeneous precipitation because the nucleation rate is too low (53). However, precipitation can occur in the presence of a sufficient concentration of suspended solids (ie, turbidity). The more these suspended solids resemble calcium carbonate in crystal structure the more likely precipitation will occur. Precipitation results in a decrease in pH, calcium hardness, and carbonate alkalinity.

$$Ca^{2+} + 2\ HCO_3^- \rightarrow CaCO_3(s) + H_2CO_3$$

When $CaCO_3$ precipitation occurs, the extent and rate is a function of the saturation index, the presence of impurities, turbidity, and the buffer intensity (54) which in turn depends on the alkalinity and pH of the water. Impurities such as Mg ions, polyphosphates (present in some source waters), and naturally occurring organic matter can inhibit precipitation of calcium carbonate.

Scale that forms at the water line is due primarily to evaporation of water. Heterogeneous precipitation (ie, scaling) may occur on some rough pool surfaces. Elevated temperature in pool heaters may cause precipitation because the solubility of $CaCO_3$ decreases with increasing temperature. Excessive scaling can lead to flow restriction and reduced heat transfer.

To avoid problems such as etching or scaling, pool water should have a zero to slightly positive saturation index. A practical operating range is 0–0.5, which corresponds to 100 to ~300% of saturation. Water can be brought to a state of approximate equilibrium (balance) by suitable adjustments in pH, alkalinity, and hardness. However, the *SI* will drift, primarily because the pH changes due to CO_2 loss and addition of sanitizer (7). An upward drift typically occurs when hypochlorites or a combination of hypochlorites and chloroisocyanurates are used for pool sanitation. By contrast, a downward drift occurs with chlorine gas or in cases of high Trichlor usage.

A practical approach is to adjust the *SI* to the midpoint of the recommended range and to monitor the pH to establish the actual drift pattern. In order to maintain proper water balance for a maximum percent of the time, the *SI* should be adjusted to the beginning of the normal drift range. Many swimming pool chemical dealers and some pool service companies have computer programs for calculating necessary water balance adjustments. When a pool is winterized, the saturation index must be adjusted for the lower anticipated temperatures.

1.7. Ancillary Chemicals. In addition to sanitizers, various ancillary chemicals are employed in swimming pools for control of algae, oxidation, stabilizing chlorine sanitizers, water balance, scale and stain prevention, water clarification, filter degreasing, and cleaning of pool surfaces. Compatibility with chlorine must be considered in selecting ancillary chemicals since many of these additives are organic materials which have chlorine demands and therefore may interfere with pool disinfection. For example, quats and chelating agents such as citrate and phosphonate are oxidized by chlorine sanitizers, the oxidation being accelerated by sunlight.

Algicides. Algal growth in pools is unsightly, a potential safety hazard to swimmers, and usually a result of poor pool maintenance. It can cause slipperiness, development of odors, cloudy and discolored water, chloramine formation, increased chlorine demand, bacterial growth, and stubborn stains. Low FAC, high temperatures, sunlight, and certain mineral nutrients (eg, nitrate and phosphate) promote algae growth. Such growth can be prevented by avoiding excessive cyanuric acid concentrations and maintaining the pH and free available chlorine in the recommended ranges supplemented by periodic shock treatment. In hot weather, the av Cl_2 concentration should maintained at the higher end of the recommended range and the pool shock treated on a weekly basis.

The three forms of algae commonly found in swimming pools are the fast-growing green algae, slow-growing blue-green algae (sometimes called black algae), and mustard or yellow algae. Green algae are relatively easy to control because they remain suspended in the water. By contrast, mustard and especially black algae are more resistant to treatment because they grow on the pool surfaces where they become firmly attached to plaster or tile grouting and can penetrate cracks. As with bacteria, studies have shown that algae (particularly mustard algae) are more difficult to control in stabilized pools.

The longer an algae infestation remains untreated the more difficult it will be to eradicate it. If algae become entrenched, shock treatment of the water with a hypochlorite (repeated as necessary) in conjunction with mechanical treatment (ie, brushing) removes most algae. Patches of algae on plaster pool walls can be treated by Trichlor tablets contained in a porous bag suspended in the affected area, whereas, algae on the pool bottom of plaster pools can be treated with granular Trichlor. An ammonium sulfate-containing product marketed for treating algae problems is based on *in situ* formation of monochloramine. Another product for treating algae contains sodium bromide and is not recommended because it will cancel the stabilization of chlorine.

Algicides other than chlorine (or bromine) are used, principally in the hotter southern and western regions of the United States. They serve as a backup to chlorine primarily as a preventive or corrective measure against unbalanced pool conditions. The most widely used algicides are the quaternary ammonium compounds (quats), of which the *n*-alkyldimethylbenzylammonium chloride type (with C_{12}–C_{16} alkyl groups) are the most common (see QUATERNARY AMMONIUM COMPOUNDS). Formulation with other algicides improves their effectiveness, eg, *n*-alkyl-dimethyldichlorobenzylammonium chloride and copper bis[2,2′,2″-nitrilotris(ethanol)-*N*,*O*,*O*′](copper triethanolamine complex) (55). Quats are absorbed on filter media (56) and consequently require high initial doses and frequent replenishments. The quats are surfactants and therefore can cause foaming at sufficiently high concentrations. A polymeric quaternary, poly(oxyethylene(dimethylimino)ethylene(dimethylimino)ethylene dichloride), also is employed and is nonfoaming at use concentrations.

Other algicides used to a smaller extent contain copper compounds (eg, copper sulfate, citrate, and gluconate) and silver compounds (eg, Ag_2O, $AgNO_3$, or colloidal silver). A blended sanitizer-algicide product contains Dichlor and copper sulfate. The $La_2(CO_3)_3$ compound (57) does not directly attack algae, but reportedly inhibits their growth by removing phosphate which is a necessary nutrient. Zinc compounds also can be used as algicides. For example, a blended product containing zinc sulfate and calcium hypochlorite has been patented (58). However, higher concentrations of zinc are necessary because it is less effective on a ppm basis than copper. The use of Simazine, 2-chloro-4,6-bis(ethylamino)-*s*-triazine, has been discontinued since the EPA has removed its registration because of toxicity concerns.

The effectiveness of various chemicals against algae has been evaluated in numerous studies under laboratory conditions (59–62). The concentrations necessary to kill algae (algicidal doses) are generally appreciably higher than those required to prevent or control the growth of algae (algistatic doses) and vary from specie to specie. Some algicides have chlorine demands which must be taken into account in maintaining the proper FAC (63).

Nonchlorine Oxidizers. Potassium peroxymonosulfate (monopersulfate) is used as an auxiliary oxidant for shock treatment. Disadvantages of peroxymonosulfate are it oxidizes urea and chloramines to nitrate ion (which is a nutrient for algae), it is not very stable (hourly loss rates in sunlight and at spa temperature are ~23 and 20%, respectively), it lowers pH and alkalinity, and is expensive. In addition, the recommended shock dose of 1 lb (2.2 kg)/10,000 gal (37,850 L) provides only 1/3 of the oxidizing capacity of 1 lb (2.2 kg) of 65% calcium hypochlorite.

By contrast to potassium peroxymonosulfate, potassium or sodium peroxydisulafates (persulfates) are less reactive but much more stable with a daily loss rate in sunlight of ~5%. Photochemical or redox (eg, via Cu^{2+} and Ag^{+}) decomposition forms reactive sulfate ion radicals which can oxidize organic matter (64). However, the efficiency under swimming pool conditions has not been determined. Decomposition produces bisulfate ion which lowers alkalinity. Mixtures of sodium peroxydisulfate and calcium hypochlorite can be used for routine maintenance and shock treatment (65). A blended granular product containing potassium persulfate and copper sulfate as well as other ingredients is marketed for pools. However, the oxidative and disinfecting performance of this system is questionable, because the oxidative efficiency of persulfate is uncertain and the system lacks an effective bactericide.

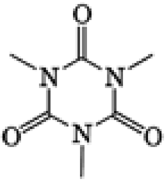
Stabilizer. Unstabilized chlorine is ~90% decomposed by sunlight in ~3 h (34). The half-life of aqueous chlorine ($HOCl/ClO^-$) depends primarily on the wavelength of light and pH. At wavelengths present in sunlight at the earth's surface (≥290 nm), ClO^- absorbs uv light much more strongly than HOCl, thus, the half-life of aqueous chlorine decreases with increasing pH due to the increasing $ClO^-/HOCl$ ratio. At ppm concentrations at the surface of the water, values of $t_{0.5}$ calculated from first-order rate constants are 57, 37, and 12 min at pH 6, 7, and 8, respectively.

Cyanuric acid is used to stabilize available chlorine derived from chlorine gas, hypochlorites, or chloroisocyanurates against decomposition by sunlight (66). Cyanuric acid and its chlorinated derivatives form a complex ionic and hydrolytic equilibrium system consisting of 10 isocyanurate species. The 12 isocyanurate equilibrium constants have been determined by potentiometric and spectrophotometric techniques (41). Other measurements of two of the equilibrium constants important in swimming pool water report significantly different and/or less precise results than the above study (67–69). A critical review of these measurements is given in Ref. 70.

A computer program allows calculation of the concentrations of HOCl, ClO^-, and all 10 isocyanurate species. A plot of species distribution for the cyanuric acid-available chlorine system at 25°C is shown in Fig. . In the presence of excess cyanuric acid, the predominant chlorinated specie is monochloroisocyanurate ion, $HClCy^-$, where Cy represents the triisocyanurate anion. Therefore, the only significant equilibria in pool water are

$$H_3Cy \rightleftharpoons H^+ + H_2Cy^-$$
$$HOCl \rightleftharpoons H^+ + ClO^-$$
$$H_2Cy^- + HOCl \rightleftharpoons ClHCy^- + H_2O$$

where Cy =



At 25°C, pH 7.5, 1.5 ppm FAC, and 25 ppm cyanuric acid, the calculated HOCl concentration is only 0.034 ppm. Although the monochloroisocyanurate ion hydrolyzes to only a small extent, it serves as a reservoir of HOCl because of rapid hydrolysis. Indeed, this reaction is so fast that $HClCy^-$ behaves like FAC in all wet methods of analysis. Furthermore, since $HClCy^-$ absorbs uv only <250 nm, which is filtered out of solar radiation by the earth's atmosphere, it is more resistant to decomposition than the photoactive ClO^-, which absorbs sunlight at 250–350 nm and represents the principal mode of chlorine loss in unstabilized pools (41). As little as 5 ppm of bromide ion prevents stabilization of FAC by cyanuric acid (34) (see CYANURIC AND ISOCYANURIC ACIDS).

The primary loss of av Cl_2 in a stabilized pool is oxidation of cyanuric acid by hypochlorite:

$$2\ H_3Cy + 9\ ClO^- \rightarrow 3\ N_2 + 6\ CO_2 + 9\ Cl^- + 3\ H_2O$$

The above reaction produces transient chloramines via the intermediate reaction: $2\ H_3Cy + 12\ ClO^- + 6\ H_2O \rightarrow 6\ NHCl_2 + 6\ CO_2 + 12\ HO^-$. The dichloramine decomposes by the breakpoint reaction: $6\ NHCl_2 + 12\ HO^- \rightarrow 3\ N_2 + 9\ Cl^- + 3\ ClO^- + 3\ H_2O$. Typical loss at a water temperature of 80–85°C is ~11%/day (71). By contrast, photochemical decomposition is very low averaging about 1–2%/day and is consistant with the fact that ~99% of the av Cl_2 is present in the form of chloroisocyanurates.

The concentration of HOCl in the normal pH range varies inversely with the total concentration of cyanurate. Increased concentration of cyanuric acid, therefore, should decrease the biocidal effectiveness of FAC. This has been confirmed by laboratory studies in buffered distilled water which showed 99% kill times of *S. faecalis* at 20°C increasing linearly with increasing cyanuric acid concentration at constant av Cl_2 at pH 7 and 9 (72). Other studies in distilled water have found a similar effect of cyanuric acid on kill times of bacteria (73–75).

Computer calculations based on the data from Ref. 72 show that the kill times are highly correlated to the HOCl concentration and poorly to the concentration of the various chloroisocyanurates, indicating that HOCl is the active bactericide in stabilized pools (76). Furthermore, analysis of the data showed that the time (min) for 99% inactivation of *S. faecalis* at pH 7.5 and 85°F was directly proportional to the ratio of ppm total cyanurate to ppm free av Cl_2 (Cy_T/Cl_T) via the following realtionship:

$$t_{0.99}(\mathrm{min}) = 0.015[\mathrm{Cy_T}/\mathrm{Cl_T}]$$

For example, at 100 ppm cyanuric acid and 3 ppm FAC, the calculated time for 99% inactivation is 0.5 min.

By contrast to distilled water, studies in swimming pool water showed greater kill times, even in the absence of cyanuric acid (74). This was attributed to unknown variables. However, since combined chlorine was not controlled, this is in reality due to swimming pool contaminants consisting primarily of nitrogenous compounds such as ammonium ion, amino acids, and creatinine. These bather introduced contaminants can react with free av Cl_2 forming bactericidally ineffective combined chlorine, resulting in increased kill times. For example, studies have shown that addition of ammonia greatly increases the kill time of *S. faecalis* by chlorine whether cyanuric acid is present or not (75). By contrast urea, a principal pool contaminant, had no effect. Although urea is a potential source of ammonia, its hydrolysis is very slow under swimming pool conditions. However, since urea is a nutrient for bacteria and algae, it is necessary to oxidize it by periodic shock treatment.

The ideal recommended cyanuric acid concentration is 30–50 ppm (Table 2). Although this range can be readily maintained when using hypochlorite sanitizers, it cannot be maintained when using chloroisocyanurates since they increase the cyanuric acid concentration (77). The National Spa and Pool Institute (NSPI) recommends a maximum of 150 ppm cyanuric acid. Many health departments limit cyanuric acid to 100 ppm. No significant increase in stabilization occurs beyond 50–100 ppm, and since high levels of cyanuric acid slow down the rate of disinfection, it's concentration should be limited. This can be accomplished by frequent back washing or if necessary partial draining of the pool and refilling with fresh water. Cyanuric acid is determined turbidimetrically after precipitation as melamine cyanurate.

Water Balance Chemicals. Water balance chemicals include muriatic acid, sulfuric acid, sodium bisulfate, and soda ash for pH control, sodium bicarbonate for alkalinity adjustment, and calcium chloride for hardness adjustment. A recent development is use of buffering agents for pH control. One of these products, sodium tetraborate, hydrolyzes to boric acid and a small amount of orthoborate (78) which provides significantly less buffering than carbonate and cyanurate alkalinity in the recommended pool pH range of 7.2–7.8 even at 100 ppm (44).

Scale and Stain Controllers. Polyacrylates (low molecular weight) and organic phosphonates, eg, (1-hydroxyethylidene)diphosphonic acid, prevent or control precipitation of $CaCO_3$ by acting as chelating agents (qv) or dispersants (qv) to prevent excessive formation of hard scale by promoting crystal distortion.

Clarifiers. Pool water may occasionally contain metallic impurities such as copper, iron, or manganese, which enter the pool with the makeup water or by corrosion of metallic parts in the circulation system. These dissolved metals can discolor the water and cause stains. Chlorine oxidizes soluble Fe^{2+} and Mn^{2+} to the highly insoluble $Fe(OH)_3$ and MnO_2, which can be removed by filtration. Water-soluble, high molecular weight polymers can be used as coagulating agents for removal of precipitated trace metals or other undesirable turbidity. These polymers also can serve as flocculating agents (qv) to increase the settling rate or strength of a chemical floc, thereby acting as a filter aid to control the depth of floc penetration (79). The polymers may be anionic, cationic, or nonionic, eg, polyacrylates, poly(styrene sulfonate), poly(diallyldimethylammonium chloride), poly(ethylene oxide), etc (80). Inorganic compounds such as aluminum sulfate and polyaluminum chloride are sometimes also used as flocculating agents for clarification or improving filtration.

Filter Cleaners. Grease and oils from bathers can affect filtration. Degreasers are employed to clean DE and sand filters. They can be surfactant or enzyme based.

Tile and Vinyl Cleaners. Cleaners (typically acid based) are employed to remove the ring of scale that forms at the water line on tile and vinyl lined pools.

1.8. Test Kits. Proper pool management requires routine analysis for free and combined chlorine and pH, and less frequently, alkalinity, hardness, and cyanuric acid. These analyses can conveniently be carried out at poolside with solution based test kits that are available at moderate cost. Test kits employing the DPD–FAS method for chlorine are more accurate than kits based on visual color comparison. Test strips for chlorine, pH, alkalinity, and cyanuric acid determinations also are available but are not as accurate as tests employing solutions.

Digital titrators are available for alkalinity and hardness that read directly in ppm. More elaborate kits employing photometers for analysis based on color intensity measurement and turbidity and meters for pH measurement are more accurate but more expensive. Other analyses such as total dissolved solids, total N, anions (NO_3^-, ClO_3^-, BrO_3^-, etc), and trace metals (Fe, Cu, Mn, etc) can be carried out as needed by analytical laboratories. Some swimming pool chemical supply stores also may perform some of these analyses.

Bacteriological analysis of pool water can be obtained through local health departments or commercial laboratories. Kits also are available for determining bacteria levels. Detailed procedures for chemical, bacteriological, and biological analysis of water are available (27).

1.9. Filtration. Efficient filtration for removal of suspended particles is essential for sparkling pool water. Filters may be of the fixed-bed, precoat, or cartridge type and operate under vacuum or pressure. The most common filter media are sand, anthracite, DE, and paper or cloth cartridges. The cartridges remove particles as small as 15 μm, sand to 25 μm, and DE to 3 μm (81). Since the visual limit is 30–35 μm, most properly operating filters do a satisfactory job. Flocculents for retention of surface dirt on sand filters are not recommended (2).

Sand filters are backwashed, whereas cartridge filters are cleaned manually by rinsing in water. Backwashing removes accumulated insoluble matter which would eventually increase resistance to flow and reduce filtration rates.

Diatomaceous earth filters require a precoat of DE after each filter cycle (see DIATOMITE). Use of compressed air (bumping) to dislodge the DE followed by recoating the filter with the dislodged DE reduces water usage and allows longer filter cycles. The DE is sometimes mixed continuously with unfiltered water before entering the filter.

The pump serves not only to circulate pool water through the filter and chlorinator but also to mix the pool water, thereby diluting and dispersing sanitizers and other additives whether added manually or through feeders. Typically, pumps are sized to achieve one pool water turnover in ~6 h.

Many pools have automatic systems for removing dirt from the pool bottom involving water jets that suspend the dirt for removal via the filter. Vacuum cleaners, which derive their suction from the filter pump, are used to remove solids from the walls and bottom of the pool. Some automatic pool cleaners moving around the bottom of the pool are efficient enough to eliminate the need for hand vacuuming.

2. Spas and Hot Tubs

The basic principles of swimming pool water treatment also apply to spas and hot tubs. However, spas and tubs are not miniature swimming pools but are unique in treatment requirements because of use patterns and a high ratio of bather to water. For example, four people in a 1.9-m^3 (500-gal) spa or tub have a sanitizer demand equal to 160 people in a 75.7-m^3 (20,000-gal) swimming pool.

2.1. Construction.

Spas are manufactured in various shapes and sizes and are generally constructed of molded fiberglass/resin or fiberglass/acrylic. Larger in-ground spas are typically made of gunnite or concrete with a marbelite plaster finish. An average spa has a depth of 0.74 m, a diameter of 2.13 m, and a water capacity of 2.08 m^3 (550 gal). Typical hot tubs are circular, 1.52–1.83 m in diameter with a 1.22 m depth and are constructed of redwood, oak, pine, cedar, cypress, teak, or mahogany. Wooden spa tubs are lined with vinyl or acrylic. The hot-water support systems of spas and hot tubs are basically the same, consisting of a pump, filter, heating system, and air blower. Pumps are sized to achieve one water turnover in ~30 min. Available filter systems include high rate sand, diatomaceous earth, and cartridge types. The heated water is violently mixed by an integrated forced-air system and venturi-type jets. The heating systems can be electric or gas.

2.2. Sanitizers.

Spa and hot-tub sanitation is dominated by chlorine- and bromine-based disinfectants. Public spas usually employ automatic feeders or generating devices to maintain a disinfectant residual. Private or residential spas also can use automatic chemical feeding or generating devices, or they can be sanitized manually with a granular or a liquid product (ie, sodium hypochlorite). The most widely used products for residential spa and tub sanitation are sodium dichloroisocyanurate and bromochlorodimethylhydantoin. Granular products are normally added before and after use, whereas solids, eg, bromine tablets, are placed in floaters, skimmers, or feeders. Bromine generating systems also can be used and are based on chemical or electrochemical oxidation of added bromide ions as discussed earlier. Copper–silver and zinc–silver cartidges are used to a small extent.

2.3. Water Quality Maintenance. The NSPI recommends an ideal residual of 3–5 ppm FAC for chlorine sanitizers with CAC not exceeding 0.5 ppm; see Table 2 (20). For bromine sanitizers, the maintenance of a 4–6 ppm ideal residual is recommended.

Spa studies have shown that the rate of FAC loss was simply a linear function of the number of bathers during use periods; cyanuric acid stabilization did not affect the loss of chlorine. However, the use of chloroisocyanurates for both sanitation and shock treatment caused a buildup of cyanuric acid to above the 150 ppm NSPI limit within 15 user periods (ie, four bathers with 15 min of exposure at 40°C), necessitating frequent changing of the water. Furthermore, these studies showed combined chlorine levels to range from 0.8 to 1.6 ppm after a four-bather exposure exceeding the NSPI limit of 0.2 ppm CAC. Shock treatment with ten times the CAC content after each user period was found satisfactory in reducing these CAC levels to ≤ 0.2 ppm. Based on these studies, it was concluded that a spa or tub should have a 4–5 ppm FAC before bather entry and maintaining the FAC in the recommended range while the spa or tub is in use (82). The spa or tub water should be shock treated after each use.

In addition to replacing spa or tub water because of cyanuric acid build-up from chloroisocyanurate sanitizers, the NSPI recommends that the water be replaced at least monthly or more frequently when often used because bathers contribute microorganisms, perspiration, body oils, lotions, etc, which affect water chemistry, total dissolved-solids concentration, water surface tension (resulting in foaming), and sanitizer demand. High bather density causes these compounds to accumulate to relatively high concentrations compared to a swimming pool that has a lower bather/water ratio. The guideline for replacing spa/hot tub water is based on the formula: $n = 88V/b$, where n is the number of days before replacement, V is the volume in m^3, and b is the number of bathers/day (3).

In wooden tubs, the maintenance of a sanitizer residual becomes complicated due to the leaching of tannins and other organic matter from the wood into the water. The sanitizer demand of these substances must be overcome in order to maintain proper residual concentrations. As the tub ages, the leaching of these materials decreases, but bleaching of the wood may occur as the lignin (qv) in the wood reacts with sanitizers.

pH control in spas and hot tubs is complicated because the violent turbulence and aeration that removes CO_2 from the water causing the pH to increase. The CO_2 loss rate also increases with temperature and carbonate alkalinity. The buffering intensity of cyanuric acid reduces the rate of pH rise. Maintaining the alkalinity at the lower end of the recommended range will moderate the upward pH drift.

2.4. Control of Microorganisms. Treatment-regime tests with $Ca(OCl)_2$ and chloroisocyanurates killed all pathogenic bacteria, including the Pseudomonas that cause skin infections, within 30 s by 2 ppm FAC at pH 7.4 (82). In a series of tests under stabilized conditions (50–100 ppm cyanuric acid), an initial concentration of 3 ppm FAC could not provide water that met the NSPI standards for bacteria or the maintenance of at least a 2 ppm FAC residual. Increasing the initial FAC to 4 ppm resulted in the bacterial criteria being met 100% of the time even when the FAC residual fell <1 ppm. For heavy bather loads an initial FAC >4ppm is recommended.

2.5. Ancillary Chemicals. Various chemicals are used in spa and hot tub maintenance including aqueous silicone solutions (polydimethylsiloxane) for defoaming, sequestrants (organic phosphonates) for scale and stain prevention, flocculating agents (polyelectrolytes) for clarification, cleaners, tints, fragrances, and nonchlorine oxidizers. Since some of these chemicals have significant chlorine demands, they might reduce the bacterial kill efficiency by lowering the FAC or by interfering in the disinfection process. The sanitizer demand of these chemicals must be compensated for to ensure the maintenance of the residual concentrations stated on the product's label.

3. Economic Aspects

3.1. Sanitizers. U.S. chlorine sanitizer consumption for swimming pools, spas, and hot tubs varies as follows: chloroisocyanurates > calcium hypochlorite > sodium hypochlorite > chlorine. (4). The global capacity for chloroisocyanurates is ~180,000 t. Chloroisocyanurates have the major share of the market, growing at ~4% from 1988 to 2002, and taking market share from other sanitizers. The overall market growth parallels the growth in pools and spas/hot tubs that are growing at ~2 and 7%/year, respectively. The estimated United States demand for calcium hypochlorite in 2003 was ~79,000 t and growing at ~2%/year (83). Other halogen-based sanitizers used to a much smaller extent are BCDMH and lithium hypochlorite.

3.2. Oznators, Ionizers, and Cartridges. Ozone generators, Cu-Ag ionizers and cartridges, and Zn-Ag cartridges are used to a small extent in pools and spas.

3.3. Oxidizers. Estimated nonchlorine oxidizer consumption in 1995 consisted of sodium peroxydisulfate and potassium peroxymonosulfate ~5000 t and hydrogen peroxide ~1600 t.

3.4. Algicides. The consumption of algicides in 2003 is estimated to be ~4000 t. Quats account for ~78% of the market which is growing at ~5%/year.

3.5. Other Ancillaries. All pool and spa owners routinely purchase pH and alkalinity adjustment chemicals. In addition all new pool startups require hardness and stabilzer chemicals. In addition many owners also purchase other ancillaries such as tile and vinyl cleaners, stain and scale inhibitors, antifoam, fragrances, tints, etc. The total market for these ancillaries is significant.

4. Health and Safety Factors

Improperly maintained swimming pools, spas and hot tubs can result in a variety of illnesses ranging from minor to life threatening.

4.1. Disease Transmission. Reported illnesses and outbreaks have been attributed to bacteria (*Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Legionella*, and *Shigella*), protozoa (Giardia and Cryptosporidium), and viruses (adenovirus, enterovirus, and Hepatitis A virus) (84,85). Giardia and Cryptosporidium are more difficult to inactivate than enteric bacteria such as *E. coli*. One of the most frequently isolated organisms found most often in spas, is *P. aeruginosa*, which is a hardy thermophilic bacteria and is most often responsible for outbreaks of folliculitis, skin dermatitis, otitis, pneumonia, and urinary tract infections.

The principal source of biological contamination entering the water is bathers who introduce microorganisms through their skin, body fluids, and fecal contamination. Since resistance to chlorine varies with the organism, it is necessary to maintain the sanitizer level above the minimum recommended level. Pools and spas with high bather loads require automatic chlorinators and continuous monitoring of disinfectant residual through measurement of the oxidation–reduction potential. In addition monitoring for *E. coli* is necessary as an indicator of fecal contamination which poses the greatest health risk.

4.2. Spa/Hot Tub Microbiology. Spa or hot-tub water is an excellent environment for the growth of microbes because of optimal temperatures and the introduction of nutrients from bathers. Diseases can be transmitted by contact with and ingestion of the water, inhalation of microorganisms contained in aerosols produced by the aerated water, and infection through close personal contact. Analysis of unsanitized spa water has shown that a load of 10^3–10^4 microorganisms/mL in a 1.1-m^3 (300-gal) spa can result from a 15-min use by a single bather.

Currently, there are no national standards governing sanitation of spas and hot tubs. Standards proposed by the NSPI are similar to those for swimming pools (20). Public spas and tubs are under the jurisdiction of local health departments. From the microbiological standpoint, the ideal recommendations exclude bacteria and visible algae. However, local health codes may allow a maximum limit of 200 bacteria/mL as determined by the SPC procedure, and no positive results in a most probable number (MPN) determination for coliforms, ie, organisms that indicate fecal contamination (27).

4.3. Spa/Hot Tub Usage. The use pattern of a spa or tub is dictated by personal preference. The water temperature of spas and tubs is normally maintained at 36.7–40.0°C. Although information from spa dealers suggests 15 min at 40°C, and 30 min at 36.7°C, individuals are known to spend longer periods. Long exposure at these temperatures may result in nausea, dizziness, or fainting. Spas and tubs should never be used while under the influence of alcohol (86). Elderly persons and those suffering from heart disease, diabetes, or high or low blood pressure should not use a spa or hot tube without prior consultation with a physician (86). Most important, the water temperature should not exceed 40°C.

4.4. Skin Irritation in Spas/Hot Tubs. A common skin irritation contacted in spas and hot tubs is a nonpruritic rash due to *P. aeruginosa* (87–89). Some cases of skin irritation (so-called bromine itch) also have been associated with use of bromine sanitizers (91). Skin infections may be enhanced by the high water temperatures which open pores and remove protective oils.

4.5. Eye and Respiratory Tract Irritation. Swimming pool water is a foreign environment to the eyes, and physiological changes can occur that result in irritation. In a comprehensive study, the irritation was $\sim$30% less at pH 8 than at 7 (92). Within the pH range 7–8, pH had a greater effect on eye irritation than free available chlorine ($\leq$ 0.5 ppm) in unstabilized water. There is no evidence that stabilized chlorine is irritating to the eyes. However, inorganic chloramines can irritate the eyes or mucous membranes and cause objectionable odors; the effect varying in the following order: $NCl_3 > NHCl_2 > NH_2Cl$. Chloramines (primarily $NHCl_2$ and NCl_3) are usually responsible for complaints of eye irritation. Swimmers may blame this condition on too much chlorine, but the problem is caused by insufficient chlorine. Because inorganic chloramines are decomposed by sunlight, they pose less of a problem for bathers in outdoor swimming pools than in indoor pools.

4.6. Disinfection By-Products. Disinfection by-products with chlorine and bromine sanitizers include chlorate and nitrate ions, inorganic and organic halamines, and halogenated organic compounds (primarily trihalomethanes, THMs). Use of ozone can lead to additional by-products, eg, bromate ion and various organic compounds (see OZONE). The average concentration of NO_3^- found in Miami, Flor., pools was well below the drinking water standard of 45 ppm (93). The primary source of chlorate is believed to be an impurity in hypochlorite sanitizers, especially sodium hypochlorite. No drinking water standard for chlorate has been issued.

The concentration of inorganic and organic chloramines in pool water is controlled by superchlorination or shock treatment. Because chloramines are decomposed by sunlight, their effect is more noticeable in indoor pools or spas. Nitrogen trichloride, the primary volatile chloramine, is a strong irritant similar to chlorine. Its effect is noticeable at >0.5 mg/m^3 (>0.1 ppm) (94). The concentration of NCl_3 depends on the extent of ventilation and typically varies from 0.2 to 0.5 mg/m^3 (0.04 to 0.1 ppm) (95).

THMs are formed by reaction of bromine and chlorine sanitizers not only with bather introduced contaminants, but also with ancillary chemicals. The average concentration of total trihalomethanes TTHMs ($\sim$0.1 mg/m^3, 20 ppb) in air close to the surface of pool water is two orders of magnitude below the OSHA permissible exposure limit (8-h time weighted average) for the main THM chloroform in air (10 mg/m^3, 2 ppm) (96). The average concentration of TTHMs in the bulk air is significantly lower. Spas, with their higher bather load, will have a higher concentration than indoor pools which will be higher than outdoor pools. The average concentration of TTHMs in pool water tend to be at or above the drinking water standard (100 ppb) (93). However, this should be tempered by the fact that swimmers or bathers do not drink pool or spa water. Saline pools have shown higher concentrations of TTHMs due to higher levels of bromoform (93).

4.7. Toxicity of Chlorine Sanitizers. Chlorine-based swimming pool and spa and hot-tub sanitizers irritate eyes, skin, and mucous membranes and must be handled with extreme care. Chlorine gas toxicity is as follows: TLV = 1ppm; acute inhalation $LC_{50} = 137$ ppm for 1 h (mouse) (95). The acute oral LD_{50} (rats) for the liquid and solid chlorine sanitizers are NaOCl (100% basis) 8.9 g/kg, 65% $Ca(OCl)_2$ 850 mg/kg, sodium dichloroisocyanurate dihydrate 735 mg/kg, and trichloroisocyanuric acid 490 mg/kg (97). Cyanuric acid is essentially nontoxic based on an oral $LD_{50} > 20$g/kg in rabbits. Although, it is mildly irritating to the eyes, it is not a skin irritant. A review of the toxicological studies on cyanuric acid and its chlorinated derivatives is given in Ref. 98.

5. Safe Storage and Handling of Sanitizers

Tests are available to determine the extent of decomposition of sanitizers under storage conditions (99). Swimming pool sanitizers should be kept in closed containers in a cool, dry area, segregated from other nonpool materials (such as ammonia, fertilizers, acids, paints, solvents, etc), and should never be mixed with each other or with other materials. Explosive NCl_3 can be generated on mixing hypochlorites and isocyanurates together (especially in the presence of water) or with nitrogen compounds (eg, ammonia, urea, and quats), mixing chloroisocyanurates with alkaline materials (eg, soda ash solution), or storing moist or wet chloroisocyanurates in closed or unvented containers. Mixing hypochlorites and chloroisocyanurates with pool acid (HCl) generates toxic chlorine gas. At very high temperatures, eg, in a fire, swimming pool chemicals release toxic or hazardous gases, eg, $Ca(OCl)_2$ gives primarily O_2 and very small amounts of Cl_2; sodium dichloroisocyanurate gives CO_2, N_2, ClCN, $(CN)_2$, Cl_2, CO, NCl_3, and N_2O; trichloroisocyanuric acid gives Cl_2, N_2, ClC(O)NCO, and trichloroisocyanuric acid vapor; and cyanuric acid gives cyanuric acid vapor and isocyanic acid (HNCO).

BIBLIOGRAPHY

"Water, Treatment of Swimming Pools" in *ECT* 3rd ed., Vol. 24, pp. 427–441, by J. A. Wojtowicz, J. P. Faust, and F. A. Brigano, Olin Corp.; in *ECT* 4th ed. Vol. 25, pp. 569–594, by J. A. Wojtowicz, Olin Corp., retired; "Water, Treatment of Swimming Pools, Spas, and Hot Tubs" in *ECT* (online), posting date: December 4, 2000, by John A. Wojtowicz, Consultant.

CITED PUBLICATIONS

1. *Swimming Pool and Spa Industry Survey*, The National Spa and Pool Institute (NSPI), Alexandria, Va., 2002.
2. *Pool-Spa Operator's Handbook*, National Swimming Pool Foundation, San Antonio, Tex., 1990, p. 11.
3. *Standard 50*, National Sanitation Foundation, Ann Arbor, Mich., 1996.
4. *The Chemical Economics Handbook*, Stanford Research Institute International, Stanford, Calif., 1995 and Feb. 2001.
5. R. E. Connick and Y-T. Chia, *J. Am. Chem. Soc.* **81**, 1280 (1959).
6. J. C. Morris, *J. Phys. Chem.* **70**, 3798 (1966).
7. J. A. Wojtowicz, *J. Sw. Pool and Spa Ind.* **1**(2), 9 (1995).
8. L. O. Petterson and U. Grzeskowiak, *J. Org. Chem.* **24**, 1414 (1959).
9. J. A. Wojtowicz, *J. Sw. Pool and Spa Ind.* **4**(1), 9 (2001); **5**(1), 19 (2004); B. B. Sandel, Olin Corp., unpublished Data on Testing of Copper-Silver Cartridge, 1992.
10. B. B. Sandel, *Symposium Series* Vol. I, pp. 80–85, 1996, NSPI National Meeting, Phoenix, Ariz.
11. R. G. Rice, *J. Sw. Pool and Spa Ind.* **1**(1), 25 (1995); J. A. Wojtowicz, *J. Sw. Pool and Spa Ind.* **4**(1), 41 (2001).
12. W. Hartwig, *J. Sw. Pool and Spa Ind.* **2**(1), 25 (1996).

13. S. M. Kutz, L. K. Landeen, M. T. Yahya, and C. P. Gerba, 4th Conference on Chemical Disinfection, Binghamton, NY April 10–13, 1988; M. T. Yayha, L. K. Landeen, S. M. Kutz, and C. P. Gerba, *J. Environ. Health* **51**, 282 (1989); M. T. Yayha and coworkers, *Can. J. Microbiol.* **36**, 109 (1990).
14. C. White, *Handbook of Chlorination*, Van Nostrand Reinhold Co., New York, 1972.
15. K. Wuhrman and F. Zobrist, *Schweiz. Z. Hydrol.* **20**, 218 (1958); Berger and coworkers, *Antimicrob. Agents Chemother* **9**, 357 (1976).
16. R. Shapiro and F. E. Hale, *J. New Eng. Water Works Assoc.* **51**, 113 (1937).
17. U.S. Pat. 4,250,910 (Feb. 1981) and U.S. Pat. 4,662,387 (May 5, 1987), L. H. King.
18. U.S. Pat. 5,004,549 (Apr. 2, 1991), R. B. Wood, R. M. Mullins, and J. A. Wojtowicz (to Olin Corp.); U.S. Pat. 5,112,521 (May 12, 1992), R. M. Mullins, R. B. Wood, and J. A. Wojtowicz (to Olin Corp.).
19. U.S. Pat. 4,876,003 (Oct. 1989), J. Casberg (to Olin Corp.).
20. *Swimming Pool and Spa Standards*, The National Spa and Pool Institute, Alexandria, Va.
21. C. Hoff, *Inactivation of Microbial Agents by Chemical Disinfectants*, U.S. Environmental Protection Agency, EPA/600/2-86/067, 1986; NTIS PB86-232-568.
22. Z. Zhang, Ph.D. dessertation, University of Houston, Houston, Tex., 1988.
23. H. C. Marks and F. B. Strandskov, *Ann. New York Academy of Sci.* **53**, 163 (1950).
24. C. P. Gerba and J. N. Naranjo, "*Comparison of the Anti-microbial Properties of Hot Tub Additives and Disinfectants*", Department of Soil, Water, and Environmental Sciences, University of Arizona, Tucson, Ariz., 1999.
25. D. S. Taylor and J. D. Johnson, in A. J. Rubin, ed. *Chemistry of Water Supply and Treatment*, Ann Arbor Publishers, Ann Arbor, MI, 1975, pp. 369–407.
26. M. Fair, G. C. Geyer, and D. A. Okun, *Water and Wastewater Engineering*, Vol. 2, John Wiley & Sons, Inc., New York, 1967, pp. 31–36; C. N. Haas, in "*Water Quality and Treatment*", American Water Works. Assoc. 4th ed., 1990, pp. 877–932.
27. *Standard Methods for the Examination of Water and Wastewater*, 19th ed., American Public Health Association, Washington, D.C., 1995.
28. E. T. Gray, D. W. Margerum, and R. P. Huffman, in F. E. Brinckman and J. M. Bellman, eds., ACS Symposium series No. 82, American Chemical Society, Washington, D.C., 1976, pp. 264–277.
29. N. A. Clarke, G. Berg, P. W. Kabler, and S. L. Chang, *International Conference on Water Pollution Research*, Pergamon Press, London, Sept. 1962.
30. A. T Palin, *Water Water Eng.* **54**, 151, 189, 248 (1950).
31. G. P. Fitzgerald and M. E. DerVartanian, *Appl. Microbiol.* **15**, 504 (1967).
32. B. M. Saunier and R. E. Selleck, *J. Am. Water Works Assoc.* **30**, 164 (1979). I. W. Wei and J. C. Morris, in A. J. Rubin, ed., *Chemistry of Water Supply and Treatment*, Ann Arbor Publishers, Inc., Ann Arbor, Mich., 1975, p. 297.
33. R. L. Valentine and C. T. Jafvert, *Environ. Sci. Technol.* **19**, 287 (1985).
34. D. Nelson, *Swimming Pool Disinfection with Chlorinated-s-triazinerione Products*, Special Report 6862, Monsanto Co., St. Louis, Mo., revised May 1975; L. H. Nowell and J. Hoigne, *Wat. Res.* **26**, 593, 599 (1992).
35. W. R. Samples, Ph.D. dessertation, Harvard University, Cambridge, Mass., 1959; J. Fuchs, *Chem. Ztg.-Chem. App.* **86**, 76 (1962).
36. W. D. Stanbro and W. D. Smith, *Environ. Sci. Technol.* **13**, 466 (1979); Z. Alouini and R. Seux, *Wat. Res.* **21**, 335 (1987).
37. Z. Alouini and R. Seux, *Wat. Res.* **22**, 1519 (1988).
38. J. A. Wojtowicz, *J. Sw. Pool and Spa Ind.* **4**(1), 30 (2001).
39. J. A. Wojtowicz, *J. Sw. Pool and Spa Ind.* **4**(1), 54 (2001).
40. L. N. Plummer and E. Busenberg, *Geochim. Geochim. Acta* **46**, 1011 (1982).

41. J. E. O'Brien, J. C. Morris, and J. N. Butler, in A. J. Rubin, ed., *Chemistry of Water Supply and Treatment*, Ann Arbor Publishers, Inc., Ann Arbor, Mich., 1975, p. 333.
42. B. Solastiouk, dessertation, Lorraine National Polytechnic Institute, Nancy, France, 1989.
43. J. A. Wojtowicz, *J. Sw. Pool and Spa Ind.* **1**(1), 7 (1995).
44. J. A. Wojtowicz, *J. Sw. Pool and Spa Ind.* **3**(2), 34 (1999).
45. J. A. Wojtowicz, *J. Sw. Pool and Spa Ind.* **3**(1), 24 (1997).
46. J. A. Wojtowicz, *J. Sw. Pool and Spa Ind.* **1**(3), 19 (1995).
47. J. A. Wojtowicz, *J. Sw. Pool and Spa Ind.* **5**(1), 35 (2004).
48. R. A. Pisigan, Ph.D. dessertation, University of Florida, 1981.
49. F. Langelier, *J. Am. Water Works Assoc.* **38**, 169 (1946); R. F. McCauley, *J. Am. Water Works Assoc.* **52**, 1386 (1960).
50. J. A. Wojtowicz, *J. Sw. Pool and Spa Ind.* **3**(1), 28 (1998).
51. J. A. Wojtowicz, *J. Sw. Pool and Spa Ind.* **3**(1), 37 (1998).
52. J. A. Wojtowicz, *J. Sw. Pool and Spa Ind.* **3**(1), 35 (1998).
53. J. A. Wojtowicz, *J. Sw. Pool and Spa Ind.* **3**(1), 18 (1998).
54. J. A. Wojtowicz, *J. Sw. Pool and Spa Ind.* **2**(2), 23 (1996).
55. R. P. Adamson, M. S. dessertation, Arizona State University, Tempe, Ariz., 1978.
56. G. P. Fitzgerald, *Appl. Microbiol.* **8**, 269 (1960); W. Cochran and J. B. Hatlen, *Stud. Med.* **10**, 493 (1962).
57. E. Herman, *Pool and Spa News* (Aug. 21, 1996).
58. U.S. Pat. 5,164,109 (Nov. 17, 1992), J. A. Wojtowicz (to Olin Corp.).
59. R. P. Adamson and M. R. Sommerfeld, *Appl. Environ. Microbiol.* **39**(2) 348 (1980); F. del Corral and F. B. Johnson, *Symposium Series* Vol. I, 1996, pp. 18–25, NSPI National Meeting, Phoenix, Ariz.
60. G. P. Fitzgerald, *Algicides*, No. PB 198130, National Technical Information Service, U.S. Department of Commerce, Springfield, Va., 1971.
61. G. P. Fitzgerald and D. F. Jackson, *J. Aquat. and Plant Mgt.* **17**, 66 (1979).
62. M. Palmer and T. E. Maloney, *Ohio J. Sci.* **55**, 1 (1955).
63. P. Fitzgerald, *Water Sewage Works* **115**, 65 (1968).
64. F. Minisci, A. Citterio, and C. Giordano, *Acc. Chem. Res.* **16**, 27 (1983).
65. U.S. Pat. 4,780,216 (Oct. 25, 1988), J. A. Wojtowicz (to Olin Corp.).
66. J. A. Wojtowicz, *J. Sw. Pool and Spa Ind.* **4**(2), 9 (2002).
67. P. Brady, K. M. Sancier, and G. Sirine, *J. Am. Chem. Soc.* **85**, 3101 (1963).
68. J. Gardiner, *Water Res.* **7**, 823 (1973).
69. M. Pinsky and H.-C. Hu, *Environ. Sci. Technol.* **15**, 423 (1981).
70. J. A. Wojtowicz, *J. Sw. Pool and Spa Ind.* **2**(2), 14 (1996).
71. J. A. Wojtowicz, *J. Sw. Pool and Spa Ind.* **4**(2), 23 (2002); J. A. Wojtowicz, *J. Sw. Pool Spa Ind.* **5**(1), 15 (2004).
72. R. Anderson, *Swimming Pool Data Ref. Annu.* **32**, 86 (1965).
73. S. Stuart and L. F. Ortenzio, *Soap Chem. Spec.* **40**, 79 (1964).
74. E. Swatek, H. Raj, and R. E. Kalbus, National Swimming Pool Institute Convention, Las Vegas, NV., Jan. 21, 1967.
75. P. Fitzgerald and M. E. DerVartanian, *Appl. Microbiol.* **15**, 504 (1967).
76. J. A. Wojtowicz, *J. Sw. Pool Spa Ind.* **2**(1), 34 (1996).
77. J. A. Wojtowicz, *J. Sw. Pool Spa Ind.* **4**(2), 17 (2002).
78. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., New York, John Wiley & Sons, Inc., 1988.
79. L. Culp and R. L. Culp, *New Concepts in Water Purification*, Van Nostrand Reinhold Co., New York, 1974, p. 84.
80. Gutcho, *Waste Treatment with Polyelectrolytes*, Noyes Data Corp., Park Ridge, NJ, 1972.

81. L. Akins, *Pool and Spa News*, (Aug. 20, 1997) p. 30.
82. F. A. Brigano and J. F. Carney, paper presented at the 84th meeting of the American Society of Microbiology, St. Louis, Mo., March 4–9, 1984.
83. *Calcium Hypochlorite Chemical Profile*, Chem. Mark. Rep., Oct. 2000.
84. R. S. Kebabjian, *J. Environ. Health* **58**, 8 (1995).
85. C. P. Gerba and P. Gerba, *J. Sw. Pool and Spa Ind.* **1**(3), 9 (1995); C. P. Gerba, C. E. Enriquez, and P. Gerba, *Symposium Series* Vol. I, 1996, pp. 31–45, NSPI National Meeting, Phoenix, Ariz. C. P. Gerba and P. Gerba, *Symposium Series* Vol. II, 1997, pp. 8–18, NSPI National Meeting, Chicago, Ill.
86. *Suggested Health and Safety Guidelines for Public Spas and Hot Tubs*, U.S. Department of Health and Human Services Publication No. 99-960, Centers for Disease Control, Atlanta, Ga., 1985.
87. *Morbidity and Mortality Weekly Rep.* **28**, 182 (1979).
88. J. Washburn and co-workers, *J. Am. Med. Assoc.* **235**, 2205 (1976).
89. F. Sausher and co-workers, *J. Am. Med. Assoc.* **239**, 2362 (1978).
90. *Morbidity and Mortality Weekly Rep.* **30**, 329 (1981).
91. P. T. Penny and R. J. G. Roycroft, *Bri. Med. J.*, August 13, 1983.
92. E. W. Mood, C. C. Clarke, and A. Gelperin, *Am. J. Hyg.* **54**, 144 (1951).
93. J. A. Beech and co-workers, *Am. J. Public Health* **70**, 79 (1980).
94. M. Hery and co-workers, *Cahiers de notes documentaires No. 156* (1994).
95. H. J. Jessen, *Z. Gesamte Hyg.* **32**, 180 (1986).
96. *Registry of Toxic Effects of Chemical Substances*, Vol. 2, U.S. Dept. of Health and Human Services, Washington, D.C., 1980 ed.
97. Material Safety Data Sheets, Arch Chemicals, Charleston, Tenn.
98. B. G. Hammond and co-workers, *Env. Health Perspect.* **69**, 287 (1986).
99. J. A. Wojtowicz, *J. Sw. Pool Spa Ind.* **5**(2), (2004).

GENERAL REFERENCES

W. Stumm and J. J. Morgan, *Aquatic Chemistry*, 3rd ed., John Wiley & Sons, Inc., New York, 1996.

C. White, *Handbook of Chlorination*, Van Nostrand Reinhold Co., New York, 1986.

SWIMMING POOL WATER: Treatment and Quality Standards, Pool Water Treatment Advisory Group, London, U.K. 1999.

J. A. Wojtowicz, *The Chemistry and Treatment of Swimming Pool and Spa Water*, Journal of the Swimming Pool and Spa Industry, Tucson, AZ, 2004.

JOHN A. WOJTOWICZ
Olin Corp., Retired

Table 1. **Chlorine Sanitizers Used in Swimming Pools**

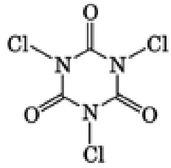
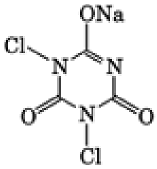
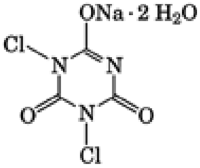
Compound	Formula	Typical form	% av Cl_2
chlorine	Cl_2	liquefied gas	100
trichloroisocyanuric acid		tablets, sticks	89–91
calcium hypochlorite	$Ca(OCl)_2$	granules, tablets, briquettes	65–75
sodium dichloroisocyanurate		granules	62–63
sodium dichloroisocyanurate dihydrate		granules	55–56
lithium hypochlorite	LiOCl	granules	35
sodium hypochlorite	NaOCl	solution	10–15

Table 2. **Recommended Swimming Pool, Spa, and Hot Tub Parameters**

Parameter	Minimum	Ideal	Maximum
FAC, ppm: pools (spas)	1 (2)	2–4 (3–5)	10 (10)
CAC, ppm: pools (spas)	0	0	0.2 (0.5)
TAB[a], ppm: pools and spas	2	4–6	10
cyanuric acid, ppm	10	30–50	150[b]
pH	7.2	7.4–7.6	7.8
Total alkalinity[c], ppm	60	80–100[d]	180
Ca hardness, ppm: pools	150	200–400	1000
Ca hardness, ppm: spas	100	150–250	800
Total dissolved solids, ppm	NA	NA	1500[e]

[a] Total available bromine.

[b] Except where limited by Health Dept. requirements, often to 100 ppm.

[c] No distinction is made between carbonate and cyanurate alkalinity.

[d] For hypochlorite sanitizers; 100–120 ppm for acidic sanitizers, chlorine, Dichlor, Trichlor, and bromine compounds.

[e] Above TDS at pool or spa start up.

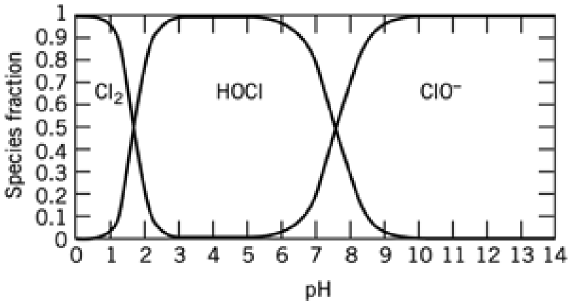


Fig. 1. Distribution of Cl_2, HOCl, and ClO^- versus pH.

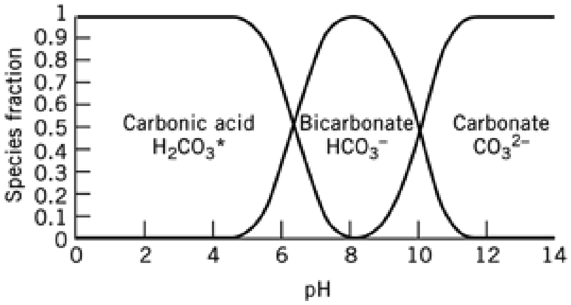


Fig. 2. Distribution of carbonic acid, bicarbonate, and carbonate versus pH.

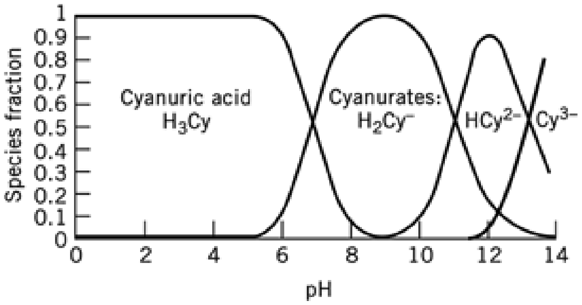


Fig. 3. Distribution of cyanuric acid and cyanurates versus pH.

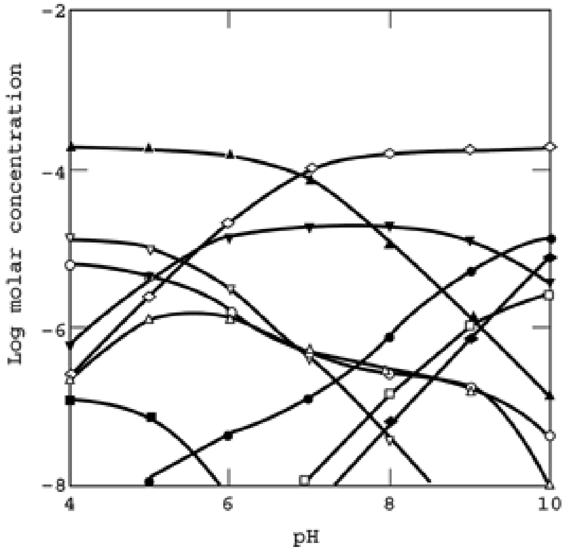


Fig. 4. Species distribution in the cyanuric acid (CA)– av Cl system at 25°C, CA ~25 ppm, av Cl ~1 ppm. ○ = HOCl, ● = ClO^-, ▽ = H_2ClCy, ▼ = $HClCy^-$, □ = $ClCy^{2-}$, ■ = HCl_2Cy, △ = Cl_2Cy^-, ▲ = H_3Cy, ◇ = H_2Cy^-, and ◆ = HCy^{2-}.