# 7.1 – Survey of Swimming Pool/Spa Sanitizers and Sanitation Systems

*Basic information on the various sanitizers and sanitation systems used in swimming pools, spas, and hot tubs is discussed from the standpoint of mode of action, disinfection, algae control, oxidation of contaminants, compatibility with ancillary chemicals, and cost. The main chemical sanitizers used in swimming pools and spas are calcium, sodium, and lithium hypochlorite, chlorine gas, chloroisocyanurates, and bromochlorodimethyl–hydantoin. Chlorine is the lowest cost and by far the most widely used sanitizer because it performs all three sanitizer functions effectively, i.e., disinfection, algae control, and oxidation. Use of bromine is limited primarily to indoor applications because it cannot be effectively stabilized. Systems employing ozone, polyhexamethyl biguanide, metallic ions (copper, silver, or zinc), persulfate–type oxidizers, UV–hydrogen peroxide, and electrolyzers are used to a small extent. In addition they do not offer an effective alternative, significant improvement in performance and/or cost effective advantage to chlorine.*

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## Sanitizer Consumption

The US sanitizer consumption is summarized in Table 1 (Wojtowicz 1993). Calcium hypochlorite, chloroisocyanurates, and sodium hypochlorite represent the major portion of the sanitizer market, whereas chlorine gas, bromochlorodimethyl–hydantoin, and lithium hypochlorite are a minor segment of the market.

## Sanitizer/Oxidizer Cost

The cost of sanitizers/oxidizers are listed in Table 2. The data show that bromine is much more expensive than chlorine and that potassium monopersulfate is very much more expensive than chlorine as an oxidizer.

# Chlorine

## Chlorine Sources

Chlorine is marketed in various forms as shown

| Sanitizer | Thousands of Metric Tons |
|---|---|
| Calcium Hypochlorite (65% av Cl) | 50.0 |
| Chloroisocyanurates | 48.8$^A$ |
| Sodium Hypochlorite ($Cl_2$ Equivalent) | 37.3 |
| Chlorine Gas | 13.6$^B$ |
| Bromochlorodimethylhydantoin | 7.7$^C$ |
| Lithium Hypochlorite | 2.9 |

A) 1992, B) 1995, C) 1993

**Table 1 – U.S. Sanitizer Consumption in Swimming Pools, Spas, and Hot Tubs (1992–5)**

| Sanitizer/Oxidizer | Weight (lb) | Cost ($) | $/lb Equiv. Av. Cl |
|---|---|---|---|
| Calcium Hypochlorite (65% av Cl) | 25 | 45 | 2.77 |
| Sodium Dichloroisocyanurate | 25 | 50 | 3.21 |
| Trichloroisocyanuric Acid | 25 | 50 | 2.22 |
| Bromochlorodimethylhydantoin | 25 | 110 | 7.59 |
| Potassium Monopersulfate | 25 | 55 | 11.22 |

**Table 2 – Sanitizer/Oxidizer Cost (at time of writing)**

in Table 3. Sanitizer usage varies geographically, e.g., in the Sun Belt, consumption varies in the order: chloroisocyanurates > calcium hypochlorite > sodium hypochlorite, whereas in the snow belt, consumption generally varies in the order: calcium hypochlorite > chloroisocyanurates > sodium hypochlorite. Granular calcium or lithium hypochlorites can be added to the pool by broadcasting the solid or by feeding a solution by metering pump. Chlorine gas is added to the pool water via a vacuum injector or a porous diffuser. Calcium hypochlorite tablets are dispensed through feeders or the skimmer. Sodium hypochlorite is added to the pool either manually or by metering pump. Dichlor is broadcast and is used primarily in spas or hot tubs. Trichlor tablets are dispensed in feeders, skimmers, or floaters.

Hypochlorite ions can also be generated electrochemically from chloride ions by dosing the pool with salt (i.e., sodium chloride). Chlorine, formed at the anode by oxidation of chloride ions, reacts with water forming hypochlorous and hydrochloric acids.

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl$$

Sodium atoms, formed by reduction of sodium ions at the cathode, react with water forming sodium and hydroxyl ions (i.e., sodium hydroxide), and hydrogen gas.

$$2Na^+ + 2e^- \rightarrow 2Na$$

$$2Na + 2H_2O \rightarrow 2Na^+ + 2OH^- + H_2$$

In an unseparated cell, the products of the anode and cathode compartments react with each other; the overall reaction is:

$$Cl^- + H_2O \rightarrow ClO^- + H_2$$

Hypochlorite ions react with hydrogen ions to form equilibrium amounts of hypochlorous acid:

$$ClO^- + H^+ \rightleftharpoons HOCl$$

Some chlorine generators add salt to the generator rather than to the pool or spa. They can employ a diaphragm that separates the anode and cathode compartments. The chlorine formed in the anode compartment is dissolved in the recycled pool water. The sodium hydroxide solution in the cathode compartment can be added to the pool for pH adjustment.

| Compound | Form | % Av. Chlorine |
|---|---|---|
| Chlorine Gas | Liquefied gas | 100 |
| Calcium Hypochlorite | Granules, Tablets | 65 and 75 |
| Lithium Hypochlorite | Granules | 35 |
| Sodium Hypochlorite, Bleach | Solution | 10–15 |
| Sodium Dichloroisocyanurate, Dichlor* | Granules | 56 and 62 |
| Trichloroisocyanuric Acid, Trichlor | Tablets | 90 |

*Marketed in hydrated and anhydrous forms.

**Table 3 – Chlorine Sources**

## Photochemical Decomposition

Chlorine is decomposed by the UV rays (>290 nm) in sunlight, e.g., about 90% decomposition occurs in three hours. The decomposition is due to the photoinstability of hypochlorite ion, which has an absorption maximum at 290 nm and absorbs UV out to about 350 nm.

## Stabilization of Chlorine

Chlorine can be stabilized against photochemical decomposition by cyanuric acid (CA) via formation of chloroisocyanurates (monochloroisocyanurate ion is the main species at pool pH), which are relatively stable to UV light because they absorb well below 290 nm. As little as 25 ppm CA reduces the extent of decomposition to about 30% after 3 hours (Nelson 1967).

## Disinfection

**Active Agent** – Disinfection by chlorine is due primarily to formation of hypochlorous acid, e.g., at pool pH chlorine gas reacts with water to produce a mixture of hypochlorous acid and hypochlorite ion.

$$Cl_2 + H_2O \rightarrow (1-x)\ HOCl + x\ ClO^- + (1+x)\ H^+ + Cl^-$$

The proportions of hypochlorous acid and hypochlorite ion vary with pH due to the equilibrium shown below (at pH 7.54, it is 50:50):

$$HOCl \rightleftharpoons H^+ + ClO^-$$

| Microorganism | Ct (ppm·min)* |
|---|---|
| *E. coli* | 0.034 – 0.05 |
| Polio 1 | 1.1 – 2.5 |
| Rotavirus | 0.01 – 0.05 |

* Ct is the product of the free chlorine concentration in ppm and the contact time in minutes. Higher temperatures will result in lower Ct values.

**Table 4 – Antimicrobial Activity of Chlorine**

**Ct values for 99% inactivation at 5°C and pH 6–7 (Hoff 1986)**

By contrast, hypochlorites such as calcium hypochlorite, ionize in water to calcium and hypochlorite ions. Hypochlorite ions partially react with hydrogen ions to form equilibrium amounts of hypochlorous acid ($ClO^- + H^+ \rightleftharpoons HOCl$).

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

**Literature Data** – Chlorine is an effective broad–spectrum disinfectant (Block 1991). It is very effective against enteric bacteria such as *E. coli* (an indicator of fecal contamination) and viruses such as Polio 1 and Rotavirus, although it is less effective against protozoa such as *Giardia* (Hoff 1986); see Table 4. The inactivation mechanism by hypochlorous acid varies with the organism. With bacteria respiratory, transport, and nucleic acid activity are adversely affected (Hass and Engelbrecht 1980).

**Effect of pH** – The rate of disinfection by chlorine varies with pH because of the change in the ratio $HOCl/ClO^-$. However, it should be remembered that $ClO^-$ is a reservoir of HOCl. As HOCl is consumed it is replenished by the equilibrium reaction: $ClO^- + H^+ \rightleftharpoons HOCl$.

**Effect of Temperature** – Although higher temperatures increase the ionization of hypochlorous acid to a small extent, the disinfection rate increases. For example, in an unstabilized pool at pH 7.5, raising the temperature from 77 to 86°F will cause an increase in HOCl ionization of ~4%, however, the disinfection rate increases by a factor of 1.4 (Wojtowicz 1996a).

By contrast, the concentration of HOCl in stabilized pools actually increases significantly with increased temperature due to increased hydrolysis of chloroisocyanurates. Indeed, the extent of hydrolysis of monochloroisocyanurate ion (the major chloroisocyanurate in pool water) increases by 200% over the above temperature range (Wojtowicz 1996a).

**Effect of Stabilization** – Although cyanuric acid stabilizes chlorine against decomposition by sunlight, it does so by reducing the concentrations of HOCl and $ClO^-$ via formation of chloroisocyanurates (Wojtowicz 1996a). However, adequate disinfection in pools is obtained by maintaining the NSPI recommended ideal free av. Cl (2–4 ppm) and maintaining cyanuric acid in the ideal range, i.e., 30–50 ppm. Stabilization does not increase much beyond 50–75 ppm, but higher concentrations of cyanuric acid can reduce the disinfection rate (Table 5). To offset this

| Cyanuric Acid, ppm | Available Chlorine, ppm |
|---|---|
| 25 | 0.75 |
| 50 | 1.5 |
| 100 | 3.0 |
| 150 | 4.5 |
| 200 | 6.0 |

**Table 5 – Minimum av. Cl for 30–sec 99% Kill Time***
***Estimated values for *E. coli* at 85°F (Wojtowicz 2001c).**

tendency, the av. Cl concentration can be maintained at a higher level or the cyanuric acid concentration can be limited by frequent back–washing of the filter.

**Effect of Contaminants** – Nitrogen compounds introduced into pool and spa water react with chlorine forming combined chlorine compounds that are relatively biocidally ineffective (Wojtowicz, JSPSI 4(1)2001:30-40). These compounds can be oxidized by chlorine. NSPI recommends superchlorination in pools (i.e., at 10 times CAC) when combined chlorine exceeds 0.2 ppm.

### Algae Control

Chlorine at 2 ppm is effective in controlling many strains of algae (Palmer and Maloney 1955). Green algae are free floating and are easy to control, whereas, the firmly attached black (i.e., blue–green) algae are the most difficult to control. Mustard (yellow) algae are loosely attached to pool surfaces and are easier to control than black algae. The key to algae control is maintaining appropriate chlorine and cyanuric acid levels combined with periodic shock treatment and brushing/vacuuming. Even a heavy infestation of black algae can be eradicated by multiple shock treatment (up to 30 ppm av. Cl) and brushing and vacuuming.

### Oxidation of Contaminants

Chlorine is an effective oxidant for most swimming pool and spa contaminants (Wojtowicz 1998a, 2001a). Oxidation of nitrogen compounds (both inorganic and organic) produces small amounts of nitrogen trichloride that may be irritating to the eyes of some bathers at sufficiently high concentrations (Wojtowicz 1998b). However, due to its volatility and decomposition by free chlorine, heat, and sunlight, it is not a significant problem in outdoor pools. Periodic overnight superchlorination or shock treatment with chlorine or hypochlorite oxidizes ammonia and organic nitrogen compounds preventing their build–up and minimizing nitrogen trichloride formation during normal chlorination of the water. Regular use of shock products containing Trichlor and Dichlor are not recommended since they greatly increase the cyanuric acid concentration.

### Reaction With Ancillary Chemicals

Because chlorine is a strong oxidant, it reacts with organic–based ancillary chemicals added to pool and spa water such as quaternary ammonium compounds, copper chelates (copper citrate and copper triethanolamine), scale and stain inhibitors (polyacrylates and hydroxyethylidene diphosphonic acid), clarifiers (polyelectrolytes), defoamers (silicones), and enzymes (Fitzgerald 1968). Consequently, these chemicals will have only a transient existence in the pool/spa water. Users should take into account the fact that ancillary chemicals have chlorine demands and will lower the free chlorine concentration of the water.

## Bromine

Elemental bromine is a member of the halogen family and thus its chemistry is similar to that of elemental chlorine.

### Bromine Sources

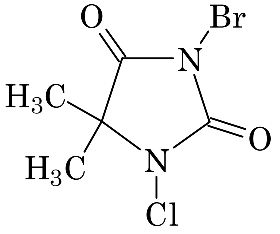

**Figure 1 – BCDMH**

**Bromine Compounds** – Commercially available bromine compounds are listed in Table 6. The primary source of bromine for swimming pool and spa sanitation is 3–bromo–1–chloro–5,5–dimethyl–hydantoin (BCDMH, see Figure 1), which has a total av. halogen content equivalent to ~56% av. Cl. Commercial product is often referred to as 1–bromo–3–

|  |  | % Theoretical |  |
|---|---|---|---|
| **Compound** | **Form** | **Av. Br** | **Equiv. Av. Cl** |
| Bromochlorodimethylhydantoin[A] | Tablets | 66.2[B] | 58.7 |
| Bromine | Liquid | 100 | 44.4 |
| Bromine Chloride | Liquefied Gas | 138.5 | 61.5 |

A) A new product is now available that is dibromodimethylhydantoin, 49.6% equivalent av. Cl

B) Also contains 29.4% av. Cl

**Table 6 – Bromine Compounds**

chloro–5,5–dimethyl hydantoin. However, this is inconsistent with the fact that the more stable N–Cl moiety prefers the electronic environment provided by the adjacent electron donating methyl groups. BCDMH is marketed in tablet form for use in feeders. Since BCDMH has a lower equivalent av. Cl content and is less soluble than Trichlor, it requires larger feeders for equivalent feed rates. BCDMH is also marketed in granular form for use in spas. In water, the bromine substituent hydrolyzes forming an equilibrium concentration of hypobromous acid. All of the bromine substituent analyzes as free bromine. By contrast, the chlorine substituent is very tightly bound, hydrolyzing to only a very slight extent, and analyzes as combined chlorine. In the presence of bromide ion and excess dimethylhydantoin ($H_2DMH$), the chlorine substituent can form the monobromo derivative. However, outdoor sunlight exposure tests under simulated swimming pool conditions show that reaction 1 does not go to completion even after 75% decomposition of total av. halogen.

$$\mathrm{BrClDMH} + \mathrm{Br}^- + \mathrm{H_2DMH} \xrightleftharpoons{\mathrm{H_2O}} 2\mathrm{BrHDMH} + \mathrm{Cl}^-$$

$$\mathrm{BrHDMH} \rightleftharpoons \mathrm{H_2DMH} + \mathrm{HOBr}$$

The hydantoin ring can be cleaved by hypochlorite ion (e.g., during shock treatment). The dichloro derivitive forms N–chloroisopropylamine, $NCl_3$, and $CO_2$ (Patterson and Grzeskowiak 1959).

Some instances of bather skin irritation have been reported in spas sanitized with BCDMH (Penny and Rycroft 1983).

Both bromine and bromine chloride produce hypobromous acid on reaction with water.

$$\mathrm{Br_2} + \mathrm{H_2O} \rightarrow \mathrm{HOBr} + \mathrm{HBr}$$

$$\mathrm{BrCl} + \mathrm{H_2O} \rightarrow \mathrm{HOBr} + \mathrm{HCl}$$

Bromine is a liquid (boiling point 59°C, 138°F) and is more difficult to meter than bromine chloride which is a gas (bp –5°C, 23°F). In addition, bromine is more expensive and only half of the bromine is usable for disinfection. Neither $Br_2$ nor BrCl are employed in sanitation of pools or spas.

Although bromine and bromochloro derivatives of Dichlor and Trichlor are known, they are not produced commercially and therefore are not available for swimming pool and spa sanitation.

***In–Situ* Generation of Av. Bromine** – Hypobromous acid and hypobromite ion can also be generated *in situ* by oxidation of bromide ion (typically supplied by calcium or sodium bromide) with chlorine compounds such as chlorine gas, hypochlorites (Ca, Li, or Na), or chloroisocyanurates (Dichlor or Trichlor). For example, reaction of bromide ion with hypochlorite ion or hypochlorous acid, formed on addition of a hypochlorite sanitizer to swimming pool or spa water, will form hypobromite ion and hypobromous acid.

$$\mathrm{HOCl/ClO^-} + \mathrm{Br}^- \rightarrow \mathrm{HOBr/BrO^-} + \mathrm{Cl}^-$$

As with hypochlorite ion and hypochlorous acid, hypobromite ion and hypobromous acid are in equilibrium with each other at swimming pool pH.

$$\mathrm{HOBr} \rightleftharpoons \mathrm{H}^+ + \mathrm{BrO}^-$$

Other oxidizing agents such as potassium monopersulfate or ozone can also be used.

$$\mathrm{Br}^- + \mathrm{H}^+ + \mathrm{KHSO_5} \rightarrow \mathrm{HOBr} + \mathrm{KHSO_4}$$

| Stabilizer | Conc. | NaBr | Av. Halogen | % Decomposition$^{C}$ |
|---|---|---|---|---|
| | ppm | ppm | as ppm av. Cl$^{B}$ | |
| Cyanuric Acid | 50 | 0 | 3.4 | 35 |
| “ | 50 | 100 | 4 | 100 |
| “ | 150 | 0 | 3.6 | 19 |
| “ | 150 | 100 | 4.6 | 96 |
| “ | 300 | 100 | 4.6 | 74 |
| BROMIshield | 50 | 100 | 5.0 | 76 |
| DMH | 50 | 100 | 4.6 | 74 |

A) Studies carried–out outdoors on a one–gallon scale in shallow glass containers in bright sunlight at temperatures of 70–85°F.

B) Initial concentration. Analysis performed using the FAS–DPD method.

C) Exposure time 4 hours.

**Table 7 – Comparative Stabilizer Studies$^{A}$ (Wojtowicz 2000a)**

$Br^- + H^+ + O_3 \rightarrow HOBr + O_2$

Bromide ion can also be oxidized electrochemically to produce available bromine. This was demonstrated in a swimming pool and a spa dosed with 2200 ppm sodium bromide (Olin Corp. 1983).

$Br^- + H_2O \rightarrow BrO^- + H_2$

Hypobromite ions reacts with hydrogen ions to form equilibrium amounts of hypobromous acid: $BrO^- + H^+ \rightleftharpoons HOBr$.

## Disinfection

As with chlorine, the disinfecting properties of bromine are due to hypobromous acid. Disinfection by bromine is less sensitive to pH because HOBr is less ionized than HOCl over the swimming pool pH range. Nevertheless, bromine is in general less effective than chlorine (at normal pool pH) against bacterial spores (Marks and Strandskov 1950), bacteria (Zhang 1988, Gerba and Naranjo 1999), and viruses (Taylor and Johnson 1972) on a ppm basis. Although bromamines are better disinfectants than chloramines, they are readily decomposed by free bromine. Use of BCDMH results in build–up of dimethylhydantoin that can reduce the concentration of hypobromous acid, resulting in a decreased disinfection rate.

## Algae Control

Swimming pool tests with electrochemically generated bromine showed that it was effective in controlling green, blue–green, and mustard algae.

## Stabilization

Although bromine reacts with cyanuric acid forming bromoisocyanurates analogous to chloroisocyanurates, it cannot be stabilized as effectively as chlorine. Indeed, very high concentrations of cyanuric acid are required to obtain significant stabilization as shown in Table 7. At 300 ppm of cyanuric acid, the extent of stabilization is similar to 50 ppm dimethylhydantoin (DMH, the parent compound of BCDMH). Some research on bromine stabilizers has recently been published (Nalepa 1999).

A product called BROMIshield is currently on the market that claims to reduce decomposition of available bromine caused by intense sunlight (Dumas 1999). This product appears to be dimethylhydantoin based on a similar degree of stabilization (see Table 7). Additionally, BROMIshield behaves like dimethylhydantoin in that it reacts with sodium hypochlorite in the presence of bromide ion to form significant amounts of combined chlorine a portion of which is still present even after 4 hours exposure to sunlight. However, if the sodium hypochlorite is first reacted with sodium bromide to form hypobromite, then little or no combined chlorine is formed on

| Compound | Av. Cl/N Mol Ratio | $Br^-$ Ion ppm | Reaction Time Min. | % Oxidation of Compound |
|---|---|---|---|---|
| Ammonia | 1.8 (3.6) | 0 | 10 | 38 (87) |
| “ | 1.8 | 40 | 10 | 79 |
| Urea | 1.8 (3.6) | 0 | 60 | 7 (8) |
| “ | 1.8 | 40 | 60 | 14 |
| Creatinine | 1.8 | 0 | 60 | 3.4 |
| “ | 1.8 | 40 | 60 | 2.6 |
| Glycine | 1.8 | 0 | 60 | 20 |
| “ | 1.8 | 40 | 10 | >26 |

**Table 8 – Effect of Bromide Ion on Oxidation of Nitrogen Compounds by Chlorine (Wojtowicz 1998a, 2001a)**

reaction with either BROMIshield or DMH. However, the stability is somewhat lower under these conditions.

### Oxidation of Contaminants

With the exception of creatinine, the main swimming pool contaminants are oxidized more rapidly by bromine than by chlorine as shown in Table 8. The mechanism involves conversion of the chlorine compounds to bromo derivatives that are less stable. Excess chlorine above the stoichiometric amount also increases the oxidation rate as in the case of ammonia.

### Reaction With Ancillary Chemicals

Like chlorine, bromine is a strong oxidant and it can react with ancillary chemicals added to pool and spa water such as quaternary ammonium compounds, copper chelates, scale and stain inhibitors, defoamers, and enzymes. Consequently, these chemicals will have only a transient existence in the pool/spa water.

## Ozone

### Properties

Ozone is an allotropic form of oxygen that contains three oxygen atoms. It is a pale blue gas at ordinary temperatures, slightly soluble in water, and has a pungent odor. Because of its instability (both thermal and explosive), it must be generated on site. The half–life of ozone in tap water at 20°C is less than 30 minutes. In addition to this thermal decomposition, aqueous ozone is also decomposed by sunlight. Because ozone is a gas, it tends to escape from aqueous solution. This tendency and the fact that ozone is toxic (the maximum allowable concentration in air is only 0.1 ppm for an 8–hour exposure), is the reason that ozone cannot be used as a primary sanitizer.

Although ozone is a stronger oxidant than chlorine from a thermodynamic standpoint, it is not always kinetically superior. For example, experimental data show that chlorine is a much better oxidant for bather contaminants such as ammonia, urea, and creatinine that are oxidized only slowly by ozone. Thus, one of the advertised benefits of ozone in swimming pool/spa treatment, that it is a stronger oxidant than chlorine, is not supported by actual data. Ozone technology has been comprehensively reviewed (Wojtowicz 1996b, 2001b).

### Ozone Generation

Ozone can be generated from the oxygen in air by ultraviolet (UV) light or electric discharge (also called corona discharge).

$$3O_2 + \text{UV light or electrical energy} \rightarrow 2O_3$$

Corona discharge (CD) ozone generators (ozonators) produce much higher concentrations than UV ozonators, i.e., 1–2 wt. % vs. <0.1 wt. %).

**UV Ozone Generators** – Low–pressure mercury lamps produce low concentrations because they also emit 254 nm radiation that decomposes ozone in addition to the 185 nm radiation that's responsible for formation of ozone. Lamps optimized for 185 nm radiation produce higher concentrations, typically about 300 ppm. Some UV ozonators have air filters and dryers but do not employ lamp cooling. UV lamps have very low energy efficiency compared to CD ozonators. Over the past two decades numerous UV ozonator manufacturers have entered the market only to go out of business a few years later.

**CD Ozone Generators** – By contrast to UV ozonators, properly designed CD ozone generators produce much higher concentrations, typically 1–2 % covering a wide range of production rates. Typical CD ozonators employ dryers to lower the moisture content of the inlet gas; a dew point of at least 60°F is required for optimum output. They may also utilize cooling to reduce the temperature of the CD cells. Some CD ozonators on the market are only marginally better than UV ozonators with ozone concentrations of only 0.06–0.2 wt. %.

## Ozone Transfer into Water

The ozone produced by ozonators is transferred into water by devices such as porous diffusers or venturis that disperse the gas into very small bubbles for more intimate contact with water. Venturis generate a vacuum that draws air through the ozonator and injects the resultant ozone–air mixture into the water circulation system. Compressors are used with porous diffusers and can also be employed to improve the effectiveness of venturis. The transfer efficiency increases with the ratio of the water to gas flow rates. For a given transfer efficiency, the aqueous ozone concentration increases with the gas phase ozone concentration. The calculated ozone absorption for UV ozonators is generally in the 70–90% range. Since UV ozonators do not decompose the unabsorbed ozone in the off gas, this can pose a potential health risk to bathers in indoor spas.

## Disinfection

Ozone at appropriate concentrations is an effective broad–spectrum disinfectant, but its biocidal properties can be affected by presence of readily oxidizable matter in the water. Ozone cannot be used as a primary sanitizer because it is both volatile and toxic. If the ozone residual is sufficient for effective control of microorganisms, the concentration of ozone above the water will exceed the permissable exposure limit (for an 8–hour exposure) of 0.1 ppm (OSHA 1975). Thus, ozone requires a primary sanitizer and is typically used in conjunction with chlorine.

## Algae Control

Ozone at appropriate concentrations is toxic to many types of algae. However, swimming pools cannot benefit from this because ozone cannot be used as a primary sanitizer. UV ozone was shown to be ineffective in algae control in two swimming pool tests (see Table 9).

## Oxidation of Contaminants

**Kinetic Data** – The reactivity of ozone varies greatly and depends on the functionality of the substrate. Reaction rate constants determined in the laboratory show that ozone reacts very slowly with bather contaminants such as ammonia, urea (the main swimming pool contaminant), and creatinine (Hoigne, *et al* 1983–1985). Although ozone reacts rapidly with amines and amino acids, it reacts slowly with many other organic compounds, e.g., aliphatic alcohols, aldehydes, and acids. Many organic nitrogen compounds yield ammonia as an intermediate product. For example, in the oxidation of the amino acid glycine, the ammonia formed is only slowly oxidized at pool or spa pH because it is primarily in the form of ammonium ion that does not react with ozone.

**Laboratory Data** – Laboratory tests showed very slow oxidation of bather contaminants such as ammonia, urea, and creatinine even at relatively high ozone and substrate concentrations (Eichelsdorfer and Jandik 1985, Wojtowicz 1989a).

## Reaction With Ancillary Chemicals

As in the case of chlorine and bromine, ozone will react with ancillary chemicals added to the pool or spa water.

## Evaluation of UV Ozonators

**Disinfection** – Two brands of commercially available UV ozonators were evaluated under swimming pool and spa conditions. The results, summarized in Table 9 indicate that typical UV ozonators by themselves are not effective for either pool or spa treatment (Wojtowicz 1985). The bactericidal effec-

| Ozonator | Test | Ozone g/h | Results |
|---|---|---|---|
| A1 | 250–gal spa | 0.25 | Poor bactericidal performance. |
| A2 | 6800–gal pool | 0.5 | Green algae bloom after 3 days of continuous operation* |
| B1 | 250–gal spa | 0.3 | Poor oxidation of urea in synthetic bather insult. |
| B2 | 6800–gal pool | 1.0 | Green algae bloom after 4 days of continuous operation* |

*Water shock treated with calcium hypochlorite prior to test. pH 7.2–7.8, 80–85°F, 80 ppm alkalinity, 300 ppm calcium hardness.

## Table 9 – Evaluation of UV Ozonators

tiveness of ozone, evaluated under spa conditions, initially showed no inactivation of bacteria at spa temperature. In a second test starting at room temperature, a very slow kill rate was observed. After one hour the temperature increased from 77 to 88°F and the inactivation was only 55%.

**Oxidation** – The oxidation of urea by ozone was evaluated in a 300–gallon spa (100°F, pH 7.5, 0.3 g ozone/hour). A total of 27 g of urea was added during the 36–hours of the test. Essentially no oxidation of urea occurred based on the fact that there was little or no change in the urea concentration and no byproduct nitrate formation was observed. Similar results were obtained in another study (Adams *et al.* 1999).

**Bromine Generation** – A UV ozonator rated at 7.5 g ozone/day was evaluated for generation of available bromine from sodium bromide.

$$O_3 + Br^- \rightarrow O_2 + BrO^-$$

Based on the amount of available bromine formed, the ozone generation rates at 25 and 35°C corresponded to 1.6 and 0.8 g/day or efficiencies of only 21 and 8%, respectively.

## Use of UV Ozone in Pools and Spas

**Pools** – UV ozone is applied directly into pool water without use of a contact chamber as with CD ozone, which is typically applied at a concentration of 1 ppm and maintained for at least 2 minutes. By contrast, UV ozonators generate an ozone concentration of only 0.02 ppm in the external recycle loop and the contact time prior to entry into the pool is less than 1 second. The average ozone concentration in the pool after one turnover (i.e., 6 hours) provided by the ozonators in Table 1 is about 40-fold lower and amounts to only 0.5 ppb at a water temperature of 85°F, assuming only ozone decomposition. Assuming no reaction with bather contaminants, about 99% of the applied ozone will decompose over the course of 6 hours. The total ozone dose, assuming no decomposition, is equivalent to only 0.03 ppm av. Cl in terms of potential oxidizing capacity. The low ozone concentration and dosage provided by UV ozonators precludes significant contribution to disinfection or oxidation of bather contaminants.

**Spas** – Ozonating the water while the spa is in use is not recommended because the unabsorbed ozone in the ozonator vent gas can amount to 60 ppm. If the spa is treated after use with ozone at the average feed rate of 0.184 g/h (see Table 2) over a 6–hour period, the calculated average ozone concentration, considering only decomposition, will be 1.6 ppb. The total ozone dose, assuming no decomposition, is equivalent to 0.4 ppm av. Cl in terms of potential oxidizing capacity. This represents only 5% of the recommended shock dose of 8 ppm av. Cl. Furthermore, most (~99%) of the applied ozone will simply decompose resulting in negligible oxidation of bather contaminants.

**Claims** – UV ozonator manufacturers typically claim lower chlorine consumption (typically 60 to 80%) and the ability to operate pools and spas at lower chlorine concentrations (0.5–1.0 ppm). However, there is a lack of published data on disinfection, algae control and oxidation of bather contaminants obtained by independent researchers under actual pool and spa conditions in support of these claims.

As discussed above, UV ozone is too dilute to significantly contribute to disinfection and oxidation of bather contaminants, consequently a reduction in chlorine concentration and usage is not possible. Accordingly, NSPI recommended chlorine levels (1–3 ppm in pools and 3–5 ppm in spas) supplemented by periodic shock treatment are necessary, (ANSI–NSPI 1995 and 1999).

**Safety** – As discussed earlier, ozone absorption is incomplete, and since UV ozonators do not provide for off gas ozone destruction, the ozone concentration above the water at the point of entry of the ozonated air into the pool or spa can be quite high (55 to 60 ppm). In indoor spas, this can cause the average ozone concentration above the spa to exceed the OSHA limit of 0.1 ppm, creating a potential health hazard to bathers.

**NSF Approval** – UV ozonators with ratings up to 1 gram per hour ozone were tested by NSF and require the use of NSF certified brominators or chlorinators delivering 4 ppm bromine or 2 ppm chlorine (NSF 1985). Even larger output CD ozonators are subject to this requirement.

**Cost** – UV ozone generators, with production rates of 0.25 to 0.44 g/h for pools of 18,000 to 50,000 gals., retail for $500 to $700. These units come with venturi type injectors but do not have air filters, dryers, or off gas ozone destruction. The cost is a function of the ozonator output and whether the unit has an air filter, dryer, or compressor.

**Deficiencies of UV Ozonators** – The following summarizes deficiencies of UV ozonators:

- Build up of toxic concentrations of ozone in indoor installations due to lack of off gas ozone destruction
- Raises water pH by removing carbon dioxide
- No separate contact vessels
- Ozone inlet concentration too low and contact time too short for significant disinfection or oxidation of bather contaminants
- Ozone output much too low to satisfy oxidizer demand of pool or spa water in a practical time
- No method to measure the low ozone concentration
- No way to tell if unit is functioning properly
- Ozone output decreases with lamp age
- No way to tell if lamps need replacement
- Some units do not have air filters or dryers
- No independent substantiation of effectiveness in disinfection, oxidation, or reduced chlorine usage

## Use of CD Ozone in Pools

**European Practice** – CD ozonators produce much higher concentrations than UV ozonators and are commonly used in Europe, primarily in large commercial or public pools. CD ozonators also require additional equipment for a complete system including: compressors, dryers, contact chambers and deozonators for treating vent gases and for treating ozone–containing water before returning it to the pool. The most widely used ozonation technique in Europe is the ozone–granular activated carbon (GAC) system that is covered by the German–developed standard (DIN 1984). It involves treating all water by coagulation, filtration, ozonation, GAC filtration, and chlorination. Ozone (about 1 ppm) is introduced into the water in the external recycle loop after a sand filter, through a porous diffuser in a contact chamber. After a reaction time of at least 2 minutes, the ozonated water is filtered through GAC to destroy unreacted ozone. This also destroys available chlorine. The dechlorinated and deozonated water (with <0.05 ppm ozone) is then dosed with 0.5 ppm av. Cl and returned to the pool. Although oxidation of contaminants is the primary purpose of ozonation, some destruction of microorganisms may also occur. In order to limit buildup of dissolved solids, a specified amount of water (~30 liters per bather) is purged from the pool.

Treating water by this process is cost effective only for large, heavily used pools (e.g., public, commercial, or private). Data from European pools employing the ozone–GAC process show that ozone can reduce operating costs by about 20%. Since ozone is not effective in oxidizing bather impurities such as ammonia, urea, and creatinine, removal of these contaminants will depend on processes that may occur in the GAC filter. For example, monochloramine can be partially converted to nitrogen and chloride ion. Although the GAC filter may become biologically active, potentially providing biodegradation of some contaminants, no data are available on the extent, if any.

**North American Practice** – Ozone–GAC systems have been installed in several US cities (Rice 1995). Modified systems are also being offered in order to reduce costs. In retrofit installations, post–filter ozone injection is employed in conjunction with a combination contact chamber/GAC filter (Hartwig 1996). For new installations, pre–filter ozonation is employed which utilizes the filter as a combination contact chamber/GAC filter/sand filter. Still this system is cost effective only for large, heavily used pools. Although DIN requires full flow ozonation, some systems employ only partial or slipstream ozonation (in some cases as low ~10%). Since ozone only increases the non–urea and ammonia COD reduction by about 20% and also requires a water purge and an effective GAC filter (i.e., biologically active), any significant departure from DIN design will be at the expense of water quality. CD ozonators are not cost–effective for residential pools because the bather load is too low. This is probably also the case for many intermediate sized public or private pools.

**Generation of Bromine** – Ozone is sometimes used to generate av. Br from sodium bromide in small European public and semi–public pools and whirlpools (i.e., spas). A spa test using a CD ozonator (7.5 g ozone/hour) at room temperature showed only a 50% bromine generating efficiency that would probably be lower at typical spa temperatures.

**Cost** – The suggested retail price of residential pool CD ozonators for 25,000 to 100,00–gal pools with ozone production rates of 0.3 to 1.0 g/h ranges from about $600 to $1800. CD ozone generators employing air feed with ozone production rates of 1.2 to 7.4 g/h retail in the $800 to $3700 range and do not come with any peripheral equipment. Commercial CD ozonators employing oxygen feed with ozone production rates of 2 to 7 g/h retail in the $4,000 to $10,000 range and do not come with off gas ozone destruction, contact chambers, or GAC filters. The cost of CD ozonators with higher production rates are as follows: 2–200 g/h (air) and 20–320 g/h (oxygen) – $10,000–$25,000; 750–1800 g/h (oxygen) – $35,000–60,000.

## Potassium Monopersulfate (PMPS)

### Properties

**Composition** – Potassium monopersulfate (PMPS, $KHSO_5$) is marketed in the form of a triple salt ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) of 85% purity. It contains ~4.5% active oxygen and is employed primarily as a non–chlorine oxidizer.

**Reaction with Halide Ions** – Potassium monopersulfate readily oxidizes bromide ion to bromine. It also oxidizes chloride ion to chlorine but at a much slower rate.

**Stability** – PMPS is decomposed by sunlight much faster than stabilized chlorine, e.g., an 8.6 ppm solution of PMPS in tap water was 75% decomposed after 6 hours (decomposition rate ~20%/hour) in sunlight (Wojtowicz 2000b). Even in the absence of sunlight PMPS decomposes at ~4%/hour at room temperature. The rate is even higher at spa temperature: ~12%/hour.

### Disinfection/Algae Control

While PMPS alone (or in the presence of cartridge derived copper and silver ions) is ineffective at typical swimming pool temperatures (~75–80°F), it is more effective at spa temperatures. For example, at 77°F PMPS provided only 16.8% inactivation of *E. coli* bacteria in 2 minutes (Gerba and Naranjo 1999), but at 104°F it provided >99.9999% inactivation. No data are available on disinfection of viruses and protozoa, or on the algicidal properties of PMPS.

### Oxidation of Contaminants

By contrast with chlorine, there is no published data on the effectiveness of monopersulfate as an oxidant for typical pool and spa contaminants such as ammonia, urea, amino acids, creatinine, etc. PMPS appears to be less reactive than chlorine since it behaves like combined chlorine during DPD analysis. By contrast with chlorine, which oxidizes ammonia and urea nitrogen primarily to elemental nitrogen, the oxidation product with PMPS is nitrate ion that is a nutrient for algae. The recommended use of PMPS at 1 lb/10,000 gal as an alternative shock treatment for pools using the copper–silver or zinc–silver cartridges will be much less effective than a chlorine shock, providing an oxidation capacity equivalent to only 2.3 ppm chlorine. Indeed, 3.3 lb of PMPS would be required to equal the oxidizing capacity of a 1 lb calcium hypochlorite shock.

### Effect on pH

PMPS lowers pH due to formation of bisulfate ions:

$$2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4 \rightarrow 3KHSO_4 + K_2SO_4 + 2O$$

### Uses

PMPS is used primarily as a non–chlorine shock in pools and spas and as a disinfectant in spas.

### Cost

PMPS is much more expensive than chlorine, e.g., the cost of a 1–lb calcium hypochlorite shock is $1.80 while the cost of the equivalent amount of PMPS (3.3 lb) is $7.26.

# Potassium Persulfate (PPS)

## Properties

**Composition** – Potassium persulfate or peroxydisulfate ($K_2S_2O_8$) is marketed as a white powder of ~95% purity.

**Stability** – The decomposition rate in stabilized swimming pool water is about 5% per day. Decomposition proceeds as follows:

$$S_2O_8^{2-} + H_2O \rightarrow 2HSO_4^- + 0.5O_2$$

In the presence of oxidizable matter, the oxygen will be consumed.

## Disinfection/Algae Control

No data are available on the effect of PPS on disinfection or algae control, however, by comparison with potassium monopersulfate it is not expected to be significant.

## Oxidation of Contaminants

Oxidation reactions of persulfate ion are normally slow but can be catalyzed by sunlight and by metal ions (eg, silver, copper, etc.) via formation of sulfate ion radicals ($SO_4^-\cdot$) (Minisci *et al* 1983):

$$S_2O_8^{2-} + \text{photon} \rightarrow 2SO_4^-\cdot$$

$$S_2O_8^{2-} + Ag^+ \rightarrow SO_4^{2-} + SO_4^-\cdot + Ag^{2+}$$

The intermediate divalent silver ($Ag^{2+}$) ions can oxidize organic matter faster than persulfate itself. Sulfate ion radicals are also more effective oxidants than persulfate. The $Ag^+$ ions formed after oxidation of bather contaminants can be reoxidized to $Ag^{2+}$ by sulfate ion radicals (or persulfate as above):

$$SO_4^-\cdot + Ag^+ \rightarrow SO_4^{2-} + Ag^{2+}$$

No data are available on silver or copper catalyzed oxidations of bather contaminants by persulfate at swimming pool concentrations.

## Effect on Water Chemistry

The end products of decomposition of persulfate are hydrogen and sulfate ions. The hydrogen ions will reduce pH and alkalinity.

## Uses

Persulfate is used to a very small extent as a non–chlorine oxidizer in combination with copper sulfate.

# Polyhexamethylene Biguanide (PHMB)

## System Description

Polyhexamethylene biguanide (PHMB) is a polymeric nitrogen compound $[-(CH_2)_6[NHC(=NH)]_2NH-]_N$ that is marketed as a 20% solution. It functions as a bacteriostat and is part of a three–component system that includes a quat, i.e., a quaternary nitrogen compound (dimethylalkylbenzylammonium chloride) and hydrogen peroxide, which function as algistat and oxidizing agent, respectively. The system also includes an enzyme–based filter cleaner and a metal chelator. After an initial dose of 10 ppm active, the concentration of PHMB is maintained between 6 and 10 ppm while the quat is maintained at 2–2.5 ppm via weekly measurement/adjustment. Peroxide is added every 3–4 weeks at a dosage of ~27 ppm. This multi–component system is more expensive than chlorine.

## Incompatibilities/Problems

Product literature indicates that PHMB is not compatible with chlorine or bromine sanitizers, copper and silver–based algicides, ozone, persulfate oxidizers, most clarifiers and cleaners, and some stain and scale inhibitors. Excessive use of PHMB, quat, and enzyme can cause foaming and impart an odor and off taste to the water. Other problems include persistent haziness or cloudy water and development of biological growths. These problems may necessitate partial drainage of the pool water and replacement with fresh water and/or temporarily increasing the pH combined with vacuuming to waste. Since quats tend to be removed by filter media such as diatomaceous earth (Fitzgerald 1960), increased dosing frequency may be necessary.

| Test Duration days | No. of Samples | Incubation Period | Bacteria Counts > 200 CFU/mL | |
|---|---|---|---|---|
| | | | Control | PHMB |
| 90 | 26 | one week | 1 | 7 |
| 100 | 35 | 2 days | 0 | 20 |

**Table 10 – Bactericidal Comparison of Chlorine and PHMB**

## Disinfection/Algae Control

PHMB is a bacteriostat; the minimum inhibitory concentration (MIC) for *E. coli* is 20 ppm (4 ppm active) and for *Pseudomonas aeruginosa* it is 100 ppm (20 ppm active) (Block 1994). Since the recommended PHMB concentration is 30–50 ppm (6–10 ppm active), *Pseudomonas aeruginosa* may not be controlled. However, the combined effect of PHMB and the quat may provide control. Because hydrogen peroxide is a poor oxidant, build–up of organic matter can promote biological growths such as water mold and pink slime.

**Swimming Pool Evaluation** – The PHMB system was evaluated in a 6800–gal swimming pool (Sandel 1996). The data are summarized in Table 10. In the first year of the test, 27% of the pool samples showed bacterial counts above 200 CFU/mL. In the second year, 57% of the pool samples showed bacterial counts above 200 CFU/mL. By contrast with the first year results, which were obtained using a 7–day incubation period, the second year results were based on only a 2–day incubation period. This is indicative of development of PHMB resistant bacteria. By contrast with the PHMB results, a calcium hypochlorite treated control pool showed negligible test results above 200 CFU/mL. In addition, the PHMB test pool showed evidence of bacterial slimes in the pool skimmer. Furthermore, total organic carbon (TOC) increased with time and is associated with the poor oxidizing properties of hydrogen peroxide. The presence of organic matter may in fact be responsible for the development of PHMB resistant bacteria.

## Oxidation of Contaminants

Hydrogen peroxide is a very poor oxidant for ammonia and urea (the main pool contaminant), and other organic matter. Thus, build–up of organic matter will occur and may cause cloudiness, development of biological growths, and inadequate disinfection.

# Copper, Silver, and Zinc Devices

**System Descriptions** – Sanitizer systems based on metal ions employ copper, silver, or zinc. The ions can be generated electrochemically (i.e., copper–silver or silver ionizers), or by dissolution (copper–silver and zinc–silver cartridges). Ionizers deliver much higher concentrations than cartridges (Table 11). The metal ion concentrations delivered by zinc–silver cartridges have not been disclosed. These devices are installed in the external recycle loop of the pool or spa. Silver is not compatible with bromine or biguanide–based sanitizing systems.

## Disinfection

**Literature Data** – The antimicrobial activity of copper and silver is thought to be due to binding to sulfhydryl groups in cellular proteins and enzymes preventing their participation in enzymatic reactions (Kutz *et al* 1988). On a ppm basis, the activity of metal ions varies in the following order: silver > copper > zinc. Compared to chlorine, silver is a poor bactericide, e.g., 86 minutes were required for 99.9% inactivation of *E. coli* in the presence of 0.03 ppm silver at 25°C and pH 7.5 (Wuhrman and Zobrist 1958). The presence of chloride or phosphate ions significantly increased kill time. For example, 10 and 100 ppm chloride ion increased the 99.9% kill time of 60 ppb silver by 25 and 70%, respectively. The 99.9% kill time was also increased by 3 minutes for each 10 ppm of hardness.

Ceramic cartridges containing finely divided metallic silver embedded in a ceramic substrate have been known since the 1930's. One problem encountered in their use was a gradual decrease in bactericidal effectiveness with time due to build–up of an organic slime that coated the silver particles necessitated periodic cleaning (White 1972). Evaluation in swimming pools showed that silver was unsatisfactory as a bactericidal agent (Shapiro and Hale 1937).

The data in Table 12 show that copper and silver, either individually or together, are poor disinfectants (Kutz *et al* 1988). With chlorine alone, a high kill rate was observed. With chlorine, copper, and silver present, disinfection improved to a small extent. Indeed, the data show that chlorine killed 99.9% of the bacteria and the copper and silver killed only 0.09%. However, the concentration of copper was above 0.3 ppm and would most probably cause staining. The data show that chlorine is necessary for adequate disinfection. It is important to mention that the tests were carried–out in well water with only 0.02 ppm of chloride ion. Since typical swimming pool water contains significant concentrations of chloride ion, disinfection rates will be lower than those shown in Table 12.

The disinfection data in Table 12 and provided by some manufacturers was obtained in the absence of chloride ion and cyanuric acid. Chloride ion decreases the bactericidal effectiveness of silver as discussed above. In addition, cyanuric acid is known to reduce the effectiveness of chlorine. Thus, the low recommended av. Cl levels shown in Table 11 might not provide satisfactory control of bacteria in stabilized pools.

**Testing of Ionizers** – In a one–month test of a copper–silver ionizer in a 16,000–gal outdoor above ground residential pool, extremely high bacteria counts (14,000 to 62,000 CFU/mL) were observed on three successive periodic samples. The pool was shocked with PMPS every two weeks. In a test of a spa ionizer, high bacteria counts (>3,000/mL) of fecal coliforms and streptococci were present in the water while bathers were in the spa despite satisfactory copper and silver levels (Sandel 1996).

**Testing of Cartridges** – Copper silver cartridges provide even lower metal ion concentrations than ionizers, consequently the small enhancement in % kill shown in Table 12 would be further reduced. A cartridge designed for pools up to 16,000 gals. was evaluated in a 6800–gal experimental aboveground swimming pool (Sandel 1992). The recommended chlorine level was 0.2 ppm. The bacteriological effectiveness of water from this pool was compared with a control pool treated only with chlorine using a modified AOAC protocol (AOAC 1981). The data, summarized in Table 13, show that water from the pool with the attached cartridge did not kill bacteria at rates sufficient to pass the disinfection standard of the AOAC even with the presence of 0.24 ppm chlorine. In addition, the effect of the copper and silver on the kill rate in the presence of chlorine was very small. Another study also reports poor bacteri-

| Device | Application | Copper ppm | Silver ppm | Zinc ppm | Chlorine ppm | PMPS ppm |
|---|---|---|---|---|---|---|
| Cu–Ag Ionizer | pool/spa | 0.3 | 0.03 | – | ~0.2 | – |
| Cu–Ag Cartridge | pool$^A$ | 0.02–0.06 | 0.01–0.06 | – | 0.4–0.6 | – |
| “ | Spa | “ | “ | – | C | B |
| Zn–Ag Cartridge | Pool$^D$ | – | F | F | 0.5–1.0 | – |
| “ | Pool | – | F | F | – | E |
| “ | Spa$^G$ | – | F | F | 0.5–1.0 | – |

A) Maintain at least 50 ppm cyanuric acid. Shock with 1 lb calcium hypochlorite or 1 lb of PMPS per 10,000 gallons when pool becomes hazy.

B) For chlorine treated 250-gal spa: before each use add 1 tsp Dichlor (~4 ppm av. Cl) and once a week shock with 1 tbs Dichlor.

C) For PMPS treated 250-gal spa: before each use add 1 tbs 85% PMPS (equiv. to ~4 ppm av. Cl) and once a week shock with 3 tbs PMPS.

D) Shock once a week with 1 lb calcium hypochlorite or 1 lb PMPS/10,000 gal.

E) Shock three times a week with 1 lb PMPS/10,000 gal.

F) No data available.

G) Shock once a week with Dichlor or PMPS according to manufacturer’s recommendations.

**Table 11 – Copper, Silver, Zinc Devices**

| Copper[B], ppm | Silver[B], ppm | Av. Cl, ppm | One–min % Kill |
|---|---|---|---|
| 0.39 | 0 | 0 | 1 |
| 0 | 0.06 | 0 | 2 |
| 0.48 | 0.04 | 0 | 7 |
| 0 | 0 | 0.20 | 99.9 |
| 0.47 | 0.04 | 0.20 | 99.99 |

A) For *E. coli* bacteria (Kutz, Landeen, Yahya, and Gerba 1988).

B) Provided by ionizer.

**Table 12 – Comparative Bactericidal Performance of Copper, Silver, and Chlorine[A]**

cidal performance for copper and silver ions provided by a cartridge. At 77°F, the copper and silver ions supplied by the cartridge itself provided an average of only 53% kill after 45 minutes against three test organisms (*S. faecalis, E. hirae, and P. aerogenosa*) and had virtually no effect on the kill rate when PMPS was present (Gerba and Naranjo 1999).

A zinc–silver cartridge attached to a 500–gal tank circulated at 40 gpm required 30 minutes for 99% kill (equivalent to 2.4 turnovers; Legend Labs). It's main competitor (copper–silver) provided only 13% kill under the same test conditions.

**Limitations of Cartridges** – Manufacturers of cartridges claim that bacteria can be removed from the water and inactivated on the surface of the cartridge packing. However, the rate of disinfection by this process will be very low because a typical pool requires about 6 hours for one turnover of the water and only a portion of the water (average ~30% for the copper–silver cartridge) passes through the cartridge. Furthermore, when the swimming pool pump is off (typically about 18 hours) no filtration of bacteria occurs. Even in spas, it typically takes about 30 minutes for one turnover of the water. Effective disinfection in pools occurs on a minute time scale. The amount of water passed through the pool cartridge in one minute is less than 0.1%. Thus, it is the chlorine in the water that will be doing virtually all of the disinfection, e.g., in one minute chlorine treats the entire contents of a 25,00–gal pool while the cartridge treats less than 69 gallons. Removal of bacteria by the cartridge results in buildup of bacterial residues/organic slimes that reduces this disinfection process and also decreases the release of silver into the water.

Potassium monopersulfate (PMPS), which is used as a non–chlorine shock with cartridges, is a poor disinfectant at pool temperatures but is more effective at spa temperatures.

|  | Av. Cl | *E. coli* CFU/mL |  |  |
|---|---|---|---|---|
| Solution | ppm | 0.5 min. | 1.0 min. | 10 min. |
| Cu–Ag from pool[A] | 0 | 100,000 | 94,000 | 77,000 |
| Cu–Ag from pool[A,B] | 0.24 | 73,000 | 49,000 | <1 |
| Trichlor control pool | 0.23 | 70,000 | 52,000 | 230 |
| “ | 2.08 | 850 | <1 | <1 |
| Phosphate Buffer[C] | 0.95 | <1 | <1 | <1 |

A) Provided by cartridge: copper ~25 ppb, silver ~30 ppb.

B) Pool chlorinated with Trichlor tablets.

C) Laboratory solution without cyanuric acid.

**Table 13 – Comparative Bactericidal Performance of Copper, Silver, and Chlorine**

| Algae | Copper Concentration, ppm[B] | | |
|---|---|---|---|
| | % Control | Algistatic[C] | Algicidal[D] |
| *Chlorella py.* (green) | 0 | 0.12 – 0.15 | |
| | 100 | 0.21 – 0.44 | >0.6 |
| *Phormidium in.* (blue–green) | 0 | 0.14 – 0.21 | |
| | 100 | 0.59 | >0.6 |
| *Pleurochloris py.* (mustard) | 0 | | |
| | 100 | 0.07 – 0.14[E] | >0.6[F] |

A) Tests in Allen's medium employing 300,000 cells/mL.

B) As copper triethanolamine.

C) Contact time (days): C) 14, D) 9–10, E) 7, F) 1.

**Table 14 – Control of Algae by Copper [A]**

## Algae Control

**Literature Data** – Silver, at 0.064 ppm, was shown to be effective against blue green algae (*Phormidium minn.* and *Plectonema sp.*) but not effective against green (Oocystis) and yellow–green algae (*Pleurochloris sp.*) (Adamson and Sommerfeld 1980).

It is thought that copper inhibits the growth of algae by reacting with protein sulfhydryl groups consequently affecting cell membrane permeability (Kuwabara and Leland 1986). Studies using Allen's medium have shown that low levels of copper (<0.6 ppm) are only algistatic toward common swimming pool algae (Fitzgerald and Jackson 1979) as shown in Table 14. The data show that copper is most effective against mustard (yellow) algae and least effective against blue–green (black) algae. Other data are consistent with these results (Adamson and Sommerfeld 1980). Algicidal concentrations are too high to be employed in pools because of the increased potential for staining.

Studies with green algae (*Chlorella vulgaris*) showed that using simulated swimming pool water instead of Allen's medium resulted in a lower MIC (minimum inhibitory concentration), i.e., 0.042 ppm vs. 0.45 ppm (Grenier and Denkewicz 1997).

Zinc is less effective than copper as an algistat by more than an order of magnitude. No data are available on the algistatic/algicidal effectiveness of PMPS, which is used as a non–chlorine shock.

**Ionizer Testing** – An ionizer with a 97:3 copper–silver electrode was evaluated in a heated 6800–gal outdoor aboveground test pool: temperature 80–85°F, pH 7.2–7.8, alkalinity 80 ppm and calcium hardness 300 ppm (Wojtowicz 1988). The pool was shock treated with calcium hypochlorite and the av. Cl allowed to dissipate prior to starting the test. The initial copper concentration was 0.3 ppm. This dropped to 0.2 – 0.25 ppm after three weeks. The silver concentration was very low, typically < 2 ppb. During the 52 days of the test, yellow–green algae developed on four different occasions, necessitating shock treatment with calcium hypochlorite. A control pool, stabilized with cyanuric acid and sanitized with calcium hypochlorite (free chlorine 1–3 ppm) over a similar time frame did not develop algae growth despite being treated three times per week with green, blue–green, and mustard algae.

**Cartridges** – The low concentrations of copper and silver provided by cartridges in conjunction with relatively low chlorine levels would probably result in questionable control of algae in stabilized pools. Indeed, regular use of a quat–type algicide is recommended by the manufacturer of copper–silver cartridges in cases of persistent algae infestation.

## Oxidation of Contaminants

Effective oxidation of contaminants is necessary for proper disinfection and algae control. Due to the low recommended average chlorine levels used with copper, silver, and zinc devices, bather contaminants will rise to higher levels, e.g., the urea concentration will be more than 10, 4, and 2.7 times higher in pools using ionizers, copper–silver cartridges, and silver–zinc cartridges, respectively. This will enhance the growth of bacteria and algae. Chlorine is a good oxidant for swimming pool contaminants when used at appropriate maintenance concentrations (1–

3 ppm FAC) supplemented with weekly or biweekly shock treatment (~8 ppm av. Cl).

The recommended use of PMPS at 1 lb/10,000 gal as an alternative shock treatment for pools using cartridges will be much less effective than a chlorine shock, providing an oxidation capacity equivalent to only 2.3 ppm chlorine. Furthermore, PMPS is decomposed by sunlight much faster than chlorine.

## Claims

**Chlorine Levels -** It will be very difficult to maintain the low chlorine levels (0.2 for ionizers, 0.4-0.6 for copper-silver cartridges, and 0.5-1.0 for zinc-silver cartridges) in water subjected to the twin demands of decomposition by sunlight and bather contaminant oxidation. It will also be difficult to measure these low recommended chlorine levels by test kit because they are at or near the bottom of the scale. Furthermore, these low chlorine levels will not provide adequate disinfection in stabilized pools.

**Chlorine Usage -** It is claimed that ionizers and cartridges can reduce chlorine usage by up to 90%. However, no actual pool or spa test data are provided in support of these claims. What little bactericidal data that is presented was obtained in the absence of cyanuric acid, which is known to decrease disinfection rates. In view, of the minimal effects of ionizers and cartridges (and the ions they provide) on disinfection, a significant reduction in chlorine usage does not appear to be feasible.

## Staining/Cloudy Water

Staining will occur over an extended period of time since all of the added copper and silver eventually precipitate from solution and are deposited on pool surfaces. Indeed, about 30% of the silver and 10% of the copper added to the water by an ionizer was found to be lost each day. In short term tests, blue staining was observed at ≥ 0.3 ppm copper. Copper can also cause gray or black staining or discoloration while silver can cause brown or black staining. Most manufacturers recommend a maximum copper concentration of 0.2 to 0.3 ppm to avoid staining. Some ionizer manufacturers include a stain remover and a stain inhibitor with their start up kits. Zinc can cause cloudy water by precipitation of basic zinc carbonate at concentrations of a few ppm.

## Cost

The cost of copper, silver, and zinc devices is summarized in Table 15. Ionizers are very expensive. Even the cartridge–based units are relatively expensive.

# Non–Chlorine Silver–Copper Formulations

Two non–chlorine granular formulations for treatment of pools and spas are available. Information on these is summarized in Table 16.

**Product 1 –** This product for pools consists of a mixture of copper sulfate and potassium persulfate (PPS). It does not contain a disinfectant. It is rather expensive at $66 for 10 lbs. Its claims are: controls algae, oxidizes, adjusts pH, clarifies water, and maintains alkalinity and hardness. However, this product does not contain any ingredients that will control alkalinity or hardness. Indeed, the product contains sodium bisulfate, an acidic compound that lowers pH and alkalinity. Additional bisulfate is formed by decomposition of PPS.

The recommended concentrations are: copper 0.2 – 0.8 ppm (preferably 0.2–0.4 ppm) and potassium persulfate 1.5 ppm minimum. Copper concentrations of ≥ 0.3 ppm can cause staining of plaster surfaces. The minimum concentration of 1.5 ppm potassium persulfate is equivalent to 1.0 ppm av. Cl in terms of oxidizing capacity. Without taking into account its oxidizing effectiveness, this concentration will be insufficient to effectively oxidize bather contaminants in the absence of an effective shock treatment. Since this system lacks an effective disinfectant, control of bacteria and other microbes will be compromised.

**Product 2 –** This system consists of two separate products, a disinfectant (silver oxide) and an oxidizer (i.e., PMPS). Dosing with PMPS before each use, and once a month treatment with silver oxide is recommended.

# Ultraviolet Light–Hydrogen Peroxide

## Equipment Description

This system utilizes a cell that contains an ultraviolet (UV) lamp. Swimming pool or spa water is circulated through the cell. Only that portion of the water within the cell is subjected to the combined effects of UV light and hydrogen peroxide. The UV cells are relatively expensive.

| Device | Application | Cost |
|---|---|---|
| Cu–Ag Ionizer | 10,000–25,000 gal Pool | \$1000–1500[A] |
| " | 200–1,000 gal Spa | \$400–900[A] |
| Cu–Ag Cartridge | 5,000–25,000 gal Pool | Flow Controller \$130[B] |
| " | 250–1000 Spa | Cartridge \$30[C] |
| Zn–Ag Cartridge | 20,000–gal Pool | Flow Controller \$100[D] |
| " | 40,000–gal Pool | Flow Controller \$329[D] |
| " | 250–1000–gal Spa | Cartridge[E] |

A) Replacement electrodes: \$100–150.
B) Cartridge cost \$90; requires replacement every 6 months.
C) Fits inside cartridge filter; requires replacement every 4 months.
D) 6–month cartridges: \$89 and \$151, respectively.
E) Requires replacement every four months.

**Table 15 – Cost of Copper, Silver, and Zinc Devices**

## Disinfection

Hydrogen peroxide by itself is a very poor disinfectant (Block 1991). For example, it required 500 ppm at 37°C (99°F) to inactivate *E. coli* in 10–30 minutes and 15,000 ppm at 20°C (68°F) to inactivate Poliovirus type 1 in 75 minutes. Ultraviolet light can inactivate bacteria and viruses. For example, the reported 99.9% inactivation time for *E. coli* is 60 seconds whereas *S. facecalis* required 165 seconds (White 1972). Although ultraviolet light can inactivate microorganisms, many bacteria can repair damage to their DNA. A major problem with this system is that it does not provide a residual sanitizer concentration in the main pool or spa water. Also turbidity can reduce the effectiveness of UV light.

## Algae Control

No data are available on the effectiveness of hydrogen peroxide as an algicide.

## Oxidation of Contaminants

Hydrogen peroxide itself is a poor oxidant for swimming pool contaminants. However, ultraviolet light decomposes hydrogen peroxide into hydroxyl radicals.

$$H_2O_2 + h\nu \rightarrow 2OH$$

Due to their extreme reactivity, hydroxyl radicals have a very short lifetime of about $10^{-6}$ seconds (Dorfman and Adams 1972). They react non–specifically with swimming pool contaminants. The mechanism of the oxidation involves hydrogen abstraction by OH followed by rapid reaction with oxygen. The efficiency of oxidizing swimming pool contaminants by OH is reduced by reaction with radical traps such as bicarbonate and carbonate ions.

Table 17 shows data on oxidation of swimming pool contaminants by UV– $H_2O_2$ (Wojtowicz 1989). Whereas ammonium ion and urea showed little or no

| Product | Application | Disinfectant | Algicide | Oxidizer |
|---|---|---|---|---|
| 1[A] | Pool/Spa | | 1.6% Copper Sulfate | Potassium Persulfate |
| 2 | Spa | 1% Silver Oxide | 1% Silver Oxide | PMPS |

A) Contains: oxidizer, algicide, clarifier, and 28% sodium bisulfate.

**Table 16 – Non–Chlorine Formulations**

reaction, amino acids underwent significant oxidation. On average the ratio of the ammonia yield to TOC reduction was 0.97 indicating that the oxidation yields ammonia, carbon dioxide, and water.

$$H_2NCH_2COOH + [OH/O_2] \rightarrow NH_3 + 2CO_2 + H_2O$$

Although creatinine underwent significant TOC reduction, very little ammonia and no nitrate formation occurred. The extent of TOC reduction will be lower at the lower concentrations of these compounds found in pools.

A UV-hydrogen peroxide system (15 gal/min.) was evaluated over a 3-week period in a 250 gal spa at 100°F using a 4-6 hour duty cycle and a synthetic bather insult. Analysis showed no oxidation of urea after 107 hours of operation.

| Compound$^B$ | % Yield of $NH_3$ | % Yield of $NO_3^-$ | % TOC Reduction |
|---|---|---|---|
| Ammonia | – | 0 | – |
| Urea | 2 | 0 | $2^C$ |
| Creatinine | 1.5 | 1 | 57 |
| Glycine | 65 | 0 | 70 |
| $\alpha$–Alanine | 59 | 0 | 46 |
| Valine | 63 | 2 | 59 |
| Lysine | 35 | 0 | 47 |
| Glutamic Acid | 58 | 0 | 69 |

A) ~23°C, time 4 hours, pH 7.4, alkalinity 80 ppm, calcium hardness 250 ppm.

B) Containing 2.26 ppm nitrogen.

C) Calculated.

**Table 17 – Oxidation of Swimming Pool Contaminants by $UV/H_2O_2^A$**

## Electrolyzers

### Equipment Description

Electrolyzers are electrolytic cells containing two electrodes, one negative (cathode) and one positive (anode). A direct current from a power supply is passed through the cell, from one electrode through the water to the other electrode. Electrolyzers are relatively expensive.

### Electrolysis of Water

Electrolyzers essentially carry out electrolysis of water, i.e., they dissociate water into its components: hydrogen and oxygen. Water ionizes to a slight extent to hydrogen and hydroxyl ions.

$$4H_2O \rightarrow 4H^+ + 4OH^-$$

The hydrogen ions are attracted to the negative electrode where they are reduced to neutral hydrogen ions that rapidly recombine to form a molecule of hydrogen gas.

$$4H^+ + 4e^- \rightarrow 4H \rightarrow 2H_2$$

The hydroxyl ions are attracted to the positive electrode where they are oxidized to hydroxyl radicals that rapidly react to form water and oxygen atoms which themselves recombine to molecular oxygen.

$$4OH^- \rightarrow 4OH + 4e^- \rightarrow 2H_2O + 2O \rightarrow 2H_2O + O_2$$

The overall reaction is:

$$2H_2O \rightarrow 2H_2 + O_2$$

To avoid an explosion between the hydrogen and oxygen, air may have to be purged through the cell.

### Swimming Pool Evaluation

This system was evaluated on a 20,000–gal pool in Las Vegas, NV from September 1994 to June 1995 (Hafer 1995). During the first phase of the test (September 14 to December 6), the pool was treated periodically with a combination of sodium hypochlorite, Dichlor, and an algicide. The av. Cl ranged from 0.09 to 0.25 ppm. Data for only 7 out of 83 days was presented. Despite the use of chlorine and algicide, black algae were observed. In addition, high bacteria counts > 200 CFU/mL were observed on numerous occasions: heterotrophic 4 out of 7 and coliforms 3 out 6. The test has been critiqued (Wojtowicz 1998b).

## Disinfection/Algae Control

Since electrolyzers do not provide a sanitizer residual, they will be ineffective in disinfecting the pool and in control of algae.

## Oxidation of Contaminants

Oxidation of water contaminants will not be very significant, because in contrast to the UV–$H_2O_2$ system, which generates hydroxyl radicals in the bulk of the water flowing through the UV cell, electrolyzers generate hydroxyl radicals in a very thin film at the surface of the positive electrode. The transient OH radicals and O atoms that are formed react extremely rapidly in this film before they have a chance to diffuse into the bulk water. Thus, most of the water passing through the electrolytic cell is unaffected by these reactive species.

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