

# Comparison of Swimming Pool and Spa Sanitizers and Sanitation Systems

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*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 bromochlorodimethylhydantoin. 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, polyhexamethylene 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 a significant improvement in performance and/or cost effective advantage to chlorine.*

## Sanitizer Consumption

Domestic sanitizer consumption data are shown in the Table 1 (Wojtowicz 1993). The Table shows that chlorine in various forms is by far the predominant sanitizer. Bromine is used to a small extent, accounting for about 5% of the market. Other sanitizers such as hexamethylene biguanide, ozone, ionizers, etc. are used to a very small extent.

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## 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.

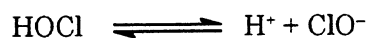
## Chlorine

### Sources and Delivery Systems

The various chlorine sanitizers and their typical available chlorine contents are shown in Table 3. Bleach is added to water by pouring around the pool or spa perimeter, granular sanitizers are added by broadcasting, and tablets are employed in feeders, skimmers, or floaters. Chlorine, hypochlorites, and trichlor are used primarily in pools, whereas dichlor and bromochlorodimethylhydantoin are used mainly in spas.

### Active Agent and pH Sensitivity

All chlorine sanitizers on dissolution in water form biocidally effective hypochlorous acid, which exists in equilibrium with the less effective hypochlorite ion, the relative amounts varying with pH according to the following equilibrium reaction.



The percentage of hypochlorous acid varies from 58 to 47% from pH 7.4 to 7.6.

## Chloramines

Chlorine reacts with nitrogen-containing bather

contaminants forming chloramines, which represent biocidally ineffective combined chlorine. Although eye irritation has been attributed to presence of certain chloramines (e.g., nitrogen trichloride), pH excursions and extended swimming periods can also cause eye

irritation. Chloramines are not a problem in outdoor pools because they are decomposed by sunlight and can also be oxidized by chlorine (Wojtowicz 1999, 2000b). Oxidation is accomplished by maintaining a sufficient free chlorine level or by periodic shock treat-

Sanitizer	Thousands of Tons
Calcium hypochlorite	50.0
Chloroisocyanurates	48.8 <sup>A</sup>
Sodium hypochlorite (Cl <sub>2</sub> equivalent)	37.3
Chlorine gas <sup>D</sup>	13.6 <sup>B</sup>
Bromochlorodimethylhydantoin	7.7 <sup>C</sup>
Lithium hypochlorite	2.9

A) 1992, B) 1995, C) 1993, D) Small amounts of chlorine are generated *in situ* via electrochemical generators.

**Table 1 – US Sanitizer Consumption in Swimming Pools, Spas, and Hot Tubs (1992-5)**

Sanitizer/Oxidizer	Weight (lb)	Cost (\$)	\$/lb Equiv. Av. Cl
Calcium Hypochlorite	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 to the Consumer**

Compound	Form	% Av. Cl
Chlorine gas	Liquefied gas in cylinders	100
Calcium hypochlorite	Granules, Tablets	65 & 75
Lithium hypochlorite	Granules	35
Sodium hypochlorite (Bleach)	Solution	10-15
Sodium dichloroisocyanurate (Dichlor)	Granules	56 & 62
Trichloroisocyanuric acid (Trichlor)	Tablets	90

**Table 3 – Chlorine Sources**

Microorganism	Ct (ppm*min)*
<i>E. coli</i>	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. Ct values will be lower at higher temperatures.

**Table 4 – Antimicrobial Activity of Chlorine  
Ct Values for 99% Inactivation at 5°C and pH 6-7 (Hoff 1986)**

ment. Indeed, the presence of significant concentrations of chloramines is indicative of insufficient free chlorine.

### Disinfection

Chlorine in the form of hypochlorous acid is a broad-spectrum disinfectant that is effective against bacteria and viruses as shown in Table 4. Ct values are higher for parasites such as *Giardia* and *Cryptosporidium*. 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).

### Stabilization and its Effect on Disinfection

Chlorine is decomposed by sunlight, e.g., unstabilized chlorine is greater than 90% decomposed in about 3 hours. However, in the presence of as little as 25 ppm of cyanuric acid, decomposition is reduced to only 35% (Nelson 1974). Since stabilization is accomplished by reducing the concentrations of hypochlorous acid and hypochlorite ion, the rate of disinfection is affected (Wojtowicz 1996). To compensate for this, higher av. Cl concentrations are necessary as the concentration of cyanuric acid increases as shown in Table 5.

### Algae Control

Chlorine is effective in controlling most algae (Palmer and Maloney 1955). Their growth can be prevented by maintaining an adequate free chlorine residual. In addition to maintaining a sufficient free chlorine level, periodic brushing and vacuuming of the pool is advised. It is also recommended that pool water be shocked every other week when the air temperature is below 85°F and every week when the temperature is above 85°F. When algae infestations occur, they can be treated with chlorine alone, e.g., a green algae bloom can be completely cleared-up by shocking the pool with chlorine or a hypochlorite. Even black algae can be eradicated by multiple shock treatments.

### Oxidation of Contaminants

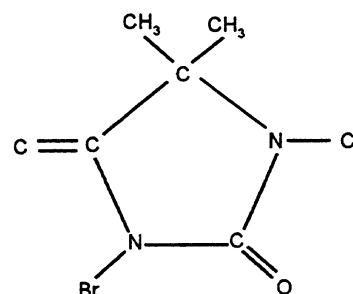
One of the requirements of a sanitizer or sanitation system is an oxidizing agent, since it is necessary to oxidize bather and other contaminants because they are nutrients for algae and microorganisms. Chlorine oxidizes both inorganic and organic contaminants, especially urea, ammonia, amino acids, and creatinine that are the main bather contaminants (Wojtowicz 1999, 2000b).

### Reaction with Ancillary Chemicals

Chlorine is a strong oxidant and will react with organic-based ancillary chemicals such as quaternary ammonium compounds, copper chelates, scale and stain inhibitors, defoamers, and enzymes. Consequently, these chemicals should not be routinely added to pool or spa water since they consume free chlorine and can affect disinfection. Furthermore, scale and stain inhibitors contain phosphorus, which is a food for algae and can also cause cloudy water at relatively low concentrations (~5 ppm).

### Bromine

#### Sources



**Bromochlorodimethylhydantoin** - Bromine is supplied by 3-bromo-1-chloro-5,5-dimethylhydantoin (BCDMH, structure shown above), which has a total av. halogen content equivalent to ~56% av. Cl. Commercial product is often referred to as 1-bromo-3-chloro-5,5-dimethylhydantoin. However, this is inconsistent with the fact

Cyanuric Acid (ppm)	Available Chlorine (ppm)
25	0.6
50	1.2
100	2.3
150	3.5
200	4.7

**Table 5 – Minimum Available Chlorine for 30-second 99% Kill Time\***

\*Estimated values for *E. coli* at 85°F (Wojtowicz 2000a).

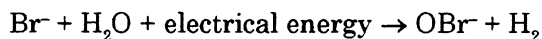
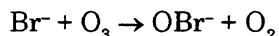
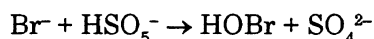
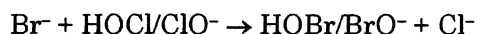
that the more stable N-Cl moiety prefers the electronic environment provided by the adjacent methyl groups. BCDMH is marketed in tablet form for sanitizing swimming pools via feeders. Since BCDMH has a lower equivalent av. Cl content and is less soluble than Trichlor, it requires larger feeders for equivalent feed rates. BCDMH is also marketed in granular form for use in spas.

In water, BCDMH reacts with excess dimethylhydantoin (DMH, the parent compound of BCDMH) forming monobromo (BrDMH) and monochloro (ClDMH) derivatives (reaction 1). The bromine substituent hydrolyzes to a small extent forming an equilibrium concentration of hypobromous acid (reaction 3). 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. It reacts slowly with bromide ion to form the monobromo derivative (reaction 2), taking several hours for completion.

- (1)  $\text{BrClDMH} + \text{DMH} \rightarrow \text{BrDMH} + \text{ClDMH}$
- (2)  $\text{ClDMH} + \text{Br}^- \rightarrow \text{BrDMH} + \text{Cl}^-$
- (3)  $\text{BrDMH} \rightleftharpoons \text{DMH} + \text{HOBr}$

There have been reports of bather skin irritation in spas sanitized with BCDMH in Canada and in the UK.

**Bromide Plus Oxidant** - Free available bromine (HOBr/BrO<sup>-</sup>) can also be generated *in situ* from calcium or sodium bromide and an oxidizing agent such as chlorine, hypochlorites, chloroisocyanurates (Dichlor or Trichlor), potassium monopersulfate, ozone, or electrical energy.



### Bromamines

As with chlorine, bromine reacts with ammonia nitrogen, forming bromamines. Although bromamines are better disinfectants than chloramines, they are less stable, being decomposed more easily by the breakpoint process and by sunlight.

### Disinfection/Algae Control

As with chlorine, the disinfecting properties of bromine are due to hypobromous acid. Bromine is in general less effective than chlorine (at normal pool pH) against bacterial spores (Marks and Strandkov 1950), bacteria (Zhang 1988), and viruses (Taylor and Johnson 1972) on a ppm basis. The concentration of hypobromous acid is less sensitive to pH changes than that of hypochlorous acid. Build-up of dimethylhydantoin will reduce the bactericidal effectiveness of bromine from BCDMH. Bromine is toxic to many species of algae at appropriate concentrations.

### Swimming Pool Evaluation

BCDMH was evaluated using a feeder in a 25,000-gal residential pool. BCDMH feeders are larger than Trichlor feeders because of slower erosion rates. Free and combined bromine averaged 2.6 and 0.5 ppm, respectively using a 24-hr pump duty

Compound	Av. Cl/N Mol Ratio	Br <sup>-</sup> Ion ppm	Reaction Time Min.	% Oxidation of Nitrogen
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	8
"	1.8	40	60	6
Glycine	1.8	0	60	60
"	1.8	40	60	>79

**Table 6 - Effect of Bromide Ion on Oxidation of Nitrogen Compounds by Chlorine (Wojtowicz 1999, 2000b)**

cycle. A total of 85 lbs. of BCDMH was used during the 3-month long test corresponding to a daily usage of 15 oz per day. In addition, 13 lbs. (average of 2.3 oz./day) of Dichlor was used for shocking the pool to control algae. The total sanitizer usage of 17.3 oz. is much higher than necessary to treat a similar pool with calcium hypochlorite, amounting to an average of 7.4 oz./day, i.e., 3.8 oz. for normal maintenance and 3.6 oz for shock treatment. Although bacteria counts were low, some algae growth was observed.

### Oxidation of Contaminants

With the exception of creatinine, the main swimming pool contaminants are more rapidly oxidized by bromine than by chlorine as shown in Table 6. The increased oxidation in the presence of bromide ion is due to formation of more reactive bromine derivatives.

### 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.

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). The main ingredient is dimethylhydantoin DMH, the parent compound of BCDMH.

The degree of stabilization of BROMIshield and DMH are similar (see Table 6). DMH is a better bromine stabilizer than cyanuric acid, e.g., 300 ppm of cyanuric acid being required to provide the same extent of stabilization as 50 ppm dimethylhydantoin. However, DMH-stabilized bromine is still much less

stable than cyanuric acid-stabilized chlorine.

Addition of a hypochlorite to water containing DMH forms considerable amounts of the 1-chloro derivative that analyzes as combined chlorine (58–73% CAC). However, if the hypochlorite is pre-reacted with sodium bromide to form hypobromite, then very little combined halogen (5–10%) is formed. The degree of stabilization is about 10% better in the former case.

### Reaction with Ancillaries

Like chlorine, bromine will oxidize ancillary chemicals added to pool or spa water.

### Ozone

#### Properties

Ozone is a gas at ordinary temperatures. It is slightly soluble in water in which it is rather unstable with a typical half-life of about 25 minutes in tap water at 20°C. In addition, ozone is readily decomposed by sunlight. It also tends to volatilize from water, which is a concern because ozone is a toxic gas with a maximum exposure level of only 0.1 ppm.

#### Generation of Ozone

Because ozone is unstable and explosive in concentrated form, it must be generated on-site. Ozone can be generated from air or oxygen using ultraviolet light (UV) or electrical energy, i.e., silent or corona discharge (CD) (Wojtowicz 1996).



The moisture content of the inlet gas and the temperature of the UV lamp or CD cell affect the ozone output.

Stabilizer	Conc., ppm	NaBr, ppm	Av. Hal. ppm <sup>A</sup>	% Decomposition <sup>B</sup>
Cyanuric Acid	50	0	3.4	35
Cyanuric Acid	50	100	4	100
"	150	0	3.6	19
"	150	100	4.6	96
"	300	100	4.6	74
BROMIshield	50	100	5.2	76
DMH	50	100	4.6	74

A) Bromide oxidizing agent: NaOCl. Analysis performed using the FAS-DPD method; calculated as av. Cl.

B) Exposure time 4 hours.

### Table 7 – Comparative Stabilizer Studies (Wojtowicz 2000)

Studies carried-out outdoors in bright sunlight at temperatures of 70-85°F in one-gallon glass containers.

**UV Ozone Generators** – UV ozone generators (ozonators) produce very low concentrations, <0.1 wt. %. 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 185nm radiation produce higher concentrations. 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.

**CD Ozone Generators** – By contrast to UV ozonators, properly designed CD ozone generators produce much higher concentrations, typically 1–2 wt. % with 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 marketed in the US are only marginally better than UV ozonators in terms of ozone output and concentration.

### Ozone Transfer into Water

The ozone produced by ozonators must be 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 flowrates. For a given transfer efficiency, the aqueous ozone concentration increases with the gas phase ozone concentration.

### Disinfection

Although ozone is an effective broad-spectrum disinfectant, the disinfection rate can be affected by the presence of readily oxidizable organic matter that consumes ozone. Ozone cannot be used as a primary sanitizer because of its volatility and toxicity. If the ozone residual is sufficient for effective control of microorganisms, then the concentration of ozone above the water will exceed the recommended limit (for an 8-hour exposure) of 0.1 ppm (OSHA). Thus, ozone requires a primary sanitizer and is typically used in conjunction with chlorine.

### Algae Control

Ozone is toxic to many types of algae. However, swimming pools cannot take advantage of this because ozone cannot be used as a primary sanitizer.

### Oxidation of Contaminants

**Literature Data** – Rate constants on the kinetics of ozone reactions with various compounds (Hoigne, *et al.* 1983–1985) indicate that the reactivity of ozone varies widely and is dependent on the functionality of the substrate. Indeed, ozone reacts very slowly with typical bather contaminants such as ammonia, urea, and creatinine.

**Laboratory Data** – Laboratory tests show 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 1989).

### Evaluation of UV Ozonators

**Disinfection** – Two brands of commercially

Ozonator	Test	Ozone g/h	Results
A1	250-gal spa	0.25 <sup>B</sup>	poor bactericidal performance
A2	6800-gal pool	0.5 <sup>C</sup>	green algae bloom after 3 days of continuous operation <sup>A</sup>
B1	250-gal spa	0.3 <sup>D</sup>	poor oxidation of urea in synthetic bather insult
B2	6800-gal pool	1.0 <sup>E</sup>	green algae bloom after 4 days of continuous operation <sup>A</sup>

A) Water shock treated with calcium hypochlorite prior to test. Temp. 80–85°F, pH 7.2–7.8, alkalinity 80 ppm, calcium hardness 300 ppm.  
Chlorine equivalent ppm/day: B) 9.3, C) 0.7, D) 11.2, E) 1.4.

**Table 8 – Summary of Evaluation of UV Ozonators**

available UV ozonators were evaluated under swimming pool and spa conditions. The results, summarized in Table 8, indicate that typical UV ozonators by themselves are not effective for either pool or spa treatment (Wojtowicz 1985). The bactericidal effectiveness of UV 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 (~55% inactivation in 1 hour at 77–88°F) that essentially ceased when the water was warmed to spa temperatures (i.e., 100–104°F).

**Oxidation** – The oxidation of urea by UV ozone was also evaluated under spa conditions. To simulate a bather load, the spa was treated with a synthetic bather load. A total of 27 grams of urea was added via the loading during the 36 cumulative hours of testing. Essentially no oxidation of urea occurred based on the fact that there was little or no change in the urea concentration and no nitrate formation was observed.

### Use of Ozone in Pools and Spas

As discussed earlier, ozone absorption is incomplete, and since UV ozonators do not provide for offgas 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.

**UV Ozonators** - Due to a high bather density, spas have a very high sanitizer demand compared to pools. Bathers introduce a substantial sanitizer demand even after a 15-minute immersion. In order to achieve satisfactory disinfection and oxidation of bather contaminants (urea, amino acids, ammonia, etc.), a spa requires 4–5 ppm FAC before bather entry, maintenance of the FAC in the recommended range (3–5 ppm) while the spa is in use, and shock treatment (8 ppm av. Cl) after each use (Brigano and Carney 1984). UV ozone cannot meet or even substantially satisfy the requirements of spas.

UV ozone is too dilute to provide a significant benefit to residential pools and spas. There is insufficient contact time at the point of injection where the concentration is highest and the final ozone concentration in the pool or spa is extremely low (a few ppb). Consequently no significant oxidation of bather contaminants can occur because of slow kinetics. Therefore, chlorine will have to perform essentially all of the oxidation of bather contaminants. This will require normal NSPI recommended chlorine levels, supplemented by periodic shock treatment and will not result in reduced chlorine usage. Based on the

observed poor performance (i.e., slow disinfection and contaminant oxidation), the capital, maintenance and utility costs associated with the use of UV ozonators are hard to justify.

**CD Ozonators** – 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. Deozonation of water utilizing granular activated carbon (GAC) also removes chlorine that has to be replenished. In European practice the design of ozone systems for treating pools is generally based on the German developed standard (DIN 1984), that utilizes flocculation, filtration, ozonation, GAC filtration, and finally chlorination. A specified amount of water (~30 L/bather) is purged from the pool in order to limit the concentration of mineral salts. Since ozone is not effective in oxidizing bather impurities such as ammonia, urea, and creatinine, removal of these contaminants will be dependent on the GAC filter where adsorbed contaminants may be consumed by means of the biological activity of the bacteria that are probably present. Data from European pools employing the ozone–GAC process show that ozone can reduce operating costs by about 20%. Treating water by this process is cost effective only for large, heavily used pools (e.g., public, commercial, or private).

In the US, the German ozone–GAC process has been modified 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). Although DIN requires full-flow ozonation, some systems employ only partial or slip-stream ozonation (in some cases as low as about 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. For new installations, pre-filter ozonation is employed that utilizes the filter as a combination contact chamber/GAC filter/sand filter. Still this system is cost effective only for large, heavily used pools. 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.

### NSF Approval

Only one UV ozonator (rated at 1 gram per hour ozone) was tested by NSF and requires the use of NSF approved brominators or chlorinators delivering 4 ppm bromine or 2 ppm chlorine (NSF 1985). Even larger output CD ozonators are subject to this requirement.

## Claims

UV ozonator manufacturers typically claim lower chlorine consumption (typically 60 to 90%) and the ability to operate pools and spas at lower chlorine concentrations (~0.5 ppm). However, these claims have not been substantiated by independent test data on disinfection or oxidation of bather contaminants under actual pool or spa conditions.

It has been previously shown that ozone is not capable of meeting the requirements of spa sanitation from the standpoint of disinfection and oxidation of bather contaminants. In outdoor residential swimming pools, the main sanitizer demand is decomposition by sunlight. Indeed, this sanitizer demand exceeds that due to bather contaminants. In addition, stabilized pools require higher chlorine concentrations than unstabilized pools for acceptable disinfection. UV ozone is too dilute to significantly assist in disinfection or oxidation of bather contaminants. Thus, a reduction in chlorine concentration and usage does not appear to be feasible.

## 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. The suggested retail price of the CD ozonators for 25,000 to 100,000-gal residential 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.

## Potassium Monopersulfate (PMPS)

### Properties

**Composition** – Potassium monopersulfate ( $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ ), is marketed as an 85% product. It contains ~4.5% active oxygen and is employed primarily as a non-chlorine oxidizer.

**Reaction with Halide Ions** – Potassium monopersulfate (PMPS,  $\text{KHSO}_5$ ) 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 in sunlight (decomposition rate ~20%/hour). Even in the absence of sunlight PMPS decomposes at ~4%/hour at room temperature. The rate is even higher at spa temperature: ~16%/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 much more effective at spa temperatures. For example, at 77°F, PMPS provided only 16.8% inactivation of *E. coli* bacteria in 2 minutes, but at 104°F it provided >99.9999% inactivation (Gerba and Naranjo 1999). No data are available 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,

Component	Disinfectant	Algicide	Oxidizer
Active Agent	PHMB <sup>A</sup>	Quat <sup>B</sup>	Peroxide <sup>C</sup>
% Active	20%		30%
Pool Conc. ppm	6 – 10	2 – 2.5	0 – 27

A)  $[-(\text{CH}_2)_6-\text{NH}-\text{C}(=\text{NH})-\text{NH}-\text{C}(=\text{NH})-\text{NH}-]_N$ ; checked weekly.  
 B) Alkyldimethylbenzyl ammonium chloride; dosed weekly.  
 C) Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ); Added once a month or as needed to control cloudiness or haziness.

**Table 9 – PHMB Swimming Pool System\***  
 \*The system also includes a stain controller and an enzyme filter cleaner.



Organism	MIC <sup>A</sup> (ppm)
<i>Staphylococcus aureus</i>	4
<i>E. coli</i>	4
<i>Pseudomonas aeruginosa</i>	20

A) MIC = Minimum inhibitory concentration

**Table 10 – Bacteriostatic Data for PHMB\***  
\*Active concentration (Block 1991)

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 cartridge 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.

#### 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.

### Polyhexamethylene Biguanide (PHMB)

#### System Description

This system consists of three main components and two ancillary chemicals as shown in Table 9. This multi-component system is more expensive than chlorine.

Test Duration days	Samples	Incubation Period	Bacteria Counts > 200 CFU/mL	
			Control	PHMB
90	26	one week	1	7
100	35	2 days	0	20

**Table 11 – Bactericidal Comparison of Chlorine and PHMB**

Device	Applica-tion	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 <sup>A</sup>	0.02-0.06	0.01-0.06	—	0.4-0.6	—
"	Spa	"	"	—	—	8.8 <sup>B</sup>
Ag-Zn Cartridge	Pool	—	E	E	0.5-1.0	C
"	Pool	—	E	E	—	D
"	Spa	—	E	E	—	—

- A) Maintain at least 50 ppm cyanuric acid. Shock with 1 lb calcium hypochlorite or 1 lb of PMPS when pool becomes hazy.
- B) Add before use: based on one tablespoon 85% DuPont Oxone (equivalent to 4 ppm chlorine). Once a week add 3 tablespoons of PMPS.
- C) Shock once a week with 1 lb PMPS/10,000 gal.
- D) Shock three times a week with 1 lb PMPS/10,000 gal.
- E) No data available.

**Table 12 – Copper, Silver, Zinc Devices**

## Incompatibilities

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.

## Problems

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.

## Bactericidal Effectiveness

**Literature Data** – Literature data (Table 10) show that PHMB itself may not control *Pseudomonas aeruginosa* since its average concentration in pools is 8 ppm.

**Swimming Pool Evaluation** – The PHMB system was evaluated in a 6800-gal swimming pool (Sandel 1997). The data are summarized in Table 11. 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 on pool surfaces.

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 poor oxidant for ammonia and urea (the main pool contaminant), and other organic matter. Thus, organic matter can build-up and may cause cloudiness, development of biological growths, and inadequate disinfection.

## Copper, Silver, and Zinc Devices

Sanitizer systems based on metal ions employ copper, silver, or zinc. The ions can be generated electrically (i.e., copper-silver or silver ionizers), or by dissolution (copper-silver and silver-zinc cartridges). Ionizers deliver much higher concentrations than cartridges (Table 12). The metal ion concentrations delivered by silver-zinc cartridges have not been disclosed. These devices are installed in the external recycle loop of the pool or spa.

Silver 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 that their bactericidal effectiveness gradually diminished with time due to build-up of an organic slime that coated the silver particles, necessitating periodic cleaning (White 1972).

## Disinfection

The antimicrobial activity of copper and silver ions 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. Com-

Copper <sup>A</sup> , ppm	Silver <sup>A</sup> , 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) Provided by ionizer.

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

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

pared to chlorine, silver is a poor bactericide, e.g., at 25°C and pH 7.5, 30 ppb silver required 86 minutes for 99.9% inactivation of *E. coli* (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. Evaluation in swimming pools showed that silver was unsatisfactory as a bactericidal agent (Shapiro and Hale 1937).

The data in Table 13 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 will result in 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.

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. 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).

Cartridges provide even lower metal ion concentrations than ionizers, consequently the small enhancement in % kill shown in Table 13 will be further reduced. A cartridge designed for pools up 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. The data, summarized in Table 14, 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.

The disinfection data in Table 13 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 lower recommended av. Cl levels may not provide satisfactory control of bacteria in a stabilized pool.

Manufacturers of cartridges claim that bacteria can be removed from the water and inactivated on the surface of the cartridge packing. However, the extent 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 16 hours or more) 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 pool water passed through the 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. Indeed, the cartridges by themselves exhibit very slow kill rates. For example, a zinc-silver cartridge attached to a 500-gal tank circulated at 40 gpm required 30 minutes for 99% kill of *E. coli* (equivalent to 2.4 turnovers; Legend Labs). At 77°F, cartridge supplied copper and sil-

Solution	Av. Cl ppm	<i>E. coli</i> CFU/mL		
		0.5 min.	1.0 min.	10 min.
Cu-Ag from pool <sup>A</sup>	0	100,000	94,000	77,000
Cu-Ag from pool <sup>A,B</sup>	0.24	73,000	49,000	<1
Trichlor control pool	0.23	70,000	52,000	230
"	2.08	850	<1	<1
Phosphate Buffer <sup>C</sup>	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 14 – Comparative Bactericidal Performance of Copper, Silver, and Chlorine**

ver ions provided an average of only 53% kill after 45 minutes against three test organisms (*S. faecalis*, *E. hirae*, and *P. aeruginosa*) (Gerba and Naranjo 1999). Removal of bacteria by the cartridge results in a buildup of bacterial residues/organic slimes that reduces this disinfection process and also decreases the release of silver into the water.

Potassium monopersulfate (PMPS) is a poor disinfectant at pool temperatures but can be effective at spa temperatures. The presence of cartridge supplied copper and silver ions had no effect on the performance of PMPS at pool temperatures (Gerba and Naranjo 1999).

### Algae Control

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 15. The data show that copper is most effective against mustard algae and is 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.

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. 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 dosed three times per week with green, blue-green, and mustard algae.

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.

The low concentrations of copper and silver provided by cartridges in conjunction with relatively low chlorine levels may result in questionable control of algae in stabilized pools. Indeed, regular use of an algicide is recommended by the manufacturer of copper-silver cartridges in cases of persistent algae infestation.

### Oxidation of Contaminants

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	% Control	Copper Concentration, ppm <sup>A</sup>	
		Algistatic <sup>B</sup>	Algicidal <sup>C</sup>
<i>Chlorella py.</i> (green)	0	0.12 – 0.15	
	100	0.21 – 0.44	>0.6
<i>Phormidium in.</i> (blue-green)	0	0.14 – 0.21	
	100	0.59	>0.6
<i>Pleurochloris py.</i> (mustard)	0		
	100	0.07 – 0.14 <sup>D</sup>	>0.6 <sup>E</sup>

A) As copper triethanolamine.

Contact time (days):

B) 14 C) 9–10 D) 7 E) 1

**Table 15 – Control of Algae by Copper\***

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

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 the copper–silver cartridge will be much less effective than a chlorine shock, providing an oxidation capacity equivalent to only 2.3 ppm chlorine. Effective oxidation of contaminants is necessary for proper disinfection and algae control. By contrast with chlorine, there is little or 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.

A silver ionizer has been marketed that was used in conjunction with hydrogen peroxide. Previous comments have shown that silver is a poor disinfectant and hydrogen peroxide a poor oxidant.

### Chlorine Consumption

Copper, silver, and zinc device manufacturers claim that chlorine consumption can be reduced by as much as 90%. However, these claims are based solely on disinfection data that in addition were obtained in the absence of cyanuric acid. It is a well-established fact that cyanuric acid increases the kill time of microorganisms such as bacteria (O'Brien 1960, Wojtowicz 1996); see also applicable discussion in chlorine section. Stabilized pools require an NSPI recommended maintenance concentration of 1–3 ppm FAC. For adequate control of algae, this should be supplemented by periodic shock treatment (biweekly when the temperature is below 85°F and once a week when it is above). The main chlorine demand in pools is due to photochemical decomposition by sunlight. The other significant chlorine demand is oxidation of

bather contaminants. The combination of these chlorine demands and the necessity of maintaining a higher FAC in stabilized pools will make it very unlikely that these systems can provide adequate disinfection, control of algae, and oxidation of bather contaminants while reducing chlorine consumption by as much as 90%.

### Staining / Cloudy Water

Staining will occur over an extended period of time since all of the added copper and silver eventually precipitates from solution and is deposited on pool surfaces. Indeed, about 30% of the silver and 10% of the copper added to the water was found to be lost each day in ionizer tests. In short term tests, blue staining was observed at  $\geq 0.3$  ppm copper. 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. Silver can cause brown or black staining. 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 16. Ionizers are very expensive. Even the cartridge-based units are relatively expensive.

### Non-Chlorine Formulations

Two non-chlorine granular formulations for treatment of pools and spas are available. Informa-

Device	Application	Cost
Cu–Ag Ionizer	10,000–25,000 gal Pool	\$1295 <sup>A</sup>
"	200–1,000 gal Spa	\$395 <sup>A</sup>
Cu–Ag Cartridge	5,000–30,000 gal Pool	Flow Contoller \$160 <sup>B</sup>
"	250–1000 Spa	Cartridge \$30 <sup>C</sup>
Zn–Ag Cartridge	20,000–gal Pool	Flow Contoller \$100 <sup>D</sup>
"	40,000–gal Pool	Flow Contoller \$329 <sup>D</sup>
"	250–1000–gal Spa	Cartridge \$45 <sup>E</sup>

A) Replacement electrodes: pool \$149, spa \$129.  
 B) Cartridge cost \$30; 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 16 – Cost of Copper, Silver, and Zinc Devices**

tion on these is summarized in Table 17.

**Product 1** – One 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. In fact it will lower alkalinity because it contains sodium bisulfate and also forms potassium bisulfate.

The oxidizer, potassium persulfate (i.e., potassium peroxydisulfate,  $K_2S_2O_8$ ), is a poor oxidant at normal pH (it works better at acidic pH). The product also contains sodium bisulfate, an acidic compound that lowers pH, however, it will not lower the pH into the acidic range because of the buffering of the water. Although persulfate ion has a high oxidation potential its reactions with bather contaminants are slow. Persulfate ion can oxidize cupric ion ( $Cu^{2+}$ ) to  $Cu^{3+}$  that may be a kinetically more effective oxidant. Sunlight decomposes persulfate ion into sulfate ion free radicals that are effective oxidants, but the decomposition rate is only about 5%/day. No data are

presented on the effectiveness of this system in the oxidation of bather contaminants.

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  $\geq 0.3$  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. In addition, no data on disinfection, algae control, or oxidation of bather contaminants such as urea and ammonia are available at pool or spa temperatures.

**Product 2** – This system consists of two separate products, a disinfectant (silver oxide) and an energizer (i.e., an activator and oxidizer). Once a month treatment is recommended. First of all, silver is a poor disinfectant. Secondly, if the oxidizer is potassium persulfate, then oxidation of bather contaminants will also be compromised. If the oxidizer is PMPS, then

Product	Application	Disinfectant	Algicide	Oxidizer
1 <sup>A</sup>	Pool		1.6% Copper Sulfate $CuSO_4$	Potassium Persulfate
1 <sup>B</sup>	Spa			"
2	Spa	1% Silver Oxide, $Ag_2O$	1% Silver Oxide, $Ag_2O$	"

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

B) Same as (a) except no copper sulfate

C) Not specified

**Table 17 – Non-chlorine Formulations**

Compound <sup>A</sup>	% Yield of $NH_3$	% Yield of $NO_3^-$	% TOC <sup>B</sup> Reduction
$NH_4Cl$	–	0	–
Urea	2	0	2 <sup>c</sup>
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) Containing 2.26 ppm nitrogen

B) Calculated

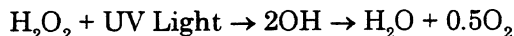
**Table 18 – Oxidation of Swimming Pool Contaminants by  $UV/H_2O_2$  \***

Laboratory study at  $\sim 23^\circ C$  in water with 40 ppm hydrogen peroxide at pH 7.4, alkalinity 80 ppm, hardness 250 ppm, irradiation time 4 hours.

acceptable disinfection can be obtained if an appropriate concentration is maintained. However, this will not occur given the once a month treatment frequency.

## Ultraviolet Light and Hydrogen Peroxide

Lamps that produce ultraviolet (UV) light have been used for pool and spa sanitation. They are used in conjunction with hydrogen peroxide that is dissociated by UV light into hydroxyl radicals.



Hydroxyl radicals are extremely reactive and short-lived. They can recombine to form oxygen and water or they can react with water contaminants.

### Laboratory Evaluation

Although hydroxyl radicals react with bather contaminants such as amino acids, byproduct ammonia is formed that is not readily oxidized because it is present as ammonium ion that is relatively unreactive toward hydroxyl radicals; see Table 18 (Wojtowicz 1988). Even after 4 hours, the TOC reduction for amino acids was still incomplete.

### Spa Evaluation

The UV-H<sub>2</sub>O<sub>2</sub> system was evaluated over a three-week period in a 250-gal. portable spa employing balanced water at 100°F and a recirculation rate of 15 gpm (Wojtowicz 1988). Hydrogen peroxide usage averaged 60 g/day and the concentration averaged 40 ppm. The spa was treated with a synthetic bather load containing primarily urea. After 107 hours of UV irradiation, analysis showed the presence of 47 ppm urea compared to 40 ppm added, indicating that no oxidation by peroxide had occurred. This was consistent with the fact that there was no increase in the nitrate content of the spa water.

### Disadvantages of UV-H<sub>2</sub>O<sub>2</sub>

- Bacteria can repair UV damage.
- Does not provide a disinfectant residual in the pool or spa.
- Poor oxidation of ammonia and urea.
- UV lamps can become coated with scale requiring cleaning and also need to be replaced from time to time due to reduced intensity.
- They are expensive.

## Electrolyzers

Electrolyzers are electrolytic cells that convert water into hydrogen and oxygen by means of electrical energy. Hydrogen atoms are transient intermediates in formation of hydrogen molecules and hydroxyl radicals and oxygen atoms are intermediates in formation of oxygen molecules. However, these highly reactive species are very short-lived and do not significantly diffuse into the bulk water but rather rapidly recombine at the electrode surface and therefore they are largely unavailable for reaction with water contaminants.

### 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 of 6. The test has been critiqued (Wojtowicz 1998).

### Disadvantages of Electrolyzers

- They do not provide a disinfectant residual and do not control bacteria or algae.
- They are not effective in oxidizing water contaminants.
- They are expensive.

## About the Author

Now retired, **John A. Wojtowicz** was a senior consulting scientist for Olin Corp. Seventeen of his 47 years of industrial experience was spent in the swimming pool chemical area and primarily involved swimming pool chemistry and process and product research on calcium hypochlorite, trichloroisocyanuric acid, and sodium dichloroisocyanurate. He holds over 55 U.S. patents and has published over 40 technical papers. He is currently a chemical consultant (Chemcon) residing at 3266 N. 151st Drive, Goodyear, AZ 85338, phone/fax #602-535-8851. His areas of expertise include swimming pool chemistry, manufacture and product and process development in hypochlorites and chloroisocyanurates, alternate sanitizers and sanitation systems (ozone, hydrogen peroxide-UV, bromine, etc.), chloramines and bromamines, computer programming, and expert witnessing.

## References

- Block, S. S. "Disinfection, Sterilization, and Preservation." Lea & Febiger, Philadelphia, PA, Fourth edition, 1991.
- Brigano, F.A. and J.F. Carney. Paper presented at the 84th Meeting of the American Society of Microbiology, St. Louis MO, March 4-9, 1984.
- DIN 19643 (English): Treatment and Disinfection of Swimming pool and Bathing Water (Berlin, Beuth Verlag, 1984).
- Dumas, Bob. "Bromine Stabilizer Passes Early Test." *Pool & Spa News*, January 13, 1999, p 1-2.
- Eichelsdorfer, D. and J. Jandik. "Long Contact Time Ozonation for Swimming Pool Water Treatment." *Ozone Science and Engineering* 7(2)(1985):93-106.
- Fitzgerald, G. P. and D. F. Jackson. "Comparative Algicidal Evaluation Using Laboratory and Field Algae." *Journal of Aquatic and Plant Management* 17(1979):66-.
- Gerba, Charles P. and Jaime N. Naranjo. "Comparison of the Anti-bacterial Properties of Hot Tub Additives and Disinfectants." Seminar at NSPI meeting in Las Vegas, NV, 1999.
- Hafer, D. "A Field Evaluation of the Bi-Polar Oxygen Sanitation System/Mineral Purification System." *Journal of the Swimming Pool and Spa Industry*, 1(3)(1995):39-51.
- Hartwig, W. "To DIN or not to DIN: Ozonation of Pool Water in Public and Commercial Pools." *Journal of the Swimming Pool and Spa Industry*, 2(1)(1996):25-33.
- Hass, C. N. and R. S. Engelbrecht. "Chlorine Dynamics during Inactivation of Coliforms, Acid-Fast Bacteria, and Yeasts." *Water Research* 14(1980):1749-.
- Hoff, J. C. "Inactivation of Microbial Agents by Chemical Disinfectants." U.S. Environmental Protection Agency, Report no. EPA/600/2-86/067, 1986.
- Hoigne, J. and H. Bader. "Rate Constants for Reaction of Ozone with Organic and Inorganic Compounds - I: Non-dissociating Organic Compounds." *Water Research*, 17(1983):173-183.
- Hoigne, J. and H. Bader. "Rate Constants for Reaction of Ozone with Organic and Inorganic Compounds - II: Dissociating Organic Compounds." *Water Research*, 17(1983):184-185.
- Hoigne, J., H. Bader, and W. R. Haag. "Rate Constants for Reaction of Ozone with Organic and Inorganic Compounds - III: Inorganic Compounds and Radicals." *Water Research*, 19(1985):993-1004.
- Kutz, S. M., L. K. Landeen, M. T. Yahya, and C. P. Gerba. "Microbiological Evaluation of Copper-Silver Disinfection Units." 4<sup>th</sup> Conference on Chemical Disinfection, Binghamton, NY April 10-13, 1988.
- Marks, H. C. and F. B. Strandkov. "Halogens and their Mode of Action." *Annals of the New York Academy of Sciences* 53(1950):163-.
- Nalepa, C.J. *et al.* "Development of a Bromine Stabilizer for Outdoor Pools." Handout, 4<sup>th</sup> Annual NSPI Water Chemistry Symposium, Las Vegas, NV November 30, 1999 (see page 12 of this publication).
- National Sanitation Foundation. Standard 50 for Circulation System Components for Swimming Pools, Spas, and Hot Tubs. Ann Arbor, MI., 1985.
- Nelson, G.D. "Swimming Pool Disinfection with Chlorinated-s-triazinetrione Products." Report No. 6862, 1975, Monsanto Chemical Co., St. Louis, MO.
- OSHA, U.S. Occupational Safety and Health Administration, Washington, DC.
- Palmer, C. M. and T. E. Maloney. "Preliminary Screening for Potential Algicides." *Ohio Journal of Science* 55(1955):1-.
- Sandel, B. B. 1992, Olin Corp. private communication.
- Sandel, B. B. "Disinfection with Chlorine Products - Some Lessons Learned." *Water Chemistry and Disinfection: Swimming Pools and Spas*, NSPI Symposium Series Volume 1, 1996, pp. 80-85.
- Shapiro, R. and F.E. Hale. "An Investigation of the Katadyn Treatment of Water with Particular Reference to Swimming Pools." *Journal of the New England Water Works Association*, 51, 113 (1937).
- Taylor, D. S. and J. D. Johnson. "Kinetics of Viral Inactivation by Bromine." in A. J. Rubin, ed., *Chemistry of Water Supply and Treatment*, Ann Arbor Publishers. Ann Arbor, MI, 1975, pp 369-407.
- Wojtowicz, J. A. Unpublished data. (1985-1990).
- Wojtowicz, J.A. "Chlorine Monoxide, Hypochlorous Acid, and Hypochlorites." Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, Vol. 5, John Wiley & Sons, Inc., New York, NY, pp 932-968, 1993.
- Wojtowicz, J. A. Letter to the Editor, *Journal of the Swimming Pool and Spa Industry*, 3(1)(1998):41-43.
- Wojtowicz, J. A. "Relative Bactericidal Effectiveness of Hypochlorous Acid and Chloroisocyanurates." *Journal of the Swimming Pool and Spa Industry*, 2(1)(1996):34-41.
- Wojtowicz, J. A. "Ozone", Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, Vol. 17, 1996, John Wiley & Sons, Inc., New York, NY.
- Wojtowicz, J. A. Letter to the Editor, *Journal of the*



- Swimming Pool and Spa Industry* 3(1)(1998): 41-43.
- Wojtowicz, J. A. (1999) "Fate of Nitrogen Compounds in Swimming Pool Water." *Advances in Pool and Spa Water Chemistry - Analysis, Measurement, and Testing*, NSPI Symposium Series Volume III 1998, pp. 40-44.
- Wojtowicz, J. A. (2000a) "Cyanuric Acid Technology." *Journal of the Swimming Pool and Spa Industry*, to be published.
- Wojtowicz, J. A. (2000b), "Oxidation of Nitrogen Compounds in Swimming Pool Water." *Journal of the Swimming Pool and Spa Industry*, to be published.
- Wuhrman, K. and F. Zobrist. "Investigation of the Bactericidal Effect of Silver in Water." *Schweiz. Z. Hydrol.* 20(1958):218- .
- Zhang, Z. "Disinfection Efficiency and Mechanisms of 1-Bromo-3-chloro-5,5-dimethylhydantoin." Ph. D. Thesis, Univ. of Houston, 1988.
-