Sanitizer and Oxidizer Product Information Summaries

John A. Wojtowicz
Chemcon

Summary sheets containing product description, properties, and performance data for various sanitizers, oxidizers, and sanitation systems shown below are based on the following published papers:

Wojtowicz, J. A., "Survey of Swimming Pool/Spa Sanitizers and Sanitation Systems", Journal of the Swimming Pool and Spa Industry 4(1)2001:9 -29.

Wojtowicz, J. A., "Use of Ozone in the Treatment of Swimming Pools and Spas", Journal of the Swimming Pool and Spa Industry 4(1)2001:41 - 53.

Some of the categories covered in the summaries include: disinfection, algae control, oxidation of contaminants, cost, and cost effectiveness.

1. *Chlorine*
2. *Bromine*
3. *Ozone: Data on Disinfection and Oxidation*
4. *Ultraviolet (UV) Ozone*
5. *Corona Discharge (CD) Ozone (DIN Design)*
6. *Corona Discharge (CD) Ozone (Modified DIN Design)*
7. *Copper, Silver, and Zinc*
8. *Copper-Silver Ionizers*
9. *Copper-Silver Cartridges*
10. *Zinc-Silver Cartridges*
11. *Potassium Monopersulfate*
12. *Potassium Peroxydisulfate (Persulfate)*
13. *Polyhexamethylene Biguanide (PHMB)*
14. *Ultraviolet Light (UV) and Hydrogen Peroxide*

About the Author

John A. Wojtowicz currently works as a consultant, and is retired from his position as senior consulting scientist for Olin Corp. Seventeen of his 47 years of industrial experience were 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 patents and has published over 40 technical papers. His areas of expertise include swimming pool chemistry, manufacture and product and process development in hypochlorites and chloro-isocyanurates, alternate sanitizers and sanitation systems (i.e.: ozone, hydrogen peroxide–UV, bromine, etc.), chloramines and bromamines, computer programming, and expert witnessing. He may be reached at Chemcon, 623–535–8851.

Journal of the Swimming Pool and Spa Industry
Volume 5, Number 1, pages 20–38

1. CHLORINE

Sources		**Form**	**% Av. Cl**	**$/lb av. Cl**
	Chlorine	Liquefied Gas	100	<1.00
	Calcium Hypochlorite	Granular & Tablets	65 (75)	2.77
	Lithium Hypochlorite	Granular	35	~8.50
	Sodium Hypochlorite	Liquid	10	~1.50
	Sodium Dichloroisocyanurate	Granular	56 (63)	3.21
	Trichloroisocyanuric Acid	Granular & Tablets	90	2.22
Active Agent	•At pool pH, all chlorine products provide free available chlorine (FAC).			
	•FAC consists of the disinfectant hypochlorous acid (HOCl) and hypochlorite ion (ClO^-).			
	•The concentration of HOCl is controlled by the equilibrium: $HOCl \rightleftarrows H^+ + ClO^-$ Ionization constant $K_A = [H^+][ClO^-]/[HOCl] = 2.88 \times 10^{-8}$ at 25°C $[HOCl]/[ClO^-] = [H^+]/K_A = 10^{-pH}/K_A = 50/50$ @ pH 7.54			
Decomposition By Sunlight	•Unstabilized chlorine is more than 90% decomposed by sunlight (≥290 nm) in a few hours due to the photoinstability of hypochlorite ion, which has maximum absorption at 290 nm but absorbs UV light out to 350 nm.			
Stabilization	•Chlorine is stabilized by cyanuric acid (CA) against decomposition by sunlight primarily by formation of monochloroisocyanurate ion, which absorbs UV light well below 290 nm (ie, 215 nm). •Photochemical decomposition is ~1%/day and thermal decomposition is ~13%/day (Wojtowicz 2002).			
Disinfection	**Effect of pH**	•Disinfection rate changes with pH due to the changing ratio $[HOCl]/[ClO^-]$.		
		•Increased ionization of HOCl at higher pH is offset by increased hydrolysis of chloroisocyanurates.		
	Effect of Temperature	•Disinfection rate increases by 260% from 75 to 85°F.		
	Effect of Cyanuric Acid	•Decreases disinfection rate by reducing the equilibrium conc. of HOCl.		
	Effect of Ammonia and Amino-N Compounds	•Decreases disinfection rate by formation of chloramines (ie, combined chlorine, CAC) that strongly bind HOCl.		
	Effect of Microorganism	**Ct (5°C, pH 6-7)** Hoff 1986	**99% Kill Time t (min.) C = 0.5 ppm av. Cl**	
	E. coli	0.034–0.05	0.068–0.10	
	Polio 1	1.1–2.5	2.2–5.0	
	Rotavirus	0.01–0.05	0.02–0.10	
NSPI Recom-Mendations		**Minimum**	**Ideal**	**Maximum**
	FAC (ppm): Pools	1	2-4	10
	FAC (ppm): Spas	2	3-5	10
*100-120 ppm for chloroiso-cyanurate or bromine treated pools.	**CAC (ppm)**	0	0	0.2
	Cyanuric Acid (ppm)	10	30–50	150
	pH	7.2	7.4–7.6	7.8
	Carbonate Alkalinity (ppm)	60	80–100*	180
	Calcium Hardness (ppm)	150	200–400	500–1,000+
Algae Control	•Chlorine at 2 ppm is toxic to many species of algae (Palmer and Maloney 1955).			
	•A newly formed green algae bloom can be completely oxidized by a single shock dose of hypochlorite chlorine, eg, 1 lb calcium hypochlorite per 10,000 gals.			
	•An infestation of black algae can usually be eradicated with a triple shock dose of hypochlorite chlorine in combination with brushing and vacuuming.			
Oxidation of Contaminants	•Chlorine oxidizes contaminants such as ammonia, urea, amino acids, creatinine, etc.			
	•Ammonia reacts with chlorine to form chloramines, some of which (eg, trichloramine) are potential eye irritants. •Ammonia chloramines absorb UV light and are therefore decomposed by sunlight.			
	•Ammonia is oxidized via **breakpoint chlorination** via the overall reaction: $2NH_3 + 3HOCl \rightarrow N_2 + 3HCl + 3H_2O$			
	•For example, 0.25 ppm ammonia N (1.26 ppm CAC as monochloramine) is 87% oxidized by 3.55 ppm av. Cl in 10 minutes at pH 7.5 and 20–25°C (Wojtowicz 1999).			
	•Oxidation of other nitrogen compounds is slower, the reaction rate varying in the following order: ammonia > amino acids > urea > creatinine			
Cost	•Chlorine in its various forms is the most economical and cost effective method of swimming pool and spa sanitation, eg, the single season sanitizer cost for a 25,000-gal. residential swimming pool in Phoenix, AZ using Trichlor tablets for maintenance and liquid bleach for shock treatment is less than $100.			

2. BROMINE

Sources	Bromine Compounds	Form	% Equiv. Av. Cl	$ per lb Equiv. Av. Cl
	Bromochlorodimethylhydantoin (BCDMH) 63.5% av. Br, 28.2% av. Cl	Granular & Tablets 90.4% purity	56.4 (actual)	7.80
	Dibromodimethylhydantoin	Granular & Tablets	49.6 (theoretical)	Not Available

Generation of Bromine	•Bromine can be generated in situ from bromide ion plus oxidizing agents such as hypochlorites, chloroisocyanurates, monopersulfate, ozone, or electrical energy.
Active Agent	•At pool pH, all bromine products provide free available bromine, ie, the disinfectant hypobromous acid (HOBr) as well as hypobromite ion (BrO^-).
	•The concentration of HOBr is controlled by the equilibrium: $HOBr \rightleftarrows H^+ + BrO^-$ Ionization constant $K_A = [H^+][BrO^-]/[HOBr] = 7.2 \times 10^{-9}$ at 25°C. $[HOBr]/[BrO^-] = [H^+]/K_A = 10^{-pH}/K_A = 82/18$ @ pH 7.5 = 50/50 @ pH 8.1
Decomposition by Sunlight	•As with chlorine, unstabilized bromine is more than 90% decomposed by sunlight (≥290 nm) in 3 hours due to the photoinstability of hypobromite ion, which has maximum absorption at 330 nm but absorbs UV light out to about 390 nm. .
Decomposition by Hypochlorite	•Hypochlorite ion can cleave the hydantoin ring, especially at higher pH, eg, dichlorodimethylhydantoin forms NCl_3, CO_2, and N-chloroisopropylamine,
Stabilization Wojtowicz 2000	•Bromine can be partially stabilized by dimethylhydantoin (DMH), eg, 50 ppm DMH reduces decomposition from ~100% to 75% in four hours.
	•By contrast, 300 ppm cyanuric acid is required to attain a similar improvement.

Factors Affecting Disinfection		
	Effect of pH	•Although the disinfection rate changes with pH due to the changing ratio $[HOBr]/[BrO^-]$, it is less sensitive to pH than in the case of chlorine.
	Effect of Temperature	•As with HOCl, disinfection rate increases with temperature.
	Effect of Dimethylhydantoin Concentration	•Decreases disinfection rate by reducing the equilibrium concentration of HOBr.
	Effect of Ammonia and Amino-N Compounds	•Disinfection rate decreases by formation of bromamines (combined bromine) that are about half as effective as free bromine but are less stable than chloramines.

Disinfection Data Gerba & Naranjo 1999

•On a ppm basis, bromine is a less effective bactericide than chlorine, eg, 3 ppm FAC from hypochlorite provided 99.99% inactivation of *S. faecalis* and *P. aeruginosa* after 2 minutes at 25°C and pH 7.5.

•By comparison, 5 ppm electrogenerated bromine (EGB) provided 92.8 and 85.5 % inactivation under the same conditions (see below).

	% Inactivation (5 ppm Free Av. Bromine, 25°C, pH 7.5)			
	S. faecalis		***P. aerugenosa***	
Time (min.)	**EGB**	**BCDMH**	**EGB**	**BCDMH**
2	92.8	66.1	85.5	85.2
4	99.9	99.8	99.99	99.8

NSPI Recommendations		Minimum	Ideal	Maximum
	Free Av. Br (ppm): Pools & Spas	2	4-6	10
	pH	7.2	7.4–7.6	7.8
	Carbonate Alkalinity (ppm)	60	100-120	180
	Calcium Hardness (ppm)	150	200–400	500–1,000+

Algae Control	•As with chlorine, bromine is toxic to many species of algae.
Oxidation of Contaminants	•Bromine oxidizes contaminants such as ammonia and urea faster than chlorine.
	•The oxidation of ammonia is similar to breakpoint chlorination: $2NH_3 + 3HOBr \rightarrow N_2 + 3HBr + 3H_2O$
	•As with chlorine, oxidation of other nitrogen compounds is slower, the reaction rate varying in the following order: ammonia > amino acids > urea > creatinine.
Eye and Skin Irritation	•Ammonia bromamines are less irritating to the eyes than chloramines. •Instances of skin irritation (itch and rash) have been reported in pools and spas treated with BCDMH (British Medical Journal 13 August 1983).
Cost	•Bromine sanitation is more expensive than chlorine sanitation.

3. OZONE: DATA ON DISINFECTION AND OXIDATION

Ozone Disinfection Data
Hoff 1986

•Although ozone is a broad-spectrum disinfectant (see data below), the disinfection rate can be affected by presence of readily oxidizable matter.

Microorganism	Ct (ppm•min) @ 5°C and 6-7 pH
E.coli	0.02
Polio 1	0.1–0.2
Rotavirus	0.006–0.06
G. Lamblia cysts	0.5–0.6
G. Mutis cysts	1.8–2.0

Laboratory Data at ~22°C and pH 7.5 on Oxidation of Swimming Pool/Spa Contaminants at High Contaminant and Ozone Concentrations (Wojtowicz 1989).

Contaminant		Ozone	Reaction Time	Mols Ozone Consumed per Mol Contaminant	
	Conc. (ppm)	ppm	Mins.	Theoretical	Calc'd.*(Found)
Urea	26.9	12.4	68	8	0.03 (0.01)
Ammonia	1.6	11.4	55	4	0.2 (0.3)
Glycine	6.7	13.8	13	7	3.2 (2.9)
Creatinine	10.1	14.5	72	18	1.6 (0.3)

*Based on published rate constants (Hoigne et al 1983-1985).

Calculated Data on Oxidation of Contaminants

•Calculated data for some bather contaminants are based on 1 ppm total N, 1 ppm CD ozone, and a 2–minute reaction time using published rate constant data at 25°C.

Contaminant	Nitrogen ppm	Contaminant ppm	Calc'd. % Contaminant Oxidation
Urea	0.876	1.877	0.002
Monochloramine	0.0443	0.163	2.2
Glycine	0.0433	0.232	14[A]
Creatinine	0.0363	0.098	0.03

A) Byproducts ammonia and formaldehyde are largely unoxidized.

Comparative Calculated Data on Oxidation of Contaminants

Initial Contaminant Oxidation Rate (% per min.)[A]

Contaminant	Ozone		Chlorine[D]	Bromine[D]
	1.6 ppb[B]	1.0 ppm[C]	2.3 ppm	4.6 ppm
Ammonim ion	0	0	3.8	7.9
Ammonia	1.6×10^{-5}	0.01	3.8	7.9
Monochloramine	1.7×10^{-3}	1.1	>3.8	>7.9
Urea	1.3×10^{-6}	8×10^{-4}	0.11	0.23
Creatinine[E]	1.1×10^{-5}	7×10^{-3}	0.06	0.04
Glycine[E]	1.5×10^{-2}	1.7	0.33	>2.6

A) pH 7.5, 20-25°C, 0.25 ppm bound nitrogen per contaminant. B) Calculated data for steady state UV ozone concentration in spas. C) Calculated for initial CD ozone conc. in swimming pool contact chamber. D) Experimental data (Wojtowicz 1998 and 2000). E) For decomposition to CO_2 and nitrate for ozone and CO_2 and nitrogen for chlorine.

Summary of Ozone's Oxidative Capabilities

•Despite its high oxidation potential (2.07 volts), the reactivity of ozone toward organic matter varies widely (over 10 orders of magnitude) and depends on the original functionality of a compound as well as that of its byproducts, eg, the initial rate constant for oxidation of the amino acid α-alanine is 6.4×10^4 L/mol/sec. whereas that for the byproducts ammonia, acetaldehyde, and acetic acid are 20, 1.5, and $\leq 3\times10^{-5}$ L/mol/sec., respectively.

•Ozone reacts exceedingly slowly with urea (the main bather contaminant) and also slowly with another bather contaminant: creatinine.

•Decomposing ozone does not appear to affect the rate of reaction.

•Ozone does not react at all with ammonium ion (the main form of ammonia at pool pH), but does react slowly with the small fraction of ammonia as well as with its chlorinated product: monochloramine.

•Ozone only partially oxidizes organic matter and reacts primarily with readily oxidzable functionalities such as amine ($-NH_2$) and sulfhydryl (-SH) groups (present in amino acids and possibly protienaceous matter) and with compounds containing reactive carbon-carbon double bonds (-C=C-).

•Both chlorine and bromine are better overall oxidants for bather contaminants as shown in the table above.

4. ULTRAVOILET (UV) OZONE	
Device Description	•A plastic enclosure containing one or more UV lamps, fitted with an air inlet and outlet.
Principle of Operation	•UV light dissociates oxygen into atoms that react with oxygen molecules forming a very low ozone conc. (0.03–0.07 vol. %) that is injected into the water via a vacuum venturi in the return line.
Claimed Ozone Output	**Pools:** 0.25–0.83 g/h; **Spas:** 0.042–0.33 g/h
Contact/Reaction Chamber	•None
Calc'd. Ozone Absorption	**Pools:** 71–87%; **Spas:** 83–94%
Ozone Offgas Destruction	•None
Calc'd. Ozone Conc. in Offgas	**Pools:** 58 ppm; **Spas:** 67 ppm
Calc'd Steady State Ozone Conc. Before Reaction	**Pools:** 0.34–0.78 ppb **Spas:** 0.35–3.0 ppb
Calc'd. Time to 99% Steady State	**Pools:** 40 min.; **Spas:** 9 min.
Testing of UV Ozonators	
Disinfection	•Spa tests with UV ozone (0.25 g/h) alone showed a very slow disinfection rate (~0.8%/min.) of bather-introduced bacteria as the water was heated from 77 to 95°F over a two-hour period. •Tests at spa temperature (~100°F) showed no killing of bacteria over a 30-min. period (Wojtowicz 1985).
	•Other tests at 106°F showed similar results (Watt et al 1999).
	•**Conclusion:** Ozone concentration too low (as shown above) for significant effect on disinfection.
Algae Control (Wojtowicz 1985)	•Swimming pool tests with UV ozone (0.5 and 1.0 g/h) resulted in green algae blooms after 3 and 4 days despite continuous ozonation.
Oxidation of Contaminants	•No oxidation of urea was observed under spa conditions over a 36-hour period at an ozone feed rate of 0.3 g/hour (Wojtowicz 1985). •Other tests showed similar results (Adams et al 1999).
	•**Conclusion:** Ozone concentration too low (as shown above) for significant effect on oxidation.
Generation of Bromine From Bromide Ion	•Spa tests at 25 and 35°C with UV ozone (0.3 g/h) resulted in available bromine generation efficiencies of only 21 and 8%, respectively.
Assessment	
Chlorine Concentration	•**Manufacturer Recommendation:** Typically about 0.5–1.0 ppm
	•**Technical Assessment:** The minimal effect of UV ozone on disinfection does not support claims of reduced chlorine maintenance concentrations. •Therefore, current NSPI recommended ideal free chlorine levels for pools (2–4 ppm) and spas (3–5 ppm) would be necessary for adequate disinfection.
Chlorine Usage	•**Claims:** up to 50–80% reduction.
	•**Technical Assessment:** The minimal effect on disinfection and lack of significant oxidation capacity does not support claims of reduced chlorine usage.
Operational and Analytical Deficiencies	•No way to tell if unit is operating properly.
	•Ozone output decreases with age of lamps.
	•No way to tell if lamps need replacement.
	•No method to measure the low ozone concentrations.
Safety	•The lack of ozone offgas destruction poses a potential toxicity problem in indoor spas due to ozone build up.
	•OSHA permissible exposure limit is 0.1 ppm for an 8-hour exposure.
NSF Testing	•Only one ozone generator (rated at 1g/h) was tested and requires NSF approved feeders delivering 2 ppm chlorine or 4 ppm bromine.
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 ozone offgas destruction.
	•The UV lamps require periodic replacement.

5. CORONA DISCHARGE (CD) OZONE: DIN 19643

CD Ozone Generation	•Typically, ozone is generated electrically (ie, by corona discharge) from very dry air. The required ozone concentration is ≥18 g/m^3 (~1.5 wt. %).	
The Ozone-Granular Activa-ted Carbon (GAC) Process DIN 1984	**Applicability**	•Large public pools with high bather loads.
	Treatment Sequence	•Flocculation (1 g/m^3 Alum), rapid sand filtration, full flow ozonation, GAC filtration, ozone offgas destruction, and chlorination.
	Ozone Dosage	•0.8–1.0 ppm if 28°C
		•1.0–1.2 ppm above 28°C
	Contact Time (min.)	•≥2 minutes; allows inactivation of microorgan-isms and a moderate reduction of COD by partial oxidation of bather contaminants.
	GAC Filtration	•Destroys ozone (to ≤0.05 ppm) and chlorine.
	Chlorine Dosage	•0.5 ppm
	Pool Turnover Time	•~2 hours
	Water Purge	•~30L/bather to limit mineral salt build-up.
Disinfection Objectives	**Combined Chlorine**	≤0.2 ppm @ pH 7.2-7.8
	Oxidation-Reduction Potential (ORP)	750 mv. @ pH 6.5-7.5 770 mv @, pH 7.5-7.8
	Effective Kill Time	~30 seconds
	Bacterial Colonies	<100 per mL
	E. coli	0 per 100 mL
Algae Control	•Although ozone is toxic to many species of algae, it is not used as the primary sanitizer.	
Chemical Oxygen Demand (COD) Reduction Data	•Studies show that the average organic pollutants entering the pool per bather correspond to a COD of 4.0 g $KMnO_4$/cu. meter.	
	•The combined **flocculation-filtration-chlorination process** reduces the COD (excluding urea and ammonia) of the water by the equivalent of 2.0 g $KMnO_4$/cu. meter. •Thus 2 cu. meters of water/bather have to be treated to remove the pollutant load.	
	•In the combined **flocculation-filtration-ozonation-GAC filtration-chlorination process**, the COD reduction is 20% higher, ie, 2.4 g $KMnO_4$/cu. m. •Thus only 1.67 cu. meters/bather have to be treated to remove the pollutant load, resulting in a smaller treatment plant.	
COD Reduction Summary	•Flocculation-filtration-chlorination: 80% •Ozonation-GAC filtration: 20%	
Effects of GAC Filtration	•GAC destroys ozone and chlorine and can convert ammonia chloramines such as monochloramine to elemental nitrogen.	
	•GAC adsorbs organic matter and microorganisms and may become biologically active, increasing contaminant removal through biodegradation.	
	•The relative effects of ozone and GAC on COD reduction are unknown, but in view of ozone's ineffectiveness in oxidizing major bather contami-nants, COD reduction by GAC may in fact exceed that due to ozone.	

Cost of Ozone Generators (not including peripheral equipment)	**Ozone Production Rate (g/h)**		**Approximate**
	Air Feed (1.5 wt. % O_3)	**O_2 Feed (10 wt. % O_3)**	**Cost**
		2–7	\$4,000–\$11,000
	12–200	20–320	\$10,000–\$25,000
		750–1800	\$35,000–\$60,000

Impact of Equipment Cost	•The additional capital requirements for a full ozone–GAC system are high and recovery of capital costs through lower operating expenses can take many years.
	•This process is cost effective only for large, heavily used pools.
Generation of Bromine From Bromide Ion	•Ozone is sometimes used to generate available bromine for sanitizing whirlpools (ie, spas). •A spa test at 25°C with a CD ozonator (5 g/h) showed an efficiency of only 50%. •The efficiency would be lower at a typical spa temperature of 40°C due to increased ozone decomposition.

6. CORONA DISCHARGE (CD) OZONE: MODIFIED DIN DESIGN			
A. Full Flow Ozonation Hartwig 1996	**Applicability**	•New installations.	
	Process Sequence	•Flocculation (optional), ozonation, mixed media filtration, ozone offgas destruction, and chlorination.	
	Filter Construction	•Requires ozone-resistant sand filters, sized to allow sufficient head space for ozone contacting.	
	Ozone Injection	•Main stream or side stream	
	Recommended Ozone Dosage	•Varies from 0.15–1.0 ppm depending on water facility.	
	Contact Time	•No data available (DIN design requires ≥ 2 min.).	
	Aqueous Ozone Destruction	•A GAC layer atop the sand media destroys the dissolved ozone as well as chlorine.	
	Chlorine Dosage	•DIN design requires 0.5 ppm.	
	Turnover Time	•~6 hours.	
Concerns	•Flocculation-filtration-chlorination can remove 80% of the pollution load.		
	•Eliminating flocculation will seriously affect contaminant removal and put more emphasis on much more expensive ozonation.		
	•The lower turnover rate will also affect contaminant removal.		
B. Partial Flow Ozonation Hartwig (1996)	**Applicability**	•Retrofit to existing installations.	
	Process Sequence	•Filtration, side stream ozonation, contacting/GAC filtration, offgas ozone destruction, and chlorination.	
	% of Full Flow Ozonation	**Typical**	•10–50%
		Recommended	•25–40%
	Recommended Ozone Dosage	•Varies from 0.15–1.0 ppm depending on water facility.	
	Contact Time	•No data available (DIN design requires ≥ 2 min.).	
	Aqueous Ozone Destruction	•A combination contact chamber and GAC filter is employed, however, some prefabricated systems do not destroy ozone in solution or in offgases.	
	Chlorine Dosage	•DIN 19643 requires 0.5 ppm.	
	Turnover Rate	•~6 hours.	
Concerns	•Lack of flocculation, use of only partial flow ozonation, and a lower turnover rate than used in DIN 19643.		
Assessment of Processes A and B			
Factors Affecting Disinfection Rate	**Combined Chlorine**	•No data available.	
	ORP	•No data available.	
	Chemical Oxygen Demand	•No data available.	
Disinfection Objectives	**Bacterial Colonies**	•No data available.	
	E. coli	•No data available.	
Algae Control	•Although ozone is toxic to many species of algae, it is not used as the primary sanitizer.		
Oxidation of Contaminants	•Since use of ozone via DIN 19643 only increases the non-urea and ammonia COD reduction by about 20% (compared to chlorination) and also requires a water purge and an effective GAC filter (ie, biologically active), any significant departure from DIN 19643 specs. will result in a lower increase in COD reduction.		
	•For example, a process without flocculation, with only 10% of full flow ozonation, and with a turnover time of 6 hours cannot be expected to even come close to the COD reduction achieved by DIN 19643.		
Cost	•Expensive compared to conventional chlorination (see Sheet 5). •Actual cost will vary according to the type of system employed.		
Cost Effectiveness	•The primary application of CD ozonation is in water facilities with high bather loads.		
	•The cost effectiveness of modified DIN systems will depend on how well they remove bather contaminants and maintain acceptable water quality.		
	•As mentioned above some of the modifications are expected to remove far less COD than DIN 19643.		

7. COPPER, SILVER, AND ZINC

Sources	**Copper**	•Copper-silver ionizers and cartridges, copper sulfate, and copper chelates with citric acid and triethanolamine.
	Silver	•Copper-silver ionizers and cartridges, zinc-silver cartridges, colloidal silver, and silver compounds such as silver oxide, and silver nitrate.
	Zinc	•Zinc-silver Cartridges.

Disinfection Data For Silver Wuhrman and Zobrist 1958	**Silver (ppb)**	**99.9% Kill Time (mins.) of *E. coli**@ 25°C and pH 7.5**
	10	432
	30	86
	90	32
	270	13
	*In water containing 60 ppb of silver, 10 and 100 ppm chloride ion increased kill time by 25 and 70%, respectively. Kill time also increased by 3 mins. for each 10 ppm hardness.	

Swimming Pool Testing Shapiro and Hale 1937	•Silver was shown to be unsatisfactory for swimming pool disinfection. •Bacteria counts were unaffected and consisted of S. aureus, S. albus, and streptococci which can cause eye, ear, nose, and throat infections.
Disinfection Data for Copper-Silver Ionizer w/o Chlorine	**Swimming Pool Test:** High bacteria counts (14,000–62,000 cfu/mL) were observed on three successive periodic tests in a 16,000-gal pool (Wojtowicz 1988)

300-gal. Spa Test with 4 Bathers at 40°C (104°F) (Sandel 1996)

	Before Use	**After 15 mins.**[B]
Standard Plate Count, SPC	<1/mL	>3,000/mL
Total & Fecal Coliform, MPN[A]	0 of 5 positive	4 of 5 positive
Fecal Stretococci, MPN	0 of 5 positive	5 of 5 positive

A) Most Probable Number. B) Even after 30 mins. SPC was >3,000 cfu/mL and Fecal Stretococci (MPN) was 5 of 5 positive.

Disinfection Data For Copper, Silver, and Chlorine Kutz, Landeedn, Yahya, and Gerba 1988	**Copper (ppm)**	**Silver (ppm)**	**Av. Cl (ppm)**	**One-Minute % Kill**
	0.39	0	0	1
	0	0.06	0	2
	0.48	0.04	0	7
	0	0	0.2	99.9
	0.47	0.04	0.2	99.99

•Tests were done in well water with only 0.02 ppm chloride.
•Chloride ion is known to reduce the bactericidal effectiveness of silver.

Disinfection Data For Zinc	•Antibacterial properties of zinc are much less than for copper or silver.

Algae Control Data For Copper Fitzgerald and Jackson 1979			**Copper (ppm)**	
	Algae	**% Control**	**Algistatic**	**Algicidal**
	Chlorella py.	0	0.12–0.15	
		100	0.21–0.44	>0.6
	Phormidium in.	0	0.14–0.21	
		100	0.59	>0.6
	Pleurochloris py.	100	0.07–0.14	>0.6

Algae Control Data For Silver Adamson and Sommerfeld 1980	•Silver at 64 ppb was shown to be effective against blue-green but not against green or mustard algae.
Algae Control Data For Zinc	•Zinc is much less effective than copper by a factor of about 10.
Oxidation of Contaminants	•Copper, silver, and zinc do not possess oxidative capacity.
Staining Potential	•Silver has a tendency to adsorb onto surfaces, creating a potential for staining.
	•Copper can cause visible localized staining above 0.2–0.3 ppm.
	•Even below this concentration, a general discoloration of pool surfaces will occur over time since all added copper and silver eventually precipitate from the water.
	•For this reason, copper and silver containing algicides should be used only on an as needed basis.
Precipitation Potential	•Zinc can precipitate as basic zinc carbonate at concentrations of a few ppm and may cause cloudy water.

8. COPPER-SILVER IONIZERS	
Device Description	•An electrolytic cell consisting of a pair of copper-silver electrodes, a DC power supply, and control panel. •Device is installed in water return line to pool or spa.
Principle of Operation	•As water flows through the cell, a DC current generates soluble copper and silver ions.
Recommended Ion Concentrations	**Copper** 0.2–0.4 ppm
	Silver ~20–40 ppb (assuming 90/10 copper-silver electrodes).
Recommended Av. Cl	0 to ~0.2 ppm.
Miantenance of Chlorine Concentration	•The extremely low recommended av. Cl will be very difficult to measure because it is at the bottom of the scale.
	•It will also be difficult to maintain under the twin demands of UV decomposition and contaminant oxidation.
Chlorine Usage	•The main chlorine demand in outdoor swimming pools is due to the combined effect of sunlight and contaminant oxidation.
	•In residential pools, chlorine consumption due to sunlight exceeds that due to oxidation of contaminants, whereas, in public pools with high bather loads, the reverse may be true.
	•The presence of copper and silver ions will not reduce this demand and the low level of chlorine will not be sufficient to satisfy this demand, consequently, significant reduction in chlorine usage (as claimed) will not be possible.
Disinfection	•Swimming pool and spa tests show unacceptable disinfection in the absence of chlorine.
	•Since copper and silver contribute minimally to the disinfection rate in the presence of av. Cl, the extremely low recommended av. Cl level of 0.2 ppm would be insufficient for adequate disinfection in stabilized pools.
	•Consequently, current NSPI recommended free chlorine levels (ie, 1–3 ppm in pools and 3–5 ppm in spas) would be necessary for adequate disinfection (and contaminant oxidation).
Algae Control	•At recommended concentrations, copper acts algistatically.
	•Copper is most effective against mustard algae and least effective against black algae.
Oxidation of Contaminants	•Copper and silver do not contribute to oxidation of swimming pool water contaminants.
	•The low level of recommended chlorine level of 0.2 ppm will not be sufficient to adequately oxidize bather contaminants.
Staining/Discoloration	•Silver tends to adsorb onto surfaces creating a potential for staining.
	•Copper can cause visible localized staining above 0.2–0.3 ppm.
	•Even below this concentration, a general discoloration of pool surfaces will occur over time since all added copper and silver eventually precipitate from the water.
	•For this reason, copper and silver containing algicides should be used only on an as needed basis.
Electrode Maintenance	•Scale build-up on the electrodes necessitates periodic cleaning with acid.
NSF Approval	•Ionizers have not been approved.
Cost	•Ionizers are very expensive given their minimal effect on disinfection.

	Gallons	Ionizer	Replacement Electrodes
Pool	10,000–25,000	$1,000–$1,500	$100–$150
Spa	200–1,000	$400–$900	$100–$150

<table>
<tr><th colspan="2">9. COPPER-SILVER CARTRIDGES</th></tr>
<tr><td rowspan="4">Device Description</td><td>•According to the patent literature the heart of the device is a canister or cartridge containing a carrier (ie, granular alumina coated with ~1% metallic silver), copper metal, and a filler material (ie, activated carbon).</td></tr>
<tr><td>•Current cartridges contain ceramic pellets (~3 mm in diameter). •In addition, copper is present in readily soluble form instead of copper metal.</td></tr>
<tr><td>•The cartridge can be inserted into a plastic housing, fitted with an inlet and outlet and a valve for flow adjustment, for installation after sand or DE filters.</td></tr>
<tr><td>•Small cartridges are also available and are installed inside cartridge filters on pools or spas.</td></tr>
<tr><td>Principle of Operation</td><td>•Flow of water (~30% of full flow) through the unit quickly dissolves the copper and very slowly dissolves the metallic silver.</td></tr>
<tr><td rowspan="2">Technical Assessment</td><td>•The cartridge only works when the pump is on and adds very little to the overall disinfection rate. •Indeed, in one minute the cartridge treats less than 0.3% of the pool water (<3% in spas), whereas chlorine in the water treats 100%.</td></tr>
<tr><td>•Silver containing ceramic cartridges (so-called candles) have been known since the 1930's. •Their bactericidal effectiveness gradually decreased due to build up of organic slimes, necessitating periodic cleaning (White 1972).</td></tr>
<tr><td>Aqueous Copper Conc.</td><td>•0.02–0.06 ppm</td></tr>
<tr><td>Aqueous Silver Conc.</td><td>•0.01–0.06 ppm</td></tr>
<tr><td>Recommended Sanitizers</td><td>Pools: Stabilize with 50 ppm cyanuric acid and maintain 0.4–0.6 ppm av. Cl
<table>
<tr><th>Spas: Sanitizer Options</th><th>Potassium Monopersulfate (PMPS) Ppm</th><th>Av. Cl as Dichlor</th></tr>
<tr><td>Each Use Dosage</td><td>9.3 (equivalent to 4.3 ppm av. Cl)</td><td>~4 ppm</td></tr>
<tr><td>Weekly Dosage</td><td>~28 (equivalent to ~13 ppm av. Cl)</td><td>~12 ppm</td></tr>
</table></td></tr>
<tr><td>Maintenance of Available Chlorine</td><td>• The low recommended av. Cl (0.4 – 0.6 ppm) will be difficult to measure because it is near the bottom of the scale. • It will also be difficult to maintain under the twin demands of UV decomposition and contaminant oxidation.</td></tr>
<tr><td>Disinfection Data: Pools
Sandel 1992</td><td>•Tests showed that low concentrations of copper (0.025 ppm) and silver (0.03 ppm) provided by a cartridge had little effect on the disinfection rate alone or in chlorine sanitized and stabilized pool water.</td></tr>
<tr><td rowspan="2">Disinfection Data: Spas
Gerba & Naranjo 1999</td><td>•Tests showed no significant killing of bacteria even though unit had been in operation for 3 days prior to introduction of bacteria.</td></tr>
<tr><td>•The cartridge also had no effect on the disinfection rate when PMPS was present.</td></tr>
<tr><td>Disinfection Concerns</td><td><table>
<tr><td>Pools</td><td>•Tests show that the cartridge has a minimal effect on disinfection, consequently, the recommended chlorine level of 0.4–0.6 ppm is considered too low for effective disinfection in stabilized pools.</td></tr>
<tr><td>Spas</td><td>•Disinfection may be affected, since PMPS is not as thermally stable as chlorine.</td></tr>
</table></td></tr>
<tr><td>Algae Control</td><td>•The concentrations of chlorine and copper and silver are considered too low for effective algae control.</td></tr>
<tr><td>Contaminant Oxidation</td><td><table>
<tr><td>Pools</td><td>•The recommended chlorine level of 0.4–0.6 ppm is considered too low for effective oxidation of bather contaminants.</td></tr>
<tr><td rowspan="2">Spas</td><td>•PMPS decomposes at 20%/hour and will be 80% decomposed in 8 hours (see Sheet No. 11).</td></tr>
<tr><td>•This thermal instability may affect its oxidative capacity.</td></tr>
</table></td></tr>
<tr><td>Chlorine Usage</td><td><table>
<tr><td>Claimed</td><td>•60–80% reduction.</td></tr>
<tr><td>Assessment</td><td>•Since tests show that the cartridge does not enhance disinfection, the cartridge is unlikely to deliver on the claim of up to 80% reduction in chlorine usage and allow effective disinfection, algae control, and contaminant oxidation.</td></tr>
</table></td></tr>
<tr><td>NSF Approval</td><td>•Copper-silver cartridges have not been approved.</td></tr>
<tr><td>Cost</td><td><table>
<tr><th></th><th>Volume Gallons</th><th>Flow Controller Plus Cartridge</th><th>Replacement Cartridge</th><th>Cartridge Lifetime</th></tr>
<tr><td>Pool</td><td>10,000–25,000</td><td>$149-199</td><td>$69-99</td><td>6 months</td></tr>
<tr><td>Spa</td><td>250–1,000</td><td>-</td><td>$30</td><td>4-months</td></tr>
</table></td></tr>
</table>

10. ZINC-SILVER CARTRIDGES		
System Description	**Pools**	•The unit consists of a plastic housing with an inlet and outlet with a flow control valve and a removable cartridge that contains zinc, silver and limestone.
		•An insert containing Trichlor tablets is available as well as a flow controller for non-chlorine operation.
	Spas	•A cartridge containing the mineral reservoir is designed to fit inside the cartridge filter.
Principle of Operation	•Flow of water through the cartridge can slowly dissolve zinc and silver.	
	•Microorganisms such as bacteria may become attached to the surface of the minerals within the cartridge and undergo inactivation.	
Technical Assessment	•The cartridge works only when the pump is on and adds very little to overall disinfection rate. •Indeed, in one minute the cartridge treats less than 0.3% (<3% in spas) of the pool water, whereas chlorine in the water treats 100%.	
	•As with copper-silver cartridges, build-up of organic slimes may affect the performance.	
Aqueous Zinc Conc.	•No data available.	
Aqueous Silver Conc.	•No data available.	
Sanitizer Options	**Pools**	•Maintain 0.5–1.0 ppm av. Cl.
		•Shock once a week with 1 lb. calcium hypochlorite or 1 lb. potassium monopersulfate (PMPS) per 10,000 gals.
		•For non-chlorine operation shock 2–3 times a week with PMPS.
	Spas	•Maintain 0.5–1.0 ppm chlorine or bromine.
		•Shock once a week with Dichlor or PMPS according to manufacturers recommendations.
Maintenance of Available Chlorine	• It will be difficult to maintain 0.5–1.0 ppm av. Cl under the twin demands of decomposition and contaminant oxidation.	
Disinfection Concerns	**Pools**	•The low recommended chlorine residual of 0.5–1.0 ppm is considered too low for adequate disinfection in stabilized pools.
		•The non-chlorine option is not expected to provide adequate disinfection or algae control.
		•Based on their poor bactericidal properties, silver and zinc ions are not expected to significantly increase the disinfection rate.
		•In the absence of chlorine, the cartridge itself provides a very slow bacterial kill rate.
	Spas	•The recommended chlorine (and bromine) levels will be insufficient to meet the demands of the higher bather density in spas (Brigano and Carney 1984).
		•Shocking once a week is considered insufficient to oxidize bather contaminants.
		•Bromine will reduce the effectiveness of silver due to insolubility of silver bromide.
Algae control	•Because the concentration of zinc and silver in the pool water are not available, their effect on algae control cannot be assessed.	
Oxidation of Contaminants	•The low recommended chlorine level of 0.5–1.0 ppm is considered too low for adequate contaminant oxidation.	
	•Shocking of the pool with PMPS is much less effective than with chlorine, eg, 1 lb of PMPS is equivalent to only 1/3 of a 1-lb shock dose of chlorine.	
Chlorine Usage	**Claims**	•50–67% reduction.
	Assessment	•The cartridge is unlikely to deliver on the claim of reduced chlorine usage and allow effective disinfection, algae control, and contaminant oxidation.
Cost	20,0000-gal. Pool	Flow Controller $100; 6-month Cartridge ~$90
	40,000-gal. Pool	Flow Controller ~$330; 6-month Cartridge ~$150
	250–1,000-gal Spa	6-Month Cartridge

11. POTASSIUM MONOPERSULFATE (PMPS)

Formula	•$2KHSO_5 \bullet KHSO_4 \bullet K_2SO_4$			
Assay	•85%			
Active Oxygen	•~4.5%			
Form	•White granular powder			
Uses	**Non-chlorine Shock in Pools**	•Dosage: 1lb/10,000 gals.		
	Sanitizer/Oxidizer in Spas	•Used alone or in combination with chlorine or silver.		
Stability in Water Wojtowicz 2000		**Decomposition Rate (% per hour)**		
	Sunlight	~23		
	Room Temperature (~70°F)	~4		
	Spa Temperature (~104°F)	~20		
Disinfection in Pools Gerba & Naranjo 1999	•Tests with *E. coli* at 25°C (77°F) show that PMPS is unsuitable as a swimming pool disinfectant with inactivations of only ~17% at 2 mins. and 75% at 45 mins..			
Disinfection in Spas Gerba & Naranjo 1999		**% Inactivation @ 40°C (104°F)**		
	Time (mins.)	***S. faecalis***	***E. hirae***	***P. aerugenosa***
	2	58	28	15
	15	>99.9999	>99.9999	>99.9999
	•Data for *E. coli* show >99.9999% inactivation in 2 mins.			
	•Data for chlorine (3 ppm) show higher 2 min. inactivations of 99.99% for *S. faecalis* and 99.97 for *P. aerorugenosa*.			
Algae Control	•No data are available on the effect of PMPS on swimming pool algae.			
Oxidation of Contaminants	**Ammonium ion**	•No reaction.		
	Ammonia	•No data available.		
	Monochloramine	•Nitrate ion is main oxidation product.		
	Urea	•Nitrate ion is main oxidation product.		
	Amino Acids, Creatinine, Uric Acid, etc.	•No data available.		
	Other Organic Matter	•No data available.		
Disadvantages and Deficiencies	•Oxidizes nitrogen compounds to nitrate ion, which is a nutrient for bacteria and algae.			
	•Not stable in water subjected to heat or exposed to sunlight.			
	•Reduces pH and alkalinity due to formation of bisulfate ion. $2KHSO_5 \bullet KHSO_4 \bullet K_2SO_4 \rightarrow 3KHSO_4 + K_2SO_4 + 2O$ $3HSO_4^- + 3HCO_3^- \rightarrow 3SO_4^{2-} + 3CO_2 + 3H_2O$			
	•The recommended 1-lb. shock dose is equivalent to only 1/3 of a 1-lb. chlorine shock.			
	•Very expensive: $55 per 25 lbs. or $11.22/lb. equivalent av. Cl.			

12. POTASSIUM PEROXYDISULFATE (PPS, PERSULFATE)		
Formula	•$K_2S_2O_8$	
Assay	•>95%	
Form	•White granular powder	
Stability in Water		**Decomposition Rate (%/day)**
	Sunlight	~5
	Swimming Pool Temperature	Very slow
	Spa Temperature	Very slow.
Uses	•Blended with Dichlor for use in shock treatment. •As non-chlorine oxidizing agent usually in combination with copper.	
Effect on Disinfection	•No data are available.	
	•By comparison with monopersulfate, persulfate itself probably has negligible anti-bacterial properties even in the presence of copper or silver ions.	
Effect on Algae Control	•No data is available.	
	•Best guess is that persulfate itself has negligible anti-algal properties.	
Oxidation of Contaminants	•PPS is normally a sluggish oxidant compared to potassium monopersulfate and requires activation as discussed below.	
	Effect of Sunlight	•Sunlight dissociates persulfate into reactive sulfate ion radicals: $S_2O_8^{2-} + UV \rightarrow 2SO_4^-$
		•Sulfate ion radicals are effective in oxidation of organic matter (Minisci et al 1983).
	Effect of Silver and Copper Ions	•Silver (and possibly copper) ions can catalyze oxidation reactions of persulfate via formation of divalent silver (or trivalent copper) (Minisci et al 1983).
		•The effectiveness at swimming pool concentrations has not been documented.
Deficiencies	•Normally reacts slowly with bather contaminants.	
	•Reduces pH and alkalinity due to formation of bisulfate ion on decomposition: $S_2O_8^{2-} + H_2O \rightarrow 2HSO_4^- + O$ $2HSO_4^- + 2HCO_3^- \rightarrow 2SO_4^{2-} + CO_2 + H_2O$	

Formulated Product	**Product**	**Application**	**Dosages**		**Cost**
			Copper ppm	**PPS ppm**	
	PPS with 1.6% copper sulfate	Pools and Spas	0.2–0.8 (0.2–0.4 ideal)	1.5 ppm	$66/10 lb.
	Concerns	•Copper concs. >0.2–0.3 ppm can cause staining.			
		•Questionable disinfection and oxidation.			
		•Product is expensive.			

13. POLYHEXAMETHYLENE BIGUANIDE (PHMB)			
System Components[A]	**Component**	**Function**	
	20 % PHMB	Bacteriostat	
	Quat[B]	Algistat	
	30% Hydrogen Peroxide	Oxidant	
	Enzyme Cleaner	Filter Cleaner	
	Chelating Agent	Trace Metal Chelation	
		Swimming Pool Concentrations	**Testing and Adjustment**
	PHMB	6–10 ppm active	Weekly
	Quat	2–2.5 ppm active	Weekly
	Hydrogen Peroxide	0–27 ppm	Every 3–4 weeks
Disinfection Data Block 1991	**Organism**	**MIC**[C] **(PHMB)**	
	E. coli	4 ppm	
	S. aureus	4 ppm	
	P. aerugenosa	20 ppm	
Swimming Pool Disinfection Testing of PHMB System Sandel 1996	•In a first year test (90 days), 27% of the of water samples showed bacterial counts >200 cfu per mL vs. 4% for a chlorine control pool.		
	•In a second year test (100-days), 57% of the of water samples showed bacterial counts >200 cfu per mL vs. 0% for a chlorine control pool.		
	•The incubation periods for the two tests were 7 and 2 days, respectively, indicating development of PHMB-resistant bacteria.		
	•Formation of bacterial slimes was also observed during the tests.		
Algae Control Data del Corral & Johnson 1996		**MIC (ppm)**	
	Algae	**Quat**	**PHMB**
	Chlorella pyrennoidosa (Green)	1.0	≤0.5
	Phormidium faveolarum (Black)	5.0	<0.5
	Eustigmatos vischeri (Yellow)	≥1 <5	> 20
Oxidation of Contaminants	•Hydrogen peroxide is a poor oxidant for ammonia, urea, and other organic matter.		
Incompatibilities[A]	•Chlorine and bromine oxidizers.		
	•Ozone and persulfate oxidizers.		
	•Copper and silver-based algicides.		
	•Most clarifiers and cleaners.		
	•Some stain and scale inhibitors.		
Potential Problems	•Excessive use of PHMB, Quat, and Enzyme can cause foaming and impart odor and off-taste to the water.		
	•Build-up of organic matter.		
	•Development of persistent haziness and cloudiness.		
	•Development of biological growths, eg, pink slime and water mold.		
	•Development of PHMB resistant bacteria (Sandel 1996).		
Cost	•More expensive than chlorine.		

A) Product literature.

B) Alkyldimethylbenzyl ammonium chloride.

C) Minimum inhibitory concentration.

<table>
<tr><th colspan="5">14. ULTRAVIOLET (UV) LIGHT AND HYDROGEN PEROXIDE</th></tr>
<tr><td rowspan="2">System</td><td colspan="4">•A flow through cell containing a UV lamp (emitting ~254 nm radiation).</td></tr>
<tr><td colspan="4">•Hydrogen peroxide.</td></tr>
<tr><td rowspan="3">Principle of Operation</td><td colspan="4">•The water, dosed with ~40 ppm hydrogen peroxide, flows through the cell.</td></tr>
<tr><td colspan="4">•UV light (ie, UV photons) dissociates hydrogen peroxide (H_2O_2) into reactive hydroxyl radicals (HO) that are the actual oxidizing agent:
$H_2O_2 + UV \rightarrow 2HO$</td></tr>
<tr><td colspan="4">•The UV light itself also can inactivate microorganisms such as bacteria.</td></tr>
<tr><td>Application</td><td colspan="4">•Small spas.</td></tr>
<tr><td rowspan="3">Factors Affecting Disinfection Rate</td><td>UV Light</td><td colspan="3">•Although UV light can inactivate 99.9% of E coli in 1 min. (White 1972), the residence time of the water in the UV cell is much less than 1 min.
•For example, assuming 1 gal. volume for the UV cell attached to a 300-gal. spa with a water flow rate of 10 gal./min. the residence time of the water in the cell is only 0.1 min.
•UV light intensity decreases with time.
•Water turbidity and build up of films on the lamp reduces UV light intensity.</td></tr>
<tr><td>Hydrogen Peroxide</td><td colspan="3">•Hydrogen peroxide is a very poor disinfectant.
•500 ppm inactivates 99% of E. coli in 10-30 mins.</td></tr>
<tr><td>Hydroxyl Radicals</td><td colspan="3">•No data available.</td></tr>
<tr><td rowspan="3">Disinfection Concerns</td><td colspan="4">• No sanitizer residual in the water outside the cell.</td></tr>
<tr><td colspan="4">•The kill time of microorganisms such as bacteria is very long because only about 1/30 of the spa water flows through the cell per minute and the residence time of the spa water in the UV cell is much less than 1 minute.</td></tr>
<tr><td colspan="4">•Bacteria can repair damage from UV light.</td></tr>
<tr><td rowspan="11">Contaminant Oxidation Data
Wojtowicz 2000</td><td>Conditions</td><td colspan="3">•Hydrogen peroxide: 50 ppm
•Nitrogen: 2.26 ppm per compound
•Alkalinity: 80 ppm
•Calcium hardness: 250 ppm
•pH 7.4
•T =~23°C.
•UV light irradiation time: 4 hours</td></tr>
<tr><td>Compound</td><td>% Yield of Ammonia</td><td>% Yield of Nitrate[A]</td><td>% TOC[B] Reduction</td></tr>
<tr><td>Ammonia</td><td>-</td><td>0</td><td>-</td></tr>
<tr><td>Urea</td><td>2</td><td>0</td><td>2[C]</td></tr>
<tr><td>Creatinine</td><td>1.5</td><td>1</td><td>57</td></tr>
<tr><td>Glycine</td><td>65</td><td>0</td><td>70</td></tr>
<tr><td>α-Alanine</td><td>59</td><td>0</td><td>46</td></tr>
<tr><td>Valine</td><td>63</td><td>2</td><td>59</td></tr>
<tr><td>Lysine</td><td>35</td><td>0</td><td>47</td></tr>
<tr><td>Glutamic Acid</td><td>58</td><td>0</td><td>69</td></tr>
<tr><td colspan="4">A) Lack of nitrate formation indicates that ammonia per se or byproduct ammonia is exceedingly slowly oxidized even by reactive HO radicals.
B) Total organic carbon. C) Calculated.</td></tr>
<tr><td>Spa Test</td><td colspan="4">•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.</td></tr>
<tr><td>NSF Approval</td><td colspan="4">•No NSF approval (NSF 1985).</td></tr>
<tr><td>Cost</td><td colspan="4">•A system for a small spa will probably cost several hundred dollars.</td></tr>
<tr><td>Overall Assessment</td><td colspan="4">•The system cannot provide adequate disinfection and contaminant oxidation.</td></tr>
</table>

15. REACTION OF ANCILLARY CHEMICALS WITH CHLORINE (Cl) AND BROMINE (Br)[A]			
	Reacts with Cl or Br[B]	**Forms Combined Cl or Br[C]**	**Other Potential Problems**
[Algicides]			
Alkyldimethylbenzylammonium chloride **Dialkylmethylbenzylammonium chloride** **Alkyldimethyldichlorobenzylammonium chloride**	Yes Yes Yes	Yes Yes Yes	•Excessive concentrations can cause foaming. •Can precipitate by formation of flocs that can cause filter problems. •Can form bromamines and chloramines.
Poly[oxyethylene(dimethylimino)ethylene-(dimethylimino)ethylene dichloride]	Yes	Yes	•Can form bromamines and chloramines.
Copper Citrate or Gluconate	Yes		•Excessive concentrations can cause staining.
Copper Triethanolamine	Yes	Yes	•Excessive concentrations can cause staining. •Can form bromamines and chloramines.
Silver Compounds (eg, silver oxide)			•Excessive concentrations can cause staining.
[Antiscalants and Stain Preventers]			
Organophosphonates (eg, hydroxyethylidene diphosphonic acid)	Yes		•Decomposition by sunlight and chlorine produces phosphate ions. •Increases concentration of phosphate, which is a nutrient for bacteria and algae and can cause cloudy water due to precipitation of calcium phosphate.
Polymeric (eg, polyacrylates)	Yes		
[Clarifiers/Flocculating Agents]			
Inorganic (eg, aluminum sulfate)			
Polymeric (eg, polydimethyldiallylammonium chloride)	Yes	Yes	
[Defoamers]			
Polydimethylsiloxane	Yes		
[Degreasers]			
Enzymes	Yes		
[Tints]			
Organic Dyes	Yes		
[Fragrances]			
Organic compounds such as alcohols, aldehydes, ketones, and esters formulated with other reactive organic ingredients such as propylene glycol and glycerine.	Yes		•Since they apparently can cause foaming, they are formulated with a defoamer such as polydimethylsiloxane.

A) Ancillary chemicals can also react with non-chlorine oxidizing agents such as potassium monopersulfate.

B) The rate of reaction will depend on the concentration and functionality of the organic matter as well as the chlorine (or bromine) concentration, temperature, and sunlight duration and intensity.

C) The greater the nitrogen content, the greater the potential for formation of combined chlorine or bromine.

References

Adams, V.D., et al, "An Evaluation of an Electrolytic Process for the Removal of Ammonia and Urea from Simulated Spa Water", Symposium Series Vol. IV, pp 44-52, 1999, NSPI National Meeting, Las Vegas, NV,

Adamson, R.P. and M.R. Sommerfeld, "Laboratory Comparison of the Effectiveness of Several Algicides on Isolated Swimming Pool Algae", *Applied and Environmental Microbiology,* 39(2)(1980):348-353.

ANSI/NSPI-4 199X Standard for Aboveground/ Onground Residential Swimming Pools.

ANSI/NSPI-5 1995 Standard for Inground Residential Swimming Pools

AOAC, Official Methods of Analysis of the American Association of Official Analytical Chemists, 15th Edition, 1990, Arlington, VA.

Bauer, C. R. and V. L. Snoeyink, "Reactions of Chloramines with Active Carbon", *Journal of the Water Pollution Control Federation,* 45(11)(1973):2290-2301.

Block, S. S., "Disinfection, Sterilization, and Preservation", Lea & Febiger, Philadeliphia, 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.

del Corral, F. and B. Johnson, "Comparitive Algicidal, Algistatic, and Bacteriostatic Evaluations of Selected Commercial Algicides", Symposium Series Vol. I, pp 18-25, 1996, NSPI National Meeting, Phoenix, AZ,

DIN 19643 (German Industry Standard: In English): Treatment and Disinfection of Swimming Pool and Bathing Water (Berlin, Beuth Verlag, 1984).

Dohan, J.M. and W.J. Masschelein, *Ozone Science and Engineering* 9(1987): 315-.

Dorfman, L.M. and G.E. Adams, "Reactivity of the Hydroxyl Radical in Aqueous Solution", National Bureau of Standards, NSRDS-NBS 46 (Washington, DC, US Government Printing Office, 1972).

Dumas, Bob "Bromine Stabilizer Passes Early Test", *Pool & Spa News,* January 13, 1999, pp 1- 2.

Eichelsdorfer, D., "Use of Ozone for Treatment of Swimming Pool Water", in Ozone Treatment of Waters for Swimming Pools, R. Rice, Ed., International Ozone Association, Norwalk, CT, 1982, pp. 82 and 91.

Eichelsdorfer, D. and J. Jandik, "Long Contact Time Ozonation for Swimming Pool Water Treatment", *Ozone Science and Engineering* 7(2)(1985):93-106.

Elliasson, B. and U. Kogelschatz, "Ozone Generation with Narrow-Band UV Radiation", *Ozone Science and Engineering* 13(3)(1991):365-373.

Fitzgerald, G. P., "Loss of Algicidal Chemicals from Swimming Pools", *Applied Microbiology* 8 (1960): 269-274.

Fitzgerald, G. P., and M. E. DerVartanian. "Factors Influencing the Effectiveness of Swimming Pool Bactericides." *Applied Microbiology* 15 (1967): 504-509.

Fitzgerald, G. P., " Compatibility of Swimming Pool Algicides and Bactericides", *Water and Sewage Works,* 115 (1968): 65-71.

Fitzgerald, G. P. and D. F. Jackson, "Comparative Algicidal Evaluation Using Laboratory and Field Algae", *Journal of Aquatic and Plant Management* 17 (1979): 66-

Gardner, J. "Chloroisocyanurates in the Treatment of Swimming Pool Water." *Water Research* 7 (1973): 823-833.

Gerba, C.P. and J. Naranjo, University of Arizona, Unpublished Data, 1999.

Grenier, J. and R. Denkewicz, "Improved Test Method for the Evaluation of Algicides and Algistats for Swimming Pools", Symposium Series Vol. II, pp 63-68, 1997, NSPI National Meeting, Chicago, ILL.

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.

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.

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.

Kinman, R.N., Water and Wastewater Disinfection with Ozone", Critical Reviews of Environmental Control, 5(1975):141-152,

Kurzman, G. E., "Ozone-Granular Activated carbon for Disinfection and Purification of Swimming Pool Water", in Ozone Treatment of Waters for Swimming Pools, R. Rice, Ed., International Ozone Association, Norwalk, CT, 1982, p. 106.

Kutz, S. M., L. K. Landeen, M. T. Yahya, and C. P. Gerba, "Microbiological Evaluation of Copper-Silver Disinfection Units", 4th Conference on Chemical Disinfection, Binghamton, NY April 10-13, 1988.

Kuwabara, J. S. and H. V. Leland, "Adsorption of Selanastrum capricornutum (Chlorophyceae) by Copper", *Environmental Science and Technology* 5(1986):197-

Lange's Handbook of Chemistry, J.A. Dean, ed., McGraw-Hill Book Co., New York, 13th Edition, 1985.

Legend Labs, St. Paul, MN

Marks, H. C. and F. B. Strandskov, "Halogens and their mode of action", *Annals of the New York Academy of Sciences* 53(1950):163-

Minisci, F., A. Citterio, and C. Giordano "Electron Transfer Processes: Peroxydisulfate, a Useful and Versatile Reagent in Organic Chemistry." Accounts of Chemical Research 1983, 16, 27-32.

Nalepa, C.J. et al, "Development of a Bromine Stabilizer for Outdoor Pools", Symposium Series Vol. I, pp 12-17, 1999, NSPI National Meeting. Las Vegas, NV.

National Sanitation Foundation (NSF), Ann Arbor, MI (see website at www.NSF.com)

National Spa and Pool Institute (NSPI), Alexandria, VA.

Nelson, G.D. "Special Report 6862 – Swimming Pool Disinfection with Chlorinated-s-triazinetrione Products." Monsanto Chemical Co. St. Louis, MO, March 1967.

Olin Corporation. Unpublished Data on Swimming Pool Evaluation of Electro-chemical Generation of Bromine. 1983.

OSHA, U.S. Occupational Safety and Health Administration, Washington, DC; see Federal Register 40, 47261 (1975).

Ozone in Water Treatment: Applications and Engineering, B. Langlais, D. A. Reckhow, and D. R. Brink, Eds. Lewis Publishers, Chelsea, MI, p113, 1991.

Palmer, C. M. and T. E. Maloney, "Preliminary Screening for Potential Algicides", *Ohio Journal of Science*, 55(1955):1- .

Penny, P.T. and R.J.G. Roycroft, "Swimming Pool Dermatoses associated with the use of Bromine Disinfectant" *British Medical Journal* August 13, 1983.

Rice, R. G. "Chemistries of Ozone for Municipal Pool and Spa Water Treatment", *Journal of the Swimming Pool and Spa Industry*, 1(1)1995:25-44.

Sandel, B.B., Unpublished Data on Testing of Copper-Silver Cartridge, 1992.

Sandel, B. B., "Disinfection with Chlorine Products – Some Lessons Learned", Symposium Series Vol. I, pp 80-85, 1996, NSPI National Meeting, Phoenix, AZ,

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(1937):113-

Snoeyink, V. in Water Quality and Treatment, F. W. Pontius, Ed., 4th Edition, McGraw-Hill, Inc., New York, NY, pp. 812-813, 1990.

Stumm, W. "The Decomposition of Ozone in Aqueous Solution", *Helvetica Chimica Acta*, 37(1954):773-

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.

Tiefenbrunner, F., "Problems with the Direct Ozonation of Swimming Pool Water", in Ozone Treatment of Waters for Swimming Pools, R. G. Rice, Ed., International Ozone Association, Norwalk, CT, 1982, p. 152.

Watt, P.M, D.I. Kennedy, J. Naranjo, J. Sandoval, and C.P. Gerba, "Comparison of the Disinfectant Capabilities of Various Spa Products", Symposium Series Vol. IV, pp 71-76, 1999, NSPI National Meeting, Las Vegas, NV.

White, C.G., Handbook of Chlorination, Van Nostrand Rheinhold, New York, 1972.

Wojtowicz, J. A., Unpublished Data on Testing of UV Ozonators, 1985.

Wojtowicz, J. A., Unpublished Data on Testing of Copper-Silver Ionizer, 1988.

Wojtowicz, J. A., Unpublished Data on Ozone Reactions, 1989.

Wojtowicz, J. A., Unpublished Data on Testing of UV-Hydrogen Peroxide, 1989.

Wojtowicz, J. A., Unpublished Data on Bromine Stabilization, 2000.

Wojtowicz, J. A., Unpublished Data on Potassium Monopersulfate Stability, 2000.

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. "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. "Fate of Nitrogen Compounds in Swimming Pool Water", Symposium Series Vol. III, 1998, pp 40-44, NSPI National Meeting, New Orleans, LA.

Wojtowicz, J. A. Letter to the Editor, *Journal of the Swimming Pool and Spa Industry*, 3(1) 1998:41-43..

Wojtowicz, J. A., "Chemistry of Nitrogen Compounds in Swimming Pool Water", *Journal of the Swimming Pool and Spa Industry*, 4(1) 2001:30-40.

Wojtowicz, J. A., "Use of Ozone in the Treatment of swimming Pools and Spas"*Journal of the Swimming Pool and Spa Industry*, 4(1) 2001:41-53.

Wojtowicz, J. A., "Cyanuric Acid Technology", *Journal of the Swimming Pool and Spa Industry*, 4(2) 2001:9-16.

Wuhrman, K. and F. Zobrist, "Investigation of the Bactericidal Effet 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.