7.2 – Use of Ozone in the Treatment of Swimming Pools and Spas

Although ozone is an effective disinfectant, it cannot be used as a primary sanitizer because of its volatility, toxicity, and short lifetime. Since ozone is unstable and hazardous, it has to be produced on–site from air by ozone generators (ozonators). Commercial units employ ultraviolet light (UV lamps) or electrical discharge (i.e., corona discharge or CD). UV ozonators produce very low concentrations of ozone compared to CD ozonators, i.e., <0.1 vs. ~1.5 wt. %.

Despite its high oxidation potential, ozone reacts very slowly with bather contaminants such as ammonia, monochloramine, urea (the main contaminant), and creatinine, even at high ozone and contaminant concentrations. Both chlorine and bromine are more effective than ozone in oxidation of these contaminants. The very low ozone concentrations produced by UV ozonators makes them even less effective than CD ozonators in oxidation of bather contaminants.

A number of UV ozonators have been evaluated and found to be unsuitable for pool or spa use. Although UV ozonator manufacturers typically claim lower chlorine consumption (typically 60 to 90%) and the ability to operate pools and spas at lower chlorine concentrations, no independent data are provided to support these claims.

In Europe, CD ozone is used in an integrated system such as the German–designed ozone–granular activated carbon (GAC) process that employs flocculation, sand filtration, ozonation, GAC filtra-tion, and chlorination and also includes a water purge. In DIN (German Industry Standard) based installations, the reduction in chemical oxygen demand (COD) of the water (other than ammonia and urea) is improved by 20% over the same process without ozone/GAC, and also reduces operating costs by 20%; however this system is cost effective only for large heavily used pools.

In North America, variations of the ozone–GAC process are employed that treat only a portion of the water resulting in lower COD reductions than obtained using DIN–based systems.

Properties of Ozone

Ozone is an allotropic form of oxygen that contains three oxygen atoms. It is a pale blue gas at ordinary temperatures and has a pungent odor. The properties, chemistry, manufacture, uses, environmental and health aspects of ozone have been comprehensively reviewed (Wojtowicz 1996).

Solubility – The solubility of ozone in water is very low and varies inversely with temperature. The solubility of gases such as ozone is described by Henry's Law: $P = K_H C$, where P is the partial pressure (atm), C is the concentration in the liquid phase (mol L^{-1}), and K_H is Henry's Law constant (L atm mol^{-1}). From the ideal gas law (PV = nRT) the following useful equation can be obtained for the equilibrium distribution of ozone between water and air:

$$[O_3]_{AQ} / [O_3]_G = RT / K_H = S$$

where: $[O_3]_{AQ}$ and $[O_3]_G$ are the aqueous and gas phase ozone concentrations (ppm), R is the gas constant (0.082 L atm K^{-1} mol^{-1}), T is the tempera-

ture (Kelvin), and S is a dimensionless constant also referred to as the solubility ratio. The value of S varies with temperature according to the following equation (Ozone in Water Treatment 1991):

$$S = \exp(-0.45 - 0.043T°C)$$

The value of S varies inversely with temperature and is equal to 0.18 and 0.11 at 85°F (29.4°C) and 104°F(40°C), respectively.

Toxicity – Because ozone is a slightly soluble gas, it tends to escape from aqueous solution. Gaseous ozone is toxic, e.g., the OSHA permissible exposure limit (PEL) in air is only 0.1 ppm for an 8–hour exposure (OSHA 1975). This concentration can be achieved by aqueous ozone concentrations of only 0.018 ppm in pools and 0.011 ppm in spas and is the reason that ozone cannot be used as a primary sanitizer. The limit for a shorter exposure (10 minutes) is 0.2 ppm. By contrast, the PEL for gaseous hydrocyanic acid is 10 ppm.

Stability – Although ozone is stable for hours in double distilled water, its half–life in single distilled or tap water at 20°C (68°C) is less than 30 minutes. In addition to thermal decomposition, UV rays in sunlight also decompose aqueous ozone. The rate constant k_D for decomposition of ozone in bicarbonate buffered water can be calculated using the following equation (Stumm 1954):

$$k_D = 1.64 \cdot 10^{23}\exp(-13{,}437/T)[OH^-]^{0.75} \text{ min}^{-1}$$

where: $T = 273 + °C$ and $[OH^-]$ is the hydroxyl ion concentration in mol/L.

Decomposition of ozone is catalyzed by hydroxyl (OH^-) ions and generates reactive intermediates such as hydroxyl radicals, which act as chain carriers. Hydroxyl radicals ($HO\cdot$) have a very short lifetime due to their extreme reactivity. Solutes such as bicarbonate and carbonate ions consume $HO\cdot$ radicals by forming less reactive radicals that interrupt the chain reaction, thereby extending the lifetime of ozone.

Oxidation Potential – Although ozone is a stronger oxidant than chlorine from a thermodynamic standpoint (standard potential E°: 2.1 vs 1.5 volts), it is not always kinetically superior. For example, experimental data show that chlorine and bromine are much better oxidants for bather contaminants such as ammonia, urea, and creatinine that are oxidized only slowly by ozone. Thus, one of the advertised benefits of ozone in swimming pool/spa treatment, that it is a stronger oxidant than chlorine, is not supported by actual data.

Ozone Generation

Because of ozone's instability (both thermal and explosive), it must be generated on site. Ozone can be generated from the oxygen in air by ultraviolet (UV) light or by electric discharge (also called corona discharge or CD).

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

UV Ozone Generators – UV ozone generators (ozonators) produce very low concentrations, typically <0.1 wt. % from air. The low–pressure mercury lamps employed produce low ozone concentrations because they not only emit 185 nm radiation that forms ozone but also 254 nm radiation that decomposes ozone. The energy efficiency of UV ozonators is very low compared to CD ozonators, i.e., 44 vs. 2 kWh/kg (Dohan and Masschelein 1987). Some UV ozonators have air filters and dryers but do not employ lamp cooling. Drying is not as critical with UV ozonators as it is with CD ozonators. More efficient lamps based on xenon excimer lasers producing 172 nm radiation have been studied experimentally but have not yet been commercialized (Elliasson and Kogelschatz 1991).

CD Ozone Generators – By contrast to UV ozonators, properly designed CD ozone generators produce much higher concentrations, typically 1–2 % by wt. from air and even higher concentrations from oxygen. Typical CD ozonators employ dryers to lower the moisture content of the inlet gas; a dew point of at least –60°C is required for optimum output. They may also utilize air or water cooling to reduce the temperature of the CD cells. Some CD ozonators sold for pool use are only marginally better than UV ozonators with ozone concentrations from air of only 0.06 to 0.2 wt. %.

Ozone Transfer into Water

Ozone Dispersion – The ozone produced by generators must be transferred (i.e., injected) into water by devices such as porous diffusers or venturis that disperse the gas into small bubbles for more thorough contact with water. Venturi–type injectors generate a vacuum (as a result of water flowing past an orifice in a constricted section of pipe) that draws air through the ozonator and into the water. Compressors are used with porous diffusers and can also be used with venturi injectors.

Ozone Absorption – The absorption of ozone (in single stage absorbers assuming no reaction or decomposition) is given by the following equation:

$$\% \, O_{3, ABS} = (SV_L / V_G)100 / (1 + SV_L / V_G)$$

where: V_L and V_G are the liquid and gas flow rates (L/min). The transfer efficiency increases with increasing water to air flow ratios. For a given transfer efficiency the aqueous ozone concentration increases with the input gas phase ozone concentration. Using multiple stages can increase the % absorption of ozone.

Calculated Data for UV Ozonators – Calculated data for UV ozonators for residential in–ground swimming pools using manufacturers specifications are shown in Table 1. The calculated values represent % ozone absorbed and aqueous ozone concentrations prior to entry into the pool and where the ozone–air mixture is in contact with the full flow of the recirculation system. They show ozone absorption in the 70 to 90% range and pool inlet ozone concentrations of only 0.01 to 0.03 ppm.

The unabsorbed ozone requires destruction especially in indoor spas. However, these units do not provide for offgas ozone destruction. The aqueous ozone concentration at the point of injection will be higher because of the lower flow rate of water in the side stream but the % ozone absorption will be lower.

Assuming 6 feet of 1.5" pipe downstream from the point of injection to the pool inlet, the contact time is only about 0.5 seconds. This is minuscule compared to the minimum of 2 minutes that's typical of DIN–based (DIN 1984) CD installations.

Similar calculations to those in Table 1 for spa ozonators are shown in Table 2. Somewhat higher gas phase ozone concentrations and % ozone absorbed are obtained but the spa inlet aqueous ozone concentrations are still quite low.

Ozone Offgas – Based on the data in Table 2, ozone absorption at the point of entry into the spa is

Volume Gallons	Air CFH	O_3 g/h	O_3 Volume %	% O_3 Absorbed[B]	Pool Inlet O_3 ppm[B]	Pool O_3 ppb[D]
30,000	50	0.83[C]	0.030	71	0.031	0.78
25,000	15	0.25	0.030	87	0.014	0.34
25,000	15	0.30	0.036	87	0.016	0.42

A) For manufacturers 1,2, and 3, respectively, of residential in–ground pools using a filter bypass venturi injection system assuming 85°F and a standard turnover time of 6 hours.

B) After bypass section prior to entry into pool.

C) Maximum output; may not be attainable under typical operating conditions.

D) Steady state ozone concentration.

Table 1 – Calculated Data for Pool UV Ozonators[A]

Volume Gallons	Air CFH	O_3 g/h	O_3 Volume %	% O_3 Absorbed[B]	Pool Inlet O_3 ppm[B]	Pool O_3 ppb[E]
800	8	0.33[C]	0.074	83	0.045	3.0
1000	3	0.042	0.025	94	0.005	0.35
975	6.5	0.18	0.050	88	0.021	1.4

A) For manufacturers 1,2, and 3, respectively, of residential spas using a filter bypass venturi injection system assuming 104°F and a standard turnover time of 30 minutes.

B) After bypass section prior to entry into spa.

C) Maximum output; may not be attainable under typical operating conditions.

D) Steady state ozone concentration.

Table 2 – Calculated Data For Spa UV Ozonators[A]

incomplete, averaging 88%. Since these ozonators do not provide ozone off gas destruction, the unabsorbed ozone will build up in the spa room. For a spa in a 10'x10'x10' room, the average ozone concentration would reach about 0.35 ppm after one hour of operation exceeding the OSHA limit of 0.1 ppm. However, the ozone concentration above the spa ozone inlet could be as high as 60 ppm.

UV Ozone Conc. in Pools and Spas – The steady state ozone concentration in pools and spas (assuming only thermal decomposition) is given by the following differential equation:

$$d[O_3]/dt = k_A - k_D[O_3]$$

Where: $d[O_3]/dt$ is the instantaneous ozone decomposition rate (ppm/min), k_A is the ozone addition rate (ppm/min), k_D is the ozone decomposition rate constant (min^{-1}), and $[O_3]$ is the instantaneous ozone concentration (ppm) in the pool or spa. Integration yields the following algebraic equation allowing calculation of the ozone concentration as a function of time.

$$[O_3] = (k_A/k_D)[1 - \exp(-k_D t)]$$

At the steady state: $d[O_3]/dt = 0$, therefore, the steady state ozone concentration is given by:

$$[O_3]_{SS} = k_A/k_D$$

Another equation for the steady state ozone concentration is:

$$[O_3]_{SS} = [O_3]_{IN} r/k_D$$

Where: $[O_3]_{IN}$ is the inlet ozone concentration (ppm) to the pool or spa and r is the turnover rate (min^{-1}).

At pH 7.5 and 85°F, $k_D = 0.11$ min^{-1} (see eq. for calculation in Properties section). In pools, it would take about 42 minutes to attain 99% of the extremely low calculated steady state ozone concentrations of 0.3 to 0.8 ppb (assuming no chemical reaction). Photochemical decomposition will further decrease the ozone concentration.

Based on the data in Table 2 and the value of k_D (0.50 min^{-1}) at 104°F, the average steady state spa ozone concentration is 1.6 ppb assuming no chemical reaction. It would take 10 minutes to attain 99% of this concentration.

Evaluation of UV Ozonators

Operational Problems – Operational problems were experienced due to the venturi–type injectors employed with the UV ozonators that created a significant backpressure on the pump. This backpressure would prevent operation of the ozonator that requires a minimum vacuum before the UV lamps became energized. In swimming pool operation, the outlet nozzle on the water return line to the pool had to be removed to eliminate the water flow restriction thereby providing sufficient vacuum for operation of the ozonator. In spa operation, the outlet nozzles could not be removed, therefore, the return line had to be repiped to empty directly into the spa.

Ozone Offgas Measurement – Swimming pool tests at 85°F with two commercial ozonators are shown in Table 3 (Wojtowicz 1985). Based on the air and water flow rates, the calculated ozone absorption was 49%. Initial ozone off gas measurements showed very low ozone concentrations indicating very high absorption. However, when the ozone off gases were trapped beneath a plastic enclosure, very high ozone concentrations were observed in very good agreement with the calculated ozone absorption.

Ozonator	O$_3$ g/h	Air L/min	Water gpm	O$_3$ in Air[A] ppm	O$_3$ Above Pool[B] (ppm)	
					As Is	Trapped
UV–250	0.25	28	40	65	~1	33
UV–500	0.5	28	40	130–140	0.2	67
"	"	28	40	80[C]	0.2	41

A) Before contact with water.

B) Above ozone inlet.

C) Output of ozonator dropped by about a half indicating that one of the lamps may have stopped working.

Table 3 – Off Gas Testing of Commercial UV Ozonators

Ozonator	Test	Ozone g/h	Results
A1	250–gal spa	0.25	Poor bactericidal performance, see Table 5
A2	6800–gal pool	0.5	Green algae bloom after 3 days of continuous operation*
B1	250–gal spa	0.3	Poor oxidation of urea in synthetic bather insult, see Table 6
B2	6800–gal pool	1.0	Green algae bloom after 4 days of continuous operation*

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

Table 4 – Evaluation of UV Ozonators

If these tests had been done indoors or in an enclosure as in UL testing, it would have been only a matter of time before the ozone concentrations exceeded 0.1 ppm. These results indicate that the testing of UV ozonators should be modified so that the ozone off gas is trapped as in these studies in order to obtain a realistic value for ozone off gassing potential. In addition, testing should include the following in order to verify that the ozonator is functioning properly and producing ozone according to the manufacturers specifications, otherwise the test results will not be meaningful.

- The airflow through the ozonator.
- The pump water flow rate
- The gas phase outlet ozone concentration

This will allow calculation of the ozonator output in g ozone/h and also the % ozone absorption.

Disinfection/Algae Control – A summary of pool and spa tests is shown in Table 4. In two swimming pool tests with different commercially available UV ozonators, algae blooms developed after 3 and 4 days, despite continuous ozonation.

Results of a spa evaluation of a UV ozonator are shown in Table 5. In the first test, the data show no inactivation of bacteria (produced by bathers) at spa temperature. In a second test starting at room temperature, a very slow kill rate of bacteria was observed that decreased with increasing temperature and eventually slowing to the point that bacterial growth actually increased.

Oxidation of Urea – Another spa test (Table 6), showed little or no oxidation of urea after 36 hours of operation at a temperature of 100°F based on little change in the urea concentration and absence of byproduct nitrate. Another study showed similar results (Adams *et al* 1999).
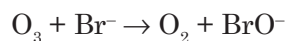
Generation of Bromine – A UV ozonator

Time, hours		Temp. °F	Bacteria, cfu/mL	% Inactivation
Test 1	0	100	2.0×10^3	–
	0.5	100	2.0×10^3	0
Test 2	0	77	1.58×10^6	–
	1	88	7.19×10^5	54.5
	2	95	3.34×10^4	97.9
	4	102	1.1×10^3	99.9
	7	102	5.43×10^3	99.7
	24	77	0	100

Table 5 – Bactericidal Evaluation of a UV Ozonator
Ozonator A1, 0.25 g/h, pH 7.5

Total Ozonation time, hours	Urea, ppm		Nitrate, ppm
	added	found	
10	13.4	11.3	
32	22.4	23.4	
36	26.9	25.1	0

Table 6 – Oxidation of Urea by a UV Ozonator
Ozonator B1, 0.3 g/h Ozone, 100°F, pH 7.5

(rated at 7.5 g ozone/day) was evaluated for generation of available bromine from sodium bromide.

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

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

Use of UV Ozonators in Pools and Spas

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

Spas – Ozonating the water while the spa is in use is not recommended because the unabsorbed ozone in the ozonator vent gas can amount to 60 ppm. If the spa is treated after use with ozone at the average feed rate of 0.184 g/h (see Table 2) over a 6–hour period, the calculated average ozone concentration, considering only decomposition, will be 1.6 ppb. The total ozone dose, assuming no decomposition, is equivalent to 0.4 ppm av. Cl in terms of

potential oxidizing capacity. This represents only 5% of the recommended shock dose of 8 ppm av. Cl. Furthermore, most (~99%) of the applied ozone will simply decompose resulting in negligible oxidation of bather contaminants.

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

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

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

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

Cost – UV ozone generators, with production rates of 0.25 to 0.44 g/h for pools of 18,000 to 50,000 gals., retail for $500 to $700. These units come with venturi type injectors but do not have air filters, dryers, or off gas ozone destruction. The cost is a

function of the ozonator output and whether the unit has an air filter, dryer, or compressor.

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

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

Use of CD Ozonators in Pools and Spas

European Practice – CD ozonators are commonly used in Europe, primarily in large commercial or public pools. They 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 (Eichelsdorfer 1982, Kurzman 1982). The most widely used ozonation technique in Europe is the ozone–granular activated carbon (GAC) system that is based on the German Industry Standard (DIN 1984). It involves treating all water by flocculation, filtration, ozonation, GAC filtration, and chlorination. Ozone (about 1 ppm) is introduced into the water in the external recycle loop after a sand filter, through a porous diffuser in a contact chamber. After a reaction time of at least 2 minutes, the ozonated water is filtered through GAC. This destroys unreacted ozone as well as all of the chlorine. The dechlorinated and deozonated water (with <0.05 ppm ozone) is then dosed with 0.5 ppm av. Cl and returned to the pool. FAC is maintained in the 0.2–0.5 ppm range and combined available chlorine (CAC) is limited to 0.2

ppm. The oxidation–reduction potential (ORP) is maintained at 770 mV. Although oxidation of contaminants is the primary purpose of ozonation, some destruction of microorganisms may also occur. A specified amount of water (~30 L/bather/day) is purged from the pool and replaced with fresh makeup water in order to limit buildup of mineral salts in the water.

Additional removal of contaminants can occur by chemical and biological action in the GAC filter. Literature data show that monochloramine can be partially converted to nitrogen and chloride ion (Bauer and Snoeyink 1972). Dichloramine and nitrogen trichloride react with GAC forming primarily nitrogen. Although the GAC filter may become biologically active (Snoeyink 1990), potentially providing biodegradation of contaminants such as ammonia, urea, and creatinine that are not readily oxidized by ozone, no data are available on the extent of biodegradation, if any.

In the combined flocculation/filtration/chlorination process, the chemical oxygen demand (COD) of the water is reduced by the equivalent of 2 $g/KMnO_4$/cu. meter. Addition of ozonation/GAC filtration reduces COD by 2.4 $g/KMnO_4$/cu. meter or a 20% increase. It would be interesting to know what the COD reduction would be without ozonation but with GAC filtration, i.e., how much COD reduction is due to ozone and how much to GAC filtration.

The limits on bacterial colonies in the pool is <100/mL, whereas the limit for *E. coli* is 0/100 mL. The goal of disinfection is a 30–sec. bacterial kill time that is ensured by maintaining an ORP of 750–770 mV. Another factor that improves water quality is the high water turnover rate: ~2 hours vs. 6 hours that is typical in US pools. Thus, pools using the DIN–based ozone–GAC process can maintain acceptable microbiological quality suggesting that the concentration of bather contaminants in the pool is not excessive.

Data from European pools show that the ozone–GAC process can significantly reduce operating costs, allowing recovery of capital costs in about 8 years. However, treating water by this process is cost effective only for large, heavily used pools (e.g., public, commercial, or private).

Ozone is sometimes used to generate av. Br from sodium bromide in small European public and semipublic pools and whirlpools (i.e., spas). A laboratory test at 25°C with a CD ozonator rated at 5 g/h showed only a 50% efficiency in generation of available bromine. The efficiency would be lower at 40 °C that is typically employed in spas.

Volume gallons	Air CFH	Ozone g/h	Ozone Vol. %	% O_3 Absorbed	Pool Inlet O_3 ppm	Pool O_3 ppb[A]
25,000	15	0.3	0.036	87	0.016	0.42
50,000	15	0.5	0.601	93	0.015	0.37
100,000	15	1.0	0.120	96	0.015	0.36

A) Steady state ozone concentration

Table 7 – Calculated Data for Pool CD Ozonators
(Manufacturer 2)

North American Practice – DIN–based ozone–GAC systems have been installed in several US and Canadian cities (Rice 1995). Modified systems are also being offered in order to reduce costs. In retrofit installations, post–filter ozone injection is employed in conjunction with a combination contact chamber/GAC filter (Hartwig 1996). For new installations, pre–filter ozonation is employed that utilizes the filter as a combination contact chamber/GAC filter/sand filter. Although DIN requires full flow ozonation, some systems employ only partial or slipstream ozonation (in some cases as low ~10%). Since ozone only increases the non–urea and ammonia COD reduction by about 20% and also requires a water purge and an effective GAC filter (i.e., biologically active), any significant departure from DIN design will be at the expense of water quality. Speaking of water quality, it would be desirable to see performance data on pools using the various modified DIN–based systems. These systems are 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.

Some manufacturers market CD ozonators that are not much better performance–wise than UV ozonators as shown in Table 7. The average pool inlet and pool steady state ozone concentrations are similar (see Table 1).

Cost – The suggested retail price of the residential pool CD ozonators in Table 6 with ozone production rates of 0.3 to 1.0 g/h ranges from about $600 to $1800. CD ozone generators employing air feed with ozone production rates of 1.2 to 7.4 g/h retail in the $800 to $3700 range and do not come with any peripheral equipment. Commercial CD ozonators employing oxygen feed with ozone production rates of 2 to 7 g/h retail in the $4,000 to $10,000 range and do not come with off gas ozone destruction, contact chambers, or GAC filters. The cost of CD ozonators with higher production rates are as follows: 2–200 g/h (air) and 20–320 g/h (oxygen) – $10,000–$25000; 750–1800 g/h (oxygen) – $35,000–$60,000.

Disinfection

Literature data indicate that ozone at appropriate concentrations is an effective broad–spectrum disinfectant as shown by the data in Table 8, where Ct is the product of the ozone concentration in ppm and the contact time in minutes. Ct values will be lower at higher temperatures. In the case of bacteria, ozone kills by rupturing the cell wall. The presence of readily oxidizable organic matter can retard or inhibit inactivation of microorganisms by ozone (Kinman 1975). Because of ozone's short half–life, continuous ozonation of the water would be necessary for adequate disinfection in pools. Whereas CD ozone can provide effective disinfection, UV ozone cannot. However, CD ozone cannot be used as a primary disinfectant because of its volatility and toxicity. If sufficient ozone is present for acceptable disinfection, then the ozone concentration above the water will exceed the maximum allowable concentration, whereas if the ozone con-

Microorganism	Ct (ppm•min)
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

Table 8 – Ct Value Ranges for 99% Inactivation of Various Organisms by Ozone at 5°C and pH 6–7 (Hoff 1986)

centration above the water is at or below the maximum allowable concentration, then disinfection will be inadequate (Tiefenbrunner 1982).

Algae Control

Although ozone at appropriate concentrations is toxic to many species of algae, pools cannot benefit from this because ozone cannot be employed as a primary sanitizer. As mentioned earlier, UV–generated ozone was shown to be ineffective in algae control in swimming pool tests.

Oxidation of Contaminants

Kinetic Data – The reactivity of ozone varies greatly and depends on the functionality of the substrate as shown by the rate constants in Table 9. For example, ozone reacts very slowly with ammonia and is unreactive toward ammonium ion. Ozone also reacts exceedingly slowly with urea, which is the main swimming pool contaminant. Although ozone reacts rapidly with amines and amino acids, it reacts slowly with many other organic compounds, e.g., aliphatic alcohols, aldehydes, and acids. Ozone only partially oxidizes organic compounds and only rarely does the oxidation go to completion to form

CO_2 and H_2O. Many organic nitrogen compounds yield ammonia as an intermediate product. For example, in the oxidation of the amino acid glycine, the ammonia formed is only slowly oxidized at pool or spa pH because it is primarily in the form of ammonium ion that does not react with ozone.

$$3O_3 + H_2NCH_2COOH + H^+ \rightarrow$$
$$NH_4^+ + 2CO_2 + 3O_2 + H_2O$$
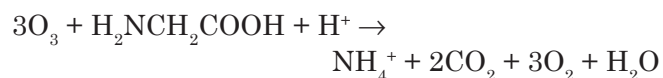
Calculated Data – The % ozone reacted with typical bather contaminants (based on 1 ppm total N) using the rate constants in Table 9 are shown in Table 10. The data show that except for glycine there is very little reaction between ozone and the main bather impurity urea as well as the minor impurities ammonia, monochloramine, and creatinine. In the case of glycine, the byproduct ammonia does not undergo significant reaction. The calculations were based on a 1 ppm dose of ozone and a contact time of 2 mins. that is typical for DIN standard installations. Lower ozone dosing, impurity levels, and contact times will result in even lower extents of reaction. The rate constants for reaction of ozone with chloro– derivitives of glycine and creatinine may differ from the unchlorinated compounds, and thus the extent of reaction may

Compound	Formula	Rate Constant (L mol^{-1} sec^{-1})
Ammonium ion	NH_4^+	0
Ammonia	NH_3	20
Monochloramine	$ClNH_2$	26
Dichloramine	Cl_2NH	1.3
Hypochlorite ion	ClO^-	120
Urea	H_2NCONH_2	~0.05
Glycine	H_2NCH_2COOH	1.3×10^5
a–Alanine	$CH_3CH(NH_2)COOH$	6.4×10^4
Creatinine *	$-CH_2N(CH_3)C(NH)NHC(O)-$	~2
Butylamine	$CH_3CH_2CH_2CH_2NH_2$	1.7×10^5
Ethyl alcohol	CH_3CH_2OH	0.37
Acetaldehyde	CH_3CHO	1.5
Acetone	CH_3COCH_3	0.032
Acetate ion	CH_3COO^-	$\leq 3 \times 10^{-5}$
Glucose	$OCH(CHOH)_4CH_2OH$	0.9

* Five–membered cyclic ring compound. See page 24 for structure.

Table 9 – Rate Constants at 20–25°C for Reaction of Ozone with Various Compounds (Hoigne *et al* 1983a, 1983b, 1985)

Compound	ppm N	ppm Compound	Calculated % Compound Oxidized
Urea	0.87	1.86	0.002
Ammonia	0.044	0.053	0.07
(Monochloramine)	(0.044)	(0.16)	(2.2)
Glycine	0.043	0.23	19[A]
Creatinine	0.036	0.10	0.03
Uric Acid	0.007	0.02	[B]

A) Does not include oxidation of byproduct ammonia.

B) Calculation not possible due to lack of information on reaction rate constant.

Table 10 – Reaction of Ozone with Bather Contaminants
Temp. 20–25°C, 1 ppm Ozone, Contact Time 2 min.

also be different. By contrast with the reaction of ozone with bather contaminants, the calculated extent of reaction with av. Cl (0.5 ppm at pH 7.5) amounts to approximately 5%, and is greater than that of all of the bather contaminants except for glycine.

Experimental Data – Experimental data on oxidation of ammonia, urea, and glycine by CD generated ozone, presented in Table 11, show very good agreement between observed and calculated values. However, it should be noted that despite very high substrate and ozone concentrations and long reaction times, the extent of reaction is very low except for glycine. But in the case of glycine the byproduct ammonia is virtually unreacted; it would require the consumption of an additional 3.8 mols of ozone to complete the oxidation. Literature data (Eichelsdorfer and Jandik 1985) also showed a pattern of slow oxidation at high substrate and ozone concentrations.

COD Reduction – German laboratory studies determined the contaminants that bathers introduce into swimming pool water; these are listed in Table 12. However, the determination of COD by titration of a heated sample with acidic $KMnO_4$ does not include ammonia and urea, both of which are not effectively oxidized by ozone. Assuming no oxidation of bound nitrogen, an average of 2.3 g of O_2 per g of TOC is required to completely oxidize typical non–urea contaminants (e.g., glycine, alanine, hippuric acid, glucuronic acid, uric acid, lactic acid, pyruvic acid, and citric acid) to CO_2 and water. Thus, the TOC in Table 11 is equivalent to 9.2 g $KMnO_4$. The observed value of 4 indicates that even a strong oxidant such as hot acidic permanganate does not completely oxidize organic matter in pool water. This is also the case with ozone.

Oxidation of Bather Contaminants By O_3, Br, and Cl – Table 13 shows data on comparative rates of oxidation of bather contaminants. The data show that except for glycine, that chlorine and bromine are superior oxidants to ozone. However, even in the case of glycine, ozone does not effectively oxidize the byproduct ammonia.

Substrate		Ozone	Reaction Time	Δmol O_3/mol Substrate	
	Conc. ppm	ppm	minutes	Calc'd.	Found
Ammonia	0.52	11.4	55	0.2	0.3
Urea	26.9	12.4	68	0.03	0.01
Glycine	6.7	13.8	13	3.2[A]	2.9
Creatinine	10.1	14.5	72	1.6[B]	0.3

A) For oxidation to CO_2, NH_3, and H_2O.

B) Value is probably higher than theoretical since the actual concentration of free creatinine has not been taken into account due to lack of data on the dissociation constant of the protonated form of creatinine.

Table 11 – Ozone Reaction with Bather Contaminants
pH 7.5, Temp. 25°C (Wojtowicz 1989a)

	Grams
COD (as $KMnO_4$)	4.0[D]
Total Organic Carbon (TOC)[A]	1.0
Urea[B]	0.7
Total Bound Nitrogen	0.9
Non–urea Nitrogen[C]	0.25

A) Does not include urea.

B) Bound nitrogen = 0.33 g.

C) Primarily amino acids, uric acid, creatinine, etc.

D) Equivalent to 1.0 g O_2. Does not include ammonia or urea.

Table 12 – Swimming Pool Bather Contaminants

The effectiveness of bromine in destruction of urea was further demonstrated in a test in a 300–gal spa sanitized with sodium dichloroisocyanurate (Dichlor) plus sodium bromide. The spa was treated daily with a synthetic bather insult equivalent to 2 people/day. Destruction of urea in the insult averaged 100% over the 65–day duration of the test (Wojtowicz 1989b).

	Initial Substrate Oxidation Rate, % Per Min.[A]			
Substrate	UV Ozone[B]	CD Ozone[C]	Chlorine (2.3 ppm)[D]	Bromine (4.6 ppm)[D]
Ammonium 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}	0.12	0.23
Creatinine	1.1×10^{-5}	7×10^{-3}	0.06	0.04
Glycine	1.5×10^{-2}	1.7	0.33	>2.6

A) pH 7.5, T = 20–25°C, each substrate contains 0.25 ppm of bound nitrogen.

B) Calculated data for steady state UV ozone concentration of 1.6 ppb.

C) CD ozone concentration of 1 ppm.

D) Experimental data (Wojtowicz 1998 and 2001).

Table 13 – Comparative Rates of Oxidation of Bather Contaminants

Reaction with Ancillary Chemicals – As in the case of chlorine and bromine, ozone can react with ancillary chemicals added to the pool or spa water.

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