5.4 – Effect of Cyanuric Acid on Swimming Pool Maintenance

Cyanuric acid is added to swimming pools to reduce photochemical decomposition of free available chlorine (av. Cl) by ultraviolet (UV) rays in sunlight. This is accomplished by formation of chloroisocyanyurates that do not appreciably absorb UV light. Recent data show that the av. Cl loss rate (at 80-85°F) caused by sunlight is only 1-2% per day at 138 ppm CA. This is consistent with the fact that over 99% of the av. Cl in CA stabilized pools is in the form of chloroisocyanurates. Virtually all of the decomposition (about 14% per day) observed in a bather-free pool in the summer time in the Phoenix area is due to thermal decomposition of chloroisocyanurates, which increases by a factor of 2 for each 5° rise in temperature. Bather load can appreciably increase the av. Cl loss rate. Cyanuric acid, in combination with its ionized form (i.e., cyanurate ion), also functions as a buffer to help stabilize pH.

Stabilization of Available Chlorine by Cyanuric Acid

Mechanism – Cyanuric acid is used in outdoor swimming pools to stabilize free available chlorine against photochemical decomposition by sunlight (Fuchs and Lichtman 1961, Nelson 1967). This is accomplished by formation of chloroisocyanurates, which do not significantly absorb UV light. The main equilibria in swimming pool water are (Wojtowicz 1996):

$$\mathrm{HOCl} \rightleftharpoons \mathrm{H^+ + ClO^-}$$

$$\mathrm{H_3Cy} \rightleftharpoons \mathrm{H^+ + H_2Cy^-}$$

$$\mathrm{H_2Cy^- + HOCl} \rightleftharpoons \mathrm{HClCy^- + H_2O}$$

$$\mathrm{HClCy^- + HOCl} \rightleftharpoons \mathrm{Cl_2Cy^- + H_2O}$$

where Cy^{3-} represents the tri-isocyanurate anion. All of the above chlorine compounds absorb ultraviolet light. The wavelengths (λ) of maximum absorption are tabulated in Table 1.

Compound	λ_{max} **nm**
Hypochlorous acid, HOCl	235
Hypochlorite ion, ClO^-	290
Monochlorisocyanurate ion, $HClCy^-$	215
Dichlorisocyanurate ion, Cl_2Cy^-	220

Table 1 – Absorption Maxima for Main Chlorine Species

Ultraviolet light from the sun is partially absorbed by the ozone layer in the upper atmosphere (the stratosphere), i.e., all wavelengths below 290 nm are absorbed. Since HOCl and the chloroisocyanurates absorb primarily below 290 nm, they are relatively stable to decomposition. By contrast, hypochlorite ion, whose absorption maximum occurs at 290 nm, absorbs UV light out to about 350 nm and therefore will be decomposed by sunlight. Since available chlorine exists predominately in the form of chloroisocyanurates, photodecomposition is greatly reduced, i.e., the available chlorine is considered to be stabilized. Addition of bromide to the pool will result in a drastic reduction in the stabilizing effect of cyanuric acid (see Wojtowicz 2001).

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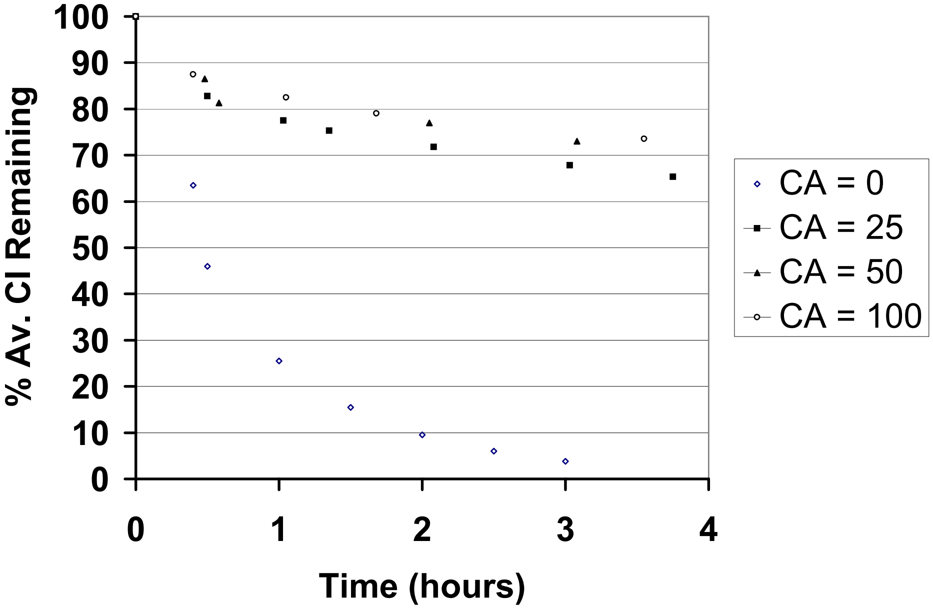


Figure 1 – Effect of Cyanuric Acid on Photochemical Decomposition of Available Chlorine (Monsanto Data)

Laboratory Data – Tests (Nelson 1967) on samples exposed to sunlight of chlorine demand-free swimming pool water at pH 7, 84-90°F containing 2.5 ppm av. Cl and 0, 25, 50, and 100 ppm CA show that cyanuric acid greatly reduces the photochemical decomposition of available chlorine (see Figure 1). The graph shows very little difference in stabilization from 25 to 100 ppm CA. The large initial drop of 12-20% over the first half hour is inconsistent with the slow linear loss of about 10% over the next 3 hours.

Other data (see Table 7, chapter 7.1) on samples of simulated swimming pool water containing 3.5 ppm av. Cl and 50 and 150 ppm CA

	Exposure	CA ppm	Av. Cl ppm[D] Initial	Final	Loss Rate %/day
Pool Water	Outdoors[A,B]	138	5.6	2.6	26
Pool Water	Outdoors[A,B]	138	8.2	3.6	27
Pool Water	Outdoors[A]	138	8.4	5.6	14
Pool Water	Outdoors[A]	138	9.2	6.2	13
Pool Water	Outdoors[A]	138	7.6	4.8	15
Pool Water	Indoors[C]	138	5.4	3.8	12
Pool Water	Indoors[C]	138	5.2	3.5	13
Tap Water	Indoors[C]	0	6.2	5.8	2
Tap Water	Indoors[C]	0	6.0	5.6	2
Tap Water	Indoors[C]	0	8.8	7.8	4

A) 25,000-gallon inground pool with no bather load; water temperature: 85°F; daytime air maximum: ~110°F; nighttime air minimum: 75-80°F. Samples taken directly from the pool and analyzed using the DPD-FAS method.
B) Bather insult added (150 mL urine per day).
C) One-gallon samples in polyethylene containers stored in the dark; air temperature 90–105°F.
D) Tests carried-out over a 3-day period.

Table 2 – Av. Cl Loss Studies

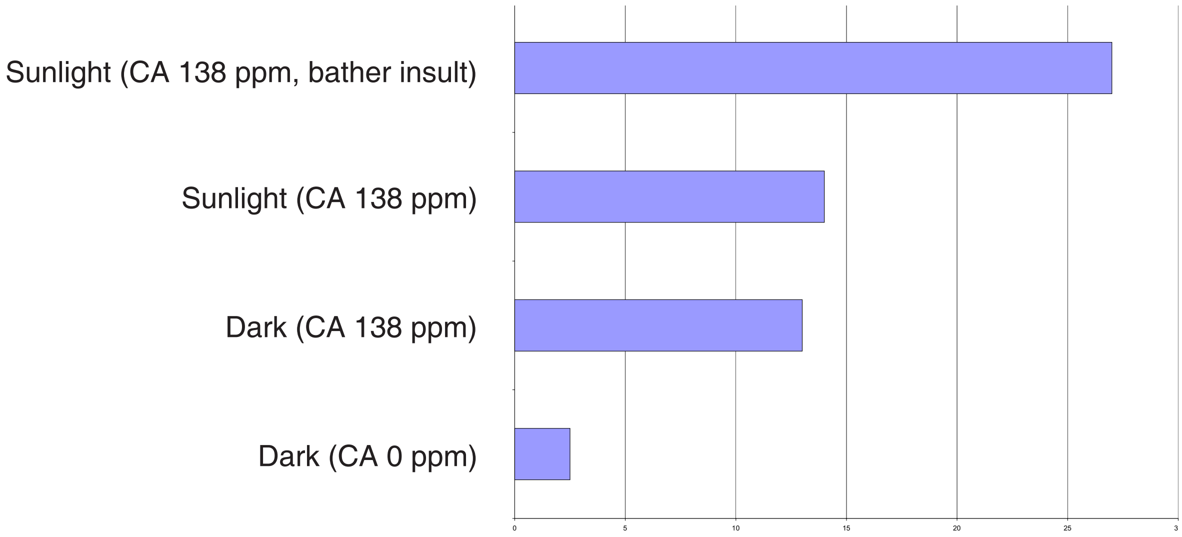


Figure 2 – Av. Cl Loss Rate (% per day)

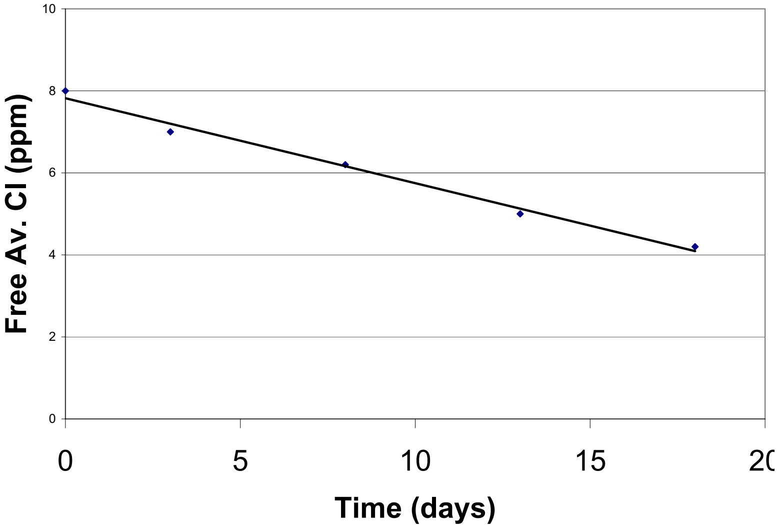


Figure 3 – Loss of Av. Cl vs. Time at 55–60ºF

show losses of 35 and 19%, respectively, after 4 hours exposure to sunlight. The data at 50 ppm CA is in reasonable agreement with the Monsanto data at the same concentration.

Recent Data – By contrast with Monsanto's data, experiments in a Phoenix area pool show a much lower av. Cl loss rate as shown in Table 2 and Figure 2. The data show that the av. Cl loss rate in bather-free stabilized water is approximately the same under outdoor and indoor conditions (i.e., in the presence and absence of sunlight), indicating that photochemical decomposition is very low (~1-2% per day). This is consistent with the fact that over 99% of the av. Cl in stabilized water is in the form of chloroisocyanurates, which do not significantly absorb UV radiation in sunlight. Virtually all of the decomposition (about 14%/day) observed in a bather-free pool in the summer time in the Phoenix area is due to thermal decomposition of chloroisocyanurates. i.e., oxidation of CA by av. Cl (Wojtowicz 2001). By contrast, the absence of CA results in a considerably lower av. Cl loss rate

(~3%) in the absence of sunlight.

Bather contaminants consume chlorine as a result of their oxidation and can significantly increase av. Cl loss rate as shown in Table 2 and Figure 2. Other factors that consume av. Cl are ancillary chemicals, algae, and windblown debris.

Effect of Temperature – Results of tests on a bather-free, CA stabilized swimming pool at a low temperature of 55-60°F are plotted in Figure 3. The average loss rate of 3.4%/day compare with 14%/day at 80-85°F. Using the loss rate of 12.5%/day at 80-85°F in the absence of sunlight gives a photochemical loss rate of 1.5%/day. Thus, the thermal loss rates of av. Cl at 55-60°F and 80-85°F are 1.9 and 12.5%/day, respectively. These results can be used to determine the activation energy (ΔE) for thermal decomposition of av. Cl in a bather-free, CA stabilized pool via the following form of the Arrhenius equation:

$$\text{Log}\,(r_2/r_1) = [\Delta E/(2.3R)](1/T_1 - 1/T_2)$$

Where: r_1 and r_2 are the av. Cl loss rates (%/day) at absolute temperatures of T_1 and T_2 (in degrees Kelvin, K = °C + 273) and R = 8.314 Joules $\text{mol}^{-1}\,\text{K}^{-1}$ is the gas constant. Inserting appropriate values of the variables gives a value of ΔE = 97.4 kJoules mol^{-1} (23.3 kcal mol^{-1}). This result means that the av. Cl loss rate increases by a factor of about 2 for each 10°F rise in temperature. The Arrhenius equation, $k = A\exp(-\Delta E/RT)$, for the loss of av. Cl in a bather-free, CA stabilized pool can be represented by the following equation, where k is the loss rate constant in %/day.

$$\begin{aligned} k &= 9.86\text{x}10^{17}\exp(-97{,}400/(RT)) \\ &= 9.86\text{x}10^{17}\exp(-11{,}713/T) \end{aligned}$$

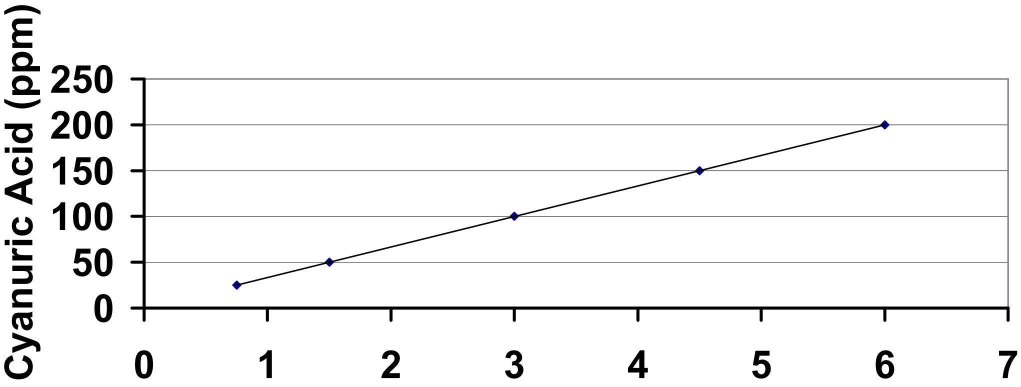
Effect of Cyanuric Acid on Swimming Pool Disinfection

Bacterial Kill Time

The following equation was obtained on analysis of literature data on the effect of cyanuric acid on the kill time of *S. facaelis* in distilled water (Wojtowicz 1996):

$$t_{0.99}\ (\text{pH } 7.5\ @\ 85°\text{F}) = 0.03 + 0.014[Cy_T/Cl_T]\ \text{min.}$$

where $t_{0.99}$ is the 99% kill time, Cy_T is the total cyanurate concentration in ppm and Cl_T is the free available chlorine concentration in ppm. This



Calculated Free Available Chlorine (ppm)
Based on Laboratory Data
(Andersen 1967 and Wojtowicz 1996)

Figure 4 – Minimum Available Chlorine for 30-second 99% Kill Time of *S. Faecalis* at pH 7.5 and 85°F

equation was used to calculate the minimum available chlorine for a 30–second 99% kill time at 85°F for various cyanuric acid concentrations which are plotted in Figure 4. The plot predicts that higher free av. Cl concentrations are required to achieve a 99% kill for *S. Facaelis* in 30 seconds at pH 7.5 at 85ºF with increasing CA concentration.

The NSPI recognizes that cyanuric acid affects the rate of disinfection by chlorine and recommends higher av. Cl levels for stabilized pools (1–3 ppm – see ANSI/NSPI–5 1995) vs. the 0.4 ppm historically recommended by other authoritative sources for unstabilized pools. In fact the NSPI has raised the ideal recommended av. Cl range to 2–4 ppm (ANSI/NSPI–4 1999 and ANSI/NSPI–5 2003, and draft versions of the BSR/NSPI/WWA–9 standards).

Many local health codes limit CA to 100 ppm and some do not allow use of CA at all.

Effect of Bather Contaminants on Disinfection in Stabilized Pools

Combined Chlorine Formation

Impurities introduced by bathers (i.e., sweat and urine) add nitrogen compounds to the water. Some of these compounds (e.g., ammonia, creatinine, amino acids, etc.) react with free available chlorine to form combined chlorine. Combined chlorine compounds are poor disinfectants because they bind chlorine very strongly, and consequently do not hydrolyze significantly to hypochlorous acid. An increase in combined chlorine reduces the concentration of free available chlorine and therefore increases the kill time of bacteria for a given total av. Cl.

Indeed, experimental data (Fitzgerald and DerVartanian 1967) show that ammonia greatly increases the kill time of chlorine whether CA is present or not. At low to moderate levels of added ammonia, the CA system as expected showed longer kill times than the CA–free system.

Studies in swimming pools report that kill times are comparatively long whether CA is present or not. Gardner (1973) states that "the reason for this is presumably the effect of ammonia and amines on the free HOCl concentration…". He also states that "The aim of break-point chlorination, however, is that the total chlorine concentration should always be kept in excess of the ammonia and amine concentration, and the effect of cyanuric acid on the HOCl concentration is then expected to be similar to the effect in the absence of ammoniacal nitrogen, i.e., as in the distilled water experiments".

Buffering Effect

Aqueous cyanuric acid and cyanuric ion form a buffer system similar to carbonic acid and bicarbonate ion, and therefore will contribute to the buffering of swimming pool water (Wojtowicz 1999).

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