Factors Affecting the Cyanuric Acid Concentrations in Swimming Pools

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Use of chloroisocyanurates for swimming pool sanitation results in a build-up of cyanuric acid (CA) with time. This is a concern because the kill time of bacteria increases with the ratio of cyanuric acid to free available chlorine at a given pH (Wojtowicz 1996). This is due to the fact that cyanuric acid reduces the concentration of hypochlorous acid. The NSPI (ANSI/NSPI–5 1995) recognizes that cyanuric acid affects the rate of disinfection by chlorine and recommends higher av. Cl levels for stabilized pools compared to unstabilized pools, i.e., 1–3 ppm vs. 0.4 ppm. In fact the NSPI has a draft proposal to raise the ideal recommended av. Cl range to 2-4 ppm (ANSI/NSPI–4 199X). Excessive concentrations of cyanuric acid should be avoided, not only to avoid compromising disinfection but also algae control. Equations for calculating the rate of build-up and the steady state concentration of cyanuric acid are developed. The NSPI recommends a maximum of 150 ppm CA and many Health Departments limit CA in public or commercial pools to 100 ppm because they recognize that CA affects disinfection. Various options are discussed for limiting or reducing the cyanuric acid concentration in swimming pools sanitized with chlorisocyanurates, including water purge, precipitation with melamine, adsorption on activated carbon, and oxidation with hypochlorite. The most practical method of controlling or limiting CA build–up is water purging. The loss rate of cyanuric acid from hypochlorite or chlorine sanitized pools is also discussed.

Journal of the Swimming Pool and Spa Industry
Volume 4, Number 2, pages 17–22

Build–up of Cyanuric Acid in Chloroisocyanurate–treated Pools

Steady State Cyanuric Acid Concentration

The increase in the cyanuric acid concentration in swimming pool water can be represented by the following differential equation:

1. $dC/dt = C_A - pC$

where: dC/dt is the instantaneous rate of change of the cyanuric acid concentration with time (ppm/week), dC and dt are differentials and represent infinitesimal changes in C and t, C_A is the cyanuric acid equivalent of the sanitizer addition rate (ppm/week), and p is the fraction of the pool water purged per week. At the steady state, dC/dt is equal to zero, therefore, the steady state cyanuric acid concentration (C_{SS}) is given by:

2. $C_{SS} = C_A/p$

Thus, the steady state cyanuric acid concentration is simply the quotient of the equivalent cyanuric addition rate and the fractional purge rate. The equivalent cyanuric addition rate is calculated from the Trichlor addition rate as follows:

3. $C_A = TCCA \cdot 28.4 \cdot 10^3 \cdot 129/(V \cdot 3.8 \cdot 232)$
$= TCCA \cdot 4155/V$

where: TCCA = trichloroisocyanuric acid (oz/week), 129 and 232 are the approximate molecular weights of cyanuric acid and trichloroisocyanuric acid, respectively, 3.8 = liters/gallon, and V is the pool volume in gallons. The purity of the Trichlor is not taken into account in the calculation, since it will have only a small effect given the fact that most Trichlor has an available chlorine of about 90.5% which is close to the theoretical value of 91.5%, i.e., a calculated assay of ~99%.

At a Trichlor addition rate of 14 oz/week to a 20,000–gal pool (equivalent to 2.9 ppm CA/week) and a purge rate of 0.01/week (i.e., 200 gal/week), the steady state cyanuric acid concentration would be 290 ppm. If the purge rate was 0.02, then the steady state cyanuric acid concentration would be 145 ppm. The actual steady state cyanuric acid concentration will depend on the actual Trichlor addition rate and water purge rate.

Increase of Cyanuric Acid Concentration with Time

Integration (i.e., conversion to an algebraic function) of equation 1 and application of boundary conditions (i.e., variable limits) gives the following equation representing the build–up of cyanuric acid with time:

4. $$C = C_0 \exp(-pt) + (C_A/p)[1 - \exp(-pt)]$$

where C_0 is the initial cyanuric acid concentration. Setting $t = \infty$ in equation 4 yields a similar relationship to equation 2.

The calculated build–up of cyanuric with time is shown in Figure 1 for a 20,000–gallon pool using a Trichlor addition rate of 14 oz/week, initial CA concentrations of 50, 100, and 150 ppm, and a purge rate of 1%/week (i.e., 200 gallons/week). The calculated CA build–up is based on a pool maintenance routine utilizing 26 backwashings per year. The graph shows that the steady state cyanuric acid concentration is unaffected by the initial concentration. It takes more than 10 years to reach the steady state concentration of 290 ppm. Even after 5 years, the cyanuric acid concentration only ranges from 78 to 87% of steady state. A similar plot (see Figure 2) showing the effect of a higher purge rate of 2% indicates a steady state CA concentration half that of Figure 1. Figure 3 shows the effect of a 2% purge rate on much higher initial CA concentrations of 200, 300, and 400 ppm. After 3 years an initial concentration of 400 ppm CA can be reduced to 200 ppm. These plots are illustrative only. The actual build–up or decay curve will depend on the length of the pool season, the Trichlor feed rate, and the water purge rate.

Since shocking with chloroisocyanurates (Dichlor or Trichlor) will increase the rate of cyanuric acid build–up in the pool, their use for this purpose is not recommended.

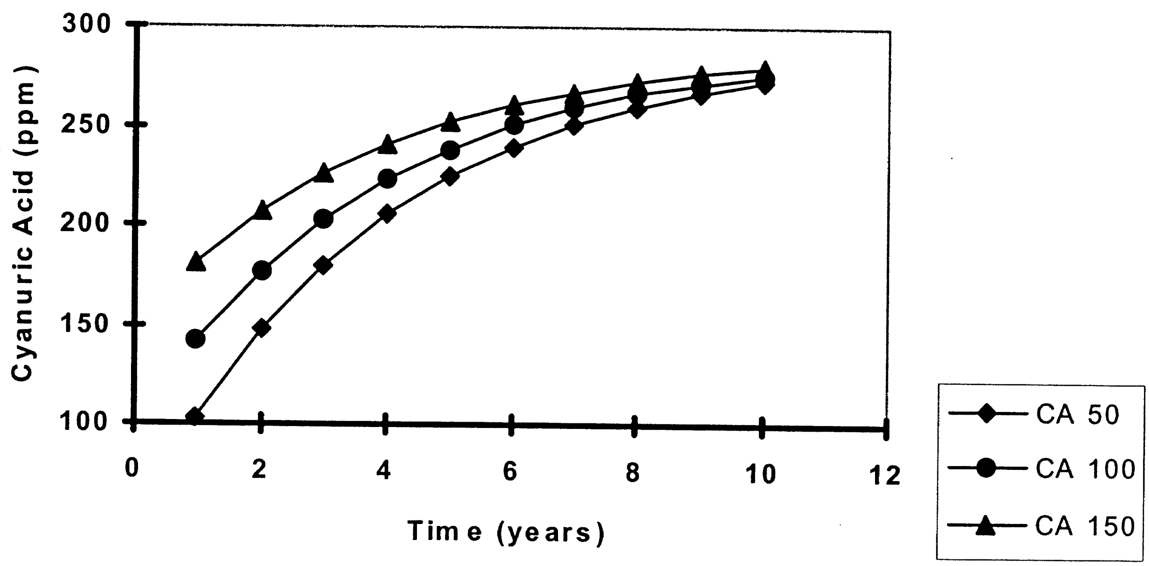


Figure 1 – CA Build–up vs. Time
V = 20,000 gal, 14 oz Trichlor/week, purge rate 0.01/week

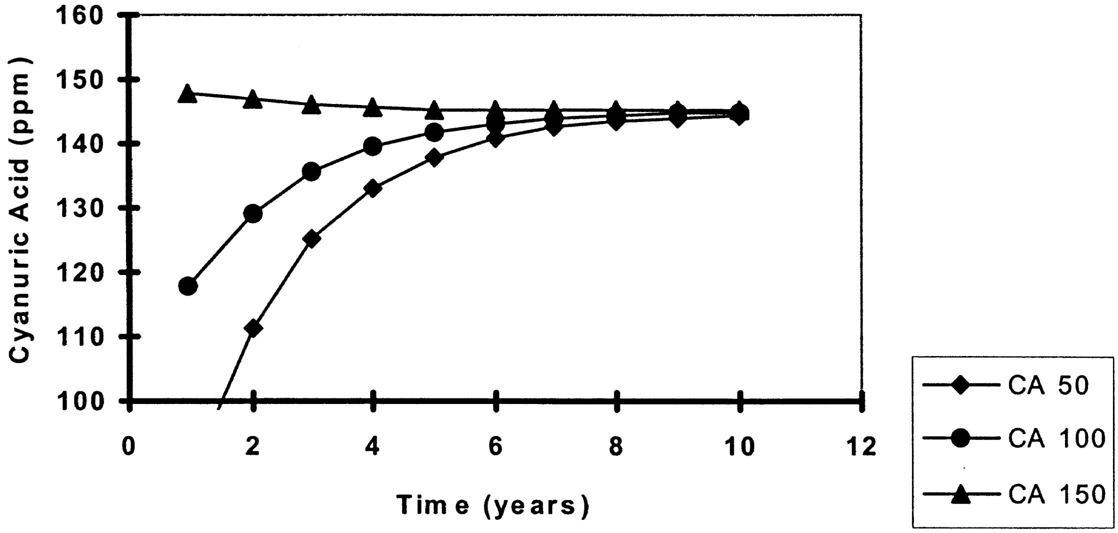


Figure 2 – CA Build–up vs. Time
V = 20,000 gal, 14 oz Trichlor/week, purge rate 0.02/week

Removal of Cyanuric Acid from Pool Water

Pool Water Purge

Purging during Filter Backwashing – A convenient way to keep the cyanuric acid concentration from building–up and maintaining it at a desired level would be to adjust the volume of filter backwash to eliminate the cyanuric acid added via the chloroisocyanurate sanitizer. Trichlor will contribute 2.9 ppm of cyanuric acid to a 20,000–gallon pool at a sanitizer addition rate of 14 oz/week. The necessary purge can be calculated using equation 3.

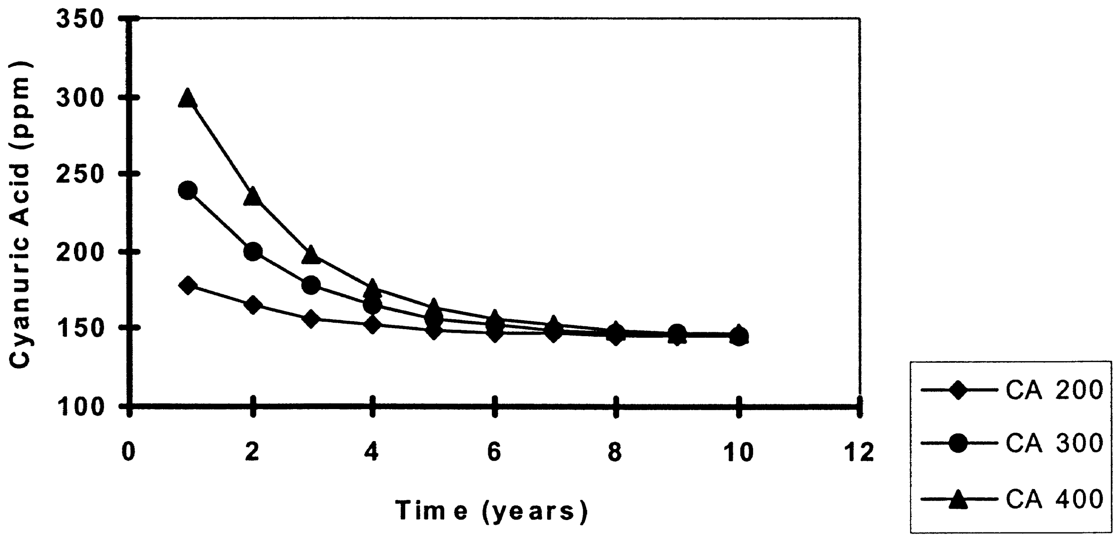


Figure 3 – CA Build–up vs. Time
V = 20,000 gal, 14 oz Trichlor/week, purge rate 0.02/week

Steady State CA Concentration (ppm)	Purge Fraction	Purge Water Gallons/week
50	0.058	1160
100	0.029	500
150	0.019	380
200	0.0145	290

Table 1 – Purge Fraction and Volume of Purge

Table 1 shows the purge fraction and volume of purge water to maintain different cyanuric acid concentrations in a 20,000–gallon pool. The calculated data show that the lower the steady state cyanuric acid concentration, the greater the purge necessary to maintain the desired CA level.

Purging at a Specific CA Level – An excessive cyanuric acid concentration can be reduced by removing a portion of the swimming pool water and replacing with fresh make–up water. The amount of purge water can be calculated by the following equation:

5. $V_P = (1 - CA_F/CA_I)V_T$

where: V_P = water purge (gal), CA_F = final CA concentration (ppm), CA_I = initial CA concentration (ppm), and V_T = total pool volume (gal). To remove 100 ppm of cyanuric acid from a 20,000–gallon swimming pool containing 300 ppm cyanuric acid would require replacing one third of the pool volume (i.e., 6,667 gallons) with fresh water. The purging can be seasonal or when the cyanuric acid concentration reaches a specific level.

Melamine–Cyanurate Precipitation

Cyanuric acid forms a slightly soluble (less than 10 ppm) precipitate with melamine according to the following reaction:

$$(HNCO)_3 + (H_2NCN)_3 \rightarrow (HNCO)_3 \cdot (H_2NCN)_3$$

This is the same reaction that takes place during determination of cyanuric acid in swimming pool water by test kit. The problem is that this will turn the entire pool cloudy and removal of the precipitated melamine cyanurate will be time consuming, requiring a combination of filtration and pool vacuuming as well as frequent backwashing of the filter. The quantity of melamine for a specific reduction in the cyanuric acid concentration can be calculated as follows:

6. $\text{Melamine (lb.)} = V \cdot 3.8 \cdot CA \cdot 126/(10^3 \cdot 454 \cdot 129) = V \cdot CA/(1.22 \cdot 10^5)$

where: V is the pool volume in gallons, 3.8 = liters/gallon, CA is the ppm of cyanuric acid to be removed, 126 and 129 are the molecular weights of melamine and cyanuric acid, respectively, and $10^3 \cdot 454$ converts mg to pounds. Approximately one pound of melamine is required to remove one pound of cyanuric acid. For example, removal of 100 ppm cyanuric acid from a 20,000–gallon swimming pool will require 16.4 pounds of melamine.

Removal of the cyanuric acid added through the sanitizer on a weekly basis would require substantially less melamine. The quantity of melamine can be calculated via the following equation:

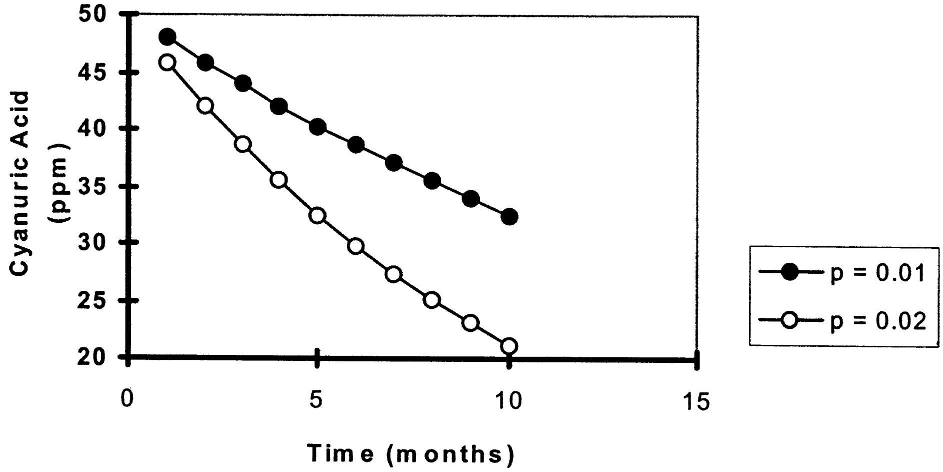
7. $\text{Melamine (oz)} = \text{TCCA (oz)} \cdot 126/232 = \text{TCCA (oz)} \cdot 0.543$

where: TCCA is the weight of trichloroisocyanuric acid and 126 and 232 are the molecular weights of melamine and trichloroisocyanuric acid, respectively. For example, a Trichlor addition rate of 14 oz/week to a 20,000 gallon pool would require 7.6 oz of melamine/week to keep the cyanuric acid at a fixed level, e.g., 50 ppm.

Adsorption on Activated Carbon

Cyanuric acid can be removed via adsorption by pumping the pool water through a cartridge filled with granular activated carbon. However, this method is costly because the loading of the carbon is not very high and the carbon requires regeneration (by combustion) resulting in some weight loss and possibly some loss in adsorption capacity. If we assume a 10% loading of the carbon, it would require about 150 pounds of carbon to

Figure 4 – Loss of CA vs. Time for Hypochlorite Treated Pools
Initial CA 50 ppm



reduce the concentration of cyanuric acid in a 20,000–gallon pool by 100 ppm. The cost of having a pool serviceman perform the operation would probably exceed that of simply purging the pool water as discussed above.

Oxidation

Cyanuric acid can be oxidized to nitrogen, carbon dioxide, and chloride ion with hypochlorite ion via the following overall reaction (Carlson 1978 and Wojtowicz 1981):

$$2(HNCO)_3 + 9ClO^- \rightarrow 3N_2 + 6CO_2 + 9Cl^- + 3H_20$$

However, the reaction is very slow at pool pH. For example addition of 50 ppm available chlorine to a pool with 300 ppm cyanuric acid would result in decomposition of only 6 ppm cyanuric acid in 24 hours in the absence of sunlight at 20 to 25°C. The loss rates would be about 40% higher at swimming pool temperatures of 80 to 85°F (or 26.7 to 29.4°C). The effect of sunlight or temperature on this reaction has not been determined.

Loss of Cyanuric Acid from Hypochlorite and Chlorine Treated Pools

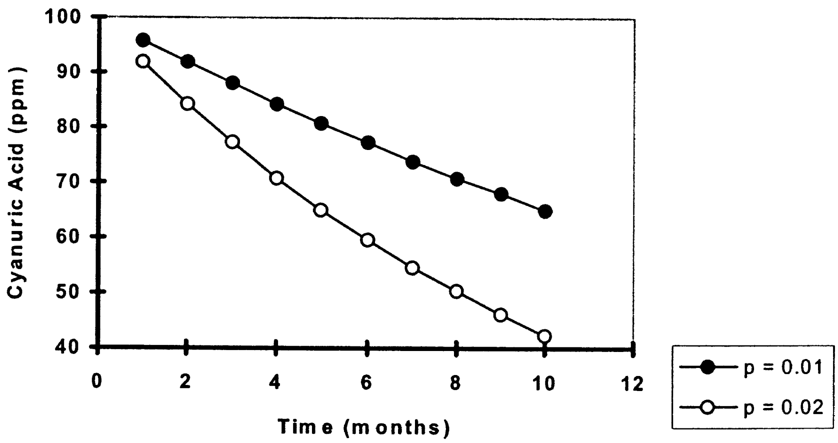
Loss due to Filter Backwashing

For hypochlorite or chlorine treated pools, C_A is equal to zero, therefore, equation 3 simplifies to:

8. $C = C_0 exp(-pt)$

This equation represents the rate of loss of cyanuric acid from hypochlorite or chlorine treated swimming pools as a function of the initial cyanuric acid concentration, time, and the water purge rate. The calculated cyanuric acid concentration as a function of time is plotted in Figure 4 for 50 ppm cyanuric acid for purge rates of 0.01 and 0.02/week. A similar plot for 100 ppm cyanuric acid is shown in Figure 5.

Figure 5 – Loss of CA vs. Time for Hypochlorite Treated Pools
Initial CA 100 ppm



Losses due to other factors

Field data (Hales 1998), derived from Southern Arizona in a predominantly sand–filter market, indicate a replacement rate of about 7 ppm CA/month for the average pool of 18,000 gallons at an average cyanuric acid concentration of about 100 ppm. This indicates a purge rate of 0.017/week, i.e., 288 gallons/week. This includes backwashing of the filter, splash–out, and carry–out. Olin data, based on CA analysis of pool water in the Connecticut area show a loss of 9.9 ppm/month at an average initial CA concentration of 69 ppm for pools ranging from 7,500 to 20,000 gallons. Filter backwashing is typically carried out for 3–4 minutes and amounts to 180–240 gallons at 60 gal/min. Splash–out is difficult to estimate because it's a function of the intensity of the activity of the bathers in the pool. Carry–out depends on the number of people using the pool, whether they are adults or children, and how many times a day that they go into and come out of the pool. If one estimates that an adult and a child carry–out 1 quart and 0.5 quarts of water, respectively, each time they use the pool and that they use the pool an average of 4 times each day, that the total carry–out would amount to 21 gallons/week for a family of 4, i.e., two adults and two children.

References

(ANSI/NSPI–4 199X Standard for Aboveground/ Onground Residential Swimming Pools)

(ANSI/NSPI–5 1995 Standard for Residential Inground Swimming Pools)

Carlson, R. H. "Sodium Hypochlorite Treatment for Removal of Cyanurate Compounds from Aqueous Waste Streams", U. S. Patent 4,075,094 Feb. 21, 1978 (to FMC Corporation).

Hales, J. Q., private communication from Pool Chlor (1998).

Wojtowicz, John A. Unpublished Data 1981.

Wojtowicz, J. A., "Oxidation of Cyanuric Acid with Hypochlorite", *Journal of the Swimming Pool and Spa Industry* 4:2(2001): 22–26.

Wojtowicz, J. A. "Relative Bactericidal Effectiveness of Hypochlorous Acid and Chloroisocyanurates", *Journal of the Swimming Pool and Spa Industry* 2:1(1996): 34–41.

About the Author

Now retired, **Mr. Wojtowicz** was a senior consulting scientist for Olin Corp. Seventeen of his 47 years of industrial experience was spent in the swimming pool chemical area and primarily involved swimming pool chemistry and process and product research on calcium hypochlorite, trichloroisocyanuric acid, and sodium dichloroisocyanurate. He holds over 55 U. S. patents and has published over 40 technical papers. He is currently a chemical consultant (Chemcon) residing at 3266 N 151st Drive, Goodyear AZ 85338, phone number 623–535–8851. His areas of expertise include swimming pool chemistry, manufacture and product and process development in hypochlorites and chloroisocyanurates, alternate sanitizers and sanitation systems (ozone, hydrogen peroxide–UV, bromine, etc.), chloramines and bromamines, computer programming, and expert witnessing.