5.2 – Factors Affecting the Cyanuric Acid Concentration in Swimming Pools

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. After reviewing the results of field testing of chloroisocyanurates in swimming pools, it was concluded that the recommended level of 0.4 ppm chlorine residual be amended to 1.5 ppm if cyanuric acid is used as a stabilizer (Robinton and Mood 1965). When chloroisocyanurates were introduced into the swimming pool market, the recommended free chlorine level was 1.0 to 1.5 ppm (Nelson 1967). This was adopted by the NSPI, subsequently widened to 1.0 to 3.0 ppm (ANSI/NSPI-5 1995), and recently increased to 2.0 to 4.0 ppm (ANSI/NSPI-5 2003). 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 chloroisocyanurates, including water purge, precipitation with melamine, adsorption on activated carbon, and oxidation with hypochlorite. The most practical method of controlling or limiting CA buildup is water purging. The loss rate of cyanuric acid from hypochlorite or chlorine sanitized pools is also discussed.

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Build-up of Cyanuric Acid in Chloroisocyanurate-treated, Backwashed Pools

Steady-state Cyanuric Acid Concentration

Rate of Build-up — 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 dt, 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.

Steady-state Concentration — At the steady-state, dC/dt is equal to zero, therefore, the steady-state cyanuric acid concentration ($C_{\rm SS}$) 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.

Effect of Trichlor Dosing — When using trichlor as a sanitizer, the equivalent cyanuric acid 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. The Trichlor addition rate can be significantly higher in hot Southwest locations.

Effect of Dichlor Dosing – The equivalent CA addition rate using Dichlor as a maintenance dose is calculated as follows:

4.
$$C_A = \frac{SDCC \cdot A \cdot 28.4 \cdot 10^3 \cdot 129}{100 \cdot V \cdot 3.8 \cdot 220}$$

where: SDCC = sodium dichloroisocyanurate (oz/week), A = % assay of SDCC, and 220 is the approximate molecular weight of SDCC. Other factors are as described above. At a Dichlor (56% av. Cl, $A = \sim 87\%$) addition rate of 21 oz/week to a 20,000-gal pool, the equivalent CA addition rate is 4.0 ppm/week. Using a water purge rate of 0.01/week, the steady-state CA concentration would be 400 ppm, which is considerably higher than with Trichlor under the same conditions.

Increase of Cyanuric Acid Concentration with Time

Time-Dependent CA Buildup – 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:

5.
$$C_t = C_0 \exp(-pt) + (C_A/p)[1 - \exp(-pt)]$$

where C_o and C_t are the cyanuric acid concentrations (ppm) initially and at time t. Setting $t=\infty$ in equation 5 yields a similar relationship to equation 2.

Build-up with Trichlor Dosing — When using Trichlor as a sanitizer (14 oz/wk), the calculated build—up of cyanuric acid with time is shown in Figure 1 for a 20,000—gallon pool for initial CA

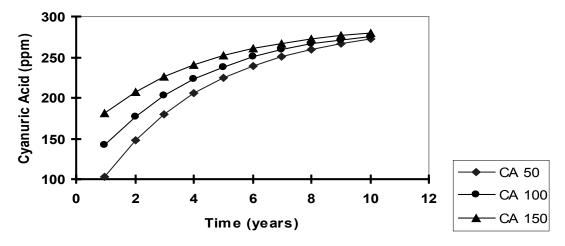


Figure 1 – CA Build-up vs. Time V = 20,000 gal, 14 oz Trichlor/week, purge rate 0.01/week

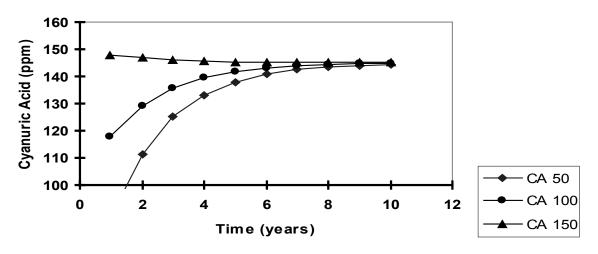


Figure 2 – CA Build-up vs. Time V = 20,000 gal, 14 oz Trichlor/week, purge rate 0.02/week

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 concen-

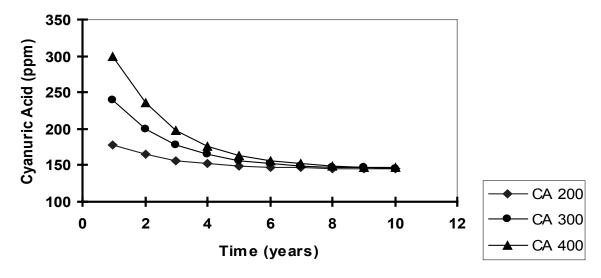


Figure 3 – CA Build-up vs. Time V = 20,000 gal, 14 oz Trichlor/week, purge rate 0.02/week

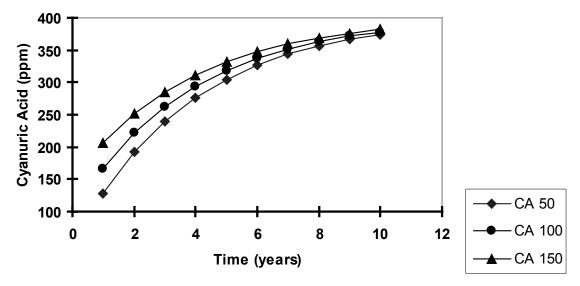


Figure 4 – CA Build-up vs. Time V = 20,000 gal, 21 oz Dichlor/week, purge rate 0.01/week

tration 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.

Build-up with Dichlor Dosing – The buildup of CA with time using Dichlor maintenance dosing is graphically illustrated in Figure 4 and shows that the rate is much higher than with Trichlor dosing shown in Figure 1.

Effect of Dichlor/Trichlor Shock – 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. For example, when Dichlor and Trichlor are used for both maintenance and shock dosing, the CA concentration can rise to very high levels (from an initial 50 ppm of CA) as shown in Table 1 and Figures 5 and 6.

CA Buildup in Non-Backwashed Pools – Some pools are not backwashed, e.g., pools with cartridge and DE filters. Consequently, the CA concentration in these pools will increase to much higher levels than in pools with sand filters that are backwashed periodically. Cyanuric acid build-up with time in non-backwashed pools is given by:

6.
$$C_t = C_0 + C_A \cdot t$$

where: t = number of weekly sanitizer additions. By contrast with backwashed pools, the CA concentration in non-backwashed pools will continue to increase with time and no steady state will develop. Table 2 compares the CA concentration in backwashed and non-backwashed pools treated with Trichlor and Dichlor with and without backwashing after 5 years.

	Ca(OCl) ₂		$\mathbf{Trichlor}^{\mathrm{B}}$		Dichlor ^B	
Shock	5 yrs	St. State	5 yrs	St. State	5 yrs	St. State
none	≤ 50	≤ 50	239	290	305	400
bi-weekly	≤ 50	≤ 50	414	530	562	754
weekly	≤ 50	≤ 50	588	771	820	1108

- A) Initial CA 50 ppm; purge rate 0.01/week.
- B) CA values will be 50% lower at a purge rate of 0.02.

Table 2. Comparison of ppm CA Buildup after 5 years vs. Purge Rate and Shocking Frequency							
	Trichlor ^A		Dichlor ^B				
Shock\Purge	0	0.01	0	0.01			
0	427	239	570	305			
biweekly	740	414	1030	562			
weekly	1052	588	1490	820			

- A) Maintenance: 14 oz/week/20K gals; shock: 23.1 oz Trichlor (90% av. Cl) or 32 oz Trichlor blend (65% av. Cl).
- B) Maintenance: 21 oz/week/20K gals; shock: 37.1 oz Dichlor (56% av. CI).

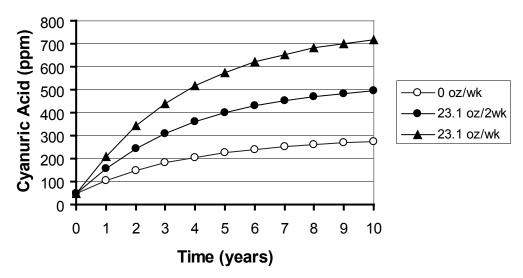


Figure 5 – CA Build-up vs. Time – Effect of Trichlor Shock Trichlor maintenance dose: 14 oz/week/20k gal Shock product: 71.8% Trichlor

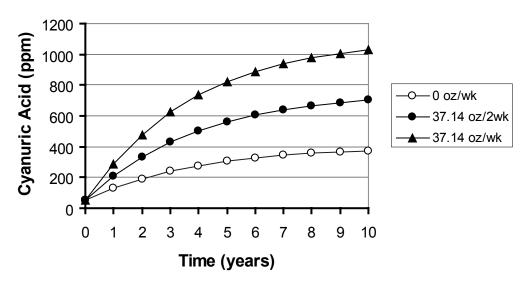


Figure 6 – CA Build-up vs. Time – Effect of Dichlor Shock Dichlor maintenance dose: 21 oz/week/20k gal

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 in pools with sand filters 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. Table 3 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:

7.
$$V_P = (1 - CA_F/CA_I)V_T$$

where: $V_{\rm p}$ = water purge (gal), ${\rm CA_F}$ = final CA concentration (ppm), ${\rm CA_I}$ = initial CA concentration (ppm), and $V_{\rm T}$ = 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:

$$(HNCO)_3 + (H_9NCN)_3 \rightarrow (HNCO)_3 \cdot (H_9NCN)_3$$

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:

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:

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 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 purg-

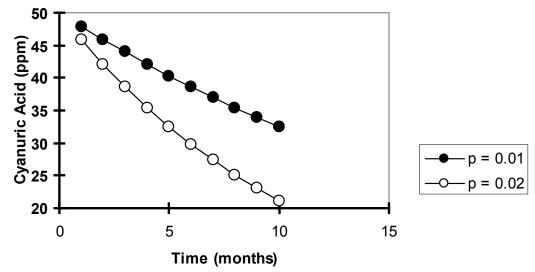


Figure 7 – Loss of CA vs. Time for Hypochlorite Treated Pools Initial CA 50 ppm

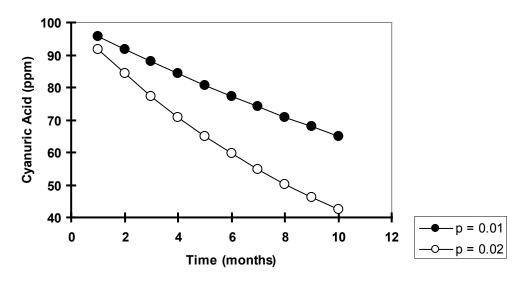


Figure 8 – Loss of CA vs. Time for Hypochlorite Treated Pools Initial CA 100 ppm

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

Table 3 – Purge Fraction and Volume of Purge

ing 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):

$$2\mathrm{(HNCO)_3} + 9\mathrm{ClO}^- \! \to 3\mathrm{N_2} + 6\mathrm{CO_2} + 9\mathrm{Cl}^- + 3\mathrm{H_2O}$$

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).

Loss of Cyanuric Acid from Hypochlorite and Chlorine Treated Pools

Loss Due to Filter Backwashing

For hypochlorite or chlorine treated pools, $\mathbf{C}_{\mathbf{A}}$ is equal to zero, therefore, equation 5 simplifies to:

10.
$$C = C_0 \exp(-pt)$$

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.

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—92

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.

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