# Cyanuric Acid Requirement Versus Free Chlorine in Pool Water

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*Relationships between hypochlorous acid and hypochlorite ion equilibria are discussed when in the presence of cyanuric acid.*

## Background

The ability of cyanuric acid to stabilize chlorine against destruction by sunlight, as well as slowing all other reactions of free chlorine is generally accepted to result from the binding of free chlorine and thereby suppressing the concentration of hypochlorite ion and of hypochlorous acid to comparatively low values. Tests by Monsanto researchers showed considerable stabilization of apparent free chlorine (initially at 2.5 ppm concentration) by cyanuric acid concentrations as low as 25 ppm (Nelson 1975, Wojtowicz 2004). (In the present paper the terms "apparent free chlorine" and "measured (or measurable) free chlorine" include not only hypochlorous acid and hypochlorite (true free chlorine) but also cyanurate-bound chlorine, which in testing with DPD shows up as "free" chlorine.)

Increases in cyanuric acid concentration above 25 ppm resulted in increased stabilization of chlorine, but with sharply diminishing returns. Such diminishing returns result from the fact that most of the "Free" chlorine is actually cyanurate bound by the time a 10:1 excess (in ppm) of cyanurate is reached.

## Estimating the Cyanuric Acid Requirement for a Given Free Chlorine Residual

Photolysis of free chlorine by sunlight results mainly from UV absorption at ~330nm wavelength by hypochlorite ion. Hypochlorous acid is also somewhat sensitive to sunlight, though to a significantly lower degree. Photolysis tends to be more rapid at higher pH due to the pH dependence of the hypochlorite ion/hypochlorous acid ratio (Nowell 1992, O'Brien 1974). Cyanurate-bound chlorine tends to be relatively stable to decomposition by sunlight. Thus, controlling solar destruction of free chlorine becomes a matter of providing a sufficient cyanurate concentration to limit the hypochlorite concentration to a low enough value to give acceptably low solar decomposition rates. Matching the stabilization of 2.5 ppm FC shown in Figure 1, but with a higher FC residual, becomes a matter of adding enough CyA to suppress the hypochlorite ion concentration to a value comparable to those achieved in the figure with 2.5 ppm FC and 25 ppm CyA.

Rigorous calculation of the concentrations of hypochlorite ion and of hypochlorous acid in the presence of cyanuric acid is complex and tedious, requiring the simultaneous solution of 11 equations. This can be done using equilibrium constants and methodology described by J.E. O'Brien in the early 1970s (O'Brien 1974). This method was used in the current paper to produce a couple of the graphs.

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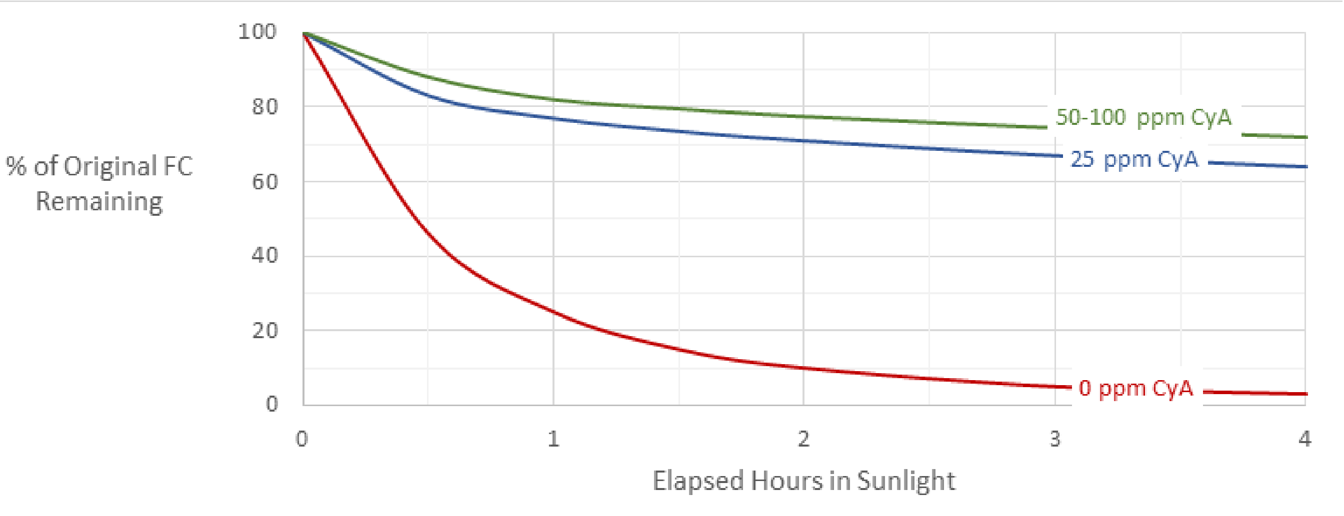

**Figure 1 — Stabilizing effect of cyanuric acid on free chlorine in moderate sunlight. From G.D. Nelson, Monsanto data.**

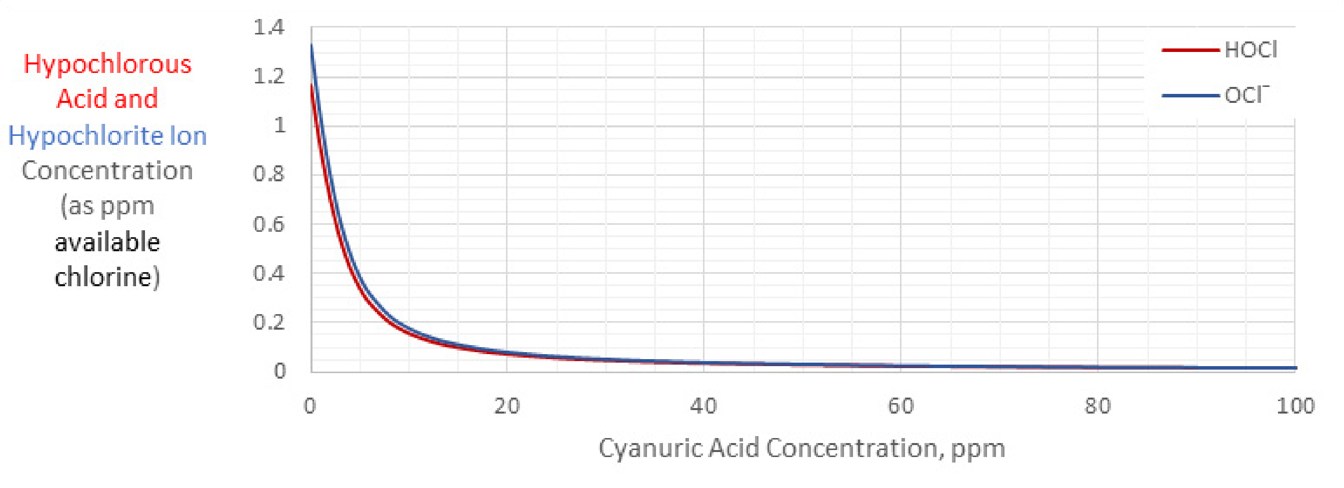

**Figure 2 — Calculated concentration of hypochlorous acid and hypochlorite ion (both expressed as ppm available chlorine). Assumed conditions: 2.5 ppm FC, pH 7.5, 1,500 ppm TDS, 81°F.**

David G. Wahman of the US Environmental Protection Agency has posted a tool online to do the complex calculations for a user, though that particular tool limits FC and CyA concentrations to 10 mg/L each (Wahman 2017).

There is, however, a simple shortcut to estimating hypochlorite concentration from the FC/CyA ratio for most common swimming pool scenarios. Richard Falk has noted that the hypochlorous acid concentration is often (inversely) tied to the concentration ratio CyA/FC (Falk 2019). Similarly, hypochlorite concentration can be estimated from the FC/CyA ratio for a number of common pool scenarios. When cyanuric acid is used, typical concentrations exceed 30 ppm, with chlorine concentrations on the order of 1–4 ppm. For such low ratios of apparent FC/total CyA namely $< 0.14$ ppm FC/ppm CyA, and concentrations of total CyA exceeding 20 ppm—hypochlorite ion concentration relates to the Apparent FC/total CyA ratio, or quotient ($Q$), as follows:

$$[OCl^-] = 1.08Q^2 + 0.529Q \qquad (1)$$

where $Q$ is the concentration ratio of apparent FC/total CyA (both expressed as ppm or mg/L) and the hypochlorite ion concentration, $[OCl^-]$, is expressed as ppm or mg/L avail-

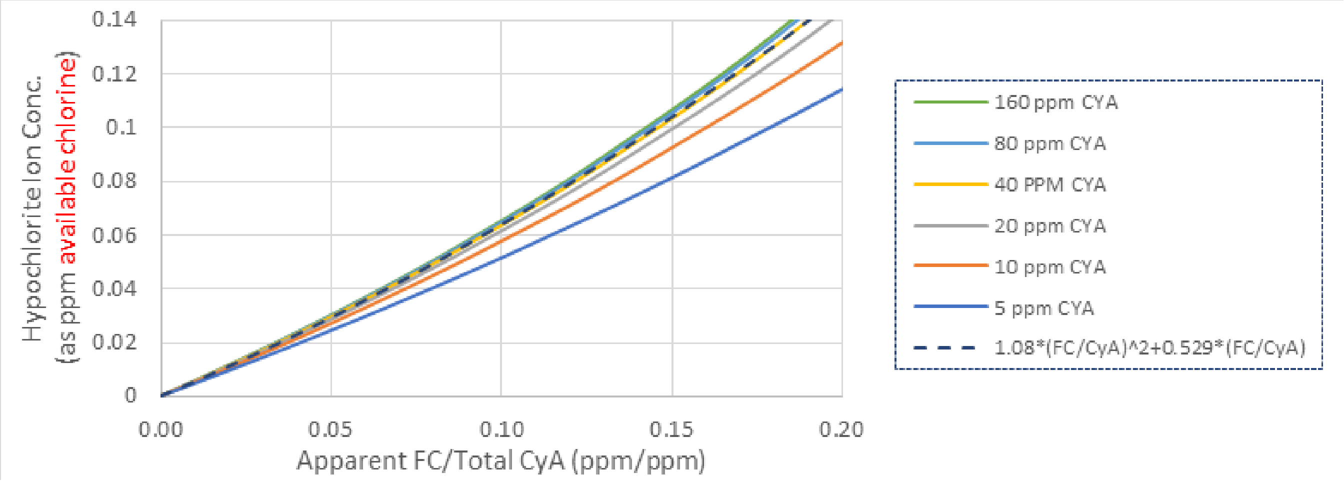

**Figure 3 — Relationship between hypochlorite ion concentration and the ratio FC/CyA at pH 7.5. All concentrations are in ppm or mg/L, and hypochlorite is expressed as the $Cl_2$ equivalent, or available chlorine.**

able chlorine. The relationship expressed in Equation (1) is less reliable at low values of CyA or high values of *Q* (or FC/CyA). This is illustrated in Figure 3. It should also be pointed out that while some proportionality between Q and hypochlorite will exist at any reasonable pool pH, Equation (1) strictly applies only near a pH of 7.5. In addition to the widely known fact that the hypochlorous acid/hypochlorite ion concentration ratio decreases with increasing pH, O'Brien has noted that binding of chlorine by cyanurate is strongest at pH 6.8 and weakens at either higher or lower pH (O'Brien 1974).

For protection from rapid depletion of free chlorine by oxidation of contaminants, hypochlorous acid concentration would be of more concern than hypochlorite concentration. There is, however, a mathematical relationship between hypochlorous acid concentration and hypochlorite ion concentration, with or without cyanurate being present. This relationship is expressed in Equation 2 where brackets indicate concentrations of the species indicated within the brackets, $K_a$ is the acid dissociation constant of *HOCl*, and $pK_a$ is –log(*Ka*). Generally, the $pK_a$ for hypochlorous acid is 7.5 ± 0.1, with $pK_a$ (and thus the $[HOCl]/[OCl^-]$ ratio) decreasing somewhat with increases in temperature or ionic strength. At a temperature of 27°C (81°F) and ionic strength of 0.0375 (TDS ≅ 1,500 mg/L) the $pK_a$ is about 7.44. (The calculations behind the graph in Figure 3 assume such conditions, as well as a pH of 7.5.) Strictly speaking, Equation 2 applies to concentrations expressed in molarity, however both hypochlorous acid concentration and hypochlorite ion concentration could be expressed as mg/L free chlorine and the same equation would apply.

Given the fairly well-defined relationship between hypochlorite concentration and the FC/CyA ratio, as shown in Figure 3 and approximated by Equation 1, and the proportional relationship with hypochlorous acid concentration, as indicated by Equation 2, it is possible to determine the required FC/CyA ratio to achieve any realistic hypochlorite ion and hypochlorous acid concentration combination. Since chlorine demand depends primarily on the concentrations of these two species, fixing these concentrations will serve to match general chlorine demand to

$$[HOCl] = [OCl^-] * \frac{[H^+]}{K_a} = [OCl^-] * 10^{(pK_a - pH)} \qquad (2)$$

other known values of FC and CyA. It is to be expected, within limits, that as the free chlorine concentration increases, a proportional increase in cyanuric acid concentration will suffice to limit chlorine loss to the same rate as at the lower concentrations of FC and CyA. Thus, for example, to match the chlorine decomposition rate of the Monsanto chart at the beginning of this paper, it is, in principle, only necessary to match the FC/CyA ratio of 2.5 ppm FC/25 ppm CyA. At 5 ppm FC the CyA would need to be increased to 50 ppm. For 10 ppm FC the CyA concentration would need to be 100 ppm, etc.

It should be noted, however, that at very high concentrations of free chlorine and cyanuric acid, there can be significant reaction between the chlorine and the cyanuric acid. This can most readily be observed with rather large FC/CyA ratios (e.g. 2:1 or 3:1) and high concentrations, as when dichlor or trichlor are moistened, resulting in the emanation of noxious fumes.

## Mathematical Modeling of Solar Decomposition

Modeling the CyA impact on solar decomposition rates in detail has failed to match the Monsanto data overall.

For the cyanurate-free loss of free chlorine due to sunlight, it is possible to get a fair match of the Monsanto data by assuming a 1.3 order dependence of the reaction rate on free chlorine concentration:

$$\frac{dC}{dt} = -k * C^{1.3} \qquad (3)$$

Some rearrangement and integration of this equation leads to the Equation (4), which can be used to generate a curve that can be fitted to the data:

1.3 Order kinetics: $C_2 = (C_1^{-0.3} + k * (t_2 - t_1))^{-1/0.3}$ (4)

1st Order $C_2 = C_1 * \exp(-k * (t_2 - t_1))$ (5)

2nd Order $C_2 = (C_1^{-1} + k * (t_2 - t_1))^{-1}$ (6)

$C_1$ and $C_2$ are the hypochlorite ion concentrations at times $t_1$ and $t_2$ respectively and k is a rate constant, adjusted to fit the data. (Note that to allow for photochemical decomposition of hypochlorous acid in parallel with hypochlorite, the same equation could be used with an adjustment to the value of the constant k to allow for the simultaneous, but slower, destruction of HOCl by sunlight.) Use of hypochlorite concentration alone, reaction order 1.3 and a k value of 0.145 gives a reasonable fit to the Monsanto data, as shown

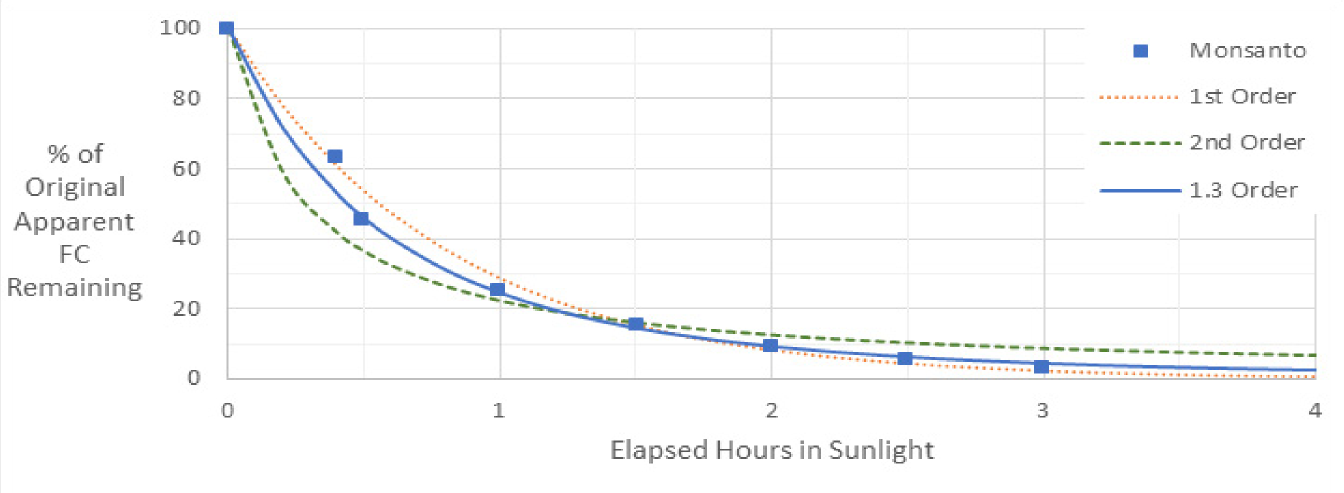

**Figure 4 — Fit of Monsanto data on solar destruction of free chlorine to 1st order, 2nd order and 1.3 order kinetics.**

in Figure 4.

It can be seen from the plot that the curve for 1st order kinetics provides too little curvature, while 2nd order kinetics provide too much curvature; but 1.3 order provides a fair fit to the reported data, apart from a possible outlier at 0.4 hour. Theoretically, 1st order kinetics involve the simplest, most expected photo decomposition reaction mechanism. The apparent 1.3 order might arise from a parallel, second order decomposition mode present simultaneously.

Assuming, then, kinetics that are 1.3 order in unbound chlorine ($HOCl + OCl^-$) and adjusting the decomposition rate downward to allow for the depressed concentration of $HOCl$ and $OCl^-$ in the presence of 25, 50 and 100 ppm CyA results in the curves shown in Figure 5.

To generate the plots in Figure 4 – 7, the procedure was as follows:

1. The starting apparent (measurable with DPD) free chlorine and total CyA concentrations (when CyA was present) were used to calculate hypochlorite ion concentration (expressed as ppm available chlorine). For the zero CyA case, it was assumed that the pH was at the $pK_a$ (~7.5) so half of the FC was hypochlorite ion. (See Equation (2)) For the cases with CyA, Equation (1) was used.
2. The decrease in the hypochlorite ion concentration was calculated using a kinetic equation. For 1.3 order reaction, Equation (4) was used. For 1st and 2nd order kinetics (Figure 4), Equation (5) or (6) was used with a rate constant (k value) of 1.25 or 3.5 respectively.
3. The resulting hypochlorite ion concentration at time $t_2$ was used to calculate the apparent FC, at time $t_2$, using Equation (7). This equation assumes that the hypochlorous acid concentration equals the hypochlorite ion concentration (pH ≈ 7.5), and subtracts twice the hypochlorite loss from the previous apparent FC. This entails an assumption that as hypochlorite is destroyed by UV light, there is a comparatively rapid Le Châtelier conversion of hypochlorous acid to hypochlorite to restore the balance between hypochlorite and hypochlorous acid concentrations demanded by the pH, as indicated in (2). So while decomposition occurs primarily via UV destruction of hypochlorite, there is facile conversion of hypochlorous acid to hypochlorite, allowing thereby a roughly equal rate of hypochlorous acid decomposition by the hypochlorite route.

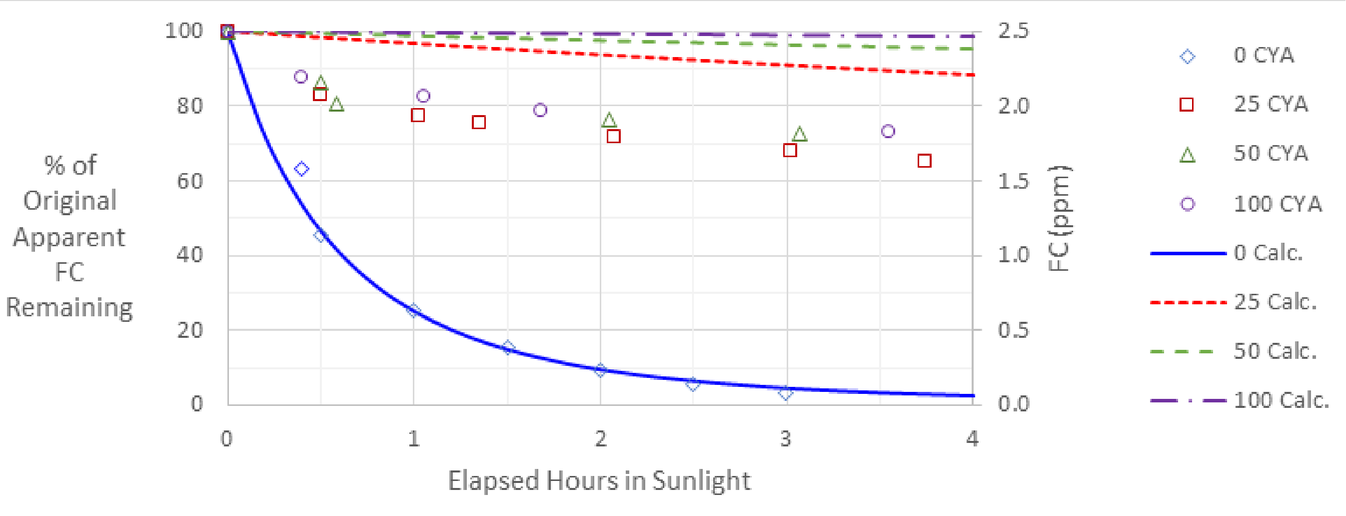

**Figure 5 – Comparison of Monsanto data with model assuming solar degradation of available chlorine does not involve any cyanurate-bound chlorine. Free chlorine starts at 5 ppm.**

$$FC_2 = FC_1 - 2 * ([OCl^-]_1 - [OCl^-]_2) \qquad (7)$$

Equation (1) was used to perform a Le Châtelier rebalance to the new hypochlorite concentration at time $t_2$ (freeing some hypochlorous acid and hypochlorite from CyA to replenish much of what was lost to solar destruction), and steps 2 and 3 were repeated. This continued in small increments of time (0.2 hours initially) until the elapsed time reached four hours.

Note that while the fit is fairly good for the cyanurate-free case, the cases involving 25, 50 or 100 ppm CyA show a marked departure of the theoretical curves from the Monsanto data points. With most of the chlorine bound to cyanurate (~95% even for the 25 ppm CyA case), the rate of solar chlorine destruction should correspondingly be very low, as shown by the theoretical (calculated) curves. The Monsanto data, on the other hand, show an initial rapid drop in chlorine concentration, even with CyA present, followed by a sudden leveling off to a rate loss more closely parallel to the theoretical predictions. Of various possible explanations for the rapid initial losses of FC, even in the CyA cases, the most plausible is the presence of chlorine demand in the water at the beginning of the tests. In citing the Monsanto data, Wojtowicz also noted the odd and sudden drop in the rate of chlorine decomposition after the first half-hour (Wojtowicz 2004). He also noted much slower loss due to sunlight than Monsanto reported, noting that the outdoor pool used

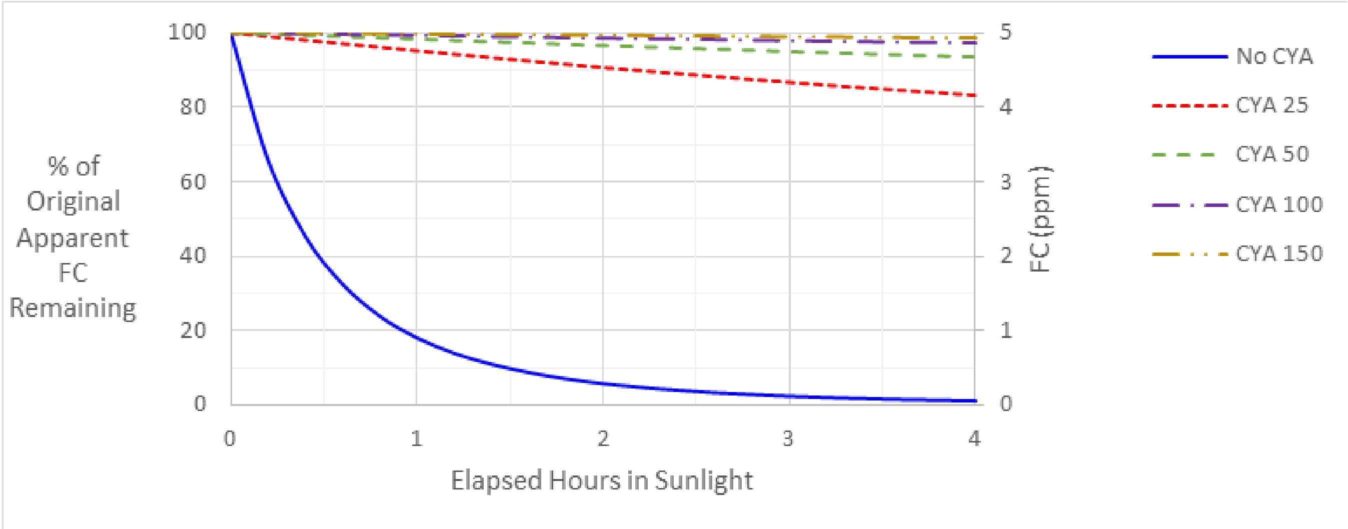

**Figure 6 – Model of stabilization of free chlorine. Free chlorine initially at 5 ppm.**

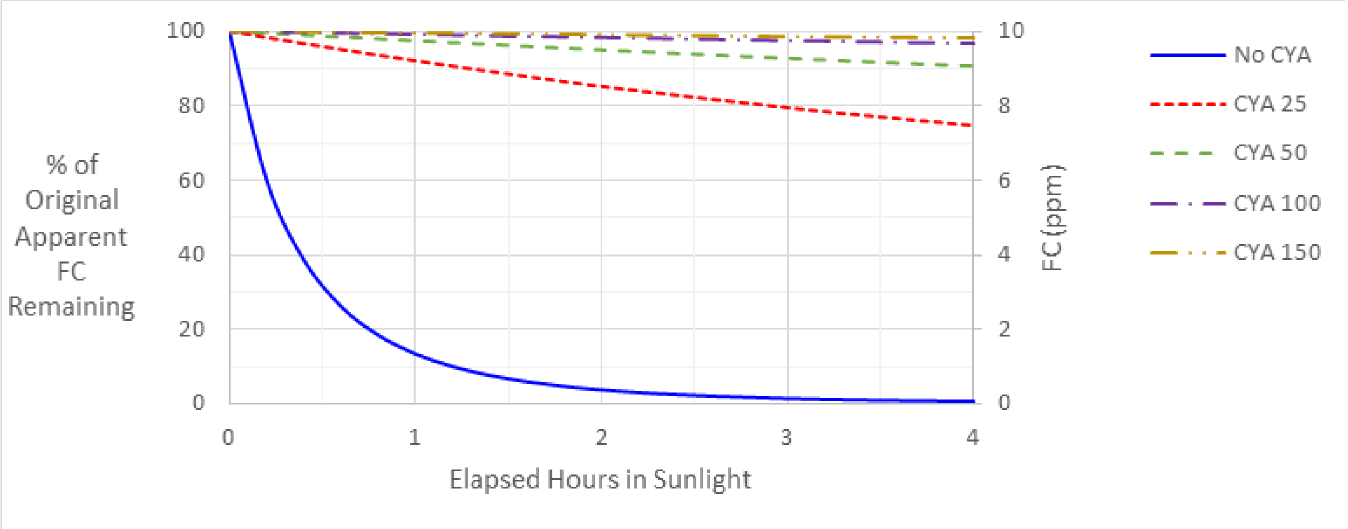

**Figure 7. Model of stabilization of free chlorine. Free chlorine initially at 10 ppm.**

for his testing (in Arizona) was not used by bathers, and therefore presumably had low chlorine demand. If the pools Nelson used for the Monsanto tests initially had chlorine demand, but were dosed to a 2.5 ppm FC concentration at the beginning of each test, satisfaction of the chlorine demand early in data collection may account for the steep initial drop in FC, followed by a large decline in the rate of chlorine loss to something closer to the theoretical predictions.

Figure 6 and Figure 7 use the same model as in Figure 5, but instead of the FC starting at 2.5 ppm, it starts at 5 and 10 ppm respectively, as shown on the right vertical axis of each plot. A comparison of the three graphs shows that to maintain the same free chlorine loss rate, when the FC is doubled, the CyA concentration must also be doubled. Thus the 100 ppm CyA curve in Figure 7 (10 ppm FC) roughly duplicates the 50 ppm CyA curve in Figure 6 (5 ppm FC) and the 25 ppm CyA curve in Figure 5 (2.5 ppm FC) in terms of FC loss rate. Each loses about 0.3 ppm FC over the course of four hours.

## The Optimum CyA/FC Ratio

For any free chlorine concentration, adding cyanuric acid serves to decrease the concentrations of hypochlorous acid and hypochlorite. This slows the rate of solar destruction, but by the same proportion also slows the oxidation of contaminants and the inactivation of pathogens. The advantage of doing this is that it makes it possible to provide relatively stable free chlorine residuals, by providing a large reserve of cyanurate bound chlorine, ready to be released as the truly free chlorine is consumed. Increasing the CyA/FC ratio provides for a more stable residual, but also slows the rate of disinfection. The optimum balance between stability and efficacy is not the same for all bodies of water. For indoor pools with no solar destruction of chlorine, it may be desirable to have little or no CyA present, to allow for the most rapid inactivation of pathogens and oxidation of bather waste, as long as the FC residual can be maintained. For outdoor bodies of water, especially shallow ones—such as kiddie pools, beach entries and flumes or slides—it may be nearly impossible to maintain a stable chlorine residual in bright sunlight unless circulation turnover times are short *and* the CyA/FC ratio is high.

In principle, a better balance between stabilization of free chlorine and disinfection rate may be obtained by operating at lower pH, since disinfection rate is proportional to hypochlorous acid concentration, while hypochlorite ion is more sensitive to sunlight. However, it may be difficult to take advantage of this fact in shallow, agitated bodies of water, since they would tend to be most subject to rapid loss of carbon dioxide, and consequent upward drift in pH. Carbon dioxide loss would be faster at lower pH and/or higher alkalinity.

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## About the Author

Stanley Pickens is a retired Senior Research Scientist from Axiall Corporation, a Westlake Company. Dr. Pickens served for over two decades on the Recreational Water Quality Committee (formerly called the Chemical Treatment and Process Committee) of the Pool &Hot Tub Alliance (formerly the Association of Pool and Spa Professionals, The International Aquatic Foundation, and National Spa and Pool Institute), writing and editing recreational water standards and educational materials. From 2014 to 2016 he served as chair of the committee. He also served on the Chlorine Stabilizer Ad Hoc Committee of the Council for the Model Aquatic Health Code from 2016 to 2020. Of his 36+ years in chemical research, 22 were focused on chemical water treatment. He has written and lectured on topics including water balance, chlorine stabilization, water-borne illness, and disinfection. He currently owns & operates Swim-Chem Consulting Services, LLC.