Relative Effects of pH and Cyanurate on Disinfection

Stanley R. Pickens, Ph.D.
Swim-Chem Consulting Services LLC

Using published equilibrium constants and adjusting for the impact of temperature and ionic strength to match common swimming pool conditions, hypochlorous acid concentration was calculated for a range of pH (7.0-9.0), free chlorine concentration (1, 2 and 4 mg/L) and chlorine stabilizer (cyanuric acid) concentration (0, 12.5, 25, 50 & 100 mg/L). The calculations show that hypochlorous acid concentration is generally much lower in the presence of stabilizer than in its absence; hypochlorous acid concentration is far less sensitive to pH than to the presence of stabilizer; and that, hypochlorous acid concentration is significantly less sensitive to pH in the presence of stabilizer than in its absence. Available disinfection rate data indicate that disinfection rates follow these same general trends seen for hypochlorous acid concentration. Raising the upper pH limit from 7.8 to 8.5 would have comparatively little impact on disinfection and water quality, while making it easier to maintain relatively constant pH, and thereby prevent the needless effects of corrosion and scale formation that can result from pH swings. It would also be appropriate to tie ideal chlorine residuals to cyanuric acid concentration, since cyanuric acid has a profound chlorine sequestering tendency.

Introduction

A number of standards and codes, such as *ANSI/APSP-11*[1] and the *Model Aquatic Health Code*[2], limit the operational pH for swimming pools and spas to the 7.2 to 7.8 range. The reasons for not allowing pH to be outside the 7.2 – 7.8 range generally include concerns about possible corrosion (especially at lower pH), scale formation (at higher pH), irritation or tissue damage, and the lower efficacy of chlorine at higher pH due to a shift toward more hypochlorite (a markedly less effective disinfectant) and away from hypochlorous acid (the dominant disinfectant in chlorinated pools) at higher pH.

Journal of the Swimming Pool and Spa Industry
Volume 6, Number 1, pages 6–19

Scale Control

The risk of scale formation at higher pH can be mitigated by proper application of a scale index, most commonly the Langelier Saturation Index. The primary limitation of the Langelier Index in open bodies of water, such as swimming pools, is failure to actually *predict* scale formation due to the tendency for pH to drift upward as carbon dioxide is lost to the atmosphere. This upward drift is most rapid when the pH is low and the alkalinity is high. The upward pH drift can lead to scale formation, unless pH is constantly controlled. Since use of pH controllers remains atypical in residential pools, it is desirable to have alternate means to limit upward drift in pH and the resulting scale formation. One method is to set a higher pH target (8.0 to 8.5) in combination with alkalinity low enough to achieve LSI (Langelier Saturation Index) balance.

Irritation and Tissue Damage

The human body can easily endure external exposure to a pH in the 8 to 9 range. The pH of some foods is in the alkaline range. For example, the pH of egg whites ranges from 7.0 to 9.0; and crackers range from 7.0 to 8.5.[3] The majority of soaps have pH values ranging from 9 to 10.[4]

Eyes are more sensitive than skin. The Annex to the *Model Aquatic Health Code* indicates that in terms of bather comfort optimum pH limits are 7.5 to 8.0.[5] No documentation was cited. A peer-reviewed study not cited in the annex to the code, however, noted that damage to corneal cells was observed after three hours of exposure to a pH outside the 6.5 to 8.5 range.[6] A 1973 study by Rylander, et al. on eye irritation by pool water generally reported no significant influence of pH variation between pH 7 and 9, though reduction of the pH from 8.0 to 7.0 resulted in higher frequency of eye irritation.[7] Eye drops and similar ophthalmic preparations typically are formulated with pH in the pH 6.5 – 8.5 range. Therefore, in the interest of bather comfort and safety, the pH of pool water should not be allowed to exceed 8.5.

Impact of pH on Disinfection

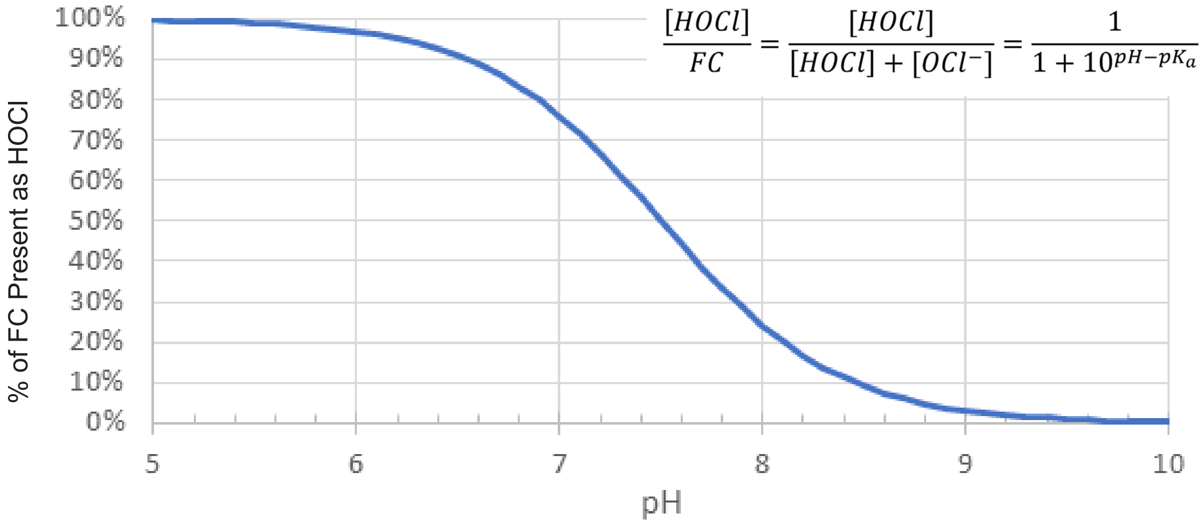
The primary reason cited in the *Model Aquatic Health Code Annex* for an upper pH limit of 7.8 is the impact of pH on hypochlorous acid concentration and the fact that, compared to hypochlorite ion, hypochlorous acid is estimated to be 100 times as effective at killing microorganisms.[8] For the same reason, pool operator training materials from various organizations, including APSP and NSPF[9], present graphs of the fraction of free chlorine in the acid (*HOCl*) form as a function of pH (Figure 1):

The *pKa* of hypochlorous acid, which appears in the equation that defines the graph, is about 7.4 to 7.5, depending on temperature and ionic strength.

Such plots and the associated guidance can, however, be misleading in many pools. Chlorine stabilizer (cyanuric acid) is commonly present, usually at concentrations exceeding 25 mg/L, especially in outdoor residential pools. Under such conditions most of the chlorine is bonded to isocyanurate, though DPD tests include cyanurate-bound chlorine in the free chlorine reading. (For this reason, in this paper the term "Free Chlorine" includes not only hypochlorite and hypochlorous acid, but also isocyanurate-bound available chlorine.) As is the case with hypochlorite, isocyanurate-bound chlorine is a relatively ineffective disinfectant. Most of the inactivation of microorganisms is accomplished by the small fraction of free chlorine present as hypochlorous acid, not hypochlorite or chlorine bonded to cyanurate. In view of this, a few key factors should be noted:

- When cyanuric acid is absent, hypochlorous acid concentrations tend to be *relatively* high—even at high pH.
- Hypochlorous acid concentration is far more sensitive to the cyanuric acid than to pH (when the pH range is limited to 7 – 8.5 and CYA concentration may range from 0 to >25 mg/L).

Figure 1 — Plot of hypochlorous acid fraction as a function of pH in the absence of cyanuric acid. Such plots are common in pool operator training materials.



- Hypochlorous acid concentration is far less sensitive to pH when measurable concentrations of cyanuric acid are present, than when cyanuric acid is absent.

Each of these points will be illustrated in the graphs and tables that follow.

Hypochlorous Acid Concentration Dependence pH and CYA

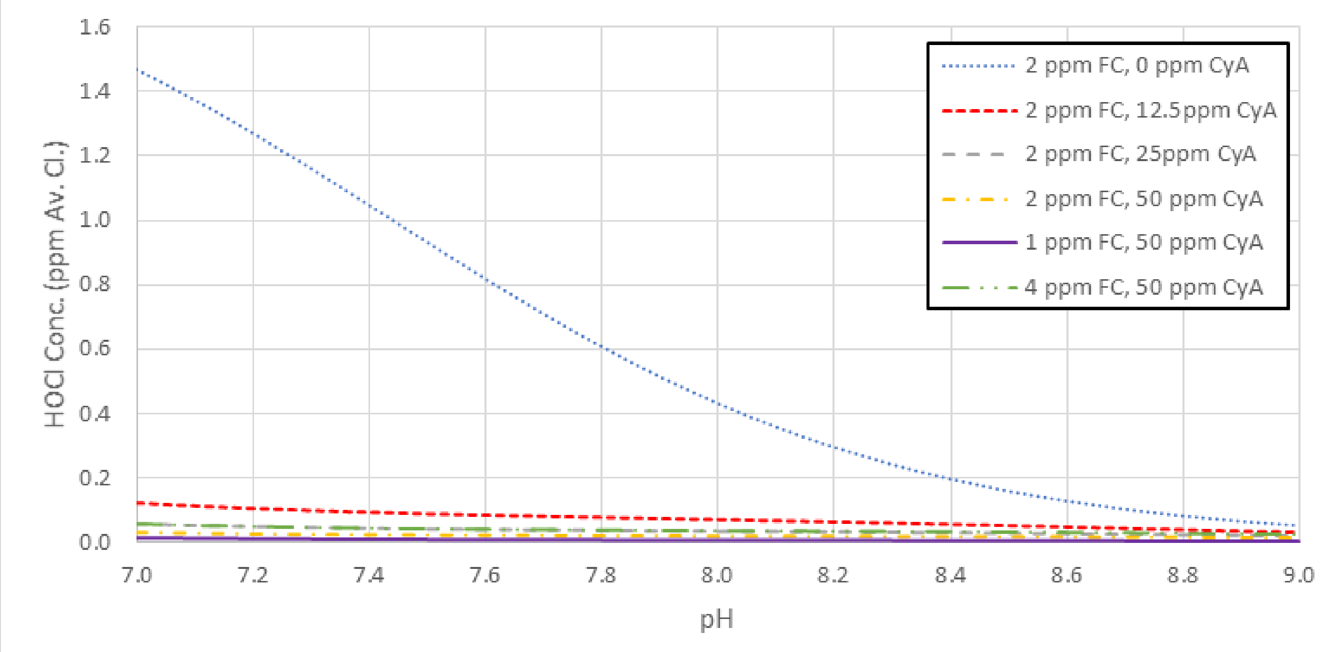
The graphs shown below illustrate the impact of pH, and measurable "free" chlorine and cyanuric acid concentrations on hypochlorous acid concentration. For all these graphs the assumed conditions were:

Temperature:	27.0°C (81°F)
Ionic Strength:	0.04 (Roughly 1,600 ppm TDS)
Free Chlorine:	1, 2 or 4 mg/L, as indicated, in most cases 2mg/L
Cyanuric Acid:	0, 12.5, 25, or 50 mg/L, as indicated. (This includes all ten possible forms cyanuric acid: ionized or uncharged, unchlorinated, monochlorinated, dichlorinated, trichlorinated, etc.)

At the temperature and ionic strength indicated, the *pKa* of hypochlorous acid is approximately 7.44.

Figure 2, below, shows the decline in hypochlorous acid concentration as pH increases. The higher, blue, dotted-line curve is for 2 mg/L free chlorine and no cyanuric acid. The shape matches that of the common reverse-sigmoidal graph shown in Figure 1, though the pH range in Figure 2 is limited, so the full sigmoidal shape of the curve is not displayed. Note that with cyanuric acid present, even at the low concentration of 12.5 mg/L (red, dashed line), hypochlorous acid concentration is much lower than the cyanurate-free curve. Clearly hypochlorous acid concentration is more sensitive to cyanuric acid concentration than to pH. The hypochlorous acid concentration in the absence of cyanuric acid at pH 8.6 is higher than the hypochlorous acid concentration with 12.5 mg/L cyanuric acid at pH 7.0. Doubling the cyanuric acid concentration has as large an impact on hypochlorous acid concentration as raising the pH one to two full units. This can be seen in Figure 3 and Figure 4, in which the free chlorine concentration is fixed at 2 mg/L and the cyanuric acid concentration ranges from 0 to 100 mg/L. The vertical axis in Figure 3 is expanded to focus on the 0 to 0.4 mg/L hypochlorous acid range. The vertical axis in Figure 4 is logarithmic, allowing the hypochlorous acid sensitivity to pH to be compared for various cyanurate concentrations.

Figure 2 — Hypochlorous acid concentration as a function of pH at various cyanurate and chlorine concentrations. Hypochlorous acid concentration is expressed in units of mg/L available chlorine.



In addition to being more sensitive to cyanuric acid concentration than to pH, hypochlorous acid concentration is far less sensitive to pH when cyanuric acid is present than when it is absent. This becomes more apparent in Figure 4, in which all the curves are for 2 mg/L free chlorine concentration and the hypochlorous acid (vertical) axis is logarithmic, and in Figure 5, which shows a plot of the ratio of *HOCl* concentration at the given pH to the *HOCl* concentration at pH 7.5 for the same combination of free chlorine and cyanuric acid. By normalizing the hypochlorous acid concentration at any given pH to the concentration at pH 7.5, all of the curves are brought into the same approximate magnitude on the vertical axis. Due to this normalization, all the curves naturally cross each other at pH 7.5 and a ratio or normalized value of 1.0. A normalization pH of 7.5 was selected because 7.5 is the midpoint of the common operating range of pH 7.2 – 7.8.

Note that the cyanurate-free curve (blue

Figure 3 — Hypochlorous acid concentration versus pH for 2 mg/L free chlorine and various cyanuric acid concentrations, as indicated.

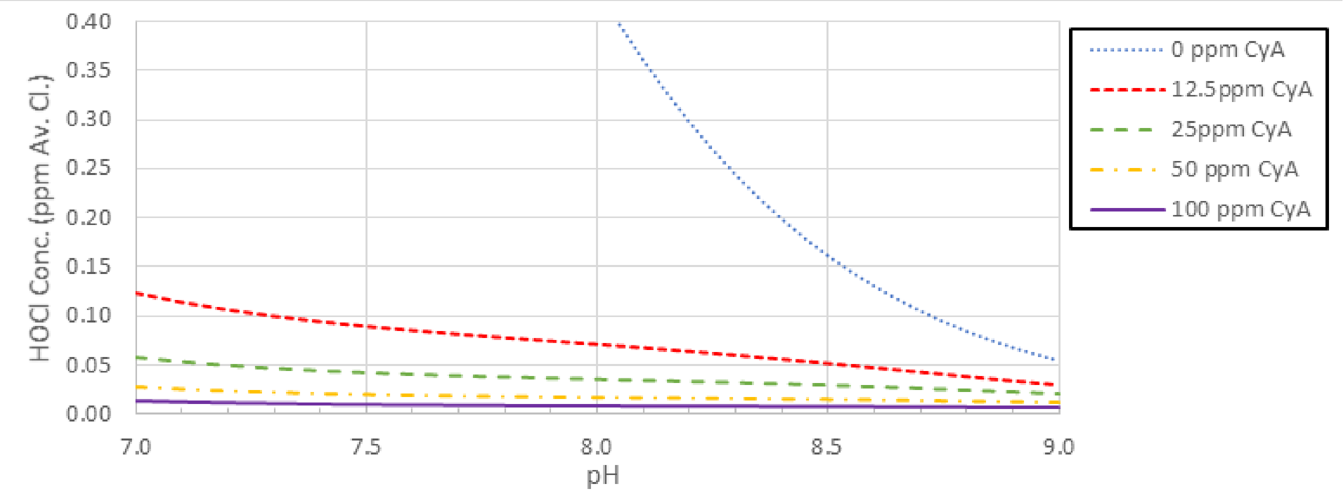
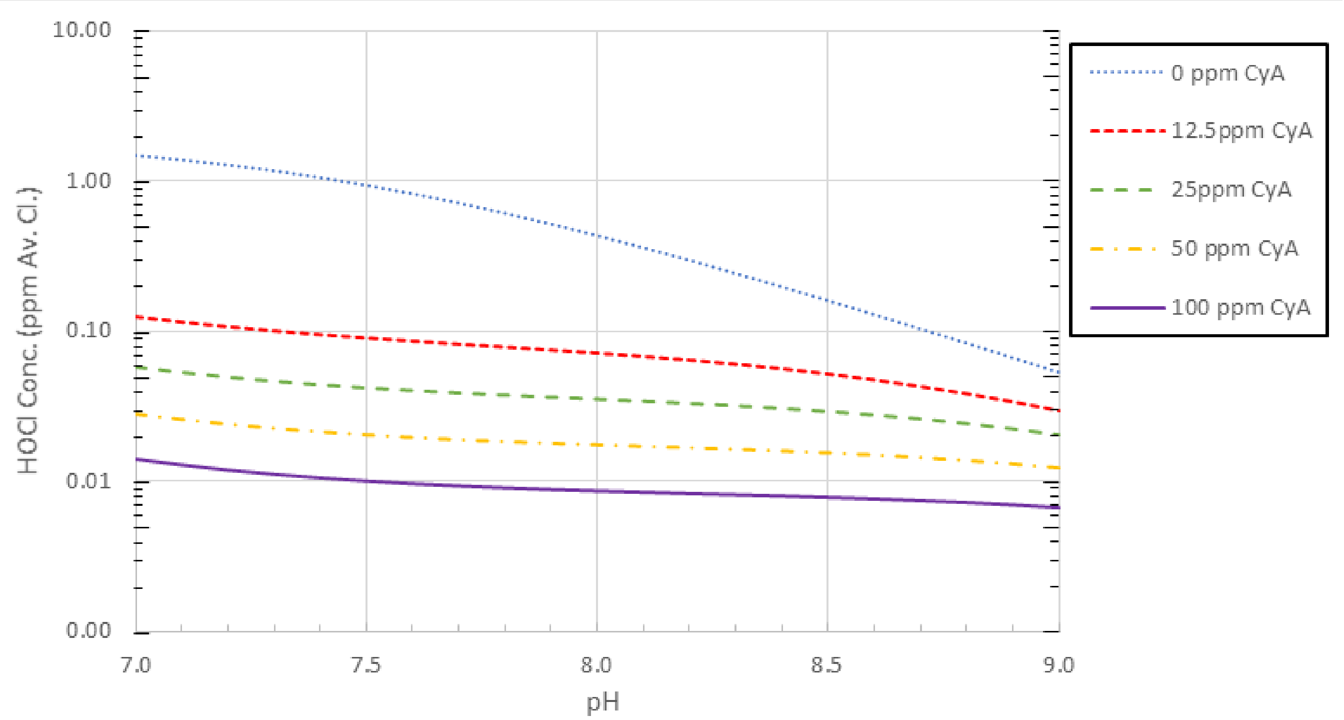


Figure 4 — Hypochlorous acid concentration as a function of pH for various cyanuric acid concentrations. The hypochlorous acid concentration (vertical axis) is logarithmic. For all curves, free chlorine is 2 mg/L, temperature 27°C (81°F) and ionic strength 0.04.



dotted line) in Figures 2 to 5 varies more with pH than do the curves in which cyanurate is present; and to some degree the sensitivity of hypochlorous acid concentration to pH decreases with increasing cyanuric acid concentration, though with diminishing additional impact as cyanuric acid concentration increases from already substantial values. This decrease in pH sensitivity as cyanurate is added may seem surprising, since cyanurate should have no influence on the hypochlorous acid acid-dissociation equilibrium constant, *Ka*, or *pKa*, or the equation shown in Figure 1. The same relationship between pH and the ratio [HOCl]/([HOCl]+[OCl$^-$]) exists with or without cyanuric acid; however, the affinity of cyanuric acid for chlorine decreases as the pH moves upward from 7.0. This is shown in Figure 6, where the concentrations of hypochlorous acid, hypochlorite anion, and the total isocyanurate-bonded chlorine are plotted versus pH. Note how the solid purple line (cyanurate-bonded chlorine) drops off, especially as the pH rises above 8. With less chlorine bonded

Figure 5 — Hypochlorous acid concentration at any given pH normalized to the concentration at pH 7.5

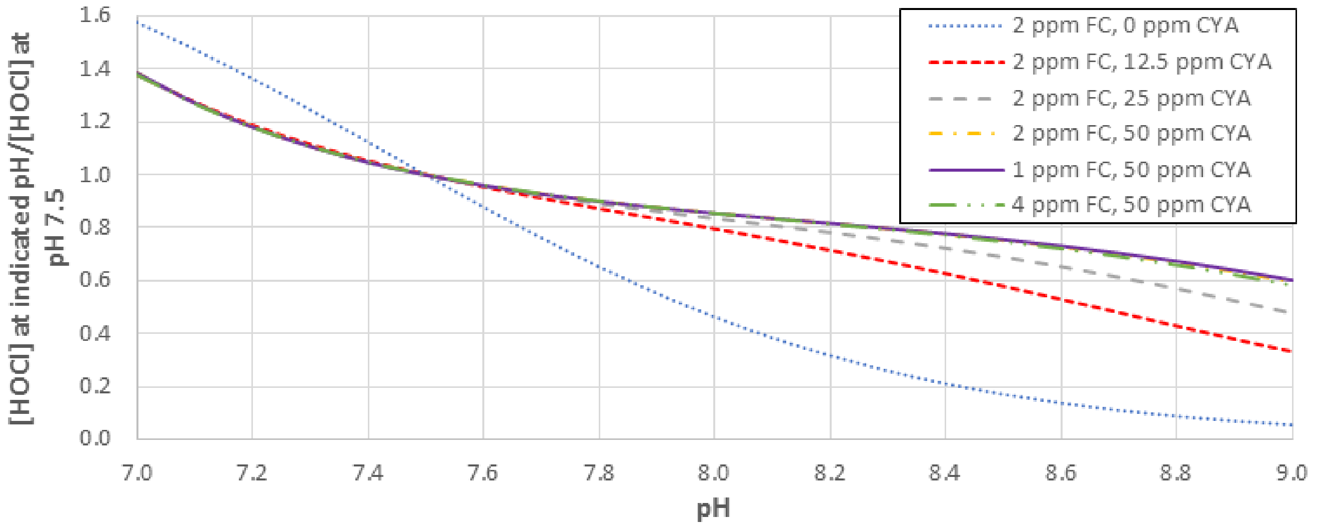
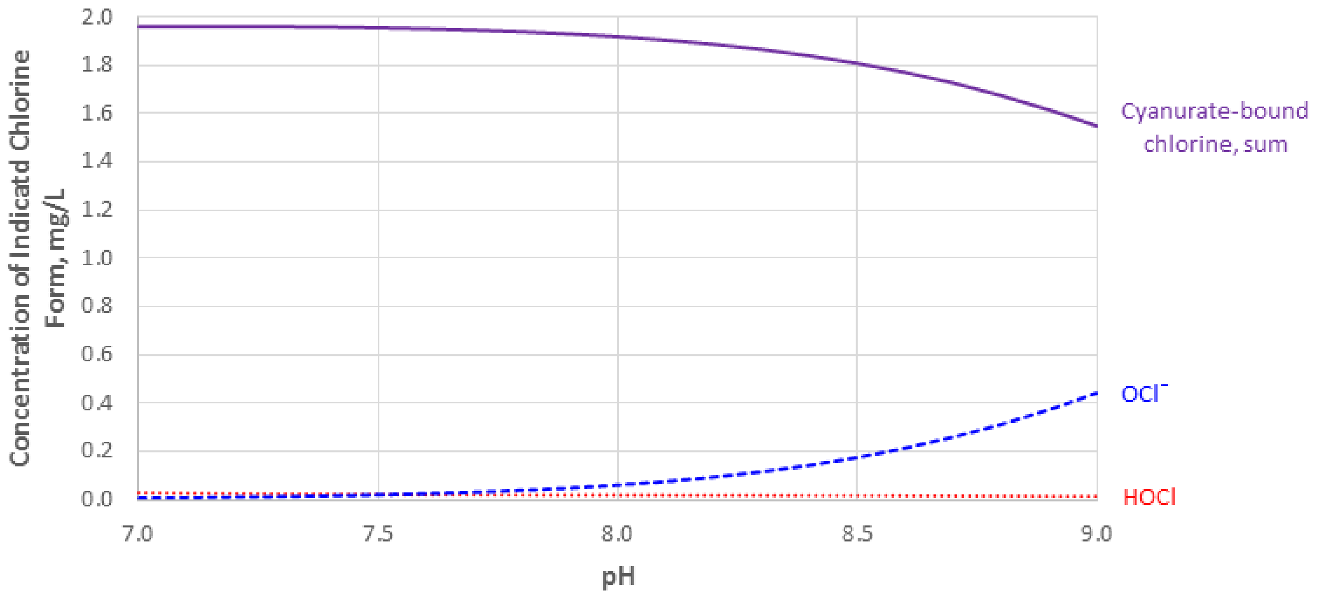


Figure 6 — Concentrations of hypochlorous acid, hypochlorite and cyanurate-bound chlorine (sum from six possible species) versus pH. Conditions: 2 ppm FC, 50 ppm CYA, 27°C (80.6°F), 0.04 ionic strength (~1,600 ppm TDS.)



to isocyanurate as pH increases, the hypochlorite ion concentration rises more and the hypochlorous acid concentration drops off less than would be the case in the absence of cyanuric acid.

For reference, Table 1 provides the numeric values plotted in Figure 5. Stabilized-chlorine pools rarely have cyanuric acid concentrations below 25 mg/L, and usually do not maintain chlorine concentrations greater than 4 mg/L. (At present the US EPA does not allow bather entry to the water when the free chlorine concentration exceeds 4 mg/L.) Consequently, the last four columns in the table are most relevant to common situations. From these columns, it can be seen that even at pH 8.5 the hypochlorous acid concentration is at least 70% of what it would be at pH 7.5 (for the same concentrations of free chlorine and cyanuric acid). If the cyanuric acid concentration is at least 50 mg/L, the hypochlorous acid concentration at pH 8.5 is at least 75% of what it would be at pH 7.5.

The net takeaway from these calculations is that hypochlorous acid concentration is far more sensitive to cyanuric acid concentration than to pH, and that when cyanuric acid is present, and hypochlorous acid is therefore lowest, sensitivity of hypochlorous acid concentration to pH is also at its lowest. It is generally acknowledged that hypochlorous acid is the primary or only significant disinfectant in chlorine treated recreational water. If the chlorine is not stabilized, hypochlorous acid concentration would be higher than in a typical stabilized pool. This is the case even if the pH is as high as 8.5 in the non-stabilized pool and as low as 7.2 in the stabilized pool. On the other hand, in stabilized pool water—where hypochlorous acid concentrations tend to be the lowest—the pH sensitivity is so low that increasing the pH limit to 8.5 would only allow the hypochlorous acid concentration to drop to 75% of what it would be at pH 7.5 or 83% of what it would be at the currently common upper limit of pH 7.8.

Table 1 — Relative Dependence of Hypochlorous Acid Concentration on pH, normalized to pH 7.5.

	HOCl Concentration at Given pH Divided by *HOCl* Concentration at pH 7.5					
pH	**2 ppm FC, 0 ppm CYA**	**2 ppm FC, 12.5 ppm CYA**	**2 ppm FC, 25 ppm CYA**	**2 ppm FC, 50 ppm CYA**	**1 ppm FC, 50 ppm CYA**	**4 ppm FC, 50 ppm CYA**
7.0	1.57	1.38	1.38	1.38	1.39	1.38
7.1	1.47	1.27	1.27	1.27	1.27	1.27
7.2	1.36	1.19	1.18	1.18	1.18	1.18
7.3	1.25	1.11	1.11	1.11	1.11	1.11
7.4	1.12	1.05	1.05	1.05	1.05	1.05
7.5	1.00	1.00	1.00	1.00	1.00	1.00
7.6	0.88	0.95	0.96	0.96	0.96	0.96
7.7	0.76	0.91	0.92	0.93	0.93	0.93
7.8	0.65	0.87	0.89	0.90	0.90	0.90
7.9	0.55	0.83	0.86	0.88	0.88	0.88
8.0	0.46	0.80	0.84	0.86	0.86	0.85
8.1	0.39	0.76	0.81	0.84	0.84	0.83
8.2	0.32	0.72	0.78	0.82	0.82	0.81
8.3	0.26	0.67	0.76	0.80	0.80	0.79
8.4	0.21	0.63	0.72	0.78	0.78	0.77
8.5	0.17	0.58	0.69	0.75	0.76	0.75
8.6	0.14	0.53	0.65	0.73	0.73	0.72
8.7	0.11	0.48	0.61	0.70	0.70	0.69
8.8	0.09	0.43	0.57	0.67	0.67	0.66
8.9	0.07	0.38	0.53	0.64	0.64	0.62
9.0	0.06	0.33	0.48	0.60	0.60	0.58

Consequently, one would expect that disinfection should be little affected by increasing the pH upper limit from 7.8 to 8.5. This invites the question of whether this expectation would be borne out by actual disinfection data.

Impact of pH on Disinfection Time

To verify whether the predictions based on calculated hypochlorous acid concentration are supported by actual disinfection data, peer-reviewed studies were sought in which disinfection rates were compared over a range of pH and cyanuric acid concentrations. One published study was located that satisfied these criteria.[10] In this paper John Anderson measured 99% kill times for *Streptococcus faecalis*, currently referred to as *Enterococcus faecalis*, at pH 7.0 and 9.0, at cyanuric acid concentrations of 0, 25, 50 and 100 mg/L, and nominal total chlorine concentrations of 0.25, 0.5 and 1.0. Data were also provided in the paper that allow estimation of free chlorine concentrations for each of the total chlorine concentrations measured. (See section on Methods.)

Unfortunately, since kill times are so short in the absence of cyanuric acid, kill times could not be accurately estimated for free chlorine concentrations >0.2 mg/L and cyanuric acid concentration of zero. Nevertheless, a couple of clear relationships are confirmed:

1. As expected, kill times (not just hypochlorous acid concentration) are far more dependent on cyanuric acid concentration than on pH.
2. Also, as expected, while kill times are longer in the presence of cyanuric acid, they are also far less dependent on pH. With 25 mg/L or more of cyanuric acid present, the kill times at pH 9.0 are generally little over twice the kill times at pH 7.0, whereas in cyanurate-free water, kill times are several times (probably >10x) longer at pH 9.0 than at pH 7.0.

One unexpected observation is that with no cyanuric acid present, kill times are far less sensitive (by about half) to pH than is hypochlorous acid concentration; whereas with at least 25 mg/L of cyanuric acid present, kill times generally appear to be somewhat more sensitive to pH than is hypochlorous acid concentration. Nevertheless, it appears clear that in the absence of chlorine stabilizer, bacterial inactivation times tend to be short, even at pH as high as 9; whereas with stabilizer present, kill times are relatively insensitive to pH.

Table 2 — Time required for 99% inactivation of S. faecalis at pH 7 vs. pH 9 for various combinations of free chlorine and cyanuric acid concentration.

Also included, at right, are estimated hypochlorous acid concentrations.

CYA (mg/L)	FC (mg/L)	99% Kill Time (minutes)			[HOCl] in units of mg/L FC		
		@ pH 7.0	@ pH 9.0	@ pH 9/@ pH7	@ pH 7.0	@ pH 9.0	@ pH7/@ pH9
0	0.18	0.3	3.5	11.7	0.14	0.006	23
0	0.41	<0.25	1.6	>6.4	0.318	0.013	24
0	0.86	<0.25	0.9	>3.6	0.674	0.029	24
25	0.19	7.2	15.5	2.2	0.002	0.001	2.3
25	0.41	3.2	7.7	2.4	0.005	0.002	2.1
25	0.88	1.6	3.3	2.1	0.01	0.005	2.2
50	0.19	11.5	29.5	2.6	0.001	0.001	2
50	0.41	4.7	12.1	2.6	0.002	0.001	2
50	0.87	2.4	5.5	2.3	0.005	0.002	2
100	0.19	21.7	55.3	2.5	0.001	0.000	1.9
100	0.41	10.2	20.4	2	0.001	0.001	1.9
100	0.86	4.1	9.4	2.3	0.002	0.001	2

Estimating Appropriate Chlorine Residuals

Given the strong dependence of hypochlorous acid concentration on cyanuric acid concentration, it seems appropriate to establish appropriate chlorine residuals as a function of the amount of cyanuric acid present. This can be done if an ideal hypochlorous acid concentration can be agreed upon. As the hypochlorous acid concentration decreases, the rate of disinfection will decrease, as will the rate of oxidation of contaminants. However, as the hypochlorous acid concentration increases, formation of irritating and toxic disinfection byproducts may also increase. Direct toxicity from the hypochlorous acid would also increase in tandem.

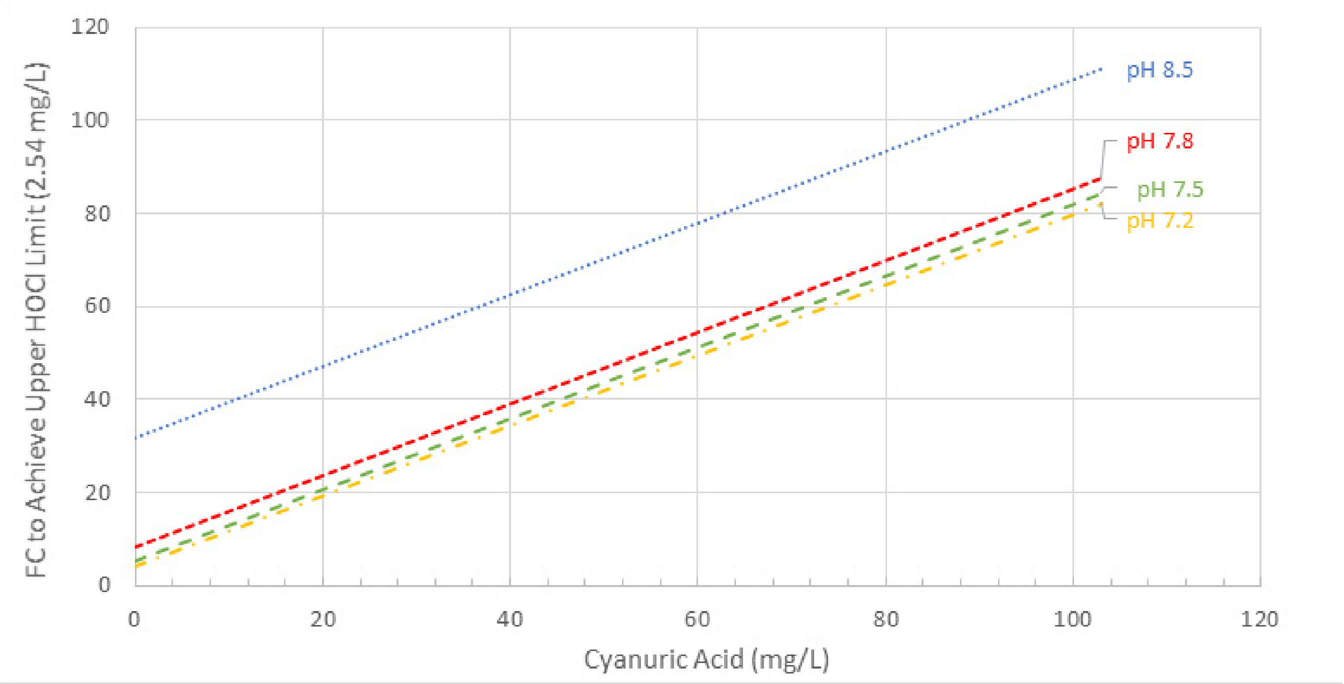
In the absence of consensus on an ideal hypochlorous acid concentration, a rough range may be estimated as follows:

- For a lower limit: A free chlorine residual of no less than 0.2 mg/L is required to insure the safety of potable water.[11] Also consider the secondary drinking water standard for pH: 6.5 to 8.5.[12] This would establish a minimum hypochlorous acid concentration (assuming the absence of cyanuric acid) of 0.0161 (expressed as milligrams free chlorine per liter), using the 0.2 mg/L FC and pH 8.5. To avoid bacterial infestation, the hypochlorous acid concentration should never be allowed to drop below this lower limit, though even this limit may not be high enough.
- For an upper limit, consider the common pool water chlorine limit of 4.0 mg/L and minimum pH of 7.2. This would, in the absence of cyanuric acid, equate to a hypochlorous acid concentration of 2.54 (expressed milligrams of free chlorine per liter). To avoid issues with chlorine toxicity and excessive formation of irritating disinfection byproducts, this upper limit should not be exceeded when bathers are present.

Using these upper and lower limits for general guidance, one can then determine the free chlorine concentrations required to establish such hypochlorous acid concentrations, as a function of pH and of cyanuric acid concentration. Figures 7 and 8 plot the free chlorine concentrations corresponding to the upper and lower hypochlorous acid limits indicated above.

It can be seen that the 0.0161 to 2.54 hypochlorous acid concentration range corresponds to a rather broad range for free chlorine, especially when variations in pH and cyanuric acid are taken into account. Few experts would be comfortable recommending hypochlorous acid concentrations

Figure 7 — Free chlorine required to provide the upper limit hypochlorous acid concentration of 2.54 mg/L (as free chlorine).

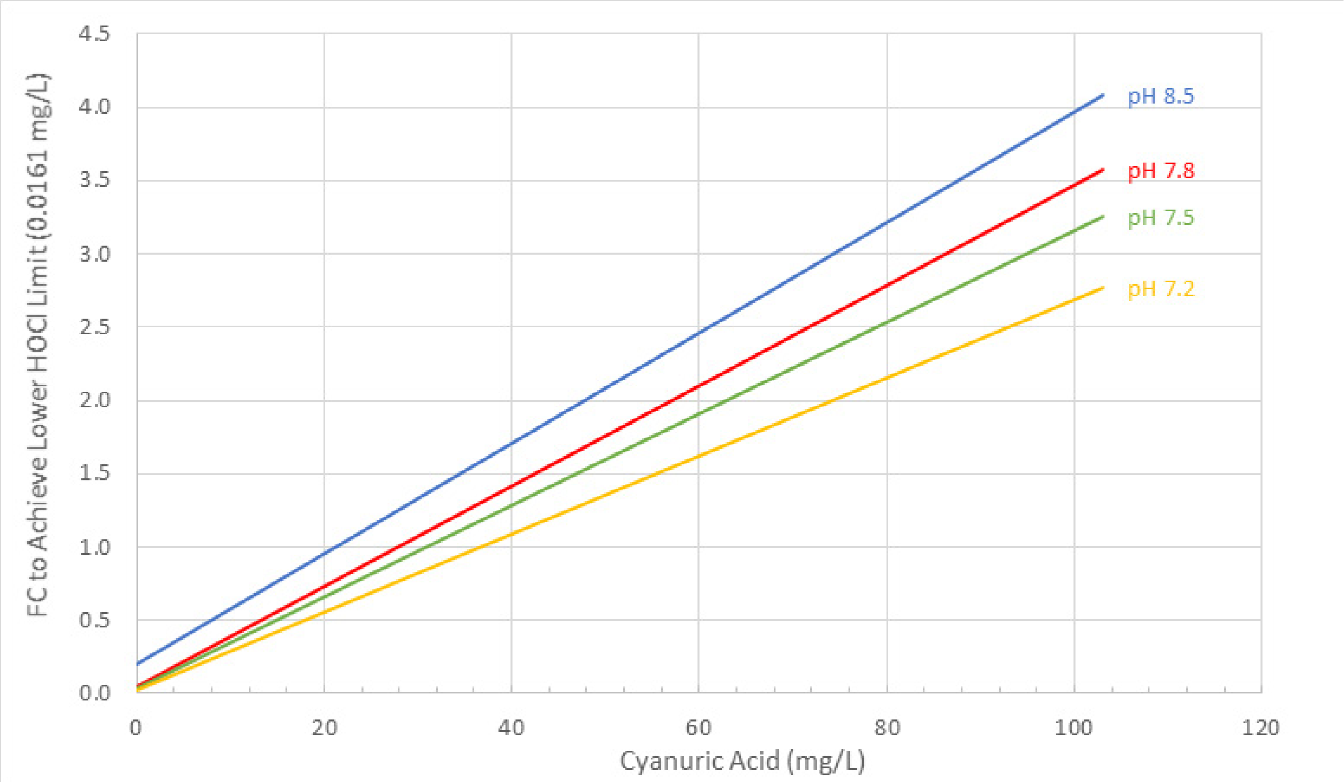


outside the 0.0161 to 2.54 mg/L concentration range when bathers are present. For most, the lower limit would be too low and the upper limit too high. A more ideal hypochlorous acid concentration would be the geometric mean of the indicated limits, 0.20 milligrams of hypochlorous acid per liter. Figure 9, below, is based on this hypochlorous acid target.

Note that even fixing the ideal hypochlorous acid concentration still allows for a wide range in free chlorine concentration, with cyanuric acid concentration having a particularly large influence on the chlorine concentration requirement. The increase in the free chlorine requirement as pH or cyanuric acid concentration increase is probably overstated by the graphs. As cyanuric acid increases to higher levels, above 10–20 mg/L, hypochlorous acid becomes a very small fraction of the total chlorine present. Under such circumstances the weak disinfecting influence of the chlorinated isocyanurates could become significant, as the concentrations of these species dwarfs the concentration of hypochlorous acid. The net result would be that if a target disinfection rate, rather than just a target $HOCl$ concentration were allowed to determine the required free chlorine concentration, a leveling off of each curve, below the lines shown in the figures at higher values of cyanuric acid. The green dashed line "pH 7.5 corr." curve in Figure 9 was generated with an assumption that, in aggregate, the active chlorine species other than hypochlorous acid (hypochlorite and the various chlorinated isocyanurates) would have 2% of the disinfecting strength of hypochlorous acid. It would be very difficult to determine the right disinfection credit to assign to the key chlorinated isocyanurates. This would vary with the number of chlorines bound to the cyanurate ring (1 to 3) and the charge, if any, of the species (0, -1, or -2). In view of this, the green dashed line is presented simply to illustrate the general type of deviation one might anticipate, not to establish the actual magnitude of the correction.

Calculations show the mono-negative, mono-chlorinated isocyanurate ($HC_3N_3O_3Cl^-$) to be the dominant chlorinated isocyanurate in the pH range of 5.5 to 10. In view of the negative charge of the ion, it is unlikely to penetrate microbial cells well enough to be very active as a disinfectant. Consequently, an efficacy greater than 2% as high as hypochlorous acid is unlikely; so, deviations greater than that shown by the green dashed line are unlikely. In all probability, actual chlorine concentration required to match 0.2

Figure 8 — Free chlorine concentration required to provide the lower limit hypochlorous acid concentration of 0.0161 mg/L (expressed as free chlorine).



mg/L *HOCl* falls between the dashed green curve and the solid green line. This suggests that even with reasonable allowance for disinfection contributions from chlorinated isocyanurates, with cyanuric acid concentrations as low as 20 mg/L, a free chlorine concentration in excess of 4 mg/L is required to match the efficacy of a 0.5 mg/L free chlorine pH 7.6 solution without cyanuric acid.

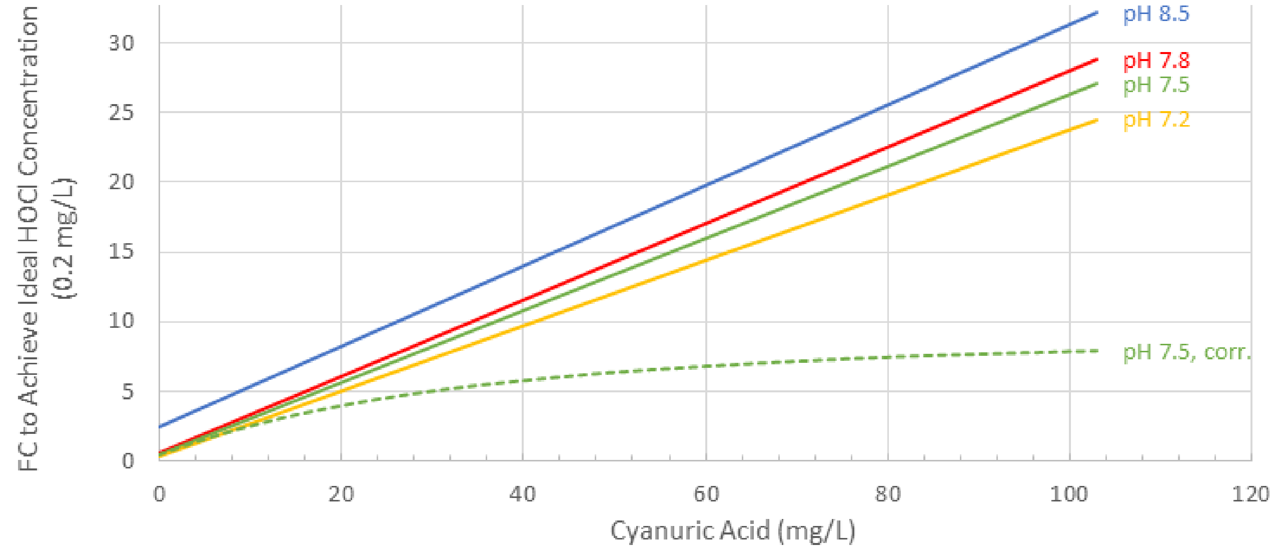
Increasing chlorine residual concentration to at least partially offset the impact of cyanuric acid should not be a concern in terms of formation of chlorinated disinfection byproducts. By lowering the concentrations of hypochlorous acid and of dissolved free chlorine, cyanuric acid also slows the formation of chlorination disinfection byproducts. Ronald L. Jones, et al. have demonstrated that addition of cyanuric acid causes a decrease in the formation of chloroform from the reaction of free chlorine with humic acid.[13]

A final note of caution: Federal law under FIFRA (the Federal Insecticide, Fungicide and Rodenticide Act) forbids use of a pesticide, for example an antimicrobial such as a chlorinating agent, in a manner inconsistent with its labeling. At present the US EPA does not allow chlorine residuals in excess of 4 mg/L in recreational water when bathers are present. Consequently, any efforts to increase chlorine residuals based on the considerations discussed in this paper would need to involve the US Environmental Protection Agency, before changes are made on product labels or in the actual operation of swimming pools. It does seem prudent, however, to bring to the EPA's attention information on the impact of cyanuric acid on disinfection, oxidation and chlorination of disinfection byproduct precursors. It should also be noted that the Conference on the Model Aquatic Health Code has an *ad hoc* committee that is conducting a more thorough investigation on the impact of cyanuric acid on the risk of exposure to pathogens from other bathers in swimming pools. The report of the committee, when available, could be quite relevant to the current subject, and includes considerations (such as diffusion, pathogen load per bather, etc.) not taken into account in the present paper.

Calculation Methods

Hypochlorous acid concentration was calculated using equilibrium constants reported by O'Brien.[14] However, critical equilibrium constants were adjusted for temperature and ionic strength, based on peer-reviewed reports of the effects of these parameters. The impact of temperature on the dissociation constant of hypochlorous acid was from Morris.[15] The impact of temperature on O'Brien's key equilibrium constants K_7 and K_9 was from Wojtowicz.[16] The acid dissociation constant for hypochlorous acid and the various protonated cyanurate species were adjusted for ionic strength using Davies' method, which has been described by Wojtowicz[17], among others.

Figure 9 — Estimated free chlorine concentrations corresponding to an "ideal" hypochlorous acid concentration of 0.2 mg/L (expressed as free chlorine). See the limitations and precautions indicated in text on the next page.



The effect of ionic strength on hydrogen ion is already accounted for in pH, and the impact of ionic strength on neutral (uncharged, non-ionic) molecules is negligible, so only the impact on anions had to be taken into account in the present work. Taking the ionic strength of 0.04 and temperature of 27°C into account the equilibrium constants are as indicated in Table 3.

Prior to calculating equilibrium concentrations of the various species, free chorine and cyanuric acid concentrations were converted from mg/L units to molarity, by dividing the mg/L concentrations by the molecular weights: 70,906 mg/mole for free chlorine and 129,074 mg/mole of cyanuric acid.

Using the adjusted equilibrium constants, it is possible—for any given combination of pH, hypochlorous acid concentration and cyanuric acid concentration (total)—to calculate the ratio of the concentration of each of the ten possible cyanurate species ($H_3C_3N_3O_3$, $H_2C_3N_3O_2^-$, $ClH_2N_3C_3O_3$, etc.) to the concentration of some common form, such as the fully protonated, unchlorinated $H_3C_3N_3O_3$ form. Then by summing all ten ratios one can calculate the ratio of the total cyanuric acid concentration (sum of all ten species) to the common form, $H_3C_3N_3O_3$. Dividing the chosen total stabilizer concentration by this ratio yields the concentration of the common form. From it, the absolute concentrations of each of the ten forms can be calculated. Likewise, from the pH and the hypochlorous acid dissociation constant the hypochlorite concentration can be calculated. The net total "free chlorine" concentration can then be calculated by summing the contributions from hypochlorous acid, hypochlorite and the various chlorinated isocyanurate species (Equation 1).

To determine the concentrations of the various species for a chosen *free chlorine* concentration rather than a pre-determined *hypochlorous acid* concentration, one can start with an initial guess of the hypochlorous acid concentration (as a very small percentage of the free chlorine, or 0 for simplicity). Then the concentrations of the ten cyanurate species and of hypochlorite are calculated as indicated above. The calculated free chlorine concentration, summed from the chlorine contributions of all the calculated active chlorine species (as in the equation above), will then differ from the chosen free chlorine concentration. For the next iteration, the calculations are repeated

Table 3 — Temperature and ionic strength adjusted pKs used in calculating concentrations of hypochlorous acid and related species.

Reaction	pK
$HOCl \rightleftharpoons H^+ + OCl^-$	7.441
$H_3Cy \rightleftharpoons H^+ + H_2Cy^-$	6.860
$H_2Cy^- \rightleftharpoons H^+ + HCy^{2-}$	11.322
$HCy^{2-} \rightleftharpoons H^+ + Cy^{3-}$	13.324
$H_2ClCy + H_2O \rightleftharpoons H_3Cy + HOCl$	3.954
$HCl_2Cy + H_2O \rightleftharpoons H_2ClCy + HOCl$	2.822
$Cl_3Cy + H_2O \rightleftharpoons HCl_2Cy + HOCl$	1.800
$H_2ClCy \rightleftharpoons H^+ + HClCy^-$	5.310
$HClCy^- \rightleftharpoons H^+ + ClCy^{2-}$	10.042
$HCl_2Cy \rightleftharpoons H^+ + Cl_2Cy^-$	3.73

Equation 1

$$FC = [HOCl] + [OCl^-] + [H_2ClCy] + [HClCy^-] + [ClCy^{2-}] + 2([HCl_2Cy] + [Cl_2Cy^-]) + 3[Cl_3Cy]$$

where $Cy = C_3N_3O_3$

with a different value for the hypochlorous acid concentration, adjusted as needed to bring the calculated total free chlorine closer to the chosen value for free chlorine. With enough iterations, it is possible to converge on a concentration for hypochlorous acid that produces a chlorine sum (Equation 1) equal to the chosen free chlorine value. The number of iterations required for convergence can be greatly reduced by use of the Newton-Raphson method. To do this, the above equation for free chlorine (Equation 1) is differentiated with respect to [*HOCl*]. The resulting differential or slope, d*FC*/d[*HOCl*], can be used in selecting the value of [*HOCl*] for the next iteration based on the difference between the calculated total FC in the current iteration and the target FC. Moving from any iteration, *i*, to the next iteration, *i*+1, a new estimate for [*HOCl*] is calculated:

Equation 2

$$[HOCl]_{(i+1)} = [HOCl]_i + \frac{FC_{target} - FC_i}{dFC/d[HOCl]}$$

Using this Newton-Raphson method to achieve rapid convergence, consistency between the chosen (target) free chlorine concentration and the calculated sum can be achieved in a few iterations. A spreadsheet was developed with 20 such iterations (to insure complete convergence), one iteration per row and the concentration of one species or the ratio of concentrations of two species, or sum of ratios, etc. per column. This spreadsheet was used for the computation of hypochlorous acid concentration for each combination of pH, free chlorine and cyanuric acid concentration cited in this paper.

For Table 1 and Figures 1 through 4 the assumed temperature was 27°C (80.6°F) and the ionic strength was assumed to be 0.04, which roughly equates to about 1,600 ppm total dissolved solids. For calculation of hypochlorous acid concentration in the disinfection work reported by Anderson, the temperature 20°C, indicated by Anderson, was used for equilibrium calculations. The ionic strength was assumed to be 0.01, roughly 400 ppm TDS.

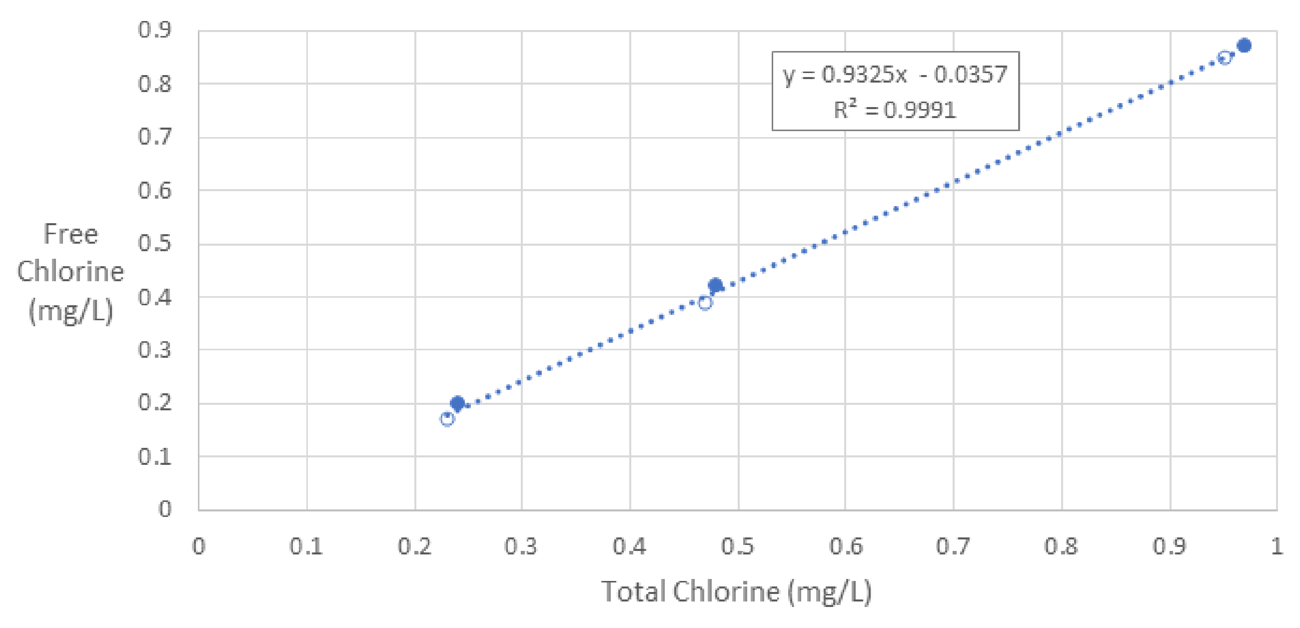
Time required for 99% inactivation of *S. faecalis* under various conditions of pH, total chlorine and cyanuric acid concentration were taken from Table 3 in the cited paper by Anderson.[10] Free chlorine concentrations were estimated by the relationship:

Equation 3

$$FC = 0.933 \times TC — 0.036$$

This relationship was discerned by plotting

Figure 10 — Plot of free chlorine versus total chlorine in Anderson's work. Filled circles are average initial values. Open circles are average final values, for the three nominal total chlorine levels.



the data from Table 1 in Anderson's paper.

With the work being reported by Anderson in 1965, free and total chlorine were measured by the, now obsolete, OTO-arsenite method. The method was discontinued by the 15th edition (1991) of *Standard Methods*, due to inaccuracy and OTO toxicity.[18] Nevertheless, Anderson's estimates of free and total chlorine were remarkably consistent. In view of this, and the evidence that combined chlorine concentrations were low in comparison to total chlorine, the free chlorine estimates are sufficiently accurate for the current purposes of showing whether hypochlorous acid concentration and disinfection rate share approximately the same relationships with pH and stabilizer concentration.

Conclusions

Available evidence based on disinfection rate data and hypochlorous acid concentration calculations indicate that:

- Disinfection rate and hypochlorous acid concentration are far more dependent on stabilizer (cyanuric acid) concentration than on pH, when pH can vary from 7 to 8.5 and cyanuric acid can vary from 0 to >25 mg/L.
- Hypochlorous acid concentration and disinfection rate are higher in the absence of stabilizer—even at pH as high as 8.5—than in the presence of 12 mg/L of stabilizer, even at a pH as low as 7.0.
- Upon raising the pH from 7.5 to 8.5, the percent decline in hypochlorous acid concentration with ≥25 mg/L stabilizer present is little more than a fifth of the percent decline without stabilizer. Best indications are that sensitivity of disinfection rate to pH is more or less the same.
- Consequently, when stabilizer is absent, hypochlorous acid concentrations and disinfection rates remain comparatively high even up to pH 8.5.
- When stabilizer is present, and therefore hypochlorous acid concentrations and disinfection rates are depressed, the *HOCl* concentration and disinfection rate are comparatively insensitive to pH. Raising the pH upper limit from 7.8 to 8.5 would not have a significant impact on bacterial kill rates or water quality in general. Operation at a higher pH (8.0-8.5) could actually improve water quality somewhat with respect to nitrogen trichloride generation during breakpoint chlorination. Conduction of breakpoint chlorination at high chlorine concentrations or low pH tends to increase the amount of noxious nitrogen trichloride formed, relative to what would be formed at higher pH. This might also explain the higher irritation at pH 7 than at pH 8, noted on page 7 in the last paragraph of the "Irritation and Tissue Damage" section.
- It would be appropriate to establish an ideal free chlorine concentration range that varies with cyanuric acid concentration, rather than being fixed regardless of cyanurate levels.
- With cyanuric acid concentrations as low as 20 mg/L, a free chlorine concentration in excess of 4 mg/L is required to match the efficacy of a 0.5 mg/L free chlorine solution at pH 7.6 without cyanuric acid.
- Due to the impact of cyanuric acid in depressing the concentration of hypochlorous acid, and the trace concentration of dissolved elemental chlorine, formation of chlorinated disinfection byproducts is also slowed by cyanuric acid.

About the Author

Stanley R. Pickens, Ph.D.
Swim-Chem Consulting Services, L.L.C.
Monroeville, PA
Phone: 412-372-5321; Mobile: 412-607-5752
stanleypickens@yahoo.com
https://www.linkedin.com/in/stanpickens

Dr. Pickens has specialized in water chemistry and water quality for 25 years. He has presented lectures at various national and international venues on water treatment issue involving potable, recreational, cooling and industrial treatment water. After obtaining a Ph.D. in inorganic chemistry from Texas A&M University, Dr. Pickens began a 35-year career in industrial research. In 2016 he retired from a position as Senior Research Scientist at Axiall Corporation and founded Swim-Chem Consulting Services, L.L.C. He is a former chair of APSP's Recreational Water Quality Committee and an APSP Fellow. He currently serves on the Council for the Model Aquatic Health Code's ad hoc committee on cyanuric acid.

References

1. Association of Pool & Spa Professionals, ANSI/APSP-11, “American National Standard for Water Quality in Public Pools and Spas”, section 7.1, 2009.
2. U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, Model Aquatic Health Code, 2nd edition, section 5.7.3.4.1, p. 214, July 2016. https://www.cdc.gov/mahc/pdf/2016-mahc-code-final.pdf, posted 7/15/2016, accessed 2/23/2017.
3. U.S. Food & Drug Administration, “Bad Bug Book–pH Values of Various Foods”, https://www.fda.gov/food/foodborneillnesscontaminants/causesofillnessbadbugbook/ucm122561.htm, updated 5/20/2015, accessed 2/23/2017.
4. Jose Tarun, et al., “Evaluation of pH of Bathing Soaps and Shampoos for Skin and Hair Care”, *Indian Journal of Dermatology*, **59** (5), 442-444, 2014. https://www.fda.gov/food/foodborneillnesscontaminants/causesofillnessbadbugbook/ucm122561.htm, NIH US National Library of Medicine, accessed 2/23/2017.
5. CDC, “Model Aquatic Health Code”, Annex, 2nd Edition, section 5.7.3.4, sub-section on “Bather Comfort”, p. 243, 2016. https://www.cdc.gov/mahc/pdf/2016-mahc-annex-final.pdf
6. R. Gonnering, et al., “The pH tolerance of rabbit and human corneal endothelium”, *Investigative Ophthalmology & Visual Science*, **18**, 373-390, 1979.
7. Rylander et al., “The effect of saline on eye irritation caused by swimming-pool water”, *J. Hyg., Cambr.*, **71**, 587-591; http://www.ncbi.nlm.nih.gov/pmc/articles/PMC2130569/pdf/jhyg00081-0170.pdf
8. “Model Aquatic Health Code,” Annex, op cit., p.242.
9. Note: As of April 1, 2019 the Association of Pool and Spa Professionals (APSP) is to be known as the The Pool & Hot Tub Professionals Association and the National Swimming Pool Foundation (NSPF) is to be known as The Pool and Hot Tub Foundation, with the two organizations being united under the umbrella of The Pool and Hot Tub Alliance. See press release, Jan. 22, 2019: https://apsp.org/Portals/0/2019%20NSPF%20Merger/Press_Release_January_22_19.pdf?ver=2019-01-22-140417-407
10. John R. Anderson, “A Study of the Influence of Cyanuric Acid on the Bactericidal Effectiveness of Chlorine”, American Journal of Public Health, 55 (10), 1629-1637, 1965.
11. Centers for Disease Control and Prevention, “Safe Water System” / “Household Water Treatment” / “Chlorination”, https://www.cdc.gov/safewater/chlorine-residual-testing.html, as updated July 17, 2014.
12. United States Environmental Protection Agency, “Secondary Drinking Water Standards: Guidance for Nuisance Chemicals”, https://www.epa.gov/dwstandardsregulations/secondary-drinking-water-standards-guidance-nuisance-chemicals, as viewed June 21, 2017.
13. Ronald L. Jones, Henry D. Caughman, Susan M. Shelor and Ellwood L. Lines, Jr., “Compositions and Methods for Controlling the Growth of Microbials in Aqueous Media”, US Patent 5,591,692, January 7, 1997.
14. J. E. O’Brien, J. C. Morris & J. N. Butler, “Equilibria in Aqueous Solutions of Chlorinated Isocyanurate”, Ch. 14 in Alan J. Rubin’s “Chemistry of Water Supply, Treatment, and Distribution”, Ann Arbor: Ann Arbor Science Publishers, Inc., 1974, ISBN 0-250-40036-7, pp. 333–358.
15. J. Carrell Morris, “The Acid Ionization Constant of HOCl from 5 to 35°”, J. Phys. Chem., 70 (12), pp 3798-3805, 1966. http://pubs.acs.org/doi/abs/10.1021/j100884a007?journalCode=jpchax
16. John A. Wojtowicz, “Reevaluation of Chloroisocyanurate Hydrolysis Constants”, J. Swimming Pool & Spa Industry, 2 (2), 112-120, 2001.
17. John A. Wojtowicz, “A Revised and Updated Saturation Index Equation”, Journal of the Swimming Pool and Spa Industry, 3 (1), 28—34, 2001.
18. Andrew D. Eaton, Lenore S. Clesceri and Arnold E. Greenberg, “Standard Methods for the Examination of Water and Wastewater”, 19th edition, Washington, DC: American Public Health Association (in cooperation with AWWA and WEF) Method 4500-Cl, “Chlorine (Residual)”, 1995, ISBN 0-87553-223-3, p. 4-36.