



Volume 6 Number 1
Spring 2019

Journal of the Swimming Pool and Spa Industry

J. Que Hales, Editor

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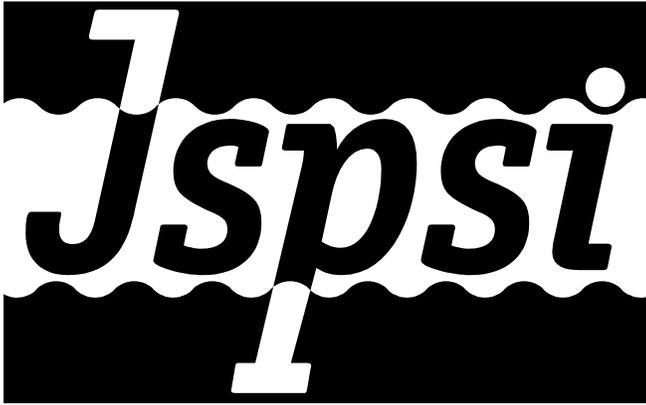
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Journal of the Swimming Pool and Spa Industry

The Journal of the Swimming Pool and Spa Industry (JSPSI) publishes papers on all aspects of the swimming pool and spa industry. Research, informative papers, bibliographies, book reviews, and symposia-in-print are presented for the general education of all technically minded individuals in the industry.

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Submission of Papers: Instructions for submission of papers appear at the end of this issue. Requests for additional information or copies of the submission criterion should be directed to editor@poolhelp.com, or the above address or phone numbers.

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Welcome!

Welcome to Volume 6 of the Journal of the Swimming Pool and Spa Industry. Many excellent publications are currently available in the pool industry, each designed for a different purpose and a different readership; from general to service to retail. This particular publication seeks to distribute and make available purely technical material covering interests of the entire swimming pool and spa industry – to publish that kind of material that is too technical for publishing in a trade magazine. Some existing technical journals publish, from time to time, articles which relate to our industry, but they don't delve deep enough, much less exclusively, into the swimming pool and spa industry. There is a wealth of material available in the technical realm, from conventional water chemistry to plaster technology, from alternative sanitizers to alternative surfaces, from plastic performance to motor curves. Some of this material describes new research, some explains conventional wisdom in a technical manner not readily available or understood in the industry today. It is the intent of the JSPSI to assemble, edit, and publish this type of material, providing an open forum for education, discussion and debate.

The journal format is time-honored in the world of academia. JSPSI will not attempt to reinvent the format, but will be structured much the same as other existing journals. The following is a list of what we expect to include in issues:

Research Papers: A wealth of research is currently being conducted in the industry, and the primary purpose of this journal will be to provide a forum for the publishing of research findings. Published material is expected to detail completed projects, although some papers describing works in progress may be accepted. Papers will include documentation as needed, including chemical formulas, mathematical support, tables, illustrations, and references.

Informative papers: Some areas of knowledge are well researched and understood in certain circles, but not in the general pool industry. For example, cement curing, metal ion and ozone activity in water, heater efficiency and emissions, motor performance curves, etc. are all well under-

stood in selected circles, but not to the industry as a whole. Informative papers will be printed which explain, at a technical level, these types of ideas for the education of those in the industry who are technically minded, but not yet exposed to that particular segment of knowledge.

Annotated Bibliographies: When appropriate, annotated bibliographies will be printed. The purpose of this type of bibliography is to collect in one location as complete a listing as possible of documentation on a particular subject. Such listings may be useful in furthering research in a given area. Unlike a simple bibliography, which merely lists all of the publications containing the data, annotated bibliographies include paragraph-long descriptive or evaluative summaries after each citation, so that the reader knows what he may expect to find without having to locate and read each separate work.

Book Reviews: Books relating to technical aspects of the swimming pool industry may be reviewed. Reviewers will be qualified, independent persons, who will evaluate books based on such factors as content, accuracy, and readability.

Letters to the Editor: Appropriate letters to the editor may be printed. Letters will be responses or rebuttals to material in previous issues of the journal, and must be technical in nature.

Short Technical Notes: Notes of a technical nature, but of short length may be included in this category. Technical notes are typically accepted and sent to publication much quicker than a paper, due to their brevity, and can therefore be useful under certain circumstances.

Abstracts: Each submission in the journal is preceded by an abstract (the summary/introductory paragraph in italics at the start of each paper). As articles pertaining to the swimming pool/spa industry appear in other journals, the abstract may be reprinted in this journal, to alert our readers to the appearance of the article.

Special Reports: These are reports which review research results of topical importance in a particular facet of the industry, and are usually commissioned in advance by the Editor.

Symposia Proceedings: The Journal occasionally sponsors and co-sponsors symposia and will, when appropriate, publish symposium proceedings in issues of the journal, either as a collection or individually. Entire symposium proceedings will be edited, but not peer reviewed. Individually published papers from symposia will, however, be subject to peer review.

Symposia-in-Print: These are collections of original research or informative papers, each individual paper being only about three to five pages

in length, all held together by a unified theme. Subjects of forthcoming Symposia-in-print will periodically be announced in the journal. A Guest Editor will be assigned to head the project, and he will in turn invite authors active in the field of the symposium to submit papers, which then go through the normal editorial review procedure. Submissions by other authors not specifically invited are considered for inclusion on equal footing with invitees.

The people behind *JSPSI*:

Editor

The Editor of the Journal of the Swimming Pool and Spa Industry is J. Que Hales. He is currently employed by Pool Chlor, a residential chemical service firm. He has been in the pool industry since 1980, working first as a residential chemical technician, and then as the owner of a small independent cleaning, repair, and retail business. He has managed the Tucson office of Pool Chlor since 1985, and also functions as the Pool Chlor corporate computer systems manager and mailing operations manager. He has a Bachelor's Degree in English from the University of Arizona. He is the co-author of many technical papers which have been reported on in various industry magazines. He has been a member of the Board of Directors of the National Association of Gas Chlorinators (NAGC, later the Swimming Pool Water Treatment Professionals, or SPWTP) since its inception, and is a past president of that organization. He has also served as a board member and President of the Southern Arizona Chapter of the National Spa and Pool Institute (SAC-NSPI/ Association of Pool and Spa Professionals. He is also a Certified Pool Operator (NSPF).

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The Editorial Review Board is a group of volunteers who have agreed to read and referee submissions to the Journal. In order to maintain an objective, independent Journal, the Editor does not determine which submissions will be published and which ones will not. The Review Board, comprised of a wide selection of professionals in the publishing, technical, and service facets of the industry, performs a blind review, meaning that the Editor removes the cover sheet and other identifying text before the Board members see the submission. They then judge suitability based on sound scientific method, clarity, readability, pertinence to the industry and the Journal, etc. Each submission is reviewed by at least three individuals, two of whom must be Board members, and one of whom may be selected as needed from the industry at large for particular expertise on a specific subject. Board members do not know which other members are reviewing a particular submission, and if a Board member chooses to abandon anonymity to contact a particular author for clarification, he/she will not compromise other reviewers (if known).

These Review Board members, along with the advisor to the editor, deserve our special thanks and appreciation. The JSPSI is a non-profit publication, and these individuals donate their time and efforts on our behalf.

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-11¹ and the Model Aquatic Health Code², 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.

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

Journal of the Swimming Pool and Spa Industry

Volume 6, Number 1, pages 6-19

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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

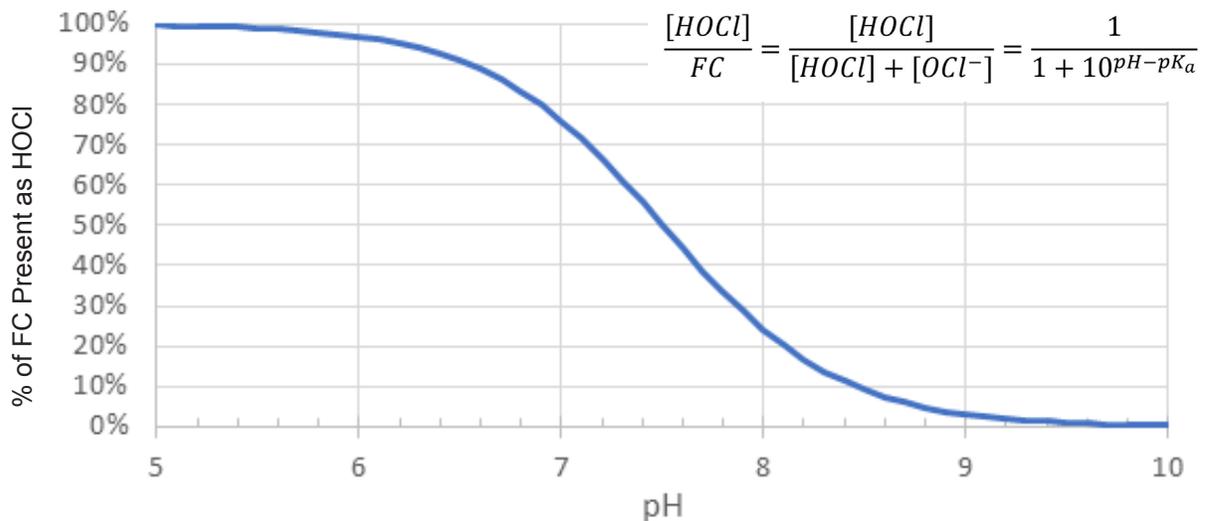
The primary reason cited in the *Model Aquatic Health Code Annex* for an upper pH limit of 7.8 is the impact of pH on hypochlorous acid concentration and the fact that, compared to hypochlorite ion, hypochlorous acid is estimated to be 100 times as effective at killing microorganisms.⁸ For the same reason, pool operator training materials from various organizations, including APSP and NSPF⁹, 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:

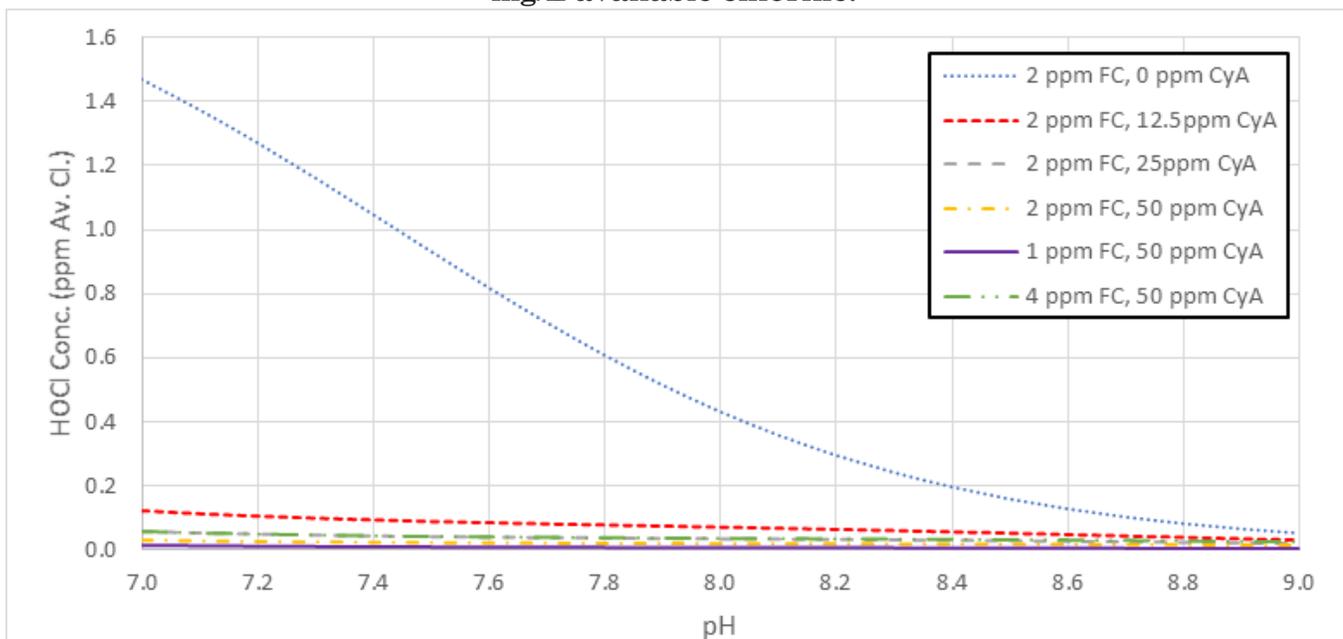
- Temperature: 27.0°C (81°F)
- Ionic Strength: 0.04 (Roughly 1,600 ppm TDS)
- Free Chlorine: 1, 2 or 4 mg/L, as indicated, in most cases 2mg/L
- Cyanuric Acid: 0, 12.5, 25, or 50 mg/L, as indicated. (This includes all ten possible forms cyanuric acid: ionized or uncharged, unchlorinated, monochlorinated,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

At the temperature and ionic strength indi-

cated, the pK_a 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.

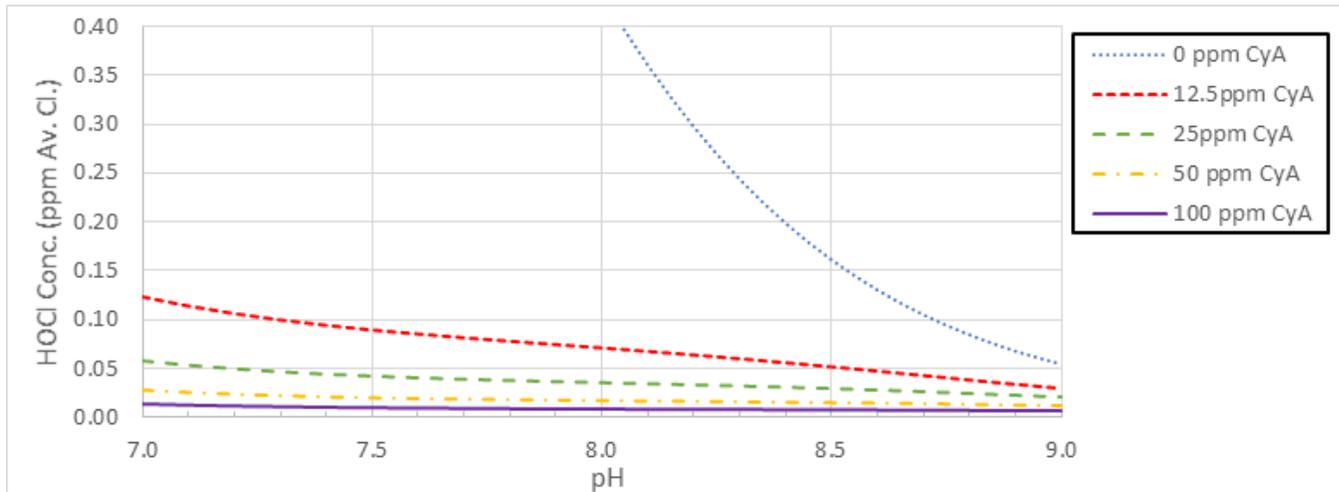
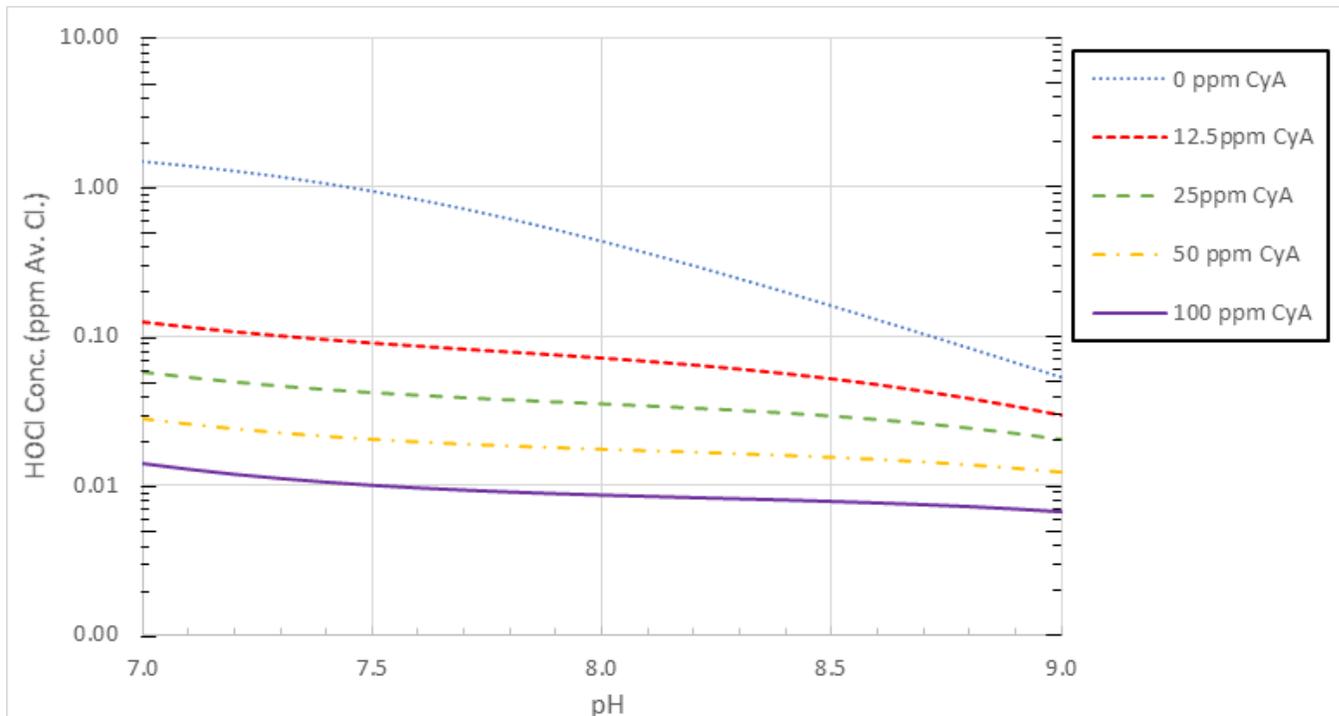


Figure 4 — Hypochlorous acid concentration as a function of pH for various cyanuric acid concentrations. The hypochlorous acid concentration (vertical axis) is logarithmic. For all curves, free chlorine is 2 mg/L, temperature 27°C (81°F) and ionic strength 0.04.



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-dissociation equilibrium constant, K_a , or

pK_a , 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

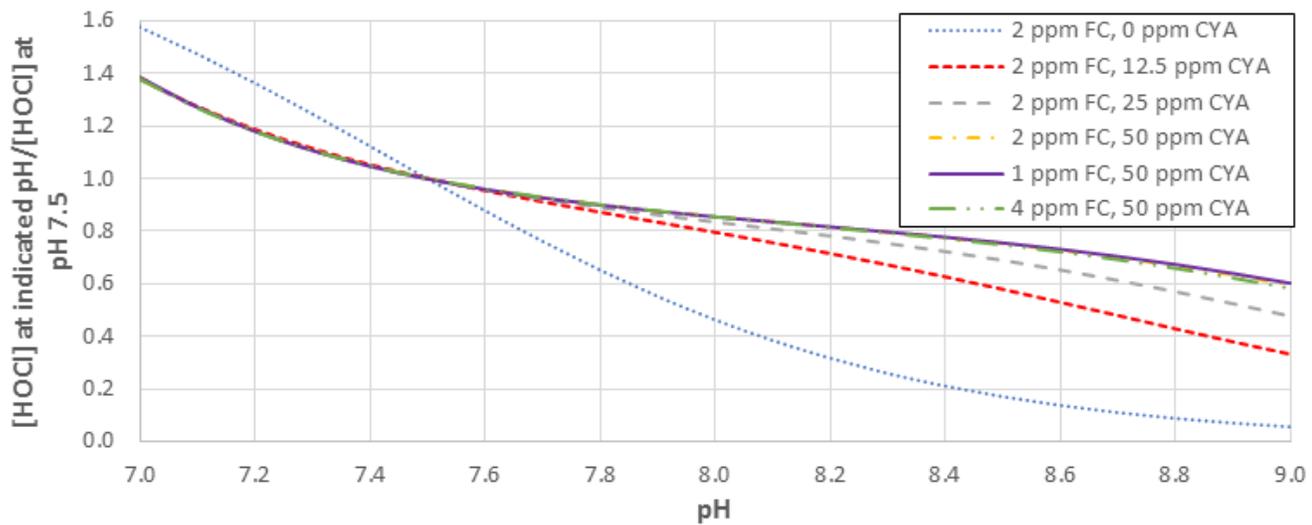
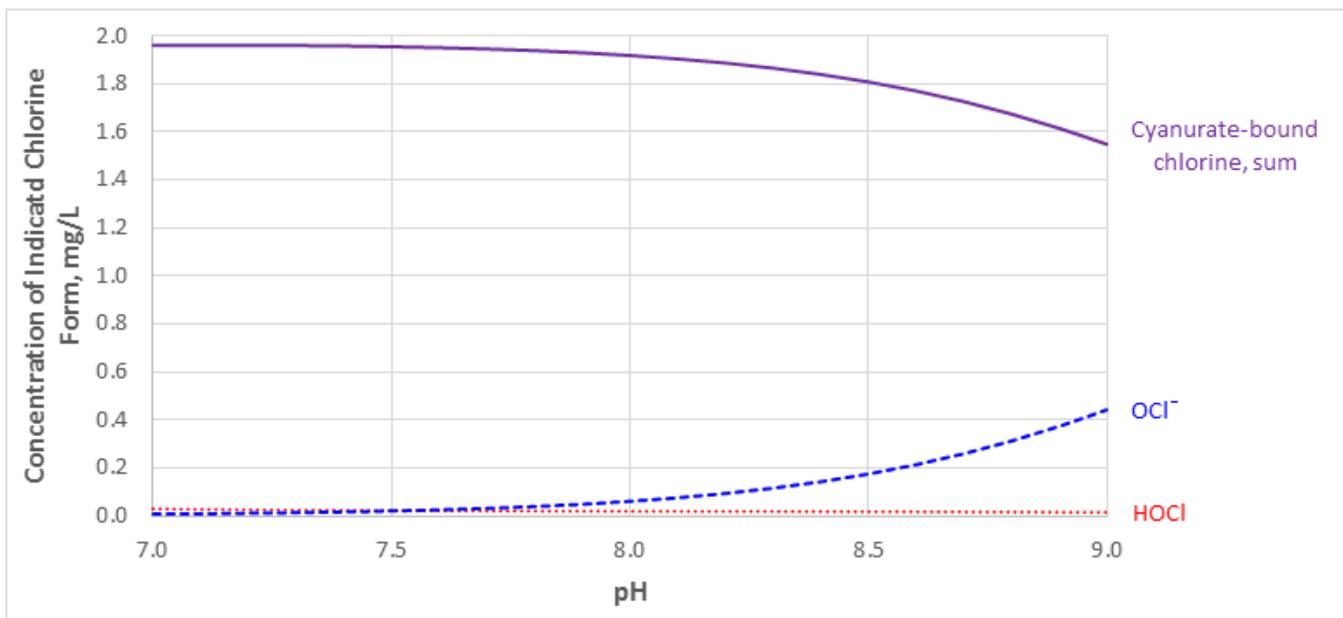


Figure 6 — Concentrations of hypochlorous acid, hypochlorite and cyanurate-bound chlorine (sum from six possible species) versus pH. Conditions: 2 ppm FC, 50 ppm CYA, 27°C (80.6°F), 0.04 ionic strength (~1,600 ppm TDS.)



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.

pH	<i>HOCl</i> Concentration at Given pH Divided by <i>HOCl</i> Concentration at pH 7.5					
	2 ppm FC,	2 ppm FC,	2 ppm FC,	2 ppm FC,	1 ppm FC,	4 ppm FC,
	0 ppm CYA	12.5 ppm CYA	25 ppm CYA	50 ppm CYA	50 ppm CYA	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

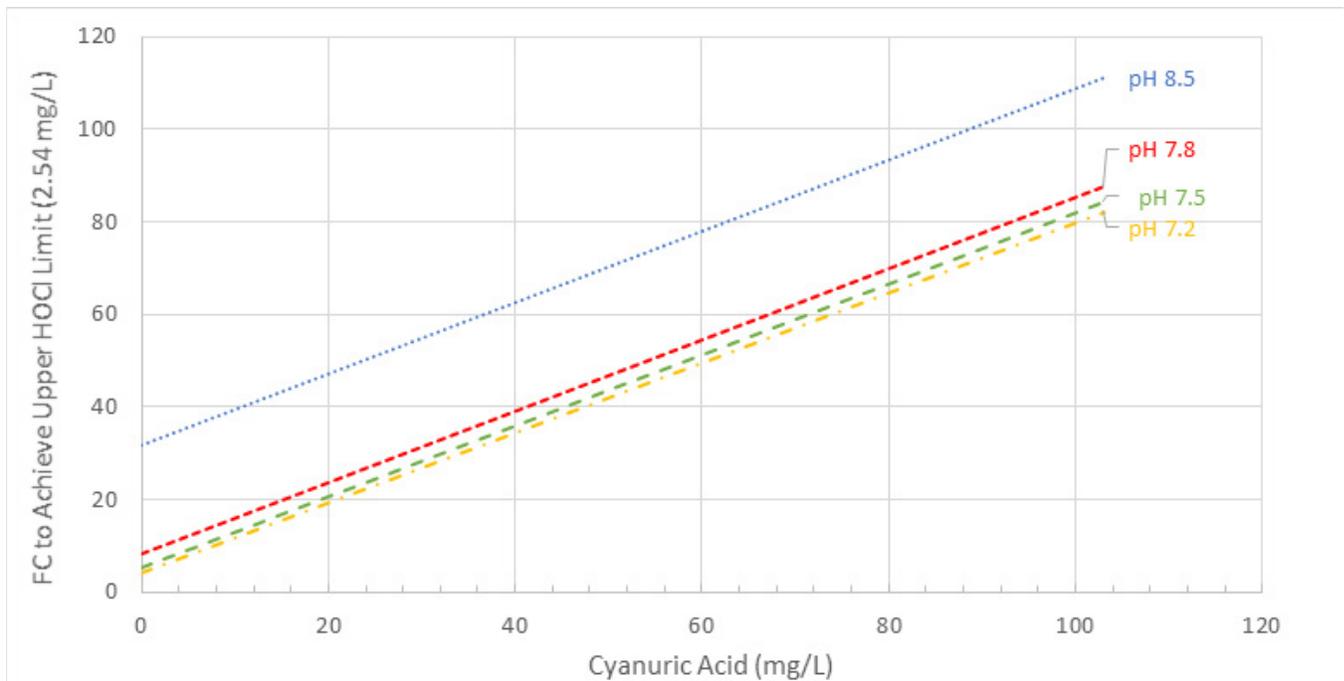
avoid bacterial infestation, the hypochlorous acid concentration should never be allowed to drop below this lower limit, though even this limit may not be high enough.

- 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).



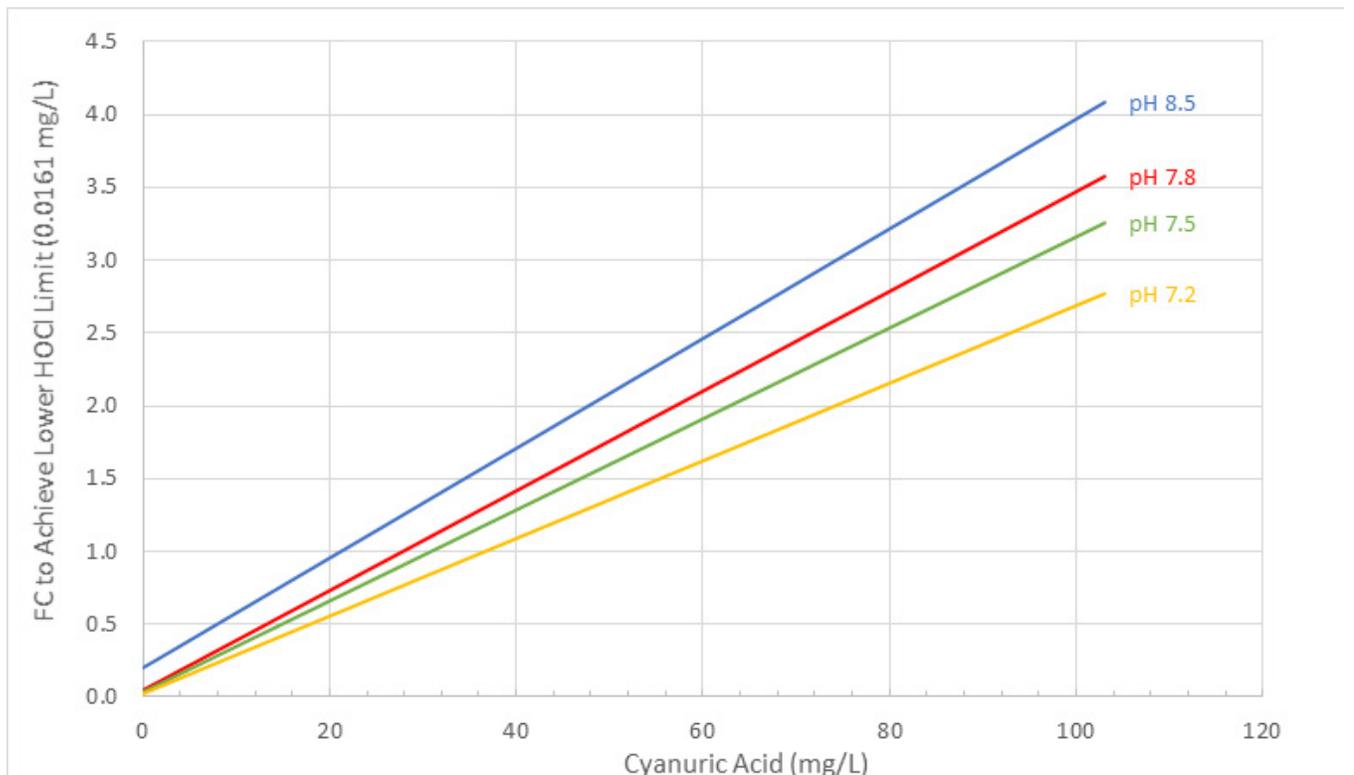
outside the 0.0161 to 2.54 mg/L concentration range when bathers are present. For most, the lower limit would be too low and the upper limit too high. A more ideal hypochlorous acid concentration would be the geometric mean of the indicated limits, 0.20 milligrams of hypochlorous acid per liter. Figure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

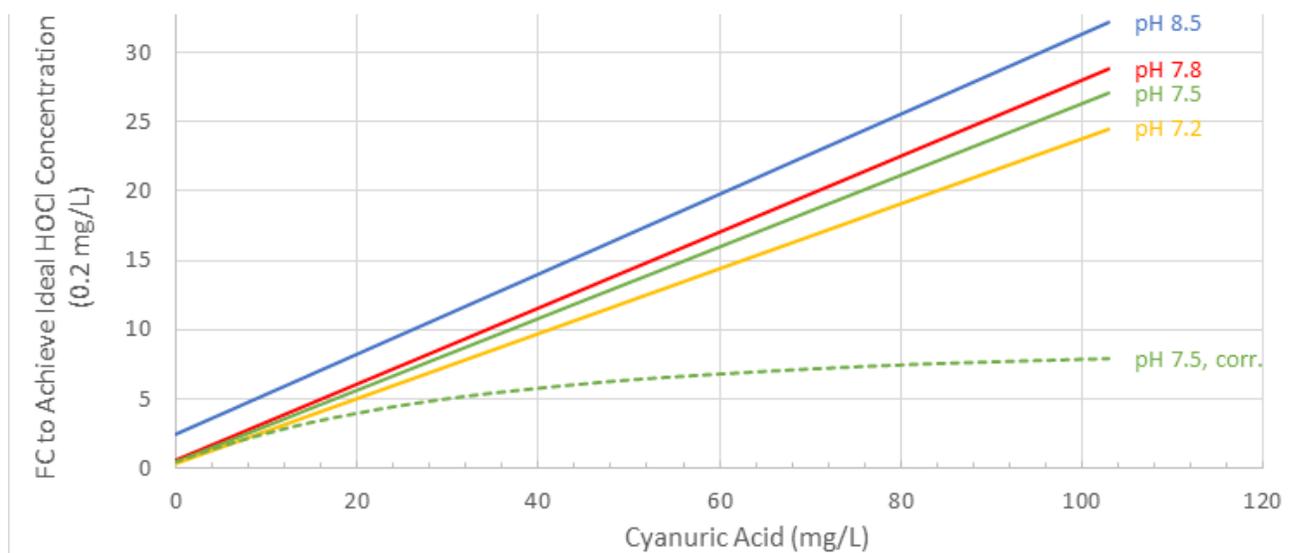
A final note of caution: Federal law under FIFRA (the Federal Insecticide, Fungicide and Rodenticide Act) forbids use of a pesticide, for example an antimicrobial such as a chlorinating agent, in a manner inconsistent with its labeling. At present the US EPA does not allow chlorine residuals in excess 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 Wojtowicz¹⁷, 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 chlorine 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 ($H_3C_3N_3O_3$, $H_2C_3N_3O_3^-$, $ClH_2N_3C_3O_3$, 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, $dFC/d[HOCl]$, 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.

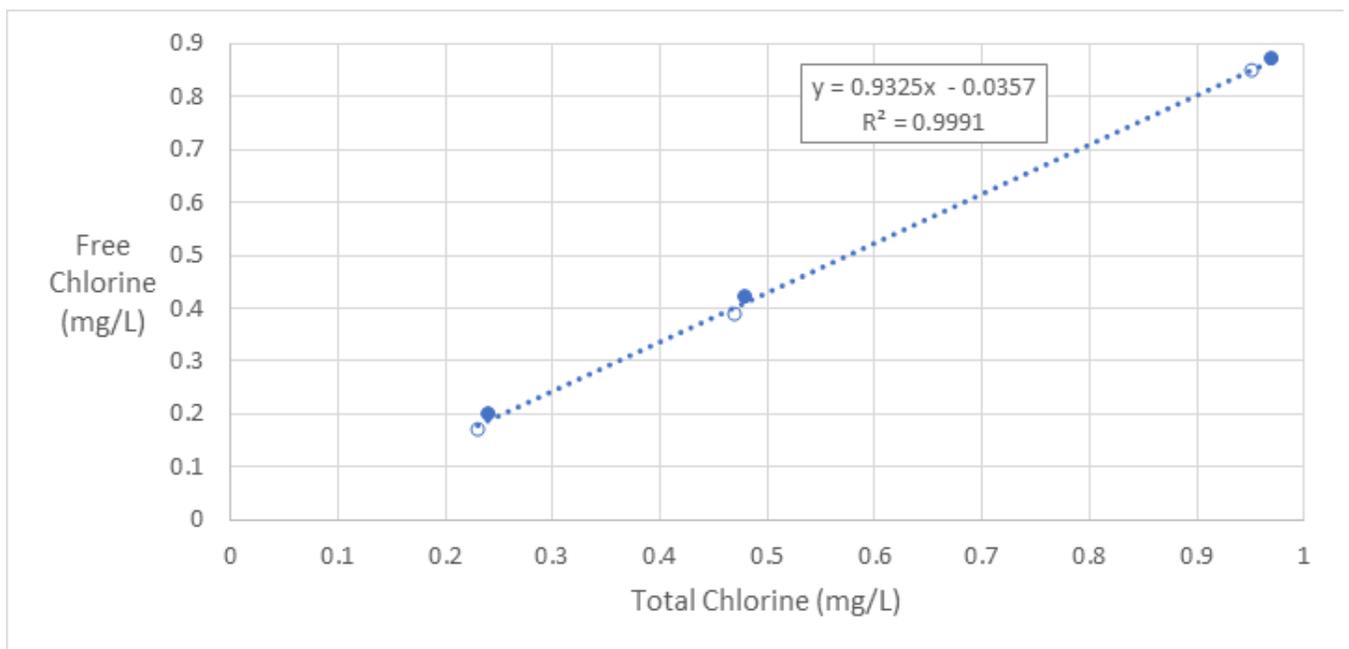
Time required for 99% inactivation of *S. faecalis* under various conditions of pH, total chlorine and cyanuric acid concentration were taken from Table 3 in the cited paper by Anderson.¹⁰ Free chlorine concentrations were estimated by the relationship:

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.

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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 issues 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., Camb.*, **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.](https://apsp.org/Portals/0/2019%20NSPF%20Merger/Press%20Release%20January%2022%2019.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.

The Relative Effect of Sodium Carbonate and Sodium Bicarbonate on Increasing Alkalinity and pH in Pool Water

Kim Skinner
onBalance

The correct alkalinity and pH results from the addition of sodium carbonate and sodium bicarbonate are given, along with an explanation of the chemistry. This information refutes incorrect material that is being presented in some industry literature and in trade show classes.

For many years, there have been some misconceptions within the swimming pool service industry regarding the effects and quantitative results when comparing sodium carbonate (soda ash) and sodium bicarbonate (baking soda) when these two chemicals are added to swimming pools.

The misinformation being promulgated in seminars throughout the industry varies. Some instructors claim that, pound for pound, sodium carbonate and sodium bicarbonate add equal amounts of alkalinity to pool water, while others claim that sodium bicarbonate actually increases the alkalinity more than sodium carbonate. Another inaccurate claim is that sodium bicarbonate will always increase the pH.

This paper will address the above misinformation and clarify the actual differences between these two chemicals when added to water.

Sodium Bicarbonate

To begin, a 1% solution of sodium bicarbonate

in distilled water has a pH of approximately 8.3. Understanding this, when sodium bicarbonate is added to water having a pH lower than 8.3, it will cause the pH to rise towards 8.3. Conversely, and what is not understood by some, is that if the water's starting pH is greater or higher than 8.3, (which does occur occasionally in swimming pools, and especially upon the filling of new plaster pools) adding sodium bicarbonate to this water will decrease or lower the pH down and towards 8.3. In general, adding sodium bicarbonate will affect the pH more significantly when the beginning pH of the water is further away from 8.3. However, the amount or content of the total alkalinity present in the water will also determine the degree or the amount of the pH change when sodium bicarbonate is added to water. The rule here is that when the content of carbonate alkalinity is low, a greater effect on the pH from the addition of sodium bicarbonate occurs. For example, if sodium bicarbonate is added to one pool that has a pH of 7.0 and an alkalinity of 20 ppm and also added to another pool that has a pH of 7.0 and an alkalinity of 100 ppm, then the greater pH increase will result with the pool that has alkalinity of 20 ppm. This is due to the greater pH buffering of water with higher amounts of alkalinity.

Sodium Carbonate

A 1% solution of sodium carbonate in distilled water has a pH of approximately 11.4. Because of this high pH condition, sodium carbonate will raise the pH in water more significantly than will sodium bicarbonate. And just as with sodium bicarbonate, sodium carbonate will also

more significantly increase the pH when a lower alkalinity level exists.

Alkalinity Contribution

The alkalinity of water is a measurement of its capacity to neutralize acids, and the measurement of alkalinity in water is generally expressed as its calcium carbonate equivalent. There are several ways to calculate the amount of contribution to alkalinity by sodium bicarbonate and sodium carbonate. The following is one example.

Sodium Bicarbonate — In order to calculate the amount of alkalinity increase by the addition of sodium bicarbonate, we must know its calcium carbonate equivalent. We know that the equivalent weight (mass) of calcium carbonate has been assigned as one hundred (100) and the equivalent weight of sodium bicarbonate is one hundred sixty-eight (168). By dividing calcium carbonate's equivalent weight (100) by sodium bicarbonate's equivalent weight (168), we know that sodium bicarbonate is only 59.5% of the equivalent strength of calcium carbonate. By determining the amount of alkalinity contributed by pure calcium carbonate, we will then be able to determine how much alkalinity is contributed by sodium bicarbonate.

If twelve (12) pounds of calcium carbonate was added to a million pounds of water, we would have twelve (12) parts (pounds) per million (pounds) of water (also known as "ppm") of alkalinity as calcium carbonate. Since water has an approximate weight of 8.34 pounds per gallon and 10,000 gallons of water weighs about 83,400 pounds, this is one-twelfth of a million pounds and one pound of calcium carbonate added to 10,000 gallons of water would make 12 ppm. Knowing this we then multiply 12 ppm by the percentage strength of sodium bicarbonate (which is 59.5%) and learn that one pound of sodium bicarbonate would add 7.14 ppm of alkalinity in 10,000 gallons of water.

Another way of arriving at this result is to calculate that one part per million alkalinity, divided by the atomic weight of calcium carbonate multiplied by 1000, and then multiplied by twice the atomic weight of sodium bicarbonate equals the amount per liter, in grams, of sodium bicarbonate to add per ppm increase desired:

$$\frac{1}{(100.09)(1000)} \times 2(84.0077) = 0.001678643$$

This amount multiplied by the conversion factor to convert from grams to pounds

$$0.001678643 \times 0.00220462 = 0.0000037$$

and then multiplied by the number of liters in a 10,000 gallon pool

$$0.0000037 \times 37853 = 0.1400561 \text{ pounds}$$

and then multiplied to increase the 0.14 pounds to 1 full pound

$$\frac{0.14 \text{ pounds}}{1 \text{ pound}} = \frac{1 \text{ ppm}}{7.14 \text{ ppm}}$$

shows that 1 pound of sodium bicarbonate is gives a 7.14 ppm alkalinity lift in a 10,000 gallon pool.

Sodium Carbonate — With sodium carbonate, the equivalent weight (as compared with calcium carbonate) is one hundred six (106). Dividing calcium carbonate's equivalent (100) by sodium carbonate's equivalent weight (106) we learn that sodium carbonate is approximately 94.3% strength of calcium carbonate. Therefore, using the above example, adding one pound of sodium carbonate to 10,000 gallons of water will result in 11.32 ppm of alkalinity.

Using the other method, one part per million alkalinity, divided by the atomic weight of calcium carbonate multiplied by 1000, multiplied by the atomic weight of sodium carbonate equals the amount per liter, in grams, of sodium carbonate to add per ppm increase desired:

$$\frac{1}{(100.09)(1000)} \times 105.9794 = 0.001058841$$

This amount multiplied by the conversion factor to convert from grams to pounds

$$0.001058841 \times 0.00220462 = 0.000002334$$

and then multiplied by the number of liters in a 10,000 gallon pool

$$0.000002334 \times 37853 = 0.088349 \text{ pounds}$$

and then multiplied to increase 0.088349 pounds to 1 full pound

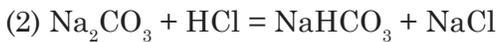
$$\frac{0.088349 \text{ pounds}}{1 \text{ pound}} = \frac{1 \text{ ppm}}{11.32 \text{ ppm}}$$

shows that 1 pound of sodium bicarbonate is gives an 11.32 ppm alkalinity lift in a 10,000 gallon pool.

As we can see from the above information, sodium carbonate increases the alkalinity of water approximately 58.5% more than sodium

bicarbonate, or a better way of comparison is that in terms of alkalinity, sodium bicarbonate is only about 63% as strong as sodium carbonate.

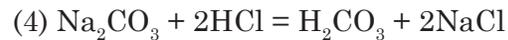
Part of the confusion regarding these two chemicals is the misunderstanding of how acid neutralizes alkalinity. A false assumption is that it takes the same amount of acid to neutralize one pound of sodium bicarbonate as it does one pound of sodium carbonate. This can better be understood if we look at the chemical formulas of sodium bicarbonate and sodium carbonate and their reaction with acid.



In Equation (1) sodium bicarbonate (NaHCO_3) is reacted with a single hydrochloric acid molecule and results in the formation of carbonic acid (H_2CO_3) and sodium chloride (NaCl). Carbonic acid is not alkalinity, nor is sodium chloride. We see that it only took one molecule of acid (HCl) to convert sodium bicarbonate (alkalinity) into an acid.

In Equation (2), we see that sodium carbonate (Na_2CO_3) is reacted with a molecule of acid (HCl) which then forms sodium bicarbonate and sodium chloride (NaCl). We can see that we have converted one form of alkalinity (sodium carbonate) into another form of alkalinity (sodium bicarbonate). This reaction hasn't eliminated all of the total alkalinity, but has reduced the alkalinity by half. Now in Equation (3), the sodium bicarbonate (created in reaction 2) is now reacted

with another acid molecule to produce carbonic acid and sodium chloride. As we can see, it took two molecules of acid (hydrochloric) reacting with sodium carbonate to form carbonic acid and two sodium chlorides. The following reaction will also help illustrate.



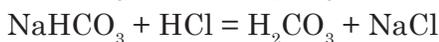
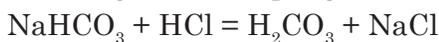
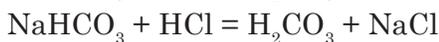
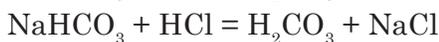
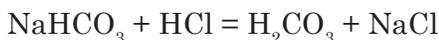
Again, this equation illustrates how it requires two molecules of acid to neutralize sodium carbonate (alkalinity) as compared to one molecule of acid for sodium bicarbonate and create carbonic acid and a non-alkaline component.

Since we see that sodium carbonate has twice the content of alkalinity as compared to sodium bicarbonate, it has been asked why sodium carbonate doesn't contribute exactly double the alkalinity increase as does sodium bicarbonate. The answer lies in the molecular weight differences between these two chemicals. As mentioned earlier, the molecular weight of sodium bicarbonate is 84 and sodium carbonate is 106. Because of this fact, sodium bicarbonate has approximately twenty percent (20%) more molecules in one pound of NaHCO_3 than there is in one pound of sodium carbonate. The equations in Illustration 1 will better illustrate.

As we can see in Illustration 1, there are five molecules of sodium bicarbonate (NaHCO_3) in the left column, with a molecular weight of 420. There are only four molecules of sodium carbonate (Na_2CO_3) in the right column, with an almost equal molecular weight of 424. This represents the 20% higher amount of sodium bicarbonate molecules as compared to sodium carbonate. Then, we see that

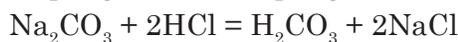
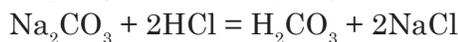
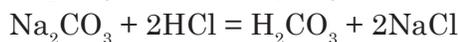
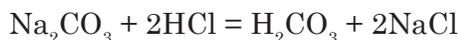
Illustration 1 – Relative Contributions to Total Alkalinity from Sodium Carbonate vs. Sodium Bicarbonate

Bicarbonate reduction with acid



Molecular weight ca. 420

Carbonate reduction with acid



Molecular weight ca. 424

there are a total of five (5) HCl acid molecules in the left column with sodium bicarbonate, and we see that there are a total of eight (8) molecules of HCl in the right column with sodium carbonate. Thus we see that sodium carbonate requires 60% more acid to neutralize its alkalinity content by weight as compared to sodium bicarbonate's alkalinity content.

This accounts for why the different quantitative results between these two compounds is not double the amount.

Due to the high pH of soda ash, adding a lot of it may precipitate calcium carbonate and thus lower the calcium level of pool water. And when that occurs, the pH and the alkalinity may not increase at all, due to the offset of sodium carbonate "in" vs. calcium carbonate "out."

About the Author

Kim Skinner began work in the pool industry at family-owned Skinner Swim Pool Plastering,

Inc. of Sun Valley, California, and later became president of Pool Chlor, a chemical service firm with offices throughout the Southwest. He has worked in the swimming pool industry for over 50 years.

Mr. Skinner has performed both laboratory and field research on pool water chemistry and on the relationships between water chemistry and pool plaster surfaces. He has developed novel processes for swimming pool chemical treatment, including the bicarbonate start-up method for new plaster pools.

He is the co-author of several technical reports on swimming pool water chemistry and plaster phenomena, which have been featured in the trade press. He has also authored material published in previous issues of the Journal of the Swimming Pool and Spa Industry. He has been a voting member of many industry committees, including the APSP Technical Committee and Recreational Water Quality Committee.

Effects of Cyanuric Acid (Chlorine Stabilizer) on Swimming Pool Plaster Surfaces

Presley Kirkland Mitchell
Kirk Mitchell & Associates, LLC

A detailed investigation of plaster coupons exposed to simulated swimming pool water with a range of concentrations of cyanuric acid (CAS No. 108-80-5) was performed. Plaster coupons were prepared in accordance with customary industry guidelines based on input and guidance documents from the National Plasterer's Council. A six-month exposure and monitoring period accompanied by pre- and post-immersion surface roughness measurements as outlined in ANSI/ASME B46.1 and light optical photo-microscopic imaging was carried out. Routine water testing was done and accompanying chemical adjustments were made to maintain conditions within acceptable swimming pool water balance parameters. No measurable surface deterioration via surface roughness and optical photo-microscopic imaging was observed up to 250 mg/L cyanuric acid, the highest cyanuric acid concentration tested.

Introduction

Cementitious material such as plaster has been a common surface finish in the in-ground swimming pool industry for over sixty years. As a semi-pervious but very durable material, plaster exhibits excellent finishing properties for swimming pool application. However, similar to other natural or man-made surfaces, care must be taken to ensure that a plaster swimming pool finish provides a useful life expectancy estimated to be 15 – 20 years by industry experts.

In the October 31, 2007 NPC Online article titled Understanding the Impact of Over Stabilization on Pool Surfaces, the author cites work performed by Dr. Dwain R. Chapman (1971) wherein the report outlines how cyanuric acid reacts with calcium hydroxide in the plaster surface by selectively leaching this essential compound from the plaster. The author accurately highlights the importance of distinguishing between carbonate ($\text{HCO}_3^{-1}/\text{CO}_3^{-2}$) and cyanurate ($\text{C}_3\text{N}_3\text{O}_3^{-m}$) alkalinity. This allows the proper correction to the calculated Langelier Saturation Index (LSI) so that chemical adjustments could be made based exclusively on the carbonate alkalinity.

In work performed by Arch Chemicals, the author reported a substantial loss of dissolved cyanuric acid from the solution after five weeks of exposure to newly prepared plaster coupons. The reported loss of cyanuric acid of 60 – 70% from the starting point of 250 ppm or 500 ppm cyanuric acid was highlighted as a surprising discovery. However, the paper never mentioned the fact that National Plasterers Council's guidelines for initial plaster startup specify that the cyanuric acid should range between 30 – 50 ppm. Photo-documentation performed using Scanning Electron Microscopy (SEM) at 250X magnification observed surface deterioration, most notably at 250 and 500 ppm cyanuric acid.

An alternate view as to the primary cause of certain types of premature plaster deterioration was put forth by onBalance in 2008. The contention of onBalance is that poorly made plaster is the primary culprit for the reported occurrence of these kinds of plaster deteriorations. They claim that it requires very aggressive water for

Journal of the Swimming Pool and Spa Industry

Volume 6, Number 1, pages 24–32

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a prolonged period of time to significantly affect well-made plaster. Their highlighted work revealed no visible discoloration, no shrinking or craze cracking with well-made plaster coupons. Conversely, they reported notable plaster deterioration/damage with plaster coupons made with commonly seen mistakes including a) high water-to-cement ratio; b) excessive calcium chloride (~3.5%); and c) aqueous submersion of coupons too soon after troweling.

The work reported here was undertaken to address a number of key uncertainties and challenge some of the assertions regarding the effect of cyanuric acid on properly prepared plaster surfaces.

Materials and Methods

Preparation of Plaster Coupons

Ten concrete substrates measuring 0.75 in. (1.90 cm) thick, 7.38 in. (18.74 cm) wide and 9.00 in. (22.86 cm) long were prepared using QUIKRETE® Crack-Resistant Concrete Mix (No. 1006) and used as the base for preparing plaster coupons for testing. The size of a plaster coupon was proportionate to a standard size pool. For example, a 20 ft (6.1 m) X 40 ft (12.2 m) X 5 ft (1.5 m) pool has a total water volume capacity of 29,925 gallons (113,266 L) and an estimated water exposed surface area of 1,536 ft² (142.7 m²). Therefore, each gallon of water in an experimental test tank will represent 0.0513 ft² (47.6 cm²) of exposed plaster surface area. 9.0 gallons [34 liters] of H₂O would correlate to a plaster coupon area of 0.462 ft² (429 cm²) and thus a coupon size of approximately 9 in (22.8 cm) by 7⅜ in (18.7 cm). The concrete substrates were allowed to air cure for approximately two weeks before application of the plaster. The finishing plaster mixture was prepared by weighing and uniformly hand-mixing 1.03 lbs. [470 grams] of Royal White® White Portland cement conforming to ASTM C-150 Type 1 and 1.65 lbs. [750 grams] of Imery's Pool Mix – White Ground Marble Aggregate. Calcium chloride (CaCl₂ – 94% Dow Flake) at 1.0% was added to the water and subsequent hand blended plaster samples were prepared by incrementally adding water in 20 to 30 mL aliquots. The total water content added to the plaster mixture used for test coupons 1A, 1B, 2A, 2B, 3A, 3B, 4A and 4B was 0.518 lbs. [235 grams] representing a water:cement ratio of 0.5. Plaster mixture used for test coupons 5

and 6 contained 0.544 lbs. [247 grams] and 0.568 lbs. [258 grams] of water representing an excess water content of 5 and 10%, respectively. Individually-prepared plaster mixtures were applied to the cured concrete substrates using a 6" (15.2 cm) trowel with similar compression and densification application. Non-plastered, underlying concrete substrate surfaces were treated with BEHR® Concrete & Masonry Waterproofer to minimize impact of bare concrete on water chemistry. The finished plaster coupons were air-cured out of direct sunlight for three days prior to immersion in individual test tanks.

Test Tank Set-up and Solution Preparation

Ten Sterilite® - 50 quart (46.9 L) HDPE containers were used during the six-month aqueous immersion experimental test period. Each tank was filled with 9.0 gallons [34 L] of water. Of this, 4.5 gallons [17 L] of water was drawn from the local N.E. Florida municipal water source. The remaining water was derived from distilled water appropriately adjusted with water balancing chemicals and additives so that the following test conditions were maintained: pH 7.2 – 7.6; total alkalinity 80 – 100 mg/L (ppm); calcium hardness 150 mg/L minimum and free available chlorine (Cl₂) 1.0 – 4.0 mg/L. Water recirculation was achieved through use of a Rio+® Aqua/Powerhead 600 pump. This pump provided a significantly shorter turnover than 6 to 8 hours; however, it is assumed that this higher dynamic flow would not affect the outcome as all experimental tanks were equipped with the same recirculation pump configuration.

A ~10,000 mg/L chlorine stock solution was prepared by volumetrically transferring ~95.2 mL of Pinch-A-Penny™ liquid chlorine (10.5% sodium hypochlorite) to a 1.0 liter volumetric flask and bringing to volume with chlorine demand-free distilled water. This standard solution was properly labeled and stored in an amber quart bottle under ambient conditions. The chlorine stock solution was periodically checked by dilution and analysis via Taylor® FAS-DPD titration Chlorine Test Kit (K1515-C). 10% stock solutions of sodium bicarbonate (NaHCO₃) and calcium chloride (CaCl₂) for adjusting water balance were prepared by dissolving 100 grams of each chemical in 1.0 L of distilled water using a volumetric flask. The

pH was adjusted to 7.2 – 7.8 by addition of 3.0 N hydrochloric acid (HCl).

A 0.27% stock solution of cyanuric acid was prepared by dissolving 41.712 grams of Sun-Coast™ Stabilizer Conditioner (98% cyanuric acid) in 4.0 gallons (15.4 L) of distilled water. This solution was constantly stirred at 2,500 rpm using a Cole-Parmer® Ultra-Compact Variable Speed Digital Mixer (Model 50006-00) and pH adjusted to 7.0 using 3.0 N sodium hydroxide (NaOH). Upon complete dissolution, the cyanuric acid solution was stored in sealed one-gallon amber containers under ambient conditions. Cyanuric acid was added to each test tank at the following concentrations by adding the proper volume of cyanuric acid stock solution: Tanks 1A, 1B – 50 mg/L; Tanks 2A, 2B – 27.5 mg/L with weekly cyanuric acid additions of 12 mg/L; Tanks 3A, 3B – 100 mg/L; and Tanks 4A, 4B, 5A and 5B – 250 mg/L.

Water Testing

Temperature and pH readings were performed with an Oakton® pH 5 Acorn Series pH/°C meter calibrated with NIST referenced buffer standards. Free and total available chlorine concentrations were determined using a Taylor® FAS-DPD titration Chlorine Test Kit (K1515-C). The combined available chlorine concentration was calculated as the difference between the free and total available chlorine concentrations. Total alkalinity (TA) and calcium hardness (CH) measurements were performed with a Taylor K-2005 Complete Test Kit.

Total dissolved solid (TDS) was measured using an Oakton® TDS/Conductivity Meter (CON110). Cyanuric acid (CYA) determination was initially performed using Taylor CYA solutions and a calibrated turbidity test procedure using an MP-9500-XMCI Multi-Test photometer. The CYA analytical method was subsequently changed to the turbidimetric disappearing black dot technique contained in the Taylor K2005C Test Kit. The accuracy of the results obtained with the Taylor CYA turbidimetric test method was confirmed via High Performance Liquid Chromatography (HPLC) with confirming spiked recovery validation technique performed by IsleChem™, 2801 Long Road, Grand Rapids, New York 14072 (www.Islechem.com). Turbidity measurements were performed using a HACH® 2100 P (Portable)

turbidimeter meeting the design criteria specified by the United States Environmental Protection Agency (EPA), Method 180.1.

Surface Characterization

Light optical photo-microscopic imaging was performed using a Zeiss Discovery V12 optical microscope at magnifications ranging from 10X to 50X. Surface roughness of the plaster coupons was quantitatively measured using a Mitutoyo SJ201P profilometer using the procedure as outlined in ANSI/ASME B46.1. This technique determines the roughness average (R_A), which is the average deviation (in micro-inches) of the measured profile from the mean plane.

Experimental Results

Accompanying the results are summary data of water chemistry data and corresponding calculations and presentation of the Langelier Saturation Index (LSI), an industry recognized index for the corrosive or scaling-tendency of the experimental aqueous conditions.

Water Chemistry Results

Table 1 summarizes the experimental water conditions with accompanying standard deviations during the entire 6-month experimental test period. These parameters were used to assess an aqueous system's tendency toward scaling or corrosion and the accompanying deposition or removal of calcium carbonate (CaCO_3) by calculating the Langelier Saturation Index (LSI).

Cyanuric Acid

The cyanuric acid concentration was originally determined using a photometric test method with reference standards. The results generated with this method were not as accurate and reproducible as desired. A new test method was employed 46 days into the experiment. The new cyanuric acid test method was the conventional turbidimetric disappearing black dot technique contained in the Taylor K2005C Test Kit. Table 2 summarizes the average and standard deviation for cyanuric acid using the new method after the initial 46 days. The applicability of the conventional Taylor CYA test was substantiated via third party analytical testing and thus there was no impact on the study.

Table 1 – Summary of Water Chemistry Results

Test Tank	pH	FAC (mg/L)	CAC (mg/L)	TAC (mg/L)	TA _(meas.) (mg/L)	CH (mg/L)	T(°C)	Turbidity (NTU)	Langelier Saturation Index (LSI)
1A	7.66 ± 0.18	2.4 ± 0.7	0.3 ± 0.1	2.7 ± 0.7	107 ± 10	165 ± 15	20.1 ± 3.5	0.32 ± 0.43	-0.11 ± 0.27
1B	7.67 ± 0.18	2.6 ± 0.7	0.3 ± 0.1	2.9 ± 0.7	111 ± 13	165 ± 15	20.2 ± 3.5	0.23 ± 0.08	-0.33 ± 0.27
2A	7.63 ± 0.22	2.1 ± 0.6	0.4 ± 0.2	2.5 ± 0.7	See a	164 ± 19	18.7 ± 3.4	0.22 ± 0.07	-0.12 ± 0.31
2B	7.65 ± 0.21	2.4 ± 0.7	0.4 ± 0.2	2.9 ± 0.7	See a	174 ± 18	20.4 ± 3.4	0.23 ± 0.05	-0.10 ± 0.29
3A	7.70 ± 0.18	2.4 ± 0.7	0.4 ± 0.1	2.8 ± 0.7	123 ± 11	176 ± 19	20.5 ± 3.4	0.21 ± 0.06	-0.02 ± 0.25
3B	7.66 ± 0.17	2.5 ± 0.9	0.4 ± 0.1	3.0 ± 0.9	126 ± 12	179 ± 21	20.4 ± 3.4	0.27 ± 0.10	-0.05 ± 0.25
4A	7.60 ± 0.16	2.6 ± 1.0	0.7 ± 0.1	3.3 ± 1.0	166 ± 18	195 ± 28	20.5 ± 3.2	0.27 ± 0.06	-0.15 ± 0.25
4B	7.63 ± 0.17	2.3 ± 0.6	0.7 ± 0.1	3.0 ± 0.7	163 ± 16	195 ± 30	20.6 ± 3.2	0.22 ± 0.07	-0.09 ± 0.26
5	7.68 ± 0.20	2.4 ± 0.7	0.7 ± 0.2	3.1 ± 0.7	158 ± 17	194 ± 33	21.0 ± 3.2	0.27 ± 0.08	-0.04 ± 0.28
6	7.70 ± 0.20	2.2 ± 0.8	0.7 ± 0.2	2.9 ± 0.8	155 ± 16	199 ± 33	20.9 ± 3.1	0.28 ± 0.07	-0.02 ± 0.28

- a. Total alkalinity adjusted upward to compensate for weekly increases in CYA and associated increase in observed results when testing total alkalinity; FAC, CAC, TAC = Free, Combined and Total Available Chlorine, respectively. TA = Total Alkalinity, CH = Calcium Hardness

Table 2 - Cyanuric Acid Test Results

Test Tank	Protocol Targeted CYA (mg/L)	Average CYA (mg/L) ± Std. Dev.
1A	50	47 ± 5
1B	50	48 ± 5
2A	27 ^a	286 ^b
2B	28 ^a	267 ^b
3A	100	108 ± 5
3B	100	113 ± 10
4A	250	246 ± 18
4B	250	258 ± 12
5	250	254 ± 11
6	250	255 ± 12

- a. Initial CYA concentration
 b. Final CYA concentration

Two separate independent laboratory validations (5 samples per test) for cyanuric acid were performed during the course of the study using HPLC analysis. The results demonstrated that the Taylor conventional turbidimetric disappearing black dot technique was an accurate and

reproducible test when performed under optimum conditions between 35 – 60 mg/L CYA which was achieved via sample dilution and reproducible lighting. The observed recorded results were within (±) 3.8 percent of the HPLC analytical results.

Equation 1

$$LSI_{(Calc)} = pH - ([9.3 + TDS_{(t)} + T_{(t)}] - [CH_{(t)} + Alk_{(t)}])$$

$$TDS_{(t)} = \text{Log}((TDS) - 1) / 10$$

$$T_{(t)} = -13.12 \times \text{Log}(\text{°C} + 273) + 34.55$$

$$CH_{(t)} = \text{Log}(\text{Calcium Hardness mg/L}) - 0.4$$

$$Alk_{(t)} = \text{Log}(\text{Total Alkalinity Corrected per Equation 2 as mg/L})$$

Langelier Saturation Index Results

The Langelier Saturation Index (LSI) is a chemical equilibrium mathematical model that provides an indicator of the degree of saturation of water with respect to calcium carbonate [CaCO₃]. LSI values were calculated using Equation 1.

LSI values less than -0.3 denote significant under-saturation of CaCO₃, indicating that the plaster will tend to dissolve. LSI values greater than 0.5 indicate significant over-saturation of CaCO₃, indicating that CaCO₃ will tend to precipitate from the water, leading to scaling. Figure 1 summarizes the average LSI and associated standard deviation of the test solutions during exposure of the test coupons. As these results show, all test tanks with the exception of 1B yielded average LSI values within the industry

acceptable range of -0.3 to +0.5. Test tank 1B had a calculated average LSI value of -0.33, which was only slightly outside of the recommended range. Therefore, all test coupons in this study were exposed to solutions that were non-aggressive according to LSI, despite the high levels of cyanuric acid.

Surface Roughness – Pre- and Post-Immersion

The surface roughness of each plaster coupon was measured pre- and post-immersion, as outlined in the Surface Characterization section. Figure 2 depicts the surface roughness (R_A) results. Only one coupon (#2A) exhibited a higher R_A value after immersion (Figure 2), indicating the plaster surface was rougher after the 6-month immersion period. The surface character of three

**Figure 1 — Langelier Saturation Index (LSI) values
for test tank/coupons**

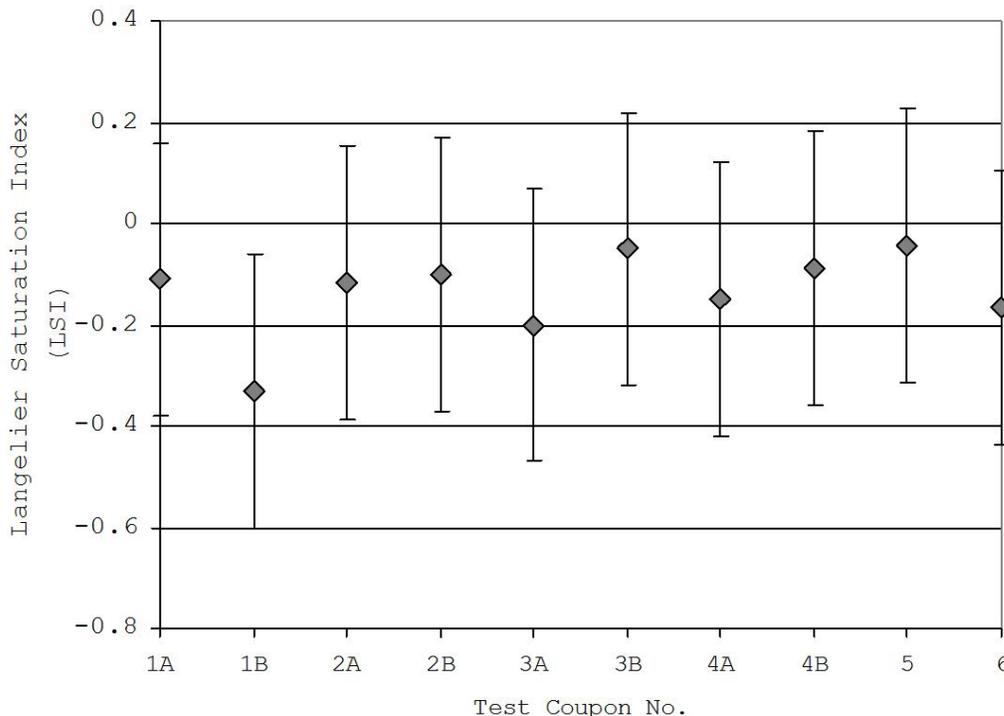
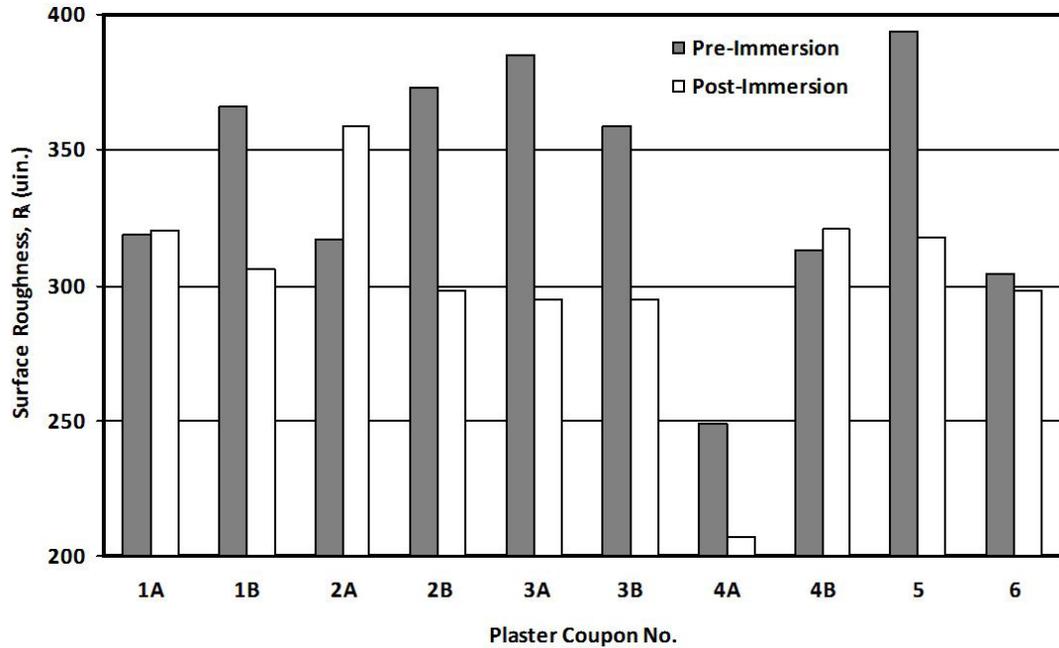


Figure 2 — Pre- and Post-Immersion Surface Roughness



plaster coupons (#1A, 4B and 6) were essentially unchanged following the six-month exposure period, whereas the remaining plaster coupons (#1B, 2B, 3A, 3B, 4A and 5) were smoother at post-immersion (Figure 2).

Light Optical Photo-Microscopic Imaging

Light optical photo-microscopic imaging was performed on all of the test coupons as outlined in the Surface Characterization section. Pre-Im-

mersion Test Coupon 4A at 15X magnification (Image 1a) and Post-Immersion Test Coupon 4A at 15X magnification (Image 1b) exhibit side-by-side optical photo-microscopic images of Test Plaster Coupon 4A at 15X magnification in the 250 mg/L CYA test solution. The post-immersion image portrays a smoother surface character which is consistent with the measured surface roughness (R_A) results shown in Figure 2.

Pre-Immersion Test Coupon 2B at 50X magnification (Image 2a) and Post-Immersion

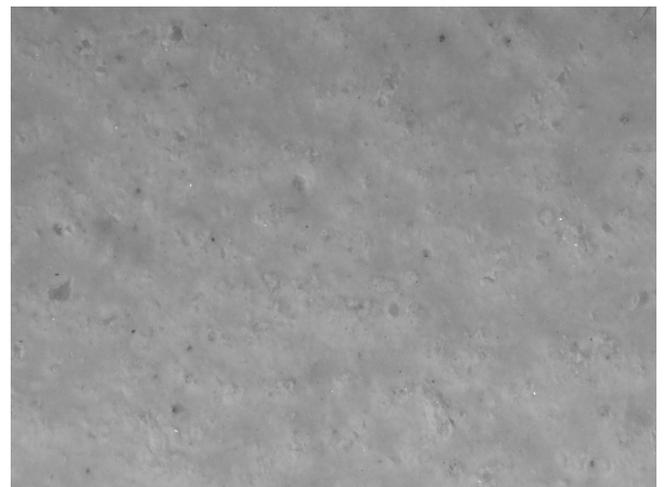
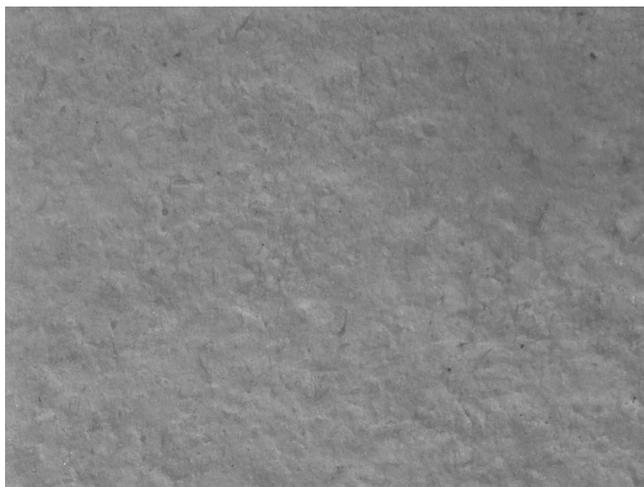


Image 1 — Light optical photo-microscopic imaging Test Coupon 4A
 Left: (a) Pre-Immersion Test Coupon 4A at 15X magnification
 Right: (b) Post-Immersion Test Coupon 4A at 15X magnification

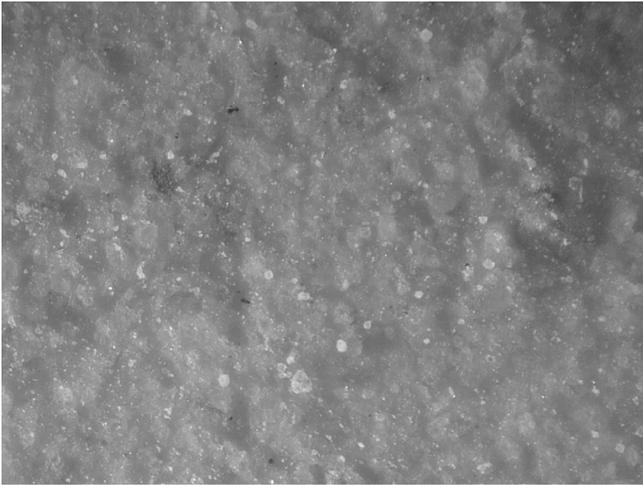


Image 2 — Light optical photo-microscopic imaging Test Coupon 2B

Left: (a) Pre-Immersion Test Coupon 2B at 50X magnification

Right: (b) Post-Immersion Test Coupon 2B at 50X magnification

Test Coupon 2B at 50X magnification (Image 2b) exhibit side-by-side optical photo-microscopic images of Test Plaster Coupon 2B at 50X magnification with steadily increasing concentrations of cyanuric acid derived from weekly incremental doses of approximately 12 mg/L. The final cyanuric acid concentration of Test Tank 2B was 267 mg/L (Table 2). No significant difference was observed between the pre- and post-immersion photos.

In addition, the post-immersion coupons do not show any of the cracking or surface modification reported in the Arch study. Very similar results were found for all the other test coupons in this study – the surface texture showed no significant differences between the pre- and post-immersion coupons.

Discussion

Accelerated deterioration of swimming pool plaster is typically associated with the application of aggressive agents directly to the plaster surface such as a) strong mineral acids; b) concentrated (non-diluted) sequestering agents; and c) application of acidic compositions directly to the surface, all defined categorically as aggressive chemical attack per NPC guidelines (Reference 1, pp. 27).

Surface finish is important to the function and esthetics of many kinds of industrial and consumer products. It is particularly important in the recreational water sector because a smooth cementitious (plaster) surface reduces the likelihood of skin abrasions and lessens the propensity

for algae growth by limiting the harboring sites for algae cells, primarily surface-clinging black (blue-green) algae.

Surface roughness using the ANSI/ASME B46.1 procedure was employed in this study as it was deemed a practical approach to directly assessing surface deterioration. This profiling technique involves a careful, detailed probing of the surface with a high resolution probe. Although other referenced work has employed the use of scanning electron microscopy (SEM), optical microscopy alone provides a limited qualitative assessment. The individual surface roughness measurement (R_A) of each plaster coupon provides a quantitative pre- and post-immersion evaluation of the surface.

As shown in Figure 2, only one coupon (#2A) exhibited a higher R_A value after the six month exposure period, pointing to a slightly rougher post-immersion surface. All other test coupons exhibited no appreciable difference between the pre- and post-immersion surfaces or a smoother post-immersion surface, even for those coupons exposed to the highest cyanuric acid levels (#4A, 4B, 5 and 6) as presented in Table 2. These observations diverge from prior work (Reference 3) performed to assess the impact of cyanuric acid on plaster surfaces but support the findings reported by onBalance (Reference 4).

Table 1 provides a summary view of the average water balance conditions over the 6-month experimental test period. Although all chemical water balance measurements are important and

must be performed in a manner consistent with quality test methods, the measurement of total alkalinity is one measurement that requires special attention, especially in the presence of cyanuric acid, an essential chlorine-stabilizing agent in outdoor swimming pools.

Cyanuric acid is a polyprotic acid as indicated by its molecular formula ($H_3C_3N_3O_3$). Within the acceptable pH range of recreational water venues (7.2 – 7.8), cyanuric acid exists as a combination of the neutral molecule and negatively charged cyanurate anions, $[H_nC_3N_3O_3^{(n-3)}]$ where n is the number of hydrogen atoms. Accordingly, the collection of cyanurate anions consumes mineral acid during the standard acid titration method for determining total alkalinity. While cyanurate anions contribute to the total alkalinity, cyanurate is not part of the carbonate (HCO_3^{-1}/CO_3^{-2}) buffering system which is employed to determine the Langelier Saturation Index (LSI). This requires correcting the measured Total Alkalinity ($TA_{[measured]}$) to determine the corrected Total Alkalinity value ($TA_{[corrected]}$), using Equation 2.

The total alkalinity values presented in Table 1 are the measured values expressed in milligrams per liter (ppm).

Figure 1 graphically highlights the average calculated Langelier Saturation Index (LSI) and accompanying standard deviation. A total of 32 data points were used to calculate the average LSI and standard deviation for each test tank shown.

The final and very important distinguishing observation from earlier published work was the overall observed ‘*steady-state*’ condition of

cyanuric acid, except for Test Tanks 2A and 2B wherein a weekly incremental dose of additional cyanuric acid was applied. As reported in Table 2, the relative percent deviation of measured and targeted cyanuric acid for Test Tanks 1A, 1B, 3A, 3B, 4A, 4B, 5 and 6 was 6.9 percent. Couple this with the negligible difference between the employed test method and the independent HPLC analyses, and the results clearly support the ‘*steady-state*’ presence of cyanuric acid which is in disagreement with the rapid decline of cyanuric acid reported by Meyer (Reference 3).

Conclusion

This study demonstrated that cyanuric acid at up to 250 mg/L, two and one-half times the generally recognized state and municipal health code maximum level, did not result in premature surface deterioration of properly prepared plaster coupons. This observation was realized when the water balance was maintained within industry accepted guidelines including the adjustment of total alkalinity to compensate for the buffering influence of cyanurate anions. Even plaster coupons produced with excess water content of 5 and 10% showed no appreciable surface degradation using the ANSI/ASME B46.1 surface roughness procedure.

Acknowledgement

The author thanks Tom Kuechler, Ph.D, David Lewis and Gary Wright, Ph.D. of the IIAHC for their comments and constructive suggestions throughout the study.

Equation 2

$$TA_{[corrected]} = TA_{[measured]} - \{CYA \times CYA \text{ Factor}\}$$

$$TA_{[measured]} = \text{Measured Total Alkalinity}$$

$$CYA = \text{Cyanuric acid concentration (mg/L)}$$

$$CYA \text{ Factor (See Table 3)}$$

Table 3 — CYA Correction Factor

pH	CYA Factor	pH	CYA Factor
7.0	0.23	7.6	0.33
7.2	0.27	7.8	0.35
7.4	0.31	8.0	0.36

Funding

The author acknowledges and appreciates the financial support from the Isocyanurate Industry Ad Hoc Committee (IIAHC), an industry consortium comprised of the following entities - Aqua Clor, S.A. de C.V., Bengbu Jingxian Hongfa Chemical Company, Ltd., Bio-Lab, Inc., Clearon Corporation, Ercros, S.A., Hebei Jiheng Chemical Co., Ltd., Heze Huayi Chemical Company, Ltd., Inquide S.A.U., Nissan Chemical America Corporation, Occidental Chemical Corporation, Shikoku Chemicals Corporation and 3V Sigma S.p.A.

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Kirk Mitchell has over 35 years of technical managerial and leadership experience with a principal focus on product and process development, governmental liaison, regulatory affairs and third party certification and listing of proprietary products and processes. He has extensive strategic and operational planning expertise with a keen sight for the right set of results. He has authored and had published numerous articles in peer-reviewed technical journals, conceived and published training manuals and been granted nine (9) co-authored patents by the U.S. Patent and Trademark Office. Kirk, a former member of the U.S. Marines, has a Masters degree in chemistry with numerous training credentials in project management, product development, technology licensing and leadership.

References

1. National Plasters Council, Technical Manual, 6th Edition, 2009
2. NPC OnLine, Preventing Interior Finish Problems, Part III, Understanding the Impact

of Over-Stabilization of Pool Finishes by Greg Garrett, Technical Advisor to the National Plasterers Council.

3. High Cyanuric Acid Levels & Plaster Degradation in Swimming Pools, Ellen M. Meyer, Pool & Spa Marketing, January 2006.
4. onBalance Conducts New Plaster Study, Pool & Spa News, August 2008 (pg. 18).
5. The Analytical Control of Anti-Corrosion Water Treatment, W. F. Langelier, Journal of the American Water Works Association, Vol. 28, 1936, pp. 1500-1521
6. Examining Scaling Indices: What Are They, Paul Pickorius and Peter S. Cartwright, Waterworld, Water and Wastewater International, Vol. 12, Dec. 2012
7. Appendix A – Association of Pool & Spa Professional® (APSP) Chemical Operational Parameters (Revised and Approved February 2012) applicable to APSP – 1 Public Inground Pools, APSP – 2 Public Spas, APSP – 3 Residential Permanent Spas, APSP – 4 Residential Aboveground/Onground Pools, APSP – 5 Residential Inground Pools, APSP – 6 Residential Portable Spas, APSP – 9 Aquatic Recreational Facilities and APSP – 11 Water Quality for Public Pools and Spas
8. California Department of Health, 2010 Building Code, Public Swimming Pools, Section 3106B.2 – Finish, pp 478
9. Oklahoma State Department of Health, OAC 310:315, Subchapter 7, Construction & Operation, 310:315-7-7(a) Materials and Finishes
10. Surface Finish – Metrology Tutorial, U.S. Department of Commerce, NISTIR 89-4088, June 1990
11. Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989, Part 2320, pp. 2-35 – 2-39
12. Effect of Cyanuric Acid on Total Alkalinity, National Spa and Pool Institute (NSPI) Informational Bulletin, CT&P -5, March 1995

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