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Jeffery Que Hales, Editor

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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 publcation 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 understood 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 proceeded 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 Jeffery 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. 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/PHTA).

Editorial Review Board

The Editorial Review Board is a group of volunteers who have agreed to read and ref-

eree submissions to the Journal. In order to maintain an objective, independent Journal, the Editor does not unilaterally 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 deserve our special thanks and appreciation. The JSPSI is a non-profit publication, and these individuals donate their time and efforts on our behalf.

Cyanuric Acid Requirement Versus Free Chlorine in Pool Water

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

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

Background

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

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

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Estimating the Cyanuric Acid Requirement for a Given Free Chlorine Residual

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

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



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



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

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

There is, however, a simple shortcut to estimating hypochlorite concentration from the FC/CyA ratio for most common swimming pool scenarios. Richard Falk has noted that the hypochlorous acid concentration is often (inversely) tied to the concentration ratio CyA/FC (Falk 2019). Similarly, hypochlorite concentration can be estimated from the FC/CyA ratio for a number of common

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pool scenarios. When cyanuric acid is used, typical concentrations exceed 30 ppm, with chlorine concentrations on the order of 1-4ppm. For such low ratios of apparent FC/ total CyA namely < 0.14 ppm FC/ppm CyA, and concentrations of total CyA exceeding 20 ppm—hypochlorite ion concentration relates to the Apparent FC/total CyA ratio, or quotient (*Q*), as follows:

$$[OCl^{-}] = 1.08Q^{2} + 0.529Q \tag{1}$$

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



Figure 3 — Relationship between hypochlorite ion concentration and the ratio FC/CyA at pH 7.5. All concentrations are in ppm or mg/L, and hypochlorite is expressed as the Cl_{2} equivalent, or available chlorine.

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

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

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

$$[HOCl] = [OCl^{-}] * \frac{[H^{+}]}{K_{a}} = [OCl^{-}] * 10^{(pK_{a}-pH)}$$
(2)

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

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

Mathematical Modeling of Solar Decomposition

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

For the cyanurate-free loss of free chlorine

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

$$\frac{dC}{dt} = -k * C^{1.3} \tag{3}$$

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

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

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

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

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



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

in Figure 4.

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

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

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

1. The starting apparent (measurable with DPD) free chlorine and total CyA concentrations (when CyA was present) were used to calculate hypochlorite ion concentration (expressed as ppm available chlorine). For the zero CyA case, it was assumed that the pH was at the pK_a (~7.5) so half of the FC was hypochlorite ion. (See Equation (2)) For the cases with CyA,

Equation (1) was used.

- 2. The decrease in the hypochlorite ion concentration was calculated using a kinetic equation. For 1.3 order reaction, Equation (4) was used. For 1st and 2nd order kinetics (Figure 4), Equation (5) or (6) was used with a rate constant (k value) of 1.25 or 3.5 respectively.
- 3. The resulting hypochlorite ion concentration at time $\mathbf{t}_{\scriptscriptstyle 2}$ was used to calculate the apparent FC, at time t_2 , using Equation (7). This equation assumes that the hypochlorous acid concentration equals the hypochlorite ion concentration (pH \approx 7.5), and subtracts twice the hypochlorite loss from the previous apparent FC. This entails an assumption that as hypochlorite is destroyed by UV light, there is a comparatively rapid Le Châtelier conversion of hypochlorous acid to hypochlorite to restore the balance between hypochlorite and hypochlorous acid concentrations demanded by the pH, as indicated in (2). So while decomposition occurs primarily via UV destruction of hypochlorite, there is facile conversion of hypochlorous acid to hypochlorite, allowing thereby a roughly equal rate of hypochlorous acid decomposition by the hypochlorite route.



Figure 5 – Comparison of Monsanto data with model assuming solar degradation of available chlorine does not involve any cyanurate-bound chlorine. Free chlorine starts at 5 ppm. 10

$$FC_{2} = FC_{1} - 2 * ([OCl^{-}]_{1} - [OCl^{-}]_{2})$$
(7)

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

Note that while the fit is fairly good for the cyanurate-free case, the cases involving 25, 50 or 100 ppm CyA show a marked departure of the theoretical curves from the Monsanto data points. With most of the chlorine bound to cyanurate (~95% even for the 25 ppm CyA case), the rate of solar chlorine destruction

should correspondingly be very low, as shown by the theoretical (calculated) curves. The Monsanto data, on the other hand, show an initial rapid drop in chlorine concentration, even with CyA present, followed by a sudden leveling off to a rate loss more closely parallel to the theoretical predictions. Of various possible explanations for the rapid initial losses of FC, even in the CyA cases, the most plausible is the presence of chlorine demand in the water at the beginning of the tests. In citing the Monsanto data, Wojtowicz also noted the odd and sudden drop in the rate of chlorine decomposition after the first halfhour (Wojtowicz 2004). He also noted much slower loss due to sunlight than Monsanto reported, noting that the outdoor pool used



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



Figure 7. Model of stabilization of free chlorine. Free chlorine initially at 10 ppm. Volume 6 Number 2 – Spring 2023

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

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

The Optimum CyA/FC Ratio

For any free chlorine concentration, adding cyanuric acid serves to decrease the concentrations of hypochlorous acid and hypochlorite. This slows the rate of solar destruction, but by the same proportion also slows the oxidation of contaminants and the inactivation of pathogens. The advantage of doing this is that it makes it possible to provide relatively stable free chlorine residuals, by providing a large reserve of cyanurate bound chlorine, ready to be released as the truly free chlorine is consumed. Increasing the CyA/FC ratio provides for a more stable residual, but also slows the rate of disinfection. The optimum balance between stability and efficacy is not the same for all bodies of water. For indoor pools with no solar destruction of chlorine, it may be desirable to have little or no CyA present, to allow for the most rapid inactivation of pathogens and oxidation of bather waste, as long as the FC residual can be maintained. 12

For outdoor bodies of water, especially shallow ones—such as kiddie pools, beach entries and flumes or slides—it may be nearly impossible to maintain a stable chlorine residual in bright sunlight unless circulation turnover times are short *and* the CyA/FC ratio is high.

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

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About the Author

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

Softening Pool Water Through Calcium Carbonate Precipitation and Removal

Que Hales, Doug Latta and Kim Skinner on Balance

Pool water was softened by reacting dissolved calcium bicarbonate (calcium hardness) in the pool water with added sodium carbonate (soda ash). This formed a filterable precipitate of calcium carbonate. The process had little effect on other dissolved solids, but a marked reduction of calcium hardness.

Swimming pool water chemistry standards commonly call for a maximum calcium hardness level of 1000 ppm. This is primarily intended to facilitate saturation index balancing of the pool water. Once calcium hardness exceeds 1000 ppm, unless the pool is drained either the pH and/or the alkalinity must generally be lowered toward the bottom of the acceptable ranges to compensate.

Draining a pool and replacing some or all of the water with fresh tap water to lower calcium levels is often preferred, since it also lowers other undesirable components of the water, including total dissolved solids, cyanuric acid, accumulated salts, disinfection byproducts, etc.

Unfortunately, there are times when draining a pool may be impractical. Reasons for not draining a pool may include cost, weak

Journal of the Swimming Pool and Spa Industry Volume 6, Number 2, pages 14–19 Copyright © 2023 by JSPSI All rights of reproduction in any form reserved. (bond-failed or delaminated) plaster, high ambient temperatures coupled with low humidity, drought restrictions, high water tables, or even particularly conservation-minded pool owners. In these circumstances an alternative to water replacement may be desirable.

Accidental Precipitation

Sodium carbonate (Na₂CO₃ or soda ash) is often added to swimming pool water to raise the pH and alkalinity. Under normal circumstances, the product should be added in such a manner as to distribute the powder evenly across the pool water surface. This method promotes the speed of blending the product (and its effects) throughout the vessel as expeditiously as possible. Even when added carefully, a precipitate may form, momentarily clouding the water. The visible clouding is not soda ash that has not yet gone into solution, but rather a precipitation of calcium carbonate. This is the result of a localized, temporary raising of the pH in the water at least into the mid-10 range, putting a relatively small area of the pool water into extreme over-saturated Langelier Saturation Index (LSI) levels. The clouding fades away as the non-stable precipitate dissolves back into the pool water, and the high-pH products blend throughout the vessel, thereby lowering the pH in the initially affected area while raising the pH of the entire pool from the starting point to the overall target level.

If added incorrectly (in a small, localized area of water rather than spreading it out across the entire surface for proper blending), the correct amount of sodium carbonate to raise, for example, 20,000 gallons from a pH of 7.4 to 7.6 may be able to increase the pH of perhaps a cubic yard of water significantly. At pH 11.5, which is in the pH range of a saturated solution of sodium carbonate, approximately 85% of the carbonate species material in water will be carbonate instead of the bicarbonate form prevalent at normal pool water pH ranges (see Figure 1). When this happens, the cloud of calcium carbonate precipitate takes much longer to dissipate. and sometimes a threshold is achieved at which the formation of a stable precipitate is actually promoted. (For a discussion of this topic, see Wojtowitz 2001 p. 45)

When this happens, the entire pool water becomes white. The precipitate must then be either filtered or re-dissolved through a significant lowering of the pH using acid.

Intentional Precipitation

One method of softening water in water treatment plants is that of "lime softening," where calcium is removed using this precipitation/filtration process. (See, for example, Lime Softening). In swimming pools, water may also be softened (i.e., calcium ions removed) by precipitation (essentially a process of sodium/calcium ion exchange) and filtration.

Equation 1 shows the reaction of sodium carbonate (added as a powder) and dissolved calcium bicarbonate (hardness in pool water), forming a filterable precipitate of calcium carbonate with a residual of soluble sodium bicarbonate (non-hardness alkalinity).

$$Ca(HCO_3)_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaHCO_3$$
 (1)

This process may also be accomplished using sodium hydroxide (NaOH, or caustic soda). Equation 2 shows the same process using sodium hydroxide, which also forms a



filterable precipitate of calcium carbonate, along with water and sodium bicarbonate alkalinity.

$$Ca(HCO_3)_2 + NaOH \rightarrow CaCO_3 + H_2O + NaHCO_3(2)$$

Sodium hydroxide (caustic soda) is generally not favored in the pool water treatment industry because it must be handled under hazardous materials precautions, is less available to the pool service technician, and is more dangerous to use.

Dosage

The potential amount of filterable precipitate that could be generated may be estimated by taking into consideration the following: The molecular weight of sodium carbonate is 105.98 and the molecular weight of calcium carbonate is 100.08. Therefore, one pound of added soda ash reacting with calcium bicarbonate in the pool water can potentially yield 0.944 lbs. of calcium carbonate precipitate. Or, 1.06 pounds of soda ash reacting with calcium bicarbonate can yield up to 1.0 lbs. of calcium carbonate. One pound of calcium carbonate precipitate translates to about 12 ppm of calcium hardness reduction in 10,000 gallons of water.

Variables

It is important to note that there are a number of variables to how much calcium carbonate precipitate will actually be formed and filtered when this process is utilized in a swimming pool. These variables include the method of addition (localizing and raising pH as much as possible), existing buffers in the pool water, the temperature of the water, the speed and efficiency of the filtration process (inhibiting re-dissolving of any precipitate), etc.

An In-field Example

A swimming pool was treated with the Soda Ash / Calcium Hardness precipitation technique. The water had a beginning calcium hardness level of roughly 1200 ppm, and the pool owner did not wish to drain the pool due to the cost of water replacement and the weather (very hot temperature).

The water was pre-tested, and the initial readings are given in the "Before" column of the accompanying Table.

The pool was dosed twice, the first time with 20 pounds of sodium carbonate and then a follow-up dose a few days later (after the pool cleared) of 50 pounds.

	Before	After 20 Pounds Soda Ash	After 50 More Pounds Soda Ash
рН	8.2	7.8	7.5
Total Alkalinity	180	154	158
Calcium Hardness	1196	972	598

a. The pH was determined using a calibrated Kruger and Eckels Model 100 pH meter using a wide-range combination electrode with a silver/silver chloride reference. The instrument precision is 0.1 pH units.

b. Total Alkalinity was determined using a 0.02 N HCl buret titration to a 4.6 pH endpoint and a temperature of 20°C, with a precision of 2 ppm [Standard Methods 2320 - Alkalinity].

The method used to determine calcium hardness was a 0.1 Molar EDTA buret titration utilizing murexide as an indicator and an NaOH solution for magnesium precipitation. The precision is 2 ppm [Standard Methods 3500-Ca - Calcium]. 16



Illustration 1 – Setting Up the Filter at a Hard Water Pool



Illustration 2 – Adding the Soda Ash in a Local Area to Create the Cloud



Illustration 3 – "Milking" the Pool so it Precipitates the Calcium

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Illustration 4 – Brushing the Pool and Cleaning the Filter Each Day



Illustration 5 – Residue on the Bottom is Removed By Adding a Suction-side Cleaner to the Filter



Illustration 6 – Result, a Clear Pool With Half the Hardness

Follow-up Readings

The results after the 20 pound and 50 pound additions are given in the Table. The result was not only a decrease in calcium hardness of nearly 600 ppm from the 70 pounds of soda ash added, but also a decrease in alkalinity of about 20 ppm and a decrease in pH of 0.7 pH units. The LSI went from roughly +1.4 to +0.4.

The slight lowering of pH and TA by the addition of soda ash and the precipitation of calcium carbonate was one of the interesting side notes of the process. One may intuit a large rise in alkalinity and pH when adding such a large dose of sodium carbonate, but instead the consequent loss of calcium carbonate offset that effect.

The filter available for precipitate removal was a Sta-rite System 3 unit with a DE cartridge. No DE was added, and the filter was opened and cleaned once per day for three days, resulting in a removal of approximately 70 pounds of precipitated calcium carbonate. A suction cleaner was attached to the filter to remove precipitate that had settled to the bottom of the pool.

The precipitate was not in the pool long enough to adhere to the interior surfaces. One caution to observe if trying this technique is that the process could potentially precipitate heavy metals such as copper or iron if they are present in significant concentrations.

References

Lime Softening. National Drinking Water Clearinghouse Fact Sheet. See <u>https://</u> <u>water-research.net/Waterlibrary/</u>

privatewell/limesoftening.pdf

Wojtowicz, John A. "Factors Affecting Precipitation of Calcium Carbonate" Journal of the Swimming Pool and Spa Industry 3:1(2001):18-23. See <u>http://www.poolhelp.com/wp-content/</u> <u>uploads/2017/05/JSPSI V3N1 pp18-</u> <u>23.pdf</u> (internal pagination follows the compiled works publication of Wojtowitz's articles)

About the Authors

J. Que Hales has been the manager of the Tucson branch office of Pool Chlor for the past 38 years. He is an active author, researcher, lecturer and publisher. He is the past president of the National Association of Gas Chlorinators, the Southern Arizona Chapter of the NSPI, and is the editor of the *Journal* of the Swimming Pool and Spa Industry.

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An Update on the Cause of Swimming Pool Plaster Efflorescence (Calcium Nodules)

Que Hales, Doug Latta and Kim Skinner - onBalance

Swimming pool plaster samples exhibiting calcium nodule growths have been analyzed by cement petrographers, and the findings are consistent with the model proposed by onBalance in a 1998 JSPSI article.

In 1998 we published an article titled "Calcium Nodules" in the Journal of the Swimming Pool and Spa Industry (Volume <u>3 Number 2 pp. 21-26</u>). In that article we proposed a mechanical and chemical model for the occurrence of calcium nodules on swimming pool plaster. The primary characteristics of the phenomenon were described as water penetration into or through various types of flaws in the plaster, leaching calcium hydroxide from within the plaster paste; and then carbonation, or conversion into calcium carbonate as the exudate reacts with alkalinity in the pool water at the exterior plaster surface.

This reaction does not involve "aggressive" pool water as some in the industry were maintaining, and in fact the presence of aggressive water inhibits nodule formation by solubilizing the calcium (derived primarily from calcium hydroxide, but also from chloride) into soluble calcium bicarbonate.

Since that time the majority of the pool industry has accepted this understanding of pool plaster calcium nodules. However, there have been a few cases where there was still

Journal of the Swimming Pool and Spa Industry Volume 6, Number 2, pages 20–26 Copyright © 2023 by JSPSI All rights of reproduction in any form reserved. 20 dispute. In those cases, samples of calcium nodules were obtained and presented for forensic analysis at petrographic laboratories. We are here presenting copies of those analyses, showing that the lab findings support and substantiate the model we presented.

Case Study oB-00015

This pool failed primarily by being extensively soft spotted. However, there were also some areas where nodule formation occurred. In one such area, a core sample was removed to acquire the nodule and we found complete bond failure between the gunite substrate and the plaster layer (see Figure 0B-00015a). Hairline cracking occurred in the plaster, allowing water to penetrate between the plaster and the gunite, and a nodule formed along the exterior crack line. A three-inch core was removed from the plaster, which including the nodule (see Figure oB-00015b). This core was sent to Dr. Boyd Clark, at the time a Senior Materials Scientist and petrographer at the RJ Lee Group (RJLG). An additional sample of the plaster (with soft spotting only, no nodule) was sent to Laura Powers, at the time a petrographer and Principal Microscopist at Construction Technology Laboratories (CTL), the subsidiary lab of the Portland Cement Association (PCA) for a second opinion.

Dr. Clark noted the bond failure:

No concrete, from the pool substrate, was observed on the opposite side (not shown), indicative of plaster delamination from the shotcrete substrate. [RJLG p. 1] Although referred to as "efflorescence" in the cement/concrete industry, he associated it with the pool term "nodule":

Relief is observed, in figure 2, decorating the length of the crack due to efflorescence, indicative of a calcium rich material. From our discussions, this phenomenon seems to be generally termed nodular growth in the swimming pool industry. [RJLG p. 2]

He also said the pool plaster surface was not etched from aggressive water:

The stereo optical images do not show evidence of "disrupted" paste indicative of an aggressive solution (surface attack due to acidic water conditions.) [RJLG p. 2]

He further notes that:

The chloride content in the paste (observed in the SEM) indicates that calcium chloride has been added to the plaster at a concentration greater than 2 Wt.%. [RJLG p. 3]

Note that two weight percent chloride-to-cement as dihydrate is a recognized high-end limit and that this limit was substantially exceeded in this pool. In fact, Dr. Clark's determination of acid soluble chloride in bulk plaster was 1.04 Wt.%, which converts to around 5% calcium chloride to cement as flake calcium chloride dihydrate [RJLG p. 3]. This substantial defect disrupted the paste, filled void spaces with Friedel's salt, and created stresses resulting in the lifting separation and craze cracking upon which the nodule formed:

This addition has resulted in extensive shrinkage cracking throughout the plaster paste. This cracking also appears to predate the formation of the affected region, highly porous paste follows the crack and calcium rich material has moved from the porous regions into the crack. [RJLG p. 3]

Powers, in her peer review report, concurred that the surface had not been etched by aggressive water:

The outer surface of the marble does not exhibit evidence of dissolution or etching.

(CTL p. 2)

She calculated the calcium chloride addition in her sample at 1.06 Wt.% (CTL p. 4), comparable to the RJLG value, and also commented on the paste distress, including the attendant Friedel's salt deposits (CTL p. 2).

This calcium nodule perfectly illustrates the bond failure-related type of formation.

References:

Boyd Clark "RJ Lee Group Project Number MAH304128" 07-08-2003 (<u>http://www.poolhelp.com/wp-content/uploads/2023/03/</u> <u>oB-00015 RJLG-MAH304128.pdf</u>)

L. J. Powers "Evaluation of Surface Discoloration – Swimming Pool Plaster" Construction Technology Laboratories Project #154801, 08-14-2003 (http://www.poolhelp. com/wp-content/uploads/2023/03/oB-00015 CTL-154801.pdf)



Figure oB-00015a – Bond Failure and Cavity Behind Crack and Nodule



Figure oB-00015b – Front of Core with Crack and Nodule Following Crack

Case Study oB-00045

This pool failed by accumulating hundreds of small white calcium nodules on craze lines throughout the pool and spa plaster surface after about a year from plastering. The pool was drained, polished (wet sanded) and refilled multiple times. Each time new nodules formed on the craze cracks.

A sample of the plaster with a nodule was cored (see Figure oB-00045) and sent to Laura Powers, at the time an Associate Principal Microscopist at Wiss, Janney, Elstner Associates.

In this case, Ms. Powers notes that there was no bond failure:

...the plaster is tightly adhered to the shotcrete. [p. 2].

Ms. Powers noted that the plaster in this pool was also significantly over-accelerated with calcium chloride:

If the assumed proportions of cement and sand are 1 part to 1-1/2 parts, the percentage of calcium chloride dihydrate by mass of cement is 4.81 at a water-cement ratio of 0.5 and 4.47 percent at a watercement ratio of 0.3. [p. 2]

She associated the problem – both cracks and nodules – with the plastering workmanship:

The elongated white nodule appears to be an extrusion at the outside end of a lowangle (approximately 10 degrees) crack that intersects the exterior surface of the plaster (Figure 4)... The crack passes around crushed marble aggregate particles suggesting that it formed fairly early, probably during finishing operations. [p. 2]

The general characteristics of the crack suggest that it was caused by finishing operations. [p. 3]

This calcium nodule, then, perfectly illustrates the craze crack-related type of formation.

Reference:

L. J. Powers "Analysis of Nodules on Pool

Plaster" WJE No. 2011.0741 (<u>http://www.poolhelp.com/wp-content/uploads/2023/03/</u>0B-00045_WJE-2011-0741.pdf)



Figure oB-00045 – Front of Core with Craze Nodules Following Cracks

Case Study oB-00058

This pool plaster failed in a way that was visually similar to the previous pool, but which actually had bond failure similar to the first (Figure oB-00058). The plaster had been repeatedly re-polished (wet sanded), yet small calcium nodules on craze lines repeatedly reappeared.

Cores 2 and 4, referenced in the report, are depicted in Figure 1 [p. 6] and Figure 2 [p. 7] of the report. The nodules on the surfaces and the bond failure of both cores are shown.

When analyzed by Laura Powers (at this time back at CTL Group), the plaster was determined to not have an intact bond with the substrate, which in this case was a combination of gunite and left-over white plaster from the previous coating:

Remnants of an older white plaster (Figs. 5 and 6) and patches of gray concrete substrate are adhered to the bottom surface of Core 2 Floor and to the back surface of the Core 4 Wall. [p. 2]

The actual nodule on Core 4 is associated with:

The delamination crack may be an artifact of troweling operations. Microcracks are

common in the surface region of Core 4 Wall (Fig. 14). The cause of microcracking is not apparent. Possible causes include finishing and curing operations. [p. 3]

The chloride content in the bulk paste is listed at 0.768 weight percent [p. 3], which is 4.4% as calcium chloride dihydrate to cement. Again, this is more than double the commonly accepted maximum dose.

These calcium nodules, then, are of interest because visually they appear to be craze nodules, but when the pool plaster is cored, it was found that each nodule was on a small crack over a bond-failed area.

Reference:

L. J. Powers "Petrographic Examination of Swimming Pool Plaster Cores from Gilbert AZ" Construction Technology Laboratories Project #150389, 04-30-2020 (<u>http://www.</u> <u>poolhelp.com/wp-content/uploads/2023/03/</u> <u>oB-00058 CTL-150389.pdf</u>)



Figure oB-00058 – Core 4 with Nodule Following Crack and Bond Failure

Case Study oB-00060

As a point of interest, although this pool has yet to be replastered or core sampled, it was covered with small nodules similar to the previous two pools. Again, the plastering contractor assumed that the nodules were craze nodules, and he was under the impression that craze nodules were the result of pool water maintenance failures. However, when the pool was drained, it was found that each nodule was located on a small, almost invisible crack which led to a sub-surface reservoir of contained water. These, then, were bond-failure nodules and are being addressed by the contractor.



Figure oB-00060a – Pool Floor with Nodules Over Cracks and Sub-Surface Trapped Water



Figure oB-00060b – Close-up of Nodule on Microcrack With Leaking Water

Garrett – Nodules on Fiberglass

In March of 1993 a calcium nodule report was written based on an analysis by Timothy S. Folks of Riverside Cement Company on behalf of Greg Garrett, who was at the time with Shasta Pools in Phoenix. The calcium nodule is described as being on a "fiberglass resurfaced pool sample."

Photographs of this calcium nodule (see for example Figure A – Garrett) were used in Mr. Garrett's pool industry presentations to insinuate that calcium nodules must be precipitated from dissolved calcium in the pool water, rather than from the pool plaster and/or cementitious substrate, since there was no pool plaster involved (see, for example, a video of Mr. Garrett making such claims here: <u>https://www.youtube.com/watch?v=4cY-oWNq-PKo</u>).

However, the lab analysis, dating previous to Mr. Garrett's presentations, shows that the defective fiberglass coating (see Figure B – Garrett) was apparently compromised with a path, in this report referred to as a "pin hole," through which water could penetrate to the previous plaster and/or the gunite substrate behind the fiberglass coating:

There is some evidence of an actual pin hole through the surface to the plaster backing. [p. 1]

It was also noted that there were other sites on the surface that could become similar nodules because of the poor quality of the fiberglass coating.

A second report was written in April of 1993, this time by Ed Holdsworth of SEM/ TEC Laboratories. It is unknown whether this calcium nodule on a fiberglass surface was from the same swimming pool as that analyzed by Mr. Folks, or if it came from a different pool.

The findings are essentially the same: a calcium nodule on a fiberglass-coated plaster pool. Mr. Holdsworth found:

...the plaster had been covered with resin/ fiberglass which should preclude the pool water reaching the plaster. [p. 1]

Removal of the glass showed several sites where the dye had reached the plaster layer. One spot corresponded to the location of the nodule... [p. 1]

...nodules can form on "glass" surfaces, but probably only when there exists a pathway

from the surface down to the base plaster. [p. 2]

The carbonate that forms the nodule derives from the plaster and not the water... [p. 2]

Any statements made by Mr. Garrett insinuating that a calcium nodule on a fiberglass pool surface does not involve plaster should therefore have been known by Mr. Garrett to contradict his lab reports at the time he made them. This information, and the reports were of course not disclosed to the industry in the mid- to late-1990s when the photographs were first being used.



Figure A – Screenshot From Garrett Video



Figure B – Screenshot From Garrett Video

References:

Timothy S. Folks "Composition of Calcium Nodule" Riverside Cement Company RLA 93022701 (http://www.poolhelp.com/wp-content/uploads/2023/03/Riverside 93022701. pdf)

Ed Holdsworth "Examination of surface

and subsurface portions of wall nodule" SEM/ TEC Laboratories 11666A (<u>http://www.poolhelp.com/wp-content/uploads/2023/03/Semtec 11666A.pdf</u>)

Case Study oB-00042 [NAGC/NPC Coupon 3]

In 1999 the National Plasterers Council and the National Association of Gas Chlorinators collaborated on a project that involved creating 12" diameter pool plaster coupons for experimentation (see Figure oB-00042a). Two matching sets of sixteen coupons – one set in Tucson AZ and another in Livermore CA – were placed in water of four different chemical (alkalinity) qualities (40, 80, 120, and 160 ppm TA), exposing both the troweled and the molded sides of each plaster coupon to the four different waters. After a few months, small calcium nodules appeared on all four guartered slices/chunks of that one coupon (out of 16) at Tucson and the same matching coupon at Livermore in all four chemistries. The other 15 coupons did not form any nodules at all although they were submerged in the same four waters (see Figure oB-00042b). Interestingly, the calcium nodules only appeared on the troweled sides, not the molded sides (see Figure oB-00042c).

A sample from each location was sent to Dr. Boyd Clark of the RJ Lee Group for analysis, one from the Tucson batch and one from the Livermore batch. In the report, they are labelled "Que's Sample" and "Kim's Sample."

As with other plaster samples described in this paper, these plaster samples were overdosed with calcium chloride. In this case, the chloride in bulk sample value was as high as 10%. Note that this is much higher than one would likely ever see in a swimming pool, but it was possible because of the "mix a small batch in a bucket" atmosphere at the trade show in question.

The conclusions found on page four of the report include:

The nodule growth on the top surface of the coupons is calcium carbonate Volume 6 Number 2 – Spring 2023 Shrinkage cracking of the coupons and leaching of calcium from the paste was promoted by calcium chloride content, apparent from the distinctive map crack pattern developed in high (10 Wt. %) calcium chloride content standard plaster.



Figure oB-00042a - Forming the Coupons



Figure oB-00042b – Nodules on Plaster Surface



Figure oB-00042c – Absence of Nodules on Molded "Backside" of Plaster Surface

Reference:

Boyd Clark "RJ Lee Group Project Number MAH011437" 03-19-2001 (<u>http://www.</u> poolhelp.com/wp-content/uploads/2023/03/ oB-NPC-03 RJLG-MAH011437.pdf)

Conclusions

In every case of which we are aware, when pool plaster exhibiting efflorescence, or nodule growth is sent to a competent forensic petrography laboratory, the same conclusions are reached – that:

- the nodules are formed using material from the cement-based plaster
- the material is calcium ydroxide
- the hydroxide carbonates in reaction with alkalinity
- the material is leached from the cement paste by ionic movement, not by etching, or aggressive attack
- the leaching occurs through cracks, pinholes, or other defects in the surface
- nodules are often associated with over-acceleration of the paste using calcium chloride
- nodules that appear to be on craze cracks may actually be associated with bond failure, although draining or even coring may be required to find the cause

• both bond-failure and craze nodules are the result of a plaster failure and not a result of the quality of chemical maintenance of the pool water

About the Authors

J. Que Hales has been the manager of the Tucson branch office of Pool Chlor for the past 38 years. He is an active author, researcher, lecturer and publisher. He is the past president of the National Association of Gas Chlorinators, the Southern Arizona Chapter of the NSPI, and is the editor of the Journal of the Swimming Pool and Spa Industry.

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- 1. The primary typeface for text used by the Journal is from the Century Schoolbook/ Times New Roman family of typefaces, and the typeface used for captions, tables, illustrations, charts, etc. is from the Helvetica/Calibri/Ariel family.
- 2. The page/column format is $8 \times 10^{\frac{1}{2}}$ pages, with double columns of $3^{\frac{3}{8}}$ each. Full double column width is 7". Full column height is $9^{\frac{3}{4}}$ ". Artwork should be designed to fit in full single or double column format.