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

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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 (HCO_3^{-1}/CO_3^{-2}) and cyanurate ($C_3N_3O_3^{-n}$) 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

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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 ft^2 (142.7m^2). Therefore, each gallon of water in an experimental test tank will represent 0.0513 ft^2 (47.6 cm^2) of exposed plaster surface area. 9.0 gallons [34 liters] of H_2O would correlate to a plaster coupon area of 0.462 ft^2 (429 cm^2) 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 ($CaCl_2$ – 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 (Cl_2) 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 ($NaHCO_3$) and calcium chloride ($CaCl_2$) 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 SunCoast™ 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-X MCI 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

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

$TDS_{(f)} = Log((TDS)-1)/10$

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

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

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

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 [$CaCO_3$]. LSI values were calculated using Equation 1.

LSI values less than –0.3 denote significant under-saturation of $CaCO_3$, indicating that the plaster will tend to dissolve. LSI values greater than 0.5 indicate significant over-saturation of $CaCO_3$, indicating that $CaCO_3$ 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

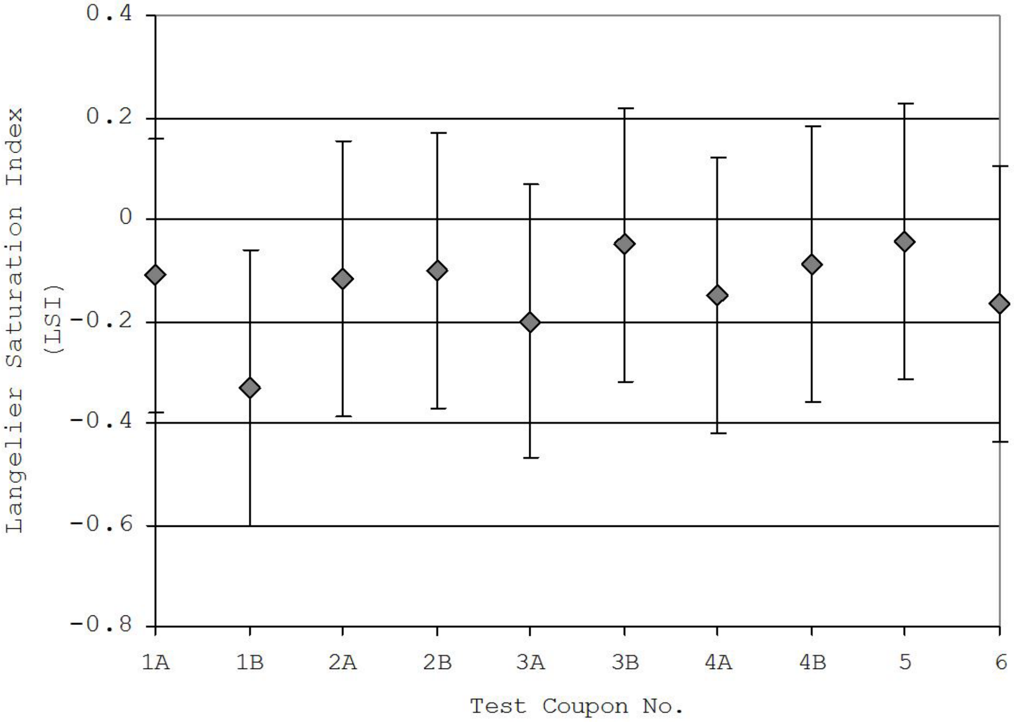
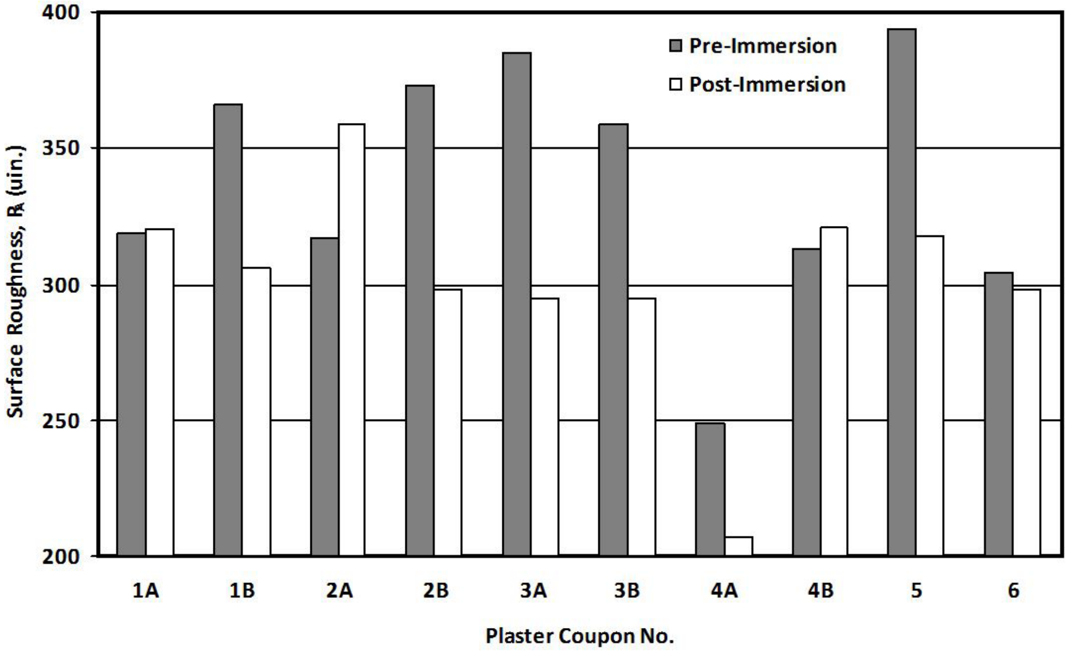


Figure 2 — Pre- and Post-Immersion Surface Roughness



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-Immersion 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

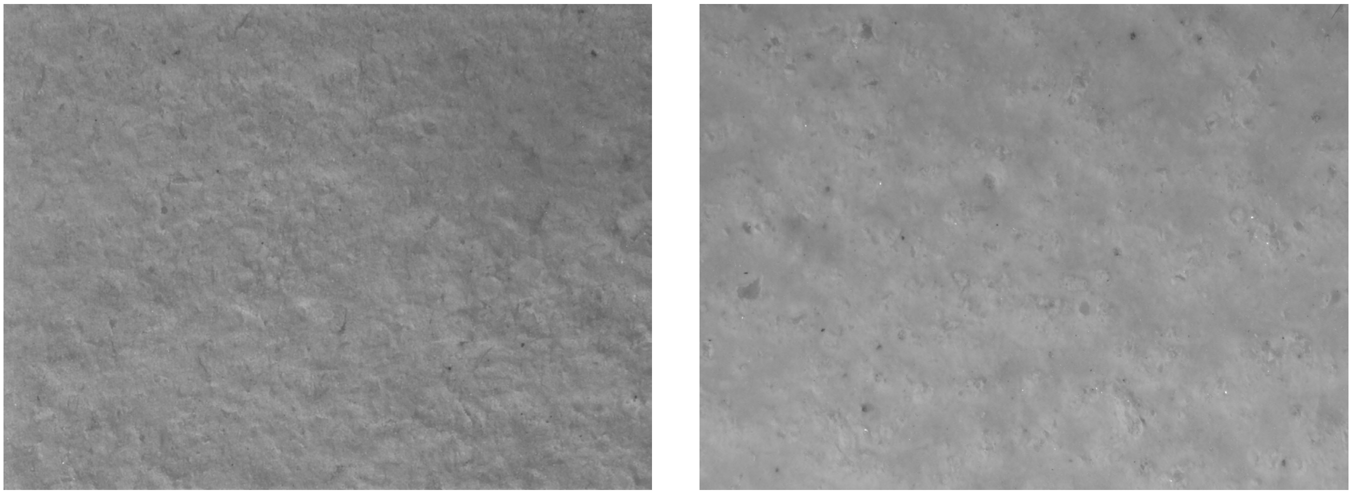


Image 1 — Light optical photo-microscopic imaging Test Coupon 4A

Left: (a) Pre-Immersion Test Coupon 4A at 15X magnification

Right: (b) Post-Immersion Test Coupon 4A at 15X magnification

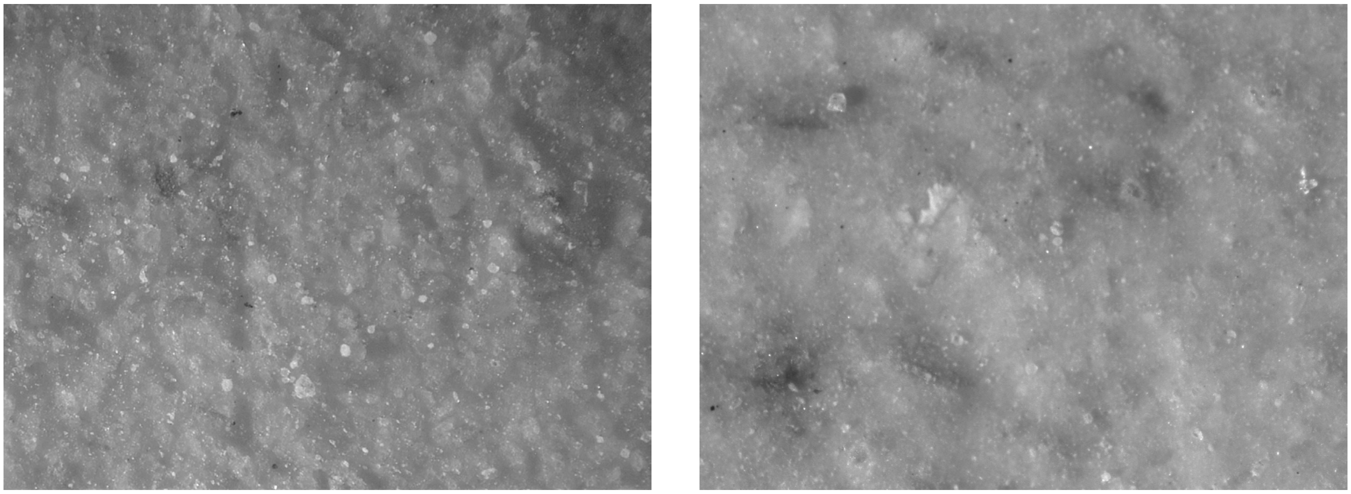


Image 2 — Light optical photo-microscopic imaging Test Coupon 2B

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.

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Equation 2

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

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

CYA = Cyanuric acid concentration (mg/L)

CYA 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

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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.

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