Factors Affecting the Calcium Carbonate Saturation Index

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Swimming pool water chemistry must be balanced in order to prevent corrosion, etching, and scaling and maintain water clarity. This is accomplished by means of the calcium carbonate Saturation Index (SI) which allows calculation of a measure of the degree of calcium carbonate saturation of pool water based on the temperature, pH, carbonate alkalinity, and calcium hardness (Langelier 1936, Larson 1942, Van Waters 1964). It is desirable to maintain the SI in an ideal operating range so that the water is neither corrosive/aggressive nor prone to precipitate calcium carbonate for a maximum percent of the time. However, the SI varies with time primarily because pH and alkalinity change due to addition of sanitizers and loss of carbon dioxide, necessitating periodic adjustments. Since acid addition for pH reduction consumes alkalinity, this needs to be taken into account when adjustments are made. Also, if the water contains other alkaline substances (e.g., cyanurate ion), the total alkalinity must be corrected to obtain the actual carbonate alkalinity (Snoeyink 1980, Stumm 1981) so that the correct SI is obtained, otherwise serious corrosion and etching problems can arise.

Factors Affecting pH Drift and Carbonate Alkalinity

Buffering – Buffering, i.e., the resistance to pH change, is necessary to prevent severe pH fluctuations when acidic or alkaline sanitizers are added to pool water. A buffer system consists of a weak acid and its anion (e.g., carbonic acid and bicarbonate). Maximum buffering occurs at a pH where the molar ratio of acid

to anion is one. This pH is also equal to the pK_a (ionization constant) of the acid which is the negative logarithm of the ionization constant. In the carbonic acid system this occurs at pH 6.3 (at 80°F and 1000 ppm TDS) where the molar ratio of carbonic acid to bicarbonate ion is equal to one. In the case of cyanuric acid, maximum buffering occurs at pH 6.8 under similar conditions. Buffers for laboratory use typically have a concentration of 0.02 molar. In swimming pools the concentration of buffering agents is much lower and therefore the buffering effect is correspondingly less; e.g., 100 ppm carbonate alkalinity is equivalent to only 0.002 molar.

The strength of buffering is measured by the buffer intensity which is the incremental change in alkalinity required to change pH by one unit, i.e., $\beta = \Delta \text{Alk}/\Delta \text{pH}$. For a diprotic acid such as carbonic acid and its salts it is expressed numerically by:

$$\beta = 2.3\{C_T[\alpha_1(\alpha_0 + \alpha_2) + 4\alpha_0\alpha_2] + OH^- + H^+\} \cdot 50 \cdot 10^3$$
$$\text{ppm CaCO}_3$$

where: C_T is the total molar concentration of carbonic acid, bicarbonate, and carbonate and α_0, α_1, and α_2 are the respective ionization fractions. For a monoprotic acid and its salt it is given by the following equation:

$$\beta = 2.3(C_T'\alpha_0'\alpha_1' + OH^- + H^+) \cdot 50 \cdot 10^3 \text{ ppm CaCO}_3$$

Since only the first ionization of cyanuric acid is important at pool pH, the above equation can be used to calculate its buffering effect; where: C_T' is the sum of the concentrations of cyanuric acid and cyanurate ion and α_0' and α_1' are the respective ionization fractions. This equation can also be used for boric acid.

Buffer intensity varies with pH and increases with concentration of carbonate, cyanurate, and borate alkalinity. On a molar basis, cyanurate ion has the higher buffer intensity at pool pH; e.g., at pH 7.5 and 0.002 M, the buffer intensities (as ppm $CaCO_3$) vary in the following order: cyanurate 30.4, carbonate 13.6, and borate 4.6. A plot of buffer intensities of 100
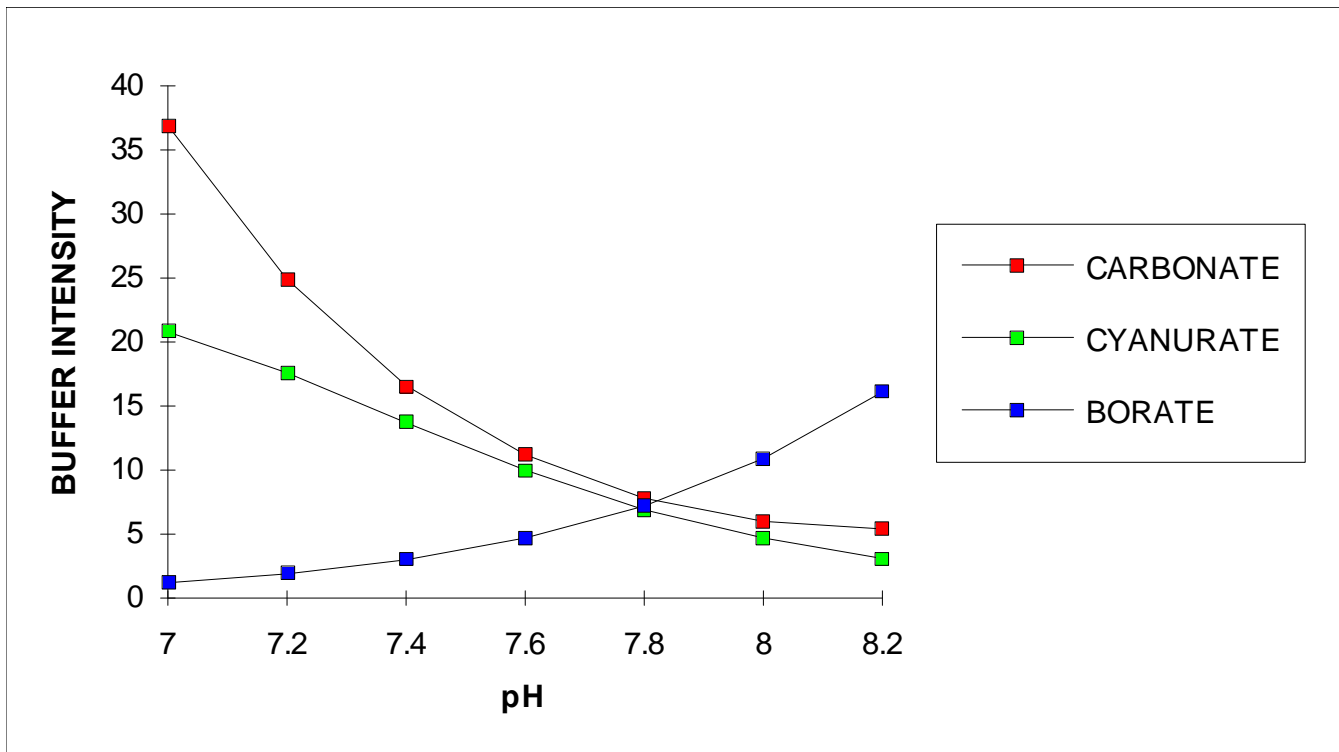
Figure 1 – Buffer Intensities of 100 ppm Each of Carbonate Alkalinity and Cyanuric and Boric Acids
1000 ppm TDS and 80°F over the 7.0-8.2 pH range

ppm each of carbonate alkalinity and cyanuric and boric acids at 1000 ppm TDS and 80°F over the 7.0-8.2 pH range is shown in Figure 1. The plot shows that the buffer intensity of carbonate and cyanurate alkalinity decrease with increasing pH whereas that of borate alkalinity increases with pH. Both carbonate alkalinity and cyanuric acid provide roughly comparable buffering at 100 ppm concentration. Compared to either carbonate or cyanurate alkalinity, the buffering effect of borate is significantly less below pH 7.8, but greater above pH 7.8.

Loss of Carbon Dioxide – Swimming pool water continually loses CO_2 because it is supersaturated with CO_2 due to periodic pH adjustments with acid (Wojtowicz 1984). If swimming pools were in equilibrium with atmospheric CO_2, very low alkalinity levels would result (i.e., only 4–17 ppm over the 7.2–7.8 pH range) (Stumm 1981), making maintenance of proper alkalinity and buffering impossible. The loss of CO_2 causes the pH to increase but does not affect alkalinity. This is shown by the following carbonic acid equilibrium.

$$H_2CO_3^* \rightleftharpoons H^+ + HCO_3^-$$

$$K_1 = [H^+][HCO_3^-] / [H_2CO_3^*]$$
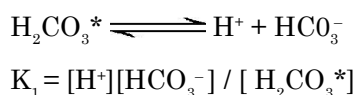
As $H_2CO_3^*$ (99.85% CO_2 and 0.15% H_2CO_3) decreases, the hydrogen ion concentration $[H^+]$ also decreases in order to maintain K_1 constant. As pH rises, a small amount of $H_2CO_3^*$ is converted to HCO_3^- and a small amount of HCO_3^- is converted to CO_3^{2-}, but alkalinity remains unchanged.

Water turnover rate (a function of pump duty cycle and pumping rate) is a major factor increasing the rate of CO_2 loss while use of a pool cover is a significant factor in decreasing the rate. The CO_2 loss rate also increases with temperature, alkalinity, and bather load. The calculated pH drift, based on test data for an outdoor pool without bathers (Wojtowicz

| Carbonate Alkalinity (ppm)	CA (ppm)	ΔpH/week
80	50	+0.24
80	100	+0.16
120	50	+0.41
120	100	+0.30

Table 1 – pH Drift Due to CO_2 Loss as a Function of Alkalinity and CA

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1984), for a 20,000 gallon pool (6 feet average depth) at pH 7.5, 80°F, and 1000 ppm TDS, and a turnover rate of 0.84 (8–hour pump duty cycle and 35 gal/min pumping rate) are given in Table 1. The buffering effect of higher alkalinity is offset by increased loss of CO_2.

By contrast, the buffering effect of cyanuric acid (CA) is evident by the lower pH drift at the higher CA level. The actual pH drift due to carbon dioxide loss will vary not only with alkalinity and cyanuric acid levels, but also with temperature (e.g., geographical location or heated pools), water quality (presence of turbidity), water turbulence (due to circulation, bather load, and wind), and maintenance and use patterns

Cyanuric Acid Addition - As discussed in Part 1 of this series (Wojtowicz 1995), addition of cyanuric acid lowers the pH by replacing a portion of carbonate alkalinity with cyanurate alkalinity:

$$H_3Cy + HCO_3^- \rightleftharpoons H_2Cy^- + H_2CO_3*$$
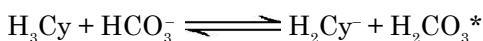
Restoration of the pH to the original value with soda ash converts more of the cyanuric acid to cyanurate (and carbonic acid to bicarbonate and carbonate), further increasing total alkalinity.

Acid Addition - Acid addition is necessary to reduce the pH when it exceeds the ideal maximum. Both muriatic acid (HCl) and sodium bisulfate ($NaHSO_4$) provide hydrogen ions (H^+) for lowering pH. The added pool acid reacts with cyanurate alkalinity forming cyanuric acid and with carbonate alkalinity forming mostly dissolved carbon dioxide and a slight amount of carbonic acid, i.e., H_2CO_3*.

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3*$$

$$H_2Cy^- + H^+ \rightleftharpoons H_3Cy$$
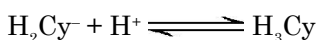
Under normal conditions carbonate alkalinity is greater than cyanurate alkalinity, thus more bicarbonate than cyanurate is neutralized, resulting in a significant loss of carbonate alkalinity from the pool water each time the pH is adjusted. For example, adjusting the pH with pool acid from 8.0 to 7.4 at 80°F, 100 ppm carbonate alkalinity, 1000 ppm TDS, and 50 ppm CA reduces total alkalinity and carbonate alkalinity by 8.6 and 5.8 ppm, respectively.

Acidic Sanitizers - Use of gaseous chlorine for swimming pool sanitation results initially in the formation of equimolar amounts of hypochlorous and hydrochloric acids.
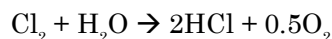
$$Cl_2 + H_2O \rightarrow HOCl + HCl$$
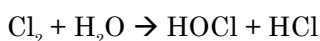
At pool pH, hypochlorous acid forms equilibrium amounts of hypochlorite ion (Morris 1966) which is decomposed by sunlight resulting in conversion of HOCl to hydrochloric acid (Nelson 1968).

$$HOCl \rightleftharpoons ClO^- + H^+$$
$$ClO^- + h\nu \rightarrow Cl^- + 0.5O_2$$
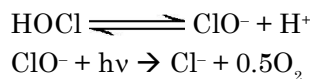
The overall reaction is:

$$Cl_2 + H_2O \rightarrow 2HCl + 0.5O_2$$

In practice some chlorine is converted to organic chlorine compounds resulting in somewhat less than two molecules of acid. In addition, some chloric acid is also formed (Young 1949). The hydrochloric and chloric acids formed react with alkalinity as discussed above. Sodium sesquicarbonate ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) can be added to replenish alkalinity and restore pH.

Chloroisocyanurates also provide equilibrium amounts of hypochlorous acid for swimming pool disinfection via hydrolysis (O'Brien 1972). In the case of Trichlor (trichloroisocyanuric acid, Cl_3Cy), complete consumption of each mol of Trichlor theoretically yields one mol of cyanuric acid, three mols of hydrochloric acid, and 1.5 mols of oxygen.

$$Cl_3Cy + 3H_2O \rightarrow H_3Cy + 3HCl + 1.5O_2$$
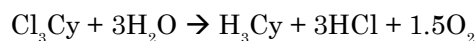
Comments regarding by-product formation discussed above also apply. Since the cyanuric acid concentration increases with time when Trichlor is used, its effect on total alkalinity increases.

Dichlor (sodium dichloroisocyanurate, $NaCl_2Cy$) decomposes similarly to Trichlor producing a like amount of cyanuric acid but only 1/3 as much HCl.

$$NaCl_2Cy + H_2O \rightarrow H_3Cy + NaCl + HCl + O_2$$
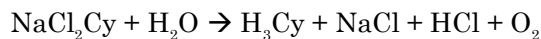
However, on an equivalent available (av.) Cl_2 basis, Dichlor contributes 1.6 times as much CA and about half as much HCl as Trichlor.

The comparative effects of maintenance doses of chlorine, Trichlor, and Dichlor on swimming pool water (10,000 gal, pH 7.5, 100 ppm carbonate alkalinity, 100 ppm cyanuric acid, and 1000 ppm TDS) are

Sanitizer	Ounces/Week	ΔpH/week
Dichlor	10.5	−0.09
Trichlor	7	−0.14
Chlorine Gas	6.8	−0.22

Table 2 – pH Drift due to Acidic Sanitizers

Sanitizer	Treatment	Ounces/Week	ΔpH/week
NaOCl	Maintenance	56.0	+0.019
"	Shock	106.5	+0.035
$Ca(OCl)_2$	Maintenance	10.5	+0.009
"	Shock	20.0	+0.016

Table 3 – pH Drift due to Alkaline Sanitizers

shown in Table 2. Sanitizer usage is based on Olin Corporation (1992a) recommendations. The pH drifts vary in the following order: Cl_2 > Trichlor > Dichlor.

Alkaline Sanitizers - Like chloroisocyanurates, solid calcium hypochlorite [$Ca(OCl)_2$] and liquid bleach (sodium hypochlorite, NaOCl) provide hypochlorous acid for disinfection: $ClO^- + H_2O \rightleftharpoons HOCl + OH^-$. However, unlike chloroisocyanurates, hypochlorites do not form acid on decomposition of the av. Cl_2 as shown by the following reaction: $Ca(OCl)_2 \rightarrow CaCl_2 + O_2$. In practice, less than one mol of oxygen is formed due to formation of organic chlorine compounds and chlorate. Sodium hypochlorite contains some sodium hydroxide while calcium hypochlorite contains very small amounts of calcium hydroxide [$Ca(OH)_2$] and calcium carbonate ($CaCO_3$). These alkaline byproducts are neutralized when the pool pH is adjusted with acid. Comparative effects of sodium hypochlorite and

calcium hypochlorite on swimming pool water (10,000 gal, pH 7.5, 100 ppm carbonate alkalinity, 100 ppm CA, and 1000 ppm TDS) are shown in Table 3 (following page). Sanitizer usage for calcium hypochlorite is based on Olin Corporation recommendations (1992b). Sodium hypochlorite affects pH more than $Ca(OCl)_2$. Compared to Dichlor and Trichlor, hypochlorites affect pH to a significantly smaller extent.

Summary - The data in Table 4 on the effect of sanitizers on alkalinity, show that chlorine gas has the greatest effect on total alkalinity, reducing it by a total of 21.2 ppm/week when used for maintenance and shock dosing. Trichlor has a much lower effect, reducing alkalinity by 2.8 ppm/week when used with $Ca(OCl)_2$ shock. Additionally, the cyanuric acid contributed converts about 0.9 ppm of carbonate alkalinity to cyanurate alkalinity. These values may be greater in the southwest where sanitizer usage is generally

Dosage[a]	Sanitizer	% Av. Cl_2	oz/week	ΔAlk (ppm/wk)	ΔCA (ppm/wk)
Maintenance	Cl_2	100	6.8	−7.2	
Shock[b]	Cl_2	100	13	−13.7[j]	
Maintenance	NaOCl[f]	10	56	+0.46	
Shock[b]	NaOCl[f]	10	106.5	+0.87[j]	
Maintenance	$Ca(OCl)_2$[g]	65	10.5[h]	+0.29	
Shock[b]	$Ca(OCl)_2$[g]	65	20[h]	+0.55[j]	
Maintenance	Trichlor	89	7[i]	−3.3	+2.8[c]
Shock[b]	NaOCl[f]	10	106.5	+0.87[j]	
Maintenance	Trichlor	89	7[i]	−3.3	+2.8[c]
Shock[b]	$Ca(OCl)_2$[g]	65	20[h]	+0.55[j]	
Maintenance	Dichlor[d]	56	10.5[i]	−1.5	+4.0[e]
Shock[b]	$Ca(OCl)_2$[g]	65	20[h]	+0.55[j]	

a) Per 10,000 gallons. b) ~10 ppm av. Cl_2. c) Reduces carbonate alkalinity by 1.3 ppm at pH 7.5. d) Sodium dichloroisocyanurate dihydrate. e) Reduces carbonate alkalinity by 1.2 ppm at pH 7.5. f) 12 trade %, 10.76% NaOCl, Sp. gr. 1.17, 0.73% NaOH. g) ~2% $Ca(OH)_2$ and ~2% $CaCO_3$; assumes 50% of $CaCO_3$ dissolves. h) Olin Corporation recommendations 1992b. i) Olin Corporation recommendations 1992a. j) These values are based on a 10 ppm shock, and would be lower if a typical 8 ppm was used, or if the shock was administered bi-weekly rather than weekly.

Table 4 – Effect of Various Sanitizers on Total Alkalinity and CA

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higher. By contrast, the alkaline sanitizers sodium and calcium hypochlorite increase total alkalinity by less than 1 ppm/week. Total alkalinity is also depleted whenever acid is added for pH adjustment. Thus, the carbonate alkalinity should be periodically adjusted with sodium bicarbonate. Alternatively, an equivalent amount of bicarbonate could be added whenever acid is added to the pool (0.68 oz. bicarbonate/oz. sodium bisulfate or 0.94 oz. bicarbonate/oz. muriatic acid). Alkalinity is also increased by makeup water.

Recommended Swimming Pool Parameters

pH - The ideal pH range is 7.2 to 7.8 for optimum disinfection, bather comfort, and stability of av. Cl_2

CA (ppm)	Total Alkalinity (ppm)
≤50	80 – 120
100	97 – 137
150	113 – 153

Table 5 – Total Alkalinity as a Function of Cyanuric Acid Level

residual. The biocidal effectiveness of chlorine varies inversely with pH (Fair 1947). The pH should be adjusted to 7.2–7.4 prior to shock treatment (with a hypochlorite) to compensate for the temporary pH jump (~0.2–0.3 pH units) due to the alkalinity of hypochlorite ion.

Alkalinity - A small but adequate amount of total alkalinity (e.g., 80–120 ppm) is necessary for buffering and to provide sufficient carbonate ion for balancing the water. This total alkalinity range applies to the recommended CA levels. In hypochlorite–treated pools, this corresponds to 65–105 ppm of carbonate alkalinity. Higher carbonate alkalinities are not recommended because pH drift due to CO_2 loss increases with alkalinity. Furthermore, higher carbonate alkalinity could result in greater precipitation of calcium carbonate when the saturation index exceeds the recommended maximum level, i.e., 0.5. In chloroisocyanurate-treated pools, the CA concentration will increase slowly with time. Above 50 ppm CA, the total alkalinity should be increased by 1/3 of the ppm CA above 50 ppm as shown in Table 5 in order to maintain proper carbonate alkalinity.

Hardness - At 100 ppm of carbonate alkalinity, a calcium hardness of 200 ppm is required for balance at pH 7.5 and 80°F. Since hardness and alkalinity are reciprocally related, lower carbonate alkalinities require higher hardness, and conversely, higher carbonate alkalinities require lower levels of calcium hardness.

Temp. °F	TF	Ca Hardness	CF	Carb. Alkalinity	AF
32	0.0	25	1.0	25	1.4
37	0.1	30	1.1	30	1.5
46	0.2	40	1.2	40	1.6
53	0.3	50	1.3	50	1.7
60	0.4	65	1.4	65	1.8
66	0.5	75	1.5	75	1.9
76	0.6	100	1.6	100	2.0
84	0.7	125	1.7	125	2.1
94	0.8	150	1.8	150	2.2
105	0.9	200	1.9	200	2.3
TDS	**Constant**	250	2.0	250	2.4
1000	12.10	300	2.1	300	2.5
2000	12.13	400	2.2	400	2.6
3000	12.14	500	2.3	500	2.7
4000–5000	12.15	600	2.4	600	2.8

Table 6 – Factors for Saturation Index Calculation

Cyanuric Acid - Moderate levels of cyanuric acid are desirable since the biocidal effectiveness of chlorine is inversely related to the cyanuric acid concentration (Andersen 1963). The ideal cyanuric acid concentration for a hypochlorite-treated pool is 40–50 ppm. For a chloroisocyanurate pool, the recommended initial CA is 20–25 ppm. The CA concentration in hypochlorite–treated pools will decrease slowly with time due to splashout and backwashing and requires readjustment at the start of a new season. By contrast, the CA concentration in a chloroisocyanurate-treated pool will slowly increase with time before leveling-off.

Calcium Carbonate Saturation Index

Calculation - At a given temperature, swimming pool water chemistry must be balanced by adjusting pH, alkalinity, and calcium hardness in order to maintain the proper saturation with respect to calcium carbonate to avoid corrosion of metallic surfaces, etching of tile grout and plaster, scaling, and cloudy water. The Saturation Index (SI) at 1000 ppm

CA (ppm)	SI* (uncorrected)	SI (corrected)
50	0.00	−0.08
100	0.00	−0.17
200	0.00	−0.47
300	0.00	−2.00

*at 84°F, pH 7.5, 100 ppm total alkalinity, 220 ppm hardness, and 1000 TDS

Table 7 – Effect of Cyanuric Acid on Saturation Index

TDS is calculated using the following equation (Van Waters 1964):

$$SI = pH + AF + CF + TF - 12.1$$

where: AF, CF, and TF are the alkalinity, calcium, and temperature factors, respectively. A list of factors is given in Table 6.

Correction for Cyanuric Acid – Since the equation for SI requires the ppm carbonate alkalinity, the total alkalinity (ppm) must be corrected for the cyanuric acid concentration (ppm CA) by means of the following equation (Wojtowicz 1995):

$$Alk_{carb} = Alk_T - 1/3 \cdot CA$$

Calculated values of the Saturation Index at various levels of cyanuric acid using uncorrected and corrected alkalinity are shown in Table 7.

The data show that the potential error in SI increases as the cyanuric acid concentration increases. The table also shows that a pool with 100 ppm total alkalinity and 300 ppm cyanuric acid will essentially have no carbonate alkalinity. While 100 ppm of total alkalinity would appear acceptable to the uninformed pool owner, it could lead to severe corrosion and etching problems under the above conditions. Thus, correcting total alkalinity for the effect of cyanuric acid will tell the pool owner when to adjust carbonate alkalinity to the ideal range (with sodium bicarbonate) in order to maintain the SI in the recommended range.

Adjustment - Proper water balance is determined by the calcium carbonate saturation index. An SI of 0 indicates full saturation with respect to calcium carbonate, whereas negative and positive values indicate under– and oversaturation, respectively. The saturation index does not remain constant primarily

	ΔpH			ΔSI[c]
Sanitizer	Maintenance	Shock Treatment	CO_2 Loss[d]	
Chlorine	−0.22	−0.370	+0.23	−0.36
Trichlor	−0.14	+0.016[a]	+0.23	+0.11
Dichlor	−0.09	+0.016[a]	+0.23	+0.16
$Ca(OCl)_2$	+0.009	+0.016[a]	+0.23	+0.26
NaOCl	+0.019	+0.035[b]	+0.23	+0.28

a) Calcium hypochlorite. b) NaOCl. c) Includes -0.09, -0.015, -0.007, +0.004, and +0.006 adjustments for changes in alkalinity, respectively. d) For 8–hr pump duty cycle equivalent to one one turnover.

Table 8 – Calculated pH and SI Drifts Per Week

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because both pH and alkalinity change with time due to addition of sanitizers and loss of carbon dioxide as discussed above. A practical operating SI range is 0.0 to 0.5, which corresponds to 100 to about 300% of saturation. Alkaline sanitizers (e.g., calcium, sodium, or lithium hypochlorite) will augment the rise in pH due to CO_2 loss and will have a positive (i.e., upward) SI drift, thus the SI is adjusted to the lower end of the ideal operating range.

By contrast, acidic sanitizers will tend to counteract the rise in pH due to CO_2 loss; Trichlor more than Dichlor. Alkaline sanitizers used for shock treatment in conjunction with chloroisocyanurates will offset the acidity that Dichlor and Trichlor form to a small extent. The SI drift of chloroisocyanurate–treated pools will depend on the magnitude of the CO_2 loss rate which varies with temperature, pump duty cycle, and bather load. Pools in Florida maintained with Trichlor and shocked with $Ca(OCl)_2$ have been observed with positive SI drifts, requiring weekly pH adjustments. However, a negative drift might occur with heavy Trichlor usage (e.g., in the southwest). Therefore, a practical approach would be to adjust the SI to the mid-point of the ideal range and to monitor the water frequently by test kit to establish the actual drift pattern.

When the SI drifts outside the operating range, it should be readjusted. In an established pool (i.e., with calcium hardness in the ideal range), it is usually adjusted by changing pH and/or alkalinity. In order to maintain proper water balance for the maximum percent of the time, the SI should be set at the beginning of the normal drift range. Since acid addition for pH adjustment consumes some alkalinity, this needs to be taken into account when adjustments are made. When a pool is winterized, it should be balanced using the lower temperatures encountered during the winter because the Saturation Index decreases with temperature.

Calculated SI Drifts — Calculated pH and SI drifts per week for chlorine, Trichlor, Dichlor, and calcium and sodium hypochlorite–maintained pools (pH 7.5, 100 ppm carbonate alkalinity, 100 ppm CA, and 1000 ppm TDS) are shown in Table 8. Except for the chlorine pool, calcium or sodium hypochlorite were used for shocking.

The calculations show that CO_2 loss exerts a greater effect on SI drift than the alkalinity introduced into the pool by hypochlorite sanitizers. The calculated SI drifts show that chlorine treated pools have a large negative drift, whereas all other sanitation systems have positive drifts; hypochlorites greater than a combination of chloroisocyanurate and hypochlorite. The actual drifts will depend on bather–load, temperature, pool geometry, pump duty cycle, and sanitizer usage.

The calcium hardness introduced by $Ca(OCl)_2$ has a negligible effect on the SI drift. For example, at pH 7.5, 80°F, 100 ppm total alkalinity, 300 ppm hardness, 100 ppm CA, and 1000 ppm TDS, the SI is increased by less than 0.01/week.

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