Swimming Pool and Spa Water Chemical Adjustments

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This paper deals with adjustments to swimming pool and spa water chemical parameters such as pH, alkalinity, hardness, stabilizer, and chlorine. It discusses test kit acid and base demand tests and provides equations for calculating required acid and base additions for adjusting pH based on the test results. It also discusses a mathematical approach for calculating acid and base additions (and associated alkalinity changes) and pH changes resulting from addition of sodium bicarbonate (for alkalinity adjustment) and cyanuric acid (for stabilizer adjustment) based on swimming pool chemical equilibria. Tables, graphs, and a general equation are provided for determining required acid and base additions for adjusting pH. In addition, equations are provided for determining required chemical additions for adjusting alkalinity, hardness, stabilizer, and chlorine concentrations.

Recommended Swimming Pool and Spa Water Parameters

The recommended ranges for swimming pool and spa water parameters are summarized in Table 1, where: FC equals the free chlorine, CC equals the combined chlorine, and FB equals the free bromine.

Table 1. Recommended Swimming Pool and Spa Parameters[A]

Parameter	Minimum	Ideal	Maximum
FC (ppm) pools (spas)	1(2)	2-4 (3-5)	10
CC (ppm)	0	0	0.2
FB (ppm)	2	4-6	10
pH	7.2	7.4-7.6	7.8
Total Alkalinity (ppm)[B]	60	80-100	180
Calcium Hardness (ppm)	150	200-400	500-1000
Cyanuric Acid (ppm)	10	30-50	150[C]
Total Dissolved Solids (ppm)	300	1000-2000	3000

A) ANSI/NSPI 2002
B) For hypochlorite sanitizers; 100-120 ppm for acidic sanitizers: chlorine, Dichlor, Trichlor, and bromochlorodimethylhydantoin.
C) Except where limited by Health Dept. requirements, often to 100 ppm.

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Factors Affecting Swimming Pool and Spa Water Parameters

Carbon Dioxide Loss – Carbon dioxide is continually evolved from swimming pool water because pools are normally supersaturated with carbon dioxide. This causes an upward drift in the pH and necessitates periodic pH adjustment with acid (Wojtowicz 1995a). In spas, the upward drift is accelerated by the higher temperature and use of aeration.

Acidic Sanitizers – Acidic sanitizers such as chloroisocyanurates can significantly retard the rise in pH because of the large quantity of acid that they produce (Wojtowicz 1995b). Gaseous chlorine can completely offset the upward pH rise due to CO_2 loss and cause a downward drift.

Alkaline Sanitizers – Alkaline sanitizers such as hypochlorites contain low levels of alkaline and basic substances that will augment the upward pH drift, but only to a small extent (Wojtowicz 1995b).

Water Evaporation – Water used to replace that lost by evaporation will increase alkalinity and hardness.

Filter Backwashing – Water used to replace that removed via filter backwashing can affect alkalinity and hardness depending on its composition.

Analysis of Swimming Pool and Spa Water via Test Kit

A summary of swimming pool and spa water analysis via test kit is presented in Table 2.

Table 2. Summary of Swimming Pool and Spa Water Parameter Measurement

Parameter	Measurement[A]
Free Chlorine (FC)	Reaction with DPD[B] produces a pink color proportional to concentration, which is quantified by comparison with a standard color scale. Alternatively, drop-wise titration with standard FAS[C] solution to extinction of the pink color can be used; the number of drops of FAS being proportional to the FC concentration.
Combined Chlorine (CC)	Addition of potassium iodide catalyzes reaction of CC with DPD and allows its determination.
pH	Treatment with phenol red indicator produces a color ranging from red (basic) to yellow (acidic). The pH is determined by comparison with a standard color scale.
Acid Demand	The sample from pH measurement is titrated drop-wise with a standard dilute acid solution to the desired pH, the number of drops being proportional to the acid demand.
Base Demand	Similar to acid demand except that a standard base solution is used.
Alkalinity	Titration with standard acid solution in the presence of mixed bromocresol green-methyl red indicator.
Calcium Hardness	A buffered sample is titrated with EDTA[D] in the presence of an indicator, eg, Eriochrome Black T.
Cyanuric Acid (CA)	Treatment of a sample with melamine solution produces turbidity (ie, a precipitate of melamine cyanurate) that is proportional to the CA concentration.

A) Carried-out using test kits, eg, Taylor.
B) N,N-Diethyl-p-phenylenediamine.
C) Ferrous ammonium sulfate.
D) Ethylenediamine tetra-acetic acid.

Swimming Pool and Spa Water pH Adjustment via Test Kit Analysis

Acid Demand – This test determines the amount of acid required to reduce the pH of swimming pool or spa water when it has exceeded the recommended range of 7.2 to 7.8 (see Table 1). The acid demand test involves titration of a pool or spa water sample with acid to a desired pH; e.g., using a Taylor test kit. A standard acid solution (dilute sulfuric acid) is added dropwise to a known volume (44 mL) of pool or spa water containing a pH indicator (phenol red) until the desired pH is obtained as determined by the color change of the indicator. Tables are available to convert the number of drops of acid solution to volume of pool acid (muriatic acid, i.e., hydrochloric acid, HCl) to decrease the pH to the desired level (Taylor 2002). Based on these Tables, the quantity of muriatic acid (31.45% HCl) required can also be calculated using the following formula:

$$V_{MA}\,(\text{fl. oz}) = 9.165 \cdot 10^{-4} \cdot N \cdot V$$

where: V_{MA} (fl. oz) equals the volume of muriatic acid, N equals the number of drops of acid demand reagent, and V equals the pool or spa volume (gals).

Dry acid, i.e., sodium bisulfate, can also be used to lower pH. Tables are available for determining the quantity of bisulfate to add based on the number of drops of reagent and pool or spa volume. The quantity of sodium bisulfate also can be calculated using the following formula, which is based on these Tables:

$$W_{BS}\,(\text{oz}) = 1.148 \cdot 10^{-3} \cdot N \cdot V/p$$

where: W_{BS} equals the weight of sodium bisulfate, N equals the number of drops of test kit acid demand reagent, V equals the volume of pool or spa, and p equals the degree of purity of sodium bisulfate.

Base Demand – This test determines the amount of sodium carbonate (soda ash) required to increase the pH of pool or spa water when the pH has dropped below the recommended range of 7.2 to 7.8, e.g., due to a high dose of gaseous chlorine or high usage of chloroisocyanurates. The base demand test involves titration of a pool or spa water sample with base to a desired pH; e.g., using a Taylor test kit. A standard base solution (dilute sodium hydroxide) is added dropwise to a known volume (44 mL) of pool or spa water containing a pH indicator (phenol red) until the desired pH is obtained as determined by the color change of the indicator. Tables are available to convert the number of drops of base solution to weight of soda ash (sodium carbonate) to increase the pH to the desired level (Taylor 2002). The quantity of 100% sodium carbonate required can also be calculated using the following formula:

$$W_{SC}\,(\text{oz}) = 5.12 \cdot 10^{-4} \cdot N \cdot V$$

where: W_{SC} equals the weight of sodium carbonate, N equals the number of drops of base demand reagent, and V equals the volume of pool or spa water (gals).

Calculation of Swimming Pool and Spa Water Chemical Parameters and Adjustments

Computer Assisted Calculations

The basic data and equations for calculating certain changes in water chemistry have been published in previous issues of the journal (e.g., see Wojtowicz 1995b, 1995c, 2001, and 2002). The changes include: acid and base requirements for adjusting pH and pH changes on addition of chlorine, sodium bicarbonate, and cyanuric acid. The input data for the calculations are: pool or spa volume, water temperature, total dissolved solids, initial and final pH, total alkalinity, cyanuric acid, boron, and av. Cl. In the case of carbon dioxide loss calculations, additional data are necessary such as pool or spa surface to volume ratio, pumping rate, and pump duty cycle.

Variables, Constants, and Conversion Factors

Various conversion factors and variable sym-

Table 3. Summary of Variables, Constants, and Conversion Factors	
Variables	**Conversion Factors**
V = pool or spa volume (gal)	28.35 g/oz
TA = total alkalinity (ppm)	29.57 mL/fl. oz
d = density (g/mL)	1000 mg/g
p = degree of purity (% assay/100)	436.5 g/lb
Constants	3.7854 L/gal
Equivalent wt. of $CaCO_3$ (50)	

bols are used in the following discussions and are summarized in Table 3.

pH Adjustment

Decreasing pH with Muriatic Acid – Addition of muriatic acid lowers the pH of swimming pool water because it is highly ionized, thereby increasing the concentration of hydrogen ions (H^+) which suppresses ionization of the respective acidic species resulting in decreased concentrations of the alkaline ions: carbonate, bicarbonate, cyanurate, and borate, i.e., the equilibria below are shifted to the right.

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$$

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3 \rightleftharpoons H_2O + CO_2$$

$$H_2Cy^- + H^+ \rightleftharpoons H_3Cy$$

$$B(OH)_4^- + H^+ \rightleftharpoons H_3BO_3 + H_2O$$

The required quantity of acid is readily calculable from the decrease in calculated total alkalinity at the new pH. Each mol of added acid neutralizes one mol of total alkalinity.

Tables 3A to 6A contain calculated values of muriatic acid required to reduce pHs in the 7.8 to 8.2 range to 7.2 at different total alkalinities (80 to 210 ppm) and cyanuric acid levels (50 to 200 ppm). The data are also shown graphically in Figures 1 to 4. The graphs show that the quantity of acid varies linearly with total alkalinity at a given starting pH. The conditions used for the calculations are: 80°F, 1000 ppm TDS, 3 ppm av. Cl, and 10,000 gals pool volume.

Multiple linear regression analysis of all of the data in Tables 3A to 6A was performed using the following equation form involving one dependent variable (V_{MA}) and three independent variables (pH, TA, and CA):

$$V_{MA} = a + b(pH) + c(TA) + d(CA)$$

where: V_{MA} equals the volume of 31.45% muriatic acid (fl oz), TA equals the total alkalinity (ppm), and CA equals the cyanuric acid (ppm). The regression analysis showed an excellent correlation coefficient (0.997) and a very low standard deviation (0.02), resulting in the following equation:

$$V_{MA} = -237.34 + 29.894(pH) + 0.244(TA) + 0.1276(CA)$$

This equation estimates the values in Tables 3A to 6A to within ± 2% on average.

Borate will affect the calculated quantity of acid. For example, the presence of 100 ppm of boric acid (17.5 ppm boron) will increase the calculated quantity of muriatic acid (required to reduce pH from 8.2 to 7.2) from 62.1 fl. oz to 78.2 fl. oz at 100 ppm CA and 170 ppm total alkalinity.

	Table 3A. Volume (fl. oz) of 31.45% Muriatic Acid				
Total Alk.	**to Reduce pH to 7.2; CA 50 ppm**				
ppm	**7.8**	**7.9**	**8**	**8.1**	**8.2**
70	22.1	24.0	25.5	26.9	28.1
80	24.2	26.3	28.0	29.5	30.8
90	26.4	28.6	30.4	32.1	33.5
100	28.5	30.9	32.9	34.6	36.2
110	30.7	33.2	35.4	37.2	38.9
120	32.8	35.5	37.8	39.8	41.6
130	34.9	37.8	40.3	42.4	44.3
140	37.1	40.1	42.7	45.0	47.1
150	39.2	42.4	45.2	47.6	49.8

Fig. 1 - pH Reduction to pH 7.2 via Acid Addition (CA 50 ppm)

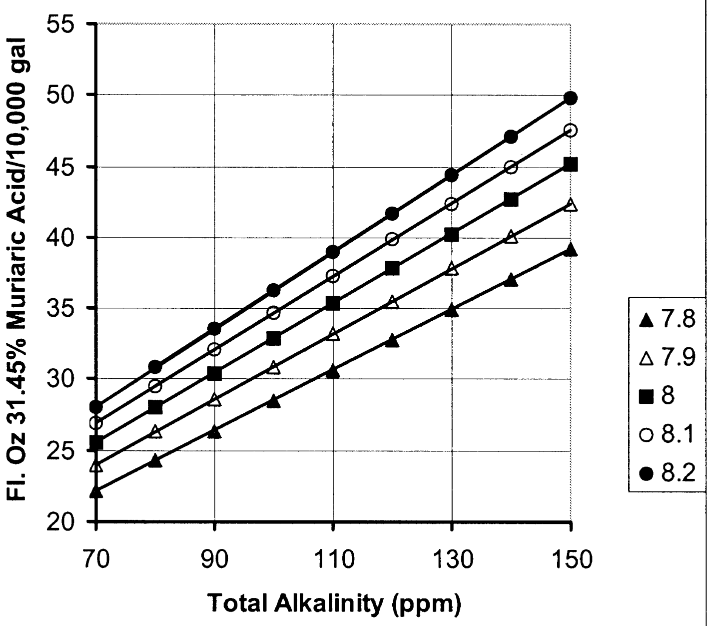


	Table 4A. Volume (fl. oz) of 31.45% Muriatic Acid				
Total Alk.	to Reduce pH to 7.2; CA 100 ppm				
ppm	7.8	7.9	8	8.1	8.2
90	32.0	34.7	36.9	38.8	40.4
100	34.2	37.0	39.4	41.4	43.1
110	36.3	39.3	41.8	44.0	45.8
120	38.4	41.6	44.3	46.6	48.5
130	40.6	43.9	46.7	49.1	51.3
140	42.7	46.2	49.2	51.7	54.0
150	44.9	48.5	51.6	54.3	56.7
160	47.0	50.8	54.1	56.9	59.4
170	49.1	53.2	56.6	59.5	62.1

Fig. 2 - pH Reduction to 7.2 via Acid Addition (CA 100 ppm)

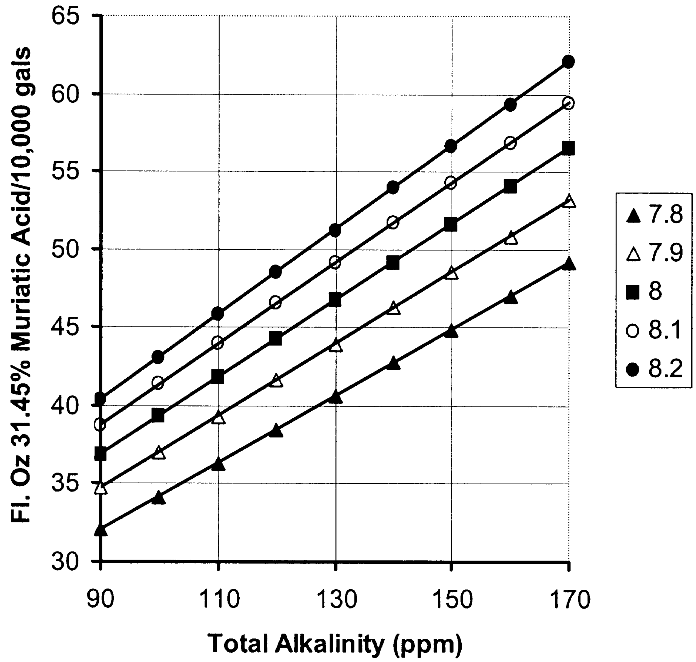


	Table 5A. Volume (fl. oz) of 31.45% Muriatic Acid				
Total Alk.	to Reduce pH to 7.2; CA 150 ppm				
ppm	7.8	7.9	8	8.1	8.2
110	42.0	45.4	48.3	50.7	52.8
120	44.1	47.7	50.8	53.3	55.5
130	46.2	50.0	53.2	55.9	58.2
140	48.4	52.3	55.7	58.5	60.9
150	50.5	54.7	58.1	61.1	63.6
160	52.7	57.0	60.6	63.6	66.3
170	54.8	59.3	63.0	66.2	69.0
180	56.9	61.6	65.5	68.8	71.7
190	59.1	63.9	67.9	71.4	74.4

Fig. 3 - pH Adjustment to 7.2 via Acid Addition (CA 150 ppm)

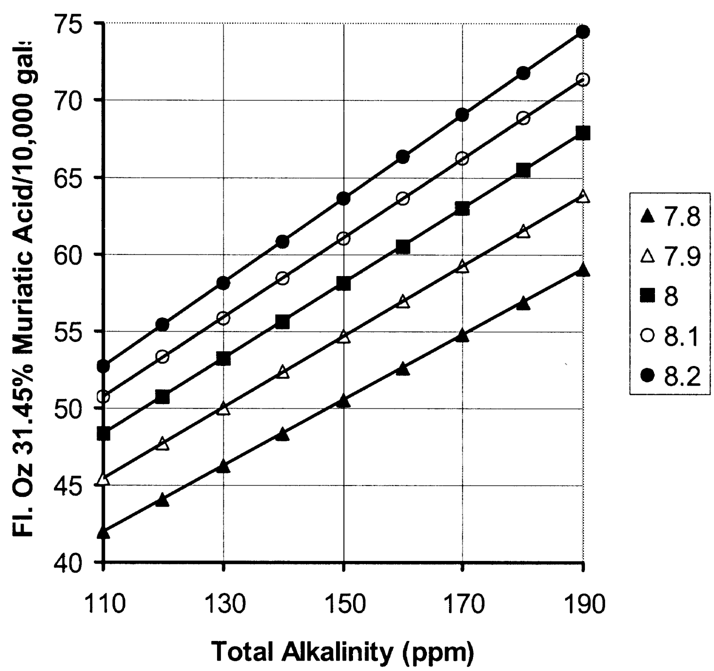
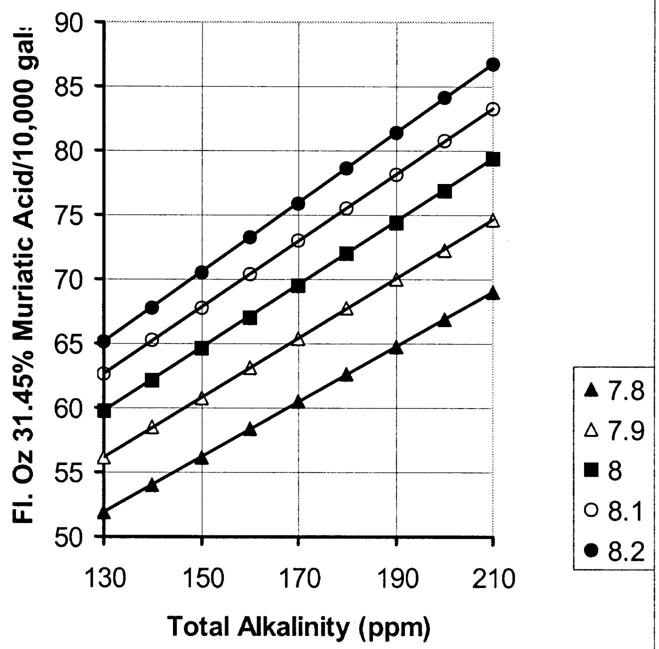


	Table 6A. Volume (fl. oz) of 31.45% Muriatic Acid				
Total Alk.	to Reduce pH to 7.2; CA 200 ppm				
ppm	7.8	7.9	8	8.1	8.2
130	51.9	56.2	59.7	62.6	65.1
140	54.0	58.5	62.1	65.2	67.8
150	56.2	60.8	64.6	67.8	70.5
160	58.3	63.1	67.1	70.4	73.2
170	60.5	65.4	69.5	73.0	75.9
180	62.6	67.7	72.0	75.6	78.6
190	64.7	70.0	74.4	78.1	81.4
200	66.9	72.3	76.9	80.7	84.1
210	69.0	74.6	79.3	83.3	86.8

Fig. 4 - pH Adjustment to 7.2 via Acid Addition (CA 200 ppm)



Tables 3B to 6B contain calculated values of muriatic acid required to reduce pHs in the 7.3 to 7.7 range to 7.2 at different total alkalinities (80 to 210 ppm) and cyanuric acid levels (50 to 200 ppm). These Tables are useful for determining the quantity of muriatic acid required to reduce pH from the 7.8 to 8.2 range to intermediate values in the 7.3 to7.7 range. For example, to calculate the quantity of muriatic acid required to reduce pH from 8.2 to7.5, one would subtract the quantity of acid to reduce pH from 7.5 to 7.2 from that required to reduce pH from 8.2 to 7.2.

Decreasing pH with Sulfuric Acid – The above equation also works equally well for 38.5% sulfuric acid (d = 1.29 g/mL).

Decreasing pH with Sodium Bisulfate – It will require 1.32 oz of 95% sodium bisulfate to provide the same pH reduction as one fl. oz of 31.45% muriatic acid. Bisulfate (i.e., bisulfate ion) lowers pH by reacting with hydroxyl ion and is converted to sulfate ion.

$$HSO_4^- + OH^- \rightarrow SO_4^{2-} + H_2O$$

Decreasing pH with Carbon Dioxide – By contrast with mineral acids (hydrochloric and sulfuric) and bisulfate, carbon dioxide decreases pH (without affecting alkalinity) by increasing the concentration of carbonic acid.

Increasing pH with Sodium Carbonate – As discussed earlier, swimming pool and spa pH tends to drift upward. Thus, acid addition is typically necessary to adjust the pH to the recommended range. By contrast, pools treated with chlorine will offset the upward pH drift due to CO_2 loss because of the acidity introduced, which lowers pH and decreases alkalinity. This will necessitate addition of soda ash, which

	Table 3B. Volume (fl. oz) of 31.45% Muriatic Acid				
Total Alk.	**to Reduce pH to 7.2; CA 50 ppm**				
ppm	**7.3**	**7.4**	**7.5**	**7.6**	**7.7**
70	5.6	10.2	14.0	17.2	19.9
80	6.2	11.2	15.4	18.9	21.8
90	6.7	12.3	16.8	20.6	23.8
100	7.3	13.3	18.2	22.3	25.7
110	7.9	14.3	19.6	24.0	27.6
120	8.4	15.4	21.0	25.7	29.6
130	9.0	16.4	22.4	27.4	31.5
140	9.6	17.4	23.8	29.1	33.4
150	10.2	18.4	25.2	30.8	35.4

	Table 4B. Volume (fl. oz) of 31.45% Muriatic Acid				
Total Alk.	**to Reduce pH to 7.2; CA 100 ppm**				
ppm	**7.3**	**7.4**	**7.5**	**7.6**	**7.7**
90	8.1	14.8	20.3	25.0	28.8
100	8.6	15.8	21.7	26.7	30.8
110	9.2	16.8	23.1	28.4	32.7
120	9.8	17.8	24.5	30.1	34.6
130	10.3	18.9	25.9	31.8	36.6
140	10.9	19.9	27.3	33.5	38.5
150	11.5	20.9	28.7	35.2	40.5
160	12.0	22.0	30.1	36.8	42.4
170	12.6	23.0	31.5	38.5	44.3

	Table 5B. Volume (fl. oz) of 31.45% Muriatic Acid				
Total Alk.	**to Reduce pH to 7.2; CA 150 ppm**				
ppm	**7.3**	**7.4**	**7.5**	**7.6**	**7.7**
110	10.5	19.3	26.6	32.7	37.8
120	11.1	20.3	28.0	34.4	39.7
130	11.7	21.4	29.4	36.1	41.7
140	12.2	22.4	30.8	37.8	43.6
150	12.8	23.4	32.2	39.5	45.5
160	13.4	24.5	33.6	41.2	47.5
170	13.9	25.5	35.0	42.9	49.4
180	14.5	26.5	36.4	44.6	51.3
190	15.1	27.6	37.8	46.3	53.3

	Table 6B. Volume (fl. oz) of 31.45% Muriatic Acid				
Total Alk.	**to Reduce pH to 7.2; CA 200 ppm**				
ppm	**7.3**	**7.4**	**7.5**	**7.6**	**7.7**
130	13.0	23.9	33.0	40.5	46.7
140	13.6	24.9	34.3	42.2	48.7
150	14.1	25.9	35.7	43.9	50.6
160	14.7	27.0	37.1	45.6	52.5
170	15.3	28.0	38.5	47.3	54.5
180	15.8	29.0	39.9	49.0	56.4
190	16.4	30.0	41.3	50.7	58.4
200	17.0	31.1	42.7	52.3	60.3
210	17.6	32.1	44.1	54.0	62.2

increases both pH and alkalinity. Dissolution of sodium carbonate in water produces hydroxyl and bicarbonate ions:

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

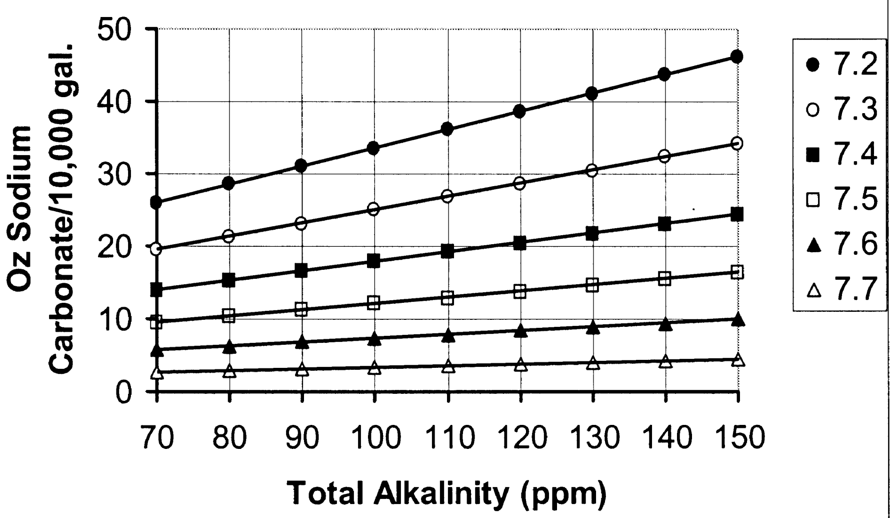
The hydroxyl ions decrease the concentration of hydrogen ions via the equilibrium: $H_2O \rightleftharpoons H^+ + OH^-$. This raises the pH, causing increased ionization of carbonic, cyanuric, and boric acids producing bicarbonate, cyanurate, and borate ions, i.e., the reverse of the reactions when acid is added as shown in the previous section.

The quantity of sodium carbonate required is calculable based on the increase in alkalinity at the higher pH. Tables 7–10 contain calculated values of sodium carbonate required to raise pH to 7.8 from initial pHs of 7.2–7.7. The conditions for the calculations were: 80°F, 3 ppm av. Cl, 1000 ppm TDS, total alkalinity of 70–210, and CA of 50–200 ppm. Plots of the data are shown in Figures 5–8. They show that the required quantity of sodium carbonate varies linearly with total alkalinity at a given pH and CA concentration.

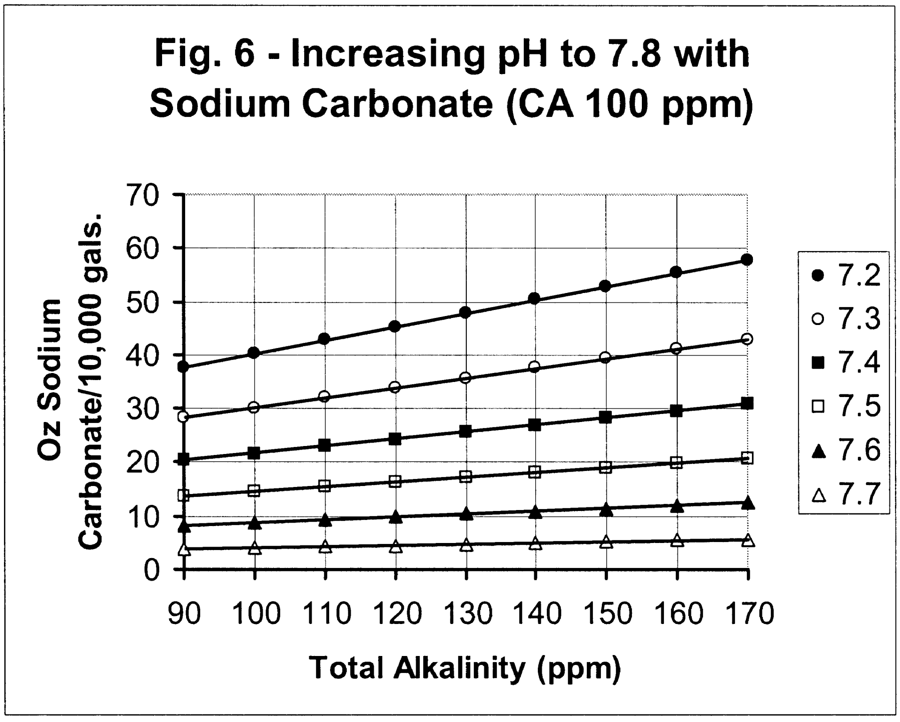
Multiple linear regression analysis of all the

T. Alk.	Table 7. Weight (oz) of Sodium Carbonate to Increase pH to 7.8: CA 50 ppm					
ppm	**7.2**	**7.3**	**7.4**	**7.5**	**7.6**	**7.7**
70	26.0	19.5	14.0	9.5	5.7	2.6
80	28.6	21.3	15.3	10.4	6.3	2.8
90	31.1	23.2	16.6	11.2	6.8	3.1
100	33.6	25.0	17.9	12.1	7.3	3.3
110	36.1	26.9	19.2	13.0	7.8	3.6
120	38.6	28.7	20.6	13.9	8.3	3.8
130	41.2	30.5	21.9	14.7	8.9	4.0
140	43.7	32.4	23.2	15.6	9.4	4.3
150	46.2	34.2	24.5	16.5	9.9	4.5

Fig. 5 - Increasing pH to 7.8 with Sodium Carbonate (CA 50 ppm)

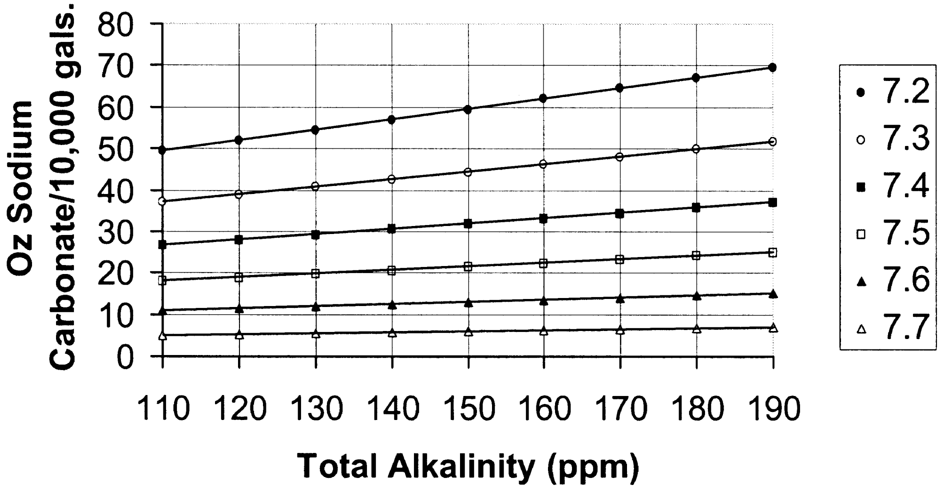


T. Alk.	Table 8. Weight (oz) of Sodium Carbonate to Increase pH to 7.8: CA 100 ppm					
ppm	7.2	7.3	7.4	7.5	7.6	7.7
90	37.8	28.3	20.4	13.8	8.3	3.8
100	40.3	30.1	21.7	14.6	8.8	4.0
110	42.8	32.0	23.0	15.5	9.4	4.2
120	45.3	33.8	24.3	16.4	9.9	4.5
130	47.8	35.6	25.6	17.3	10.4	4.7
140	50.3	37.5	26.9	18.1	10.9	5.0
150	52.9	39.3	28.2	19.0	11.4	5.2
160	55.4	41.2	29.5	19.9	12.0	5.4
170	57.9	43.0	30.8	20.8	12.5	5.7



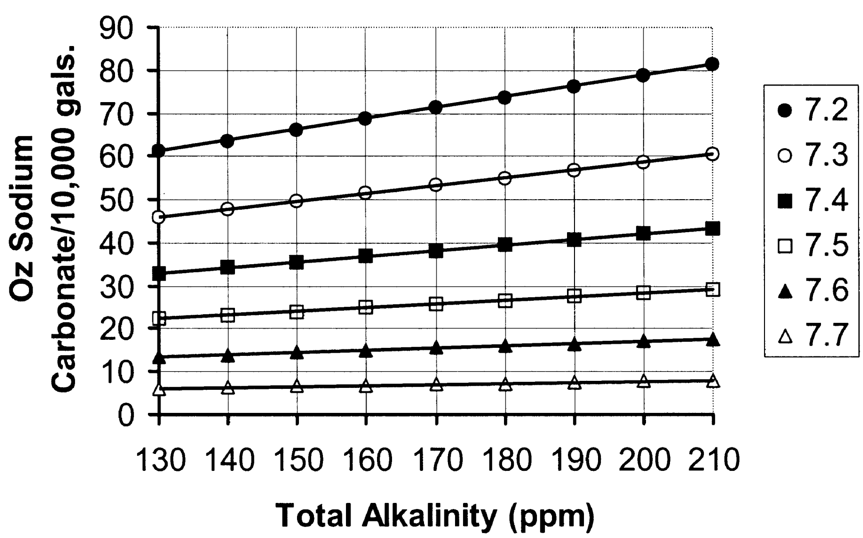
T. Alk.	Table 9. Weight (oz) of Sodium Carbonate to Increase pH to 7.8: CA 150 ppm					
ppm	7.2	7.3	7.4	7.5	7.6	7.7
110	49.5	37.1	26.7	18.1	10.8	4.9
120	52.0	38.9	28.0	18.9	11.3	5.2
130	54.5	40.7	29.3	19.8	11.9	5.4
140	57.0	42.6	30.6	20.7	12.4	5.6
150	59.5	44.4	31.9	21.5	12.9	5.9
160	62.0	46.3	33.2	22.4	13.5	6.1
170	64.6	48.1	34.5	23.3	14.0	6.3
180	67.1	50.0	35.8	24.2	14.5	6.6
190	69.6	51.8	37.1	25.0	15.1	6.8

Fig. 7 - Increasing pH to 7.8 with Sodium Carbonate (CA 150 ppm)



T. Alk.	Table 10. Weight (oz) of Sodium Carbonate to Increase pH to 7.8: CA 200 ppm					
ppm	**7.2**	**7.3**	**7.4**	**7.5**	**7.6**	**7.7**
130	61.2	45.9	33.0	22.3	13.4	6.1
140	63.7	47.7	34.3	23.2	14.0	6.3
150	66.2	49.5	35.6	24.1	14.5	6.6
160	68.7	51.4	36.9	24.9	15.0	6.8
170	71.2	53.2	38.3	25.8	15.5	7.0
180	73.7	55.1	39.6	26.7	16.1	7.3
190	76.3	56.9	40.9	27.6	16.6	7.5
200	78.8	58.8	42.2	28.4	17.1	7.7
210	81.3	60.6	43.5	29.3	17.6	8.0

Fig. 8 - Increasing pH to 7.8 with Sodium Carbonate (CA 200 ppm)



data in Tables 7–10 did not yield a satisfactory predictive equation as in the case of acid addition, because the data was not linear with respect to pH. Therefore, the data from each Table was regressed separately using the following equation form consisting of the dependent variable W_{SC} (oz sodium carbonate) and the independent variable pH:

$$W_{SC}=(A_1+A_2 \cdot F)+(B_1+B_2 \cdot F) \cdot pH+(C_1+C_2 \cdot F) \cdot pH^2$$

where: A_1, B_1, and C_1 are regression constants and A_2, B_2, and C_2 are constants for extrapolating total alkalinity, and F equals $(TA_a - TA_o)/10$ where TA_a is the actual total alkalinity, and TA_o is the lowest total alkalinity for a given CA level and is equal to 70, 90, 110, and 130 for the data in Tables 7–10, respectively. The constants are summarized in Table 11.

These equations estimate the values in Tables 7–10 to within ±2% on average.

Because of chlorine's propensity for lowering pH, pool service companies using chlorine for sanitization maintain pH at or above 7.8. Pools are treated once a week, and typically, the av. Cl averages about 3 ppm before chlorination. The water is treated with about 8 oz chlorine/10,000 gal, which is equivalent to 6 ppm av. Cl. Total alkalinity and stabilizer are maintained at about 100 ppm. The total alkalinity will be reduced by 4.23 ppm. If the pH is at 8.0 when the chlorine is added, it will decrease to 7.54. Raising the pH to 7.8 will require 13.4 oz of soda ash and will raise the total alkalinity by 9.4 ppm. When all of the added av. Cl has decomposed to HCl, the total alkalinity will be reduced by an additional 4.23 ppm. Thus, the net change in total alkalinity will be about +0.9 ppm.

If the quantity of soda ash is just sufficient to neutralize all of the acidity due to chlorine, there should be no net change in alkalinity as shown below and will require 1.5 lb of soda ash per pound of chlorine or 12.0 oz in the above example.

$$Cl_2 + H_2O \rightarrow HOCl + HCl$$

$$HOCl \rightarrow HCl + 0.5O_2$$

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$$

Overall: $Na_2CO_3 + Cl_2 \rightarrow 2NaCl + CO_2 + 0.5O_2$

However, pool alkalinity can still change due to the effects of filter backwashing and makeup water.

Increasing pH with Sodium Hydroxide – Addition of sodium hydroxide (caustic soda) to water raises pH by increasing the concentration hydroxyl ions. In the above example, it would require 21.7 fl. oz of 30% sodium hydroxide to increase the pH to 7.8. This would raise the total alkalinity from 95.8 to 104.2 ppm. Decomposition of all of the added chlorine would reduce the total alkalinity back to its original value of 100 ppm, thus no change in alkalinity would occur and is in agreement with the following reaction stoichiometry obtained on substitution of sodium hydroxide in place of soda ash in the above reaction sequence:

$$2NaOH + Cl_2 \rightarrow 2NaCl + H_2O$$

Alkalinity Changes after pH Adjustments

Decrease in Alkalinity after Mineral Acid Addition – Mineral acid (i.e., hydrochloric or sulfuric) addition for pH adjustment lowers alkalinity by reacting with bicarbonate, carbonate, cyanurate, and borate (if present) ions as

Table 11. Summary of Constants for Calculating Soda Ash Addition

CA	A_1	A_2	B_1	B_2	C_1	C_2
50	2732.097	302.340	-683.781	-76.358	42.768	4.821
100	3939.389	301.702	-985.481	-76.189	61.607	4.810
150	5144.099	301.527	-1286.436	-76.149	80.393	4.808
200	6336.031	302.088	-1584.076	-76.291	98.964	4.817

discussed earlier. The decrease in total alkalinity (ΔTA) is calculable from the quantity of acid added.

$$\Delta TA = (\text{fl. oz acid}) \cdot 29.57 \cdot d \cdot p \cdot 1000 \cdot 50 / (EW \cdot V \cdot 3.7854)$$

where: d equals 1.16 for muriatic acid and 1.29 for sulfuric acid, p equals 0.3145 for muriatic acid and 0.385 for sulfuric acid, EW is equivalent weight – 36.46 for hydrochloric acid and 49.04 for sulfuric acid. The above calculation yields similar results (to within 1%) for each acid. Thus, one quart (i.e., 32 fl oz) of 31.45% muriatic acid and 38.5% sulfuric acid added to 10,000 gal of pool water reduces alkalinity by 12.5 and 12.7 ppm, respectively, as calculated by the following condensed formulas:

$$\Delta TA = 3912.0 \cdot V_{MA}/V$$

$$\Delta TA = 3962.8 \cdot V_{SA}/V$$

where: V_{MA} equals the volume (fl oz) of muriatic acid and V_{SA} equals the volume (fl oz) of sulfuric acid.

Decrease in Alkalinity after Sodium Bisulfate Addition – The change in total alkalinity when sodium bisulfate is used for pH adjustment is calculated as follows:

$$\Delta TA = W_{BS} \cdot 28.35 \cdot p \cdot 1000 \cdot 50/(120 \cdot V \cdot 3.7854) = 3120.5 \cdot W_{BS} \cdot p/V$$

where: W_{BS} equals the weight (oz) of sodium bisulfate, 120 is the molecular weight of sodium bisulfate. Assuming a degree of purity of 0.95 (i.e., 95% purity), each pound (i.e., 16 oz) of sodium bisulfate added to 10,000 gal of pool water will reduce total alkalinity by 4.7 ppm.

Increase In Alkalinity after Sodium Carbonate Addition – The increase in total alkalinity (ΔTA) resulting from addition of sodium carbonate (soda ash) can be calculated using the following formula:

$$\Delta TA = W_{SC} \cdot 28.35 \cdot 1000 \cdot 50/(53 \cdot V \cdot 3.7854 \cdot p) = 7065.4 \cdot W_{SC}/(V \cdot p)$$

where: W_{SC} equals the weight (oz) of sodium carbonate, and 53 equals the equivalent weight of sodium carbonate. Assuming a typical degree of purity of 0.998 (i.e., 99.8% purity), each pound (i.e., 16 oz) of soda ash added to 10,000 gals of pool water will increase the total alkalinity by 11.3 ppm.

Alkalinity Adjustment

All tap and well water contain varying amounts of alkalinity depending on the source. In new pools the alkalinity may require adjustment to the recommended range (see Table 1). In established pools, makeup water to replace evaporation losses will increase the pool or spa alkalinity. In addition, alkaline sanitizers will increase alkalinity to a small extent, whereas acidic sanitizers will decrease alkalinity to a significant extent (Wojtowicz 1995b). High alkalinity is lowered by acid addition whereas low alkalinity is increased with sodium bicarbonate.

Increasing Alkalinity with Sodium Bicarbonate – Sodium bicarbonate is used to increase total alkalinity. Addition of sodium bicarbonate to pool water will increase the concentration of bicarbonate ions, which will repress ionization of carbonic acid resulting in a lower hydrogen ion concentration and a higher pH.

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

However, the effect is very small. For example, increasing the total alkalinity by 20 ppm with sodium bicarbonate in pool water at 80°F, pH 7.5, total alkalinity 80 ppm, cyanuric acid 100 ppm, 3 ppm av. Cl 3 ppm, and TDS 1000 ppm will increase the pH to only 7.55.

The quantity of sodium bicarbonate (W_{SB} (lb)) can be calculated using the following equation:

$$W_{SB} = \Delta TA \cdot 84 \cdot V \cdot 3.7854/(50 \cdot !000 \cdot 453.6 \cdot p) = 1.40 \cdot 10^{-5} \cdot \Delta TA \cdot V/p$$

where: ΔTA equals the increase in total alkalinity (ppm), 84 equals the molecular weight of sodium bicarbonate, and p is typically 1.0, i.e., 100% assay. Tables are available showing dosages for various water volumes.

Decreasing Alkalinity with Mineral Acid – The quantity of mineral acid necessary to reduce total alkalinity (TA) by a specified amount can be calculated using the following equations obtained by rearrangement of equations used earlier.

$$V_{MA} = 2.556 \cdot 10^{-4} \cdot (\Delta TA) \cdot V$$

$$V_{SA} = 2.523 \cdot 10^{-4} \cdot (\Delta TA) \cdot V$$

where: V_{MA} equals the volume (fl oz) of 31.45% muriatic acid, V_{SA} equals the volume (fl oz) of sulfuric acid. Reduction of total alkalinity by 10 ppm requires 1.6 pints of muriatic acid.

Decreasing Alkalinity with Sodium Bisulfate – Similarly, the earlier equation can be rearranged to give the quantity of bisulfate (W_{BS} oz) necessary to reduce total alkalinity by a specified amount.

$$W_{BS} = 3.205 \cdot 10^{-4} \cdot (\Delta TA) \cdot V/p$$

Hardness Adjustment

Increasing Hardness – All source water contains some calcium hardness. If necessary, the calcium hardness (CH) can be adjusted to the recommended range by the addition of calcium chloride (typically the dihydrate $CaCl_2 \cdot 2H_2O$). The required dosage is readily calculable using the following equation:

$$W_{CC} = \Delta CH \cdot V \cdot 3.7854 \cdot 147/(100 \cdot 1000 \cdot 453.6 \cdot p)$$
$$= 1.227 \cdot 10^{-5} \cdot \Delta CH \cdot V/p$$

where: W_{CC} equals lbs of calcium chloride dihydrate, DCH equals the increase in calcium hardness (ppm), 147 equals the molecular weight of calcium chloride dihydrate, 100 equals the molecular weight of calcium carbonate, and p equals the degree of purity of calcium chloride dihydrate (typically 0.98). Raising calcium hardness (expressed as ppm calcium carbonate) by 10 ppm requires 1.25 lb of 98% calcium chloride dihydrate per 10,000 gals of pool water. Tables are available showing dosages for various water volumes.

Decreasing Hardness – Alkaline sanitizers such as calcium hypochlorite add small amounts of calcium hardness to the water (Wojtowicz 1995b). Makeup water to replace evaporation losses also adds calcium hardness to pool or spa water. Makeup water used to replace water removed by backwashing can reduce calcium hardness if its hardness is lower. Thus, frequent backwashing can keep hardness in the recommended range.

Stabilizer Adjustment

Increasing Stabilizer Concentration – The stabilizer concentration is adjusted by addition of cyanuric acid (CA). In a new pool, the stabilizer concentration can be adjusted to 50 ppm by addition of 4.2 lb of cyanuric acid (99% assay) per 10,000 gal of water. The CA dose for other concentrations and water volumes can be calculated using the following equation:

$$CA\ (lb) = \Delta CA \cdot V \cdot 3.7854/(1000 \cdot 453.6 \cdot p)$$
$$= 8.345 \cdot 10^{-6} \cdot \Delta CA \cdot V/p$$

where: ΔCA equals the ppm increase in the CA concentration.

Decrease in pH after Cyanuric Acid Addition – Addition of cyanuric acid to swimming pool or spa water will increase the hydrogen ion concentration as the result of ionization, therefore, lowering the pH.

$$H_3Cy \rightleftharpoons H_2Cy^- + H^+$$

The effect is significant. For example, increasing the cyanuric acid concentration to 50 ppm in pool water at 80°F, pH 7.5, total alkalinity 100 ppm, initial cyanuric acid 0 ppm, av. Cl 3 ppm, and TDS 1000 ppm will lower pH to 6.99. At this point, there are two options:

1. Let the pH drift and under normal conditions it will eventually increase to 7.5 and even higher due to loss of carbon dioxide. For a 20,000–gal pool with an average depth of 5 feet, a pumping rate of 42 gal/min, a 24–hour pump duty cycle, the pH will reach 7.50 after only about 2.4 days.

2. Add base to immediately increase the pH to the original value of 7.5.

In the first case there will be no change in alkalinity, whereas in the second, there will be and will depend on the base added. With soda ash, it will require 86.8 oz to increase the pH back to 7.5. This will increase the total alkalinity to 130.7 ppm. Instead of soda ash, sodium hydroxide (i.e., caustic soda) can be added and will result in a much lower increase in total alkalinity. It will require 86.8 fl. oz of 30% sodium hydroxide and will increase the total alkalinity to 116.8 ppm, about half that of soda ash.

Decreasing Cyanuric Acid Concentration – In hypochlorite or chlorine sanitized pools or spas, the cyanuric acid concentration decreases with time due to backwashing, splash out, and decomposition requiring periodic adjustment. By contrast, in water sanitized with chloro-isocyanurates the CA concentration normally increases with time. Excessive CA concentrations can be reduced and controlled by adjusting the backwashing frequency and duration (Wojtowicz 2002).

Summary of Ancillary Chemical Dosages

A summary of ancillary chemical dosages used for adjusting pH, alkalinity, hardness, and stabilizer is shown in Table 12.

Chlorine Sanitizer Adjustment

The required dosage of solid sanitizers (W_{SAN} including gaseous chlorine) can be calculated using the following formula:

$$W_{SAN}\,(oz) = \Delta FC \cdot V \cdot 3.7854/(1000 \cdot p \cdot 28.35)$$
$$= 1.34 \cdot 10^{-4} \cdot \Delta FC \cdot V/p$$

where: ΔFC equals the increase in free chlorine, p equals the degree of purity of sanitizer (i.e., % av. Cl/100). The required dosage of liquid chlorine sanitizers such as sodium hypochlorite can be calculated using the following formula:

Table 12. Summary of Ancillary Chemical Dosages

Parameter	Additive	% Purity	lb/10 ppm/10K gals
Alkalinity (Increase)	Sodium Bicarbonate	100	1.40
Alkalinity (Decrease)	Hydrochloric Acid	31.45	1.6 (pints)
"	Sulfuric Acid	38.5	1.6 (pints)
"	Sodium Bisulfate	95	2.11
Hardness (Increase)	Calcium Chloride	77	1.25
Stabilizer (Increase)	Cyanuric Acid	99	0.84

Table 13. Summary of Chlorine Sanitizer Dosages

Sanitizer[A]	% Av. Cl	Oz/ppm/10K gal
Sodium Hypochlorite (solution)	12[B]	9.1 fl. oz
Lithium Hypochlorite	35	3.81
Calcium Hypochlorite	65	2.05
Calcium Hypochlorite	75	1.78
Sodium Dichloroisocyanurate[C]	56	2.39
Sodium Dichloroisocyanurate	62	2.15
Trichloroisocyanuric Acid	90	1.48
Chlorine (gas)	100	1.34

A) Granular except where noted otherwise
B) Density =1.17 g/mL
C) Dihydrate

$$W_{SH}\text{ (fl. oz)} = \Delta FC \cdot V \cdot 3.7854/(1000 \cdot p \cdot d \cdot 29.57)$$
$$= 1.28 \cdot 10^{-4} \cdot \Delta FC \cdot V/(p \cdot d)$$

where: W_{SH} (fl. oz) equals the volume of sodium hypochlorite. Calculated dosages for various chlorine sanitizers are summarized in Table 13.

References

ANSI/NSPI–4 1999 Standard for Aboveground/ Onground Residential Swimming Pools

ANSI/NSPI–5 1995 Standard for Residential Inground Swimming Pools

ANSI/NSPI–5 2003 Standard for Residential Inground Swimming Pools

Taylor Technologies, Inc., "Pool & Spa Water Chemistry", Sparks, MD, 2002.

Wojtowicz, J.A. 1995a "Swimming Pool Water Balance – Part 2: Factors Affecting the Calcium Carbonate Saturation Index", Journal of the Swimming Pool and Spa Industry 1(2)1995:9–15.

Wojtowicz, J.A. 1995b "Swimming Pool Water Balance – Part 3: Factors Affecting Loss of Carbon Dioxide", Journal of the Swimming Pool and Spa Industry 1(3)1995:19–26.

Wojtowicz, J.A. 1995c "Swimming Pool Water Balance – Part 1: The Effect of Cyanuric Acid and other Interferences on Carbonate Alkalinity Measurement", Journal of the Swimming Pool and Spa Industry 1(1)1995:7–13.

Wojtowicz, J.A. "Swimming Pool Water Balance – Part 4: Calcium Carbonate Precipitation Potential", Journal of the Swimming Pool and Spa Industry 2(2)1996:23–29.

Wojtowicz, J.A., "The Carbonate System in Swimming Pool Water", Journal of the Swimming Pool and Spa Industry 4(1)2001:54–59.

Wojtowicz, J.A., "Factors Affecting the Cyanuric Acid Concentration in Swimming Pools", Journal of the Swimming Pool and Spa Industry 4(2)2002:17–22.

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