Factors Affecting Loss of Carbon Dioxide

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As part of a study on factors affecting the saturation index of swimming pool water, a computer program was written to simulate the chemistry of swimming pools. One of the key parameters in this program is the rate of carbon dioxide loss. Laboratory tests under static conditions had shown that carbon dioxide is readily lost to the atmosphere resulting in increased pH with time. Because carbon dioxide loss raises pH, it also increases the saturation index, making cloudy water formation, i.e., precipitation of calcium carbonate, more favorable.

Carbon dioxide is continuously evolved from swimming pool water because pools are normally supersaturated with carbon dioxide. This causes an upward drift in pH. Generation of carbon dioxide by oxidation of organic matter in the water by available chlorine will only slightly offset this drift. However, acidic sanitizers such as trichloroisocyanuric acid can significantly retard the rise in pH, because of the relatively large quantity of acidity they produce. By contrast, alkaline sanitizers such as hypochlorites will augment the pH drift, but only to a small extent.

Data involving residential pools in California (1979) and Florida (1981) as well as test pools in Florida (1987 and 1988) showed that the major portion of added acid is needed to restore pH due to carbon dioxide loss. Acid addition reduces carbonate alkalinity. Use of gaseous carbon dioxide in place of mineral acid for pH adjustment was shown to be feasible. This allows reduction of pH without affecting alkalinity.

The rate of carbon dioxide loss from a bather–free test pool was measured under a variety of conditions. The kinetics of volatilization of carbon dioxide was shown to be second–order rather than first–order in excess dissolved carbon dioxide as predicted by the film diffusion model. Whereas first–order rate constants were dependent on alkalinity, second–order rate constants were essentially independent of it. This indicates that the process may involve facilitated transport of carbon dioxide across the water–air interface, i.e., it is enhanced by bicarbonate and carbonate ions.

Pump duty cycle and use of a cover were major factors affecting carbon dioxide loss. Alkalinity of the water also had a significant effect on pH rise due to its effect on the initial concentration of carbon dioxide which in turn affects the loss rate. A general equation was developed for calculating the specific carbon dioxide transfer rate constant as a function of temperature, surface–to–volume ratio, and turnover rate of the pool. The rate constant is also dependent on other factors such as bather load, wind velocity, etc., which are not taken into account in the model due to obvious mathematical difficulties. Use of a cover when the pool is not in use, maintaining a moderate alkalinity, in conjunction with minimal pump runs can minimize pH drift due to carbon dioxide loss.

Theory

Carbonic Acid Equilibria – The carbonic acid equilibrium system can be represented as follows:

1. $CO_2(g) \rightleftharpoons CO_2(aq)$
2. $CO_2(aq) + H_2O \rightleftharpoons H_2CO_3$
3. $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$
4. $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

The concentration of carbonic acid is negligible in comparison to dissolved carbon dioxide, e.g., only 0.15% of the latter is hydrated to carbonic acid at 25°C. Although the ionic equilibria shown above are established rapidly, the hydration–dehydration of dissolved carbon dioxide is not as fast. Values for the hydration and dehydration rate constants and activation energies at 20–25°C are shown in Table 1 (Stumm and Morgan 1982). Although these rate constants are relatively small in comparison to those for ionic reactions, the hydration–dehydration equilibrium reaction should be established in only a few minutes.

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Rate Constant	sec^{-1}	Activation Energy ΔE kcal/mol
k hydration	0.025–0.030	15
k dehydration	10–20	16

Table 1 – Kinetic Parameters for $CO_2(aq)–H_2CO_3$ Equilibrium

Effect of CO_2 Evolution – Loss of aqueous carbon dioxide reduces the carbonic acid concentration, causing a shift in the equilibria toward carbonate, i.e., higher pH. As a result, some bicarbonate is converted to carbonate. However, this does not affect carbonate alkalinity, i.e., bicarbonate and carbonate, since the decrease in equivalents of bicarbonate is equal to the increase in equivalents of carbonate.

In stabilized pools, an additional equilibrium is ionization of cyanuric acid (CA):

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

Thus, a fraction of the total alkalinity will be due to the concentration of cyanurate ion which is pH dependent. When the pH rises due to carbon dioxide loss, a fraction of the bicarbonate alkalinity is converted not only to carbonate but to cyanurate ion as well. However, total alkalinity is conserved in the process.

Driving Force For CO_2 Evolution – Carbon dioxide is evolved because swimming pool water is normally supersaturated with carbon dioxide. This arises from the fact that swimming pool water at its normal pH range has higher alkalinities than can be accommodated under equilibrium with atmospheric carbon dioxide (i.e., 0.033 vol.%). Indeed, water in equilibrium with the atmosphere would contain only 4 to 11 ppm of alkalinity over the pH range 7.2 to 7.6. Because of the natural tendency of perturbed thermodynamic systems to drift toward equilibrium, the excess carbon dioxide will be evolved, raising the pH to higher levels where higher alkalinities are allowed. If sufficient time is allowed, the equilibrium distribution of carbon dioxide between water and air will be given by:

$$[CO_2(aq)]\gamma_{CO_{2(aq)}}/(P_{CO_2}\gamma_{CO_{2(g)}}) = K_H$$

Where: $[CO_2(aq)]$ and P_{CO_2} are the aqueous concentration (mol/L) and the partial pressure (atmospheres) of CO_2, $\gamma_{CO_{2(aq)}}$ and $\gamma_{CO_{2(g)}}$ are the respective activity coefficients (which are approximately equal to one), and K_H is Henry's Law constant (mol/L/atm). The temperature dependent equation for K_H is (Plummer and Busenberg 1982):

$$\begin{aligned}\text{Log } K_H &= -108.3865 + 0.01985076T - 6919.53/T \\ &\quad - 40.45154 \text{ Log } T + 669365/T^2\end{aligned}$$

Since the system is periodically displaced from its upward drift toward equilibrium by acid addition, the pH is lowered by neutralization of bicarbonate, forming an equivalent amount of dissolved carbon dioxide and a small amount of carbonic acid. Thus, although a swimming pool is open to the atmosphere, it never gets to equilibrium with the atmosphere because of chemical additions which cause the pH to vary with time resembling a sawtooth pattern.

The dissolved carbon dioxide concentration is readily calculable from the pH, carbonate alkalinity, cyanuric acid content, temperature, and dissociation constants (adjusted for ionic strength) of carbonic and cyanuric acids. At 82°F, the equilibrium concentration of aqueous carbon dioxide is only 0.45 ppm and is independent of pH. Unfortunately, thermodynamics does not provide information on the kinetics of approach to equilibrium. Because of this and the fact that no applicable data were found in the literature, it was necessary to experimentally develop the appropriate kinetics for use in the computer program.

Mechanism Of CO_2 Evolution – Loss of carbon dioxide from aqueous solution can be modeled using the film diffusion model (Lewis and Whitman 1924). The latter assumes two stagnant layers at the liquid–air interface, one in the liquid phase and one in the gas phase. Gas molecules travel by molecular diffusion through the layers. Since molecular diffusion in air is roughly 100–1,000 times faster than in water, diffusion through the liquid phase is the rate controlling process for all but the very soluble gases (e.g., HCl, NH_3, and SO_2). The liquid film at the surface layer is assumed to be in locally laminar flow whereas the bulk liquid is in turbulent flow with complete mixing. Although this model lacks physical reality, except possibly under very calm conditons, it yields results similar to more sophisticated physically tenable models.

At low pH (<5) carbon dioxide behaves essentially as an inert gas and the exchange rate is governed by normal diffusive transport. However, at higher pH (>5) ionic gradients (i.e., bicarbonate and carbonate) contribute significantly to the exchange of carbon dioxide across the interface (Bolin 1960, Hoover and Berkshire 1969, and Emerson 1975). Dissolved carbon dioxide and the various carbonate species are assumed to be in thermodynamic equilibrium in the bulk solution. However, the carbon dioxide concentration in the liquid film is apparently not equilibrated due to the concentration gradient across the surface layer. The molecular and ionic reactions in the carbonic acid equilibrium system will shift in the appropriate direction in an attempt to restore equilibrium. Thus, the exchange of carbon dioxide across the surface layer will be facilitated by participation of bicarbonate and carbonate in the diffusion process.

Kinetics of CO_2 Evolution – Steady–state gas transfer across a plane surface in the two–layer film diffusion model (Figure 1) is described by Fick's First Law in one dimensional form:

$$F = (1/A)dn/dt = D\Delta C/z = k_g(C_g - C_{sg}) = k_l(C_{sl} - C_l)$$

Where: F is the flux in mols (n) per unit time (sec) per unit area A (cm^2), D is the diffusion coefficient of CO_2 (cm^2/sec) for a surface layer of thickness z (cm), ΔC is the concentration difference (mol/cm^3) across the surface layer, k_g and k_l are the exchange constants or transfer coefficients (cm/sec) for the gas and liquid films (i.e., the velocities with which the carbon dioxide molecules traverse the gas and liquid films), C_g and C_l are carbon dioxide concentrations (mol/cm^3) in the bulk gas and liquid, and C_{sg} and C_{sl} are the carbon dioxide concentrations (mol/cm^3) in the gas and liquid films. The surface layer thickness (z) varies inversely with the degree of agitation. Although k_l for a hypothetical completely stagnant system can be calculated from fundamental principles (i.e., semi–infinite linear diffusion), in real systems k_l is a function of hydrodynamics and can also be influenced by impurities, e.g., surface active agents. The higher the agitation, the greater the value of k_l and conversely, the lower the agitation the smaller the value of k_l.

It is assumed that the exchanging gas obeys Henry's law:

$$C_{sg} = HC_{sl}$$

where: $H = 1/K_H$ is Henry's law constant (atm/mol/L). Elimination of C_{sg} and C_{sl} between the previous two equations gives:

$$\begin{aligned}(1/A)dn/dt &= (C_g - HC_l)/(1/k_g + H/k_l)\\ &= (C_g/K_H - C_l)/(1/k_l + 1/Hk_g)\end{aligned}$$

Since liquid phase resistance is the rate controlling process, this simplifies to:

$$(1/A)dn/dt = k_l(C_g/H - C_l) = k_l(C_l^* - C_l)$$

where C_l^* is the equilibrium liquid phase carbon dioxide concentration. Loss of carbon dioxide from solution will cause a decrease in the flux with time. A kinetic equation for the loss of carbon dioxide with time can be obtained by suitable modification of the above and initial equations. Dividing both sides by V, the volume of solution, and rearranging gives:

$$dC/dt = -(k_lA/V)(C_l^* - C_l - C) = -(k_lA/V)(C_{ex} - C)$$

Where: dC/dt represents the instantaneous carbon dioxide loss rate ($mol/cm^3/sec$), C_{ex} is the excess carbon dioxide in the water, and C is the amount lost in time t. Integrating and applying boundary conditions gives the following equation for the change in concentration of excess carbon dioxide with time (for convenience concentrations in ppm and time in days are employed, accordingly k will have units of day^{-1}):

$$\log_e [C_{ex}/(C_{ex} - C)] = k_ltA/V = kt$$

Thus, according to the film diffusion model, carbon dioxide loss from solution should obey first–order kinetics in the absence of enhancement. Good first–order kinetics were obtained for evasion of carbon dioxide from distilled water (pH ~4) which was mechanically agitated (Bohr 1897).

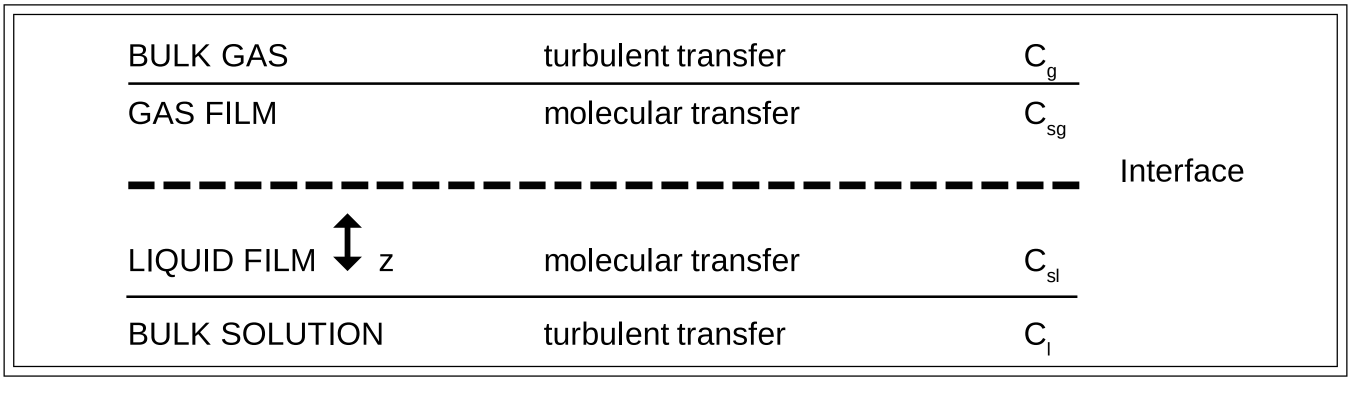

Figure 1 – Film Diffusion Model for Transport of CO_2 at the Water–Gas Interface

Laboratory Tests – Static tests in plastic tanks showed that the pH rise due to CO_2 loss increased with alkalinity and decreased with surface–to–volume ratio.

Swimming Pool Tests

Procedure – Following preliminary laboratory tests, larger scale testing was carried–out in an outdoor 6,800–gal swimming pool (with sand filter) which was stabilized with cyanuric acid (~69 ppm). The average water hardness was 440 ppm. The temperature of the pool was maintained in the 80–84°F range by means of a propane heater. The circulation pump was rated for 60 gpm. Since the pumping rate depends on the resistance of the filter and piping, the actual volumetric rate was typically about 35 gpm. The av. Cl, determined by thiosulfate titration, was maintained in the 0.5–1.8 ppm range (average 1.13 ppm) by periodic addition of calcium hypochlorite (average of 1.6 oz every other day). This dosage was significantly lower than that recommended (2.05 oz every other day plus 6.0 oz every other week for superchlorination), due to the absence of a bather load. Calculations showed that the alkalinity of the sanitizer had a negligible effect on the pH during the typical test period of 7 days. At the lowest pool alkalinity (54 ppm), the weekly addition of calcium hypochlorite would cause a pH increase of only ~0.01 and a carbon dioxide consumption of <2%.

Kinetics – The swimming pool test results are summarized in Table 2. Initial analysis of carbon dioxide evolution data from the swimming pool tests showed inconsistent values of k. The first–order rate constants not only decreased significantly with time during each test but also varied with alkalinity. By contrast, second–order constants were less variable and essentially independent of alkalinity. This indicates that the mechanism of carbon dioxide loss does indeed involve facilitated transport across the air–water interface, as discussed earlier. Therefore, the kinetics of carbon dioxide loss in these studies can be more adequately represented by the following differential equation:

$$dC/dt = -k_1A/V(C_{ex} - C)^2 = -k(C_{ex} - C)^2$$

Integration and application of boundary conditions, gives the following equation for k:

$$k = C/[tC_{ex}(C_{ex} - C)]$$

Where the second–order rate constant k has units of $(ppm \cdot day)^{-1}$. Rearranging gives:

$$C/(C_{ex} - C) = kt/\ C_{ex}$$

Plotting $C/(C_{ex} - C)$ against t should give a straight line with an intercept of zero and a slope of k/C_{ex}. A plot for one run is shown in Figure 2.

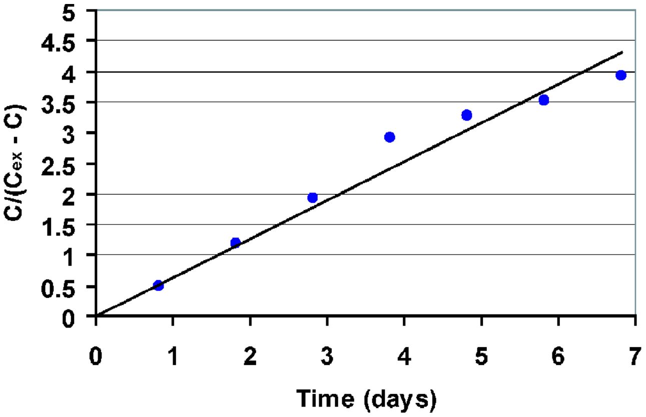

Figure 2 – Second–Order Plot for Carbon Dioxide Loss (Carb. Alk. 54 ppm, CA 69 ppm, Hard. 440 ppm)

A possible mechanism that supports the observed second–order kinetics is as follows:

$$CO_2(aq) \rightleftharpoons CO_2(g)$$

$$H_2CO_3 \rightleftharpoons CO_2(aq) + H_2O$$

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

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

Overall:

$$2HCO_3^- \rightleftharpoons CO_2(g) + H_2O + CO_3^{2-}$$

Since $CO_2(aq)$ is proportional to HCO_3^-, the carbon dioxide loss rate will follow second–order kinetics. Support for this mechanism comes from the fact that only when the latter equation is taken into account does the calculated pH rise agree with the experimental values.

Pump Duty Cycle (h)	Carb. Alkalinity (ppm)	pH_i	pH_f	ΔpH	k $(ppm/day)^{-1}$
24	54	7.33	7.82	0.49	0.19
24	79	7.39	8.03	0.64	0.21
24	96	7.33	8.03	0.70	0.17
24[a]	83	7.35	7.51	0.16	0.016
8	73	7.34	7.70	0.36	0.066
0	67	7.35	7.50	0.15	0.034

a. Pool cover installed.

Table 2 – Summary of Swimming Pool Tests on pH Drift due to CO_2 Loss Temperature 80–84°F, Cyanuric Acid 69 ppm

The data in Table 2 show that the rate constant (or transfer constant) for carbon dioxide evolution depends on pump duty cycle (ie, the water turnover rate) and use of a cover. In addition, it will depend on the water temperature and the surface to volume ratio of the pool. These and other factors will be discussed in the following sections.

Effect Of Alkalinity – In initial tests, the rate of carbon dioxide loss was determined over a range of alkalinities, i.e., 54 – 96 ppm. It was found that although pH increased with time, the alkalinity remained essentially constant, in agreement with theory, demonstrating that no precipitation of calcium carbonate occurred. The data show that the pH drift per week (for a 24–h pump duty cycle) varies approximately linearly with alkalinity. A plot of pH against time for the lowest and highest alkalinity is shown in Figure 3.

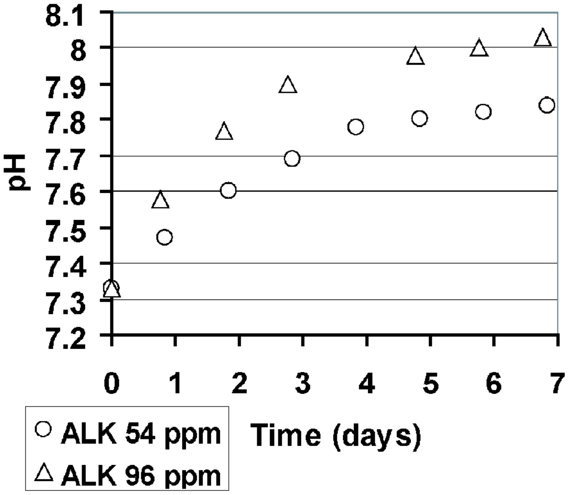

Figure 3 – Effect of Carbonate Alkalinity on pH rise due to Carbon Dioxide Loss

(CA = 69 ppm)

Temperature – The effect of temperature on the specific rate constant for loss of carbon dioxide from water can be obtained from data on determination of the rates of invasion and evasion of carbon dioxide in an aqueous system under efficient mechanical mixing conditions (Bohr 1897). Calculation of the activation energy from the temperature dependence of evasion coefficients yields a value of 5.00 kcal/mol. This value is similar to that (4.84 kcal/mol) obtained from the temperature dependence of Henry's law constant (Plummer and Busenberg 1982) for the gas–liquid carbon dioxide equilibrium, and thermochemical calculations employing standard enthalpy values (ΔH_f°) for the reaction (Lange's 1985):

$$CO_2(aq) \rightleftharpoons CO_2(g)\ \Delta H\ (25°C) = 4.64\ \text{kcal/mol}$$

Using a value of 5.0 kcal/mol for the activation energy, values of the rate constant for carbon dioxide loss from water can be obtained at other temperatures by means of the Arrhenius equation.

$$k = Ae^{-\Delta E/RT}\ (\text{ppm/day})^{-1}$$

Where: ΔE = 5,000 cal/mol, the gas constant R = 1.987 cal/mol/deg, and T is the absolute temperature (Kelvin). The value of the preexponential factor A will depend on the turnover rate and the surface–to–volume ratio of the swimming pool as well as whether a pool cover is employed.

Effect Of Pool Cover – Covering the pool with a plastic blanket (lying on the surface of the water) resulted in over a tenfold reduction in the carbon dioxide transfer rate constant (Table 2). This is in agreement with theory for a gas–liquid equilibrium system in which a physical barrier is expected to reduce the transfer rate of carbon dioxide to the air. A plot of pH against time with and without a pool cover is shown in Figure 4.

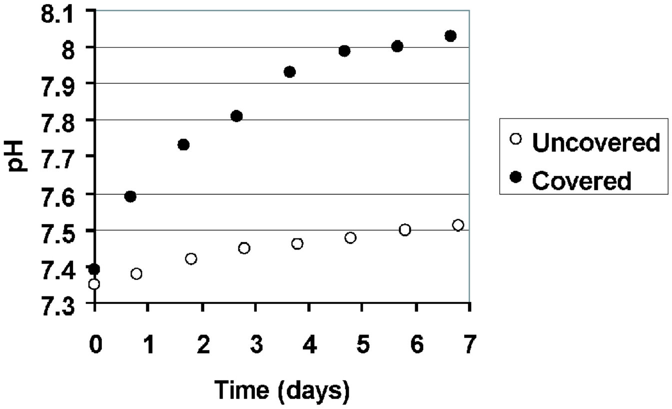

Figure 4 – Increase in pH due to Carbon Dioxide Loss (24–hour pump duty cycle)

Effect of Pool Heater – The data in Table 2 show that the heater has little or no effect on loss of carbon dioxide (specifically the run using the pool cover). Despite 24–hour pump and heater duty cycles the rate constant was decreased tenfold by use of a pool cover. Although water temperature does affect the carbon dioxide loss rate, the hot surfaces of the heater apparently do not cause significant localized outgassing of carbon dioxide.

Surface To Volume Ratio – As indicated above, the transfer constant k is dependent on the surface–to–volume ratio (S/V = SVR) of the pool water. Since k varies directly with SVR, values for other pools can be calculated via the simple proportion:

$$k_1 SVR_2 = k_2 SVR_1$$

The value of SVR for the test pool was 0.28. The surface–to–volume ratio is actually equivalent to the reciprocal of the mean pool depth (where L = length, W = width, and h = average depth).

$$SVR = L \cdot W/(L \cdot W \cdot h) = 1/h.$$

Turnover Rate – It was seen that the transfer constant in the film diffusion model is a function of the diffusion coefficient (D) of carbon dioxide and the liquid film thickness (z). The latter varies with degree of mixing as discussed earlier. The degree of mixing is proportional to the turnover rate (TR) which is a function of the pump duty cycle (PDC, hours), the pumping rate (PR, gpm), and the volume (V, gal) of the pool.

$$TR = PDC \cdot PR \cdot 60/V \ day^{-1}$$

A plot of pH against time for different pump duty cycles is shown in Figure 5. Typically, residential pools achieve one turnover in about 8 hours. Based on the known volume of the test pool (6,800 gal) and the typical pumping rate of 35 gpm, the following equation is obtained for k as a function of turnover rate:

$$k = 0.0341 + 0.009 \cdot TR + 0.0016 \cdot TR^2 \ (ppm/day)^{-1}$$

The observed and calculated data are summarized in Table 3.

Effect Of Wind – Since the carbon dioxide exchange coefficient is a function of turbulence, it will be affected by wind velocity. However, weather bureau data was not available to evaluate its effect.

Effect Of Evaporation – In theory, evaporation of water can enhance carbon dioxide loss, however, the effect under normal conditions will be small. For example, evaporation of one inch of water from a 20,000–gal pool represents only 1.7% of the total volume. Typical evaporation rates in sunbelt locations average 50 to 60 inches per year. If this occurred during the six hottest months, it would amount to only about 2 inches per week.

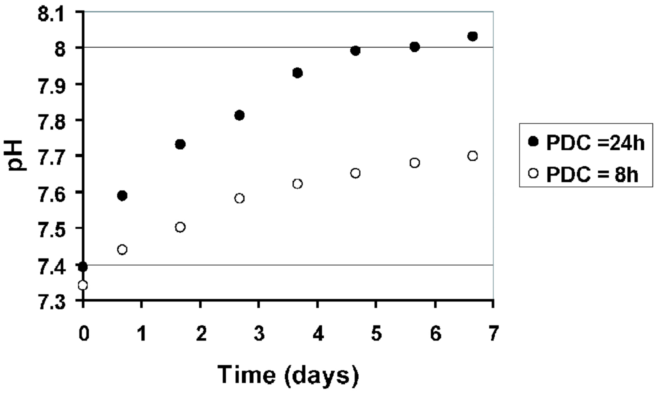

Figure 5 – Effect of Pump Duty Cycle (PDC) on Loss of Carbon Dioxide (CA = 69 ppm)

		Rate Constant (ppm/day)$^{-1}$	
PDC	**TR**	**Observed**	**Calculated**
0	0	0.034	0.034
8	2.47	0.066	0.067
16	4.94	–	0.12
24	7.41	0.19	0.19

Table 3 – Effects of Pool Turnover Rate on CO_2 Loss Rate Constant
Volume 6800 gal, T 82°F, TDS 1000 ppm

Effect Of Suspended Solids And Pool Surfaces – Suspended solids and swimming pool surfaces (including the filter) can in principle facilitate outgassing of carbon dioxide via heterogeneous nucleation of gas bubbles. However, the potential effects may be rather minimal, based on the small pH drift observed when the pool was covered but with the pump going continuously.

Effect of Bather Pollutants – The pH drift due to loss of carbon dioxide to the atmosphere will be offset only slightly by carbon dioxide formed by oxidation of organic matter by chlorine, since most organics are not mineralized (ie, converted to CO_2 and water) to a significant extent. Although urea is ultimately completely oxidized to carbon dioxide, the effect on pH drift will be small. It is estimated that on average, each bather introduces 739 mg of urea (mostly from urine and a small amount from sweat) into swimming pool water (Gunkel and Jessen 1986). For a bather load of four people/day in a 20,000–gal pool, this will result in a CO_2 formation rate of only 0.03 ppm/day.

Effect of Sanitizers – The pH drift will be modified according to the acidity or alkalinity of the sanitizer (Wojtowicz 1996). Trichloroisocyanuric acid (Trichlor) will have the greatest effect because it forms three mols of strong acidity (HCl) and one mol of weak acidity (CA) per mol. By contrast, calcium hypochlorite will have the least effect because it introduces only 0.19 mol alkalinity per mol.

General Equation For CO_2 Transfer Rate Constant – If one combines the three main parameters affecting the loss of carbon dioxide from an uncovered bather–free pool, i.e., temperature, surface–to–volume ratio, and turnover rate, the following general equation is obtained for calculating the carbon dioxide transfer constant:

$$k = (0.0341 + 0.009 \cdot TR + 0.0016 \cdot TR^2)(SVR/.28)(4296.4e^{-2516.36/T})\ (ppm/day)^{-1}$$

A computer program was written for calculation of the pH drift due to loss of carbon dioxide based on carbonic and cyanuric acid equilibria and the above equation.

Calculated pH drifts due to CO_2 Loss for Various Conditions – Calculated pH drifts due to carbon dioxide loss for a 20,000–gal swimming pool with an average depth of 6 feet, under various conditions at an initial pH of 7.5 are shown in Table 4. Alkalinity and turnover rate have the greatest effect on pH drift due to carbon dioxide loss. By contrast to turnover rate, which directly affects the carbon dioxide loss rate, the effect of alkalinity is due to its influence on the initial concentration of carbon dioxide. At a given pH, the initial carbon dioxide varies directly with alkalinity. Therefore, the higher the initial carbon dioxide the greater the carbon dioxide loss rate, and the greater the resultant pH drift. The increased buffer intensity of the higher alkalinity is masked because the carbon dioxide loss rate varies as

Parameter	Range	C. Alk	CA	TR	ΔpH/Week
Carb. Alkalinity	50–200 ppm		100	1	0.08–0.59
Cyanuric Acid	0–200 ppm	100		1	0.58–0.15
Temperature	70–90°F	100	100	1	0.22–0.25
Turnover Rate	0–3	100	100		0.19–0.32

Table 4. Calculated pH drifts due to CO_2 Loss for Various Conditions
V = 20,000–gal, T = 80°F, TDS = 1000 ppm, PDC = 8 h, PR = 41.7 gpm

Study	No. of Pools	% of Acid used due to CO_2 Loss
Florida 7,500–gal test pools	6	92
Florida residential pools	143	93
California residential pools	40	96

Table 5. Calculated CO_2 Loss Estimates from other Studies

the square of concentration, whereas buffering varies linearly with alkalinity. However, the effect of buffering on limiting the pH rise is evidenced by the effect of cyanuric acid at constant carbonate alkalinity. Temperature has a very small effect on CO_2 loss.

CO_2 Loss Estimates From Other Studies – Data from other studies involving residential pools in California (1979) and Florida (1981) as well as Florida test pools (1987 and 1988) indicate that the major portion of added acid is required to restore pH due to carbon dioxide loss as shown in Table 5.

Swimming Pool pH Control With Carbon Dioxide Gas – Since loss of carbon dioxide raises the pH of swimming pool water, it follows that treating the water with gaseous carbon dioxide will restore and maintain the pH in the desired range. This could be done automatically by means of a pH probe, controller, solenoid valve, and carbon dioxide cylinder. In a one–week experiment in the test pool, gaseous carbon dioxide from a cylinder was effectively used to make pH adjustments for pH drift due to carbon dioxide loss. It is worth noting that this method of pH adjustment conserves alkalinity, i.e., no alkalinity is consumed in the pH adjustment. By contrast, pH adjustment with pool acid results in a decrease in alkalinity of 5.3 ppm/lb of 32% HCl added to a 10,000–gal pool.

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