The Addition of Muriatic Acid

Results and Implications of Using Varied Methods of Muriatic Acid Application in Swimming Pool Water

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The lowering of Total Alkalinity (TA) and/or pH in swimming pools utilizing muriatic acid has been an accepted procedure in the pool industry for many decades. The reactions involved have been documented and published in widely available texts.

Recently, however, a myth has been seeping into the literature and into chemistry seminars provided to service personnel. This particular myth is that different methods of acid application have the effect of producing different amounts of alkalinity and pH reduction in the pool. This paper demonstrates the fallacy of this myth.

In recent years a myth has developed in the service industry regarding the most effective methods of acid addition for "maximum" efficiency. The basic concept concerns the idea that the manner in which acid is introduced to the water influences the amount of pH vs. alkalinity reduction.

The methods promoted are as follows:

For the reduction of pH, it is recommended the acid be "trickled" into the water while walking around the perimeter of the pool. It is maintained, according to those who promote the myth, that by thus trickling in the acid, pH will drop, but the alkalinity in the pool will be only slightly affected.

For the maximum reduction of alkalinity, it is recommended that the acid be poured into a single location in such a manner as to create what is variously referred to as a "column", "well", or "cloud" of water with an extremely low pH. It is theorized that when a relatively small volume of water is lowered in pH to levels below 5.5 (or 4 or lower depending on the source), carbonates (CO_3) are converted directly into gaseous carbon dioxide (CO_2).

Anecdotal evidence refers to gas bubbles or vapor forming near where the acid was added, with the inference that the bubbling/vapor is CO_2.

Recommendations vary as to the optimum method of concentrated acid addition because of the need to protect the interior pool surface and the filtration system from the effects of such low pH ranges. Although most recommend acid addition in the deep end, some recommend adding the acid with the circulation system on, while others recommend turning the system off. It is suggested that swimming pool acid (i.e., 31.45% muriatic acid) can be added in such a concentrated fashion without it coming into detrimental contact with the interior surface or filter system.

Based on the diversity of authors and publications involved, the myth is spreading and gaining acceptability at a rapid pace. Yet examination of the claims show that they do not make sense.

Acid Column Claim: While pouring acid in a localized area, the pH is lowered dramatically in a localized column of the pool water. Yet the claim is that once this low pH column of water mixes in, this acid addition will somehow not significantly lower the pH of the entire pool! Also, somehow the alkalinity of the entire pool will be significantly (or extraordinarily) reduced – reduced by an amount above and beyond what that given amount of acid would normally provide when added by a different method! We are to understand that this skewed effect is somehow – by means of chemical shortcuts – associated with a CO_2 gas–off from the affected column and a hypothetical direct conversion of carbonate to carbonic.

Acid Dilution Claim: When trickling in diluted acid around the pool, the pH of a localized area of water is not lowered significantly; rather, a gradual

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reduction of the pH is achieved throughout the pool. Yet the claim is that, after mixing, this method will lower the pH of the entire pool water more dramatically, or more effectively than when a column is used! In addition, it is claimed that very little alkalinity reduction will result from this method of application. Somehow we are to understand that the diluted, dispersed acid does not affect the alkalinity level of the pool the same way acid in a concentrated, localized form would.

Origins of the Acid Column Myth

The acid column myth, as near as can be ascertained, originated with a pool serviceman, and was spread through the service trade organizations. The serviceman observed what he thought were different results from pouring acid into pools, consistent with the methods summarized above. It appears that someone subsequently attempted to develop a chemical rationale for the supposed phenomenon without actual field testing, which, incidentally, would have shown that conclusions drawn from the original observations were in error. Since the phenomenon in reality does not occur, the chemical rationale is also incorrect, and will be shown to be impossible in this paper. To demonstrate the fallacy of the myth, basic alkalinity and pH reactions, the solubility of carbon dioxide, and Henry's Law must be understood. The following points are key issues that will be addressed:

1. In most swimming pools, there is essentially no alkalinity in the carbonate form. There is virtually *no carbonate alkalinity below pH 8.3.*
2. Any reduction of alkalinity below pH 8.3 converts bicarbonate to CO_2.
3. Dissolved CO_2 does not contribute to alkalinity since it is an acid.
4. At normal pool operating temperatures and in the absence of aeration, there is never enough bicarbonate in the water to cause the formation of CO_2 bubbles.
5. Areas of low pH do not foster any increased tendency for CO_2 offgassing.

Alkalinity, pH and Carbon Dioxide

The basic chemistry involved in the acid reduction of alkalinity and pH in swimming pools is as follows:

[Please note that there are more detailed reactions taking place, but that simplified versions of these reactions are used for clarity and are consistent with simplifications used in swimming pool chemistry texts. The symbols and equations used represent components of, and changes in the water, but are not meant to be inclusive of every component or change.]

Present in water is alkalinity. There are primarily three types: bicarbonate (HCO_3^-), carbonate ($CO_3^=$), and hydroxide (OH^-), also known as hydroxyl.

With the pH range of pool water normally maintained from 7.2 to 8.2, bicarbonate will generally be the only significant type present. While it may be possible to have a very small percentage of carbonate alkalinity exist at these pHs, it begins to be more prevalent at pHs above 8.3. This is due to the fact that dissolved CO_2 in water reacts with carbonate and hydroxide alkalinity, and converts them to bicarbonate.

When adding acid, hydrogen ions (H^+) are added to the water. The addition of these hydrogen ions will lower the pH and decrease the alkalinity by the following process: acid will react with the carbonate alkalinity (if present) to form bicarbonate alkalinity ($CO_3^= + H^+ \rightarrow HCO_3^-$). Hydrogen ions also react with the bicarbonate ions in solution to form carbonic acid. ($HCO_3^- + H^+ \rightarrow H_2CO_3$) Carbonic acid is simply dissolved CO_2 in water ($H_2CO_3 \rightleftharpoons CO_2 + H_2O$). The pH is lowered because, by definition, the greater the hydrogen ion concentration, the lower the pH. The alkalinity is lowered because once bicarbonate alkalinity receives a hydrogen ion, it becomes carbonic acid (dissolved CO_2) and ceases to be alkalinity in any form. These reactions are instantaneous. Overall changes in the pool are not a result of reaction time, but are rather a function of the process variously referred to as mixing or blending, which may be accelerated by circulation.

The acid column myth states that a low pH of 5.5 or 4.0 (depending on the source) is required for maximum "<u>production</u>" of carbon dioxide. However, bicarbonate alkalinity is transformed into carbonic acid (by hydrogen ions) in normal pool pH ranges (7.2 to 8.2). If enough acid is added, the pH will begin to descend below 7.2 as more CO_2 is formed, but the "production" of carbon dioxide occurs at any pH below 8.3, and is not dependent on low pHs for "maximum" production. Also, some proponents of the acid column method believe that a very low pH is necessary to convert carbonate alkalinity directly to carbon dioxide. They claim that if the pH is not lowered sufficiently, the carbonate alkalinity will only be converted into the bicarbonate form, resulting in no reduction of alkalinity. This claim is apparently based on the belief that carbonate and bicarbonate alkalinity are of equal quantitative measure. However, this is not true. Carbonate alkalinity has double the quantitative measure as does bicarbonate alkalinity. The carbonate ion must accept two hydrogen ions as compared to one accepted by the bicarbonate ion to be converted into carbonic acid ($CO_3^= + 2H^+ \rightarrow H_2CO_3$ and $HCO_3^- + H^+ \rightarrow H_2CO_3$). Once the carbonate ion has accepted (only) one hydrogen ion, it becomes bicarbonate and at that point it is of equal quantitative measure to any other bicarbonate alkalinity ($CO_3^= + H^+ \rightarrow HCO_3^-$). The carbonate ion cannot be converted directly to carbon dioxide. Again, it must first be converted to bicarbonate and then into carbonic acid – which requires two hydrogen ions ($2H^+$). The difference in quantitative measure between bicarbonate and carbonate is illustrated by the fact that soda ash added to pool water increases alkalinity about 60% more than sodium bicarbonate. (Which also seems to be misunderstood by some in the service industry).

There are no shortcuts. Since no unique species or combinations of chemicals occur when water has stabilized after an acid addition, how can abnormal changes in alkalinity occur? The hydrogen introduced to the water via the muriatic acid will have a predictable effect regardless of the method of introduction. A specific amount of acid will convert a specific amount of bicarbonate alkalinity into a specific amount of carbonic acid.

Henry's Law

After the addition of acid to a pool with a pH lower than 8.3, carbonic acid is formed, increasing the concentration of CO_2 in the water. With this higher concentration, the potential for CO_2 (from carbonic acid) at the water's surface to begin to dissipate into the atmosphere also increases. This process is predicted by Henry's Law, which states that "the concentration of a dissolved gas is proportional to the gas pressure above the liquid ($C = k \cdot P_{gas}$)". Petrucci notes that "equilibrium between the gas above and the dissolved gas within a liquid is reached when the rates of evaporation and condensation of gas molecules become equal," and that pH does not affect the solubility of CO_2 in H_2O. (Petrucci 1982) If dissipation occurs, free CO_2 is removed, leaving water behind ($H_2CO_3 \rightleftharpoons CO_2\uparrow + H_2O$). The pH of the pool water increases as a result of the CO_2 loss. If, however, *insufficient* CO_2 is in the water, Henry's law predicts that CO_2 from the atmosphere will dissolve into the water until equilibrium is reached, thereby increasing the water's carbonic acid level (soluble CO_2) and decreasing pH. The potential for either of these things to occur is dependent on the total CO_2/H_2CO_3 concentration at the water's surface. Air always has some carbon dioxide present, about .04% (the *Merck Index* cites atmospheric CO_2 levels in earth's temperate zones at 0.027 – 0.036% – Merck 1993), and according to *Standard Methods for the Examination of Water and Wastewater* (AWWA 1992), surface waters normally contain <10 ppm dissolved CO_2. Henry's Law predicts that the equilibrium concentration of CO_2 in water at room temperature would be 0.64ppm:

0.64ppm = 1600ppm (CO_2 solubility) times $4 \cdot 10^{-4}$

(volume fraction of CO_2, or .04% divided by 100)

This CO_2 gas exchange process is ongoing in a pool environment, both because of frequent chemical additions affecting the balance, and because of the fact that gas release only occurs at the surface of the water (where the CO_2–rich or CO_2–poor water is in contact with atmospheric CO_2) – a slow phenomenon. As CO_2 dissipates from the water at the surface, a general CO_2 dilution process occurs, equalizing the dissolved CO_2 level of the entire pool. This process continues as long as the natural equilibrium is not achieved. If full equilibrium in a plaster pool were ever to be reached, the resulting pH will be at a natural level of about 8.0 to 8.3. (The carbonic/bicarbonate buffer pH level = 6.4. The bicarbonate/carbonate buffer pH level = 10.2. When the primary alkalinity species is bicarbonate and little or no dissolved CO_2 is present the pH will approach the midpoint, which is 8.3.)

The acid column theory states that when adding acid, the pH must be reduced to 5.5 or 4.0 or lower (depending on which source is consulted) to achieve maximum "release" of carbon dioxide, which in turn reduces the alkalinity. This concept is false for two reasons. First, excess carbon dioxide (from carbonic acid) will, over time, release into the air regardless of the pH, as predicted by Henry's Law. It is not necessary to have a pH of 5.5 or 4.0 or below to accomplish this. Second, as indicated earlier, even if excess carbonic acid (or carbon dioxide) is present in water, it is not in any form of alkalinity and will not titrate out as any kind of alkalinity. Carbonic acid will not revert back into alkalinity unless a base (alkaline) material such as soda ash is added to the water. Therefore, there is no need to remove carbon dioxide from the water to achieve the desired results of lowering alkalinity. Stumm et al. note that "Alkalinity does not change as a result of CO_2 loss... The case of the addition or removal of dissolved carbon dioxide is of particular interest... Any increase in carbon dioxide...increases both the acidity of the system and the total concentration of dissolved carbonic species. Unlike the case for the addition of strong acid, however, alkalinity remains unaffected by increases or decreases in $[H_2CO_3]$." (Stumm et al. 1981).

The Solubility of Carbon Dioxide

The acid column theory deals with the idea that, given a sufficiently low pH, CO_2 will *immediately* escape the pool by gassing off, or forming bubbles of free carbon dioxide which rise and escape from the pool. However, for CO_2 to gas off in any location of the pool other than directly on the surface, "free CO_2" must reach a sufficient concentration to no longer be soluble; i.e. to be in sufficient concentration to form a bubble at the column location. According to the Merck Index

(Merck 1993) the solubility of carbon dioxide at 20°C is 88 ml CO_2/100 ml H_2O. The molar volume of CO_2 at 0°C (volume occupied by 44g CO_2) = 22.4 L. Using the Ideal Gas Law (Charles' Law) at 20°C the molar volume is 22.4 L times 293°K ÷ 273°K, or 24 $^{L}/_{mole}$. The vapor density is 44 $^{g}/_{mole}$ ÷ 24 $^{L}/_{mole}$ = 1.83 $^{g}/_{L}$. The weight of 88 ml = (.088)(1.83) = 0.161g. This 0.161g ÷ .1L = 1.6$^{g}/_{L}$, or 1600$^{mg}/_{L}$ or 1600ppm. The unlikelihood of a carbon dioxide concentration exceeding this 1600ppm solubility level is best understood by considering the following fact: if **all** of the alkalinity in the pool were somehow converted to CO_2 (assuming a starting point of 250 ppm bicarbonate alkalinity and a pH of 8.3) the CO_2 level would be... 220 ppm! (Calculation 1). The muriatic acid contains no CO_2, so the only available source of CO_2 is (a) the alkalinity and (b) any existing dissolved carbon dioxide, which would be minimal (see the discussion of Henry's Law). This level of CO_2 is so far below the 1600 ppm saturation level of carbon dioxide that it would be virtually impossible for a CO_2 bubble to form. If, as mandated by the acid column parameters, only that water volume in the localized acid column is affected by the low pH, only that volume is available to contribute to the gas–off. This restricts even further the amount of CO_2 available to form the hypothetical bubbles. How then can a low pH restricted to a localized area of the pool be expected to generate enough CO_2 to form bubbles? It can't.

If no CO_2 is gassed off, all components of the equation are still present, and those constituents *must* reach their normal equilibria and result in the *same* changes in pH/alkalinity, regardless of how they are introduced to the pool. If CO_2 *is* lost, either via a surface or acid column gas–off, *still* the components remaining *must* arrange themselves according to established equilibria. The only difference between the two possibilities is the change in pH due to the loss of CO_2 – there can be no difference in the amount of alkalinity decrease.

Chemical Scenarios

An examination of several possible scenarios may be instructional at this point. Scenario A shows the chemical effect if the acid column theory were correct, and Scenario B shows the correct (i.e. actual) result. Scenario C shows the effect of acid addition by dilution. The total volume of the pool, for this exercise, is assumed to be 20,000 gallons, with a starting pH of 8.3 and a starting alkalinity of 250 (i.e., pH and alkalinity sufficiently high as to warrant the addition of the acid).

Scenario A An acid column is successfully created in the water, where the pH is 4.0 in the column. ***All** of the CO_2 in the affected area gasses off from that region*, and then the circulation system blends the water in the entire pool. What are the resultant pH and alkalinity changes in the region, and subsequently in the entire pool?

If 2 quarts of muriatic acid were added to 20,000 gallons with a starting alkalinity of 250ppm as $CaCO_3$ the maximum volume that can be reduced to 0 alkalinity (ca. pH 4.6) by this addition is about 1000 gallons. (see Calculation 2) However, since the lowest quoted pH requirement for "maximum" CO_2 production is 4.0 the total volume of water that could be reduced to pH 4 by this addition is slightly less, approximately 990 gallons.

If all of the CO_2 in this 990 gallon region were quickly released as gas in the form of CO_2 bubbles, the pH of the water in this region would increase to approximately 4.3. The pH of the acid column region would increase because of the loss of some acid (carbonic acid, or dissolved CO_2). It would only increase to 4.3 because of the excess muriatic acid left over in this region.

As the decarbonated water mixed with the remaining untreated pool water the excess muriatic acid (approx. 1% of the original amount added) would be

$$\frac{250}{(100.09\text{g } CaCO_3/_{mole})(1000\ ^{mg}/_{L})} = 0.0025 \text{ moles } CaCO_3$$

(note that at pH 8.3 and lower alkalinity is bicarbonate...)

$CO_3^{=} + H_2CO_3 \rightarrow 2HCO_3^{-}$

0.0025 moles of $CaCO_3$ gives 2(0.0025) = 0.005 moles HCO_3^{-}

0.005 moles $HCO_3^{-} \rightarrow$ 0.005 moles CO_2

$(0.005)(44^{g}/_{eq}\ CO_2)(1000^{mg}/_{g})$ = 220 ppm CO_2

Calculation 1 – The amount of CO_2 available from the neutralization of 250 ppm alkalinity

The total amount of acid in 2 quarts muriatic =

$$\frac{(2\ \text{qts})(.946\ ^{L}/_{qt})(.3145\ \%\text{HCl})(1.16\ \text{spec. grav.})(1000\ ^{g}/_{kg})}{36.46\text{g}\ ^{HCl}/_{mole}} = 18.93\ \text{moles}$$

Since $2HCl + CaCO_3 \rightarrow CaCl_2 + H_2CO_3$

$$(18.93\ \text{moles HCl})\ \frac{1\ \text{mole}\ CaCO_3}{2\ \text{moles HCl}} = 9.47\ \text{moles}\ CaCO_3\ \text{can be neutralized by 2 quarts}$$

If water contains 250ppm $CaCO_3$, each gallon contains

$$\frac{(250\text{mg}\ CaCO_3/_{L})(3.785\ ^{L}/_{gal})}{(100.09\text{g}\ CaCO_3/_{mole})(1000\ ^{mg}/_{L})} = 0.00945\ \text{moles}\ CaCO_3\ \text{in each gallon}$$

$$\frac{9.47}{.00945} = 1002, \approx 1000\ \text{gallons}$$

Calculation 2 – Amount of water that can be lowered to 0 alkalinity with 2 quarts muriatic acid

(From Calculation 2 we see that 9.47 moles $CaCO_3$ can be neutralized by 2 quarts, and that at 250ppm alkalinity each gallon contains 0.00945 moles $CaCO_3$.)

$$\frac{(250\text{ppm TA})(9.47\ \text{moles}\ CaCO_3\ \text{reduction by 2 qts})}{(0.00945\ \text{moles}\ CaCO_3/_{gal})(20{,}000\ \text{gallons})} = 12.5$$

Calculation 3 – Alkalinity reduction in 20,000 gallons by 2 quarts acid

neutralized by the remaining alkalinity in the yet untreated portion of the pool. After the alkalinity in an additional 10 gallons of water was reduced to 0, the remaining acid would be gone. After the neutralized water mixed with the rest of the pool water the final alkalinity would be 237.5 (as $CaCO_3$) (see Calculation 3). The amount of dissolved CO_2 in the water would be the equivalent amount of CO_2 available in the remaining 10 gallons of water neutralized after the offgassing of CO_2 in the acid column, which, after blending, would be 0.11 ppm. The final pH of the solution would be approximately 8.3.

If this process were possible, as the acid column theorists maintain, the effect they predict is “dramatic” or “maximum” alkalinity reduction with little pH reduction. Yet, contrary to the theory's pH prediction, in this scenario, the test pools which will be described later showed *predictable* alkalinity reduction and *full* pH reduction when employing the acid column addition method.

Scenario B An acid column is successfully created in the water, where the pH is 4.0 in the column. ***None*** *of the CO_2 in the affected area gasses off from that region*, and then the circulation system blends the water in the entire pool. What are the resultant pH and alkalinity changes in the region, and subsequently in the entire pool?

If the acid were added, and *none* of the CO_2 in the 990 gallon region of pH 4 were offgassed, the excess acid remaining in solution would react and neutralize another 10 gallons of water. Of course, this is what in reality occurs since a total CO_2 concentration of 220ppm is far below the solubility limit of CO_2 of 1600ppm (Merck 1993). As the water mixed the resultant alkalinity would be 237.5 (see Calculation 3), the concentration of dissolved CO_2 would be 220 times $^{1000}/_{20,000}$ or 11ppm, and the resultant pH decrease would be 0.6 pH

Assuming a starting pH of 8.3 and an alkalinity of 250, the pH reduction from the addition of the 2 quarts of acid may be calculated.

Amount of CO_2 available from neutralization of 250 ppm alkalinity:

$$\frac{250}{(100.09\text{g } CaCO_3/_{\text{mole}})(1000\ ^{\text{mg}}/_{\text{l}})} = 0.0025 \text{ moles } CaCO_3$$

(note that at pH 8.3 and lower alkalinity is bicarbonate...)

$CO_3^{=} + H_2CO_3 \rightarrow 2HCO_3^{-}$

0.0025 moles of $CaCO_3$ gives 2(0.0025) = 0.005 moles HCO_3^{-}

0.005 moles $HCO_3^{-} \rightarrow$ 0.005 moles CO_2

$(0.005)(44^{\text{g}}/_{\text{eq}}\ CO_2)(1000^{\text{mg}}/_{\text{g}}) = 220 \text{ ppm } CO_2$

when bicarbonate is dissolved $HCO_3^{-} + H_2O \rightleftharpoons H_2CO_3 + OH^{-}$

$$k_b = \frac{[H_2CO_3]+[OH^-]}{[HCO_3^-]} = 10^{-7.6} = \frac{k_w}{k_a}$$

base dissociation reaction with $k_b = k_w/k_a$ $\quad k_a = 10^{-6.4}$ $\quad k_w = 10^{-14}$

$k_b = 10^{-7.6} = 2.5\text{x}10^{-8}$

after addition of 2 quarts acid $\quad [HCO_3^-] = 237.5\text{ppm}$

$$\frac{2(237.5)}{(100.09)(1000)} = .00475$$

$[H_2CO_3] + [HCO_3^-] = .005$

$[H_2CO_3] = .005 - .00475 = .00025 = 2.5\text{x}10^{-4}$

$$\frac{k_b[HCO_3^-]}{[H_2CO_3]} = [OH^-] = \frac{(2.5\text{x}10^{-8})(0.00475)}{2.5\text{x}10^{-4}} = 4.75\text{x}10^{-7}$$

$$[H^+] = \frac{k_w}{[OH^-]} = \frac{10^{-14}}{4.75\text{x}10^{-7}} = 2.1\text{x}10^{-8}$$

$\text{pH} = -\log 2.1\text{x}10^{-8} = 7.7$

Calculation 4 – pH reduction in 20,000 gallons by 2 quarts acid

units, resulting in a final pH of 7.7 (see Calculation 4).

This is what actually happened in the test pools (described later) when the acid column addition method was used. Note the discrepancy between this scenario and the results predicted by the acid column theorists (as in Scenario A) – the alkalinity reduction is identical with the acid column predicted reduction, but the full expected pH reduction agrees with that of the test pools, not that of Scenario A.

Scenario C Acid is added to the water via dilution and distribution, therefore the pH never drops below 7.0 at any location in the pool. ***None*** *of the* CO_2

in the pool gasses off, and then the circulation system blends the entire pool water. What are the resultant pH and alkalinity changes in the pool?

If the acid were added slowly, the total reduction of alkalinity would be equivalent to the amount of acid added. After mixing the resultant alkalinity would be 237.5 (see Calculation 3). The total possible amount of dissolved CO_2 would be 11ppm, and the lowest possible final pH would be 7.7 (see Calculation 4).

This is what actually happened in the test pools when the dilution/distribution method was employed. Note the discrepancies between this scenario and the results predicted by the acid column theorists. They claim that this method is for lowering pH, and will not produce conditions needed for total alkalinity decrease. They also predict that with this addition method, full pH reduction should occur, with the alkalinity reduction being "slight" or insignificant. Yet the calculations predict full reduction of both pH *and* alkalinity, and that is what happened in the test pools (described later).

In all cases, as the dissolved CO_2 equilibrates with the atmosphere the pH will gradually rise toward 8.3 as any excess dissolved CO_2 (carbonic acid) is slowly removed.

These scenarios, with the accompanying documentation in the calculations, illustrate the fact that the alkalinity reduction will be the same *regardless of the application method*, and also *regardless of whether CO_2 offgassing occurs*. Alkalinity reduction is not properly referred to with relative terms such as "optimum". The proper terms would be "predictable" and "constant", independent of application method. On this point the acid column/acid distribution theorists are incorrect regardless of the CO_2 solubility issue. Scenario A has been shown to be impossible, and the results for Scenarios B and C are identical. Scenarios B and C, with the accompanying proofs, also are totally consistent with actual field results in both test pools. This is what sound theory predicts as well as what is experimentally observed. This fact, coupled with the above–mentioned facts relative to CO_2 solubility, show that both the alkalinity and pH predictions of the acid column/acid dilution theorists are incorrect.

Controlled Testing

Initial field tests were conducted in Livermore, California in plaster pools, and it was verified that the alkalinity reduction was identical with both methods of adding acid. Additionally, the resulting pH decrease was also identical. Careful, independent experiments were then conducted in Tucson, Arizona in both an above–ground vinyl–lined pool and an in–ground plaster pool to verify the results under controlled, documented conditions. A pH meter with 3 submersible probes and datalogging equipment (described below) was used to verify low pH's as demanded by the acid column method. Initially the alkalinity and pH was increased with sodium bicarbonate, soda ash, and sodium hydroxide to create conditions where the addition of 2 quarts of acid would be a normal procedure. (These same chemicals were used subsequently between tests to reestablish test conditions.) The water was allowed to stabilize, and then the acid was added via the different methods. Tests were also conducted to determine the pH at the bottom of a non–circulating pool after concentrated acid has been added in a localized area.

The initial controlled testing (tests #1 – #6) was performed in a vinyl–lined above–ground pool which, according to the dealer, had a manufacturer's stated volume of 13,000 gallons of water. Acid applications were conducted using various methods of application. Each method of application was tried twice in the vinyl pool and once in the plaster pool (tests #7 – #9) to verify repeatability of the results.

Chemical calculations previous to the first acid addition indicated that the amount of alkalinity decrease expected in 13,000 gallons of water by the addition of 2 quarts of muriatic acid would be about 19¼ ppm. In actuality, all 6 tests resulted in an alkalinity decrease of 18 ppm. Subsequent measurement of the pool showed that the installer had hollowed out a bowl in order to install an effective main drain. With this taken into account, the calculated volume (Diameter • Diameter • Average Depth • 5.9) was 13,900. This adjustment led to the development of the "Note on Calculating Pool Volume" in the Alkalinity Dosages paper published in the previous volume of *JSPSI* (Skinner and Hales 1995).

The plaster pool had a volume of 11,400 gallons, and in that pool the decrease in alkalinity was 22 ppm with all three methods of application.

Experimental Methods

Testing was conducted in two ways. In order to verify that the pH did indeed drop to the required levels, submersible pH probes were inserted into the pool in three locations. These probes were wide–range combination electrodes with silver/silver chloride references. Probe 1 was located 18" above the main drain, probe #2 was located directly on the main drain, and probe #3 was located in the hair/lint strainer (pump pot). The probes were connected to a Model 600 Electronic pH recorder and data logger, manufactured by Kruger & Eckels. The Recorder/data logger was custom manufactured specifically for this type of testing by, and after consultation with Gerald Eckels. The probes were set to sample pH at 30 second intervals and values were directly downloaded into a computer graphing software package designed for the datalogger.

The second method of testing involved the collection of sample water from approximately 18" below surface and 18" from the edge, previous to the acid application. This water was tested for pH, Total Alkalinity, Total Hardness, Calcium Hardness, Total Dissolved Solids, Iron, Copper, Chlorine, and Cyanuric Acid at the Pool Chlor lab approximately ½ mile from the test site, with testing beginning 5–10 minutes after sampling. Subsequent to the acid application, pH and alkalinity were tested twice daily for three days. Testing protocols were as follows:

pH – Electronic meter measurement utilizing a Kruger & Eckels Model 100 pH meter coupled to a wide range combination electrode with a silver/silver chloride reference. Accuracy +/– .05 pH units

Total Hardness – .01 M EDTA buret titration utilizing Eriochrome Black T as indicator and an EDTA magnesium precipitator. The result is recorded as mg/L as Calcium Carbonate ($CaCO_3$). Accuracy +/– 2 mg/L (ppm)

Total Calcium Hardness – .01 M EDTA buret titration utilizing Murexide as indicator and an NaOH solution for pH adjustment (magnesium precipitation). The result is recorded as mg/L as Calcium Carbonate ($CaCO_3$). Accuracy +/– 2 mg/L

Hardness – Calcium – The percentage of Total Hardness present as Calcium Hardness.

Total Alkalinity – 0.0200 N HCl buret titration using a pH 4.6 endpoint as measured by the pH meter described above. The result includes carbonate, bicarbonate, and hydroxide alkalinity, and is recorded as mg/L as Calcium Carbonate ($CaCO_3$). Accuracy +/– 2 mg/L

Total Dissolved Solids – Electronic meter measurement using a Myron L Model 512 DS meter. Range 0 – 2500 Accuracy +/– 50 mg/L, Range 0 – 5000 Accuracy +/– 100 mg/L

Total Iron – Electronic meter measurement using Hach Model DR–100 colorimeter utilizing the 1,10–phenanthroline method. The result is recorded as mg/L as iron (Fe). Range 0 – 2.0 mg/L Accuracy +/ – .05 mg/L

Total Copper – Electronic meter measurement using Hach Model DR–100 colorimeter utilizing the bicinchininate method. The result is recorded as mg/L as copper (Cu). Range 0 – 3.0 mg/L Accuracy +/– .05 mg/L

Total Chlorine – Iodometric buret titration using 0.0025 N Sodium Thiosulfate as titrant, sulfamic acid for pH adjustment, and potassium iodide and starch as color indicators. The result is recorded as mg/L as total chlorine (Cl), and includes both free and combined forms. Accuracy +/– .1 mg/L

Cyanuric Acid – Melamine precipitation column turbidity test using Aquality cyanuric acid test kit. The result is recorded as mg/L as cyanuric acid. Range 0 – 100 Accuracy +/– 10 mg/L

Temperature – Glass sealed mercury thermometer. Range 0 – 120° Fahrenheit Accuracy +/– 1 ° F.

Nine tests were performed under closely controlled conditions in order to document results from the various methods of acid addition. The methods and locations were:

#1 – Acid Column – aboveground vinyl pool
#2 – Dilute & Distribute – aboveground vinyl pool
#3 – Acid Puddle – aboveground vinyl pool
#4 – Acid Column – aboveground vinyl pool
#5 – Dilute & Distribute – aboveground vinyl pool
#6 – Acid Puddle – aboveground vinyl pool
#7 – Acid Column – inground plaster pool
#8 – Dilute & Distribute – inground plaster pool
#9 – Acid Puddle – inground plaster pool

#1, #5, #9 In the first application method (acid column method) the muriatic acid (with dye added) was poured into the pool undiluted at a single surface location in a short amount of time with the filtration/circulation system turned on. Acid was poured in the deep end of the pool so that probe #2 would verify the pH of the "acid column". The dye verified the flow and pH of the acid (a pH–sensitive dye, the sodium salt of phenol red, was used at a concentration of approximately 2 grams per quart). **Full pH and alkalinity reduction occurred using this method in each of the three repetitions.** Although a definite "acid column" (pH lower than 4.0 in a localized, defined area) was created, at no time were there visual bubbles or effervescence. A copy of the Lab Water Analysis for test #1 is provided in Figure 1. A composite pH graph of these three tests is provided in Graph 1.

#2, #4, #7 In the next application method (dilute & distribute method) the dyed acid was poured into a five gallon bucket containing 3 gallons of pool water. This solution was then gently agitated for mixing, and then, with the system running, the acid was dribbled into the pool approximately 18" from the edge, while walking a complete circuit of the perimeter of the pool. **Full pH and alkalinity reduction occurred using this method in each of the three repetitions.** A copy of the Lab Water Analysis for test #2 is provided in Figure 2. A composite pH graph of these three tests is provided in Graph 2.

#3, #6, #8 Since the second method represented a "best case scenario" of how acid may be added to a pool, a final application method (static concentrated, or acid puddle method) was used for contrast. The location of the probes remained the same. This time the dyed acid was introduced undiluted and in a single location at the deep end of the pool. The circulation system was left off for twenty minutes, and then turned on for the rest of the test period (three days). **Full pH and alkalinity reduction occurred using this method in each of the three repetitions.** Although a definite "acid puddle" (pH lower than 2.5 in the bowl of the pool) was created, at no time were there visual bubbles or effervescence rising from the puddle. A copy of the Lab Water Analysis for test #3 is provided in Figure 3. A composite pH graph of these three tests is provided in Graph 3. A set of photographs illustrating the "puddle" formation is provided in Figure 4.

Conclusions

Results of testing showed that both the alkalinity and pH reduction were virtually identical with all three methods of adding acid, once the pool water had been circulated for a few minutes. There was no practical result or valid chemical rationale for undiluted application of muriatic acid (either with the system on or off), and ample evidence that such application subjects both random, non–uniform areas of the pool surface, as well as the circulation system, to pH levels generally considered undesirable or damaging. Once the filter system was engaged, the amount of time required for the effect of the mixing/blending was measured in minutes regardless of the method employed, and full reduction and a homogenous water mass was always complete inside of 24 hours. For decades muriatic acid has been used as an efficient, inexpensive method of producing a desired reduction in pH/alkalinity, and testing showed that, if done properly (i.e. dilute and distribute with the water circulating), the optimum desired result will be achieved without subjecting any part of the surface or system to adverse conditions.

It may be instructive at this point to note that there are times when pool plaster is intentionally subjected to low pH levels – for example in the case of acid washing the plaster, either with the pool filled or drained. It is not the authors' contention that these processes are detrimental or invalid. The etching or acid–washing of the plaster surface to remove minerals or materials deposited on the surface is done *intentionally* by professionals using controlled procedures, with care taken to *uniformly* affect the pool

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Expressed as ppm

	Date / time	1:30pm	5:00pm	9:30am	2:00pm	1:00am
pH	pH meter reading	8.35	7.8	7.6	7.8	7.8
Total Hardness	$CaCO_3$	678				
Total Calcium	$CaCO_3$	452				
Hardness - Calcium	%Ca	66%				
Total Alkalinity	$CaCO_3$	228	210	212	212	210
Total Dissolved Solids	ppm	2200				
Total Iron	Fe	0				
Total Copper	Cu	.52				
Total Chlorine	Cl_2	0.44				
Total Cyanuric Acid	ppm	95				
Temperature	°F	62°				

Added 2 qts. muriatic acid, "column", or "roll-in" method w/ system on at 2:00 pm 11-10-93. System set for main drain suction only, ran continuously for the duration (3 days) of the test. Lowest observed pH in any part of the pool during any part of the process was 2.2 under area of application.

Figure 1 – "Acid Column" Lab Results – Test #1

Expressed as ppm

	Date / time	11/15 10:00am	11/15 4:30pm	11/16 10:00am	11/16 5:15pm	11/17 11:30am
pH	pH meter reading	8.05	7.4	7.5	7.6	7.6
Total Hardness	$CaCO_3$	672				
Total Calcium	$CaCO_3$	438				
Hardness - Calcium	%Ca	65%				
Total Alkalinity	$CaCO_3$	224	208	206	204	206
Total Dissolved Solids	ppm	2100				
Total Iron	Fe	0				
Total Copper	Cu	.375				
Total Chlorine	Cl_2	0				
Total Cyanuric Acid	ppm	100				
Temperature	°F	51°				

Added 2 qts. muriatic acid, “dilute & distribute” method w/ system on at 10:20 am 11-15-93. System set for main drain suction only, ran continuously for the duration (3 days) of the test. Lowest observed pH in any part of the pool during any part of the process was 7.2.

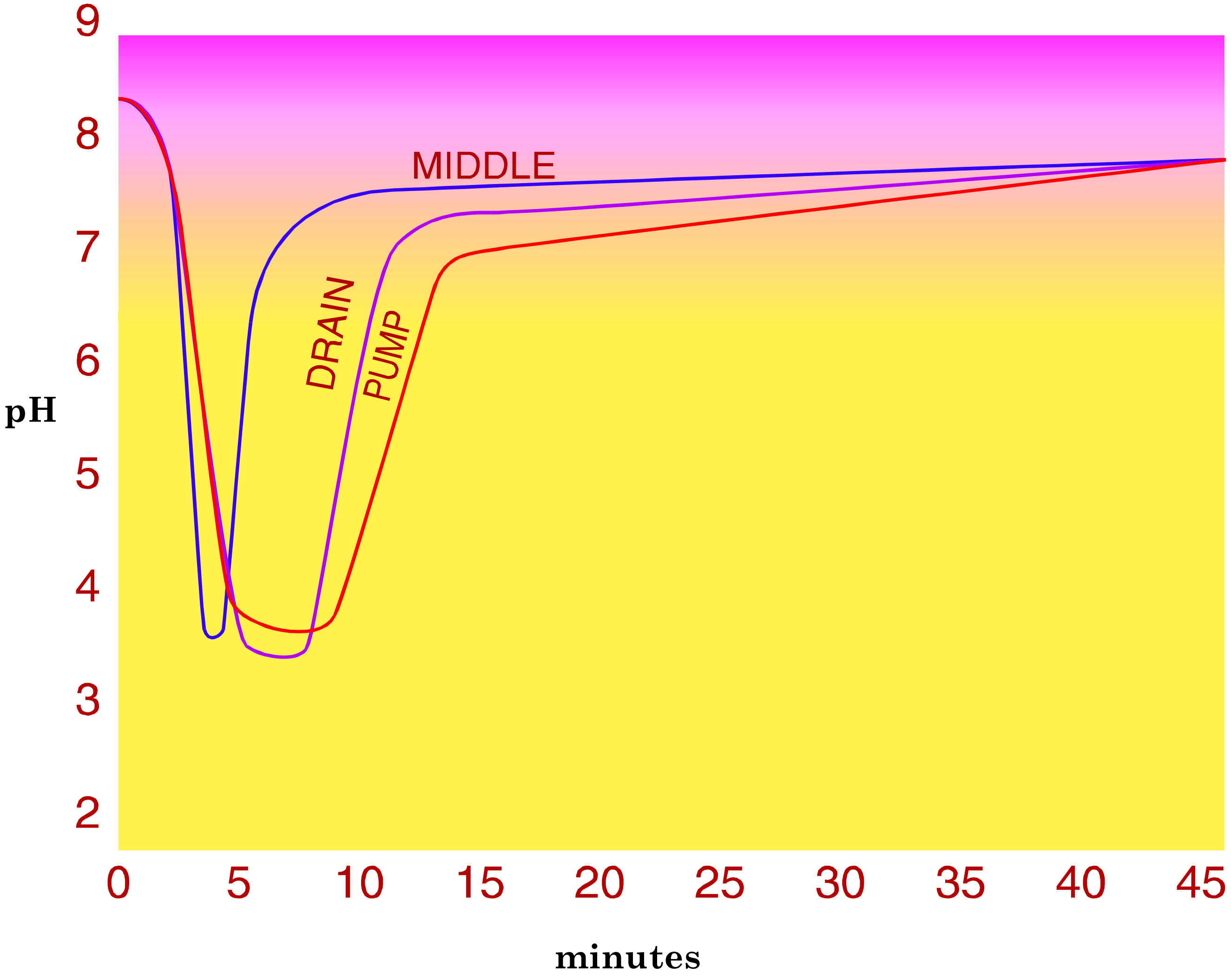
Figure 2 – “Dilute and Distribute” Lab Results – Test #2

Expressed as ppm

	Date / time	11/23 10:00am	11/23 3:00pm	11/24 9:30am	11/24 4:15pm	11/25 8:00am
pH	pH meter reading	8.3	7.65	7.9	7.95	8.0
Total Hardness	$CaCO_3$	674				
Total Calcium	$CaCO_3$	446				
Hardness - Calcium	%Ca	66%				
Total Alkalinity	$CaCO_3$	216	198	196	198	198
Total Dissolved Solids	ppm	2150				
Total Iron	Fe	0				
Total Copper	Cu	.45				
Total Chlorine	Cl_2	.27				
Total Cyanuric Acid	ppm	100				
Temperature	°F	57°				

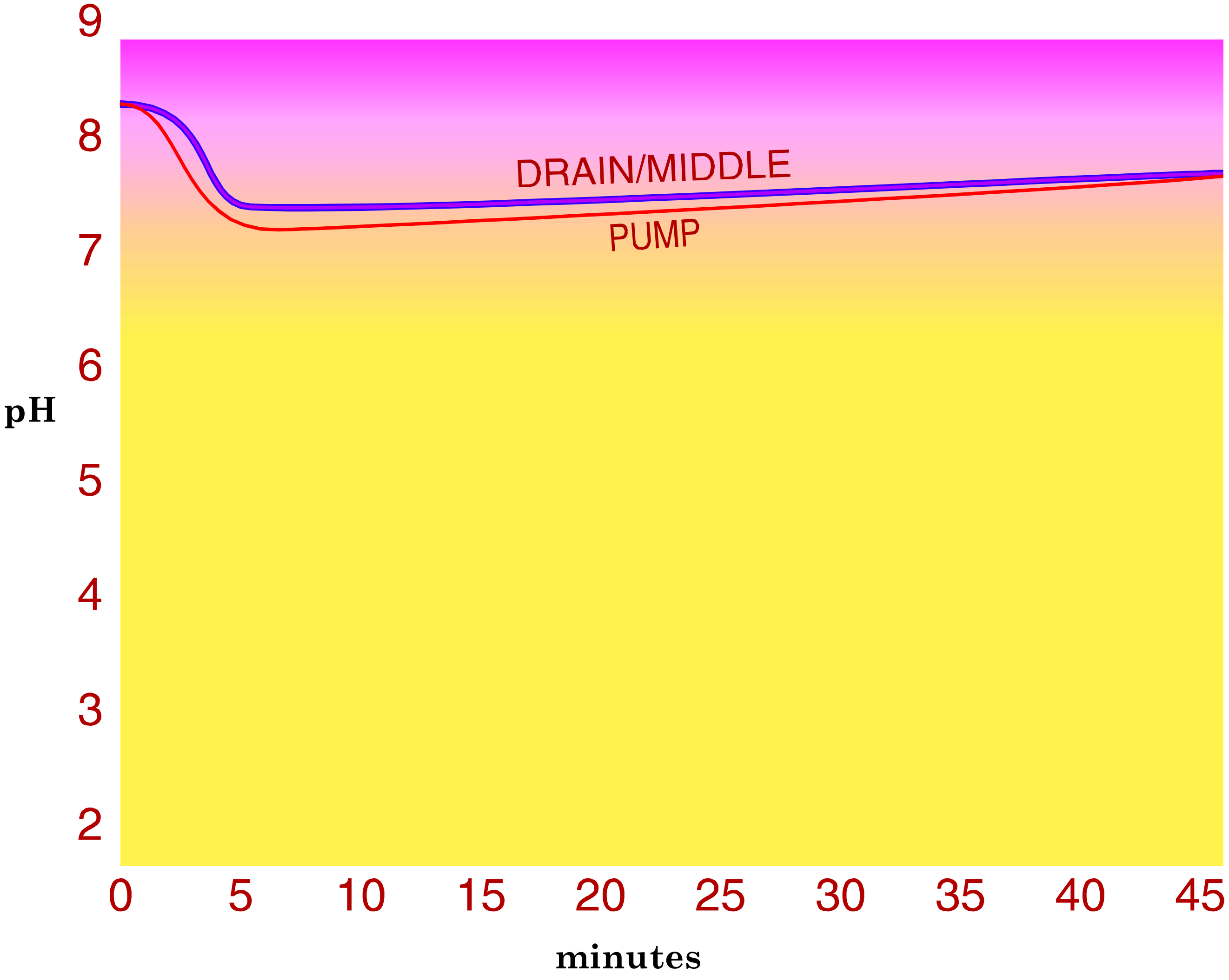
Added 2 qts. muriatic acid, “puddle” method w/ system off at 10:07 am 11-23-93. System set for main drain suction only, water static for first 20 minutes of the test, then system ran continuously for the duration (3 days) of the test. Lowest observed pH in any part of the pool during any part of the process was 2.1 on the bottom and in the main drain.

Figure 3 – “Acid Puddle” Lab Results– Test #3



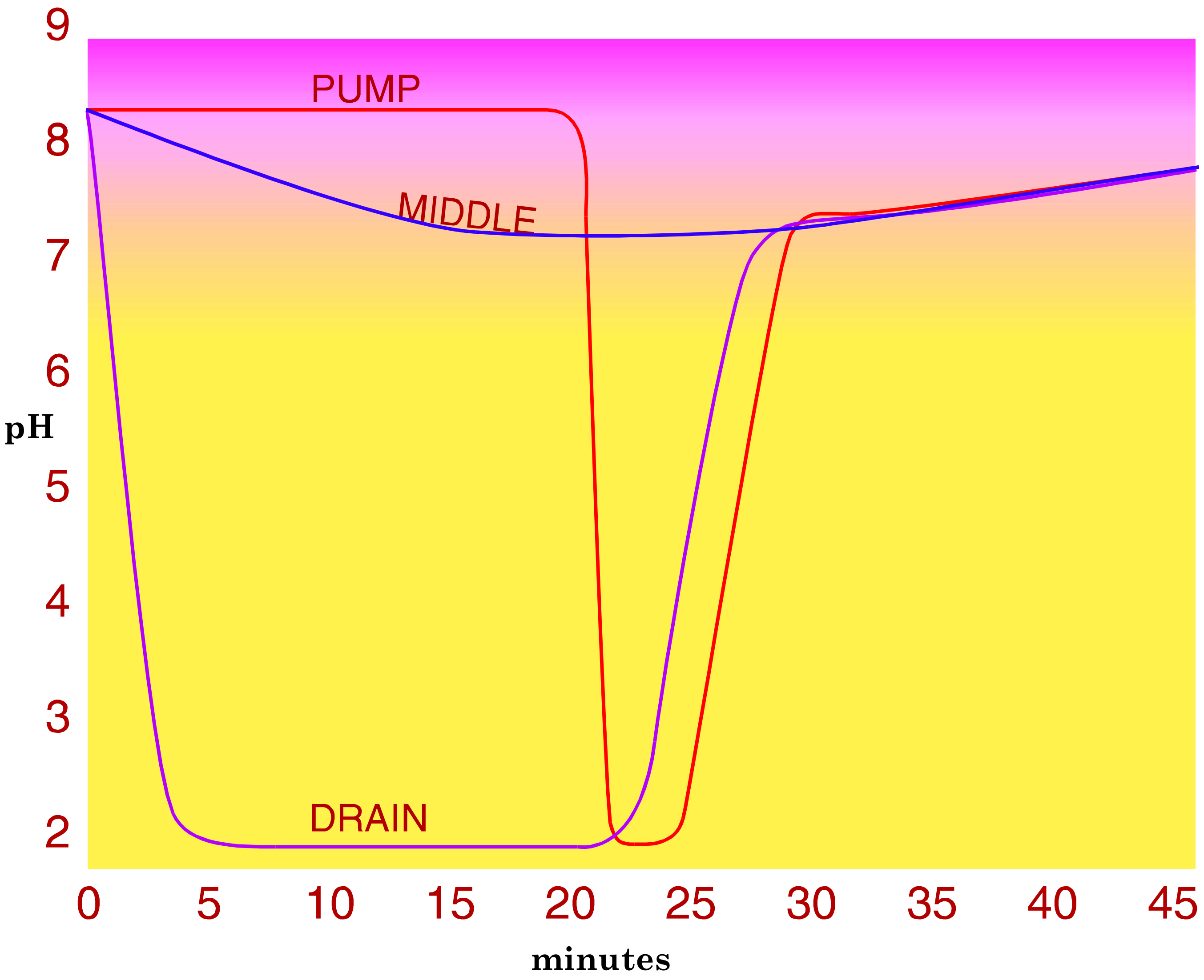
Graph A – Acid Column

This is a composite profile of the pH changes when undiluted acid was "rolled in" using the acid column technique, with the filter system on. Probes were located in the hair/lint strainer, on the main drain, and 18" above the main drain. With a starting pH of 8.3 the overall pH drop from the addition of 2 quarts acid in a 11 - 14 thousand gallon pool was approximately .6 pH units. The requirements of the technique call for a localized area of pH lower than 5 (or 4.4). This requirement was met in all three probe locations for periods of 1 to 4 minutes. The acid dropped past the middle probe fairly quickly (1 minute or less), puddled briefly (ca. 3 minutes), and slightly diluted into the pump area for about 4 minutes. The pH in all areas of the pool rebounded to safe levels approximately 10 minutes after the acid application. The pH in all three areas rebounded to approximately 7.7 after 45 minutes. The water was in a condition commonly accepted as extremely detrimental to the plaster in the main drain area for over 4 minutes, and in an extremely detrimental condition in the pump area for over 6 minutes.



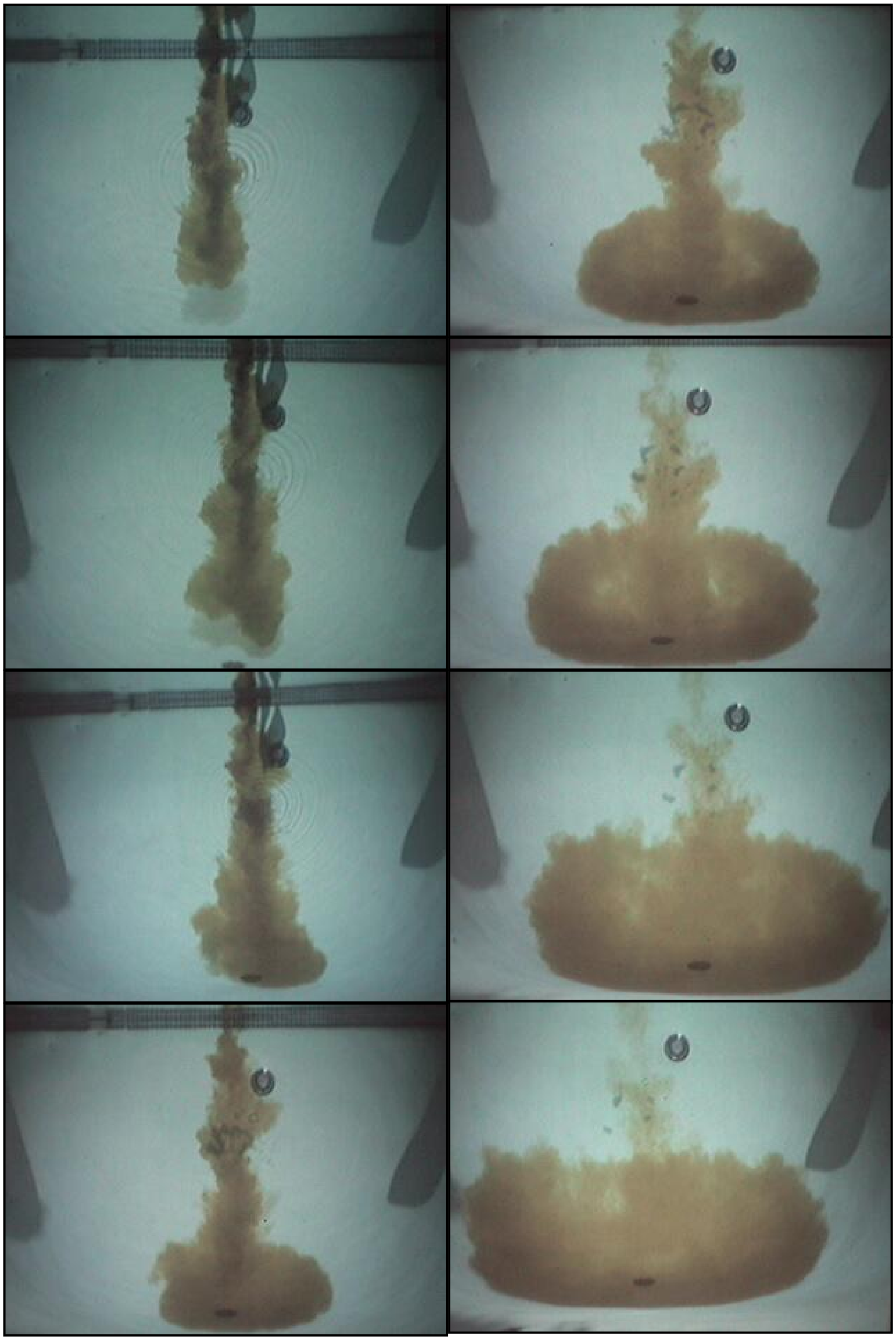
Graph B – Dilute and Distribute

This is a composite profile of the pH changes when the acid was diluted and distributed around the pools with the filter system on. Probes were located in the hair/lint strainer, on the main drain, and 18" above the main drain. With a starting pH of 8.3 the overall pH drop from the addition of 2 quarts acid in a 11 - 14 thousand gallon pool was approximately .6 pH units. When the acid is sufficiently diluted and "walked around" the perimeter of the pool, the lowest the pH ever dropped was to approximately 7.2 in the pump. Main drain and middle pH only went down to around 7.4. The pH in all three areas rebounded to approximately 7.7 after 45 minutes. At no time was the pH at a level commonly considered to be detrimental to the plaster or equipment.



Graph C – Acid Puddle

This is a composite profile of the pH changes when the acid was "puddled" on the bottom by adding undiluted acid with the filter system off. Probes were located in the hair/lint strainer, on the main drain, and 18" above the main drain. With a starting pH of 8.3 the overall pH drop from the addition of 2 quarts acid in a 11 - 14 thousand gallon pool was approximately .6 pH units. The pH in all three areas rebounded to approximately 7.7 after 45 minutes. Since the water was static for the first 20 minutes of the test, the acid slipped under the middle probe and only affected it slightly. The pH at the main drain plummeted immediately to 2.1 and remained there until the system was turned on, at which time the acid puddle was drawn into the pump. As soon as the puddle had passed into the piping system, the pH at the drain and then the pump climbed rapidly with the contact from water drawn from unaffected areas of the pool. The breakdown of the concentrated puddle was minimal until the puddle was drawn into the circulation system. The pH 18" off the pool floor was never low enough to cause harm, but the pH at the bowl of the pool was low enough to be what is generally considered extremely detrimental to plaster for an extended period of time, and presumably would have remained so until water movement from an outside source (pump or brushing) could force the puddled acid apart. The pH in the pump was at a level considered to be extremely detrimental for a 3 to 4 minute period as the slug of acidified water passed through it.



This sequence of photographs was taken in Livermore, California and shows the path of the muriatic acid (colored with phenol red dye) from the point of application to the puddle. For these photographs, a single quart of acid was used. The puddle remained well defined for more than 25 minutes, and was dispersed at that time by turning on the circulation system. The pH in the puddle was 2.1, and the pH inches away from the edges of the puddle was unaffected.

Figure 5 – Acid Puddle Illustration

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surface. Incidentally, only while performing such a procedure have the authors been able to see bubble formation in pools – when calcium carbonate is being dissolved as a result of the acid application. Even spot applications are done intentionally with professional, controlled techniques. It is the authors' contention that acid application to etch/clean should be undertaken only when that is the intent and when it is beneficial to do so, but not undertaken inadvertently when the actual intent is only to affect the water balance. The process of acid application that *this* study deals with (i.e.: acid column creation), subjects random localized areas of the plaster (typically in the deep bowl of the pool) and also the circulation system to etching chemical conditions.

An informal poll of servicemen, builders, and homeowners indicated that not all service technicians will turn the pool system on to help dilute the acid that is added. Some service technicians incorrectly believe that having the pool equipment off will help achieve the lower pH desired in a localized area for maximum reduction of alkalinity. This practice seems particularly dangerous with the advent of newer pools, since many are smaller and shallower, creating a greater potential for damage.

It is unfortunate that industry professionals are promoting the acid column concept for reducing alkalinity. At what cost is the industry adopting new programs and what amount of risk is the industry willing to take in order to save what, even if the theory had any validity, must be only a few pennies in time and acid?

The basic testing procedure employed has been given in detail in order that anyone desirous of independently verifying these results and conclusions may duplicate the experiments. The only real requirements for duplication are a precise method of pH and alkalinity determination and a willing swimming pool. The authors of this paper welcome any constructive comments or criticism from interested parties.

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References

Petrucci, Ralph H. *General Chemistry* 3rd. Ed., Macmillan Publishing Co., p. 293

American Water Works Association. *Standard Methods for the Examination of Water and Wastewater* (AWWA, 1992, 18th ed., p. 4–12 section 4500)

Merck Index (10th ed., 1993, p. 251)

Stumm, Werner and Morgan, James J. *Aquatic Chemistry* (John Wiley & Sons, New York 1981) pp. 184, 187

Skinner, Kim and Hales, J. Que. *Dosages for Adjusting Alkalinity*, Journal of the Swimming Pool and Spa Industry, pp. 14–20

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