The role of CO_2 in pool water

A series of e-mail articles from the research group onBalance, January 2006

The role of CO_2 in pool water #1

While some service techs go about their business taking care of various swimming pools, and specifically after they lower pH by adding acid, they may ask themselves why the pH of the water begins to rebound (rise back up again) afterwards. Also, they may wonder why this pH rebound happens faster in some pools than in others.

The answer lies in the behavior of carbon dioxide in the water. Carbon dioxide (also known as CO_2 & carbonic acid) is formed when acid is added to swimming pool water, and it is this compound that affects the changes in pH of pool water.

Carbon dioxide (CO_2) is a common, essential compound in nature. It is found almost everywhere, from what flowers and trees breathe in, to what humans and animals breathe out; and to the bubbles in the soda you drink. In its warmer phase it is a gas, and in its colder phase it becomes a solid – dry ice. Our atmosphere (the air we breathe) contains a relatively small amount of gaseous carbon dioxide – only about 0.03% to 0.06% – which is fortunate, since levels around 10% or higher would cause us all to lose consciousness! Because it exists in the air, a slight amount of carbon dioxide can be absorbed by water.

In water, CO_2 primarily exists as aqueous CO_2 (gas in, but not fully reacted with the water), but a small amount also combines with water to form carbonic acid: $CO_2 + H_2O = H_2CO_3$, and the slightly acidic nature of this compound lowers the pH somewhat.

CO_2 in Pool Water #2

Carbon dioxide plays an important role in the make up and balancing of pool water. When dissolved in water, carbon dioxide has a direct effect on the water's pH. The more CO_2 in the water, the lower the pH, and the less CO_2, the higher the pH. Pool water with no dissolved CO_2 (but with a minimum alkalinity of 100 ppm) will have a pH of about 8.4 (as long as no other chemicals have been added). On the other hand, pool water that is saturated with CO_2 will have a pH down around 5.

Although CO_2 can be introduced to water from the air, it is also produced in pool water by simply adding acid. As we all know, when acid is added, both the alkalinity and the pH are lowered. The *alkalinity* is lowered because, with normal pool water parameters, the added acid reacts with bicarbonate alkalinity in the water, converting it to carbonic acid – which is then no longer alkalinity.

For you who enjoy formulas, bicarbonate and acid form carbonic acid and chloride, or $HCO_3 + HCl = H_2CO_3 + Cl$, and then all but a fraction of a percent of the carbonic acid shifts to aqueous CO_2: H_2CO_3 <==> $CO_{2\ (aq)}$ + H_2O. Depending on the amount of acid added, a specific and calculatable amount of alkalinity is eliminated.

CO_2 in Pool Water #3

After adding acid to the pool water, the *pH* goes down (at first) because of the effect on pH of the increasing amount of $CO_{2\ (aq)}$ produced by the acid. Shortly afterwards, the pH begins to rebound and eventually can return to its original level. This is due to the equilibrium relationship between the amount of CO_2 in the water and the amount of CO_2 in the air above the water. This is known as Henry's Law. Since the acid addition forms more $CO_{2\ (aq)}$ in the water than is dictated by the equilibrium, most of the $CO_{2\ (aq)}$ created by the addition of acid will then begin to release and off-gas into the atmosphere – which will gradually raise the pH level *but not the alkalinity*.

It may be instructive at this point to mention that the "natural" level of CO_2 in balanced pool water after it has had sufficient time to reach equilibrium with the atmosphere is from about 0.5 ppm to 2.0 ppm and the pH will be around 8.0 to 8.3. This pH range is dependent on total alkalinity.

Since it is dissolved CO_2 in water that keeps calcium soluble in water, we want to maintain pool water with just enough CO_2 to keep the pH down in the mid to high 7 range. Too much CO_2 in water creates low pH conditions that are aggressive to pool plaster, and no CO_2 creates high pH conditions that are scale forming to pool surfaces. Of course, etching and scaling are something service techs are always trying to prevent from happening.

CO_2 in Pool Water #4

CO_2 can also be added to pool water by simply injecting pure CO_2 into the water, or by adding dry ice (frozen CO_2) to water. The pH will drop, and if a large amount of CO_2 is absorbed into the water, the pH could go below 6.0. Despite the fact that the pH could be lowered dramatically, *no change or reduction will occur in the alkalinity* under this scenario. This fact bears repeating because it is incorrectly being taught in some seminars. The amount of CO_2 in water does not affect the content of alkalinity, only the pH is affected.

The process of injecting CO_2 into water (especially spas) is becoming more and more popular. Systems have been designed to add CO_2 into the water when sanitizers such as bleach are used. The concept behind this is to use CO_2 to offset the high pH effects of bleach. This system works quite well to keep the pH in check and in balance (7.2 – 7.8) except for the fact that the total alkalinity will gradually increase over time, but this is only due to the small amount of alkaline properties of the bleach.

Therefore, small amounts of acid will eventually need to be added to control total alkalinity levels, and it won't be necessary to experience the vicious cycle of adding larger doses of acid followed by offsetting doses of sodium bicarbonate or soda ash to maintain pH and alkalinity. But, because the content of the CO_2 being injected in the water is higher than the natural level (equilibrium, or 8.2-8.3), most of it will off-gas over time. Therefore, a continual addition of CO_2 will be needed to keep the pH from rising. Although this may be done manually, it is much easier by dosing the CO_2 with a pH controller.

CO_2 in Pool Water #5
Why the pH rebounds.
While some of the following information has already been mentioned, let's specifically address the question raised at the beginning of this update series. Why does the pH eventually rise after acid initially makes it drop? Again, the answer lies in the fact that whenever the pH is below 8.2-8.3, there is generally more CO_2 in water than its natural equilibrium level with the atmosphere. Because of this, the extra CO_2 will off-gas into the atmosphere over time. The pH rises because CO_2 is off-gassing from the pool water. Unless checked, the pH will continue to rise until the CO_2 reaches its equilibrium or about 8.3. The more alkalinity (over 80 ppm), the stronger pull to a pH of 8.3. This is one of the difficulties that pool service techs have to deal with. Generally, there is no getting around this.

But there are exceptions to the above rule. For instance, a common but occasionally unrecognized factor which interferes with CO_2 off-gassing or absorption is a pool cover. This particular situation will be cover in our next update. Incidentally, this entire update discussion on carbon dioxide was published by Service Industry News in their Sept. 15, 2004 issue.

CO_2 in Pool Water #6
When pools are covered with non-gas permeable covers, such as the common blue bubble solar blankets or solid vinyl or plastic automatic safety covers, the exchange of gas from water to air and air to water is blocked.

Especially with newer plaster pools, a vast supply of hydroxide (a component of the plaster surface) is exposed to the water and its chemistry. If a pool cover blocks the otherwise natural process of CO_2 off gassing, the CO_2 reacts with the plaster surface and, together with hydroxide, form carbonate, thereby reducing CO_2 in the water. Eventually, all aqueous CO_2 could be depleted, causing the pH to climb to 8.4, and the pool cover would not allow more CO_2 from the atmosphere to dissolve into the water to keep the pH from rising even higher than 8.4. At this point, dissolved calcium would probably begin to precipitate and produce scale on the floor and walls.

In vinyl, painted, and fiberglass pools, on the other hand, no ready source of hydroxide is available, so pool covers on these pools can keep the pH artificially low when inhibiting the ability of CO_2 to off-gas. When acid or an acidic sanitizer is added to this type of pool that has a non-permeable cover on it, the CO_2 generated (by the acid) will stay in the water, and will not be able to off-gas. Therefore, the pH will probably remain unchanged (low) until either other chemicals are added, or the cover is removed.

When non-permeable covers are used, pH needs to be watched carefully. Ideally, the cover should be removed for enough time to allow gases to equilibrate (perhaps 6 to 8 hours, twice a week for residential pools). When this is not an option, careful control of pH using acids and bases must be maintained. How will you know if the pool contains the right amount of CO_2? The pH will be balanced.

CO_2 in Pool Water #7 – How Long for pH change?

So how long does it take for CO_2 to off-gas after adding acid? Or, why does the "rebound" happen faster in some pools than others, or faster one time than another in the same pool? CO_2 off gassing, and its relative speed, are dependent on several factors, which include water temperature, circulation, total alkalinity, ratio of water volume to air-exposed surface, and atmospheric pressure. These factors affect both the rate and the percentage of either off-gassing or absorption.

Factors which *accelerate* off-gassing (and speed pH rebound) include higher water temperatures, increased circulation, and especially increased aeration. Factors which *inhibit* off-gassing (thus slowing down pH rebound) include decreased aeration, decreased circulation, and low temperature. Factors which promote absorption of CO_2 (which drops pH) include high total alkalinity, a pH above 8.4, and low water temperature.

Service techs can easily observe for themselves the speed at which CO_2 off-gasses by watching the speed at which the pH increases, or returns to normal in their pools. They will detect how some pools have a major change in the pH within a day or so, maybe even in just a few hours, while some pools take over a week to have a significant change in the pH. Obviously, however, adding any more chemicals affects the pH and the process starts all over.

CO_2 in Pool Water #8
Rapid Alkalinity Reduction

Another practical application relating to CO_2 in water is the process of lowering high alkalinity levels in a short amount of time without allowing the pH to drop below the ANSI/APSP-recommended minimum of 7.2. The traditional methods involve either adding enough acid at a single time to remove the right amount of alkalinity (in which case the pH likely goes lower than desired), or adding smaller amounts of acid at intervals, allowing the pH to slowly rebound, and then repeating the small acid dose, over and over until the desired alkalinity level is reached, which takes hours or days.

The "CO_2-savvy" method is accomplished by adding acid to water while off-gassing (by increased aeration and/or increased surface exposure) as much as possible. Aeration can be accomplished by turning on venturi jets, spa air bars, or other features or devices that create air bubbles in the water. Aeration is quite effective at rapidly reducing the CO_2 in the water by increasing the surface area of water to air, which is where the off gassing occurs. Increased surface exposure includes longer circulation times, and using water features such as fountains – which might not technically aerate, but still increase the total amount of water exposed to air.

The routine (popularized online by Ben Powell) involves adding just enough acid to lower the pH to 7.2, and then circulating and aerating the water as much as possible. The acid lowers the alkalinity, and the aeration accelerates the process of CO_2 off gassing, thereby increasing the pH. Then more acid may be added, to pH 7.2, and so on – until the alkalinity reaches the desired target. In a relatively short period of time (at least, compared to traditional methods) the target alkalinity is reached without a) taking a lot of time, or b) allowing the pH to drop below safe and desirable ranges.