CWS White Paper

pH, Buffers, Total Alkalinity, Chlorine and PoolMoss®
Everything You Wanted to Know, But Were Afraid to Ask

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Introduction

It's all about hydrogen ions and water. Hydrogen, you remember, the most abundant molecule on earth, is in the upper right-hand corner of the periodic table of elements. It is just one proton and one electron. Two hydrogen molecules combine with one oxygen molecule to form water. The hydrogen ion (H+) in water has a positive charge; the mirror image chemical is the hydroxyl ion (OH-) that has a negative charge. These two ions are like a teeter-totter. When one is up, the other is down. An acid has a high concentration of hydrogen ions and a low concentration of hydroxyl ions. A base is just the opposite. Put an acid and a base together carefully because they react with vigor to make water and release a lot of energy. To understand pH, buffers, total alkalinity, and chlorine in any body of water like a pool, spa, pond or drinking water, you have to understand hydrogen ions.

pH

The term pH refers to the concentration of hydrogen ions in water. It is a logarithmic, not a linear, scale. Higher numbers refer to a decrease in the concentration of hydrogen ions while lower numbers reflect a higher concentration of hydrogen ions. That means that when the pH changes from 6 to 7, the actual change in the concentration of hydrogen ions is 10 fold lower, and a pH change from 6 to 8 is a 100 fold lower. Therefore, seemingly small changes in pH mean large changes in hydrogen ion concentration.

Buffers

Buffers are molecules that can combine with and release hydrogen ions. Many different molecules can act as buffers. The most recognized buffer in the pool and spa industry is bicarbonate. Depending on the pH of a solution, it can either release hydrogen ions in the water, or combine with hydrogen ions in the water to remove them from the solution. Many other molecules also act as buffers. Many amino acids and proteins made from amino acids are buffers. Long chain sugar molecules can also act as buffers. Buffers stabilize the pH of a solution over a range of hydrogen ion concentrations and are most effective when the pH of the solution is near the pKa of the buffer. Buffering capacity is also dependent on the concentration of the buffer. Buffers perform best over different pH ranges. Pick the pH you want, add the right buffer, and the pH of the solution will stay stable over the range of that buffer. It is a chemical version of balance.

Bicarbonate is also one of the buffer systems in your blood. As the hydrogen ion concentration fluctuates in our blood, the bicarbonate and proteins in our blood combine with hydrogen ions if there are too many, or release hydrogen ions if there are too few, to keep the pH stable. It works well at a pH of 7.4 (that's the pH of our blood when we are healthy) because our bodies can rapidly control the CO_2 levels through a process called physiological buffering. It is not, however, an optimal buffer for recreational water systems. The bicarbonate buffer system has a pKa of 6.1, which is quite far from the operating pH of 7.2-7.6 typically seen in swimming pools. As stated above, buffers are most effective when the pH is close to the pKa. This would explain why controlling and maintaining a stable pH can be so difficult. Because the operating pH is more than one unit from the pKa of the buffer, the system is living on the edge of the ability of the bicarbonate buffer system to work effectively. Why is a bicarbonate buffer system used in pools if there are better options? The first reason is that it is the buffer system that exists in tap water (and what is measured when we measure alkalinity). The second reason is that the chemicals used to control pH are relatively inexpensive. The third reason is that the use of a more appropriate buffer, with the right pKa (i.e. a phosphate buffer system), would require the use of additional chemicals, increasing cost and the complexity of the aquatic water system.

Total Alkalinity vs. Alkalinity

This confused us when we first started paying attention to the pool and spa water chemistry terminology. In chemistry, we learned that alkalinity is the absence of hydrogen ions resulting in a high pH. When we read the indicator strips and saw total alkalinity we thought we were measuring the hydroxyl ions in the water. A lot of hydroxyl ions mean a low concentration of hydrogen ions or an alkaline solution. These readings didn't make sense, so we asked a dumb question and Tom Schaffer from US Aquatics, Inc. (he is a CPO instructor and has 30+ years industry experience) told us that total alkalinity, as viewed in the pool and spa industry, is a measure of bicarbonate buffer. Low total alkalinity reflects a low level of bicarbonate buffer in the water solution; it does not reflect the alkalinity (concentration of hydroxyl ions) of the solution.

Tom also told us about pH bounce when the bicarbonate level gets too low. This made sense to us once we knew what total alkalinity means. If there is too little buffer in a solution, adding hydrogen ions (acid) overwhelms the buffering capacity and will result in a meteoric fall in pH. This occurs if bicarbonate is the predominant buffer in the solution and the total alkalinity goes below 60. That's why many state regulations require pool operators to keep total alkalinity above 60, so there is enough buffer to keep the pH stable.

If the total alkalinity is high, like in some source water, then there is so much bicarbonate that it is very difficult to get the pH to go down or to increase the number of free hydrogen ions in the solution. If you add enough hydrogen ions by adding acid, then a balance can be achieved to keep the pH stable. Add more bicarbonate buffer and you will have to add more acid to balance the solution. A high total alkalinity can also affect the use of CO_2 to increase hydrogen ion concentration thus lowering the pH of the solution. To understand this effect we have to understand the chemistry of CO_2, water, bicarbonate and acid. CO_2 alone is not acidic. When CO_2 is dissolved in water, a slow chemical reaction occurs to form carbonic acid. Carbonic acid then gives off hydrogen ions and forms bicarbonate. All these reactions are in equilibrium and occur at different rates. If the bicarbonate level in a pool is very high, then the reaction to form hydrogen ions from carbonic acid is driven in the opposite direction. As a result, adding more CO_2 cannot increase hydrogen ion concentration and simply off gases from the pool water into the air without changing the water's hydrogen ion concentration.

pH and Chlorine

When chlorine (or bromine) is added to the mix, the chemistry becomes more involved. We will talk about hypochlorous acid, not chlorine. Hypochlorous acid is the ion formed when chlorine is added to water. Hypochlorous acid is also the oxidative molecule that kills bacteria, algae and cryptosporidium. The ORP (oxidation reduction potential) probe measures the oxidative potential of the water. Since hypochlorous acid is the major oxidizer in pool water, the ORP is used to constantly monitor the pool water and to add chlorine when the ORP goes below a set level. Hypochlorous acid is very reactive, so it combines with a lot of other molecules to form new molecules. Hypochlorous acid changes when the pH goes above 7.6. It basically morphs into a form that doesn't react anymore, so it doesn't kill anything.

Remember, because the scale is logarithmic, that a change in pH from 7.3 to 7.6 results in one- half the concentration of hydrogen ions. This is a very large change. Hypochlorous acid works a lot better at pH 7.2 to 7.4. That's why keeping the pH at this level reduces the amount of chlorine needed to maintain a desired free available chlorine level.

pH, Total Alkalinity, Buffers and PoolMoss® Pro

PoolMoss® contains the leaves of one species of Sphagnum moss. It affects the pH, buffer and total alkalinity of the water it touches. If you test the water in a wetland bog that contains Sphagnum moss it will be acidic (high hydrogen ion concentration). Sphagnum moss leaves and therefore PoolMoss®, have a cation exchange system that binds positive ions, like iron and calcium, and pumps hydrogen ions into the water causing the water to become acidic.

During testing in pools and spas, we also found that the PoolNaturally® system stabilized pH and lowered total alkalinity over time. What was interesting is that even with the lowered total alkalinity we found no pH bounce or pH instability at all. This prompted us to allow the total alkalinity to equilibrate and see what happened. To our surprise, and the pleasant surprise of the pool owners and operators, they didn't need to add bicarbonate to elevate total alkalinity to prevent pH bounce. Using the PoolNaturally® system, we recommend keeping the pH between 7.2 and 7.4 and letting the total alkalinity equilibrate to a steady state over time. This results in a net decrease in the bicarbonate and acid needed to maintain stable water.

Using CO_2 with the PoolNaturally® system works very well. Because the total alkalinity is low, there is a low concentration of bicarbonate in the water.

This facilitates the conversion of CO_2 to carbonic acid and then to hydrogen ions and bicarbonate.

We also documented a decrease in chlorine delivered to the pool needed to maintain a stable free available chlorine (hypochlorous acid) level. The oxidative state of the water also became stabilized as measured by ORP. The end result is stable water using less chemicals.

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