Alkalinity & pH Relationships

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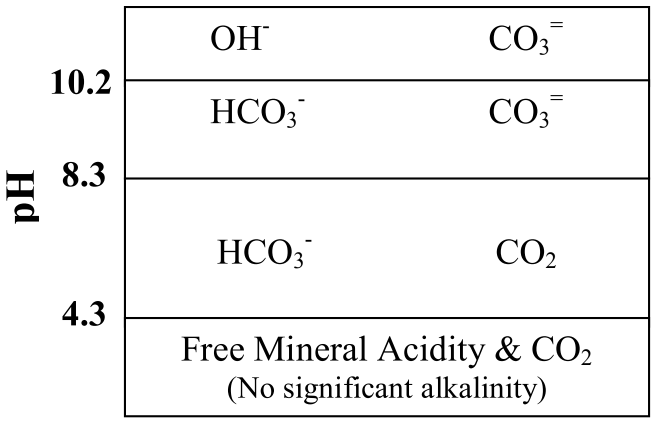
Whether you are new to the water field or an old timer, alkalinity and pH relationships can still be confusing. Alkalinity is defined as the acid absorbing property of water. The major acid absorbing constituents that we typically deal with are hydroxide (OH^-), bicarbonate (HCO_3^-) and carbonate ($CO_3^=$) ions.

Take a look at the alkalinity and pH diagram presented here. At a pH of approximately 4.3 and below, we see there is no alkalinity present. There is only free mineral acidity (FMA) and dissolved carbon dioxide. (Dissolved carbon dioxide is sometimes expressed as carbonic acid, H_2CO_3.)



As we increase the pH, we see that between 4.3 and 8.3, the dissolved carbon dioxide starts to convert to bicarbonate ion. This conversion is complete at a pH of about 8.3, where only bicarbonate is present.

Increasing the pH beyond 8.3, the bicarbonate ion is converted to carbonate ion. Conversion is nearly complete at a pH around 10.2 with almost all the bicarbonate being converted to carbonate.

Further increasing the pH past 10.2, we start seeing measurable levels of hydroxide ions along with the carbonate ions.

Alkalinity Testing

The P-, M-, and OH-alkalinity tests are all related to these significant pH's. Acid is added until a pH endpoint is achieved allowing the alkalinity components to be measured.

M-Alkalinity

The M-alkalinity is a measure of the amount of acid it takes to drop the pH to approximately 4.3. As can be seen from the diagram, this would directly measure the amount of any bicarbonate, carbonate, and hydroxide alkalinity present, depending upon the starting pH. For example, if the starting pH is 9.0, the M-alkalinity test will measure the amount of bicarbonate and carbonate alkalinity, but will not measure hydroxide alkalinity because no measurable levels were present.

P-Alkalinity

The P-alkalinity is a measure of the amount of acid required to drop the pH to approximately 8.3. As can be seen, this would measure the amount of any carbonate or hydroxide alkalinity present. Since the carbonate alkalinity is being converted to bicarbonate alkalinity, this test does not measure bicarbonate alkalinity.

OH-Alkalinity

The OH-alkalinity is a measure of the amount of acid required to drop the pH to approximately 8.3 after the carbonate has been precipitated out with barium as barium carbonate. You can also use an equation to calculate OH-alkalinity depending upon the P- to M-alkalinity. The relationship that applies to most situations we see is $OH = 2P-M$. This calculation should agree reasonably well with the OH-alkalinity test. If there is a difference, it may be due to interference from neutralizing amines increasing the acid absorbing ability of the water.

Conclusions

When thought of in terms of the diagram presented and the pH endpoints, hopefully you have a better understanding of alkalinity and pH relationships.