Focustronic Educational Program

Secrets of KH

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FOCUSTRONIC
SETTING NEW STANDARDS

Introduction

The concepts of alkalinity and pH are one of the most important factors in a marine water system. In particular, the subject alkalinity is easy to misunderstand and is sometimes not described correct. It is my vision to shed some light on the subject with this paper.

pH

The pH value is a measure of the number of hydrogen ions, H, in a solution. The higher the pH value, the fewer hydrogen ions, and conversely, the lower the pH value, the more hydrogen ions. A solution with a pH value below 7.0 we call an acidic solution, and a solution with a pH value above 7.0 we call alkaline.

The value itself, is a number between 0-14, and is purely mathematically the negative logarithm of the hydrogen ion concentration:

$pH = -\log [H^+]$

pH	*Conc.of hydrogen ions mol/l*
0	10^{0}
4	10^{-4}
7	10^{-7}
9	10^{-9}
14	10^{-14}

The marine-water on a coral reef or in a coral reef aquarium contains a relatively large amount of basic ions, mainly bicarbonate (HCO_3) and carbonate ions (CO_3). Therefore, the water is slightly alkaline and maintains a pH value around 8.2. However, it is quite common with a daily variation, where the pH value in the morning can go all the way down to 7.9 and in the evening rise to 8.4. This is because during the day the algae and corals consume carbon-dioxide due to its photosynthetic activity. The carbon dioxide level then drops in the water. Because carbon dioxide is an acid, the decrease in carbon dioxide leads to an increase of the pH value. The reverse happens at night.

Both too high and too low pH values inhibits the skeleton formation ability of the corals and are also stressful for the fish. Try to be in the range 8.0-8.4, and also avoid too fast oscillations.

Mandatory to achieve a stable pH value is to ensure that the so called **alkalinity** is sufficient, and besides that also secure a good gas exchange by using a proteinskimmer.

Alkalinity

Alkalinity is a summary of the ability of the water to neutralize an acid, ie. the ability of water to absorb and neutralize hydrogen ions, H. In a natural marine water (with a pH around 8.2) the following ions, thanks to their ability to absorb hydrogen ions, contribute to the alkalinity:

- *HCO_3 =Bicarbonate*
- *CO_3 = Carbonate*
- *$B(OH)_4$ = Borate*

Actually there exists more ions that contribute to the alkalinity, but they are in such a low amount so we can ignore them.

The ions above together make up what we call **Total Alkalinity**. The carbonate and hydrogencarbonate ions together make up what we call **Carbonate Alkalinity**. And the borate ions make up what we call **Borate Alkalinity.**

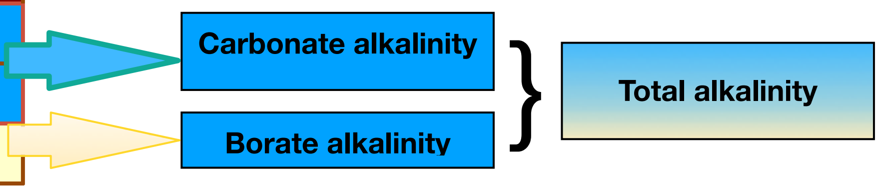
So in summary:

Total alkalinity = Carbonate Alkalinity (HCO_3+CO_3) + Borate Alkalinity ($B(OH)_4$)

As we said in beginning the carbonates dominates among the alkalinity contributors, so carbonate alkalinity is just slightly lower than total alkalinity In figures, during normal conditions (pH 8,2 and Borate concentration around 4 ppm) the borate alkalinity contributes to around 0.3dKH and the rest is carbonate alkalinity.

The figure below illustrates how much each ion contributes to the total alkalinity at a pH of 8.2.

Alkalinity ions	*Contribution to total alkalinity (at pH 8.2)*
HCO_3^-	90%
CO_3^{2-}	7%
$B(OH)_4^-$	3%



pH stabilising function

The alkalinity ions act as hydrogen ions acceptors as we said. So, by this way of absorb hydrogen ions (and release if they are in its acid form), the alkalinity will minimize the pH fluctuations, and act like a buffer.

If we for instance look at the hydrogencarbonate ion,(the major contributor to the alkalinity), this ions can both release a hydrogen ion or receive one, thus minimize pH fluctuations in **both** directions.

Here is the reaction that happens for hydrogencarbonate when **pH decrease** (add an acid/H-ions):

$$HCO_3 + H \Rightarrow H_2CO_3$$

Here is the reaction that happens for hydrogencarbonate when **pH increase** (removal of H-ions):

$$HCO_3 \Rightarrow CO_3 + H$$

The total reaction is like this and how it affects by pH:

$$H_2CO_3 \Leftrightarrow HCO_3 + H \Leftrightarrow CO_3 + H$$

A pH increase forces the reaction going to the right

$$H_2CO_3 \Leftrightarrow HCO_3 + H \Leftrightarrow CO_3 + H$$

A pH decrease forces the reaction going to the left

So, depending on environmental pH , the carbonate reaction above goes back and forth <u>in purpose to stabilize the pH.</u>

CO_2 influens on alkalinity

One common misunderstanding is that by adding CO_2 we increase alkalinity. At a first glance this seems logic, because when we add CO_2 we force this reaction to the right and thus some new HCO_3 and CO_3 is formed.

$$H_2O + CO_2\uparrow \Leftrightarrow H_2CO_3 \Leftrightarrow HCO_3\uparrow + H \Leftrightarrow CO_3\uparrow + H$$

BUT, look again at the reaction:

$$H_2O + CO_2\uparrow \Leftrightarrow H_2CO_3 \Leftrightarrow HCO_3\uparrow + H\uparrow \Leftrightarrow CO_3\uparrow + H\uparrow$$

At same time as we create new HCO_3 and CO_3 by introducing CO_2, **we also create same amount of H ions!** And H-ions have a lowering effect on alkalinity. So the effect on total alkalinity is +- 0!

So to summary: **Increase or decrease of CO_2 in the water will NOT affect total alkalinity,** but only the ratios that build up the total alkalinity.

Table summarize:

	Carbonate alkalinity	Borate alkalinity	Total alkalinity
CO_2 ↑	↑	↓	↔
CO_2 ↓	↓	↑	↔

Building blocks

As the total alkalinity is to 97% made up of carbonates, the **total alkalinity value perfect reflects the access of building blocks for coral skeleton formation**. When a coral builds up the skeleton ($CaCO_3$), it require same amount of Ca-ions as CO_3-ions.

$Ca^{2+} + CO_3^{2-} \Rightarrow CaCO_3$

That means that the consumption-ratio of calcium and carbonates due to coral growth is 1:1.

This is the reason why we as a basic rule always wants to add calcium and carbonates in this ratio 1:1. To make this easy, most modern recipes are designed that if you add same volume of the calcium-solution as the carbonate-solution, you will add exact same numbers of calcium-ions as carbonate-ions. We call this balanced dosing and balanced recipes.

Note: Calcium is only consumed by calcareous-formation processes. But when comes to carbonates they are not only involved in calcareous formation, but also in bacterial activity of different kind. For instance nitrification consumes alkalinity, and denitrification produces alkalinity. So if the balance is not perfect between nitrification and denitrification, a tank can temporary experience that calcium and carbonates are not consumed in exact 1:1 ratio.

Still, the advice is in most situations to keep balanced dosing with equal dose from the calcium and carbonate bottles, and rather adjust manually as this is normally temporary deviations.

Sometimes though, due to chronic unbalance between nitrification/denitrification, you can have to abandon the basic rule, and deliberately dose not equal from the KH and Ca channels. If that´s the case, measure calcium at least once a week, and as soon as calcium values matches the KH values again, go back to equal dose from all bottles.

Here is a table that helps you decide if the consumption of calcium and carbonates is reasonable close to 1:1.

Note: Do NOT overreact and chase numbers. These values are based on natural seawater values and a consumption rate of exact 1:1. Accept a corresponding calcium value of +- 20 ppm from the "perfect one" before consider go for a temporary unbalanced dosing regim.

KH value (dKH)	Ca value (ppm) if perfect balanced	Acceptable range
6	413	390-430
6.5	417	390-435
7	420	395-440
7.5	424	400-445
8	427	405-450
8.5	431	410-455
9	434	415-455
9.5	438	420-460
10	441	420-460
10.5	445	425-465
11	448	430-465
11.5	452	435-465
12	455	440-465

Measure alkalinity

When we speak about alkalinity, KH, we always mean Total alkalinity. Therefore, all KH/alkalinity-tests on market measure total alkalinity. Thats good, because that is exactly what we want. Reason of that is:

- Like I have explained above: Total alkalinity is independent in CO_2, and thus always give you the correct value.
- One of the major function of alkalinity is to buffer the sea water, so we wants a number that reflects that properties.

- As mentioned, total alkalinity makes up by carbonate alkalinity to approx 97%, so by given the total alkalinity we for sure **also** knows the status of carbonates, aimed to be the building block for coral skeleton formation.

When we want to measure KH, the basic methods is to add an acid to that amount so all alkalinity-contributing ions has been converted to its acid. When this have happened, the pH of a marine water will be around 4.2-4.5. So by just detecting this so called *end titration point*, either by an electrode, or by a pH indicator that change color at this pH area, we can then calculate the total alkalinity of the water.

Science is beauty

/Jonas Roman

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