Alkalinity

Dallas Warren - September 7, 1997

What is alkalinity?

Alkalinity is a measure of the pH buffering capacity of water. (In this case alkalinity is not usedin the chemistry context, as alkalinity is typically used to indicate that the solution has a pHabove 7.0, i.e. it is basic or alkaline). It indicates the concentration of carbonate $(CO3)2-$,hydrogen bicarbonate $(HCO3)-$, borate $(BO3)3-$, sulphate $(SO4)2-$, and hydroxide $(OH)-$ anions.The actually value is determined by the amount of free acid, hydrogen ions (H+), required toneuralise all of the above anions.

Why is alkalinity important?

Alkalinity is what provides the correct and stable pH for a reef aquarium, if maintained atsufficient levels. A correct and stable pH, i.e. nonfluctuating, is important for the health of anaquariums inhabitants. Many authors state that alkalinity is important as it is a measure of theability to resist a drop in pH. This is true, but it is only half of the story. It is also a measure ofthe ability to resist an increase in the pH, i.e. the "buffering" of the water works in bothdirections. Some components of the alkalinity buffer system are also utilised by organisms, suchas hard corals, and so have to be present in sufficent amounts for good health and growth.Additionally, the higher the alkalinity, the greater the ability of the system to absorb the additionof an acid or a base with only small change in the actual pH.

Alkalinity levels of 3.0 to 6.0 meq/ml are recommended to keep a stable pH in a reef aquarium.

How does a buffer work?

A buffer is a series of chemical species in a solution that resists a change in pH when either abase, eg hydroxide ions $(OH-)$, or an acid, eg hydrogen ion (H+), are added to a solution.It doesthis by acting as a reservoir for H+, donating them to the solution when the concentration fallsand taking them from the solution when the concentration rises.

The buffering system involves a base and an acid, in relatively high concentrations, inequilibrium with each other. The base acts as a hydrogen ion absorber and the acid as a hydrogendonator. When this equilibrium is upset by the addition of H+ or $OH-$, which in effect removesH+, then the acid and base alter their concentrations until equilibrium is again achieved. Whenthis equilibrium is reattained the pH is close to the original pH.

It is possible to buffer a solution at any pH by the choice of an appropriate acid/base pair.

For seawater and human blood the important buffering system involves carbonic acid (H2CO3),hydrogen bicarbonate $(HCO3)-$, carbonate $(CO3)2-$ and of course hydrogen (H+).

The chemical reactions involved are as follows:

CO2(gas) <<=>> CO2(aqueous)

H2O(liquid) + CO2(aqueous) <<=>> H2CO3(aqueous) ---- (1)

H2CO3(aqueous) <<=>> (HCO3)-(aqueous) + H+(aqueous) ---- (2)

(HCO3)-(aqueous) <<=>> (CO3)2-(aqueous) + H+(aqueous) ---- (3)

The more important reaction for the buffering system is number 2. In this reaction H_2CO_3 isacting as the acid and $(HCO_3)^-$ as the base. If H^+ is added to the system the $(HCO_3)^-$ acts as abase and removes the excess hydrogen ions from solution by forming H_2CO_3. And visa versawill occur if H^+ is removed from solution, then the H_2CO_3 dissociates, releasing more H^+ intothe solution. The pH is thus stabilised by the equilibrium between the acid and base, adding orremoving H^+.

Reaction number 3 performs a similar function. From this it can be seem that the entireequilibrium system is rather complex, with the formation of one species effecting the equilibrium position of another reaction and therefore the concentration of the other species involved.

The pH of a buffered solution is determined by the ratio of the concentrations of the base and theacid species i.e. [Base]/[Acid]. Therefore as the concentration of the acid increases over that ofthe base, then the pH will fall and visa versa. This effect can be use to alter the pH of a solutionwithin a certain range to what ever value is required.

Although this is not that simple within a complex system of a reef aquarium. Luckily it is notrequired to worry about this, as if the alkalinity is maintained at sufficient levels then the pHtends to the natural value of 8.0-8.4.

As the ratio [Base]/[Acid] determines the pH, therefore want to minimise the change of this ratioupon the addition/removal of H^+. The buffering capacity, i.e. the ability to absorb theaddition/removal of H^+ with only a small pH change, is determined by the magnitude of the acidand base concentrations.

This is easily seen when considering the ratio [Base]/[Acid]; the larger the acid/baseconcentrations, the smaller the percentage change in these concentrations after the addition/lossof H^+, resulting in a smaller change in the ratio.

Therefore to get the best buffering capacity and maintain a stable pH then this ratio has to remainalmost constant. This will occur when the the amount of H^+ that is added/removed is smallcompared to the concentration of the buffer species. As a result, the higher the concentration ofthe acid/base buffering species the greater the buffering capacity of the solution.

This is why if a high alkalinity level is used, then the aquarium has a more stable pH.

It should also be noted that a solution is better able to resist pH changes in any direction if theratio [Base]/[Acid] is one.

Q: How can alkalinity be maintained?

Alkalinity has a natural tendency to decrease over time in an enclosed system. This is due to theproduction of acids as by-products of biological processes and the utilisation of some of thebuffering species by various organisms. In order to maintain the proper levels of alkalinity moreanions have to be added to the system.

The source of these anions are as follows:

The Atmosphere: Carbon dioxide from the atmosphere dissolves into the water and then reactswith water to form H_2CO_3 as shown in reaction 1 above.

Carbon Reactors: Works the same as for the atmosphere, just more can be introduced into thesystem by operating under elevated pressures without having to rely on slower diffusion from theair into the water.

Water Changes: These introduce the buffer species into the system with the new water, whethersynthetic or natural.

Powdered Buffers: These are powders containing the important buffering anions such as CO_3^{2-},$(HCO_3)^-$ and other minor components, and are added periodically to elevate the alkalinity.

Calcium Reactors: These not only help maintain the calcium levels, but also the alkalinity.Dissolvess CO_2 into the

water and, because of the lowered pH, the $(CO_3)^{2-}$ associated with thecalcium ions.

OK, that concludes my talk on Alkalinity, now onto all those questions ;-)

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Q: What are the pros and cons of additives like Bi-Onic?

B-Ionic is a two part additive. What is does is add the caclium with one of the solutions then thealkalinity, which is the anion, such as HCO_3^- in the other. The good thing about these guys isthat the two components are separte, therefore can add higher concentrations to the tank in onehit. If the Ca and $(CO_3)^{2-}$ was in the same bottle at such a concentration $CaCO_3$ wouldprecipitate They are good for smaller tanks, but for larger ones they can get a bit expensive DBW

Q: Are all Buffers created equal?

OK, I suspect this is asking about buffer powders, which are the easiest way to add alkalinity to atank. The better ones will also contain the minor buffering components, which is H_3B_03 ... it isrelitively minor compared to the carbonate buffering system, but it is still important. If you can,go for one that you know has this in it.

Q: What is the relationship between Carbonate Hardness (dKH) and alkalinity?

dKH is a measure of alkalinity, along with the other units of measuring alkalinity, such as meq/land ppm $CaCO_3$.

2.8 dKH = 1.0 meq/l = 50 ppm $CaCO_3$ .... I think that is the conversion from memory, but don'thold me to it ;-)

Q: Does that mean that if u bring your alkalinity up while your ph is wrong it will stay wrong?

If the alkalinity is taken up correctly, then the pH should adjust to the correct range. The problemis that if the ratio of the acid to base is out, HCO_3^- and H_2CO_3, then the pH range that it willsettle down to will not be correct. If your pH is in the incorrect range, I would suggest somewater changes to get the ratio back to the correct value. Additionally check your pH test kit orprobe.

Q: I have tried some buffering powders, can they add anything to the water that is not wanted ina reef like, phosphate, silicate etc...?

Not to my knowledge, they typically contain calcium, magnesium, strontium and a few othermetals, with carbonate, sulphate and borate.

Q: What does kalkwasser do in terms of Alkalinity stabalization?

Dosing kalkwasser (damn I hate that word, can't spell it ;-)), or calcium hydroxide introducescaclium, Ca^{2+}, and hydroxide, OH^- to the tank. The OH^- will remove some of the H^+ from thebuffering system, and then free those parts of the buffer to adsorb additional H^+ generated byorganisms. That is how I understand it currently, but that may not be 100% correct DBW

Q: Is Seachem marine buffer a "good" supplement to use?

I am currently using that one myself on OZ REEF, and with good results so far. Everyone elsethat I have talked to that have used it have had good results as well. It has good mix of metalsand anions. DBW

Q: what is the relationship between alkalinity and calcium levels?

OK, this is actually a reverse relationship based on this equilibrium ...

Ca2+ + (CO3)2- <<=>> CaCO3

With the species on the right handside being a solid. So if there is a high calcium level, then apoint will be reached where CaCO3 can form, and will use up the alkalinity. And the visa versais true too, if a high alkalinity is used, then a point will be reached where the CaCO3 will form,removing calcium from solution. It is a hard thing to balance, so if one is too high, then the otherwill be adversely affected

Q: When dripping kalkwasser, sometimes the alkalinity increases while the Ca decreases. Othertimes Ca increases and Alk decreases. Is there a simple explanation to what might be going on?

That I have not had the opportunity to talk to someone about ... but I will give my thoughts onwhat I think may be occuring... When the calcium levelsare decreasing, the alkalinity may behigh, as a result the Ca are taken out of solution into CaCO3. And visa versa for the alkalinity,back to the previous question I suspect.

Q: any practical advice on adding supplements, whther kalkwasser or powders?

Do addtions gradually, marine life dislikes rapid changes in pH or ion concentration. Withpowders mix in a small amount of water first, then add to the tank in a high current area. Withcaclium hydroxide do slowly, as CaOH has a high pH, as very basic. If you add it too quicklythe pH will get too high. I recommend calcium reactors as the best way to do it....and don't worryabout price, as stay tunes as I am about to put plans online on how to make cheap one, verysimple to make too ;-)

Q: How does one know when the alkalinity to calcium ratio is balanced???

Good question that one :-)

It all comes back to the pH, alkalinity and calcium levels. If you are constantly fighting thelevels, going up and down, fluctuating, then it is most likely that something is amiss. Aiming forthe recommend levels is a good idea, as these are close to what is found on a natural reef, and canbe maintained without too much trouble once things are in balance

Q: what is the common name of h3bo3?

Boric acid. Also (BO3)3- is the borate anion

Q: Does sand in the aquarium help to keep the alk stable?

If the sand is CaCO3 and if the pH close to it is low enough to dissolve it. This is the same effectat that which a calcium reactor uses. I have not heard of any conclusive evidence that the sanddoes keep the alkalinty stable, but many people have said that there alkalinity and calcium levelsare maintained by it.

Q: Most literature I've read indicate that alkalinity levels above 5.0 meq/l are artificially high andmay initiate a "snowstorm" of CaCO3 precipitate. As such, they recommend a level of 3.0-3.5meq/l as a good range instead. You earlier indicated a desirable range of 3.0 to 6.0 meq/ml. Canyou elaborate on the difference between your recommendations and those found in otherliterature?

OK, personally I like to keep my tank at levels around that of nature seawater, which is the rangeof 3.0-3.5 meq/l, which is where OZ REEF is currently. The higher levels can be used, and isused and advocated by several other people. The reason it is used is that the pH is much more stable, and because of the excess availablity of the anions present , growth rates of the organismsthat use them is also elevated.

I am still unsure of the actual levels where the Ca will precipitate out, and I am on the look outfor values indicating this. When I find out it will be added to the article that I have on OZ REEFMarine Park.

Q: What substrate do you prefer to use in a calcium reactor?

The best sort is one that is mostly CaCO3 and any of the other trace elements involved in thebuffering process. Aragonite sand is the best one, I cannot fill you in on brands as I am over herein Australia and we don't get the range you do. On draw back of calcium reactors is that if youhave a poor calcium sand, then you can add phosphates and silicates to the system.

Q: Would the use of argonite and dolomite help stablize alkalinity?

Well, aragonite is a crystal form of CaCO3, and the other is calcite. Aragonite is twice assoluble as calcite. Dolomite on the other hand is CaMg(CO3)2 I suspect that dolomite is also lesssoluble than aragonite. The only way that these guys will stabilse the alkalinity is if the pH dropsto a level where it can be dissolved, and this occurs below 7.0. In a reef tank, I am unsure if therelevels are reached, it is possilbe that in the sand bed it gets this low, but this point is currently upin the air.

Q: You said earlier that sand will help maintain alk, are you refering to coral sand, live sand?

Yeah, coral sand, live sand, aragonite, etc All the same thing really. Live sand is just sand thathas interstitial fauna living in it.

Q: LFS states that the only test that tests usable calcium is the seachem one, is this true?

The Seachem kit may in fact only really test for the calcium that their product, Reef Caclium,provides and that is chelated with EDTA. I am of the opinion currently that the chelated may notbe such a good idea, even though can get to higher Ca levels. Other than those points, I have notanymore to tell you on that.

<EricEE> Seachem's test kit is designet to compensate for the fact that they use EDTA as achelating agent. Seachem's test is NOT accurate if you're using kalkwasser or a reactor for thatspecific reason.

I would just like to invite everyone to have a look at my site, OZ REEF Marine Park,www.ecr.mu.oz.au/~dagley/. You can checkout of heaps of pics of my tank and some otherinteresting articles too.