

The Contrarian Reef

Leo Morin, Ph.D

At Seachem, we get many questions from hobbyists, not all directly related to our product line. We do our best to be helpful and answer questions without bias. We do not, however, follow the crowd, so that sometimes our views may seem contrarian. Here are some of the issues that come up repeatedly.

CALCIUM SUPPLEMENTATION

The most frequently recommended practice for reef maintenance is the addition of limewater or calcium hydroxide solution either in a continuous drip or when replacing water of evaporation. Because of the very high pH (>12) of this material, the addition has to be done slowly and carefully. For example, Tullock (MFM, Oct., 1993, p 4.) recommended one fluid ounce per 50 gallons each day of limewater containing 1.8 g of calcium hydroxide per gallon.

Aside from the potential pH hazards to the aquarium, the zone of high pH that is formed when the limewater mixes with the tank water creates a chemical environment ideal for precipitation of both the calcium being added and the carbonate buffer present in the tank. Beyond this, it is chemically improbable that this addition of minute quantities of calcium has any significant impact on calcium concentration. The addition of one ounce of limewater per 50 gallons per day amounts to less than 0.04 mg/L (ppm) per day. Put another way, it would take 25 days at this rate to increase the calcium concentration by 1 ppm. In sea water containing some 380 mg/L calcium, 1 ppm is insignificant. Calcium hydroxide, although itself rich in calcium and economically available from most food stores as pickling lime, is poorly soluble and caustic and so must be used in the form of limewater, which is an exceptionally poor source of calcium.



Calcium chloride and organically chelated calcium are clearly better sources of calcium without the inherent inadequacies of limewater. Calcium chloride is readily soluble, does not notably alter pH, calculating exact amounts to use is easy, and it is readily available from many home or hardware stores as 96% pellets. It is used mainly as road salt. The 4% impurities are mainly other calcium, magnesium, and sodium salts, which pose no hazard to the reef aquarium. The chloride ion already predominates in sea water, so that the addition that comes with calcium chloride supplementation is relatively minor. Like limewater, calcium chloride will precipitate alkalinity as calcium carbonate, but this is less severe than with lime-

water, since calcium chloride does not produce zones of high pH that favor such precipitation.

Organically chelated calcium has the advantages of being both more readily available biologically and more stable in sea water, requiring smaller and less frequent dosing than other additives, as well as diminishing the need to maintain calcium at 380 mg/L or higher. As for calcium chloride, calculating proper dosage is simple. Some prefer not to use chelated calcium, because of concern about adding organics to the aquarium. This is not a valid concern. The amount of organics added with chelated calcium is insignificantly small when compared to the organics released by most reef creatures, even in a no feed, no nutrients approach. Since chelated calcium products are lactate, gluconate, or cross-linked gluconate chelates, the naive misconception that these products contain sugars has arisen. While these components are related to sugars, they are oxidized aldehydes and do not react or behave as sugars any more than chloride ions, predominant in sea water, react or behave as chlorine. When regularly monitored by redox measurements, the addition of chelated calcium has no significant impact on redox.

ALKALINITY

Alkalinity is another area of confusion for aquarists and recommendations about this are often equally confused. The first problem with alkalinity is the term itself. It is not well defined and means different things to aquarists, chemists, environmental engineers, and water treatment engineers. It is often confused with calcium content and hardness. Some units used to report concentration of alkalinity do not help. Expressing alkalinity as grains/gallon calcium carbonate or, in the hobby, as German degrees (KH), defined as parts calcium oxide per 100,000 parts water, only adds to the confusion. Calcium concentration is measured as mg/L (ppm) and it is not hardness nor is it alkalinity. Hardness is a measure of divalent metal cations and primarily reflects the combined calcium and magnesium concentration in freshwater. Hardness is not a measure of carbonate, even though it is often expressed as some unit related to calcium carbonate. Alkalinity would be better called buffer capacity. Alkalinity is the ability of the water to resist changes in pH on the addition of acid. Most of the buffering in sea water comes from its bicarbonate, carbonate, and borate content. It makes little sense to express buffering capacity as some unit related to calcium oxide or calcium carbonate. The value should be expressed in terms consistent with sound chemistry (related to the amount of acid required to measure it) and the S.I. (international) system of units. The expression meq/L (milli-equivalents per liter) satisfies these criteria. Even without defining terms, it is almost intuitive that 1 meq of alkalinity will neutralize 1 meq of acid. Alkalinity is measured by titrating a known volume of sea water with a known concentration of acid until a pH indicator marks the complete consumption of alkaline components by the acid: the amount of acid required is equivalent to the amount of alkalinity or buffer capacity.

HOW MUCH ALKALINITY DOES A REEF AQUARIUM REQUIRE?

Natural sea water has an alkalinity of about 2.5 meq/L. Recommendations range from the same as sea water to as much as 4 times that amount. It has been suggested that to deviate in any way from natural sea water is an experi-

ment and should not be done. While this is true to some extent, it is not sound for all parameters of sea water chemistry. An alkalinity of 2.5 meq/L is fine for the open ocean, but a reef tank is not the open ocean. The accumulation of organic and inorganic acids, even CO₂ as carbonic acid during night hours, can easily take its toll on an alkalinity of only 2.5 meq/L in a confined aquarium environment. To put this buffer capacity in perspective, consider that in most biological studies, such as tissue or cell culture—and reef tanks have more in common with test tube culture than the open ocean—buffers are required to be in the range of 50 - 200 meq/L. Another way to look at it: less than a single fluid ounce of commercial muriatic acid added to 50 gallons of sea water will completely consume its alkalinity at 2.5 meq/L. A buffer capacity of 2.5 meq/L is almost no buffer at all. We recommend 5 meq/L, and even this is minimal buffering. We do not recommend more, not because it would be harmful, evidence indicates otherwise, but because at greater than 5 - 6 meq/L it becomes almost impossible to maintain a calcium concentration approximating 380 mg/L. In a fish only tank (not reef), it is advisable to maintain higher alkalinity and ignore the calcium content. We do not subscribe to the notion that natural sea water is the perfect media for sea life, but it is a good starting point. We have little information on most constituents of sea water, so that to deviate from them very much tends to be experimental, but for some constituents, such as alkalinity, we have enough experience to be confident that reasonably increased alkalinity is beneficial. The same might be said for slightly lower salinity than is generally found in sea water.

REDOX

Redox is another poorly understood measurement in the hobby. Redox is measured with an electrode, very much like pH is measured with an electrode. Just as electrode pH measurements are very much dependent on a properly functioning and calibrated electrode, true redox measurements are even more dependent on function and calibration of the electrode. Unfortunately, redox calibrators do not have the stability characteristic of pH calibrators. While accuracy and precision are dependent on electrode function, many hobbyists have the natural inclination to

assume that digital read-outs are highly accurate, regardless of the condition of the electrode. The assumption behind redox measurements is that organics depress redox and the removal of organics raises redox. All organics are assumed to be harmful. High redox is associated with oxygenation and good water quality. In fact, redox is a measure of the ratio or equilibrium between oxidizing and reducing substances in the water. It does not address the issue of whether these oxidants or reductants are harmful or beneficial. The underlying assumption is that oxidants are good, reductants are bad. Redox measurements can be useful if they are made reliably and the aquarist is aware of what can alter measurements without necessarily reflecting a decline or improvement in water quality. The addition of strong oxidizing agents, such as ozone, peroxide, permanganate, persulfate, or hypochlorite, will produce an immediate rise in redox of themselves, and this has no particular benefit. Ultimately, these oxidants will oxidize something oxidizable and that may be of benefit, but the benefit was not reflected by the initial rise of redox from the oxidants themselves. Likewise, the addition of reductants, such as vitamin C, other vitamins, amino acids, some nutrients, dechlorinating or ammonia removing compounds, will cause a drop of redox, but this does not reflect a decline in water quality. Even innocent fluctuations, such as pH, alkalinity, or temperature rise, will cause a drop in redox. Day or night, feeding, filtering media, water changes, all of these have innocent effects that are not faithfully reflected by redox changes. High nitrates are undesirable, yet nitrates will cause an upward swing in redox. Redox measurements are a tool. Used intelligently they can be helpful, used compulsively they can be dangerous. Provided an aquarium is well oxygenated and well maintained with water changes and some form of chemical treatment such as skimming and organic filtration, it is more likely that damage will be caused by too high a redox than by too low a redox, usually because someone feels compelled to raise redox by adding some strong oxidizing agent. Using a redox meter is a lot like investing in stocks. If you follow the normal ups and downs too closely, you will probably end up losing it all. It is very possible to maintain a successful reef aquarium without ever taking a single redox measurement.

OZONE

Another area of concern is ozone. Ozone is a very unstable triatomic form of oxygen and is a very powerful oxidizer. It is often recommended for use with skimming. In freshwater, ozone oxidizes organic material and ultimately breaks down to free diatomic molecular oxygen. In sea water, however, ozone reacts instantly (microseconds!) not only with organics, but first with iodide, bromide, and chloride ions to form hypoiodite, hypobromite, hypochlorite (bleach!), also iodine and bromine. The latter two are just as bad as chlorine. Ozone also reacts with available manganese, iron, magnesium, and even calcium ions and depletes them from solution. Ozone is non-discriminating and destroys useful amino acids, vitamins, and other deliberately added nutrients as well as the undesirable organics. Ozone cannot escape into the tank itself, being too short-lived, but its byproducts, predictable (bleach) and unpredictable (what did that unidentified organic released by that anemone incompletely break down to?) can. With all the proper caveats in place, ozone can be used safely, but is it worth it?

PHOSPHATE

Despite rumors to the contrary, phosphate is not among the most toxic substances known to man. Phosphate is essential for all life forms, even viruses and corals. Phosphate is a major component of DNA and RNA and life cannot get very far without one or both of these. Phosphate has limited solubility in sea water, most of it precipitating naturally as magnesium and calcium phosphates, major components of detritus. Phosphate is harmless to fish and most invertebrates. Excess phosphate, greater than 0.1 - 0.2 mg/L (ppm), can interfere with the growth of some corals and promotes the proliferation of hair algae. Common sources of phosphate are seasonal peaks in municipal water supplies, the biota of the aquarium, food, and activated carbon. Contrary to some manufacturers' claims, all carbons contain and leach phosphate. Phosphate in carbon does not arise from phosphoric acid washing of carbon, but from the organic material used to manufacture the carbon. Acid washed carbons are washed with sulfuric or hydrochloric acid, not phosphoric acid.

Usually, carbons most suited for water filtration (macro-porous) leach the most phosphate. Carbons designed for gas filtration (microporous) leach the least. A few macro-porous carbons available leach relatively less because they have been pre-washed or acid washed to remove soluble components.

RED SLIME

This one is simple. Do not use red slime killing products, usually erythromycin. Aside from jeopardizing nitrification and denitrification, antibiotics just kill off all susceptible strains of algae or bacteria, then a few weeks later the resistant survivors take over. Your slime killer stops working. The safest way to suppress red slime is with light, specifically with the long UV available in actinic sources. Increase the actinic light or other UV source and remove any glass or thick acrylic between the light and the water. UV sterilizers do not help with this because they do not illuminate the aquarium.

“BERLIN SYSTEM”

Finally, something else that keeps coming up. The new philosophy is that if the nitrate concentration is too high, it is because you have a too efficient nitrification filter. The solution is to dismantle the wet-dry or other filter and start relying solely on reef rock to do the job. Somehow, if you use reef rock as your sole biological filter you will have a balance between nitrification and denitrification. Somehow, all that ammonia that is now being converted to nitrate will be processed in some other mysterious way so as not to form nitrate. It has been suggested that you don't even need a skimmer. Lots of reef rock and that's it! Maybe some aquarists can make this work for more than two weeks, but I do not think experimenting with such a precarious—yes, precarious!—system (and that is using the word loosely) is something to do unless you are ready to gamble a lot of reef creatures and money. It has been suggested that those who do not agree with this approach simply do not understand the chemistry of reef rock. In all humility, I have to admit I do not understand the mysterious new age chemistry alluded to by some of the proponents of this approach. If you have a high nitrate concen-

tration, it makes more sense to find a way to remove the nitrate, either by regular water changes or some kind of denitrification filter or agent. If you have too much nitrate, seek to improve the denitrifying capacity of your rock and filter material, not short circuit your nitrifying filter. Also, seek to remove ammonia before it is converted to nitrite: a well vented wet-dry or ammonia tower can have significant impact by venting free ammonia directly to the air; also enhanced chemical filtration and skimming can remove many amino-organics before they are bacterially converted to ammonia. It is also important to consider that nitrate in itself is not likely the real problem, but rather other not easily measured impurities for which nitrate is a useful marker. All the more reason not to neglect water changes and to consider supplemental chemical, bacterial, and algal filtration.

Reef keeping is as much an art as it is a science. There is no single best way to practice this art, but any approach should be viewed with caution when it evokes the suspension of basic chemical principles or plain good sense.