When Do Calcium and Alkalinity Demand Not Exactly Balance?
By Randy Holmes-Farley

Calcium and alkalinity are generally supplied to reef aquaria in order to offset losses caused by the formation of calcium carbonate. There are many ways to replace these loses, and every method has its own pros and cons. While the purpose of this article is not to detail these methods, there is one important aspect of the consumption of alkalinity and calcium that has a strong bearing on the way such replacement methods are designed and used, and how well each of them may work in a given aquarium. Specifically, the consumption of alkalinity and calcium are tied together due to calcium carbonate containing a relatively constant ratio of calcium to alkalinity. Replacing them using a method that has that same ratio is typically more convenient and often more accurate and effective than trying to constantly measure them both and adjusting them independently.

There are, however, certain scenarios where the consumption ratio deviates from that expected for pure calcium carbonate. How and why that happens is the purpose of this article. Understanding such issues can help aquarists know how to deal with such situations, and to understand if observed mismatches are real consumption effects, or are related to other factors, such as dosing pump errors, testing errors, or poorly designed or described products.

All of the sections of this article are relatively self-contained, so if only a single topic or two is of interest, there's no need to read it all. If all you want is a quick summary of the entire topic, reading just the summary may be best.

Summary

1. Mismatches in real calcium and alkalinity demand are small. Unless total demand is very low, the mismatch may not be noticed for weeks or months. When total demand is very low (such as alkalinity demand less than 0.3 dKH per day), then these effects can become more significant.

2. Large mismatches in observed demand are likely due to issues such as mismatched dosing pumps, poorly designed products, large water changes with a mix not matching the aquarium, or to testing errors, often driven by not watching calcium long enough to get an accurate measure of the decline over time.

3. Nitrate is a common player in real demand mismatches, though the effect is most often fairly small. Rising nitrate depletes alkalinity. Falling nitrate (by consumption) or dosing of nitrate (followed by consumption) adds alkalinity. If nitrate is steady at any level (without dosing nitrate) then there is no ongoing effect of nitrate on alkalinity. Sulfur denitrators strongly deplete alkalinity (or add unbalanced calcium if they are also set up to dissolve calcium carbonate), but carbon denitrators do not.

4. Dosing ammonia can deplete alkalinity, or be alkalinity neutral, depending on the specific forms used.

5. The incorporation of magnesium and strontium in place of calcium in calcium carbonate lowers the demand for calcium, relative to alkalinity. The amount of magnesium incorporated is a large function of the organism depositing the calcium carbonate. Coralline algae is among the larger users of magnesium relative to calcium, and a tank where coralline algae is the biggest consumer of alkalinity and calcium will have a lower calcium to alkalinity demand ratio than one where hard corals drive most of the calcification. Strontium effects are typically quite small, but the amount incorporated is a function of the amount of strontium in the water and can thus variably impact the calcium to alkalinity demand ratio.

6. Water changes have a couple of effects. Exporting nitrate by water change tends to deplete alkalinity, and without nitrate, water changes can still alter the apparent demand ratio when the alkalinity and calcium in the new water do not match the aquarium.

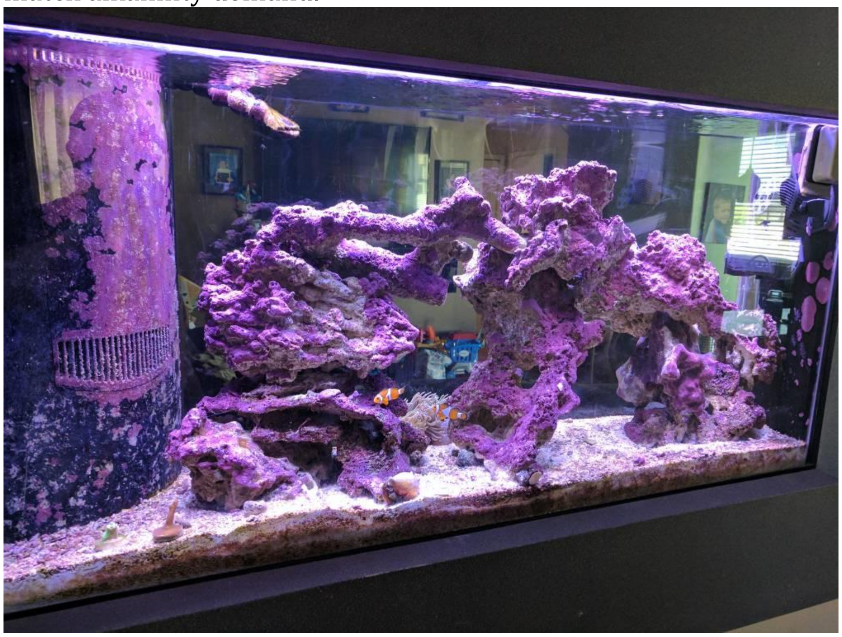
7. If top off water contains any calcium or alkalinity, it can alter the apparent demand ratio. Tap water can contain as much alkalinity as seawater, and thus this effect can be significant.

8. Because of these various deviations, no dosing method that ties alkalinity to calcium can be perfectly balanced for every aquarium, and occasional corrections or adjustments may be needed. These methods include $CaCO_3/CO_2$ reactors, limewater/kalkwasser, and various one, two and three part dosing methods (e.g., Tropic Marin All For Reef, ESV B-ionic, and Tropic Marin Balling as an example of each type, respectively). Overall, I believe that such methods are better than independent dosing of alkalinity and calcium (largely due to the inability to accurately detect calcium changes day to day), and most reef aquarists use one or more of these balanced methods. Note, however, that not all such products claim 1:1 dosing of the two parts (e.g., Red Sea Foundation Elements), and at least one that claims to be (Seachem Reef Fusion) is not designed with a proper ratio for 1:1 dosing.

Calcium Carbonate Formation Background

The deposition of calcium carbonate takes place in hard corals to form their skeletons, and in other internal structures such as spicules in certain soft corals. It also takes place in a wide range of other organisms, ranging from coralline algae to snails to clams. Deposition of calcium carbonate also takes place outside of biological systems, such as on heaters and pump impellers, where the increased temperature results in decreased solubility of calcium carbonate, and hence a greater likelihood of precipitation. Such abiotic deposition can also take place in sand and on rock, where bare calcium carbonate surfaces can act as seed crystals to precipitate calcium and carbonate that are supersaturated in normal seawater and in most reef aquaria.

Figure 1. Coralline algae in the aquarium of Reef2Reef member triolede ployment. Coralline algae incorporates a relative large percentage of magnesium in place of calcium in its calcium carbonate compared to many corals, and is one of the primary reasons for calcium demand to not exactly match alkalinity demand.



In each of these cases, what is being deposited is largely calcium carbonate. Since calcium and carbonate are present in pure calcium carbonate at exactly equal concentrations (one ion of calcium to one ion of carbonate), the removal rate of calcium and carbonate by all of the deposition mechanisms described above should be approximately the same. To a great extent, aquarists use alkalinity as a surrogate measure of carbonate (and bicarbonate). The exact balance between calcium and carbonate demand in a reef aquarium is therefore equally well described as a balance between calcium and alkalinity demand.

Reef aquarists take great advantage of the 1:1 matching of calcium and alkalinity demand in reef aquaria by using additives that supply calcium and alkalinity in this same ratio. In this way, over- or under-dosing of such balanced calcium and alkalinity additives should not result in skewing the aquarium water's chemistry toward too much calcium and too little alkalinity, or too much alkalinity and too little calcium. On the other hand, independent additions of calcium and alkalinity, even with careful and frequent measurement, often lead to such imbalances due to testing imperfection.

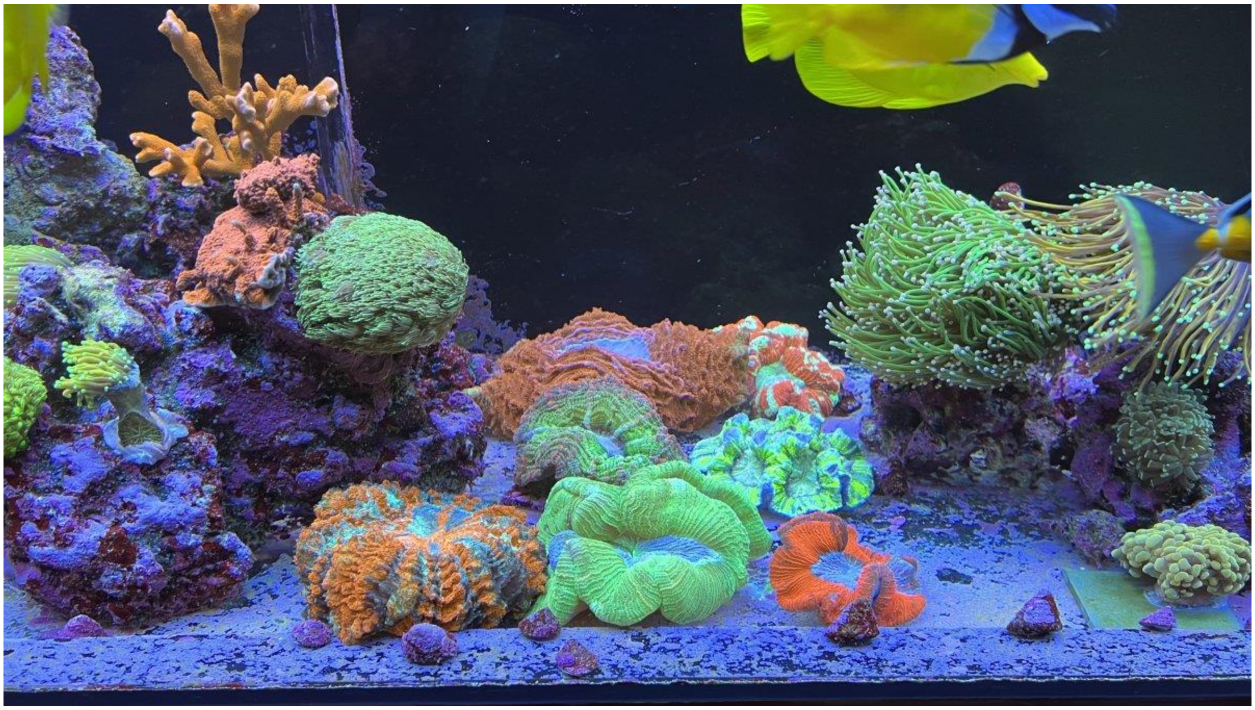
There exist a variety of such balanced additives, and many have been described and compared in detail in previous articles. They include calcium carbonate/carbon dioxide ($CaCO_3/CO_2$) reactors, limewater (kalkwasser), the two or three part additive systems, and some one-part systems (e.g., All for Reef or Salifert All In One). As a class, I strongly recommend them over any other unbalanced additive methods for most reef aquarists.

There are, however, several reasons that calcium and alkalinity balance is not always perfect. In many reef aquaria using only balanced additive systems, the levels will slowly drift away from perfect balance, and will require occasional correction. Whether this correction is needed weekly, monthly or yearly, and in what direction, will depend on the system's details. Before discussing these real calcium and alkalinity demand imbalance issues, however, I will also describe one "mechanism" that confounds many aquarists by appearing to represent a drift in the balance, but that really does not. The "mechanism" arises in the simple fact that alkalinity rises and falls much faster than does calcium because seawater has a much bigger reservoir of calcium than it does alkalinity.

Calcium and Alkalinity Demand: Calcium Carbonate Mathematics

Calcium carbonate formation consumes its two components in an exact 1:1 ratio. In the units used by aquarists, this ratio corresponds to 2.8 dKH (1 meq/L; 50 ppm CaCO3 equivalents) for every 20 ppm of calcium. Not surprisingly, this is also approximately the ratio of alkalinity to calcium that is supplied when calcium carbonate is dissolved, as in a $CaCO_3/CO_2$ reactor. Fortuitously for the aquarist, this is also the ratio supplied when calcium hydroxide is dissolved, as with the use of limewater (kalkwasser).

Figure 2. Several hard corals in the aquarium of Reef2Reef member Miami Reef. Miami Reef uses a balanced 3 part DIY alkalinity and calcium system using calcium chloride, sodium hydroxide, and Tropic Marin Balling Part C to balance out the ionic composition. One of the benefits of a two or three part dosing system is that one can easily adjust the doses slightly off the prescribed 1:1 dosing to match any deviations in the alkalinity to calcium demand ratio.



Apparent Excess Demand for Alkalinity

One of the most common complaints of new aquarists is that their aquaria seem to need more alkalinity than their balanced additive system, such as limewater or All for Reef, is supplying. While there are reasons this may actually be the case over the long term (these will be detailed later in this article), frequently these aquarists are seeing a "chemical mirage" rather than a real excess demand for alkalinity.

One of the interesting features of seawater is that it contains a lot more calcium than alkalinity. By this, I mean that if all of the calcium in seawater (420 ppm) were to be precipitated as calcium carbonate, it would consume 59 dKH of alkalinity (nearly 10 times as much as is present in natural seawater). In a less drastic scenario, let's say that calcium carbonate is formed from aquarium water starting with an alkalinity of 8.4 dKH that it is allowed to drop to 5.6 dKH (a 33% drop). How much has the calcium declined? It is a surprise to many people to learn that the calcium would drop by only 20 ppm (5%). Consequently, many aquarists observe that their calcium levels are relatively stable (within their ability to reproducibly test it), but alkalinity can vary up and down substantially. This is exactly what would be expected, given that the aquarium already has such a large reservoir of calcium.

Therefore, the first "deviation" from the rule of calcium and alkalinity balance really isn't a deviation at all. If an aquarist is supplying a balanced additive to his aquarium, and calcium seems stable but alkalinity is declining, it may very well be that what is needed is more of the balanced additive, not just alkalinity. This scenario should be assumed as the most likely explanation for most aquarists who should look for more esoteric explanations for alkalinity decline only if calcium RISES substantially while alkalinity falls. Likewise, if alkalinity is rising and calcium seems stable when using a balanced calcium and alkalinity additive system, the most likely explanation is that too much of the additive system is being used.

The real imbalance effects described later in this article take effect slowly, and are manifested over weeks, months and years. This short term "chemical mirage" caused simply by the mathematics of calcium and alkalinity additions can be seen in a single addition. Any effect that develops rapidly over the course of a few days is almost certainly not a true demand imbalance.

The following scenarios show what can happen to a reef aquarium whose dosage with a balanced additive system does not match its demand. Table 1 shows what can happen when the dosing is inadequate. Alkalinity drops fairly rapidly. After one day, many aquarists might conclude that they need additional alkalinity, when in reality, they need more of both calcium and alkalinity to stabilize the system.

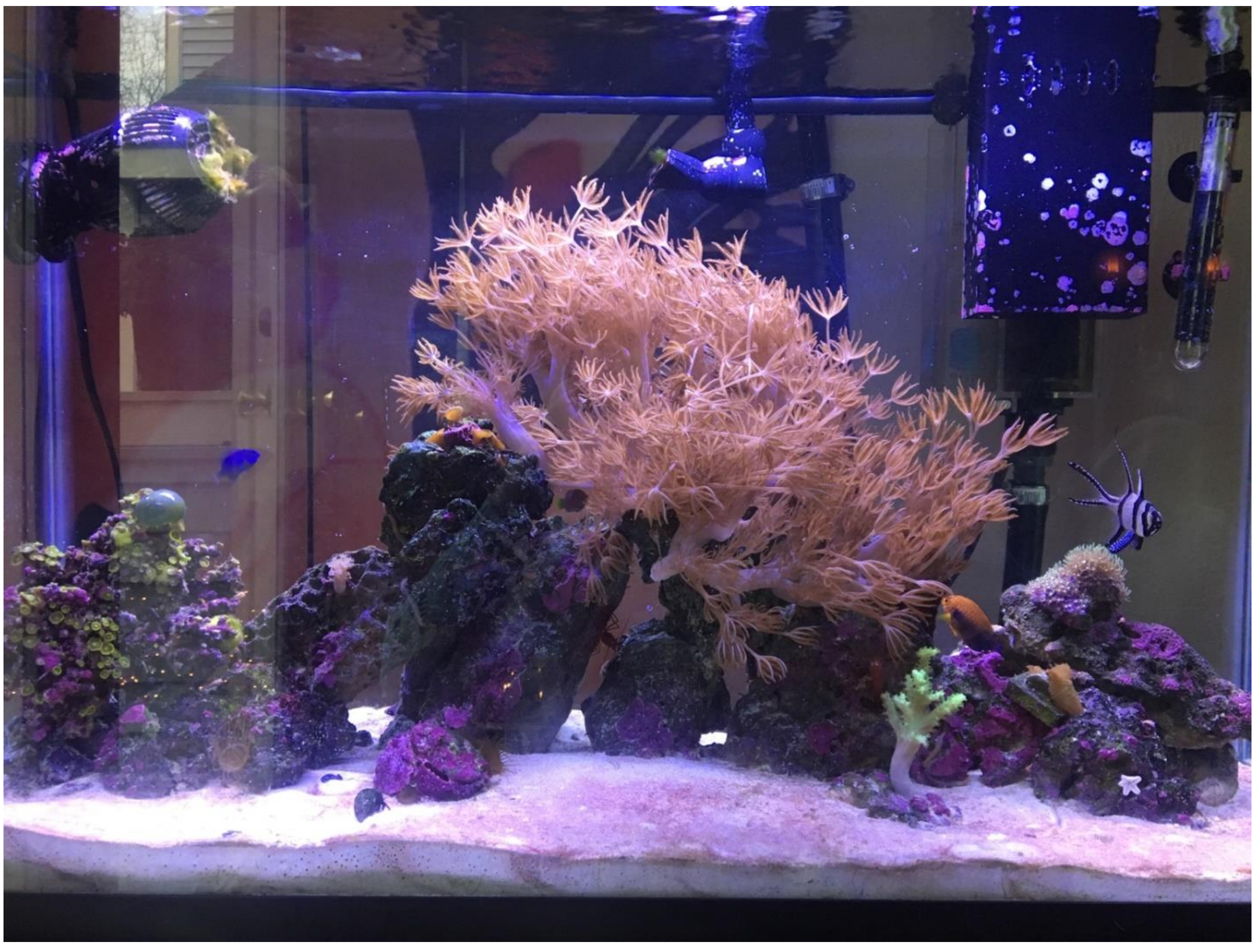
Table 1. Calcium and alkalinity declines in a reef aquarium where balanced additions *are not meeting* demand.

Day	Calcium (ppm)	Alkalinity (dKH)
1	450	11.2
2	440	9.8
3	430	8.4
4	420	7
5	410	5.6

Table 2 shows what happens when too much of a balanced additive is added. After a day or two, many aquarists would conclude that alkalinity is rising too much, but that calcium is fairly stable. Again, what is needed is less of the balanced additive, not just less alkalinity.

Table 2. Calcium and alkalinity increases in a reef aquarium where balanced additions are *greater than* demand.		
Day	**Calcium (ppm)**	**Alkalinity (dKH)**
1	410	7
2	420	8.4
3	430	9.8
4	440	11.2
5	450	12.6
6	460	14
7	470	15.4

Figure 3. A xenia soft coral growing in the aquarium of Reef2Reef member kpnosal. While many soft corals do use calcium and alkalinity to form internal structures made from calcium carbonate, Xenia seems to have few if any such structures. Consequently, it does not significantly impact the demand for calcium or alkalinity in reef aquaria.



Real Excess Demand for Alkalinity: Magnesium and Strontium

Many aquarists will correctly dispute the notion I professed in the introduction, that calcium and alkalinity are exactly balanced, because coral skeletons are not pure calcium carbonate. In fact, they contain significant amounts of magnesium and a smaller amount of strontium. Abiotically precipitated calcium carbonate also contains such ions. In short, magnesium and strontium enter the calcium carbonate structure in place of calcium, reducing the amount of calcium required for a given amount of carbonate. Consequently, the aquarium is skewed toward less calcium demand and more alkalinity demand for this reason.

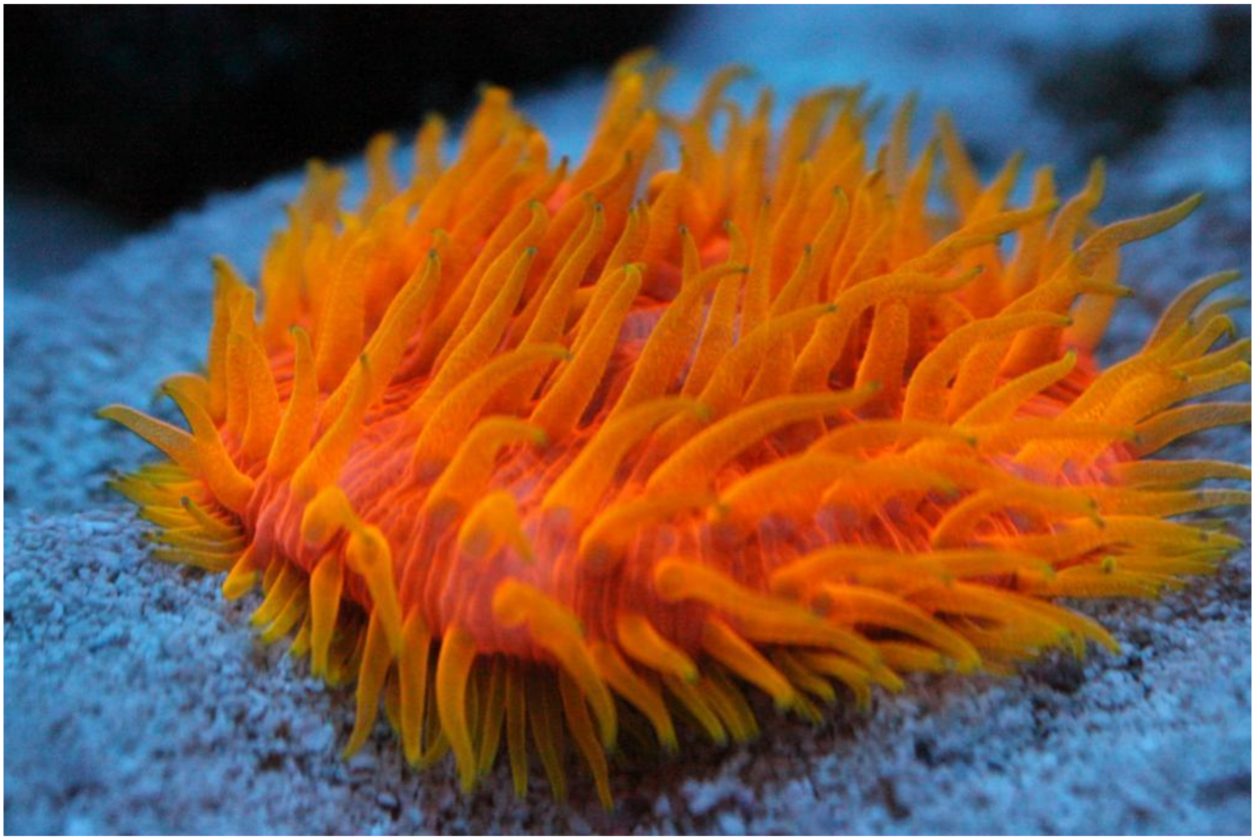
How big is this effect? In terms of magnesium, it is hard to say exactly how big the effect will be because the amount of magnesium deposited depends strongly on the species involved, and ranges from much less than 1% magnesium by weight in the skeleton, to more than 4%. Consequently, the magnesium demand in one aquarium may be very different from the magnesium demand in a second aquarium whose calcium demand is exactly the same.

Importantly, coralline algae (Figure 1) actually deposits a high magnesium calcite instead of the aragonite deposited by most hard corals, and thus incorporates a relatively large fraction of magnesium relative to calcium (about 10 parts calcium by weight to 1 part magnesium by weight, or about 4 % magnesium in the calcium carbonate overall). Hence, aquaria where coralline algae is one of the largest users of calcium and alkalinity will be among the most skewed to using less calcium than a perfect balance.

Figure 4. Coralline algae may be the largest user of calcium and alkalinity in this aquarium of Reef2Reef member Nerdist Aquarist. It provides an attractive backdrop to the aquarium, and he likely has a relatively high magnesium to calcium requirement and hence a lower than average calcium to alkalinity demand ratio.

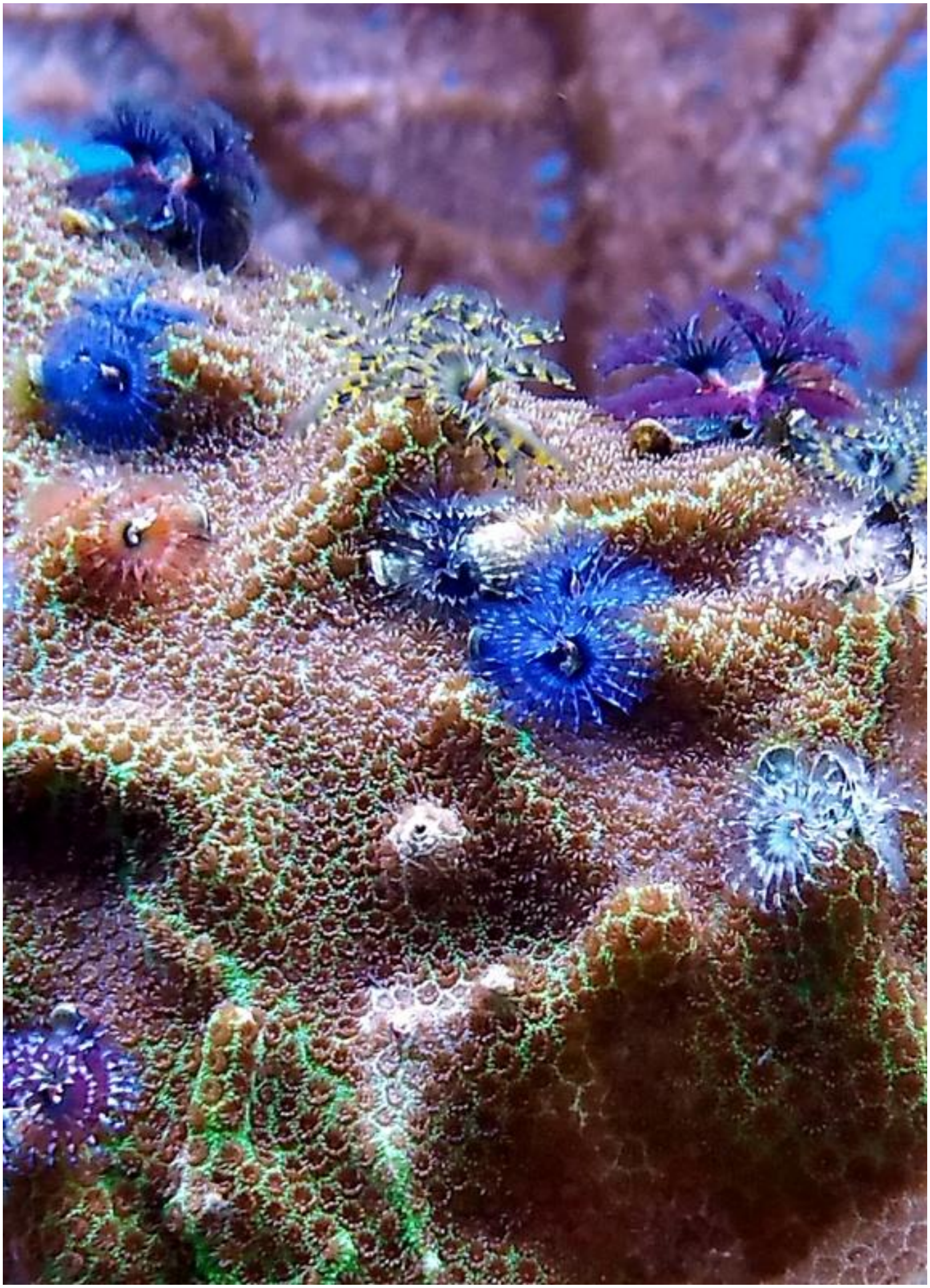
We can roughly calculate the magnitude of the effect of magnesium incorporation, despite the variability. Depositing pure calcium carbonate requires 20 ppm of calcium for every 2.8 dKH of alkalinity. Substituting magnesium to the extent of 4% by weight in the skeleton (as in some coralline algae species) decreases the calcium content by 16.5% (because magnesium is lighter than calcium and calcium only occupies 40% of the mass of calcium carbonate to begin with). Thus, the demand is then only 16.7 ppm calcium for every 2.8 dKH of alkalinity. The change in the balance of the demand caused by magnesium incorporation into organisms will depend on the exact species driving the demand, but can be larger than the other causes described in this article.

Figure 5. A fungia coral in the aquarium of Reef2Reef member FloMojo. Fungia corals are reported to be among those with the lowest percentage of magnesium in their skeletons, at only 0.09 to 1.2% magnesium by weight.



Strontium has a rather smaller effect. Corals, coralline algae, and abiotically precipitated calcium carbonate in natural seawater typically have roughly one strontium ion for every 100 calcium ions (whether these are dispersed within calcium carbonate, or as a separate strontium carbonate miniphases). In a reef aquarium, where the strontium level can be twice the natural level, this strontium incorporation can be higher, on the order of one strontium ion for every 50 calcium ions. The replacement of calcium by strontium in the carbonate crystals has the effect of reducing the calcium demand from 20 ppm per 2.8 dKH of alkalinity to 19.8 per 2.8 dKH for natural levels of strontium, and to 19.6 ppm per 2.8 dKH at double the natural level. This strontium effect is smaller than the magnesium effect, but can be comparable to the other effects described in this article. In addition, the amount of substitution by ions other than calcium in forming carbonates may depend on other factors, including temperature and (as with the strontium example above) the relative concentrations of the ions present.

Figure 6. A porites coral with Christmas tree worms in the aquarium of Reef2Reef member Leon1988. Porites species vary with respect to the amount of magnesium incorporated, from less than 0.1% to over 1% magnesium in the skeleton.



Alkalinity Decline in the Nitrogen Cycle

One of the best known chemical cycles in aquaria is the nitrogen cycle. In it, ammonia excreted by fish and other organisms is converted into nitrate. This conversion produces acid, H^+ (or uses alkalinity depending on how one chooses to look at it), as shown in equation 1:

(1) $NH_3 + 2O_2 \rightarrow NO_3^- + H^+ + H_2O$

For each ammonia molecule converted into nitrate, one hydrogen ion (H^+) is produced. If nitrate is allowed to accumulate to 50 ppm, the addition of this acid will deplete 2.3 dKH of alkalinity.

However, the news is not all bad. When this nitrate proceeds further along the nitrogen cycle, the depleted alkalinity is returned in exactly the amount lost. For example, if the nitrate is allowed to be converted into N_2 in a sand bed, one of the products is bicarbonate, as shown in equation 2 (below) for the breakdown of glucose and nitrate under typical hypoxic conditions as might happen in a deep sand bed:

(2) $4NO_3^- + 5/6\ C_6H_{12}O_6$ (glucose) $+ 4H_2O \rightarrow 2\ N_2 + 7H_2O + 4HCO_3^- + CO_2$

In equation 2 we see that exactly one bicarbonate ion is produced for each nitrate ion consumed. Consequently, the alkalinity gain is 2.3 dKH for every 50 ppm of nitrate consumed.

Likewise, equation 3 (below) shows the uptake of nitrate and CO2 into macroalgae to form typical organic molecules:

(3) $122\ CO_2 + 122\ H_2O + 16\ NO_3^- \rightarrow C_{106}H_{260}O_{106}N_{16} + 138\ O_2 + 16\ HCO_3^-$

Again, one bicarbonate ion is produced for each nitrate ion consumed.

It turns out that as long as the nitrate concentration is stable, regardless of its actual value, there is no ongoing net depletion of alkalinity. Of course, alkalinity was depleted to reach that value, but once it stabilizes, there is no continuing alkalinity depletion because the export processes described above are exactly balancing the depletion from nitrification (the conversion of ammonia to nitrate). This also applies to all types of organic carbon dosing schemes, unless the organic added actually provides alkalinity when it is metabolized, such as with formate in All For Reef or acetate in Salifert All in One.

There are, however, circumstances where the alkalinity is lost in the conversion of ammonia to nitrate, and is never returned. The most likely scenario to be important in reef aquaria is when nitrate is removed through water changes. In that case, each water change takes out some nitrate, and if the system produces nitrate to get back to some stable level, the alkalinity again becomes depleted.

If, for example, nitrate averages 50 ppm at each water change, then over the course of a year with 10 water changes of 20% each, the alkalinity will be depleted by 4.5 dKH over the course of that entire time period. This process is one of the primary reasons that fish-only aquaria that often export nitrate in water changes need occasional buffer additions to replace that depleted alkalinity, even if nitrate is the same after each water change.

While the magnitude of the depletion described in the paragraph above due to water changes is fairly easy to understand, it also can be converted into units that clarify the imbalance. The impact of alkalinity depletion on the calcium and alkalinity demand balance depends, of course, on the amount of calcium and alkalinity added (and consumed) over the course of that same year.

For a typical reef aquarium (for example, an aquarium using a daily addition of saturated limewater equal to 2% of the tank's volume), the amount of alkalinity added during the course of a year is very large: 834 dKH. Likewise, the amount of calcium added is 5,957 ppm Ca++. If that extra 4.5 dKH of alkalinity lost by water changes containing nitrate is added to create a slightly larger demand of 838.8 dKH over the course of a year, the new ratio for the alkalinity to calcium consumed is changed very little: from 20.0 ppm calcium for each 2.8 dKH to 19.9 ppm for each 2.8 dKH of alkalinity. **Consequently, while the effect of nitrate production on alkalinity is enough to be noticed over the course of a year, it is substantially smaller than some of the other effects discussed in this article, and is unimportant for aquaria that maintain low nitrate levels.**

Effects of Nitrate Dosing

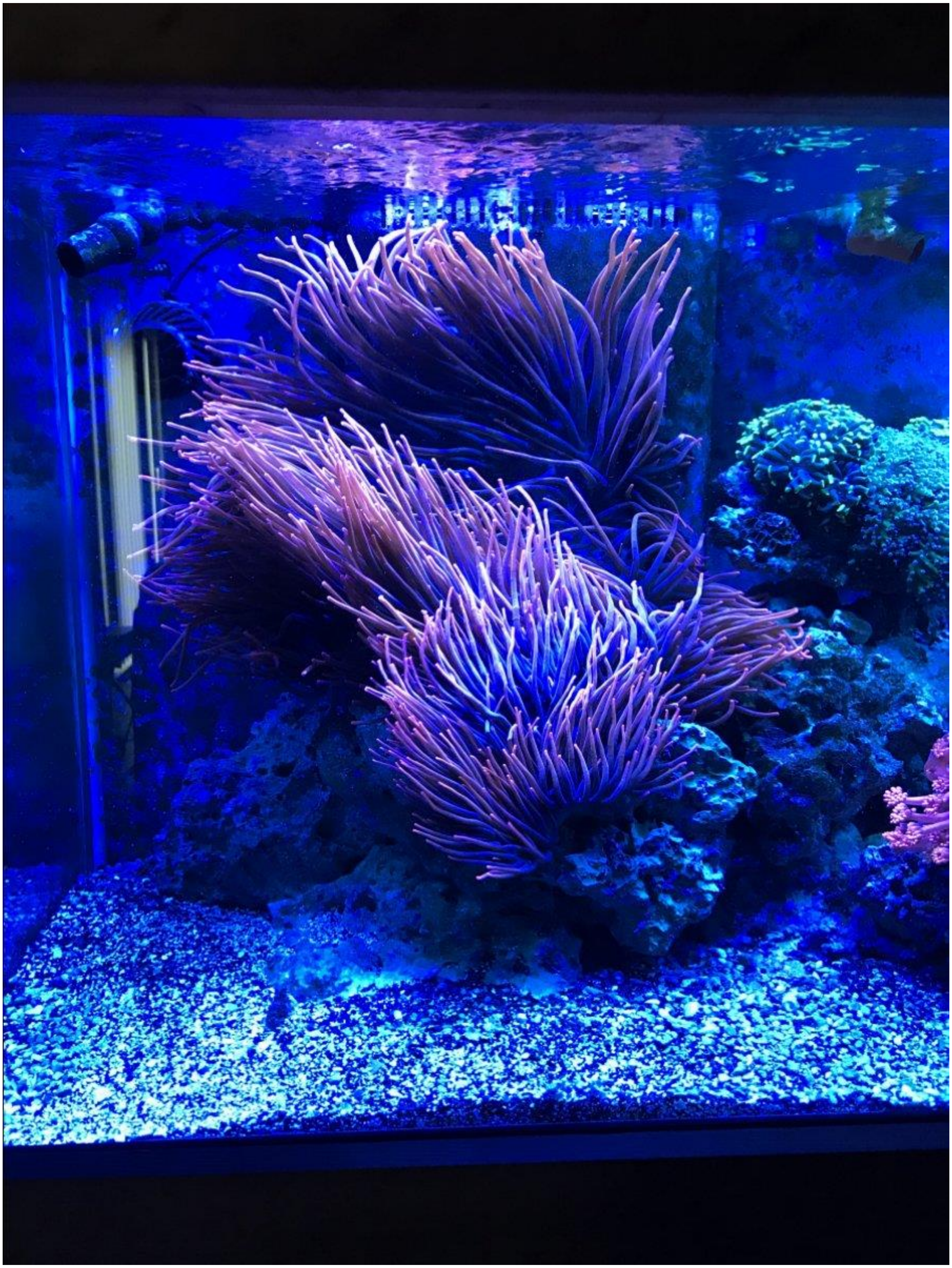
Taking equations 2 and 3 from above, representing nitrate being consumed by either denitrification (#2) or by incorporation into tissues (#3)

(2) $4NO_3^- + 5/6\ C_6H_{12}O_6$ (glucose) + $4H_2O \rightarrow 2\ N_2 + 7H_2O + 4HCO_3^- + CO_2$

(3) $122\ CO_2 + 122\ H_2O + 16\ NO_3^- \rightarrow C_{106}H_{260}O_{106}N_{16} + 138\ O_2 + 16\ HCO_3^-$

we see that if we are dosing nitrate and it is consumed, there is generation of alkalinity (as bicarbonate in these equations, HCO3-). In both cases, the addition is 2.3 dKH for each 50 ppm of nitrate dosed and consumed. That amount is significant enough that in a low alkalinity demand reef aquarium, alkalinity may actually rise over time without any standard alkalinity additives being used. In all aquaria, it is sufficient to throw off the standard ratio of alkalinity to calcium consumed.

Figure 7. Bubble tip (E. quad.) anemones in the aquarium of Reef2Reef member Hitman. While anemones themselves are not net consumers of alkalinity or calcium, they may use alkalinity in the water as a source of CO2 for photosynthesis. In this aquarium, nitrate was being dosed, which will tend to supplement alkalinity as the nitrate is consumed.



Effects of Ammonia Dosing

There are several different DIY recipes available for aquarists wanting to dose ammonia to low nitrate systems. One of these, using ammonium chloride, tends to deplete alkalinity, and one using ammonium bicarbonate is net neutral toward alkalinity. Some aspects of the recipes are copied below so that readers can understand the effect.

Ammonium Chloride

Ammonium chloride, NH_4Cl, is essentially ammonia (NH_3) plus hydrochloric acid (HCl). Dosing NH_3 followed by consumption by organisms to form tissue is a net alkalinity neutral process. I'm ignoring the fact that if it is converted into nitrate, alkalinity is lost, because if that nitrate is later used, all the lost alkalinity comes back.

However, the HCl that is effectively dosed will steadily deplete alkalinity. Adding the equivalent of 50 ppm nitrate (0.81 meq/L; coming from NH_4Cl) will have depleted 2.3 dKH of alkalinity. That may need to be made up for in some other fashion, such as adding more alkalinity supplement.

Ammonium Bicarbonate

Ammonium bicarbonate, also known as baking ammonia, NH_4HCO_3 is essentially ammonia (NH_3) plus CO_2 and water.

As mentioned above, dosing NH_3 followed by consumption by organisms to form tissue is a net alkalinity neutral process. The CO_2 and water also do not impact alkalinity. Thus, ammonium bicarbonate is a net alkalinity neutral way to dose ammonia. The same is true of ammonium hydroxide (basically ammonia plus water)

Effects of Sulfur Denitrators

In sulfur denitrators, bacteria use elemental sulfur and produce N_2 from the sulfur and nitrate according the following equation (or something similar):

(4) $2\ H_2O + 5\ S + 6\ NO_3^- \rightarrow 3\ N_2 + 5\ SO_4^{2-} + 4\ H^+$

The production of acid (H^+) in this reactor can tend to reduce the aquarium alkalinity. It has also been suggested to pass the effluent of such a reactor through a bed of aragonite to use the acid (H^+) produced to dissolve the calcium carbonate, and thereby provide calcium and alkalinity to the aquarium. While that is a fine idea to boost pH and alkalinity, it doesn't solve the imbalance of alkalinity being consumed relative to calcium. The dissolving calcium carbonate merely shifts the balance to adding calcium instead of depleting alkalinity.

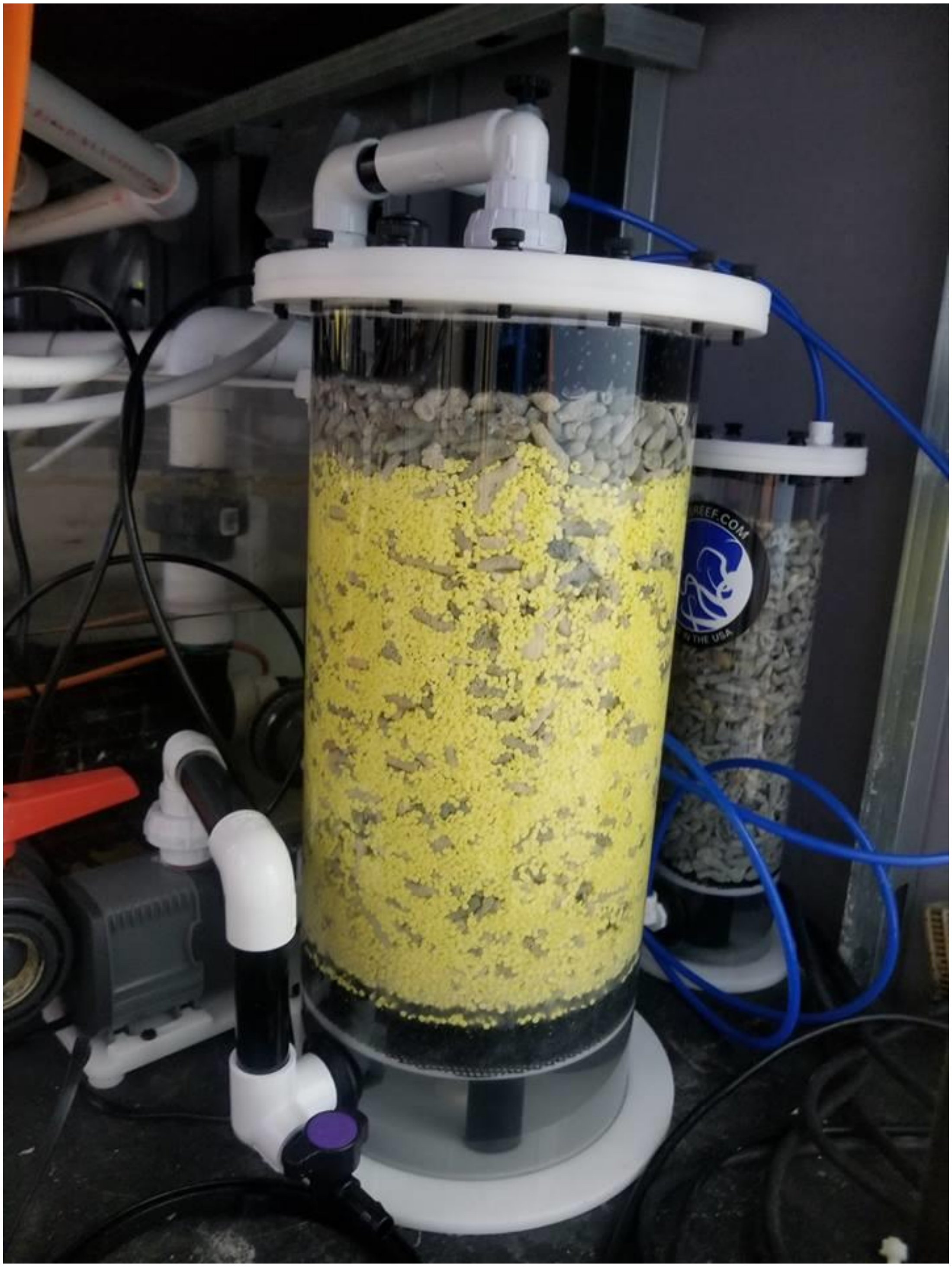
To estimate the magnitude of the effect of a sulfur denitrator on the relative demand ratio, we start with an estimate of how much nitrate might be removed. Say 10 ppm of nitrate per week.

10 ppm nitrate = 0.16 mmole/L of nitrate

Since 4 moles of H^+ are produced for every 6 moles of nitrate consumed, this will produce 0.107 mmoles/L of H^+ per week, or effectively deplete 0.3 dKH of alkalinity per week. Added to the 0.46 dKH of alkalinity that was depleted when ammonia was converted to 10 ppm of nitrate, and **we see that producing 10 ppm of nitrate and then removing it with a sulfur denitrator**

depletes 0.76 dKH which is not an insignificant amount of alkalinity to deplete in a time frame such as a week.

Figure 8. A sulfur denitrator used by Reef2Reef member cumbeje. The sulfur granules are yellow, and the grey material is calcium carbonate, used to offset the pH and alkalinity decline (though it does not alter the calcium to alkalinity imbalance, it just shifts it to adding calcium instead of depleting alkalinity).



Effects Due to Water Changes (without nitrate export)

Another reason that calcium and alkalinity demand is not exactly balanced in many aquaria has to do with water changes. Many aquarists (including myself) do not attempt to match the calcium and alkalinity levels in water change water to the aquarium water. Consequently, each water change will alter these levels in the aquarium, and will alter the observed balance between calcium and alkalinity demand. What direction the change takes, however, will depend on the salt mix chosen and the aquarium water parameters. Commercial salt mixes vary from high calcium and normal alkalinity to high alkalinity and low calcium.

For example, if the aquarium is maintained at 420 ppm calcium and 11 dKH of alkalinity, and the water change has 500 ppm calcium and 7 dKH of alkalinity, each 20% water change will increase calcium by 16 ppm, and will drop alkalinity by 0.8 dKH. Using the same water change scenario used in the nitrate calculations above (10 changes of 20% each over the course of a year), these water changes will increase calcium by 160 ppm and drop alkalinity by 8.4 dKH.

For a typical aquarium (assuming a daily addition of saturated limewater equal to 2% of the tank's volume), the amount of alkalinity added during the course of a year is 834 dKH. Likewise, the amount of calcium added is 5,957 ppm Ca++. If that amount of alkalinity demand is increased by 8.4 dKH to 842.4 dKH over the course of a year, and the calcium demand is decreased by 160 ppm to 5797 ppm, the new ratio for the total demand becomes 19.30 ppm Ca++ per 2.8 dKH of alkalinity. Consequently, the effect of water changes can be significant, but will depend entirely on how much the aquarium water deviates from the water change water, and on the amount of water changed.

Figure 9. A sophisticated automatic water change system in use by Reef2Reef member CoralReefer2110. Automatically changing water is a great way to minimize the amount of work needed by the aquarist each time water is changed.

The Effect of Top-Off Water

A final factor that can impact the apparent calcium and alkalinity demand is the possibility of delivering calcium or alkalinity or both in top-off water. Water that is purified by reverse osmosis (RO) followed by deionization (DI), and water that is purified by distillation will not deliver any significant amount of calcium or alkalinity (regardless of the apparent pH when such a measurement is taken). The same is true for water purified by DI only. Water purified by only RO may have a small amount of calcium or alkalinity in it, depending on the nature of the source water.

The greatest chance for effects to tank water calcium and alkalinity levels comes from the use of tap water or spring water (neither of which do I recommend for reef aquaria without careful testing). In an article describing concerns with the use of tap water in reef aquaria, I showed that water from municipal water supplies can range from 0 to 93 ppm calcium and 0 to 15 dKH of alkalinity. Obviously, tap water with close to zero calcium and alkalinity will not appreciably impact the calcium and alkalinity balance. At the extremes, however, these values can have a large impact.

If we assume that an aquarium receives 2% of its tank volume daily to replace evaporated water, then one extreme is a case where over the course of a year, 679 ppm of calcium is added, and no alkalinity. At the other extreme, 112 dKH of alkalinity is added, and no calcium.

For a typical aquarium (using 2% of the tank volume daily in saturated limewater), the amount of alkalinity added during the course of a year is 834 dKH. Likewise, the amount of calcium added is 5,957 ppm Ca++, given the demand ratio of 2.8 dKH of alkalinity for every 20 ppm of calcium discussed above. If that amount of alkalinity demand is decreased by 112 dKH, due to alkalinity in tap water, to 721 dKH over the course of a year, and the calcium demand is unchanged, the new ratio for the total apparent demand becomes 23.1 ppm Ca++ per 2.8 dKH of alkalinity. Likewise, if the calcium demand is decreased by 679 ppm of calcium, to 5278 ppm, the new apparent demand ratio becomes 17.7 ppm Ca++ per 2.8 dKH of alkalinity. These extreme cases may not actually happen anywhere, since the extreme case for calcium and the extreme case for alkalinity occur in the same city (Kansas City in 2003), so they partially offset each other. Nevertheless, the effect easily could be half as large in many cities, and it is apparent that this effect of tap water can be significant, and may even dominate the other effects.

Figure 10. Two tridancid clams in the aquarium of Reef2Reef member Narideth. *Tridacna* species of clams deposit calcium carbonate in their shells, and can be a significant source of calcium and alkalinity demand in reef aquaria with many clams. In general, they would be expected to have a largely balanced demand for alkalinity and calcium, just as corals do.

Other Effects

Other effects may also skew the demand for calcium and alkalinity in aquaria. These include foods that contain calcium or, rarely, alkalinity, and various additives that aquarists use. Most additives do not contain alkalinity (except, of course, buffers and anything claiming to control pH or supply alkalinity), although sodium silicate and borax (borate) do provide alkalinity. Since many additives do not even say what they contain, it is hard to say what effect they might have, but I'd expect most of them to be inconsequential in this respect.

How Are Additive Systems Really Balanced?

Since, for the reasons described above, the demand for calcium and alkalinity may not be precisely balanced at 20 ppm calcium per 2.8 dKH alkalinity (matching pure calcium carbonate formation), the question arises, what ratio is used in balanced additive systems?

According to the ESV web site, the two part system B-ionic has a balance of 19.3 ppm calcium per 2.8 dKH of alkalinity when dosed at 1:1. That value is probably a fine balance for the calcium and alkalinity ions given the effects of magnesium and strontium incorporation. A one part system, Tropic Marin All For Reef uses 20.1 ppm calcium for each 2.8 dKH of alkalinity. It might accumulate calcium slowly in an aquarium with a lot of coralline algae. Seachem Reef Fusion uses 22.7 ppm of calcium for each 2.8 dKH of alkalinity when dosed 1:1, and it will clearly accumulate calcium over time if dosed 1:1 in most aquaria, despite its claim of being designed for 1:1 dowsing.

Clear, settled limewater has a ratio of approximately 20.0 ppm Ca^{++} to 2.8 dKH of alkalinity. It has no significant magnesium in it, and its strontium level is very low. For those dosing cloudy limewater, lime solids that I have measured contain enough magnesium to drop the ratio to about 19.9 ppm calcium per 2.8 dKH of alkalinity.

While the following published analyses are fairly old now, they likely are representative of the sorts of materials currently available. Koralith $CaCO_3/CO_2$ reactor media has slightly less magnesium and strontium than does the lime that I tested, and would have a ratio of 19.9 ppm calcium per 2.8 dKH of alkalinity. A different brand of media, Super Calc Gold, has more magnesium, with a resulting ratio of about 19.8 ppm calcium per 2.8 dKH of alkalinity. A third brand, Nature's Ocean crushed coral, has a similar level of magnesium, resulting in a ratio of 19.8 ppm calcium per 2.8 dKH of alkalinity. All of these brands may fall short of the rate of incorporation of magnesium in reef aquaria, as has been discussed in previous articles. Some aquarists have taken to adding a small amount of dolomite (a material containing both calcium and magnesium carbonates) to their $CaCO_3/CO_2$ reactors to add an appropriate amount of magnesium.

Which Mechanisms Predominate in Reef Aquaria?

Mechanisms resulting in a deviation from an exact balance between calcium and alkalinity will obviously vary between aquaria with different calcifying species and with different husbandry practices. Some of the mechanisms may have opposite effects on the balance, partially canceling each other out in some aquaria (e.g., water changes with a high alkalinity/low calcium salt mix vs. magnesium and strontium incorporation). Consequently, it isn't possible to say which effect will dominate reef aquaria in general.

In my reef aquarium, I used only Instant Ocean salt and I did not add any additional calcium except as limewater/kalkwasser for a number of years (during which time I performed regular 1% daily water changes). My calcium level (472 mg/L by ICP) was higher than one would normally expect for Instant Ocean (between 350 and 400 mg/L at that time). That long term rise in calcium is the expected result when using limewater to maintain alkalinity, while magnesium is being incorporated into deposited calcium carbonate.

Conclusion

A variety of processes prevent reef aquarists from experiencing exactly balanced demand for calcium and alkalinity. These include the effects of incorporation of magnesium and strontium into coral skeletons, the varied effects relating to nitrate, the effects of water changes with new water that does not match the aquarium water in terms of chemical ions present, and top off water that contains calcium or alkalinity. Aquarists may also be fooled into thinking they are seeing imbalanced demand when in reality they are simply observing the fact that on a percentage basis, alkalinity goes up and down much faster than calcium. Understanding how and when these differences arise should allow reef aquarists to better deal with them, and not take inappropriate actions to "correct" them.

Happy Reefing!