Calcium and Alkalinity: How to Achieve Proper Levels in Your Aquarium

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One of the aspects of keeping small polyp stony (SPS) corals that is starting to gain significant attention is the need to supplement calcium by the easiest means possible. Before stony corals were maintained, little attention was paid to maintaining the proper level of calcium. Water changes and the dissolution of the calcium substrate were thought to be able to keep the levels high enough, so that no additional supplementation was utilized.

When the Berlin System for keeping corals was introduced in the late 1980's, the concept of supplementing calcium in the tank was first described. This was important, in that prior to this series of articles, little attention was paid to the coral's need for calcium in order to thrive and grow. Initially, the only method described was that of using calcium hydroxide dissolved in water (kalkwasser) to replace evaporated water. As tanks became more sophisticated and stony corals and clams became the dominant animals in these tanks, more sophisticated methods for maintaining calcium levels have been developed. Over the past ten years, it has finally been demonstrated that virtually all corals, as well as coralline algae require calcium in order to thrive.

The reason that no single method of calcium supplementation is utilized exclusively is that, to date, no system has proven to be perfect. Despite the shortcomings of these methods, it is still relatively easy to maintain the calcium level in most tanks above 400ppm (parts per million), the level of natural seawater, as long as these problems are understood and managed. It is very important that calcium levels be kept this high, particularly for stony corals, for these reasons:

- If calcium levels are low, the corals will not grow, and what little growth does occur, will result in thin, spindly branches.
- In addition, if growth is not occurring, the coloration of the coral, particularly at the tips, will not be as vivid as when the coral is growing well.

> In nature, seawater bathes coral reefs in many minerals and elements. Of all the minerals and elements present in natural seawater, no mineral is consumed as quickly or in as large amounts as calcium. Hard corals, which are the building blocks of the coral reef, demand large amounts of calcium to build their skeletons. Providing enough calcium to meet the demands of all the corals, invertebrates, and algae in a closed ecosystem creates a real challenge for the hobbyist.

It is necessary to understand the limits of each method of supplementation before choosing a method for one's system. The methods that are currently being employed include:

- Calcium chloride and buffer
- Kalkwasser (sometimes referred to as limewater)
- Kalkwasser reactor
- Balanced liquid or dry supplements
- Calcium reactors
- Calcium reactor and kalkwasser combinations

I have used each of these methods over the past ten years, so I feel comfortable discussing their advantages, as well as their shortcomings. However, I do not consider myself an expert on calcium supplementation, as I am still tinkering to try and optimize my calcium supplementation system.

Calcium chloride and buffer

Using calcium chloride in combination with buffer was probably the first method for maintaining calcium levels employed by most old reef hobbyists. Once it was understood that its use could rapidly deplete the buffering capacity of a tank, the use of buffering compounds were added in combination. This methodology is indeed a simple and easy way to maintain calcium levels for a small system, or one that does not consume a lot of calcium.

Advantages: The advantages of calcium chloride and buffer are:

- Calcium chloride is widely available and inexpensive.
- Calcium chloride dissolves rapidly and it is possible to mathematically determine how much is needed.

Disadvantages: When this method is employed, it tends to be used as a bolus type of supplementation method. That is, when it is determined that the calcium levels are low, a large amount of calcium chloride is dumped in to correct the problem. When the proper level of calcium is reached, the addition of calcium chloride is stopped.

- If a measurement of alkalinity is not undertaken, the calcium level may be fine, but the alkalinity level drops too low. This causes one of the coral's main sources for carbon to be reduced. If this is not corrected, a drop in pH may occur

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due to the tank's loss of buffering capacity. When this is realized, buffer is usually added to make up for the reduced alkalinity. At this point, one of two things happen:

- The calcium level drops and the cycle is repeated, or
- The system becomes stable for a short time and then additional supplements are added as needed. Even if the system is stable for a short time, depending on the buffer used, some elements may start to accumulate to unnatural levels. Sodium and bromide in particular may build up, as they are contained in high levels in most buffers. As a result, some animals may begin deteriorating for no apparent reason. If the source of the problem is determined, then the only course of action to remedy the problem is to do more frequent, and larger, water changes. This can shock the animals, or possibly get the system back to the point where the problem originated.

This system may work fine in tanks where lesser amounts of calcium are consumed, for example, tanks with small amounts of coralline algae and a small population of soft corals. In these tanks, the above problems should not occur.

Kalkwasser

The use of calcium hydroxide (kalkwasser), when introduced by Alf Nielsen in 1990, probably did more to enable us to keep SPS corals than just about any other advancement in reefkeeping to that point. Before this discussion by Mr. Nielsen, calcium supplementation was more or less an afterthought. However, once it was explained how vital it was to have adequate calcium available in order for SPS corals to thrive, a whole new group of corals suddenly were being cultivated. Up until this time, as noted above, calcium chloride and buffer were the calcium supplementation method of choice. However, once the use of kalkwasser was explained, it became the method of choice for most of the last decade. After using this method for the past ten years, the advantages and disadvantages of its use have become apparent.

Advantages: European aquarists have been using kalkwasser for the past twenty years with great success. Some of the advantages of this method are:

- Kalkwasser is simply calcium hydroxide dissolved in water, so it is very straightforward to use.
- There are many different manufacturers of kalkwasser, including Kent, Seachem, and Warner Marine, with all of them having relatively the same high quality.
- Kalkwasser adds virtually nothing to the water that is deleterious (harmful), only calcium and hydroxide ions.
- Kalkwasser precipitates out phosphate, which allows calcification to occur better. Due to its high pH, phosphate precipitates out as calcium phosphate.
- Kalkwasser is also relatively easy to make and is inexpensive. All that is required is to add the dry powder to water and shake it up. *Note:* Allow the cloudy mixture to settle out and then use the clear liquid as make-up water.
- Now there are even kalkwasser reactors available that do the mixing and stirring. These have come to be called "Nielsen reactors," after their initial advocate.

Disadvantages: Unfortunately, there are also some shortcomings to the use of kalkwasser. The disadvantages include:

- Kalkwasser dissolves poorly in water; only approximately 1.5 grams are able to dissolve in a liter of water. As a result, if the tank's evaporation rate is low, it is difficult to maintain the calcium level through the use of kalkwasser alone.
- Kalkwasser is also a caustic (corrosive) alkaline agent, so care must be taken when mixing it up so that the dust is not inhaled.
- Kalkwasser has a very high ph (12.00+), so it should ***not*** be dumped into the tank in large quantities or it will raise the tank's pH levels to excessively high levels. *Note:* This can be used to an advantage by dosing it slowly at night when the tank's pH typically drops. As a result, dramatic changes in pH can be reduced.
- Over time, the use of kalkwasser lowers the alkalinity in the tank. As a result, buffer also has to be added from time to time when kalkwasser is used.
- The biggest drawback is that kalkwasser needs to be fresh. It should not sit in its mixed form for very long or else it interacts with atmospheric carbon dioxide and converts into insoluble calcium carbonate. As a result, kalkwasser should be mixed up daily before it is added to the tank.

As noted above, I have used kalkwasser as my method of calcium supplementation for my SPS tank for the past ten years. As a result of my experience, it is my opinion that this is a very good way to supplement calcium for small- to medium-sized SPS tanks, as long as adequate evaporation is occurring. For most of these tanks, as long as the majority of the kalkwasser is trickled in at night, and buffer is added regularly, there should be few problems. The dynamics of every tank changes over time, and this is why regular testing is necessary.

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Kalkwasser reactors

An alternative to kalkwasser is to use a kalkwasser reactor to mix up and deliver the kalkwasser. Calcium hydroxide is simply added daily to the reactor, which slowly delivers fresh kalkwasser over the course of the day o replace water that evaporates.

Advantages: Some advantages to using kalkwasser reactor are:

- The kalkwasser is continually mixed throughout the day.
- Some reactors include a pH probe to control the quality of the kalkwasser.

Disadvantages: Disadvantages of using kalkwasser reactor are:

- If this device is employed, it may be necessary to also use a carbon dioxide reactor, such as that made by Ultralife, to keep the pH of the tank from going too high. This is because daytime is when most of the evaporation takes place and when most of the kalkwasser will be added into the tank. This could result in the pH rising above the maximum desired level of 8.5 during the day. The carbon dioxide would then be released into the tank via a pH controller, such as a Neptune controller, and an electronic solenoid to keep the pH at the desired level.
- If you need to use kalkwasser as a bolus (large quantity all at once), then it may be necessary to use a carbon dioxide reactor. This dramatically increases the cost of dosing kalkwasser, and thus may make some of the alternatives a better choice.

Balanced liquid or dry supplements

To overcome the problems described above, several manufacturers have devised balanced formulas for maintaining both calcium and alkalinity. Products include Tropic Marin® BioCalcium, Two Little Fishes C-Balance®, and Seachem Reef Advantage CalciumTM.

Advantages: Advantages to using balanced liquid or dry supplements include:

- These compounds, both dry and wet, are capable of maintaining both high calcium levels and alkalinity, while not causing a build-up of unwanted compounds over time. *Note:* Some hobbyists have reported that their salinity levels do increase over time.
- These balanced formulas are easy to use in that once the desired levels of calcium and alkalinity are achieved, all that is necessary is to add equal amounts of the two-part compound to the tank according to the directions.
- It is possible to automate delivery of the liquid compounds by having dosing pumps administer the dose gradually over the course of the day. This helps prevent shock to the tank's inhabitants, even though there is already little chance of shock.
- When the tank's inhabitants grow or when more animals are added, all that needs to be done is to simply increase the amount added daily.

Disadvantages: There are also several shortcomings in the use of this method.

- Liquid compounds are somewhat expensive. Relative to the other methods used, it is the most expensive method for maintaining calcium over the long term. This method of calcium supplementation is great for smaller tanks, or tanks with a small quantity of SPS corals and coralline algae, but somewhat cost prohibitive for large SPS tanks.
- It is somewhat tedious to measure out the same additives every day and consistently add the same small measurements of each.
- If the alkalinity/calcium balance gets out of whack, it will be necessary to restore the balance through some other means which could affect these agents.

Liquid compounds have become very popular. This method was employed on some of my tanks for over two years and it was quite successful. It was so successful in fact, when I discontinued it, several of my corals seemed to go through a withdrawal phase and declined in health, even though the tank was immediately switched to another method of supplementation.

Calcium reactors

As calcium supplementation has become more automated, one of the more sophisticated means of achieving the desired goal is the use of the calcium reactor. Carbon dioxide (CO_2) is pumped, at a fixed rate, into a chamber filled with a calcareous media (aragonite) or Korallith. The CO_2 lowers the pH in the chamber to an acidic level, which dissolves the calcium into the water. The amount of calcium that is released is controlled by the flow rate of water through the chamber, as well as by the rate of release of the carbon dioxide bubbles. This process also dissolves nearly all of the minerals and trace elements corals need to grow. The dissolved solution increases alkalinity (carbonate hardness) to stabilize pH while

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replenishing minerals (trace elements).

Advantages: Calcium reactors are popular for several reasons:

- Over the long term, this method is relatively inexpensive in that all that is needed are carbon dioxide and a calcareous media.
- When used properly, this method provides a very precise means of maintaining calcium levels within a system.
- There are now calcium reactors on the market that can handle even the largest tanks, so it is possible to find a reactor for every tank size.

Disadvantages: Like all methods, calcium reactors are not without some drawbacks.

- These units are relatively expensive initially. In addition to the reactor itself, a properly set up unit will also require a tank for carbon dioxide, a regulator and needle valve, and a means for assessing pH.
- Care must be taken in the selection of the media. Some media may contain a lot of phosphate, so that as the media dissolves, phosphate is released, as well. Fortunately, in the last year, phosphate-free media such as Korallith is now available.
- The amount of carbon dioxide being introduced needs to be closely monitored so that excessive carbon dioxide is not leaked into the tank. If this occurs, a constantly low pH reading will result. However, when a properly functioning needle valve and bubble counter are being used in combination with a pH monitor, there usually is no problem.
- Calcium reactors may increase alkalinity to excessively high levels if they are not monitored closely. This can be controlled by the addition of calcium chloride from time to time, or by adjusting the flow rate and the rate of carbon dioxide introduced.

I have now been using a reactor for over five years on one of my tanks, and other than getting it adjusted initially, it has produced very few problems. While there are considerable start-up costs associated with implementing such a system, a calcium reactor may prove to be a wise long-term investment by saving you time, money, and frustration while maximizing your coral growth. For more information see: Calcium Reactors.

Calcium reactor and kalkwasser combination

One of the latest advances is to use both a calcium reactor and a kalkwasser reactoron a tank that consumes a large amount of calcium. This combination maintains both calcium and alkalinity levels even better than using a single reactor and also results in a reduction in phosphate levels and stable pH. In my opinion, this may be the optimum way of maintaining calcium levels in a large SPS tank. However, it should be noted, as with most aspects of reefkeeping, there are always numerous ways to achieve the desired result, so the experimentation within the hobby will continue. This is how the hobby has progressed to the point it is at now, where SPS corals are commonplace, and their growth rates in some tanks can exceed the rates seen in the wild. Understanding and implementing proper calcium supplementation and alkalinity may seem difficult at first, however, over time, with proper testing and patience, keeping these compounds at their proper levels is actually quite simple.

Testing

Regardless of the system used, while supplementing calcium, there is a need to frequently test the tank's water for the calcium level. Once a good method for supplementing calcium is chosen, we often quit testing thinking that we are done. Calcium supplementation is not a static process; as coral colonies, both soft and stony, grow, and as coralline algae spreads, these organisms all take up more and more calcium. As a result, the supplementation of calcium generally needs to be increased over time. If testing is not done regularly, it is very easy for the levels to drop precipitously, owing to this increase in demand. For this reason, it is my experience that calcium levels should be assessed every two weeks or so, or even better, once per week. To do this, several reliable test kits are available. At the same time, alkalinity should also be measured, as there is a relationship between calcium levels and alkalinity that should be monitored. These same companies also make very good alkalinity/KH test kits. The reason that both of these measures need to be monitored is that if the calcium levels get high (over 500ppm), there is a tendency for the alkalinity to drop. Conversely, if alkalinity levels get too high, calcium levels will tend to fall, as calcium precipitates out in the form of insoluble calcium carbonate. Therefore, when calcium is measured, the level should be between 400ppm and 450ppm, while the alkalinity level should be between 2.5-3.5 meq/L (milliequivalents per liter) or 7-10 dKH (carbonate hardness as measured in degrees).

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