Chapter 14

Calcium and carbonate in closed marine aquarium systems

DIETER BROCKMANN[1] AND MAX JANSE[2]

[1] Gartenweg 3, 89079 Ulm, Germany
dieter.brockmann@uni-ulm.de
[2] Burgers' Zoo, Antoon van Hooffplein 1, 6816 SH Arnhem, The Netherlands
m.janse@burgerszoo.nl

ABSTRACT
The chemistry of calcium and hydrogen carbonate is closely interconnected in marine water. For instance, both ions are of vital importance for the physiology of marine life and play important roles in the buffer system of the marine ecosystem. They are necessary for the calcification process in corals as well as calcareous algae. However, in closed marine aquarium systems the prolific growth of calcium consuming organisms like corals and calcareous algae and chemical processes can rapidly reduce their concentrations followed by instability of the system and decrease in coral growth. Consequently, it is necessary to keep the concentration of both ions constant in their natural range (calcium concentration: app. 420 mg.L^{-1}, alkalinity 2.5-3.5 mEq.L^{-1}) to be successful in the long term culture and reproduction of coral organisms. This paper describes the chemistry of calcium and carbonates within reef aquarium systems. In addition, innovative techniques are presented helping to keep the concentrations of calcium and hydrogen carbonate ions constant in their natural range including additions of calcium hydroxide solutions (*kalkwasser*), calcium chloride / sodium hydrogen carbonate solutions and calcium reactors. The efficiency of these methods with respect to the increase of the calcium and carbonate concentrations as well as their positive and negative sides are discussed.

INTRODUCTION

Calcium is one of the major elements in seawater. It is critical for the formation of a variety of biological structures, including the skeletons and shells of algae, scleractinians and other invertebrates. Carbonate, on the other hand, functions as skeleton element of corals and other invertebrates, as buffer system as well as nutrient for algae.

Calcium carbonate is super saturated in seawater and prone to precipitate. In nature, variation of the calcium concentration is mostly very low and due to a change in salinity caused by for instance changes of temperature or influx from rivers. In reefs, calcification reactions of organisms have only little effect on the calcium concentration due to the large volume of the surrounding sea water. In closed aquarium systems the situation is different. Here, variation in calcium and carbonate concentrations is larger due to a relative small tank volume. Also higher concentrations of organics and phosphates and in relation to the volume high calcification load of the different invertebrates and algae can decrease the calcium concentration rapidly.

The goal of this chapter is to summarize the mechanisms of calcium and carbonate consumption both biological and chemical in aquarium systems. In addition, different techniques are described to supplement calcium and carbonates to a closed marine aquarium system.

CALCIUM AND ALKALINITY

The calcium level in natural sea water is around 420 mg Ca^{2+}.L^{-1} (Spotte, 1979). It is advised to keep the calcium level in aquaria in this range

(390 and 430 mg $Ca^{2+}.L^{-1}$). In the calculations of this chapter a concentration of 420 mg $Ca^{2+}.L^{-1}$ is used.

Calcium carbonate is supersaturated in natural seawater and aquaria and precipitates chemically forming for example calcium carbonate. Calcification on the other hand is the process of a life form to produce calcium carbonate. Both calcium and carbonates are necessary for these reactions. In this perspective, the alkalinity of the water is important. The alkalinity of a solution is its ability to neutralize acid. It can be said, that with a high alkalinity only little pH changes will occur, when acids are added to the system. In contrast, large pH changes occur when acids are added to a solution low in alkalinity.

Alkalinity in seawater is mostly formed by the carbonate-bicarbonate-system and is expressed in milli-equivalent per liter ($mEq.L^{-1}$). To a much lesser extend other compounds like borates participate in the alkalinity. The formation of the carbonate-bicarbonate equilibrium is expressed in the equations 1 to 3. The equilibrium depends on the pH. At the pH of seawater in the range of 7.9 and 8.3 about 90 % of the alkalinity is formed by bicarbonate, the rest is carbonate and to a very lesser extent carbonic acid. The higher the pH the more carbonate will be formed (equation 3). Addition of carbonate or bicarbonate will increase alkalinity.

Equation 1

$$CO_2 \text{ (aq)} + H_2O \quad \leftrightarrows \quad H_2CO_3$$

Equation 2

$$H_2CO_3 \quad \leftrightarrows \quad H^+ + HCO_3^-$$

Equation 3

$$HCO_3^- \quad \leftrightarrows \quad H^+ + CO_3^{2-}$$

In natural seawater the alkalinity is approximately 2.1 to 2.5 $mEq.L^{-1}$ (Spotte, 1992; Delbeek and Sprung, 1994). Another expression for alkalinity is carbonate hardness expressed in German degree (dKH), where 1 $mEq.L^{-1}$ equals 2.8 dKH.

Due to photosynthetic activity and a reasonable small tank volume alkalinity needs to be higher in captivity than in nature. It is advised to keep the alkalinity in aquarium systems with corals between 2.5 and 3.5 $mEq.L^{-1}$ (or 7.0 and 9.8 dKH).

CALCIUM LOSS

Calcium can be lost due to precipitation or consumption. Calcium carbonate is super saturated in seawater which is possible due to different chemical equilibriums. Consequently, calcium carbonate precipitates rapidly from seawater, given the opportunity. In nature the amount of dissolved calcium depends primarily on the equilibrium described in equation 4 (Libes, 1992; Holmes-Farley, 2002).

Equation 4

$$CaCO_3 \text{ (s)} \quad \leftrightarrows \quad Ca^{2+} \text{(aq)} + CO_3^{2-} \text{(aq)}$$

The calcium and carbonate concentration in natural seawater depends on the apparent solubility product (K_{sp}^*) and is expressed as the super saturation index (Ω) in formula 1 (Libes, 1992; Holmes-Farley, 2002)

Formula 1

$$\Omega = \frac{[Ca^{2+}]_{aquarium} * [CO_3^{2-}]_{aquarium}}{K_{sp}^*}$$

$$= \frac{[Ca^{2+}]_{aquarium} * [CO_3^{2-}]_{aquarium}}{[Ca^{2+}]_{saturation} * [CO_3^{2-}]_{saturation}}$$

When the water is saturated the index is 1. At super saturation the index is larger than 1. In normal seawater, the product of calcium and carbonate is about 3 times the K_{sp}^* of aragonite and 5 times that of calcite (Holmes-Farley, 2002). Aragonite and calcite are different crystalline forms of calcium carbonate. In nature the super saturation index is affected positively with increasing salinity and CO_2-concentration and decreasing temperature, pressure and pH (Libes, 1992; Spotte, 1992; Hallock, 1997; Holmes-Farley, 2002). The CO_2-concentration is the most important factor, which is affected by temperature, pressure and salinity and affects directly the pH. In addition to these factors, alkalinity, phosphate, sulphate and magnesium have a direct effect on the calcium level in aquaria. These factors are more prone to variation in aquaria than in nature.

Magnesium has also a direct effect on the calcium concentration. Magnesium interferes with the process of precipitation of calcium carbonate (Spotte, 1992; Holmes-Farley, 2003). Grguric *et al.* (1999) describe the

losses of calcium and magnesium in a closed aquarium system. The precipitation on the rocks had a Mg/Ca ratio of 2.2. Measurement and calculation of the carbonate balance of this precipitant proved it to be a magnesium-calcium carbonate-complex. New calcium carbonate surfaces in an aquarium will quickly attain a thin coating of magnesium calcite ($Mg/CaCO_3$). The extent to which this happens depends on the relative amounts of calcium and magnesium in the water and the underlying mineral, and is apparently much more extensive on calcite than aragonite (Spotte, 1992; Holmes-Farley, 2003). Magnesium calcite is not a good nucleating site for precipitation of additional calcium carbonate and precipitation of calcium carbonate will slow down (Holmes-Farley, 2003).

Phosphates rise easily in aquaria systems especially with high bioloads in fish or sea mammal exhibits. Phosphate levels as high as 5 mg $PO_4^{3-}.L^{-1}$ are not abnormal in these habitats. Coral systems must have much lower phosphate levels, to a maximum of 0.2 mg $PO_4^{3-}.L^{-1}$. When phosphates are available a calcium phosphate-complex can easily be formed as an insoluble layer on the substrate or as crystals. Hebbinghaus (1994) describes that the addition of calcium and carbonates to a system will result in an increase of calcium carbonate and calcium phosphate precipitation and thus helps to reduce the phosphate level.

Finally calcium can be bound to organic compounds. These organics can be natural (e.g. proteins and carbohydrates) or (un) intentionally added chemicals like EDTA, vitamin C, polygluconate, and polyphosphates (Holmes-Farley, 2002). The formed complexes may be discarded from the system via protein skimmers. At Burgers' Ocean, Arnhem three protein skimmers on coral systems had a 8 to 12% higher calcium level in the discarded foam compared to the aquarium water after equalizing to the same salinity. These figures are much lower than found by Sondervan (2001) where the difference was 30%. Still the effect on the calcium concentration of the aquarium water will be neglectable, since only small quantities of solution will be discarded via a protein skimmer.

CALCIFICATION

Calcium is consumed by many different algae and animals via a process called calcification. The importance of calcium to teleosts and elasmobranches from the seawater is not described. It is unknown whether calcium depletion will have an effect on fish health. Calcareous algae and scleractinia consume the largest portion of calcium in aquaria. Calcium carbonate is formed using calcium and bicarbonate in a molar ratio of 1:2.

Equation 5

$$Ca^{2+} + 2HCO_3^- \leftrightarrows Ca(HCO_3)_2 \leftrightarrows CaCO_3 + H_2CO_3$$

Calcareous red algae will form magnesium calcite with a magnesium fraction of around 18 M % (Medakovic et al., 1995). Scleractinia will form of stronger type of calcium carbonate: aragonite. High rates of calcification in hermatypic scleractinia are possible due to the symbioses with zooxanthellae (Muller-Parker and D'Elia, 1997). Strontium, magnesium and trace elements are included in the calcium carbonate skeleton in variable amounts depending on species and concentration of the element in the water.

Gattusa et al. (1998) conducted a calcification experiment with the scleractinia *Stylophora pistilata* in water with different aragonite saturation levels. The rate of calcification increased exponential as a function of increasing aragonite saturation state above the 100% saturation level. A plateau was reached at values greater than 300%, where 300% equals about the natural calcium carbonate super saturation. Higher concentration does not increase calcification. So higher levels of calcium are not necessary to increase calcification in aquaria.

On coral reefs the mean calcification rates are known to be approximately 4 kg $CaCO_3.m^{-2}.y^{-1}$ (Davies, 1983; Smith, 1983; Barnes and Chalker, 1990) to even as high as 10 kg $CaCO_3.m^{-2}.y^{-1}$ (Smith, 1983). No exact data are available for calcification rates in a multiple species coral aquarium.

CALCIUM SUPPLEMENTATION

Several techniques can be applied to increase the calcium and carbonate concentrations in the aquarium. The most commonly used methods including the addition of calcium chloride, calcium hydroxide and the calcium reactor are discussed in detail. In addition to these techniques calcium and carbonates are also made available through dissolution processes

in the aquarium itself. Moreover, carbonates are produced in large amounts through the metabolism of the tank inhabitants.

Leaching of calcium from artificial rock, consisting of cinder blocks or concrete may occur in new aquarium systems. Grguric *et al*. (1999) describe an increase of 75.4 mg Ca^{2+}.kg^{-1} seawater due to leaching from artificial rock in a 2.9 million liter fish tank. Wickens and Helm (1981) describe the use of calcium carbonates (as coral sand) in an external filter system to replace the loss of calcium. However, this will have a limited effect due to (1) an overgrowth of the sand particles by magnesium-calcium carbonate complex (Spotte, 1979) and (2) the very low solubility of $CaCO_3$ in seawater at pH 8.0 or higher.

The coral reef mesocosm of the Pittsburgh Aqua-Zoo has been observed to lose approximately 2.5 to 5.0 cm of carbonate sediment per year (Lang, 1993). Explanations might be a possible dissolution of $CaCO_3$ or a redistribution or compaction phenomena within the sediment. Jaubert (1989) describes a similar dissolution of calcium carbonate in its sand filter system, which includes a 5 cm thick plenum or water buffer below the sand. Due to the activity of nitrifying and denitrifying bacteria and the activity of the meiofauna, acids and carbon dioxide are produced which decrease the pH in the sand bed. When the pH drops below 7.0, calcium carbonate will start to dissolve in the coral sand (see Chapter 12).

When the calcium level in the aquarium ($C_{Ca, aquarium}$) is lower than in fresh seawater ($C_{Ca,refresh}$), water changes ($V_{refresh}$) may have marginal positive effects on the calcium concentration. However, this technique has a very limited effect especially in highly proliferating coral systems due to the constant consumption of large amounts of calcium ions. The effect is described in Formula 2.

Formula 2

$$dC_{Ca} = \frac{V_{refresh}}{V_{aquarium}} * (C_{Ca, refresh} - C_{Ca, aquarium})$$

dC_{Ca} = increase of calcium conc.   [mg Ca^{2+}.L^{-1}]
$V_{aquarium}$ = volume of the aquarium   [L]

Quantification of supplementation

Addition of calcium and carbonates should only be done when calcium levels are tested on a regular basis, to prevent too large variation in both concentrations. A 2 to 4 days calcium depletion test will give some idea of the daily calcium consumption of the system. Care must be taken not to decrease more than 20 mg Ca^{2+}.L^{-1} to prevent adverse effects from the test. During the testing period the external addition of calcium, magnesium and carbonate should be stopped. The required calcium level ($C_{Ca, required}$) in a coral aquarium should be between 390 and 430 mg Ca^{2+}.L^{-1}.

In coral systems (or low phosphate systems) a calcium depletion test can also be tested by using the change in alkalinity (A in mEq.L^{-1}) or carbonate hardness (KH in °dKH). Formula 3 describes the calculation of the amount of calcium consumed ($N_{Ca,t}$) per time interval (t in days) through the system. In this formula the consumed amount of calcium equals the amount of calcium that needs to be added to a system, unless the calcium concentration in the aquarium ($C_{Ca, aquarium}$) is much lower than the required ($C_{Ca, required}$) concentration. Part of the difference must be added ($N_{Ca, diff}$) to the daily addition until the required concentration is reached (Formula 4). The total amount of calcium ($N_{Ca, total}$) supplemented to a system is expressed in Formula 5.

Formula 3

$$N_{Ca, t} = \frac{(C_{Ca, t=0} - C_{Ca, t=n})}{n} = \frac{0.05 * (A_{t=0} - A_{t=n})}{n}$$

$$= \frac{0.14 * (KH_{t=0} - KH_{t=n})}{n} \qquad [\text{g } Ca^{2+}.d^{-1}]$$

Formula 4

$$N_{Ca, diff} = \frac{(C_{Ca, required} - C_{Ca, aquarium})}{n} * V_{aquarium}$$

$$[\text{g } Ca^{2+}.d^{-1}]$$

Formula 5

$$N_{Ca, total} = N_{Ca, t} + N_{Ca, diff}$$

$$[\text{g } Ca^{2+}.d^{-1}]$$

It is important to adjust the calcium level in the aquarium slowly, so the system can adjust to the higher calcium concentration. Since coral skeletons consist of calcium carbonate it is important to add not only calcium, but also carbonates.

For the production of one mole calcium carbonate, one mole of calcium and 2 moles of bicarbonates are needed (equation 5).

Calcium chloride / sodium hydrogen carbonate

Solutions of calcium chloride ($CaCl_2$) and sodium hydrogen carbonate ($NaHCO_3$) are already used since the early 1990 to adjust both the calcium level and the alkalinity and thus to support the calcification of stony corals (see for instance Pawlowsky, 1994; Brockmann and Nilsen, 1995a; Balling, 2002). This method makes use of two separate stock solutions prepared from calcium chloride ($CaCl_2.2H_2O$) and sodium hydrogen carbonate ($NaHCO_3$). Adding both solutions to the tank water gives rise to the following equation.

Equation 6

$$CaCl_2 + 2NaHCO_3 \leftrightarrows Ca^{2+} + 2HCO_3^- + 2\,NaCl$$

In addition to sodium hydrogen carbonate ($NaHCO_3$) sodium carbonate (Na_2CO_3) can be used to prepare the stock solution (Pawlowsky, 1994). Some commercial recipes use a mixture of both chemicals. The advantage is a better control of the pH.

The solubility of $CaCl_2.2H_2O$ in deminelarized water is very high (1000 $g.L^{-1}$ at 20 ^oC). For aquarium use a stock solution of 7.35% $CaCl_2.2H_2O$ (w/v or 73.5 $g.L^{-1}$) is normally prepared. If $CaCl_2$ or $CaCl_2.6H_2O$ is used the stock solution should be 5.60% or 10.96%, respectively. The solubility of $NaHCO_3$ is approximately 95.5 $g.L^{-1}$. The stock solution should be 8.4 % (w/v). Equal volumes of both stock solutions are given to the tank water on a regular basis using a dosage system to add the correct molar ratio of $Ca^{2+} : HCO_3^- = 1 : 2$ (see also equation 6). The absolute amount needed, however, is dependent on the calcium consumption of a given tank.

The amount of calcium that needs to be added daily to the system ($N_{Ca, total}$ in g) (see Formula 5) using the above stock solution of $CaCl_2.2H_2O$ ($N_{CaCl2, stock}$) is expressed in Formula 6. The addition of $CaCl_2.2H_2O$ together with $NaHCO_3$ can also be calculated by weight ($N_{CaCl2, weight}$) (Formula 6 - 9).

Formula 6

$$N_{CaCl_2, stock} = N_{Ca, total} * 0.025 = N_{NaHCO_3, stock} \quad [L]$$

Formula 7

$$N_{CaCl_2.2H_2O, weight} = N_{Ca, total} * 3.67 \quad [g]$$

Formula 8

$$N_{NaHCO_3, weight} = N_{Ca, total} * 4.18 \quad [g]$$

Formula 9

$$N_{CaCl_2.2H_2O, weight} = N_{CaCl_2.6H_2O} * 1.49 = N_{CaCl_2} * 0.76 \quad [g]$$

The main disadvantage of calcium chloride / sodium hydrogen carbonate method is the addition of sodium chloride (see equation 6). Addition of 147 g of $CaCl_2.2H_2O$ and 168 g of $NaHCO_3$ to a system will give rise to 100 g $CaCO_3$ or 40 g Ca^{2+}, however this will also add 117 gram sodium chloride (NaCl). This results in an important – maybe detrimental - effect: the sodium chloride concentration increases in the tank water compared to the other elements. Consequently, when using $CaCl_2$- and $NaHCO_3$-solutions over a prolonged period sodium- and chloride-ions accumulate and the ion balance is disturbed, with possible adverse effects on the life forms. However, due to the best knowledge of the authors the latter effect is not yet systematically researched. Nevertheless, to counteract the ion imbalance and its putative detrimental effect NaCl-free "sea salt" mixtures can be used for water changes (Renke, 2000; Balling, 2002). For each liter of the stock solutions described above, 25.0 g of the NaCl-free sea salt mixture (instead of the complete sea salt mixture) is used for water changes (Balling, 2002). Unfortunately NaCl-free salt mixtures dissolve only poorly in water as its components might react with each other. It is therefore recommended to increase the amount of water change and thereby mix the NaCl-free sea salt mixture with the complete sea salt mixture. By doing this, 25.0 g of the NaCl-free salt mixture substitute for 83.5 g of the complete sea salt mixture (Balling, 2002).

It is very important to add both stock solutions in different regions of the aquarium system in areas with a high water movement. Otherwise calcium carbonate will precipitate following equations 6 and 7. The precipitated $CaCO_3$ is of no use for the aquarium system due to its insolubility.
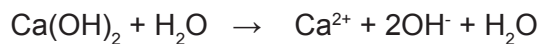
Kalkwasser

Addition of kalkwasser to increase the calcium level of the tank water was originally described by Wilkens (1973) and is nowadays widely used with great success among aquarists keeping tanks with sessile invertebrates (e.g.

Wickens and Helm, 1981; Brockmann, 1991; Delbeek and Sprung, 1994; Grguric *et al.*, 1999). Kalkwasser is an aqueous solution containing calcium (Ca^{2+}) and hydroxide (OH^-) ions. It can be prepared using either calcium oxide (CaO, equations 7 and 8) or calcium hydroxide ($Ca(OH)_2$, equation 8).

Equation 7

$$CaO + 2H_2O \quad \rightarrow \quad Ca(OH)_2 + H_2O + energy$$

Equation 8

$$Ca(OH)_2 + H_2O \quad \rightarrow \quad Ca^{2+} + 2OH^- + H_2O$$

Dissolution of CaO in water is an exothermic reaction producing energy (heat; see equation 7). Due to this side effect, which may cause problems if the calcium oxide is dissolved in a glass container, most aquarists use $Ca(OH)_2$ to produce kalkwasser. Still calcium hydroxide is an aggressive and corrosive chemical and should be handled with extreme care.

$Ca(OH)_2$ dissolves poorly in water. Approximately 1.26 gram of solid $Ca(OH)_2$ dissolves in 1 liter of demineralized water at 20 °C (Holleman and Wiberg, 1976) which gives rise to a concentration of 682 mg Ca^{2+}-ions per 1 liter of kalkwasser. The solubility of $Ca(OH)_2$ is temperature dependent: it decreases with increasing temperature. Moreover, $Ca(OH)_2$ dissolves better in freshwater than in saltwater.

In case of a calcium deficiency, the theoretical amount of kalkwasser ($V_{kalkwasser}$) that has to be added to a system can be calculated via Formula 5 and Formula 10.

Formula 10

$$V_{kalkwasser} = N_{Ca,total} / 0.68 \qquad [L]$$

The theoretical amount of kalkwasser which can be added to a system depends on the evaporation rate of a given tank. For instance, approximately 5 L of water evaporate daily from a tank containing 800 L. If all the evaporated water is refilled with saturated kalkwasser, 3.41 g of Ca^{2+}-ions are given back to the system which increases the Ca^{2+}-concentration at 4.26 mg.L^{-1}. In comparison to other methods described in this chapter this is pretty low and the amount of calcium ions deriving from kalkwasser is not sufficient to support maximum calcification rates of stony corals in closed aquarium systems as

shown by a rough calculation of Fosså and Nilsen (2001).

Kalkwasser is prepared by adding an excessive (app. 2 g $Ca(OH)_2$ powder per liter) amount of solid calcium hydroxide to freshwater, mix the suspension vigorously and allow it to settle for some hours. The clear supernatant, which constitutes the kalkwasser, is added to the tank in an area with strong water movement to avoid precipitation of $CaCO_3$. (Of note: solid calcium hydroxide or calcium oxide must NOT be added directly to the tank at any time! This would cause uncontrolled pH fluctuations of the tank water and direct precipitation of $CaCO_3$.) On the bottom of the container containing kalkwasser undissolved calcium hydroxide is found together with precipitated calcium carbonate. The latter is formed by the reaction of calcium-ions with carbon dioxide present in the water or attracted from the air (see equations 9 and 10).

Equation 9

$$2OH^- + CO_2 \quad \rightarrow \quad CO_3^{2-} + H_2O$$

Equation 10

$$Ca^{2+} + CO_3^{2-} \quad \rightarrow \quad CaCO_3(s)$$
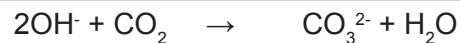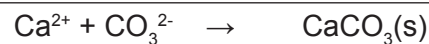
When the clear solution is used up, freshwater can be added again together with some calcium hydroxide to form a new batch. When this procedure is repeated at a maximum of 7 times the amount of insoluble calcium carbonate is strongly increased and the precipitate should be discarded.

For obvious reasons only saturated kalkwasser should be used. However, saturated kalkwasser has several limitations. First of all, it has a pH of 12.4 at 25 °C (Brockmann, 1991). Consequently, rapidly dosing uncontrolled amounts of kalkwasser to the tank water can have serious consequences as the buffering system of the tank water can neutralize only a limited amount of OH^- ions. Addition of kalkwasser to a tank with a depleted buffering system will quickly increase the pH of the tank water to dangerous levels, especially in smaller tanks. Secondly, addition of kalkwasser to the tank will decrease the buffering capacity of the tank water. It is quite often observed, that the alkalinity drops from 2.5-3.2 mEq.L^{-1} to only 1.4 mEq.L^{-1} or even less due to the precipitation of $CaCO_3$ (see equations 3 and 4). However, the depletion of the buffering capacity can be counteracted by dosing carbon dioxide directly

into the tank water (Brockmann and Nilsen, 1995b). Moreover, addition of old kalkwasser with a large amount of precipitated calcium carbonate may cause a decrease in alkalinity. Pure calcium carbonate, with its alkaline micro-environment, may induce a further calcium carbonate (Delbeek and Sprung, 1994) or magnesium/calcium carbonate precipitation (Spotte, 1992) and thus decrease the alkalinity. Also when adding calcium hydroxide to a tank, water with a calcium and carbonate level higher than saturation a calcium carbonate precipitation will be formed, resulting in a depletion of the alkalinity (Calfo, 2002).

Unfortunately, kalkwasser is highly unstable. Due to its alkaline pH it attracts CO_2 from the air, reacts with it to form calcium carbonate ($CaCO_3$, see equations 9 and 10), which precipitates. Old kalkwasser will be therefore of no use because of its very low Ca^{2+}-concentration. Consequently, kalkwasser can be stored for only two to three days depending on the container used and should be used as fresh as possible.

Because of its high pH saturated kalkwasser should be added only in small amounts (drop wise) to the tank water when the lights are still off and in an area with strong current. If the lights are off the pH of the tank water is low (7.9 or even less) due to CO_2 production of its inhabitants and the buffer capacity is high.

Nilsen (1990) describes a reactor where the calcium hydroxide is mixed with a magnetic spinner set on a time clock. Demineralized water is pumped into the reactor chamber with a dosage pump connected to a reservoir. A level sensor in the aquarium that measures the amount of water evaporated drives the dosage pump which pumps kalkwasser into the aquarium. However, such equipment should be controlled by a pH-meter to avoid dangerous pH levels in the tank water.

An advantage of kalkwasser is that the hydroxide ions of the kalkwasser neutralize organic acids, and thus may help to maintain the alkalinity and pH (Delbeek and Sprung, 1994; Calfo, 2002). Unfortunately, this holds only true in tanks driven with small amounts of kalkwasser.

Calcium reactor

Hebbinghaus (1994) described an innovative method adding calcium and carbonate to aquarium systems, the 'Calcium reactor'. In the calcium reactor carbon dioxide is added to a reactor filled with a calcareous medium through which controlled amounts of tank water are pumped. The following reaction takes place:

Equation 11

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^-$$
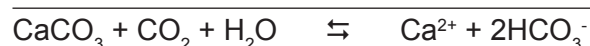
Comparing equation 5 with equation 11 indicates that both substances needed for the calcification process are produced in the right ratio: 1 mol of calcium and 2 mol of hydrogen carbonate.

The cost of this technique is relative high, but the advantages are numerous. The addition of bicarbonates will stabilize the pH in the aquarium and supports the calcification of invertebrates (see equation 5) as the Ca^{2+}-ions do. As strontium, and to a lesser extend magnesium and some trace elements are incorporated in the skeletons of stony corals dissolving coral gravel in a calcium reactor will introduce these elements to the system thus help to keep the concentration of trace elements constant.

On the other hand, several disadvantages of the calcium reactor must be mentioned. (i) The pH of the tank water may drop slightly due to the use of excessive amounts of CO_2 in the reactor. (ii) CO_2/HCO_3^- is added to the aquarium system. If there are high concentrations of nutrients like nitrate and/or phosphate in the system filamentous algae may grow. (iii) In dependence on the calcareous medium used a calcium reactor can leach large amounts of phosphate originating from an organic layer on the outside and in the pores of the media. This can easily be seen in Figure 1, which demonstrates the leaching of phosphate from a Calcium reactor, which was freshly filled with 1.5 kg of coral gravel (dosage of CO_2 55 bubbles per minute, with a water flow of 67 drops per minute). High concentrations of phosphate (> 0.2 mg $PO_4^{3-}.L^{-1}$) are detrimental for coral reef systems as phosphate on the one hand inhibits the calcification process and kills the coral and on the other hand gives rise to enhanced growth of filamentous algae. There are several techniques available to counteract the increase of the phosphate concentration due to the leaching from the calcium reactor. (a) The reactor is rinsed with fresh or demineralized water and CO_2 and the flow through is not pumped back to the system until the phosphate concentration drops below 0.2 mg $PO_4^{3-}.L^{-1}$ which is usually reached after a couple a days. (b) The coral gravel is washed with mild acid followed by a wash with demineralized water
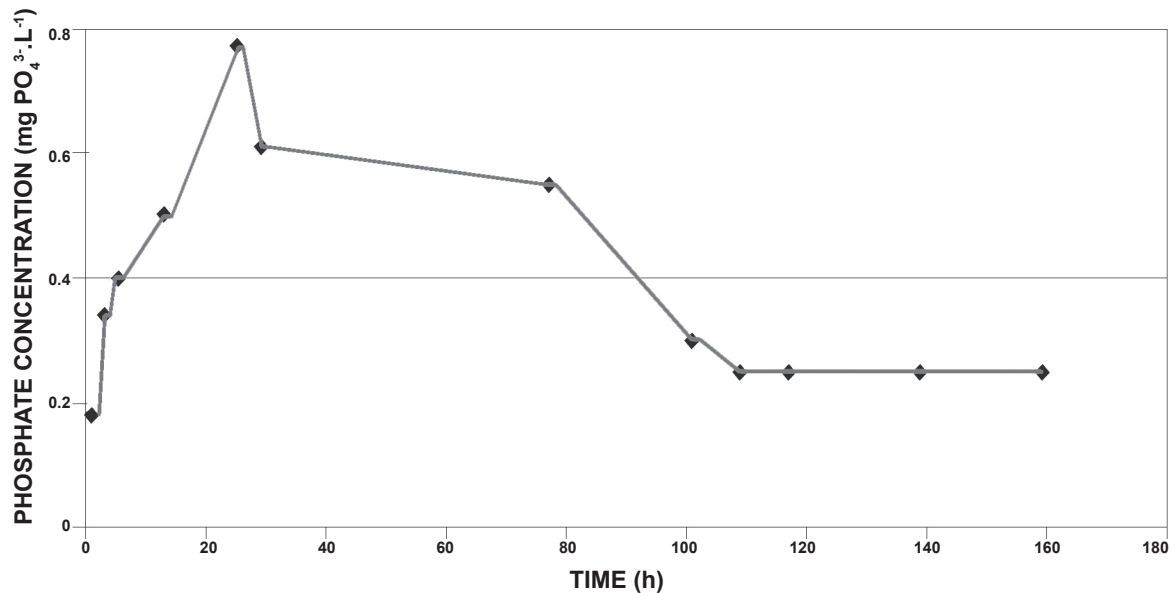
Figure 1: Changes in the phosphate-concentration of the effluent of a Calcium reactor in the presence of carbon dioxide.

before usage. (c) The flow through is pumped through a container containing a phosphate adsorbing material (like Rowaphos®). If the phosphate concentration is less than 0.2 mg.L^{-1} the flow through can be directly pumped back into the aquarium system. (d) An artificial CaCO$_3$ material can be used to fill the calcium reactor. Such a material should be free of phosphate, however this always should be tested. (e) The effluent of the calcium reactor is sent to waste in the first days, so excessive phosphates are rinsed from the gravel, before the reactor is installed within the aquarium circuit.

Calcium reactors should have an internal circulation, which ensures a better CO$_2$ usage and a higher efficiency of the reactor. The CO$_2$ bottle should have a double valve with two pressure gauches, so the bottle pressure can be diminished to a constant 1 to 2 bar, while fine adjustment can be done with a second valve. A non-return valve in the CO$_2$ hose prevents water to enter a nearly empty bottle. A bubble counter can be used to visualize and adjust the carbon dioxide addition to the reactor. A more reliable, but expensive technique is the usage of a pH sensor placed in front of the circulation pump, steering an automatic valve in the CO$_2$ hose and thus dose the amount of carbon dioxide to a set pH inside the reactor. The pH sensor should be cleaned every two weeks and calibration should be done on a regular base. The effluent from the reactor should be brought into the aquarium at a place with a strong current to prevent precipitation.

Zöllner and Ilmberger (2000) created an innovative calcium reactor: the rotating calcium reactor. In this reactor type the reaction chamber containing the calcium carbonate substrate is horizontally mounted. A timer driven motor gives rise to a slow rotation of the reaction chamber (one rpm), thereby preventing clogging of the substrate and the formation of CO$_2$-bubbles attaching to the substrate as well as the production of small canals through which the carbon dioxide enriched water runs. The mixing of the substrate is further supported by small buttresses, which are fixed in an angle of 90° in the reaction chamber. The rotating calcium reactor gives rise to a very high efficiency. Such reactors are now commercially available.

Although different substrates are described to be used in calcium reactors best results will be obtained with coral gravel or pure artificial calcium carbonate substrate, both in a particle size of 3-6 mm, to prevent the reactor from clogging and ensure an even flow of water through the reactor which results in the highest efficiency of the reactor. If the particle size is too small the efficiency of the reactor is reduced. Usage of coral sand can produce excessive concentrations of phosphate, aluminum and silicium (Sebralla, 2003). Hiller (2002) compared three different commercial calcium reactor substrates where the phosphate level varied between 2 and 6 mg PO$_4^{3-}$.L^{-1} and a Ca^{2+}/PO$_4^{3-}$ ratio ranging from 500 to 1925.

The amount of calcium (N$_{Ca,total}$) added to a system via a calcium reactor depends on the reactor type, reactor size, type of medium, CO$_2$-dosage (or reactor pH) and the flow through (Q$_{effluent}$ in l/h) and is expressed by Formula 11.

Formula 11

$$N_{Ca, total} = Q_{effluent} * (C_{Ca, effluent} - C_{Ca, aquarium}) \quad [mg.L^{-1}]$$

The calcium concentration ($C_{Ca,effluent}$) of the effluent depends on the pH in the reactor. By changing the effluent flow and/or the pH in the reactor the calcium dosage can be easily adjusted to the daily calcium consumption (Formula 3) of the aquarium systems.

CONCLUDING REMARKS

Calcium proved to be in a fragile equilibrium in marine aquarium systems due to pH, alkalinity, salinity, magnesium-, sulphate- and phosphate-concentration. Large amounts of calcium carbonate are consumed by the inhabitants of reef exhibits. Consequently, the replenishment of both, calcium and carbonate, is necessary in these exhibits.

Several techniques are described in this chapter to add calcium and carbonates to marine aquarium systems. Every addition technique has advantages and disadvantages. Which kind of technique is used, depends on the amount of calcium consumption in the system, type of collection (fish or corals) and the financial situation. The amount of Ca^{2+}- ions added to an aquarium system with kalkwasser is limited in comparison to calcium chloride addition or usage of a calcium reactor. The most important disadvantage of saturated kalkwasser is, however, its high pH which limits the amount of kalkwasser which can be added to a given aquarium system. An important advantage of kalkwasser is its ability to precipitate phosphate and thus helps to keep the concentration of this nutrient low.

Increasing the calcium and carbonate concentration by adding calcium chloride and sodium hydrogen carbonate solutions is very efficiently. However, the main disadvantage is the generation of an ion-imbalance which can be counteracted by the use of NaCl-free sea salt mixtures for water changes.

Calcium reactors are excellent techniques to add calcium and carbonates to aquarium systems. They are easy to adjust and besides calcium and carbonate they add trace elements to the system. However, it is the most expensive technique described in this chapter and care must be taken not to add too much carbon dioxide to the aquarium.

In addition, it might be necessary to combine different methods for the replenishment of calcium and carbonate in order to obtain optimum results with respect to the keeping of calcium carbonate consuming animals and algae. For instance, a combination of a calcium reactor and kalkwasser may be helpful to reduce fluctuations in pH, thereby reducing the negative side effects of both methods when used alone. Such a combination is actually used by a lot of aquarists world wide with great success.

Whatever technique is chosen, additions to aquarium systems, especially coral systems should be carefully done. Changes always should go gradually. Regular monitoring of the chemical changes are of utmost importance, so life in the aquarium will benefit maximal from the additions.

REFERENCES

Balling, H.W., 2002. The Balling-Methode. Koralle, 14:72-75. (in German)

Barnes, D.J. and B.E. Chalker, 1990. Calcification and photosynthesis in reef-building corals and algae. In: Dubinsky, Z (Ed.) Ecosystems of the world. bd. 25: Coral reefs. Elseviers, Amsterdam: 109-133.

Brockmann, D., 1991. What is kalkwasser? Das Aquarium, 269:23-26. (in German)

Brockmann, D. and A.J. Nilsen, 1995a. A critical comparison of the most commonly used methods for dosing calcium in seawater aquariums, pt. I. Aquarium Frontiers Summer: 2-27.

Brockmann, D. and A.J. Nilsen, 1995b. A critical comparison of the most commonly used methods for dosing calcium in seawater aquariums, pt. II. Aquarium Frontiers Fall: 2-25.

Calfo, A., 2002. Book of coral propagation. Volume one, Version 1.0 Reef gardening for aquarists, Reeding Trees publication, Monroeville, USA: 450 pp.

Davies, P.J., 1983. Reef growth. In: Barnes, D.J. (Ed.) Perspectives on coral reefs Manuka: Austalian Institute of Marine Science: 69-106.

Delbeek, J.C. and J. Sprung, 1994. The reef aquarium Volume 1, 1st edn, Ricordea Publishing, Coconut Grove, USA: 544 pp.

Fosså, S.A. and A.J. Nilsen, 2001. The coral reef aquarium.: Birgit Schmettkamp Verlag, Bornheim, Germany, 158-161. (in German)

Gattuso, J. -P., M. Frankignoulle, I. Bourge, S. Romaine and R.W. Buddemeier, 1998. Effect of calcium carbonate saturation of seawater on coral calcification. Global and Planetary Change, 18:37-46.

Grguric, G., J.A. Komas and L.A. Gainer, 1999. Differences in major ions composition of artificial seawater from aquarium tanks at the New Jersey State Aquarium. Aquarium Sciences and Conservation, 2:145-159.

Hallock, P., 1997. Reefs and reef limestone in earth

history. In: Birkeland, C. (Ed.) Life and death of coral reefs, Chapman & Hall, New York: 13-42.

Hebbinghaus, R., 1994. The Löbbecke calcium reactor. DATZ, 47(8):517-522. (in German)

Hiller, G., 2003. Calcium reactor substrate and phosphate levels. Advanced Aquarist's Online Magazine, 2(4), www1.

Holleman, A.F. and F. Wiberg, 1976. Textbook of inorganic chemistry, Walter de Gruyter, Berlin: 692 pp. (in German)

Holmes-Farley, R., 2002. Chemistry at the aquarium. Calcium. Advanced Aquarist's Online Magazine, 1(3), www1.

Holmes-Farley, R., 2003. Chemistry at the aquarium. Magnesium in reef aquaria. Advanced Aquarist's Online Magazine, 2(10), www1.

Jaubert, J., 1989. An integrated nitrifying-denitrifying biological system capable of purifying sea water in a closed circuit aquarium. 2nd International Aquarium Congres, Monaco 1988. Bulletin de l'Ínstitute océanographique, Monaco, 5:101-106.

Lang, G.T., 1993. An introduction to the biogeochemical cycling of calcium and substitutive strontium in living coral reef mesocosms. Zoo Biology, 12:425-433.

Libes, S.M., 1992. An introduction to marine biogeochemistry. Chapter 15 Calcite, alkalinity, and the pH of seawater, John Wiley & Sons, New York: 242-261.

Medakovic, D., S. Popovic, N. Zavodnik, B. Grezeta and M. Plazonic, 1995. X-ray diffrication study of mineral components in calcareous algae (Corallinaceae, Rhodophyta). Marine Biology, 122:479-485.

Muller-Parker, G. and C.F. D'Elia, 1997. Interactions between corals and their symbiotic algae. In: Birkeland, C.(Ed.) Life and death of coral reefs, Chapman and Hall, New York: 96-113.

Nilsen, A.J., 1990. The successful coral reef aquarium. Part 3 Calcareous water. FAMA ,13(11):32-37.

Pawlowsky, E., 1994. Calcium in a Coral Reef Aquarium. Das Aquarium, 301:28-35. (in German)

Renke, E., 2000. Calcium chloride and sodium bicarbonate for marine aquaria. Der Meerwasser-Aquarianer, 3:37-40. (in German)

Sebralla, L., 2003. Kalkwasser - calcium reactor pro and contra. Les Lettres Recifales, 32:25-27. (in German or French)

Smith, S.V., 1983. Coral Reef Calcification. In Perspectives on coral reefs. (Ed. Barnes, D.J.) Manuka: Austalian Institute of Marine Science: 240-247.

Sondervan, P.J., 2001. The relationship of calcium loss with trace element concentrations in seawater life systems. Bulletin de l'Institute océanographique Monaco, 20(1):139-148.

Spotte, S., 1979. Seawater aquarium. The captive environment, John Wiley & Sons, New York: 413 pp.

Spotte, S., 1992. Captive seawater fishes, 1st edn, John Wiley & Sons, New York: 942 pp.

Wickens, J.F. and M.M. Helm, 1981. Seawater treatment. In: Hawkins, A.D. (Ed.) Aquarium Systems. London: Academic Press: 63-128.

Wilkens, P., 1973. The Saltwater Aquarium for Tropical Marine Invertebrates, Wuppertal, Germany: Engelbert Pfriem Verlag: 216 pp.

Zöllner, A. and K. Ilmberger, 2000. The rotating calcium reactor. Der Meerwasser-Aquarianer, 4:40-41. (in German)

INTERNET RESOURCES

www1.   www.advancedaquarist.com