



PLEASE NAME ME!

March 2003

Editorial....

Welcome to the third issue of our new MASWA newsletter. I am stepping in for David whilst he is on his honeymoon. David is a hard act to follow, to which I have unceremoniously messed up by being late back from a job. It has made me realise how important a role certain members have in organising meetings. THANK YOU! David. I had to do a bad job this time so we all appreciate David when he gets back. 8 small print pages in this newsletter, so make sure you're sitting down.

Terry Peake

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Upcoming Monthly Meetings....

March 26th

Mr. Marc Quiad
10 Westminster Rd
LEEMING

April 30th

Elmer Ellison

May 28th

Phillipe Dor

June 25th

?

Meetings start promptly at 7.30pm!

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Newsletter Contributions

If you would like to make a contribution to the newsletter please don't hesitate to contact the Newsletter Editor, David Bloch on the phone number or email address listed above. Contributions to the newsletter need to be received no later than 7 days prior to the next meeting date. Don't be shy – I don't care if you can't spell or use a computer. Hand written transcripts are fine!

M.A.S.W.A host meeting tips.

If you are going to host a meeting after being up for about 48Hrs, make sure you get someone to host it with you. It was pointed out by my wife, that during the obligatory speech and aquarium description. I lost the plot! And started to drift off into, where ever you go, and whatever you talk about, when you are overtired.

February Meeting Rundown....

The February meeting was at Terry & Val's place (Yours truly) the reef was in a fair condition as it is a relatively new tank compared to some at M.A.S.W.A.

Several comments were made on the professional layout; however Terry said he could not take all the credit for this. A few M.A.S.W.A. members came over saw what Terry was doing..... Pushed him to one side and took over. Namely Simon, Dion and Nigel. Thanks guys.

The size of the tank is 10ft X 2ft X2ft which is about 1000 litres including the sump. As most of you are aware, Terry is an electronic engineer, but in this case, he removed all the toys so new members would not think that you have to have all the gadgets we build up over time, to run a successful mini reef.

As usual a raffle was held and it was fantastic to see I won second prize (should be more of it) Dion scored again (should have been me). Nathan ran a mini auction of some clams and coralamorphs (that's how I spell it, using crayon) A little bit of money was raised for M.A.S.W.A.

The soft coral Terry won at the last meeting was looking great (whew)

March Meeting Information....

This month we will be attending the home of Marc Quaid. Unfortunately I haven't seen Marc reef, but I like surprises and can't wait to see what is in store for us all. One of the best things about M.A.S.W.A. is seeing everyone's tank and getting different ideas. See you there. The address is **10 Westminster Rd, LEEMING** and starts promptly at **7.30pm**.

Calcium reactors

*By Dr. Terry Peake
Sanjay Joshi
Dr. Dallas Warren.
Mr. Craig Bingman.*

If you are like me, I was confused over all the advice and information around on calcium reactors. To help with some understanding of the chemistry involved, I contacted a friend of mine in Victoria. His name is Dr Dallas Warren. As he is a research fellow, with credentials in chemical engineering (In my opinion, the hardest discipline of learning) , I figured if any one knows about chemistry it would be Dallas. What I decided to do was ask Dallas for his input on a few articles on the web, and present here the outcomes of his opinion. So without further ado... here it is.

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Calcium Carbonate Reactors Sanjay Joshi:

Although calcium carbonate reactors have been around for a while, I first saw calcium carbonate reactors about two years ago, when Jeff Turner of Exotic Aquaria showed me videotape of some German reef tanks. Several of them were using these devices to maintain the carbonate hardness levels in their predominantly small polyp stony (SPS) corals.

I was very intrigued by the idea of using a reactor, since I was fighting a losing battle with trying to maintain the Ca and alkalinity levels in my 180G

SPS coral tank through the use of Kalkwasser only. Not only did this device have the potential to address my problem; it seemed like a dream for a consummate lazy aquarist like me. No adding and mixing Kalkwasser daily, no hassles with trying to increase evaporation and adding humidity to basement, and other hassles that I am sure you are all aware of.

Before delving into the reactors let us first take a look at how it works. The basic idea of the reactor is the reverse process of calcification. A calcium carbonate media is dissolved using carbonic acid (generated by addition of CO₂ to water) to provide the Calcium and bicarbonate ions, in the same proportion that is used during calcification.



So the calcium carbonate reactor is basically a device that brings the three ingredients together in a manner so as to allow efficient production of Ca and bicarbonate.

Basic Design

There are two basic types of designs that have been used to construct the reactor. The open circulation kind and the recirculating kind. The current trend is to use the recirculating type of design, so I will not spend much time with the open circulation kind.

In a recirculating type of reactor the mixture of CO₂ and H₂O is continuously circulated in the chamber through the calcareous medium in a closed circulation loop. Water from the tank/sump enters the reactor through an inlet and exits through an outlet, both of which are connected to the main recirculating loop.

Typical recirculation rates are in several hundred gph, while typical input/output rates are in several litres/hr. Water entering the reactor comes in at tank alkalinity levels and effluent leaving the reactor has much higher alkalinity (depending on the settings). The amount of CO₂ added is typically measured in bubbles/min (unfortunately there is no standard bubble size, so this is a dubious measure when comparing different reactors).

All the commercially available reactors basically use a variation of techniques to create the circulation loop, the manner in which CO₂ is injected, how the water is input to the reactor, and how the effluent is drawn. The Knop reactor for example, has a top to bottom circulation loop, whereas the MKR reactor has a reverse flow circulation loop through the media. Some require an external pump to input the water into the reactor, whereas others use gravity or siphon to introduce water into the reactor.

You can easily see the variations in design by looking at the commercially available designs, but they all essentially do the same thing - provide a mixing chamber for the three ingredients - calcareous medium, CO₂ and water. So let us stick to the basic principles and not get into a product review, at this point.

There are basically two adjustments that can be made to the reactors - the amount of CO₂ being added and the effluent flow rate. Keeping the same amount of CO₂ and increasing the effluent flow rate will result in a reduction in the alkalinity of the effluent, Increasing the amount of CO₂ while maintaining the same effluent flow rate will result in a increase in the effluent alkalinity. So, using these parameters we can adjust the resulting alkalinity of the tank.

The most important ingredient in the Ca reactor is the Calcareous Medium used. It is the only ingredient whose "quality" is attributed to the problems one could encounter when using a reactor. The factors of concern are

(a) the chemical composition of the medium

Since the calcareous medium is dissolved in the reactor, it is reasonable to expect that all the compounds contained in the medium are susceptible to dissolution and subsequent introduction into the tank. Magnesium, Strontium, Phosphates, and other heavy metal salts present in the medium will also dissolve and enter the tank via the effluent. This has both positive and negative effects. On the positive side, one may be able to stop adding additional Strontium and other trace elements. On the negative side we may be adding large amounts of undesirables such as phosphate, copper, heavy metals, etc that will contribute to the problems that I will discuss later. I wish the companies selling these would provide a complete chemical assay of their medium (To be fair to the companies - I have not tried calling them to get it either).

(b) the particle size of the media.

The particle size of the media impacts the total surface area of the calcareous media exposed to the carbonic acid formed in the reactor. The larger the particle size the less total surface area available for the carbonic acid to react with the medium. So a medium with a larger particle size will dissolve more slowly, and has larger inter particle space which results in less trapping of powdered particles in the medium, and easier flow through the medium.

Smaller particles provide a much large surface area, and will dissolve at a faster rate. This has its own disadvantages. The medium turns to powder

(mushy) much faster than the larger grained particles. This powder mush being light in weight is easily suspended in the water in the reactor and over a short period of use (2-3 months) results in chalky effluent being introduced into the tank. Further, the powder particles tend to stay trapped in the medium and sometimes when the reactor "burps" it spews a lot of chalky effluent into the tank. Using finer grained particles also puts more back pressure on the pump used for circulation.

Given that the circulation rate in the reactor is very high compared to the rate at which the effluent is drawn I don't think that the rate of dissolution due to the particle size (with in certain range) is a sensitive parameter in the operation of the reactor.

I found with the Caribsea Sea Flor as the medium in the reactor, it would turn powdery in a about 2-3 months of use, and start creating a haze in my tank. I am right now experimenting with Caribsea Geomarine and have been using it for a month so far.

Problems often Identified with the use of a Calcium Carbonate Reactor

(1) Depressed tank pH

For an aquarium at equilibrium conditions there is a certain quantity of CO₂ that can be maintained without reducing the pH. As this amount of CO₂ is increased, additional CO₂ will decrease the pH. Thus when adding the effluent back to the tank, there will always be some additional CO₂ that will be added to the tank, that can result in a drop in the tank pH. This drop in pH will be higher if the tank initially has low alkalinity.

In my tank I have not seen any depression in tank pH. In fact, the tank runs at a higher pH since I added the reactor. This is possibly due to the fact that the tank is now running at higher alkalinity values and hence less susceptible to pH drop. I also think that since I am running a downdraft skimmer it may help to "blow off" the excess CO₂.

(2) Increase in Phosphates

A common criticism levelled against these reactors is that they can increase the phosphate levels in the tank. The reasons cited are:

(a) the medium used contains phosphates which redissolve and are introduced into the tank

I have not done any chemical assays of calcareous mediums available to determine which one is high in phosphates. In an Aquarium Frontiers (May/June 1997) article Greg Schiemer stated that the effluent using Caribsea Sea Flor tested at 0.25-

.30 ppm of phosphate, but there was no measurable increase in the phosphate levels in his tank. I have seen similar results in my tank.

At the rate at which this extra phosphate is being added to the water, it is either being removed by the skimmer or being bio assimilated. If the phosphate issue is a concern to you and is in fact increasing the phosphate levels in your tank, then you may want to try some of the "purer" brands of calcareous medium that are being advertised. I have not used them so I can't really say much about them or their claims.

(b) Since most people using these reactors stop using Kalkwasser, they give up the capability of using the phosphate precipitating properties of Kalkwasser.

This may be of some concern in tank where the phosphate transport/removal mechanisms are poor to begin with. Using a "better quality" substrate can minimize the impact of this.

(c) The drop in the pH of the tank, causes a release of phosphates already bound in the tank substrates (live sand, etc). I think this is essentially a non-issue. If your tank pH is dropping so much so as to cause the substrate in your tank to redissolve then you should be in big trouble already.

(3) Increase in Algae and Diatoms

The increase in available CO₂ in the tank often acts like a fertilizer for the and coupled with the phosphate additions from the medium can fuel an increase in algae growth. Further, the calcareous medium may also contain silicates that are released into the tank, thus increasing the diatom growth.

Whether or not these problems will manifest themselves in an aquarium depends to a large extent on the prevailing conditions of the tank - its ability to degass excess CO₂, transport/removal of phosphate, availability of herbivores to keep the algae in check, etc.

My advice to people thinking of using Calcium Carbonate reactors is to first get your tank running in peak condition without the reactor. Once you are over the typical tank problems such as red slime, hair algae, diatom blooms, and you have a trouble free tank then evaluate whether you really need or want a Ca reactor. Most tanks can be run very well without them, and the only reason to use one on these tanks is the lower maintenance factor.

Adjusting the Reactor (and some reactor Math)

Once you have decided to add a reactor, how do you go about adjusting it, i.e. determining the effluent flow rate and the amount of CO₂ to be added.

The following discussion is based on several personal conversations with Dr. Craig Bingman, and the experience of several others in the Fishroom.

Let us assume that the reef system contains T litres of water. Set the CO₂ flow rate to approx. 20-30 bubbles/min and the effluent flow rate to a slow enough drip and let the reactor run for several hours until it reaches a steady state. Measure the effluent flow rate in litres/hr - say its L litres/hr.

Now measure the alkalinity in the tank, and the alkalinity of the effluent. The difference between the two values will give you the increase in alkalinity due to the reactor. Let us say this is d meq/L.

Assuming no calcification and use of alkalinity, this will result in an increase in tank alkalinity that is given by the following formula:

$$\text{Increase in tank alk/day due to the reactor} = (d \times L \times 24) / T - (1)$$

Now measure the tank alkalinity after a day. The difference between the increase in alkalinity due to the reactor and the actual increase in alkalinity will give you the daily consumption of alkalinity for your tank. Let us say this value is c meq/L.

So now we need to adjust the reactor so that the daily increase due to the reactor is approximately c meq/L. This will give us the setting at which the reactor will replenish the alkalinity that is consumed daily.

Looking at the equation (1), we can see that there are 2 ways in this can be achieved.

- (1) adjusting d - the increase in effluent alkalinity
- (2) increasing L - effluent flow rate

The effluent alkalinity can be increased by increasing the amount of CO₂, and keeping the effluent flow rate constant. Increasing the flow rate will result in a decrease in effluent alkalinity if the CO₂ flow rate is not simultaneously increased.

Which one of these is a better adjustment?. My opinion is that increasing the amount of CO₂, and

keeping the flow rate is a better choice, since it adds less CO₂ to the tank.

Similarly to reduce the alkalinity of the effluent, it is better to reduce the amount of CO₂ added.

I don't want to bore you all with the math and chemistry details but I feel that a basic understanding is necessary to avoid the trial and error, and test and adjust solutions. You can use the above equation to calculate, for example, what the value of d should be, given a certain effluent rate and the desired increase in alkalinity - rather than making wild guesses and adjustments.

Conclusion

Calcium carbonate reactors are a very useful device, and when used with the proper care and understanding of its advantages, and associated problems addresses a constant struggle faced by most aquarists - Ca and alkalinity.

For a consummate lazy aquarist like me it has been worth every penny. I built myself a DIY one, and I know I will be deluged with requests for plans. I have not taken the time to write and sketch the plans, but I will refer to the plans on the web by John Payter

<http://www.concentric.net/~Jfpnn3/calcium.htm>.

Mine is very similar, but I used acrylic tube so I can see inside the reactor. A 4.5" OD acrylic tube works with 4" PVC fittings.

I am sure I have not covered all aspects of Ca reactors in this talk, but I am sure we can cover those when we get to the Q&A.

In case you need to get in touch with me after this talk, you can send me email at sjoshi@psu.edu.

Intermission ☺
Article two

Article two....

Some Chemistry Behind Ca(OH)₂ and CaCO₃/CO₂ Reactors Craig Bingman

There is a deep underlying reason why the two "best" ways of maintaining calcium and alkalinity in reef tanks have such drastically different pH's. Both of these methods (limewater and CaCO₃/CO₂ reactors) achieve balanced inputs of calcium and alkalinity by relying on the natural balance of calcium and alkalinity in calcium carbonate. While it is possible to get limited amounts of calcium carbonate equivalents into solution by allowing aragonite to dissolve in deep

sand beds, or by running topoff water through Halimdea hash _a la_ Adey, calcium carbonate is at best a sparingly soluble substance, so you can't get much of it into solution those ways. It makes sense that corals would use some sparingly soluble substance for skeletal material. Organisms that try to make skeletons out of soluble substances stand the test of evolutionary pressure. You can imagine them having the same problem as the wicked witch of the west? in the Wizard of Oz.... pour a little water on them and they are melting....

So we need to do something to coax calcium carbonate to dissolve in water. Calcium carbonate by itself gives a pH similar to seawater (when you equilibrate it against the atmosphere in seawater... so we can either go higher in pH or lower in pH. It turns out that both work. The high pH side is of course limewater, and the low pH side is the kalkreactor.

Underlying this is a very simple piece of chemistry... the concept of a solubility product. The ion concentrations relevant to the solubility of calcium carbonate are calcium and carbonate, curiously enough. Note that bicarbonate is not directly relevant, and hydroxide ion isn't relevant (except in the high pH limit of limewater.) Granted, in a given solution with various forms of inorganic carbon present, all of these values are going to be interrelated, but calcium and carbonate ions are where it is at for this discussion.

So, aside from chelating the calcium ions, there isn't much way to affect their activity. However, by adding carbon dioxide to a solution, you can drop the pH to the point that the carbonate ion concentration is very low. That is how kalkreactors work. You can also imagine a solution that limits the carbonate ion concentration by starting out with essentially zero dissolved inorganic carbon. That is how limewater works.

So, it isn't terribly surprising that there are two major ways of coaxing calcium and alkalinity into solution, and that they have dramatically different pH values. Fundamentally, there are really two ways to do this... get rid of inorganic carbon (limewater) or add so damned much inorganic carbon that the carbonate ion concentration goes down (kalkreactor.)

You should never directly mix the output of a kalkreactor with limewater, because you will make an extraordinarily highly supersaturated solution with respect to calcium carbonate at that point. Remember that the two gambits for getting calcium carbonate in soluble form work by moving to the very high CO₂ limit and the zero CO₂ limit. When you mix them, you wind up right back in the middle, and calcium carbonate is going to fall out

of solution. If you mix them separately in your system, then they both have a chance to do what they are supposed to before they spontaneously flop out of solution.

You should never mix limewater with seawater, because you will absolutely precipitate the magnesium as magnesium hydroxide when you do that. This is why there are no Nilsen-style reactors that are closed-loop systems.

No, Nilsen-style reactors are not necessarily volume limited, because you can dispense milky limewater (a suspension of calcium hydroxide) with them.

Are Nilsen reactors necessarily better or worse than kalkreactors? No, they aren't. The only reason why kalkreactors are more favored in this country is.. well, there are two or three.

1. they aren't commercially available.
2. you need to add calcium hydroxide more often than you need to replenish the calcium carbonate in a kalkreactor. Since a desire to find a system that demands little attention is what often drives people to go with one of these systems, kalkreactors are a little gentler on the lazier aquarists.
3. Nilsen reactors may be somewhat more difficult to adjust than CaCO₃/CO₂ reactors, although once you get that down, they are in principle no more difficult to run than a kalkreactor.
4. you need one more technical gadget with the Nilsen-style reactor, a pH controller.

The Nilsen system does have advantages that the calcium carbonate/carbon dioxide reactor doesn't have... or perhaps we should call it a property because it isn't free. If you use a pH controller, you have a really great way to keep the system pH reasonably high 24 hours per day. In fact, you could clamp it at just about any value you like. That isn't true for kalkreactors, and when people try to modulate pH with a controller and a solenoid, they find that they are more difficult to adjust.

I have a follow up question regarding the following statement "You should never mix limewater with seawater, because you will absolutely precipitate the magnesium as magnesium hydroxide when you do that. This is why there are no Nilsen-style reactors that are closed-loop systems."

Yeah, it is a bit frightening when I re-read what I've written. I guess it was clear that what I meant is that you should never use sea water to prepare limewater.

Why don't we have localized precipitation of magnesium hydroxide in our tanks when we drip in limewater? My guess is that we do, but that if we have sufficient mixing the microscopic bits of precipitate go right back into solution. Is this correct? (I gather that this is the case for the calcium carbonate that forms when limewater is dripped in as well?).

Yes, there is probably localized precipitation, but the material formed (brucite is the name for magnesium hydroxide the mineral) is not stable at seawater pH. The partial pressure of carbon dioxide needs to be orders of magnitude lower than NSW for brucite to be stable. That condition is never satisfied in your tank outside of the tiny area where a droplet of limewater hits the tank water. It is of course satisfied very well in limewater solution.

This is also the reason why the "special" limewater mix on the market that contains both calcium hydroxide and magnesium hydroxide is... well, a bit silly. Magnesium hydroxide is rock insoluble at limewater pH values.

Regarding other questions... about Nilsen reactor plans. There is a call for such things occasionally, but I'm personally unaware of extremely well debugged plans laying around on the web somewhere. Regarding the questions asked, my personal preference would be to use an overhead mixer rather than a stir bar, and gravity output from the lime container. Obviously some sort of metered input.

Some ages ago, I remember some chap giving a talk at the Brooklyn Aquarium society... he was quite proud of his Nilsen-esque limewater additions. I think that he used a modified fish feeder to slowly meter lime into the mixing container.

And.. again, these devices are more trouble than a simple CaCO₃/CO₂ reactor. There are some advantages, though. I remember when Alf put a CaCO₃/CO₂ reactor on his system, that had been managed (very successfully) for many years with his own limewater reactor. The results were not great, and I believe that he broke the tank down some time after that. There was a massive proliferation of algae and also those pesky anemones. The algae was probably related, the anemones... maybe yes, maybe no.

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MASWA Message Board....

Newsletter Naming Competition

With the launch of the new format MASWA newsletter we would like to give the newsletter its own identity - a name. We are holding a competition to see who comes up with the best suggestion for a name. The winner will have the choice of a free 1 year subscription to MASWA or an aquarium shop voucher to the value of \$24. The winner will be decided by the committee and announced at the March general meeting.

Meeting Venues WANTED!

If you would like to host a meeting, whether it is to show off your setup, or get a bunch of heads together to solve your problems, WE WANT YOU! Don't worry if your tank is only just beginning or you have an algae bloom, we have seen it all before and can help you if you need it. Please speak to any of the committee members if you would like to volunteer your home to us!!!! There are currently vacancies for meetings from June to November. Don't be scared, we don't bite (except maybe Tony!).

Water testing

The parameters that are currently able to be tested are Calcium, Alkalinity, Phosphate, Nitrate, Silicate and Salinity (Temperature testing will also be available, but is obviously only viable for the meeting host's aquarium). **If you wish to have your water tested at a meeting, please bring along roughly 200ml of water in a clean, screw-top container** (a spring water bottle is best). Make sure you rinse the container with your aquarium water before filling it.

Live Sand Again, Please....

We would like to request that anyone who has a healthy established live sand bed to bring along a small cup full of sand to either donate to the raffle or give to the meeting holder for their tank. You cannot ever get enough life in your sand! The greater the diversity of micro-organisms in your sand bed the more successful your aquarium will be – it's that simple.

Buy, Sell and Swap....

REEF AQUARIUM AND CABINET

122cm X 75cm X 61cm black silicon aquarium with 2X overflow and 2X inlet holes on pine cabinet. Includes all plumbing, 50cm cube glass sump,

downdraft protein skimmer (no pump), gravity feed water top up valve and hanging light hood (not including lights!). **\$850 ONO.**

Contact David on:

email: fishnut@optusnet.com.au

mobile: 0412 079 886

METAL HALIDE CONTROL GEAR

Metal halide control gear for 150 watt light. Control gear only - does not include lighting plug and cord or bulb holder and bulb. The asking price **\$75 ONO**

Contact David on

email: fishnut@optusnet.com.au

mobile: 0412 079 886

INCOMPLETE CALCIUM REACTOR

Acrylic tube 200mm in diameter. Is not completed and needs to be finished off. Does not include pump. The asking price **\$50 ONO.**

Contact David on:

email: fishnut@optusnet.com.au

mobile: 0412 079 886

METAL HALIDE GEAR

Metal halide control gear, lamp holder and reflector (including 400 W bulb). The asking price **\$165 ONO.**

Contact Carl on:

email: carlevans@optusnet.com.au

mobile: 0409 785 251