WATER CHEMISTRY IN MARINE AQUARIA

WITH SPECIAL EMPHASIS ON REDOX, AND ITS INTERACTIONS WITH NITRIFICATION, DENTRIFICATION, PROTEIN SKIMMING, OZONE, AND MORE

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Saltwater is well known as one of the most complex liquids on earth. Many complicated chemical reactions take place in the oceans, and even more so in the closed systems that are represented by marine aquaria.

This article will attempt to show the part played by the highly important parameter known as redox value, as well a pH and others, and to try to explain why it is essential to understand its complexities. I will give my opinions on the best way to obtain the stable, desirable values that are critical to keeping successful saltwater aquaria, with particular emphasis on reef aquaria.

Redox is the name given to the measurement of “reduction-oxidation” reactions which take place in a medium (e.g., saltwater), and which involve the transfer of electrons. This transfer changes the valency (oxidation number) of the involved chemical compounds, as we will see later. The transfer of electrons is much slower than the changes in other types of chemical reactions, which typically are acid-base equations, and take place by proton transfer. This kind of transfer (proton) is usually a rapid reaction, while the redox transfer of electrons is slow. This must be taken into account when trying to achieve a desired redox value in a marine aquarium.

The redox meter is able to calculate the “potential” of the medium in which the supplied probe is inserted, as the probe can measure in millivolts the charged electron acceptors, principally oxygen. Generally in the marine aquarium, we need a fairly high reading, i.e., mV number, to keep the closed system at the optimum quality that tends to occur in nature on a reef. The values recommended will be referred to later in this article.

The reactions that comprise the redox equations may be divided into two categories. First there are those that involve the oxidation of organic carbon compounds, such as fats, carbohydrates, and proteins. The oxidation of the fats and lipids yields carbon dioxide (CO_2) and water. The CO_2 may have an effect on the pH of the aquarium, especially in those that have an alkalinity level that is less than optimum. Second the redox oxidation of protein usually creates ammonia, plus smaller quantities of phosphates, and sulphates.

Thus the redox (oxidation) of the se impurities in the marine aquarium can be represented as follows:

Fats + Carbohydrates + O_2 —> H_2O + CO_2
Proteins + O_2 —> H_2O + CO_2 + NH_3

The ammonia, as most of us are aware, is further oxidized by specialized bacteria, *viz. Nitrosomonas* species to nitrous acid, which the buffering compounds in the aquarium convert to nitrite (NO_2); while NO_2, in turn, is further oxidized by *Nitrobacter* species to nitric acid, which is again buffered to nitrate (NO_3).

The bacteria involved in the equations above are autotrophic, i.e., they use inorganic compounds as an energy source, and as this is abundant in the aquarium (provided the normal guidelines are followed), there should be no problems in obtaining the needed quantities, if modern filters are employed and the proper protocols are observed; however, redox reactions are also involved in the “reduction” of the undesirable nitrates (NO_3), as well as any phosphates (PO_4 inorganic and PO_3 organic) that may accumulate.

The build-up of nitrates has been shown to cause the retraction and slow death of most of the very beautiful species of hard and soft corals.

The accumulation of phosphate is known to cause (when present in measurable levels, and coupled with low redox values) rapid growth of the cyanobacteria known erroneously as Red Algae. It is important to be aware that, in the case of phosphates, all the test kits on the market currently measure the value known as PO_4, or inorganic PO4; none of them can obtain values for PO_3, which is organic phosphate, and which can often be the real cause of much of the destructive growth of the cyanobacteria. There will shortly be a development in the marketplace which will address this problem.

The redox equations which are involved in the "reduction" process also are created by a biological process known as "dentrification." In this process electron transfer takes place with the aid of bacterial action, the bacterial species involved are anaerobic species, and must have an energy source with specialized conditions which involve virtually no oxygen presence and hence, negative redox values. This reaction takes place by conversion first of the NO_3 to NO_2, and then to gaseous nitrogen and oxygen. The bacteria which cause the reactions to take place use either oxygen or nitrate as electron acceptors while oxidizing electron donors.

In order for this dentrification to take place, an organic carbon energy source is needed. This is most often introduced by adding methanol to the reaction. Aquarists please, however, be warned, the amounts which are required are very precise. Under dosing, or overdosing, can result in either toxic nitrites (NO_2) or hydrogen sulphide (H_2S) being produced, both of which can bring about fatal results.

The equation of reduction of nitrate (or oxidation of methanol) can be schematically represented as:

(NO_3) – (Nitrate) + CH_2OH (Methanol) —> N2 (as gas) + HCO_3 (mainly as a Bicarbonate) + H_2O

The reader will observe that some buffer is replaced by this equation in the form of carbonate. It is important to be aware, however, that even if the aquarium is set up to maintain both nitrification and dentrification in ideal conditions, that the process of nitrification depletes the buffer capacity or alkalinity of the aquarium, to a larger extent, than the dentrification process replaces it. The importance of this for the marine aquarist is thus transparent, so the aquarist must regularly monitor the buffer capacity (alkalinity) of his aquarium and replenish it whenever the level falls below the ideal amount.

The redox value is measured with a reference electrode in mV or millivolts, and the standard employed is a hydrogen value of 1 mV. Most (but not all) electrodes commercially available in the hobby today are electrodes which are platinum, silver/silver chloride types, with a one-to-three molar solution of silver chloride. When the electrode is a potassium bromide electrode, or if the filling solution of the electrode differs from the molar solution that a redox unit has been calibrated for, then the values that will be shortly mentioned are not applicable, and must be recalibrated to allow for the variable.

However, as mentioned, most of the electrodes are of the platinum, silver/silver chloride types, with a three molar solution. The value that has been found to be the best for a reef type aquarium, by the writer, as well as Red Sea's other scientists, is between 325mV and 350mV. Although there are references in the American literature to values of 400mV and more, this has been proven to be a high risk, both in Europe and Israel, as under some circumstances, such levels which are usually created by the addition of ozone can cause very dangerous compounds of chlorine and bromine, such as hypochlorite and hypobromide OBr^- or BrO_3^-, etc. This excessive use of ozone also causes depletion of the iodine level which is essential to the well being of many invertebrates.

This **unregulated** use of ozone can also kill the essential nitrifying bacteria, thus causing many other undesirable problems. Does this mean, therefore, that the use of ozone in the marine aquarium is undesirable? On the contrary, ozone, when used in a controlled manner, has **many** useful effects, which can greatly add to the efficiency of the closed system.

Ozone, because of the nature of the O_3 molecule, which has high electron acceptor values, greatly adds to the oxidation processes, as well as accelerating the breakdown of proteins and other organic matter. The cleaner and purer waters produced by such action lead to higher redox values.

Acceleration of the oxidation of NO_2 (nitrite) to NO_3 (nitrate), as well as the partial oxidation of organic phosphates to inorganic phosphates, is also a benefit of the use of ozone if correctly applied. The treatment of these simpler forms of impurities is easier than dealing with the more complex organics.

The higher the redox value produced and the cleaner the water, the more efficient will be the processes of nitrification as well as a reduction of the numbers of free swimming bacteria of all kinds.

The points made above have important implications for the setting up of a marine aquarium and the aspiring aquarist should ensure the following:

1) Treatment with ozone is desirable but should invariably be done **after** the biological filter and **never** before it, or into it.

2) Ozone is best used **in conjunction with a protein skimmer**, as the combined use of the two enhances the breakdown of the organic compounds, while at the same time has the effect of discharging to the atmosphere excess ozone gas.

3) **Residual ozone** which as mentioned can react with chloride and bromide, which are abundant in seawater, to form highly dangerous compounds, should be reduced by techniques which we will explain shortly. When measured with a "residual ozone test," a value below .05ppm should be obtained **before** returning the water to the aquarium.

Aquarists, please note for the purposes of technical accuracy, the residual ozone tests on the market do not measure residual ozone (although that is what they are invariably called), but actually measure the harmful compounds which ozone can create if uncontrolled, as mentioned above. Therefore, when using ozone the aquarist should ensure that he purchases and uses such a residual test to ensure optimum results.

4) There is today on the market a protein skimmer, developed by a world famous German research laboratory, which by its unique construction virtually **eliminates any residual ozone before the water is returned to the aquarium** so that no undesirable compounds can possibly be formed.

5) The use of carbon filters (contactors) after treatment with ozone has been quoted by certain authors (Spotte) to remove any residual. This probably works by the catalytic reaction whereby, for example, a hyperbromide compound, e.g., BrO, would be broken down into Br + O_2.

When selecting a carbon to use in marine aquaria, it is most important to obtain one with a really high CTC value. This CTC value is a standardized scientific test, using carbon tetrachloride to evaluate the absorbing capability of the carbon. The higher the value, the more impurities it will absorb. It has been found in the last few years that a "blended" carbon gives the best results, such as is marketed by Rainbow Products and one or two other companies.

Problems with the Introduction of Ozone

As explained above, ozone can be very beneficial in helping to maintain a high redox value in the aquarium, as well as reducing the amounts of bacteria and other undesirables. To use it for optimum results means not only ensuring that it is introduced at the best place in the cycling of the aquarium water, but also ensuring that the levels of ozone are kept under control.

This today can be done by obtaining a redox meter which will shut off the ozone generator when a predetermined optimum redox value has been achieved.

There are several redox meters available from several suppliers today which can be coupled to an ozone generator. Also controller/generator instruments which combine the production of ozone with built-in automation to switch on the ozone, or turn it off, as when a predetermined redox level has been achieved.

The choice of such instruments is up to the aquarist who, if purchasing two separate instruments, must ensure that the two units will "handshake" or be compatible together. Generally, the cost of the combined units is less than buying two separate units.

One should also be aware that many of the so-called ozone generators that rely on the production of ozone by a bulb or similar method of discharge, gradually reduce the amounts of ozone produced so that after a period of time they no longer produce the amounts that may be needed. Alternatively, those units that produce ozone by the corona method of discharge are usually constant in the amounts they are rated at.

On the reefs in nature the amount of bacteria, especially pathogenic types, are few, and this is concurrent with a relatively high redox value as, generally speaking, the higher the redox value the more sterile the water. Please, however, remember the remarks above. If one tried to achieve **too high** a redox value, which is nearly always done with the aid of ozone, then undesirable compounds can often result, which can be fatal.

Articles by Kipper, as well as our own measurements at Red Sea Fish pHarm, where we are located beside a coral reef, confirm that the redox values vary considerably, from a low of about 200mV to a high of around 350 mV. We have found that in a closed system, a level of about 300-325mV to be ideal , and never give any negative side effects.

As well as using the dentrification method to break down nitrates (NO_3) which, when used with anaerobic bacteria should be coupled with negative redox readings, there are some other alternatives, which will also achieve the same result.

The most popular currently is the algae scrubber method advocated by Dr. Adey of the Smithsonian Institute in his excellent book *Dynamic Aquaria*. We have used variants of this method in our marine hatchery in Eilat, where we are now breeding several species of marine fish including several which, as far as we know, have never before been bred commercially. The larvae in a marine hatchery can stand virtually no nitrates, just as the corals prefer very low values. There are those who have contrary opinions about the method, but pragmatically speaking, we have obtained excellent results, although it is not a system that will be easy to adopt to smaller marine reef aquaria.

Another method (of eliminating NO_3) is by using high quality "live rock," coupled with what is now termed "living sand." When one walks along the typical beach and kicks the sand, down a few inches you will often see black, rather evil-smelling sand, in which there is no oxygen. Here, anaerobic bacteria are thriving, and of course "dentrifying" any nitrates, as well as breaking down other compounds that may be present, such as rotting seaweed. With good live rock in the aquaria, this can take place within the many small crevices, where aerated water is not flowing. The problem with relying on such a method is that it is very difficult to get into a precise balance the amount of rock (of the right quality) which will always sustain the amount of biomass you are placing in the aquaria. If one is conservative, has a high quality dealer who really sells only the best and “recent” live rock, and you do not overload your tank, this method will work very well indeed.

Of course you can also ensure the elimination of nitrates by growing various *Caulerpa* in the aquarium, and this will almost certainly ensure that you will have no nitrates and probably no phosphates, as the will take up these chemicals, and even ammonia (before it becomes converted to NO_2 and NO_3). The problem then becomes, that if you have some tangs or other algae eaters in the aquarium, they will eat back the *Caulerpa* until it no longer plays a useful role, while if one hasn’t algae-eating fish or invertebrates, then the *Caulerpa* will eventually take over the tank, very often at the expense of the beautiful corals you so wanted to admire and see thrive.

I would like, at this juncture, to caution the reader about several products on the market which claim to filer out nitrates. We at Red Sea have tested all the products that have been extensively advertised and none of them do what is claimed. The most that they will do is a **very small reduction** when the nitrate levels are already far too high and the resulting reduction is of no consequence if you want to keep corals or breed marines. Thus, if eliminating nitrates is important to you, invest in one of the other methods mentioned above. I would mention that if you only want to keep fish without invertebrates then nitrate levels are not important, as no deleterious effects have been observed with the vast majority of species, although some butterflies may be an exception. There will shortly be, on the market, a new patented system of eliminating nitrate (NO_3), which will be the subject of further articles.

Like all articles on marine aquaria, I expect this one will also raise many questions and doubtless there will be opposing points of view, some expressed vehemently. I am not of the opinion that there is only one way to be successful, although for the beginner it is most useful if he can be guided by methods and equipment that will work.

If there is one certain piece of advice which almost every experienced shopkeeper and marine aquarist could agree upon, it is **patience**. Do not attempt to build the entire reef aquarium in a day, or a week. The really beautiful ones you have seen were most certainly the result of many months of slow work leading up to the desired result, and throwing money at a new aquarium too quickly will more often lead to failure and frustration than success. Only buy from a shop where the reef display tank or tanks tell you that the shop owner has a really good understanding of the “how-to.” If he does not have such a beautiful display, what makes you think he can advise you how to keep one successfully?

It is gratifying today, however, to find more and more shops that have taken the trouble to study or employ qualified personnel to advise the customers professionally and so ensure their success.

Happy reef-keeping!

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