

Carbon Dioxide: Friend or Foe?

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By Randy Holmes-Farley

Carbon dioxide is an extraordinarily important molecule for reefkeepers. No, not just because global warming due to atmospheric CO₂ may impact natural reefs, but because it has a huge impact on the processes taking place in a reef tank. You can't see it or smell it, although perhaps surprisingly, you can taste it. Nevertheless, CO₂ has a direct impact on things ranging from pH to calcification to growth rates.

Let me back up a bit and describe what CO₂ is, and then proceed to how it impacts our reef tanks. CO₂ is a gas at room temperature, and consists of a central carbon atom and two oxygen atoms arranged in a linear fashion (Figure 1). When dissolved into water, the CO₂ becomes hydrated to form carbonic acid (H₂CO₃). This hydration step takes a few seconds, and though that may seem fast, many organisms, from bacteria to humans use an enzyme called carbonic anhydrase to greatly speed up the process.

Once carbonic acid forms, it very quickly equilibrates with the other acids and bases in solution. It can, for example, lose one or two protons (H⁺). The extent to which this happens depends upon the pH and a variety of other factors. In seawater at pH 8.1, most of it (87 percent) will lose one proton to form bicarbonate, a small amount will lose two protons to form carbonate (13 percent), and a very small amount will remain as H₂CO₃ (<>1 percent). All of these forms, however, interconvert faster than the blink of an eye, so one cannot identify one as carbonate and one as bicarbonate for more than a tiny fraction of a second. All one can really say is that on average X percent is in the form of bicarbonate, and Y percent in the form of carbonate.

One final point on the nature of these species before we go on to more interesting properties. In seawater, carbonate forms soluble ion pairs with a variety of metal ions. Most notably, it forms ion pairs with magnesium (more than half of the total carbonate), calcium and sodium. Only about 14 percent of it remains "free." In a sense, an ion pair comprises one magnesium ion and one carbonate ion attached to each other, unlike most other ions in solution that move about independently. These ion pairs are also rapidly forming and breaking down in solution, so, once again, the best description is that on average a certain percentage are paired and a certain percentage are not. This pairing may sound esoteric, but it is important in understanding the complex interrelationships between calcium, magnesium and alkalinity. Bicarbonate also forms the same types of ion pairs, but to a much smaller extent, with nearly 80 percent of it remaining "free".

pH

One of the most obvious effects of CO₂ on reef tanks is on the pH. Any process that adds CO₂ to the tank will drive down the pH. These include calcium carbonate reactors, the respiration of organisms and breathing into a skimmer air intake (try it!). Likewise, processes that remove CO₂ from the tank tend to drive up the pH. These include limewater addition and photosynthesis. These effects are readily understood by looking at Equation 1. If you add CO₂ to the left hand side, the reaction is pushed to the right, producing protons (H⁺) and lowering the pH. If you remove CO₂, the equilibrium shifts to the left, taking up H⁺ and raising the pH. This effect is found in the open ocean as well, where the pH is found to change as the amount of CO₂ in the water changes with location.

An interesting development in the past few years in reef keeping is recognition of the importance of indoor air quality. CO₂ often builds up considerably in tightly sealed homes and offices. This excess CO₂ tends to drive down the pH, and many people have found themselves with unacceptably low pH values. Opening a window has, in many cases, been a satisfactory solution to this problem.

Limewater and CO₂

When limewater (or the German, kalkwasser) is added to a reef tank, CO₂ is especially important. Limewater consists primarily of calcium ions (Ca⁺⁺) and hydroxide ions (OH⁻) in solution. There is some CaOH⁺ around as well, but on addition to seawater it quickly dissociates into additional calcium and hydroxide ions.

When added to a tank, these hydroxyl ions proceed to combine with a host of other ions. One important reaction is the combination with hydrogen ions, reducing the H⁺ concentration, and thus increasing the pH:

The hydroxide ions that are added also shift the bicarbonate/carbonate equilibrium (equation 1) to the right, toward carbonate.

One immediate effect is that the concentration of carbonic acid (H_2CO_3) is reduced. Because the carbonic acid concentration is in equilibrium with gas phase CO_2 , as soon as the carbonic acid is reduced below the equilibrium level, the system becomes deficient in CO_2 , and more is then pulled in from the atmosphere. The CO_2 pulled in then becomes carbonic acid, which in turn mostly breaks down into H^+ and bicarbonate:

In this last equation, we can see the importance of atmospheric CO_2 to the system: it has kept the pH from rising too much by causing the production of H^+ , and it has provided additional carbonate alkalinity in the form of HCO_3^- (a semantic point here: the OH^- itself provided alkalinity, but not "carbonate alkalinity"). Because aeration often cannot keep up with the demand for CO_2 in such tanks, the pH often runs higher than natural seawater (~8.2). This effect is, in fact, why some people use CO_2 in conjunction with limewater. In this case, they do not choose to rely on atmospheric CO_2 , but want to add it faster or to a greater extent than would happen naturally by aeration.

Calcium Carbonate Reactors and CO_2

To an even greater degree than limewater, calcium carbonate reactors are dependent upon CO_2 . Calcium carbonate consists primarily of calcium ions (Ca^{++}) and carbonate ions (CO_3^{--}) in solid form. When mixed with seawater, however, it will not dissolve to any extent because seawater is already supersaturated with respect to calcium carbonate. In fact, clean calcium carbonate surfaces will act as nucleating sites for precipitation of calcium and carbonate from solution, actually reducing the concentration of both.

The way that $CaCO_3$ reactors solve this problem, of course, is by using CO_2 to lower the pH inside of the reactor. This is accomplished by the mechanism shown in Equation 5. But why does this change the solubility of calcium carbonate? The dissolution of calcium carbonate is shown below:

In a very real sense, the equilibrium solubility of calcium carbonate (or any solid) is a competition between ions dissolving off of the surface and ions precipitating onto it. When there are few ions in solution, the movement is mostly one-way: off the surface. However, as the concentrations of calcium and carbonate rise, the precipitation reaction begins to become significant. When the solubility limit is reached, the number of ions going into solution is exactly balanced by the number of ions precipitating onto the surface.

So what does this have to do with CO_2 ? Well, as CO_2 is added to the reaction chamber, the pH drops as shown in Equation 5. This in turn shifts the bicarbonate/carbonate equilibrium back toward bicarbonate and reduces the carbonate concentration:

The reduction in carbonate concentration as the pH is reduced is dramatic. As the pH of seawater drops from 8.2 to 7.2, the carbonate concentration will drop by nearly a factor of 10. It is this drop in the concentration of carbonate that permits more $CaCO_3$ to dissolve before equilibrium is reached.

So why use CO_2 instead of another acid, like hydrochloric, to facilitate dissolution? Well, if the processes described above were all that took place, the pH of the tank would keep on dropping as acid was added. Think of it this way: if fluid is continuously dumping into the tank at a pH of 6.0 to 7.0, why doesn't the pH eventually drop down to this level?

The answer is CO_2 ! If one were using a different acid, like HCl, the pH would, in fact, decline forever. You add acid to dissolve the calcium carbonate and then the calcium carbonate is removed in coral skeletons. What's left? The acid that you used to dissolve the media to begin with remains.

With CO_2 , however, you remove the acid on a continuous basis, though most people don't think about this aspect. The "acid" is removed by blowing off CO_2 to the atmosphere, in a skimmer, on the tank surface, etc.

Thus, the tank itself has too much acid in it to be in equilibrium with the air, and blows off some of the acid as CO_2 . Because this process is not instantaneous, tanks that use such reactors often run at a lower pH than natural seawater, and likewise lower than those that use limewater.

There is a second effect of reduced pH on the solubility of calcium carbonate that may also be very important in $CaCO_3$ reactors. All of the discussion to this point has been based on the equilibrium solubility. Equilibrium solubility is, in effect, the amount that will dissolve if given long enough to "finish" dissolving. However, the dissolution of many solids is slow,

and equilibrium may not be reached in the time frame required in any given application. The dissolution of aragonite in seawater is generally slow, and is typically governed more by kinetic (rate) issues than by the equilibrium solubility.

The kinetics of solubility can be impacted by many factors, such as temperature (higher temperatures make nearly all reactions reach equilibrium faster), particle size (smaller particles have higher surface area and thus dissolve faster) and the movement of the fluid in relation to the particle surface (higher flow carries away dissolved ions, reducing the likelihood of reprecipitation).

In the case of CaCO_3 , however, pH can also have a big impact on the kinetics of dissolution and not just on the equilibrium solubility. The previous discussion showed how acid (H^+) combines with carbonate (CO_3^{++}) to form bicarbonate (HCO_3^-) and effectively reduces the carbonate concentration. The actual rate of dissolution of aragonite in undersaturated seawater has been shown by several research groups to depend upon the concentration of carbonate.

Here again, one might think of this effect in terms of the off (dissolution) and on (precipitation) rates. If there is very little carbonate in solution, there are far more carbonate ions coming off of the surface than going down onto it. Here, the overall rate of dissolution is relatively fast. Alternatively, as the carbonate concentration rises towards the equilibrium solubility, more and more carbonate ions are precipitating onto the surface. In this case, the overall rate of dissolution is relatively slow. Consequently, the rate of dissolution of calcium carbonate depends upon the carbonate concentration, and hence is faster at lower pH.

There may be an additional impact of low pH on the kinetics of dissolution of CaCO_3 , though I don't know how important it is in seawater. As the pH is lowered, carbonate ions attached to the surface of the CaCO_3 crystal may become protonated to become HCO_3^- . Because calcium bicarbonate is readily soluble in seawater, this bicarbonate ion may come off of the surface much more rapidly than when it was a carbonate ion. Likewise, a calcium ion attached to this bicarbonate may desorb from the surface more readily than when it was attached to a carbonate. Consequently, this mechanism will increase the rate of dissolution of CaCO_3 as the pH is reduced. I do not know if anyone has experimentally determined whether this effect or the effect of reduced carbonate concentration predominates in the dissolution of CaCO_3 in acidified seawater.

Overall, the effect of CO_2 is to increase both the equilibrium solubility of the calcium carbonate and the rate at which the calcium carbonate dissolves. In my opinion, neither of these effects alone is probably adequate for optimal performance of a CaCO_3 reactor, but both together can provide a very useful device.

Conclusion

I hope that this brief venture in the world of CO_2 has shown how important it is in many of our systems. The next time that you are exhaling near your tank, take a minute to think what is going to happen to that CO_2 once it hits the water. Unfortunately, this article has only scratched the surface of the world of CO_2 and carbonates. Future articles may delve deeper into these mysteries, such as the very interesting and important relationships between calcium, magnesium, phosphate and carbonate.

For those interested in further pursuing these and other issues involving the chemistry of CO_2 in natural waters, I'd recommend two books. *Chemical Oceanography* by Frank J. Millero (Second Edition, 1996; CRC Press) provides a very detailed examination of many aspects of seawater chemistry. *Aquatic Chemistry Concepts* by James F. Pankow (1991; Lewis Publishers) provides a sophisticated mathematical treatment of the chemistry of natural waters, though much of it is applied to fresh water.