IS YOUR POND RUNNING ON EMPTY?

(or the importance of the carbonate cycle)

by Dick Roemer, North Carolina

We all know what happens when our automobiles run out of gas. Actually several things happen, and none of them are good–a long walk to a gas station, water in fuel injectors, etc. The results in your pond can be even more drastic if your pond runs out of one of its major ingredients. That ingredient is carbonates and the results of running out of carbonates in the pond can be a drastic drop in the pH, followed by a great rise in toxic compounds like ammonia as the biological filter shuts down due to the low pH. This is followed by death of the fish. I have seen cases where *every* fish in a pond died suddenly due to these effects and all because the pond ran out of carbonates.

This phenomenon is not discussed much in the Koi literature because most of the books and magazines come from the West coast where the water is much different than what we have here in the East. The water out West naturally has three or four (or more) times as much dissolved carbonates as our water here in the East. Also, most of the ponds in the West are made of concrete, which is rich in carbonates, while almost all of the ponds being constructed now on the East coast are made with plastic or rubber liners which provide none of these vital ingredients. So the folks out West can pretty much take carbonates for granted, and not think (or write) about them much. As a result, we here in the East haven't had much to go on with regard to carbonates. Yet carbonates form a vital, life giving and life saving part of our ponds' existences. We have a tendency to operate all the time on the very ragged edge of running out of carbonates in our ponds, and when we do step over the edge, disaster is right behind!

Ok, you say, so what is this carbonate stuff all about, what does it do, and how can it have such a big effect on my pond? If it's so important, how come I have gotten along so far without knowing anything about it?

First of all, carbonates are absolutely essential to a biological filter and even to the fish themselves. I have been saying carbonates when I mean the family of carbonate compounds. In this family, the most important one is the bicarbonate ion (HCO_3^-). It is one half of the old familiar sodium bicarbonate ($NaHCO_3$) or Baking Soda. That's the *Arm & Hammer* stuff we all have used to raise the pH of a pond or aquarium or to remove odors from a refrigerator.

The bicarbonate ion is actually a *buffer* in a pond, able to raise the pH if it is too low or less well known and more remarkable, to lower the pH if it is too high. How can it do that? The normal process in a pond is for the bicarbonate to keep pH stable by "absorbing" the acidic ions (H^+) that are produced by the bacteria in the biological filter. When this happens, we get water and carbon dioxide. The carbon dioxide is driven out of the pond by our aeration devices (waterfalls or air stones) and the water is left behind. The chemical formula is:

$$HCO_3^- + H^+ = H_2O + CO_2$$

bicarbonate + acid = water + carbon dioxide

Notice what a nice balance there is. There are three oxygen atoms on the left side of the equal sign, three on the right side. Two hydrogen atoms on each side, and one carbon. Nothing is lost, we have as much of each after the chemical reaction of "absorbing" the acid ion as we had before. What is lost, however, is the bicarbonate ion. The bicarbonate has been transformed into carbon dioxide (CO_2) and driven off as a gas. We also lost the acid which had been produced by the bacteria in the biological filter. But because the bicarbonate is *consumed* in the reaction, we must continually *replace* it.

But how can the bicarbonate act as a buffer--to go the other way, lowering the pH if it is too high? In that case, which we don't normally see in a pond, the bicarbonate ion would give up its hydrogen as an ion, thus adding acid, lowering pH, and becoming a carbonate ion (CO_3^{--}).

$$HCO_3^- = CO_3^{--} + H^+$$

bicarbonate = carbonate + hydrogen ion (acid)

The carbonate ion tends to unite with a calcium ion (Ca^{++}) becoming a solid, calcium carbonate. That is the stuff oyster shells, marble chips and concrete are made of. Notice again that everything balances on both sides of the equation, all the H, O, and C atoms are equal in number on each side, and the plus and minus signs are also in balance.

I have written both equations with an equal sign "=" for simplicity. Actually, a chemist writes both of these equations with a "<=> " symbol to show that the chemical reaction can go both ways. Whether they go from left to right or from right to left depends on the relative concentrations of the compounds involved and on the pH of the water (and on other things as well). Many pond keepers add oyster shells or marble chips to the filter in order to get the benefit of the last equation going from right to left—that is the oyster shells or marble chips tend to dissolve (absorbing a hydrogen ion in the process) and providing the needed bicarbonate ion to "absorb" another hydrogen ion. If you have a concrete pond, this happens fast enough so that you might never have to worry about the carbonate balance in your pond. I first added marble chips in 3/4″ size to the filters in my liner pond and now I have replaced them with whole oyster shells in an attempt to increase the bicarbonate level. I can't honestly say how much help it has done, or how fast they dissolve (not very fast to be sure).

So we see that bicarbonate acts as a *buffer* in the water. The complete equation (from *Fish and Invertebrate Culture* by Steven Spotte) is

$$CO_{2\,(Gas)} = CO_{2\,(Ag)} + H_2O = H_2CO_3 =$$

carbon dioxide = carbon dioxide + water = carbonic acid =

$$H^+ + HCO_3^- = H^+ + CO_3^{--}$$

acid + bicarbonate = acid + carbonate

He says the reaction is extremely pH sensitive. This means that the carbonates will react quickly to a shift in pH and will work to bring the pH back to the proper range. This range is about 7.4 to 7.8. This means that this is the range you should find in your pond. If it's lower, you probably don't have enough bicarbonate. If it's higher, it is not a concern, because it will be stable at that level. If you add something with acid in it to lower the pH, you won't see any lowering of the pH because the carbonates will resist any change. The only thing that will happen is that you will be destroying some of the bicarbonate in the pond. Add enough acid, and all of the bicarbonate becomes exhausted, and the next drop of acid, from the biological filter or from your addition, will cause the pH to plummet with all of the damages described in the beginning of this article! So, never add anything to your pond to lower pH, NEVER. Spotte also says the equation above shifts to the right as pH increases. The action in a pond, however, is from right to left due to the steady addition of the H+ acidic ions from the biological filter. The carbonate ions (CO_3^{--}) and bicarbonate ions (HCO_3^-) "absorb" the acid ions—so long as these carbonates are present in the water. When they run out, the acid builds up and trouble begins!

Proper levels of bicarbonate

How do you know if you have enough bicarbonate ions in the water? The test involved is called "total alkalinity." I think that is a terribly obscure description of what we are looking for, but that's what we're stuck with! It's further complicated by having about six (!) measuring scales to describe how much of the stuff is in the water! The one I'm going to talk about is parts per million (ppm).[1]

The starting point in talking about total alkalinity (might as well get used to the term) is that you should not go below about 40 parts per million in the pond as a minimum. Steve Meyer said at the 1990 AKCA Seminar that the desired range is 50 to 100 ppm. In the book, *Practical KOI Keeping, Volume I*, published by the AKCA, Joe Cuny says that the level shouldn't go below 15 ppm. I think that is pushing things way too close to the edge. In a more recent edition of *KOI USA*, July/August 1989, Dr. Bob Vessey says total alkalinity between 80 and 120 ppm is acceptable and below 40 ppm is dangerous. I try to maintain at least 80 ppm in the pond at all times and accept anything above that. This level of bicarbonates can be maintained here in the Virginia suburbs of Washington, D.C. if water changes are done often enough as the tap water has about 70 to 90 ppm. Alan Hobron reports that his tap water in Staten Island, N.Y., ranges from 12 to 32 ppm, however, so water changes alone won't let him maintain an adequate level of bicarbonate. He adds a spoonfull of *Arm & Hammer* every day to his 750 gallon pond to maintain 80 ppm. Bob Vessey, in Florida, reported in the May/June 1990 issue of *KOI USA* that a member of his club who used well water was having trouble keeping fish alive. Bob tested the well water for total alkalinity and found it contained only 10 ppm of total alkalinity. Bob called such toxic water chemistry the "unseen killer."

Testing for Total Alkalinity

There are several test kits to determine your pond's total alkalinity level. The Mardel company makes a chemically impregnated plastic strip that you dip in the water. A color change gives a reading for total alkalinity. The reference colors are 0, 80, 120, 180, 240, and 300 ppm. If your goal is to stay above 40 ppm, it is very difficult to tell from these "Dip and Read Strips" if you are above or below that level. Other members who use that test kit add enough *Arm & Hammer* baking soda to bring the level up to 80 ppm. The folks at TETRA make a kit that includes a test for total alkalinity (they

1. Officially the ppm is expressed as calcium carbonate equivalents. In case you see other measurements, here are the conversion formulas: 50 ppm = 1 Meq./L = 2.8 German degrees of hardness (DKH) = 3.5 English DKH = 5.0 French DKH = 2.92 grains per gallon.

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call it "carbonate hardness") that reads in degrees of hardness, where one degree of hardness equals 17 ppm.

Another test kit for total alkalinity is made by the Taylor Company and is sold in swimming pool supply stores. In this test, 5 drops of a Total Alkalinity Indicator (R-0008) is mixed with 25 ml (0.88 oz) of pond water. Then, their next reagent, Sulfuric Acid .12N (R-0009) is added, one drop at a time, until the color changes from green to red. The total alkalinity in ppm is ten times the number of drops it took to make the color change. For example, if it took four drops, the total alkalinity is 40 parts per million. The complete Taylor test kit that I bought cost about $30 a few years ago, but it also included tests for pH, chlorine, calcium hardness and cyanuric acid, as well as a circular slide rule that related the total alkalinity, temperature, and calcium hardness to give a pH in balance with the other three variables. (They say if your actual pH is more than 0.3 above that balanced pH, you will have lime deposits on your swimming pool piping, or if more than 0.3 below, there will be etching (dissolving) of your concrete swimming pool.)

A much cheaper alternative to buying the complete Taylor test kit is to simply buy the two refill reagents and use them according to the directions given above. No color chart is needed since the change in the test sample from green to red and the number of drops it needed gives the total alkalinity reading.

Correcting Low Levels of Total Alkalinity

The current four-pound package of *Arm & Hammer* Baking Soda has a table of the amount to add to correct low total alkalinity levels. They say to add 3 pounds per 10,000 gallons to raise total alkalinity by 20 ppm. Expressed in amounts needed per 1,000 gallons, it's 0.15 pounds to raise total alkalinity by 10 ppm. Or, 1 pound will raise 5,000 gallons by 13 ppm.

Summary

Maintaining a proper level of bicarbonate in the pond is necessary for the proper operation of a biological filter and the health of the fish. There are simple tests to determine when your pond is running on empty and there are simple ways to replace the bicarbonates lost through the biological filtration process. Water changes replace bicarbonates if your water supply has an adequate level to begin with. In addition, you can add crushed coral, limestone chips, or oyster shells to your filter to help the replacement of carbonates. Finally you can add *Arm & Hammer* Baking Soda to keep your pond safe and healthy for your fish. ❖