<u>Cactus and Alkalinity</u>

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Foreword – Some of this is a repeat of our article in the CSSJ. “Acidic Solutions” by Malcolm Burleigh, Elton Roberts and D Russell Wagner, 2008, 80_5, pp245-250. That article was written in 2007 and we have developed our theoretical arguments further and also have changed and improved our practices substantially.

Our sole wish is to help people who are experiencing problems with their plants. We feel that this may apply to all types of container culture and possibly to all horticulture in general. The occurrence of highly alkaline water seems to be quite prevalent. For this reason we would allow and actually encourage the dissemination of this article as long as you don’t misquote us or take our statements out of context.

This article is broken into Introduction, Practice, Theory and a Glossary that may help you with your pH adjustment.

Introduction -- Cacti in the desert –
We often hear references to desert soil being alkaline. Maybe this is because there are so many alkali dry lakes in the desert, the assumption is that desert soils must also be alkaline. Cacti in their natural habitat get their water directly from rain. These plants normally grow on a minimum of soil in rocky areas. Many appear to come out of cracks in the rock. The pH of rain is acidic due to the carbon dioxide from the atmosphere dissolving in the rain water. It is this water that the cacti prefer.

We have seen that dropping the pH of our alkaline water by adding acid has vastly improved the lives of the cacti that we grow. This is reflected in new growth and flowering of our plants. This effect seems to be quite general for many plants. However, it is more striking for cacti, since we keep our plants in the same pots for years without disturbing them. The fact that they do not like their roots disturbed mitigates for not repotting them but increased alkalinity is a serious problem that then gets the cactus grower into a losing situation. These problems may readily be corrected by dropping the pH of the water for your plants. Alkalinity is due to bicarbonate in the water. Dropping the pH of the water leads to a decrease in the water alkalinity. <u>The sole use of adding acid is to decrease the bicarbonate concentration.</u>

Municipal water supplies often have high alkalinity. This alkalinity serves to prevent pipe corrosion and since many of the pipes in older towns are made of Lead this becomes a safety issue. Leaking pipes are another safety issue, since this will cause ground water to be aspirated into the pipe. Well water can also be especially alkaline. As a result soils quickly become intolerably alkaline for the plant. Once this happens, the plant stops growing and starts to die. Since the pH of normal rain is about 5.1, it may be best to drop the pH of your water to that level. This may be done with any number of acids.

<u>Use of lower pH in horticultural practice</u> – There are few references to suggest that cactus growers ought to use a low pH water on their plants. The best reference for the use of lower pH for cacti we have seen is from Buxbaum(1). In his book on Cactus Culture he emphasizes that pH=6.0 is the proper pH for water for cacti. Buxbaum also shows pictorial evidence for the much slower growth of cacti at higher pH. He offers many examples of the poor response of cacti to higher pH.

Bailey and Bilderback, Alkalinity Control for Irrigation Water Used in Nurseries and Greenhouses, also suggest a lower pH of ca. 5.4 to 6.0[2]. They also discuss the acids that are in common use and methods for adjusting the pH. They suggest that the main reason for better response at low pH is the availability of the elements necessary for plant growth. This article which is available on the Internet, contains many excellent pointers for nursery growers.

The use of acid to decrease the pH of irrigation water is also common in large-scale agricultural practices. Many companies in agricultural areas such as the Central Valley of California sell large systems for addition of acid to correct the pH of irrigation water. We were referred to Verdegaal Bros. Inc. by a farmer in the Modesto area. They referred to the article of Bailey and Bilderback when we wanted to find out how much acid they were using.

The use of lower pH in hydroponics is also well known and there are several pH indicators on the market that allow the pH to be readily and cheaply measured. These are discussed below. pH measurements of rainfall during thunderstorms reveal that the pH of rainwater fluctuates over very short time intervals, falling to 3.6 directly after lightning strikes[3]. Obviously plants are habituated to low-pH water.

<u>Practice</u> –
<u>Elton Roberts' story</u> -- I built my first hothouse to grow cacti in the early 1970s in California's Sierra Mountains at an elevation of about 3000 feet. But when I moved to my present location 24 years ago my plants stopped growing, although conditions had not noticeably changed. If I repotted the plants into new soil they would grow and get to look good again, but before long they would go into decline.

When an azalea finally died I was inspired to use gypsum. I gave that to all my plants. The positive effect lasted only six months. A nurseryman suggested I use aluminum sulfate and I spent another $200 on a pH meter. I dropped the pH to about six but the problem was that it caused the water to become milky. Since I had a pH meter I experimented with vinegar and found out that it only took one tablespoon in five gallons to drop the pH from 7.8 to 6.0.

I didn't pursue the idea further, because about that time I found a pH-balanced fertilizer. When it was no longer available, I bought a fertilizer with sulfur in it. The sulfur is supposed to keep the pH of the soil on the acidic side, but it didn't work. I found, by calling the manufacturer that the sulfur was supposed to encourage a bacterial growth that was responsible for maintaining low pH in the soil. But these bacteria evidently don't grow in a dry cactus mix, and a low pH was not maintained. By the fall of 2006 my plants were looking pretty bad. *Echinomastus johnsonii* var *lutescens*, normally the diameter of a tennis ball, was hardly bigger than a ping-pong ball. So, remembering my old tests I mixed up a batch of vinegar-spiked water and watered my plants with it. Within a week they were pushing new spines. I had happened upon a simple fact that commercial nurseries take for granted but that hobbyists are largely unaware: for best growth, most plants need slightly acidic water. For cacti, I now believe it to be essential. Since 5% vinegar is more expensive, I have eventually gone to sulfuric acid. This is the cheapest material that can be used.

<u>Malcolm's story</u> -- Elton had been bugging me to drop my water pH for some time. I told him my water was OK after all, I live in Minnesota, the "Land of Sky Blue Waters". I demurred until the spring of 2007 when I decided to check the pH of the water in St Paul. **<u>It was 8.2</u>**! Elton suggested that I throw in some vinegar, so in April I began by adding vinegar or citric acid to my water to achieve a pH of about 6. I eventually settled at a pH of about 5.0.

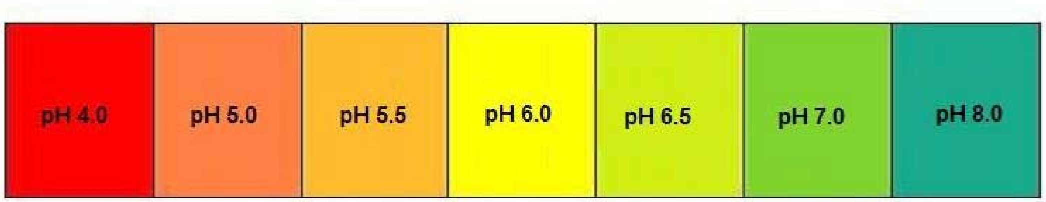
Acidified water has been a real boon in my garden. I have set up a whole pumping system for my plants and currently use citric acid to lower the pH. It is cheaper than vinegar and can be purchased on-line. My first glimmer was several sets of Opuntia seeds that I had started. A week after I had started them I noticed a bulge several of the pots. When I looked there, the large cotlyedon leaves of the Opuntias were trying to push their way out of the soil. Before this

Opuntias were always the slowest seeds to sprout. There followed a succession of growth on other plants that I had trouble with. By late May I was so impressed that I bought a sump pump and began to treat all my plants with pH-adjusted water.

We have many other stories from people who have tried this and seen new growth with their plants.

<u>Acidifying your water</u> -- Starting out -- In order to lower your pH you must be able to measure it. The cost of pH meters has dropped a lot and you may now purchase them starting at about $150. If you have a commercial greenhouse that is nice but it still is a substantial outlay of cash.

It seems as though the hydroponics growers have been aware of the necessity of correct pH for some time. They generally suggest a pH of 5.6 to 6.0. Our suggestion would be to purchase a colorimetric indicator kit. These are available from hydroponics stores. They are generally from $6-8. The two brands I have seen are General Hydroponics® and Sunleaves® They have a spectrum of color going from:



Color gamut

Low pH=	red
Correct pH =	reddish-yellow (about 5.0)
High pH =	blue green

Vinegar is a good acid to start with. Purchase a gallon bottle of 5% white vinegar. (Some of the cheaper brands contain 4% so be careful to read the label. You will have to adjust your vinegar add accordingly). Beginning with a five-gallon bucket of tap water, add incremental volumes of vinegar and measure the pH using a good pH meter. Or record the color using your colorimetric kit. Keep track of the results and make note of the total volume required to reach a pH of about 5.0. Any number of acids may be used to lower your water's pH. Citric acid, acetic acid (vinegar), nitric acid, phosphoric acid, and sulfuric acid are possibilities, *but do not use muriatic acid (often sold for swimming pools) as this is another name for hydrochloric acid, and is very bad for plants.* If you have access to pH data and $CaCO_3$ hardness of your local water, I refer you to the above discussion above.

Note that phosphorous and nitrogen are both present in fertilizers, and you must take this into account if you use nitric or phosphoric acids. Citric and acetic acids do not present these problems. Sulfur is a necessary plant nutrient. Plants are not damaged by receiving too much sulfur, therefore, sulfuric acid is a good option for larger collections. Sulfuric acid is available in large quantities from auto supply stores. It has proven to be the cheapest acid to use. We suggest using acids such as either vinegar of citric acid with very alkaline water. Very alkaline waters generally contain very high calcium levels. Sulfuric acid although it is cheap will cause gypsum, calcium sulfate, to form. It is not very soluble and will cause deposits on your valuable plants. The calcium salts of citric acid and acetic acid (vinegar) are very soluble though.

If you have high alkalinity you should be very careful about calculating the amount of acid to add and take time with it. pH rebound will be significant and you must allow your sample to equilbrate before calculating the actual amounts to add.

Delivery systems for watering with low pH – There are several ways that you can water your plants with low pH water. The cheapest would be to use a five-gallon bucket and adjust the pH in the bucket. We are sure that you will quickly tire of this procedure and find it necessary to upgrade to a more automatic system.

Sump pumps are available in hardware stores for under $100 that may be used in conjunction with a larger container such as a 55gal drum. The best type is one that has an on-off float. Running these pumps dry can be disastrous to the impellers. Plastic garbage cans make excellent reservoirs. Have a hose system set up to deliver water to all of the places that you want.

The more expensive Dosatron may be used for larger operations. It can be adjusted to dilution factors from 1:66 to 1:500. The dilution rate is independent of the flow rate. This is the Cadillac of the watering systems. It will run about $300-400.

The added benefit these operations give you is the ability to add your fertilizers and other chemicals such as pesticides and wetting agents into the water. Many fertilizers have a downward pH adjustment built into them, and it would help to measure the pH of your favorite fertilizer mixture. You must adjust the pH after you have placed the fertilizer into the water.

For plants with heavy mineral deposits on the pots, caused by alkaline conditions, it may take some time for the acidic water to have its full effect. Older clay pots may also leach a lot of minerals, and their outsides will turn white for a while as the mineral buildup is slowly dissolved away.

Theory – Water hardness is an old term that refers to certain dissolved salts. These are often salts of calcium and magnesium. These ions cause a precipitation reaction with soaps.

Calcium Bicarbonate + Sodium Stearate → Sodium Bicarbonate + Calcium Stearate
(Precipitate)

Consequently water containing these salts is said to be "hard". Generally the counter-ion to these salts is bicarbonate but often sulfate and chloride can be present. Much of the soluble salts can be precipitated, if the counter-ion is bicarbonate, by heating the water. This part of the "hardness" is called "temporary" and the other "permanent". These counter-ions precipitate as the insoluble calcium and magnesium carbonate.

$$Ca^{++} + 2(HCO_3)^- \rightarrow CaCO_3 \text{ precipitate} + H_2O + CO_2 \text{ (to atmosphere)}$$

Alkalinity -- *The problem for plants is caused by the presence of bicarbonate in the water.* The common term for bicarbonate is "alkalinity" These are soluble bicarbonates of calcium, magnesium and sodium in the water. Bicarbonate is often referred to as a buffer. This refers to the fact that the amount of acid necessary to drop the pH is greater than theoretical. But the buffering is not actually germane to the argument. Bicarbonate is the cause of alkalinity in the water.

Since our cacti and other succulents grow for very long times in the same pot, the amount of bicarbonate will reach high levels quickly, if the water has elevated levels of bicarbonate. Elevated levels are quite common. The pH of most city water is kept quite high (pH>8). In addition, well water may also be alkaline, if it comes from limestone strata. This alkalinity severely inhibits the ability of your plants to absorb water and importantly, the elemental nutrients that they need to grow.

The alkalinity is controlled by the following equilibrium:

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$$

The concentrations of each of these materials in water affect the concentration of the others. Mathematically this can be expressed as the following equation. The numbers in parentheses are the concentrations in moles/liter:

$$(HCO_3^-) \times (H^+) / CO_2 = 4.27\times10^{-(7)} = K_a$$

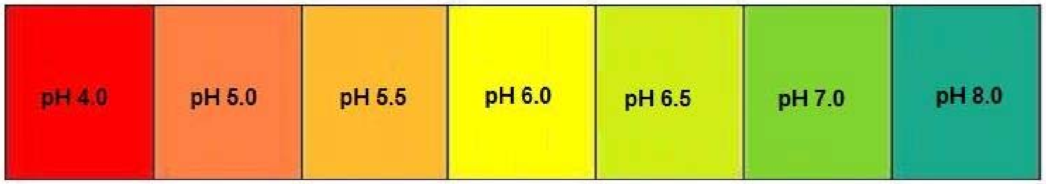
K_a is termed the equilibrium constant. Additionally under ordinary circumstances, although the CO_2 may change, it will eventually equilibrate to an equilibrium level due to the CO_2 in the atmosphere replenishing the diminished CO_2. Or the water can lose the excess CO_2 like soda losing its fizz.

Removing bicarbonate -- The best and easiest way to remove the excess bicarbonate from the water is to add acid, which will drive the equilibrium to the left. Increasing the hydrogen ion (acid) concentration lowers the amount of bicarbonate and raises the amount of CO_2 in the water.

$$\text{Acid} + \text{Bicarbonate} \rightarrow CO_2 + H_2O$$

Definition of pH -- The best way to follow the reaction is to measure the pH of the water. This is defined as the negative logarithm of the hydrogen ion concentration. This is an odd number invented by chemists to confuse people. Neutral is defined as pH = 7 this means that the H^+ and the OH^- concentration are both 10^{-7}. This is a very small number but still is meaningful. If the H+ concentration were 100 times as high the pH would then be 5. (Please refer to the glossary for further help.)

Measuring pH -- The pH may be measured using a pH meter. These will give a direct reading of the pH of the water. Another way to measure the pH is by a series of dyes that change color at different pH. There are about 20 to 30 of these dyes in general use. They are not as exact as a pH meter but in some situations, such as a greenhouse where the environment is not that controlled, a small bottle of indicator solution may prove much more reliable than a pH meter. pH meters must be calibrated and can give erroneous readings if not used properly. They also start at $150 for the reliable models. On the other hand an excellent pH indicator may be purchased for $6-8. These are available from hydroponics suppliers. They use a combination of Methyl Red and Bromothymol Blue. Methyl Red goes from red to yellow starting at a pH of 4.8 to 6.0. Bromothymol Blue goes from yellow to blue at a pH from 6.0 to 7.6. In this way they form a natural rainbow spectrum of color which is fortuitously in the right range of our interest.



Color gamut

Bromothymol Blue	6.0	7.6
	Yellow	Blue
Methyl Red	4.8	6.0
	Red	Yellow

Acid strength -- The strength of an acid may be described by the value of its equilibrium constant. That is often expressed as the pK value in a similar manner to the pH value. The pK value of the reaction bicarbonate/CO_2 reaction is 6.37. The acid of choice must have a pK value significantly less than this value to work properly.

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$$

Acetic acid has a pK value of 4.75 and so vinegar (5% acetic acid) is a good one to start with since it is readily available and quite safe. Citric acid has three acid groups and thus has several pK values 3.02, 4.75 and 5.06. Consequently it is excellent for dropping pH. These two acids also have soluble calcium and magnesium salts and so will not cause crusty salts to form.

Many people use nitric and phosphoric acid. If you use these you should be aware that nitric acid is very caustic and can cause severe skin burns. Phosphoric acid is safe. In order to use either of these acids you must take them into your fertilizer calculations. Pure phosphoric acid contains 72.5% phosphorus and pure nitric acid contains 22.2% nitrogen. Sulfuric acid is by far the cheapest acid to use. Although it is caustic, if reasonable precautions are taken it can be used with good effect. For high strength sulfuric acid add the acid to the water not the water to the acid! *Do not use hydrochloric acid or its technical grade, muriatic acid.*

Getting started adding acid -- Add incremental amounts of acid to a known volume of water such as five gallons and measure either the color or the pH on your meter until you get to your desired pH. We shoot for a peachy color on the indicator, slightly higher than 5.0.

Another way is to know the value of your water alkalinity. Most municipal water systems in the USA have websites that will give you the pH of your water as well as the alkalinity. The alkalinity number to look at is the CaCO3 equivalents of alkalinity.

These equivalents then should be matched with the equivalents of acid you are adding. I will give you several equivalent weights to start off with. These can be calculated from the molecular weight. The atomic weights must be added.

CaCO3 has a molecular weight of 40+12 + (16x3) = 100 but since it will sorb two acid groups, its equivalent weight is 50. The online municipal water web sites give the CaCO3 in PPM. This is the same mg/li (milligrams/liter). Malcolm's water is currently listed at 50ppm this means that his acid equivalents are 1.0meq/li. (Milli (m) means one thousandth.).

An equivalent of acetic acid for instance is 60g of acetic acid. A meq or milli-equivalent of acetic acid is 60/1000g = 0.06g. This would be 1.2g of vinegar. The equivalent weight of any diluted acid may be calculated by dividing by the dilution percentage. The equivalent weights of the various acids are listed in the glossary.

For a bicarbonate hardness of 0.1meq/li it is necessary to drop the pH to about 5.0 in order to remove about 95% of the bicarbonate. With higher levels it will be necessary to go even further. At a 10 times Malcolm's alkalinity level of 1.0meq/li even going to an initial pH of 5.0 leaves you with about 9 times as much bicarbonate as Malcolm has by setting his pH at 5.0. More care must be taken with high alkalinity, we discuss this in pH rebound. There is a chart in the glossary that will help you.

We caution you that going too far adding acid can be as bad for the plant as high alkalinity. So you should definitely avoid going too far.

<u>pH rebound</u> -- Another thing that you will see especially with high levels of alkalinity is a pH rebound. When we first saw this phenomenon we very perplexed. You add the acid to your water and it drops to the pH that you want to have. If you do not use the water for several days, you will see that the pH has rebounded almost to the level that you started. Malcolm's sister told us about this and we had both seen it too. Since Malcolm was using a small vial to use the colorimetric indicator it was very noticable.

We were mystified. Malcolm thought that either this was some alkaline material in the air in St Paul or a volatile acid. Vinegar is not any more volatile than water. When he switched to Citric acid as an acid the same thing happened. The acid that is volatile is actually the Carbon Dioxide! CO2 is absorbed into water from the atmosphere. It has an acidic reaction. If you heat water, most of the CO2 will be boiled off in a short time. After that, the water will slowly absorb CO2 over a period of time. As this happens the pH will fluctuate. Pure water has an equilibrium pH of about 5.1 caused by 0.39ml of CO_2 per liter.

As we add acid to the water the following reaction takes place:

$$\text{(Acid)} + \text{(bicarbonate alkalinity)} \rightarrow CO_2 + H_2O$$

If you add acid to a solution of Sodium Bicarbonate (Baking Soda) you will see the CO_2 effervescing very plainly. Since water contains much less bicarbonate we do not see the effervescence. But as you add acid to highly alkaline water the CO_2 becomes super-saturated in the water. As the CO_2 comes out of the water the pH will rebound back. If you have very alkaline water you may want to take some time as you do initial testing on your water due to the pH rebound.

Since the alkalinity is caused by bicarbonate in the water, when you add Vinegar you are destroying bicarbonate and creating CO2.

The pH of the water is controlled by the following reaction

$$CO2 + H2O \dashrightarrow HCO3 \text{ (bicarbonate)} + H+\text{(Acid)}$$

The reaction is controlled by the following equation where the values in parentheses represents the molar concentration of the various materials:

$$\{(HCO_3^-) \times (H^+)\} / (CO_2) = K_a$$

K_a is a constant known as the equilibrium constant. We have a solution of bicarbonate which also has CO2 dissolved in it.

The initial pH is controlled by the amount of CO_2 and the amount of bicarbonate in the water. If the CO_2 is absent this will raise the initial pH. The city of St Paul reports a pH of 9.0 with a bicarbonate level at 1 meq/l. This indicates a level of CO_2 that is 1.3% of equilibrium. When Malcolm measured it after taking it a few hours to work in a bottle, it was 8.2, suggesting that the level had risen to about 8%. A perfectly saturated water should read about a pH of 7.1. (That's St Paul water!) Higher levels will read differently.

<u>An example</u> -- Here is an example of what can happen and it illustrates the problem well. Robert Swan wrote to us from Maryland –"Our city water has a pH of 7.4 and alkalinity of 110 PPM. Using a pH meter and test strips the pH goes down to 5.8 when I add 4 Tablespoons of vinegar to 10 gallons of water. Seems like a lot of vinegar but I guess that is okay. However, if the treated container of water sits for a few days, the pH goes back up to 7.4 when I test it. Am I going crazy or does the vinegar evaporate? Help!"

<u>Here is our answer</u> -- The hardness is given in equivalent amounts of Calcium Carbonate ($CaCO_3$). This has a molecular weight of 100 but an equivalent weight of 50 since it produces two moles of bicarbonate. The equilibrium solubility of atmospheric CO_2 in water is listed below. This is a number we got off of the internet higher temperatures will favor a lower solubility. 4TBSP of vinegar in 10 gal. translates to 0.00135 eq/li.

Malcolm's hardness	50	PPM = Mg/li
Malcolm's hardness	0.0010	eq/li
Swan's Hardness	110	PPM = Mg/li
Swan's Hardness	0.0022	eq/li
Equilibrium CO2 in H2O	0.39	ml gas/liter water
Equilibrium CO2 in H2O	0.000174	Moles /li
5% HAc	0.83	Moles /li
Ka CO2	4.27×10^{-7}	

The pH calculation for the final pH comes out to be a bit over 6.1 instead of the 5.8 you mentioned. This means that you have destroyed about 60% of your bicarbonate but still have about 40% left.

pH	H+	K	CO2	HCO3
7.47	3.37E-08	4.27E-07	0.000174	0.0022
		Vinegar add	0.00135	-0.00135
6.12	7.65E-07	4.27E-07	0.001524	0.00085
				39%

Of course you are left with an excess of CO_2 in the water and it will eventually evaporate which will raise the pH of the water to close to what it was before.

pH	H+	K	CO2	HCO3
7.06	8.73E-08	4.27E-07	0.000174	0.00085

We would suggest you put more vinegar into your tank. Probably more like 6.6 tbsp/10gal. This should bring the pH down to about 4.7.

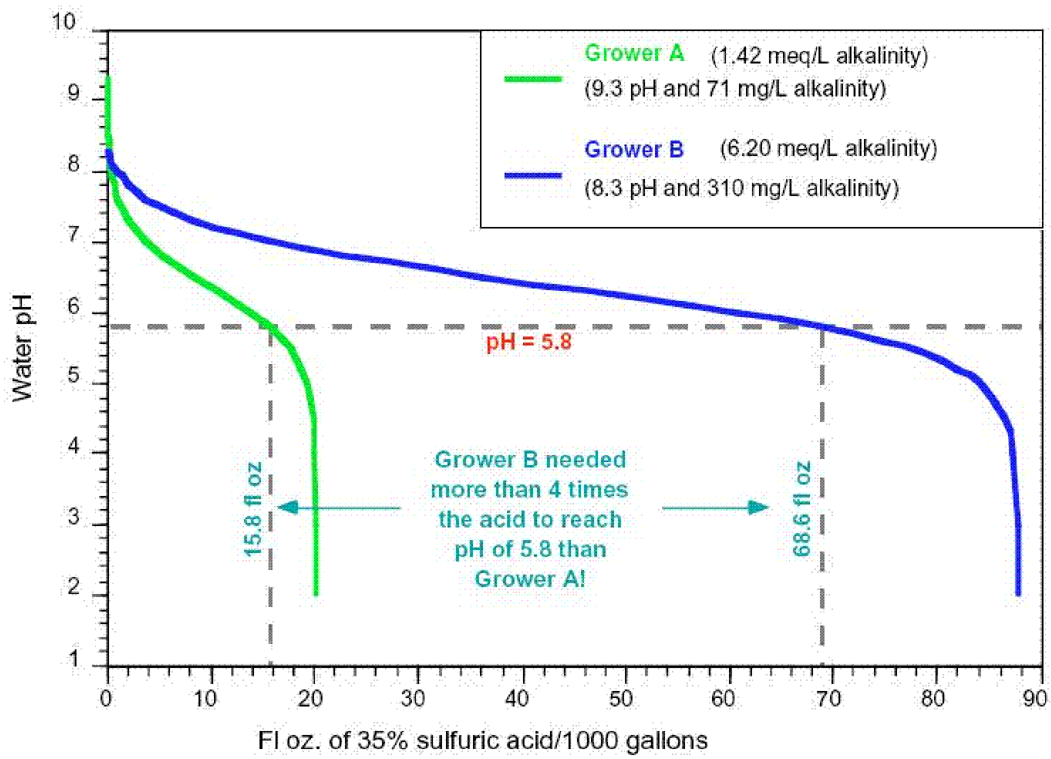
pH	H+	K	CO2	HCO3
7.47	3.37E-08	4.27E-07	0.000174	0.0022
		Vinegar add	0.00215	-0.00215

4.70	1.98E-05	4.27E-07	0.002324	0.00005
				2%

This pH should eventually correct to about 5.8.

pH	H+	K	CO2	HCO3
		Vinegar add	0.00215	-0.00215
5.8	1.48E-06	4.27E-07	0.000174	0.00005

The bottom line is that you should not give too much regard to the initial pH but focus on how much acid it takes to drop the pH to about 5.0, taking care to allow for pH rebound with very highly alkaline waters. The degree of alkalinity does not necessarily follow the pH. (See figure below) The most important issue is the amount of bicarbonate in your water. This is always determined by how much acid you must add in order to drop the pH.



Titrations of two different waters with sulfuric acid. Notice that although the beginning pH of Grower A water is a full unit higher than Grower B water, it takes more than 4 times the acid to drop Grower B water to pH 5.8, due to the greater alkalinity in Grower B water.

Excerpted from Bailey and Bilderback [(2)]

If you aren't a chemist and are thoroughly confused and we lost you on equivalent weight and moles/liter, all you have to remember is, the higher the alkalinity the lower you have to drop the initial pH. The initial pH is controlled by both the bicarbonate and the CO2 in the water. If you have the hardness values for your water then you can use that to judge how much acid to add to your water. We have also put a glossary at the end which will help you wade through the calculations. It would also help if you have an Excel ® program.

There is a lot of variability in local waters. Malcolm's sister in Modesto has an alkalinity level of about 8.5 times as great as mine. Elton's is only slightly higher than Malcolm's St. Paul MN water and he lives about 2 miles away from his sister as the crow flies. Malcolm's cabin water, near St Cloud MN is about 5 times as alkaline as his home water.

Quite often we have people tell us that they drop the pH of their water by letting it set in a bucket for several days. Although it may alter the pH as we have described above, this does not affect the concentration of bicarbonate. This can only be done by reaction with stronger acids.

Cacti and Limestone -- In the Chihuahuan Desert, especially, many desert plants are found associated with limestone strata. This association with limestone is so strong that having geological maps of the limestone areas is a good way to find these plants. These soils have been measured as having a high pH value. The assumption then is that the soil is very alkaline.

Let us then examine the relation of pH to alkalinity since the relationship is certainly not simple. Rain has CO_2 dissolved in it, lowering the pH of the water. Limestone reacts with the CO_2 in the water creating soluble calcium bicarbonate.

$$CO_2 + H_2O + CaCO_3 \rightarrow Ca^{++} + 2(HCO_3^-)$$

This reaction raises the pH of the original rainwater. When the concentration of bicarbonate is equal to that of the original CO_2 in the water the pH will be about 6.4. However, this level is still acidic and the progression to higher pH is much slower as the pH increases. The bicarbonate levels in contact with the plant roots in limestone strata after a rainstorm are a fraction of the levels that are seen in the alkaline ground water. Measurements made of the soil pH during the dry periods before the monsoon rains arrive, when there is nothing left but bicarbonate in the surrounding soil are not indicative of what the roots see during their cycles of growth after a rain [4]. This water percolates into the ground and eventually the water table can get to very high levels of bicarbonate. Since the equilibrium value for CO2 in water is 0.174meq/l, the highest it can get in the limestone soil is about 0.35 meq/l after extended periods. This is a low level, about 1/3 of the level of Malcolm's water. The harder to grow genera that seem to love limestone, Ariocarpus, Escobaria, Turbinicarpus, and other genera do not grow when given alkaline water, but will immediately start growing when given acidic water.

Warning -- The pH increase caused by limestone creates some confusion with cactus raisers. We often see references to adding lime to your cactus soil. This is a big mistake since lime and limestone are very different materials. Lime is calcium hydroxide and the pH of lime is so high that it is deadly for the plants.

Conclusion -- Some plants show adverse reaction to alkaline water sooner than others do. These are the plants that have a reputation of being difficult to grow. Among them are the high elevation plants of North and South America, such as *Pediocactus*, *Sclerocactus*, *Micropuntia*, *Rebutia*, *Sulcorebutia* and the rare and hard to come by Opuntioids from South America. Also other deep desert species such as Echinomastus, *Escobaria*, *Neolloydia*, *Glandulicactus* and plants like *Mammillaria tetrancistra* and *Herrerae* and many others succumb readily to alkaline water. The slow growing *Ariocarpus* may not show signs of dying quickly but in time they will succumb like the others. Plants with small diameter stems and young plants that do not have much water storing capacity will succumb quickly to alkaline water. These plants and the rest of the cactus family along with all other succulents will show signs of growth soon after receiving acidified water.

References

1. Cactus Culture Based upon Biology. Franz Buxbaum, pp. 34 – 44 Blandford Press, London, 1958
2. Doug Bailey and Ted Bilderback, 1998, Alkalinity Control for Irrigation Water Used in Nurseries and Greenhouses, North Carolina State University, http://www.ces.ncsu.edu/depts/hort/hil/hil-558.html

3. Railsback, LB. 1997. Lower pH of acid rain associated with lightning: evidence from sampling within 14 showers and storms in the Georgia Piedmont in summer 1996. Science of the total environment. 198: 233-241.
4. The Genus Turbinicarpus in San Luis Potosi by Cactus & Co. libri

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Glossary of terms and explanations --

Alkalinity – This actually refers to any material that raises the pH of the aqueous solution. But here we are defining it as bicarbonate since just about all of the alkalinity of the water in the world is caused by bicarbonate.

Alkalinity correction for PPM $CaCO_3$ – This is a table that will tell you of the amounts of vinegar to add to 5 gallons of your water. It may also be listed as mg/li. It will leave bicarbonate equivalent to 2.5PPM of CaCO3.

The final pH should eventually become 5.8 for all of these additions.

PPM CaCO3	TBSP vinegar	Initial pH
50	1.5	5.0
100	3.0	4.7
150	4.5	4.6
200	6.1	4.5
250	7.6	4.4
300	9.1	4.3
350	10.7	4.2
400	12.2	4.2
450	13.7	4.1
500	15.3	4.1

The equation for acetic acid and PPM alkalinity can be expressed as:

(Tbsp/vinegar / 5 gallons) = 0.0307 x (PPM of CaCO3) - 0.0768

Ions and counter-ions – It's a universal rule that there are the same amount of positive ions and negative ions in a solution. Some of these ions like magnesium for instance have two plus charges on them and they have to be balanced with two minus charges from two other molecules or a double minus charge from molecules like sulfate.

pH – The symbol "p" refers to the negative log of the hydrogen ion concentration. Chemists have done this because the concentration normally can vary by at least 14 orders of magnitude. These would normally be negative numbers if we used "log". This can be confusing since a higher acid concentration is a lower number. The point at which the OH^- and H^+ concentration is 10^{-7} and so a pH of 7 is considered neutral.

The equilibrium reaction is:

$$H_20 \leftrightarrow H^+ + OH^-$$

$$(H^+) \times (OH^-) = 10^{-14}$$

Equilibrium – This is a point when the reactants in a system are going as fast in one direction as they are in the other. Thus an acid, HA, will react in this way.

$$HA \leftrightarrow H^+ + A^-$$

The reaction hasn't stopped! But there are just as many molecules of HA going to $H^+ + A^-$ as there are $H^+ + A^-$ going to HA.

Equilibrium constant – There is a relation of the reactants at equilibrium. The equation for the above reaction is:

$$(H^+) \times (A^-) / HA = K_A$$

If more A^- is added to the solution this will cause the amount of HA to increase and the amount of H^+ to decrease thereby raising the pH. For this reason, A^- is called the conjugate base to the acid HA.

pK_A – This is the same operator "p" done on the equilibrium constant. If the amount of A^- and HA are made equal then the equation above becomes:

$$(H^+) = K_A$$

Then the pH is equal to the pK. Buffers are made in this way since addition of either acid or it's conjugate base change the pH only slightly.

Atomic weight, Molecular weight, Equivalent weight -- The elements are composed of an inner core of heavy protons and neutrons with an outer cloud of very light electrons. In order to know how many of these we have when we weigh we have to know their relative weights. Oxygen has been defined as having an atomic weight of 16.0000. There are isotopes of the various elements which have different numbers of neutrons but the same protons. Since the negative electrons match up with the positive protons. We call all of the elements that have the same protons as being the same element. But there are two stable varieties of Carbon, two of Hydrogen. Oxygen actually has four. So the chemists mess up. Fluorine is the smallest element with only one isotope. We normally round these off to one with the exception of Chlorine, which is split and is 34.5.

Molecular weight is just the addition of the atomic weights So CO2 = 12+16+16= 44 water is 16+1+1=18 and do forth.

Equivalent weight must be considered when you are using the chemical to run a reaction. The molecular weight of Sulfuric Acid H2SO4 is 1+1+32+16+16+16+16=98. But since there are two acid groups on Sulfuric acid it's equivalent weight is half or 49.

These equivalents then should be matched with the equivalents of acid you are adding. I will give you several equivalent weights to start off with. These can be calculated from the molecular weight. The atomic weights must be added.

Element	At, Wt.
Hydrogen H	1
Carbon C	12
Nitrogen N	14
Oxygen O	16
Sodium Na	23
Phosphorus P	31
Sulfur S	32
Potassium K	39
Calcium Ca	40

Equivalent weights of common acids

Acid	Eq.Wt.
acetic acid	60
5% vinegar	1200
citric acid hydrate	70
phosphoric acid	49
sulfuric acid	49
nitric acid	63

Mole, Equivalent – This is also called a gram-atom. A mole of sulfuric acid weighs 98grams. Thus an equivalent of Sulfuric Acid weighs 49g.

Molarity, Normality – 1 molar is a mole of a substance dissolved in a liter of solution. E.g. take 98g of sulfuric acid and put it into a volumetric flask then add water until you reach one liter. Only be careful since you must first add some water to the flask then add the acid, then add more water to the mark. Never add 100% sulfuric acid to water. That's 1mole/li.

One normal (1N) sulfuric acid would be 49g (one equivalent) in one liter. This is 1eq/li.

Milli – since molar numbers in solution are very fractional we often multiply the number by 1000. So this number is actually quite a bit smaller. A millimeter is one thousandth of a meter.

Molecular weight of NPK – When you see 20-20-20 you might think that you have equal amounts of Nitrogen, Phosphorus and potassium but you would be wrong! Nitrogen is reported as N = 14. Phosphorus is reported as P_2O_5, it's pentoxide and potassium is reported as its oxide K_2O. So the equivalent weight if N is 14, the equivalent weight of phosphorus is $\{(31x2) + (16x5)\}/2 = 71$. Potassium is $(39+39+16)/2 = 47$. When you recalculate for equivalence the ratios become 67%, 13%, 20%.

Element	Horticultural equivalent weight
Nitrogen = N	14
Phosphorus = P	71
Potassium = K	47

Bailey and Bilderback mistakes – Their article is the best that we have seen on the whold subject. It is written for agricultural and large commercial greenhouse use. They had several mistakes though :

Citric acid. -- They failed to use the last acid group on citric acid. They probably considered it not to be strong enough but our additions tell us that all the acid groups are OK and the equivalent weight of Citric acid is 70, for the hydrate.

Indicators -- For their indicators they mention Methyl Red and Bromocresol Green. However we feel that Bromothymol Blue is the correct material. Bromocresol Green turns at too low of a pH.

PPM – This is a very common term and you will see it in many references. It is also milligrams per liter or if you want grams per thousand liters. Just to give you some English reference, 1ppm would be about 1oz in about 7500gallons or 1oz in 62500lb.

Trace elements for fertilizer. Here is an estimate of the ppm for a 20-20-20 fertilizer. This is an educated guess. There may be other necessary elements such as Cobalt and Selenium. When compounding these, it is very helpful to chelate some trace elements using citric acid. (Fe, Mn, Zn, Cu) Make a concentrate of these and add citric acid. If you have a clear solution you are OK.

N = Nitrogen	20,000ppm
P = Phosphorus	20,000ppm
K = Potassium	20,000ppm
Ca = Calcium	5,000ppm
Mg = Magnesium	2000ppm
S = Sulfur	1,000ppm
Fe = Iron	100ppm
Cl = Chlorine	100ppm
Mn = Manganese	50ppm
Zn = Zinc	20ppm
B = Boron	20ppm
Cu = Copper	6ppm
Mo = Molybdenum	0.1ppm
Se = Selenium	?
Co = Cobalt	?