

Understanding Alkalinity and Hardness - Part II

1.0 Introduction

This article is Part II in a series descriptive of the so called significant seven water characterization parameters which, by themselves, give good overall representation of the character of a water sample's fitness for brewing. The seven are pH, alkalinity, calcium hardness, magnesium hardness, chloride, sulfate and chlorine/chloramine concentrations. I have previously written about pH (Ref 2. and 3.) and chlorine/chloramine (Ref. 4.) in Brewing Techniques. Part I of this series (Ref 1.) introduced alkalinity and hardness. I discussed what these are, how they are measured and what the effects of the ions associated with them are on beer brewed with water containing them. In Part II I will continue discussion of their effects on mash pH and then go on to discuss means of adjusting alkalinity and hardness in either direction. I'll touch on the traditional means of softening/decarbonation (boiling and treatment with lime) and their limitations and will show how slight modification of these techniques can be used to achieve more complete decarbonation and excess magnesium removal.

2.0 Kohlbach's Residual Alkalinity

Barley contains an enzyme called *phytase* which survives the heat of the kiln in pale malts. This enzyme causes the organic phosphate *phytin*, which is also found in malt, to release inorganic phosphate forming the B vitamin myo-inositol which is beneficial to yeast in the fermenter. This phosphate reacts with calcium to produce hydrogen ions and precipitate calcium phosphate. Phytin itself has a strong affinity for calcium and a phytic acid molecule can combine with up to four calcium ions thus releasing additional hydrogen ions. Thus calcium in strike water has a pH lowering effect on the mash and is in large part precipitated. Magnesium acts in a similar way but to a lesser extent.

Kohlbach observed experimentally that approximately 3.5 mEq/L of calcium would yield 1 mEq/L of hydrogen ion but that it took twice as much magnesium (7 mEq/L) to get the same 1 mEq/L of hydrogen ion. He then defined residual alkalinity as the alkalinity of the water minus the amount of hydrogen released by the phytin reaction

$$RA_{\text{mEq/L}} = Alk_{\text{mEq/L}} - \frac{[Ca]_{\text{mEq/L}}}{3.5} + \frac{[Mg]_{\text{mEq/L}}}{7} \quad (2.1)$$

$[Ca]_{\text{mEq/L}}$ symbolizes the calcium concentration in mEq/L and is, thus, the calcium hardness in equivalence units. If we multiply everything in Equation (2.1) by 50 we obtain units of ppm as CaCO_3 thus

$$RA_{\text{ppm}} = Alk_{\text{ppm}} - \frac{[Ca]_{\text{ppm}}}{3.5} + \frac{[Mg]_{\text{ppm}}}{7} \quad (2.2)$$

We can, in similar fashion, multiply both sides of Equation (2.1) by any of the equivalence based scale factors I enumerated in Part I (Ref. 1.) and thus calculate residual alkalinity in any of the units in which hardness and alkalinity are expressed as long as alkalinity and hardness are in consistent units. Kohlbach, for example, worked with "German degrees of hardness" (dH)¹.

Note that formulas for RA have appeared in error in at least two recent texts of which the author is aware and this

may cause the incorrect forms to spread throughout the literature. On the other hand, the RA formula in Ref 5. is correct. If a published formula shows *RA* increasing with either increasing calcium or increasing magnesium concentration then you will know that the formula is in error.

Kohlbach also observed that if pale malt was mashed with distilled water and subsequently with water with varying degrees of residual alkalinity, dough-in pH was shifted by 0.03 pH units in the alkaline water mash for each German degree of residual alkalinity (Ref. 6.). Translated to mEq/L this is 0.084 pH units per mEq/L or 0.00168 pH units per ppm as CaCO₃. Using this observation with Equation (2.1) we have

$$pH_{mash} = pH_{dist} + 0.00168 \text{ Alk}_{ppm} - \frac{[Ca]_{ppm}}{3.5} + \frac{[Mg]_{ppm}}{7} \quad (2.3)$$

in which pH_{dist} represents the pH of a test mash made with distilled (or otherwise deionized water) and the particular pale malt to be used. pH_{dist} usually will have a value between 5.7 and 5.8.

Equation (2.3) is the possibly the most important result of all we have discussed thus far. It will permit you to at least estimate the dough-in pH of pale beers made with a particular water sample and it is for this reason that we seek information about our liquor's alkalinity and hardness.

¹ 1 dH is equivalent to 17.9 ppm as CaCO₃.

2.1 Interpreting Residual Alkalinity

Residual alkalinity is very useful in planning a brew both generally and in particular. This is aided greatly by plotting Equation (2.3) as I have done in Figure 2.1. This plot depicts diagonal lines with constant values of residual alkalinity and thus constant pH shift. The lines are labeled with both the RA and the predicted pH for an assumed pH_{dist} of 5.75. To use the plot, one enters it on the vertical axis with the alkalinity of the mash water and on the horizontal axis with the sum of all the calcium hardness plus half the magnesium hardness. Where only the total hardness is known assume that 60% of it is from calcium and 40% from magnesium and, therefore, use 0.8 times the total value in entering the hardness axis.

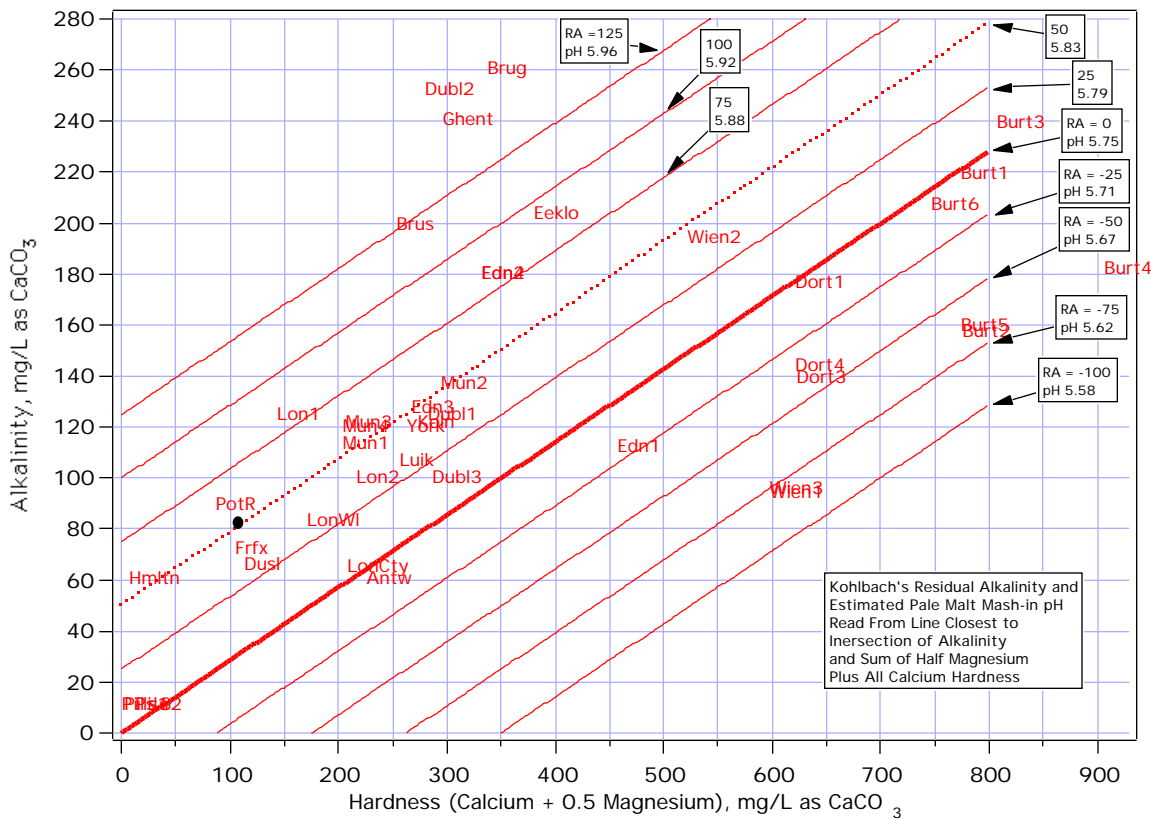


Figure 2.1 Fixed Values of Residual Alkalinity and pH Shift Plotted vs. Alkalinity and Hardness

Example: At my last brew day my well water showed alkalinity of 82 ppm as $CaCO_3$, calcium hardness of 78 ppm as $CaCO_3$ and magnesium hardness of 54 ppm as $CaCO_3$. What is the residual alkalinity and predicted pH of a pale malt mash made from this water?

Solution: Half the magnesium hardness plus the calcium hardness is 105. The small dot at 82 on the alkalinity axis and 105 on the hardness axis represents my water. It lies very close to the dashed $RA = 50$ line which is labeled with a predicted pH of 5.83 representing an increase of 0.08 pH units above the nominal pH 5.75 on which the chart is based.

If your water sample as plotted on Figure 2.1 falls below the dashed line ($RA = 50$) you can generally assume it will give an acceptable mash pH as is. This is not, of course, a black and white situation. My water falls right on this line which tells me that I should at least be alerted to the possibility of mash pH being higher than I like. The sensible thing to do in such cases is to be prepared to make a pH mash adjustment based on measurement in the mash tun or, better still, to do a mini test mash before the brewing session.

The dot representing my water falls between the labels “PotR” which means “Potomac River”, near which I live and “Frfx” which means “Fairfax” symbolizing water from the Fairfax County (VA) Water Authority which serves much of the county in which I live. Other symbols on the chart represent the hardness and alkalinity of waters, as reported in various published sources, of cities like Dusseldorf, London, Munich, Vienna, Burton, Dortmund, Edinburgh, Dublin, Pilsen and Brussels. Thus, if you plot your water on Figure 2.1 you can easily and quickly see how it compares, in terms of hardness and alkalinity only, to the waters of famous brewing cities. In some cases you can make deductions about the nature of the beers brewed in those cities. Consider Burton. There are several Burton labels on the chart and these represent different reported values for Burton water from various sources. While they vary somewhat in reported alkalinity level they all agree that Burton water is very hard. This hardness is, however, enough to offset the substantial alkalinity of Burton water so that all but 1 of the labels falls below the solid ($RA = 0$) line on the plot. Thus given a water sample with any of the reported Burton profiles one ought to be able to make a pale beer, i.e. one in which no dark malt is required and this is, of course, exactly the kind of beer we associate with Burton.

The reader must be made aware of two points in this regard

1. Many of the published city mineral profiles are seriously in error. This is easily confirmed by doing a simple internal consistency check which consists of calculating the pH required of the samples by the reported ion concentrations. Many, if not most reported water profiles require this pH to be 10 or 11 or even higher which is not a reasonable value.
2. Even where the values are correctly reported the chart does not convey information about how it may be processed by the breweries which use it.

3.0 Dealing with Excess Residual Alkalinity

The previous discussion makes it clear that from the perspective of mash pH alone it is not really alkalinity (bicarbonate) which is the source of problems with mash pH but residual alkalinity. Thus in the example of Burton water we find that while the alkalinity is approximately 200 ppm as $CaCO_3$ there is plenty of calcium and magnesium to offset it to the extent that the residual alkalinity is actually negative (for the majority of Burton water specifications at least). There are several ways to reduce residual alkalinity:

1. Neutralize the bicarbonate by the addition of mineral (usually hydrochloric, sulfuric or phosphoric) or organic (usually lactic) acid.
2. Remove the bicarbonate.
3. Dilute the bicarbonate.
4. Increase calcium and or magnesium thus releasing malt acid which neutralizes the bicarbonate.

5. Combinations of the above

Note that some authors, e.g. DeClerk (Ref. 11.) find neutralized bicarbonate flavor negative, especially when sodium is present. Brewers who feel this way will concentrate on bicarbonate removal or dilution rather than neutralization. In this same regard we note that "neutralization", be it by any of the acid sources listed above, actually results in removal of much of the bicarbonate. The mechanism is discussed in Section 3.3.

In the paragraphs which follow I'll discuss these means of residual alkalinity reduction. Figure 3.1 is similar to Fig 2.1 in Part I and should help you to understand the mechanisms involved. In Part I, I discussed how the relative proportions of each of the three carbo species (carbonic, bicarbonate, carbonate) depended on the pH of the water. At high pH the shift is towards the right of the diagram and at low pH it is towards the left. Calcium carbonate is not very soluble in water so that if the pH becomes high enough that the relative concentration of carbonate ion increases and if calcium is present insoluble calcium carbonate forms and drops out of solution. When some calcium carbonate precipitates the equilibrium between bicarbonate and carbonate is upset as there is proportionally less carbonate. This causes some bicarbonate to convert to carbonate in an attempt to rebalance the proportion. This results in release of hydrogen ions which tends to lower the pH. Lowering of the pH causes some bicarbonate to convert to carbonic, consuming some of the hydrogen ions and raising the pH. Carbonic acid will decompose into carbon dioxide gas and water if the dissolved carbonic acid level is higher than a value proportional to the atmospheric pressure of carbon dioxide which is normally 0.03% to 0.05% of an atmosphere. Escaping carbon dioxide imbalances the relative amounts of bicarbonate and carbonic and more bicarbonate converts to carbonic to try to restore this balance thus consuming more hydrogen and driving the pH back up. There are thus multiple balancing acts at work at once here. Eventually *equilibrium*, the point after which no further changes occur is reached. At equilibrium carbon dioxide in the air is balanced by carbonic acid in solution. The carbonic acid concentration is simultaneously in balance with the bicarbonate ion concentration which is, in turn, in balance with the carbonate ion concentration and that is in an equilibrium with the solid calcium carbonate. The numerical values of all these concentrations can be worked out but the details are tedious and are not needed to understand how we can deal with bicarbonate in brewing. As strange as it may seem, the tiny amount of carbon dioxide in the air is the controlling factor. For normal CO₂ levels the system is in equilibrium at pH near 8.3 and the alkalinity is about 40 ppm as CaCO₃.

The significance of the last paragraph is that any water which is in contact with calcium carbonate will eventually decarbonate itself to alkalinity of about 40 ppm CaCO₃ - a level which is below the 50 ppm limit we like to see. The treatments described below are aimed at speeding the process along as it sometimes takes a very long time for equilibrium to be established if we don't intervene. They work either by converting bicarbonate to carbonic which subsequently decomposes into CO₂ gas which escapes or to carbonate in which case calcium is supplied (if not already present) which coalesces with the carbonate forming insoluble calcium carbonate (chalk) which falls out of solution. Conversion to CO₂ is achieved by lowering pH (adding acid) or heat. Raising pH is achieved by heat (which drives off CO₂ gas resulting in elimination of carbonic acid) or by adding base, often in the form of calcium hydroxide which also provides the calcium.

The following equations model the reactions of Figure 3.1



In describing the individual processes I will lump the ones of these that are in effect into a single equation describing the overall reaction.

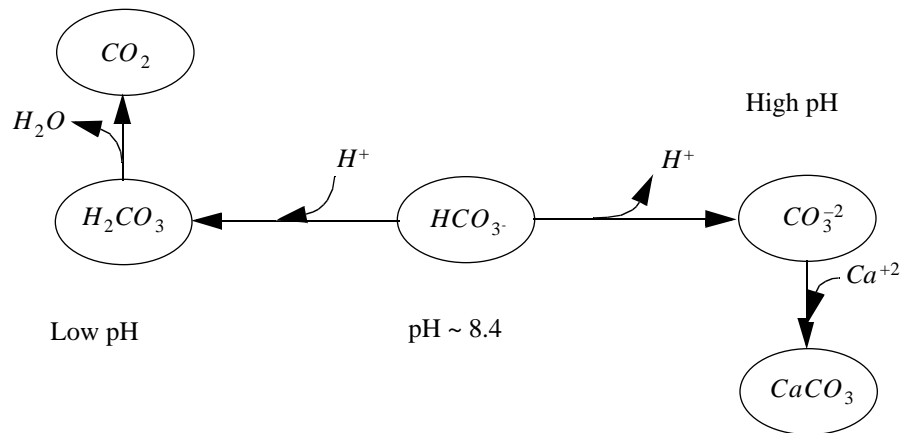


Figure 3.1 Flow of carbo species during decarbonation. Reversing arrowheads shows flow when carbonic acid dissolves limestone.

3.1 Reducing Residual Alkalinity by Dilution

Dilution is a very simple matter both in terms of explaining how it works and in its implementation. The brewer adds deionized (DI) or low ion content water to the water he wishes to treat in a volume calculated to bring about the dilution of bicarbonate he wishes. Thus if 1 part of DI water is added to 2 parts of tap water the alkalinity after mixing will be about two thirds of what it was in the undiluted tap water. If equal amounts of tap and DI water are mixed the alkalinity will be half. If two parts of DI water are added to 1 part tap water, 1 third and so on.

When the proportion of DI water to tap water is large and the DI water and tap water differ appreciably in pH there will be a shift towards the pH of the DI water and this will result in a redistribution of the carbo species so that the reduction in alkalinity will be slightly different than the dilution ratio but this error is very small and can be ignored.

Obviously it is not only bicarbonate which gets diluted when DI water is added to tap water but all other ions as well. Brewers using this technique to reduce residual alkalinity may wish to supplement calcium, magnesium, sulfate and chloride by adding appropriate salts.

3.2 Reducing Residual Alkalinity by Adding Calcium and Magnesium

Equation (2.2) shows that adding a 3.5 millivals (mEq/L) of calcium ion reduces residual alkalinity by 50 ppm as CaCO_3 and that adding 7 mEq/L of magnesium ion has the same effect. It is convenient to make small RA adjustments this way and the addition of gypsum (calcium sulfate dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is probably the most widely practiced method of RA adjustment in home and craft brewing. As its molecular weight is 172.17 and the calcium ion is doubly charged each gram of gypsum contributes 11.6 mEq of calcium ion and also adds 0.557 gram of sulfate ion. The effects of sulfate must be considered when adding gypsum for RA reduction. I will cover this in the third article of this series.

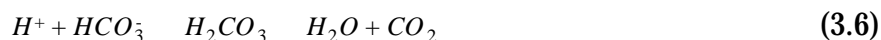
Calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) is used frequently by craft brewers and by some homebrewers when a source of calcium is desired which will not increase sulfate levels. It has a molecular weight of 147.02 and each gram contributes 13.6 mEq of calcium and 0.482 grams of chloride to the water in which it is dissolved.

Magnesium sulfate heptahydrate (Epsom salts, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) may be used where it is desired to combat RA with magnesium. This is not usual practice as magnesium is half as effective as calcium (on a mEq/L basis) and magnesium is problematical in excess. Epsom salts have a molecular weight of 246.47 and contribute 8.11 mEq magnesium and 0.389 gram of sulfate per gram used.

Be sure to obtain food grade versions of any of these three salts you decide to use. Gypsum is available at homebrew shops and calcium chloride has started to appear at better ones. Epsom salts are available at any pharmacy.

3.3 Reducing Residual Alkalinity by Neutralizing Bicarbonate

Neutralization involves adding acid, from one of three sources to be discussed until the pH reaches the desired value for the application. In the case of mash this is in the 5.2 - 5.8 region. In the case of sparge water it is generally in the same range i.e. a value below 6. Hydrogen ions from the acid combine with carbonate ions to form bicarbonate ions and with bicarbonate ions to form carbonic acid which under the hot conditions of mash and sparge, decomposes into water and carbon dioxide which escapes as shown in and discussed in Part I. At pH 5.8 all but 20% of the original carbo moles convert to gas most of which escapes. The net effect on the bicarbonate can be summarized by the single equation



Thus “neutralizing” bicarbonate with acid actually results removing 80% of it from the water.

3.3.1 Neutralizing With Mineral or Organic Acid

In treating with acid the amount required is calculated from the alkalinity and volume of water required, measured out and added to either the water or the mash. Accurate computation the amount of acid required is somewhat involved and usually not justified as the acid will need to be added in small increments and the result checked as you go anyway. For those who wish all the details, they can be found at Ref. 8. The following simplified calculation will tell you roughly how much acid is required.

1. Calculate the residual alkalinity in mEq/L or convert the residual alkalinity in ppm as CaCO₃ to mEq/L by dividing by 50.
2. The answer from Step 1 is the approximate number of milliequivalents (mEq) of acid you will need to neutralize the residual alkalinity per liter of water being treated. Multiply by the number of liters of water to be treated or the number of liters in the mash.
3. If your acid is labeled by its normality (i.e. 1 N, 3 N - hydrochloric and perhaps sulfuric would be the only ones likely to be labeled this way) divide the mEq from Step 2 by the normality of the acid to obtain the approximate number of mL of acid required. For acids not labeled with normality, multiply the mEq from Step 2 by 96 if using citric acid, by 90 for lactic, by 98 for phosphoric and sulfuric acids, 36.5 for hydrochloric and 75 for tartaric acid to get the number of milligrams of acid required. If the acid is a solid (citric, tartaric), measure it out. If the acid is a liquid labeled as, for example, 88% lactic acid, convert the percentage to a fraction by dividing by 100 (for 88% use 0.88) then divide the required milligrams by the fraction to get the approximate number of mL of acid required.
4. Measure out the amount of acid required. If acidifying a mash add the acid to the mash in small portions (say 10% of the total at a time), stir very thoroughly, wait a couple of minutes and then check pH. If acidifying sparge water it is not necessary to wait. pH can be checked immediately.
5. Repeat Step 4 until the target pH is reached. If acidifying a mash, you may wish to decrease the amount of the incremental additions as you approach the target pH.

The reason for the small incremental addition of acid is that the simplified 3 step calculation I have given has got lots of approximations in it and the chances are that the amount of acid you measure out will be in error by quite a bit.

Beer is food so use only food grade acid to acidify but keep in mind that just because something is food grade doesn't mean you can't hurt yourself with it so be careful. Lactic acid is pretty safe and is readily available in food grade form from homebrewing stores so it is probably a good choice. It, and any other acid you use will flavor the beer. The lactic flavor is quite distinct and certainly desirable in certain beer styles (Lambic, Wit and Berliner Weisse are obvious examples but lactic acidification is sometimes used by German lager brewers who use lactic producing bacteria to sour some mash which is then added to the main mash). Sulfuric and hydrochloric acids are, from the flavor viewpoint, good choices because brewers often want chloride and sulfate (I'll be discussing them in Part III) in their brews but they are dangerous in concentrated form and probably difficult for the average home brewer to acquire in food grade. Phosphoric acid is a popular choice, especially for sparge water adjustment. It is relatively flavor neutral, is available as a 28% food grade solution and is fairly safe to handle. Tartaric and citric acids belong more to the vintner than the brewer and, as they are solids, will require a reasonably accurate balance to measure out. Liquid acids are much to be preferred as a reasonably good graduated cylinder is much less expensive than a good balance.

3.3.2 Neutralizing With Acid from Dark Malt

The procedure for neutralizing alkalinity with dark malt is theoretically the same as it is for adding other acids. The difference is that malts are not labeled as to their acidity. It is possible to determine malt acidity by titration and the result is thus called “titratable acidity”. The procedure is quite simple. A sample of malt is crushed and a portion is weighed and placed in a beaker with enough deionized water to make a thin mash. Alkali, typically sodium hydroxide, of calibrated strength is titrated into the beaker until a nominal pH is reached. The amount of base, measured in mEq, consumed in reaching this pH is the amount of alkalinity that the malt will neutralize in coming to this pH. Table 1 lists some examples of the acid yields of 4 dark malts in reaching three typical values of target strike pH. As the data show, the amount of acid released and thus the amount of alkalinity which can be neutralized depends strongly on the pH to which it is desired to bring the mash pH. As the table shows, the very dark malts have considerable acidity and thus considerable ability to neutralize alkalinity. One kg of the 600°L patent malt has the ability to deliver the equivalent of 6 mL of hardware store strength (usually about 8 N) hydrochloric acid in lowering pH to 5.5.

Table 1: Examples of Dark Malt Titratable Acidity

Malt Type	Titratable Acidity to pH 5.3, mEq/Kg	Titratable Acidity to pH 5.5, mEq/Kg	Titratable Acidity to pH 5.7, mEq/Kg
DWC Munich	0	2.5	7.5
DWC Caramel Pils	2.5	8	16
DWC Caravienne	17	25	34
600°L Patent	40	48	60

The data in Table 1 cannot be used to compute exact quantities of malt required to reach a given pH any more than Figure 2.1 can be used to predict mash pH in the absence of treatment precisely. The usefulness of these data are in their ability to help the brewer plan. As an example of this let us suppose I am planning to brew a lager beer using my well water with its residual alkalinity of 50. I'd mash about 10 pounds of pilsner malt hoping to obtain 6 gallons OG of about 13°P and use about 12 quarts of water to do it (i.e. 3 gallons). The residual alkalinity value predicts a mash pH of a little over 5.8 which is about the starting limit for lagers which are to be decocted. I'd like to be a little lower than that and so plan to throw in a pound of caramel pils. According to the table this would neutralize from 12.5 to 17 mEq of residual alkalinity if the final pH were to fall between 5.5 and 5.7. The water has residual alkalinity of 1 mEq/L and as I'm planning to use about 12 liters of it I'd have about 12 mEq of residual alkalinity to deal with. Thus the 1 pound of caramel pils would more than neutralize the residual alkalinity at the pH 5.7 level and the mash pH ought, as a consequence, to be below 5.7

3.3.3 Neutralizing With Malt Phosphate Derived Acid by Adding Calcium

Neutralizing residual alkalinity by increasing calcium is probably the most popular means of lowering mash pH in home and craft brewing. Many all grain brewers do it without realizing why they are doing it. I am referring here to the very common practice of adding some amount of calcium sulfate (gypsum) to the mash or mash water. Calcium sulfate, $CaSO_4 \cdot 2H_2O$, has a molecular weight of about 174. This means that the number of milligrams of the salt per mEq of calcium in it is half this number, 87. If we take the simple approach of merely wanting to neutralize any positive residual alkalinity with gypsum we follow these steps.

1. Calculate the residual alkalinity in mEq/L or convert a ppm as $CaCO_3$ value to mEq/L by dividing by 50.
2. Multiply the result of Step 1 by 3.5 to get the mEq/L of calcium required to neutralize the RA.
3. Multiply the result of Step 2 by 87 to get the number of mg/L of gypsum required to supply the calcium
4. Multiply the mg/L by the number of liters to be treated if the whole water volume is to be treated or by the number of liters in the mash if the gypsum is to be added to the mash.
5. Add the gypsum to the mash or to the water. Stir thoroughly, wait a few minutes and check mash pH.

Note that if the gypsum is added to water there will be no change in pH - the reaction with malt phytin is required. For this same reason, addition of gypsum for sparge water acidification is not effective. Acid must be added for that job (see next section).

If the gypsum is to be added to the mash, you may wish to divide it into say 3 portions and add them one at a time with thorough mixing and a wait before checking pH. This may prevent overshooting the target pH.

3.4 Reducing Residual Alkalinity by Removing Carbonate

Calcium carbonate is not very soluble in water. If the product of the molar concentration of calcium and carbonate ions exceeds a threshold value the water is super saturated with this salt and calcium carbonate (chalk) will eventually precipitate. "Eventually" is a big word here and we will have more to say about this later.

The inequality

$$[Ca^{+2}][CO_3^{-2}] > K_s \quad (3.7)$$

describes the conditions at which saturation occurs. K_s has a value of 3.31×10^{-9} at 25° C and 7.58×10^{-10} at 90° C. The square roots of these values give the basic solubilities of chalk at the two temperatures and high pH: 0.057 mM/L (5.7 mg/L) at 25° C and 0.027 mM/L (2.7 mg/L) at 90° C.

Inequality (3.7) suggests that we can remove bicarbonate from a water sample by

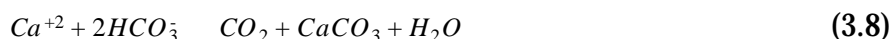
1. Converting bicarbonate to carbonate thus increasing the ion product on the left side of Ineq. (3.7)

2. Increasing the calcium concentration (by adding a calcium compound) thus increasing the ion product.
3. Increasing the temperature thus decreasing the solubility of calcium carbonate while at the same time driving off carbonic acid which results in increased pH and conversion of bicarbonate to carbonate

Combinations of these are effective. Adding lime (calcium hydroxide) simultaneously increases the pH and the calcium ion concentration. Adding calcium chloride (or sulfate) and heating simultaneously increases the ion product and lowers the solubility. In the sections which follow I discuss methods based on these ideas.

3.4.1 Decarbonating by Boiling

If a sample of water which contains calcium and bicarbonate ions is heated the following well known overall reaction



takes place (the underlining indicates that the product so designated precipitates). The basis for this is that CO₂ is not very soluble in water at high temperature so as the water is heated it escapes. This causes carbonic acid to decompose into water and CO₂ leaving less carbonic acid than required by the carbonic/bicarbonate equilibrium at the given pH. Bicarbonate converts to carbonic consuming hydrogen ions (see Figure 3.1) in the process. This results in a raised pH. Raised pH causes more bicarbonate to convert to carbonate thus causing the ion product of the inequality to be exceeded. Calcium carbonate precipitates. This causes more bicarbonate to convert to carbonate in an attempt to rebalance the bicarbonate/carbonate equilibrium and so on.

For this to work it is essential that CO₂ be able to escape. Escape is facilitated by sparging the water with any gas which contains little or no CO₂. The two obvious candidates are air and steam. Thus it is not necessary to actually boil the water being decarbonated if it is sparged with air to sweep out the CO₂. Aeration can be accomplished by pouring the hot water back and forth between two containers but that has never struck me as a very safe thing to do with large volumes of hot water. Agitation with a paddle that breaks up the surface should also suffice. An effective and safe technique uses a pump to force the hot water through a nozzle or shower head and spray it back into the heating vessel. If the water is brought to a boil the steam serves to sweep out the CO₂. Only a few minutes of boiling are required to eliminate the CO₂ and start the precipitation of carbonate. In fact if your water is very hard and alkaline you will probably find it turns milky well before the onset of boiling. It is nevertheless important to let the boil proceed for a few minutes. Longer boiling times may be used, of course, if it desired to eliminate chlorine (short boil will do) and or chloramine (longer time may be required) at the same time. See Ref. 4.

It is also essential that the calcium carbonate precipitate can be removed from the water. This is traditionally accomplished by allowing the water to stand. If the water is of low alkalinity very little precipitate will form and the particles will be tiny. The speed at which suspended particles fall to the bottom of a container depends on their size. Thus relatively large yeast flocs fall to the bottom of a fermentation vessel much faster than the much smaller individual cells. So it is with chalk particles. To be sure, therefore, that the chalk will be removed when the water is boiled I strongly recommend that a teaspoonful or so of chalk be added to each five gallons of water being treated. This chalk will not dissolve but its particles will serve as "seeds" for the accretion of the calcium carbonate which is to come out of solution during the boiling or heating. It will, in general, be impossible to decarbonate water with levels of temporary hardness of less than about 200 - 250 ppm as CaCO_3 unless this is done. By adding chalk I am able to decarbonate test samples of my well water (alkalinity about 90 ppm as CaCO_3) which I cannot decarbonate without it to about 63 ppm. Note that it is only possible to remove the alkalinity to the extent of the temporary hardness by boiling. Temporary hardness is the alkalinity minus the hardness (practically speaking the calcium hardness) if the difference is a positive number. If hardness is greater than alkalinity then all the alkalinity can theoretically be removed. It is possible to remove more alkalinity by adding a calcium salt as explained in Section 3.4.3.

The following procedure for decarbonation by heating is recommended. A pH meter or strips can be a great help.

1. **Add 1 tsp chalk per 5 gallons of water being treated.**
2. **Raise the pH of the water to 8.5 or above by whatever combination of heating, aeration or boiling are necessary to accomplish this. The higher the pH the better.**
3. **Allow the water to settle. As soon as the precipitate is firmly, but completely, settled decant the water.**

With respect to Step 2, do whatever it takes. If agitation and aeration alone will raise the pH to over 8.5, then there is no need for heating. Usually heating is a help though as I have pointed out it may not be necessary to boil. The higher the pH which can be reached the more bicarbonate will be removed. This is shown by the heavy solid line in Figure 3.2 which depicts the alkalinity of solutions in equilibrium with calcium carbonate at various values of pH. As this curve shows, the higher the pH, the lower the alkalinity. You probably won't be able to get the pH above 9 by heating/aeration or boiling but you may want to experiment with a small volume of water just aerating it at first, then heating and aerating and then finally boiling with a pH measurement at each step. If heating to 180°F with aeration gets you to pH 8.3 and boiling only carries you to pH 8.4 then there isn't much point in boiling.

The solid curve shows the amount of alkalinity that will remain in the water after cooling as a function of the pH of the water when cooled. It does not matter what the level of the original hardness and alkalinity were as long as they were the same. The result is only a function of the pH. The other curves will be discussed when I talk about calcium salt addition.

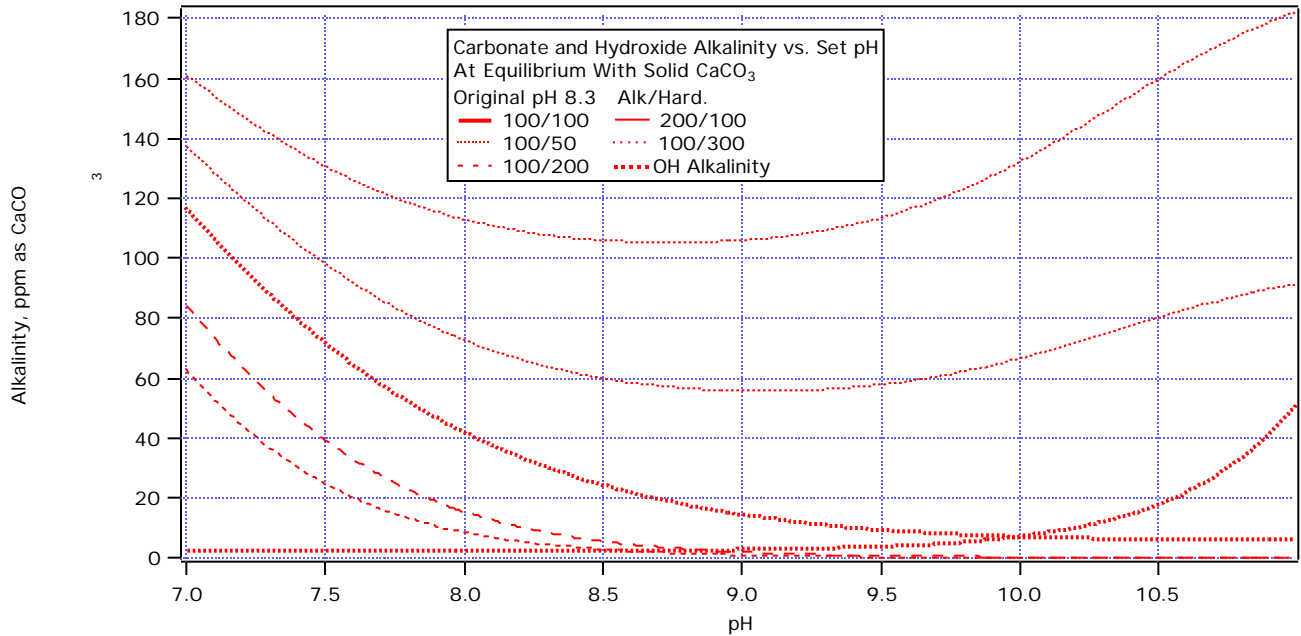
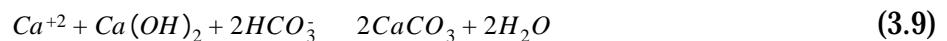


Figure 3.2 Final Alkalinity vs. pH for Various Combinations of Original Alkalinity and Calcium Hardness. Original pH 8.3

You will not be able to achieve the results given on Figure 3.2 because you will not be able to remove all the precipitated carbonate. For example, when I boiled my well water I reached pH 8.5 and centrifuged the sample to remove most of the precipitate. I was only able to reduce the alkalinity to 56 even though the curve says that theoretically I should be able to reach about 25 at this pH. Part of the reason for this is that water which has been boiled over chalk is not in equilibrium with the carbon dioxide in the air which will start to dissolve in the water as soon as its temperature begins to lower from boiling. This carbon dioxide leads to a chain of events exactly the reverse of those that you initiate when you boil water (see Figure 3.1 and follow the arrows backwards). Chalk begins to redissolve. Your best defense against this is to decant the water off the chalk as soon as you can bearing in mind that the longer you wait the more chalk will settle but also the more will redissolve. It helps to work with a large volume of water with a small surface area as the CO₂ enters through the surface. As with any of the procedures I recommend, the proof of the pudding is in a post treatment alkalinity test.

3.4.2 Decarbonating with Lime

If slaked lime (calcium hydroxide) is added to a water sample containing bicarbonate ions the following overall reaction takes place



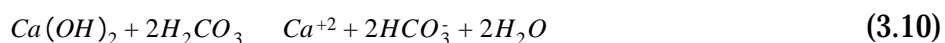
This equation shows that 1 millimole of lime will react with 2 milliequivalents of bicarbonate. As the molecular weight of slaked lime is 74.09 each gram is 135 mM and will treat 27 mEq of bicarbonate or 1350 mg as CaCO₃. The

equation shows that a mEq of calcium must be present for each mEq of carbonate to be removed thus this method, without modification, will remove bicarbonate only to the extent of the temporary hardness. You can get more bicarbonate out by adding extra calcium and I'll discuss this trick in Section 3.4.3.

Example: Forty liters of water with temporary hardness of 300 ppm as CaCO_3 are to be decarbonated with lime. How much is required?

Solution: Convert 300 ppm as CaCO_3 hardness to mEq/L by dividing by 50 to get 6 mEq/L. Each mEq required half a mM thus 3 mM of lime is required for each liter of water to be treated. For 40 liters this is 120 mM which, with molecular weight of 74 mg/mM is 8800 mg or 8.8 grams.

If the pH of the sample is such that there is appreciable carbonic present ($\text{pH} < 8$) some extra lime is required to convert the carbonic to bicarbonate:



In the previous example if the pH were 7 there would be 1.5 mM/L of carbonic present in addition to the 6 mEq/L of bicarbonate (Part I contains the curves and equations needed to reach this conclusion). As Equation (3.10) shows each mM of carbonic requires half a mM of lime so that the 1.5 mM/L would need 0.75 mM/L to be converted. For the 40 liters this amounts to an extra 2.2 grams.

DeClerk, in describing this method (Ref. 9. and 10.) suggests that the amount of lime required both for reaction with bicarbonate and neutralization of carbonic be calculated and that three small test batches of water be treated with 10% less than the calculated amount, the calculated amount and 10% more than the calculated amount. The test batch most successfully decarbonated determines the dose to be used in treatment of the actual brewing water. If DeClerk had portable pH meters or pH test strips available he might have preceded differently. Here is my recommended procedure for decarbonating water with lime:

1. Add 1 tsp. of chalk for each 5 gallons of water to be treated to the water.
2. Multiply the temporary hardness of the water by 0.74 to get a rough idea of the amount of lime required (in mg) to treat 1 L. Then multiply by the number of liters to be treated and divide by 1000 to get the number of grams required for the entire volume.
3. Increase the result from Step 2 by 20-30% and place this in a small beaker or flask. Add enough water to get this into suspension.
4. Add the slurry from Step 3 to the water in initially large and then smaller increments. Stir thoroughly and check pH after each addition.
5. Continue additions fairly rapidly until a pH between 9.5 and 10 is reached.
6. Monitor pH. As precipitation takes place the pH will fall back (see Figure 3.1)
7. At this point add only small amounts of additional slurry to maintain the pH in the 9.5 - 10 region.
8. pH will continue to drop as CO_2 from the air is dissolved but the rate of drop will slow. When it does, stop addition of lime and let the water sit while the precipitate settles.
9. Decant the water from the precipitate and measure hardness and alkalinity.

DeClerk indicates that a well run plant should be capable of decarbonating to less than 1 mEq/L (50 ppm as CaCO_3) and you should be able to approach that provided that total hardness exceeds alkalinity.

As with all the other chemicals I've discussed the lime used in treating your brewing water should be food grade slaked lime. It is sold as "pickling lime" in stores that sell home canning supplies and can often be found even in super markets. From the viewpoint of just the chemistry, "quick lime", CaO , will serve just as well as slaked lime because it quickly reacts with water converting to the slaked form. It releases a lot of heat in doing this and is thus dangerous in storage if it gets wet. I do not recommend it for small scale brewers.

3.4.3 Reducing Residual Alkalinity by Simultaneously Increasing Calcium and Removing Bicarbonate

The methods of Sections 3.4.1 and 3.4.2 are limited to reducing the alkalinity by an amount limited to the numerical value of the temporary hardness. An obvious scheme for further reduction of bicarbonate is the addition of additional calcium and magnesium to the point where the total hardness is numerically greater than the alkalinity at which point all the alkalinity can theoretically be removed and in practice you may get down to close to 50 ppm as CaCO_3 .

In addition to raising the temporary hardness level to the alkalinity level, increased calcium raises the ion product in Inequality (3.1) so that the water is more saturated at a given pH level and more chalk is precipitated. The effects of this can be seen in Figure 3.2. whose curves show the theoretical alkalinity levels after treatment (including cooling to room temperature if heat was involved) as a function of the pH or the post treatment water. Individual curves are distinguished by the original levels of alkalinity and hardness of the water. Calcium added in the form of lime for lime treatment or calcium salts is included in the original hardness. The top two curves show the effects of temporary hardness less than the alkalinity. The minimum alkalinity is found to be just over the difference between the alkalinity and the calcium hardness. Furthermore, bicarbonate which cannot be removed converts to carbonate at higher pH and adds to alkalinity if lime is used to raise the pH too far. This makes it clear that one should always add extra calcium before using either heat or lime (the extra calcium in the lime may be enough) if maximum removal of bicarbonate is the goal.

3.4.4 Decarbonation by Gross Treatment

By gross treatment we mean treatments which do not target bicarbonate specifically but are rather designed to reduce the content of all ions in the water, including bicarbonate. Distillation, ion exchange and reverse osmosis are all in this class. We will have little more to say about them here as there have been a fair number of recent articles which deal with them to some extent. It is clear that water that has all ions reduced appreciably will be impoverished with respect to desirable ions (calcium, sulfate, chloride) as well as the undesirable bicarbonate.

3.4.5 Example of Decarbonation Effectiveness

Brewers who live near the coasts of the United States will not generally find their water so alkaline that it needs decarbonation. In the middle west and parts of the west where the water is much harder decarbonation is often required but is usually done at the water treatment plant in order to minimize the probability of scale forming in the distribution system. Brewers with well water will have to deal with decarbonation themselves.

Very hard water (i.e. water with high levels of temporary hardness) are easily decarbonated by boiling or lime treatment. Heavy precipitate forms spontaneously as soon as the water is heated. It is more of a challenge to decarbonate relatively soft water.

The following table shows what I was able to do experimenting with my well water run over a neutralizer (a crushed limestone bed which raises pH by dissolving small amounts of calcium carbonate). The processed water has an alkalinity of about 90, calcium hardness of about 89 and magnesium hardness of about 25. As the calcium hardness and alkalinity are about equal and calcium carbonate is less soluble than magnesium carbonate it will be mostly calcium carbonate which precipitates.

Table 2: Decarbonation Example Results^a

Treatment	Calcium Chloride Added	Post Treatment		
		Alkalinity, ppm as CaCO ₃	Calcium Hardness	Magnesium Hardness
None	0	109	92	53
Boiling	0	56	40	56
Boiling	2 mM/L	43	244	43
Lime	0	62	42	56
Lime	2 mM/L	21	203	64
Lime Split ^b	0	27	61	10

a. These experiments were done on water from the same source but not the same water sample. This may explain some of the discrepancies in the data.

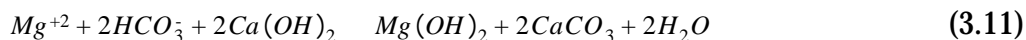
b. With aeration as described in text

3.5 Reducing Hardness

When water is decarbonated by either boiling or lime addition, calcium is removed to the extent that alkalinity is reduced i.e. if the alkalinity is reduced x ppm as CaCO₃ then the calcium hardness is reduced by approximately this same amount. This softening of the water is not usually thought desirable to the extent that many brewers will supplement calcium with gypsum or calcium chloride to make up for this loss incurred in decarbonating. We showed earlier that if this is done before decarbonation it can aid in the decarbonation process.

Magnesium carbonate is considerably more soluble than calcium carbonate so that only small amounts are precipitated during decarbonation operations. Excess magnesium hardness may result in sour bitterness or laxative qualities in a beer brewed with water which has it so that brewers confronted with such a water may need to treat it to remove some magnesium. Non chemical treatments as discussed in Section 3.4.4 are effective in reducing magnesium hardness as is dilution.

Magnesium hardness may be reduced by raising the pH to the point where insoluble magnesium hydroxide will form and precipitate.



DeClerk (Ref 12.), recommends calculation of the amount of lime required to *decarbonate* the water and addition of that amount to two thirds of the water volume to be treated. After allowing the water to sit for an hour the remaining third of the volume is added back in. This water reacts with the excess lime to precipitate its calcium bicarbonate and, if the lime dose was calculated correctly, the pH returns to about 9.5 and the alkalinity is minimized. DeClerk refers to this as “split-treatment”. It is clear that if the first step were completely effective in removing magnesium that the magnesium hardness of the final volume of treated water would be about a third of that of the untreated water. Reduction by this amount should be sufficient for most brewing applications but we can do better. I recommend the following procedure for removing magnesium from water:

1. Follow Steps 1 - 5 Section 3.4.2. but continue to add lime until a pH of 12 is reached.
2. After assuring that the pH is stable at 12 let the water rest while the precipitate settles.
3. When the water over the precipitate is clear, decant it into a separate vessel.
4. Add some calcium carbonate to serve as nucleation sites.
5. While stirring, bubble air through the water until the pH falls back to 9.6
6. Again allow the precipitate to settle and decant the clear water.

It is in Step 3 and beyond that we differ from the usual “split treatment” processing. Rather than neutralizing the excess lime with bicarbonate from untreated water which also contains more of the magnesium we are trying to eliminate we neutralize with carbonic acid from that unlimited, free supply of that acid, the air. The process can clearly be speeded up by sparging with carbon dioxide from a cylinder rather than using the tiny CO₂ content of the atmosphere.

Where very soft water is required for certain styles such as Bohemian Pilsner, a combination of decarbonation/softening by lime addition and dilution can be used. Dilution of tap water with a large volume of deionized water is a simpler approach in most cases.

3.6 Increasing Hardness and Alkalinity

Increasing hardness and alkalinity is much easier to do than decreasing them. Once the available water hardness and alkalinity have been determined and the desired levels (this is a large subject in itself which I will discuss briefly in the next article in this series) for these values are in hand it is a simple matter to calculate the amount of supplementation which is needed. It is also a simple matter to determine how much of a given salt is required to increase the levels of calcium and magnesium by a desired amount and I did that in Section 3.2 where I talked about increasing calcium and magnesium levels for RA reduction. It is a little trickier to determine the amount of carbonate or bicarbonate required to increase alkalinity by a given amount. Detailed calculations can be made but as it is generally incremental addition of a roughly estimated amount of carbonate which is done in practice we need not bother with the complex calculations.

4.0 References

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Appendix A

Appendix, maybe

Boiling does not remove all bicarbonate and so only lowers alkalinity somewhat rather than eliminating it completely. At the same time, not all water can be decarbonated by boiling. Water that is susceptible to this treatment is very hard and very alkaline. We can get a rough idea as to whether a particular sample will precipitate chalk when heated to near boiling by computing the saturation pH:

$$pH_s = pK_2 - pK_s - \log \frac{[Ca]_{ppm}}{100000} - \log \frac{Alk_{ppm}}{50000} \quad (4.1)$$

where pH_s is the pH value above which the water is super saturated with calcium carbonate, pK_2 has a value of 10.33 at 25° C or 10.13 at 90° C, pK_s has a value of 8.48 at 25° C and 9.12 at 90° C, $[Ca]_{ppm}$ is the calcium hardness in ppm as CaCO₃ and Alk_{ppm} is the alkalinity in ppm as CaCO₃. I can't give a hard and fast rule but waters with saturation pH values less than about 6.7 or 6.8 seem to be good candidates for decarbonation by boiling. Waters with higher saturation pH's may drop carbonate but it is often so finely divided that it stays in suspension and it is difficult to separate the decarbonated water from it. Any water whose actual pH is larger than its saturation pH is *super saturated* and will, theoretically, eventually drop a precipitate. This is indeed true and one of the main reasons saturation pH is calculated in the water industry is precisely to see if well water is saturated or not. Well water whose saturation pH is less than its actual pH will, even if extremely slowly, deposit a film of calcium carbonate on the insides of the pipes it flows through thus protecting them from the corrosive effects of water by keeping water out of contact with the metal. When we boil water escaping CO₂ raises the pH, typically to values of 8.5 or greater. Also, the decreased value of pK_2 and increased value of pK_s reduce the saturation pH making the *saturation index* (the difference between pH and pH_s, sometimes called the Langelier Index) even greater.

Decarbonation by boiling is seldom practiced by commercial brewers because it requires both energy and time for the precipitant to settle