Alkalinity, Hardness, Residual Alkalinity and Malt Phosphate: Factors in the Establishment of Mash pH

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ABSTRACT

The influence on mash pH of the hardness and alkalinity of brewing liquor and of inorganic phosphate released by hydrolysis of malt organic phosphates at strike are reviewed. The acid base chemistry of bicarbonate in equilibrium with atmospheric carbon dioxide and solid phase calcium carbonate is modeled and the model used to predict liquor hardness and alkalinity as a function of carbon dioxide partial pressure. This model is extended to include the effects of inorganic malt-derived phosphate precipitation and example estimates of the amount of alkalinity neutralized by phosphate are given. These results approximate Kolbach's observations and it is, thus, intended that the model, though greatly simplified, lend insight into the significance of Kolbach's residual alkalinity formula. Kolbach's formula is presented in a graphical form which permits convenient assessment of the effects of liquor hardness and alkalinity on mash tun pH.

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INTRODUCTION

Key in understanding evaluation and treatment methods for brewing (or any) water is an understanding of the chemistry of bicarbonates. It is often assumed in the study of brewery water sources that the bicarbonate system is the only buffer with appreciable effect because at mash and liquor pH all other acids are either fully dissociated ($pK << pH$ e.g. sulfuric, nitric) are completely un-dissociated ($pK >> pH$ e.g. silicate, borate) or are present in such small amounts (e.g. phosphate) as to have minimal buffering effect. The same is true of bases for example the hydroxides of metal ions. Thus while chloride, sulfate, nitrate, sodium and calcium ions are found in brewing liquor in appreciable concentration they can be ignored in terms of their buffering effects on liquor or mash pH. Phosphate is not present to appreciable extent in normal water supplies because of its tendency to precipitate dissolved calcium. Because of this phosphates were widely used as water softeners in the days before eutrophication became a major environmental concern. Phosphates are found in malt and their ability to precipitate liquor calcium is significant to brewers not so much because it softens the liquor (supplemental calcium is often added to replace that which is precipitated) but rather because the precipitation produces hydrogen ions which neutralize liquor alkalinity and thus help to lower mash pH into the desired range for enzyme activity (~ 5.2 - 5.6).

The addition of gypsum (and or other calcium salts) to brewing water to aid in establishment of proper mash pH is a very common practice especially in the brewing traditions of some areas of the world. But it is not the only means of setting mash pH. Addition of acid (mineral or organic) from any source, be it from a chemical supply house or the organic acids in high kilned malts or sour mash, have the same effect as the acids released when phosphate precipitates. Thus the knowledgeable brewer has several means of lowering mash pH at his disposal. Only the acid released by calcium phosphate precipitation is discussed in this paper.

The basis for this paper is deLange (2003). Here we expand somewhat on the level of detail. For a fuller understanding texts such as Stumm et. al. (1981) are a good place to start.

CHEMISTRY OF CARBONIC ACID, BICARBONATE ION, CARBONATE ION AND CALCIUM CARBONATE

Dissolution of Limestone

To begin our discussion let us assume that we have a lump of limestone (calcium carbonate) in a beaker which is partially filled with water and is exposed to air containing a small but finite amount of carbon dioxide. A limited amount of the limestone will dissolve in the water dissociating into Ca^{+2} and CO_3^{-2} ions. A small amount of carbon dioxide will also dissolve in the water forming carbonic acid which dissociates to some extent thus releasing protons which react with CO_3^{-2} ions forming bicarbonate: HCO_3^-. This causes additional limestone to dissolve to replace the CO_3^{-2} ions which took on protons to become bicarbonate. Figure 1 diagrams the process. We will analyze this diagram in some detail with the goal of calculating the pH and the concentrations of carbonic acid,

bicarbonate ion, carbonate ion and calcium ion which can be expected in the solution at equilibrium with the carbon dioxide in the air and solid limestone. The general concept is that material moves around the diagram to equalize chemical potentials such that the Gibbs energy of the system is minimized.

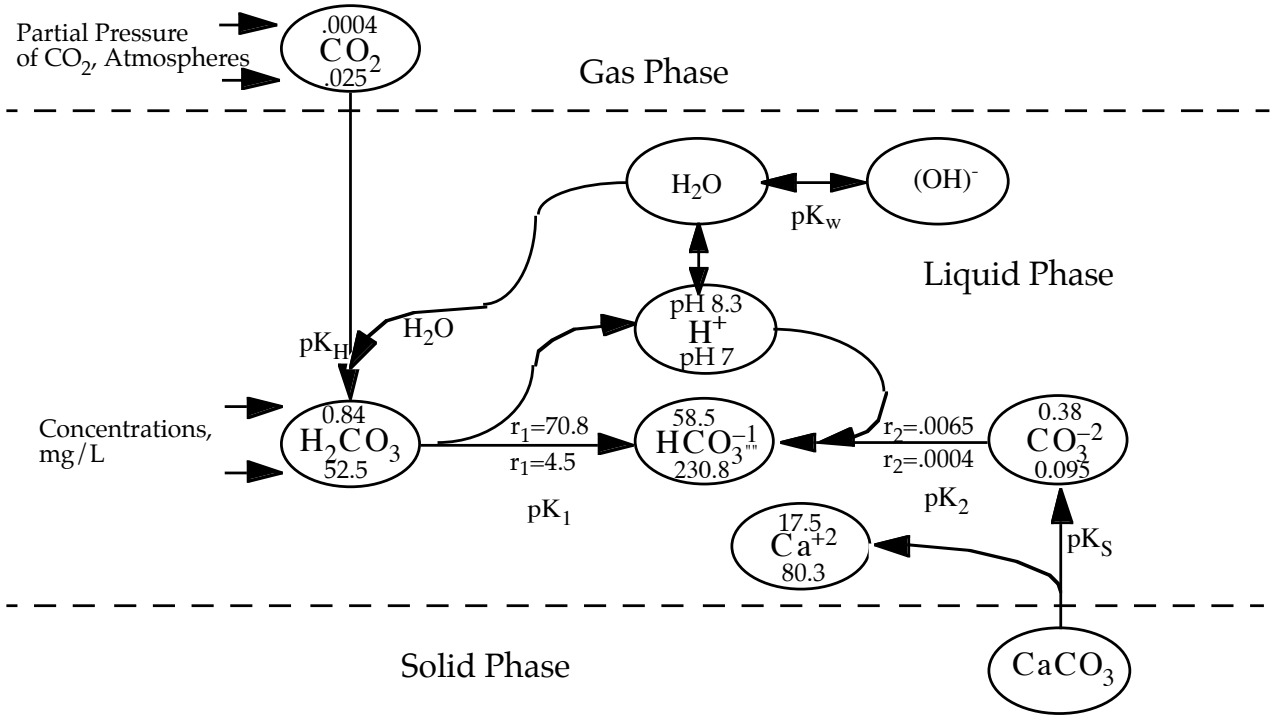

Figure 1: Carbo system in contact with limestone and carbon dioxide at two partial pressures of CO_2 showing flow of species as limestone dissolves. Reversing arrowheads shows flow of material when chalk is precipitated. All five reactions discussed in the text take place simultaneously. Small numbers in ovals are concentrations in mg/L at the two pressures (indicated in CO_2 oval).

We start with the dissolution of carbon dioxide in water:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \tag{3.1}$$

This reaction is subject to the law of mass action:

$$\frac{\{H_2CO_3\}}{\{CO_2\}\{H_2O\}} = K'_H \tag{3.2}$$

where $\{x\}$ means the chemical activity of x. The activity of a dissolved substance is given by its concentration[1] multiplied by an activity coefficient, γ_x, which is close to 1 for the dilute solutions we will be discussing here (and equal to 1 for an infinitely dilute ideal solution which is defined as one in which the ions being far enough apart that their electric charges do not interact). Thus

$$\{x\} = \gamma_x[x] \tag{3.3}$$

where $[x]$ is the concentration of x in moles per liter. For a gas the activity is its partial pressure multiplied by an activity coefficient with the product often being called the fugacity. For the very low pressures of carbon dioxide with which we are concerned the distinction between fugacity and pressure is small enough that we can ignore it and we will work with the partial pressure of CO_2 which we symbolize by P_{CO_2}. As is common practice we define $K_H = K'_H\{H_2O\}$[2] and then take the negative logarithm (we indicate that we have done this by use of the operator p) of each side of Equation (3.2) to get[3]

$$p[H_2CO_3] - pP_{CO_2} = pK_H \tag{3.4}$$

K_H is called the Henry Coefficient[4] and $pK_H = 1.41$ at 20°C if the pressure is expressed in atmospheres. Equation

[1] Concentration can be defined in terms of the mole fraction (i.e. the ratio of the number of molecules of the substance in question to all the molecules in the solution), the molar mass of the substance per kilogram of solution or the molar mass per liter of the solution. The choice influences the definition of the activity coefficient. Clearly moles per liter of solution is the most convenient of the three. For the dilute solutions under consideration moles per liter and moles per kilogram have values close enough to one another to permit the use of either.

[2] These solutions are generally dilute enough that the concentration of water can be considered as 1 L of water per L of solution.

[3] Recall that $\log(xy) = \log x + \log y$ and that $\log\left(\frac{x}{y}\right) = \log x - \log y$. Also $\log x^a = a \log x$.

[4] Note that the Henry coefficient is often defined as the ratio of the partial pressure of a gas to the mole fraction of the gas in the solution with which it is in equilibrium.

(3.4) can be solved for the concentration of carbonic in terms of the partial pressure of CO_2 by rearranging and then applying the inverse p operator (change the sign and then raise 10 to the resulting power) to both sides:

$$\left[H_2CO_3\right] = 10^{\left(-pP_{CO_2} - pK_H\right)} \quad (3.5)$$

Carbonic acid can give up a proton (hydrogen ion):

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \quad (3.6)$$

The extent to which this happens is governed by the equilibrium constant[5] K_{c1} and the equilibrium condition is:

$$\frac{\left\{H^+\right\}\left\{HCO_3^-\right\}\gamma_b}{\left\{H_2CO_3\right\}\gamma_c} = K_{c1} \quad (3.7)$$

which is often referred to as the Henderson-Hasselbalch equation but is in fact just the law of mass action applied to Equation (3.6). Here we have left the hydrogen ion activity represented as the activity but have written the activities of the other ions in terms of their concentrations and activity coefficients.

Application of the p operator gives a form similar to Equation (3.4)

$$pH + p\left[HCO_3^-\right] - p\left[H_2CO_3\right] = pK_{c1} - p\gamma_b + p\gamma_c \quad (3.8)$$

Note that we have written pH to mean $p\left\{H^+\right\}$ for while pH is now defined operationally (i.e. in terms of standard buffers) the current pH scale very closely approximates $p\left\{H^+\right\}$.

As accurate values for actual activity coefficients are difficult to obtain chemists often use an approximation given by the activity coefficient of an average ion, x:

$$p\gamma_x = z_x^2 pf_m \quad (3.9)$$

where z_x is the charge on ion x and

$$pf_m = A\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right) \quad (3.10)$$

with I being the ionic strength of the solution given by

$$I = \frac{1}{2}\sum_i z_i^2\left[x_i\right] \quad (3.11)$$

where z_i is, as above, the charge on ion and $\left[x_i\right]$ represents its molal concentration. A depends on temperature with a value of about 0.506 at 20°C and 0.511 at 25°C. Thus the activity coefficient of a particular ion depends on the charge of that ion and the concentration and charges of all the other ions in the solution.

[5] Related to the energy required to remove the proton from the ion or molecule: $\Delta G^o = \ln(10)RTpK$.

Using Equation (3.9) in Equation (3.8) gives

$$pH + p\left[HCO_3^-\right] - p\left[H_2CO_3\right] = pK_{c1} - pf_m \quad (3.12)$$

with the adjustment for carbonic being 0 because it is uncharged. Examining Equation (3.12) we see that the change brought about by recognizing that the solution is not ideal could be thought of in terms of a shift in pK_{c1} i.e. we could define $p\hat{K}_{c1} = pK_{c1} - pf_m$ and carry on as if the solution were ideal with this new value of the equilibrium constant. The problem with doing this is that pf_m is dependent on the concentration of all charged species in the solution including those whose concentrations depend on it (the bicarbonate in Equation (3.12), for example). For the majority of brewing calculations pf_m has a value of 0.05 or less: just enough to make the decision to consider it or ignore it difficult. For completeness we will continue to carry it in this discussion but encourage the reader to ignore it for the majority of his own calculations.

We can substitute from Equation (3.4) into Equation (3.8) to obtain

$$pH + p\left[HCO_3^-\right] - pK_H - pP_{CO_2} = pK_{c1} - pf_m \quad (3.13)$$

and obtain an expression for bicarbonate in terms of pH and the partial pressure of CO_2:

$$\left[HCO_3^-\right] = 10^{\left(pH - pK_{c1} + pf_m + pK_H - pP_{CO_2}\right)} \quad (3.14)$$

At 20°C $pK_{c1} = 6.35$.

The bicarbonate ion can also release its proton

$$HCO_3^- \leftrightarrow H^+ + CO_3^{-2} \quad (3.15)$$

in which sense it is an acid[6] and this dissociation is governed by a third equilibrium equation

$$pH + p\left[CO_3^{-2}\right] - p\left[HCO_3^-\right] = pK_{c2} - 3pf_m \quad (3.16)$$

Substitution for the bicarbonate from Equation (3.14) gives an expression in terms of the pH and partial pressure of carbon dioxide:

$$2pH + p\left[CO_3^{-2}\right] - pK_H - pP_{CO_2} - pK_{c1} + pf_m = pK_{c2} - 3pf_m \quad (3.17)$$

which can be solved for the concentration of carbonate ion:

$$\left[CO_3^{-2}\right] = 10^{\left(2pH - pK_H - pP_{CO_2} - pK_{c1} - pK_{c2} + 4pf_m\right)} \quad (3.18)$$

[6] Or it can take up a proton, $HCO_3^- + H^+ \leftrightarrow H_2CO_3$, in which sense it is simultaneously a base under the Lowry-Bronstead definition. Such species are said to be amphoteric.

At 20°C $pK_{c2} = 10.38$.

Calcium carbonate is not very soluble in water. The limits of solubility are expressed by:

$$\left[Ca^{+2}\right]\left[CO_3^{-2}\right] \le \gamma K_{Sc} \tag{3.19}$$

where K_{Sc} is the solubility product of calcium carbonate and γ is an activity coefficient. Equality represents equilibrium. If the product is less than K_{Sc} the solution is stable with respect to calcium carbonate, if greater, it is unstable and precipitation will occur. Using the p operator on this equation we have

$$p\left[Ca^{+2}\right] + p\left[CO_3^{-2}\right] = pK_{Sc} - 8pf_m \tag{3.20}$$

Note that the solubility is fairly strongly dependent on the ionic strength of the solution. The value of K_{Sc} depends on the crystalline form of the limestone. For calcite at 20°C $pK_{Sc} = 8.45$, for aragonite $pK_{Sc} = 8.31$ and for vaterite $pK_{Sc} = 7.87$. Thus calcite is the least soluble of the three forms.

The maximum calcium concentration is

$$\left[Ca^{+2}\right] = 10^{(-pK_{Sc} - 2pH + pK_{c2} + pK_H + pP_{CO_2} + pK_{C1} + 4pf_m)} \tag{3.21}$$

which is a function of the variables pH and pP_{CO_2} and the constants pK_{Sc}, pK_{C2}, pK_H and pK_{c1}. To find a value for $\left[Ca^{+2}\right]$ we first find the value for pH which causes the total electronic charge in a litre of the water to be 0. This must include the charges from hydrogen and hydroxyl ions whose relative quantities are governed by the dissociation of water:

$$H_2O \leftrightarrow H^+ + OH^- \tag{3.22}$$

with

$$pH + p\left[OH^-\right] = pK_W - pf_m \tag{3.23}$$

The charge neutrality condition becomes

$$2\left[Ca^{+2}\right] + 10^{-pH} - \left[HCO_3^-\right] - 2\left[CO_3^{-2}\right] - 10^{-(pK_W - pH)} = 0 \tag{3.24}$$

If we substitute the values for $\left[Ca^{+2}\right]$ from Equation (3.21), $\left[HCO_3^-\right]$ from Equation (3.14) and $\left[CO_3^{-2}\right]$ from Equation (3.18) we get an equation in terms of pH, the equilibrium constants and the partial pressure of CO_2. This is somewhat simplified if we first define

$$r_{c1} = \frac{\left[HCO_3^-\right]}{\left[H_2CO_3\right]} = 10^{(pH - pK_{c1} + pf_m)} \tag{3.25}$$

which is the ratio of the concentration of bicarbonate to carbonic and

$$r_{c2} = \frac{\left[CO_3^{-2}\right]}{\left[HCO_3^-\right]} = 10^{(pH - pK_{c2} + 3pf_m)} \tag{3.26}$$

which is the ratio of concentration of carbonate to bicarbonate. Using these definitions the neutrality equation becomes:

$$2\left(\frac{10^{-pK_{Sc} + 8pf_m}}{r_{c1}r_{c2}P_{CO_2}10^{-pK_H}}\right) + 10^{-pH} - r_{c1}P_{CO_2}10^{-pK_H} - 2r_{c1}r_{c2}P_{CO_2}10^{-pK_H} - 10^{-(pK_W - pH - pf_m)} = 0 \tag{3.27}$$

Equation (3.27) is easily solved for pH using numerical methods such as root bisectors or Newton's method[7]. Once the pH is known one can find r_{c1} and r_{c2} from Equations (3.25) and (3.26) and then use them to compute the individual terms of Equation (3.27)[8]. The first term is the calcium concentration, the second the hydrogen ion concentration, the third (ignore the minus sign) the bicarbonate ion concentration, the fourth (ignore the sign) the carbonate ion concentration and the fifth (ignore the sign) the hydroxyl ion concentration, all in units of moles per liter.

Using the values of the equilibrium coefficients given in the preceding text we can prepare curves such as Figure 2. The parallel vertical lines denote the usual range of partial pressure of atmospheric CO_2. Looking in this region we see that we can expect the pH of water at equilibrium with the atmosphere and limestone to be about 8.3 with alkalinity of about 1.1 mEq/L (55 ppm as calcium carbonate) and equivalent calcium hardness (also 1.1 mEq/L) and these numbers are typical of surface waters. Beneath the ground, partial pressures of carbon dioxide can be orders of magnitude greater than at the surface because of the presence of respiring bacteria. Thus ground waters may be substantially harder and more alkaline than surface water. It is also important to note that ground water which has been pumped to the surface takes appreciable time to come to equilibrium and that treatment by the water authority may also result in water arriving at the brewery which is not in equilibrium with the air.

It is often useful to have the mole fractions of the various species in a carbo system. These depend only on pH and pf_m. If ~~we have~~ a solution contains x moles/liter of dissolved carbon dioxide ~~we~~ it will have $r_{c1}x$ moles/liter of bicarbonate ion and $r_{c1}r_{c2}x$ moles/liter carbonate. The total moles of "carbo" are then $x(1 + r_{c1} + r_{c1}r_{c2}) \equiv xd$ and we can define three values which represent the fractions of each of the three carbo moieties:

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[7] In both of these methods values of the charge are calculated for two "trial" pH's. In a root finder if the signs of the net charges are different the pH for charge neutrality must be within the interval spanned by the trial values, if not, without. In Newton's method the two are used to calculate the slope of charge with respect to pH. In either method the "trial" values are refined until a pH is found within a specified tolerance.

[8] In fact the solution values of all these terms will have been computed by the last pass of the root finder.

$$f_{1c} = \frac{1}{d} \tag{3.28}$$

$$f_{2c} = r_{c1} f_{1c} \tag{3.29}$$

and

$$f_{3c} = r_{c2} f_{2c} \tag{3.30}$$

A graph of these three fractions vs. pH is a useful tool for understanding the flow of material in bicarbonate chemistry. Such a graph (for $pf_m = 0$) is given in Figure 3.

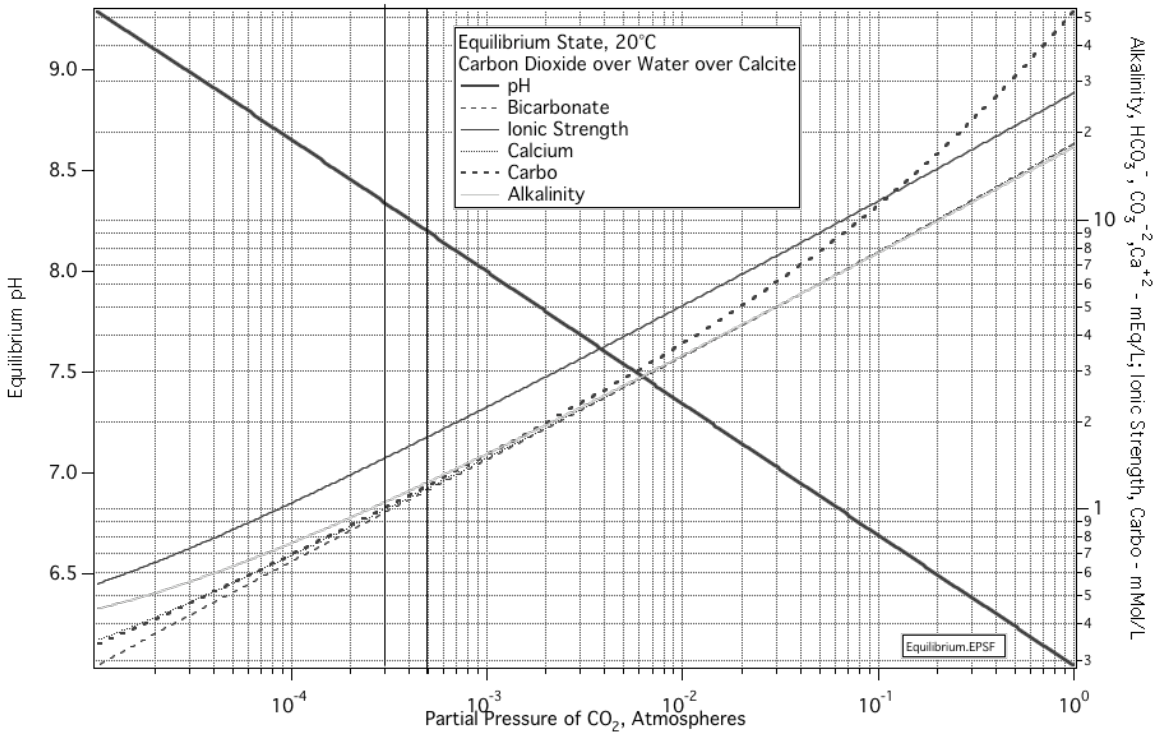

Figure 2: Equilibrium State of pure water over calcite subject to various partial pressure of carbon dioxide at 20∞C. Vertical lines indicate normal atmospheric limits of r_{CO_2}.

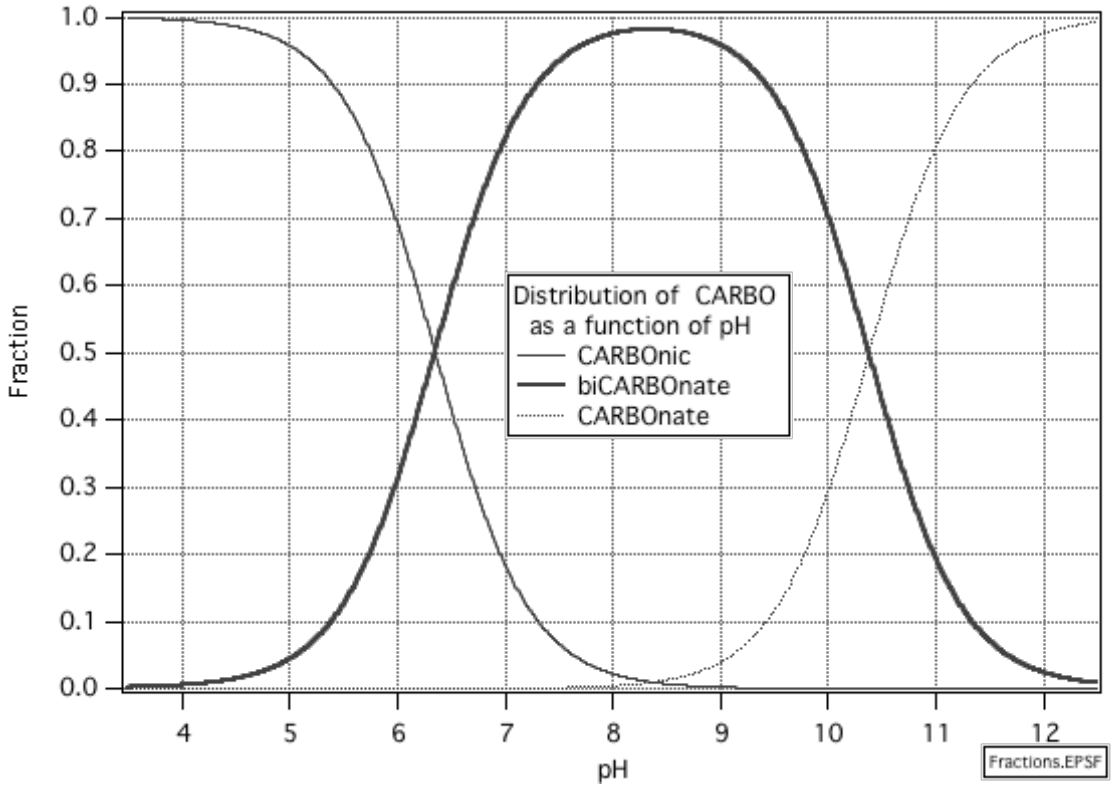

Figure 3: Distribution of carbonic, bicarbonate and carbonate as a function of pH in an ideal solution.

Decarbonation of Liquor

Having discussed the means by which nature dissolves limestone in the water we use for brewing we will mention briefly means for removing it or rather means for removing bicarbonate which is problematical for brewers because it tends to buffer pH at levels higher than ideal for mash tun enzyme activity. Figure 1 shows carbo flowing into the liquor simultaneously from the air and from the solid phase limestone. Similarly we can approach the removal of carbo from either end of Figure 1. By heating the liquor we reduce the solubility of carbon dioxide[9] which leaves the solution as a gas (especially if the liquor is sparged with another gas such as air or steam). As CO_2 escapes the equilibrium (ratio of CO_2 to HCO_3^- is reduced) is upset and bicarbonate levels must drop to reestablish it. Bicarbonate decreases through conversion to carbonic but this requires protons and reducing their number tends to raise the pH. Increased pH caused bicarbonate to convert to carbonate thus producing protons which replace those consumed in forming carbonic. If the increased carbonate is such that the product of the carbonate and calcium concentrations exceeds K_{Sc} some of the carbonate will coalesce with calcium and will precipitate as chalk. The loss of the precipitated carbonate upsets the bicarbonate/carbonate equilibrium and further conversion of bicarbonate to carbonate takes place. This produces more protons which tends to lower the pH and so on. Precipitation of carbonate will continue until the solubility product drops below K_{Sc} (note that K_{Sc} is smaller at higher temperatures i.e. heat reduces the solubility of calcium carbonate as well as that of carbon dioxide). Thus the decarbonation reaction brought about by removing carbon dioxide results in precipitation of calcium carbonate by a mechanism exactly the reverse of the one by which calcium carbonate is dissolved when CO_2 is forced into water. The diagram of Figure 1 still applies but all the arrowheads are reversed i.e. all the reactions precede in the direction opposite to that described in our previous discussion.

A preferable (because it uses less energy) method of decarbonation is to increase the liquor calcium and carbonate contents simultaneously by the addition of lime (quick, CaO, or hydrated-slaked, $Ca(OH)_2$). Lime increases pH causing bicarbonate to convert to carbonate so that the solubility product of Equation (3.20) is exceeded and chalk precipitates. As with heating protons are released but note that some of these go to neutralize the OH^- ions rather than convert bicarbonate to gas, $HCO_3^- + OH^- \rightarrow CO_3^{-2} + H_2O$. Figure 1 (with all arrows reversed) still applies, however, and, as with heating, carbo leaves the solution both as a gas and as a solid. By either method it should be possible to bring the liquor to a pH of about 8.3 and to an alkalinity level of about 1 mEq/L.

ALKALINITY

Alkalinity is a measure of the resistance of a water sample to acidification i.e. of its buffering capacity. It is defined as the amount of hydrogen ion (protons) required to decrease the pH of a sample to a particular value of pH called the end point. Two types of alkalinity are commonly discussed: the phenolphthalein alkalinity (based on an endpoint of $pH = 8.3$) and total alkalinity (based on an endpoint near $pH = 4.3$). It is the latter that is of significance to brewers.

The procedure for determining alkalinity is simple. One tenth of a liter of sample is titrated with 0.1N strong (i.e. pK low enough that the acid is essentially fully dissociated at the end point pH, e.g. hydrochloric or sulfuric) acid until the end point is reached. The number of mL of acid used is the number of milliequivalents of H^+ required to bring 1 L of the sample to the end point. This is the definition of alkalinity expressed in milliequivalents (often called millivals) per liter. The value is often multiplied by the equivalent weight of calcium carbonate, 50 mg/mMol, in which case the result is said to be in units of "ppm as calcium carbonate". If the endpoint is in a region where most of the bicarbonate and carbonate have been converted to carbonic (see Figure 3) the value obtained doesn't depend much on the actual endpoint chosen. Moll, in his chapter in Hardwick (1994) suggests 4.3 (methyl orange) as the end point, while Eaton (1995) recommends that the end point be chosen such that H^+ and HCO_3^- be equivalent but this authority, which is incorporated by reference into the ASBC Methods of Analysis (1992), also indicates that any value is acceptable as long as it is stated in the report.

Examination of Figure 1 makes it clear that the hydrogen ion consumed in shifting from one pH value to another lower one, pH_e, is given by the decrease in the molar concentration of carbonate plus the increase in the molar concentration of carbonic. Small additional amounts of hydrogen ion are required to neutralize OH^- and raise the concentration of H^+ to $10^{-pH_e+pf_e}$. The alkalinity then is:

$$alk = C_T[(f_{3c,i} - f_{3c,e}) + (f_{1c,e} - f_{1c,i})] + 1000[10^{-pH+pf_e} - 10^{pH_i-pf_i} + 10^{-pH_i+pK_W-pf_i} - 10^{-pH_e+pK_W-pf_e}] \quad (4.1)$$

where i subscripts pertain to the initial conditions of the sample and e pertain to the end point. C_T is the total carbo and is in mMol/L. A look at Figure 3 suggests that

[9] At 100°C the Henry coefficient (as defined here) is about one third of what it is at room temperature (20°C). This has the same effect, see Eqn. (3.2) or (3.5), as lowering the partial pressure of CO_2 to one third of its atmospheric value (to .01 - .017%) and Figure 2 indicates that we could expect pH to rise to 8.5 - 8.6 from this effect alone with attendant reduction in hardness and alkalinity which can also be read from the curves should equilibrium under these conditions be reached. Sparging with steam, also discussed in the text, tends to reduce the partial pressure of CO_2 even further.

where the sample pH is less than about 8.3 the alkalinity is approximately the number of equivalents of bicarbonate in the sample:

$$alk \approx C_T f_{2c,i} \qquad (4.2)$$

where, as it is an appoximation, we choose to ignore the relatively small terms directly related to pH.

PHOSPHATE

Malt contains a fair amount of phosphate, in fact as much as 1% of its weight (as P_2O_5) according to Briggs (1981). The term phosphate refers to compounds which involve the ions of phosphoric acid. Within malt most phosphate is bound in phytin i.e. salts of the organic acid myo-Inositol Hexakis-(dihydrogenphosphate). Phytin is hydrolyzed in the mash tun releasing inorganic phosphate and the B vitamin myoinosital. This reaction is catalyzed by the enzyme phytase which is destroyed in all but low kilned malts. The inorganic phosphate will, in the presence of calcium ion, precipitate calcium and phosphate mostly in the form of hydroxyl apatite ($Ca_{10}(PO_4)_6(OH)_2$) though other salts may be precipitated as well. This reaction releases protons in the same way that precipitation of calcium carbonate does (as discussed in Section 3.2) but in addition the precipitation of hydroxyl apatite releases 2 more (see Equation (5.5) below). These protons are available to combine with bicarbonate thus "neutralizing" it and in the course of doing so establishing lower mash pH than would be found were calcium absent. Figure 4 shows the additional reactions coupled with the carbonate reactions from Figure 1. Although this figure may appear quite complex it actually represents a considerable simplification. The production of inorganic phosphate from phytin is not diagrammed nor is the acid/base behavior of phytic acid (12 protons; 12 pKs) nor is the ability of phytin to bind calcium directly. Neither more do we consider the precipitation of other calcium phosphates (such as $CaH(PO_4)$ or $Ca_4H(PO_4)_3$ which may precipitate at mash tun pH. Nevertheless, consideration of the simplified model of Figure 4 may be of some value for the insight it lends into the mechanism by which mash liquor calcium combats water alkalinity. For the remainder of this section, thus, we will limit discussion to inorganic phosphate precipitated in the form of hydroxyl apatite. The phosphate reactions of interest are formally identical to the ones for carbonate except that phosphorous pentoxide (P_4O_{10}) is a solid and has such an affinity for water that the reaction with water is, practically speaking, irreversible and that there is a 3rd proton to consider:

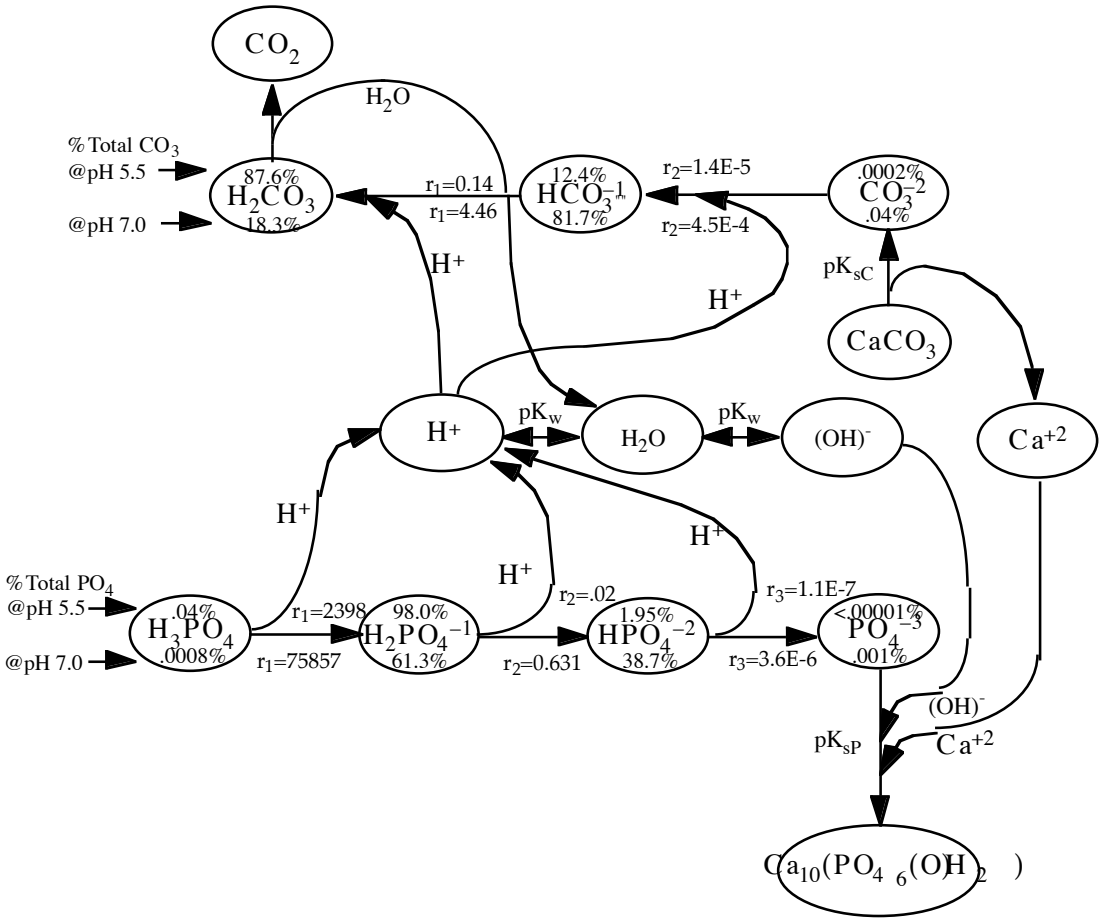

Figure 4: Conceptual diagram summarizing 9 chemical reactions involved in acidulation of mash by malt phosphate. Percentages in ovals are fraction of total carbonate or phosphate in indicated protonation state. Small numbers near arrows ~~indicates~~ indicate molar ratio of less protonated to more protonated species. For example at pH 7 18.3% of carbo species is carbonic and bicarbonate moles are 4.46 times carbonic moles; 61.3% of phosphate is monobasic.

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4 \quad (5.1)$$

$$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^- \quad (5.2)$$

$$H_2PO_4^- \leftrightarrow H^+ + HPO_4^{-2} \quad (5.3)$$

$$HPO_4^{-2} \leftrightarrow H^+ + PO_4^{-3} \quad (5.4)$$

$$10Ca^{+2} + 6(PO_4^{-3}) + 2H_2O \leftrightarrow \underline{Ca_{10}(PO_4)_6(OH)_2} + 2H^+ \quad (5.5)$$

Each equation, except the first, is governed by an equilibrium condition:

$$r_{P1} = \frac{[H_2PO_4^-]}{[H_3PO_4]} = 10^{(pH - pK_{P1} + pf_m)} \quad (5.6)$$

$$r_{P2} = \frac{[HPO_4^{-2}]}{[H_2PO_4^-]} = 10^{(pH - pK_{P2} + 3pf_m)} \quad (5.7)$$

$$r_{P3} = \frac{[PO_4^{-3}]}{[HPO_4^{-2}]} = 10^{(pH - pK_{P3} + 5pf_m)} \quad (5.8)$$

$$[Ca^{+2}] = 10^{\frac{-pK_{SP}}{10} + 9.4\,pf_m + \frac{6p[PO_4^{-3}]}{10} + \frac{2}{10}(pK_W - pH)} \quad (5.9)$$

where, as with bicarbonate, we have introduced r_{Pn} to be the ratio of the concentration of the phosphate (the P subscript designates phosphate) species which has lost n protons to the concentration of the species which has lost $n-1$.

The values for the equilibrium constants at 25°C are, respectively, $pK_{P1} = 2.12$, $pK_{P2} = 7.20$, $pK_{P3} = 12.44$ and $pK_{SP} = 114$ (the P indicates that these are phosphate constants). As with carbonic the r's can be used to calculate the concentration of each species as a fraction of all the molecules containing phosphorous. The method is the same ($f_1 = 1/d$ etc.) except that this time $d = 1 + r_1 + r_1r_2 + r_1r_2r_3$ and there are 4 fractions including $f_{P4} = r_{P3}f_{P3}$ for the PO_4^{-3} ion.

The solubility product for hydroxyl apatite, $pK_{SP} = 114$, suggests that it is quite insoluble. If, for example, the total phosphate in a solution amounts to 1 mMol/L at pH 7, $f_4 = 1.4x10^{-6}$ so that the concentration of PO_4^{-3} would be $1.4x10^{-9}$ mole/L. Substituting this value into Equation (5.9) gives 0.04 mEq/L as the saturation value for calcium. Conversely at pH 5.5, more typical of the mash tun, $f_4 = 2.2x10^{-9}$ so that the PO_4^{-3} concentration would be $2.2x10^{-12}$ mol/L for 1 mMol/L total phosphate and calcium would be saturated at a level of 3.9 mEq/L. The strategy in using calcium to control mash pH is to supply enough of it that the mash is saturated with respect to hydroxyl apatite down to the target pH so that hydroxyl apatite precipitates. When this happens Figure 4 (or the equations) indicate that for each millimole of precipitated apatite approximately 14 milliequivalents of protons are produced: 6 in the conversion of monobasic phosphate to dibasic, 6 in the conversion of dibasic phosphate to tribasic and 2 from the water molecules that furnish the two hydroxyl ions. This is so because most malt phosphate is in the monobasic form as is demonstrated when a distilled water mash is made. Even at pH 6 about 94% of phosphate is monobasic, at pH 5.7 it is about 97%. Thus in converting to the tribasic form as is required for precipitation two conversions are required and two protons are thrown off for each mononbasic ion converted.

The fact that we can approximately determine the number of protons given up when apatite precipitates suggests a strategy for calculating the amount of calcium we might need to reach a desired mash pH. The first step is to determine the quantity of protons required. This can be done handily using the alkalinity definition of Equation (4.1) with pH_i being the pH of the liquor and pH_e being the desired strike pH. The use of Equation (4.1) for this purpose requires that the total carbo be known and that value can be obtained by measuring the alkalinity as described in Section 4.0 and then solving Equation (4.1) for C_T using the measured value for alk with pH_i set to the sample pH value and pH_e to the titration end point.

We now use the fact that production of 1 mole of hydroxyl apatite produces 14 equivalents of protons. As 1 mole of hydroxyl apatite contains 6 moles of phosphate we conclude that each mole of phosphate precipitated produces two and a third (2.333) equivalents of protons. We also note, from Equation (5.5) that each mole of phosphate precipitated requires $20/6$ (three and one third) equivalents of calcium ion. Dividing the proton requirement by the protons per mole of phosphate precipitated gives the number of moles of phosphate required and multiplying that by 3.333 gives the number of moles of calcium required to be precipitated with the phosphate. If we have an idea as to how much phosphate was available to start with we can subtract the amount precipitated to obtain a value for the amount left. That amount, multiplied by f_{P4} at the strike pH gives the amount of PO_4^{-3} which would be left in the liquor and that value, used in Equation (5.9) tells us how much calcium is left in solution. The sum of the calcium precipitated plus the calcium remaining in solution is the total calcium required. If this is more than the amount of calcium supplied by the liquor then supplemental calcium will be required.

The foregoing method assumes 2.3333 protons per PO_4^{-3} ion precipitated but this is not exact. The solution can be refined by calculating an approximate answer as just described and then using numerical techniques to solve the system of 9 equations suggested by Figure 4 including Equation (3.23) for the dissociation of water plus a tenth charge neutrality equation, Equation (3.24), augmented to include the charged phosphate moieties. This is simpler than it might at first appear because we will usually want

to ignore the equilibrium of carbon dioxide in the air as available water is frequently saturated with respect to CO_2. Similarly, while available water is often saturated with respect to $CaCO_3$ at liquor pH it is usually not so at strike/mash pH.

Using such techniques we can prepare plots such as Figure 5 which assumes that phosphate salts totaling 1 mMol/L and proportioned such that if mixed with distilled water[10] would give a pH of 5.7 are added to liquor of varying degree of alkalinity and with calcium equivalent to the alkalinity (i.e. 100% permanent hardness). The total amount of calcium required to prevent the pH from shifting upward from the distilled water pH is then calculated as described. In preventing the pH shift we say the protons released by the precipitation of calcium have neutralized the water's alkalinity. Alkalinity in excess of the amount which can be so neutralized (because of an insufficiency of calcium) and which would, thus, result in a pH shift, is called "residual alkalinity" and is the subject of the next section.

The figure shows the calcium required for neutralization, the fraction of the total phosphate precipitated and the ratio of the calcium required to the alkalinity neutralized all as a function of alkalinity. Note that under the assumptions of Figure 5 the ratio is somewhat over 3 mEq/L calcium for each mEq/L of alkalinity neutralized over a fairly broad range of plotted alkalinities.

Figure 6 is calculated in the same way as Figure 5 but in the latter set of calculations we doubled the amount of phosphate and assumed the distilled water pH to be 5.6 rather than 5.7. The effects are apparent. First, doubling the phosphate approximately doubles the maximum amount of liquor alkalinity which can be neutralized (from 2.4 mEq/L to 4.2). Second, the amounts of calcium required per unit of neutralized carbonate is reduced to a bit over 2 mEq/L per mEq/L of alkalinity. This is because less calcium is required to saturate a high phosphate solution than a low one.

[10] This models malt which comes to a particular pH when water is added because of buffers contained within grist. We recognize that phosphates are not the only buffers in real grists.

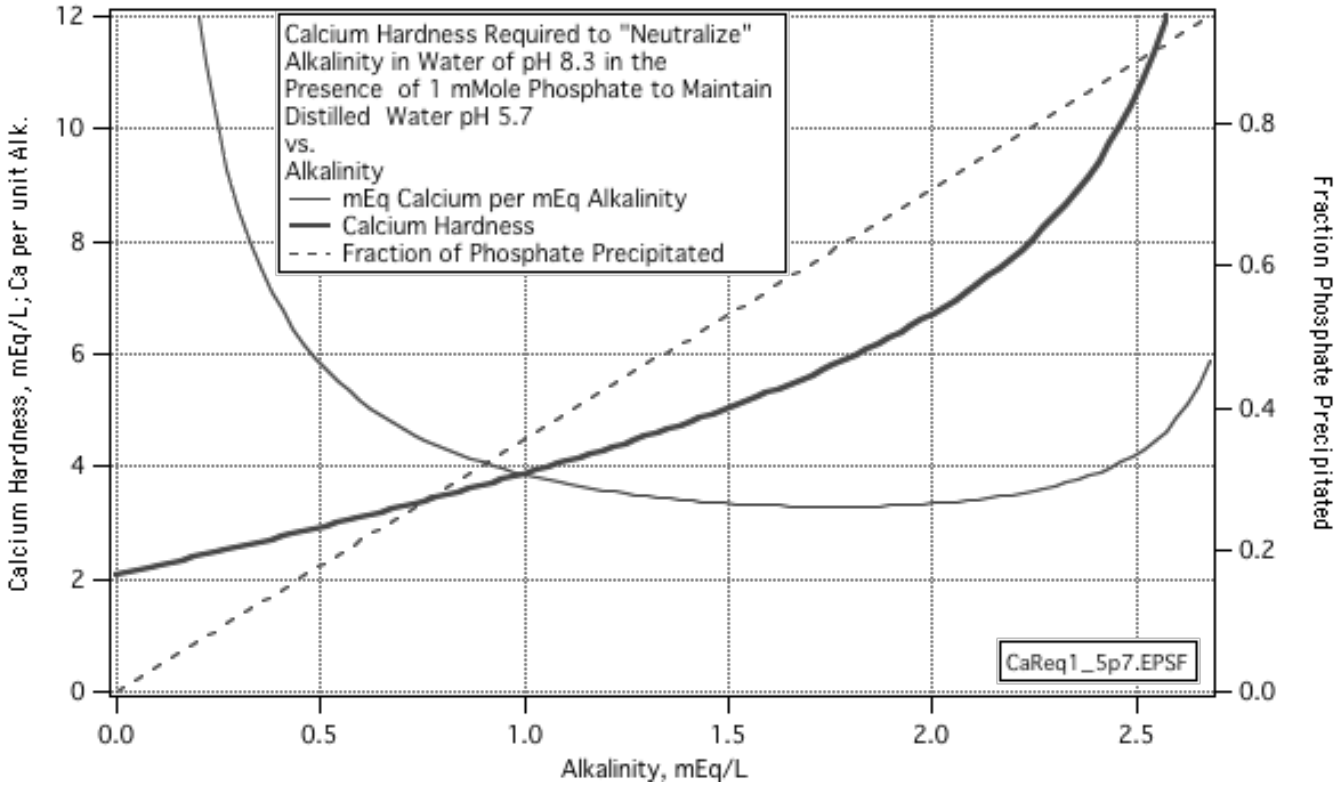

Figure 5: Calcium required to maintain distilled water mash pH (5.7) in a mash with total phosphate of 1 mMol/L as a function of alkalinity of mash liquor (pH 8.3) alkalinity.

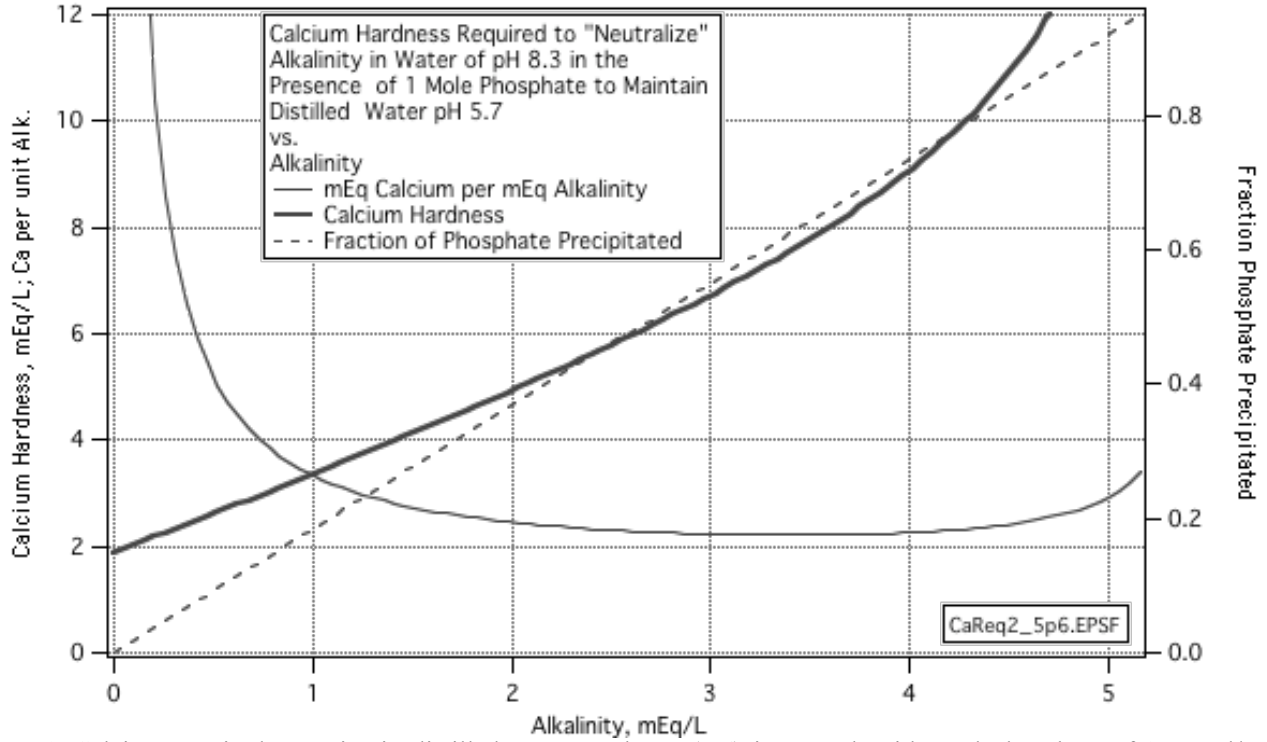

Figure 6: Calcium required to maintain distilled water mash pH (5.6) in a mash with total phosphate of 2 mMol/L as a function of alkalinity of mash liquor (pH 8.3) alkalinity.

KOLBACH'S RESIDUAL ALKALINITY

In the previous section we showed how precipitation of calcium with phosphate neutralizes alkalinity and used our model to calculate the amount of calcium required per unit of neutralized alkalinity. Paul Kolbach (1953) observed that in mashes consisting of pale malt, each 3.5 mEq/L of calcium could neutralize (in the sense of preventing a pH

shift relative to distilled water) 1 milliequivalent/L of water alkalinity. This is in at least approximate agreement with our model but we must stop short of claiming our model ~~as~~ is anything more than a teaching device at this point. Kolbach also found that seven milliequivalents of magnesium would neutralize 1 mEq/L of alkalinity. Alkalinity beyond that which could be neutralized by calcium and magnesium he termed "residual alkalinity". As a simple formula

$$RA = alk - \frac{[Ca^{+2}]}{3.5} - \frac{[Mg^{+2}]}{7} \qquad (6.1)$$

If $RA > 0$ then not all liquor alkalinity is neutralized by phosphate precipitation and pH will be higher than in a distilled water mash. If, on the other hand, more protons are emitted than are required to neutralize the liquor alkalinity, the excess protons will acidify the mash to a pH lower than would be obtained with distilled water. Note that $[Ca^{+2}]$ means concentration in mEq/L as previously in this article in which case the alkalinity, alk, must also be expressed in mEq/L and then the residual alkalinity, RA, will ~~then~~ be in these same units. But other consistent units are also possible. For example, in the United States, 50 times the mEq/L, referred to as ppm as $CaCO_3$, is often used.

If we give half the magnesium hardness plus the calcium hardness a name such as "effective calcium hardness" or just "effective hardness" and assign a symbol to it, say, $D = [Ca^{+2}] + [Mg^{+2}]/2$, then $RA = alk - D/3.5$. We find it useful to rearrange this to $alk = RA + D/3.5$ which plots on a graph of alkalinity vs. effective hardness as a straight line with slope $1/3.5$. A series of such lines for various values of residual alkalinity is shown on Figure 7. Also noted on this plot, at coordinates corresponding to the approximate reported effective hardness and alkalinities of their water supplies[11], are the names of several brewing cities of renown (some cities appear more than once because there are multiple reports as to the compositions of their waters). Figure 7 is thus a convenient tool for comparing one's own water supply to the water of these cities.

A second finding of Kolbach was that each unit of residual alkalinity (as $CaCO_3$) shifts the pH relative to a distilled water mash by 0.00168. Thus a city with water yielding a RA of +100, such as Eeklo (Belgium) would be expected to have mash pH 0.17 units higher than a distilled water mash. Assuming this to be 5.75 would imply 5.92 with the +100 RA water which is clearly too high. By contrast a water with RA of -75 would yield a mash tun pH of about 5.62 which is acceptable. Vienna, with its very hard water and Burton with its extremely hard water would thus both give an acceptable strike pH without the use of external acid.

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[11] Note that the plot uses units of ppm as $CaCO_3$. All values (alkalinity and hardness) should be divided by 50 to convert these values to mEq/L (mVal). The diagonal lines are separated by 0.5 mEq/L of residual alkalinity.

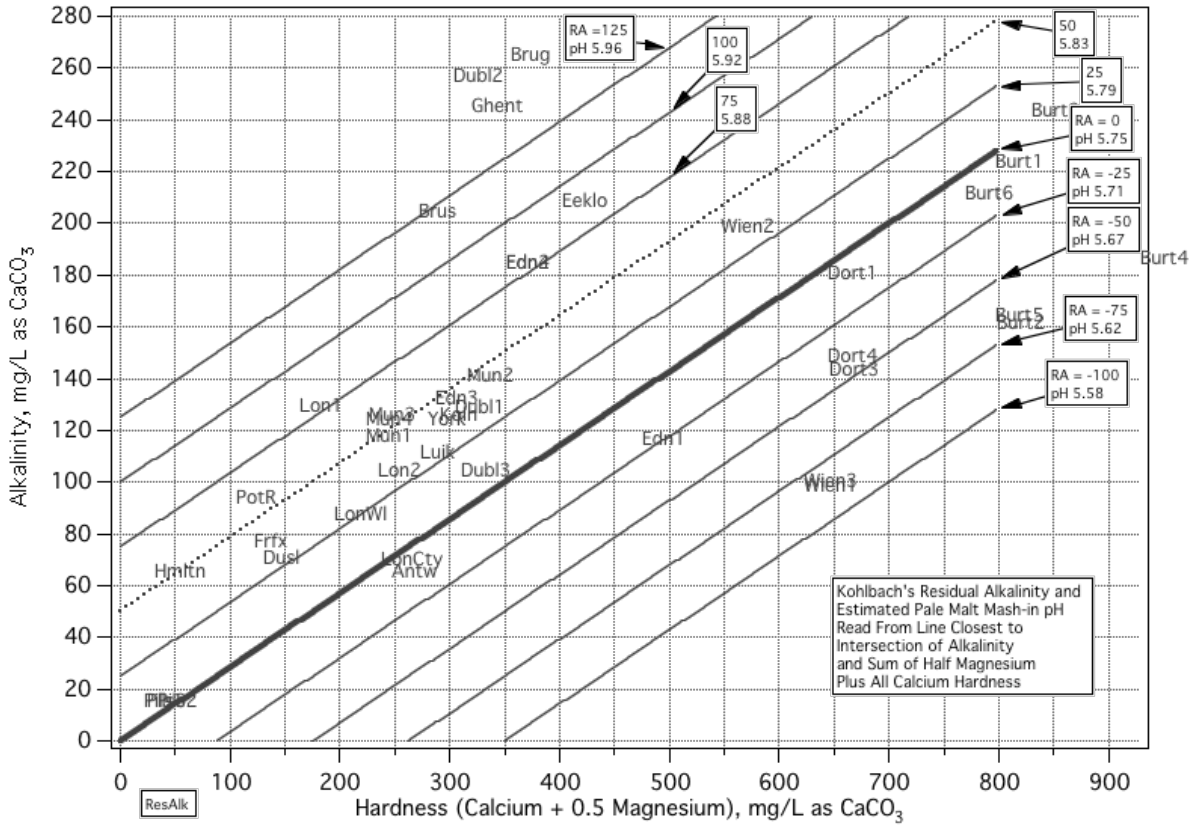

Figure 7: Residual alkalinity and mash pH prediction chart

Readers can, of course, plot their own water's coordinates on Figure 7 and by so doing get a rough idea of what pH a base malt only grist might produce at strike. If this is unacceptable, the approximate amount of acid required to set the pH to a desired value is easily estimated. Assume, for example, water like Munich's with an RA of 50 leading to a mash pH with base malt of about 5.83. The RA can shifted by adding 1 mEq/L of acid per liter of liquor for each 50 units of shift desired. Thus the Munich water can be brought to 0 RA by the addition of 1 mEq/L of acid. This would result in a mash pH of about 5.75. If it is desired to have a lower pH, say pH 5.67, the RA would need to be brought to -50 and another mEq/L would required. These 2 mEq/L acid could be supplied by adding, e.g. 0.2 mL of 10 N acid per litre of liquor to the mash. It is also quite possible to obtain this acid from dark malt. The amount of dark malt required can be calculated from its titratable acidity.

We would be remiss if we did not point out that residual alkalinity and the implied pH shift represent approximations of what will actually happen in the mash tun. Given this calculations should be used only as a starting point in the design process. Actual dark malt or mineral acid additions should be determined by experimentation with test mashes.

REFERENCES

1. Briggs, D. E., J.S. Hough, R. Stevens, and T. W. Young "Malting and Brewing Science", Chapman and Hall, London 1981 Vol. I p90.
2. DeClerck, Jean "A Textbook of Brewing", Chapman and Hall, London, 1957
3. DeClerck op. cit. pp 80 – 84
4. deLange, Andrew J. "Deconstructing Water Residual Alkalinity and Mash pH", The New Brewer, July/August 2003
5. Eaton, Andrew D., L. S. Clesceri, A.E. Greenberg, Ed. "Standard Methods for the Analysis of Water and Wastewater", 19th Edition, APHA, AWWA, WEF, Washington, DC 1995 (note: the 20th edition is out) pp 2-25 - 2-28
6. Hardwick, William A. Ed. "Handbook of Brewing", Marcel Dekker, New York, 1994, Chapter 8 "Water" by M. M. Moll
7. ibid. p276
8. Kolbach, Paul "Der Einfluss des Brauwassers auf das pH von Würze und Bier", Wissenschaftliche Beilage Monatsschrift fur Brauerei 6 Jahrgang Nummer 5 Mai 1953
9. Methods of Analysis of the American Society of Brewing Chemists, Eighth Revised Edition, ASBC St. Paul, 1992
10. Standard Methods op. cit. pp 2-36 - 2-38
11. Stumm, Werner and J. Morgan "Aquatic Chemistry, An Introduction Emphasizing Chemical Equilibria in Natural Waters", Wiley, New York, 1981