

The effect of brewing water and grist composition on the pH of the mash

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Mash pH is an important brewing parameter that lays the foundation for the pH of subsequent brewing processes and the final product. During the mash, a proper mash pH is important for optimal enzymatic activity. While home brewers have a general understanding of how brewing water mineral content and acidity of the grist affect each other to settle on a mash pH, little has been published about the quantitative effects. This paper tries to shed some light on how malt and water react with each other. It also proposes a means of estimating mash pH from water and grist composition. The distilled water mash pH of various base malts has been determined as well as the titratable acidity of specialty malts. In both cases it was found that darker malts are in general more acidic but a number of exceptions to this rule exists. Of the specialty malts tested, Cara and base malts have more acidity per color than roasted malts which showed little difference in their acidity despite their fairly large color range. The effect of water alkalinity and calcium and magnesium hardness was evaluated. It was found that Kolbach's pH change based on residual alkalinity is generally used incorrectly in (home) brewing and that it depends on more factors than just the residual alkalinity of the brewing water when mash pH is of interest. Different sources of alkalinity were evaluate. Chalk that is added to brewing water without being dissolved by CO₂ does a very poor job in raising mash pH and loses most of its effectiveness at addition rates higher than 400-500 ppm. In order to be effective chalk needs to be dissolved with CO₂. Finally mash thickness and grist preparation (milling) were evaluated. Mash thickness had a profound impact on how much pH changes when the residual alkalinity changes while milling has the same effect but to a much lesser extend.

1 Introduction

When grist and brewing water are mixed at dough-in the mash will settle at a pH that is determined by the buffer strength and other pH characteristics of both the water and the grist. Depending on the mashing procedure used and the grist, that pH may change during mashing. A mash pH in the range of 5.3 – 5.7 is generally accepted as adequate for brewing.

Early on in brewing, brewers noticed that some beers do better with their water while others don't come out right. This was a major factor in the development of regional styles and was the result of finding the a suitable grist composition for the brewing water that was available at that location.

During the mid 20th century Kolbach investigated the relation between brewing water composition and 12 Plato cast out wort pH. The result of that work was the discovery that mash pH is affected by the water's alkalinity and its calcium and magnesium hardness. He defined Residual Alkalinity as¹

$$\text{Residual Alkalinity} = KH - \frac{CH - \frac{1}{2} MH}{3.5}$$

where:

1 Paul Kolbach, *Der Einfluss des Brauwassers auf das pH von Würze und Bier*, Monatszeitschrift für Brauerei, Berlin 1953, Translation by A.J.deLange available at:
http://ajdel.wetnewf.org:81/Brewing_articles/KolbachPaper.pdf

KH: carbonate hardness

CH: calcium hardness

MH: magnesium hardness

All hardness values are given in degree German Hardness (dH) which is an equivalent measure of the molar concentration of the ions and their charges.

Residual Alkalinity is the Alkalinity that is left after the alkalinity neutralizing reactions between malt phosphates and calcium and magnesium ions in the water have been considered.

Kolbach's work also found that changing the residual alkalinity by 10 dH changes the cast out wort pH by 0.3 units. I.e. the use of a water with a residual alkalinity of 10 dH (3.55 mEq/l) results in a cast out wort pH that is 0.3 units higher than the pH of a cast out wort that has been prepared with the same grist and brewing procedure but with distilled water.

DeLange modeled the reaction between phosphate and calcium which releases protons and thus counteracts the pH raising effect of alkalinity². This reaction is the basis of Kolbach's residual alkalinity. He found that the effectiveness of calcium, i.e. how much calcium equivalents are needed to neutralize 1 equivalent of alkalinity, depends on the amount of phosphate available, the mash pH and the alkalinity itself.

2 A.J. DeLange, Alkalinity, Hardness, Residual Alkalinity and Malt Phosphate: Factors in the Establishment of Mash pH. Copy available at:
http://ajdel.wetnewf.org:81/Brewing_articles/Cerevesia/Final_gallery



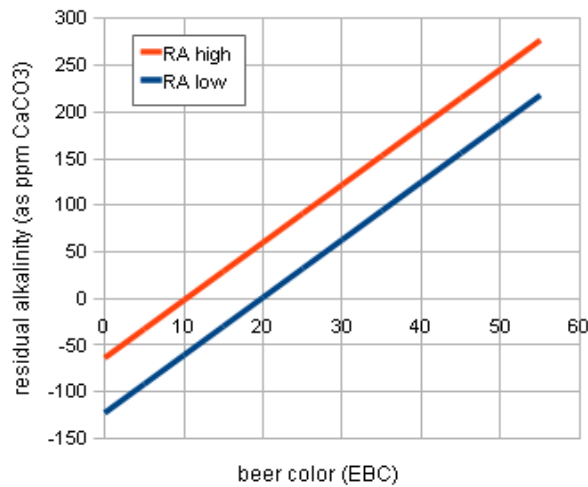


Figure 1: relationship between beer color and optimal water residual alkalinity (Palmer)

DeLange also proposed the use of the titrateable acidity of base and specialty malts to estimate the amount of alkalinity that can be neutralized by the use of these malts³. 1 mEq of titrateable malt acidity would neutralize 1 mEq of water alkalinity if the titration end pH matches the mash pH that is achieved with that grist and the water used.

To guide brewers in estimating the needed residual of their brewing liquor when brewing a beer with a given color Palmer proposed the relationship shown in Figure 1⁴. The top residual alkalinity curve represents values that should be used for beers that get most of their color from roasted malts while the low residual alkalinity curve is for beers that get all or most of their color from base and/or caramel/crystal malts.

The relative affordability of reverse osmosis water systems allow many home brewers to build their brewing water from very soft water and based it on their brewing needs. This gives brewers an unprecedented level of control over their brewing water and allows the brewer to match the water to the grist.

As a result a need for a better understanding of the effects of grist and brewing water composition as well as various

3 A.J. DeLange, Understanding Alkalinity and Hardness Part II, Copy available at: http://ajdel.wetnewf.org:81/Brewing_articles/BT_Alkalinity_II/AlkalinityPtII.pdf

4 John Palmer, Mash Residual Alkalinity Adjustment Worksheet Version 2.5, available at: http://howtobrew.com/section3/Palmers_Metric_RA_ver2e.xls



Figure 2: Mashing the mash samples in a water bath.

brewing parameters on the mash pH exists and was the motivation for the work presented in this paper.

2 Methods and Materials

Unless otherwise noted in Results and Discussions, the following methods and materials were used

The experiments for this paper were small scale mashes done in baby food jars set in a water bath. (see Figure 2) That water bath was used to preheat the strike water and maintain a mash temperature that was between 60 and 65 C. While there were temperature differences between different series, all mashes within a given series were done at the same temperature. The mash time was 10 min. Each series consisted of up to 12 experiments.

Once the mash time expired, samples were cooled to 24 – 26 C within 3-5 min in an ice bath and their pH was tested with a Milwaukee SM101 pH meter. The meter was calibrated before each series of experiment using 4.00 and 7.00 buffer solutions at 25 C.

To minimize measurement errors associated with weighing very small amounts of salts, stronger solutions of various brewing salts and distilled water were made and the desired water profile was created by mixing these stronger solution and, if necessary, distilled water. The distilled water was obtained from a drugstore and tested 0 with a TDS meter.

Weights were either measured with a precision 0-100 g scale (the precision of that scale is 0.01g) or a 0-2000g scale (the precision of that scale is 1g). The latter was used for weighing the water used to create batches of stronger brewing salt solutions mentioned earlier.

The standard strike water amount used was 50g. The standard mash thickness was 4 l/kg which resulted in a standard grist weight of 12.5 g. Some experiments,

however, changed that.

Most experiments were done with a pulverized grist. The grist was ground to a fine power using a small electrical coffee grinder (Hamilton Beach 15-cup Coffee Grinder, model No 80344) on its finest setting.

A fully adjustable JSP Maltmill set to the desired mill gap spacing with a feeler gauge was used to crush malt for experiments that used a crushed grist.

In this paper the European Brewing Convention's (EBC) measure for malt and beer color is used. When the malt color was only available in degree Lovibond, the following formula was used for conversion⁵

$$^{\circ} EBC = (^{\circ} L \cdot 2.65) - 1.2$$

Titration experiments were either done with a 0.1 M NaOH (sodium hydroxide) solution or muriatic acid (HCl) diluted to about 0.5 % (w/w). The sodium hydroxide solution was obtained from a home brew supply store while the muriatic acid was purchased at a hardware store. The correct strength of each batch of diluted muriatic Acid was determined from the initial muriatic Acid strength, its weight and the weight of distilled water that was added. It was then recorded and used calculate the amount of acid equivalents added during titration.

Alkalinity was determined by titration to a pH of 4.3 measured with a pH meter.

Only SI units are used in this paper. While it is very common to express alkalinity as either ppm as CaCO₃ or dH (German Hardness), mEq/l is used as the measure of alkalinity in this paper. The following conversion can be used to calculate ppm as CaCO₃ or dH:

$$1 \text{ mEq/l} = 50 \text{ ppm as CaCO}_3 = 2.81 \text{ dH}$$

3 Results and Discussion

The order in which the results are listed here is not necessarily the order in which the experiments have been performed. The first sections focus on the distilled water mash pH of base malts and specialty malts as well as the titrateable acidity of specialty malts. Next are experiments and discussions about the effect that water composition has on mash pH. The final set of experiments evaluates the effects of mash thickness and grist preparation.

3.1 Distilled water mash pH of base malts

When base malts are mixed with water, the resulting mash pH depends on the acidity of the malt. Most malt has a natural buffer that creates a distilled water mash pH of about 5.7 – 5.8. That mash pH can be lowered by acidic melanoidins present in more highly kilned malts. This series of experiments evaluated the distilled water mash pH of a number of commonly used base malts.

The results are shown in Figure 5 and Table 2. While a loose correlation ($R^2=0.54$) between malt color and distilled water mash pH exist, there are a number of notable exceptions. The sample of Weyermann Munich I malt, which has half the color of the darker Weyermann Munich II malt, had a lower distilled water mash pH than a sample of the darker malt.

A number of lightly kilned malts, around a malt color of 4 EBC, showed distilled water mash pH values ranging from 5.56 to 6.04.

Based on these results it cannot be said that a darker base malt color always results in a lower distilled water mash pH. The distilled water mash pH of a given base malt needs to be known if a reasonably accurate mash pH prediction is expected.

3.2 Mixing base malts

If malts act like acids and the distilled water mash pH is an indication of the amount of acid contained in a malt and not the strength of the acid, the distilled water mash pH of a mix of base malts is expected to be the weighted average of the distilled water mash pH values of the individual base malts. This assumption was supported by this experiment where Weyermann Pilsner, Weyermann Munich Type I and Weyermann Munich Type II were mixed with each other. Figure 6 and Table 2 show the results. The mash pH for these base malt mixes was slightly lower than expected from the weighted average of the contributing base malts. But since the numbers for 100% Pilsner, Munich I and Munich II were taken from the previous series, it is possible that another, not controlled, factor caused that pH shift.

For the purpose of predicting the distilled water mash pH of a base malt mix it is assumed that it is sufficient to use the weighted average of the distilled water mash pH values of the used base malts.

$$pH = \sum pH_{bi} \cdot g_{bi}$$

where

pH_{bi} : distilled water mash pH of the base malt *i*

g_{bi} : grist portion of the base malt *i* (between 0 and 1)

⁵ <http://www.unc.edu/~rowlett/units/dictD.html>,

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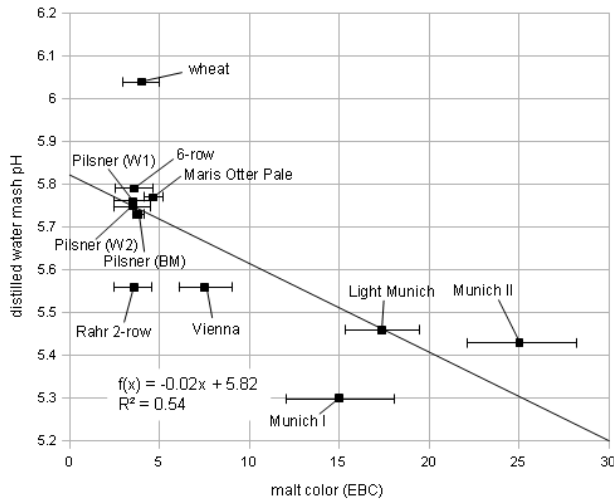


Figure 5: Distilled water mash pH for various base malts. (pulverized grist, 4 l/kg mash thickness, 10 min at 65 C)

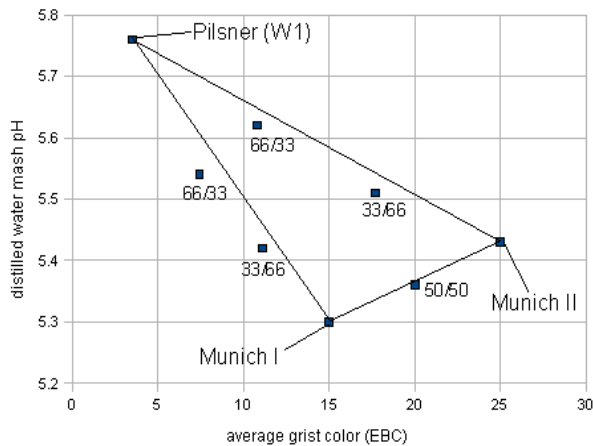


Figure 6: The distilled water mash pH for mashes made with 3 different malts and each mash used up to two different malts in the grist. The triangle represents the arithmetic mean of the grist color and distilled water mash pH. (pulverized grist, 4 l/kg mash thickness, 10 min at 65 C)

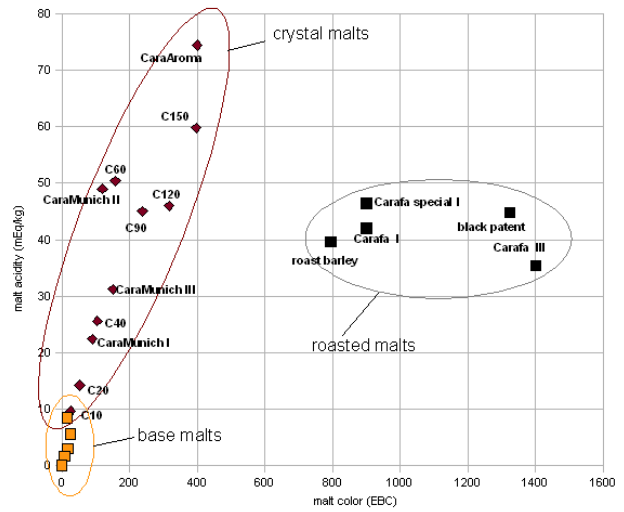


Figure 3: The acidity of various specialty malts. The orange points represent some of the darker base malts that have been evaluated in the previous section. The grouping of crystal type and roasted malts is remarkable. (pulverized grist, mash thickness 8 l/kg, 10 min at 65 C, cooled to 25 C for titration)

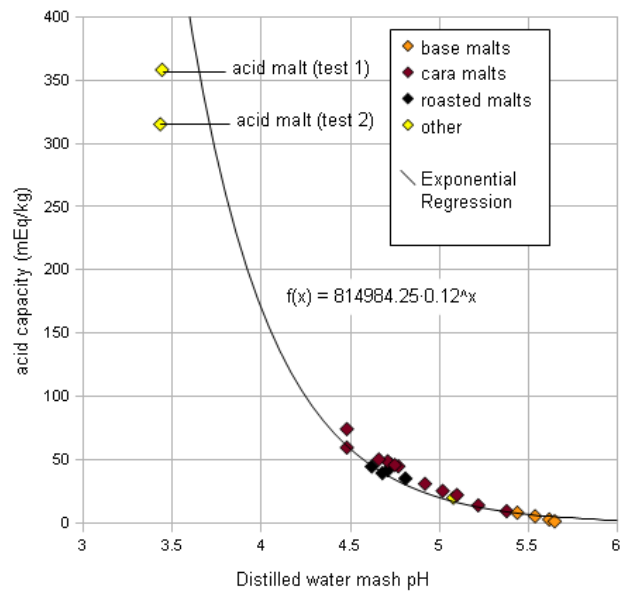


Figure 4: correlation between the distilled water mash pH of base and specialty malts and their specific acidity. (pulverized grist, mash thickness 8 l/kg, 10 min at 65 C, cooled to 25 C for titration)

3.3 The acidity of specialty malts

Another source of color and acidity in grists is specialty malts. Since they tend to be used in only small amounts compared to base malts but provide a lot of acidity to the grist, a different approach in evaluating them was taken. In addition to evaluating the pH of distilled water mashes prepared with these malts, these mashes were titrated to a pH of 5.7 with sodium hydroxide.

Figure 3 shows the results. One observation is that roasted and crystal type malts form distinct clusters. While the specific acidity (titratable acidity per kg of malt) of crystal malts increases at a slope of about $0.13 \text{ mEq}\cdot\text{kg}^{-1}\cdot\text{EBC}^{-1}$ ($r^2 = 0.77$), roasted malts have a specific acidity of about $40 \text{ mEq}\cdot\text{kg}^{-1}$ regardless of their color. As with the distilled water mash pH for base malts there are also outliers among the crystal malts. The tested sample of Weyermann CaraMunich II, for example, had with $49 \text{ mEq}\cdot\text{kg}^{-1}$ a higher specific acidity than the darker CaraMunich III ($31.2 \text{ mEq}\cdot\text{kg}^{-1}$). The same was true for Briess' Crystal 60L when compared to Crystal 90L and Crystal 120L.

The following formula can be used to estimate the acidity of crystal type specialty malts ($r^2 = 0.77$):

$$a_i = 14 + 0.13 \cdot C_i$$

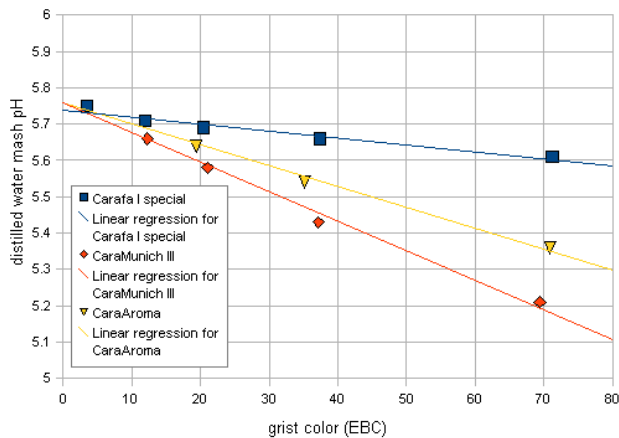


Figure 7: the distilled mash pH of a grist with pilsner malt and 3 different specialty malt. Pilsner malt was mixed with 3 different specialty malts at different grist percentages. This data confirms that the CaraMunich malt has a lower acidity per color than the CaraMunich III and the CaraAroma malt (pulverized grist, mash thickness 4 l/kg, 10 min at 63°C)

where:

a_i : specific acidity of the specialty malt i in $\text{mEq}\cdot\text{kg}^{-1}$

C_i : color of the specialty malt i in EBC

A stronger correlation exists between specific acidity and the distilled water mash pH of specialty malts. This is shown in Figure 4. While not linear, the correlation is strong enough that it could be used as a reliable means of determining the malts specific acidity from its distilled water mash pH.

Acidulated malt (Weyermann Sauermalz) was also included in the titration tests. One titration test determined a specific acidity of $315 \text{ mEq}\cdot\text{kg}^{-1}$ while another test determined $358 \text{ mEq}\cdot\text{kg}^{-1}$. This corresponds to a lactic acid content of 2.85 % and 3.22 % by weight and matches Weyermann's specification of ~ 3% (w/w)

3.4 Distilled water mash pH of grists with specialty malts

When specialty malts become part the grist, they lower the distilled water pH of that grist though the addition of acids. But since the relationship between the distilled water pH of specialty malts and their specific acidity is not linear, the pH shift caused by specialty malts was evaluated as a function

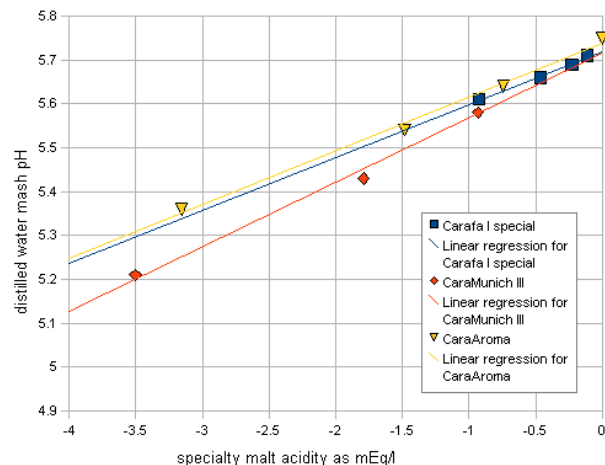


Figure 8: The distilled water pH of mashes with varying amounts of different specialty malts plotted over the specialty malt acidity per unit of strike water. (pulverized grist, mash thickness 4 l/kg, 10 min at 63°C)



of the resulting average grist color and the specific acidity added by that specialty malt.

How increasing amounts of a specialty malt in a grist affect the distilled water mash pH is shown in Figure 7 and Table 5. Again it is apparent that crystal malts provide a stronger acidity per color than roasted malts like Weyermann's Carafa I special.

Together with the specific malt acidity data that was determined in 3.3 "The acidity of specialty malts" it is possible to plot the distilled water mash pH over the specialty malt acidity divided by the amount of strike water. The resulting unit is mEq/l; the same unit as alkalinity which will be discussed later.

The form of the plot shown in Figure 8 suggests that the decrease in mash pH caused by the specialty malt is a linear function of the acidity that the specialty malt added to the grist. In other words, if the acidity of the specialty malt is known the mash pH decrease can be calculated based on mash thickness and the grist percentage of the specialty malt. The slope of the linear function was determined as follows:

malt type	pH·l·mEq ⁻¹	r ²
Carafa I special	0.12	0.99
CaraMunich III	0.15	0.99
CaraAroma	0.12	0.99
all	0.14	0.97

And with that the pH delta caused by specialty malts can be written as:

$$\Delta pH = \frac{-0.14 \left(\sum a_i \cdot g_i \right)}{R}$$

where:

$g_{s,i}$: grist portion of the specialty malt i (between 0 and 1)

$a_{s,i}$: specific acidity of specialty malt i (mEq·kg⁻¹)

R : mash thickness (l·kg⁻¹)

3.5 Distilled water mash pH of a grist containing base and specialty malts

Based on the previous findings the following formula is proposed for estimating the distilled water mash pH of a grist containing base and specialty malts:

$$pH = \left(\sum pH_{bi} \cdot g_{bi} + 5.7 \cdot \sum g_{s,j} \right) - \frac{0.14 \cdot \sum a_{s,j} \cdot g_{s,j}}{R}$$

where

pH_{bi} : distilled water mash pH of the base malt i

g_{bi} : grist portion of the base malt i (between 0 and 1)

$g_{s,j}$: grist portion of the specialty malt j (between 0 and 1)

$a_{s,i}$: specific acidity of specialty malt j (mEq·kg⁻¹)

R : mash thickness (l·kg⁻¹)

In English, the average of the distilled water mash pH values for the base malts and pH 5.7 (the titration end point) for the specialty malts is adjusted by the pH shift caused by the acidity of the specialty malts.

3.6 The effect of water alkalinity

So far only the grist's effect on the distilled water mash pH has been evaluated. But brewing water is not distilled water. It's mineral content, in particular bicarbonates, calcium and magnesium also affect mash pH.

Alkalinity is a measure of the buffer capacity of the water's carbonate buffer system. It is well known that it has a profound impact on mash pH. The initial experiment evaluated how 3 different grists (single base malt, base malt mix and base malt with specialty malt) reacted with water over a wide alkalinity range. Water samples were prepared with distilled water and hydrochloric acid (negative alkalinity) or distilled water and sodium bicarbonate (positive alkalinity).

The results are shown in Figure 9 and Table 3. The mash pH values can reasonably well approximated with a linear function with a slope of 0.061 pH·l·mEq⁻¹ (r² = 0.97). The pH value at an alkalinity of 0 mEq·l⁻¹ corresponds to the distilled water pH of the grists which has been discussed earlier. Based on these findings the expected mash pH can be written as a function of the grist's distilled water mash pH and the water's alkalinity:

$$pH = pH_{grist \text{ distilled water}} + s_{pH} \cdot Alk_{water}$$

where

$pH_{grist \text{ distilled water}}$: is the distilled water pH of the grist as calculated in the previous section

s_{pH} : the pH over alkalinity slope which has been found to be ~0.06 pH·l·mEq⁻¹ for 4 l/kg mashes

Alk_{water} : is the alkalinity of the water in mEq·l⁻¹.

Later experiments show that the pH-alkalinity slope s_{pH} depends on mash thickness and to some extent also on grist preparation (milling).

It can be argued that an exponential function the the data for the pilsner malt grist better than a linear function. While this is true a linear fit is not far off, especially in the alkalinity range that eventually matters in brewing, and makes further discussion of the effects of alkalinity on mash pH easier.



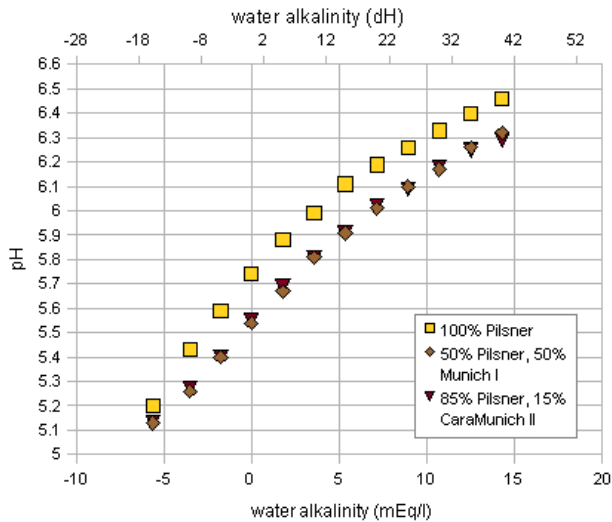


Figure 9: various grists and their mash pH over an extended alkalinity range. (pulverized grist, mash thickness 4 l/kg, 10 min at 63C, water general hardness 0 mEq/l)

Especially since it allows the definition of a pH/alkalinity slope s_{pH} .

If the slope s_{pH} is expressed as pH/dH where dH is the alkalinity expressed as German Hardness, it is 0.022 pH/dH which is different from the 0.03 pH/dH that Kolbach found in his work. But Kolbach's⁶ work measured the pH of the cast out wort and not the pH of the mash. The cast out wort is more dilute and equivalent to a much thinner mash. 3.10 "Mash thickness" Will show that this slope increases as the mash thickness decreases.

3.7 The effect of calcium and magnesium in the brewing water

Calcium and magnesium are known to affect mash pH though acidic reactions with malt phosphates. These reactions are the basis of Kolbach's concept of residual alkalinity. To evaluate the effects of calcium and magnesium, two series of 12 mashes each were done with Pilsner malt. The first series evaluated the effect of calcium and the second series evaluated the effect of magnesium.

For the calcium series waters with different alkalinity and calcium concentrations were prepared. The results are shown in Figure 10 and Table 6.

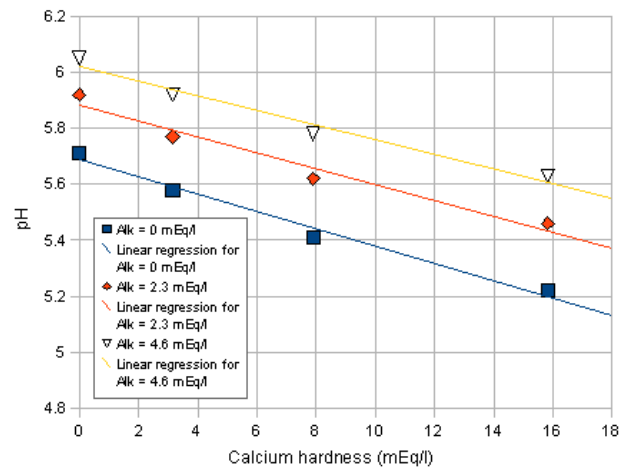


Figure 10: mash pH as a function of the calcium content of the brewing water (pulverized grist, mash thickness 4 l/kg, 10 min at 63 C).

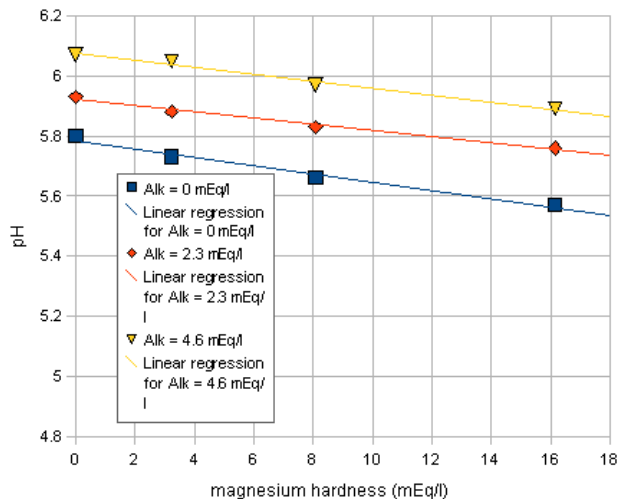


Figure 11: pH over the magnesium hardness of the brewing water for waters with 3 different alkalinities (Pilsner malt, pulverized grist, mash thickness 4 l/kg, 10 min at 63 C).

By expressing the calcium content of the brewing water as mEq/l, which is the unit of alkalinity, the slope of the pH decrease with increasing calcium content was found as:

mEq Ca to neutralize			
Alkalinity (mEq/l)	pH·l·mEq ⁻¹	r ²	1 mEq alkalinity
0	-0.031	0.984	2.6
2.3	-0.028	0.965	2.8
4.6	-0.026	0.971	3.1
average	-0.028		

6 Paul Kolbach, *Der Einfluss des Brauwassers auf das pH von Würze und Bier*, Monatszeitschrift für Brauerei, Berlin 1953, Translation by A.J.deLange available at:
http://ajdel.wetnewf.org:81/Brewing_articles/KolbachPaper.pdf



In in these experiments average pH over alkalinity slope for constant concentrations of calcium was $0.080 \text{ pH} \cdot \text{l} \cdot \text{mEq}^{-1}$ which is different to the $0.061 \text{ pH} \cdot \text{l} \cdot \text{mEq}^{-1}$ that was found in 3.6 “The effect of water alkalinity“. It is possible that Calcium has an effect on that relationship as well it addition to its own pH lowering properties. This has not been investigated further.

Based on that average $\text{pH} \cdot \text{l} \cdot \text{mEq}^{-1}$ slope, that was found during these experiments for waters with the same calcium content, 2.6 – 3.1 equivalents of calcium are needed to neutralize one equivalent of alkalinity. This is similar to Kolbach's results, who found that $3.5 \text{ mEq} \cdot \text{l}^{-1}$ calcium neutralize $1 \text{ mEq} \cdot \text{l}^{-1}$ alkalinity. DeLange showed that the amount of calcium needed to neutralize 1 equivalent depends on the phosphate concentration⁷ which is dependent on mash thickness.

The results were similar for magnesium with the difference that the pH lowering effect of magnesium is only half that of calcium. Figure 11 and Table 7 show the results. The s_{pH} slope for waters with the same calcium content in these experiments was $0.067 \text{ pH} \cdot \text{l} \cdot \text{mEq}^{-1}$. This is fairly close to the $0.061 \text{ pH} \cdot \text{l} \cdot \text{mEq}^{-1}$ that was found in 3.6 “The effect of water alkalinity“.

The following slopes were determined for the relationship between the magnesium hardness and the mash pH:

mEq Mg to neutralize			
Alkalinity (mEq/l)	$\text{pH} \cdot \text{l} \cdot \text{mEq}^{-1}$	r^2	1 mEq alkalinity
0	-0.014	0.980	4.8
2.29	-0.010	0.985	6.5
4.57	-0.012	0.985	5.7
average	-0.012		

Depending on the water's alkalinity it took 4.8 to 6.7 equivalents of Magnesium to neutralize one equivalent of alkalinity. Which is again close to the 7 that were reported by Kolbach.

Within the errors of measurement, Kolbach's findings that that magnesium is about half as effective as calcium in neutralizing alkalinity and lowering pH, have been confirmed.

3.8 Source of Alkalinity

So far, the source of brewing water alkalinity was sodium bicarbonate (NaHCO_3). But earlier experiments with suspended vs. dissolved chalk in the brewing water showed

differences in the resulting mash pH⁸ between the two. This topic was explored in more detail with the following set of experiments. Chalk was suspended in distilled water at a concentration of $\sim 1200 \text{ mg/l}$. This chalk suspension was divided into two vessels while maintaining an even distribution. One vessel was pressurized with CO_2 and shaken to dissolve that CO_2 in the water. Following a rest the chalk dissolved and the water cleared. Any chalk that didn't dissolve settled at the bottom. During the test the clear liquid was decanted and used to prepare waters of different chalk concentrations through the addition of varying amounts of distilled water.

To verify the alkalinity of the produced waters (with suspended chalk and with dissolved chalk) samples of both waters were titrated to a pH of 4.3 with HCl of known concentration. The following alkalinity values were found:

	calculated alkalinity mEq/l	titrated alkalinity mEq/l
suspended chalk	24.1	22.6
dissolved chalk	24.1	23.4

Both samples titrated to the same alkalinity within the expected error of measurement. The sample with the suspended chalk showed a slower pH response to the addition of HCl since the chalk had to be dissolved by the acid.

The experiments were done with Weyermann Pilsner malt and a 80/20 mix of Franco Belges light Munich malt and Weyermann CaraMunich II malt.

The results are shown in Figure 12 and Table 8. When chalk is dissolved in water the pH rise is proportional to the chalk concentration in the brewing water. If chalk is not dissolved it is less effective in raising the mash pH and the slope flattens out at concentrations higher than 500 mg/l . As a result chalk dissolved with CO_2 has more pH raising potential than chalk suspended in the brewing water or chalk added to the mash.

To compare the residual alkalinity of brewing water prepared with dissolved chalk it was compared to brewing water prepared with sodium bicarbonate. 3.6 “The effect of water alkalinity“ already showed that a nearly linear relationship exists between the alkalinity of brewing water prepared with sodium bicarbonate and the mash pH. Figure 13 compares that relationship between sodium bicarbonate water and dissolved chalk water. The raw data is available in Table 9 and Table 10.

7 A.J. DeLange, Alkalinity, Hardness, Residual Alkalinity and Malt Phosphate: Factors in the Establishment of Mash pH. Copy available at:
http://ajdel.wetnewf.org:81/Brewing_articles/Cerevesia/Final_galley

8 Kai Troester, How much Alkalinity does 1 ppm of chalk really add? (<http://braukaizer.com/lifetype2/index.php?op=ViewArticle&articleId=128&blogId=1>)



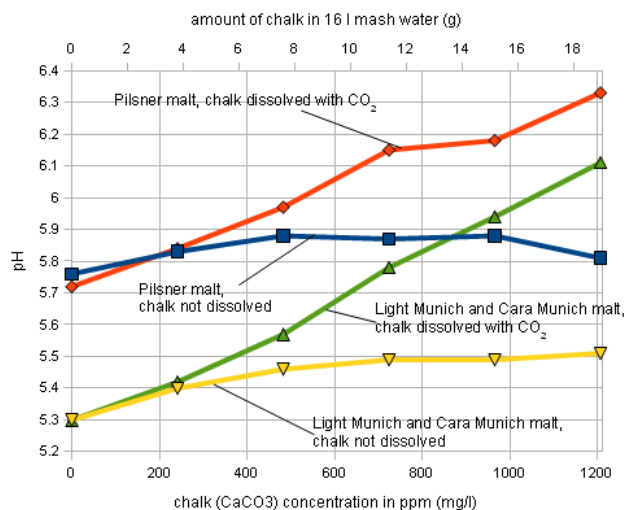


Figure 12: The pH as a function of the Chalk (CaCO_3) concentration in the mash water. Suspended and dissolved chalk data is shown here for the two different grists (100% Weyermann Pilsner and 80%/20% Franco Belges Light Munich/Weyermann CaraMunich II). (pulverized grist, mash temp 68C, mash time 25 min, mash thickness 4 l/kg)

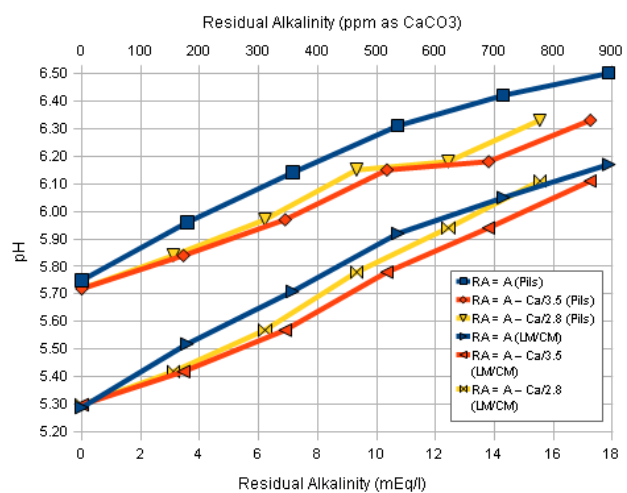


Figure 13: pH vs. residual alkalinity of sodium bicarbonate and dissolved chalk waters. See text for explanation. (100% Weyermann Pilsner malt and 80%/20% Franco Belges light Munich / Weyermann CaraMunich II malt, pulverized grist, mash temp 68C, mash time 25 min, mash thickness 4 l/kg)

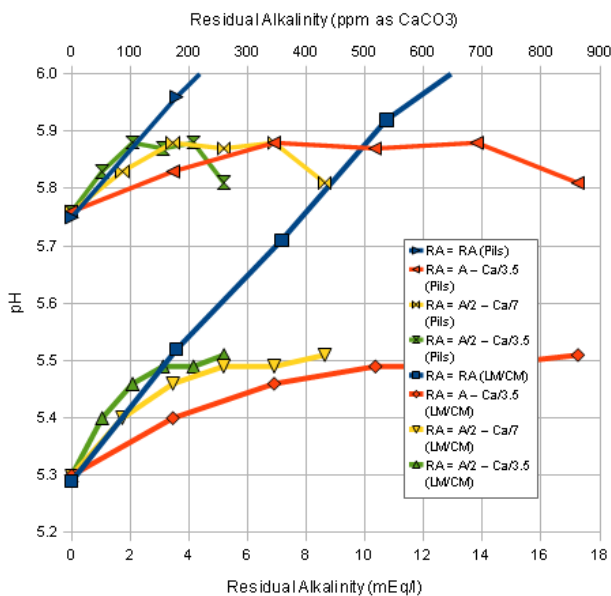


Figure 14: pH for waters prepared with sodium bicarbonate and waters prepared with suspended chalk. (100% Weyermann Pilsner malt and 80%/20% Franco Belges light Munich / Weyermann CaraMunich II malt, pulverized grist, mash temp 68C, mash time 25 min, mash thickness 4 l/kg)

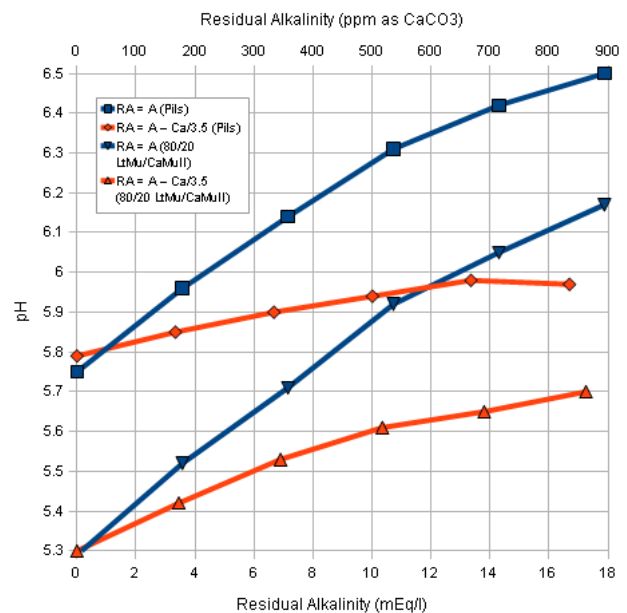


Figure 15: pH for mashes prepared with sodium bicarbonate ($\text{RA}=\text{A}$) or sodium bicarbonate and calcium chloride waters ($\text{RA}=\text{A}-\text{Ca}/3.5$) (100% Weyermann Pilsner malt and 80%/20% Franco Belges light Munich / Weyermann CaraMunich II malt, pulverized grist, mash temp 68C, mash time 25 min, mash thickness 4 l/kg)

RA = A labels the data for the sodium bicarbonate water. Since it doesn't contain any calcium or magnesium, its residual alkalinity equals the alkalinity contributed by the bicarbonate. Chalk, however, also adds calcium in addition to alkalinity and its residual alkalinity, as defined by Kolbach, is $RA = A - Ca/3.5$. In addition to that, another variation of the chalk water pH data is plotted. 3.7 "The effect of calcium and magnesium in the brewing water" showed that the alkalinity neutralizing power of calcium is about 1/2.8 its molar concentration. Hence a graph assuming $RA = A - Ca/2.8$ is plotted as well. For the Pilsner malt grist this assumption ($RA = A - Ca/2.8$) was a better fit to the sodium bicarbonate curve while for the Light Munich / CaraMunich grist the assumption $RA = A - Ca/3.5$ was a better fit. The following slopes (unit $\text{pH} \cdot \text{l} \cdot \text{mEq}^{-1}$) were determined from the data

	NaHCO_3	$\text{CaCO}_3 + \text{CO}_2$
	$RA = A$	$RA = A - Ca/3.5$ $RA = A - Ca/2.8$
100% Pilsner	0.042	0.035 0.039
80/20% Lt Munich/CaraMunich	0.050	0.048 0.054

The same comparison with sodium bicarbonate water was done for suspended chalk waters. Since no CO_2 was used to dissolve the chalk the majority of the chalk remained undissolved in the brewing water. Only the amount that could be dissolved by the atmospheric CO_2 had a chance to dissolve. This amount was considered small and neglected in these experiments.

The results are shown in Figure 18, Table 11 and Table 12.

As seen before, suspended chalk is not able to raise the pH above a certain threshold. That threshold, however, correlates with the distilled water mash pH and thus the grist composition and not the actual pH of the mash. This indicates that it is a function of the chalk concentration and not the mash pH.

There is some ambiguity around the alkalinity and residual alkalinity that is contributed by undissolved chalk. Most spreadsheets used by home brewers, assume that chalk contributes only half its alkalinity potential to the mash (i.e. the addition of 100 ppm CaCO_3 results in an alkalinity of only 50 ppm as CaCO_3). To evaluate that, the curves for suspended chalk have been plotted for 3 different residual alkalinity formulas:

$RA = A - Ca/3.5$: In this case 100 ppm of suspended chalk actually contribute 100 ppm of alkalinity as CaCO_3 or 2 mEq/l and all of its calcium takes part in the alkalinity neutralizing reaction where it takes 3.5 equivalents of calcium to neutralize 1 equivalent of alkalinity (Kolbach's data)

$RA = A/2 - Ca/3.5$: In this case 100 ppm of suspended chalk contribute only 50 ppm alkalinity as CaCO_3 or 1 mEq/l. But since only half the alkalinity is contributed it is assumed that only half the calcium takes part in the alkalinity reducing reaction. This is what is assumed by most (home) brewing water calculation spreadsheets.

$RA = A/2 - Ca/7$: In this case 100 ppm of suspended chalk contribute only 50 ppm alkalinity as CaCO_3 or 1 mEq/l. But since only half the alkalinity is contributed it is assumed that only half the calcium takes part in the alkalinity reducing reaction. Instead of 3.5 equivalents it takes 7 equivalents of calcium to neutralize 1 equivalent of alkalinity.

While the data is not precise enough to confirm this, it appears as if up to a residual alkalinity contribution of ~3-4 mEq/l only half the chalk's alkalinity and half its calcium should be considered in residual alkalinity calculations (i.e. $RA = A/2 - Ca/7$).

The surprising data for suspended chalk needed some further investigation. For that a strong sodium bicarbonate solution (3970 ppm NaHCO_3) and a strong calcium chloride solution (3570 ppm $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) were prepared. These solutions were mixed to produce a water profile that matched the alkalinity and calcium content of the dissolved chalk water that was prepared for the earlier experiments. Upon standing it was apparent that this resulting water was over saturated with CaCO_3 since a precipitate was forming and settling.

The results are shown in Figure 15, Table 12 and Table 13. A curve similar to what was observed for suspended chalk can be seen for water prepared with sodium bicarbonate and calcium chloride. There are some irregularities that were not investigated further. The curve for the Pilsner malt grist and the $\text{NaHCO}_3 + \text{CaCl}_2$ water is flatter than the one for the Munich/CaraMunich malt grist. One explanation is, that the $\text{NaHCO}_3 + \text{CaCl}_2$ water mix for the Pilsner malt experiments was prepared more than 24 hrs before the experiment and had more time to precipitate chalk while the water for the Munich/CaraMunich malt experiments was mixed within 20 min of the experiment and had less time to precipitate chalk. The waters for these experiment were created by preparing a batch of mixed NaHCO_3 and CaCl_2 water and then diluting that batch with distilled water to create water samples of desired strength.

Another irregularity is apparent if the data from these experiments is compared with the data from 3.7 "The effect of calcium and magnesium in the brewing water". Those experiments also used sodium bicarbonate and calcium chloride to create specific brewing water samples but the pH over RA slope was steeper and matched that of just sodium bicarbonate water. At this point it is assumed that



the lower concentrations of ions, that were mixed during these experiments, may not have caused chalk to precipitate.

Two mash samples of the last experiments were titrated with sodium hydroxide to determine their buffer strength. Sample C was part of the sodium bicarbonate series for the light Munich / CaraMunich grist and had a mash pH of 5.75 at an alkalinity of 7.15 mEq/l. Sample L was part of the $\text{NaHCO}_3 + \text{CaCl}_2$ series for the same grist. It's mash pH was 5.7 and the calculated residual alkalinity was ~ 17 mEq/l. Sample C required 2.34 mEq/l sodium hydroxide to reach a pH of 6.0 and sample L required 2.42 mEq/l sodium hydroxide to reach the same pH. This means that both samples had about the same buffer capacity and the flatter pH over RA curve was not the result of a stronger buffer capacity of the mash prepared with $\text{NaHCO}_3 + \text{CaCl}_2$ water.

At this point no explanation can be given for the different pH behavior between waters with dissolved and undissolved chalk. In particular since both waters showed the same alkalinity in titration experiments.

3.9 mash titration

For this experiment a mash sample was prepared with distilled water and 80% Franco Belges Light Munich and

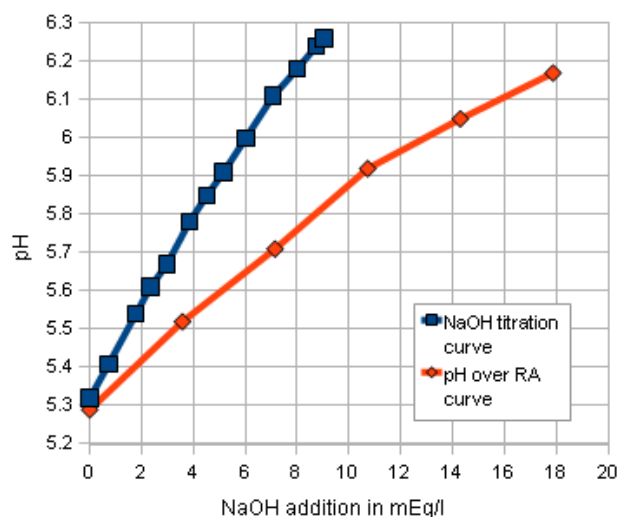


Figure 16: mash titration curve compared to a pH over alkalinity curve. (80%/20% Franco Belges light Munich / Weyermann CaraMunich II malt, distilled water, pulverized grist, mash temp 68C, mash time 25 min, mash thickness 4 l/kg, titration temperature 25 C)

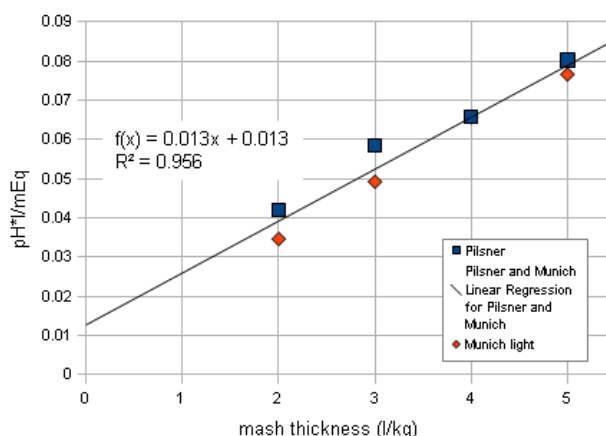


Figure 17: The pH/alkalinity slope (spH) over mash thickness (pulverized grist, 10 min mash at 63 C)

20% Weyermann CaraMunich II malt. The mash thickness was 4 l/kg. 0.1 M sodium hydroxide was used to titrate the cooled mash sample (25 C) to a pH of 6.26. The results are shown in Figure 16 and Table 14.

If this titration curve is expressed as mEq/l where l is the volume of the strike water used in the mash⁹ and plotted together with a pH over alkalinity curve for the same mash, the titration curve has a slope that is about twice as steep as the slope for the alkalinity curve. The slope for the mash titration was found as $0.104 \text{ pH} \cdot \text{l} \cdot \text{mEq}^{-1}$ while the slope for the pH-alkalinity curve was only $0.050 \text{ pH} \cdot \text{l} \cdot \text{mEq}^{-1}$. A similar relationship was found for the pH lowering effect specialty malt malt acidity has.

3.10 Mash thickness

As expected, mash thickness has an effect on mash pH as well. It was evaluated with a 100% Pilsner (Weyermann) and a 100% Light Munich (Franco Belges) grist. The data is shown in Figure 18, Table 16 and Table 15. Just like most of the other results the relationship seems to be linear for both mash thickness and alkalinity within the examined range of parameters. In these experiments the water did not contain any calcium or magnesium.

The higher the residual alkalinity of the water, the more does mash thickness affect mash pH. Since they contain more water per malt and therefore more alkalinity per unit of malt, thinner mashes show a higher mash pH than thick mashes for waters with the same alkalinity. The slope of that pH increase over the increase of the mash thickness is similar between Pilsner and Munich malt mashes. Mashes

⁹ The amount of water added by the sodium hydroxide solution was neglected for simplicity.

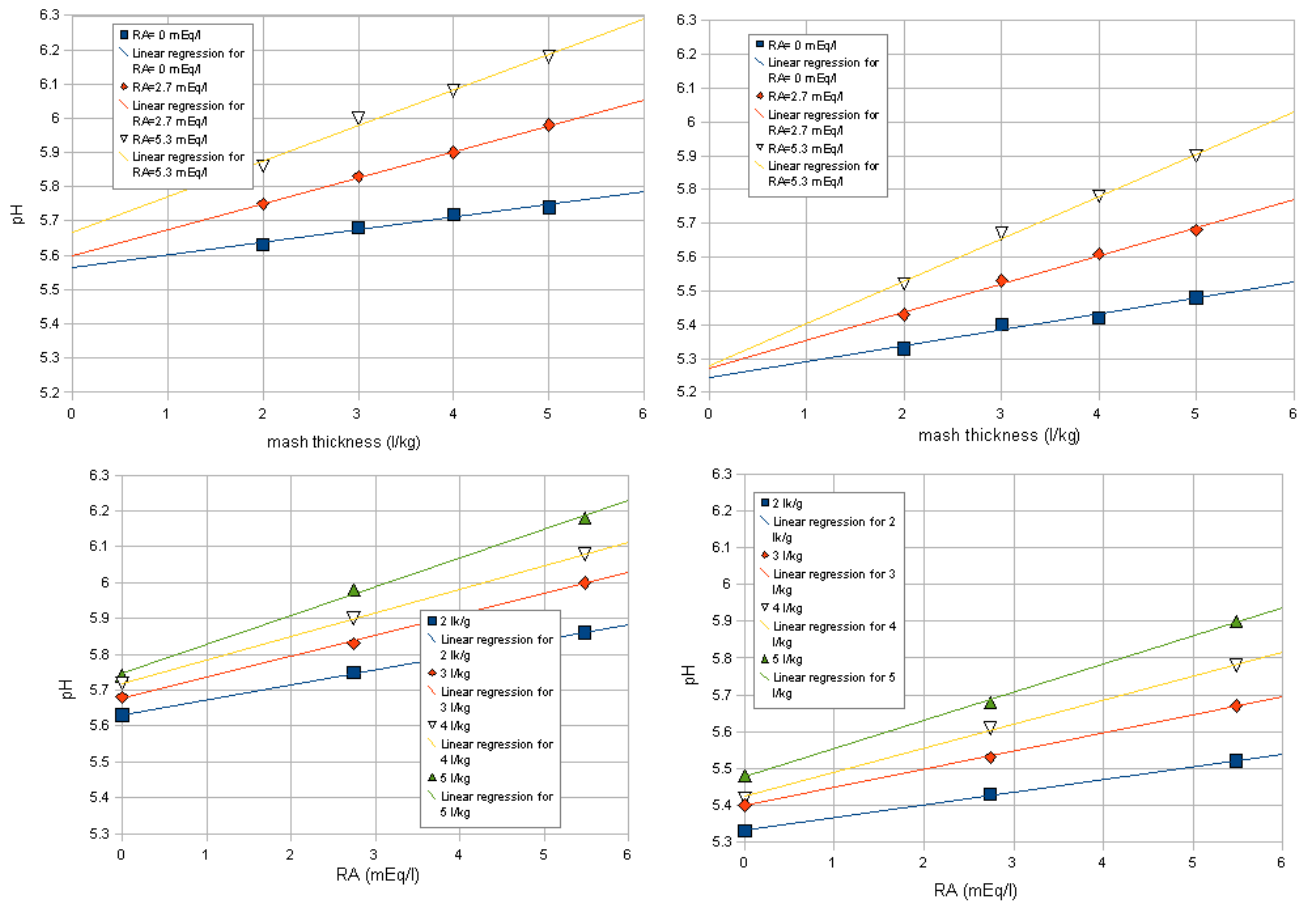


Figure 18: mash thickness and pH. Graphs showing the reaction between Pilsner malt (left hand side), light Munich malt (right hand side) and waters with varying residual alkalinity. The top graphs show the dependency between mash thickness and mash pH for different RA waters while the bottom charts show the dependency between residual alkalinity for different mash thicknesses. (pulverized grist, 10 min mash at 63 C)

with specialty malts were not evaluated but are expected to behave similar based on the observation made in Figure 9.

Conversely, the thicker the mash the less effect does a change in alkalinity have on mash pH. I.e. mash thickness affects s_{pH} , the $pH \cdot l \cdot mEq^{-1}$ slope that is used to predict mash pH changes from (residual) alkalinity changes. For the four mash thicknesses evaluated, the following pH over mEq/l slopes were determined:

mash thickness l/kg	Munich light		Pilsner	
	$pH \cdot l / mEq$	pH / dH	$pH \cdot l / mEq$	pH / dH
2	0.035	0.012	0.042	0.015
3	0.049	0.018	0.058	0.021
4	0.066	0.023	0.066	0.023
5	0.077	0.027	0.080	0.029

which can be approximated with the following equation (Figure 17):

$$s_{pH} = 0.013 \cdot R + 0.013$$

where

s_{pH} : the pH over alkalinity slope in $pH \cdot l \cdot mEq^{-1}$

R : mash thickness in l/kg

Kolbach's work showed showed a slope of 0.03 pH/dH or 0.084 $pH \cdot l \cdot mEq^{-1}$. In these experiments this matched the data for mashes with a mash thickness of about 5 l/kg. In contrast to this analysis, Kolbach's work focused on a 12 Plato cast out wort pH. This is a wort that is more dilute than a mash and would be equivalent to much thinner



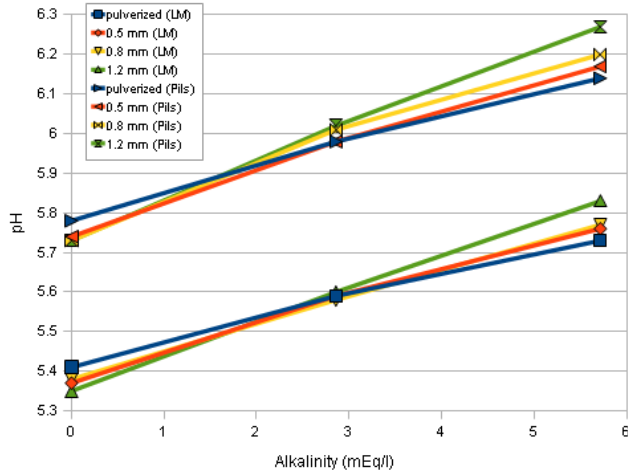


Figure 19: pH over brewing water alkalinity for malt milled at different mill gap settings. Weyermann Pilsner malt (Pils) and Franco Belges Light Munich (LM) were evaluated. A mill gap setting of 0 mm refers to pulverized grist (water prepared with NaHCO_3 , mash temperature 63 C, mash time 10 min, mash thickness 4 l/kg)

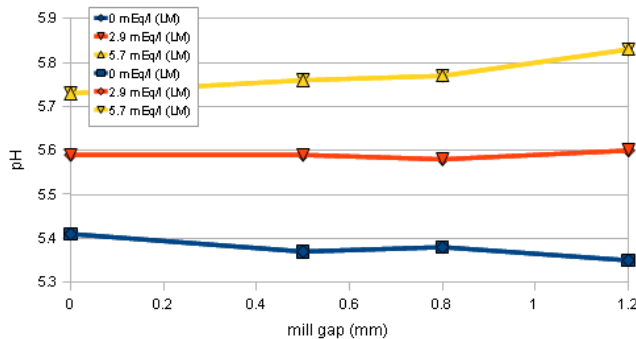


Figure 20: pH over mill gap setting for waters with 3 different alkalinity values. A mill gap of 0 mm refers to a pulverized grist. (Franco Belges Light Munich, water prepared with NaHCO_3 , mash temperature 63 C, mash time 10 min, mash thickness 4 l/kg)

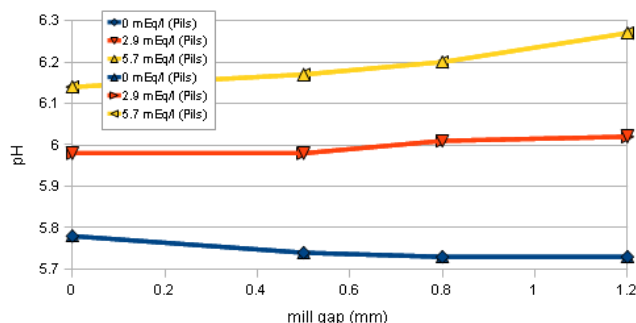


Figure 21: pH over mill gap setting for waters with 3 different alkalinity values. A mill gap of 0 mm refers to a pulverized grist. (Weyermann Pilsner, water prepared with NaHCO_3 , mash temperature 63 C, mash time 10 min, mash thickness 4 l/kg)

mashes.

3.11 Grist preparation

So far the experiments have been done with pulverized grists which are not a common form of grist preparation for most breweries. The last series of experiments for this paper evaluated the effect that the mill gap setting of a 2-roller mill has on the mash pH of a Pilsner malt (Weyermann) and a Light Munich malt (Franco Belges) grist.

Figures 19, 20 and 21 as well as tables 17 and 18 show the results. The mill gap setting has a slight impact on s_{pH} to the effect that it is flatter for more finely ground grists and steeper for more coarsely ground grists. In particular these values were determined from the data:

	Pilsner Malt	Light Munich
mill gap (mm)	$\text{pH} \cdot \text{l} \cdot \text{mEq}^{-1}$	$\text{pH} \cdot \text{l} \cdot \text{mEq}^{-1}$
0	0.063	0.056
0.5	0.075	0.068
0.8	0.082	0.068
1.2	0.094	0.084

These differences are likely the result of a greater release of buffering compounds from the more finely ground malt which make it more difficult for the water alkalinity to raise the mash pH.

The distilled water mash pH of more finely ground malt tends to be slightly higher than that of coarsely ground malt. This might not always be true and the result of measurement errors. It could, however, be explained through the assumption that acidic compounds are more readily released from the malt compared to strongly buffering compounds that reside in the endosperm and whose release into the mash depends on the accessibility of that endosperm to the mash liquid.

4 Conclusion

Investigation of a number of parameters that affect mash pH in brewing showed that the relationships commonly used for predicting mash pH are based on a misinterpretation of Kolbach's work who evaluated the effect of brewing water composition on a cast out wort of 12 Plato.

But it has been shown that Kolbach's findings still apply qualitatively and that his definition of residual alkalinity is close to the observations made in the experiments conducted for this paper. In particular it was demonstrated to what extent calcium and magnesium reduce the mash pH

through acidic reactions with the malt. In these reactions calcium is twice as effective than magnesium. In addition to that the relationship between mash pH and alkalinity is linear over the range that was evaluated and is of interest in brewing practice. This allows for a prediction of the pH change based on the water's alkalinity as well as calcium and magnesium content. The slope of that linear function depends on mash thickness and to a lesser extend on grist preparation.

When chalk is added to the brewing water or the mash, it needs to be dissolved with CO₂ in order to contribute its full alkalinity potential. If that is not done or chalk is allowed to precipitate from the water it loses its effectiveness at higher concentrations. Without being dissolved Chalk additions past 500 ppm have little or no effect on mash pH

The grist composition effects mash pH as well. In general, the higher the weighted average color of the malts used in

the grist, the lower the mash pH. A number of exceptions however exist to this rule. Some base malts which are lighter in color may have a lower mash pH than darker base malts.

Specialty malts reduce the mash pH by contributing acidity to the mash. When tested and put in relation to the malts color, crystal malts have more acidity per unit of color than roasted malts. All the roasted malts that were tested, showed nearly the same acidity while having a fairly wide range of colors.

While additional work is needed to confirm the results from these small scale mashing experiments in large scale mashes, sufficient data has been presented in order to give the interested brewer guidance in estimating a mash pH based on a given grist composition and brewing water composition or the expected change of mash pH based on grist and/or brewing water changes.



5 Appendix

5.1 Tables

short name	maltster	lot number	color (EBC)
Pilsner (W1)	Weyermann	J47E (WEY)	3.5±1
Munich II	Weyermann	J33A (WEY)	25±3
Maris Otter Pale (F&S)	Tomas Facett & Son	TF&S 293	4.63±0.5
Munich I	Weyermann	I34A (WEY)	15±3
6-row	Briess	Briess	3.57±1
Pilsner (BM)	Best Malz	Best Malz KG20080364	3.8±0.2
Wheat	Weyermann	J088 (WEY)	4±1
2-row	Rahr	Rahr	3.57±1
Munich Light (FB)	Franco Belges	Franco Belges	17.35±2
Pilsner (W2)	Weyermann	J10F (WEY)	3.5±1
Vienna	Weyermann	J33A (WEY)	7.5±1.5

Table 1: Base malts used for the experiments

malt name	malt color (EBC)	distilled water pH
Pilsner (W1)	3.5±1	5.76
Munich II	25±3	5.43
Maris Otter Pale	4.63±0.5	5.77
Munich I	15±3	5.3
6-row	3.57±1	5.79
Pilsner (BM)	3.8±0.2	5.73
Wheat	4±1	6.04
2-row	3.57±1	5.56
Munich Light (FB)	17.35±2	5.46
Pilsner (W2)	3.5±1	5.75
Vienna	7.5±1.5	5.56

Table 2: Results of the base malt and distilled water mash pH experiments (pulverized grist, mash temp 63 C, mash time 10 min, mash thickness 4 l/kg)

RA (dH)	RA (mEq/l)	100% Pilsner pH	50% Pilsner, 50% Munich I pH	85% Pilsner, 15% CaraMunich II pH
-15.75	-5.61	5.2	5.13	5.13
-9.85	-3.5	5.43	5.26	5.27
-4.92	-1.75	5.59	5.4	5.4
0	0	5.74	5.54	5.55
5.02	1.79	5.88	5.67	5.69
10.05	3.58	5.99	5.81	5.81
15.07	5.36	6.11	5.91	5.91
20.09	7.15	6.19	6.01	6.02
25.12	8.94	6.26	6.1	6.09
30.14	10.73	6.33	6.17	6.18
35.16	12.51	6.4	6.26	6.25
40.18	14.3	6.46	6.32	6.29

Table 3: various grists mashed with waters over an extended range of alkalinities (pulverized grist, mash thickness 4 l/kg, 10 min at 63C, water general hardness 0 mEq/l)



malt name	maltster	malt color (EBC)	acidity (mEq/kg)	DI pH	type
Munich II	Weyermann	22 ±3	5.6	5.54	base
Munich I	Weyermann	15 ±2	8.4	5.44	base
Munich Light	Franco Belges	17.35	3	5.62	base
Vienna	Weyermann	7.5 ±1.5	1.6	5.65	base
Cara Munich III	Weyermann	150 ±10	31.2	4.92	crystal
Cara Munich II	Weyermann	120 ±10	49	4.71	crystal
Cara Munich I	Weyermann	90 ±10	22.4	5.1	crystal
Cara Aroma	Weyermann	400 ±50	74.4	4.48	crystal
Crystal 10L	Briess	25.3 ±?	9.6	5.38	crystal
Crystal 20L	Briess	51.8 ±?	14.2	5.22	crystal
Crystal 40L	Briess	104.8 ±?	25.6	5.02	crystal
Crystal 60L	Briess	157.8 ±?	50.4	4.66	crystal
Crystal 90L	Briess	237.3 ±?	45	4.77	crystal
Crystal 120L	Briess	316.8 ±?	46	4.75	crystal
Crystal 150L	Briess	396.3 ±?	59.8	4.48	crystal
roast barley	Briess	793.8 ±?	39.6	4.68	crystal
black patent	Briess	1323.8 ±?	44.8	4.62	roasted
carafa iii	Weyermann	1400 ±100	35.4	4.81	roasted
carafa i	Weyermann	900 ±100	42	4.71	roasted
carafa I (sp)	Weyermann	900 ±100	46.4	4.73	roasted
Buiscuit	unknown	unknown	20.2	5.08	other
Sauermalz	Weyermann	5 ±2	315.2	3.43	other
sauermalz	Weyermann	5 ±2	358.2	3.44	other

Table 4: base and specialty malt titration (pulverized grist, mash thickness 8 l/kg, 10 min at 65 C, cooled to 25 C for titration)

Carafa I special		
grist %	grist color (EBC)	pH
1	11.97	5.71
2	20.43	5.69
4	37.36	5.66
8	71.22	5.61
CaraMunich III		
grist %	grist color (EBC)	pH
6	12.29	5.66
12	21.08	5.58
23	37.2	5.43
45	69.43	5.21
CaraAroma		
grist %	grist color (EBC)	pH
0	3.5	5.75
4	19.36	5.64
8	35.22	5.54
17	70.91	5.36

Table 5: Distilled water mash pH of a pilsner malt grist with 3 different specialty malts. (pulverized grist, mash thickness 4 l/kg, 10 min at 63C)



Alk (mEq/l)	Ca (mEq/l)	pH			
0	0	5.71	Alk = 0 mEq/l	slope	-0.0306
0	3.16	5.58			
0	7.91	5.41			
0	15.82	5.22			
2.29	0	5.92	Alk = 2.3 mEq/l	slope	-0.0282
2.29	3.16	5.77			
2.29	7.91	5.62			
2.29	15.82	5.46			
4.57	0	6.05	Alk = 4.6 mEq/l	slope	-0.0259
4.57	3.16	5.92			
4.57	7.91	5.78			
4.57	15.82	5.63			

Table 6: effect of calcium on the mash pH of a pilsner mash (pulverized grist, mash thickness 4 l/kg, 10 min at 63 C)

GH (mEq/l)	Alk (mEq/l)	pH			
0	0	5.8	Alk = 0 mEq/l	slope	-0.014
3.23	0	5.73			
8.07	0	5.66			
16.14	0	5.57			
0	2.29	5.93	Alk = 2.3 mEq/l	slope	-0.010
3.23	2.29	5.88			
8.07	2.29	5.83			
16.14	2.29	5.76			
0	4.57	6.07	Alk = 4.6 mEq/l	slope	-0.012
3.23	4.57	6.05			
8.07	4.57	5.97			
16.14	4.57	5.89			

Table 7: pH as a function of magnesium hardness and water alkalinity (Pilsner malt, pulverized grist, mash thickness 4 l/kg, 10 min at 63 C)

100% Pilsner Malt (Weyermann)			89% Light Munich malt (Franco Belges) + 20% CaraMunich II (Weyermann)		
ppm CaCO3	suspended	dissolved	ppm CaCO3	suspended	dissolved
0	5.76	5.72	0	5.3	5.3
241	5.83	5.84	241	5.4	5.42
483	5.88	5.97	483	5.46	5.57
724	5.87	6.15	724	5.49	5.78
965	5.88	6.18	965	5.49	5.94
1207	5.81	6.33	1207	5.51	6.11

Table 8: Brewing water chalk concentration and pH (pulverized grist, mash temperature 68 C, mash time 25 min, mash thickness 4 l/kg)

NaHCO ₃ water		CaCO ₃ + CO ₂ water			
RA = A	pH	RA = A – Ca/3.5	pH	RA = A – Ca/2.2	pH
0.0	5.75	0.0	5.7	0.0	5.7
3.6	5.96	3.5	5.8	2.6	5.8
7.2	6.14	6.9	6.0	5.3	6.0
10.7	6.31	10.4	6.2	7.9	6.2
14.3	6.42	13.8	6.2	10.6	6.2
17.9	6.5	17.3	6.3	13.2	6.3

slope (pH*/l/mEq)	0.042	slope (pH*/l/mEq)	0.035	slope (pH*/l/mEq)	0.046
r ²	0.974	r ²	0.982	r ²	0.982

Table 9: pH for brewing water prepared with different concentrations of sodium bicarbonate and chalk dissolved with CO₂. (100% Weyermann Pilsner malt, pulverized grist, mash temperature 68 C, mash time 25 min, mash thickness 4 l/kg)

NaHCO ₃ water		CaCO ₃ + CO ₂ water			
RA = A	pH	RA = A – Ca/3.5	pH	RA = A – Ca/2.2	pH
0.0	5.29	0.0	5.30	0.0	5.30
3.6	5.52	3.5	5.42	2.6	5.42
7.2	5.71	6.9	5.57	5.3	5.57
10.7	5.92	10.4	5.78	7.9	5.78
14.3	6.05	13.8	5.94	10.6	5.94
17.9	6.17	17.3	6.11	13.2	6.11

slope (pH*/l/mEq)	0.050	slope (pH*/l/mEq)	0.048	slope (pH*/l/mEq)	0.063
r ²	0.986	r ²	0.995	r ²	0.995

Table 10: pH for brewing water prepared with different concentrations of sodium bicarbonate and chalk dissolved with CO₂. (80% Franco Belges Light Munich / 20% Weyermann CaraMunich II, pulverized grist, mash temperature 68 C, mash time 25 min, mash thickness 4 l/kg)

NaHCO ₃ water		CaCO ₃ water					
RA = RA (Pils)		RA = A – Ca/3.5 (Pils)		RA = A/2 – Ca/7 (Pils)		RA = A/2 – Ca/3.5 (Pils)	
mEq/l	pH	mEq/l	pH	mEq/l	pH	mEq/l	pH
0.0	5.75	0.0	5.76	0.0	5.76	0.0	5.76
3.6	5.96	3.5	5.83	1.7	5.83	1.0	5.83
7.2	6.14	6.9	5.88	3.5	5.88	2.1	5.88
10.7	6.31	10.4	5.87	5.2	5.87	3.1	5.87
14.3	6.42	13.8	5.88	6.9	5.88	4.2	5.88
17.9	6.50	17.3	5.81	8.6	5.81	5.2	5.81

Table 11: pH for 100% pilsner grist and brewing waters prepared with sodium bicarbonate or suspended chalk (pulverized grist, mash temperature 68 C, mash time 25 min, mash thickness 4 l/kg)

NaHCO ₃ water		CaCO ₃ water					
RA = RA (LM/CM)		RA = A – Ca/3.5 (LM/CM)		RA = A/2 – Ca/7 (LM/CM)		RA = A/2 – Ca/3.5 (LM/CM)	
mEq/l	pH	mEq/l	pH	mEq/l	pH	mEq/l	pH
0.0	5.3	0.0	5.30	0.0	5.30	0.0	5.30
3.6	5.5	3.5	5.40	1.7	5.40	1.0	5.40
7.2	5.7	6.9	5.46	3.5	5.46	2.1	5.46
10.7	5.9	10.4	5.49	5.2	5.49	3.1	5.49
14.3	6.1	13.8	5.49	6.9	5.49	4.2	5.49
17.9	6.2	17.3	5.51	8.6	5.51	5.2	5.51

Table 12: pH for 80% light Munich and 20% CaraMunich II grist and brewing waters prepared with sodium bicarbonate or suspended chalk (pulverized grist, mash temperature 68 C, mash time 25 min, mash thickness 4 l/kg)



Pilsner				80% light Munich, 20% CaraMunich II			
NaHCO ₃ water		NaHCO ₃ +CaCl ₂ water		NaHCO ₃ water		NaHCO ₃ +CaCl ₂ water	
RA = A (mEq/l)	pH	RA = A – Ca/3.5 (mEq/l)	pH	RA = A (mEq/l)	pH	RA = A – Ca/3.5 (mEq/l)	pH
0	5.75	0.0	5.79	0	5.29	0.0	5.3
3.58	5.96	3.3	5.85	3.58	5.52	3.5	5.42
7.15	6.14	6.7	5.9	7.15	5.71	6.9	5.53
10.73	6.31	10.0	5.94	10.73	5.92	10.4	5.61
14.3	6.42	13.4	5.98	14.3	6.05	13.8	5.65
17.88	6.5	16.7	5.97	17.88	6.17	17.3	5.7

Table 13: pH for mashes prepared sodium bicarbonate or sodium bicarbonate and calcium chloride waters. (pulverized grist, mash temperature 68 C, mash time 25 min, mash thickness 4 l/kg)

mEq/l	pH		
0	5.32	slope	0.104
0.74	5.41	r ²	0.995
1.78	5.54		
2.34	5.61		
2.98	5.67		
3.84	5.78		
4.52	5.85		
5.16	5.91		
6.02	6		
7.08	6.11		
8	6.18		
8.74	6.24		
9.04	6.26		

Table 14: Mash titration. (80%/20% Franco Belges light Munich / Weyermann CaraMunich II malt, distilled water, pulverized grist, mash temp 68C, mash time 25 min, mash thickness 4 l/kg, titration temperature 25 C)

Pilsner (Weyermann)

GH = 0 mEq/l	mash pH			pH*/mEq	r ²
mash thickness (l/kg)	RA= 0 mEq/l	RA=2.7 mEq/l	RA=5.3 mEq/l		
2	5.63	5.75	5.86	0.042	0.999
3	5.68	5.83	6	0.058	0.999
4	5.72	5.9	6.08	0.066	1.000
5	5.74	5.98	6.18	0.080	0.997

pH/d(l/kg)	0.0370	0.0760	0.1040
r ²	0.9675	0.9993	0.9869
pH at 0 l/kg	5.56	5.6	5.67

Table 15: data for the effect of mash thickness and water alkalinity on the mash pH of a Pilsner malt. (pulverized grist, 10 min at 63 C)



Munich Light (Franco Belges)

GH = 0 mEq/l	water			pH*/mEq	r ²
mash thickness (l/kg)	RA= 0 mEq/l	RA=2.7 mEq/l	RA=5.3 mEq/l		
2	5.33	5.43	5.52	0.035	0.999
3	5.4	5.53	5.67	0.049	1.000
4	5.42	5.61	5.78	0.066	0.999
5	5.48	5.68	5.9	0.077	0.999

pH*kg/l	0.0470	0.0830	0.1250
r ²	0.9625	0.9934	0.9955
pH at 0 l/kg	5.24	5.27	5.28

Table 16: data for the effect of mash thickness and water alkalinity on the mash pH of a Light Munich malt. (pulverized grist, 10 min at 63 C)

Alkalinity	mash pH for Franco Belges Light Munich			
mEq/l	pulverized (LM)	0.5 mm (LM)	0.8 mm (LM)	1.2 mm (LM)
0	5.41	5.37	5.38	5.35
2.86	5.59	5.59	5.58	5.6
5.71	5.73	5.76	5.77	5.83
pH*/mEq	0.056	0.068	0.068	0.084
R ²	0.995	0.995	1.000	0.999

Table 17: mash pH for different mill gap settings and water alkalinities for a Franco Belges Light Munich grist (water prepared with NaHCO₃, mash temperature 63 C, mash time 10 min, mash thickness 4 l/kg).

Alkalinity	mash pH for Weyermann Pilsner			
mEq/l	pulverized (Pils)	0.5 mm (Pils)	0.8 mm (Pils)	1.2 mm (Pils)
0	5.78	5.74	5.73	5.73
2.86	5.98	5.98	6.01	6.02
5.71	6.14	6.17	6.2	6.27
pH*/mEq	0.063	0.075	0.082	0.095
R ²	0.996	0.996	0.988	0.998

Table 18: mash pH for different mill gap settings and water alkalinities for a Weyermann Pilsner malt grist (water prepared with NaHCO₃, mash temperature 63 C, mash time 10 min, mash thickness 4 l/kg).

used for	DI water weight	NaHCO ₃	CaCl ₂ *2H ₂ O	MgSO ₄ *7H ₂ O	CaCO ₃	total hardness	Alkalinity	titrated alkalinity
	g	g	g	g	g	mEq/l	mEq/l	mEq/l
The effect of calcium	1005		2.34			31.64		
mash thickness	1022	1.57					18.27	18.94
the effect of calcium and magnesium	1384	1.33					11.43	11.97
alkalinity sources	1461				1.55	21.15	21.2	19.99
alkalinity sources	2429				1.55	12.75	12.72	12.22
extended alkalinity range	1500	2.21					17.88	18.05
alkalinity sources	403.2	1.6					47.22	37.6
alkalinity sources	403.2		1.44			48.44		
alkalinity sources	1500				1.81	24.06	24.12	22.62
alkalinity sources	1500				1.81	24.06	24.12	23.37
the effect of magnesium	502			2		32.28		

Table 19: The different batches of brines used to create the waters used in the experiments

