

The Influence of Brewing Water on the pH of Wort and Beer

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While at the October 1951 congress of the VLB I set forth, in terms of the state of knowledge of the day, the pH values in wort and beer which brewers should strive to achieve, today I would like to consider the possibility of pH regulation within the framework of the Reinheitsgebot in the course of which I will take up the effects of brewing water.

The Residual Alkalinity of Brewing Water

Water contains three ions which influence the pH of wort: bicarbonate, calcium and magnesium. The bicarbonate ion has a pH raising effect, the other two lower it. The pH lowering effect of magnesium ions is only half that of calcium ions. Depending on the ratio of the water's content of bicarbonate on the one hand and calcium and magnesium on the other, the pH raising effect of the bicarbonate is more or less compensated or balanced. Thus experiment has shown that to balance 1 equivalent of bicarbonate ion 3.5 equivalents of calcium ion or 7 equivalents of magnesium ion are required. With respect to the pH raising property of the total alkalinity of the brew water, thus, a definite part is balanced. The remainder, the residual alkalinity, can serve as a measure of the pH raising effect of the water.

Because the "Wochenschrift für Braueri 1941, Nr. 44" in which the calculation of residual alkalinity was explained is no longer available in many breweries I will give here an example calculation. We take here the well water of Dortmund which belongs to the group of historically important brewing waters. It contains 16.8° temporary and 25.2° permanent hardness which means that the total alkalinity, expressed in German degrees [1 German degree, dH, is equal to 0.3574 mEq/L or 17.1 ppm as calcium carbonate¹], is the same as the temporary hardness. In this case the temporary hardness can be used as a measure of the bicarbonate ion content. Furthermore, Dortmund water contains 367 mg

¹ Comments such as this enclosed in brackets are supplied by the translator to help the reader with German brewing units of measure and terms which may not be familiar to the English language reader

CaO and 35 mg MgO per liter i.e. the calcium hardness is $367/10 = 36.7^\circ$ and the magnesium hardness $38 \times 1.4/10 = 5.3^\circ$. Because a degree of magnesium hardness has only half the effect of a degree of calcium hardness one can calculate the pH reducing effect of magnesium in terms of calcium hardness by division by 2. 5.3° magnesium hardness is thus equivalent to $5.3/2 = 2.7^\circ$ calcium hardness. The sum “calcium hardness + 1/2 magnesium hardness” = the effective hardness. This becomes here $36.7 + 2.7 = 39.4^\circ$. A degree of total alkalinity will be balanced by 3.5° of calcium value. The balanced alkalinity thus amounts to $39.4/3.5 = 11.3^\circ$. The total alkalinity of 16.8° diminished by the balanced alkalinity of 11.3° gives the residual alkalinity of 3.5° .

The lower the residual alkalinity, the lower is also the pH of the wort. With a brewing water of residual alkalinity = 0 one obtains a wort with the same pH as with distilled water. There are, however, also waters which contain so much calcium and magnesium ions that the pH-raising effect of bicarbonate ion is more than offset. In these cases a negative residual alkalinity results. Decarbonated waters with substantial permanent hardness often have a negative residual alkalinity. The Dortmund well water can, for example, be easily decarbonated to 2.5° . Thereby will the total alkalinity likewise fall to 2.5° and the decarbonated water will contain just $36.7 - (1.6.8 - 2.5) = 22.4^\circ$ calcium hardness. Because the magnesium hardness is not effected by the decarbonation the new calcium value is $22.4 + 2.7 = 25.1^\circ$ and the balanced alkalinity comes to $25.1/3.5 = 7.2^\circ$. The residual alkalinity of the decarbonated water is therefore $2.5 - 7.2 = -4.7^\circ$. By decarbonating Dortmund water one can prepare a wort whose pH is less than what that of wort made with distilled water would be.

The two computation examples may also be represented in tabular form:

Dortmund Well Water

	Before Decarbonation	After Decarbonation
Temporary Hardness, °dH	16.8	2.5
Permanent Hardness, °dH	25.2	25.2
CaO mg/L	367	224
MgO mg/L	38	38
Total Alkalinity, °dH	16.8	2.5
Calcium Hardness, °dH	36.7	22.4
Magnesium Hardness	5.3	5.3
Calcium Value, °dH	39.4	25.1
Balanced Alkalinity, °dH	11.3	7.2
Residual Alkalinity	5.5	-4.7

It has already been implied that the temporary hardness is not always equal to the total alkalinity. In waters with small temporary hardness which are the so called sodium bearing waters the total alkalinity is greater than the temporary hardness. Brewing water technical analyses should, therefore, contain the total alkalinity or rather a value from which the total alkalinity in °dH can be calculated for example the methyl orange

alkalinity (= cc n/10 HCl used in the titration of 100 cc of the water [sample] against methyl orange) From the methyl orange alkalinity one obtains the total alkalinity in °dH by multiplication by 2.8.

The pH of Wort

We have seen that the pH of wort is dependent on the residual alkalinity of the water. It remains to find a numerical relationship between the residual alkalinity and the pH of wort.

From experience there are insufficient experimental results for us to be able to indicate to at least some extent precisely how much the pH of the wort changes when the residual alkalinity changes by a particular amount. We have, however, earlier (3) carried out laboratory experiments with various waters from which the influence of residual alkalinity on wort pH was determined with tolerable accuracy. It must, at the same time, be considered that one obtains different values according as to whether the pH is measured in the mash, the runnings, the kettle or at knockout. The following comments relate principally to the pH of the wort at knockout as this has the greatest influence over conditions in the fermentation and lagering vessels.

From the previously mentioned laboratory experiments it can be concluded that a water of 10° residual alkalinity raises the pH of a 12°P wort at knockout something like 0.3 when one compares the pH with the pH of a 12°P knockout wort prepared with distilled water. A water with a residual alkalinity of -10° will, by contrast, lower the pH of knockout wort around 0.3. Based on this assertion one can calculate fairly accurately the pH shift that results from a specified change in residual alkalinity. The Dortmund well water, for example, with residual alkalinity of 5.5 would produce a knockout wort whose pH would lie around $0.3 \times 5.5/10 = 0.16$ higher than the pH of a knockout wort that one would obtain with the same malt and the same mash program but with distilled water. The decarbonated Dortmund water with residual alkalinity of -4.7° would, by contrast relative to the pH of a wort from distilled water, cause a pH lowering of about $0.3 \times 4.7/10 = 0.14$. At the same time the decarbonation pH shift amounting to $0.16 + 0.14 = 0.30$ indicates a change in the residual alkalinity of $5.5 + 4.7 =$ around 10°.

It would, naturally, be even more gratifying if we could, on the basis of the residual alkalinity, predict not only the pH shift which would be brought about by a specified water treatment but also the expected pH value itself. But that is, naturally, not possible because the pH of the knockout wort depends not only on the residual alkalinity but also on the malt and mashing program. A rough calculation can be made, however, on the assumption that one would obtain, by brewing a pale malt grist of average composition using a normal decoction mashing program but with distilled water or water of 0 residual alkalinity, a knockout wort of pH 5.50. A residual alkalinity of 5.5 as in Dortmund water, should then give a wort with pH near $5.50 + 0.16 = 5.66$ and a water with residual alkalinity of -4.7, as in decarbonated Dortmund water, a similar wort with pH of about $5.50 - 0.14 = 5.36$.

As I earlier set forth in (1) one obtains in the preparation of the strongly hopped beers in the Pilsner style a pH of about 5.4 in the knockout wort. We come, thus, to the somewhat surprising conclusion that one can, through decarbonation of water with high permanent hardness, reach, without artificial acidulation, the knockout pH values desired with high hop charges. One clearly obtains the same result by the addition of gypsum or calcium chloride to water of low permanent hardness. To reach the residual alkalinity of -4.7° which decarbonated Dortmund water exhibits, one must add to a water which has from its source but 2.5° temporary hardness or which he has brought to 2.5° temporary hardness by decarbonation, enough gypsum or calcium chloride that the permanent hardness is around 22.5° . When, as in the example discussed at the beginning of this paper, the mains water in question has no permanent hardness at all around 54 grams of CaSO_4 or 45 grams of CaCl_2 would be required.

One will naturally only decide to use such additions when he is convinced that he will, by so doing, encounter no brewing problems whatsoever. In my opinion the Dortmunder example speaks directly to this in that the flavor is not degraded in the least. In this context it is interesting to hear that in the USA water is frequently improved through the addition of gypsum. According to Mayer and Laufer(4) one seeks in general a CaSO_4 content in water of 300 mg/L or 30g/hL. The MgSO_4 content should not, by contrast, exceed 100 mg/L. In regard to this it is noteworthy that in the USA it is possible to control the pH of mash or wort by the addition of lactic, sulfuric or hydrochloric acids. We have this possibility [in Germany, because of the brewing laws in place at the time the paper was written] only through the use of lactic acid in the form of Sauermalz [malt which contains about 2% lactic acid as a consequence of the way in which it is prepared] or Sauergut [lactic acid prepared in the brewery by inoculating unhopped wort with lactobacillus].

It is interesting to compare the amount of acid required in acidulation to the amounts of CaSO_4 and of CaCl_2 needed for a pH shift of the same magnitude. According as to whether the acidity of the mash or the wort in the kettle is to be set one chooses, as is well known, between acidulation of the mash and acidulation of the wort. By acidulation of the mash the pH of both runoff and knockout wort are lowered while through acidulation of the wort only the pH of the knockout wort is set lower. The gypsum in the water (or the addition of calcium chloride) afford a combined acidification of the mash and wort because the part of the gypsum which is contained in sparge water acidifies only kettle and knockout wort. One can take the following from the many published sources concerning the relationship between applied acid levels and wort pH:

1. To lower pH in the runoff by 0.1 about 0.54 equivalents of acid must be added to the mash per 100 kg of malt.
2. To lower pH in the knocked out wort by 0.1 about 0.32 equivalents of acid must be added to the kettle wort.

The following table shows required acid additions for an 0.1 pH shift [this table is in part of the document which is very hard to read – the numbers may not be correct]

Acid	Strength	Add to mash, grams	Add to mash, cc	Add to kettle, grams	Add to kettle, cc
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Lactic	100%	58		29	
Lactic	50%	72	60	36	30
Hydrochloric	37%	63	53	32	27
Sulfuric	98%	33	17	16	8

With respect to calcium sulfate and calcium chloride additions to brewing water (strike and sparge) the rates are as follows: For a pH reduction of around 0.1 in runoff about 300 g of CaSO₄ or 250 g of CaCl₂ should be added per 100 kg malt.

For a pH reduction of 0.1 in the knockout wort around 250 g of CaSO₄ or 210 g of CaCl₂ per 100 kg must be added.

100% lactic acid is not stable but one needs the 100% data in order to calculate how much Sauermalz or Sauergut is required for a specified pH drop. With respect to the pH of mash through addition of Sauermaltz, for example, Proteolytmalz [a form of Sauermalz presumably so named because it helps move mash pH into the range where proteolysis is enhanced], a lowering of 0.1 pH requires, for example, about $58/20 = 2.9$ kg of Sauermalz with 2% lactic acid content per 100 kg of mash tun charge.

The neutralization of the carbonate of brewing water by addition of acid, a brewing preparation procedure, which is often applied in foreign countries, constitutes an (indirect) acidulation of mash and wort in which both strike and sparge water are included. According as to whether sulfuric or hydrochloric acid are added either the sulfate or chloride content of the water is increased. The total hardness of the water is not decreased but rather the carbonate hardness is converted to permanent hardness. Decarbonation by acid addition accordingly reduces the residual alkalinity of the water more strongly than decarbonation with lime because the carbonate hardness is removed. The neutralization of Dortmund water to a final assay of 2.5° carbonate hardness gives, for example the following conditions

Parameter	Value
Total Hardness	2.5° dH
Calcium as CaO	367 mg/L
Magnesium, as MgO	38 mg/L
Calcium Hardness	39.4° dH
Residual Alkalinity	-8.8° dH

Had the decarbonation been accomplished with lime the residual alkalinity would be found to be -4.7° as opposed to the -8.8° value in the table.

It is regrettable that this simple decarbonation treatment cannot be used in Germany because the Biersteuergesetz [Beer Taxation Law – derived from the Reinheitsgebot] forbids addition of acid to brewing water. Does an addition of acid to water really violate the spirit of the Reinheitsgebot? Certainly not if the acid level is only sufficient to neutralize the carbonate. The addition of calcium sulfate, for example, to brewing water is permitted, But the addition of sulfuric acid to water containing calcium carbonate

produces nothing except calcium sulfate. As technologists we must, therefore support the idea, that water which is treated with acid with the goal of carbonate neutralization, can be regarded as water in the spirit of the Biersteuergesetz.

The prohibition against the use of neutralized water does not, of course, apply to cleaning water. One might, for example, prevent adsorption of carbonate by filtering material by using decarbonated water is to wash the filter medium. Neutralization with hydrochloric or sulfuric acid is simple and inexpensive. Per degree of carbonate hardness and per hectoliter 3.50 grams corresponding to 2.96 cc of 37% hydrochloric acid or 1.79 grams corresponding to 0.87 cc of 98% sulfuric acid are required.

The pH of Beers

All malt Helles Vollbiers [light colored beers with original extract between 11 and 14° P] usually have a pH between 4.4 and 4.7. The lower the pH is, the better the biological stability. One should, therefore, strive for the lowest pH possible. This is however easier said than done. In particular, it is not possible to lower the pH by means of a simple decarbonation of the brewing water with lime. Such is very frequently said and written but it is not generally accepted as being true. For this reason I would like to approach this question more closely.

The calcium content of the water is reduced during decarbonation. The result of this is reduced precipitation of calcium phosphate in the mash and with it an increase in buffering. The decarbonation also causes a lowering of the pH in the mash and, accordingly, stronger action of phytase and the proteolytic enzymes which then causes an increase in the creation of buffers. Decarbonation with lime thus gives more acidic but more strongly buffered wort. It follows that in wort with lowered pH as in wort from decarbonated water, less acid will be produced during fermentation than in wort from untreated water. In the final analysis one has what we so often experience in practice: beers that barely differ in pH. The example of the original Pilsners proves that the situation is really thus. Pilsner water contains little carbonate hardness and is, with respect to the pH question a mostly carbonate free water with low permanent hardness. The pH of Pilsner knockout wort must, in accordance with the low level of carbonate hardness, be relatively low. The beer has, however, a somewhat high pH: we have, for example, measured 4.57 (6).

Furthermore, the acidification of the mash through acid addition is not a useable means for lowering the pH of the beer. If one mashes with Sauermalz or adds Sauergut to the mash one obtains more acidic knockout wort but the pH of the beer, by contrast, changes little because the more strongly the wort is buffered the lower the pH. This also means that if one adds Sauergut or Sauermalz extract to the wort, i.e., if he acidulates the wort the buffering will not be thereby increased and not only the wort but also the beer will exhibit a lower pH.

In contrast to decarbonation with lime it is possible to lower the pH of beer through the addition of gypsum or calcium chloride to the water. The increase in the calcium hardness reduces, under essentially the same conditions, the buffer content of the wort so that the pH shift caused by the fermentation is increased. The current research is not yet extensive enough to justify a numerical relationship between gypsum and pH value but it is possible to assume that it is quite small within the normal pH range of 4.4 to 4.7. With high gypsum levels it is perhaps possible to reach values of less than 4.4.

Gypsum or calcium chloride addition thus represents a water preparation treatment which merits attention in more than one respect. I would not wish at this point by any means to generally advocate large gypsum additions but it is important to me to point out the relevant possibilities. It is ultimately matters of practice that determine to what extent gypsum has useful effect in beer production. Many things are still problematic. For example one speaker reported observing enhanced flocculation of yeast after gypsum addition. Another brewery wrote to me since then that decarbonation had led to deterioration in flocculation to the point that filtration difficulty was a concern.

References [these are in smaller type and very difficult to read so they are probably incorrect]:

1. P. Kohlbach, Brauerei. Wiss. Beilage 1951, 77
2. P. Kohlbach, Woche. Brauerei 1941, 23
3. P. Kohlbach u. K. Schwabe, Woche. Brauerei 1941, 195
4. Mayer u. Laufer, Erho de la Brasserie 1952 Nr. 3
5. W. Windisch, P. Kohlbach u. F Schild, Woche. Brauerei 1951, 415

Translators' Note: The available original was in the form of pages from the original publication which had been faxed to John Palmer who in turn scanned them and e-mailed the scans as pdf files to me. The resulting second generation images were nearly illegible in most cases and totally illegible in others. Kai Troester was able to decipher several of these which I couldn't and also helped with cleanup of several bits of the translation.

Thanks to Kai!