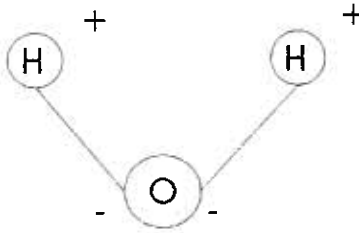


Water II

Presented by: Doug Rhoades

Water is by a wide margin the most abundant beer constituent. Water is an excellent solvent, a fact that is crucial in brewing. Without it, our efforts to dissolve grain constituents in the mash and hop constituents in the kettle boil would be for naught. The key to the solvent properties of water lies in the polarity of the bonds in its molecules. In particular the water molecule H_2O can be represented as follows:



When common salts are dissolved in water, they disassociate into their ions. These ions are held in solution by the polar charges in the water molecule. For instance, sodium chloride disassociates into sodium⁺ and chloride⁻ ions that migrate to the negative and positively charged sides of the water molecules in solution.

Other salts are only partly soluble in water. This is the case of calcium sulfate ($CaSO_4$) for example. Adding it to water will yield disassociated calcium Ca^{++} and sulfate SO_4^- ions held in solution by the above mentioned polar bonding. However, there will also be un-dissolved salts, which typically will precipitate from solution. The total effect is indicated as an equilibrium equation:



Another salt relevant to brewing is magnesium sulfate ($MgSO_4$). It too is only partial soluble:

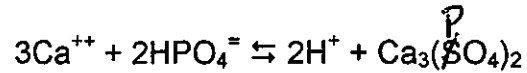


Traditional water analysis has been bedeviled by vague terms like "water hardness," which can mean many different things and can be measured in many different ways. Modern brewing theory has tended to focus on the ions present in water because they can be directly related to specific reactions in brewing, both desirable and undesirable.

Perhaps the most important water ion for brewing is calcium Ca^{++} . Proper enzymatic activity in the mash requires that the pH be within a specific range (5.2 – 5.6). Generally the pH of both malt and water is above the desired range and

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something needs to be done to "sour the mash." A calcium-rich water will do this naturally. The key here is the interaction of calcium ions with phosphates in malt, namely KHPO_4 and KH_2PO_4 . This interaction will liberate hydrogen ions (H^+) and hence reduce pH of the solution according to the following equation:



The most common water salts that contribute calcium ions are calcium sulfate (CaSO_4) and calcium chloride (CaCl_2).

Typically, gypsum salt is used to add calcium to the mash. A point to remember in this regard is that gypsum is not pure calcium sulfate, but also contains hydration water molecules:



That is, gypsum has residual moisture content, commonly called water of hydration. This is created during production of gypsum for the food industry. This moisture content must be taken into account in careful water treatment program.

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As a beginning to this discussion, the molecular weights for various ions and molecules are shown below:

Molecular Weight Table	
Atom (ion)	Molecular Weight
Br ⁻	79.904
C	12.011
Ca ²⁺	40.080
Cl ⁻	35.453
CO ₃ ⁼	60.009
F ⁻	18.998
H ⁺	1.008
H ₂ O	18.015
K ⁺	39.098
Li ⁺	6.941
Mg ²⁺	24.305
N	14.007
Na ⁺	22.990
O ⁼	15.999
P	30.974
S	32.060
SO ₄ ⁼	96.058

One mole of gypsum would contain one mole of calcium, one mole of sulfate and two moles of water. Therefore the molecular weight of gypsum would be:

Ca ⁺⁺	40.08
SO ₄ ⁼	96.0576
<u>2H₂O</u>	<u>36.0304</u>
Total	172.1680

Note that one mole of gypsum weighs about 172 grams and contains 40 grams of calcium ions. Thus, to increase the calcium content of water by 50 mg/l, it is necessary to add:

$$\left(\frac{172}{40}\right)(50) = 215 \text{ mg/l gypsum}$$

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Conversely, adding 100 mg/l of gypsum yields an increase of:

$$\left(\frac{40}{172}\right)(100) = 23.2 \text{ mg/l calcium}$$

$$\left(\frac{96}{172}\right)(100) = 55.8 \text{ mg/l sulfate}$$

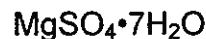
One must of course vigorously stir in the salt to insure that the reaction is driven to completion, as follows:



Epsom salts can be used to increase the magnesium content of the mash. Magnesium ions also play an important role as a cofactor in several enzymatic reactions during fermentation. The desired range is:

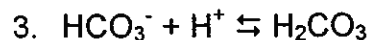
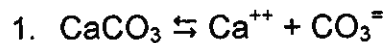
$$\langle \text{Mg}^{++} \rangle = 10 - 15 \text{ mg/l}$$

Concentrations can be determined using the formulas as provided above. Epsom salts have the structure:

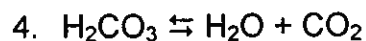


The molecular weight for Epsom salt is 246 g/mole. Since Epsom salts have a pronounced bitterness, excessive amounts can be more harmful than a deficiency of them. Moreover, malt also brings magnesium ions to the mash. Thus only rarely is it necessary to make magnesium corrections.

With some exception, the second task of a rational water treatment program is to ensure that carbonate (and bicarbonate) levels are at appropriately low levels. These ions are normally associated with the salt calcium carbonate (CaCO_3), and react in the following way:



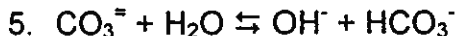
The last compound, carbonic acid (H_2CO_3), is essentially CO_2 via:



Some of the CO_2 may be dissolved in water or evolve as a gas.

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The harmful ions are $\text{CO}_3^{=}$, HCO_3^- . This can be seen from reactions (2) and (3), which can be rewritten as:



These ions tend to promote an increase in pH because hydroxyl ions (OH^-) are liberated and, as noted above, they do this in the mash exactly when it is desirable to reduce the pH to provide a better environment for malt enzymes. Carbonic acid (H_2CO_3 or CO_2), in contrast, is harmless and without significance for the mash.

Alkalinity, like hardness, is an archaic term, yet it does have value for brewers. It is typically measured by titration, and hence reflects the way water will react to the addition of H^+ ions.

The starting point for many treatment procedures is observing that equilibrium in the system depends on pH. The following table summarizes this effect:

pH	% $\text{CO}_3^{=}$	% HCO_3^-	% H_2CO_3
10	32	68	0
9	5	95	0
8	0	97	3
7	0	81	19
6.5	0	58	42
6	0	30	70
5.5	0	12	88
5	0	4	96

The units used in the table are mg/l as CaCO_3 .

Observe that as pH is decreased, more of the harmful material is converted into harmless carbonic acid. To cite an example, suppose we have water with:

Alkalinity = 200 mg/l as CaCO_3 , pH = 8

At this pH, we have:

$$\ll\text{CO}_3^{=}\gg = 0$$

Alkalinity is defined as:

$$7. \text{Alkalinity} = \ll\text{HCO}_3^-\gg + 2\ll\text{CO}_3^{=}\gg + \ll\text{OH}^-\gg - \ll\text{H}^+\gg$$

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By applying the above equation, and assuming the last two terms can be ignored, (since the pH is 8):

$$\ll\text{OH}^-\gg = 10^{-6} \times 10^3 = 0.001 \text{ mg/l as CaCO}_3$$

$$\ll\text{H}^+\gg = 10^{-8} \times 10^3 = 0.00001 \text{ mg/l as CaCO}_3$$

With the above terms being negligible, this will round to:

$$\ll\text{HCO}_3^-\gg = 200 \text{ mg/l as CaCO}_3$$

This calculation is typical in that $\ll\text{OH}^-\gg$, $\ll\text{H}^+\gg$ and $\ll\text{CO}_3^{2-}\gg$ usually can be ignored in salt calculations, and that alkalinity is due primarily to the presence of HCO_3^- ions.

From the table, we see that at a pH of 8, HCO_3^- consists of 97% of the total carbonates (T). This means to say 97% of:

$$T = \ll\text{CO}_3^{2-}\gg + \ll\text{HCO}_3^-\gg + \ll\text{H}_2\text{CO}_3\gg$$

Therefore:

$$T = \frac{\ll\text{HCO}_3^-\gg}{0.97} = \frac{200}{0.97} = 206.2$$

Also:

$$\ll\text{H}_2\text{CO}_3\gg = 206.2 - 200 = 6.2 \text{ mg/l as CaCO}_3$$

Suppose we want to reduce the alkalinity to achieve 20 mg/l. To do this, the pH must be reduced until the HCO_3^- content is less than 20 mg/l. For example, at a pH of 5.5:

$$\ll\text{HCO}_3^-\gg = 0.12T = 0.12 \times 206.2 = 24.7$$

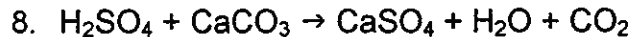
At the same time, this reduction in pH increases the carbonic acid content to:

$$\ll\text{H}_2\text{CO}_3\gg = 206.2 - 24.7 = 181.5$$

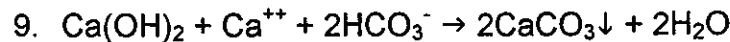
The classic procedure for reducing pH is to add lactic acid ($\text{CH}_3\text{CCHOHCOOH}$) until the desired value is obtained. From the reaction, calcium lactate is formed. It should be noted that two moles of lactic acid would be required to neutralize one mole of CaCO_3 .

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Sulfuric acid is also used to neutralize alkalinity (i.e. CaCO_3). Here the relevant reaction system is:



Here, one mole of sulfuric acid is required to neutralize one mole of CaCO_3 . Another approach would be to use lime (CaOH_2 , calcium hydroxide) to neutralize the ions HCO_3^- according to:



In this case, the salt CaCO_3 is precipitated out of solution. Three points should be made about the above procedures:

- Calcium ions are removed in each method. This must be taken into account.
- None of the procedures fully removes the carbonate material. This means that all of the reactions cited can be reversed, "unmasking" the carbonates.
- The added materials, especially the acids, can affect beer flavors.

Effective procedures for treating alkaline water which avoid some of the above problems are boiling and aeration. The reaction system is:



Here calcium carbonate is precipitated out of solution. In addition, aeration promotes the evolution of CO_2 as a gas. Both heat and aeration are needed to keep the reaction from reversing (giving \rightleftharpoons instead of \rightarrow), where CaCO_3 re-dissolves according to (1) – (3).

In yet another water treatment procedure, some brewers lower the alkaline content by diluting with distilled water. It can be assumed that the effect is proportional because combining 1 liter of water with 1 liter of distilled water will cut the alkalinity in half.

It is important to note that the above discussion of alkalinity is relevant only to mashes containing primarily pale and amber malts. If dark malts are used, at say 10% of the grist, the brewer will typically find no difficulty in establishing a proper mash pH even with highly alkaline water. This is because dark malts have a higher acidity than pale malts, and in this respect, the alkaline water actually provides a favorable environment since it will neutralize some of the excess acidity of the dark malts.

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The measurement of mash pH will vary with respect to temperature in the mash. The following table illustrates this effect:

Temperature (°C)	Temperature (°F)	Mash pH (distilled water)	Mash pH (alkalinity 50 mg/l as CaCO ₃)
18	64.4	5.84	6.03
35	95.0	5.70	5.90
52	125.6	5.65	5.80
65	149.0	5.50	5.70
78	172.4	5.40	5.55

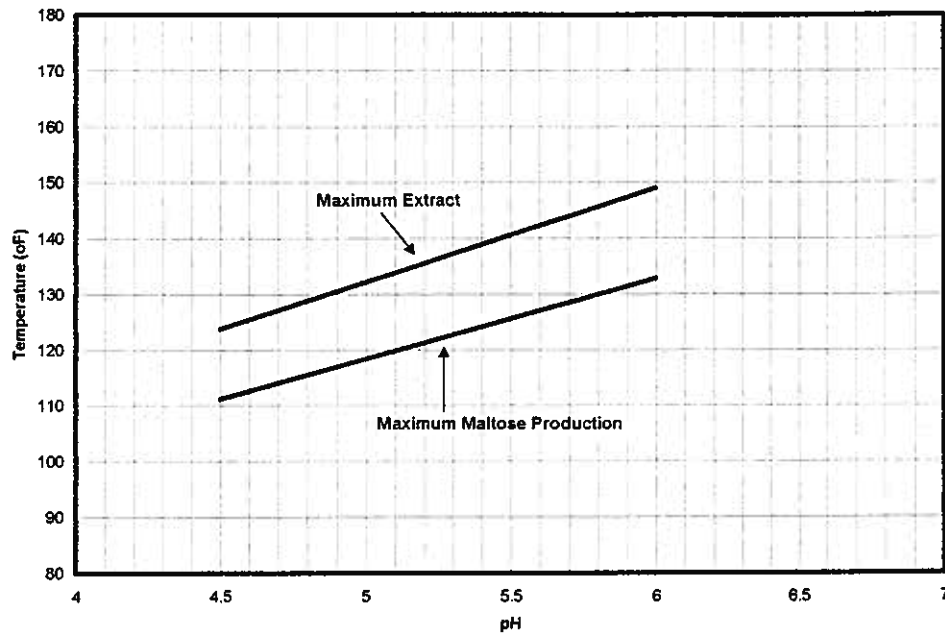
Many mashing systems are used throughout the world. As far as starch conversion is concerned, it is the environment that is created, rather than the way the environment is achieved (decoction or infusion) that is most important. In this regard the following are the most crucial:

- time
- temperature
- pH
- mash thickness

The time-temperature relationship for malt enzymes is the most important of the above listed parameters. The second factor in order of importance is the pH of the mash. It has been shown that the combined action of the amylase enzymes is most effective when the mash pH is in the range of 5.2 to 5.6, with the lower part of this range being preferred.

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In addition, for a given pH there is a temperature range where the best results are obtained. This is illustrated in the chart below.



As the mash pH drops, the desired temperature for maximum conversion is lower. For this reason many traditional mashing systems have used two or more temperature rests in that part of the mash devoted to starch conversion. One rest is typically 130°F to 140°F, which is optimal for amylase activity. During this rest, 70 to 80% of the starch is converted. A second rest in the range of 149°F to 158°F is used to finish off the starch conversion at a faster rate.

Modern brewing practice has emphasized well-modified malt whose starch can be satisfactorily converted at temperatures above optimal amylase activity levels. With these malts only the higher temperature rest is generally used. It must be emphasized that the proportions of sugars formed will depend on the temperature chosen. This is illustrated in the following table.

Carbohydrates expressed as % of wort solids	140 F	151 F	154 F
Maltose	48.3	43.9	37
Trisaccharides	14.3	13.6	12.7
Sucrose	3.4	4.2	5
monosaccharides	10.1	9.5	10.2
Dextrins	15.5	21.2	26.2
% Extract	76.2	75.3	74.6
% Fermentability	76.1	71.2	65.1

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The values of pH reported previously were those measured at the temperature of enzymatic reaction. The extent to which pH will vary with temperature in the mash depends on the alkalinity of the mash water (see chart on page 8).

Some Practical Applications

An important point to remember is that ppm hardness is expressed as if it were calcium carbonate, not that it really is. Both calcium and sulfate content are permanent hardness values. You will not be able to remove calcium using the boiling/aeration procedure mentioned above if there's sulfate present.

If your water is high in hardness and pH is near a normal 7.0, you have lots of permanent hardness. Referring to the mineral needs of certain beer styles, you will be doomed to brew styles of beer such as classic Burton-style ale or Dortmund-style export. You could try a Pilsner, but you will have the characters that sulfates, sodium, chloride and magnesium contribute to the overall character of the beer.

Water with 150 to 200 ppm hardness and pH in the 7.2 and higher range will have quite a bit of detrimental carbonate temporary hardness. Boiling with aeration could help in this case.

A pH higher than 7.5 and hardness greater than 250 ppm indicate that the water has a lot of temporary carbonate/bicarbonate hardness. Only some of it will precipitate out with boiling because there won't be enough calcium to combine with the carbonates to form calcium carbonate as a precipitate. Furthermore, there won't be enough calcium left for necessary reactions during the mash. In this case, you should determine how much food-grade acid (such as phosphoric acid, sulfuric acid or lactic acid) to add to the wort in order to neutralize the carbonates without sacrificing excessive calcium. In some cases calcium sulfate may need to be added.

When to stop sparging?

The quality of an extract will change as it trickles from the lauter-tun. The concentration of sugars decreases as the sparge water dilutes the runoff. Consequently the specific gravity of the runoff decreases. At the same time the pH of the runoff increases. When this occurs, undesirable compounds such as harsh-tasting polyphenols and tannins, haze-forming starch and insoluble proteins, are more easily extracted and brought out of the grain bed and into the brewpot.

For beers requiring a delicate and smooth finish, stop the runoff when the specific gravity falls below 1.008 or pH is greater than 6.0, whichever comes first. For more robust beers or beers not requiring extreme finesse, stop the runoff

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when the specific gravity falls below 1.002 to 1.004 or pH becomes greater than 6.2, whichever comes first.

Generally the pH and the amount of undesirable materials begin increasing dramatically when the runoff is between 1.004 and 1.008 specific gravity. They will really zoom when the specific gravity drops below 1.004.

The above sparge guidelines all assume sparge water of low calcium hardness (0-50 ppm).

What about mash extract procedures?

For those using mash-extract procedures, all of the above still applies. Perhaps even more so in order to keep from releasing tannins. When a relatively small weight of specialty grains is steeped in a large volume of water, the result is a very thin mixture. The pH is only slightly affected by the malt. This means the pH of the solution during steeping will be higher than the pH of a normal mash, which has an oatmeal-like consistency.

To combat this problem the pH of the steep can be adjusted to around 5.4. You will not be able to use gypsum or calcium chloride to lower the pH as all-grain brewers can. These salts lower pH by reacting with phosphates from the malt. Steeping mixtures don't contain much malt and lowering the pH with water salts is difficult to say the least. Again, food-grade lactic, phosphoric or sulfuric acids are alternatives. The key to adding acids is to add them slowly with continual stirring and monitoring of pH.