WATER CHEMISTRY FOR DUMMIES

Colin Weaver, September 2003

INTRODUCTION

No, I'm not insulting my audience, for I am the dummy in the title of this talk. I am by no means an expert on this subject. When I set out to write this, I had only been mashing for 2 months and my knowledge of water chemistry amounted to a few vague facts from reading the odd post on rec.crafts.brewing. Researching to this has been a voyage of discovery, which will ultimately result in better beer. (That's the point, after all!)

When starting mashing, whether as an all-grain brewer or a partial masher, the topic of water chemistry and water adjustment is unavoidably drawn to your attention. If you are lucky and live in an area with relatively benign water, like Brisbane, it is possible to get by with minimal or no adjustment to water without ill effects. My first two all-grain beers were made with no attention to water chemistry other than a quick boil to remove chlorine, and yet acceptable beers resulted. I became interested in water chemistry and pH issues after noticing two defects in these beers: a slight astringency that aged out over time, and thin body with harsh bitterness. Clumsy attempts at correcting these problems with poorly measured doses of *calcium sulphate* (CaS04 - gypsum) resulted in worse beers than my initial attempts at mashing, at which point I decided that a little knowledge is dangerous and set out to learn more.

WHY IS WATER CHEMISTRY IMPORTANT?

Mineral ions, collectively referred to as salts, are present in varying concentrations in most water. These ions have a major effect on the chemistry of the mash, the pH of the wort, and the extraction of bitterness, flavour and aroma compounds from hops. Consequently, the water of historically significant brewing centres like Pilsen, Munich, and Burton-on-Trent has dictated many of the characteristics of the styles brewed there. For example the refined bitterness of a Pilsner derives not just from the finest Saaz hops, but also from soft water with very low concentrations of calcium, sulphate, magnesium, sodium and chloride ions. The same Pilsen water which makes the greatest of all lagers would not make a good Strong Bitter or India Pale Ale; these styles require a much harder water with concentrations of many salts, particularly calcium and sulphate, many times higher than the ideal water for a Pilsner. Yet another water, with different concentrations of these salts, makes superb dry stout in Dublin.

By learning about water chemistry and adjustments, the home brewer can hope to brew the best possible beer with his/her local water, and brewing better examples of specific styles by adjusting the water to suit.

If brewing with water from a regulated supply, the profile for your water is almost certainly available from your council or water authority on request. Here in Brisbane, we are fortunate to have relatively up-to-date reports posted on a Brisbane City Council sponsored web site. The water report for Brisbane is available here:

http://www.ourbrisbane.com/government/watersupply/quality/chemical/

READING A WATER REPORT

On opening a water report you are presented with a bewildering array of detail. Many of the indices and proportions of trace salts are of little relevance, although it is good to know that Brisbane water has reassuringly low levels of arsenic, lead and mercury.

The trace salts that are relevant to brewing are always quoted either as **mg/L (**milligrams per litre), or as **ppm** (parts per million). These two units are equivalent and fully

interchangeable, for example the Brisbane report shows that our water contains 23 mg/L of *calcium* (Ca), which is the same as 23 ppm.

Harness and Alkalinity measurements are quoted "as CaCO3", which means that the hardness or alkalinity contributed by the compound is the same as would be caused by a specific amount of *calcium carbonate* (CaCO3 - chalk). For example, the Brisbane water report shows magnesium hardness (hardness caused by magnesium compounds) as equivalent to 54 mg/L of CaCO3, but the actual concentration of magnesium is much lower. The key hardness and alkalinity measurements are: *total alkalinity as CaCO3*, and *total hardness as CaCO3*. With these measurements, and the levels of key salts, brewing software like BreWater 3.0 can calculate how much acid should be added to achieve a specific water pH, how much calcium carbonate (CaCO3) is likely to be precipitated by pre-boiling the water, and to the level of *carbonate hardness* (CO3) in the water.

The relevant measurements for brewing purposes are the concentrations of *calcium* (Ca), *sulphate* (SO4), *magnesium* (Mg), *sodium* (Na) and *chloride* (Cl). The level of *carbonates* (CO3) in the water is also important, but is rarely listed as such in water reports. Fortunately given the other measurements brewing software can calculate a reasonably accurate value for *carbonate hardness*.

By extracting the relevant values from the Brisbane report into a table including brief descriptions of the effects of the measured quantities, a much more understandable picture emerges:

Test	Units	Effect on Brewing	Ideal brewing range	Brisbane
pH		Astringency from tannin extraction if too high. Sharp sourness if too low.	Should settle in range of 5.2 - 5.4 in mash, rising to no more than around 5.6 during sparge.	7.9
Alkalinity (total)	equivalence to CaCO3 mg/L	Astringency and high mash pH if too high and not balanced with acids.	-	89
Hardness (total)	equivalence to CaCO3 mg/L	Astringency and high mash pH if too high and not balanced with acids	-	110
Calcium (Ca)	mg/L	Aids bitterness extraction from hops, enhances hot and cold break, benefiical to yeast, participates in buffering reaction in mash which helps establish optimal mash pH of 5.2	50 mg/L - 200mg/L. May be lower in Pilsners.	23
Chloride (Cl)	mg/L	Accentuates bitterness and mouthfeel. When combined with sulphate can cause harsh bitterness.	Less than 100 mg/L.	65
Magnesium (Mg)	mg/L	Benefical to yeast in low concentrations, but causes "objectionable" flavours in higher concentrations.	10 mg/L - 30 mg/L	13
Sodium (Na)	mg/L	Enhances malty sweetness.	Less than 100 mg/L.	38
Sulphate (SO4)	mg/L	Accentuates hops, causes dry sharp character.	Less than 100 mg/L, except for Burton-on-Trent pale ales where it may be as high as 700 mg/L.	22
Carbonates (CO3) *	mg/L	Causes harsh hop bitterness, colour development in beer, and inhibits protein coagulation (break formation).	Less than 50 mg/L.	108.5

* = value for Carbonates was calculated by BreWater 3.0 software. For water with a pH between 7.0 and 9.0, this may be estimated by multiplying total alkalinity by 1.22.

ANALYSING THE BRISBANE WATER REPORT

So, what's our water like? The simple answer is that there's not a lot wrong with it apart from lower than ideal levels of calcium and sulphate and a bit much bicarbonate. The levels

of chloride, magnesium, sodium and carbonate hardness are all within normal brewing ranges. A low level of sulphate means that hops will tend to impart a relatively soft flavour, although bitterness is accentuated by a moderately high level of chloride and malty sweetness enhanced by the presence of sodium. The level of calcium is also low, although apparently not low enough to cause major problems with mash chemistry.

BABB members are making excellent beers of many styles, even Pilsners, without any adjustment of water other than perhaps some acidification of the sparge water. Members with access to a pH meter have reported that their mash pH settles in the correct range without any special attention to their water. Some acidification of sparge water, to pH < 6.0, is desirable particularly if fly sparging.

There is little need to adjust your water if you simply wish to brew good beer using local water, however three potential problems are evident in our water.

Firstly, Brisbane water has a very low sulphate level. This is not a problem for most styles, and indeed Pilsners are traditionally made with water containing even less sulphate than our water. Brisbane water may present a problem if attempting to reproduce a style noted for sulphate enhanced hops character, such as many English ales. Without the required levels of sulphates, attempts at these styles made with Brisbane water are likely to lack the assertive hops character that is typical of, say, English Pale Ale. This may easily be correct by adding a measured quantity of *calcium sulphate* (CaSO4 - gypsum) to strike water, which has the added benefit of providing extra calcium for the mash. For example, if using 15 litres of strike water, a sulphate concentration of 96 mg/L may be obtained by adding 2 grams of gypsum to the mash, also increasing calcium to 54 mg/L as a side effect.

Secondly, Brisbane water has a very low level of calcium. If the water is not boiled, approximately 23 mg/L of calcium is present, which is less than half the concentration that is desirable for optimal mash performance. Consequently, mashes using only pale base malts and <u>un-boiled</u> Brisbane water may settle at higher than optimal mash pH. In practice, this does not appear to be a problem, and the many mashes and partial mashes I have performed using untreated, un-boiled water have performed acceptably. The mash pH may be lowered by addition of acids, use of acidulated malt, or the presence of darker specialty malts which all tend to acidify the mash environment. If attempting mash pH correction with acids, access to a pH meter is desirable! Calcium may be increased to approximately 54 mg/L by adding either 2g of gypsum or 1g of *calcium carbonate* (CaCO3 - chalk) to the mash for each 15 litres of strike water.

The third, and major problem occurs if Brisbane water is boiled to remove chlorine and chloramine added by the water treatment plants. A side effect of this boiling process is to reduce the hardness and alkalinity of the water by precipitating *calcium carbonate* (CaCO3 - chalk). Unfortunately, the very low calcium level of our water, combined with moderately high hardness, results in potentially <u>all of the available calcium precipitating out as chalk</u>. The BreWater 3.0 software predicts that boiling our water will result in a small reduction in total hardness and alkalinity, but the remaining water will contain NO calcium at all. This will result in problems with mash pH settling too high, unless adjusted with acids, and also in poor break formation.

The calcium problem may be corrected in one of three ways:

- Add calcium back to the mash in the form of *calcium carbonate* (CaCO3 - chalk) or *calcium sulphate* (CaSO4 - gypsum). If using boiled water that has lost all its calcium, 2g of chalk or 3g of gypsum per 15 litres will give approximately 50 mg/L calcium, however addition of this much gypsum will drive sulphate levels over 100 mg/L as sulphates are not removed by boiling.
- De-chlorinate the water using sodium metabisulphite or potassium metabisulphite (campden tablets). This causes a small increase in sodium content of the water, but avoids precipitating any calcium that is present.
- Acidify the mash using addition of acids, dark malts, or acidulated malt. A trial-and-error approach to find the right levels is required, and you will need a pH meter.

I prefer the first approach; boiling the water to drive off chlorine removes all calcium that was present, however it also drops the high (109 mg/L) bicarbonate level of Brisbane water to a more manageable 75 mg/L. If brewing pale lagers, pre-boiling the water, then adding just enough chalk to raise calcium levels to 40 mg/L is probably the best method. I will be trying this approach the next time I brew a lager, using 1.5g of chalk with my usual 15 litres to 5Kg of grain ratio.

SALTS FOR WATER ADJUSTMENT

Various salts are commonly used for water adjustment. You may have to hunt around for some of these, and even order from interstate. ESB and Grain and Grape both sell gypsum, chalk, calcium chloride and magnesium chloride. For Brisbane water, chalk and gypsum are the only additions that are really necessary, but for completeness all are listed here.

Additives & Ion Concentrations (1 gram per 10 litres)

Additive	Ca	SO4	Mg	Na	Cl	CO3	Hardness	Alkalinity
Gypsum (CaSO4)	23.3	55.8	----------	----------	----------	----------	58.1	----------
Chalk (CaCO3)	40.0	----------	----------	----------	----------	60.0	100.0	100.0
Calcium Chloride (CaCl2)	27.3	----------	----------	----------	48.2	----------	68.0	----------
Salt (NaCl)	----------	----------	----------	39.3	60.68	----------	----------	----------
Baking Soda (NaHC03)	----------	----------	----------	27.4	----------	71.4	----------	59.6
Epsom Salt (MgSO4)	----------	39.0	9.8	----------	----------	----------	40.8	----------

This table shows the effect on ion concentrations of adding **1 gram** of an additive to **10 litres** of water. It is based on a similar table in Ken Schwartz' water primer, but converted to metric units. For example, the table shows that adding 1 gram of chalk to a mash containing 10 litres of strike water will increase the calcium available to the mash by 40 mg/L. Side effects of additions on carbonate levels hardness and alkalinity are as shown.

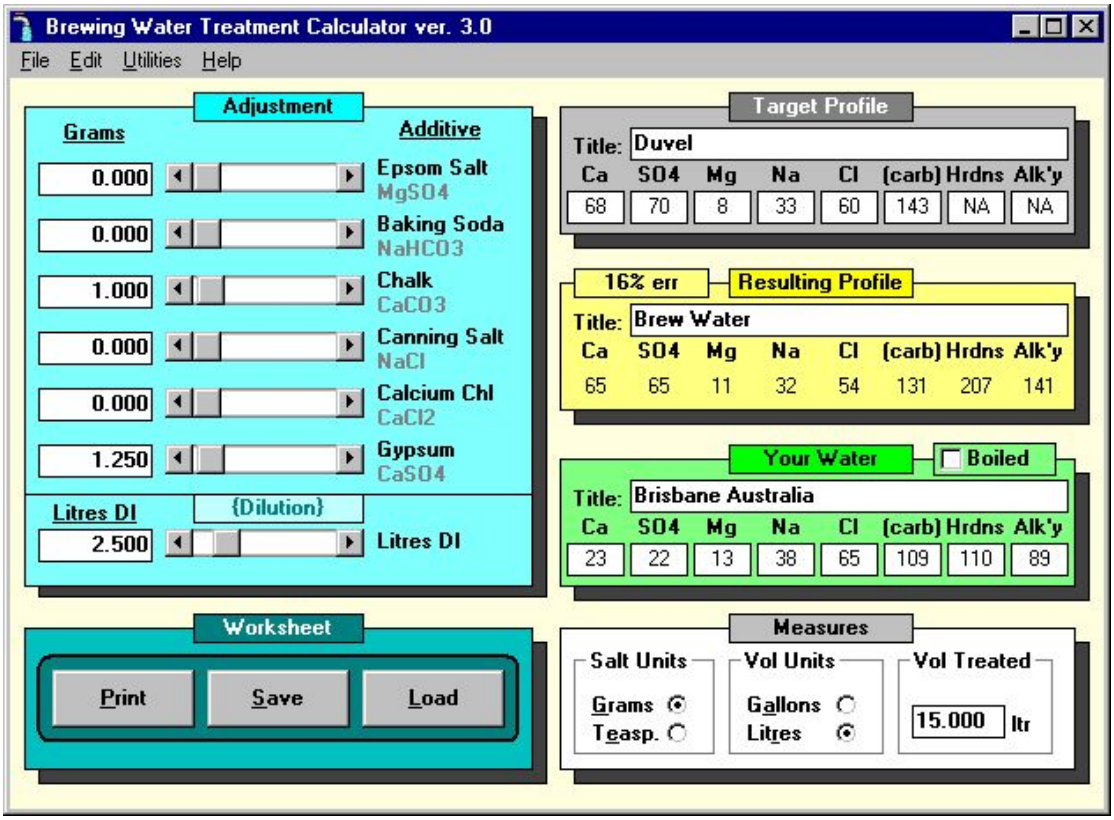
Additions should be very carefully measured; an accurate set of electronic scales is essential. When I first started using gypsum, very harsh bitterness resulted as I just heaped it in with a teaspoon. I now know that I added many times the amount necessary and caused harsh bitterness and hops flavour extraction in the boil.

BREWATER 3.0 SOFTWARE

It is possible to calculate water additions just with the above table and a calculator, but there is an easier way. The latest version of ProMash includes a water chemistry calculator, and your water adjustments may be included in a ProMash recipe printout. I personally find ProMash difficult to use, and prefer the excellent freeware utility BreWater 3.0, written by Ken Schwartz of El-Paso, Texas.

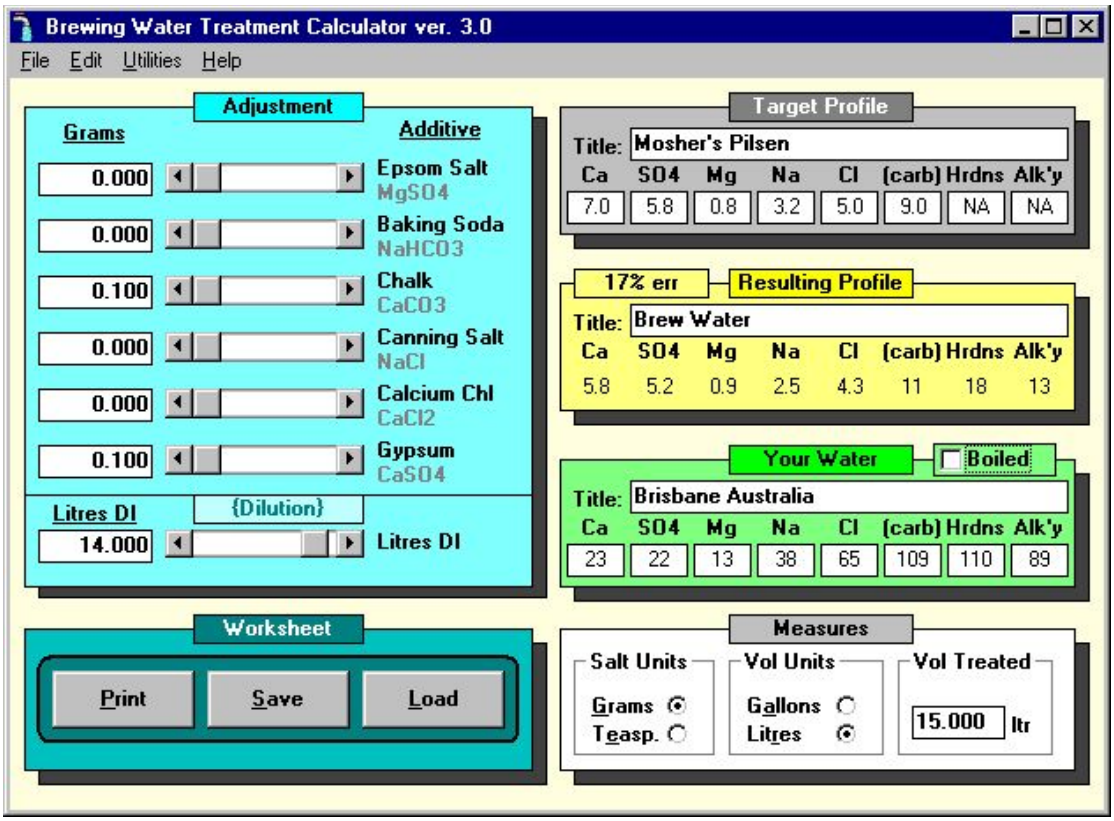
Use of BreWater is as simple as entering the profile for our local water from the council water report, entering the desired water profile, then either manually tweaking various additives (including distilled water to reduce ion concentrations) or using a goal seeking mode where the software attempts to deduce the correct additives automatically.

The screen below shows a BreWater calculation to match the known water profile used to brew Duvel, which uses water that is already quite similar to Brisbane water.



The local water shown is Brisbane water. The target water is the known profile for Duvel. Many such profiles, including Pilsen, Munich, London and Dublin are included with both BreWater and ProMash. BreWater calculates that to obtain a water profile close enough to that for Duvel, each 15 litres of water must be treated with 1g of chalk and 1.25g of gypsum. A dilution of 2.5 litres of distilled water to 12.5 litres of Brisbane water closely matches the levels of other ions with target water, however a good result can still be obtained without doing this. This information may be printed in a report format as well.

To reproduce the very soft water of Pilsen, dilution with large amounts of distilled water is required. The worksheet is shown below.



The local water shown is Brisbane water. The target water is the known profile for Pilsen. BreWater calculates that to obtain a water profile close enough to that used to make Pilsner Urquell, 14 litres of distilled water and 1 litre of unboiled Brisbane water should be combined with tiny (0.1g) additions of chalk and gypsum.

CONCLUSION

Brisbane water is good water for general brewing, and can be adjusted to match just about any common profile by addition of distilled water and tiny amounts of chalk or gypsum. I have deliberately avoided talking about the reasons why calcium is so critical in the mash, primarily because I do not yet understand the chemistry involved. In particular, I would love to know why every source I consulted recommends that the mash contains at least 50 mg/L calcium, yet the great Pilsners are all made with water containing around one tenth this concentration.

INTERNET RESOURCES

Brisbane Water Report:
http://www.ourbrisbane.com/government/watersupply/quality/chemical/
Ken Schwartz' Water Chemistry Primer:
http://home.elp.rr.com/brewbeer/water/wcprimer.html
Ken Schwartz' BreWater 3.0 software:
http://home.elp.rr.com/brewbeer/water/bw3setup.exe
Australian Craftbrewers:
http://www.craftbrewer.org/
Go to "Materials and Methods" for articles including water chemistry.