

Key Concepts in Water Treatment.

Introduction.

The crucial role played by water in the historical evolution of world beer styles is undisputed. Before the underlying chemistry was understood, native water supplies determined what styles could and could not be produced throughout the brewing world. Despite this, the topic remains poorly understood and largely neglected by many brewers, partly due to its overly complicated and often confusing presentation in much of the available brewing literature.

In reality, the subject is much simpler than it appears. There are really only four ions to be learned about, and only three salts will ever be needed. By grasping a few basic principles, brewers can develop and adjust their own water treatment plans for different beer styles and observe some improved results. Like any area of brewing, it can be learned gradually and implemented progressively as familiarity builds. This paper attempts to convey the necessary principles by extracting the relevant information from existing texts and assembling it into a (hopefully) more coherent and digestible format.

Relevant quotations are presented from *Fix: Principles of Brewing Science, 1999*, and *Noonan: New Brewing Lager Beer, 1996*. This information is then summarized, and appropriate recommendations for treatment of Melbourne water are given. Finally, an example of a rational program for water treatment is suggested, and practical techniques for implementing the required salt additions are provided.

1. Melbourne Water Profile.

Firstly, it is worth having a look at Melbourne's water supply. The following data from the South East Water 2005 Water Quality Report shows the concentrations in ppm (parts per million) of the ions of importance in brewing.

Ion		min	mean	max
Calcium	Ca ²⁺	3	5	13
Magnesium	Mg ²⁺	1	2	26
Sodium	Na ⁺	4	8	73
Bicarbonate	HCO ₃ ⁻	6	12	110
Chloride	Cl ⁻	6	12	93
Sulphate	SO ₄ ²⁻	1	3	10
pH		6.4	7.5	8.5

Some of the outlying maxima are a little disconcerting, but hopefully they are rare. For practical water treatment purposes, the mean concentrations are so low as to be considered zero. It soon becomes evident that Melbourne water is *calcium deficient* and requires calcium addition for all brewing. The same applies to rainwater. It should be also be mentioned that all tap water should be pre-boiled or carbon filtered to remove chlorine (chlorine Cl is a gas, not to be confused with the chloride ion Cl⁻).

2. Ions of major importance in brewing.

The six ions of concern to brewers can be broken down into 3 groups:

- calcium and bicarbonate are of major importance in the entire brewing process.
- chloride and sulphate are a secondary flavour consideration only in some beer styles.
- magnesium and sodium are of lesser importance and can be largely ignored.

This section looks at the first group. A major reason that calcium and bicarbonate are so important is that they are the only two ions which significantly affect pH in brewing.

2.1 Calcium Ca^{2+}

Calcium is the principal ion of hardness in water. It is the most important ion in brewing as it is the only ion which is essential in the brewing of *all* beer, regardless of style.

Noonan: “Calcium increases mash acidity. Calcium is advantageous to the brew. Calcium stimulates enzyme activity and improves protein digestion, stabilizes α -amylase, helps gelatinize starch and improves lauter run-off. It also extracts fine bittering principles of the hop and reduces wort colour.....improves hot-break flocculation.....essential part of yeast cell composition.....neutralizes substances toxic to yeast, such as peptone and lecithin. It improves clarification during aging, as well as the stability and flavour of the finished beer.”

Fix: “Calcium ions react with malt phosphates and hence decrease pH. Calcium ions afford thermal protection for mash enzymes (*Comrie, 1967*). In addition, they continue to interact with malt phosphate during wort boiling, and this ongoing reaction is the primary reason that the pH decreases in the kettle boil. Calcium ions inhibit colour formation during the boil and facilitate protein coagulation.....they favourably affect yeast flocculation and beer clarification during maturation (*Harrison et al., 1963; Saltukoglu and Slaughter, 1983; Taylor, 1990*). A widely accepted rule in brewing is to have calcium concentrations of at least 50ppm, and values in the range of 100-150ppm are common. In most practical brewing situations, the available water is calcium deficient.”

Summary: Calcium is the “good guy” in brewing. It is necessary and highly beneficial not only in the mash, but also in the boil, ferment and maturation stages. Melbourne water is clearly calcium deficient, and the essential first step in treating it is the addition of calcium to at least 50ppm.

2.2 Bicarbonate HCO_3^-

Bicarbonate is the principal ion of alkalinity in water. It is the ion formed when carbonate CO_3^{2-} dissolves in water, eg. when adding calcium carbonate CaCO_3 (chalk) to brewing liquor.

Noonan: “Bicarbonate resists increases in the mash acidity by neutralizing acids as they are formed. It also hinders gelatinization of starch by α -amylase, impedes trub flocculation during the cold break, and increases the risk of contamination in the ferment. It contributes a harsh, bitter flavour that is overwhelming in delicate lagers. Most water supplies are slightly alkaline, due to the buffering by the strongly basic reaction of even a small amount of bicarbonate. At over 50ppm Alkalinity as CaCO_3 , (30ppm HCO_3^-) water reacts sluggishly to acidulation in the mash and kettle.”

Fix: “The traditional rule used by brewers of pale beer is that the bicarbonate concentration be below 25ppm as CaCO₃ (15ppm HCO₃⁻) (*Owades, 1985*). There is a positive synergism between carbonates from brewing liquor and dark malts. The latter contain complex Maillard products (including melanoidins) some of which contribute a rather harsh and biting acidity. The carbonates tend to moderate this characteristic by giving a mellow and “fine malt” palate. Hop constituents tend to have the reverse effect. It is easy to demonstrate that highly hopped beers made with highly alkaline water have a biting and crude bitterness.”

Summary: Bicarbonate is very much the “bad guy” in most brewing situations. Bicarbonate has a host of deleterious effects on brewing processes and beer flavour. Bicarbonate is a strong alkaline buffer which resists the brewer’s efforts to acidify the mash. Its only role in brewing is in dark beers, to counteract the high acidity of dark malts. Most brewing water treatment activity worldwide is aimed at removing bicarbonate, but fortunately Melbourne water meets the 15ppm criterion.

3. Importance of Mash pH.

Fix: “.....mash pH has been known for a long time to be very important (*De Clerk, 1957*). The classic rule is for the chilled wort to have a pH of 5.0 - 5.2 and, to achieve this level, it is desirable to establish a mash pH in the range 5.2 - 5.4 (*Hind, 1950*). This range, first of all, is favourable to enzymatic activity.....the enzymes’ activities do not decrease by much if the pH levels are more acid, but there is typically a sharp decrease if the pH becomes more basic (alkaline)” :

Amylase Activity at 60°C

pH	Activity (%)
4.8	98
5.0	99
5.2	100
5.4	95
5.8	85
6.2	65

“Another equally important factor is that high pH mashes, say above 5.5, tend to lead to dull malt flavour that lacks definition (*Narziss, 1992*). Hop flavours are also negatively affected.....in modern practice, the focus has turned to the pH (rather than the specific gravity) of the wort collected from the sparge because pH increases with the extraction of undesirable astringents. A general rule is to terminate the sparge when the pH of the collected wort increases much beyond 0.1 pH units higher than the mash pH. In any case, it should not exceed 5.5.”

Noonan: “.....pH is of utmost importance to the brewer. Appropriate acidity is a prerequisite of a successful brewing cycle. Enzyme activity, kettle break, and yeast performance rely on conducive acidity in the mash, wort, and beer”.

Summary: The ideal pH for all mashes is in the range 5.2 – 5.4. Too low is better than too high, for reasons of enzyme efficiency and possible extraction of astringents during end sparging. The mash pH affects the pH throughout the remainder of the brewing cycle, including that of the finished beer.

3.1 Effects of calcium and bicarbonate on mash pH.

As mentioned above, calcium reduces pH while bicarbonate increases pH. These effects are quantified in Kolbach's equation, which predicts the pH of a 100% pale malt mash. It is not necessarily a useful brewing tool, but it does illustrate some of the key principles underlying mash pH :

$$\text{mash pH} = 5.8 + 0.028 \times [(\text{ppm HCO}_3^{2-} \times 0.034) - (\text{ppm Ca}^{2+} \times 0.04) - (\text{ppm Mg}^{2+} \times 0.033)]$$

- Note that calcium reduces mash pH (minus sign) while bicarbonate increases mash pH.
- Note also that magnesium has a similar effect to calcium, but in practice magnesium concentrations are so low that this effect is usually ignored.
- Most importantly, note that if all these ionic concentrations are close to zero, as in Melbourne water, the mash pH remains 5.8. This is way too high. The addition of 90ppm of calcium will only reduce the pH to 5.7 - still too high. This explains why very pale beers require further mash acidulation.

3.2 Effect of malt colour on mash pH.

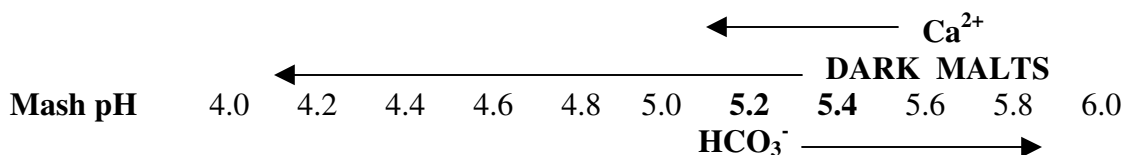
The third factor in determining mash pH is malt colour – dark malts reduce pH significantly. This is due to acidic compounds, including melanoidins, formed at their higher kilning temperatures. The following figures from *Noonan* show that the darker the malt, the lower the mash pH :

Pale malt:	pH 5.7 – 6.0
Vienna / Munich:	pH 5.5 – 5.7
Crystal:	pH 4.5 – 4.8
Chocolate:	pH 4.3 – 4.5
Black:	pH 4.0 – 4.2

Depending on their proportion in the grist, coloured malts may be sufficient to give proper mash acidity. Very dark grists may even be too acidic.

3.3 Achieving correct mash pH in practice.

The three factors determining mash pH can be represented thus:



Having first corrected any calcium deficiency in the brewing liquor, the task of brewers is then to balance the bicarbonate content with the malt colour of the mash in order to achieve optimum pH.

Beer colour is a reasonable predictor of mash pH. In practice, it turns out that bicarbonate is only demanded in extremely dark beers, eg. porters and stouts, to counteract the high acidic content of the large quantities of roast malts used in these styles. Very dark brown beers, eg. dunkels, dark Trappist ales, may also benefit from some bicarbonate. Experience shows that copper to brown beers generally hit the target range without further treatment, and amber beers will be thereabouts or a touch high. Pale beers however will be significantly high, and further efforts are required to increase acidity. Pale lagers are generally the palest of beers and therefore present the greatest challenge, and several methods are commonly used to acidify the mash:

- acid rest during mashing cycle
- direct addition of acid (eg. lactic or phosphoric) to brewing liquor to pH 5.5 or even less;
- conducting a sourmash
- addition of some acidulated malt to the mash (eg. 1 – 10% of the grist).

4. Ions of secondary importance in brewing.

This section deals with chloride and sulphate. These ions are introduced into the beer when calcium deficiency is corrected by the addition of calcium chloride or calcium sulphate (gypsum). The choice of which to use is determined by the flavour attributes desired in the beer.

4.1 Sulphate SO_4^{2-}

Noonan: “Gives beer a dry, fuller flavour, although the taste can be exceptionally sharp. With sodium and magnesium, it is cathartic (purgative). Above 500ppm it is strongly bitter, and levels are generally kept at less than 150ppm unless the beer is very highly hopped. With intensely bitter beers, sulphate at 150-350ppm gives a cleaner, more piquant bitterness. Increasing amounts of sulphate give a cleaner hop flavour. Well hopped beers brewed with gypsiferous liquor commonly exhibit a finer, less coarse bitterness than is obtained with other liquor profiles.”

Fix: “High sulphate levels and dark beers are not a particularly good marriage. The effects are a drying and astringent afterfinish.”

Summary: Appropriate in pale, hoppy, bitter beers to give a cleaner hop flavour and bitterness, eg. IPA, Pale Ales, German Pilsener, or any pale beer where a drier crisper finish is being sought, perhaps a Dortmunder or a Tripel. Sulphate would be inappropriate in a Bohemian Pilsener where a soft rounded bitterness is desirable. Sulphate is to be avoided altogether in dark beers.

4.2 Chloride Cl^-

Noonan: “Accentuates bitterness, but also increases mellowness, improves clarity. The “salt” taste of chloride generally enhances beer flavour and palate fullness, but the salt flavour is reduced by the presence of calcium. Usually found at levels of 1-100ppm, but levels may be as high as 250 ppm for British mild ales.”

Summary: Chloride is beneficial, or at least benign, in all beers, even at quite high levels. Unlike sulphate, chloride doesn't cause problems in dark beers. These attributes makes calcium chloride extremely versatile and the obvious first choice for getting calcium into the mash.

5. Ions of lesser importance in brewing.

This relates to magnesium, present in magnesium sulphate $MgSO_4$ (Epsom salts) and to sodium, present in sodium chloride $NaCl$ (table salt). For beginners, these salts would appear to have little use in brewing.

5.1 Magnesium Mg^{2+}

Fix: “Magnesium plays a role in mash acidification by a mechanism similar to calcium. However this effect is small and is usually ignored. The major role magnesium plays is in the fermentation where magnesium is an important co-factor in various yeast metabolic activities. Actually, malt supplies sufficient magnesium for this purpose, and in addition, at too high a concentration, magnesium ions will contribute a harsh bitterness (*Krauss et al., 1983*). As a consequence, magnesium salts are rarely used for treating water in modern brewing.”

Noonan: “In concentrations of 10-30 ppm, magnesium accentuates the beer’s flavour, but it imparts an astringent bitterness when present in excess. At levels higher than 125 ppm it is cathartic and diuretic.”

5.2 Sodium Na^+

Noonan: “The sour salty taste of sodium can accentuate beer’s flavour when it is found in reasonable concentrations, but it is harsh and unpleasant in excess. It is poisonous to yeast, and brewers generally avoid water that contains sodium in excess of 50 ppm, especially where softness is characteristic of the beer flavour.

6. Practical Water Treatment in Melbourne.

6.1 Which salt to add?

The three objectives of water treatment have now been identified and prioritized:

1. *rectify calcium deficiency*
2. *control pH by balancing bicarbonate levels with malt colour*
3. *confer specific flavour characteristics in some cases by addition of sulphate*

In practice, these three objectives are achieved simultaneously by the addition of one of three salts depending on the style of beer:

calcium carbonate $CaCO_3$ - very dark beers only

calcium chloride $CaCl_2$ - all other beers

calcium sulphate $CaSO_4$ - pale beers only, especially if hoppy and bitter
and a crisp dry character is required

For very pale beers consider further mash acidification by the methods mentioned at the end of Section 3.4

6.2 How much salt to add?

When calculating brewing salt additions, many brewers have relied on the standard published table, regurgitated in numerous brewing texts, which gives the supposed water profiles of various historically famous brewing cities. This table is noticeably absent from *Fix (Principles of Brewing Science, 1999)*.

Instead, using words such as “dubious” and “misleading”, *Fix* devotes two pages to a critique of these published figures, warns brewers against their “indiscriminate use” and advises: “Instead of using historical examples as a guide, the best overall strategy is to first make sure the technical requirements of the mash are met, ie. a proper pH, and then to adjust the mineral content by using the finished beer’s flavour as the guide”.

Putting this advice into practice, a table such as the following might constitute a more rational approach:

Beer colour	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	acid rest and/or acid addition
black	80	-	-	120	No
dark brown	50	-	-	75	No
copper to brown	50	90	-	-	No
gold to amber	100	180	-	-	Consider
straw	100	180	-	-	Yes

For pale hoppy beers where a dry finish is required, substitute sulphate for chloride:

gold to amber	115	-	280	-	Consider
straw	115	-	280	-	Yes

These figures represent a reasonable starting point. Ideally, mash pH should be verified using a pH meter, and adjustments made accordingly.

6.3 How to add salt?

A simple and accurate way to add brewing salts is to make up a concentrated stock solution of each salt, which can then be added to the brewing liquor at the appropriate dilution rate using a 100ml measuring cylinder (available from laboratory glassware outlets for about \$15, these double as an excellent hydrometer flask when not in use). The stock solution can be stored indefinitely and dispensed from a plastic bottle. This saves having to calculate and weigh salts every time you brew. Write the ppm concentrations on the bottle to help you memorize them. Following are the formulae for stock solutions of the three salts required, and some suggestions for their use in various beer styles:

calcium chloride $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ Composition by weight: 27.2% Ca^{2+} 48.3% Cl^-

Stock solution: Use a measuring jug to dissolve a 100g packet of CaCl_2 in about 400ml of cold water (this takes a few minutes) then top up with cold water to 540ml. A Powerade type drink bottle (approx 600ml) with re-sealable nozzle makes a convenient dispensing bottle.

Add to brewing liquor at 1:1000 dilution (eg. add 30ml to 30 litres, 50ml to 50 litres etc.) This will give 50 ppm Ca^{2+} and 90 ppm Cl^- , satisfying the minimum Ca^{2+} requirement for all beers. Try doubling this rate for pale beers to help get the mash pH down. Addition of calcium chloride by this method is an ideal first step in tackling water treatment for all beers. Later on, you can consider adding calcium carbonate and calcium sulphate to your repertoire.

For these two salts, larger stock solutions are required due to their poor solubility, and the bottle will need to be shaken and dispensed quickly before the precipitate resettles.

calcium carbonate CaCO_3 Composition by weight: 40% Ca^{2+} 60% CO_3^{2-}

Stock solution: add 40g to water and top up to 2 litres.

Add to brewing liquor at 1:100 dilution. This will give 80 ppm Ca^{2+} and 120 ppm HCO_3^- , a good level for stouts and porters. Try a bit less for dunkels and other dark brown beers.

calcium sulphate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ Composition by weight: 23.3% Ca^{2+} 55.8% SO_4^{2-}

Stock solution: add 100g packet to water and top up to 2 litres, store in a milk or fruit juice bottle.

Add to brewing liquor at 1: 100 dilution (eg. 300ml in 30 litres, 500ml in 50 litres etc.) This will give 115 ppm Ca^{2+} and 280 ppm SO_4^{2-} , a good level for pale ales and German pilsner. Consider doubling this rate for a Burton IPA.

For brewers preferring to add these two salts dry:

calcium sulphate: add 0.5 grams per litre of brewing water to give 115ppm Ca^{2+} and 280ppm SO_4^{2-}

calcium carbonate: add 0.2 grams per litre of brewing water to give 80 ppm Ca^{2+} and 120ppm HCO_3^-

Conclusion.

The old notion that “soft” water such as Melbourne’s is suitable for brewing all styles of beer can no longer be accepted by serious brewers. The addition of calcium alone usually leads to increased extraction and improved clarity, especially in pale beers, while carbonate does lend a desirable softness to stouts and porters. Whatever further potential benefits to beer flavour can be achieved by water treatment will remain unknown until brewers start to explore its frontiers.

There is more to brewing than water treatment, but it should at least be seen as a prerequisite for great beer. The following quote (*Noonan, Scotch Ale, 1993*) sums it up nicely: in reference to a competitor, “Mr. Thompson our brewer always spoke highly of their fine water and abundant supply, and he thought that if they only put in the malt they would be dangerous opponents.”