

Water makes up something like 90-95% of beer, and yet we often ignore it, at least early in our brewing career, or until we have a problem that can only be fixed by addressing a problem with the water we are using. For most of us that will be the water supplied to the taps in our house. Luckily the water we get in the Hunter is truly great brewing water we can make most any beer with it and we can get away without bothering too much with water chemistry, I know I did for many years.

First up let's be clear, we aren't looking at 'Water' but what is dissolved in the water and how that affects the beer we are making. There are various chemicals and mineral salts that can affect our beer some in a good way and some do harm.

Let's look at things we don't want in our water.

Chlorine is going to be the big one – Chlorine is the element Chlorine, it is a Halogen along with Fluorine, Bromine and Iodine, these are all extremely reactive which is why about 1ppm of Cl is put into the water, it is so reactive that it smashes up the DNA of bacteria, viruses and parasites like Giardia, killing them. By the time it reaches our taps it will be lower than that.

It's only been just over 100 years since the first municipal water supplies were treated, making it far less likely for us to contract cholera, dysentery, typhoid etc, You would have to argue that this is a good idea.

The down side being that Chlorine will react with organic chemicals (mostly Phenols) and form any of a number of chemicals collective called Chlorophenols. These chemicals are really offensive and can be quite off-putting even in the low ppb range, if they can't be detected as a discrete flavour they can still reduce the enjoy ability of the beer at ridiculously small concentrations. Getting rid of Chlorine is a good idea.

It is important to note that Chlorine isn't the same as Chloride; Chlorides like Sodium Chloride (common salt) and Calcium Chloride may be beneficial and won't cause these off flavours

Iron can cause problems over about 1-1.5ppm, a quick look at our Typical Analysis will show that we are way under that, if however you live in a really old house with galvanised pipe work or are using bore water it can be an issue, excess iron will add an unpleasant metallic flavour.

Good rule of thumb would be if the water is leaving rust stains, there is too much iron. You would be well advised to choose a different water supply or look at a reverse osmosis or ion exchange water treatment system.

There are a couple of other things we can do without in our brewing water.

Nitrates and Nitrites are mostly from agricultural runoff, as are excessive levels of pesticides and herbicides; these aren't high enough to be a problem in our municipal water, if you are using tank or bore water in or around an agricultural area they would be worth looking at.

All of the above other than iron and other metals could be effectively removed with a carbon filter. A two stage Particulate and Activated Carbon filter would be a great investment and would for most of us yield water that is going to be truly great for brewing.

If you don't want to spend the money on a filter system, just adding a little Sodium or Potassium Metabisulphite will quickly remove Chlorine and any excess will reduce dissolved oxygen. Vitamin C will also work but Metabisulphite is faster, more effective and a lot cheaper.

Carbonate and Bicarbonate can cause problems with the pH being too high for ideal enzyme activity, we are pretty lucky here in the Hunter when it comes to Carbonates, we will be looking at them some more later.

There are ways to reduce Carbonates, worth looking at if your carbonate levels are too high.

Which brings to the "what do we want in our water"?

This can be broken up into three sections based on the effects on brewing and the beer we make:-

- Chemical Effects

The increased perception of hop bitterness from Sulphate; the mellowing effect of chlorides; the isomerisation of alpha-acids; reduced pH...

- Enzymatic Effects

Improved mash yield, more alpha amylase activity; better yeast health,

- Physical Effects

Better coagulation of protein in the kettle, reduced colour formation during the boil, improved colloidal stability of the finished beer

Arguably the king of brewing salts Calcium, there are a bunch of other trace elements that play a role in brewing but the one that isn't supplied in sufficient quantities from most malt and water is Calcium.

We will look at a couple of others at the end; it is also worth mentioning Magnesium.

There is some talk around about Magnesium being much more important in lager brewing than may have been thought previously – I'm going to leave this one alone, let's say the jury is still out on how good Mg is. Where as we know how vital Ca is, the conventional wisdom is "apart from trace amounts anything Mg can do Ca can do better".

Calcium has the following effect on brewing: -
Lowers the pH

- Ca reacts with Phosphates in the water and from the malt forming insoluble Calcium phosphate. NB once the phosphates are used up it can't lower the pH further, it's nearly impossible to get below 5.7pH by adding Calcium Salts even in distilled water, this is higher than ideal.

- Stimulates both Proteases and Amylases
This improves the mash yield.

- Protects Alpha Amylase from heat degradation

Same amount of Alpha does more work and works hotter can help with late extracted starch

- Reduces the amount of Oxalates

Calcium Oxalate also called beer stone is reduced if there is enough Ca present (should be 4.5X more Ca than Oxalate) Calcium Oxalate can cause Haze and gushing in beer.

- Encourages flocculation

Both in the kettle and of the yeast at the end of fermentation

Most researchers say between 50-100ppm of Calcium is enough to achieve the above outcomes. There are no real downsides to Ca levels under 250ppm

Good time to take a look at your water analysis, first the map, then the typical analysis for your water.
Most of us will be getting our water from Grahamstown or Dungog

TYPICAL COMPOSITION OF HWC TREATED WATER **1 July 2002 to 30 June 2012**

Parameter	Units	ADWG 2011		Dungog			Grahamstown ***			Water Treatment Plant			
		Health	Aesthetic	10th Percentile	90th Percentile	Median	10th Percentile	90th Percentile	Median	Lemon Tree Passage			
										10th Percentile	90th Percentile	Median	P
Alkalinity at pH 4.5 as Calcium Carbonate***	mg/L			35	41	39	18***	26***	21***	54	61	58	
Aluminium	mg/L		<0.2	0.04	0.12	0.08	0.04	0.12	0.08	0.03	0.09	0.06	
Arsenic	mg/L	<0.01		0.0001	0.0006	0.0002	0.0001	0.0006	0.0003	0.0001	0.0003	0.0002	
Cadmium	mg/L	<0.002		0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	
Calcium	mg/L		(2)	14	17	16	10	23	11	20	25	23	
Chloride	mg/L		<250	8	13	11	37	47	42	22	29	26	
Chromium	mg/L	<0.05		0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	
Colour Apparent	Hazen Units		<15	1.6	2.9	2.5	1.8	4.5	2.8	1.7	4.8	3.6	
Conductivity	uS/cm		(1)	93	124	108	231	297	257	197	227	207	
Copper	mg/L	<2	<1	0.001	0.008	0.003	0.001	0.006	0.003	0.008	0.025	0.012	
Cyanide	mg/L	<0.08		0.01	0.05	0.05	0.01	0.05	0.05	0.01	0.05	0.05	
Fluoride	mg/L	<1.5		0.91	1.04	0.99	0.91	1.04	0.99	0.91	1.04	0.98	
Hardness as Calcium Carbonate***	mg/L		<200	41	49	46	45***	77***	51***	59	72	66	
Iron	mg/L		<0.3	0.01	0.04	0.02	0.01	0.04	0.01	0.01	0.05	0.03	
Lead	mg/L	<0.01		0.001	0.002	0.001	0.001	0.002	0.001	0.001	0.003	0.001	
Magnesium	mg/L		(2)	1.3	1.6	1.4	4.7	6.0	5.3	1.9	2.2	2.1	
Manganese	mg/L	<0.5	<0.1	0.001	0.009	0.002	0.001	0.018	0.004	0.002	0.014	0.008	
Mercury	mg/L	<0.001		0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	
Nickel	mg/L	<0.02		0.001	0.001	0.001	0.001	0.001	0.001	0.0004	0.001	0.001	
Nitrates	mg/L	<50		0.03	0.26	0.11	0.03	0.18	0.09	0.44	0.75	0.62	
Nitrites	mg/L	<3		0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	
pH **	units		6.5-8.5	7.4	7.7	7.6	7.3	7.5	7.4	7.4	7.7	7.5	

What Does it Mean?

Well I asked the chemist at Hunter Water. Looking at the top line Alkalinity

There is a 10% chance that the average for Dungog will be 35mg/L (ppm) or less

An 80% chance that the average will be 39ppm and

And a 10% chance that the average will be 41ppm or more

The range is so small that we can use the Median figure, and if we wanted to round it to a convenient whole number it won't make any practical difference. So I'm going to call it 40ppm of Alkalinity for Dungog, 25 for Grahamstown and 60ppm for Lemon Tree Passage.

For Calcium let's call it 16, 11 and 23ppm respectively. I would be very tempted to add 100ppm of Ca to all of them just to be sure. Makes sure there is plenty of Ca and keeps us well under the limit.

The two most common Brewing Salts are Calcium Sulphate (Gypsum) and Calcium Chloride

Calcium Sulphate is sold as a Dihydrate (has two water molecules attached to it) and there is the weight of the sulphate to take into account to, so Calcium Sulphate is 36% Calcium. Calcium Chloride is also sold as the Dihydrate (six waters attached) and it is 27% Calcium. Another one I want to mention is Calcium Lactate pentahydrate (yep five waters) it is 13% Calcium. Note that Calcium Chloride will suck water out of the air – keep it tightly closed in an airtight jar.

This is important, when you add Ca^{2+} or Mg^{2+} ions (called Cations), you also add the Sulphate, Chloride or Lactate ions (Anions). Conversely if you want to add Sulphate, Chloride or Lactate you will get Ca or Mg coming along for the ride.

Which Salt to Choose?

That is a good question, it's a bit like salt and pepper, it's largely a matter of taste

Sulphate increases the perception of bitterness, too much tastes harsh.

Chloride gives a mellowing effect, too much tastes salty.

Lactate has little effect on flavour, about 90% of the 'acidity' in a mash comes from Lactic Acid from bacteria.

There are plenty of thoughts on which salt works best in which beer, a great place to start is 2 Sulphate to 1 Chloride, this gives a well balanced flavour profile. Generally a good guide is more Sulphate in hoppy beer, more Chloride in mellow beers.

How much to add?

Let's say we want to add 100ppm of Calcium Sulphate to 32L of water, remember that Gypsum is 36% Calcium

We have $32\text{L} * 100\text{ mg/L} * 36\%$

$32 * 100 * 36 / 100 = 1152\text{mg} / 1000$ to get from milligrams to grams. its only 1.152g

pH

pH is simply a way to count Hydrogen ions in solution (H^+), the more there are the more acidic a solution is, the less the more alkaline it is likely to be, with 7pH being neutral (pH generally regarded as Power or Potential of Hydrogen), but why 7pH as Neutral.

Well water is a truly bizarre molecule, even at near its boiling point some of it is organised like ice, and some of it is "disassociated" or broken up into ions like Hydrochloric Acid (HCl) in water becomes the ions H^+ and Cl^- .

A tiny fraction of the water disassociates into H^+ and OH^- it turns out that at 20°C $1 * 10^{-14}$ of the water is in this form, half of it is Hydrogen so we have $1 * 10^{-7}$ hydrogen ions/L. pH is defined as the negative Log of the concentration so we get a pH of 7 being neutral as there are the same number of alkaline OH^- ions to balance the H^+ .

Log is a way to express numbers it excels at really big and stupidly small numbers, Log_{10} is the Log in base 10 (yes they use other bases – but we don't have to (whew)) Log of 10 is 1, Log 100 is 2, Log 1000 is 3 and so on. Log of 0.1 is -1, Log of 0.01 is -2, Log of 0.001 is -3 and so on. In 1L of water at 20°C there are 0.0000001 moles of H^+ ions (not many) You can call that ppm or mg/L if you like all same as H^+ weighs 1 atomic mass unit.

No there won't be an exam and if you don't get it don't worry; it's just good to know that it isn't voodoo.

The take home is that we can't just add pH numbers together. Going back to our typical analysis we see that the three water sources have pH's of 7.6, 7.4 and 7.5 so they are all slightly alkaline.

If we mixed 1L of pH7 water with 1L of pH4 acid, the pH wouldn't be pH5.5 because the pH4 is 1000 times more acidic than the pH7 (we get $(0.0001 + 0.0000001) / 2$ (in 2L) or about pH4.3)

Ok no more of that.

The main effects of a properly adjusted pH on a brew are: -

- Improves enzyme activity
- Limits the extraction of tannins
- Reduces colour formation

- Makes the mash more filterable
- Helps hot break formation

And

- Decreases the utilisation rate of Alpha Acids – but bitterness tastes smoother

We generally say the ideal pH for mashing is pH5.4-5.6 as mentioned above in distilled water it is nearly impossible to get below about pH5.7 with pale malt and we have some Carbonate in our water making it alkaline, think of that as a handicap before we start.

- We can use darker malts; the formation of Milliard products during kilning will slightly decrease the pH.
- We could add Acid Malt; 1% of grist will lower the pH by pH0.1
- We could add acid.

At each stage (Mashing, Boiling, Fermenting and Packaging) there is an ideal pH and each step depends on the one before. My personal recommendation is that we use Lactic Acid, as previously it is naturally occurring in beer, it is also a lot safer than most strong industrial acids, if you or the kids spill it on yourself it probably won't leave scars for life.

For 88% Lactic Acid

About 0.55mL/ kg of grist will reduce the pH by 0.1

About 0.27mL/L will reduce the pH by 0.1 in the kettle or the fermenter

So say we mash in 5kg of grist, we have added all the salts we want to add, wait a few minutes and measure the pH, it is 5.9 and we want it to be 5.4 we need to take off 0.5 points of pH

$0.55\text{mL/kg} * 5\text{kg} * 5 = 13.75\text{mL}$ (last 5 is 5* a change of 0.1pH)

Or substitute about 250g (5% of 5kg) of your base malt for Acid Malt (1% moves 0.1pH)

Ideally in the mash pH5.4-5.6

In the kettle start of boil pH5.6

In the kettle end of boil pH5.2

End of ferment 4.0

Remember that if the mash is out, every following step will be to.

If you really care, get a decent pH meter, some of the appropriate salts and some lactic acid.

Remember that the pH meter should read to 0.1, be a two point calibration and you really do need to calibrate every brew day.

Chlorine removal

I have had a couple of people ask me about Chlorine removal, as in the notes previously posted a Carbon filter will remove Chlorine

Camden Tablets