Brewing Liquor: Balancing the Ions

Alan Osbiston

7th September 2024

Brewing Liquor: Balancing the Ions

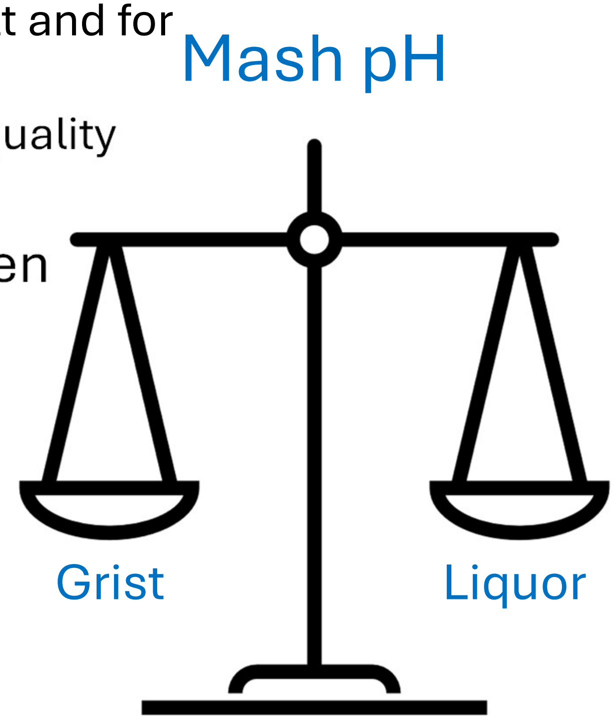
1) Requirements for Brewing
2) Know Your Water
3) Process

1) Requirements for Brewing

- Essential Requirements for the Perfect Mash & Fermentation:
  - Calcium / Ca^{2+}
  - Alkalinity
- Condiments for turning Good Tasting Beer into Great Tasting Beer
  - Sulphate / SO_4^{2-}
  - Chloride / Cl^-

Mash pH

- Mash pH needs to be between 5.2-5.6
  - Best environment for extraction of enzymes form the malt and for
  - Amylases to degrade starch
  - Produces better fermentation, head retention & flavour quality
  - Influences the pH of the wort & final beer
- pH of mash is dependent on the equilibrium between
  - Grist
    - Organic Phosphates in base malts increase pH
    - Darker malts/Roasted adjuncts are acidic and reduce pH
  - The Liquor
    - Calcium
    - Alkalinity *not pH*



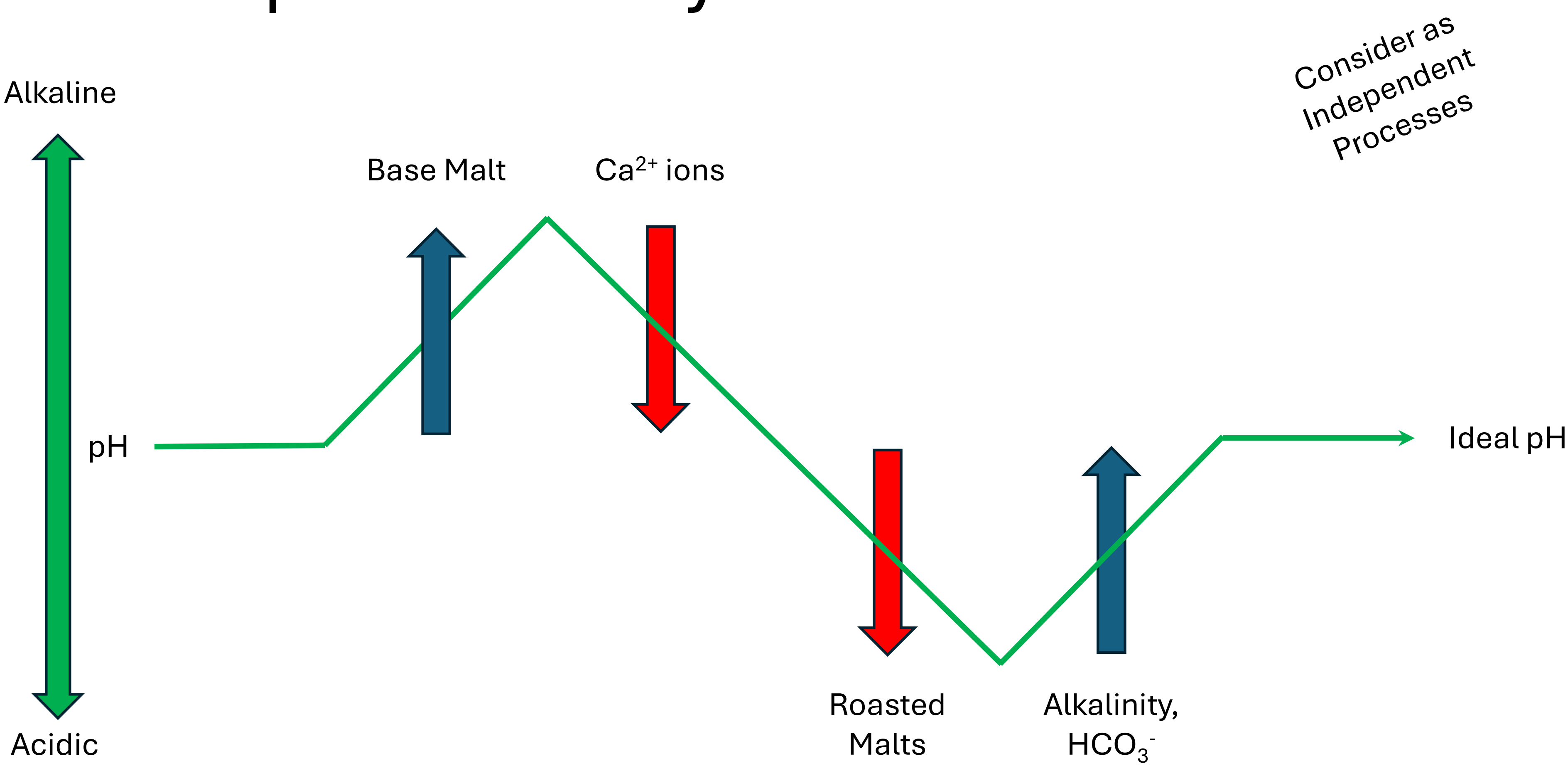
Calcium / Ca^{2+}

- Organic Phosphates in base malts act as buffers and will raise pH to ~5.8
- Ca^{2+} ions react with these to precipitate various phosphate species but mainly Hydroxy Apatite, and release H^{+} ions which reduce the mash pH.
- So, in Pale beers where there are little or no roasted malts Ca^{2+} ions are essential to reduce mash pH
- Ca^{2+} ions are also essential for a healthy fermentation: yeast flocculation & metabolism

Alkalinity

- Melanoidins & Organic Acids are created by Maillard reactions during the kilning & roasting of malts.
  - The darker the malts the more acidic they are.
- Alkalinity of the Liquor
  - The only buffer in tap water is the alkalinity from the Carbonic/Bicarbonate/Carbonate equilibrium.
  - Principally from dissolved Calcium Carbonate/Chalk found in groundwater
  - These Ions must be in solution to have an effect in the mash
  - Throwing Chalk into the mash tun will have little effect.
  - Adding Sodium Bicarbonate may increase alkalinity but will also add Sodium ions which may not be desirable

Mash ph - Summary



Flavouring Effects/Condiments

- Sulphate / SO_4^{2-}
  - can make the hop character more assertive or dryer
  - very high levels (>400ppm) can taste minerally
  - Commonly added in the form of Calcium Sulphate/Gypsum
  - May be added as Magnesium Sulphate/Epsom Salts
- Chloride / Cl^-
  - Provides a rounder, fuller, sweeter quality to the malt character
  - Commonly added in the form of Calcium Chloride or as Sodium Chloride (non-iodised salt free of anti-caking agents)

Flavouring Effects/Condiments

- Sulphate to Chloride Ratio
  - Hop to malt balance
  - Dryness to fullness balance
  - Beware as it is the absolute concentrations of the ions that make a difference
  - The effect of
    - 30:30ppm is not equal to 300:300ppm
    - 5:1ppm probably has the same effect as 5:5ppm

Flavouring Effects/Condiments

- All additions are added in the form of salts and you cannot add any single ion without the associated anion or cation:
  - Calcium Ca^{2+}
    - may be perceived as minerally >200ppm
  - Magnesium Mg^{2+}
    - works half as well as Ca^{2+} in lowering mash pH
    - necessary yeast nutrient
    - 15ppm sufficient for most beers but Porters & Stouts benefit from up to 30ppm
    - can impart an unpleasant sour & bitter taste above 80ppm
  - Sodium Na^{+}
    - salty taste in combination with Cl^{-} >150ppm

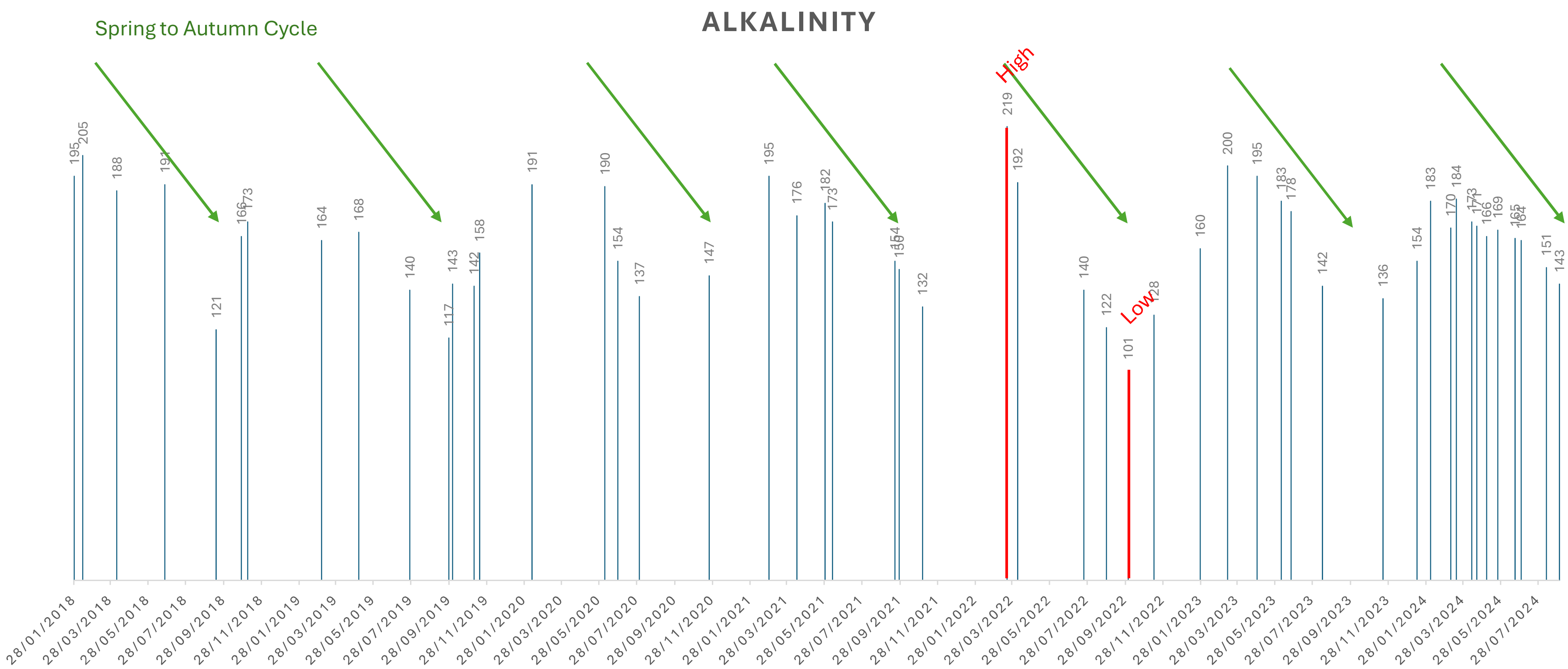
Flavouring Effects/Condiments

- Evenso, traces of other metal ions in ground water are beneficial to yeast health and the fermentation process
- Enzymatic reactions use metal ions as co-factors
  - Calcium
  - Potassium
  - Magnesium
  - Zinc
  - Manganese

2) Know Your Water

- Use annual Water Report from Water Company
  - for Average SO_4^{2-} & Cl^- concentrations
- Measure Alkalinity for each brew
  - Alkalinity changes on a daily basis:
    - Water companies constantly switch the source of water depending on demand and environmental factors such as rainfall

7 Years' Alkalinity Results – Chelmsford Tap



2) Know Your Water

- Use Annual Water Report from Water Company
  - for Average SO_4^{2-} & Cl^- concentrations
- Measure Alkalinity for each brew
  - Alkalinity changes on a daily basis:
    - Water companies constantly switch the source of water depending on demand and environmental factors such as rainfall
  - Infer Ca^{2+} concentration from Alkalinity:
    - Although both Mg^{2+} & Ca^{2+} will be bound to the CO_3^{2-}, Mg^{2+} will be at relatively low levels and both perform a similar function in brewing, so it is easier to count both as Ca^{2+}
    - There will also be a similar contribution of Ca2+ ions from the SO_4^{2-} content

Water Report

2024 WATER QUALITY REPORT FOR DRINKING WATER IN YOUR AREA with DATA AVERAGED OVER 12 MONTHS – Jan 2023 to Dec 2023

Name of water supply zone: ***Z605 BILLERICAY & BRENTWOOD***

Water source(s): ***Ground and Surface (Mixed) Water***

Brewers information:

Scale/units	Average	Maximum	Minimum
$CaCO_3$ mg/l Calcium Carbonate	276.76	309.43	241.47
mg/l Chloride	67.71	75	62
mg/l alkalinity (HCO_3)	207.05	233.34	176.40
mg/l Ca - Calcium	97.29	110.44	83.82
mg/l Mg -Magnesium	8.16	8.52	7.76
mg/l Sodium	39.97	44.42	36.26
mg/l Sulphate	80.45	92.11	69.9

Water Report

Table of sampling results showing parameters looked for in drinking water. Some are naturally occuring in the raw untreated water and others are checked as part of the the water treatment process.

Parameter (Z605)	Units	No. of samples taken in year	PCV limit	No. of samples above PCV	Min	Mean	Max
1,2-dichloroethane	ug/l	24	3	0	< 0.200	< 0.200	< 0.200
2,4-D	ug/l	24	0.1	0	< 0.011	< 0.011	< 0.011
aldrin	ug/l	24	0.03	0	< 0.003	< 0.003	< 0.003
aluminium	ug/l Al	52	200	0	< 3.900	< 5.959	11.669
chloridazon	ug/l	24	0.1	0	< 0.013	< 0.013	< 0.013
chloride	mg/l Cl	24	250	0	62	67.708	75
chlorthalonil	ug/l	24	0.1	0	< 0.007	< 0.007	< 0.007
chlortoluron	ug/l	24	0.1	0	< 0.003	< 0.003	< 0.003
residual disinfectant - total	mg/l	180		0	0.11	0.563	1.07
selenium	ug/l Se	8	10	0	< 0.830	< 0.830	< 0.830
sodium	mg/l Na	8	200	0	36.264	39.968	44.416
sulphate	mg/l SO4	24	250	0	69.9	80.447	92.106
taste (quantitative)	DN	52	>0	0	0	0	0
tebuconazole	ug/l	24	0.1	0	< 0.004	< 0.004	< 0.004

2) Know Your Water

- Use Annual Water Report from Water Company
  - for Average SO_4^{2-} & Cl^- concentrations

3) My Process

Strategy

1) Use Tap Water as the starting point
2) Use RO water to dilute Tap Water to achieve 3) & 4)
3) Make the smallest number of additions
4) Add only Ions that would naturally occur in ground or surface water

Notes on Additions

Adjusting the Alkalinity

- Downside to using 100% RO water is that it contains nothing.
  - Adding Sodium Bicarbonate may increase alkalinity but will also add Sodium ions which may not be desirable
  - Adding Calcium Carbonate/Chalk to increase alkalinity is not practical as its solubility is very very low: 0.015 g/L
  - These Ions must be in solution to have an effect in the mash: throwing Chalk into the mash tun will have little effect.

Notes on Additions

Adjusting the Alkalinity

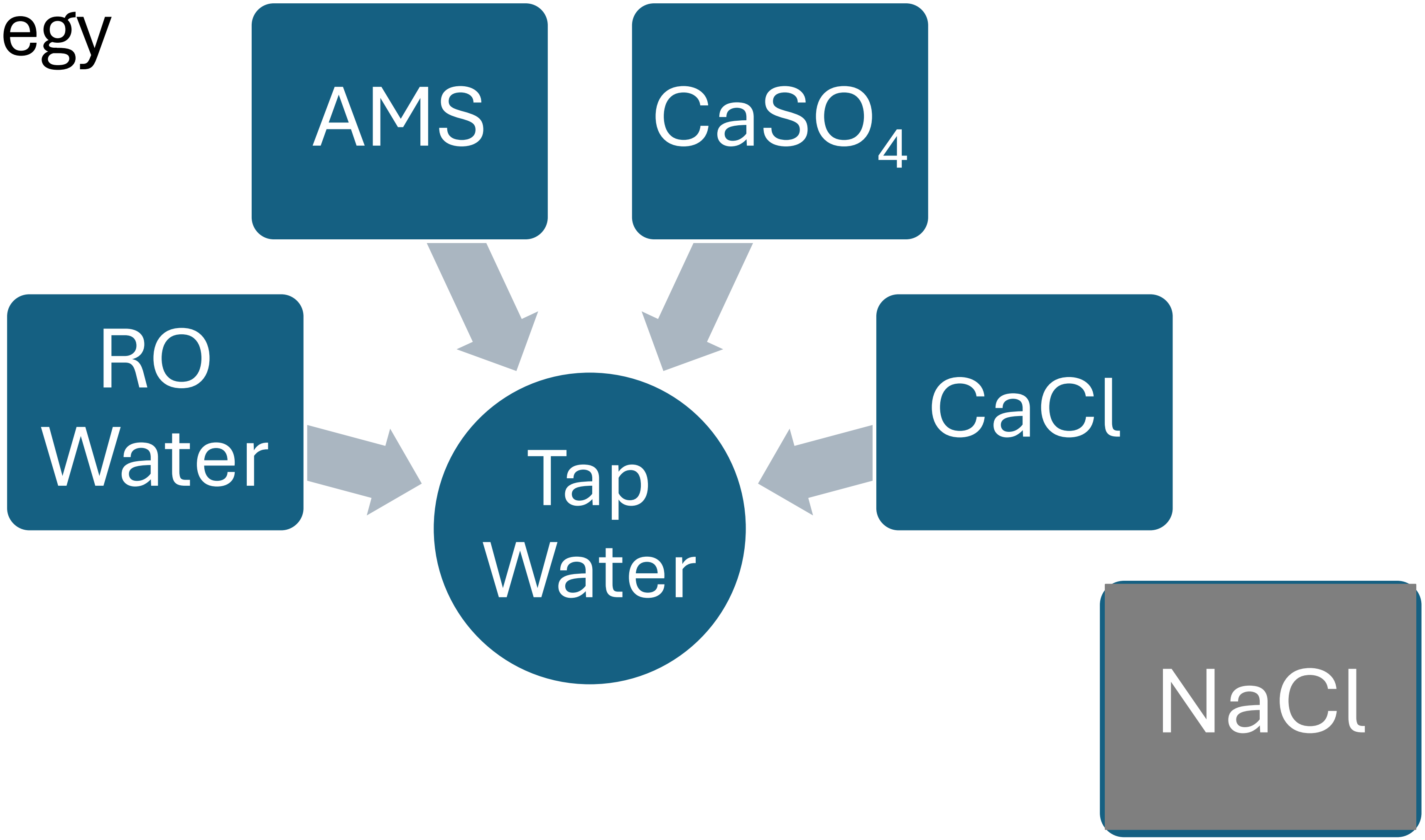
- Start with Tap water so that the task is to reduce Alkalinity
  - The simplest method to reduce alkalinity is to dilute tap water with DI or RO water
  - Adding Acids is good but they will have other effects:
  - Using AMS to reduce alkalinity adds Cl^- & SO_4^{2+} ions from Hydrochloric & Sulphuric Acids. Both Cl^- & SO_4^{2+} ions are already present in ground & surface water and are likely to be ions you wish to add to achieve the desired profile
  - Adding Lactic may give undesirable flavour effects similar to lactobacillus if over done
  - Phosphoric acid will reduce alkalinity but will have the side effect of precipitating out Ca^{2+} ions. Although PO_4^{3}- has little effect on flavour

Notes on Additions

Adjusting for Ca^{2+}, Cl^- & SO_4^{2+}

- Downside of using 100% RO water:
  - Ca^{2+} will need to be added using Calcium Chloride and/or Calcium Sulphate.
  - As there is no Ca^{2+} in RO then the resulting amounts of Cl^- & SO_4^{2+} may be too high
- Calcium Chloride is very soluble in water whereas Calcium Sulphate/Gypsum less so but manageable: 2.036 g/L
- As mentioned before Calcium Carbonate/Chalk has very poor solubility in water: 0.015 g/L

Strategy



3) My Process

1) Allow Chlorine to Air-Off Overnight
   - Only Chlorine is used in UK. Chloramine is used in USA
   - No need to add Campden/Metabisulfite tablets
2) Test Alkalinity
   - Hanna Alkalinity Checker
   - Fresh water
3) Decide Water Profile
   - Water: A Comprehensive Guide for Brewers by Palmer & Kaminski
   - Use Colour, Strength & Bitterness to determine Alkalinity, Ca^{2+}, Cl^{-} & SO_4^{2-} concentrations

Categorising the Style

Strength	Light	OG=1.030 to 1.045	Best Bitter
	Medium	OG=1.045 to 65	
	Strong	OG=1.065+	
Colour	Pale	0-18 EBC	
	Amber	18-36 EBC	Best Bitter
	Brown	35-70 EBC	
	Black	70+ EBC	
Bitterness	Soft	10-20 IBUs	
	Moderate	20-35 IBUs	Best Bitter
	Assertive	120+ IBUs	

Water: A Comprehensive Guide for Brewers – Palmer & Kominski

Water Profiles for Ale Styles

Strength	Colour	Bitterness	Ca^{2+}	SO_4^{2-}	Cl^-	Alkalinity (as $CaCO_3$)	Styles
Light Ale	Pale	Moderate	50-100	100-200	50-100	0-80	Blonde Ale; American Wheat; Bitter
Light Ale	Amber	Soft - Moderate	50-150	100-200	50-100	40-120	Mild; Scottish 60/70/80; Bitter; Best Bitter *
Light Ale	Brown/Black	Moderate	50-75	50-150	50-100	80-150	Brown Ale; Porter; Dry Stout
Medium Ale	Pale	Soft - Moderate	50-100	0-50	0-100	0-80	Weizen, Witbier, Cream Ale, Blonde Ale, Kölsh
Medium Ale	Pale	Moderate - Assertive	50-150	100-400	0-100	40-120	American Pale Ale, Saison, American IPA, DIPA
Medium Ale	Amber	Moderate - Assertive	50-150	100-300	50-100	40-120	Altbier, Californian Common, ESB, Irish Red, English IPA, Roggenbier, Belgian Pale, Saison
Medium Ale	Brown/Black	Moderate - Assertive	50-75	50-150	50-150	80-160	American & English Brown; Porter, Robust Porter; Sweet, Dry, American & Foreign Extra Stout; Dunklwiezen
Strong Ale	Pale	Moderate	50-100	50-100	50-100	0-40	Belgian Blonde, Tripel & Strong Golden
Strong Ale	Amber	Moderate - Assertive	50-100	50-100	50-150	40-120	Strong Scotch Ale; Bière de Gard, Dubbel; Old Ale; Barley Wine
Strong Ale	Brown/Black	Moderate - Assertive	50-75	50-100	50-150	120-200	Baltic Porter; Extra, American & Russian Imperial Stout; Wiezenbock; Belgian Dark Strong; Old Ale

inski

Water Profiles for Lager Styles

Strength	Colour	Bitterness	$Ca^{2}+$	SO_4^{2-}	Cl^-	Alkalinity (as $CaCO_3$)	Styles
Light Lager	Pale	Soft	50	0-50	50-100	0-40	American Lite Lager, Standard American Lager, Munich Helles
Medium Lager	Pale	Moderate - Assertive	50-75 35-150	50-150	50-100	0-40 40-80	American Premium Lager, German Pils, American Pils
Medium Lager	Amber	Soft - Moderate	50-75	0-100	50-100	40-120	Vienna, Oktoberfest
Medium Lager	Brown/Black	Soft - Moderate	50-75	0-50	50-150	80-120	American Dark, Munich Dunkel, Schwarzbier
Strong Larger	Amber	Soft - Moderate	50-75	0-50 0-100	50-150	40-80	Helles/ Maibock, Traditional Bock, Doppelbock
Strong Larger	Brown/Black	Soft - Moderate	50-75	0-50 0-100	50-150	80-150	Traditional Bock, Doppelbock, Eisbock, Baltic Porter

Water: A Comprehensive Guide for Brewers – Palmer & Kominski

3) My Process

1) Allow Chlorine to Air-Off Overnight
   - Only Chlorine is used in UK. Chloramine is used in USA
   - No need to add Campden/Metabisulfite tablets
2) Test Alkalinity
   - Hanna Alkalinity Checker
   - Fresh water
3) Decide Water Profile
   - Water: A Comprehensive Guide for Brewers by Palmer & Kaminski
   - Use Colour, Strength & Bitterness to determine Alkalinity, Ca^{2+}, Cl^{-} & SO_4^{2-} concentrations
4) Calculate Tap Water Dilution & Additions
   - Use My Water Treatment Spreadheet
5) Adjust & Check

Brewing Liquor: Balancing the Ions

Alan Osbiston

7th September 2024

Glossary

- Alkalinity
  - Indicates the total amount of acid that will be neutralized
- Target mash pH range is 5.2-5.6
- Final runnings of sparge needs to be below pH5.8 and above 1.008 SG / 2.0 Brix to avoid extracting tannins & off flavours

Glossary

- Buffer
  - A buffer works by resisting changes in pH. Remember that pH is only referring to the number of H^+ in the solution so any other chemical that
  - Most buffer works by being in equilibrium between it's weak base and weak acid form. In this case $CaCO_3$ (calcium carbonate) acts as a buffer in the bicarbonate form (HCO_3). So $CaCO_3$ will first disassociate into Ca^{2+} and CO_3^{2-}, you will then need to add some acid into the solution to change CO_3^{2-} into HCO_3. $(H^+) + (CO_3^{2-}) \rightarrow (HCO_3^-)$. In that form it can resist changes in pHcan resist changes in H^+ will be a good buffer.

Glossary

- Water Solubility:
  - $CaCO_3$ – Chalk 0.015 g/L
  - $CaSO_4.2H_2O$ – Gypsum 2.036 g/L