Better Living Through Brewhouse Water Chemistry

Joe Walts
Ale Asylum
5/17/2012

Overview

- Many small craft brewers, and even some regional ones, don't pay much attention to water chemistry.
  - For some, the consequence is minimal. Potable surface water (e.g. water from lakes and rivers) is great for brewing.
- Water treatment can be extremely complicated, but simply getting in the right ballpark can dramatically improve the flavor and stability of your beer.
  - However, trying to account for every variable will yield diminishing returns.
- I'm not a chemist, and some of these calculations are based on a very limited set of experimental data. Your feedback will make us all smarter.

Fundamental Concepts

- Malt is a pH buffer that’s strongest around 5.4-5.8.
  - In general, dark malts are more acidic than light malts.
- Water with carbonate alkalinity is a pH buffer that’s strongest at a higher pH than malt.
- The influence of alkalinity will increase as the water-to-grain ratios of your mashes increase.
- Calcium and magnesium will lower mash pH, but not by very much.
- Adding acids to eliminate carbonates will result in lower mash pHs. When carbonates are absent, acids will continue to lower mash pHs.

A Quick Word on Units

- Water reports often give ion concentrations in mg/L or ppm (parts per million). For brewers, the two units are interchangeable.
- The charge-based unit mEq/L (milliequivalents per liter) is convenient for water chemistry. For a given ion:
  - mEq/L = mg/L x Ionic Charge / Molar Mass
- Alkalinity is often given as mg/L as CaCO3, even if the report simply says ‘mg/L’. mg/L as CaCO3 is simply equal to 50 x mEq/L.

Baseline Water

- Baseline water = water in your hot liquor tank.
- Low alkalinity will reduce tannin extraction during sparging, as well as chalk buildup in hot water pipes and tanks.
  - 1 mEq/L is a good target because it's near the natural decarbonation limit of water with sufficient calcium, which means that very little chalk will precipitate.
- If you treat your water in a cold or ambient liquor tank, you can use treated water to cool your wort. This will reduce chalk in your heat exchanger

Removing Alkalinity

- My preferred method is to add lactic acid.
- It doesn't precipitate solids, and can therefore be used in hot liquor tanks without causing excessive mineral buildup.
- Unlike slaked lime and phosphoric acid, lactic acid won't deplete your water of calcium.
- It's easy to find and relatively safe to handle.
- In my experience, proper lactic acid treatments give beer a soft mouthfeel.

Step 1: Calculate Lactic Acid Addition to Baseline Water

- Ab = 1000 x (S / 100) x (99.5 / 100) / 90.09 / ((S / 100) / 1.2 + (1 – S / 100))
  - Acidity of lactic acid for baseline water in mEq/L
  - S = Strength of lactic acid as a mass percentage. 88% is common.
- Vlab = (TA1 – TA2) x Vwb x 117.348 / Ab
  - Vlab = Volume of lactic acid in mL
  - TA1 = Total alkalinity of source water in mEq/L
  - TA2 = Target total alkalinity of baseline water in mEq/L
  - Vwb = Volume of baseline water to treat in bbl

Adding Calcium

- Calcium is important for yeast flocculation[1] and beer clarity[2]. Based on vague conventional wisdom, I aim for a minimum concentration of 2.5 mEq/L in my water.
- If needed, calcium can be added to your baseline water or as separate additions to your mash and kettle.
- Two common salts used to add calcium are calcium chloride and calcium sulfate (gypsum).
  - Molar Mass of $CaCl_2 \times 2H_2O$ = 147.02 g/mol
  - Molar Mass of $CaSO_4 \times 2H_2O$ = 172.17 g/mol
- Calcium sulfate is often thought to enhance hop character. This is rubbish[3]. It can make your beer taste more English or lager-like, though.

Step 2: Calculate Calcium Chloride and Calcium Sulfate Additions

- CaN = (Ca1 – Ca2) x Vw x 117.348 x MM / 2 / 1000
  - CaN = Calcium chloride or calcium sulfate to add in grams
  - Ca1 = Initial calcium concentration in mEq/L
  - Ca2 = Desired calcium concentration in mEq/L
  - Vw = Volume of water to treat in bbl. For baseline water additions, Vw = Vwb from Step 1. For mash additions, Vw = mash water volume. For kettle additions, Vw = sparge water volume minus water volume retained by spent grain.
  - MM = Molar mass of CaCl2 or CaSO4 in g/mol

Optimal Mash pHs

- Brewing scientists hold differing opinions:
  - Bamforth: 5.6-6.1 maximizes extract and fermentability, but 5.0-5.5 maximizes soluble nitrogen and FAN[4]. Most mashes are 5.3-5.5[5].
  - Kunze and Narziss[6, 7]: 5.5 is optimal for starch conversion, but 5.2-5.4 is ideal for beer flavor and stability.
  - DeLange: "the biggest single improvement in my brewing in the last 5 years or so came when I started actively controlling pH to between 5.3 and 5.4."[8]
- Values are for room temperature measurements.
- Common pH strips read low by about 0.3[9].

Mash pH Sampling

- In my experience, pH drops during conversion rests.
    - pH measurements near the end of conversion are repeatable, and are good indicators of kettle wort pH.
    - Controlling pH near the end of conversion results in higher pHs (i.e. better for amylases) when the enzymes are most active.
- If you take pH samples from vorlauf or first runnings wort, your samples may be diluted by lauter tun foundation water.
- Bottom line: my calculations target a pH of 5.4, I pull samples near the end of starch conversion, and I'm happy with measurements between 5.2 and 5.5.

Grainbill Assumptions

- Assume the following:
  - pH of a mash with distilled water and Pilsner malt will be 5.65.
  - Acidulated malts will drop mash pH by 0.1 for every % weight of the grainbill they comprise.
  - Dark-roasted malts will drop mash pH by 0.028 for every % weight of the grainbill they comprise.
  - Pale malted wheat will raise mash pH by 0.003 for every % weight of the grainbill it comprises
  - Other types of malt will drop mash pH by 0.00027 for every % weight of the grainbill they comprise per degree Lovibond above typical Pilsner malt (assume typical Pilsner malt is 1.8 Lovibond).
- Note that we're assuming dark-roasted malts contribute a fixed amount of acid regardless of color, while the acidities of "other" malts increase linearly with color[10]. Above ~105 degrees Lovibond, "other" malts are more acidic than dark-roasted malts.

Step 3: Estimate Distilled Water Mash pH of Grainbill

- $pHd = 5.65 - 0.1 \times PA - 0.028 \times PR + 0.003 \times PW - Sum(0.00027 \times POn \times (COn - 1.8))$
  - PA = Total weight percentage of acidulated malts in the grainbill
  - PR = Total weight percentage of dark-roasted malts in the grainbill
  - PW = Total weight percentage of pale malted wheat in the grainbill
  - POn = Weight percentage of each other type of malt in the grainbill
  - COn = Color, in degrees Lovibond, of each other type of malt in the grainbill

Residual Alkalinity

- RA = TA – Ca/3.5 – Mg/7
  - RA = Residual alkalinity in mEq/L
  - TA = Total alkalinity in mEq/L
  - Ca = Calcium ion concentration in mEq/L
  - Mg = Magnesium ion concentration in mEq/L
- Assume mash pH shift = 0.059 x Total mEq of RA / lbs of Grain.

Step 4: Calculate Initial Residual Alkalinity of Mash Water

- Simply plug values of your mash water into the general residual alkalinity formula.
- RAi = TAi – Ca/3.5 – Mg/7
  - RAi = Initial residual alkalinity of mash water
  - TAi = Initial total alkalinity of mash water = TA2 from Step 1
  - Ca = Calcium concentration of mash water. If you plan to add calcium salts to your baseline water or mash water, Ca = Ca2 from Step 2
  - Mg = Magnesium concentration of mash water

Step 5: Calculate Target Residual Alkalinity of Mash Water

- This is the residual alkalinity of mash water that will result in your target mash pH.
- RAt = (pHt – pHd) x Wg / 0.059 / (Vwm x 117.348) + 0.05
  - RAt = Target residual alkalinity in mEq/L
  - pHt = Target mash pH
  - pHd = Distilled water mash pH from Step 3
  - Wg = Grainbill weight in lbs
  - Vwm = Mash water volume in bbl

Step 6: Calculate Lactic Acid Addition to Mash

- D = 100 x (1 – 1 / (1 + 10^(pHt – 3.83)))
  - D = dissociation percentage of lactic acid in mash
  - pHt = Target mash pH
- Am = 1000 x (S / 100) x (D / 100) / 90.09 / ((S / 100) / 1.2 + (1 – S / 100))
  - Acidity of lactic acid for mash in mEq/L
  - S = Strength of lactic acid as a mass percentage. 88% is common.
- Vlam = (RAi – RAt) x Vwm x 117.348 / Am
  - Vlam = Volume of lactic acid in mL
  - RAi = Initial residual alkalinity from Step 4
  - RAt = Target residual alkalinity from Step 5

Step 7: Calculate Calcium Carbonate Addition to Mash

- You'll only need calcium carbonate if you want to raise the residual alkalinity of your mash water (i.e. $RAt > RAi$). If you plan to add acid to your mash, this step will not be necessary.
- $CaCO3 = (RAt - RAi) \times Vwm \times 117.348 \times 100.09 / 2 / 0.714 / 1000$
  - CaCO3 = Calcium carbonate to add in grams
  - RAi = Initial residual alkalinity from Step 4
  - Vwm = Mash water volume in bbl
- Due to the limited solubility of calcium carbonate as a mash addition, don't use this equation if the target total alkalinity of your mash water exceeds 5 mEq/L[11].

Example: Initial Parameters

- Water supply:
  - TA = 6.78 mEq/L
  - Ca = 3.992 mEq/L
  - Mg = 3.702 mEq/L
- Baseline water volume = 100 bbl
- Mash water volume = 48.4 bbl
- Target total alkalinity of baseline water = 1 mEq/L
- Lactic acid strength = 88%
- Total grainbill = 4,000 lbs
  - Pilsner malt = 3,175 lbs = 79.3% of grainbill
  - Munich II malt (9L) = 770 lbs = 19.3% of grainbill
  - Carafa Special II malt = 55 lbs = 1.4% of grainbill

Example: Steps 1-4

- Acidity of lactic acid = 1000 x (88 / 100) x (99.5 / 100) / 90.09 / ((88 / 100) / 1.2 + (1 – 88 / 100)) = 11.39 mEq/L
- Lactic acid to baseline water = (6.78 - 1) x 100 x 117.348 / 11.39 = 5,955 mL
- Ca > 2.5 -> No calcium salts needed.
- Distilled water mash pH of grainbill = 5.65 – 0.028 x 1.4 – 0.00027 x 19.3 x (9 – 1.8) = 5.57
- Initial residual alkalinity of mash water = 1 – 3.992 / 3.5 – 3.702 / 7 = -0.669 mEq/L

Example: Steps 5-7

- Target residual alkalinity of mash water = (5.4 – 5.57) x 4,000 / 0.059 / (48.4 x 117.348) + 0.05 = -1.979 mEq/L
- Lactic acid dissociation = 100 x (1 – 1 / (1 + 10^(5.4 – 3.83))) = 97.4%
- Acidity of lactic acid = 1000 x (88 / 100) x (97.4 / 100) / 90.09 / ((88 / 100) / 1.2 + (1 – 88 / 100)) = 11.149 mEq/L
- Lactic acid to mash = (-0.669 + 1.979) x 48.4 x 117.348 / 11.149 = 667 mL
- Acid addition to mash -> no calcium carbonate needed.

Additional Resources

- A.J. DeLange's brewing website, which has a lot of information about water chemistry:
  - http://http://hbd.org/ajdelange/
- Kai Troester's website about the affects of pH on brewing processes (note that the targets and assumptions outlined in this presentation do not always match Kai's):
  - http://braukaiser.com/wiki/index.php?title=How_pH_affects_brewing
- My water treatment spreadsheet, which will do the math for you:
  - Download at http://sites.google.com/site/republicbrewpub/
  - File name is Water_Barrels.xlsx

Sources

- 1: http://www.wyeastlab.com/hb_clarification.cfm
- 2: Jean De Clerck. A Textbook of Brewing, Volume One. Siebel Institute of Technology, 1994.
- 3: Van Havig. “Maximizing Hop Aroma and Flavor Through Process Variables”. MBAA Technical Quarterly Volume 47, 2010, Quarter 2.
- 4: Charles W. Bamforth. Scientific Principles of Malting and Brewing. American Society of Brewing Chemists, 2006.
- 5: Michael J. Lewis and Charles W. Bamforth. Essays in Brewing Science. Springer Science+Business Media, LLC, 2006.
- 6: Wolfgang Kunze. Technologie Brauer und Maelzer. Second-hand reference from http://braukaiser.com/wiki/index.php?title=How_pH_affects_brewing.
- 7: Ludwig Narziss and Werner Back. Abriss der Bierbrauerei. Second-hand reference from http://braukaiser.com/wiki/index.php?title=How_pH_affects_brewing.
- 8: http://www.homebrewersassociation.org/forum/index.php?topic=3657.0
- 9: http://www.braukaiser.com/wiki/index.php?title=ColorpHast_vs_pH_meter
- 10: http://braukaiser.com/wiki/index.php?title=Mash_pH_control
- 11: http://braukaiser.com/wiki/index.php?title=Building_brewing_water_with_dissolved_chalk