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#ElevateBeer

A Study of Mash pH and its effects on Yield and Fermentability

And Plan B: Exploring the effect of Residual Alkalinity and Water-to-Grist Ratio on Mash pH

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Source Water

- Surface Water is typically low in minerals and high in organics.
  - Surface water generally needs more chlorination than ground water.
- Ground Water is typically low in organics but higher in minerals.
  - Ground water is typically higher in alkalinity than hardness.
- Many cities change their water source during the year.

Source Water Treatment

- Carbon Filtration
  - Always a good first step
  - Removes residual chlorine/chloramine
  - Removes organic chemicals and odors
  - Often used in conjunction with Ultra-violet Light
- Alkalinity Reduction (optional)
  - Acidification – Neutralizes alkalinity, adds acid anion
  - Ion-exchange – Selective removal of ions *(Softening)*
  - Reverse Osmosis – Strip, then rebuild

What is Water Hardness?

- Hardness = The sum of Calcium and Magnesium measured as calcium carbonate
  - We WANT calcium and magnesium in our mash/beer.
  - Permanent Hardness = Ca/Mg Sulfates & Chlorides
  - Temporary Hardness = Ca/Mg Bicarbonate, Carbonate
  - SOFT = Not Hard.

What is Alkalinity?

- Total Alkalinity = the sum of carbonate species in water (from limestone)
  - <u>Alkalinity ≅ Temporary Hardness</u>
  - This is why we say we want to get rid of temporary hardness.
  - Alkalinity raises Mash pH, makes beer less acidic, but duller

What is "As $CaCO_3$"?

- Calcium Carbonate is limestone.
- It is the major source of hardness, alkalinity, and scale on plumbing.
- Therefore, Hardness (Ca^{+2}, Mg^{+2}) and Alkalinity (HCO_3^{-1}, CO_3^{-2}) are measured in terms of their <u>equivalents</u> "as $CaCO_3$"

Measuring Concentration as $CaCO_3$

- Calcium, magnesium, and bicarbonate can be measured as themselves, i.e., Ca^{+2} 40 ppm
- Or they can be measured as their calcium carbonate potential, i.e., “as $CaCO_3$.
- The equivalent weight of $CaCO_3$ is 50 g/eq.
- 40 ppm Ca = 40/20 x 50 = 100 ppm Calcium Hardness as $CaCO_3$

Water Affects Beer Flavor

- Seasoning Balance: Sulfate to Chloride Ratio
  - More Sulfate = drier, more assertive hops
  - More Chloride = rounder, fuller, sweeter malt
- Amount of Seasoning
- Water Residual Alkalinity drives Mash pH,
  Mash pH drives Beer pH,
  Beer pH drives beer flavor expression.

Sulfate to Chloride Ratio

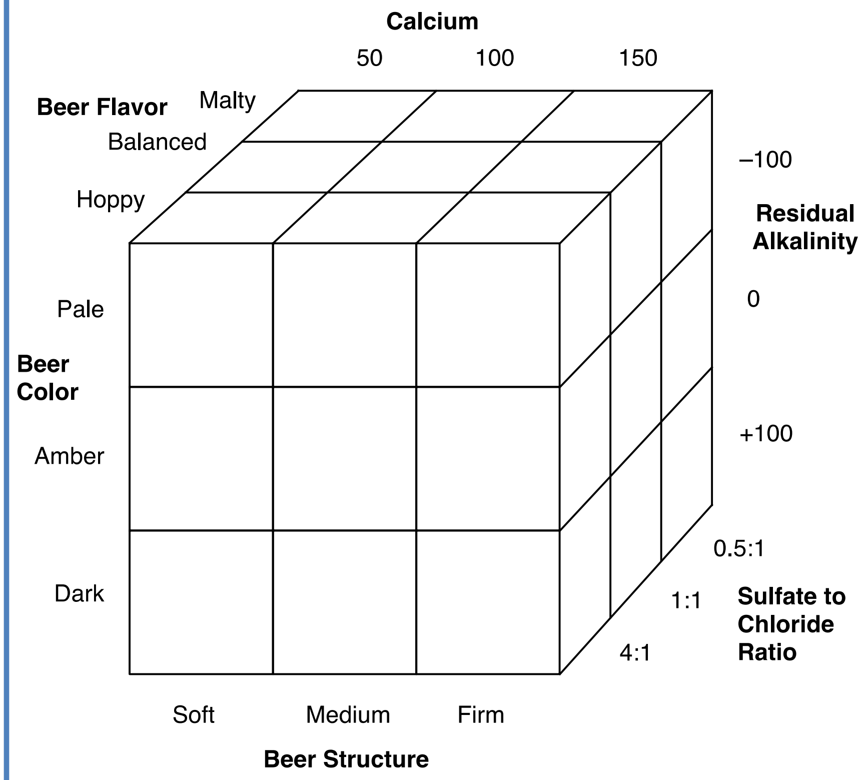
- The Ratio can affect the balance of the beer
  – Dryness vs. Fullness
- It is not magic – 40:10 ≠ 400:100
- Useful range is 9:1 to 0.5:1
  - Maximum suggested sulfate is 400 ppm
  - Maximum suggested chloride is 150 ppm
  - Recommend not to exceed 100 ppm chloride for high ratios.
  - Recommend to not exceed combined sum of 500 ppm.

TDS Effect – Total Dissolved Solids

- Light vs Heavy Seasoning
- Bohemian Pilsner
  - Rich, malty beer backed by large soft bitterness. Smooth finish balanced between malt and hops. No sharp edges.
- German Pils
  - Crisp and bitter hop forward character, followed by clean malt and dry finish. This is a beer defined by clean edges.
- Dortmunder Export
  - Balanced rich malt and firm dry bitterness. A “castle” of beer structure.

Adjusting Water for Style Summary

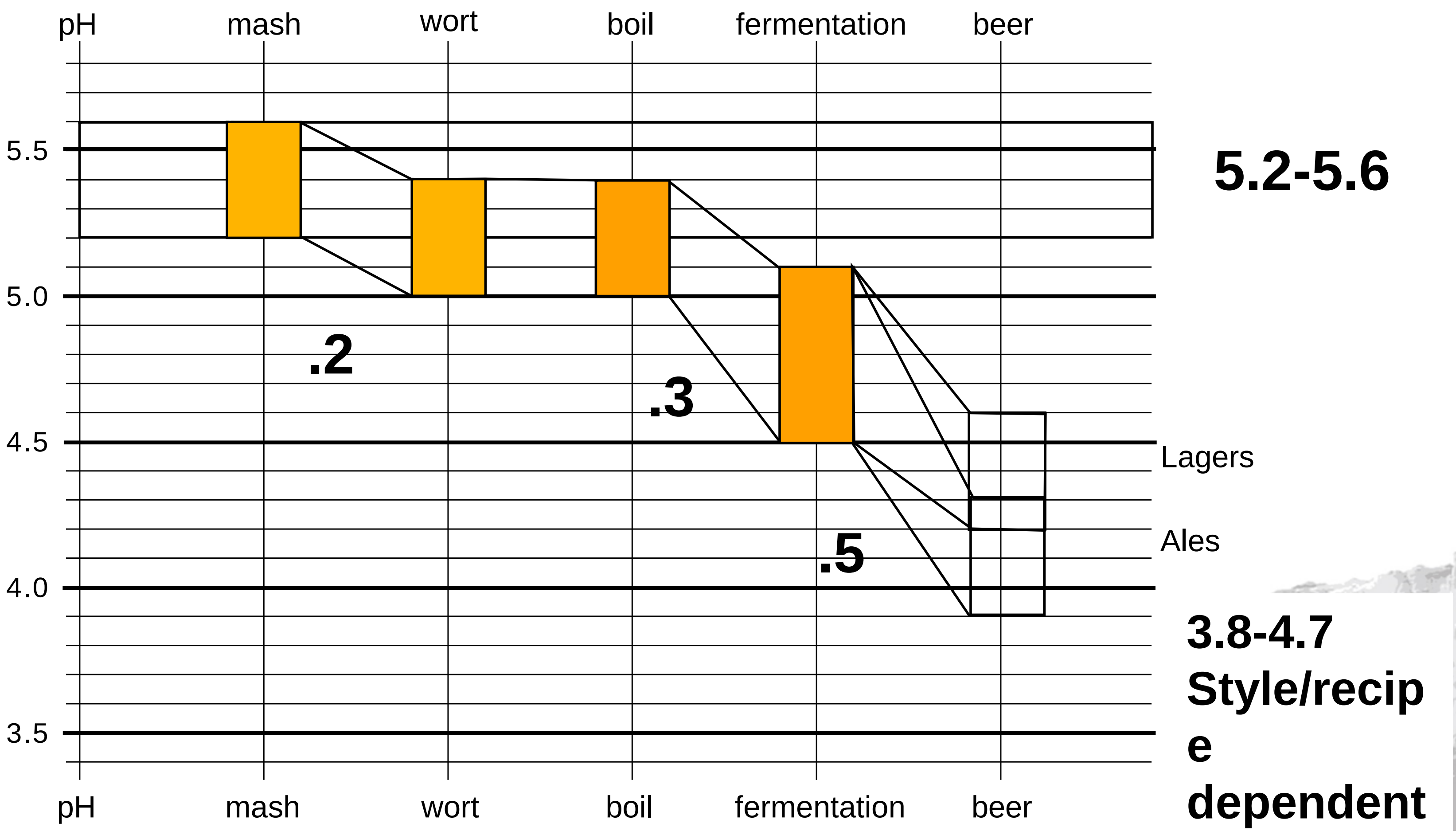
- Mash pH should be 5.2-5.6 (paler = lower)
- Beer pH should be 4.0-4.4 (paler = lower)
- To Adjust water for style, in *general*:
  - Define the style by Flavor, Color, & Foundation.
  - Read water profile by Calcium, Residual Alkalinity, and Sulfate-to-Chloride Ratio.



Why Do We Care About Mash pH?

- “The key point for control of pH throughout the brewing process is during mashing. This is due to the major influence that can be exerted at this stage on the content and format of the buffer systems that will operate subsequently in the wort and beer.”
  - Taylor, D.G., The Importance of pH Control during Brewing, *MBAA Tech. Quart.* 27:131-136, 1990.

Mash pH Sets Up Beer pH



What Does Beer pH Do?

- The beer pH affects how the beer flavors are perceived by the palate.
- Spaghetti Sauce Example
  - pH is too acidic: It’s bright but not rich, one dimensional.
  - pH is too basic: It’s rich but dull, boring.
  - pH just right: Bright, Rich, Complex flavors.
- Beer Flavor is the same:
  - pH is too high, malt character is dull, bitterness is heavy.
  - pH is too low, malt flavor is sharp, but one dimensional, hop character is reduced.

Mash pH is the Equilibrium between Water Chemistry and Malt Chemistry

- The affect of water chemistry can be quantified by Kolbach's Residual Alkalinity.
- The affect of malt chemistry can be quantified by
  - The distilled water mash pH of the malt (ie., Congress Mash pH)
  - The titrated acidity of the malt for the pH range in question.
    - The buffering capacity of malt (ΔmEq/kg/ΔpH) is not linear.

Pale Ale Experiment - 2014

Parameter	Big Rapids, MI	Adjusted
Calcium	40	130
Magnesium	19	19
Total Alkalinity	180	70
Sulfate	10	230
Chloride	10	10
Sodium	15	15
Residual Alkalinity	140	-35

Big Rapids Water vs Adjusted

Parameter	Big Rapids	Adjusted
OG	1.048	1.048
FG	1.011	1.011
IBU	40	40
Mash pH	5.5	5.25
Beer pH	4.6	4.5

Data originally presented at AHA National Homebrewers Conference 2014, courtesy of Crankers Brewery, Big Rapids, MI.

Stout Experiment - 2016

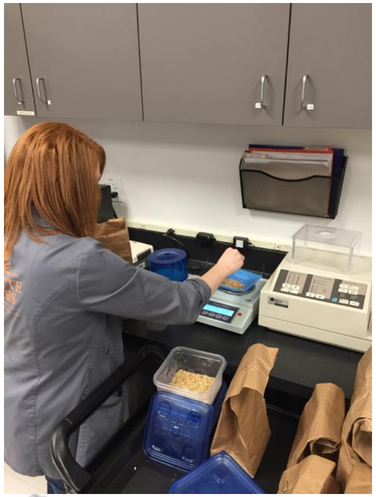
- 3rd Congresso Technico dos Cervejeiros Artensanais in Florianopolis, Brazil.
- Brewed same Stout with 2 waters
  - High RA 140 ppm as $CaCO_3$ Mash pH = 6.2
  - Low RA 14 ppm as $CaCO_3$ Mash pH = 5.3
- Triangle Test of 134 conference attendees
  - 78/134 correctly identified the different beer.
  - P value = .00000001 ($P < 0.05$ for significance)

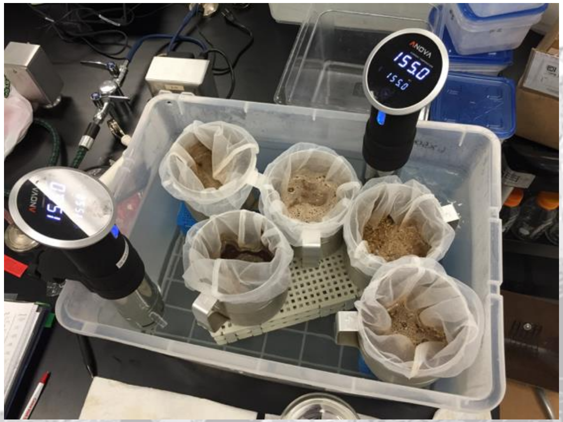
The “original” Conf. proposal

- Originally, the idea was to explore several water chemistries and their effect on the yield, fermentability and flavor of a pilot porter recipe.
- The results of that experiment would be used to design a couple of pilot batches at Ballast Point Brewing.

Experiment Parameters

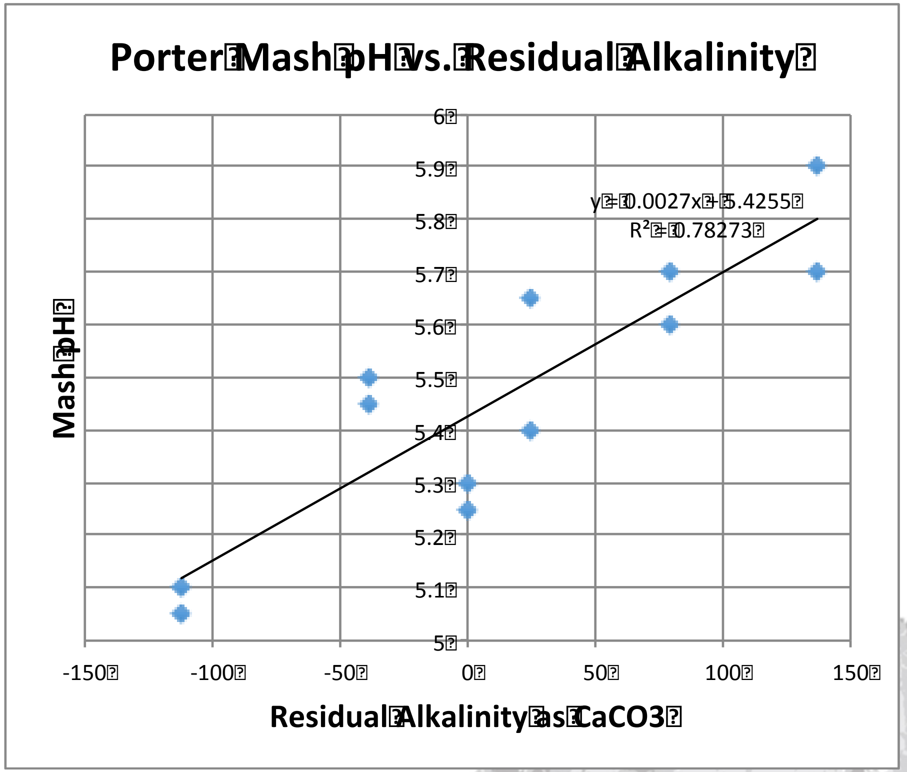
- Porter recipe: 64% base malt, 8% C80L, 8% Flaked Barley, 8% Victory, 8% Chocolate, 2% Black.
- 200g in 800ml of water
- 5 Waters, plus Distilled
  - 1: RA = –112
  - 2: RA = -39
  - 3: RA = 79
  - 4: RA = 137
  - 5: RA = 25
  - 6: Distilled (0)
- 2 Samples per condition.





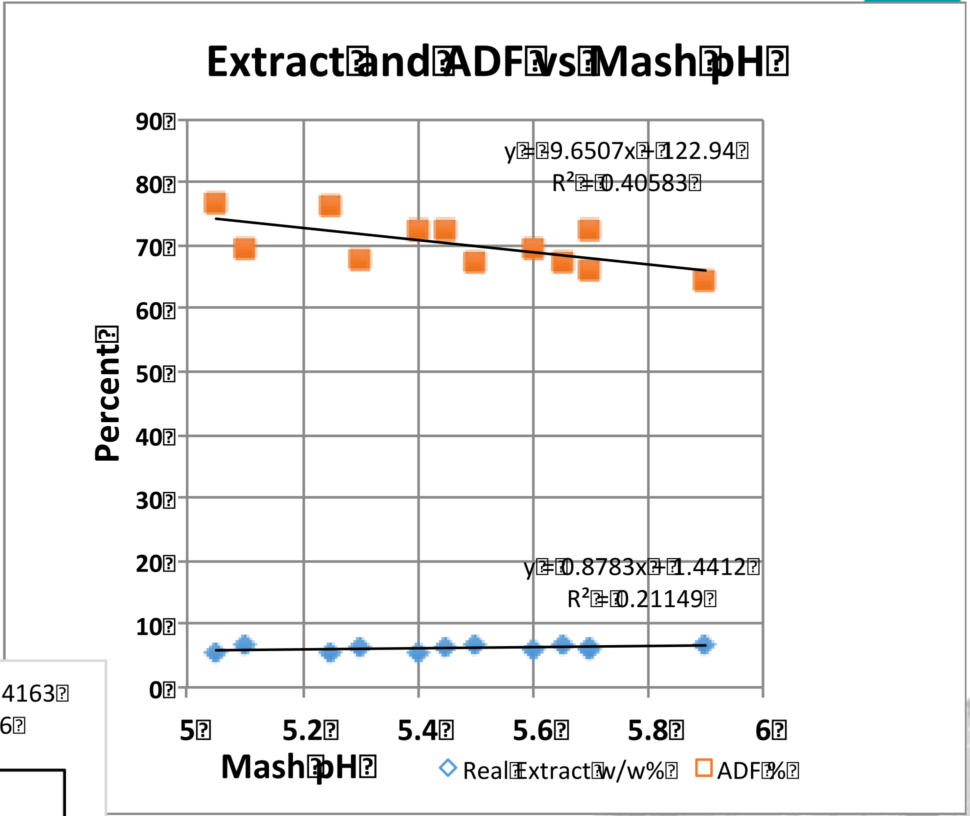
Results of Experiments

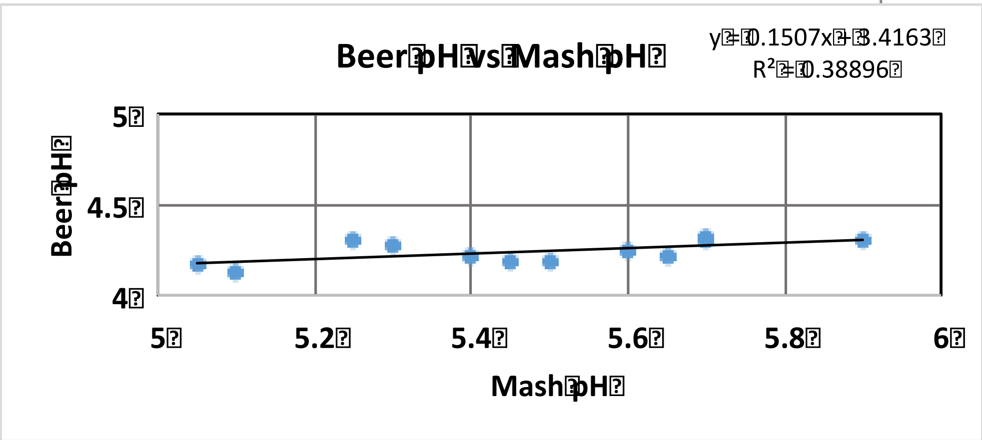
- Mini-mashes of 250g in 1 liter of water at 150-155°F (65-68°C) in water bath at 155°F (68°C) for 1 hour.
- BIAB Method – Wort drained from grain bag and pH and fermentation samples taken.
- 100 ml of wort were force fermented using WLP001.



Results of Mini-mash Experiment

- The results of the mini-mashes and forced fermentations were largely inconclusive.
- The most likely issues were the small volumes and high pitching rates obscuring the differences between samples.





Only a general trend was evident in the data.

Plan B: Exploring Mash pH and RA

- There is not much published data on mash pH as a function of residual alkalinity.
  - Troester, K., The effect of brewing water and grist composition of the pH of the mash., http://braukaiser.com/documents/effect_of_water_and_grist_on_mash_pH.pdf, 2009.
    - Troester noted that amount of effect seemed to vary between malts, and with water to grist ratio.
    - His results were in the same ballpark as Kolbach.
  - Barth, R., Zaman, R., Influence of Strike Water Alkalinity and Hardness on Mash pH, J.ASBC 73(3):240-242, 2015.
    - Barth and Zaman determined that the 3.5 factor for calcium hardness was not even close to their data.
    - The factor could be as large as 7-15 based on their data for pilsner, pale ale, and Munich malts.

Review of Residual Alkalinity

- The concept of residual alkalinity started with Kolbach, Schwabe, and Haussmann in 1941.
- Wochenschrift für Brauerei LVIII. Jahrgang No. 44, November 1st 1941, pp.231/232
- They determined that 3.5 equivalents of calcium hardness would neutralize 1 equivalent of alkalinity, and it's effect on wort pH.
  - I don't know if their basis was experimental or stoichiometric.

Review of Residual Alkalinity

- Residual Alk = Total Alk – (Ca/3.5 + Mg/7)
    - In mEq/L or milli-val or ppm as $CaCO_3$
- This concept has been applied to the brewing water and the mash for many years with reasonable success.
- It is recognized that other factors are at play: Specific malts and buffering, mash rests, water:grist ratio, etc.

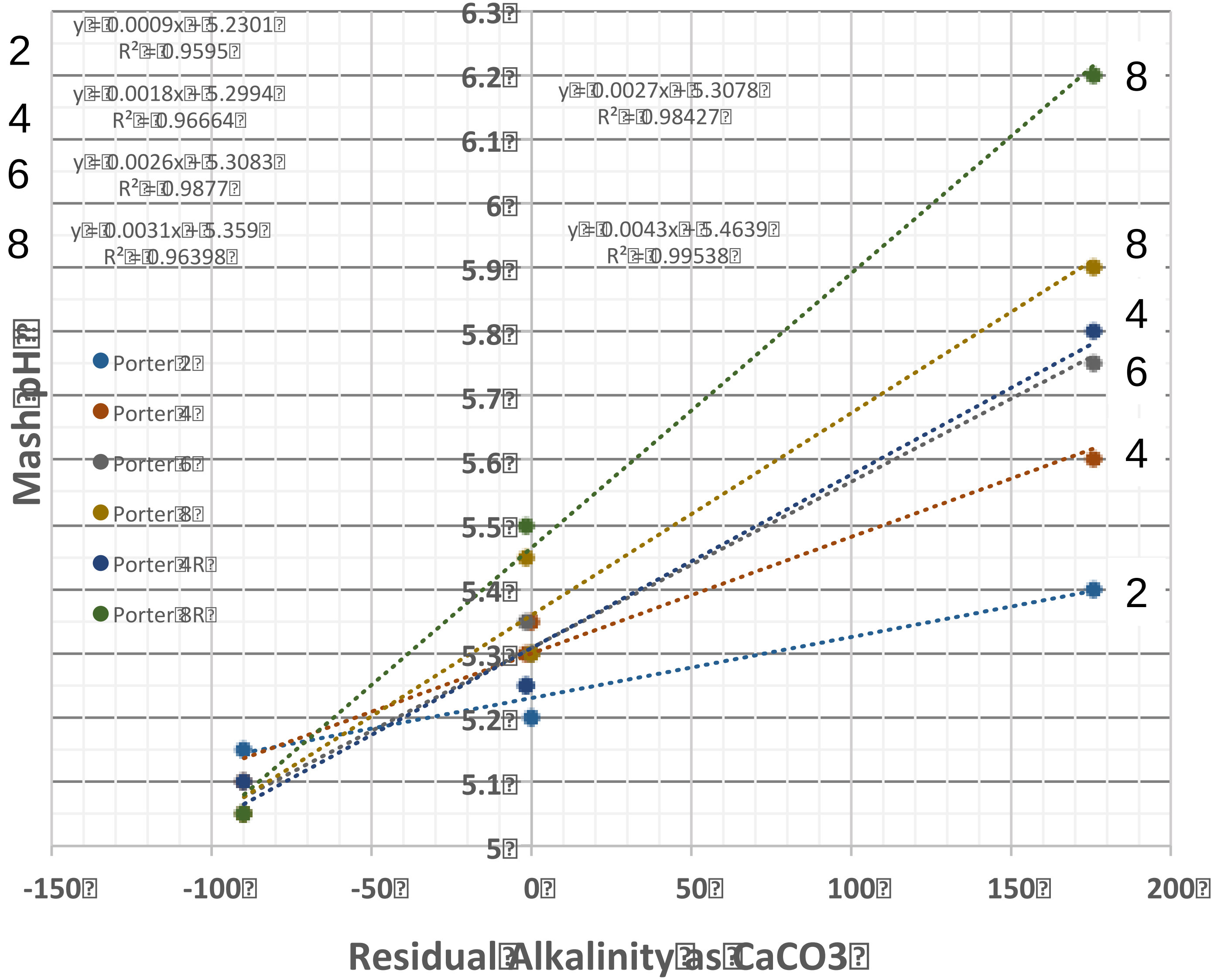
Plan B: Explore RA and R (L/kg) as it effects Mash pH

- A simplified porter recipe was used to examine mash pH as a function of R.
- 3 of the 5 waters plus distilled were used.
- Samples were mashed for 15 minutes between 150-160°F (65-71°C) in 155°F bath.
- After 15 minutes, grain bag removed, wort samples were cooled to room temperature and pH measured.

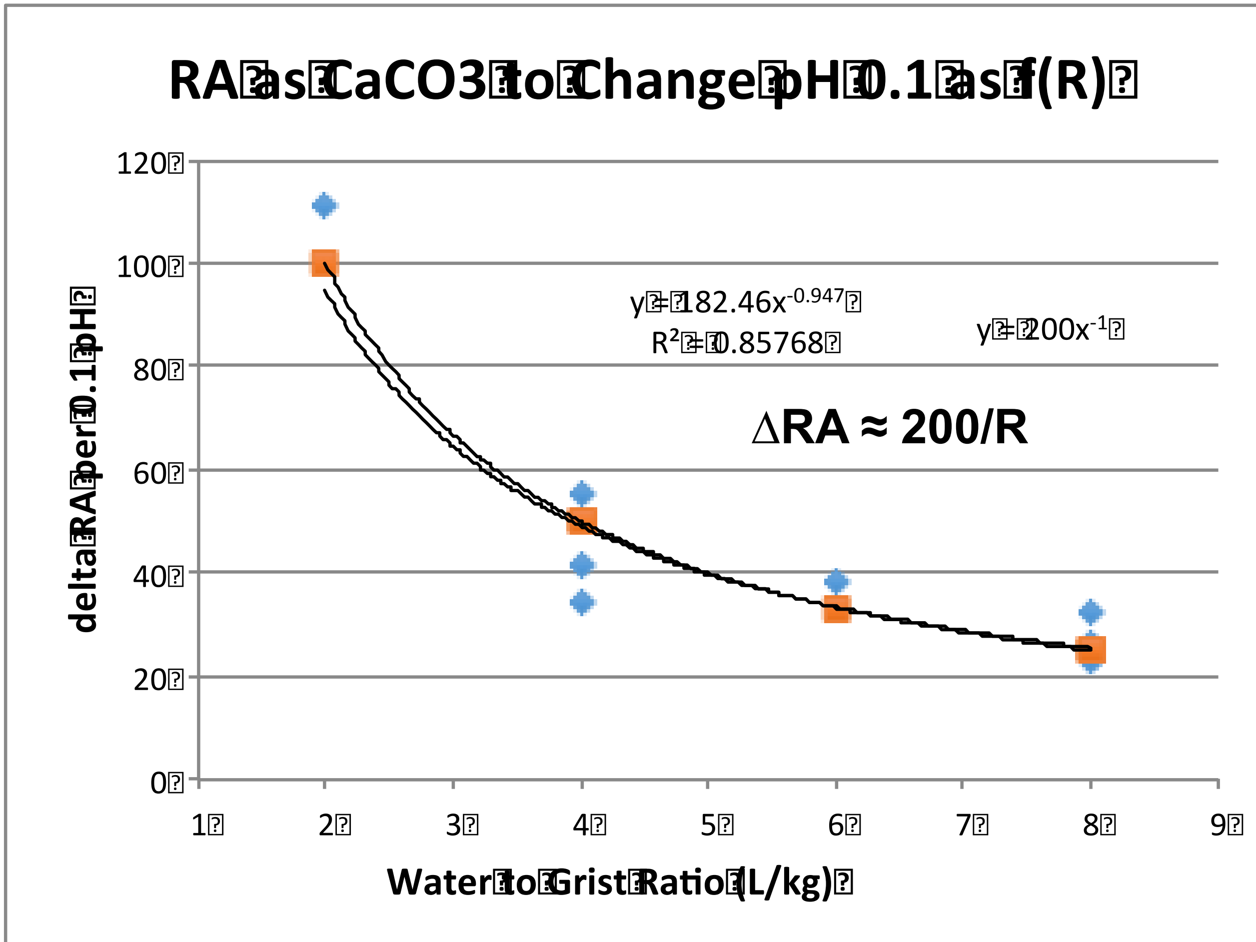
Simple Porter pH Data

RA	mEq/L Alk	mEq/L Ca	Porter 2	Porter 4	Porter 6	Porter 8	Porter 4R	Porter 8R
-90	**0**	**2.5**	5.15	5.1	5.05	5.05	5.1	5.05
0	**0**	**0**	5.2	5.35	5.3	5.3		
-2	**1.75**	**2.5**	5.25	5.3	5.35	5.45	5.25	5.5
176	**4.4**	**1.25**	5.4	5.6	5.75	5.9	5.8	6.2
Ppm/0.1 pH			*111*	*55.6*	*38.46*	*32.25*	*37*	*23*

Change in Mash ph vs Residual Alkalinity as f(R)

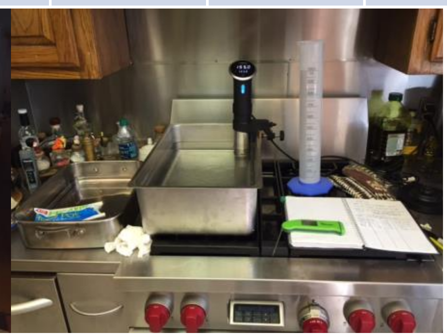


ΔRA inversely proportional to R



pH Data on Pilsner & Base malt

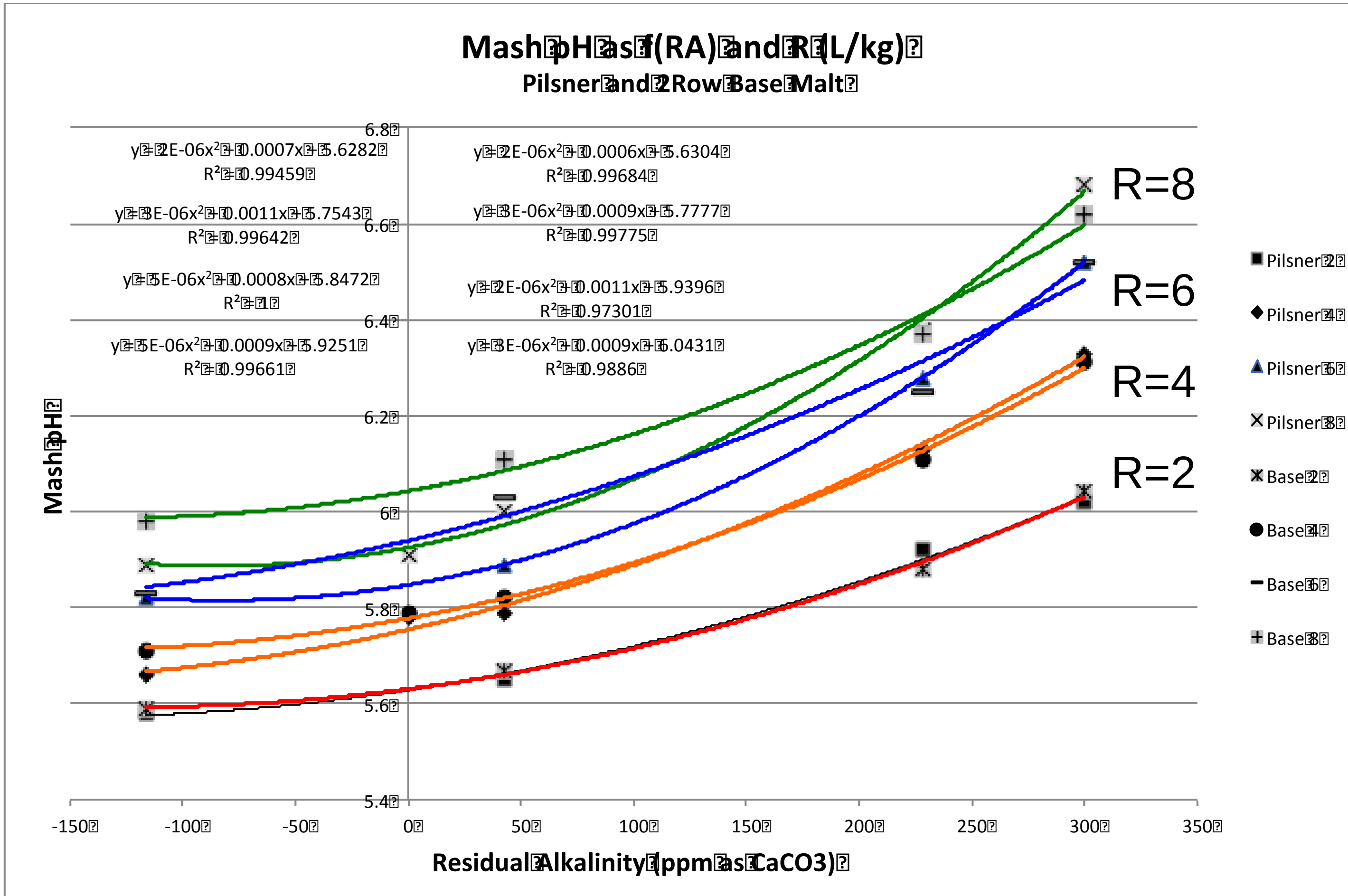
RA	mEq Alk	mEq Hard	Pilsner 2	Pilsner 4	Pilsner 6	Pilsner 8	Base 2	Base 4	Base 6	Base 8
300	***6***	***0***	6.02	6.33	6.52	6.68	6.04	6.31	6.52	6.62
228	***6***	***2***	5.92	6.13	6.28	6.38	5.88	6.11	6.25	6.37
43	***3***	***3***	5.65	5.79	5.89	6	5.67	5.82	6.03	6.11
0	***0***	***0***		5.78		5.91		5.79		
-116	***2***	***6***	5.58	5.66	5.82	5.89	5.59	5.71	5.83	5.98



100g of malt, 150-155F (65-68C), 15 minutes. R = 2, 4, 6, 8 L/kg

Increasing Effects

Alkalinity seems to have a stronger effect to raise pH than hardness does to lower it.



Summary

- Residual Alkalinity is known to directly affect mash pH.
- Magnitude of effect varies inversely with water-to-grist ratio R, for a particular water.
  - My data suggests about 1 mEq/L RA per 0.1 pH at a mash ratio of 4 L/kg although this varies with malt type, and specific amount of RA.
- High positive values of RA raise mash pH to a greater degree than negative values reduce mash pH.