Water Quality from a Craft Brewing Perspective

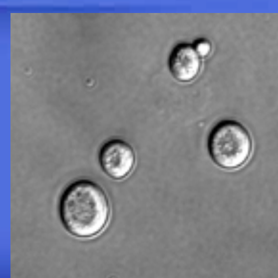
Jim Mellem – Sierra Nevada Brewing Co.
MBAA Northwest Spring Meeting -- 2011

Overview of Presentation

- **Some background knowledge**
- Simple tests to determine water quality
- Experiments with calcium additions

Which of these raw materials do you pay the most / least attention to?






Where does your water come from?

- Municipal
  - Advantages: Analytical testing, steady supply
  - Disadvantages: Price fluctuations, well switching, mystique (?)
- Private well
  - In control of water supply
  - Need to test for microorganisms, harmful inorganics and organics
  - May have to deepen well during drought, think about runoff, pumping to deliver, etc.

Water Quality Reports

- Totally free!
- Varies by water district
- Typically broken down into a few major sections
  - Public Information (water source, conservation, etc.)
  - Health Based Standards
    - Arsenic, chromium, tetrachloroethylene, coliform, etc.
    - Regulated by government
  - Secondary Standards
    - Calcium, color, hardness, odor, pH, sodium

Courtesy California Water Corporation

Comparison of Water Quality Reports: Means

Quality Standard for City / Major Brewery* in Area	Chico, CA (Sierra Nevada Brewing Co.)	St. Louis, MO (Anheuser – Busch InBev)	Milwaukee, WI (Miller Coors)	Ft. Collins, CO (New Belgium Brewing)
Free Chlorine (ppm)	0.60		0.05	0.64
Chloramines (ppm)		2.46		
Calcium (ppm)	25.0	26.3	35.5	16.6
Magnesium (ppm)	15.0	12.1	12.0	1.7
Sodium (ppm)	13.0	24.9	8.3	2.8
Iron (ppb)	< 3.0 (in house)	1.4	< 3.0	19.0
Chloride (ppm)	10.0	22.7	13.4	2.4
Sulfate (ppm)	6.3	91.5	26.5	12.7
pH	7.80	9.16	7.51	7.90
Turbidity (NTU)	0.1	< 0.11	0.04	0.13

* Brewery may not use municipal water, or treat water in house!

Comparison of Water Quality Reports: Ranges

Quality Standard for City / Major Brewery* in Area	Chico, CA (Sierra Nevada Brewing Co.)	St. Louis, MO (Anheuser – Busch InBev)	Milwaukee, WI (Miller Coors)	Ft. Collins, CO (New Belgium Brewing)
Free Chlorine (ppm)	0.20 – 0.80		0.01 – 0.16	
Chloramines (ppm)		1.88 – 3.08		
Calcium (ppm)	16.0 – 52.0	18.8 – 34.7	34.0 – 38.0	
Magnesium (ppm)	10.0 – 31.0	6.9 – 19.7	12.0 – 13.0	
Sodium (ppm)	7.7 – 38.5	14.6 – 36.4	5.7 – 13.0	Not Available
Iron (ppb)	< 3.0 (in house)	2.0 – 4.1	7.6 - < 3.0	
Chloride (ppm)	2.0 – 41.0	15.5 – 40.5	12.2 – 28.2	
Sulfate (ppm)	1.2 - 15.0	58.5 – 197.1	26.0 – 27.0	
pH	6.9 – 8.4	7.9 – 10.0	7.1 – 7.8	
Turbidity (NTU)	ND – 0.4	< 0.11	0.01 – 0.08	

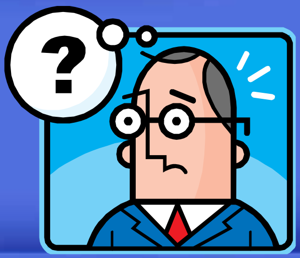
* Brewery may not use municipal water, or treat water in house!

Overview of Presentation

- Some background knowledge
- **Simple tests to determine water quality**
- Experiments with calcium additions

What are you trying to do?

- Microbiological ?
- Remove minerals ?
- Control brewhouse pH ?
- Focus on cations / anions?
- Focus on fouling ?

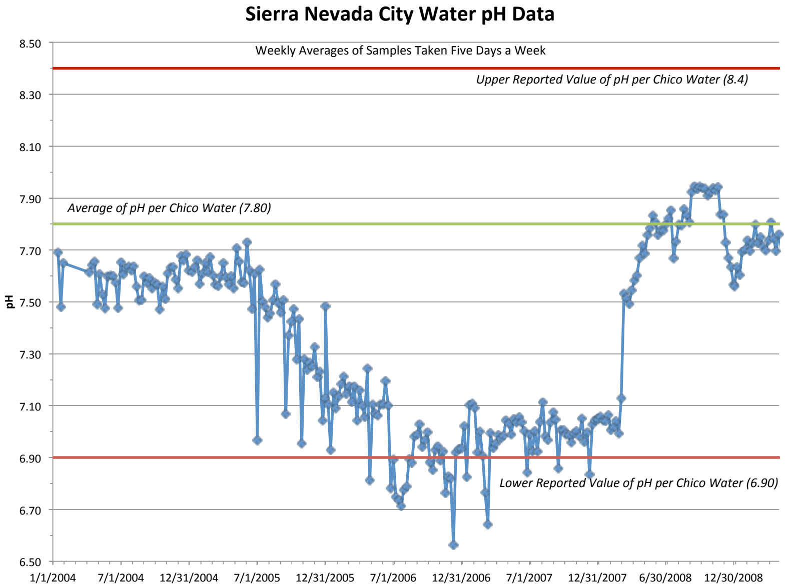


Make sure that your data finds a good use!

The Basic Analyses for Brewers

- pH
- Hardness
  - Sum of calcium & magnesium carbonate
- Alkalinity
- Total Dissolved Solids
- Chlorine
- Inorganic baselines → Sodium, iron, sulfates, silica, chlorides.

How consistent is your water supply?
What is the big picture for your brewery?



Flowchart of Analysis for Residual Alkalinity

Calcium Analysis
- EDTA Titration @ pH 12 - 13

Hardness Analysis
- EDTA Titration @ pH 10.1
- Total Hardness = Ca + Mg

Alkalinity Analysis
- Sulfuric Acid Titration
- Phenolphthalein & bromocresol green indicators

Residual Alkalinity (RA) Calculation
- RA = Alkalinity – ([Ca/3.5]) – ([Mg/7])
- Each unit of RA shifts the pH by 0.0017.

EDTA Titrimetric Test for Calcium

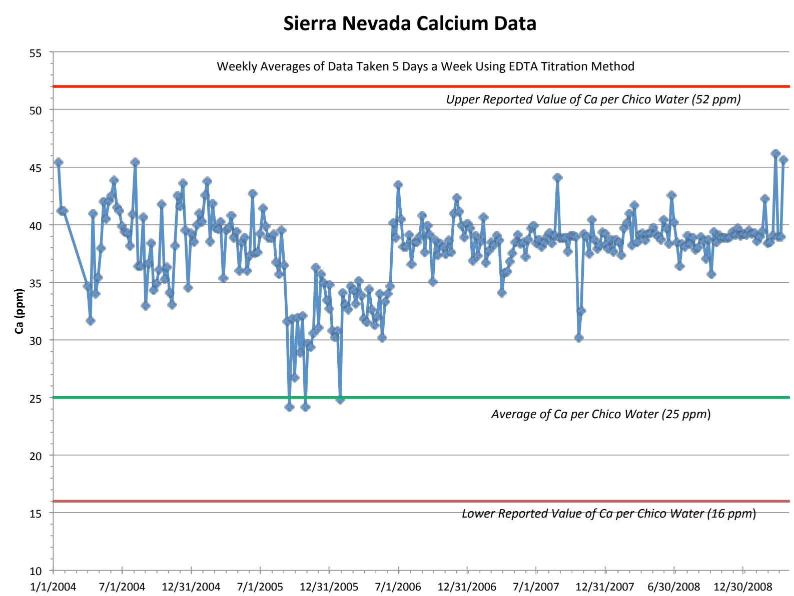
- EDTA will bind to calcium at a one-to-one ratio (steric hinderances).
- Use indicator to monitor color change
  - Hach Cal Ver 2 → Hydroxynapthol Blue
  - Murexide or Eriochrome Blue Black R also approved
- pH needs to be at 12-13 using potassium hydroxide solution – precipitates magnesium hydroxide, leaving behind calcium.

Color Change Using EDTA Titration for Calcium

Red / pink color at start

Blue / purple near end of titration

Sky blue color at end of titration



EDTA Titrimetric Test for Total Hardness

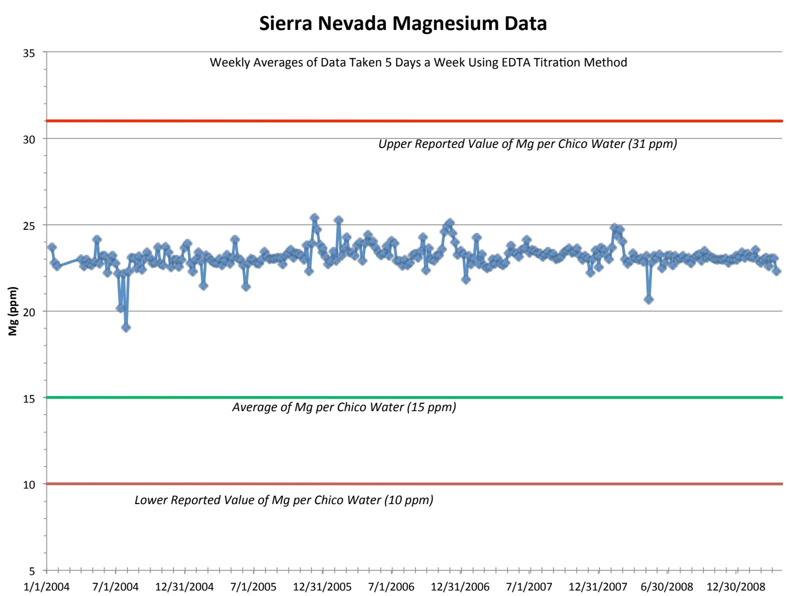
- Similar to calcium test of EDTA titration – only no precipitation of magnesium.
- Uses an organic amine to buffer solution to pH 10.1.
- Approved indicators
  - Hach Manver 2 → Calmagite
  - Erichrome Black T
- Total hardness = Calcium hardness + magnesium hardness
- Hard water >150 ppm, soft water < 75 ppm

Color Change Using EDTA Titration for Total Hardness

"Wine red" color at start

Sky blue color at end

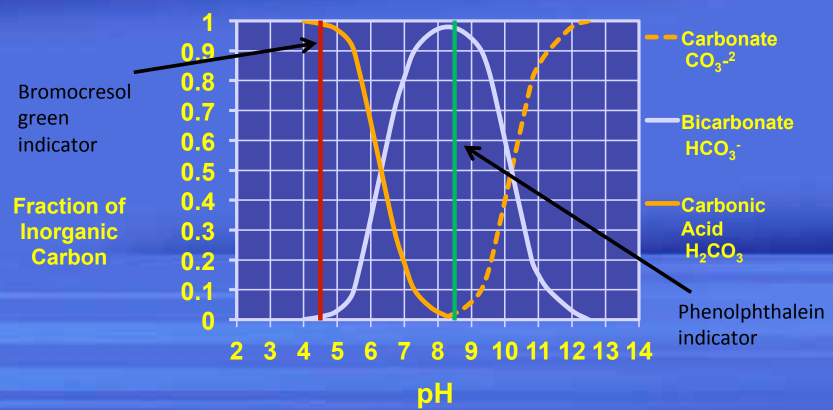
Be careful! Reaction is reversible!! Guideline is for stable color for 3- 5 seconds.



Alkalinity

- Ability of water to neutralize a strong acid.
- Primarily a function of carbonate and bicarbonate concentrations.
- Tested with titration with sulfuric acid.
- Uses two pH endpoints
  - Phenolphthalein (pH 8.3) – *if needed!*
  - Bromocresol green (pH 4.5)

Graph of Key Alkalinity Components



Modified chart from Gordon Whittaker (Coors Molson)

Alkalinity Comparisons

Quality Standard for City / Major Brewery* in Area	Alkalinity as $CaCO_3$ Average (ppm)	Alkalinity as $CaCO_3$ Range (ppm)
Chico, CA (Sierra Nevada Brewing Co.)	120	90 - 220
St. Louis, MO (Anheuser – Busch InBev)	53.5	21 – 98
Milwaukee, WI (Miller Coors)	99.0	94 - 130
Ft. Collins, CO (New Belgium Brewing)	36.4	N/A
Historical Values from *The Practical Brewer*		
Burton-on-Trent, England (Bass)	272	N/A
Pilsen, Czech (Pilsner Urquell)	15.3	N/A

* Brewery may not use municipal water, or treat water in house!

Residual Alkalinity

- Based on the work of Paul Kolbach in 1950's.
- Observed in pale malt mashes:
  - 3.5 equivalents of calcium neutralize 1 equivalent of alkalinity (7:2).
  - 7 equivalents of magnesium neutralize 1 equivalent of alkalinity (7:1).
  - Coverts bicarbonate to carbonic acid.
- $\text{Relative Alkalinity (RA)} = \text{Alkalinity} - \frac{\text{Ca}}{3.5} - \frac{\text{Mg}}{7.0}$

Residual Alkalinity

- For every degree shift in Residual Alkalinity we obtain a +/- 0.00168 effect on the pH of a standard mash made with distilled water.
  - Assumes no dark malts, same grist!
- Example: Chico Average City Water
  - Ca = 25 ppm (62.5 as $CaCO_3$)
  - Mg = 15 ppm (61.7 as $CaCO_3$)
  - Alkalinity = 120 ppm as $CaCO_3$
- $\text{Residual Alkalinity (RA)} = 120 - \frac{62.5}{3.5} - \frac{61.7}{7.0}$
- Residual Alkalinity = + 93.3
- So this would result in a mash pH being + 0.16 than a mash with distilled water.

Comparison of Water Quality Reports: Residual Alkalinity Means & Ranges

Quality Standard for City / Major Brewery* in Area	Chico, CA (Sierra Nevada Brewing Co.)	St. Louis, MO (Anheuser – Busch InBev)	Milwaukee, WI (Miller Coors)	Ft. Collins, CO (New Belgium Brewing)
Ca as $CaCO_3$ (ppm)	62.5	65.75	88.75	41.5
Mg as $CaCO_3$ (ppm)	61.7	49.8	49.4	7.0
Alkalinity (ppm)	120	53.5	99.0	36.4
Residual Alkalinity	+ 93.3	+ 27.6	+ 66.6	+ 23.5
Effect on pH	+ 0.16	+ 0.05	+ 0.11	+ 0.03
Maximum RA (Maximum Alkalinity, minimum Ca & Mg)	+ 202.7	+ 80.5	+ 98.7	N/A
Minimum RA (Minimum Alkalinity, maximum Ca & Mg)	+ 34.6	- 15.4	+ 59.2	N/A

* Brewery may not use municipal water, or treat water in house!

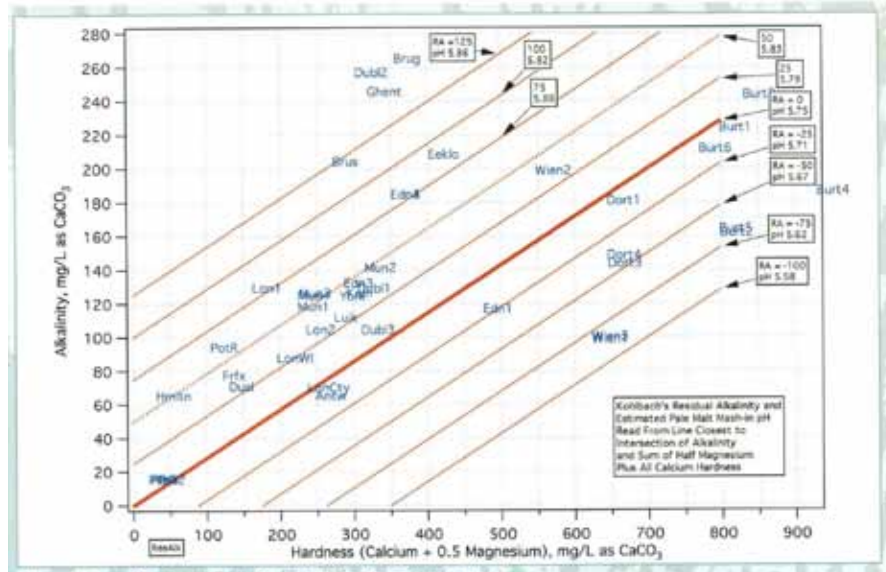


Figure 5.1 **Residual alkalinity and mash pH prediction chart.**

From The New Brewer July/August 2003

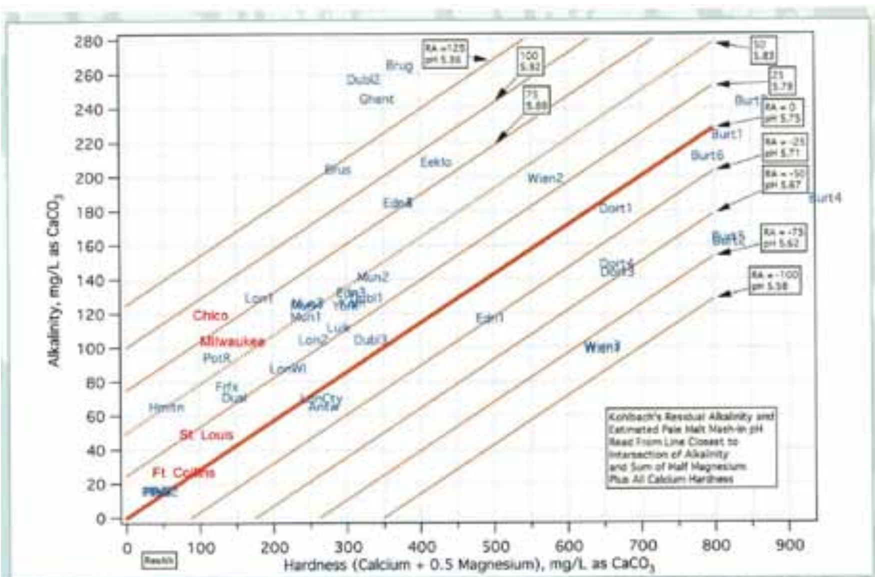


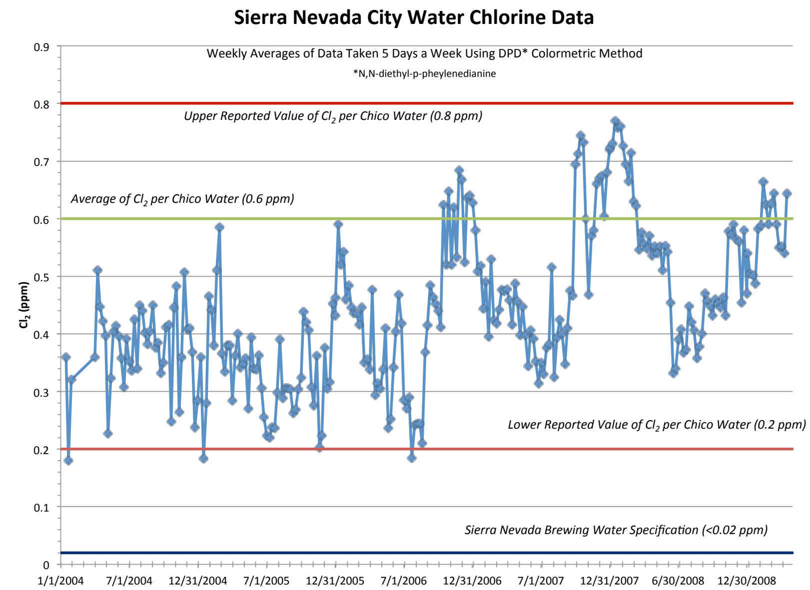
Figure 5.1 **Residual alkalinity and mash pH prediction chart.**

From The New Brewer July/August 2003 – Modified to include American brewing cities

Chlorine Testing

- Two major ways to test
  - 1) Reaction with potassium iodine
  - 2) Reaction with DPD
- Reaction of DPD at 515 nm is simplest
- Detection limits typically down to ~ 10 ppb.
- Issues in brewing arise not with chlorine, but with chloramines.
- Odor Thresholds (The Practical Brewer, MBAA)
  - Free chlorine 5 – 20 ppm
  - Dichloramine 0.5 – 0.8 ppm
  - Trichloramine 0.02 – 0.05 ppm

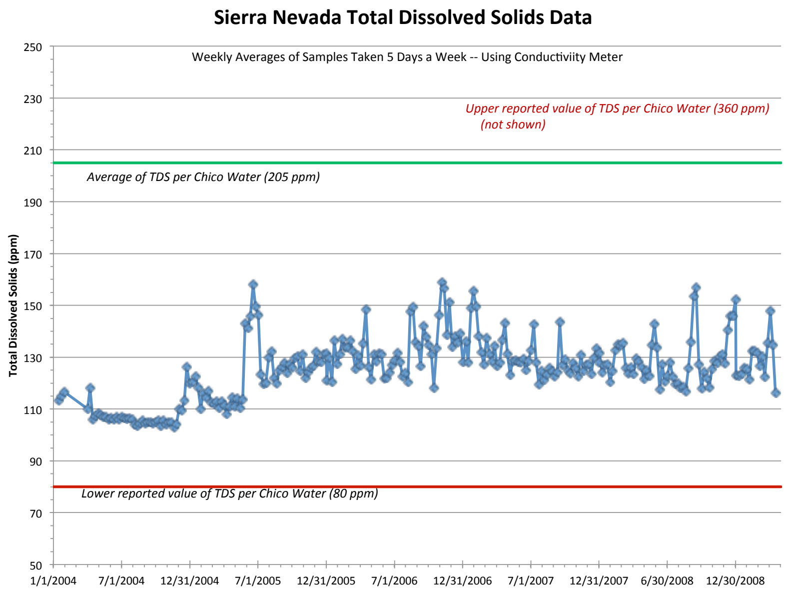
Colorimetric Test for Chlorine



Total Dissolved Solids

- Used as a check of overall water quality.
- Higher dissolved solids can lead to:
  - Issues with taste – where are the solids coming from?
  - Issues with cooling tower scaling
  - Issues with kettle fouling
- Secondary standard (non-hazardous) in USA is < 500 ppm.
- Measured gravimetrically (time consuming!) or by electrical conductivity (easy!).

Testing For Total Dissolved Solids



Anions of Particular Interest

- Chlorides → Lead to saltiness, however lower concentrations create desired dryness.
- Sulfates → Create drying effect. May lead to increased SO_2 production by lager yeast.
- Tested by various gravimetric procedures or ion chromatography.

Other Elements to Consider

- Iron → Bad for flavor stability. Good for some Belgian beers . . . ..
- Zinc → Rarely present in water sources at appreciable quantities. Needed for yeast health / toxic at high quantities.
- Copper → Yeast micronutrient. Bad for flavor stability in excess. Can bind sulfur compounds.
- Silica → Can be a health benefit. Extracted from malt and present in municipal waters.

Methods of Elemental Analysis

- Colorimetric
  - Variety of test kits for each element
  - Less accurate
  - May not work with beer
- Atomic Absorption
  - Tests elements based on electron excitement
  - Can only do one element at a time
- Inductively Coupled Plasma
  - Same basis as atomic absorption
  - Ability to do multiple elements at once.

What Does Your Water Taste Like?

Overview of Presentation

- Some background knowledge
- Simple tests to determine water quality
- **Experiments with calcium additions**

Review of Calcium Additions

- Advantageous of calcium salts in mash
  - Precipitates oxalic acid
  - Increases flocculation
  - Promotes alpha-amylase activity
  - Lowers pH through precipitation of alkaline phosphates
- $3\ Ca^{+2}$ (as salt) + $2\ HPO_4^{-2} \rightarrow Ca_3(PO_4)_2 + 2\ H^+$
  - Plenty of phosphates in malt – up to 1% of weight!*

* Briggs et. al. *Malting & Brewing Science, Vol. One*

Experiments with Calcium Levels

- Sierra Nevada using a combination of calcium sulfate & calcium chloride in mash and kettle, *and* acidified brewing water.
- Experiment looked at replacing acidification of brewing water with increased calcium salts.
- Calcium chloride was chosen to minimize further sulfate additions to Sierra Nevada Pale Ale.
  - High concentrations (350 – 400 ppm) lead to harshness.
- Experiments took place in 10 bbl pilot brewery. Each experiment brewed twice for 20 bbl fermenter.

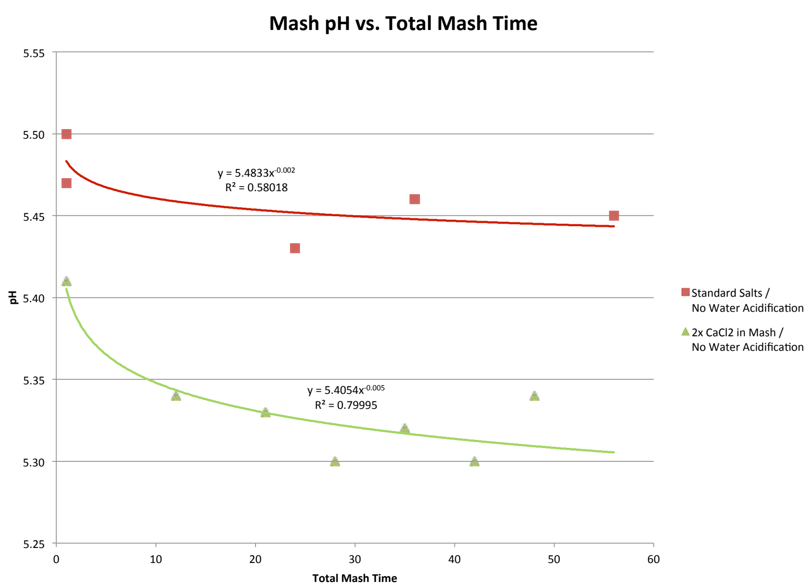
Experiments with Calcium Levels

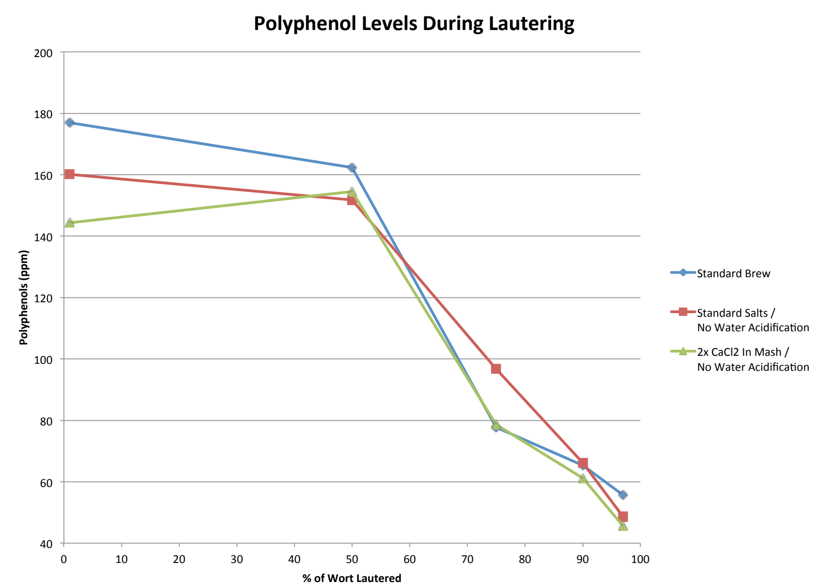
- Residual Alkalinity of acidified water of -6
- Residual Alkalinity of regular city water +40
- Experiment doubled the amount of calcium added to the mash by using $CaCl_2$.

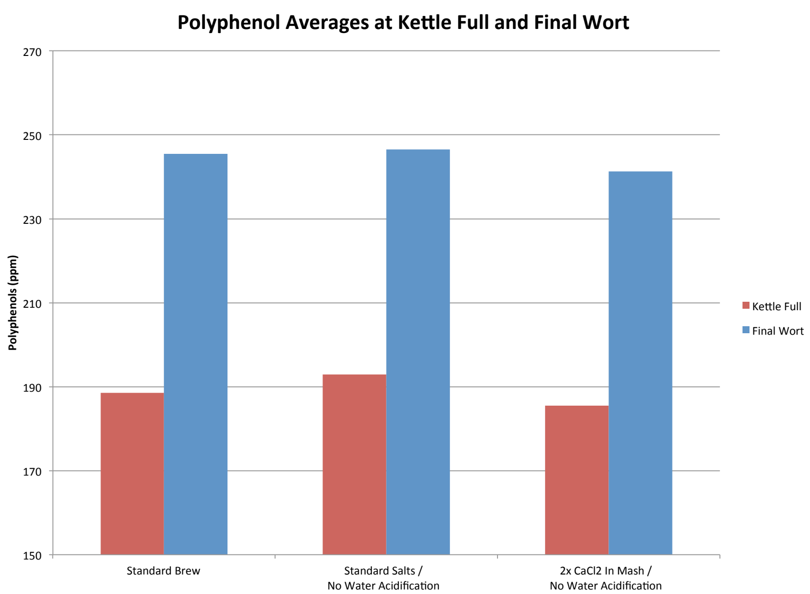
Special Description	Brewing Liquor pH	Amount of $CaSO_4$ in Mash (relative weight)	Amount of $CaCl_2$ in Mash (relative weight)	Amount of $CaSO_4$ in Kettle (relative weight)
Standard Brew	5.35	60	10	35
Standard Salts / No Water Acidification	7.80	60	10	35
2x $CaCl_2$ In Mash / No Water Acidification	7.80	60	69	35

Experiments with Calcium Levels

Special Description	Standard Brew	Standard Salts / No Water Acidification	2x $CaCl_2$ In Mash / No Water Acidification
Mash pH	5.30	5.49	5.38
1st Runnings Lauter pH	5.24	5.36	5.27
Last Runnings Lauter pH	5.56	5.91	5.83
1st Runnings Gravity (°Plato)	17.8	17.5	17.7
Last Runnings Gravity (°Plato)	1.30	1.25	1.30
Lautering Time (minutes)	77	78	78
Final Wort pH	5.17	5.37	5.31
Final Wort Gravity (°Plato)	13.3	13.3	13.4
Final Beer pH	4.37	4.37	4.41
Final Beer Gravity (°Plato)	3.00	2.75	2.78
Bitterness Units	38	38	40
Color	11	12	13

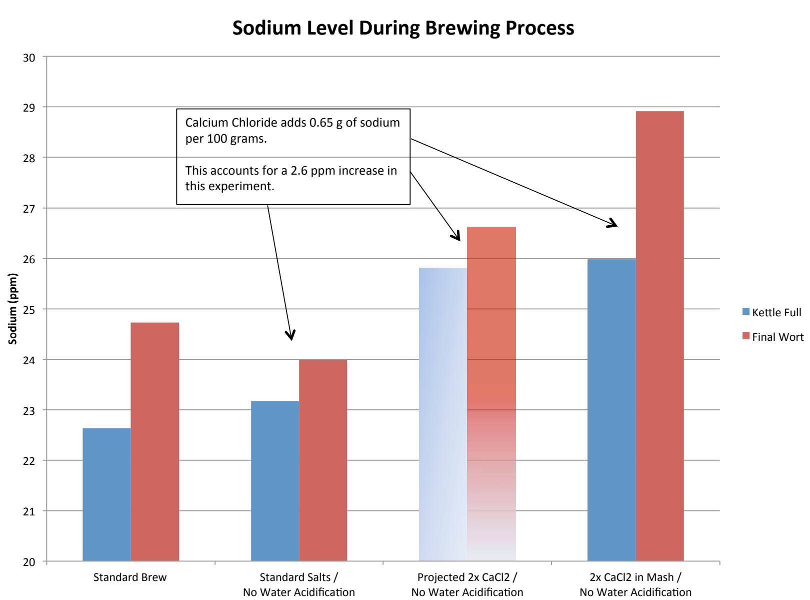


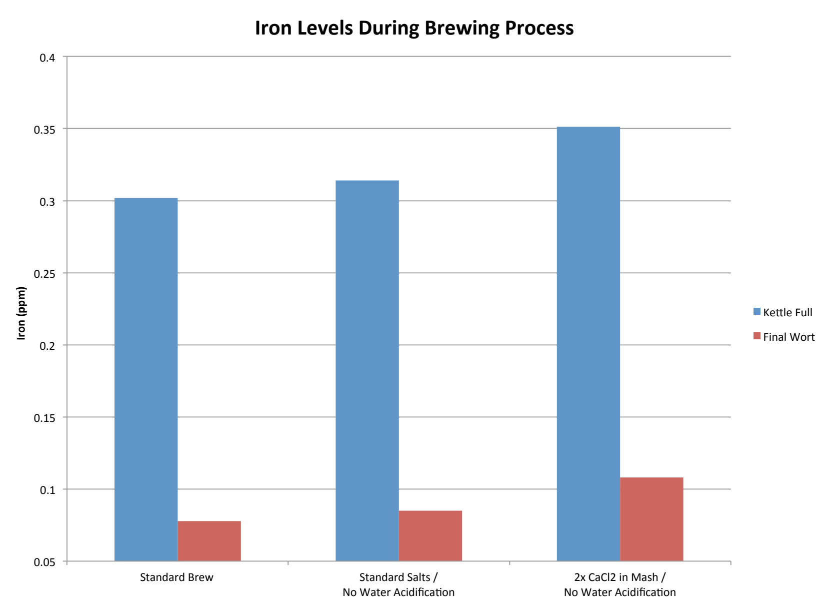


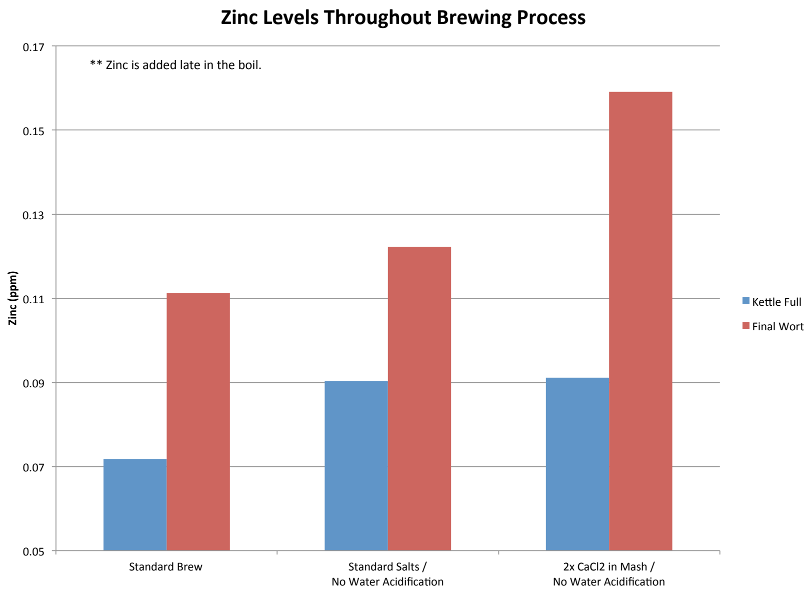


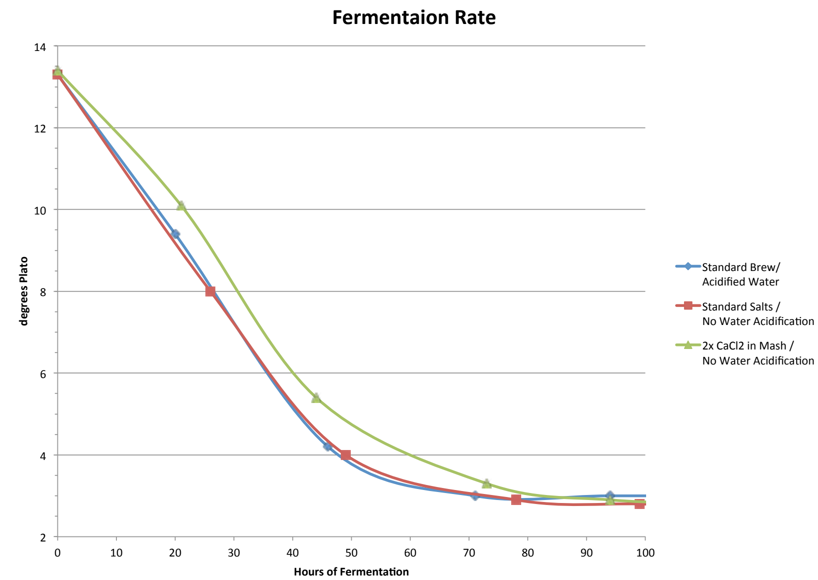
Calcium Efficiency Calculations

Special Description (all units in ppm)	Standard Brew	Standard Salts / No Water Acidification	2x $CaCl_2$ In Mash / No Water Acidification
Brewing water calcium	19	19	19
Calcium added to mash	85.1	85.1	170.2
Calcium at start of boil	43.8	39.7	67.4
Calcium increase from water	24.8	20.7	48.4
% of calcium carryover of mash addition	29.1 %	24.3%	28.4%
Calcium added to kettle	41.3	41.3	41.3
Calcium at final wort	54.3	50.9	81.2
Calcium increase from start of boil	10.5	11.2	13.8
% of calcium carryover from kettle addition	25.4 %	27.1 %	33.4 %









Sensory Results: Triangle Test

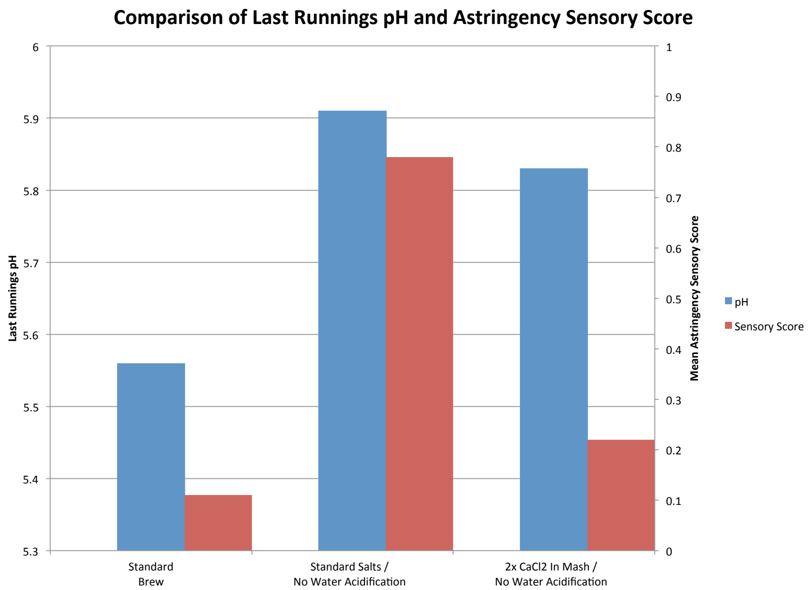
- Sensory triangle testing was done with in-house trained panelists (n=38) after twenty-one days of aging in bottle.

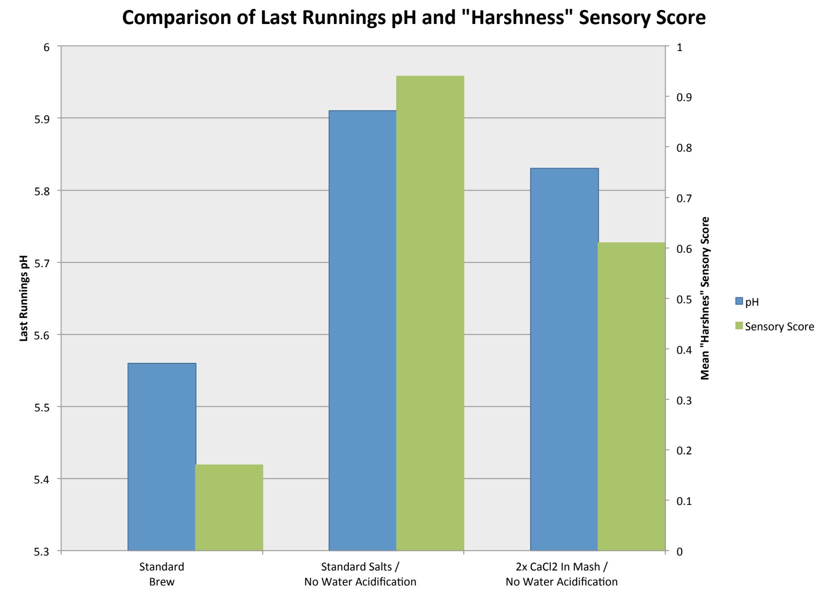
Comparison Between:		Statistically Significant Difference (α = 0.05)?
Experiment #1	Experiment #2	
Standard Salts / No Water Acidification	Standard Brew	YES
2x $CaCl_2$ In Mash / No Water Acidification	Standard Brew	YES

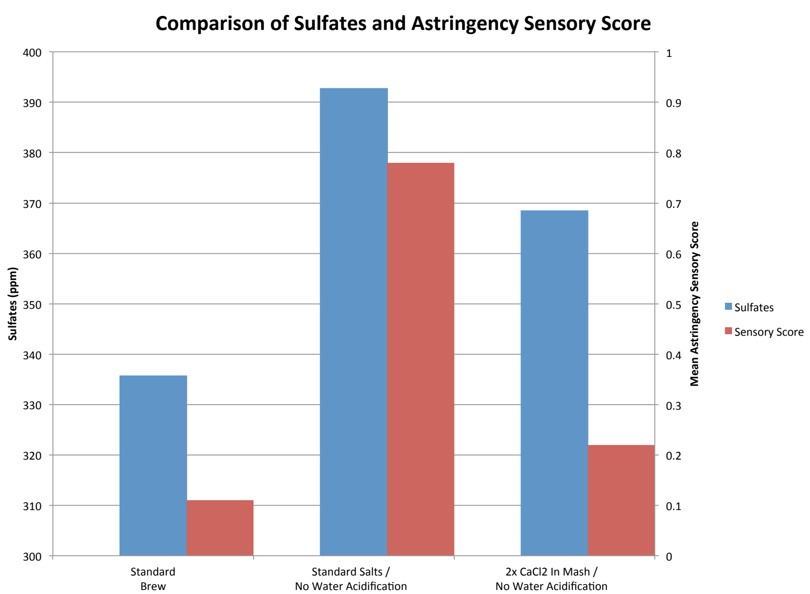
Sensory Results: Descriptive Panel

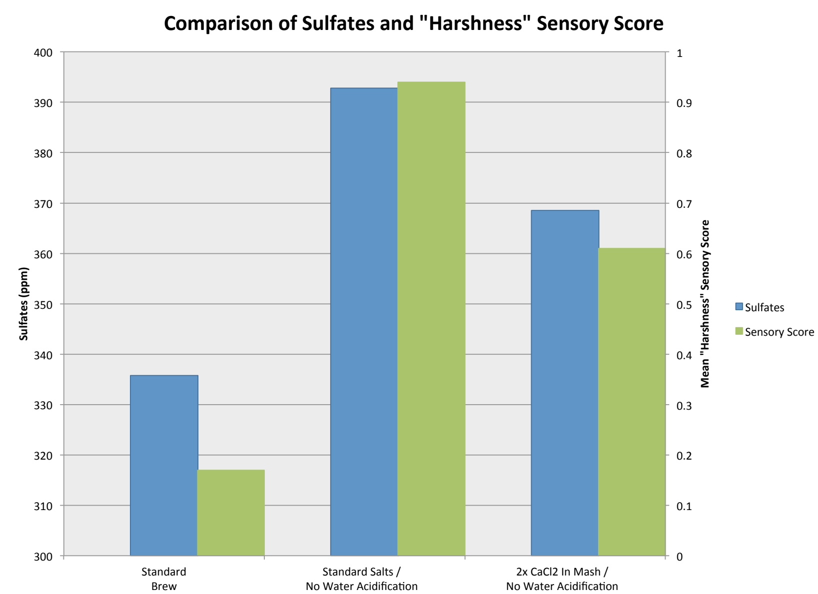
- Panelists were asked to rate the three experimental brews on five attributes using a pre-defined 0-8 scale.
- Samples statistically different noted with bold and subscripts at the 5% confidence level.

Sensory Score	Target Value for Pale Ale	Standard Brew	Standard Salts / No Water Acidification	2x $CaCl_2$ In Mash / No Water Acidification
Bitter	4	3.89	3.94	3.72
Sour	0	0.22	0.33	0.56
Astringency	0	0.11^{b}	0.78^{a}	0.22^{ab}
Harshness	0	0.17^{b}	0.94^{a}	0.61^{ab}
Acceptability (1 = highest acceptable)	1	2.44^{b}	2.56^{b}	3.11^{a}


Comparison of Last Runnings pH and Astringency Sensory Score
Last Runnings pH
Mean Astringency Sensory Score
pH
Sensory Score
Standard Brew
Standard Salts / No Water Acidification
2x CaCl2 In Mash / No Water Acidification


Comparison of Last Runnings pH and "Harshness" Sensory Score
Last Runnings pH
Mean "Harshnes" Sensory Score
pH
Sensory Score
Standard Brew
Standard Salts / No Water Acidification
2x CaCl2 In Mash / No Water Acidification


Comparison of Sulfates and Astringency Sensory Score
Sulfates (ppm)
Mean Astringency Sensory Score
Sulfates
Sensory Score
Standard Brew
Standard Salts / No Water Acidification
2x CaCl2 In Mash / No Water Acidification


Comparison of Sulfates and "Harshness" Sensory Score
Sulfates (ppm)
Mean "Harshness" Sensory Score
Sulfates
Sensory Score
Standard Brew
Standard Salts / No Water Acidification
2x CaCl2 In Mash / No Water Acidification

Calcium Level Experiment Conclusions

- Difference in mash pH, last runnings pH, and wort pH did not translate to a difference in beer pH.
- Sensory differences showed lack of water acidification led to a harsher, more astringent beer.
  - Possibly due to harsher polyphenols being extracted (total polyphenols were equal).
  - Possibly due to sulfate precipitation.

Calcium Level Experiment Conclusions

- The additional chlorides did not lead to a salty taste for the beer via informal sensory results.
- All experiments showed the same level of calcium carryover (~25 – 35%).
- Additional calcium chloride led to higher zinc, iron, and sodium levels.
- Fermentation rates / performance was similar.

Additional Resources

- *The Practical Brewer*; Chapter 2 on Water by Gil Sanchez
- *Standard Methods for the Examination of Water & Wastewater*; American Public Health Association
- "Deconstructing Water Residual Alkalinity and Mash pH" The New Brewer July/August 2003 by A.J. deLange
- Your friendly water supplier – see your bill!

Acknowledgements

- Sierra Nevada Water Treatment Team
  - Fred Strachan, Eric Brogden, Jason Dotson
- Sierra Nevada Research & Development Team
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  - Cathy Haddock, Sensory Specialist
- Ken Grossman


Thank you!