Brewing H_2O Chemistry

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Significance of Water in Beer

Water is often an underappreciated and little-monitored ingredient in beer—especially compared to the time and resources spent selecting hops, testing yeast strains, and reviewing malt COAs. Yet, beer is 85–95% water, along with ethanol, sugars, carbon dioxide, salts, vitamins, esters, aldehydes, organic acids, higher alcohols, and inorganic ions that make up the remaining 5–15%. The mineral composition of water, chemicals used in water treatment, and flavors imparted to water from the environment can have a significant impact to the final beer flavor, appearance, and shelf-life. Historically, specific beer styles have been highly dependent on the mineral content of the water used to brew the beer. Famous examples include lagers from Pilsen made with low mineral content water and pale ales from Burton-on-Trent brewed with water containing elevated levels of calcium sulfate.

Water Sources

Water sources can be separated into surface water from lakes, rivers, reservoirs, streams, and groundwater, which is water that moves through the top layers of soil and rock then is stored in aquifers. The source of water can have a significant impact on the mineral content. Typically, water from aquifers contains higher concentrations of minerals, which concentrate as water is filtered through the soil and rock layers. This filtration can also remove contaminants that can be present in surface water. Additionally, depending on the source of water, the mineral composition can vary significantly throughout the year.

A small number of breweries have water rights and can pull their water from aquifers and treat the water on-site. Most breweries source their water from city municipalities relying on the city for treatment. A general treatment process to produce potable water for consumption includes:

1) Prescreen the water to remove large particulates.
2) Flocculate to turn small particles into large/heavy particles that can be removed.
3) Sedimentation to remove large particles that have settled out.
4) Filter the water through various materials to remove dissolved material and microorganisms.
5) Sterilize to kill any remaining viruses/bacteria/parasites and prevent further growth of these organisms.
6) Storage.

Additional treatment can include the addition of fluoride to improve dental health or carbon filtration to remove off-flavors.

Water Quality

In the United States, drinking water standards are set by the Environmental Protection Agency (EPA) and can be found on the EPA's website. The primary standards set by the EPA list the microorganisms, disinfectants (and by-products), inorganic and organic chemicals, and radionuclides that need to be monitored along with their maximum concentration that can be found in drinking water. The EPA also has a list of secondary drinking water standards that are non-mandatory. The set of secondary standards are to improve "aesthetic considerations" related to taste, color, odor, and turbidity. The Food and Drug Administration sets the quality standards for bottled water, which are in line with the standards set by the EPA. Internationally, the World Health Organization (WHO) sets guidelines for safe drinking water.

If your brewery's water is sourced from a city treatment plant, you should have access to a basic water quality report including pH, water hardness, chlorine, turbidity, sodium, and alkalinity. Many cities have extensive water testing capabilities and can provide more in-depth reports noting seasonal variability, ions or organics that could be detrimental to flavor, or reports specific to your region of the city even with water being treated at a single site for a city, differences in some water parameters can be measured in different regions of the city due to pipe composition and length from the treatment plant.

There are many routine parameters measured in drinking water. Soren Sorensen (a scientist at the Carlsberg Laboratory) originally defined pH and the pH scale more than 100 years ago; pH is simply the measurement of the acidity of a solution. The pH scale ranges from 0–14, with 0–7 categorized as acidic, pH 7 is neutral, and 7–14 categorized as basic. Drinking water has a pH range from 6.5–8.5. It is ideal to monitor pH routinely at the brewery as pH can vary as the mineral content changes throughout the year.

The alkalinity of water is a measure of the acid-neutralizing components in water (primarily the carbonate and bicarbonate ions). Alkalinity is measured by titrating a water sample with an acid to a specific pH and is usually represented as mg/L of $CaCO_3$ (it can also be represented as mEq/L—see Equation 1). From the alkalinity measurement, the concentration of a neutralizing acid (such as lactic or phosphoric acid) can be calculated to neutralize the water for mashing.

$$\frac{mEq}{L} = \frac{\frac{mg}{L}\, x\ ionic\ charge}{molar\ mass}$$

Equation 1. Milliequivalents

Water hardness is a measure of the divalent cations in water (summed as Ca^{+2} and Mg^{+2}). Water hardness is broken down into 4 categories: soft water has 0–60 mg/L $CaCO_3$, 61–120 mg/L as moderately hard, 121–180 mg/L as hard, and over 180 mg/L as very hard. Hard water can lead to issues with scale in industrial processes. Permanent hardness is caused by sulfate and chloride ions and temporary hardness (which can be removed by boiling water) is the result of bicarbonate compounds. Monitoring water hardness is critical to understanding how to adjust salt additions in the brewhouse.

Several other water parameters are critical to monitor to ensure they will not impact beer quality. Chlorine is used as a disinfectant and can result in the formation of trihalomethanes (THMs). THMs are carcinogens and can also impart off-flavors in beer. Chlorine can also react with phenols resulting in the formation of chlorophenols, which will give beer a plastic-like off-aroma and have very low flavor thresholds. See the ASBC Beer Flavor Database (found under the *Methods of Analysis*) for additional information on chlorophenols.

Geosmin and 2-methylisoborneol (MIB) can be formed by algae in surface water supplies. Geosmin has a strong beet aroma and is flavor-active at part per trillion (ppt) levels. MIB has a musty/earthy aroma and is also flavor-active at ppt levels. Both compounds can be difficult to remove by water treatment and can come and go through the year.

Iron is another cation that can be found in water with the concentration dependent upon the source of the water. At part per billion (ppb) levels, iron can impart an off-flavor to beer (metallic). In addition, iron can result in oxidative reactions in beer, which can significantly reduce the shelf life of beer (see Haber-Weiss and Fenton Reactions).

In addition to monitoring water quality reports and working with your city water quality lab (in many cases, the city will notify you of any changes to the incoming water) to ensure the consistency and quality of your brewery's incoming water, the water should be tasted regularly by brewers and/or a sensory panel. Many of the off-flavors or seasonal variation can be detected by simply setting up routine water tasting (it is also ideal to visually inspect the water to ensure there is no turbidity).

Incoming Water Treatment

There are many steps that breweries can take to remove ions, oxygen, or off-flavors from water. To completely strip water of organics and ions, a process such as reverse osmosis (RO) could be used. RO is expensive to set up and energy intensive. Ion exchange could be used to soften brewing water, but it is also a costly option to set up and maintain. Another common process to treat brewing water used postbrewhouse is to deaerate the water by boiling followed by carbon filtration. This will remove oxygen from water (which can be harmful to beer flavor stability) and will also significantly reduce residual chlorine (which can make this water more susceptible to microbial growth).

Beyond removing ions or organics from incoming water, salts and acid can be added to water. Calcium salts are commonly added to control mash pH (along with influencing the final flavor of the beer). Calcium controls pH by reacting with phosphates (see Figure 1).

$$3Ca^{2+} + 2HPO_4^{2-} \rightarrow Ca_3(PO_4)_2 + 2H^+$$

Figure 1: Calcium reaction with phosphate to reduce pH

Different calcium salts can impact finished beer flavor. Gypsum/calcium sulfate ($CaSO_4$) and calcium chloride ($CaCl_2$) are both routinely added salts. The sulfate from gypsum can enhance bitterness where the chloride ion can lead to enhanced body and fullness. It is critical to balance the chloride-to-sulfate ratio and ensure that it is aligned with the style of beer being brewed. Acids, such as lactic or phosphoric, can also be added to control pH. There are several reasons to control pH in the brewhouse. These can include targeting optimum pH ranges for enzymatic activity, minimizing astringency, optimizing conversion of alpha acids to iso-alpha-acids, removing oxalate, and to improve fermentation performance. Salt and acid additions can also have an impact to final beer pH as is shown in the *ASBC Fishbone Reference* (Figure 2, next page).

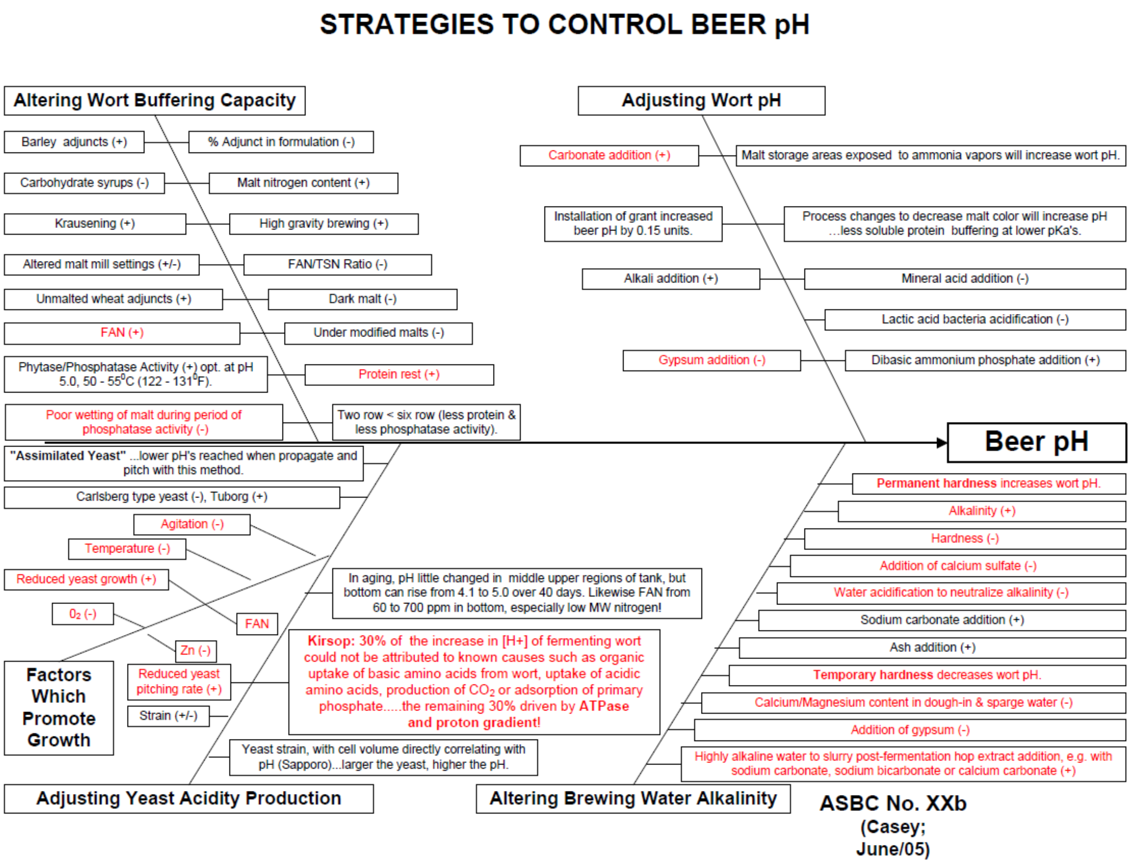

Figure 2: *ASBC Fishbone Reference* for strategies to control beer pH

Sustainability and Effluent Treatment

Breweries generate significant quantities of wastewater during the brewing process (this can vary from 3–7+ barrels of waste effluent per barrel of finished beer). Depending on the municipal water district and amount of waste effluent generated, the cost for waste disposal can be significant.

Brewery waste effluent comes from several sources, including packaging (the quantity is dependent on the type of packaging line), utilities, brewhouse, and the cellar. Each source has the potential for significantly different pH levels, temperatures, and biological oxygen demand (BOD) or chemical oxygen demand (COD) concentrations. BOD is an indirect measurement of the amount of dissolved oxygen used by aerobic microorganisms in decomposing organic matter in water. COD is a measurement of the amount of oxygen used to oxidize organic material in water. Process and waste beer streams have significant COD and BOD levels ranging from a COD of 1000 mg/L to 4000 mg/L and a BOD of up to 1500 mg/L. The pH range is dependent upon the cleaning agents used within the brewery. In general, process and waste beer will have an acidic pH as low as 3–4 and caustic waste from brewery cleaning will have a basic pH above 7. Prior to the effluent being released into the sewer system, it is ideal for effluent to be treated to reduce the temperature below 40 °C, change the pH to range from 6–10, reduce the BOD to below 25 mg/L, and reduce the COD to below 125 mg/L. In addition, if the waste is to be treated on-site, further pretreatment may be required.

With the varying pH level in brewery waste, it is critical to have the capability to adjust both acidic and caustic effluent. Ideally, caustic waste streams should be collected and stored separately from acidic waste streams. Once the waste streams are segregated, they can be mixed together to generate the desired pH. Although this is ideal, it is not always practical within a brewery. Waste effluent is continually being generated within the brewery and depending on where most of the effluent is being produced, it is very difficult to separate caustic from acidic waste. One option for treating caustic waste is to bubble unused CO_2 from the fermentation process to neutralize the caustic waste. Other options for neutralizing caustic waste include the use of strong acids such as sulfuric or hydrochloric acid or the use of weaker acids. For the treatment of acidic waste, a strong base, such as sodium hydroxide, can be used or a weaker base, such as sodium carbonate.

To reduce BOD/COD requires a more complex treatment process. Both aerobic and anaerobic treatment options are available to reduce BOD/COD in brewery effluent. Aerobic waste treatment involves mixing effluent (composed of organic matter and nutrients), with oxygen and microorganisms, which convert the effluent into carbon dioxide, ammonia, and water (Figure 3).

$$\text{Organic matter and nutrients} + O_2 + \text{Microorganisms} \rightarrow CO_2 + H_2O + NH_3 + \text{New Bacteria}$$

Figure 3. Aerobic metabolism

The microorganism sludge can consist of protozoa, bacteria, fungi, and algae. However, bacteria are the most significant microorganisms due to substantially faster growth rates. Typically, brewery effluent contains the required nutrients for the microorganisms to grow. However, in some instances nitrogen and phosphorous nutrients will need to be added to the effluent prior to aerobic treatment.

Anaerobic treatment involves a three-step process: hydrolysis, acidogenesis, and methanogenesis as shown in Figure 4.

1) Hydrolysis

$$\text{Sludge (fats, proteins, and polysaccharides)} + \text{Hydrolytic bacteria} \rightarrow \text{Sugars, amino acids, and fatty acids}$$

2) Acidogenesis

$$\text{Sugars, amino acids, and fatty acids} + \text{Acid-forming bacteria} \rightarrow \text{Acetic acid} + \text{Aldehydes} + \text{Ketones} + \text{Alcohols} + NH_3 + CO_2 + H_2O + H_2$$

3) Methanogenesis

$$\text{Acetic acid} + \text{Aldehydes} + \text{Ketones} + \text{Alcohols} + NH_3 + CO_2 + H_2O + \text{Methanogenic bacteria} \rightarrow CH_4 + CO_2 + H_2O$$

Figure 4. Anaerobic metabolism

Table 1 (next page) provides a comparison of the advantages and disadvantages of aerobic and anaerobic treatment.

Table 1: Comparison of aerobic and anaerobic processing

Treatment	Advantages	Disadvantages
Aerobic	• Can manage changing levels of BOD • Excellent BOD removal	• High sludge production • Cost of aeration
Anaerobic	• Generation of methane • Low sludge formation • Small foot-print	• Sludge susceptible to high loading of BOD. • Slow start-up times.

Incoming water quality can have a significant impact to the quality and adherence to style of a brewery's finished beer. There are many water quality parameters that should be routinely monitored to ensure the quality and consistency of your water supply. Water can be adjusted using salts and acids if needed to meet the chemistry targets for your recipe. Breweries use significant quantities of water in their process and should take reasonable steps to manage the wastewater effluent.

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