

Quickie Water Chemistry Primer

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By far water treatment is more important when mashing than it is for extract brewers, although extract brewers may need to make adjustments to very "bad" water, or even "build" water from scratch, to make a better brew.

"Building" water simply refers to adding controlled amounts of certain salts to water of known "ionic profile", to yield water with a new profile with the desired characteristics. Typically one would refer to one of the many published profiles for "classic" brewing cities and try to emulate that water. Distilled or other ion-free water is normally the starting water of choice, unless one has an accurate and reliable analysis of his/her tap water to use (they're free for the asking from your local utility; how accurate and reliable they are is another thing!).

Unfortunately, it is usually difficult or impossible to exactly match (or even to closely approximate in some cases) a given profile without resorting to elaborate techniques and additives to which most of us have no access. Even then we can normally only hope for a reasonable approximation. But we can also come pretty close in many cases with the addition of a few readily-available salts to either ion-free water (distilled, RO, deionized), or tap water (if we know the tap water's "profile"). As we will see, this is usually more than adequate for accomplishing our goals.

Most published profiles concentrate on the levels of calcium (Ca), sulphate (SO₄), magnesium (Mg), sodium (Na), chloride (Cl), and carbonate (CO₃). Other water constituents have only secondary effects on the beer (if any), and in the amounts found in regulated municipal supplies, they can be ignored. (One exception might be iron, which will ruin your beer if it's too strong. If you can taste it in the tap water, it's too high; use different water. This is normally a problem only in well water or in homes with old rusty pipes!) We can add each of these ionic components by adding measured amounts of gypsum, epsom salt, non-iodized table salt, baking soda, chalk, and calcium chloride dihydrate. These are readily-available either in grocery or drug stores, or from homebrew supply houses. Calcium chloride is one you might have to search a bit for, but it's out there.

Let's assume you have water profile in front of you; you want to build the perfect Burton Pale Ale water. The question is: how much of these salts do I add to get the ion levels I want? Adding one gram of the salts shown to one gallon of ion-free water yields the following increase in the ppm (or mg/l) concentration of their constituent ions (contributions of hardness and alkalinity are also shown):

Additive	Ca	SO ₄	Mg	Na	Cl	CO ₃	Hrdns	Alk'y
=====	=====	=====	=====	=====	=====	=====	=====	=====
Gypsum	61.5	147.4	-----	-----	-----	-----	153.6	-----
Chalk	105.8	-----	-----	-----	-----	158.4	264.2	264.2
CaCl ₂	72.0	-----	-----	-----	127.4	-----	179.8	-----
Salt	-----	-----	-----	103.9	160.3	-----	-----	-----
Bkng Sda	-----	-----	-----	72.3	-----	188.7	-----	157.4
Epsom	-----	103.0	26.1	-----	-----	-----	107.8	-----
- Hardness and Alkalinity are "as CaCO ₃ "								

Since you cannot add just one ion without adding another, this is a trial-and-error hit-or-miss effort. However, you can streamline the process somewhat by starting with Epsom salt (since this is the only source of magnesium). Add enough to set the magnesium to the correct level. If you haven't gone "over" on sulphate, then add gypsum until your sulphate is on target. Next, play with baking soda and/or salt to set the sodium and chloride. Finally, if calcium needs boosting, add chalk or calcium chloride (if available). You'll probably have to revise your recipe several times to fine-tune it.

As we will see, of these ions, only calcium and carbonates play a significant role in mashing (alkalinity arises from carbonate and can be *qualitatively* treated as equivalent in effect). However, the other ions are involved in other beer characteristics and need to be considered as well.

Highlights of Mash Chemistry

For the most part, we are concerned with the impact of these major-player ions in the mashing process, as well as impact on flavor and other finished-beer characteristics. Following is a very brief rundown of what happens in the mash with respect to the water ions.

The mash contains a number of chemicals based on phosphorous, which are weak acidic buffers. It's these phosphates that cause the pH of a mash to drop into the "high-five's" when neutral water ($\text{pH} = 7$) is used. But the mash enzymes work best at lower pH's around 5.2. So we often must aid the acidification of the mash. Calcium reacts with the phosphates to form insoluble compounds which precipitate out of the mash. In addition, hydrogen ions are released in this process. Hydrogen ions (H^+) are the defining constituent of acids, so we get acidification not only from removal of the buffering ("stabilizing") phosphates, but by the addition of H^+ ions. So calcium is crucial to proper mash acidification.

Carbonates (including bicarbonates) have the opposite effect; they are alkaline which means they will counteract acids and raise the pH. Carbonates will stay carbonates or tend to become bicarbonates depending on the pH; the exact mix of the two is not important as they have much the same effects on the mash anyway. To an extent, in small quantities, they help prevent overacidification of the mash (they too are "buffers"), and therefore some carbonate level is probably helpful, but in general we want to eliminate as much as possible. Carbonates will react with calcium to form insoluble precipitates, so they can strip out the calcium we need to set the pH. Grain bills with lots of dark roasted grains are more acidic than pale mashes and can therefore tolerate greater carbonate levels. This is why brewing darker beers successfully is often easier than is brewing lighter beers. Carbonates can be removed by boiling the water and allowing any calcium to react and form precipitates; decarbonated water is decanted off the precipitate once cooled. This requires that there is already some calcium in the water being boiled, however, and in any case not all the carbonates will be removed. When "building" brewing water using salt additions to match a certain target ion profile, consider the target profile's carbonate numbers a "maximum" target and don't worry if you come up "low" on this ion.

"Hardness" and "Alkalinity" are of course not ions, but are secondary measures of water quality having to do with the presence of certain ions. Hardness comes from calcium and magnesium content, and alkalinity comes from carbonate and bicarbonate. Alkalinity is related to pH but is not a direct measure of it. However, it IS a direct measure of the "buffering" capacity of the solution, or its "resistance" to attempts to lower its pH. In other words, the higher the alkalinity, the more acid would be required to begin to change the pH. Two solutions with identical pH's but differing alkalinities will require different levels of acidification to lower the pH to a given number. Both Hardness and Alkalinity are often quoted to be "as CaCO_3 ". This is a commonly-used reference method meant to identify the equivalent amount of CaCO_3 (also known as "scale") which would generate the hardness and alkalinity figures, regardless of the actual source.

The other ions dealt with in simple "water construction" have no (or only minor) roles in the mash chemistry, but are important in the flavor of the finished product. General effects of the ions on beer character:

Calcium (Ca): Aids in extraction of fine bittering principles from hops. Enhances protein coagulation (hot and cold break). Beneficial to yeast. Aids shelf life. 50 - 200 ppm is typical.

Sulphate (SO_4): Lends a dry, sometimes "sharp" character; accentuates hops. Normally best below 150 ppm but can go as high as 700 ppm or more in Burton-style ales.

Magnesium (Mg): Beneficial to yeast in small amounts, but is objectionable in high concentrations. Best kept to 10 to 30 ppm.

Sodium (Na): Adds a "fullness" and "sweetness" to beer in reasonable concentrations. Keep under 100 ppm (usually under 50), especially in the presence of sulphate.

Chloride (Cl): Adds a "fullness" and accentuates bitterness. Keep under 100 ppm (usually under 50), especially in the presence of sulphate.

Carbonates (CO₃): Harshens hop bitterness; reddens beer; hinders protein coagulation. Best kept below 50 ppm; high levels of calcium can offset it, as can use of dark roasted grains.

This is where extract brewers can benefit. Considering that extract is basically concentrated wort, the mashing chemistry is in the past; you can't undo it, so focus now on controlling these "flavor ions" in the water. This might be difficult since you don't know what ions may now be present in the extract, or what their concentrations are. A general guideline might be to use distilled or RO water for extract brewing, perhaps adding a teaspoon or so of gypsum (to obtain beneficial calcium -- but watch the sulphate!!), and MAYBE a small pinch (literally) of canning salt or Epsom salt. Lighter, more delicate extract brews are best left to very little or no salt additions, while minerally beers such as pale ales and stouts might benefit from a bit of help.

Comments About Using Salts

Arguably, it's more important to obtain a proper mash pH than it is to get all your ions right on target. However, many beer styles are strongly characterized by the water used to brew them. Burton ales and Pilsen lagers are examples of beers defined by their constituent waters. Especially when using baking soda or chalk, let the pH of the mash be your guide, moreso than the numbers in the resulting water profile.

Epsom Salt: Most drug stores should have this item. It's used for soaking feet and also as a laxative.

Baking Soda: A good alternative to chalk for adding a touch of carbonate buffering IF you can tolerate the sodium it adds (refer to your target profile). Dissolves readily in reasonable quantities. Use only part of the calculated amount at first; after striking the mash, add the rest slowly while monitoring the pH to ensure that it doesn't begin to rise out of the "ideal" range (~5.0 - 5.5).

Chalk: Will only dissolve at the rate of less than 1/4 gram per five gallons! Bubbling CO₂ through the water will acidify it, allowing the chalk to dissolve more easily, but this will take time, and subsequent aeration is required to bring the pH back up to a stable level. You can also just mix it well directly into the mash; the mash acidity will aid in dissolution, but this approach is perhaps less accurate and you must be sure to mix it in thoroughly. As with baking soda, start with a small amount and add the balance while monitoring pH.

Canning Salt: I chose to specify "CANNING" salt as opposed to "table salt" specifically to emphasize a point: NEVER use regular iodized table salt! Iodine is toxic to yeast and there are usually other additives such as silicates that might be undesirable. "Canning" salt is pure non-iodized sodium chloride and will say on the label "pure salt" ("pickling" and "Kosher" salts are normally non-iodized as well). I paid \$1.59 for a five-pound bag. This is essentially a lifetime supply.

Calcium Chloride: Excellent for boosting chloride without increasing sodium; also for boosting calcium without adding sulphate. May be hard to find. The accompanying table assumes you are using the common dihydrate form of CaCl₂; ion concentration figures will not be accurate if other forms are used.

Gypsum: Excellent and readily-available source of calcium. Be careful about your sulphate content when adding gypsum.

Some "Water Recipes"

These recipes are general-purpose "idealized" formulas for creating water from distilled for all-grain brewing. Refer to the above text for ideas for extract brewers. These recipes are for five gallons of ion-free water; scale up or down as needed. They are definitely "ballpark" profiles and can be adjusted liberally as desired. I'll "leave it as an exercise to the reader" to verify the resulting ppm concentrations.

When chalk is called for, you'll have to get it dissolved either by bubbling CO₂ through the water (which works but takes time), or you can stir the proper amount directly into the mash, and let the mash's acidity dissolve the chalk. By "proper amount" I'm referring to a proportion matching the actual strike water used rather than the full five gallons on which these recipes are based. If you strike with 14 quarts, mix 70% of the amount shown (14 qt out of five gallons) directly into the mash. When sparging, stir the chalk directly into the sparge water, then acidify your sparge water to your favorite pH (5.7 is typical). This should help dissolve it (to incorporate the desired concentration of calcium) while neutralizing the detrimental effects of the alkaline carbonate by lowering the pH. Remember that we're trying to emulate the makeup of the water naturally found in regions where these beers are brewed; whatever the local brewer would do to those "natural waters", we should do too.

As of this writing, I have had success with the Burton profile given here but have not personally tried the others. These recipes are based on published profiles; I make no claims as to their suitability other than that the recipes should yield the indicated ion concentrations.

Burton Pale Ale -- A toned-down, "idealized" profile. Enough sulphate to bring out the hops without overdoing it. Low alkalinity helps ensure proper mash pH. Model: Moshers 'Ideal Pale Ale'. 1 gram baking soda, 1 gram canning salt, 3.5 grams Epsom salt, 9 grams gypsum. Ca=111, SO₄=337, Mg=18, Na=35, Cl=32, CO₃=38, Hardness=352, Alkalinity=31.

English Ale -- More or less a London water profile. Model: A. J. deLange's "Ale" from HBD1965. 2 grams Epsom salt, 2 grams chalk, 0.3 gram canning salt, 0.8 gram gypsum. Ca=52, SO₄=65, Mg=10, Na=6.2, Cl=9.6, CO₃=63, Hardness=173, Alkalinity=106.

Light Lager -- Very small amounts of ions; just enough to acidify the mash. Model: Mosher's "Ideal Pale Lager". 1 gram Epsom Salt, 0.5 grams baking soda, 1 gram chalk, 0.5 grams canning salt. Ca=21, SO₄=21, Mg=5.2, Na=18, Cl=16, CO₃=51, Hardness=74, Alkalinity=69.

Medium Lager -- Malty, amber lagers like Oktoberfest. Loosely based on Papazian's Munich. 1 gram Epsom salt, 3.5 grams chalk, 0.5 grams canning salt. Ca=74, SO₄=21, Mg=5.2, Na=10, Cl=16, CO₃=111, Hardness=207, Alkalinity=185.

Dark Lagers -- Bocks, for example. Model: Mosher's "Ideal Mild Ale / Dark Lager". 2.5 grams Epsom salt, 2 grams chalk, 2.5 grams canning salt, 2.5 grams gypsum. Ca=73, SO₄=125, Mg=13, Na=52, Cl=80, CO₃=63, Hardness=236, Alkalinity=106.

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