Brewing With Madison Water

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Madison's water supply is not particularly well suited for brewing a wide variety of beer styles. Dark stouts and porters are easily made here but lighter colored beers such as pale ales and pilseners are more of a challenge given the high alkalinity of our water. Mash efficiency suffers as a result of high alkalinity and some harsh or astringent off-flavors may become evident as well. We can address these problems by making adjustments to the chemistry of our water in order to make it more suitable for brewing more authentic beer styles.

What follows is a general outline of water properties and their importance in brewing beer. A water report of average values for Madison's water is included and we'll take an extensive look at how to interpret it so we can make adjustments specifically for Madison water. Finally, we'll discuss the practicality of various water adjustment strategies and determine how to calculate adjustments to achieve our desired result.

Please note that much of this material is included for reference. It is not critical for you to understand the chemistry or know how to perform some of the more complex calculations. You may choose to skip to the end of this document for the "answers" to different water profile formulations using Madison water.

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*__pH__ is an important parameter not just in the mash but also for sparge water, wort stability, and in the final packaged beer. If you are not familiar with the meaning of pH, you should stop right here and consult some introductory chemistry or brewing books that cover the subject. Briefly, 7.0 is neutral, above 7 is alkaline (also referred to as basic), and less than 7 is acidic. Specifically, pH is a measure of hydrogen ion concentration in a solution.

In the mash it is important to achieve a target pH of 5.1 to 5.5 (usually the ideal pH is considered to be 5.2). When measuring pH of liquids at mash temperature using pH papers it is important to take into account the affect temperature has on pH readings. (I recommend ColorpHast Test Strips from EMD Biosciences. Unfortunately they are quite expensive but you can double your value by cutting them in half length-wise.) Note that at mash temperatures pH values are approximately 0.3 points less than the pH value at room temperature. For example, if you pull a few drops out of your mash and let it cool to room temperature you would subtract 0.3 to the room temperature pH to get the actual mash pH. In other words, if your mash sample measured pH=5.5, then your actual mash pH would equal 5.2.

In the mash, the target pH of 5.2 is important for allowing diastatic enzymes in the mash to function as optimally as possible. (α-amylase & β-amylase break down sugars and some proteolytic enzymes break down proteins) We also want to make sure that our sparge water pH is less than 6.0 to avoid tannin and polyphenol extraction during the sparge. Finally, the reduced pH of the resulting wort helps to reduce harsh hop bitternes and also provides a greater resistance to microbiological infection as bacteria don't thrive as well in acidic environments.

Major players in Mash Chemistry and pH

*__Calcium (Ca^{+2})__ is a major player because of the acidifying effect it has in the mash. Calcium reacts with phosphates that are present in malted barley to release hydrogen ions into the mash. This lowers the pH of the mash (that's a good thing). Another important role for calcium is its ability to protect mash enzymes from denaturing at mash temperatures. In particular, the optimal temperature range for α-amylase can be extended from the upper limit of 162°F (72°C) all the way up to 167°F (75°C) in a high calcium mash. This increased enzyme stability allows for rapid conversion of starches to fermentable sugars. Finally, calcium in the wort helps to reduce color formation (useful for making very light colored pilseners), helps precipitate proteins and oxalates which contributes toward a more clear beer, and assists with yeast flocculation.

*__Magnesium (Mg^{+2})__ functions similarly to but is much less potent than calcium. Magnesium is important for healthy yeast function but high levels can contribute negatively sour and bitter flavors.

*__Bicarbonate (HCO_3^{-1})__ is a major player in that it can raise the pH of the mash if it is present in abundance. This can be problematic if you are trying to brew pale beers as it makes achieving acceptable mash pH levels quite difficult. Some consider excess bicarbonate to be flavor-negative in some styles (particularly light colored and/or hoppy beer styles). Bicarbonate is directly related to alkalinity which is a way of describing the ability of water to resist pH change. In chemistry you'd refer to this property as a "buffering capacity".

*Note that Ca^{+2} and Mg^{+2} are referred to as **cations** (meaning they are ions with positive charge) whereas HCO_3^{-1} is referred to as an **anion** (meaning it is an ion with negative charge).

*__Alkalinity__ is directly related to bicarbonate concentration and is a way of describing the ability of water to resist pH change. The term alkalinity is used to describe the water's buffering capacity. High alkalinity means it strongly resists your efforts to reduce pH with acid. (i.e. you need more acid to lower the pH). Low alkalinity means you can easily reduce pH with acid (i.e. you don't need much acid to lower the pH). **Residual Alkalinity** refers to the alkalinity that is not neutralized after mashing in and needs to be addressed by further acid addition.

*__Hardness__ is often misunderstood and this is largely due to the peculiar way in which it is reported in water reports. It is often reported "as $CaCO_3$". **Total Hardness** is a measurement that reflects the total calcium and magnesium cations as if they were to bind bicarbonate anions. **Temporary Hardness** is a measure of how much calcium and magnesium would precipitate if you boiled the water and had enough bicarbonate available to bind to both cations. Subtract Temporary Hardness from Total Hardness and you're left with **Permanent Hardness** which is a measure of calcium and magnesium that would not precipitate after boiling to remove the temporary hardness. The conventional definition of hardness is confusing but for brewing purposes we won't be specifically concerned with it in and of itself.

Major players in Beer Flavor Contributions

- **-Sodium ions (Na^{+1})**
- **-Chloride ions (Cl^{-1})**
- **-Sulfate ions (SO_4^{-2})**

*__Sodium__ accentuates malt sweetness.
*__Chloride__ enhances "fullness" and malt flavor as well.
*__Sulfate__ increases bitterness and provides for a more dry bitterness as well.

Note that the ratio of sulfate to chloride can alter beer flavor as well. A 2:1 sulfate to chloride ratio is suited to bitter beers. Conversely, a 1:2 sulfate to chloride ratio is suited for more balanced beers. A 1:3 ratio will help achieve a more malt accented beer.

Water Profiles from Notable Brewing Centers

(average values are reported as ppm or mg/Liter)

	Pilsen	Dortmund	Vienna	Munich	London	Edinburgh	Burton	Dublin	Madison
Calcium	10	225	163	109	52	100	352	118	70
Magnesium	3	40	68	21	32	18	24	4	41
Sodium	3	60	8	2	86	20	44	12	9
Chloride	4	60	39	36	34	45	16	19	19
Sulfate	4	120	216	79	32	105	820	54	21
Total Hardness #	37	728	688	359	262	324	979	312	344
Bicarbonate	3	220	243	171	104	160	320	319	364
Alkalinity*	3	180	199	140	85	131	262	261	298
Residual Alkalinity*	-6	-4	43	50	29	49	-4	174	224

*Alkakinity and Residual Alkalinity in the table above is a calculated value which is NOT ordinarily reported by water utilities.
Reported "as $CaCO_3$"

***Let's use Madison's average values to understand how to interpret the water report. You can obtain water reports specific to your home at:**

http://www.cityofmadison.com/water/serviceCustomer.cfm

Ion	Average (ppm)
Calcium (Ca^{+2})	**70**
Magnesium (Mg^{+2})	**41**
Sodium (Na^{+1})	**9**
Chloride (Cl^{-1})	**19**
Sulfate (SO_4^{-2})	**21**
Total Hardness	**344**
Bicarbonate (HCO_3^{-1})	**364**
Alkalinity*	**298**
Residual Alkalinity*	**224**

***Calcium**: ideal range is 50-150 ppm for brewing. Madison water is well within range at 70 ppm. However, we'll need to adjust calcium levels when we make efforts to neutralize alkalinity for brewing lighter colored beers.

***Magnesium**: ideal range is 10 to 30 ppm for brewing. Madison water is high in this ion at 41 ppm. This is probably not problematic but if it reaches levels above 50 ppm it can cause a sour/bitter character to emerge.

***Sodium**: ideal range is 0-150 for brewing. There's a great deal of latitude with sodium. Malt sweetness is accentuated at levels between 70-150 which may be useful for some styles. Madison water, at 8.5 ppm is on the low end of that range.

***Chloride**: ideal range is 0-250 ppm for brewing. Again, a great deal of latitude exists with chloride and this is good because it means $CaCl_2$ will be a good option for making adjustments. A "more full" and sweet beer results from increased levels of chloride. Madison water is at the low end of this range at about 19 ppm. The ratios of chloride to sulfate interplay in ways that affect different styles of beer as described below.

***Sulfate**: ideal range is 50-150 ppm for brewing. High levels increase bitterness and gives a more dry bitterness. Madison water is low in sulfate at about 20.5 ppm and this is good because it means gypsum ($CaSO_4$) will be a good option for making adjustments.

Note that a sulfate to chloride ratio of 2:1 is suited to bitter beers and the sulfate:chloride ratio of 1:2 is more ideal for more balanced beer styles. A 1:3 ratio will help with malt accented beers. This effect is often neglected but is useful to know. Madison water is at nearly a 1:1 ratio which means the effect of this ratio is not a significant contributer to flavor in unaltered Madison water.

***Bicarbonate**: ideal range for pale colored beers is 0-50 ppm, ideal range for amber colored beers is 50-150ppm, and 150-250 ppm for dark beers. Madison water is very high in bicarbonate at 364 ppm which makes it a challenge for brewing pale colored beers. **This is the ion (along with calcium) to which Madison homebrewers must pay most of their attention.**

***Alkalinity**: Madison water is extremely alkaline at 298 ppm (as Calcium Carbonate) which means it has a high buffering capacity. Specifically, this means that it resists change in pH quite strongly. We'll need to take measures to neutralize this alkalinity.

***Total Hardness**: Total hardness for Madison water is 344 ppm and is measured as Calcium Carbonate for simplicity. Madison water's temporary hardness is 298 ppm. Permanent hardness is largely a reflection of the calcium and magnesium that remains soluble. Madison water's permanent hardness is 46 ppm. (344-298=46)

***pH**: Madison water is at pH 7.47. This isn't terribly important to know in and of itself but it is important with respect to its relationship to alkalinity. Mash pH and sparge water pH are the important values to consider in brewing.

Water Adjustment Strategies

There are several options available for adjusting your brewing water. Some are more practical than others depending on what you have to work with. We'll address these methods and their usefulness with respect to Madison water. It is important to remember that by and large we are mostly interested in adjusting **mash** water. Adjusting all of the water can be useful and/or desirable but the mash water is what is most important to address.

***Mashing regime:** An acid rest is a method of taking advantage of malt phytase which is an enzyme that functions optimally at 35°C/94°F and reacts with malt phytin to lower pH. This strategy is useful only for water that is low in alkalinity and is very time consuming (a two to three hour rest). This is not a very useful strategy with Madison water due to its high alkalinity.

***Sour Mash:** Standard malt can be steeped in water to allow naturally present lactic acid bacteria to produce lactic acid. This results in a low pH sour mash that can be blended in low amounts with a standard mash to lower the pH. As a point of reference, a standard pale malt mash in untreated Madison water yields a pH of 6.1. If you leave the mash at room temperature for 24 hours the pH drops to 4.2. The disadvantage to this method is that a sour mash doesn't smell too good and you have to be careful not to use too much or you'll taste the sourness in the final beer.

***Using specialty malts:** Highly kilned malts contain more malt phosphates than base malts and those phosphates react with calcium to liberate H^+ ions and lower the pH. Munich malt is a very good example of a malt which contains more phosphate than pale or pilsener malts and can be used as a base malt. Roasted malts are even more effective at lowering pH especially with highly alkaline water. The stouts of Dublin demonstrate this. Roasted malts at 15% of the grain bill in a mash with Madison water still only yields a mash pH of about 5.7 which is slightly higher than what we'd like to achieve (pH 5.2-5.5). An addition of $CaCl_2$ or gypsum will be very useful in achieving a pH of 5.2 for dark beers. Obviously we can't use roasted malts to make pale beers so this strategy has limited use potential for light colored beers.

One option for lighter colored beers is the use of acid malt which is a light colored malt typically used by German brewers. Acid malt contains lactic acid (the maltster intentionally lets lactic acid bacteria do it's thing) which lowers mash pH. This is a similar concept to the sour mash but in this case the maltster has already done the work for you and you avoid a stinky mess in your house. For example, a pale base malt mash in deionized water would yield a pH of about 5.8 whereas acid malt in deionized water would yield a pH of about 4.0.

***Dilution with Deionized Water:** This is probably the most straightforward approach as it requires only simple math to achieve your objective. For example, if you dilute your water to 50% tap:50% deionized water then you simply multiply your ion concentrations by 0.50. If your tap water is diluted to 25% tap:75% deionized water then you multiply your ion concentrations by 0.25. (Always multiply by the percent tap water.) In a technical sense this isn't perfectly accurate in terms of ion dilutions but it is extremely close.

However, it is very important to remember that if you're trying to dilute the water to reduce the high bicarbonate in Madison water you're also diluting all of the other ions as well. This is important because you'll likely need to add calcium back to the water since the calcium concentration was also diluted. This means you'll need to add back either calcium chloride or gypsum.

But wait!….you also must remember that you can't add one ion without adding another with it. The same can be said for subtraction of ions as well. If you add calcium in the form of gypsum you're also adding sulfate ions. If you add calcium in the form of calcium chloride you're also adding chloride ions. Keep this in mind when you take into account the style of beer you're brewing. (gypsum for hoppy beers vs. calcium chloride for malty beers)

NOTE: Gypsum does not readily dissolve in straight water so it is really only useful in the mash itself where it can dissolve due to a more acidic environment.

***Pre-boiling:** This is a strategy for removing bicarbonates by precipitating them in the form of calcium carbonate ($CaCO_3$). Boiling Madison's water will cause calcium and bicarbonate ions to combine to form a white precipitate. You'll probably notice the white scum that forms in your kitchen pots when you boil water for an extended period of time. This is calcium carbonate coming out of solution.

When you boil the water most of the available calcium will be completely removed (this reflects temporary hardness) but you will remove a significant amount of bicarbonate which achieves the objective of lowering alkalinity. (i.e. it won't be as difficult to lower the pH of the mash)

Boiling Madison water leaves a deficiency of calcium ions and removes about 190 ppm of bicarbonate. That still leaves you with about 170 ppm of bicarbonate and thus about 140 ppm of alkalinity to neutralize. You can increase the amount of bicarbonate removed if you add about 70 ppm of calcium via calcium chloride. The extra calcium from the calcium chloride will help to precipitate more calcium carbonate. In the end the last 50 ppm of bicarbonate cannot actually be precipitated due to reasons a chemist would have to explain.

So the amount of calcium chloride needed to add 70 ppm of calcium would be about 1 gram per gallon of water. Note that 1 gram/gallon of $CaCl_2$ would also add 127 ppm of chloride ions. **Add the calcium chloride to the water before boiling it!**

Theoretically the amount of calcium sulfate (gypsum) needed to add 70 ppm of calcium would be about 1.15 grams per gallon of water. Note that 1.15 grams/gallon of gypsum would also add 169 ppm of sulfate ions. **Remember that gypsum is not soluble in water so it will not be very useful for this application!** You can however use this amount of gypsum based on your total brewing water volume but add it all to the mash. This will neutralize any mash alkalinity and also add an abundance of calcium to hit optimal mash pH ranges. You'll still have about half of the original bicarbonate remaining in the final beer so keep that in mind.

This is a relatively straightforward method but it's also energy intensive. After boiling allow the water to sit overnight to allow the precipitated calcium carbonate to settle to the bottom of the vessel. The next day decant the water into your kettle and leave the white precipitated calcium carbonate behind.

***Slaked Lime Treatment:** Slaked lime treatment was a method often employed in Germany and Austria which achieves the same result as pre-boiling but is much less energy intensive and less calcium depletion occurs. Slaked lime is calcium hydroxide ($CaOH_2$) and is a white powder that you can often find in the canning section of a grocery store labeled as “pickling lime”.

When slaked lime is added to Madison water it dissociates into Ca^{++} ions and OH^- ions. The Ca^{++} ions combine with bicarbonate to form calcium carbonate (just as it does in boiling) whereas the OH^- ions combine with the hydrogen (H^+) ion that was liberated from the bicarbonate ion to form a H_2O molecule. The bonus of this method is that calcium is added, bicarbonate is removed, and the byproduct is water!

To ensure the slaked lime treatment goes to completion it’s useful to add a small amount of calcium chloride to the Madison water to provide all of the necessary calcium to remove as much of the bicarbonate as possible.

To treat Madison water with this method, add 0.5 grams of calcium chloride per gallon of water. Mix thoroughly to dissolve. Then add 1 gram of slaked lime per gallon of water and mix thoroughly again. Allow the water to sit overnight to allow precipitated calcium carbonate to settle to the bottom of the vessel. The next day decant the water into your kettle and leave the white precipitated calcium carbonate behind.

The end result is water that has only about 50 ppm of bicarbonate and still retains about 36 ppm of calcium. You’ve only added about 63 ppm of chloride from the calcium chloride addition and now you have excellent brewing water for making almost any style of beer.

As with pre-boiling, supplementing gypsum prior to slaked lime treatment is not very useful with this method since the gypsum is not soluble in water. It’s best to stick with calcium chloride for the treatment and then adjust mash pH with gypsum for hoppy styles or additional calcium chloride for malty styles.

The drawback to this method is that you need a large vessel to hold the treatment water and it takes a day for the precipitate to settle out. It’s similar to boiling in this regard. It’s also very important not to overuse slaked lime as it can actually increase pH and (and alkalinity to a lesser degree) if used in excess.

***Adding Ions Via Salt Additions:** You can lower mash pH by adding calcium in the form of Calcium Sulfate ($CaSO_4$) which is also referred to as gypsum or with

Calcium Chloride ($CaCl_2$) Remember that you'll also be adding the anion (sulfate or chloride depending on your choice of salt) and you must take that into consideration depending on what flavor impact is acceptable. Use gypsum for hoppy styles and calcium chloride for malty styles. You can also use a combination of the two to keep anion concentrations to a minimum.

Treating Madison water with only salt additions is not particularly useful unless you're brewing dark beers. These salt additions will not reduce bicarbonate although they will reduce mash pH. The amounts of salt needed will be significantly high for light colored beers if bicarbonate is still present. This means the sulfate or chloride concentrations will be substantially high as well due to the large salt addition. Ideally you'd want to add salts in tandem with other treatment methods. Salt additions (particularly calcium chloride) are useful for hitting ideal mash pH when brewing dark beers.

***Acid treatments:** Another option for adjusting mash pH is using acids such as lactic, phosphoric, or hydrochloric acids. These can be effective but again it doesn't remove bicarbonate and requires careful pH measurement that is usually beyond the practical scope of a homebrewer. Acids are most useful for adjusting sparge water pH to 6.0 or less.

For adjusting Madison tap water to use as sparge water the following amounts of acid are approximations for achieving a **sparge** water pH of 6.0 or less:
25% phosphoric acid: 5.3 milliliters/gallon
88% lactic acid: 1.4 milliliters/gallon

If you're using pre-boiled Madison water use the following approximations:
25% phosphoric acid: 2.6 milliliters/gallon
88% lactic acid: 0.7 milliliters/gallon

If you're using slaked lime treated Madison water use the following approximations:
25% phosphoric acid: 0.78 milliliters/gallon
88% lactic acid: 0.2 milliliters/gallon

Important Note These amounts are to be used as a guideline and ideally you'd add a little less that these amounts and measure the pH to see how close you are. Add the remaining acid if necessary to hit your target. Do this at least once to confirm the amounts and then for subsequent brew sessions you can approximate in a pinch if you don't have time or ability to measure pH.

***Five Star "5.2":** The contents of this product are proprietary so it's not clear what is actually in this product. It is added to the mash as proscribed by the manufacturer and in most cases will adjust the pH to 5.2 automatically. The drawback is that again, using this product with Madison water means that high bicarbonate levels remain. Also note that this product cannot be used to adjust sparge water pH. It is only designed to be used in the mash. You could probably use it successfully with mash water that has been treated to remove bicarbonate by one of the above methods but this would have to be verified by measuring pH.

Final Notes on Brewing With Madison Water

- Check your home plumbing to make sure that your water softener is only softening your hot water. Cold water does not need to be softened. The purpose of a water softener is to remove calcium and magnesium ions and exchange it for sodium ions. This is to prevent your water heater and hot water lines from becoming filled with precipitated calcium carbonate. (remember that heat causes calcium carbonate to precipitate out of solution) You don't want to use your house softened water for brewing because it is loaded with sodium and has no calcium or magnesium. As an aside Madison water softeners should be set to about 20 gpg (gpg = grains per gallon in this case)
- Don't get caught up with trying to match water profiles of the famous brewing cities of the world. Just because a city is famous for a certain style of beer does not mean that their water profile is required to brew that style. For example, brewers in pilsen actually have to treat their mash water in some way (usually acid rests) because they don't have enough calcium in their water to lower the pH of the mash to the low 5 range. Munich brewers cannot brew helles without treating their water. And contrary to popular belief, you can brew good dark beers with low to moderate bicarbonate water.
- Remember that measuring mash pH means that you measure it at room temperature and subtract 0.3 from the pH reading to get the actual mash pH. (pH readings are lower at high temperatures)
- Remember that gypsum does not dissolve in water very well. Gypsum is to be used in the mash or boil kettle only. Calcium chloride will dissolve in water very easily. It's also important to remember that these two salts do not change the pH of water itself. They do change mash pH.
- If you pre-boil or treat with slaked lime it's important to let the calcium carbonate settle to the bottom and remove the water from the precipitate. You're trying to get rid of that white stuff!
- Most of this document is geared toward Madison's water so the treatment regimes are specific to Madison and should not be passed along to anyone brewing with water that is not similar to Madison's. If you want information regarding water outside of Madison municipal sources feel free to contact Mark Garthwaite to construct a guide specific to your water.