Hardness

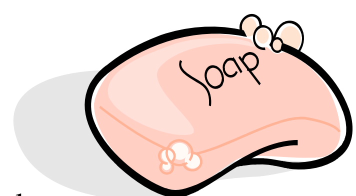
Removing hardness from water is called softening and hardness is mainly caused by calcium and magnesium salts. These salts are dissolved from geologic deposits through which water travels. The length of time water is in contact with hardness producing material helps determine how much hardness there is in raw water.

The two basic methods of softening public water supplies are chemical precipitation and ion exchange. Other methods can also be used to soften water, such as electrodialysis, distillation, freezing, and reverse osmosis. These processes are complex and expensive and usually used only in unusual circumstances.

Water becomes hard by being in contact with soluble, divalent, metallic cations. The two main cations that cause water hardness are calcium (Ca^{2+}) and magnesium (Mg^{2+}). Calcium is dissolved in water as it passes over and through limestone deposits. Magnesium is dissolved as water passes over and through dolomite and other magnesium bearing formations. Because groundwater is in contact with these geologic formations for a longer period of time than surface water, groundwater is usually harder than surface water.

Although strontium, aluminum, barium, iron, manganese, and zinc also cause hardness in water, they are not usually present in large enough concentrations to contribute significantly to total hardness.

OBJECTIONS TO HARD WATER



Hardness was originally defined as the capacity of water to precipitate soap. Calcium and magnesium precipitate soap, forming a curd which causes “bathtub ring” and dingy laundry (yellowing, graying, loss of brightness, and reduced life of washable fabrics), feels unpleasant on the skin (red, itchy, or dry skin), and tends to waste soap. To counteract these problems, synthetic detergents have been developed. These detergents have additives known as sequestering agents that “tie-up” the hardness ions so they cannot form troublesome precipitates.

Hard water forms scale, usually calcium carbonate, which causes a variety of problems. Left to dry on the surface of glassware, silverware, and plumbing fixtures (shower doors, faucets, and sink tops), hard water leaves an unsightly scale called water spots. Scale that forms inside water pipes eventually reduces water pipe carrying capacity. Scale that forms within appliances, pumps, valves, and water meters causes wear on moving parts.

When hard water is heated, scale forms much faster. This creates an insulation problem inside boilers, water heaters, and hot-water lines, and increases water heating costs.

The degree of hardness consumers consider objectionable depends on the degree of hardness to which consumers have become accustomed, as described here:

Soft:	0 to75 mg/L as $CaCO_3$
Moderate:	75 to 150 mg/L as $CaCO_3$
Hard:	150 to 300 mg/L as $CaCO_3$
Very Hard:	Above 300 mg/L as $CaCO_3$

Water should have a total hardness of less than 75 to 85 mg/l as $CaCO_3$ and a magnesium hardness of less than 40 mg/l as $CaCO_3$ to minimize scaling at elevated temperatures.

Many systems allow hardness in finished water to approach 110 to 150 mg/L to reduce chemical costs and sludge production. Use of synthetic detergents has reduced the importance of hardness for soap consumption; however, industrial requirements for high quality feed water for high pressure boilers and cooling towers have generally increased. As industrial waste treatment costs increase, demand for higher quality potable water has increased dramatically. Industries purchasing water from municipal supplies often add water treatment, depending on the quality of the municipal supply and the intended plant or process use.

HARDNESS MEASUREMENTS

Water hardness is unfortunately, expressed in several different units and it is often necessary to convert from one unit to another when making calculations. Most commonly used units include grains per gallon (gpg), parts per million (ppm), and milligrams per liter (mg/L).

Grains per gallon is based on the old English system of weights and measures, and is based on the average weight of a dry kernel of grain (or wheat). Parts per million is a weight to weight ratio, where one ppm of calcium means 1 pound of calcium in 1 million pounds of water (or 1 gram of calcium in 1 million grams of water). Milligrams per liter (mg/L) are the same as ppm in the dilute solutions present in most raw and treated water (since pure water weights 1000 grams per liter).

To Convert	To	Multiply by
Grains per gallon	Milligrams per liter	17.12
Milligrams per liter	Grains per gallon	0.05841

Since calcium carbonate is one of the more common causes of hardness, total hardness is usually reported in terms of calcium carbonate concentration (mg/L as $CaCO_3$), using either of two methods:

Calcium and Magnesium Hardness

Hardness caused by calcium is called calcium hardness, regardless of the salts associated with it. Likewise, hardness caused by magnesium is called magnesium hardness. Since calcium and magnesium are normally the only significant minerals that cause hardness, it is generally assumed that:

Total Hardness = **Calcium Hardness** + **Magnesium Hardness**
(mg/L as $CaCO_3$) (mg/L as $CaCO_3$) (mg/L as $CaCO_3$)

= 2.50 X Calcium conc. (mg/L as Ca^{2+}) + 4.12 X Magnesium conc. (mg/L as Mg^{2+})

Carbonate and Non-carbonate Hardness

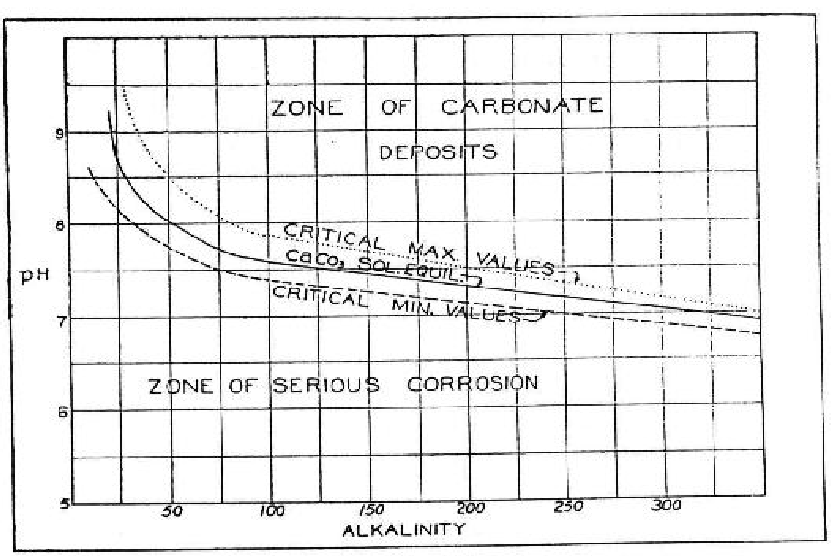
Carbonate hardness is primarily caused by the carbonate and bicarbonate salts of calcium and magnesium. Non-carbonate hardness is a measure of calcium and magnesium salts other than carbonate and bicarbonate salts (such as calcium sulfate, $CaSO_4$, or magnesium chloride, $MgCl_2$). Total hardness (which varies based on alkalinity) is expressed as the sum of carbonate hardness and non-carbonate hardness:

Total hardness = **Carbonate hardness** + **Non-carbonate hardness**
(mg/L as $CaCO_3$) (mg/L as $CaCO_3$) (mg/L as $CaCO_3$)

ALKALINITY

Alkalinity is a measure of water's capacity to neutralize acids, and is important during softening. Alkalinity is the result of the presence of bicarbonates, carbonates, and hydroxides of calcium, magnesium, and sodium. Many of the chemicals used in water treatment, such as alum, chlorine, or lime, cause changes in alkalinity. Determining alkalinity is required when calculating chemical dosages for coagulation and water softening. Alkalinity is also used to calculate corrosivity of water and estimate carbonate hardness.

Alkalinity (expressed as calcium carbonate $CaCO_3$)= bicarbonate ion concentration [HCO_3] + carbonate ion concentration[$C0_3$] + hydroxyl ion concentration [OH]



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