Hard water

NOTE: Mountain Regional Water District's Water is approx 300 mg/l of Hardness, as CaCO3, which is equivalent to approximately 17.5 grains per US gallon (gpg) of hardness.

Hard water is <u>water</u> that has a high <u>mineral</u> content. This content usually consists of high levels of metal <u>ions</u>, mainly <u>calcium</u> (Ca) and <u>magnesium</u> (Mg) in the form of <u>carbonates</u>, but may include several other metals as well as <u>bicarbonates</u> and <u>sulfates</u>. While it is not generally dangerous to safety or health, it does generally cause potentially costly nuisance problems in the home and in industry. On the other hand, hard water is considered to be ideal for brewing certain styles of <u>beer</u>, and <u>Kentucky's</u> distinctive <u>Bourbon whiskey</u> in part owes its flavor to the high calcium content of its groundwater. Some hard water chemicals, particularly <u>silicates</u> and calcium carbonate, are also effective <u>corrosion inhibitors</u>, and can prevent damage to pipes or contamination by potentially toxic <u>corrosion</u> products.

The simplest way to know if water is hard or soft is the lather/froth test. If the water is very soft, when you wash your hands the soap will tend to lather up easily, whereas with hard water it will not. <u>Toothpaste</u> will also not <u>froth</u> well in hard water. More exact methods of hardness detection use a wet <u>titration</u> method to determine hardness.

For many uses, including drinking (aside from taste), it does not matter whether water is hard or soft. For instance, to put out fires, water your lawn, wash the mud off the streets or float your boat, water would have to be pretty hard to cause a problem. But for bathing, washing dishes and clothes, shaving, washing your car and many other uses of water, hard water is not as efficient or convenient as "soft water." Hard water can cause limescale deposits in kettles, washing machines and pipes. Soft water also tastes "sweeter" than hard water.

What is hard water?

Earlier generations coined the phrase "hard water" because it made cleaning difficult. Hardness is caused by compounds of calcium, magnesium, and a variety of other metals. All freshwater sources contain calcium and magnesium in varying quantities. Water dissolves, suspends, and/or exchanges certain trace elements and compounds from many things that it contacts on its travels. For example peat will soften water where as lime will harden it

Total water hardness (including both Ca and Mg) is reported as $\underline{\text{ppm }w/v}$ (or mg/L) of CaCO₃. Water hardness usually measures the total concentration of Ca and Mg, the two most prevalent divalent metal <u>ions</u>, although in some geographical locations <u>iron</u>, <u>aluminium</u>, and <u>manganese</u> may also be present at elevated levels. Calcium usually enters

the water from either CaCO₃, as <u>limestone</u> or from <u>mineral</u> deposits of CaSO₄. The predominate source of magnesium is <u>dolimitic</u> limestone, CaMg(CO₃)₂.

Types of Hard Water

A common distinction is made between 'temporary' and 'permanent' hardness.

Temporary Hardness

Temporary hardness is hardness that can be removed by boiling or by the addition of lime (calcium hydroxide). It is caused by dissolved calcium bicarbonate in the water.

Calcium carbonate is less soluble in hot water than in cold water, so boiling (which promote the formation of carbonate) will precipitate calcium carbonate out of solution, leaving water that is less hard on cooling.

Permanent Hardness

This is hardness (mineral content) that cannot be removed by boiling. It is usually caused by the presence of calcium and magnesium sulfates in the water, which are more soluble as the temperature rises.

Types of measurement

It is possible to measure the level of hard water by obtaining a free water testing kit. These are supplied by most water softening companies. There are several different scales used to describe the hardness of water in different contexts.

- mmol/l
- mg/l calcium carbonate equivalent
- grains/gallon (gpg) 1 gr/U.S. gal = 17.11 mg/L
- parts per million weight/volume (ppm w/v or ppm m/v)

The precise mixture of minerals dissolved in the water, together with the water's acidity or alkilinity (pH) and temperature will determine the behaviour of the hardness, so single number on a scale does not give a full description. Descriptions of hardness correspond roughly with ranges of mineral concentrations:

- Soft: 0 20 mg/l as calcium
- Moderately soft: 20 40 mg/l as calcium
- Slightly hard: 40 60 mg/l as calcium
- Moderately hard: 60 80 mg/l as calcium
- Hard: 80 120 mg/l as calcium
- Very Hard: >120 mg/l as calcium

Problems caused by hard water

While hard water is not generally unhealthy (see below), it can cause many potentially costly nuisance problems.

Hard water also causes scaling, which is the <u>precipitation</u> of minerals to form a rock-hard deposit called limescale. Scale can clog pipes and can decrease the life of toilet flushing units by 70% and water faucets by 40%. It can coat the inside of tea and coffee pots, and clog and ruin water heaters.

In the home environment, hard water requires more soap and synthetic detergents for laundry and washing. It takes half as much soap for cleaning with soft water. Hard water and soap combine to form "soap scum" that can't be rinsed off, forming a "bathtub ring" on all surfaces, and it dries leaving unsightly spots on your dishes.

Using soap on the body in hard water can cause the formation of a scum often referred to as "curd." The formation of scum and curd is caused when calcium and magnesium form insoluble salts with <u>anions</u>. This curd remains on the skin even after rinsing, clogging pores and coating body hair. This can serve as a medium for bacterial growth, causing diaper rash, minor skin irritation and skin that continually itches.

In industry, hard water contributes to scaling in <u>boilers</u>, <u>cooling towers</u> and other industrial equipment. In these industrial settings, water hardness must be constantly monitored to avoid costly breakdowns. Hardness is controlled by addition of chemicals and by large-scale softening with <u>zeolite</u> resins.

Health considerations

Some studies have shown a weak inverse relationship between water hardness and cardiovascular disease in men, up to a level of 170 mg calcium carbonate per litre of water. The World Health Organisation has reviewed the evidence [1] and concluded the data were inadequate to allow for a recommendation for a level of hardness.

A later review [2] by František Kožíšek, M.D., Ph.D. National Institute of Public Health, Czech Republic gives a good overview of the topic, and conversely to the WHO, sets some recommendations for the maximum and minimum levels of calcium (40-80 mg/l) and magnesium (20-30 mg/l) in drinking water, and a total hardness expressed as the sum of the calcium and magnesium concentrations of 2-4 mmol/l.

Very soft water is more likely to corrode (i.e. react chemically) with metal pipes in which it is carried, and as a result it may have elevated levels of <u>cadmium</u>, <u>copper</u>, <u>lead</u> and <u>zinc</u>.

Softening

A water softener works on the principle of <u>cation</u> or ion exchange in which ions of the hardness minerals are exchanged for <u>sodium</u> or <u>potassium</u> ions, effectively reducing the <u>concentration</u> of hardness minerals to tolerable levels.

The most economical way to soften household water is with an ion exchange water softener. This unit uses <u>sodium chloride</u> (table salt) to recharge beads made of <u>ion exchange resin</u> that exchange hardness minerals for sodium. Artificial or natural <u>zeolites</u> can also be used. As the hard water passes through and around the beads, the hardness mineral ions attach themselves to it, dislodging the sodium ions. This process is called "ion exchange". When the bead or sodium zeolite has no sodium ions left, it is exhausted, and can no longer soften water. The resin is recharged by flushing (often *back*-flushing) with saltwater. The high excess of sodium ions force the hardness ions off the resin beads. The excess sodium is rinsed away, and the resin is ready to start the process all over again. This cycle can be repeated many, many time before the resin loses its ability to react to these forces.

Some softening processes in industry use the same method, but on a much larger scale. These methods create an enormous amount of salty water that is costly to treat and dispose of.

Temporary hardness, caused by hydrogen carbonate (or <u>bicarbonate</u>) ions, can be removed by boiling. For example, calcium hydrogen carbonate, often present in temporary hard water, is boiled in a kettle to remove the hardness. In the process, a scale forms on the inside of the kettle in a process known as "furring of kettles". This scale is composed of insoluble calcium carbonate.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O$$

Hardness can also be reduced with a lime-soda ash treatment. This process, developed by Thomas Clark in 1841, involves the addition of slaked lime (calcium hydroxide — Ca(OH)₂) to a hard water supply to convert the hydrogen carbonate hardness to carbonate, which precipitates and can be removed by filtration:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$$

The addition of sodium carbonate also softens permanently hard water containing calcium sulfate, as the calcium ions form calcium carbonate which is insoluble and sodium sulfate is formed which is soluble. The calcium carbonate formed sinks to the bottom. Sodium sulfate has no effect on the hardness of water.

$$Na_2CO_3 + CaSO_4 \rightarrow Na_2SO_4 + CaCO_3$$

It is desirable to soften hard water, as the latter does not readily form lather with soap. Soap is wasted when trying to form lather, and in the process, scum forms.