Hard and Soft Water

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Hard water

- **Hard water** is the type of water that has high mineral content (in contrast with *soft water*).
- Hard water minerals primarily consist of calcium (Ca^{2+}), and magnesium (Mg^{2+}) metal cations, and sometimes other dissolved compounds such as bicarbonates (HCO_3^-) and sulfates (SO_4^{2-}).
- Calcium usually enters the water as either calcium carbonate ($CaCO_3$), in the form of limestone and chalk, or calcium sulfate ($CaSO_4$), in the form of other mineral deposits.

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Hard water

- The predominant source of magnesium is dolomite [$CaMg(CO_3)_2$].
- Hard water is generally not harmful.
- The total water 'hardness' (including both Ca^{2+} and Mg^{2+} ions) is read as parts per million (ppm) or weight/volume (mg/L) of calcium carbonate ($CaCO_3$) in the water.
- Ppm (Ca) is usually defined as one milligram of calcium carbonate ($CaCO_3$) per litre of water

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Hard water

- Although water hardness usually only measures the total concentrations of calcium and magnesium (the two most prevalent, divalent metal ions), iron, aluminium, and manganese may also be present at elevated levels in some geographical locations.
- Hardness in water can cause water to form scales and a resistance to soap.
- It is also water that doesn't produce lather with soap solutions, but produces white precipitate (scum).

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Temporary hardness

- Temporary hardness is caused by a combination of calcium ions and bicarbonate ions in the water.
- It can be removed by boiling the water or by the addition of lime (calcium hydroxide).
- Boiling promotes the formation of carbonate from the bicarbonate and precipitates calcium carbonate out of solution, leaving water that is softer upon cooling.

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Temporary hardness

- The following is the equilibrium reaction when calcium carbonate ($CaCO_3$) is dissolved in water:
- $CaCO_3(s) + H_2CO_3(aq) \leftrightharpoons Ca^{2+}(aq) + 2HCO_3^-(aq)$
- Boiling the water will remove hardness as long as the solid $CaCO_3$ that precipitates out is removed.
- After cooling, if enough time passes the water will pick up CO_2 from the air and the reaction will again proceed from left to right, allowing the $CaCO_3$ to "re-dissolve" into the water.

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Permanent hardness

- Permanent hardness is hardness (mineral content) that cannot be removed by boiling.
- It is usually caused by the presence of calcium and magnesium sulfates and/or chlorides in the water, which become more soluble as the temperature rises.
- Permanent hardness can be removed using a water softener or ion exchange column, where the calcium and magnesium ions are exchanged with the sodium ions in the column.

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Permanent hardness

- Hard water causes scaling, which is the left over mineral deposits that are formed after the hard water had evaporated.
- This is also known as limescale.
- The scale can clog pipes, ruin water heaters, coat the insides of tea and coffee pots, and decrease the life of toilet flushing units

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Water Softening

- A water softener reduces the dissolved calcium, magnesium, and to some degree manganese and ferrous iron ion concentration in hard water
- A water softener works on the principle of cation or ion exchange in which ions of the hardness minerals are exchanged for sodium or potassium ions, effectively reducing the concentration of hardness minerals to tolerable levels and thus making the water softer and giving it a smoother feeling

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Water Softening

- The most economical way to soften household water is with an ion exchange water softener.
- This unit uses sodium chloride (table salt) to recharge beads made of the ion exchange resins that exchange hardness mineral ions for sodium ions.

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Water Softening

- As the hard water passes through and around the beads, the hardness mineral ions are preferentially absorbed, displacing the sodium ions.
- This process is called ion exchange.

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Water Softening

- Temporary hardness, caused by hydrogen carbonate (or bicarbonate) ions, can be removed by boiling.
- Calcium bicarbonate, often present in temporary hard water, may be 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".
- This scale is composed of calcium carbonate.
- $Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O$

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Water Softening

- Hardness can also be reduced with a lime-soda ash treatment.
- This process 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:
- $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$

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Water Softening

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

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

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Ion-exchange resin

- The water to be treated passes through a bed of the resin.
- Negatively-charged resins absorb and bind metal ions, which are positively charged.
- The resins initially contain univalent hydrogen, sodium or potassium ions, which exchange with divalent calcium and magnesium ions in the water.

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Ion-exchange resin

- As the water passes through the resin column, the hardness ions replace the hydrogen, sodium or potassium ions which are released into the water.
- The "harder" the water, the more hydrogen, sodium or potassium ions are released from the resin and into the water.

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Ion-exchange resin

- Resins are also available to remove carbonate, bi-carbonate and sulphate ions which are absorbed and hydroxyl ions released from the resin.
- Both types of resin may be provided in a single water softener

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Disadvantages of Hard Water

- These "hardness ions" cause three major kinds of undesired effects.

(1) metal ions react with soaps and calcium-sensitive detergents, hindering their ability to lather and forming a precipitate

$$2C_{17}H_{35}COONa + Ca^{2+} \rightarrow (C_{17}H_{35}COO)_2Ca + 2Na^+$$

- Presence of "hardness ions" also inhibits the cleaning effect of detergent formulations

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Disadvantages of Hard Water

(2) calcium and magnesium carbonates tend to precipitate out as hard deposits to the surfaces of pipes and heat exchanger surfaces.

- The resulting build-up of scale can restrict water flow in pipes.
- In boilers, the deposits act as an insulation that impairs the flow of heat into water, reducing the heating efficiency and allowing the metal boiler components to overheat.
- In a pressurized system, this can lead to failure of the boiler

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Disadvantages of Hard Water

(3) Presence of ions in an electrolyte, in this case, hard water, can also lead to galvanic corrosion, in which one metal will preferentially corrode when in contact with another type of metal, when both are in contact with an electrolyte

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