Environmental Technology in Mining

Chapter 3.1.1.1 Water Quality

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y del Medioambiente

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3) Physical properties of water
4) Chemical properties of water

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Before continuing…..
is the issue “water quality” interesting for a mining engineer?

Capacidades y Competencias del Ingeniero Técnico de Minas y Grados en Ingeniería

P07 Sondeos de captación y explotación de aguas subterráneas.

Capacities and Competencies of the Technical Mining Engineer and Degrees in Mining Engineering

P07 Boreholes for the collection and exploitation of groundwater

Competencias y atribuciones profesionales de los ingenieros de minas

2) Sectores de actividad propios o compartidos con otras ingenierías

Gestión de recursos y medio ambiente

- Ordenación del territorio, planeamiento urbanístico, movimiento de tierras, planificación y gestión sostenible de recursos minerales, aguas subterráneas, aguas minerales y termales, petróleo y gas natural, espacio subterráneo y otros recursos geológicos

Agua

- Hidrogeología. Prospección, captación, distribución y utilización de aguas subterráneas

Competencies and professional attributions of mining engineers

2) **Own or shared with other engineers activity sectors**

[…] Groundwater, mineral water […]

Hydrogeology. Prospecting, collection, distribution and use of groundwater.

Example of mineral water composition

Manantial FONTOIRA
Composición analítica (mg/l): residuo seco: 199 (180ºC); bicarbonatos: 152 sulfatos: 8,9; cloruros: 12,4; calcio: 3,4; magnesio: 7,5 y sodio: 11,0.
Control periódico por el Laboratorio Dr. Oliver Rodés. Enero 2017.

Manantial FUENMAYOR
Composición analítica (mg/l): residuo seco: 280 (180ºC); bicarbonatos: 305 sulfatos: 22,8; cloruros: 4,3; calcio: 77,0; magnesio: 20,8 y sodio: 1,6.
Control periódico por el Laboratorio Dr. Oliver Rodés. Marzo 2016.

Manantial PEÑA UMBRÍA
Composición analítica (mg/l): residuo seco: 242 (180ºC); bicarbonatos: 298 sulfatos: 7,3; cloruros: 11; calcio: 55; magnesio: 28 y sodio: 5,4.
Control periódico por el Laboratorio IPROMA. Noviembre 2015.

Manantial SANTOLÍN
Composición analítica (mg/l): residuo seco: 255 (180ºC); bicarbonatos: 274 sulfatos: 6,5; cloruros: 4,8; calcio: 92,4; magnesio: 2,73 y sodio: 2,0.
Control periódico por el Laboratorio Dr. Oliver Rodés. Febrero 2016.

Example of mineral water composition

Example of mineral water composition

Mineral composition (mg/L)

Calcium 80	Magnesium 26	Potassium 1
Sodium 6.5	Nitrates 3.8	Bicarbonates 360
Sulfates 14	Silica 15	Chlorides 10

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Natural Water Characteristics

https://www.freepik.es/vector-gratis/ciclo-agua-ilustrado-pasos_19184220.htm

Natural Water Characteristics

What is the source of natural substances in water?

Natural Water Cycle → impurities (natural substances)

- Precipitation → mineral matter, gases (traces)
- Run over and through the ground → soil particles, organic matter, bacteria
- Groundwater → mineral matter

Properties of water

- High ability to dissolve…:
  - Gases:

Gas solubility (kg/m^3) is proportional to the gas partial pressure on water surface.

As gas partial **pressure** ↑ (increases), gas **solubility** in water ↑ (increases)

Example: the higher the altitude => the lower the atmospheric pressure => the lower the oxygen solubility in water

As **temperature** ↑ (increases), gas **solubility** in water ↓ (decreases).

Example: in summer, the amount of oxygen in a river will be lower => it can be a problem for fish

Solubility of Oxygen in mg/l as a function of Altitude and Temperature
Fresh Water, Moist Air

TEMP °C	Altitude in meters					
	0 m	500 m	854 m*	1000 m	1500 m	2000 m
	760	717	688	676	638	602
0	14.61	13.78	13.22	12.99	12.25	11.55
5	12.77	12.04	11.55	11.35	10.70	10.09
10	11.28	10.64	10.20	10.03	9.45	8.91
15	10.07	9.49	9.10	8.95	8.43	7.94
20	9.08	8.55	8.20	8.06	7.59	7.15
25	8.25	7.76	7.44	7.31	6.88	6.48
30	7.54	7.10	6.80	6.68	6.28	5.91

T ºC

Altitude (m)

https://slideplayer.com/slide/12193280/

Properties of water

- High ability to dissolve…:
  - Solids:

Due to the dipolar character of water, it is good at dissolving ions and other polar molecules

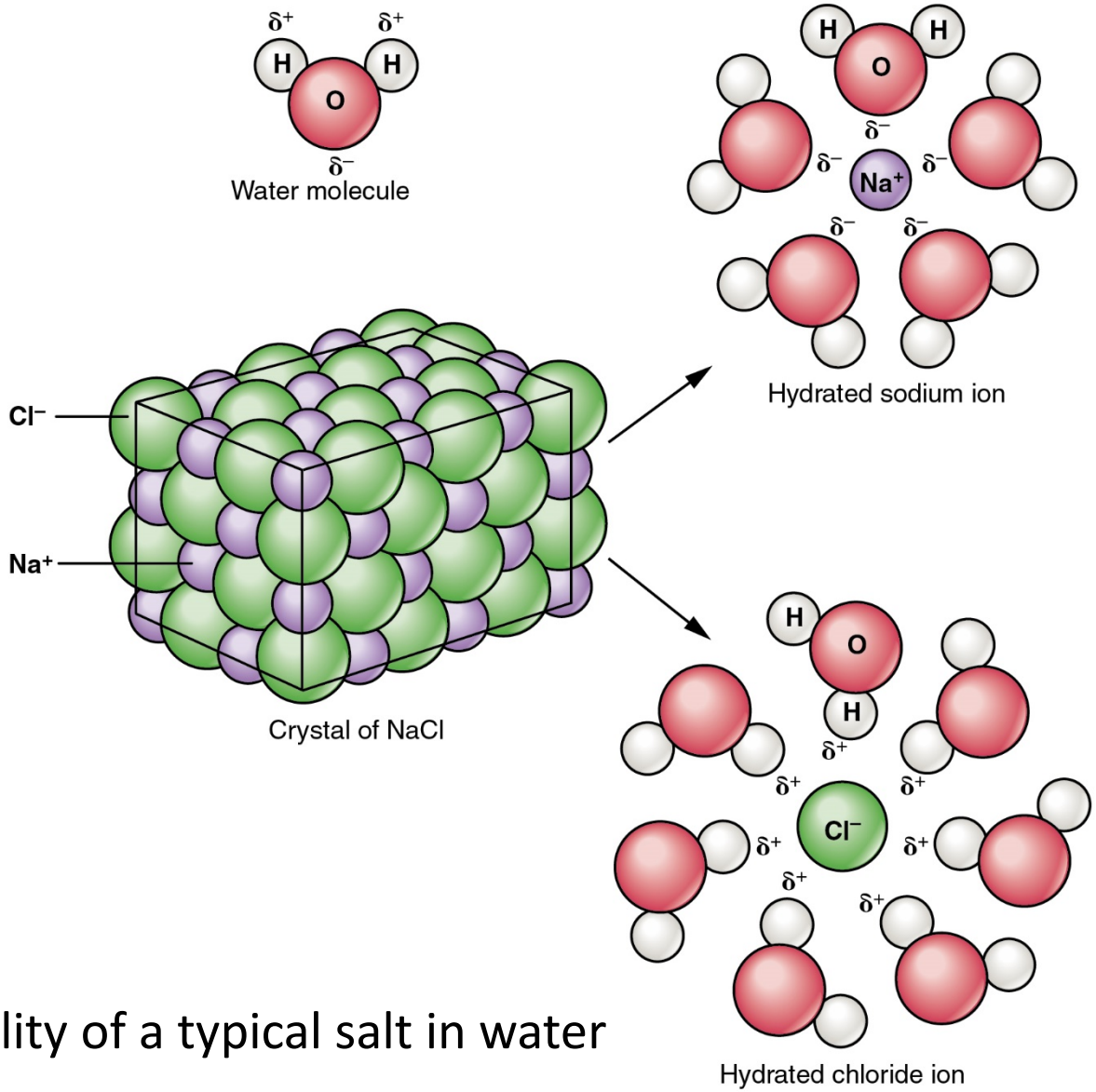
As **temperature** ↑ **(**increases), solids **solubility** in water ↑ (increases)

Exceptions!:

Ca and Mg carbonates **$CaCO_3$** , **$MgCO_3$**: ↑ **T,** ↓ **solubility**

(This will cause precipitates in hot tubes, washing machines, irons, etc.)

Properties of water



Solubility of a typical salt in water

https://commons.wikimedia.org/wiki/File:214_Dissociation_of_Sodium_Chloride_in_Water-01.jpg

Water impurities / pollution

- Impurities:

  Substances in water other than H_2O (usually refer to natural substances)

- Pollution:

  Presence in water of foreign substances that lower its quality → constitute a health hazard or impair the usefulness of water (drinking, bathing, cultivating shellfish, …)

- Categories of impurities/pollution:
  - Physical: *turbidity, color, temperature, taste and odor*
  - Chemical: *alkalinity, hardness, toxics and other compounds*
  - Microbiological: *indicators of fecal contamination*
  - Radiological

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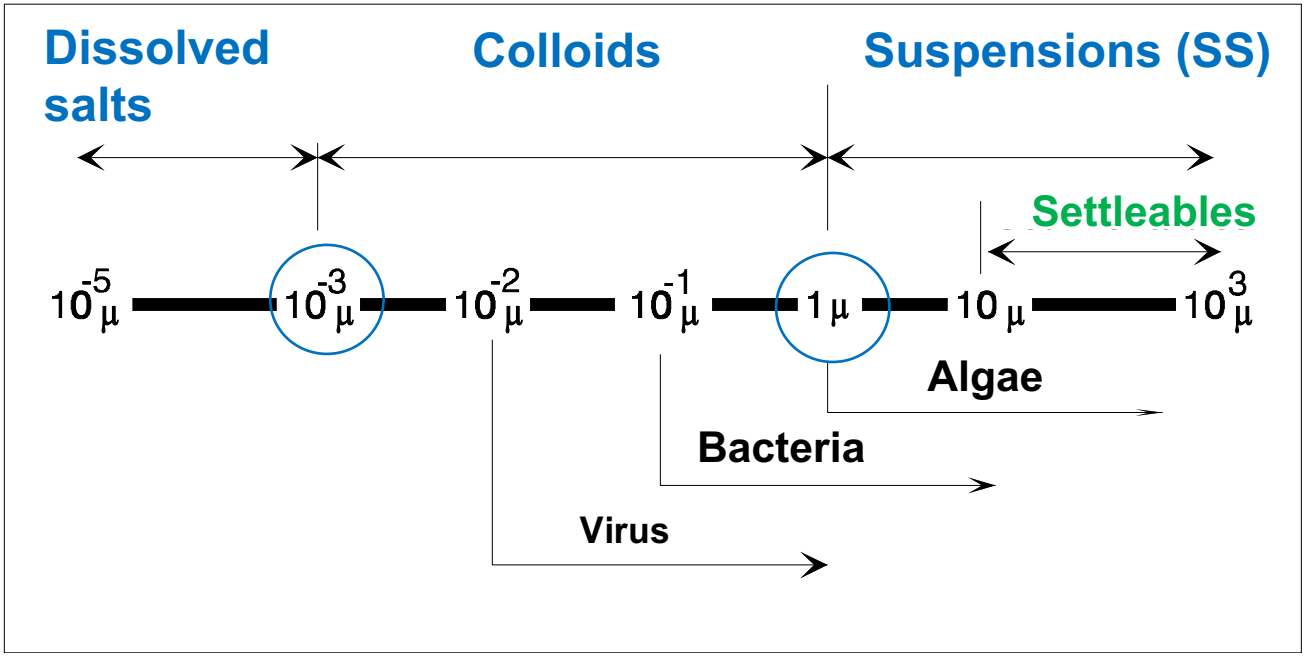
Physical properties

Types of solids in water



Physical properties

Types of solids in water

- Particulate solids:
  - Suspended solids (SS):
    - Large enough to be filtered by a glass filter disc (1µm)
    - Can be removed through physical methods
  - Colloidal particles:
    - Size between dissolved and suspended solids
- Dissolved solids (DS):
    - Atoms, molecular compounds
    - Homogeneously dispersed in the liquid → only one phase
    - Require a phase change to be removed (precipitation)

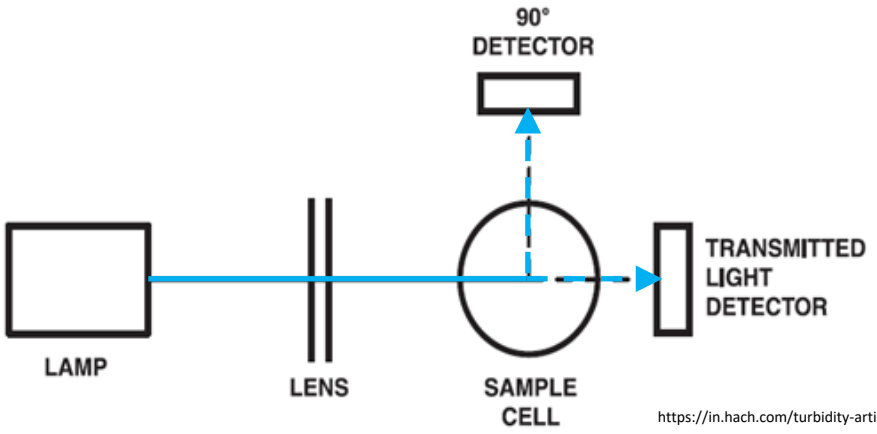
Physical properties

- Turbidity:
  - Given by suspended and colloidal material (particles)
  - Measured through the refraction of light (compared to a reference chemical). Device: nephelometer (Turbidity Meter)
  - NTU (Nephelometric Turbidity Units)

Physical properties

- Turbidity:

Nephelometer principle of measurement



https://in.hach.com/turbidity-article-turbidity101

Hanna instruments

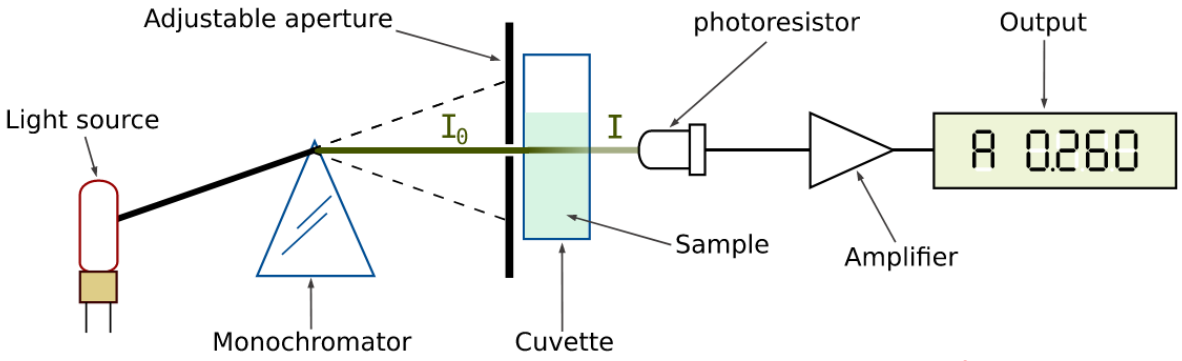
Nephelometer or Turbidity Meter

https://www.renkeer.com/wp-content/uploads/2023/08/Solution-Turbidity-Comparison.jpg

Formazin Reference Turbidity Standards

Physical properties

- Color:
  - Given by dissolved and colloidal compounds
  - Measured by the ability of water to absorb light



Spectrophotometry

https://upload.wikimedia.org/wikipedia/commons/0/05/Spetrophotometer-en.svg

GYassineMrabetTalk This W3C-unspecified vector image was created with Inkscape ., CC BY-SA 4.0 <https://creativecommons.org/licenses/by-sa/4.0>, via Wikimedia Commons

  - True color: without colloids
  - Units (most common): Platinum-cobalt units (Pt-Co)

- Taste and odor
  - Given by dissolved compounds (Fe, Mn, Cu, Na…) and gases (H_2S, …)

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Chemical properties

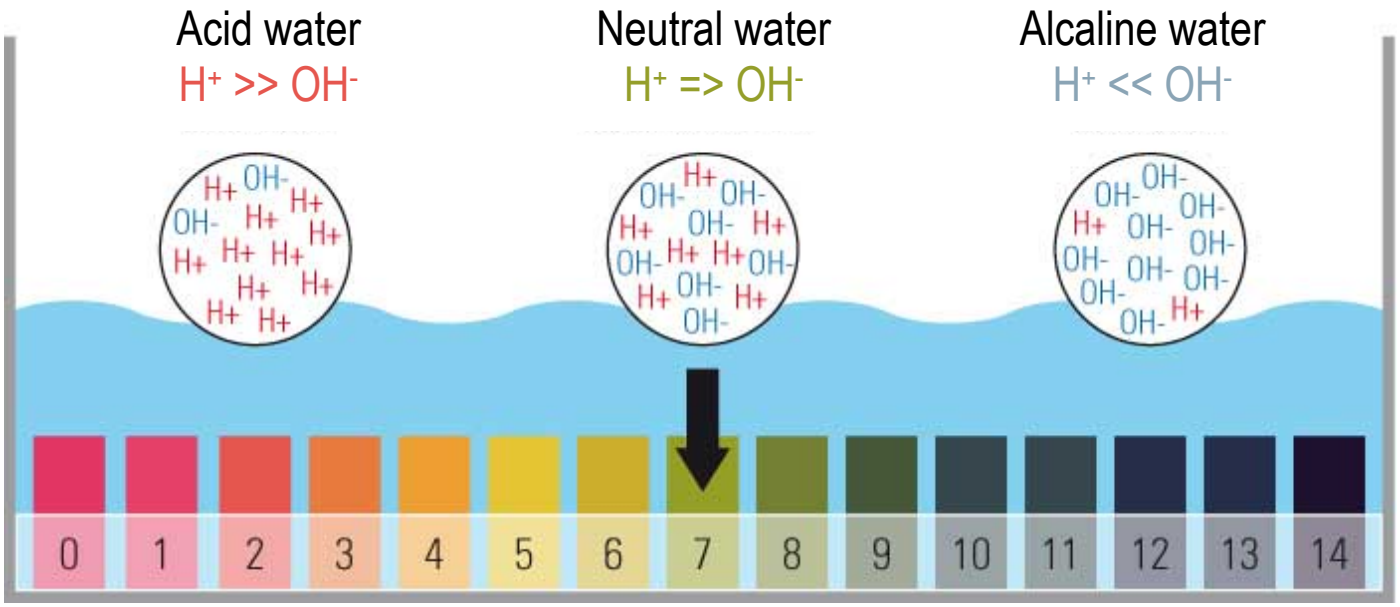
- pH

Measurement of the acidity or basicity of an aqueous solution.

$pH = - \log [H^+]$

↑ concentration of H^+ => ↓ pH

Chemical properties



https://aguapuraysana.com/ph-del-agua-destilada-acido-basico/

Solutions with a pH < 7 are said to be acidic
Solutions with a pH >7 are said to be basic or alkaline.

Pure water has a pH = 7
Natural water 6 < pH < 9

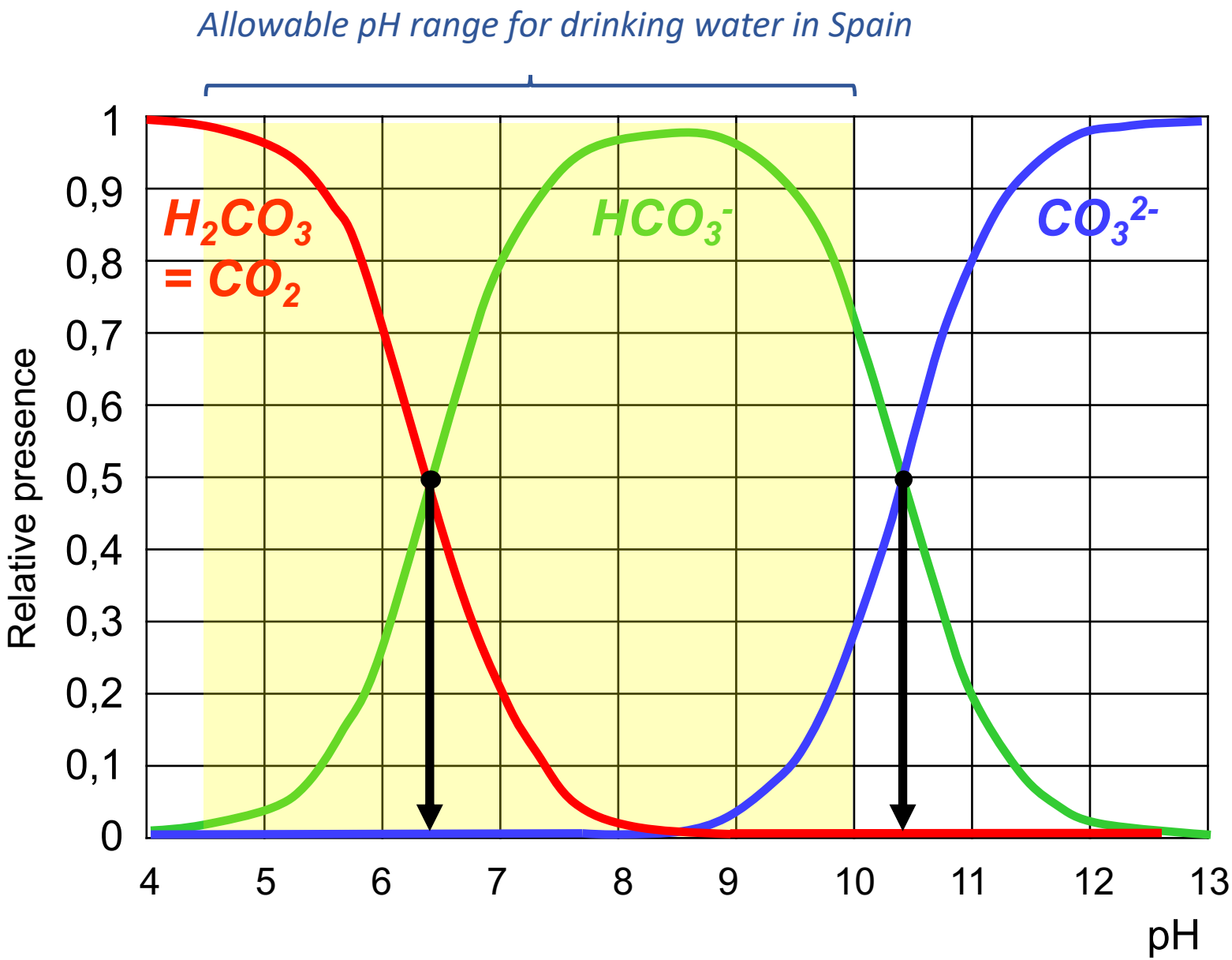
Chemical properties

- Types of solids in water

Main dissolved solids in natural water:

Anions	Name
HCO_3^- CO_3^{2-}	bicarbonates carbonates
SO_4^{2-}	sulfates
Cl^-	chlorides
F^-, NO_3^-, PO_4^{3-} ,	Fluorides, nitrates, phosphates

Cations	Name
Ca^{2+}	calcium
Mg^{2+}	magnesium
Na^+	sodium
K^+, Li^+, Fe^{2+}, Mn^{2+} , Zn^{2+}, NH_4^+	potassium, lithium, ferrous, manganese, zinc, ammonium

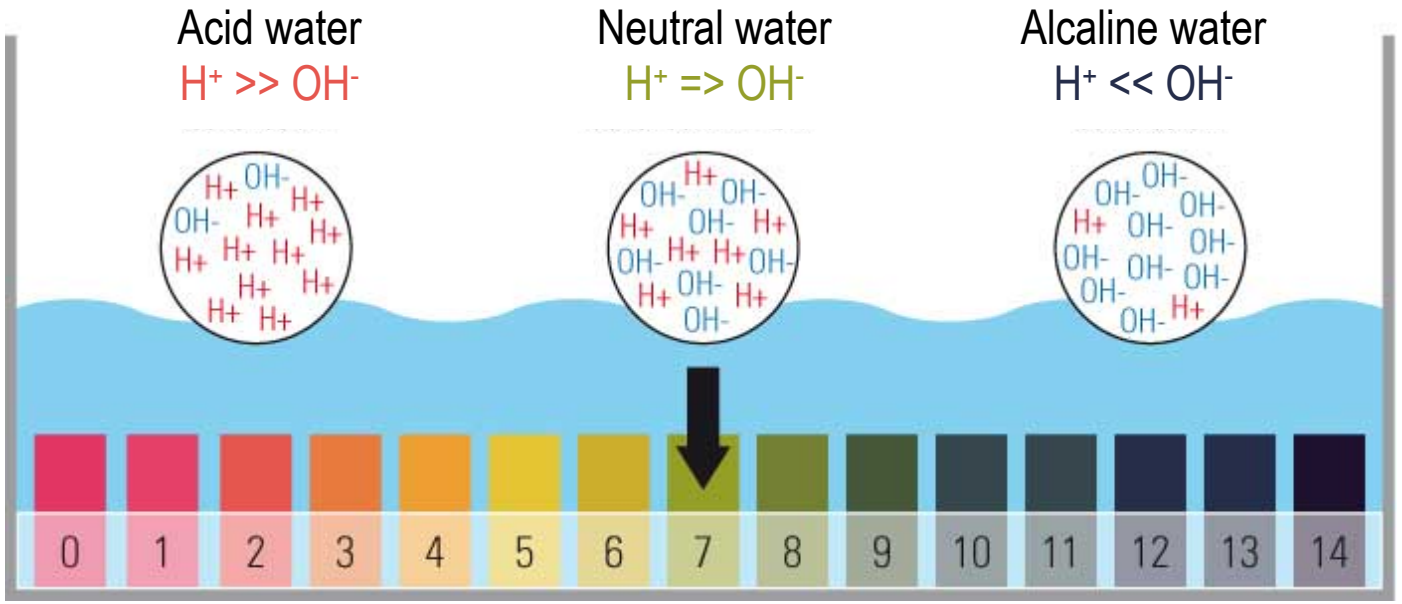


Formas de carbono inorgánico a diferentes pH

Chemical properties

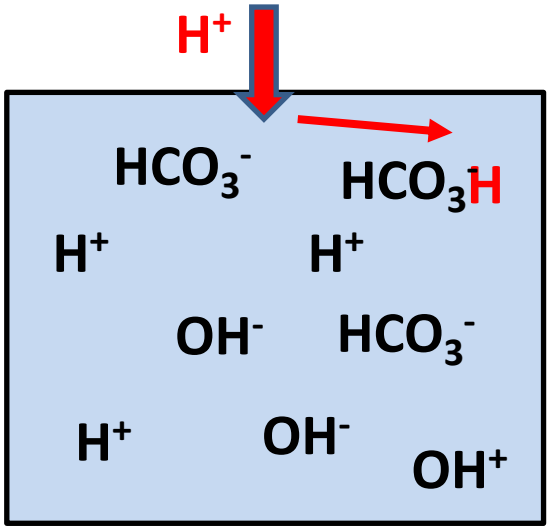
- Alkalinity:
  - Water capacity to neutralize acids
    (water capacity to resist to acidification)
  - Measured as the quantity of acid required to lower water pH to 4.5 (total alkalinity)

Chemical properties

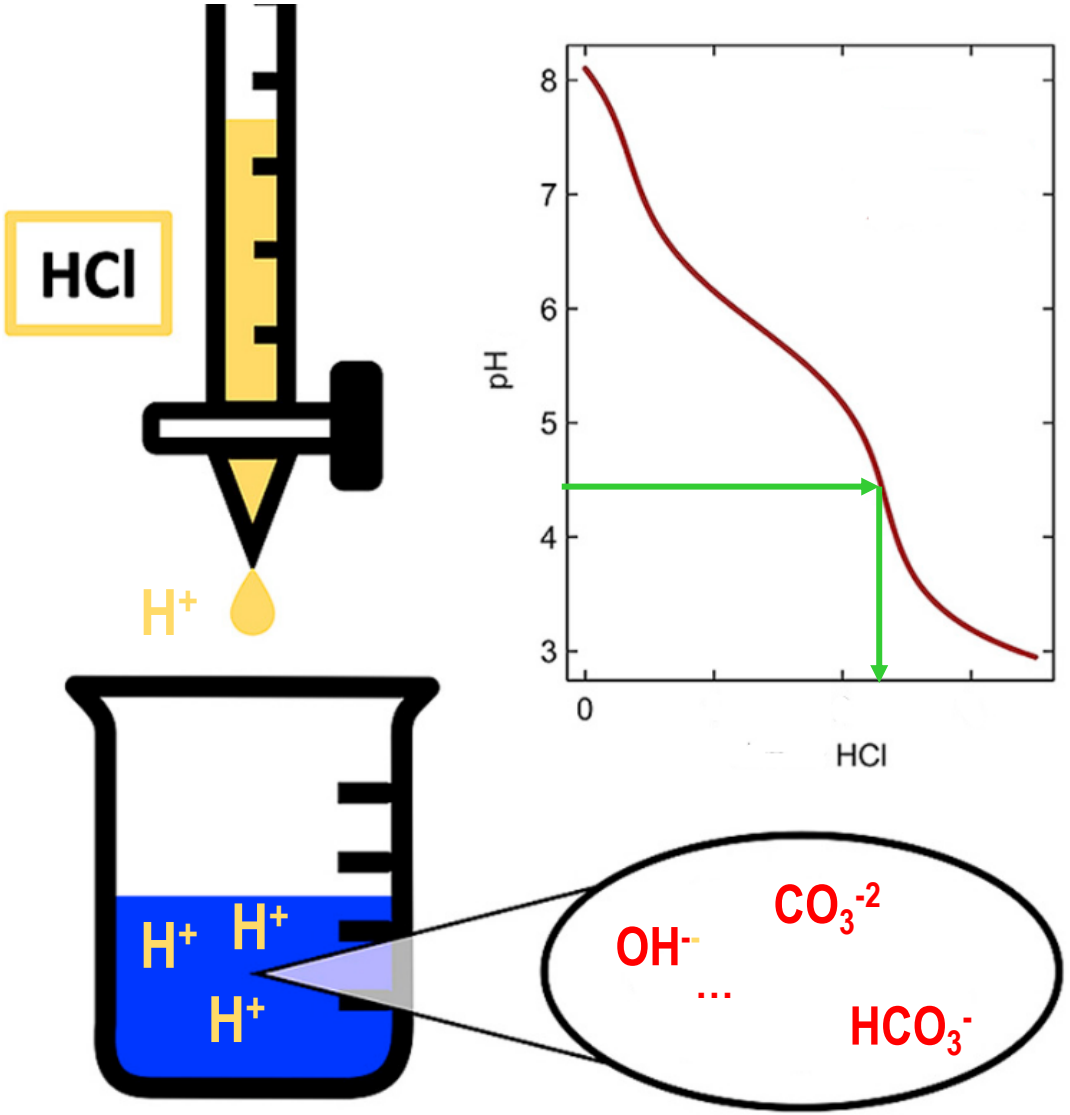


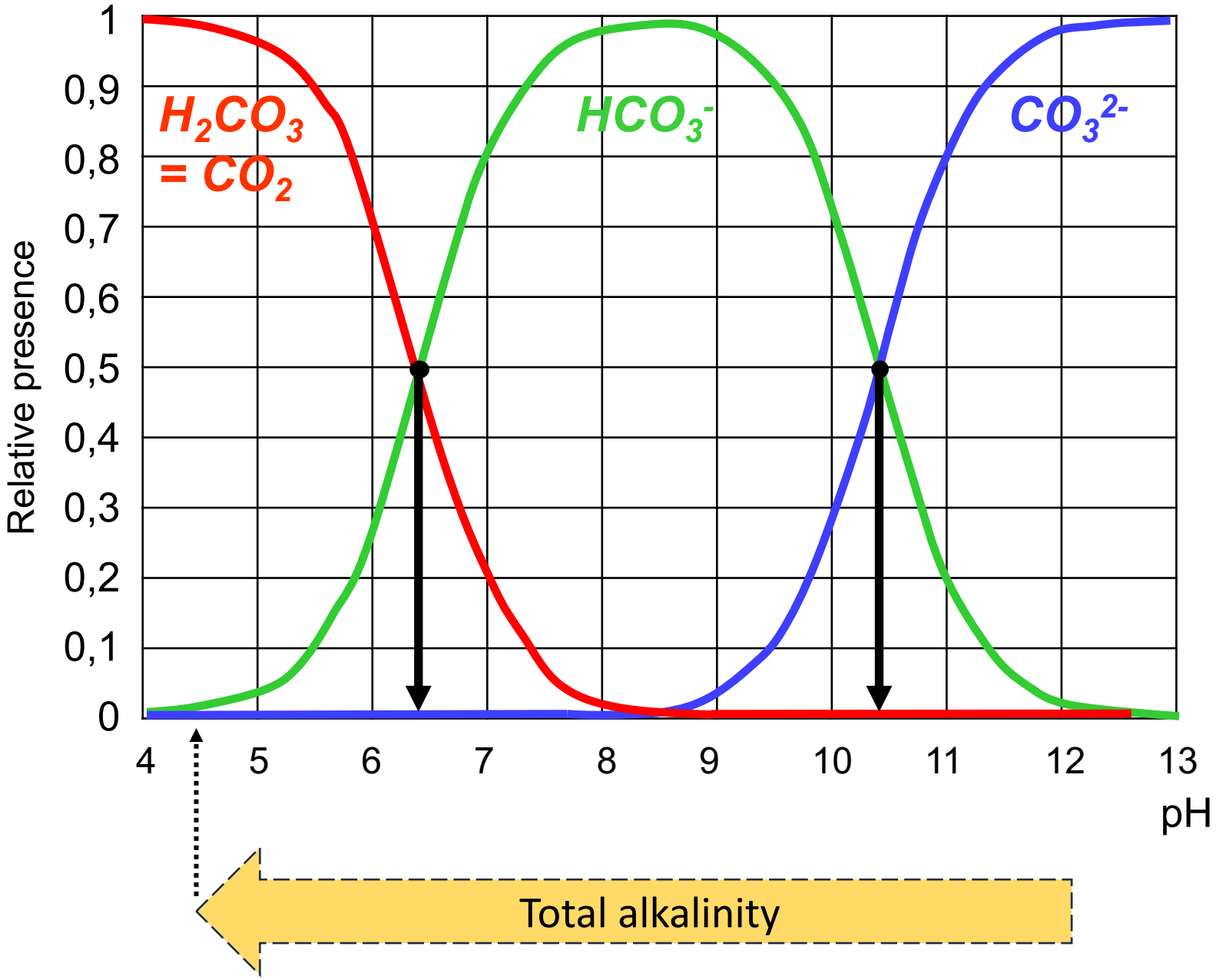
https://aguapuraysana.com/ph-del-agua-destilada-acido-basico/

How do bicarbonates neutralize acids?



Chemical properties




Relative presence
1
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
H_2CO_3
$= CO_2$
HCO_3^-
CO_3^{2-}
4
5
6
7
8
9
10
11
12
13
pH
Total alkalinity

Chemical properties

- Alkalinity:
  - Units: moles/L, meq/L, mg/L $CaCO_3$

$$\text{Alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$ moles/L

  - $[OH^-]$ and $[H^+]$ negligible in most natural waters (pH = 6 – 8)

→ usually alkalinity is calculated as the sum of carbonates and bicarbonates

Chemical properties

- Range of alkalinity in natural waters

Alkalinity Parts Per Million (or mg/L)	**Effect(s)**
30 - 400 ppm	Reasonable range for alkalinity domestic drinking water
150 - 200 ppm	**Perhaps the ideal range for drinking water alkalinity**
<150 ppm	May be corrosive to pipes if the underlying water has a low pH
>200 ppm	Potential for scale formation on and fixtures (clogging risk)

Chemical properties

• Alkalinity: neutralization

• Acidic or alkaline wastewaters require **neutralization** prior to:

- Discharge into receiving waters
- Chemical subsequent treatment
- Biological treatment (pH = 6.5-8.5)

• Chemical **reaction** for neutralization:

$$\text{Acid} + \text{Base} \rightarrow \text{Salt} + H_2O$$

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O$$

$$HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O$$

Chemical properties

- Alkalinity: neutralization

Types of processes

- Mixing acidic and alkaline waste streams
- Acidic wastewater neutralization through limestone bed
- Mixing acid wastewater with lime slurry
- Mixing basic (alkaline) wastewater with acid

Chemical properties

- Hardness:

  Sum of polyvalent cations

  - Mainly Ca^{2+} and Mg^{2+} coming from the dissolution of
    - Limestone: $CaCO_3$ and $MgCO_3$
    - Gypsum: $CaSO_4$ and $MgSO_4$

Total hardness, TH ≈ Ca^{2+} + Mg^{2+} = CH + NCH

- Carbonate or temporary hardness, CH, associated to HCO_3^- Can be removed by boiling.

- Noncarbonate hardness, NCH, associated to SO_4^{2-}, Cl^-,… Cannot be removed by boiling.

Chemical properties

- Temporary hardness (TH = CH):

Caused by the presence of dissolved bicarbonate minerals (calcium bicarbonate and magnesium bicarbonate).

$Ca(HCO_3)_2$ $Mg(HCO_3)_2$

When dissolved, these salts yield:

- calcium and magnesium cations (Ca^{2+}, Mg^{2+}) and
- carbonate and bicarbonate anions (CO_3^{2-}, HCO_3^-).

Chemical properties

- Temporary hardness (TH = CH):

Temporary hardness can be reduced either by boiling the water, or by softening processes.

Boiling promotes the formation of carbonate from the bicarbonate and precipitates calcium/magnesium carbonate out of solution, leaving water that is softer upon cooling.

Boiling reaction:

Precipitates Releases CO_2

$$Ca^{2+}_{(aq)} + 2HCO_3^-{}_{(aq)} \rightarrow CaCO_3^{2-}{}_{(aq)} \downarrow_{(s)} + CO_2 \uparrow_{(g)} + H_2O$$

aq =aquaeous s= solid g=gaseous

Chemical properties

- Temporary hardness (problems for domestic use):
  - Causes precipitates in the bath tub
  - Leaves deposits on water heaters
  - Problems with skin and hair

https://www.descalcificadoraguas.com/wp-content/uploads/2018/09/signos-del-agua-dura.jpg

https://www.camarounds.com/wp-content/uploads/2021/10/Tuberias-que-necesitan-descalcificarse.jpg

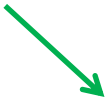
https://reparacion-electrodomesticos.es/images/blog/2018-05-30-reparacion-lavadoras-lavavajillas-por-cal.jpg

Chemical properties

- Permanent hardness (PH=NCH):
  - Hardness (mineral content) that cannot be removed by boiling.
  - Usually caused by the presence of calcium sulfates and/or magnesium sulfates and chlorides in the water, which do not precipitate out as the temperature increases.
  - Ions causing permanent hardness of water can be removed using a water softener, or ion exchange column.

Total hardness = Temporary hardness + Permanent Hardness

Carbonates and bicarbonates of Ca and Mg



Sulfates, chlorides, …of Ca and Mg

Chemical properties

- Total hardness: Problems for domestic use:
  - Does not lather well (↑ use of soap, detergents)
  - Creates difficulties at cooking some vegetables (↑ time)

	SOFT WATER	MEDIUM WATER	HARD WATER
GEL	25ml	37ml	46ml
LIQUID	35ml	35ml	55ml
POWDER	75g	100g	130g

https://www.ariel.co.uk/en-gb/how-to-wash/how-to-do-laundry/washing-in-hard-water

Amount of a certain detergent needed for clothes washing as a function of water hardness

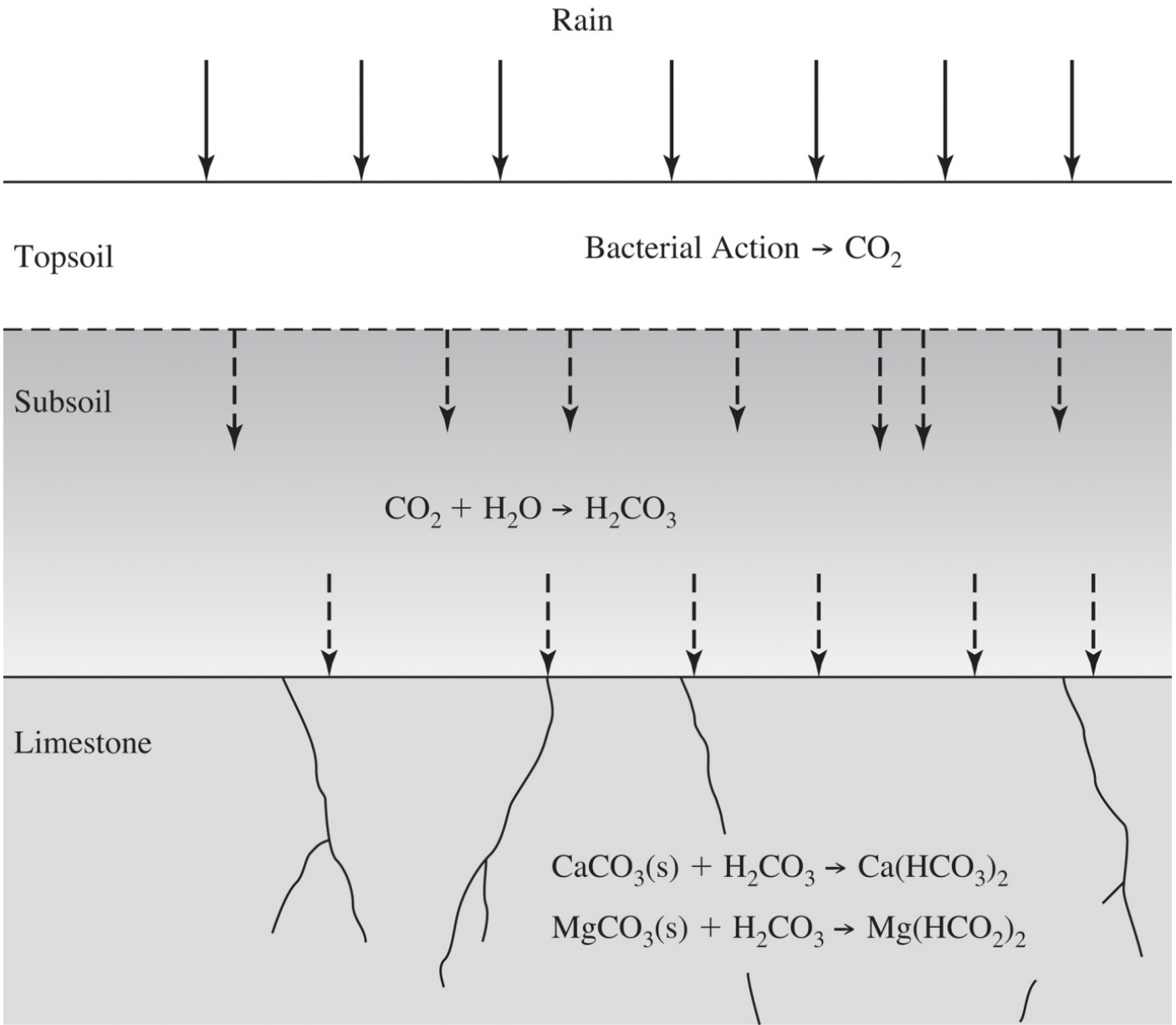
Chemical properties

- Classification of water according to hardness

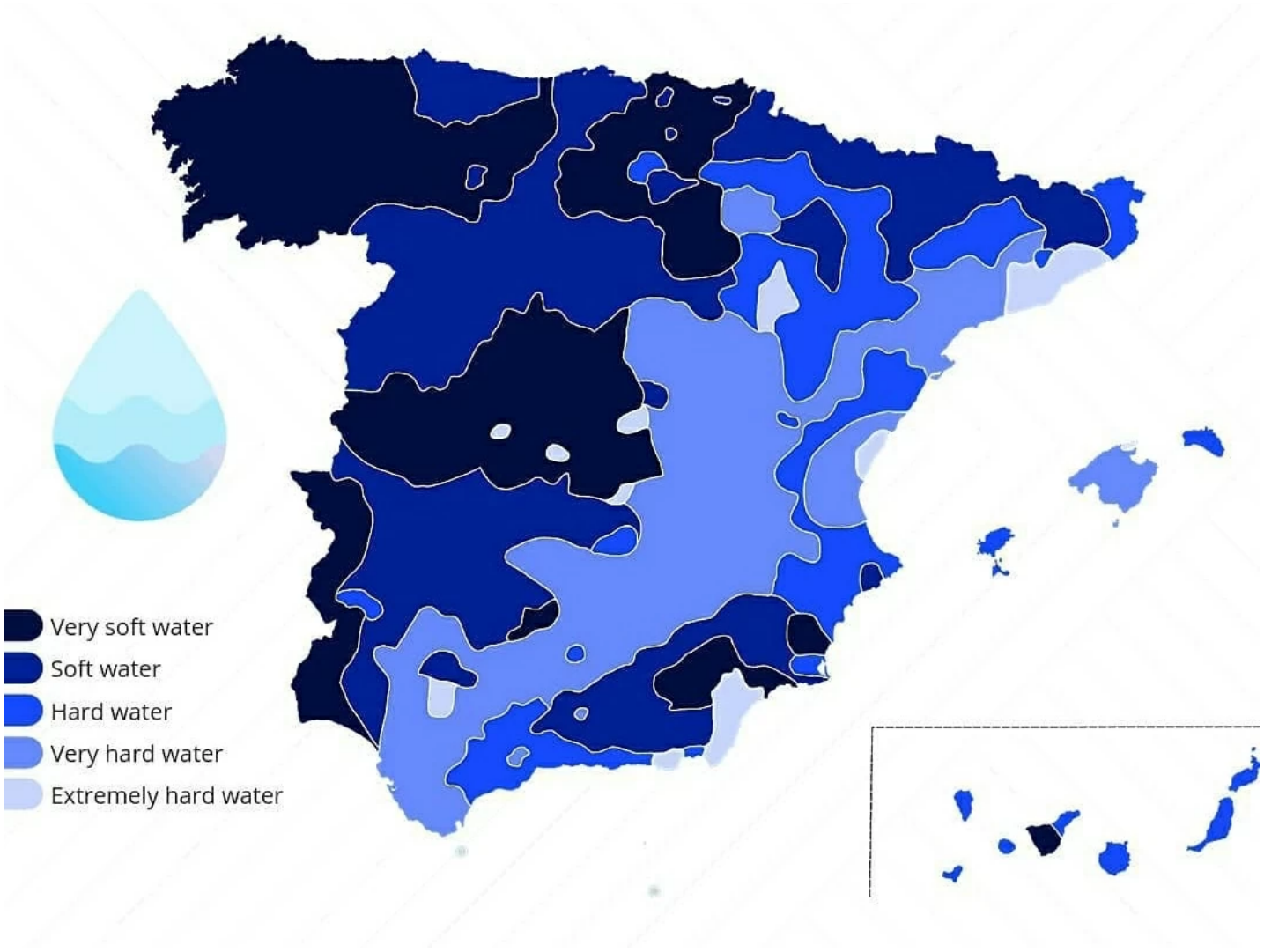
Hard water classification

Hardness range ($mg/L\ CaCO_3$)	Description
0–75	Soft
75–100	Moderately hard
100–300	Hard
>300	Very hard

Formation of hardness in natural water



Hardness of the water in Spain



https://br.ifunny.co/picture/hardness-of-the-water-in-spain-very-soft-water-soft-I6JofVGP8?s=cl

Chemical properties

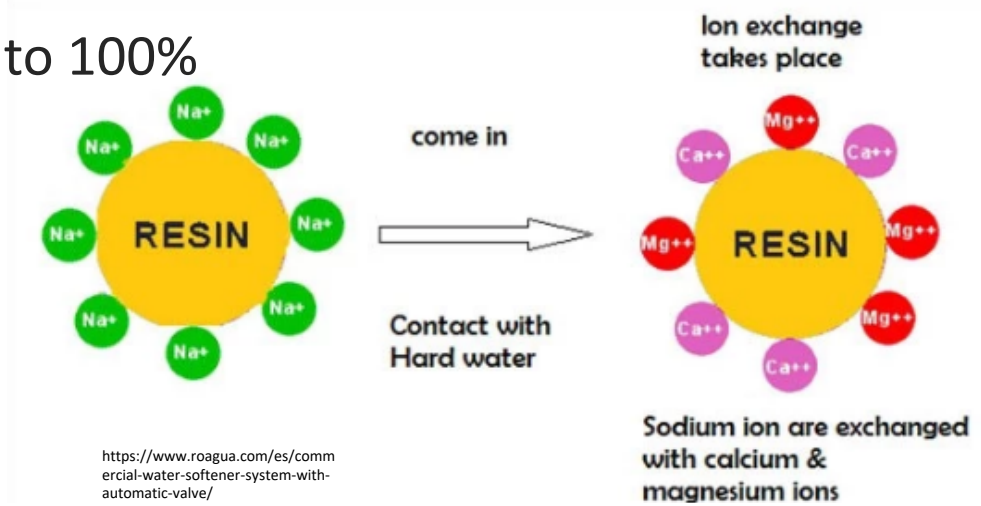
- Hardness removal: ion exchange softening

  Fundamentals:

  - Water containing hardness is passed through a column containing the ion-exchange material (R)
  - Ca^{2+} and Mg^{2+} are exchanged with an ion of the ion-exchange material R (usually Na^{+})

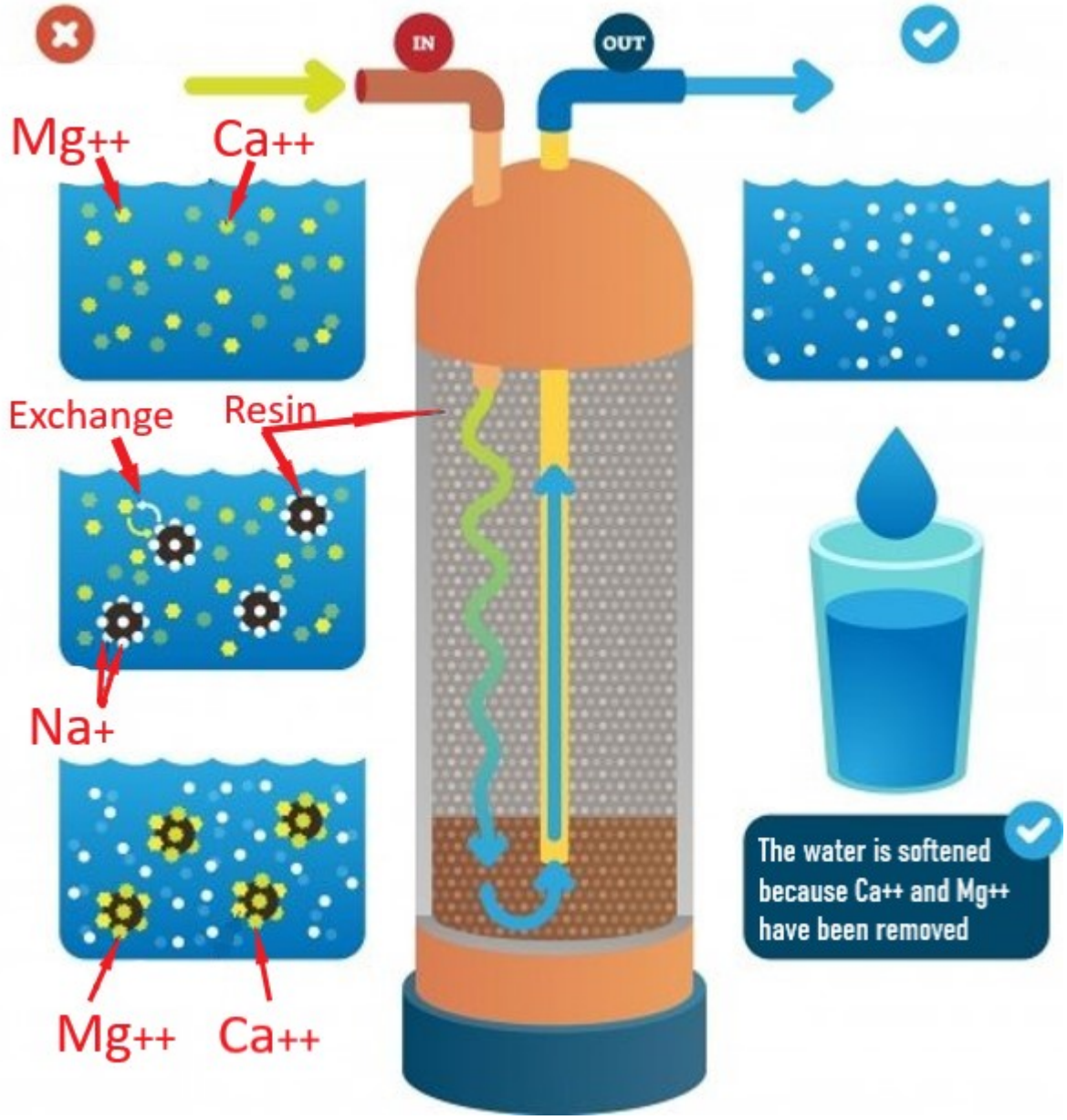
$$Ca(HCO_3)_2 + 2NaR \rightleftharpoons CaR_2 + 2NaHCO_3$$

  - Alkalinity remains unchanged
  - Removal efficiency close to 100%



Chemical properties

How a Water Softener Works

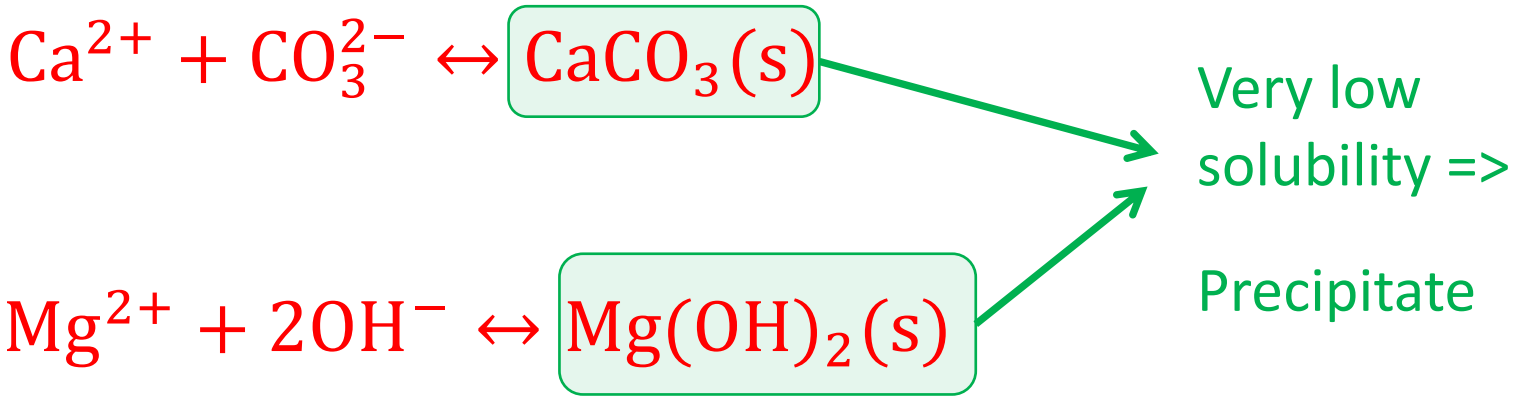


Modified from: https://www.energy.gov/energysaver/purchasing-and-maintaining-water-softener

Chemical properties

- Hardness removal by precipitation

Adding Lime [$Ca(OH)_2$] and Soda [Na_2CO_3]



Chemical properties

- Hardness bar chart

Useful to establish the different hardness components when only the concentration of ions is given

Example 1:

Total hardness = 250 mg/L $CaCO_3$

Alkalinity = 200 mg/L $CaCO_3$

Example 2:

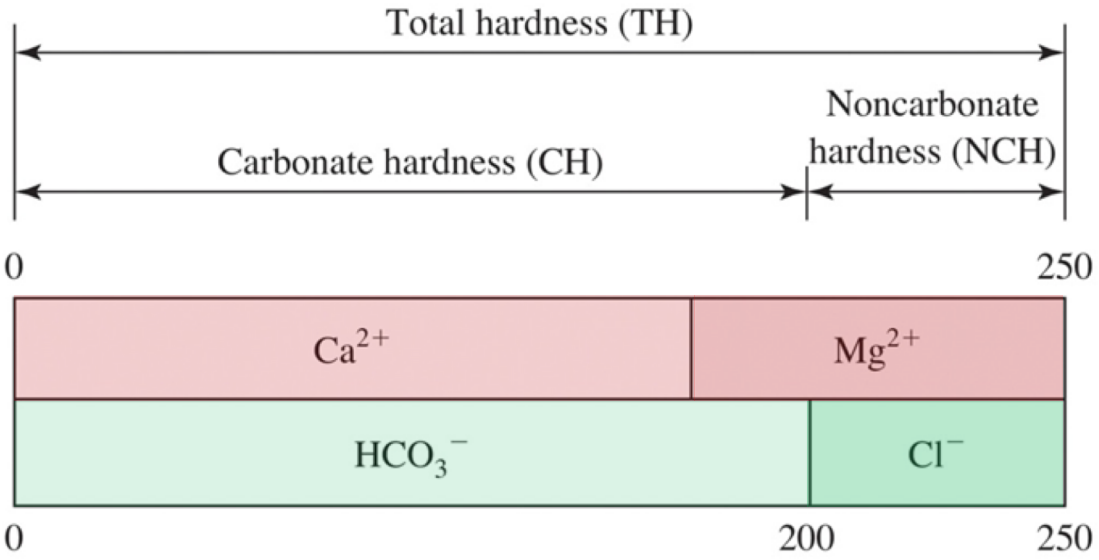
Total hardness = 250 mg/L $CaCO_3$

Alkalinity = 275 mg/L $CaCO_3$

Chemical properties

- Hardness bar chart

TH > Alk
CH = Alk
NCH = TH -CH



Example 1:

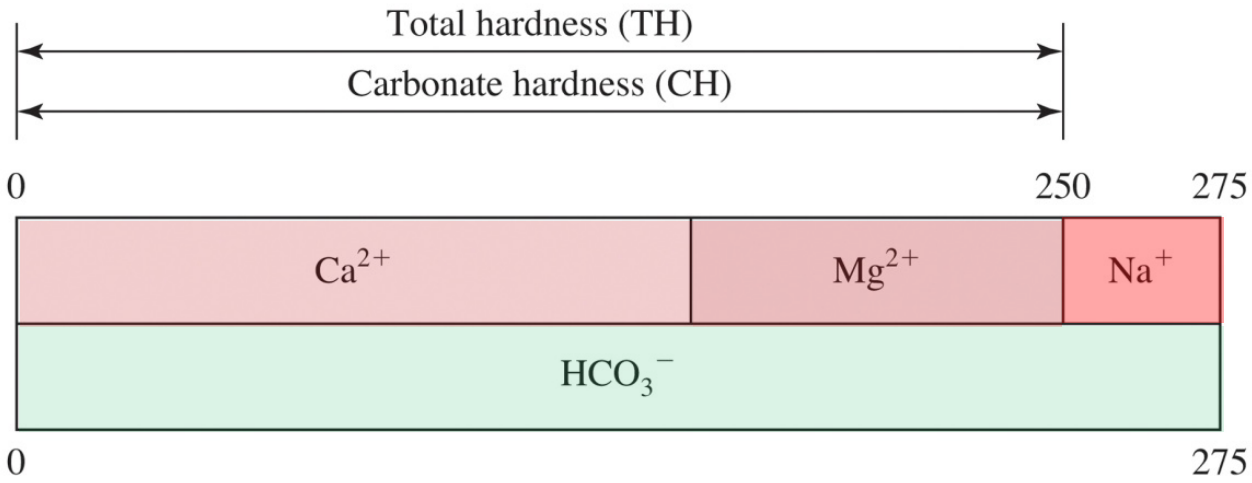
Total hardness = 250 mg/L $CaCO_3$

Alkalinity = 200 mg/L $CaCO_3$

Chemical properties

- Hardness bar chart

TH < Alk
CH = TH
NCH = 0



Cations

Anions

Example 2:

Total hardness = 250 mg/L $CaCO_3$

Alkalinity = 275 mg/L $CaCO_3$

Chemical properties

- Dry residue

Mass of solid matter which remains after the evaporation of water (mg/L)

This residue is composed mainly by salts (but may contain also other substances such as organic matter).

When water is heated at 180ºC :

$$Ca^{2+}_{(aq)} + 2HCO_3^-{}_{(aq)} \rightarrow CaCO_3^{2-}{}_{(s)} + CO_2{}_{(g)}\uparrow + H_2O{}_{(g)}\uparrow$$

aq =aquaeous s= solid g=gaseous

Chemical properties

- Dry residue

Calculate the loss of weight of dry residue after heating at 180 ºC

$$Ca^{2+}_{(aq)} + 2HCO_3^-{}_{(aq)} \rightarrow CaCO_3^{2-}{}_{(s)} + CO_{2\,(g)}\uparrow + H_2O_{\,(g)}\uparrow$$

MW: Ca =40, H = 1, C=12, O=16
Loss of weight = CO_2 and H_2O

$$\text{Loss of weight} = \frac{(12+16\cdot 2)+(2\cdot 1+16)\ g/mol}{2\cdot(1+12+3\cdot 16)g/mol} = 0.508$$

Sol: 0.508 g lost per gram of HCO_3^-

Chemical properties

- Equivalent Weight

Mass of a substance which produces the same effect as the equivalent weight of other substance (*practical, not exact definition*)

E.g.

1 equivalent of Ca^{++} gives the same hardness as 1 equivalent of $CaCO_3$

$$EW = MW/n$$

- EW: equivalent weight (g/eq, mg/meq)
- MW: molecular weight = sum of atomic weights (g/mole)
- n: valence of the element (in chemical elements)

  number of hydrogen ions required to replace the cation (in compounds)

Chemical properties

- Valence of ions in natural water

Anions	name	n	Cations	name	n
HCO_3^- CO_3^{2-}	bicarbonates carbonates	1 2	Ca^{2+}	calcium	2
SO_4^{2-}	sulfates	2	Mg^{2+}	magnesium	2
Cl^-	chlorides	1	Na^+	sodium	1
F^-, NO_3^-, PO_4^{3-} ,	Fluorides, nitrates, phosphates	1, 1, 3	K^+, Li^+, Fe^{2+}, Mn^{2+} , Zn^{2+}, NH_4^+	potassium, lithium, ferrous, manganese, zinc, ammonium	1, 1, 2, 2, 2, 1

Chemical properties

- Equivalent Weight EW= MW/n

Example: express 300 mg of Ca^{++}/L in mg of $CaCO_3$ /L

	MW (mg/mmole)	n (meq/mmole)	EW (mg/meq)
Ca^{2+}	40	2	20
$CaCO_3$	40 + 12 + 3*16 = 100	2	50

1 equivalent of Ca^{++} gives the same hardness as 1 equivalent of $CaCO_3$

20 mg of Ca^{++} gives the same hardness as 50 mg of $CaCO_3$

300 mg of Ca^{++}/L = 300*50/20 = 750 mg $CaCO_3$ /L

$$mg/L\ CaCO_3 = (mg/L\ as\ species) \cdot EW_{CaCO_3} / EW_{species}$$

50

MW: Ca=40, C=12; O=16; H=1; Na=23

Chemical properties

Example:

What is the Equivalent Weight of $NaCO_3H$?
MW: Ca=40, C=12; O=16; H=1; Na=23

Sol: 84 g/eq

EW= MW/n = (23+12+16*3+1)/1 = 84 g/eq

Chemical properties

- Concentration units

mg/L = ppm (mass, assuming 1 L = 1 kg)

moles/L

meq/L

mg/L as $CaCO_3$

°F (French degrees): 1 °F = 10 mg/L as $CaCO_3$ (used for *hardness*)

Chemical properties

- Concentration units

Example:

100 mg/L of $NaCO_3H$ have been measured. Express the concentration of sodium bicarbonate as ppm, mg/L $CaCO_3$ and °F

Sol: 100 ppm, 59.52 mg/L $CaCO_3$, 6 °F

100 mg/L $NaCO_3H$ = 100 ppm

mg/L $CaCO_3$ = (mg/L as species)· EW_{CaCO_3} / $EW_{species}$

= (100 mg/L) · 50 / 84= 59.52 mg/L $CaCO_3$

59.52 mg/L $CaCO_3$* 1 °F/(10 mg/L $CaCO_3$) ≈ 6 °F

Chemical properties

Example:

Given a chemical analysis:

- Check anions and cations balance
- Obtain total, temporary and permanent hardness
- Obtain alkalinity
- Draw hardness bar chart
- Compare estimated dry residue with measured value

Chemical properties: example

Components	Formula	Content (mg/L)
Bicarbonate	HCO_3^-	222.2
Chloride	Cl^-	9.3
Sulfate	SO_4^{2-}	56.5
Calcium	Ca^{2+}	71.3
Magnesium	Mg^{2+}	10.9
Potassium	K^+	4.4
Sodium	Na^+	15.9
Silica	SiO_2	33.3
Dry residue	-	314

Mineral water: Fuensanta

Chemical properties: example

MW/n C/EW

Components	Formula	Content (C)	MW	n	EW	Content	Content
		mg/L	mg/mmol	meq/mmol	mg/meq	meq/L	mg $CaCO_3$/L
Bicarbonate	HCO_3^-	222,2	61	1	61	3,64	182,13
Chloride	Cl^-	9,3	36,5	1	35,5	0,26	13,10
Sulfate	SO_4^{2-}	56,5	96,1	2	48,0	1,18	58,79
Calcium	Ca^{2+}	71,3	40,1	2	20,0	3,56	177,81
Magnesium	Mg^{2+}	10,9	24,3	2	12,2	0,90	44,86
Potassium	K^+	4,4	39,1	1	39,1	0,11	5,63
Sodium	Na^+	15,9	23	1	23	0,69	34,57
Silica	SiO_2	33,3	60				
Total		423,8					
Dry residue		314					

	PM (g/mol)
H	1
C	12
O	16
Cl	35,5
S	32,1
Ca	40,1
Mg	24,3
K	39,1
Na	23
Si	28

Sum of anions	254,0	mg $CaCO_3$/L
Sum of cations	262,9	mg $CaCO_3$/L

Hardness	222,7	mg $CaCO_3$/L	(100-300)	Hard Most hardness (80%) is calcium H.
Alkalinity	182,1	mg $CaCO_3$/L	(150-200)	In the ideal range
Temporary hardness	182,1	mg $CaCO_3$/L		Most hardness (82%) is temporary
Permanent hardness	40,5	mg $CaCO_3$/L		

Dry residue 310,9 mg/L

Chemical properties

- Other natural elements cause:

  - Taste:

    chloride (Cl^-), iron (Fe), manganese (Mn), zinc (Zn)

  - Color:

    Fe, Mn

  - Other effects:
    - Sodium (Na^+) → circulatory or kidney ailments
    - Sulfate (SO_4^{2-}) → laxative
    - Fluoride (Fl^-) → dental fluorosis

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Chapter review

- Water quality is an interesting subject for Mining Engineers
- Multiple sources of impurities in natural water
- Properties of water: solubilization
- Physical properties: solids content, turbidity, color
- Chemical properties: pH, alkalinity, hardness (temporary and permanent), dry residue
- Analysis of the composition of a mineral water