

Drinking Water Chemistry

CTB3365x Introduction to water treatment

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This lecture

- *Ion balance*
- *pH*
- *Carbonic acid equilibrium*
- *Saturation index (SI)*
- *Hardness*

Periodic table

hydrogen 1 H 1.0079																	helium 2 He 4.0026	
lithium 3 Li 6.941	beryllium 4 Be 9.0122											boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180	
sodium 11 Na 22.990	magnesium 12 Mg 24.305											aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948	
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80	
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29	
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 ✱	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 ✱ ✱	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnium 110 Uun [271]	ununium 111 Uuu [272]	unibium 112 Uub [277]	ununquadium 114 Uuq [289]					

* Lanthanide series

** Actinide series

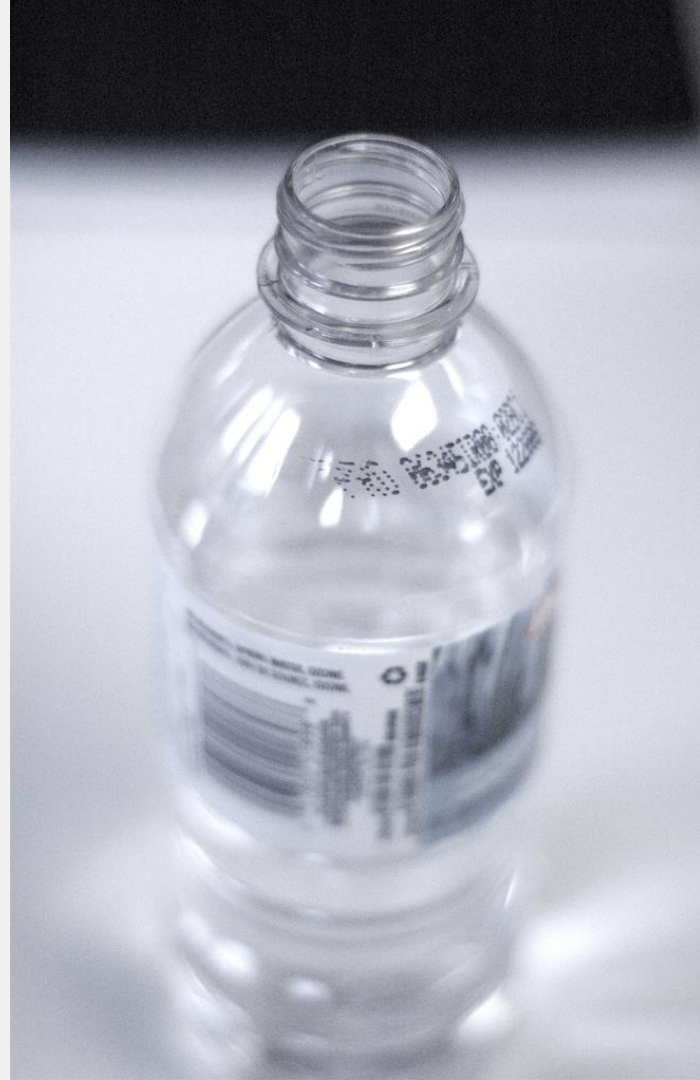
lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

Ion balance

- *Electrical neutrality*
- *Major ions usually represent most of the dissolved ions in water*
- *The sum of the milliequivalents of major cations and anions should be nearly equal*

Why Ion Balance calculations?

- *To check results of water quality analyses of the laboratory*
- *To assure that you included all major ions of your water sample in the analysis*



Ion Balance

$$\sum \frac{C_i}{M_i * z_i} = \sum \frac{C_i}{M_i * z_i}$$

Cations *Anions*

With

c = concentration (mg/L)

M = molar mass (g/mol)

z = valance (-)

Calculating ion balance (pg. 225)

Cations	Concentration (mg/L)	Anions	Concentration (mg/L)
Na ⁺	63	Cl ⁻	73
K ⁺	5	HCO ₃ ⁻	151
Ca ²⁺	45	NO ₃ ⁻	1
Mg ²⁺	9	SO ₄ ²⁻	?
Fe ²⁺	4		
Mn ²⁺	1		
NH ₄ ⁺	2		

What is the sulfate concentration in this sample?

Ion balance

- Make a **table** with the **concentration** (c), **molar mass** (M) and **valancy** (z) of all anions and cations (e.g., in spreadsheet)
- Calculate **total valence concentration** (meq/L) for the cations: $\sum c_i/M_i * z_i$

Example

compound	Na⁺
c	63 mg/L
M	23 g/mol
z	1

Calculating ion balance (pg. 225)

Cations	Concentration (mg/L)	Valence concentration (meq/L)
Na ⁺	63	2.74
K ⁺	5	0.13
Ca ²⁺	45	2.25
Mg ²⁺	9	0.73
Fe ²⁺	4	0.14
Mn ²⁺	1	0.04
NH ₄ ⁺	2	0.11
		TOTAL: 6.14 meq/L

Calculating ion balance

- Principle of *electrical neutrality*
- For anions: $\sum c_i / M_i * z_i = 6.14 \text{ meq/L}$
- $\text{SO}_4^{2-} = 6.14 - 2.06 - 2.48 - 0.01 = 1.60 \text{ meq/L}$
- $1.60 \text{ meq/L} = 160/2 = 0.80 \text{ mmol/L} = 76.8 \text{ mg/L}$

Ionisation of water

- *Ionisation of water with H^+ and OH^- ions*
- $K_w = [H^+] \times [OH^-]$ (ion product of water)
- **Neutral** water solution: $[H^+] = [OH^-] = 0.0001 \text{ mmol/L}$

pH

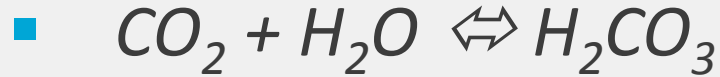
- *Decimal logarithm*
- *Neutral solution: $pH = 7$ (at $25^{\circ}C$)*
- *Simplified:*

$$pH = - \log_{10} [H^{+}]$$

$$pOH = - \log_{10} [OH^{-}]$$

$$\text{At } 25^{\circ}C: \quad pH + pOH = 14$$

CO₂ dissociation



$$K_1 = [H^+][HCO_3^-] / [H_2CO_3] = 4.5 \cdot 10^{-7} \text{ (at } 25^\circ\text{C)}$$

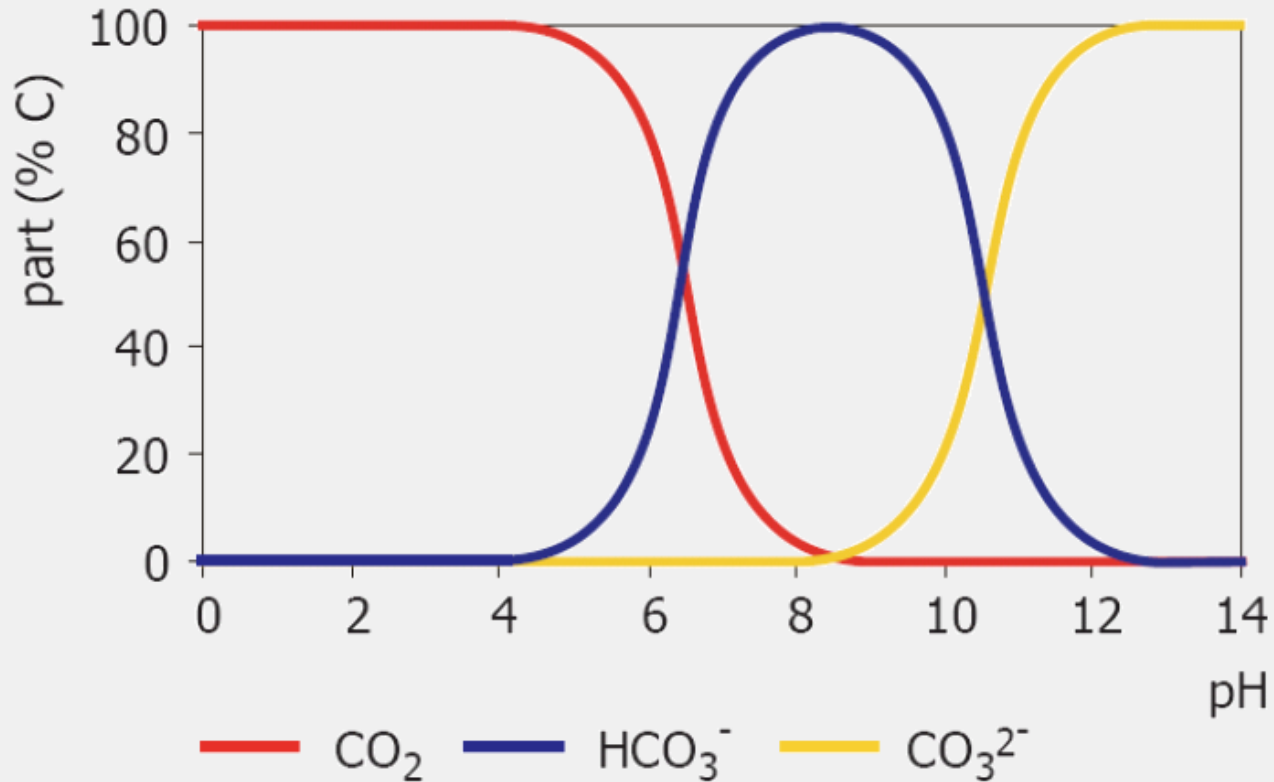


$$K_2 = [H^+][CO_3^{2-}] / [HCO_3^-] = 4.7 \cdot 10^{-11} \text{ (at } 25^\circ\text{C)}$$

pK

- $pK = -\log(K)$
- $pK_1 = pH + \log \{[H_2CO_3]/[HCO_3^-]\} = \mathbf{6.35}$ (at 25°C)
- $pK_2 = pH + \log\{[HCO_3^-]/[CO_3^{2-}]\} = \mathbf{10.33}$ (at 25°C)
- If concentrations between '{ }' are equal, $pK = pH$

Relationship pH and C



Calculating pH

*pH of soda if **4.4g** of CO_2 is added to
1L of **demineralized** water*



Calculating pH

- ***Added CO_2 (or H_2CO_3) = $4.4 / 44 = 0.1 \text{ mol}$***
- ***$x \text{ mol } \text{CO}_2$ dissociates, making $x \text{ mol } \text{H}^+$, $x \text{ mol } \text{HCO}_3^-$ and $(1-x) \text{ mol } \text{CO}_2$ (neglecting HCO_3^- transformation to CO_3^{2-})***
- ***Use $K_1 = x \cdot x / (0.1-x) = 4.5 \cdot 10^{-7}$***
- ***$x = 0.21 \text{ mmol/L}$***
- ***$\text{pH} = -\log(0.00021) = 3.68$***

pH if 1 mmol/L HCO_3^- is dosed?

- $$\begin{aligned} \text{pH} &= \text{p}K_1 - \log([\text{H}_2\text{CO}_3] / [\text{HCO}_3^-]) \\ &= 6.35 - \log(99.79 / (0.21+1)) \\ &= 6.35 - 1.92 \\ &= \mathbf{4.43} \end{aligned}$$

Calcium carbonate equilibrium

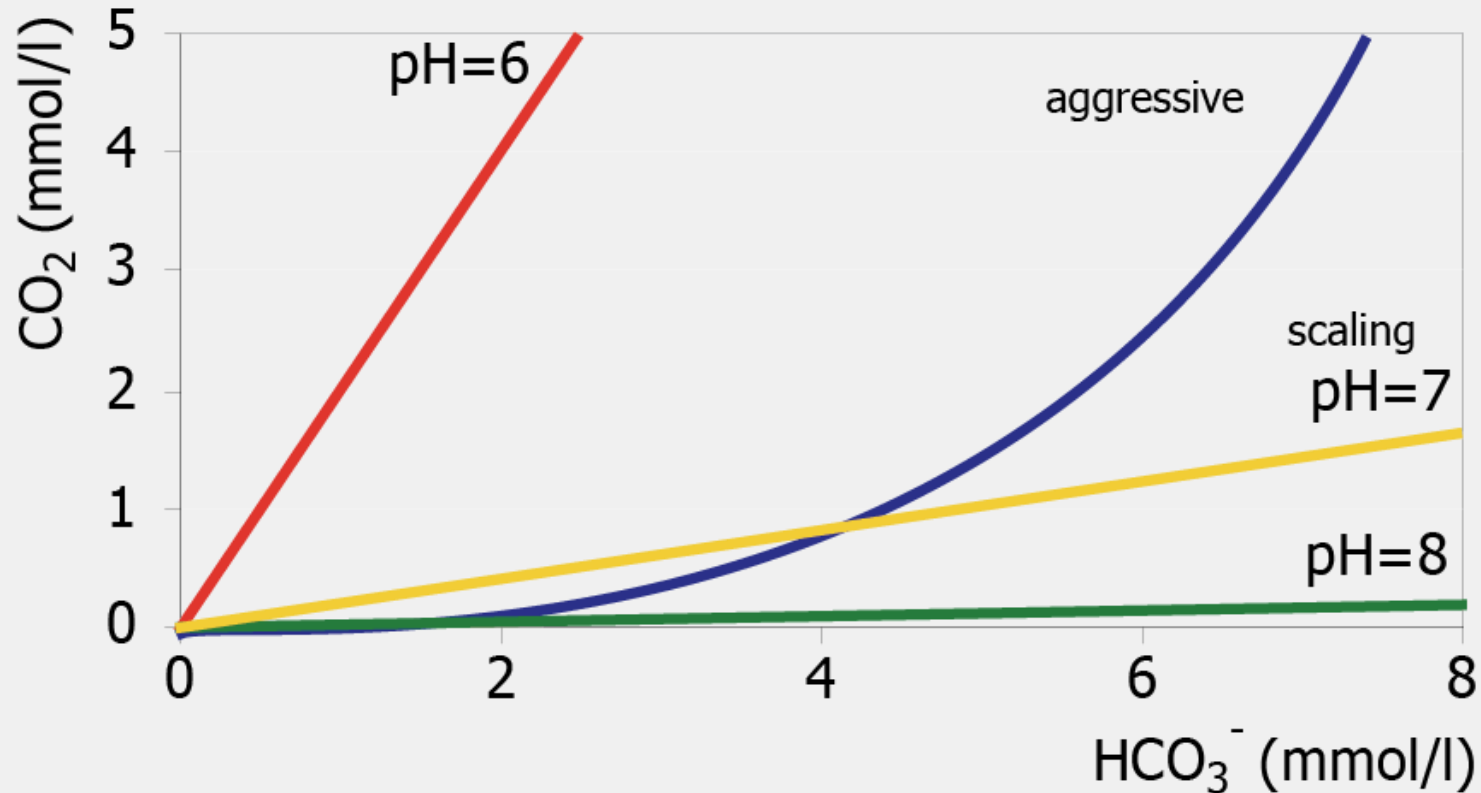
- *Calcium carbonate is difficult to dissolve in water:*
 - $\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3$
 - $K_s = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 3.8 \cdot 10^{-9} \text{ (at } 25^\circ\text{C)}$

If CO_3^{2-} is removed from water, more CaCO_3 can dissolve

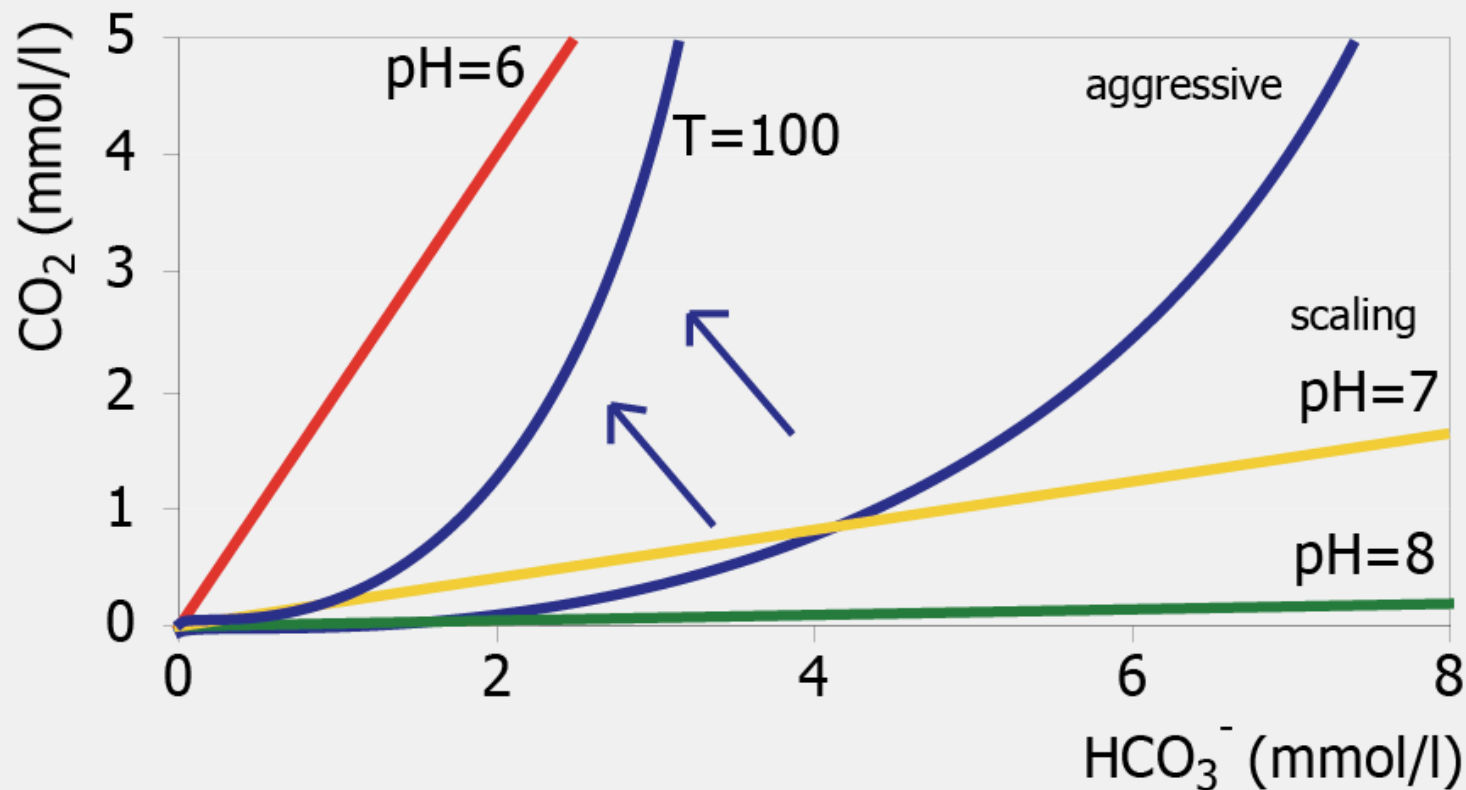
Calcium carbonate equilibrium

- *Through CO_2 calcareous rock and lime stone can be dissolved:*
 - $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^-$
 - $K = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 / [\text{CO}_2] = 3.6 \cdot 10^{-5} \text{ (at } 25^\circ\text{C)}$
- *If all calcium originates from CaCO_3 : $[\text{Ca}^{2+}] = [\text{HCO}_3^-] / 2$*

Tilmanns' diagram



Tilmanns' diagram



Aggressive water

Increasing pH by the removal of CO₂, through:

- ***Gas transfer***
- *Adding a **base** (e.g., lime)*
- *or, by reaction with **CaCO₃** (e.g., marble filtration)*

Calcium carbonate equilibrium constants

	pK		
	10°C	25°C	100°C
K_s	8.36	8.42	9.20
K_1	6.46	6.35	6.45
K_2	10.49	10.33	10.16
K_w	14.53	14.00	11.27

Saturation Index (SI)

- The *degree of over- or undersaturation* of calcium carbonate:
 - $SI = pH - pH_s = \log ([Ca^{2+}] \cdot [CO_3^{2-}] / K_s)$
 - $pH_s = pK_2 - pK_s - \log ([Ca^{2+}][HCO_3^-])$

Parameter	Unit	Value
K ⁺	mg/L	7
Na ⁺	mg/L	46
NH ₄ ⁺	mg/L	1
Fe ²⁺	mg/L	4
Mg ²⁺	mg/L	9.5
Ca ²⁺	mg/L	78
Cl ⁻	mg/L	63.5
HCO ₃ ⁻	mg/L	200
SO ₄ ²⁻	mg/L	95
CO ₂	mg/L	36
O ₂	mg/L	0
pH	-	7.1

What is the Saturation Index (SI) of this sample?

Saturation Index (SI)

- $pH_s = pK_2 - pK_s - \log([HCO_3^-][Ca^{2+}])$
- *in mol/L (!):* $([HCO_3^-][Ca^{2+}]) = 6.39 * 10^{-6}$
- $pH_s = 10.49 - 8.36 - \log(6.39 * 10^{-6})$
- $SI = pH - pH_s = 7.06 - 7.32 = \mathbf{-0.26}$

Saturation Index (SI)

- *SI > 0: CaCO₃ precipitating*
- *SI < 0: CaCO₃ dissolving (aggressive)*

Drinking water should be slightly precipitating to prevent dissolution of (cement-bound) materials during distribution

Hardness



Hardness

- *The sum of dissolved **calcium & magnesium ions***
- *Typically expressed in **mmol/L***
- *In the Netherlands the term '**German hardness**' is also used*
- ***1 °GH or 1 °D = 0.178 mmol/L***

Calculating hardness 'Spa Reine'

Mineral		Concentration (mg/L)
Sodium	Na^+	3
Calcium	Ca^{2+}	5
Magnesium	Mg^{2+}	1
Chloride	Cl^-	5
Sulfate	SO_4^{2-}	4
Nitrate	NO_3^-	2
Bicarbonate	HCO_3^-	15



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Bicarbonate	HCO_3^-	15



Calculating hardness 'Spa Reine'

$$\begin{aligned}\textit{Calcium} &= \text{concentration} / \text{molar mass} \\ &= 5 \text{ mg/L} / 40.078 \\ &= 0.125 \text{ mmol/L}\end{aligned}$$

$$\begin{aligned}\textit{Magnesium} &= \text{concentration} / \text{molar mass} \\ &= 1 \text{ mg/L} / 24.305 \\ &= 0.041 \text{ mmol/L}\end{aligned}$$

$$\begin{aligned}\textit{Total hardness} &= 0.17 \text{ mmol/L or } 0.93 \text{ }^{\circ}\text{GH}\end{aligned}$$

Guidelines for tap water

- *Dutch Decree of Water Supply: **>1** and **<2.5 mmol/L***
- *Water should be **non-aggressive** and **non-scaling** (during heating)*
- *pH: **>7.0** and **<9.5***
- *Saturation Index (SI) = **>-0.2***

Drinking Water Chemistry

CTB3365x Introduction to water treatment

Dr. ir. Doris van Halem – Assistant Professor in Drinking Water