Drinking Water Chemistry

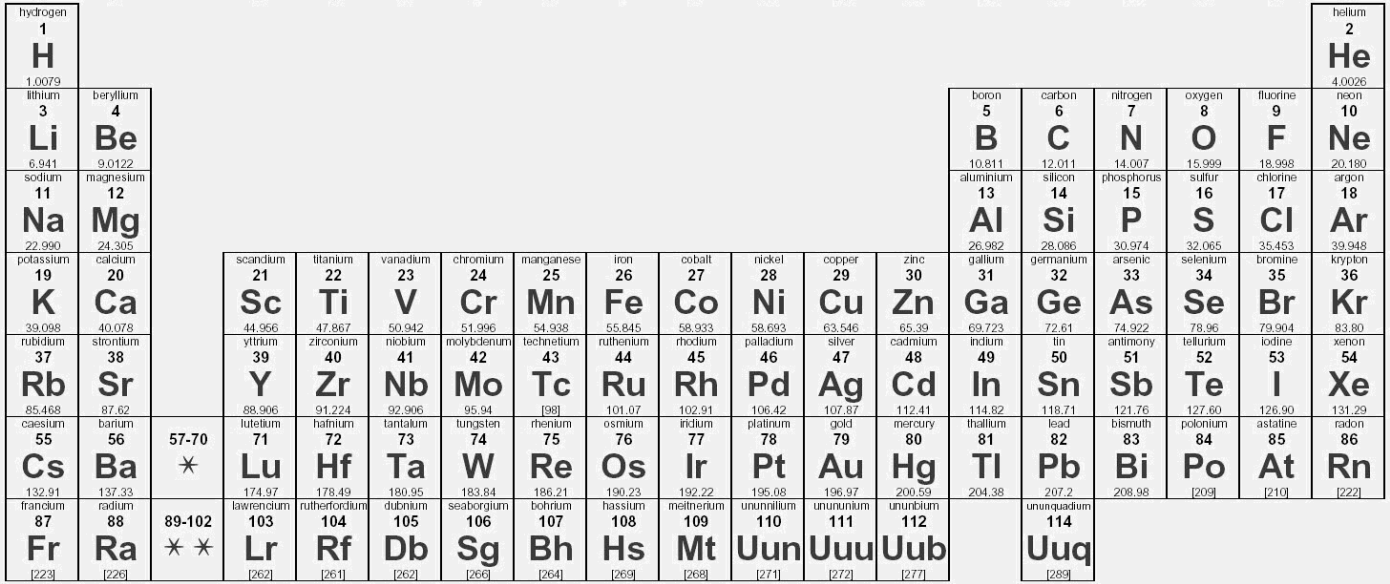
CTB3365x Introduction to water treatment

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

This lecture

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

Periodic table



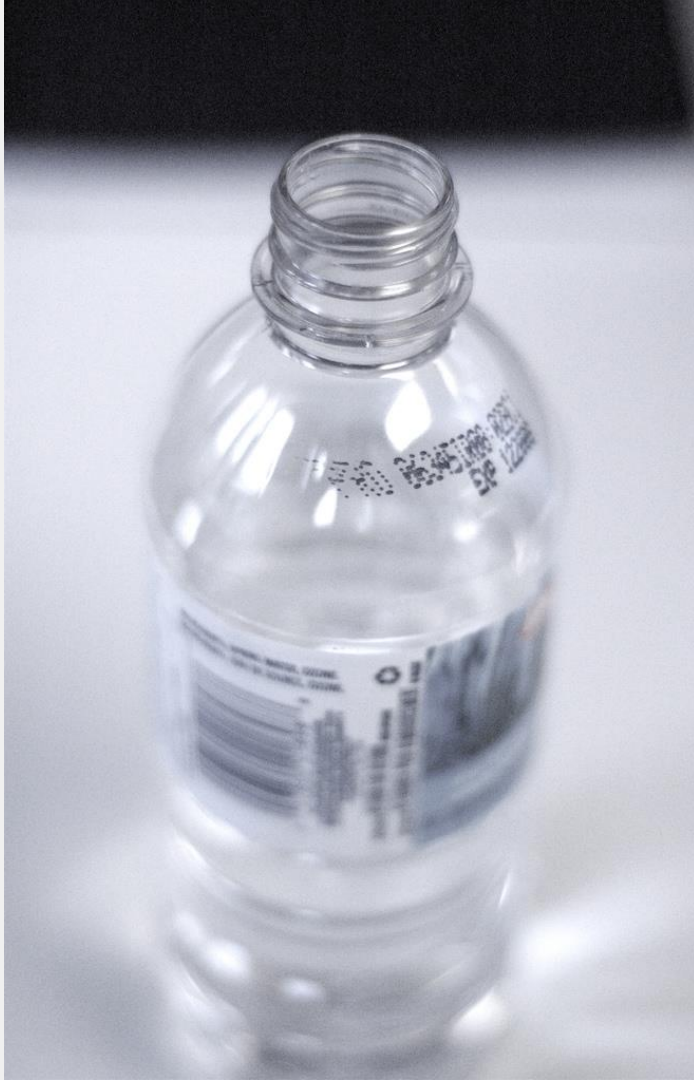
Ion balance

- ***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

$$S\frac{c_i}{M_i * z_i} = S\frac{c_i}{M_i * z_i}$$

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: $\sum c_i / M_i * z_i = 6.14$ meq/L*
- *$SO_4^{2-} = 6.14 – 2.06 – 2.48 – 0.01 = 1.60$ meq/L*
- *1.60 meq/L = 160/2 = 0.80 mmol/L = 76.8 mg/L*

Ionisation of water

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

pH

- ***Decimal logarithm***
- *Neutral solution: pH = 7 (at 25°C)*
- *Simplified:*

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

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

At 25°C: $pH + pOH = 14$

CO_2 dissociation

- $CO_2 + H_2O \Leftrightarrow H_2CO_3$

- $H_2CO_3 \Leftrightarrow H^+ + HCO_3$

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

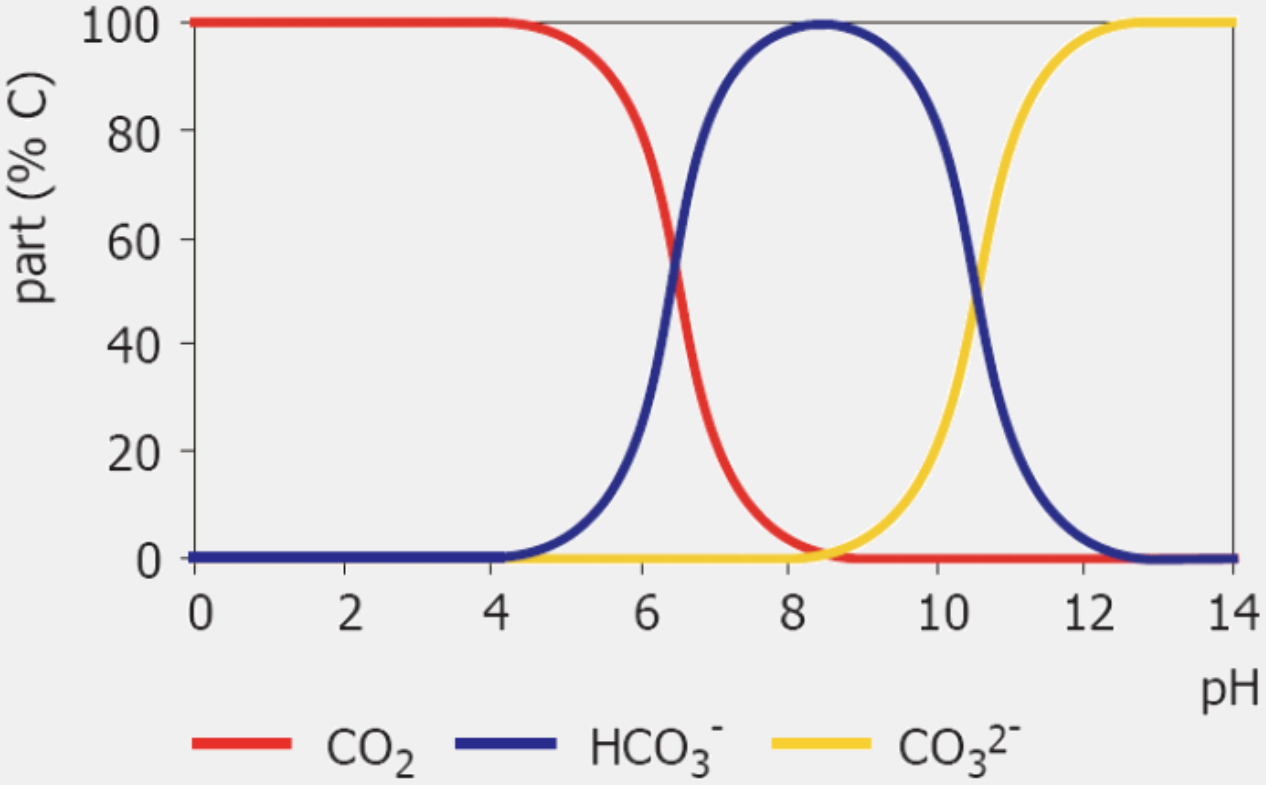
- $HCO_3^- \Leftrightarrow H^+ + CO_3^{2-}$

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

pK

- ***pK = -log(K)***
- ***pK_1*** *= pH + log {[H_2CO_3]/[HCO_3^-]} =* ***6.35*** *(at 25°C)*
- ***pK_2*** *= pH + log{[HCO_3^-]/[CO_3^{2-}]} =* ***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 mol*
- *x mol CO_2 dissociates, making x mol H^+, x mol HCO_3^- and (1-x) mol CO_2 (neglecting HCO_3^- transformation to CO_3^{2-})*
- ***Use K_1*** *= x . x / (0.1-x) = 4.5 . 10^{-7}*
- ***x*** *= 0.21 mmol/L*
- ***pH*** *= - log(0.00021) =* ***3.68***

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

- $\mathbf{pH} = pK_1 - \log([H_2CO_3] / [HCO_3^-])$

  $= 6.35 - \log(99.79 / (0.21+1))$

  $= 6.35 - 1.92$

  $= \mathbf{4.43}$

Calcium carbonate equilibrium

- *Calcium carbonate is difficult to dissolve in water:*
  - $Ca^{2+} + CO_3^{2-} \Leftrightarrow CaCO_3$
  - $K_s = [Ca^{2+}][CO_3^{2-}] = 3.8\ 10^{-9}$ *(at 25°C)*

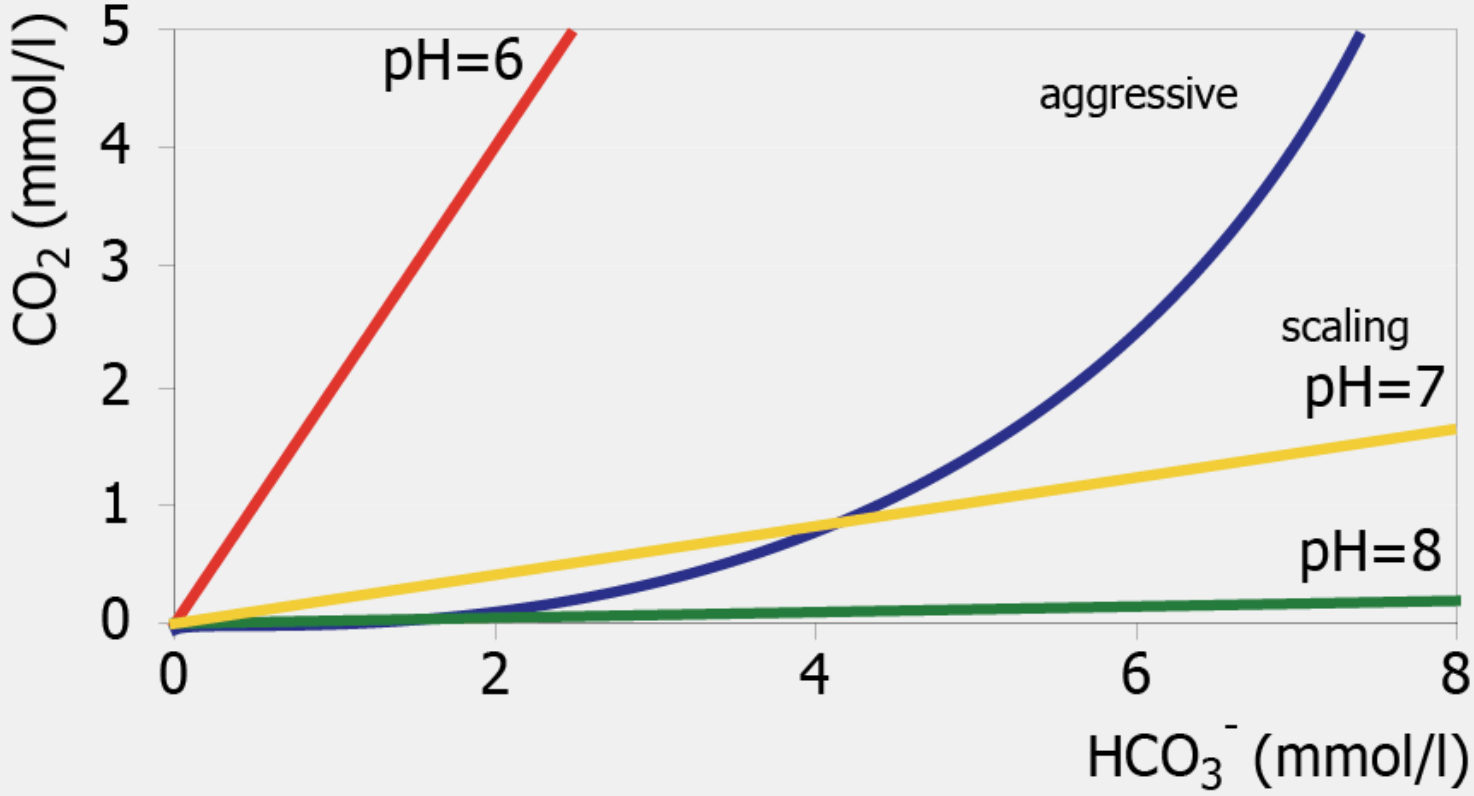
If ***CO_3^{2-} is removed*** *from water,* ***more $CaCO_3$*** *can* ***dissolve***

Calcium carbonate equilibrium

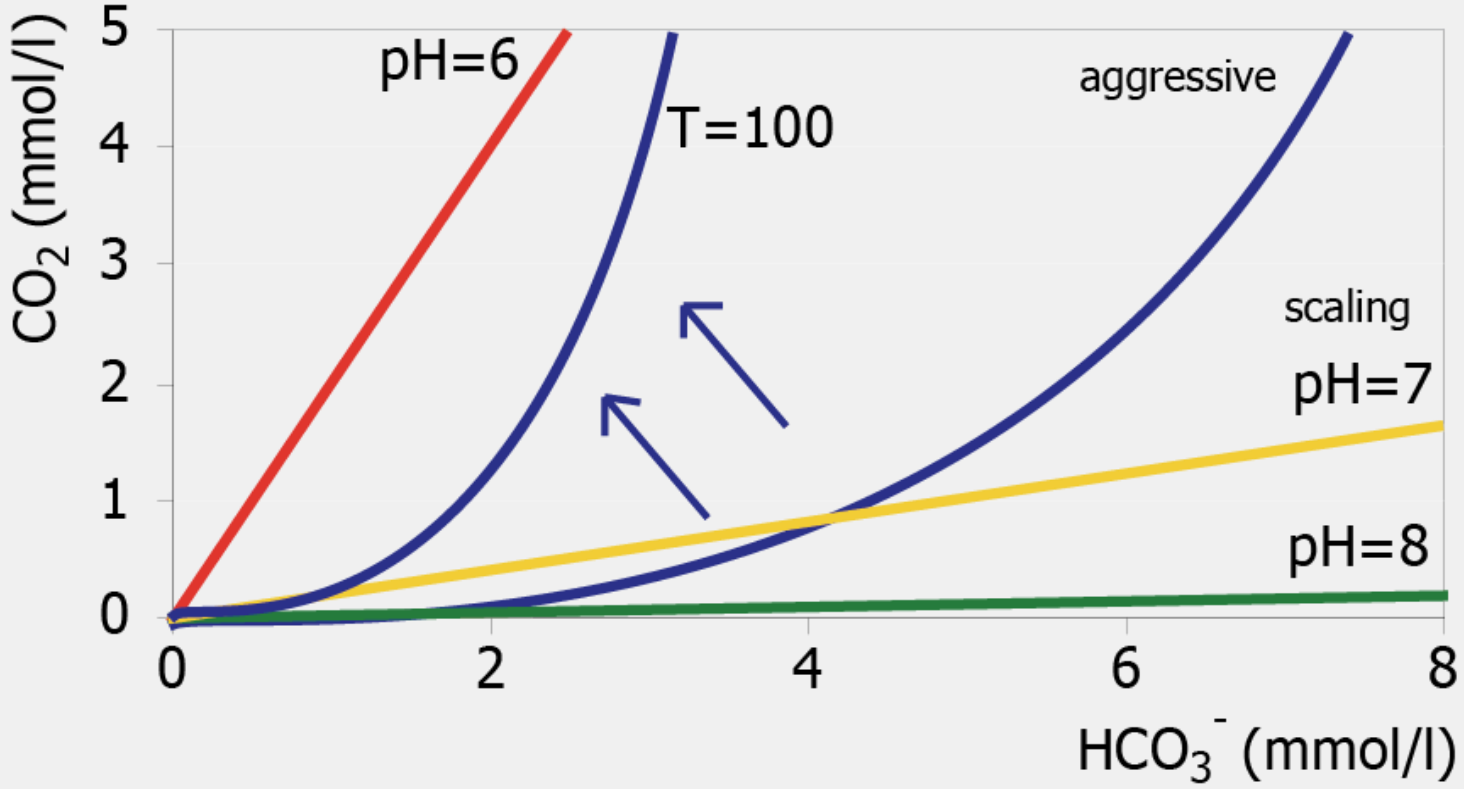
- *Through CO_2 calcareous rock and lime stone can be dissolved:*
  - *$CaCO_3 + CO_2 + H_2O <-> Ca^{2+} + 2HCO_3^-$*
  - *$K = [Ca^{2+}][HCO_3^-]^2/[CO_2] = 3.6\ 10^{-5}$ (at 25°C)*

- *If all calcium originates from $CaCO_3$: $[Ca^{2+}] = [HCO_3^-] / 2$*

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* $\boldsymbol{CaCO_3}$ *(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:*
  - $SI = pH - pH_s = \log (([Ca^{2+}] \,.\, [CO_3^{2-}]) / K_s)$
  - $pHs = pK_2 - pK_s - \log ([Ca^{2+}][HCO_3^{-}])$

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)

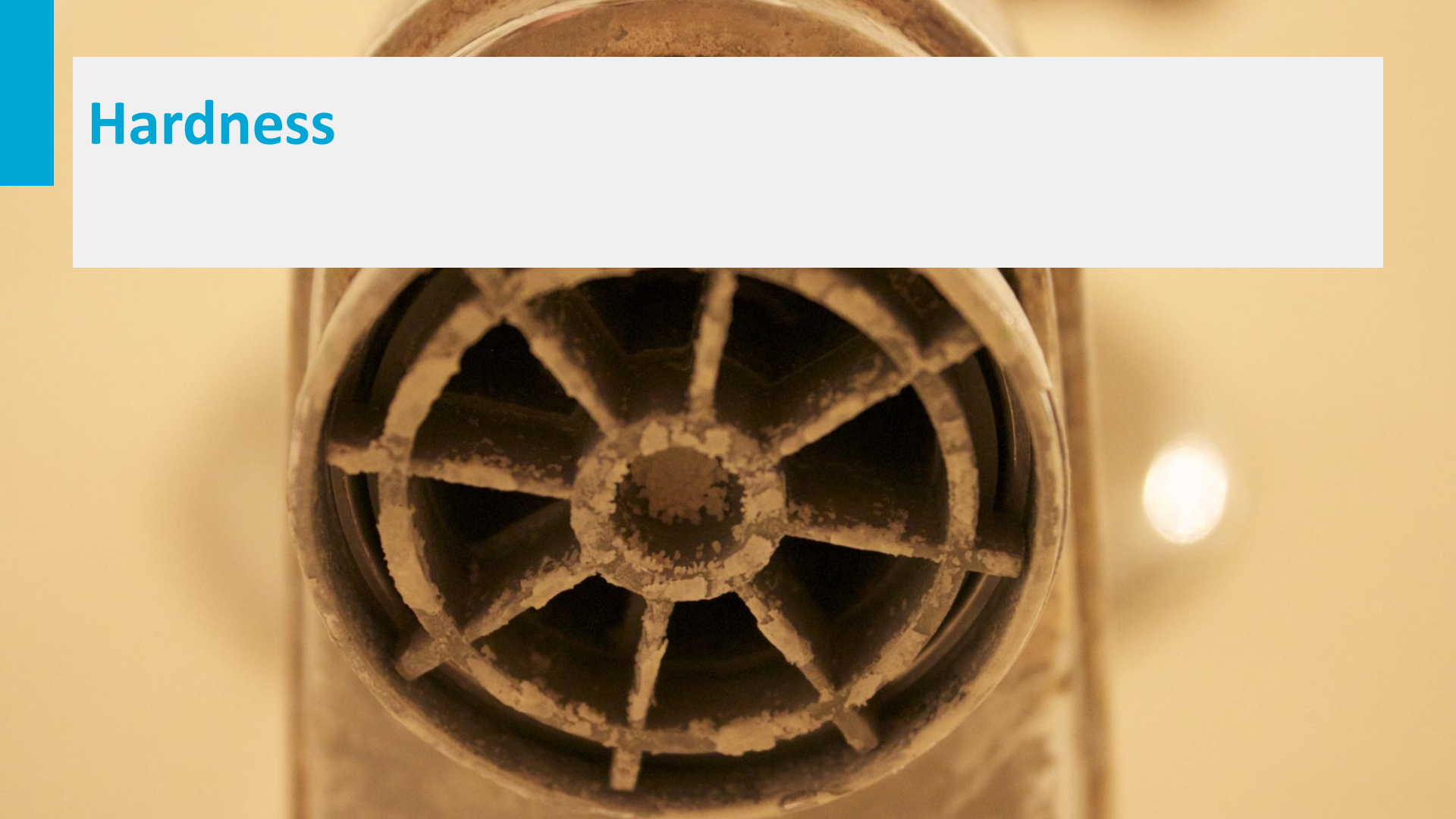
- $\mathbf{pH_s} = pK_2 - pK_s - \log([HCO_3^-][Ca^{2+}])$
- *in* **mol/L** *(!):* $([HCO_3^-][Ca^{2+}]) = 6.39 * 10^{-6}$
- $\mathbf{pH_s} = 10.49 - 8.36 - \log(6.39 * 10^{-6})$
- $\mathbf{SI} = pH - pH_s = 7.06 - 7.32 = \mathbf{-0.26}$

Saturation Index (SI)

- *SI > 0: $CaCO_3$ precipitating*
- *SI < 0: $CaCO_3$ 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

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

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

Calculating hardness ‘Spa Reine’

Calcium	=	concentration / molar mass
	=	5 mg/L / 40.078
	=	0.125 mmol/L
Magnesium	=	concentration / molar mass
	=	1 mg/L / 24.305
	=	0.041 mmol/L
Total hardness	=	0.17 mmol/L or 0.93 °GH

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