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Aalto University
School of Engineering

Physical & chemical treatment processes of water and waste

Lecture 2&3 Mass transfer, mixing & pH, alkalinity and hardness

WAT - E2120

Anna Mikola   TkT   D Sc (Tech)

Lecture outline

Lecture on gas transfer

- Mass and gas transfer

- Theory
- Important equations
- Practical applications

Demo exercises

Group discussion on gas transfer

Mixing, pH, alkalinity and hardness

Mass transfer - basics

- Transfer of material from one homogenous phase to another

- Concentration increases in one phase and decreases in the other

- Driving force is pressure or concentration gradient

- Transfer stops at equilibrium

- No conversion reactions!!

- Basic mass transfer equation (Fick's first law)

$$r = -Dm\,\frac{\partial C}{\partial x}$$

- r = mass transfer rate

- D_m = diffusion coefficient

- C = concentration of constituent being transferred

- x = distance

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Mass transfer between different phases

Phase equilibria	Type of process	Examples of processes
Gas → solid Liquid → solid	Adsorption Ion exchange	Activated carbon Selective removal of compounds
Gas → liquid	Absorption	Addition of gases to water, NH_3 scrubbing in acid
Solid → liquid Solid → gas	Desorption	Sediment scrubbing Reactivation of GAC
Liquid → gas	Evaporation Gas stripping	Drying Removal of gases

Quite familiar phenomena..
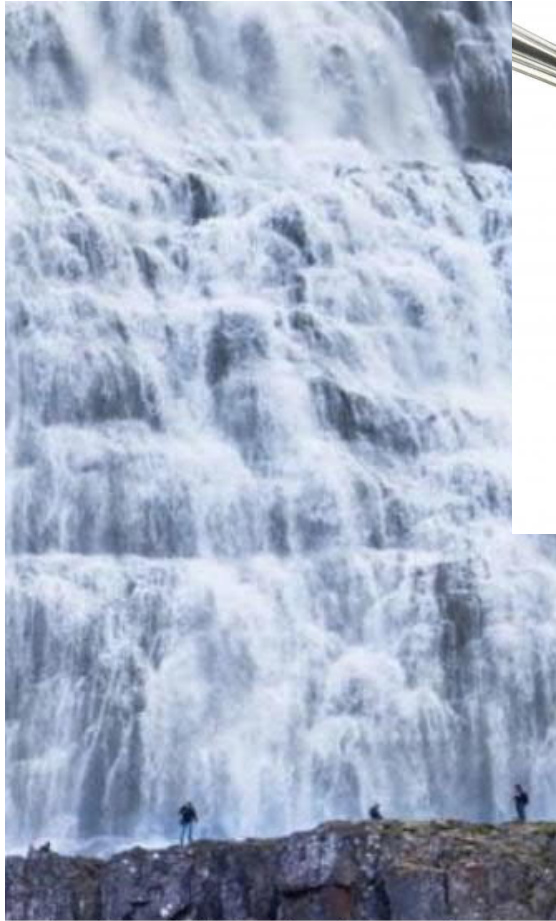
Mass transfer basics

Diffusion

- **Caused by chemical potential difference (= gradients), often concentration**

- **Mainly caused by Brownian motion of molecules**

- **Fick's law = substances move from more concentrated area to less concentrated area**

Convection

- **Due to bulk motion of the fluid**

- **Can work in favour of or against diffusion**

Diffusion coefficient

- Increases when particle size decreases

- Increases when viscosity of the liquid decreases

- Increases when temperature increases

- In turbulent flow regime replaced by coefficient of dispersion

$$D_m = \frac{RT}{6\pi\gamma r_P N}$$

R universal gas law constant

T temperature

ɣ dynamic viscosity

r_P radius of particle

N Avogadro's number

Liquid – gas equilibrium - Henry's law

The amount of gas dissolved in liquid is directly proportional to the pressure of the gas in the solution.

$$p_g = \frac{H}{P_T} x_g$$

p_g = mole fraction of gas in air

H = Henry's law constant

P_T = total pressure

x_g = mole fraction of gas in water

The equilibrium or saturation concentration (presented by Henry's contant) is different for different gases.

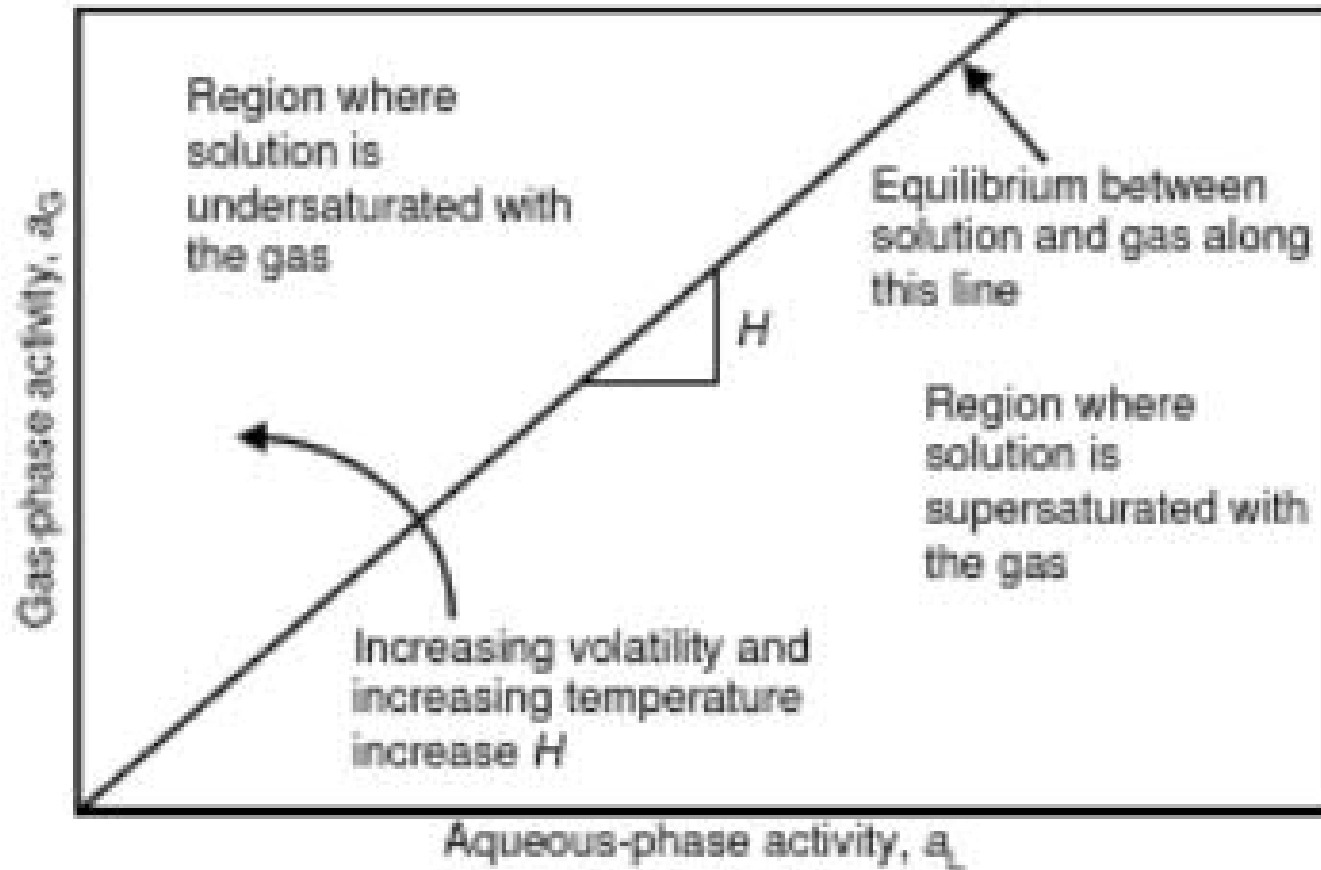The equilibrium concentration depends also on temperature and on liquid.

Principle of Henry's law

Henry's constants for different gases

Compound	H^a H_{pm} (atm/(mol/L_L))	H_{cc} or H_{mm} (L_L/L_G)^b
Nitrogen	1590	65.0
Hydrogen	1280	52.3
Carbon monoxide	1050	42.9
Oxygen	769	31.4
Methane	769	31.4
Cyclohexane	182	7.44
Radon	108	4.41
Ozone	90.9	3.72
Carbon dioxide	29.4	1.20
Carbon tetrachloride	29.4	1.20
Tetrachloroethylene (PCE)	17.5	0.715
Chlorine	10.8	0.441
Hydrogen sulfide	10.0	0.409
Trichloroethylene (TCE)	10.0	0.409
Ethylbenzene	8.33	0.340
Toluene	6.67	0.273
Benzene	5.56	0.227

Compound	H^a H_{pm} (atm/(mol/L_L))	H_{cc} or H_{mm} (L_L/L_G)^b
o-Xylene	4.55	0.186
Chloroform	4.00	0.163
Chlorine dioxide	1.00	0.0409
Sulfur dioxide	0.833	0.0340
Bromoform	0.556	0.0227
2,2',5,5'- Tetrachlorobiphenyl	0.250	0.0102
Ethyl acetate	0.143	5.84×10^{-3}
Hydrogen cyanide	0.100	4.09×10^{-3}
Acetone	0.040	1.64×10^{-3}
Ammonia	0.017	6.95×10^{-4}
Methanol	4.6×10^{-3}	1.88×10^{-4}
Phenol	5.0×10^{-4}	2.04×10^{-5}
Acetic acid	2.0×10^{-4}	8.17×10^{-6}

^{a}Values are for 25°C and are based on compilation by Sander (1999).
^{b}Values in this column are valid for any units of concentration, provided that the same units are used for both the liquid and gas phases.

Application of Henry's law
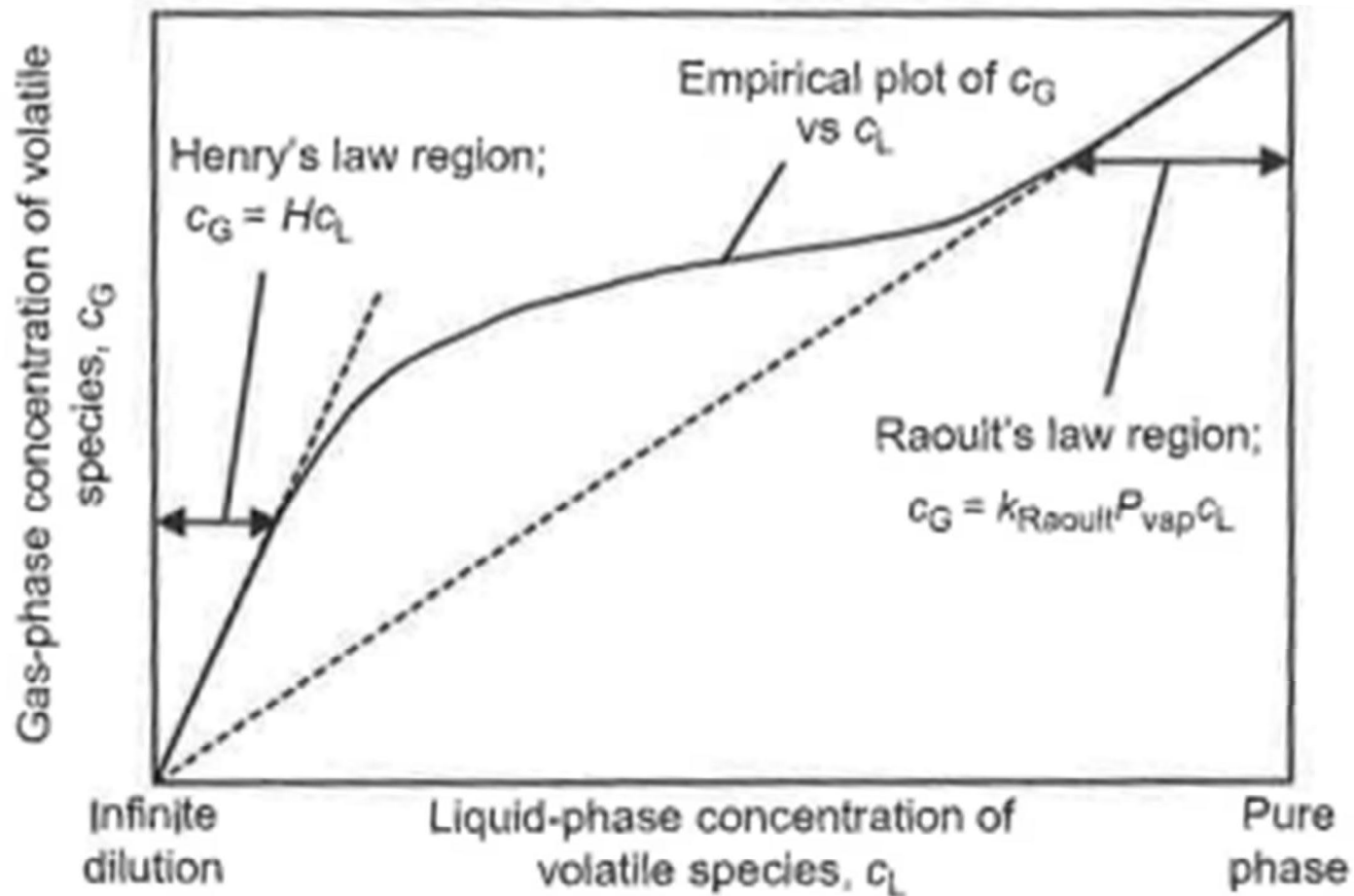
Example of saturation concentration of oxygen in water

What is the saturation concentration (mg/l) of oxygen in water at 25° C and 1 atm?

From Henry's law

$$x_g = \frac{P_T}{H}\textbf{p}_\textbf{g}$$

Let's check Henry's constant

$\textbf{H}_\textbf{pc}$ **= 769 l atm/mol$_\textbf{O2}$**

Pressure is given

1 atm

We still need the partial pressure of oxygen in air

Air contains 21% of oxygen → $\textbf{p}_\textbf{g}$ = 0,21

From Henry's law

$$x_g = \frac{P_T}{H}\textbf{p}_\textbf{g} = 2{,}73 \times 10^{-4} \textbf{ mole / l}$$

Saturation concentration = (2,73 x 10^{-4} mole / l)(32 g/mol) = 8,74 mg/l

Example of saturation concentration of oxygen in water

What is the saturation concentration of oxygen in water at 20° C and 1 atm?

Henry's constant H_{px} = 41100 atm is given.

Air contains 21% of oxygen → p_g = 0,21 mole O_2/mole air

From Henry's law

$$x_g = \frac{P_T}{H}p_g = 5,11 \times 10^{-6} \text{ mole gas / mole water}$$

One liter of water contains 55,6 mole

$$\frac{n_g}{n_g+n_w} = x_g = 5,11 \times 10^{-6}$$

$n_g + n_w \approx 55,6$ → $n_g \approx 2,84 \times 10^{-4}$ mole / l

Saturation concentration = $(2,84 \times 10^{-4}$ mole / l$)(32$ g/mol$) = 9,09$ mg/l

Saturation concentration of oxygen in clean water

T,C	mg/L	T,C	mg/L
0	14,62	21	8,91
1	14,22	22	8,74
2	13,83	23	8,58
3	13,46	24	8,42
4	13,11	25	8,26
5	12,77	26	8,11
6	12,45	27	7,97
7	12,14	28	7,83
8	11,84	29	7,69
9	11,56	30	7,56
10	11,29	31	7,43
11	11,03	32	7,31
12	10,78	33	7,18
13	10,54	34	7,07
14	10,31	35	6,95
15	10,08	36	6,84
16	9,87	37	6,73
17	9,67	38	6,62
18	9,47	39	6,52
19	9,28	40	6,41
20	9,09		

Note: Henry's constants are presented in many different forms!!

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Note: Henry's constants are presented in many different forms!!

TABLE 5-1. Units Commonly Used for Henry's Law Constants[a]

Dimensions Used for Gas-Phase Concentration	Dimensions Used for Aqueous-Phase Concentration	Symbol	Units of H
Mass concentration (μg i/L of gas)	Mass concentration (μg i/L of solution)	H_{cc}[b]	$\dfrac{\text{L liquid}}{\text{L gas}}\left(\dfrac{L_L}{L_G}\right)$
Molar concentration (mol i/L of gas)	Molar concentration (mol i/L of solution)	H_{mm}[b]	$\dfrac{\text{L liquid}}{\text{L gas}}\left(\dfrac{L_L}{L_G}\right)$
Partial pressure (atm)	Mass concentration (mg i/L of solution)	H_{pc}	$\dfrac{\text{atm-}L_L}{\text{mg } i}$
Partial pressure (atm)	Molar concentration (mol i/L of solution)	H_{pm}	$\dfrac{\text{atm-}L_L}{\text{mol } i}$
Partial pressure (atm)	Mole fraction (mol i/total moles of solution)	H_{px}	atm
Mole fraction[c] (moles of i/total moles of gas)	Molar concentration (mol i/L of solution)	H_{ym}	$\dfrac{L_L}{\text{mol of gas}}$
Mole fraction[c] (moles of i/total moles of gas)	Mole fraction (mol i/total moles of solution)	H_{yx}	$\dfrac{\text{mol of solution}}{\text{mol of gas}}$

Note: Henry's constants are presented in many different forms!!

Table 1. Conversion factors between several Henry's law solubility constants H (at $T^\ominus = 298.15\,\mathrm{K}$ and $\varrho^\ominus = 997\,\mathrm{kg\,m^{-3}}$).

	$H^{cp} = \ldots \frac{\mathrm{mol}}{\mathrm{m^3\,Pa}}$	$H^{cp} = \ldots \frac{\mathrm{M}}{\mathrm{atm}}$	$H^{cc} = \ldots$	$H^{bp} = \ldots \frac{\mathrm{mol}}{\mathrm{kg\,Pa}}$	$H^{bp} = \ldots \frac{\mathrm{mol}}{\mathrm{kg\,atm}}$	$H^{xp} = \ldots \frac{1}{\mathrm{atm}}$	$\alpha = \ldots$
$H^{cp} = 1\,\frac{\mathrm{mol}}{\mathrm{m^3\,Pa}}$	1.00000	101.325	2478.96	1.00301×10^{-3}	101.630	1.83089	2271.10
$H^{cp} = 1\,\frac{\mathrm{M}}{\mathrm{atm}}$	9.86923×10^{-3}	1.00000	24.4654	9.89893×10^{-6}	1.00301	0.0180695	22.4140
$H^{cc} = 1$	4.03395×10^{-4}	0.0408740	1.00000	4.04609×10^{-7}	0.0409970	7.38573×10^{-4}	0.916150
$H^{bp} = 1\,\frac{\mathrm{mol}}{\mathrm{kg\,Pa}}$	997.000	1.01021×10^5	2.47152×10^6	1.00000	1.01325×10^5	1825.40	2.26428×10^6
$H^{bp} = 1\,\frac{\mathrm{mol}}{\mathrm{kg\,atm}}$	9.83962×10^{-3}	0.997000	24.3920	9.86923×10^{-6}	1.00000	0.0180153	22.3467
$H^{xp} = 1\,\frac{1}{\mathrm{atm}}$	0.546182	55.3419	1353.96	5.47826×10^{-4}	55.5084	1.00000	1240.43
$\alpha = 1$	4.40316×10^{-4}	0.0446150	1.09152	4.41641×10^{-7}	0.0447493	8.06171×10^{-4}	1.00000

Example: Badly filled sample bottle

You have taken a sample in a sealed bottle of water and you are supposed to analyze ammonia concentration. The volume of the sample bottle is 100 ml and the temperature is 25 ° C. In the lab you notice that the bottle contains an air bubble with a volume of 2,5 ml.

- If the sample originally contained 10^{-5} mol/l of ammonia, what concentration will you measure in the solution, assuming that it has equilibrated with the air bubble?

- How would the ratio of concentrations change if you were analyzing radon in the water?

Total number of moles of ammonia in the bottle is 0.0975 l*10⁻⁵ mol/l, so 0.0975 *10⁻⁵ moles.

$$n_{tot} = n_G + n_L = c_G V_G + c_L V_L = \frac{P_i}{RT} V_G + \frac{P_i}{H_{pm}} V_L$$

We will now calculate the partial pressure of ammonia in the gas phase:

$$Pi = \frac{n_{tot,i}}{\left(\frac{V_g}{RT}\right) + \left(\frac{V_L}{Hmp}\right)} = \frac{9.75 * 10^{-7}}{\left(\frac{0.0025}{0.082 * 298}\right) + \left(\frac{0.0975}{0,017}\right)} = \frac{9.75 * 10^{-7}}{(1.02 * 10^{-4}) + (5,74)}$$

$$= \frac{97.5 * 10^{-8}}{5,740102} = 16.99 * 10^{-8} \ atm$$

Now we could find the equilibrium concentration of ammonia in solution:

$C_L = \frac{Pi}{Hpm} = \frac{16.99*10^{-8}}{1.7*10^{-2}} = 9.99 * 10^{-6}$ **mol/L – this is the concentration that will be measured in the solution.**

This is 99.9% of the total concentration of ammonia in the bottle, so 0.1% of ammonia is in the air bubble.

According to Henry's law we could now calculate the partial pressure of radon in the gas phase:

$$Pi = \frac{n_{tot,i}}{\left(\frac{Vg}{RT}\right) + \left(\frac{V_L}{Hmp}\right)} = \frac{9.75 * 10^{-7}}{\left(\frac{0.0025}{0.082 * 298}\right) + \left(\frac{0.0975}{108}\right)}$$

$$= \frac{9.75 * 10^{-7}}{(1.02 * 10^{-4}) + (9.04 * 10^{-4})} = \frac{97.5 * 10^{-8}}{10.06 * 10^{-4}} = 9.69 * 10^{-4} \, atm$$

Now we will find the equilibrium concentration of radon in solution:

$C_L = \frac{Pi}{Hpm} = \frac{9.69 * 10^{-4}}{108} = 8.97 * 10^{-6}$ **mol/L – this is the concentration that will be measured in the solution.**

This is 89.7% of the total concentration of radon in the bottle, so 10.3% of radon is in the air bubble.

There will be more radon in gas phase, compared to ammonia due to their very different Henry's constants.

Gas-liquid mass transfer

Often described with two-film theory

- Assumes gas film and liquid film on both sides of the interface

- Assumes that the bulk-liquid and bulk-gas are perfectly mixed

- Under steady-state conditions the rate of mass transfer in gas film must be equal to liquid film

Optionally surface-renewal model

 - surface is randomly replaced

Or penetration model

 - unsteady mass transfer during the contact time of gas/liquid

The two-film theory
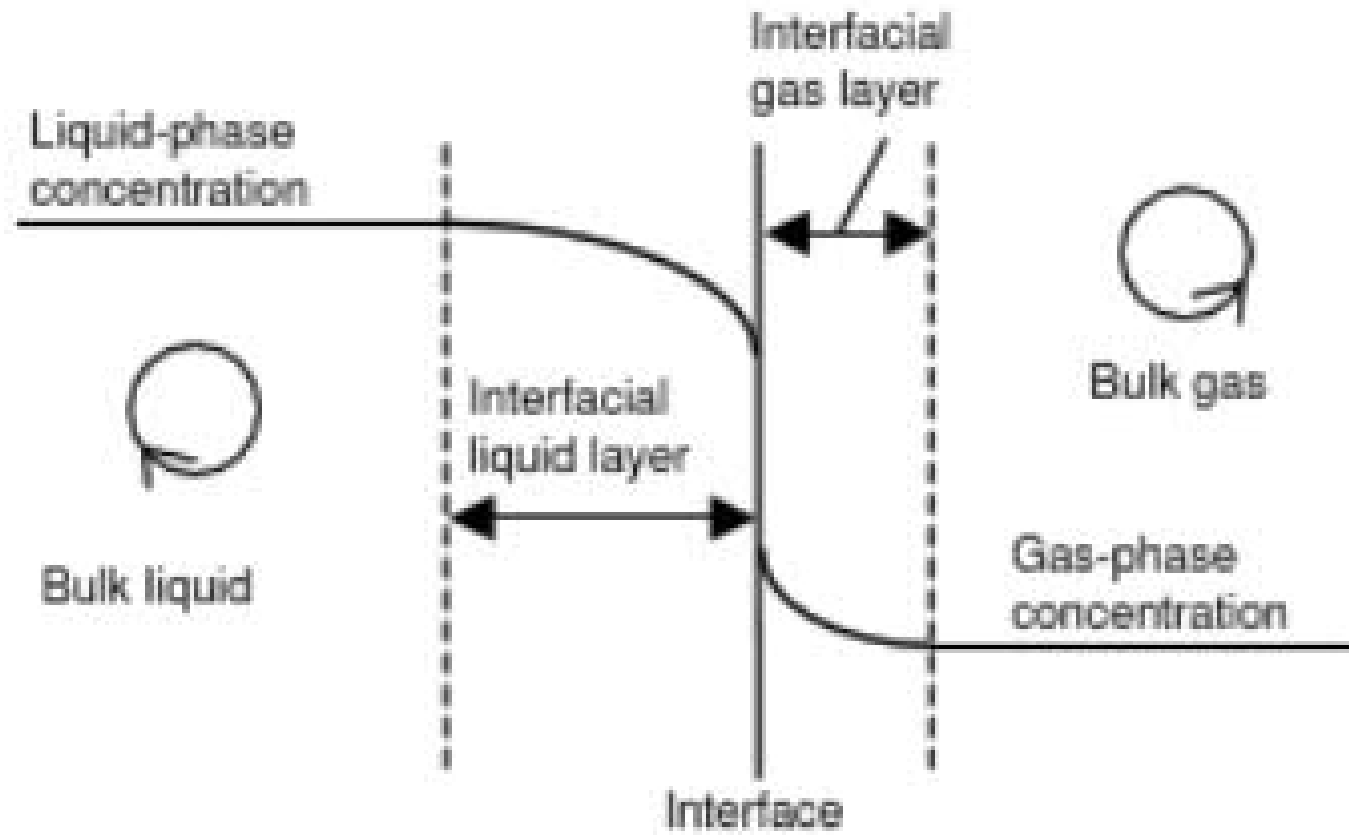
Absorption of gases to liquid 1/2

From Fick's first law

$$r = k_G (P_G - P_i) = k_L(C_i - C_L)$$

k_G gas film mass transfer coeff
k_L liquid film mass transfer coeff

From Henry's law

$$r = K_L (C_s - C_t)$$

C_s saturation concentration
C_t concentration at time t

Usually overall coefficients K_L and K_G are used

K_L is used if liquid film resistance controls (= the case e.g. for water and oxygen)

Mass transfer rate per unit volume is obtained by multiplying by area A and dividing by the volume V

$$r_V = K_L \frac{A}{V}(C_s - C_t) = \boxed{K_L a(C_s - C_t)}$$

Absorption of gases 2/2

A mass balance for an open basin:

Accumulation = rate of mass transfer + inflow – outflow

From $\frac{\partial C}{\partial t}$ = K_La (C_s – C_t)

In case of absorption:

$$\frac{Cs - Ct}{Cs - C0} = e^{-(k_L a)t}$$

In case of desorption of gases:

$$\frac{Ct - Cs}{C0 - Cs} = e^{-(k_L a)t}$$

Note: Initial state is supersaturation (C_0 – C_s)

Demo exercise – Desorption of benzene

A quantity of benzene was spilled into a water storage basin. Estimate the time required for the concentration to drop by 50% due to volatilization . K_la in this case for benzene 0,144 m/h.

It can be assumed that the concentration of benzene in the atmosphere is 0 →

$$\frac{C_t}{C_0} = e^{-(KLa)t}$$

Thus $\frac{0,5C_0}{C_0} = e^{-(KLa)t}$

Solving for time

$K_L a\, t = \ln 2$

$t = 0,69 / K_L a$

$K_L a$ for benzene 0,144 m/h

→ T = 4,8 h

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Air bubbles in a reactor basin – a researcher approach
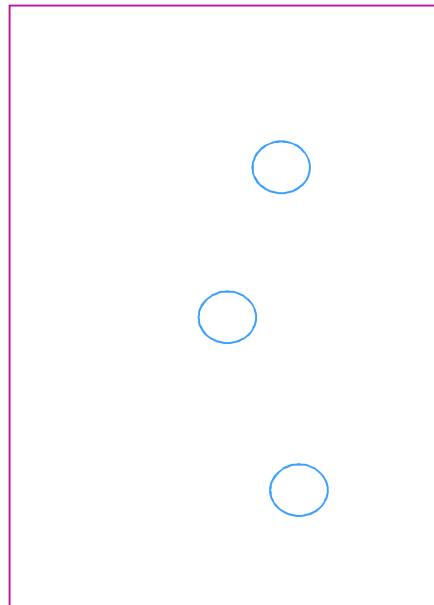
Concentrations

Pressure

Bubble size

Temperature

Flow pattern

Viscosity

Resistance due to surfactants etc.

Air bubbles in a reactor basin – an engineer approach

In practice the oxygen transfer rate is calculated e.g.

$$r = \alpha \, K_L a \, \theta^{T-20} \, (\beta C_s - Ct)$$

α is the correction factor for K_L taking into account the difference between clean water and process water (e.g. wastewater)

ß is the correction factor for the saturation concentration in process water

Note: here a is the surface area of bubbles per unit volume.

Note: Temperature correction using Arrhenius equation θ^{T-20}

Group discussion

Based on the gas transfer theories what could be a good technical solution for a efficient reactor?

Discuss different ideas in small groups (15 min)

Discussion together to compare the ideas (10 min)

Examples of gas liquid transfer applications

Stripping of gases – packed towers

VOC removal

From water: stripping, activated carbon adsorption
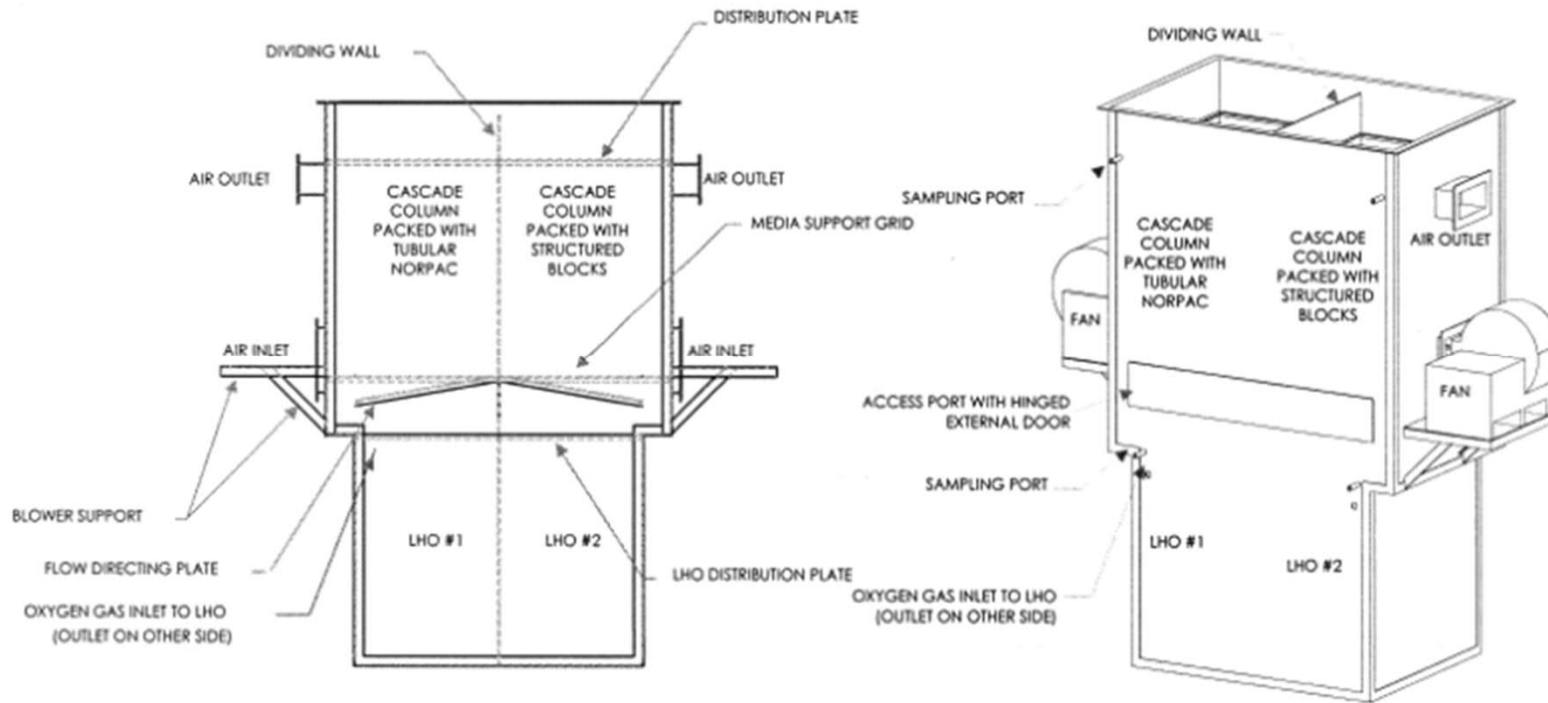
From soil: soil vapor extraction

Fliteway technologies
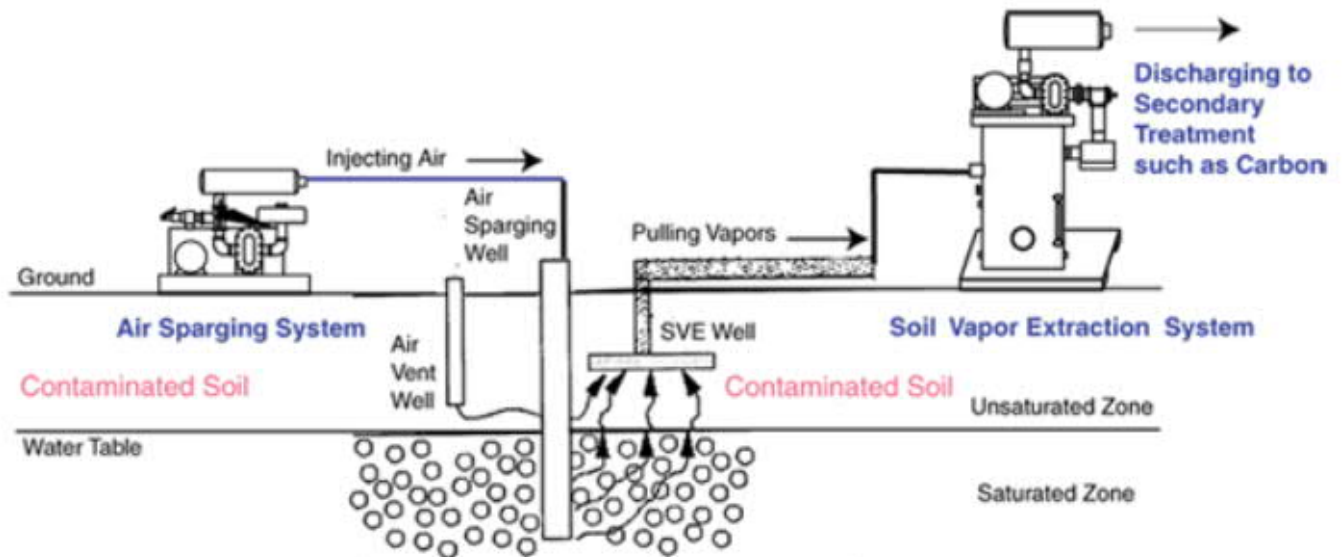
Examples of gas liquid transfer applications
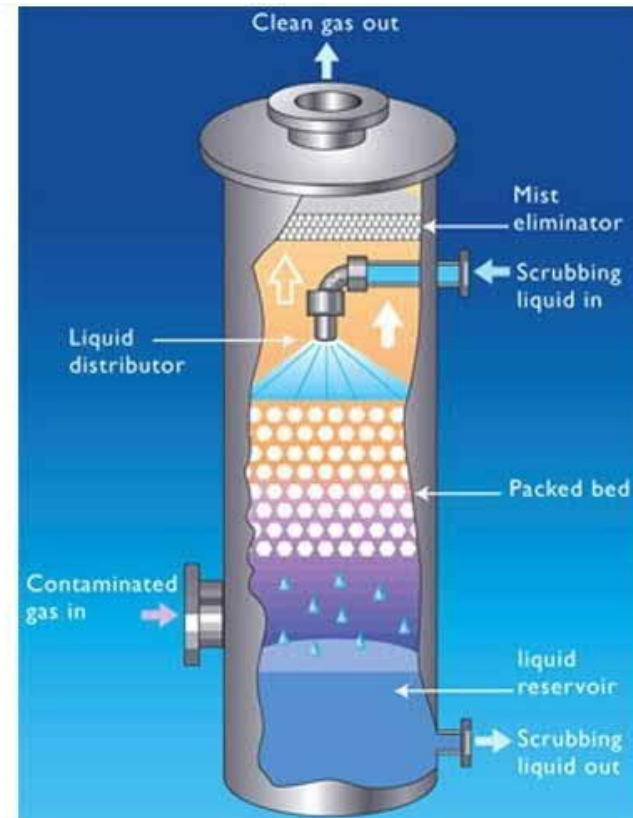
Aeration
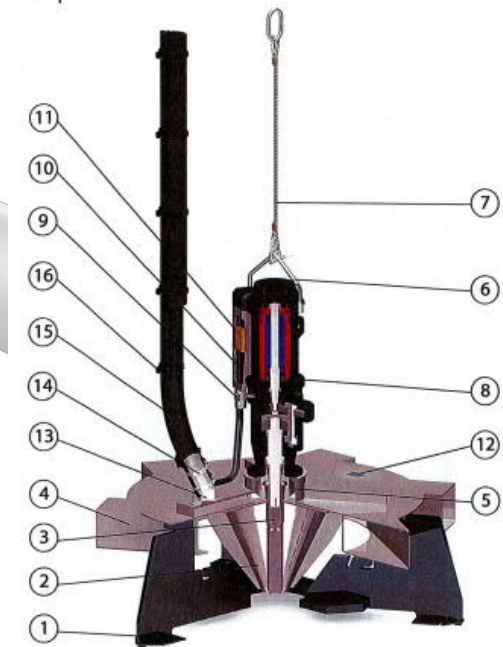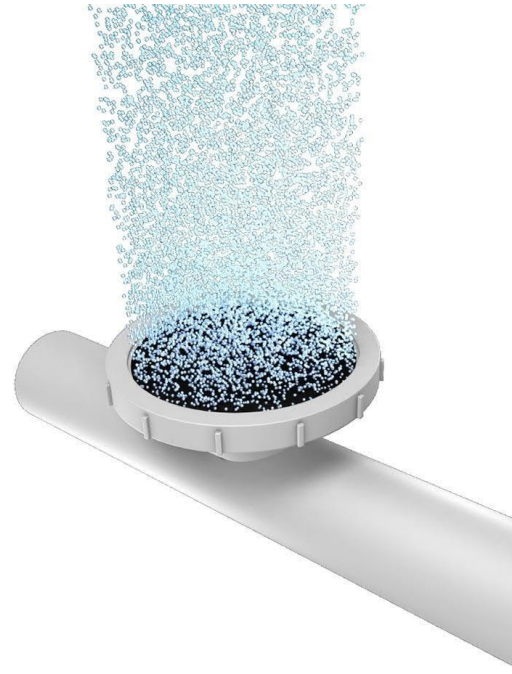
CO2 stripping

Examples of gas liquid transfer applications
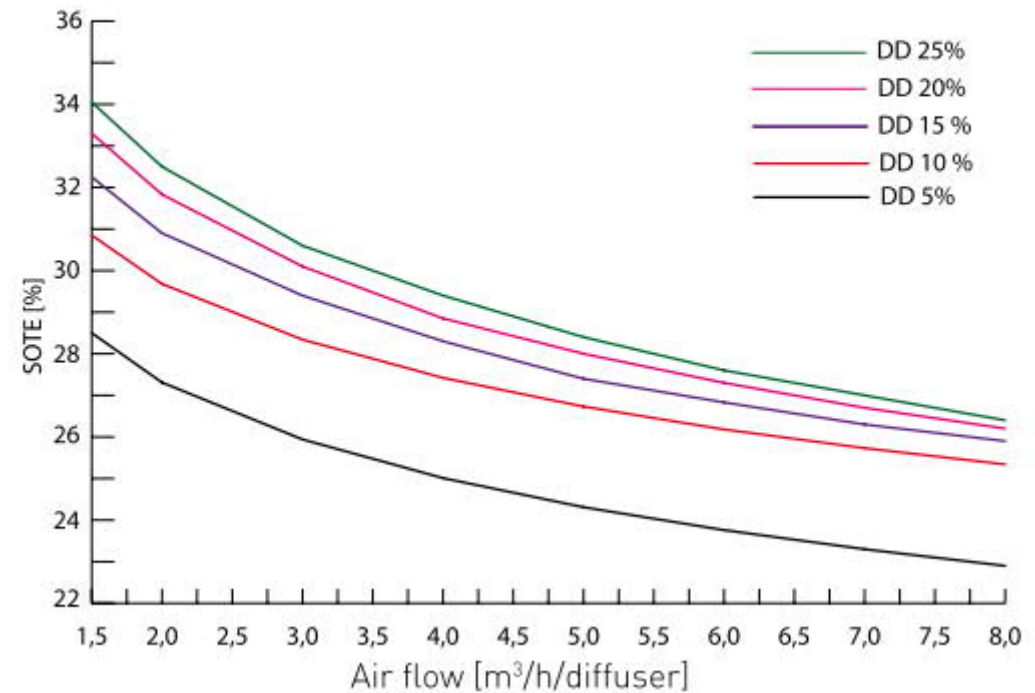
Ozone diffusion
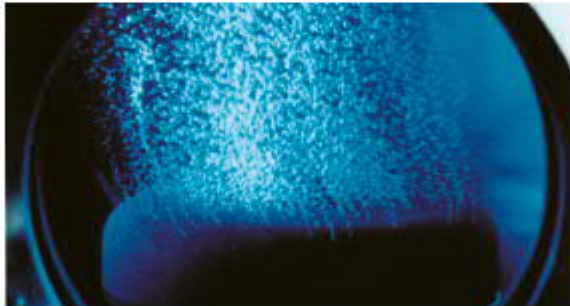
Scrubbers – towers, plates, venturis

What is affecting the aeration efficiency with bottom diffused air

- Water depth

- Aerator type

- Bubble size

- Aerator density and coverage (flow conditions)

Standard oxygen transfer efficiency, SOTE

Ammonia absortion and stripping

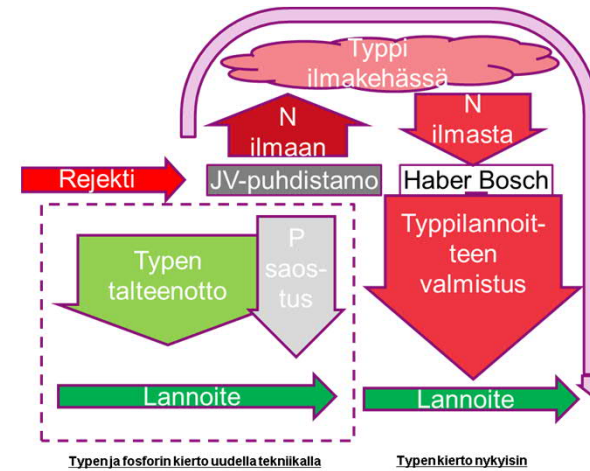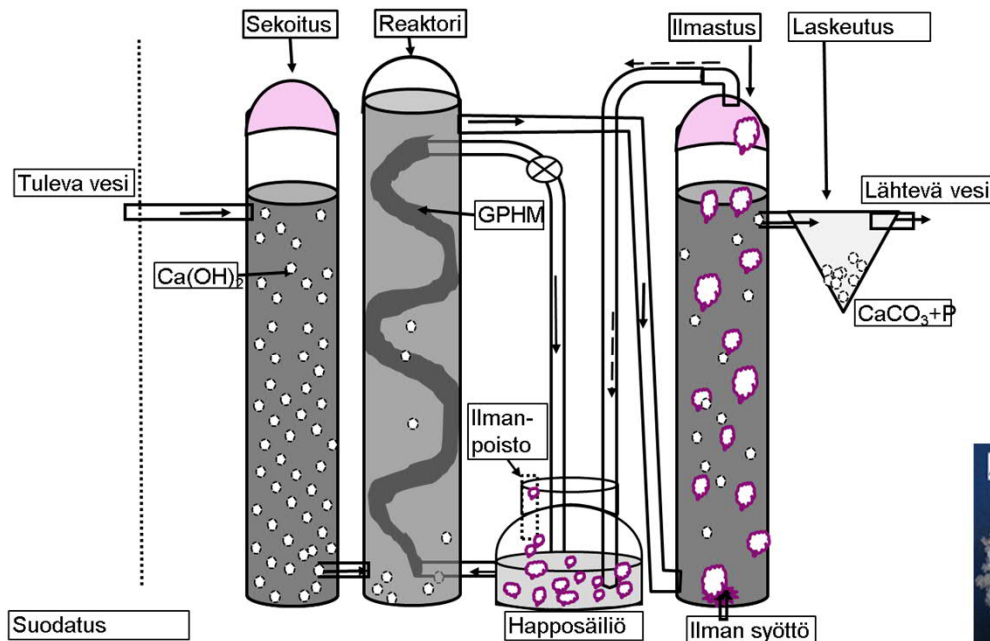**Nitrogen and phosphorus harvesting from different concentrated liquid waste streams (Post doc Surendra Pradhan)**


Figure 1. (A) $(NH_4)_2SO_4$ produced by NHT, (B) commercial $(NH_4)_2SO_4$

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GHG emission studies from advanced nutrient removal processes

Comprehensive inventory of N$_2$O emissions from an advanced WWTP and implementation of N$_2$O in the plant wide process model

Total greenhouse gas emissions from the Viikinmäki wastewater treatment process (CO$_2$ equivalents)

CH$_4$ 14% 3 320 t

CO$_2$ 0% 113 t

N$_2$O 86% 20 260 t
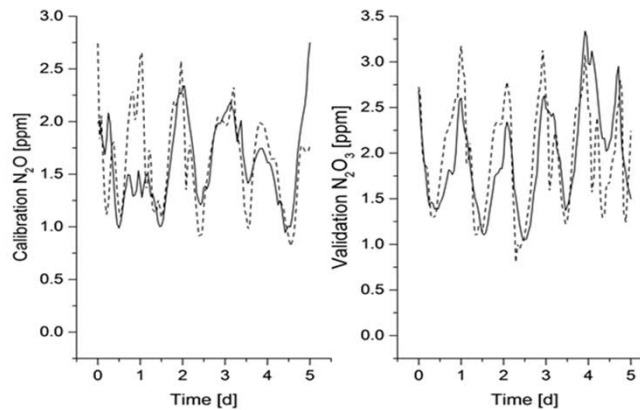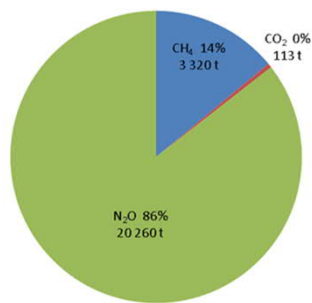
Nitrous Oxide Production at a Fully Covered Wastewater-Treatment Plant: Results of a Long-Term Online Monitoring Campaign

Heta Kosonen,[†] Mari Heinonen,[*,‡] Anna Mikola,[†] Henri Haimi,[†] Michela Mulas,[†,‖] Francesco Corona,[‡,⊥] and Riku Vahala[†]

Mixing

Velocity gradient G

Mixing is important in different reactions and processes

The mixing intensity is expressed as velocity gradient or G-value.

$$G_c = \sqrt{\frac{P}{\mu \cdot V}}$$

in which:

G_c	=	velocity gradient for rapid mixing	(s^{-1})
P	=	dissipated power	(W)
μ	=	dynamic water viscosity	$(N \cdot s/m^2)$
V	=	volume of mixing tank	(m^3)

Mixing systems can be:

- Mechanical
- Static

In case of mechanical mixing, thed dissipated power is evaluated by the power consumed.

In static mixing the dissipated power is calculated from the head loss in the mixing tank using equation:

$$P = \rho \cdot g \cdot Q \cdot \Delta H$$

in which:

ρ	=	density of water	(kg/m^3)
g	=	gravity constant	(m/s^2)
Q	=	flow	(m^3/s)
ΔH	=	head loss over mixing tank	(m)

pH, alkalinity, hardness

pH - basics

Water dissociates on H^+ and OH^-

For pure water

$\{H+\}\{OH-\} = Kw = 10^{-7} \times 10^{-7} = 10^{-14}$

$pH = -\log \{H+\}$

At pH 2 → $\{H+\} = 10^{-2}$

At pH 10 → $\{H+\} = 10^{-10}$

When acid is added to water, it ionizes and H^+ increases and consequently OH^- must decrease in order to keep the ionization equilibrium

Strong acids/bases are strongly ionized, week acids / bases are poorly ionized

Alkalinity - basics

Alkalinity is the acid neutralization capacity

Mainly due to salts of weak acids and strong bases

Most important:

Hydroxide OH$^-$

Carbonate CO$_3$ $^{2-}$

Bicarbonate HCO$_3$$^-$

Less important: phosphates, silicates…

Hydroxide alkalinity can be calculated from pH

Hydroxide alkalinity = $10^{(pH-pKw)}$

[OH$^-$] 1 mole/l = 50000 mg/l of CaCO$_3$

Calculation and measurement of alkalinity

$[H^+]$ + alkalinity (mol/l) = $[HCO_3{-}]$+2$[CO_3{}^{2-}]$ + $[OH^-]$

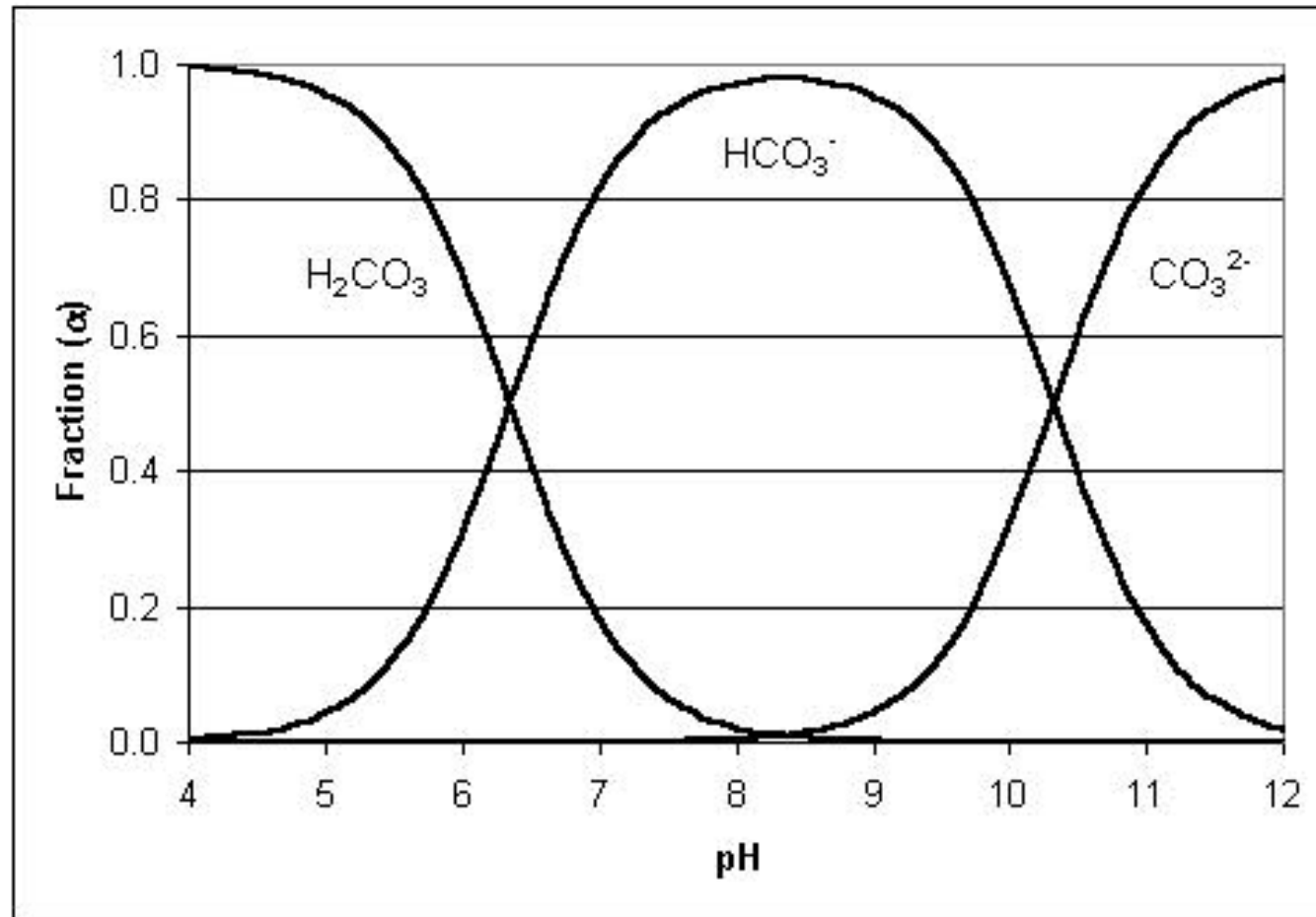Alkalinity is measured by titration with sulfuric acid

Usually given as mmol/l (= meq/l)

Other units of alkalinity: equivalent $CaCO_3$

Acidity: usually caused by CO_2 in the water, also mineral acidity

CO_2 from the atmosphere and from biological processes

Carbonate equilibrium

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Relevance of pH in treatment processes

pH control

- Removal of CO_2 by aeration

- The most commonly used alkaline reagents are ($Ca(OH)_2$), ($NaOH$), (Na_2CO_3) e.g. pH control for nitrification

- Sulphuric and hydrochloric acids (H_2SO_4, HCl) are used to increase the acidity of the water, i.e.decrease the pH, e.g.in coagulation, neutralisation

Application of alkalinity in treatment processes

- **Chemical coagulation – sufficient alkalinity needed**
- **Water softening**
- **Corrosion control**
  - Langelier saturation index
  - Aggressive index
- **Buffer capacity, especially in biological processes**

CO_2 – alkalinity – pH

  - interactions

Example: removal of CO_2 to increase pH – what is the effect on alkalinity?

Hardness - basics

Reflects the nature of geological formations

Caused by multivalent metallic cations mainly Ca^{2+}, Mg^{2+}

Expressed as mmol/l, German hardness (dH) or equivalents $CaCO_3$

mmol/l = 100x mg/l $CaCO_3$

$$Hardness \left(\frac{mg}{l} \, of \, CaCo3\right) = M^{2+} \frac{50}{EW \, of \, M}$$

EW = equivalent weight

In this case atomic weight divided by the usual valence

Consequences and removal of hardness

- **Ineffectiveness of soap**
- **Scale formation especially in warm environments (boilers, heating system pipes…)**
  - Causes clogging, material damages and heat losses
  - Protects against corrosion

Hardness can be removed by removing Ca and Mg

Methods:
- **Precipitation and filtration**
- **Ion exchange**