AquaSPICE

Advancing Sustainability of Process Industries through Digital and Circular Water Use Innovations

Technologies Mentioned in BREFs

AquaSPICE Course 2024

Laurence Palmowski & Team

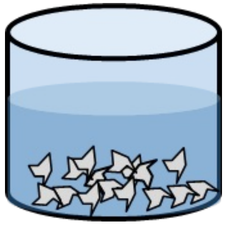
The AquaSPICE project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 958396.

Technologies mentioned in BREFs

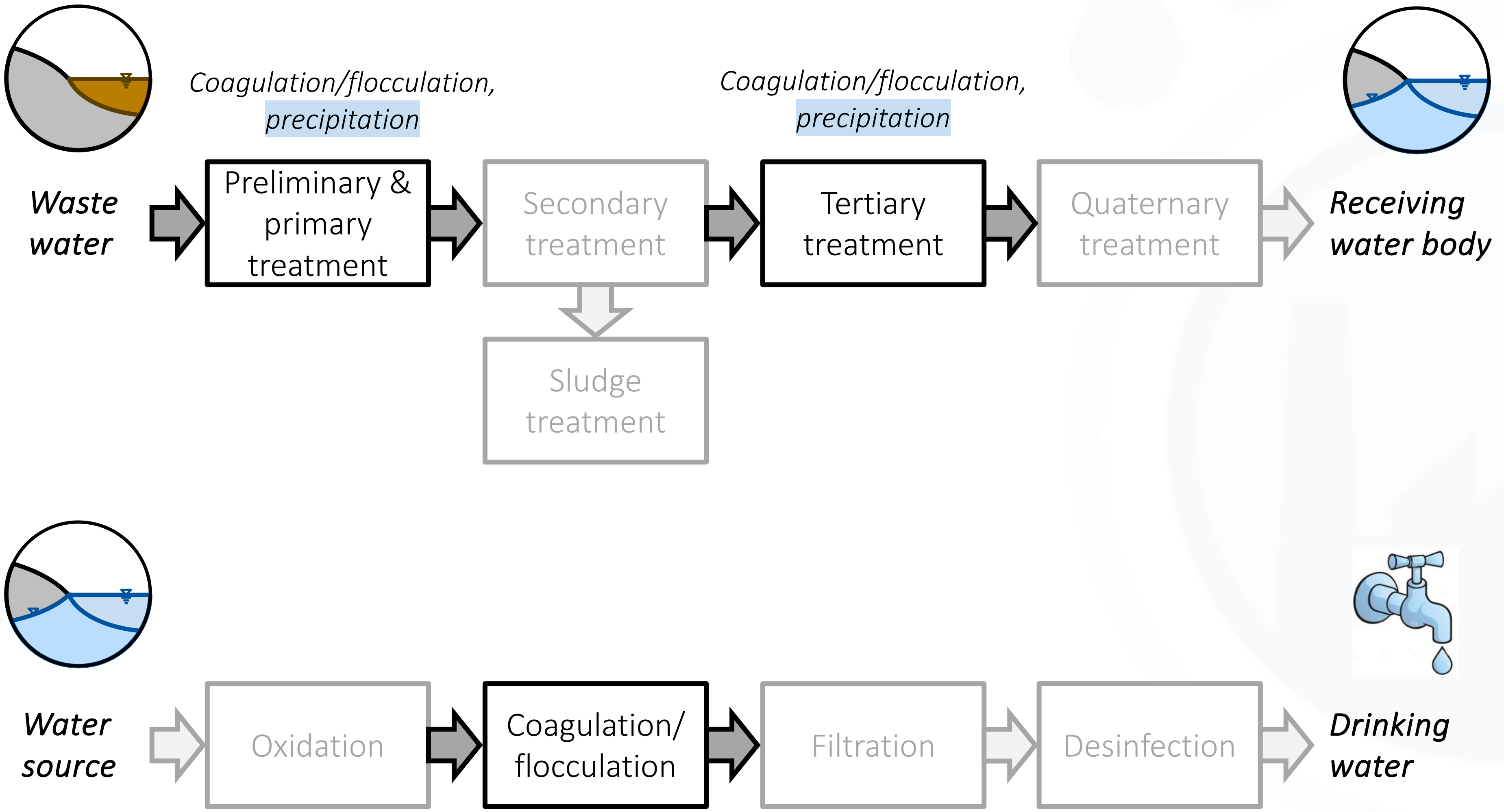
Structure

1. Suspended solids removal
    1. Coagulation/Flocculation
    2. Sedimentation
    3. Flotation
    4. Filtration
2. Physico-chemical treatment processes
    1. Precipitation
    2. Oxidation
    3. Thermal treatment processes (Evaporation,Distillation/Rectification, Stripping)
3. Biological treatment processes
4. Membranes

Precipitation

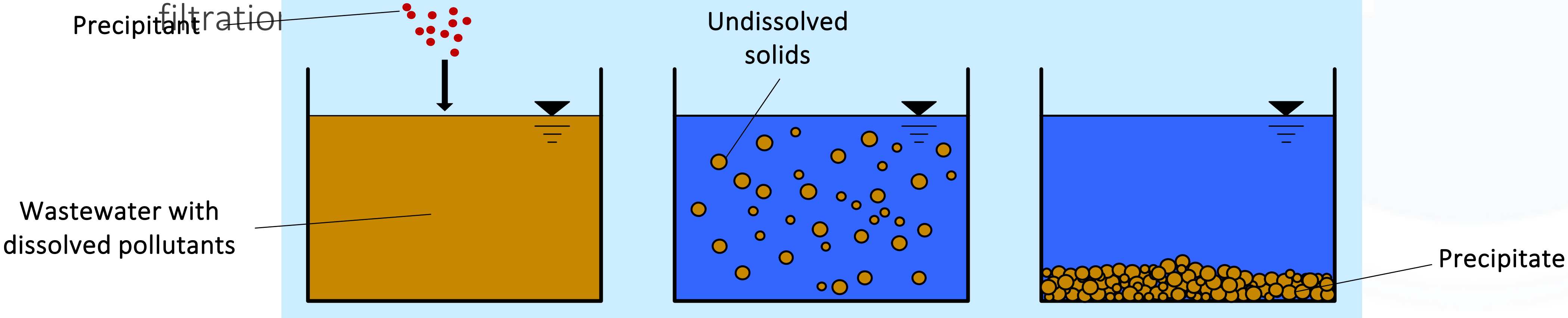


Precipitation Unit Processes



Precipitation Fundamentals

- Goal: removal of **dissolved** pollutants, especially heavy metals, from wastewater
- Principle:
  1. Chemical reactants, so called **precipitants**, are added to wastewater to have a **chemical reaction** with the dissolved pollutants
  2. The resulting compounds have a **low solubility** in water and are therefore present in an undissolved, solid state
  3. The solid product, called **precipitate**, can then be removed by mechanical processes (e.g. filtratio



Dissociation vs. Precipitation

- Dissociation (=dissolution) and precipitation: 2 competing phenomena

e.g.

$$Me(OH)_z \underset{\text{Precipitation}}{\overset{\text{Dissolution}}{\rightleftharpoons}} Me^{z+} + zOH^-$$

- Equilibrium constant K and ionic product K_{IP}

$$K = \frac{c(Me^{z+}) \cdot c^z(OH^-)}{c(Me(OH)_z)}$$

$$K_{IP} = c(Me^{z+}) \cdot c^z\,(OH^-)$$

- Solubility product K_{SP}

$$K_{SP} = c_{sat}(Me^{z+}) \cdot c_{sat}^z(OH^-)$$

The solubility product is the product of the ion concentrations in a **saturated solution** at a given temperature

Saturation

- If ionic product K_{IP} < solubility product K_{SP}
  - Solution is **not saturated**. More substance can be dissolved until precipitation occurs.

- If $K_{IP} = K_{SP}$
  - Solution is **saturated**; equilibrium

- If $K_{IP} > K_{SP}$
  - Solution is **oversaturated**.

    Precipitation occurs until value of K_{sp} (saturation) is reached again

Precipitation of Cations or Metals

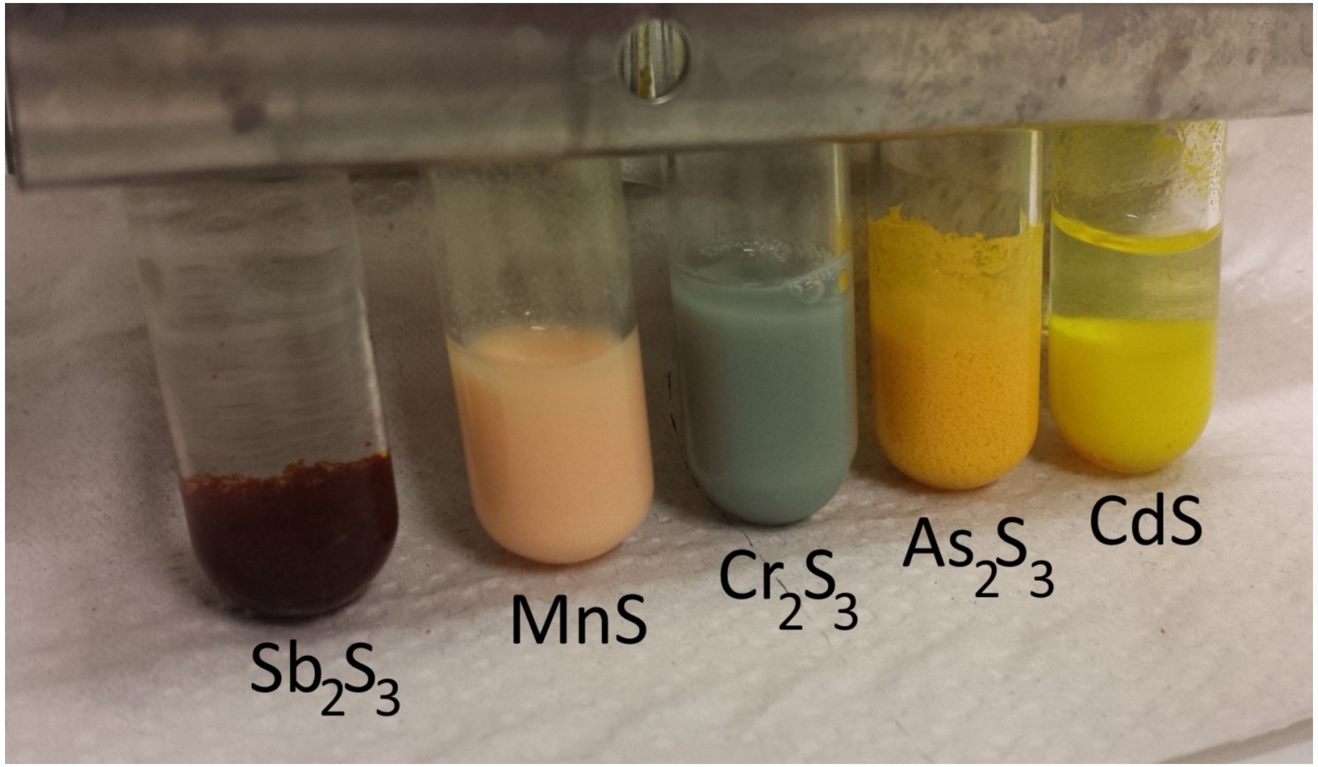
Examples

Pollutants: Sb^{3+}, Mn^{2+}, Cr^{3+}, As^{3+}, Cd^{2+}

Precipitant: $H_2S \Leftrightarrow 2H^+ + S^{2-}$

Reaction: $2\,Sb^{3+} + 3\,S^{2-} \Leftrightarrow Sb_2S_3 \downarrow$

Precipitate



[1]

[1] Johannes Schneider, https://de.m.wikipedia.org/wiki/Datei:Mit_Ammoniumsulfid_gef%C3%A4llte_Niederschl%C3%A4ge_von_Antimon,_Mangan,_Chrom,_Arsen_und_Cadmium.jpg

Examples for Precipitation of Cations or Metals

Name	Precipitant	Compound (example)	Solubility product K_{SP} [(mol/l)^n]	Stoichiometry (example)
Hydroxide/ neutralization Precipitation	NaOH $Ca(OH)_2$	$Cr(OH)_3$	$3 \cdot 10^{-28}$	$Cr^{3+} + 3OH^- \Leftrightarrow Cr(OH)_3$
Sulphide precipitation	H_2S	HgS	$4 \cdot 10^{-53}$	$Hg^{2+} + S^{2-} \Leftrightarrow HgS$
Carbonate precipitation	Na_2CO_3	$PbCO_3$	$1.5 \cdot 10^{-15}$	$Pb^{2+} + CO_3^{2-} \Leftrightarrow PbCO_3$
Ammonium precipitation	$Mg_3(PO_4)_2$	$MgNH_4PO_4$		$NH_4^+ + Mg^{2+} + PO_4^{3-} \Leftrightarrow MgNH_4PO_4$

Examples for Precipitation of Anions

Name	Precipitant	Compound	Solubility product K_{SP} [(mol/l)^n]	Stoichiometry
Fluoride precipitation	$Ca(OH)_2$	CaF_2	$3.4 \cdot 10^{-11}$	$2F^- + Ca^{2+} \Leftrightarrow CaF_2$
Sulphate precipitation	$Ca(OH)_2$	$CaSO_4$	$6.1 \cdot 10^{-5}$	$SO_4^{2-} + Ca^{2+} \Leftrightarrow CaSO_4$
Phosphate precipitation	$Ca(OH)_2$ $FeCl_3$	$CaHPO_4$ $FePO_4$	$5 \cdot 10^{-6}$	$Ca(OH)_2 + H_3PO_4 \Leftrightarrow CaHPO_4 + 2H_2O$

pH Dependency of Precipitation I/II

Chemistry Basics

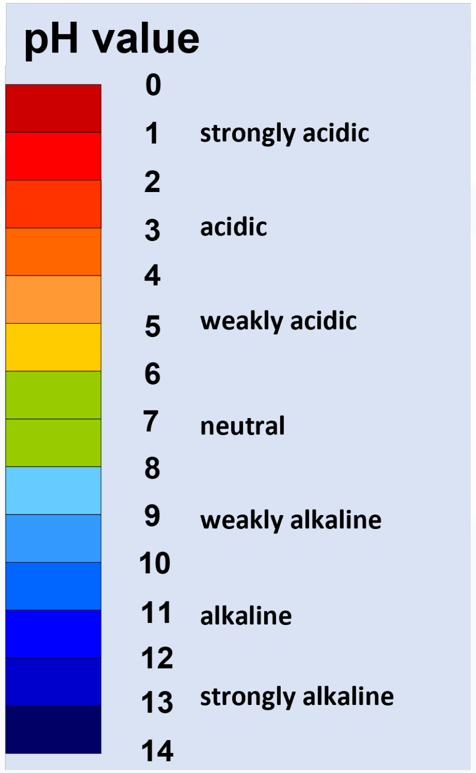
- pH plays a crucial role in chemical precipitation reactions. It **affects the solubility** of compounds and the efficiency of precipitation processes.
- Definition of pH:
  - Dissociation reaction of water

    $$H_2O \Leftrightarrow H^+ + OH^-$$

  - pH definition

    $$pH = -\log \frac{c(H^+)}{mol \cdot l^{-1}}$$

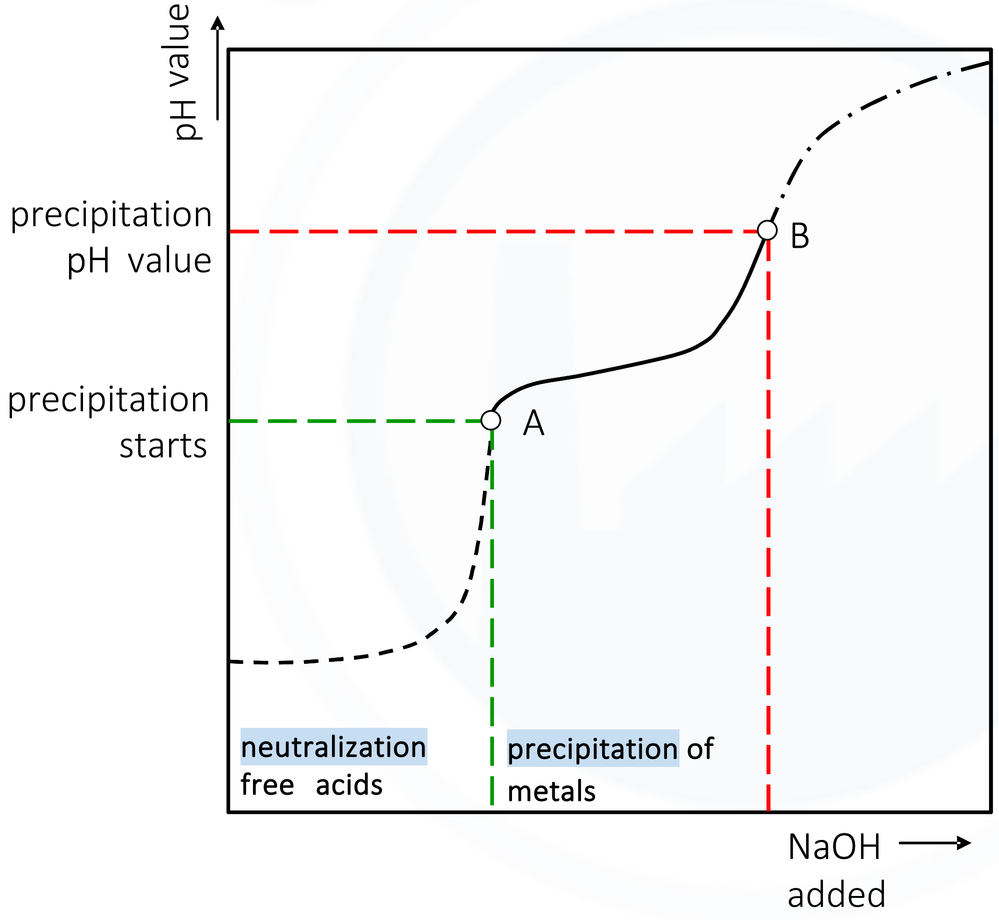
- Arrhenius concept for acids and bases:
  - Acids form H+ ions in water, e.g.: $HCl \Leftrightarrow \mathbf{H^+} + Cl^-$ → pH↓
  - Bases form OH- ions in water, e.g.: $NaOH \Leftrightarrow Na^+ + \mathbf{OH^-}$ → pH↑
  - Acids and Bases neutralize each other: $Na\mathbf{OH} + \mathbf{H}Cl \Leftrightarrow NaCl + \mathbf{H_2O}$



pH Dependency of Precipitation II/II

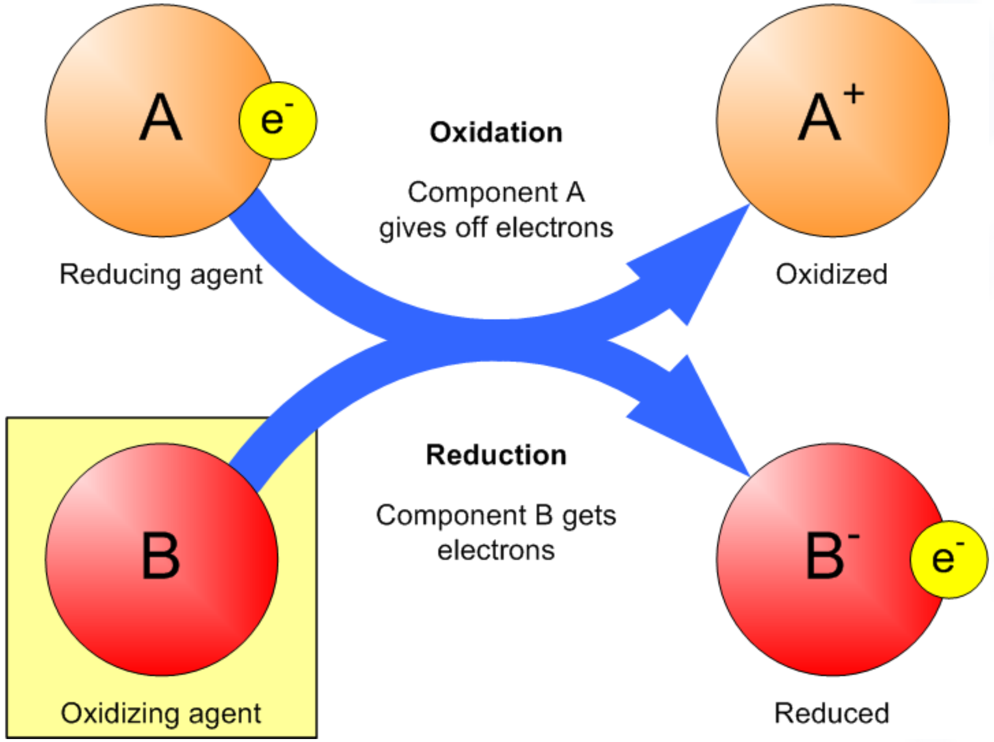
Neutralization Precipitation

- **Neutralization precipitation** using hydroxide (OH^-) as precipitant
  - By adding hydroxide to acidic wastewater (e.g. from mining industry, chemical manufacturing, etc.), free acids are neutralized before a certain pH is reached for metal precipitation
  - Examples:
    - Precipitation of ferric (Fe^{3+}) hydroxide
      $Fe(OH)_3$ A: 2.8 B: 3.5
    - Precipitation of ferrous (Fe^{2+}) hydroxide
      $Fe(OH)_2$ A: 7.0 B: 8.9



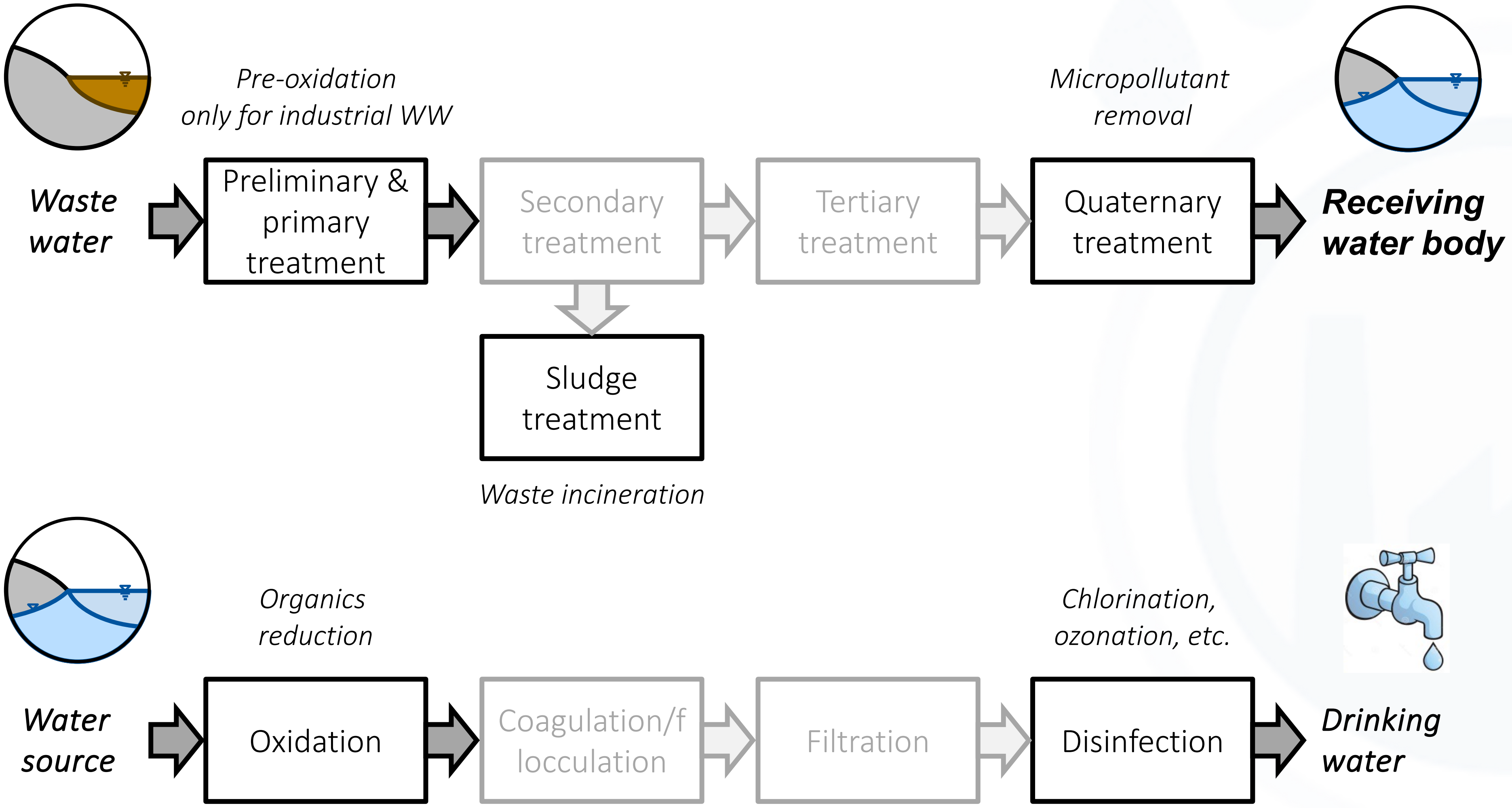
Oxidation

Reduction-Oxidation („Redox“) Reactions



Oxidation reactions introduce oxygen or other **powerful oxidizing agents** to the wastewater, **breaking down suspended or dissolved, mostly organic pollutants** (reducing agents) into simpler, less harmful forms.

Chemical Oxidation Unit Processes



Oxidation in Wastewater Treatment

- Aim for **inorganic** substances:
  - Transformation into a more **environmentally friendly** compound
  - Transformation into a compound, whose **elimination is possible**

- Aim for **organic** substances:
  - Partial oxidation for transformation into a **biodegradable** substance
  - **Complete removal** by total oxidation to CO_2 and water

- Examples:
  - Degradation of pesticides (e.g. atrazine, aldicarb, alachlor, carbofuran), phenolic compounds, aromatic compounds and aldehydes

Oxidation Processes Overview

At Different Temperature Ranges

- **Oxidation at temperatures** below 100°C and at normal pressure
  - Use of suitable oxidizing agent (O_2, O_3, H_2O_2, etc.)
  - Activation by catalysts or UV-radiation if necessary

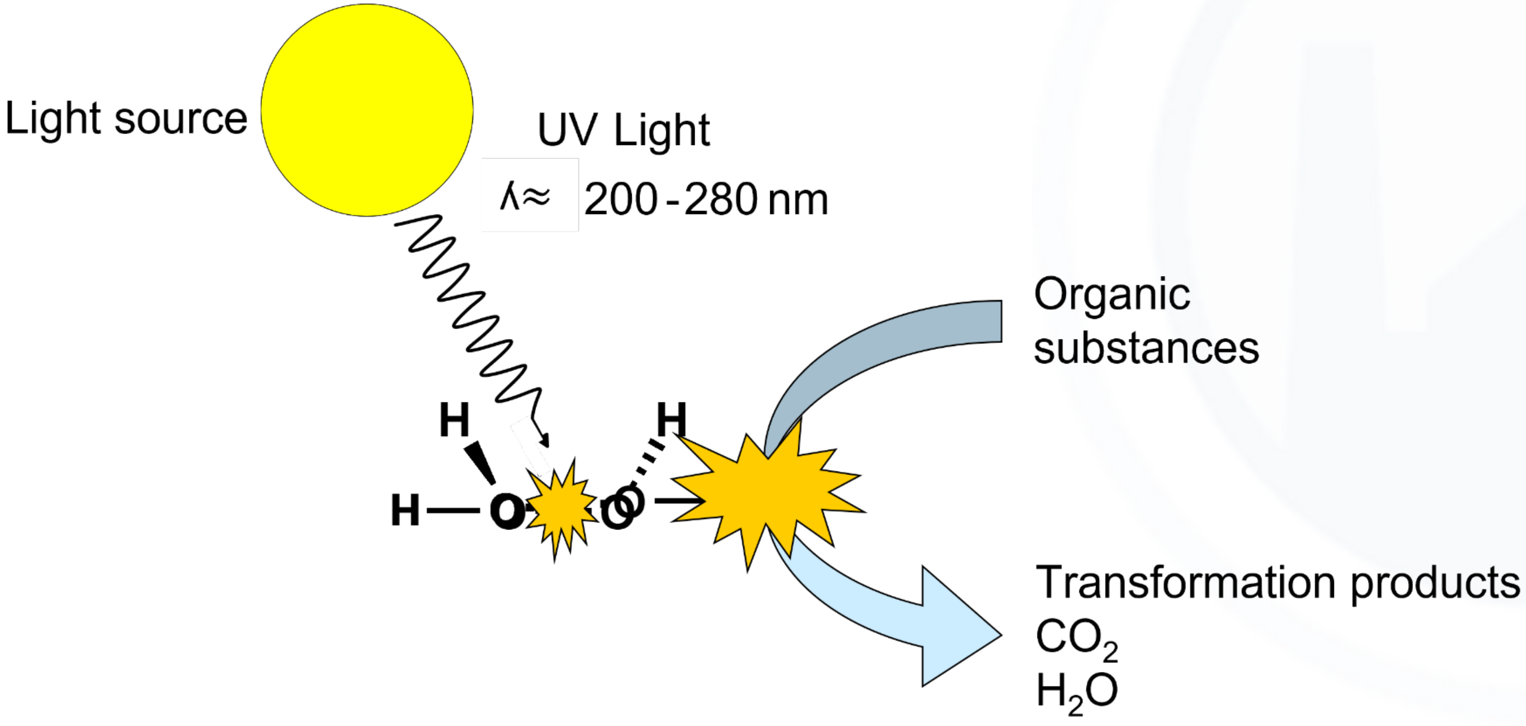
    ⇒ Advanced Oxidation Processes (AOP)

- Oxidation at moderate temperatures (approx. 180 – 330°C) and high pressure (approx. 10 – 220 bar)
  - Wet air oxidation (high and low pressure processes)
  - Activation by catalyst if necessary

- Wastewater incineration (750 – 1,200°C)

Advanced Oxidation Processes (AOPs)

- Most common AOP oxidizing agents: hydrogen peroxide (H_2O_2), Ozone (O_3)
  - Often: Activation by UV light
- For all advanced oxidation processes in common: Generation of highly reactive ·OH radicals



Wet Air Oxidation

- Oxidizing agent: Oxygen (O_2) in air

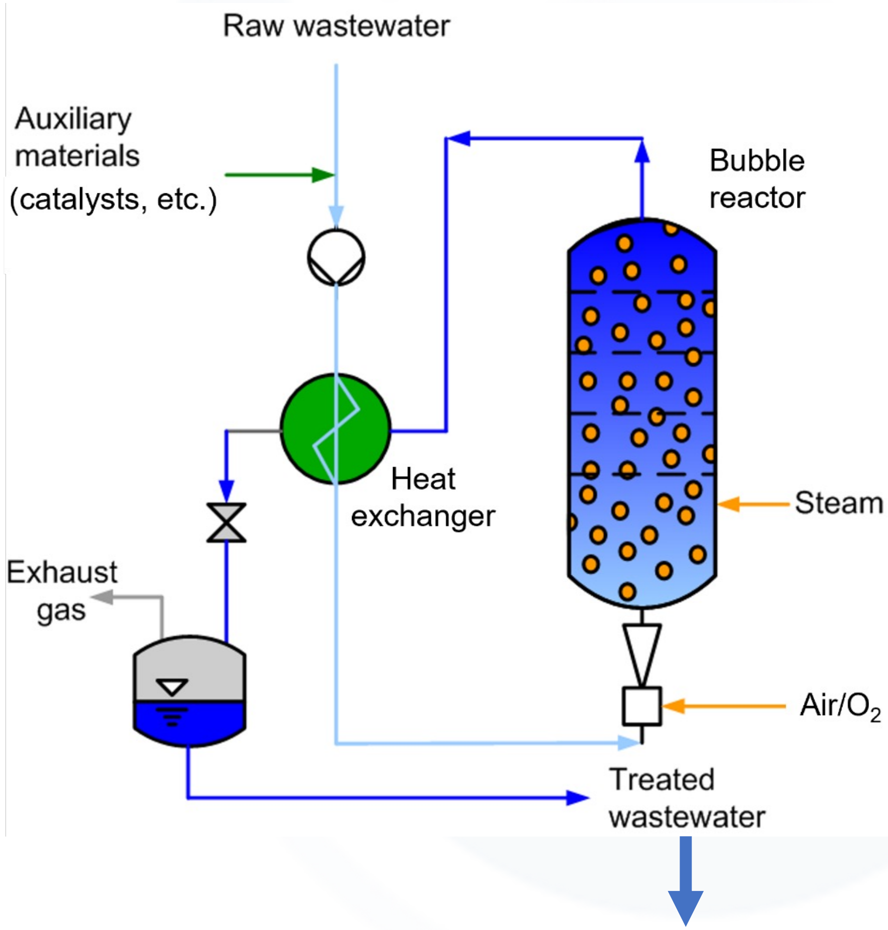
- Bubble reactor:
  - Air bubbles through pressurized wastewater
    - T = 120-330 °C
    - p = 10-220 bar to prevent evaporation of water

  → Conditions result in **higher O_2 solubility**

  → **Better O_2 availability for oxidation reaction**

  - Dissolved O_2 reacts with pollutants (mostly **complex** organic componds)

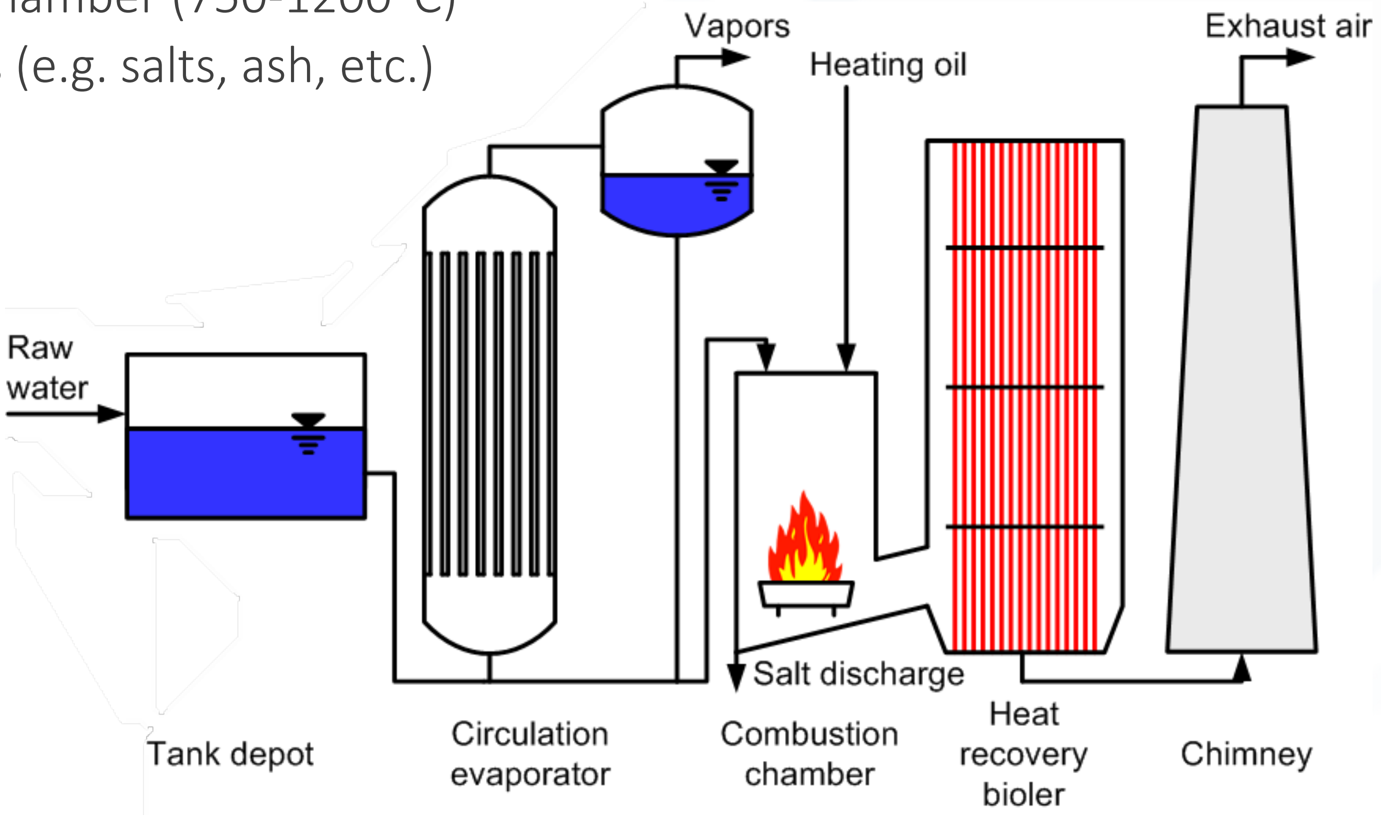
  - Treated wastewater contains reaction products (mostly **simple** organic componds)



→ Further treatment necessary

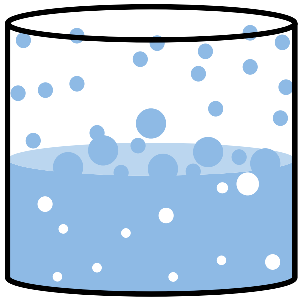
Wastewater Incineration

- Goal: Burning of organic compounds to H_2O and CO_2
- For wastewater with high content of combustile organic materials
  1. Reduce water content by evaporation
  2. Incineration in combustion chamber (750-1200°C)
  3. Removal of residual materials (e.g. salts, ash, etc.)



→Very energy-intensive process

Thermal Processes



Thermal Processes: Structure

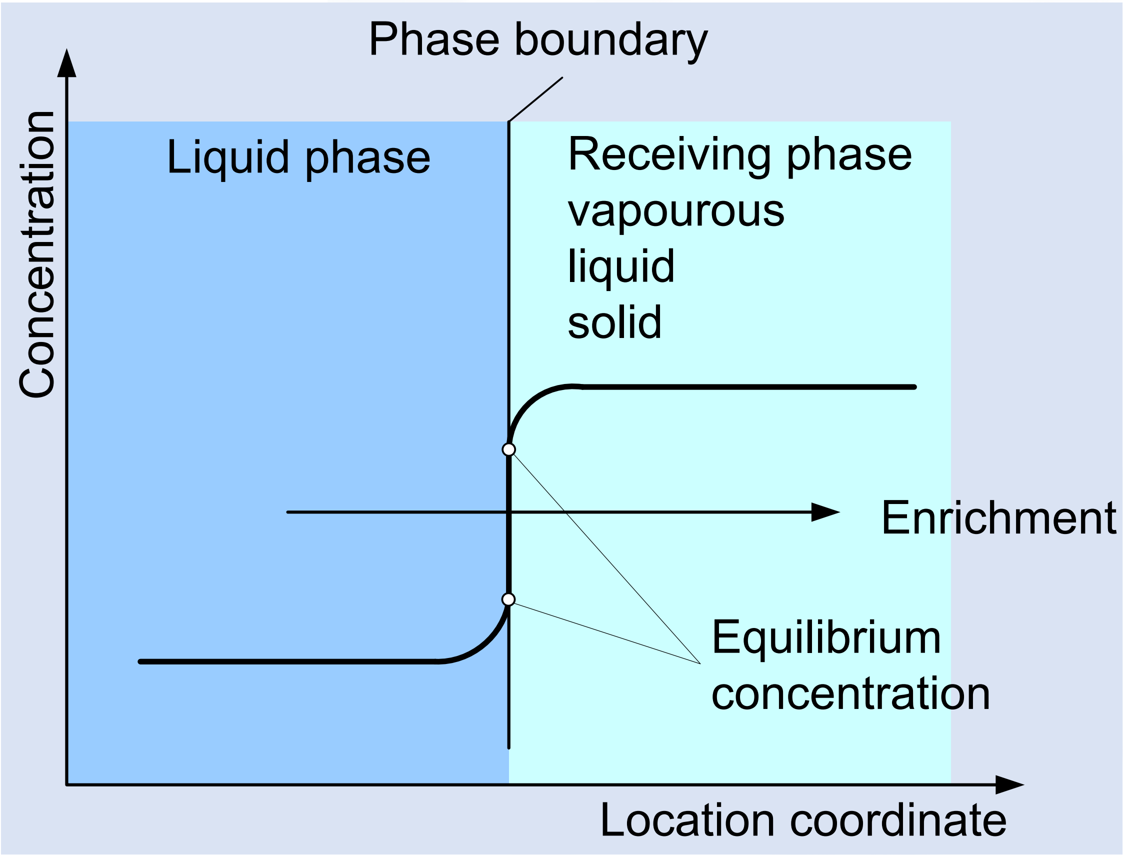
- Basics on processes based on liquid/gas equilibrium
- Evaporation
- Distillation (and fractional distillation or rectification)
- Stripping

Gas-Liquid Equilibrium

- Thermal processes: Mass (and often also energy) transport between two phases (often liquid and gas), driven by concentration or temperature gradients

- Important state: Equilibrium
  - Definition: When two phases are in an equilibrium, the rate of change of the properties of each phase is equal, and there is no net transfer of matter between the phases.

[2]

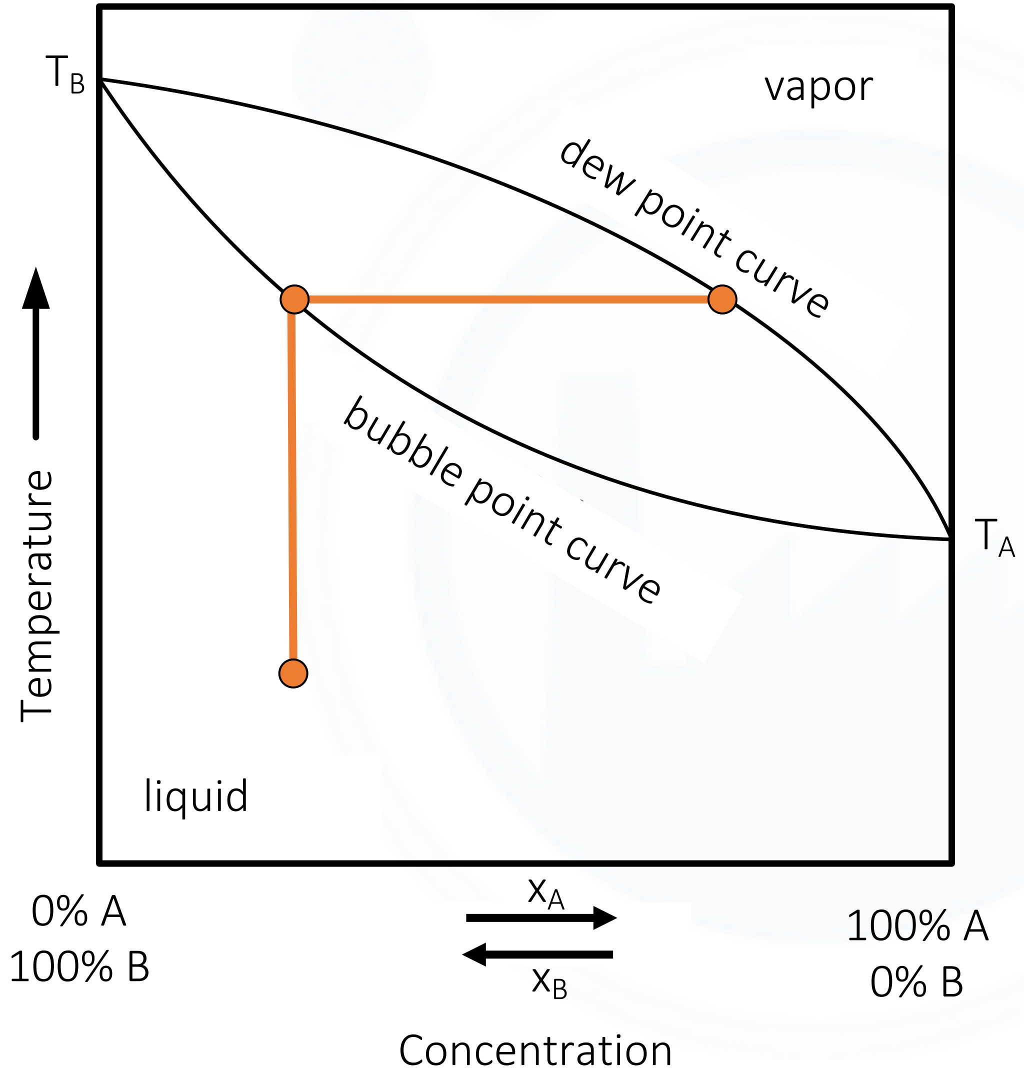


[2] ATV-Handbuch (1999): Industrieabwasser – Grundlagen

Ideal Binary Mixture: Boiling-Point Diagram

- **Two phases** and **at least two substances** with **different boiling points**:
  - Substance A: low boiling temperature T_A
  - Substance B: high boiling temperature T_B

- Difference in concentration of the 2 phases → separation
  - Concentration of low boiling substance (A) in vapor phase
  - Concentration of high boiling substance (B) in liquid phase



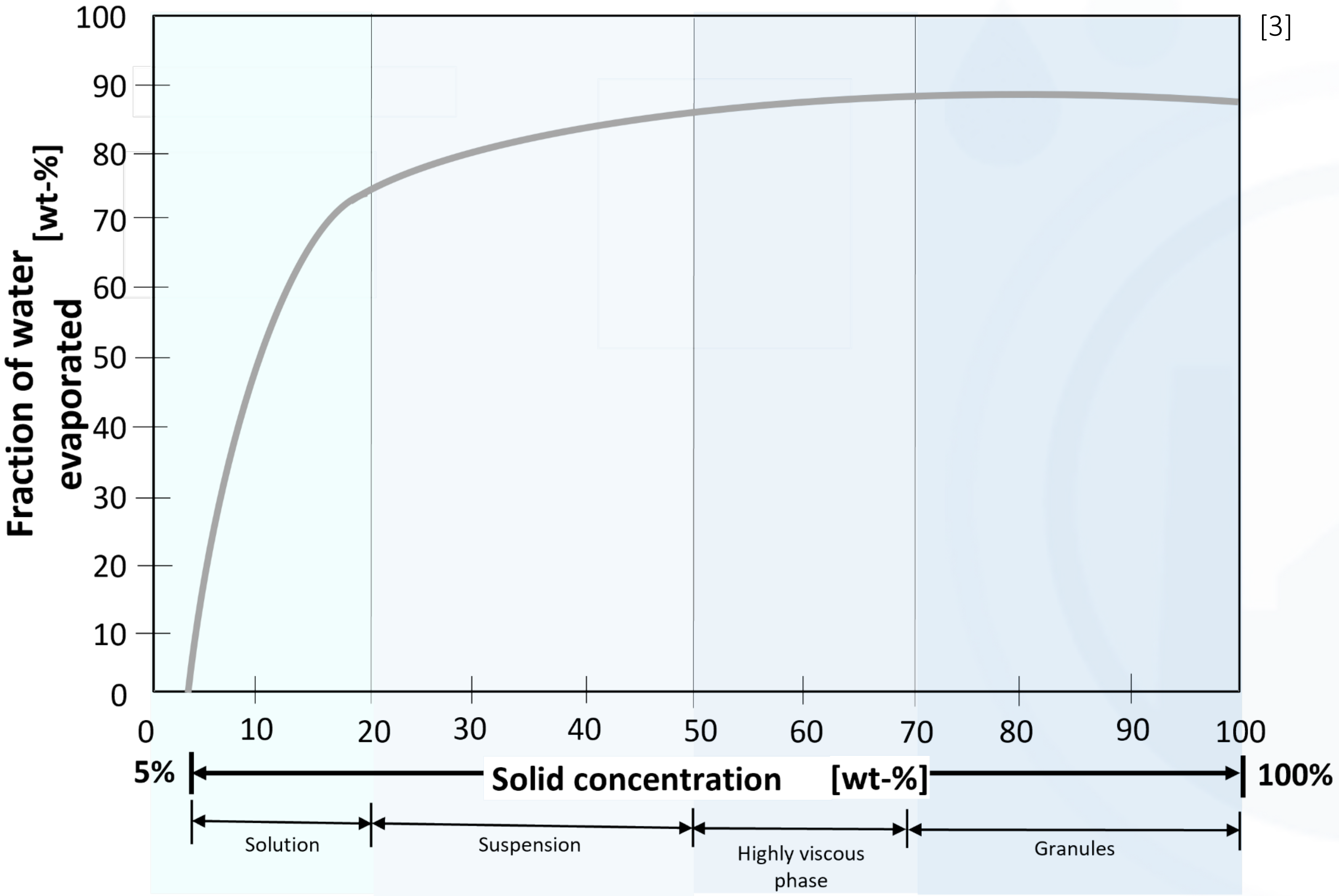
Evaporation

Evaporation for Wastewater Treatment

- Goal: Separation of substances which posses very low or no vapor pressure from water e.g. salts, heavy metals
- Fundamental process of evaporation (here: batch process)
  1. Heating wastewater to boiling point → evaporation of water
  2. When saturation is reached, remaining dissolved solids start to precipitate, the solution becomes a suspension
     - Problem: Fouling - Formation of incrustation on heat transfer surfaces
     - Counteraction: e.g. smooth surfaces, small temperature differences, mechanical cleaning system
  3. With further evaporation the suspension becomes thicker and more viscous, thus the boiling point increases
     - Problem: Formation of clumps and foam or hardening
  4. Remained solid could be burnt or dried
- End product: Powder/ granulate and evaporated water with low boiling contaminants → **water is not fully purified by evaporation**

Stages of Evaporation

Example: Evaporation for Separation of Dissolved Solids and Water



[3] Handbuch Industrieabwasser, 4. Aufl.

Stages of Evaporation

Characteristics, Challenges and Process Requirements

[4]

Solid concentration[w%]

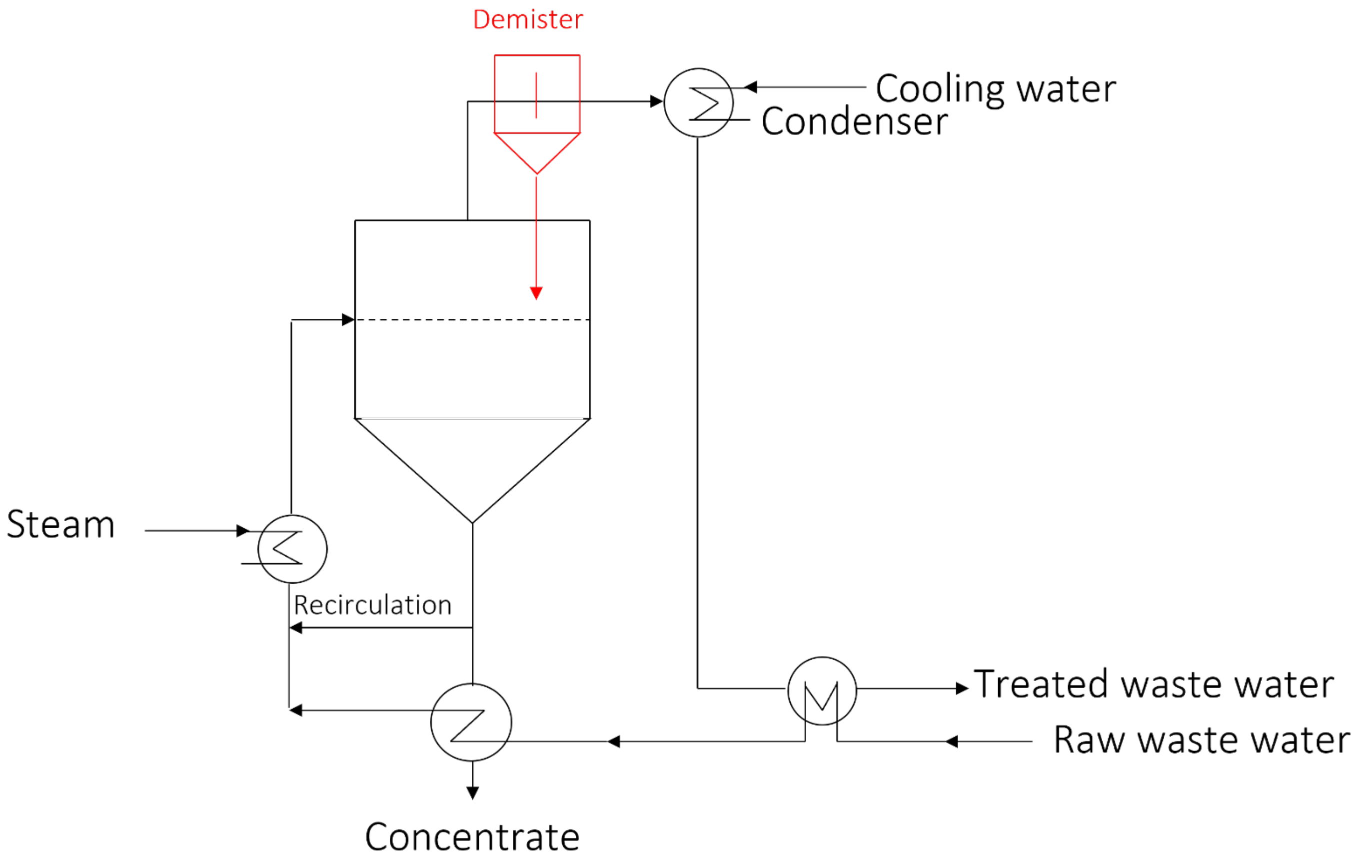
5% — 20% — 50% — 70% — 100%

	Solution (5%–20%)	Suspension (20%–50%)	Highly viscous phase (50%–70%)	Granules (70%–100%)
Process	Evaporation		Transition	Drying
Problems	Input of thermal energy	Sticking High viscosity Clumps formation Foam formation High temperature Post-polymerization		Diffusion Separation: vapor – solid
Process requirements	Good heat transfer	High forces, Self purification Low residence time		Good mass transfer, Long residence time, Low vapor velocity

[4] Handbuch Industrieabwasser, 4. Aufl

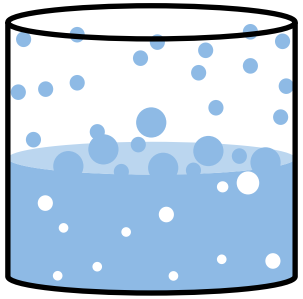
Process Example and Evaporator Designs

- One stage evaporation process



- Designs of evaporators
  - Circulation evaporator
  - Flash evaporator
  - Falling-film evaporator
  - Thin Film evaporator
  - ...

Distillation | Rectification | Stripping

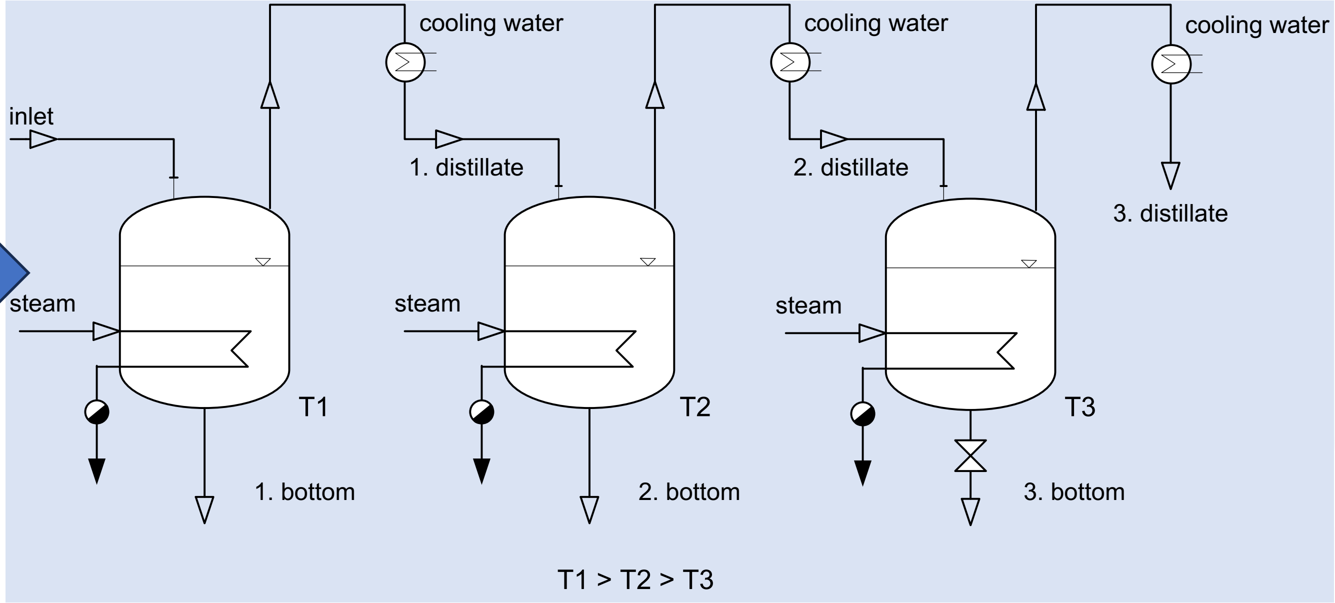


Distillation

- **Evaporation** as a wastewater treatment process concentrates contaminants
- **Distillation/Rectification** also involves heating wastewater to create vapor, but the **focus is on separating water from contaminants** (using different boiling points of components)
- The vapor is condensed back into liquid form, primarily obtaining **purified water**

Repeated single distillation as a continuous process

- Any desired distillate quality is attainable (as long as no azeotrope exists)
- High energy input (condensation at every level)
- Small yield

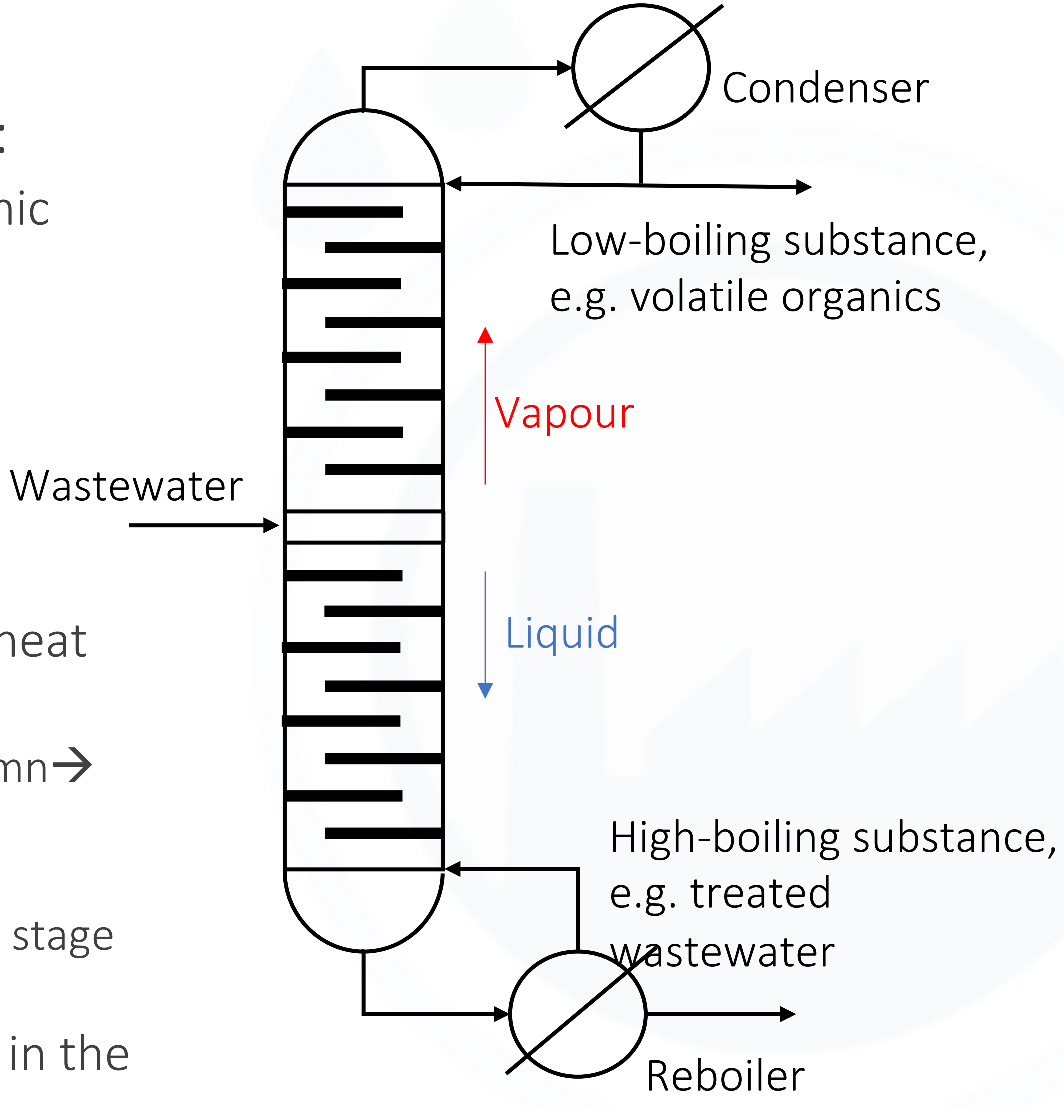


Rectification

Multi-Stage Distillation in a column

- Applications for industrial wastewater treatment:
  - Wastewaters with high concentration of Volatile Organic Carbon (VOC) compounds, such as organic solvents
    - Examples: pharmaceutical and chemical industries
  - Recovered solvents can be reused

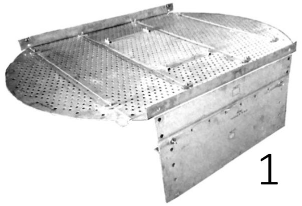
- Procedure within Rectification column:
  - One part of a feed liquid mixture is evaporated under heat supply
    - Vapour goes up the column, liquid goes down the column→ counter flow
    - Due to the equilibrium behavior of the substances the compositions of liquid and gaseous phase differ for any stage throughout the column
  - enrichment of volatiles at the head and of high boilers in the column bottom



Rectification Column Internals

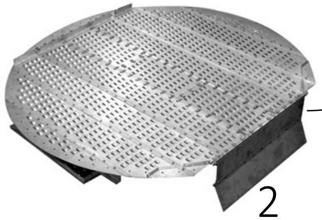
Trays:

- Sieve Trays

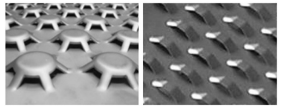


1

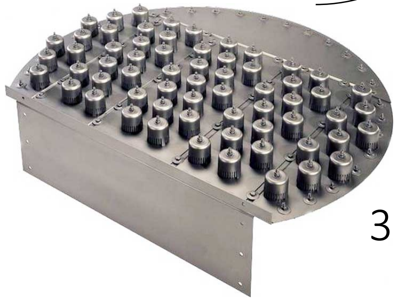
- Valve Trays



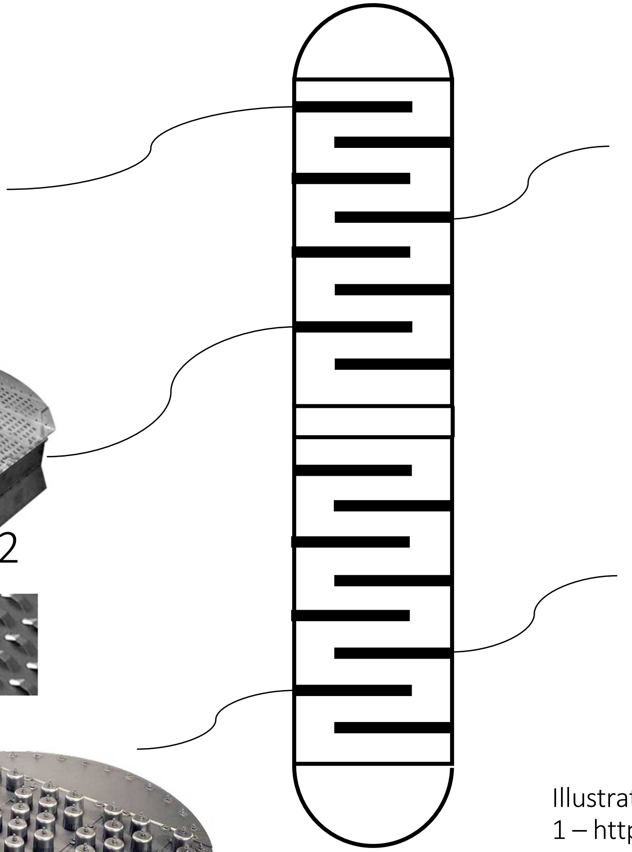
2



- Bubble Cap Trays



3



Packings:

4

- Struktured packings

- Random packings

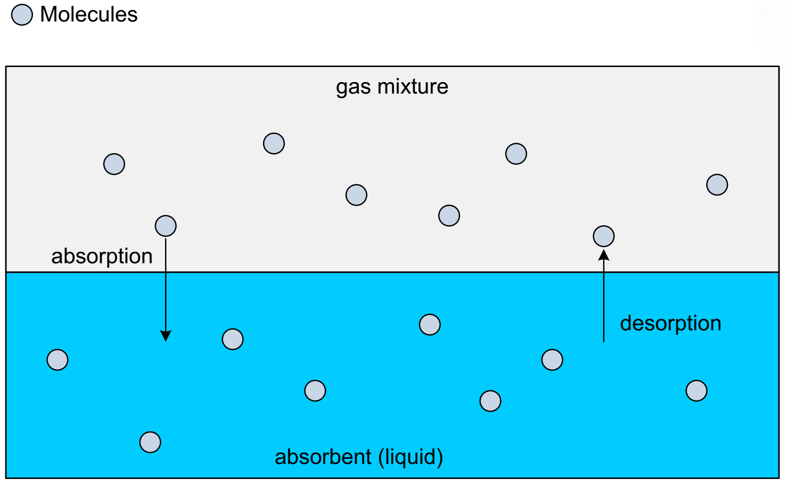
5

Illustration Sources:
1 – https://www.munters.com/en/munters/products/mass-transfer/sieve-trays/
2 - https://www.munters.com/de/munters/Produkte/mass-transfer/kevin-valve-tray/
3 - https://www.wermac.org/equipment/distillation_part2.html
4 - https://www.sulzer.com/-/media/files/products/separation-technology/distillation-and-absorption/brochures/structured_packings.pdf
5 - https://www.sulzer.com/-/media/files/products/separation-technology/distillation-and-absorption/brochures/random_packing.pdf?la=en

Column internals design goal: Maximize vapour-liquid contact → improved separation

Stripping

- Goal: removal of volatile pollutants from wastewater (e.g. benzene, toluene, ammonia,…)
- Separation principle:
  - wastewater is brought in contact with a gas (such as air or steam)
  - Volatile wastewater contaminants are released into gas phase
  - Constant removal of loaded gas phase and simultaneous inflow of fresh inert gas
- Process Requirement: Big contact surface area bewteen liquid and stripping gas



Control Questions

1) What are thermal processes?
2) What is evaporation? How does it work? What are the goals?
3) Which evaporators do you know? – Name at least four.
4) Explain distillation/rectification. What are the internals in a technical column?

AquaSPICE

Advancing Sustainability of Process Industries through Digital and Circular Water Use Innovations

Thank you!

Laurence Palmowski & Team