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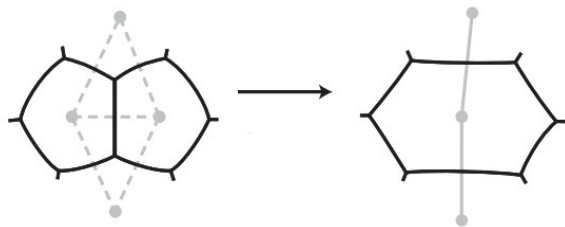
Lecture 12: Froth flotation

Structure

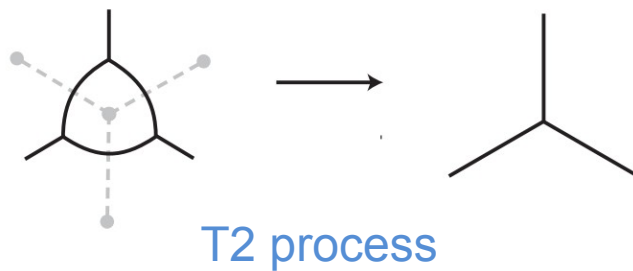
- Review lecture 11
- Mineral flotation
- Surfactants in Flotation
- Particle attachment
- Froth zone
- Cell design
- Related applications

Foam stability

- Two modes of foam destruction:
- A: Coalescence / Film rupture
→ Increased bubble size / reduced foam volume



- B: Coarsening
→ increased bubble size

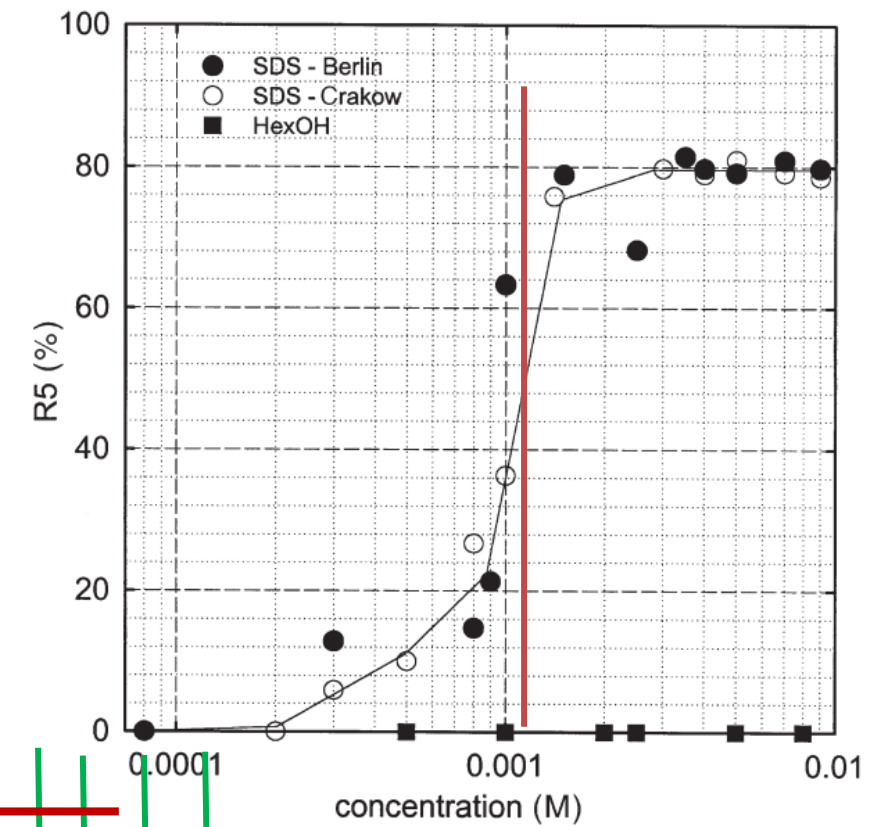
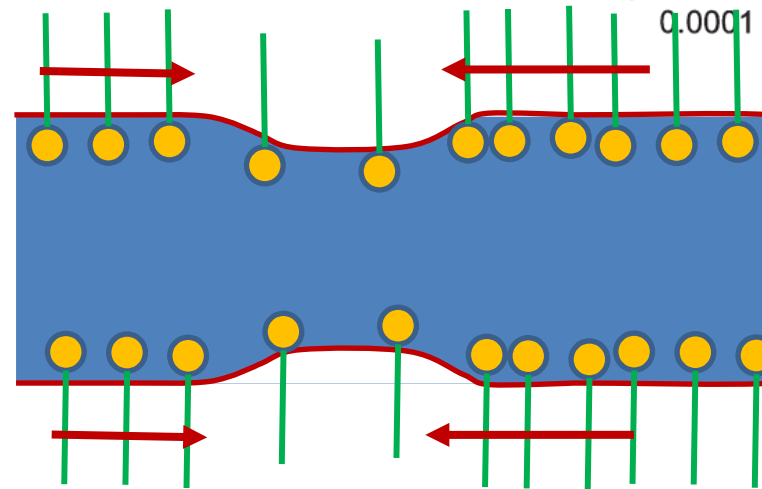
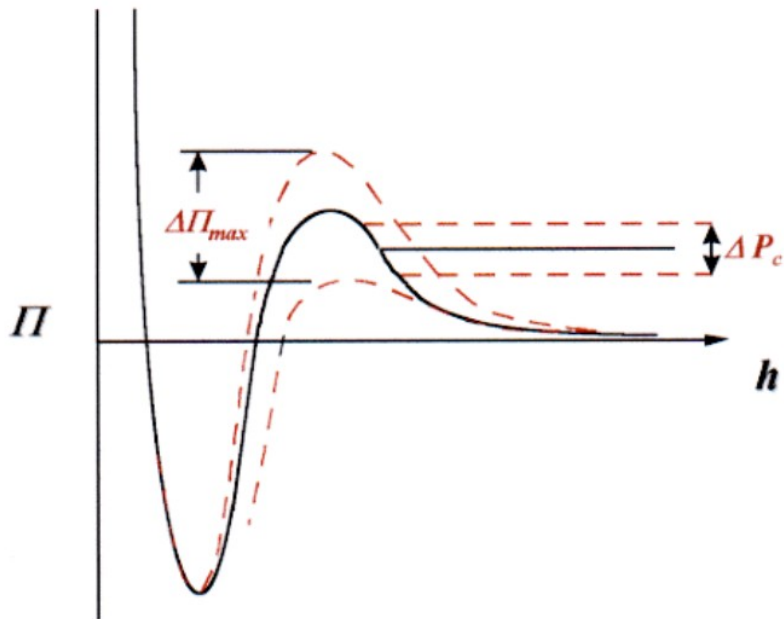


T2 process



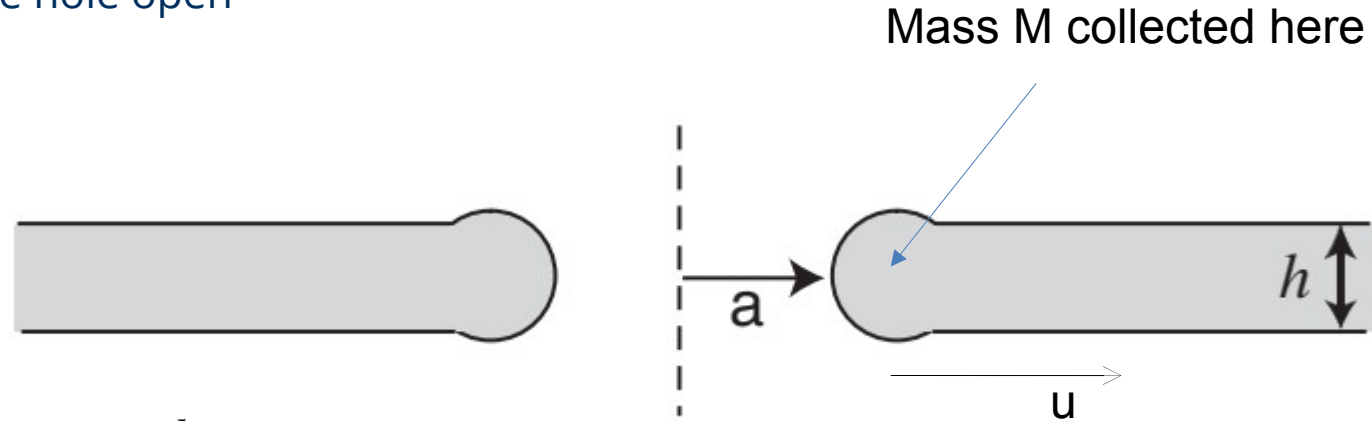
Film stability

- Film stretching → locally lower surface coverage
- Marangoni effect cures weak spots



Film rupture velocity

- Surface tension pulls the hole open



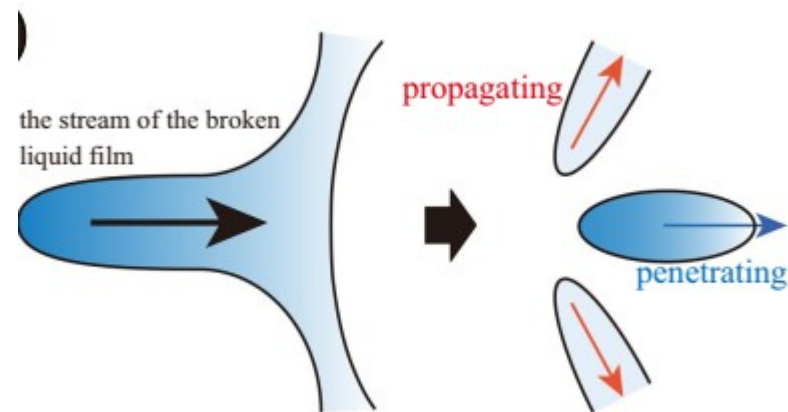
$$\frac{d(M u)}{dt} = F = 2 \gamma 2 \pi a, u = \frac{da}{dt}$$

$$M = \rho_l \pi a^2 h$$

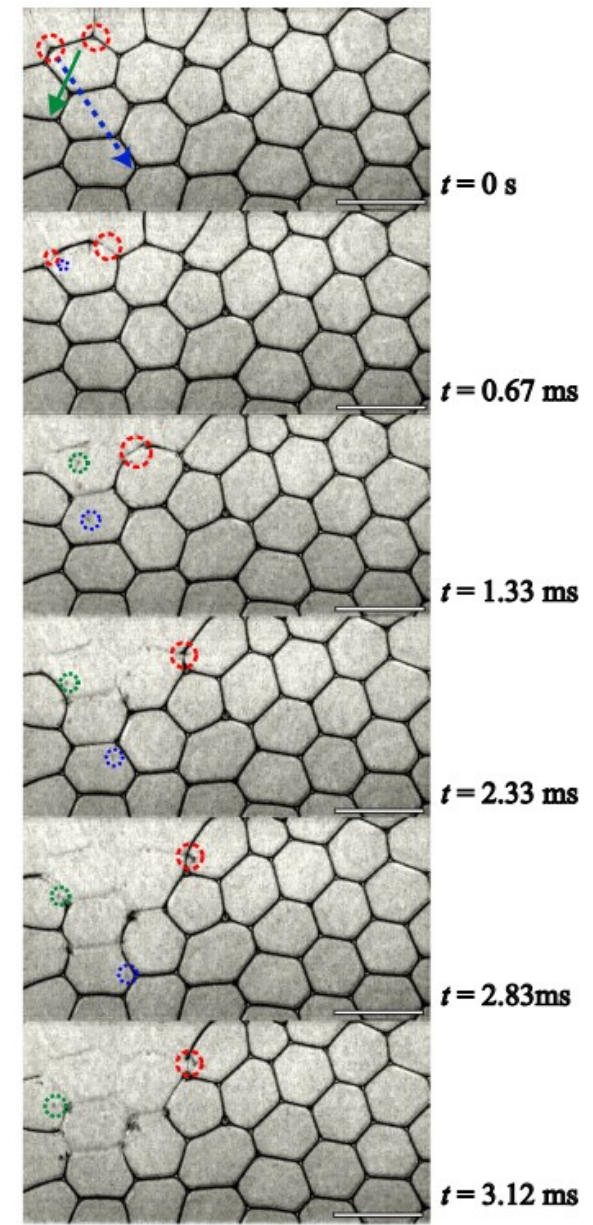
$$u = \sqrt{\frac{2\gamma}{\rho_l h}} \xrightarrow{h \approx 50 \text{ nm}} u \sim 40 \text{ m/s} \xrightarrow{R_e \approx 1 \text{ mm}} t \sim 25 \text{ ms}$$

Rupture avalanche

- Film rupture might release droplets
- Impact of droplets causes next film rupture



[Yanagisawa & Kurita, 2019]

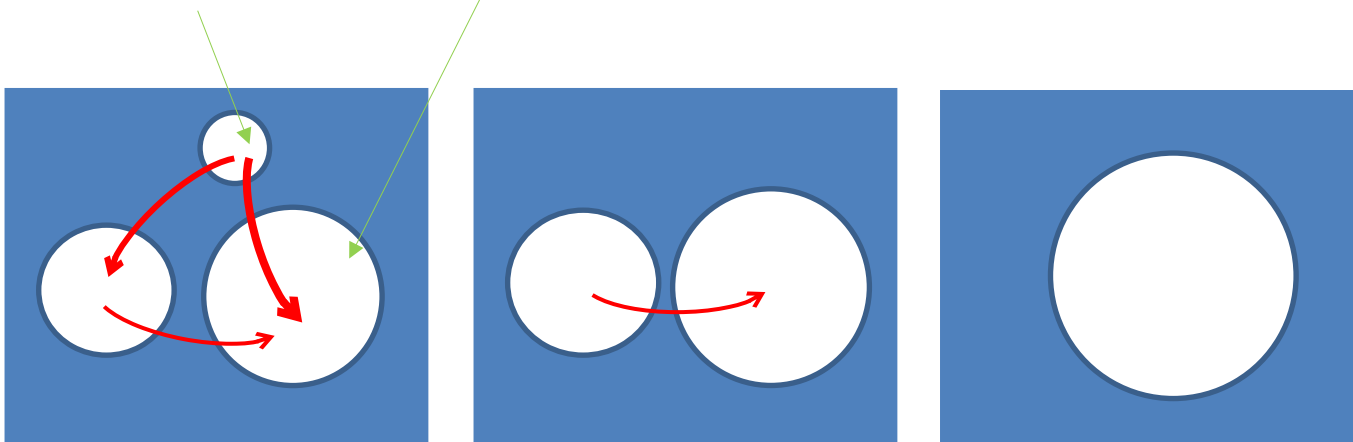


Ostwald ripening vs. von Neumann-Mullins coarsening

- Ostwald ripening for bubbly liquid
- Von Neumann-Mullins coarsening for dry foam

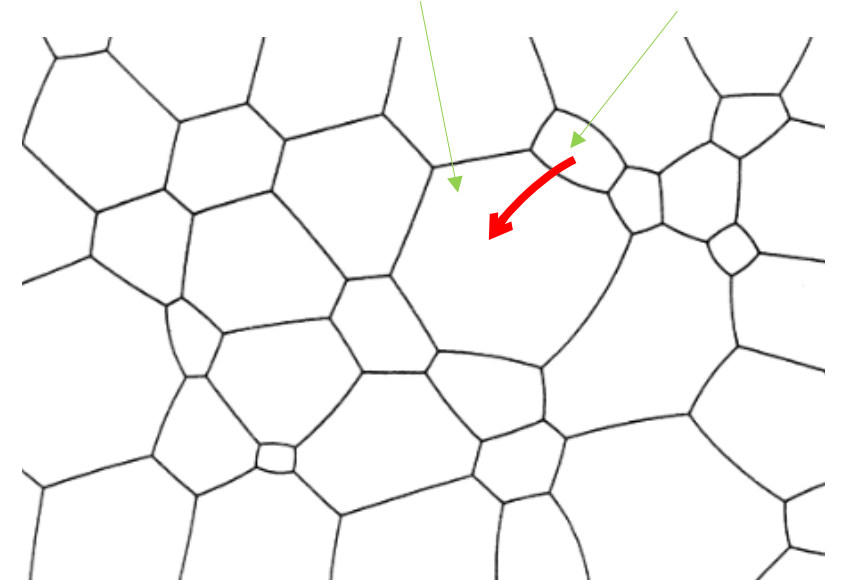
$$\Delta p = \frac{2\gamma}{R_1} - \frac{2\gamma}{R_2}$$

High pressure **Low pressure**



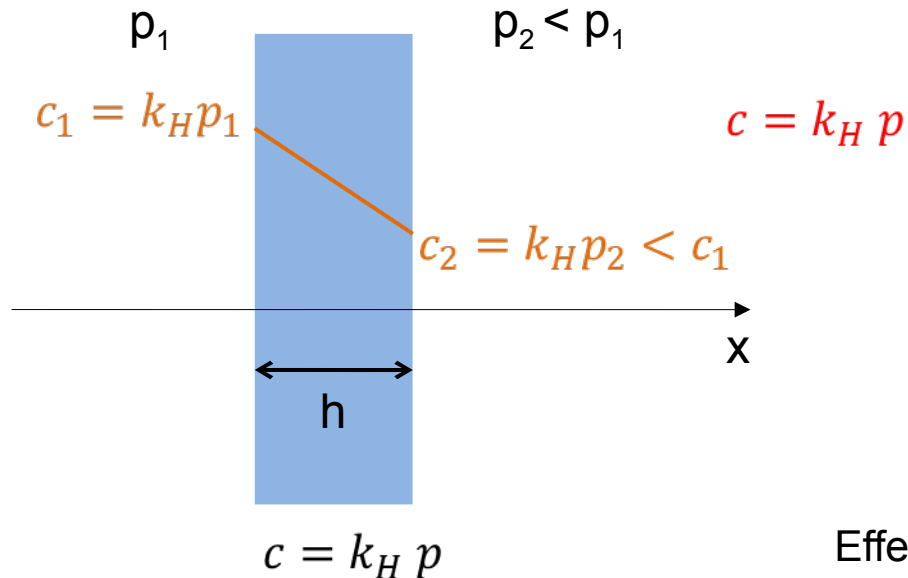
$$\Delta p = 2\gamma H_{i,j}$$

Low pressure **High pressure**



Gas diffusion

- Equilibrium over liquid lamella (steady state)
- Neglecting transport to/from the interface (pure gas)



$$\frac{\Delta c}{h} = \frac{\partial c}{\partial x} = -k_H \frac{p_1 - p_2}{h}$$

Effective diffusion coefficient D_{eff}

$$\frac{\Delta V}{A \Delta t} = D_f k_H \frac{p_1 - p_2}{h} \frac{RT}{p_0} = D_{\text{eff}} H_{1,2} \rightarrow \boxed{D_{\text{eff}} = D_f k_H \frac{2\gamma RT}{h p_0}} \quad [D_{\text{eff}}] = \text{m}^2/\text{s}$$

$\Delta p = 2\gamma H_{i,j}$

Molecular flux through Area A (Fick's law):

$$\frac{\Delta n}{\Delta t} = -D_f A \frac{\partial c}{\partial x}$$

$$p_0 V = n R T$$

Volumetric flux through Area A:

$$\frac{\Delta V}{\Delta t} = \frac{\Delta n RT}{\Delta t p_0} = -D_f A \frac{\partial c}{\partial x} \frac{RT}{p_0}$$

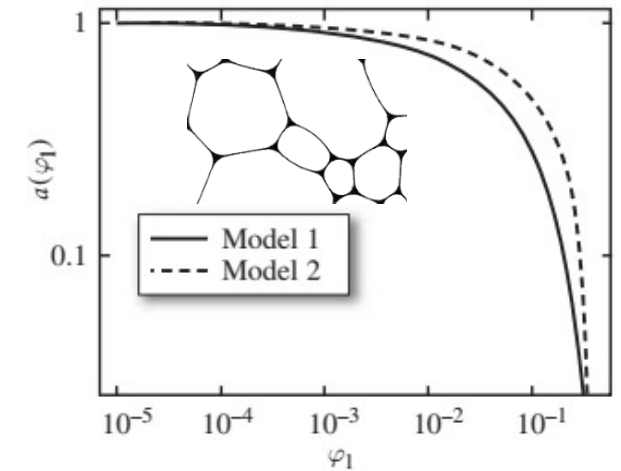
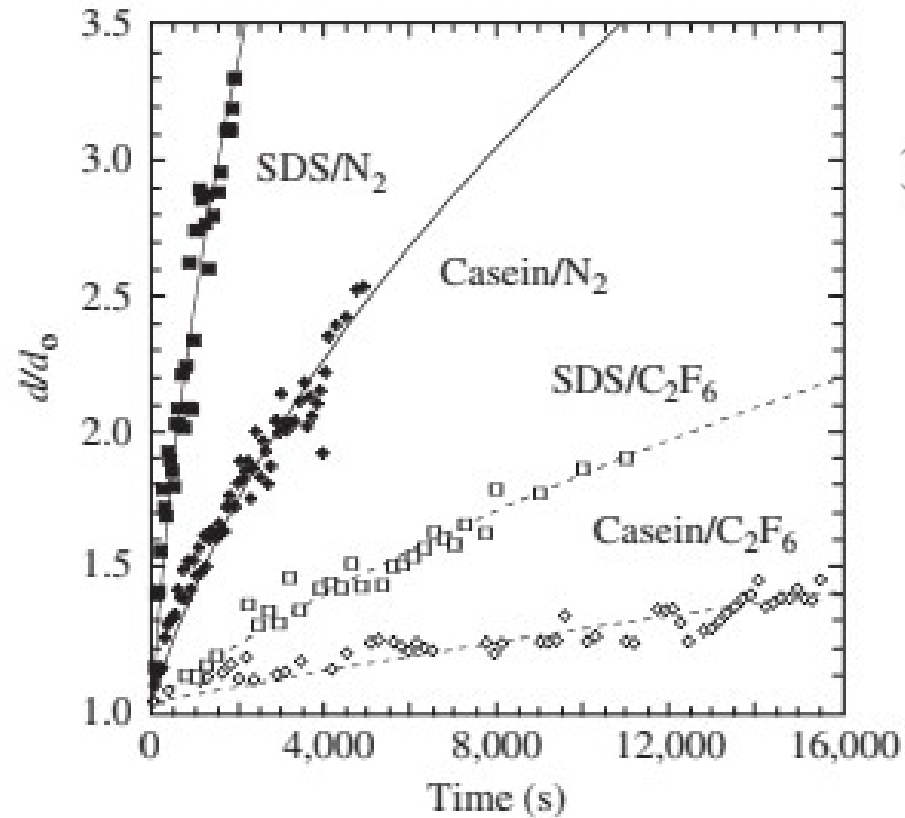
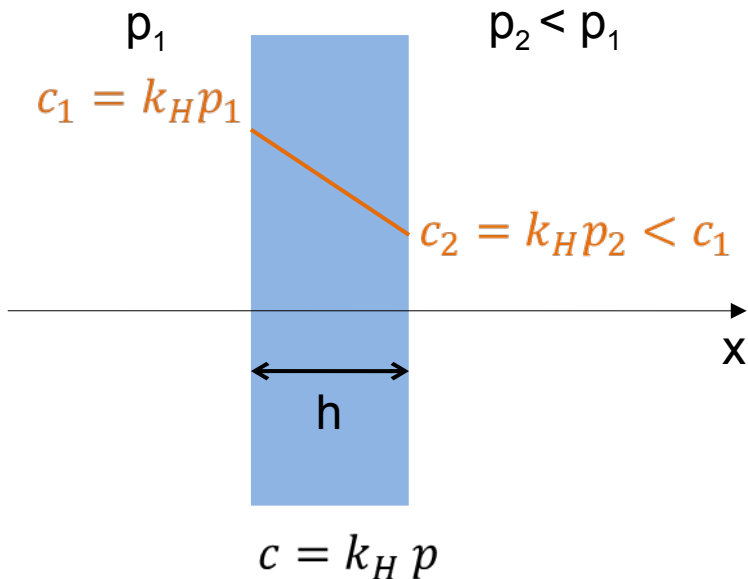
$$\Delta V = \Delta n \frac{RT}{p_0}$$

Gradient over lamella:

$$\frac{\Delta V}{A \Delta t} = D_f k_H \frac{p_1 - p_2}{h} \frac{RT}{p_0}$$

Gas diffusion

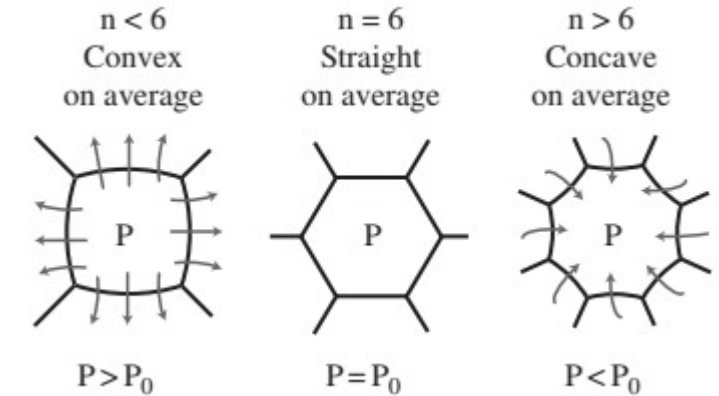
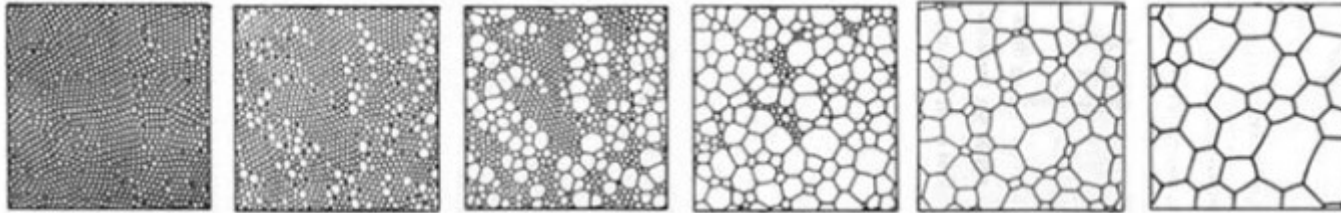
- C₂F₆ → very stable foam
- N₂, CO₂ → fast coarsening



$$D_{eff} = D_f k_H \frac{2\gamma RT}{h p_0} a(\varphi_l)$$

Growth of bubble size

- Small bubbles → small number of neighbours → convex, high mean curvature H_{ij}
- Small bubble vanish, larger bubbles grow



- Average bubble size evolution:

$$R = R_0 \sqrt{1 + \frac{t}{t_c}}$$

$$t_c \approx \frac{\langle V(t=0) \rangle^{2/3}}{b D_{eff}}, b \approx 1$$



Exercise: time scale for Coarsening

- Time for a foam to double its average bubble radius by coarsening?
- SDS foam, 50 nm film thickness
- A) 0.1 mm bubble radius, CO₂, 10 % liquid fraction

$$k_H = 3.4 \times 10^{-6} \frac{\text{mol}}{\text{m}^3 \text{Pa}}$$

$$D_f = 1.9 \times 10^{-9} \frac{\text{m}^2}{\text{s}}$$

$$t_c \approx \frac{\langle V(t=0) \rangle^{2/3}}{b D_{eff}} = 290 \text{ s}$$

$$\frac{R}{R_0} = 2 = \sqrt{1 + \frac{t}{t_c}} \rightarrow t = 3 t_c = 870 \text{ s} = 14 \text{ min}$$



- B) 5 mm bubble radius, C₂F₆, 0.1 % liquid fraction

$$k_H = 5.8 \times 10^{-7} \frac{\text{mol}}{\text{m}^3 \text{Pa}}$$

$$D_f \approx 1.2 \times 10^{-9} \frac{\text{m}^2}{\text{s}}$$

$$t_c \approx \frac{\langle V(t=0) \rangle^{2/3}}{b D_{eff}} = 3.4 \times 10^6 \text{ s}$$

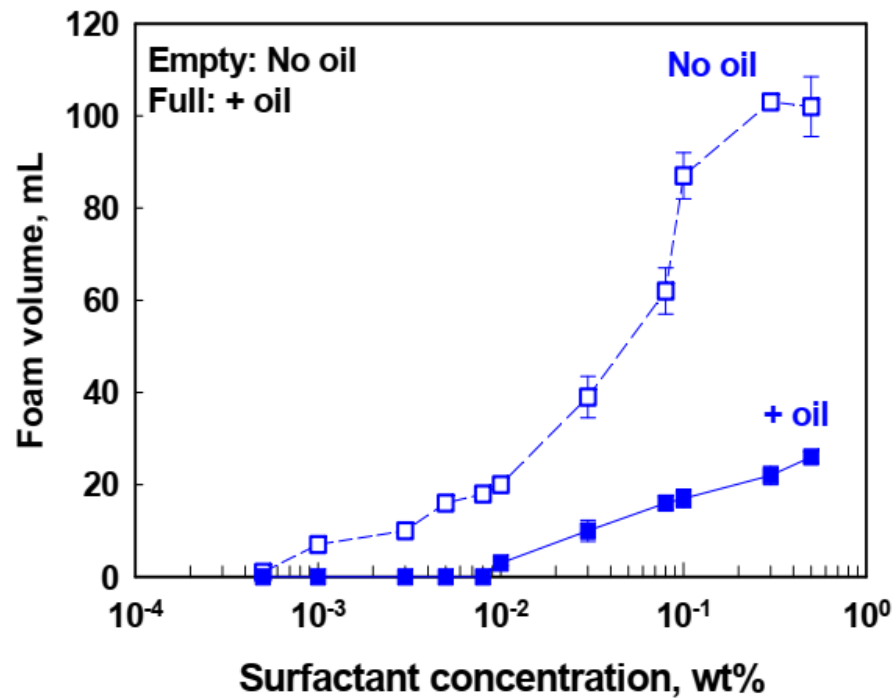
$$\frac{R}{R_0} = 2 = \sqrt{1 + \frac{t}{t_c}} \rightarrow t = 3 t_c = 10^7 \text{ s} = 100 \text{ days}$$

Air: 12 days



Bartsch test

- Shaking with defined frequency, time
- Measurement of resulting foam volume



Bikerman standardized test

- Constant gas flow rate through a porous plate
- Measurement of (steady) resulting foam height

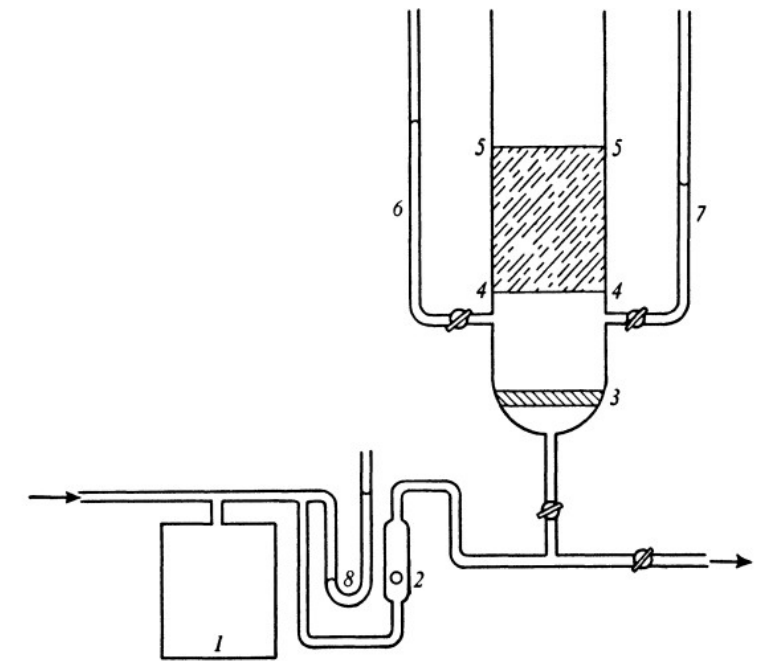
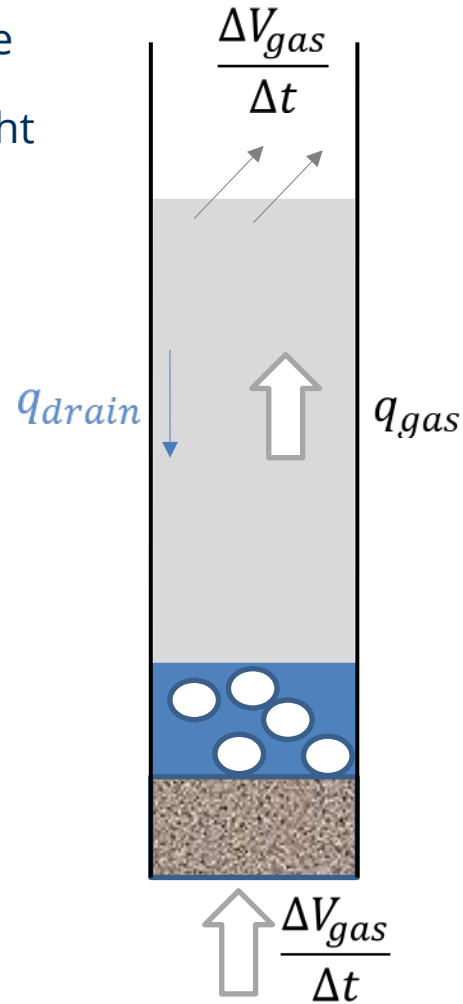
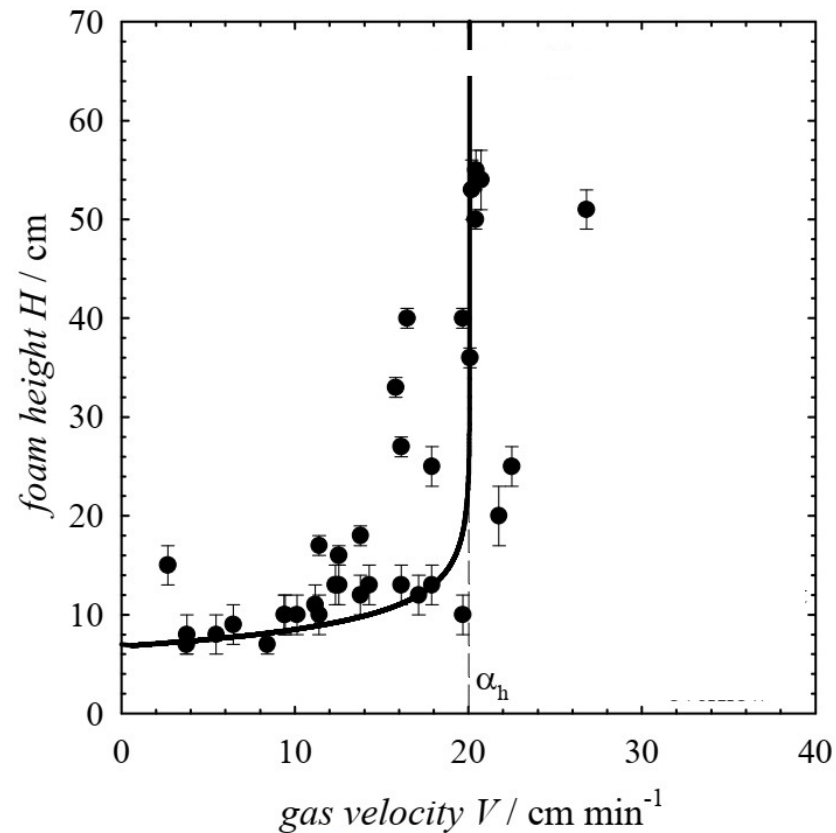
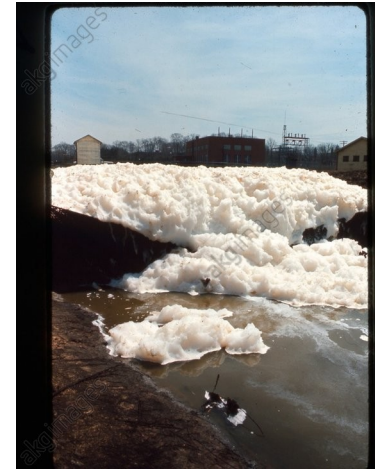


Fig. 3.6. Determination of the liquid volume in foam during bubbling. 1 is the nitrogen reservoir; 2 is the flow meter; 3 is the porous plate; 4, 4 and 5, 5 are the boundaries of the foam column; 6 is a buret; and 7 and 8 are manometers (after reference ⁴⁹).

[Bikerman, Foams, 1973]

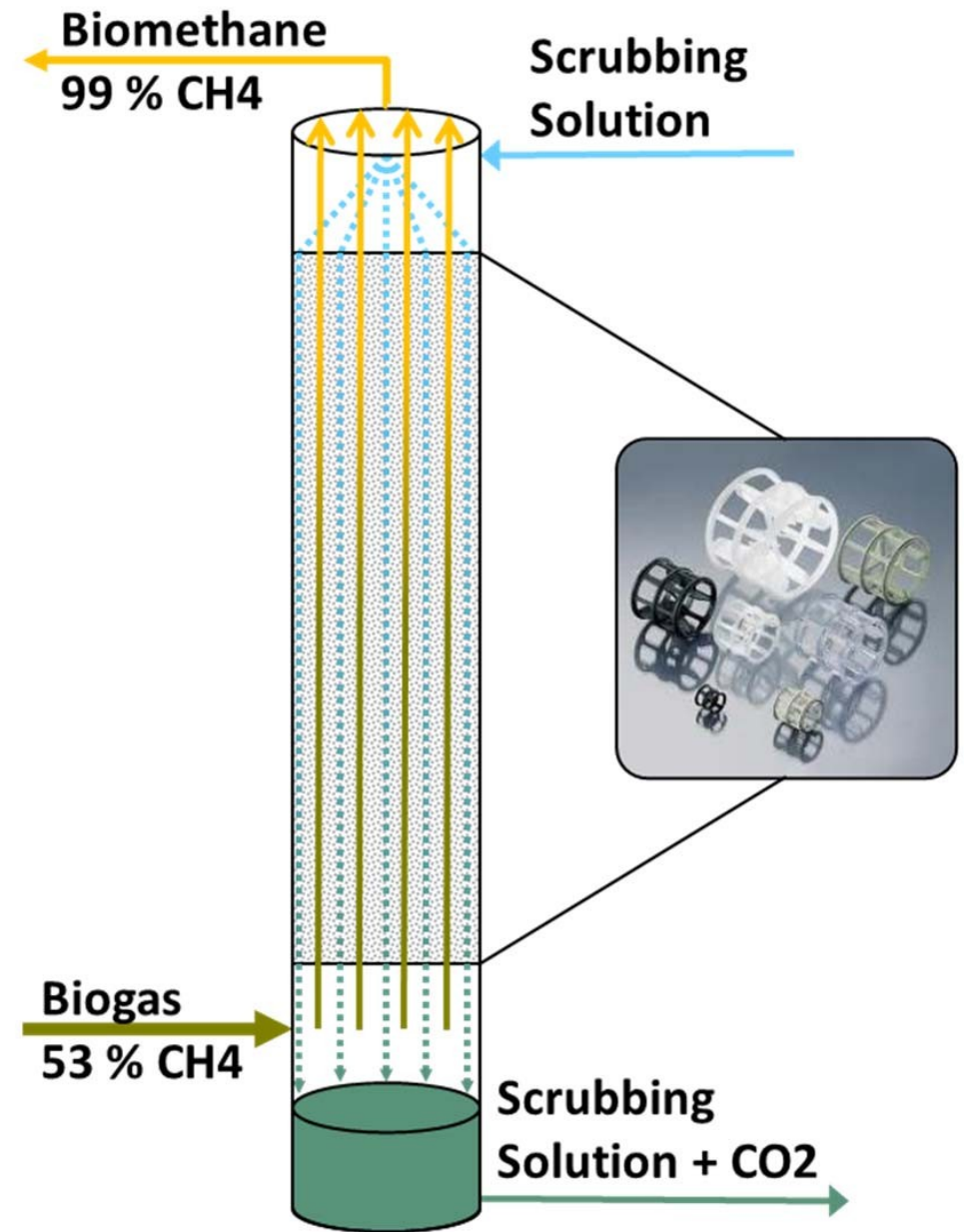
Structure

- Review lecture 10
- Film rupture
- Coarsening
- Stability testing
- Defoaming



Typical applications

- Removal of CO₂ from biogas
- Packed bed of wrinkled bodies → foam generation
- Foam blocks device, reduces efficiency
- Scrubbing solution contains defoaming agent
- → film rupture



Types of Antifoams

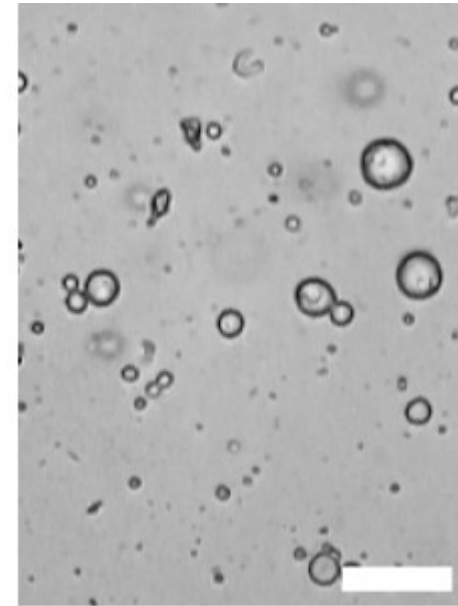
- Additives to the solution that prevent foam formation and/or destroy foam
- Solid antifoams
 - silica, wax, polymer
- Liquid antifoams
 - triglycerides
 - silicon oils, mineral oils
- Solid+liquid antifoams
 - oil + particles

Silica particles



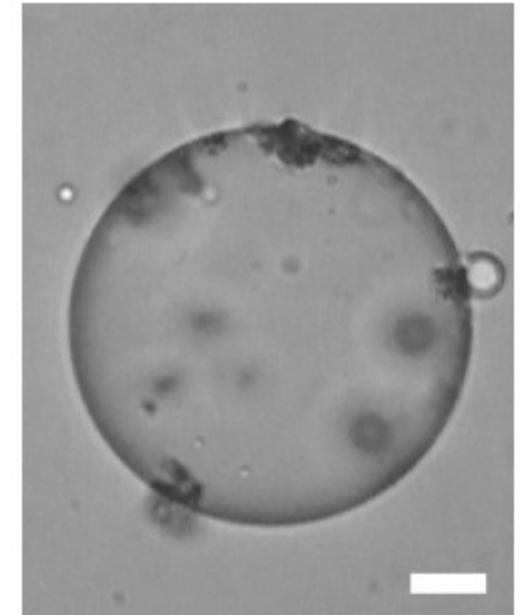
100 nm

Oil emulsion



30 μm

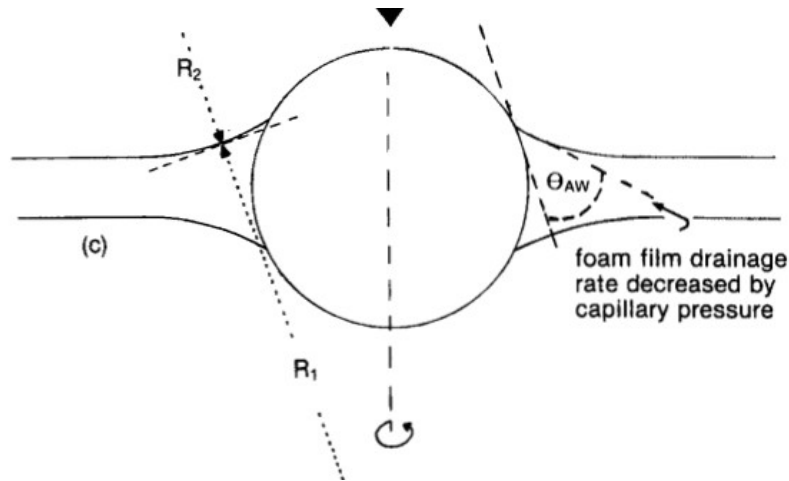
Oil+particles



1 μm

Film stabilisation by particles

- Depending on contact angle
- Hydrophilic particles ($\theta < 90^\circ$) reach to stable position

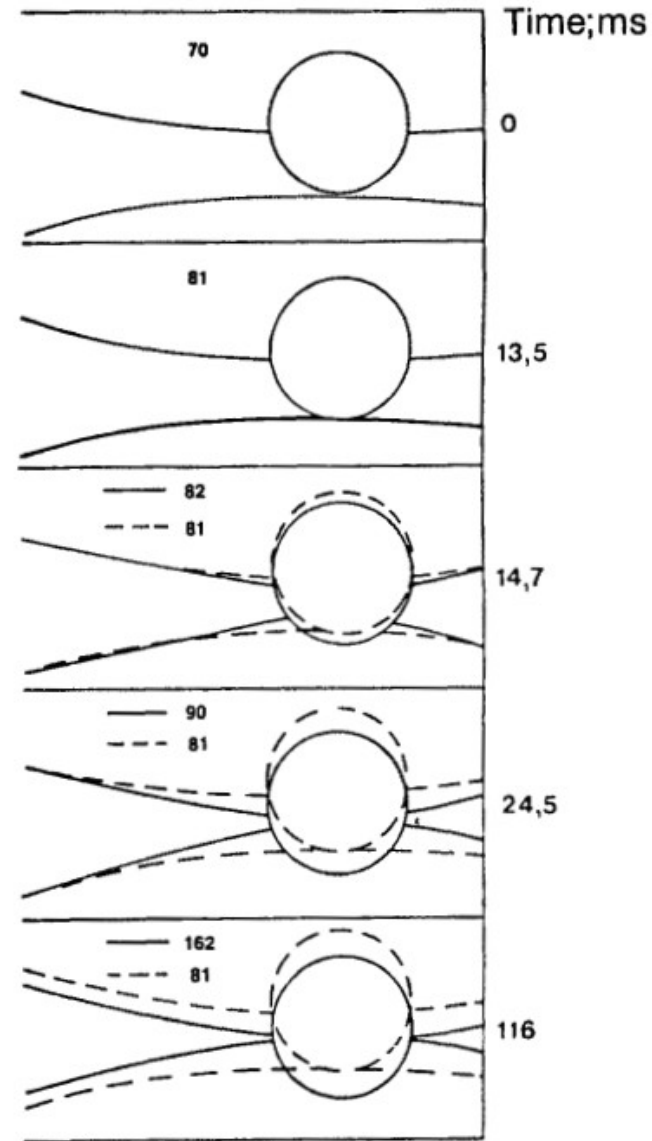


	Endogenous Particle Stabilization (EPS)	Solid Particle Stabilization (SPS)	Oxide Network Particle Stabilization (ONS)
Barrier Effect: Schematic	Particles develop from the melt during solidification and are part of the microstructure.	Ceramic particles are deliberately added to the melt.	Oxides are accidentally produced during melt atomization.
Barrier Effect: Experimentally	Coarse Fine	Two approaching interfaces Cell wall	

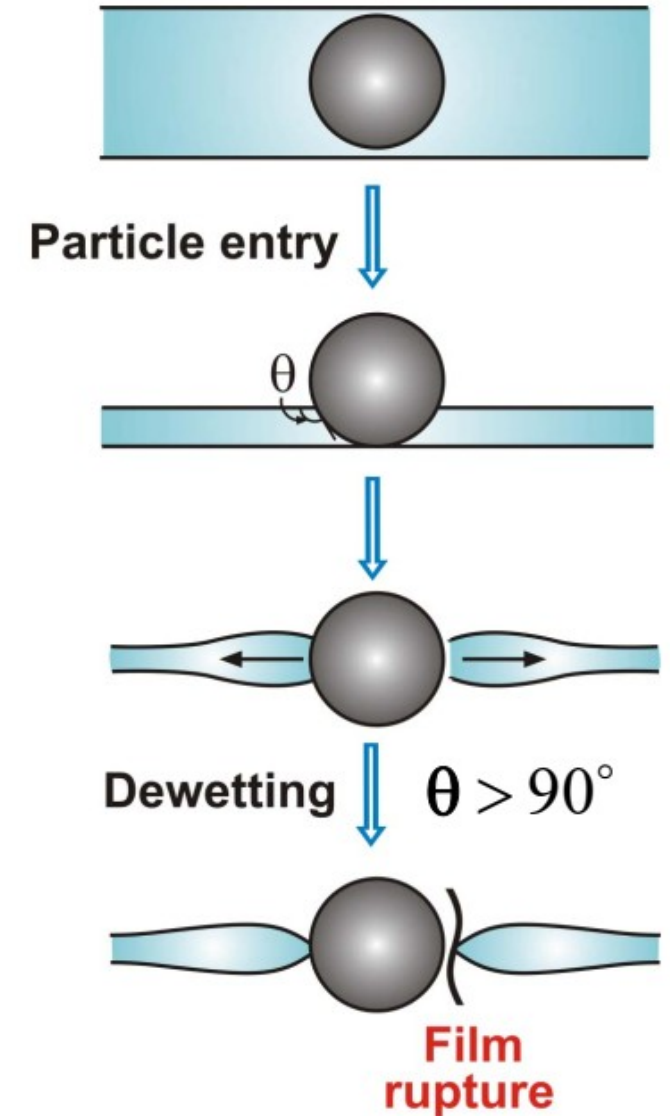
[Körner et al., 2005]

Film rupture by particles

- Depending on contact angle
- Hydrophobic particles ($\theta > 90^\circ$)
- Cause de-wetting and film rupture

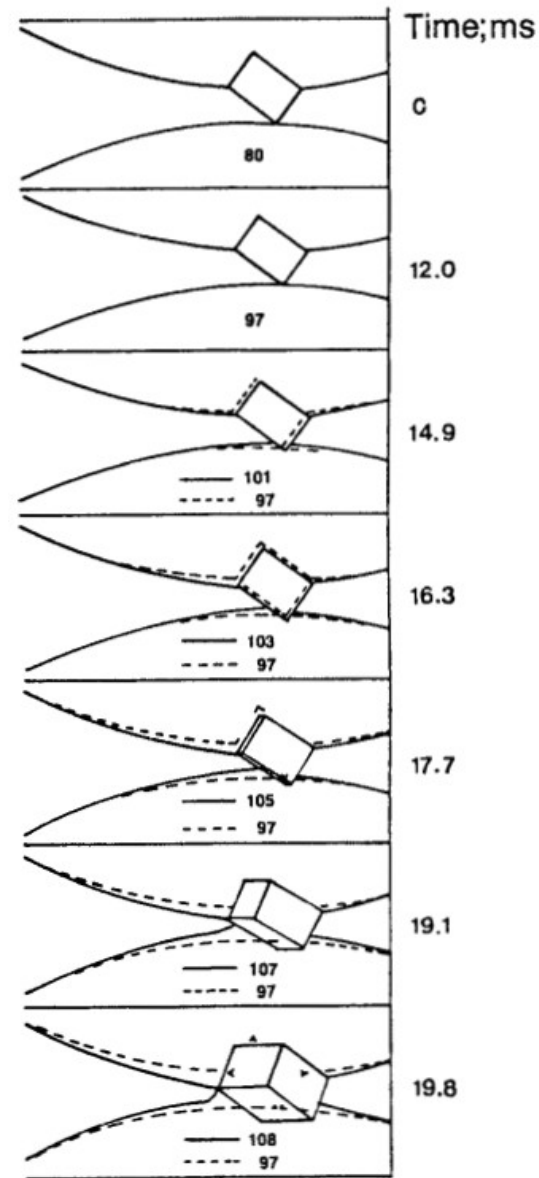


[Garret, Defoaming, 1992]

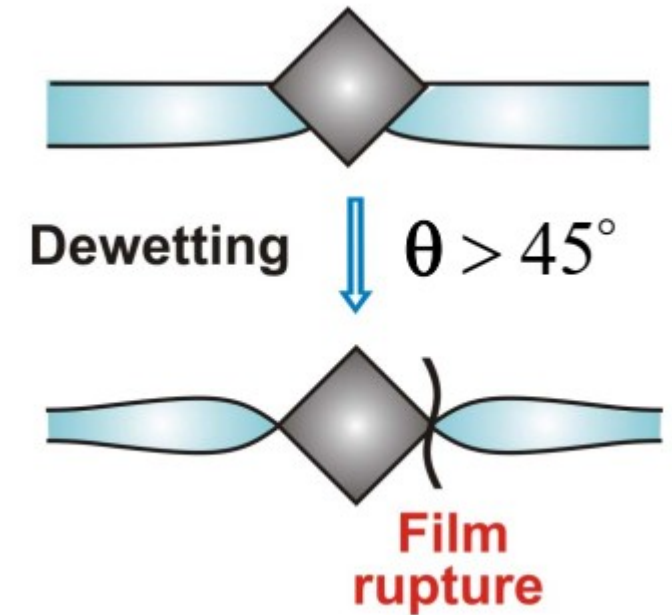


Film rupture by particles

- Shape of particles can support film rupture
- Sharp edges prevent stable situations
- Relevant e.g. for mineral particles

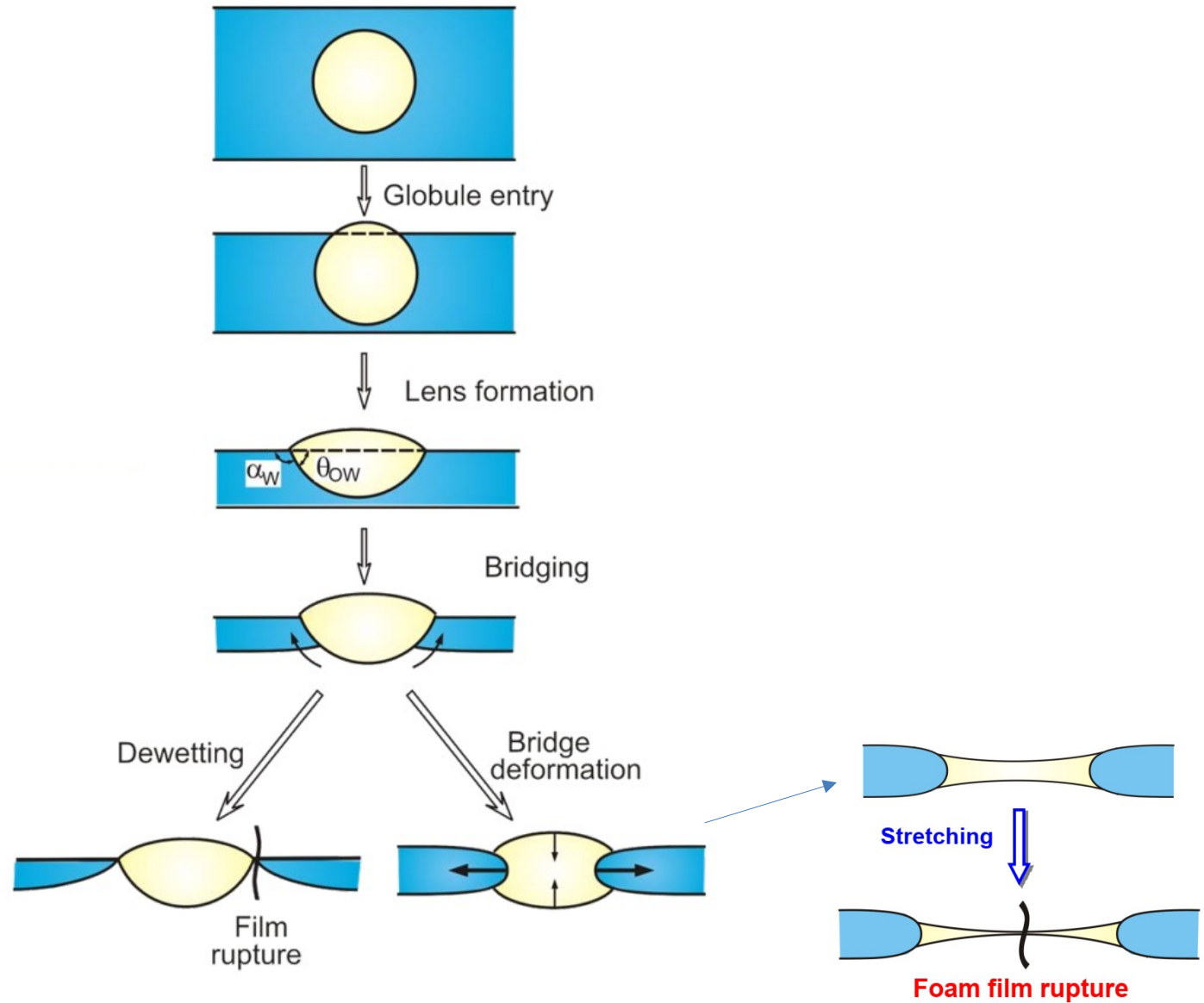


[Garret, Defoaming, 1992]



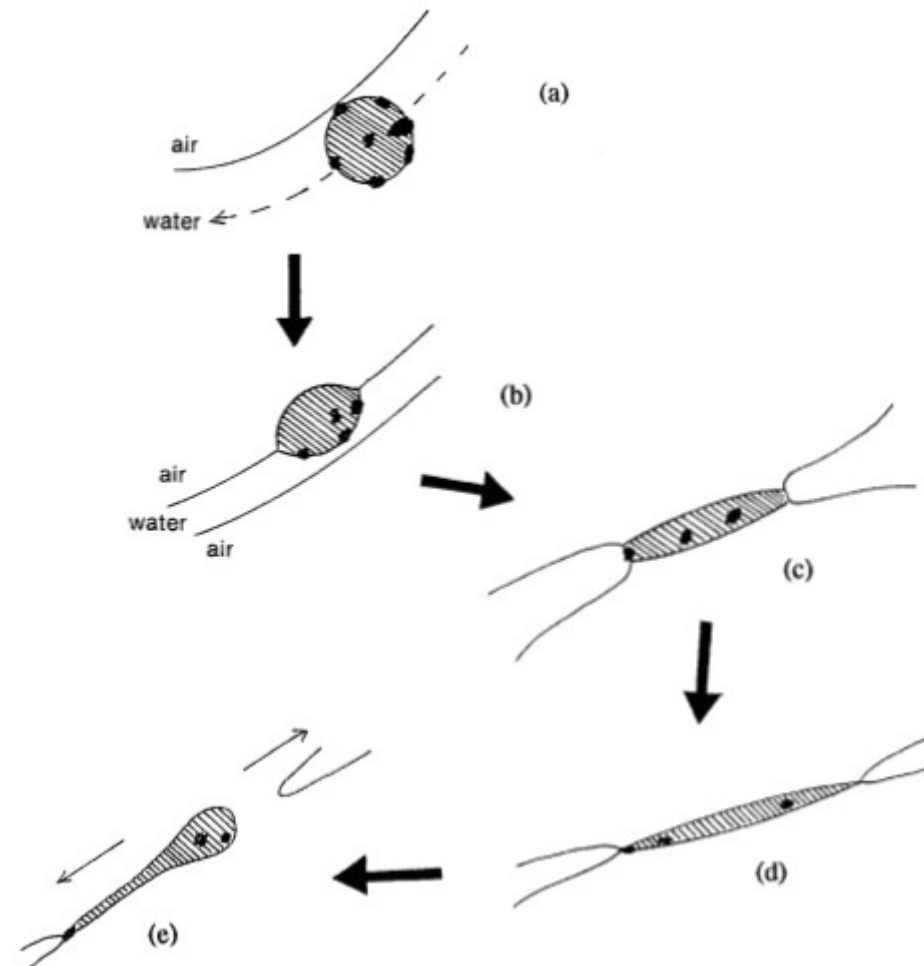
Film rupture by liquids

- Droplets adsorb at water-air interface
- Droplet bridges film
- Either dewetting or bridge-stretching
- Depending on contact angles
- Depending on drop rheology



Film rupture by compounds

- Particles support rupture of air-water-oil film
- Oil ruptures film by de-wetting

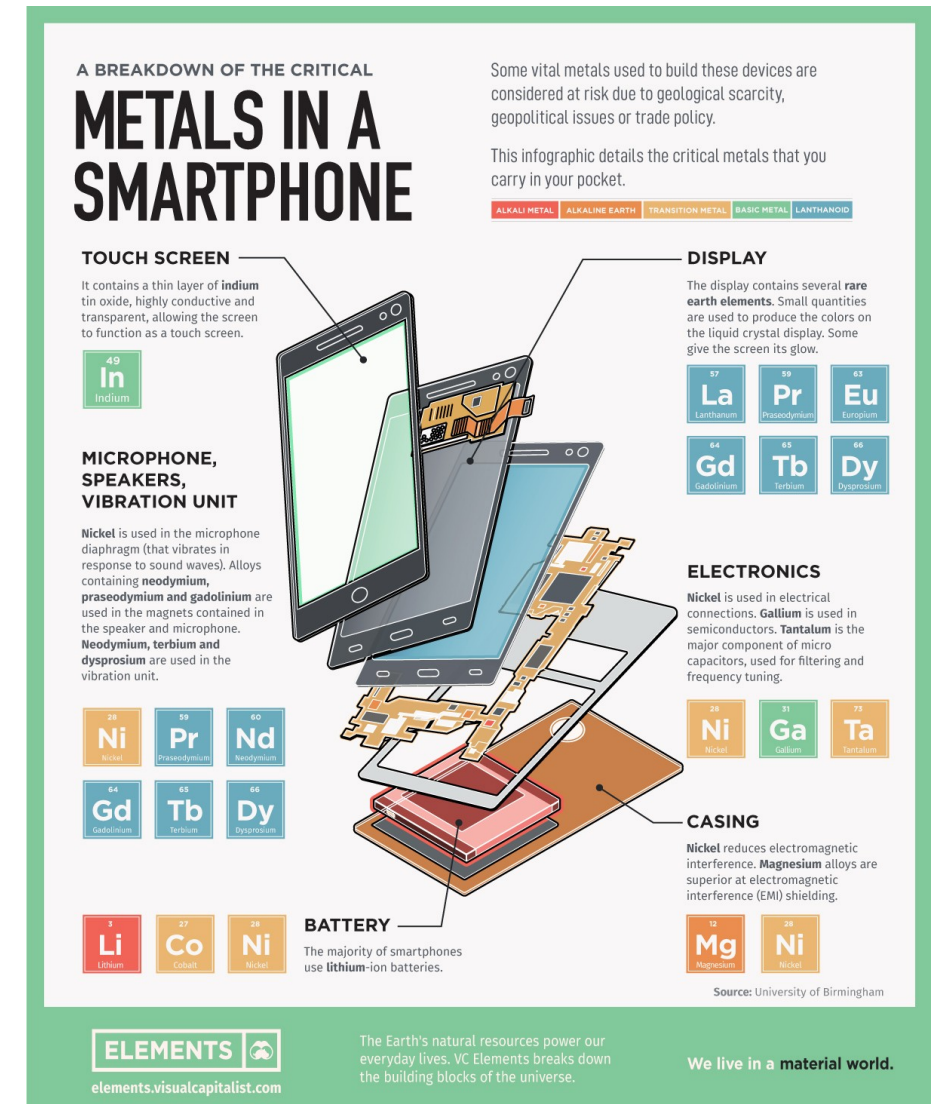
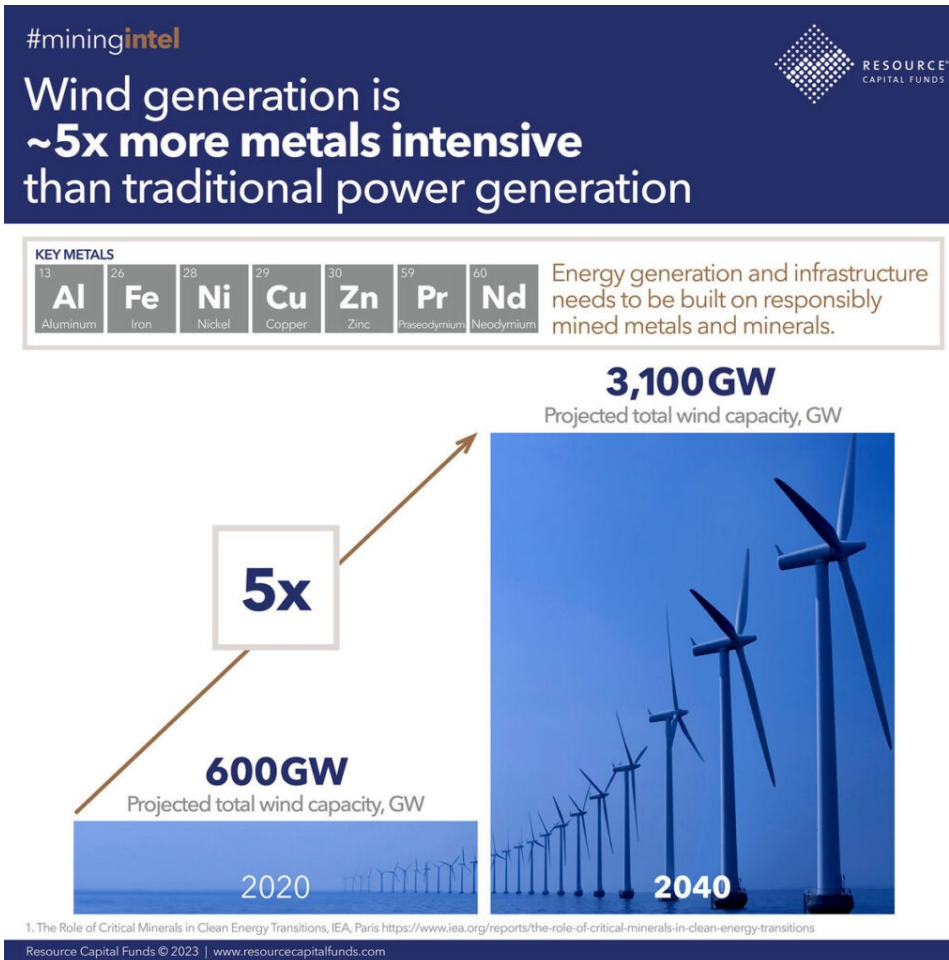


[Garret, Defoaming, 1992]

Structure

- Review lecture 11
- Mineral flotation
- Surfactants in Flotation
- Particle attachment
- Froth zone
- Cell design
- Related applications

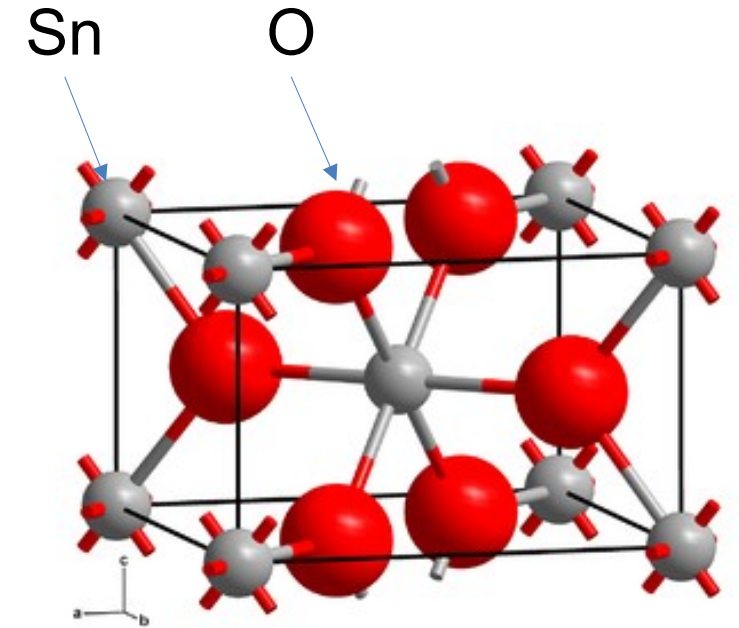
Metal usage



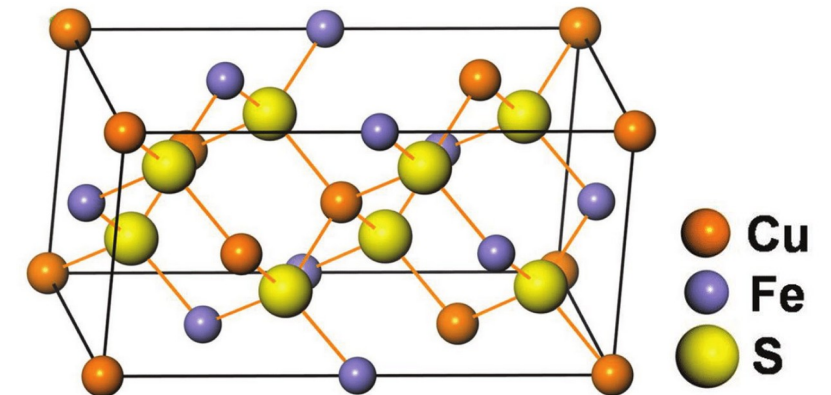
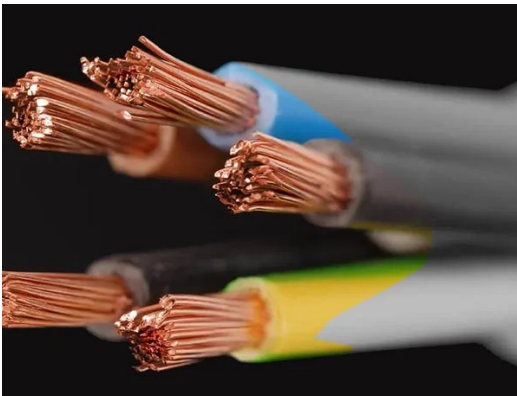
Metals and minerals



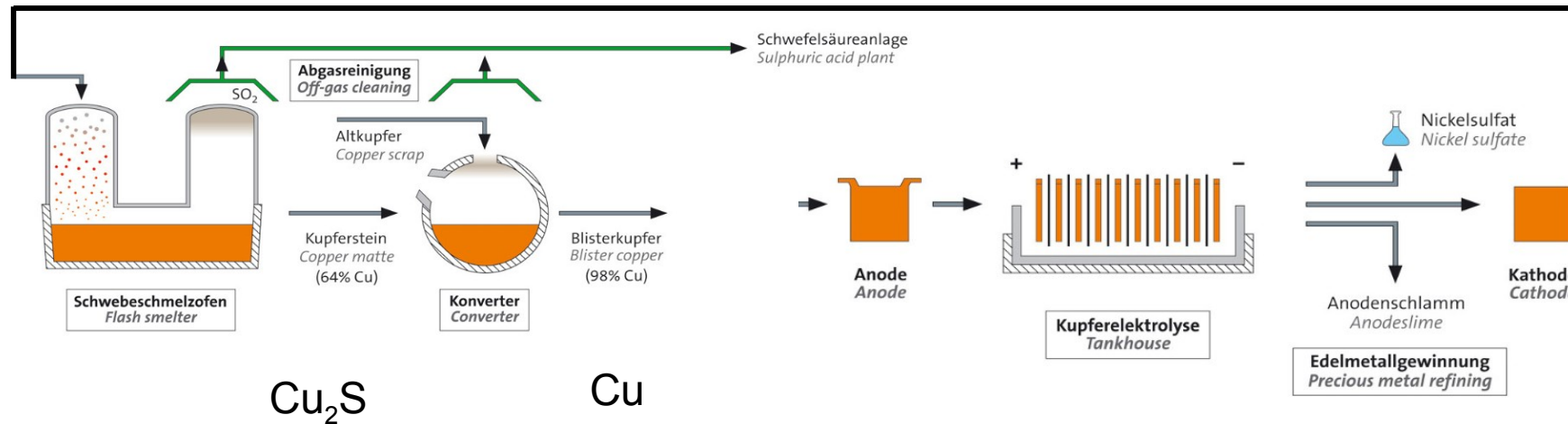
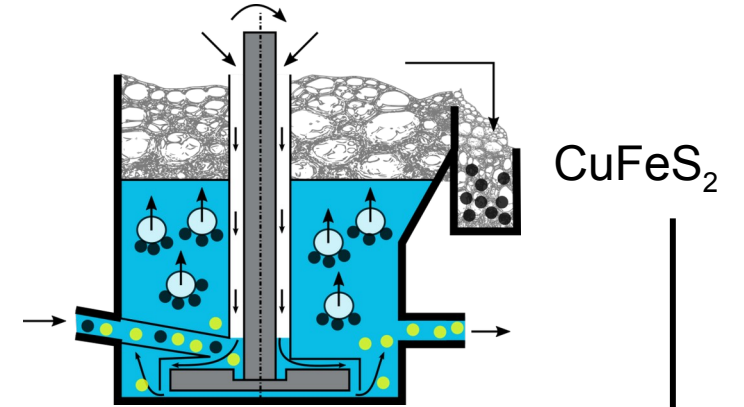
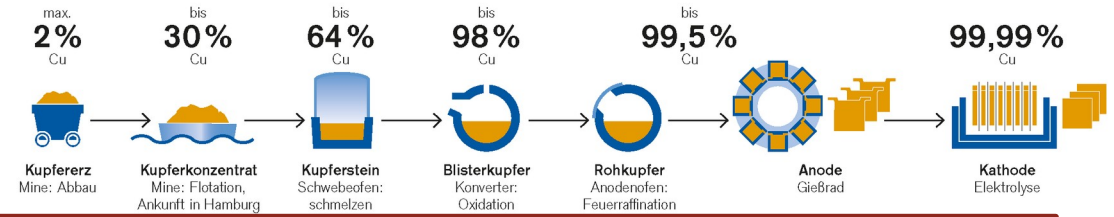
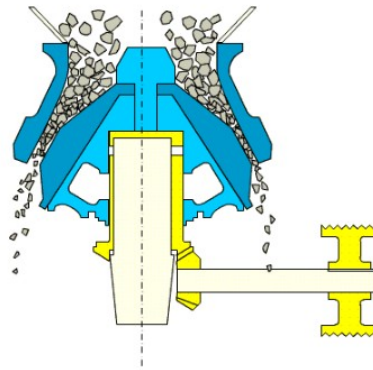
Kassiterit = SnO_2



Chalkopyrit = CuFeS_2



From ore to copper



Sorting in early industrialization

- 18th century: Bal Maidens in Cornwall
- Typically women of age between 8 and 24
- Sorting ore for crushing



Mineral separating techniques

- How to separate valuable mineral particles from valueless gangue particles?



Grinded
material

Separation techniques in mineral processing and
recycling

Density sorting

> ca. 2-5 mm

Magnetic
separation

> ca. 500 μm

> ca. 100 μm (high field gradient mag. sep.)

Electric
separation

Physical-
chemical
separation

ca. (40...200) μm

Flotation patent

- First historically acknowledged patent on flotation in 1877
- Graphite flotation
- Bessel Brothers, Dresden, Germany

Adolph Bessel,
der Erfinder der Flotation



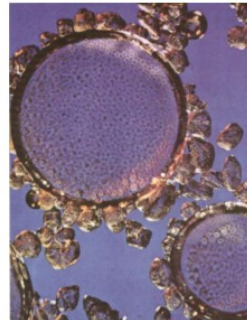
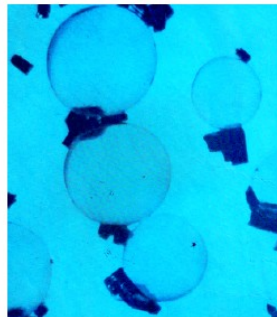
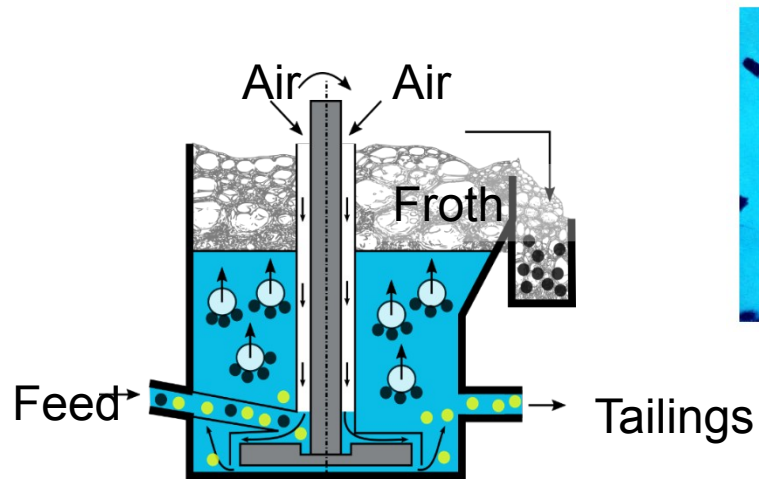
Froth flotation

- Most important separation technique in mining
- Extraction of valuable mineral particles from valueless gangue particles
- Billion tons of ore are processed every year
- 2% of world's primary energy goes into mineral processing

- Also employed for paper recycling, waste water treatment
- Research regarding electronic waste and lithium-ion battery recycling

Froth flotation

- Grinded particles added to surfactant solution
- Collectors (surfactants) render mineral particles hydrophobic, suppressors render gangue hydrophilic
- Bubbles are introduced, pick up particles, transport to top
- Frothers (surfactants) cause generation of meta-stable froth zone
- Overflowing froth extracts particles

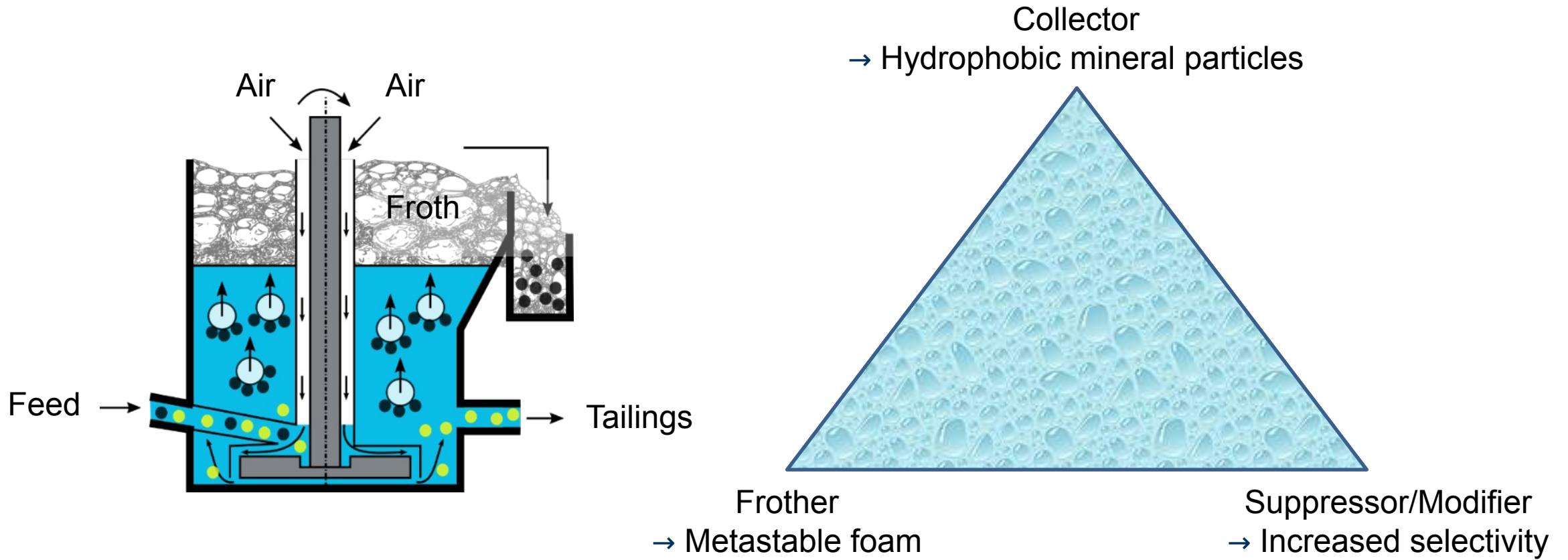


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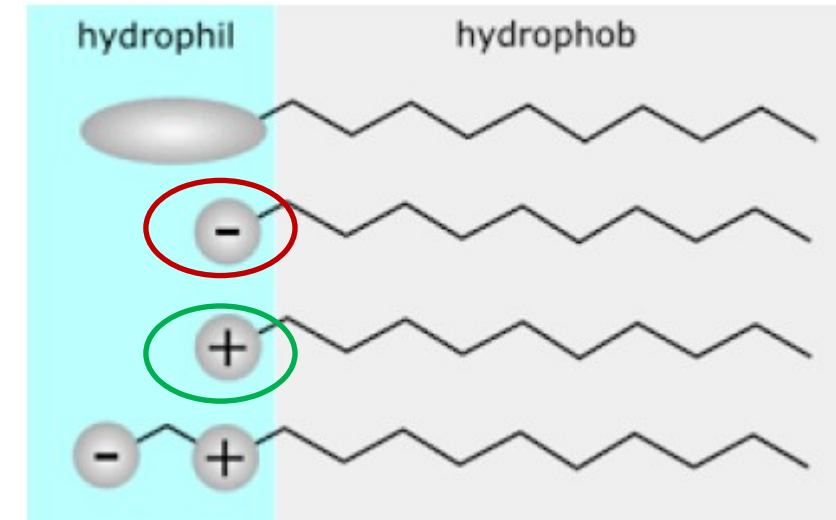
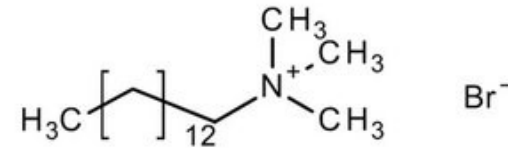
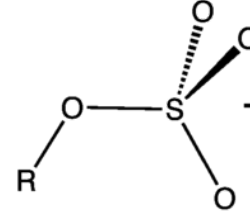
Types of surfactants

- Important branch of chemical industry
- Purposely designed molecules for different classes of ores/minerals

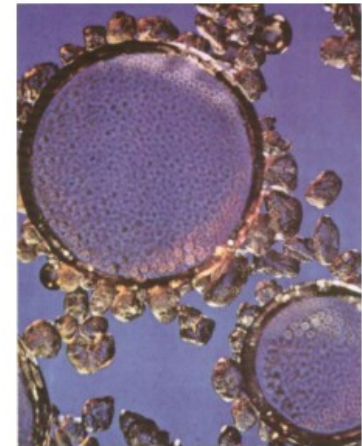
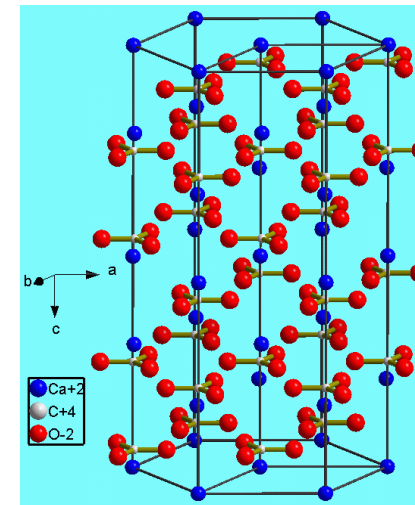


Collector

- Ionic surfactants
- Typical **anionic** surfactants: organosulfates (e.g. SDS)
- Typical **cationic** surfactants: quaternary ammonium cations (e.g. TTAB)

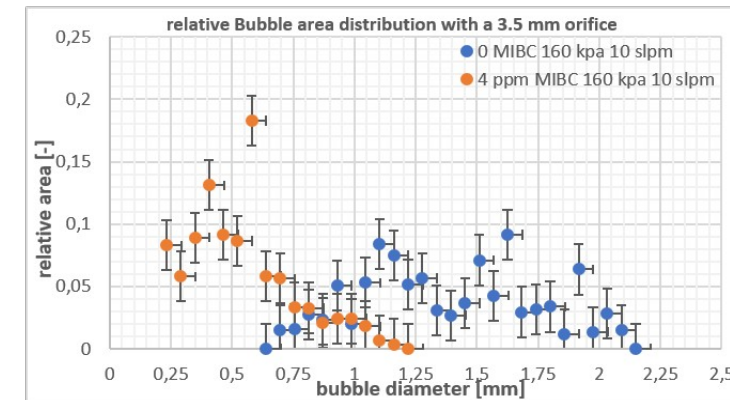
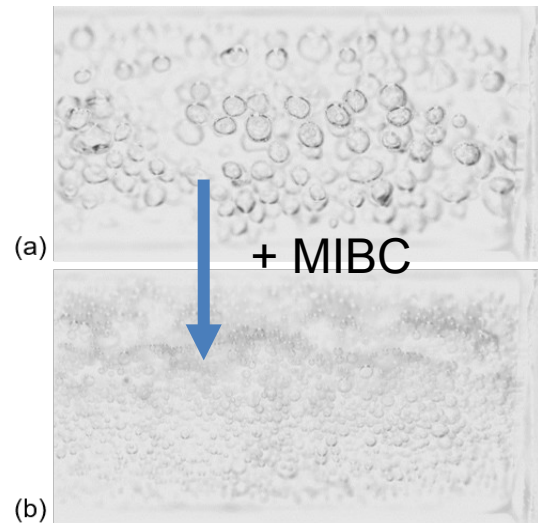
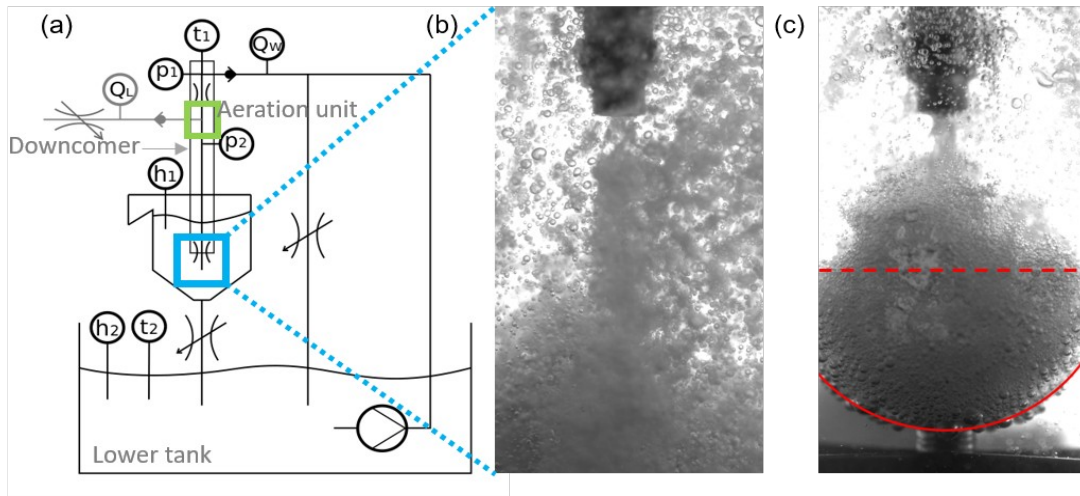
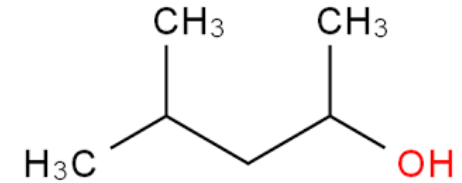
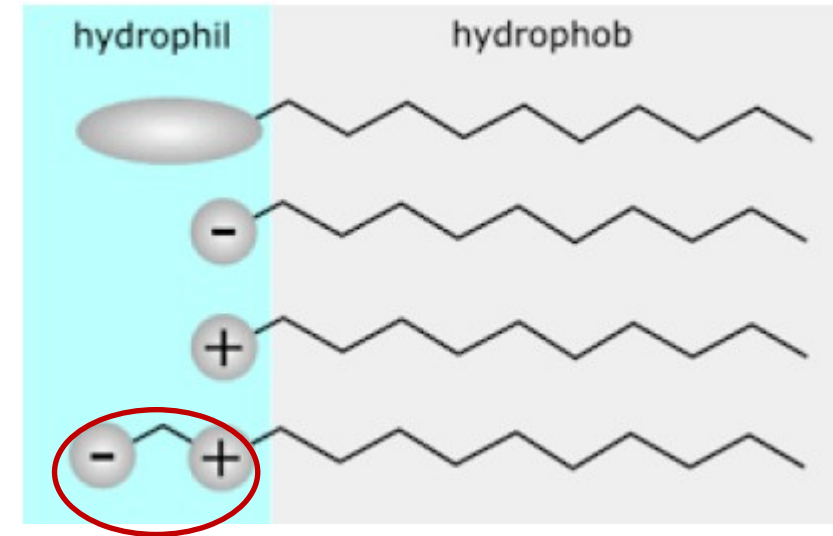


- Optimum at $C_{12} \dots C_{14}$
- Compromise between solubility (few C-atoms) and surface activity (many C-atoms)
- Particles are conditioned **before** entering the flotation cell



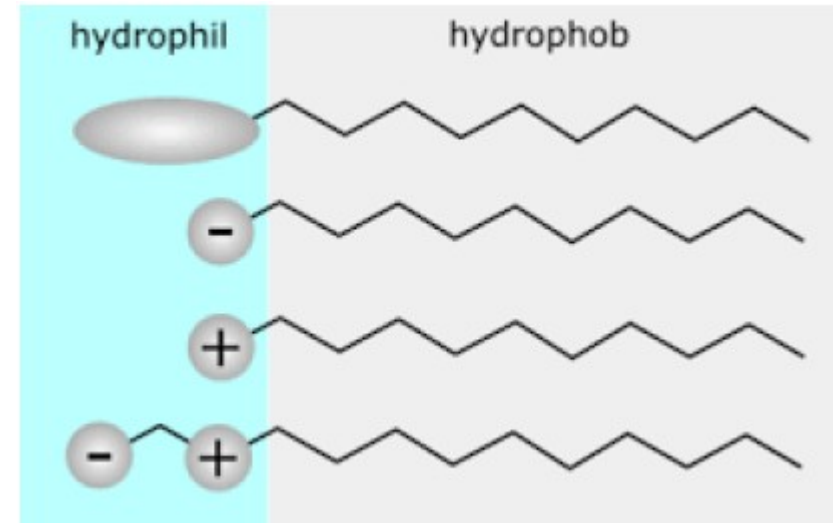
Frother

- Typical frother: methyl isobutyl carbinol - MIBC
- Hydroxy-group is polar, but not charged (=hydrophilic)
- Molecule is unpolar, otherwise (= hydrophobic)
- → generates small bubbles
- → generates meta-stable froth



Frother vs. Collector

- Both are surfactants
- Purposely designed molecules for different classes of ores/minerals

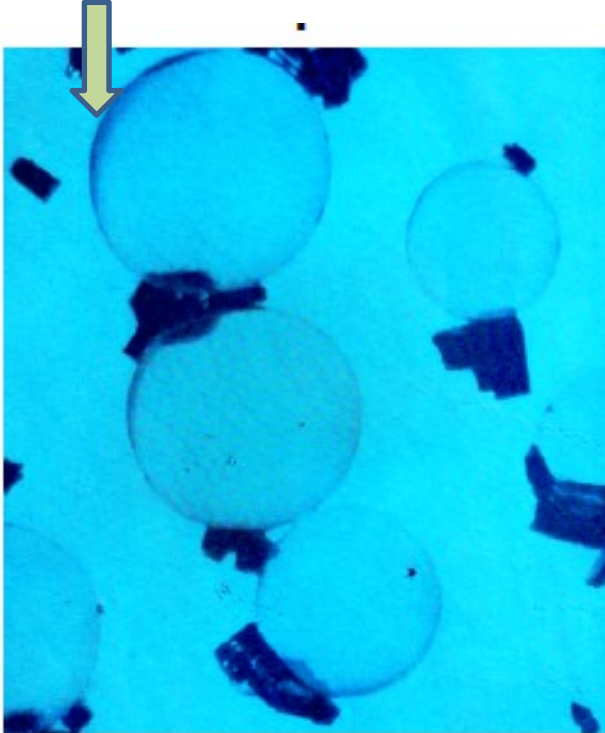


	Collector	Frother
Type	Ionic surfactants, charged head group	Non-ionic surfactants, polar head group
Function	- Adsorbs at solid-liquid interface - Hydrophobizes mineral particles	- Adsorbs at air-liquid interface - Creates metastable froth - Hinders bubble coalescence

Frother vs. Collector

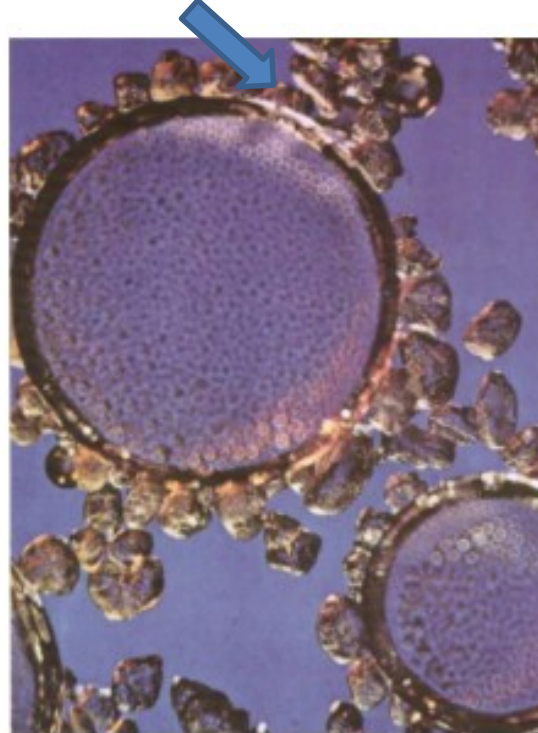
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Frother

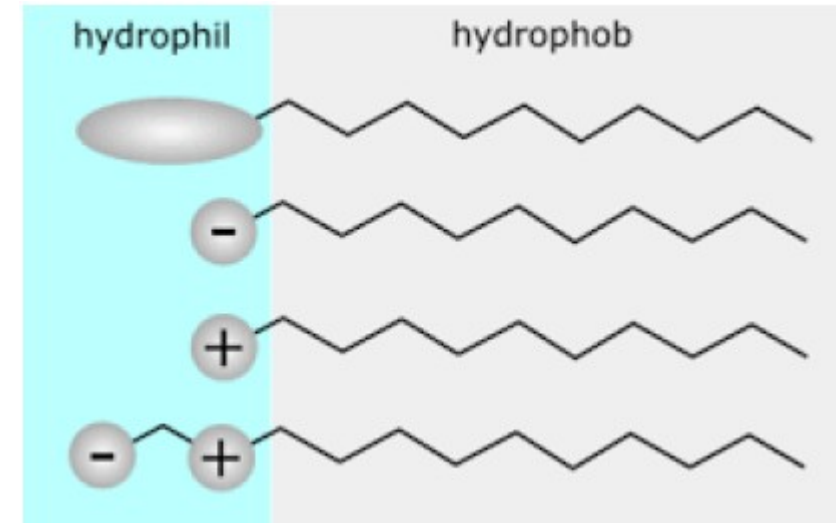


Quelle: Gaudin, Flotation

Collector



Quelle: FLSmidth

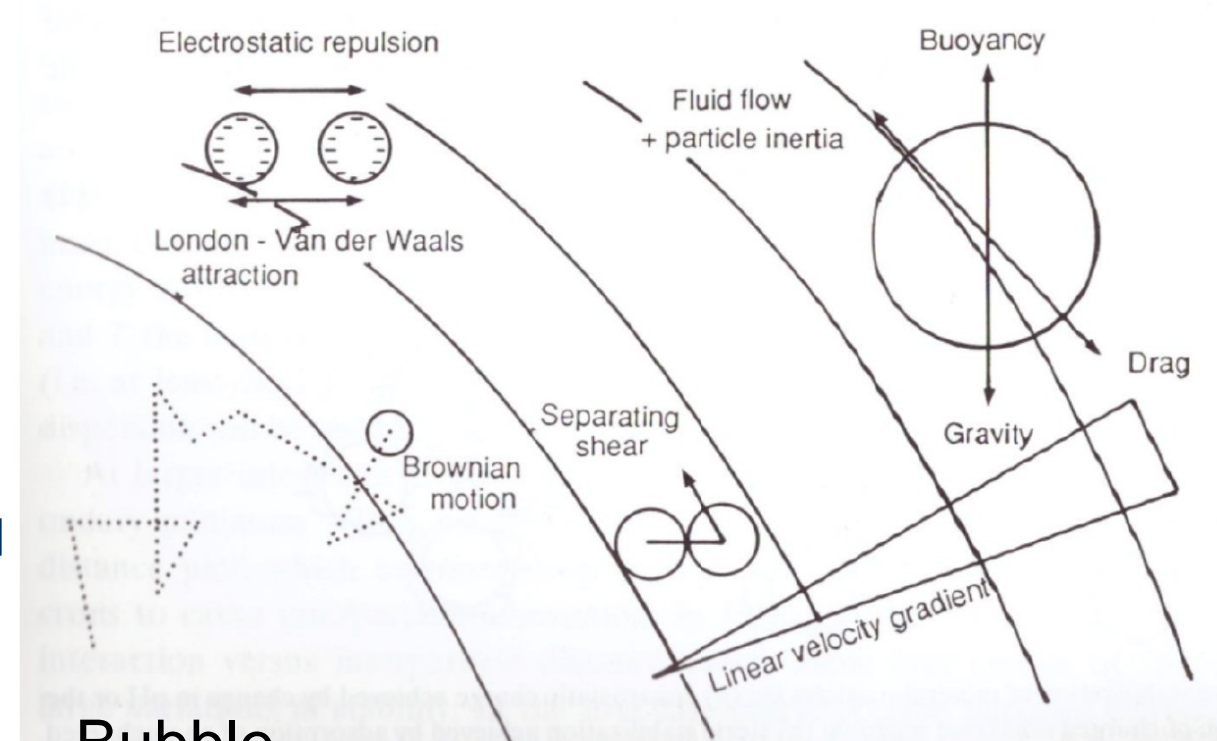


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Particle-bubble collision

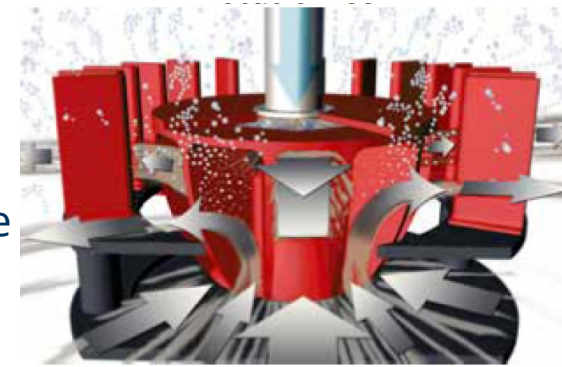
- I) Collision controlled by:
 - Long-range hydrodynamic forces:
→ inertia, drag, buoyancy, gravity, shear
 - Short-range hydrodynamic forces
→ modified stokes drag [Nguyen & Evans, JMF, 2002]
- II) Attachment controlled by
 - Short-range surface forces
van-der-Waals, electrostatic, hydrophobic interaction
 - Brownian motion



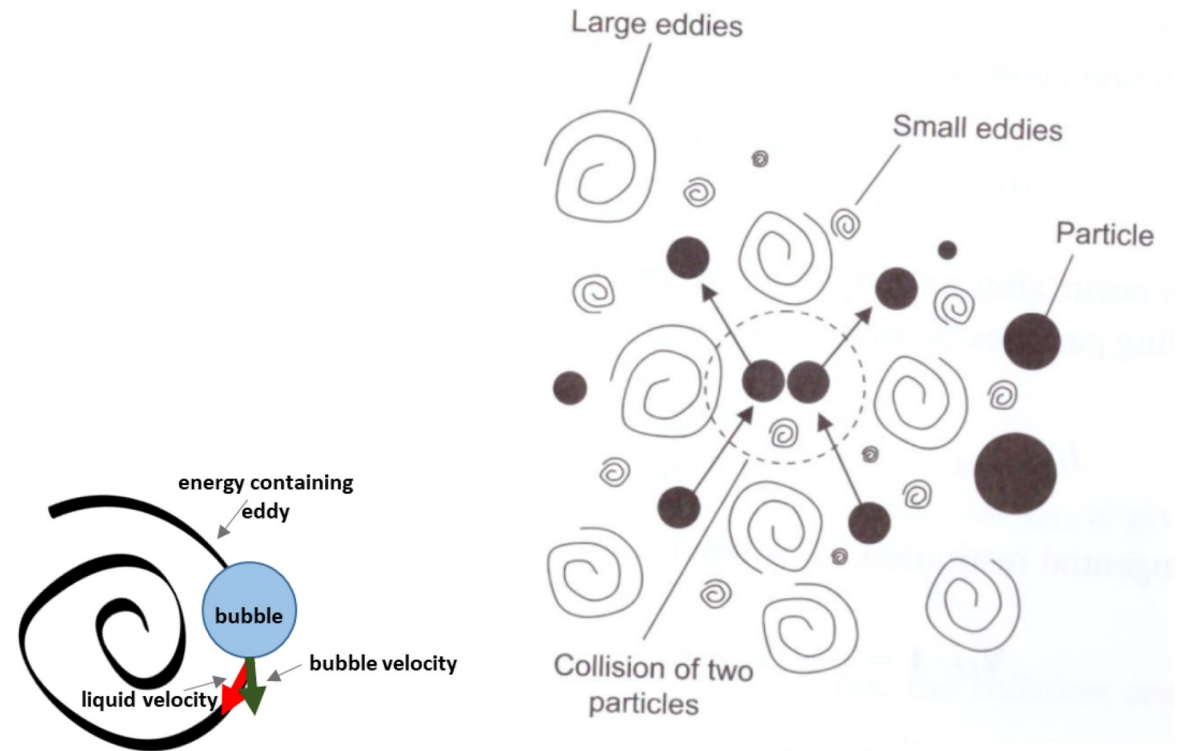
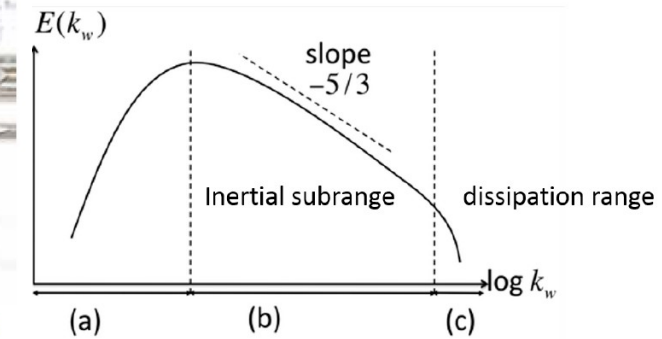
Bubble

Long range hydrodynamics

- Controlled by relative velocity between particle and bubble
- Depends on local turbulence
 - Turbulent kinetic energy, spectrum, dissipation
- Classification into two eddy sizes:
 - I) Eddy > bubble
 - → influences bubble movement
 - II) Eddy < bubble
 - → influences movement of particles near bubble



Rotor stator unit in detail (Outotec Flotation technologies)



Yeoh et al.

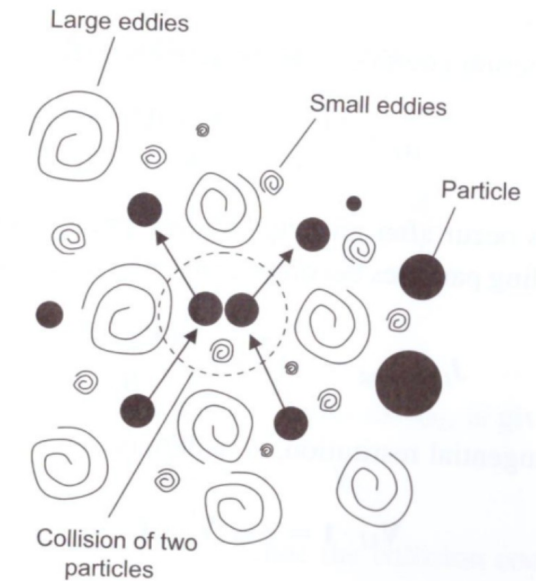
Particle transport

- Stokes-number: $St = \frac{\tau_p}{\tau_f}$ $\tau_{f,laminar} = \frac{d_b}{u_b}$ $\tau_{f,turbulent} = \frac{1}{f_{turbulence}}$

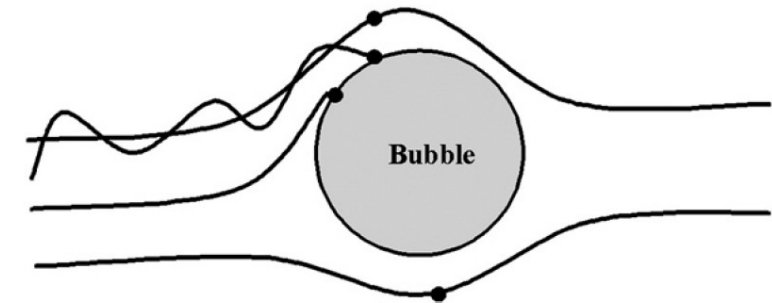
- Particle acceleration:

$$F = m \frac{du_p}{dt}, \frac{\rho_f}{2} u_{rel}^2 C_D \frac{\pi}{4} d_p^2 = \frac{4\pi d_p^3 \rho_p}{24} \frac{du_{rel}}{dt} \rightarrow u_{rel} = U e^{-t/\tau_p} \quad \tau_p = \frac{4\rho_p d_p^2}{3\mu_f C_D Re_p}$$

- Stokes-number $\ll 1$ (small particles)
- Particle follow the fluid streamlines – low collision probability
- Stokes-number $\gg 1$ (large particles)
- Particles deviate from streamlines – high collision probability

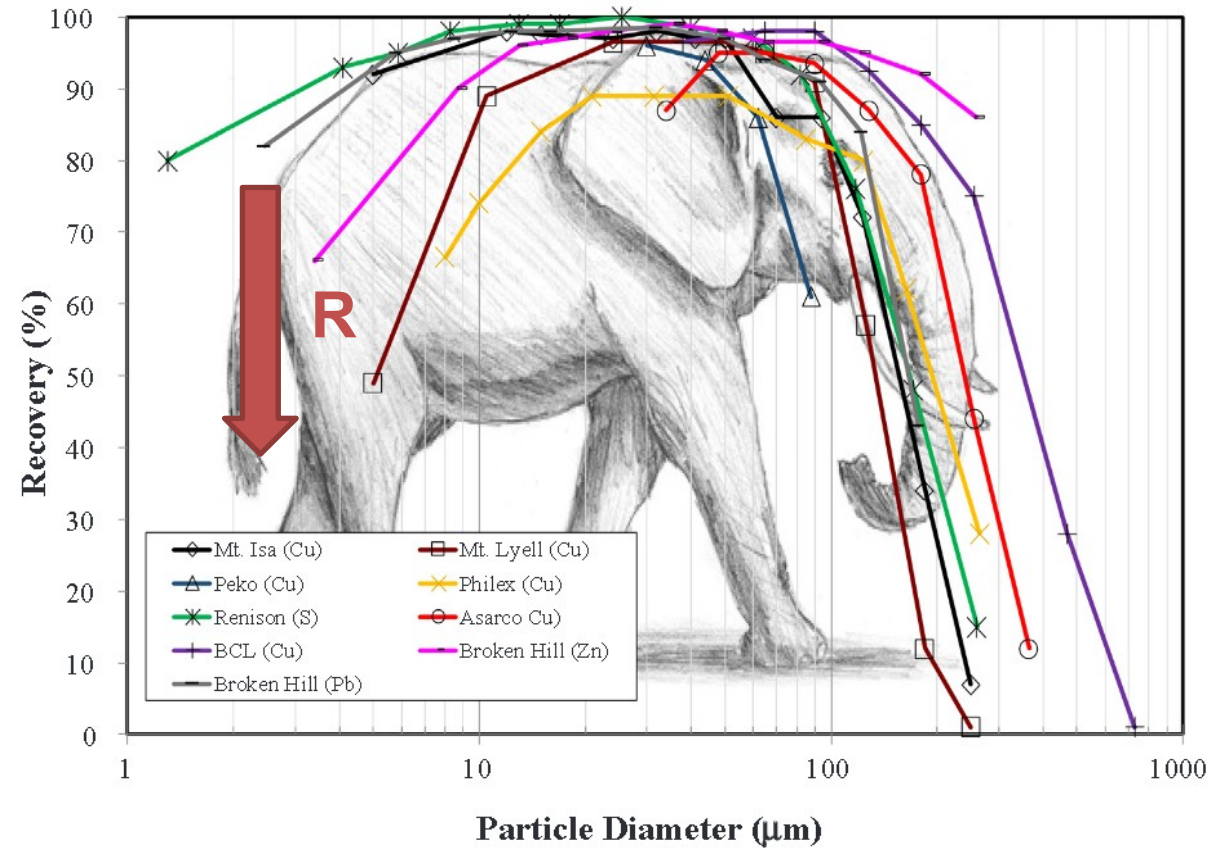
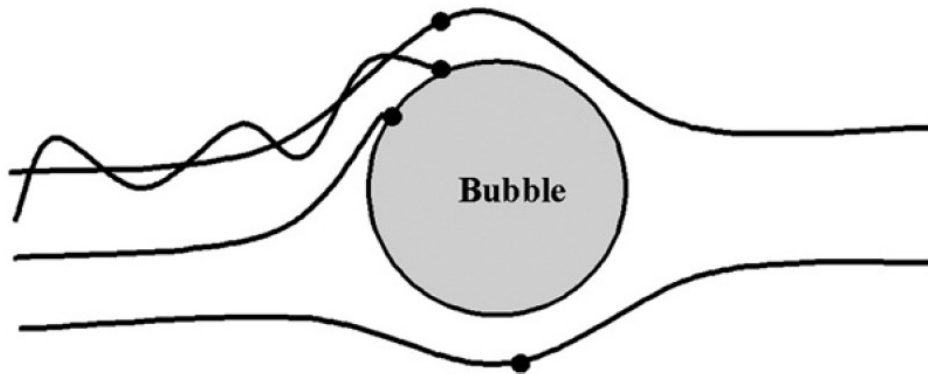


Yeoh et al.



Fine particle flotation

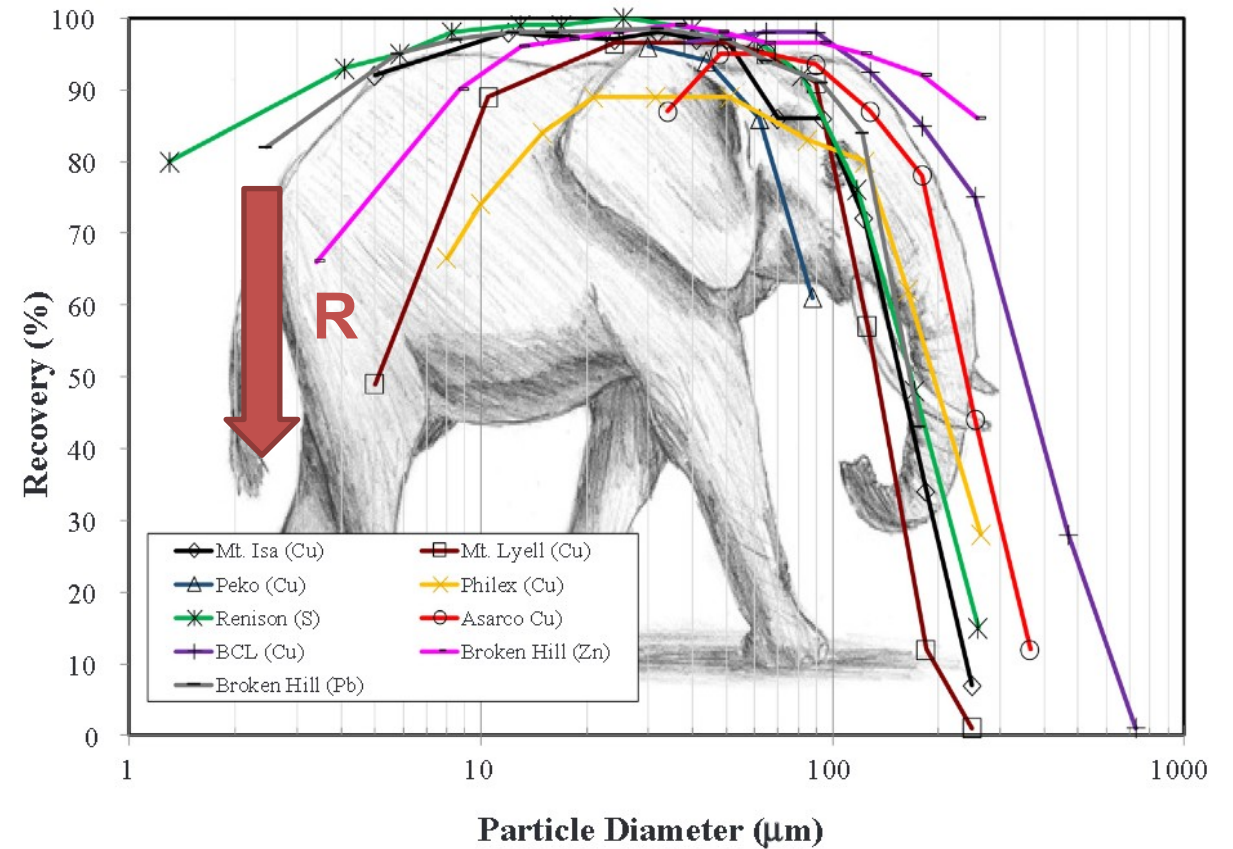
- Fine particles: $d < 20 \mu\text{m}$
- nearly inertialess
- low Stokes number
- following of fluid streamlines
- low collision probability



$$St = \frac{\tau_p}{\tau_f} \quad \tau_p = \frac{4\rho_p d_p^2}{3\mu_f C_D Re_p}$$

Fine particle flotation

- High demand of minerals → more fine grinding
- → requirement of sorting fine particles!

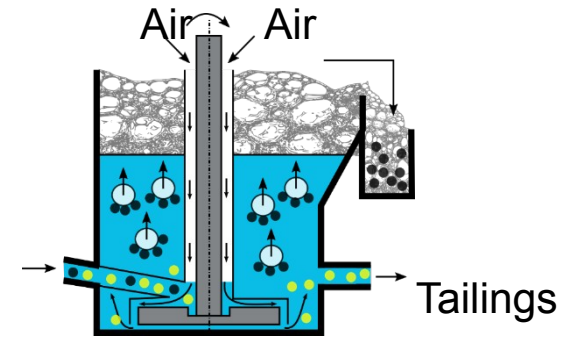


Quantifying flotation efficiency (= recovery of valuables)

- Flotation is a rate processes: $\frac{dN_p}{dt} = -kN_p = -Z_{pb}E_{coll}$

N_p : numbers of particles

k – rate constant



- Aim: understanding recovery from first principles:

- Collection efficiency E_{coll} :

$$E_{coll} = P_c \times P_a \times (1 - P_d)$$

Encounter frequency Z_{pb} :

$$Z_{pb} = 5N_pN_b(d_p + d_b)^2 \cdot \sqrt{(\bar{u}_p)^2 + (\bar{u}_b)^2}$$

[Abrahamson, 1975, Chem. Eng. Sci.]

- Collision probability P_c : e.g.

$$P_c = \frac{3}{2} \left(\frac{d_p}{d_b} \right)^2 \left[1 + \frac{3}{16} \left(\frac{Re}{1 + 0.249Re^{0.56}} \right) \right]$$

[Yoon, Luttrell, Min. Process Extr. Metall. Rev. (1989)]

rms-value of particle velocity fluctuations:

$$\bar{u}_p = 0.4 \frac{\epsilon^{4/9} d_b^{7/9}}{\nu^{1/3}} \left(\frac{\rho_p - \rho_l}{\rho_l} \right)^{2/3}$$

[Liepe, Möckel, 1977]

Design goals for flotation cells

- High turbulence:

- → High turbulent Fluctuations $(u_p'), (u_b')$

$$Z_{pb} = 5 N_p N_b (d_p + d_b)^2 \sqrt{(u_p')^2 + (u_b')^2}$$

- → High dissipation of turbulent kinetic energy

$$u_p' = 0.4 \frac{\epsilon^{4/9} d_b^{7/9}}{\nu^{1/3}} \left(\frac{\rho_p - \rho_l}{\rho_l} \right)^{2/3}$$

- → Small bubbles

$$We_{crit} \approx 1 < We = \frac{\rho u_c^2}{2\gamma/r_b} \quad \Rightarrow \text{Bubble break-up}$$

$$u_c \sim \frac{\partial u}{\partial r} r_b$$

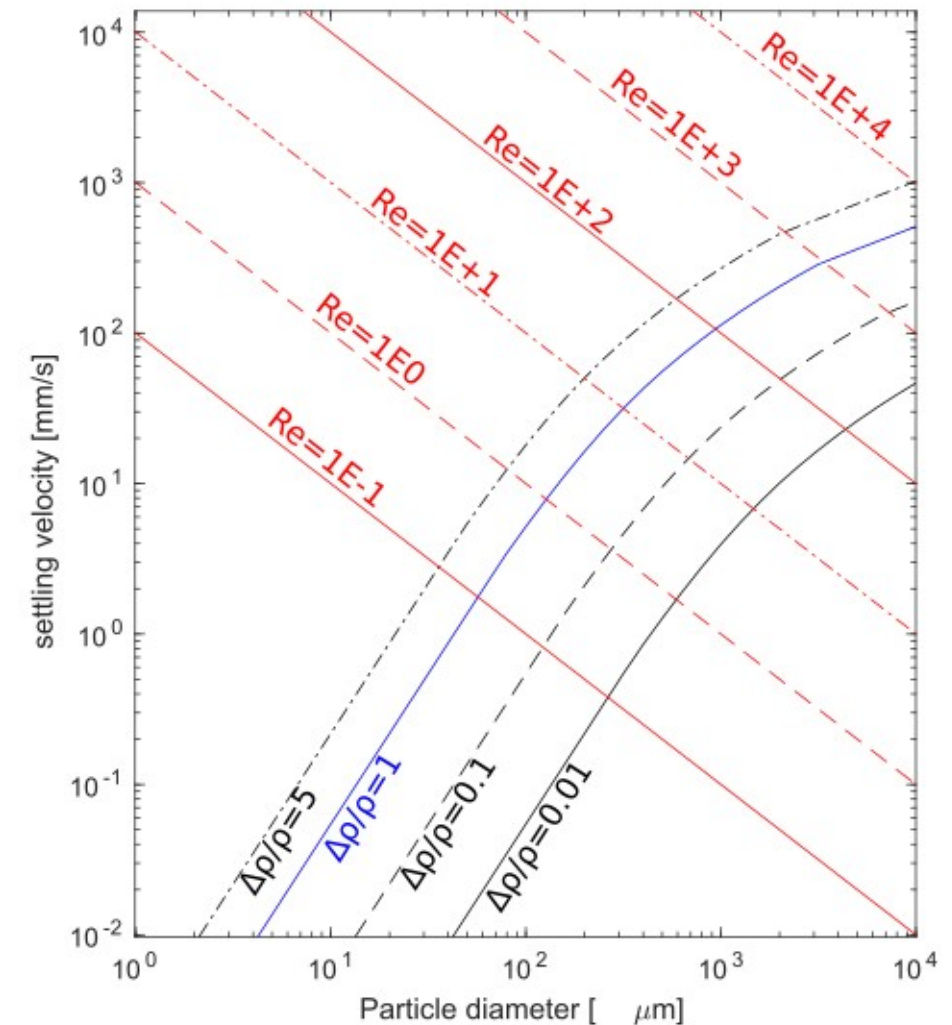
$$P_c = \frac{3}{2} \left(\frac{d_p}{d_b} \right)^2 \left[1 + \frac{3}{16} \left(\frac{Re}{1 + 0.249 Re^{0.56}} \right) \right]$$

- BUT: Energy consumption! Desorption!

$$E_{coll} = P_c \times P_a \times (1 - P_d)$$

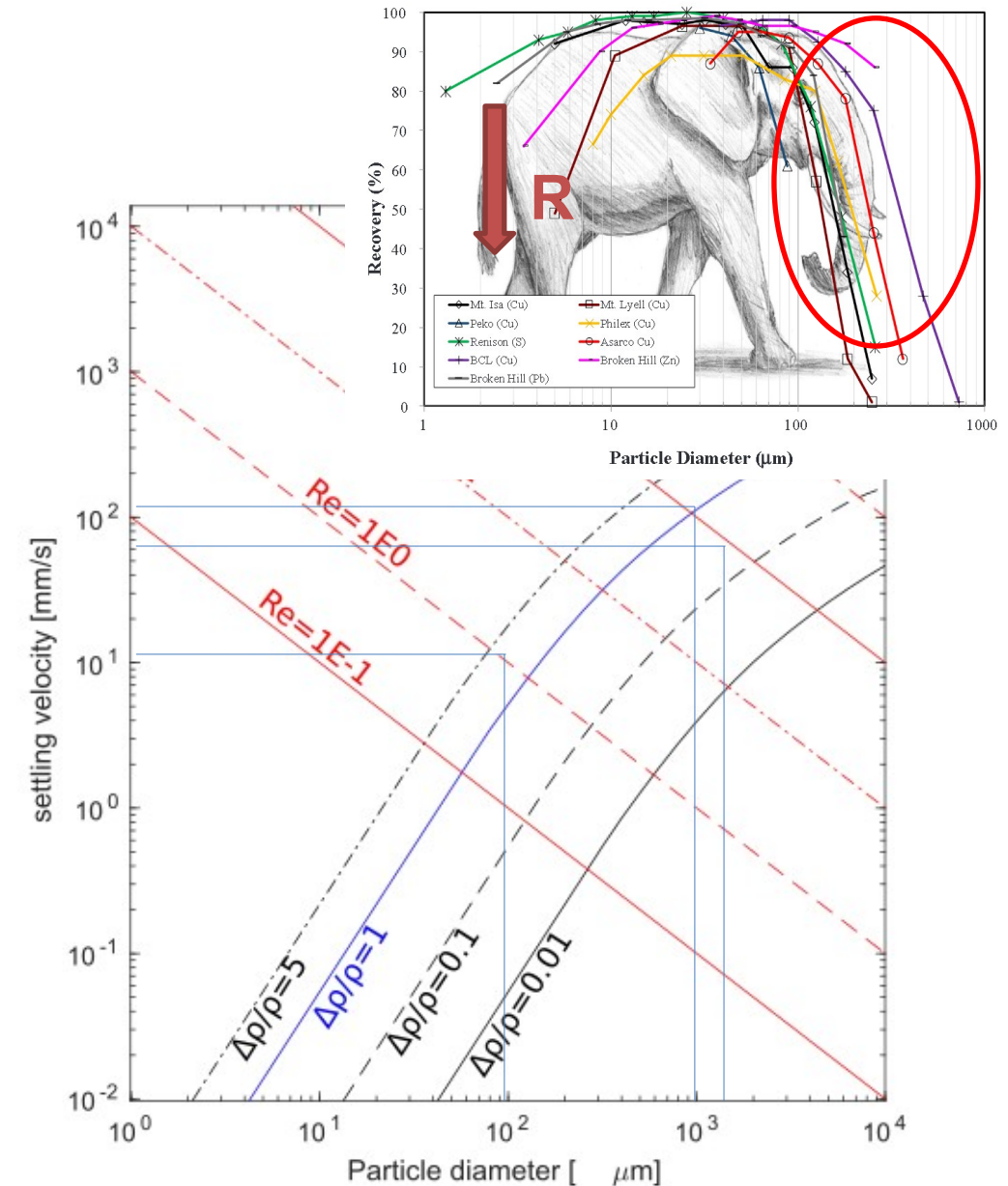
Exercise: Settling and rising velocity

- Bubble with 1 mm diameter, round particles, $\rho_p = 3000 \text{ kg/m}^3$
- → Rising/settling velocity?
- → Dwelling time ($h=1 \text{ m}$)
- A) single bubble
- B) Bubble with 5 particle of 0.1 mm diameter
- C) Bubble with 3 particle of 0.5 mm diameter
- D) Particle with 0.1 mm diameter (no bubble)



Exercise: Settling and rising velocity

- Bubble with 1 mm diameter, round particles, $\rho_p = 3000 \text{ kg/m}^3$
- → Rising/settling velocity?
- → Dwelling time ($h=1 \text{ m}$)
- A) single bubble → 100 mm/s → $T=10 \text{ s}$
- B) Bubble with 5 particle of 0.1 mm diameter
- → $\Delta \rho / \rho = 0.985 \rightarrow 100 \text{ mm/s} \rightarrow T=10 \text{ s}$
- C) Bubble with 3 particle of 0.5 mm diameter
- → $\Delta \rho / \rho = 0.182 \rightarrow 60 \text{ mm/s} \rightarrow T=17 \text{ s}$
- D) Particle with 0.1 mm diameter (no bubble)
- → $\Delta \rho / \rho = 2 \rightarrow 10 \text{ mm/s} \rightarrow T=100 \text{ s}$

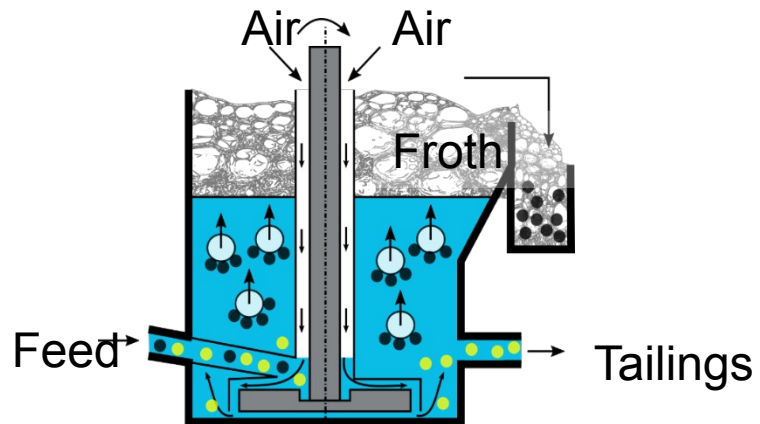


Structure

- Review lecture 11
- Mineral flotation
- Surfactants in Flotation
- Particle attachment
- Froth zone
- Cell design
- Related applications

Froth zone in flotation

- Meta-stable foam, typically large bubbles
- High solid/liquid ratio
- Launderers to collect foam efficient



Processes in the froth

- Drainage, liquid fraction gradient
- Coalescence (film rupture) due to
 - hydrophobic particles
 - low frother concentrations
 - non-ionic frothers
- Froth life-times of seconds (gas diffusion negligible)
- Coalescence $\Rightarrow$ particle clustering, particle drop-back

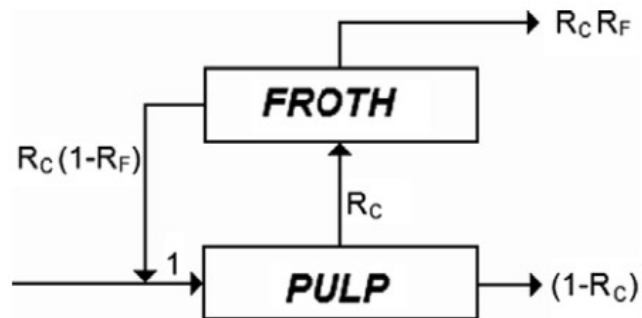
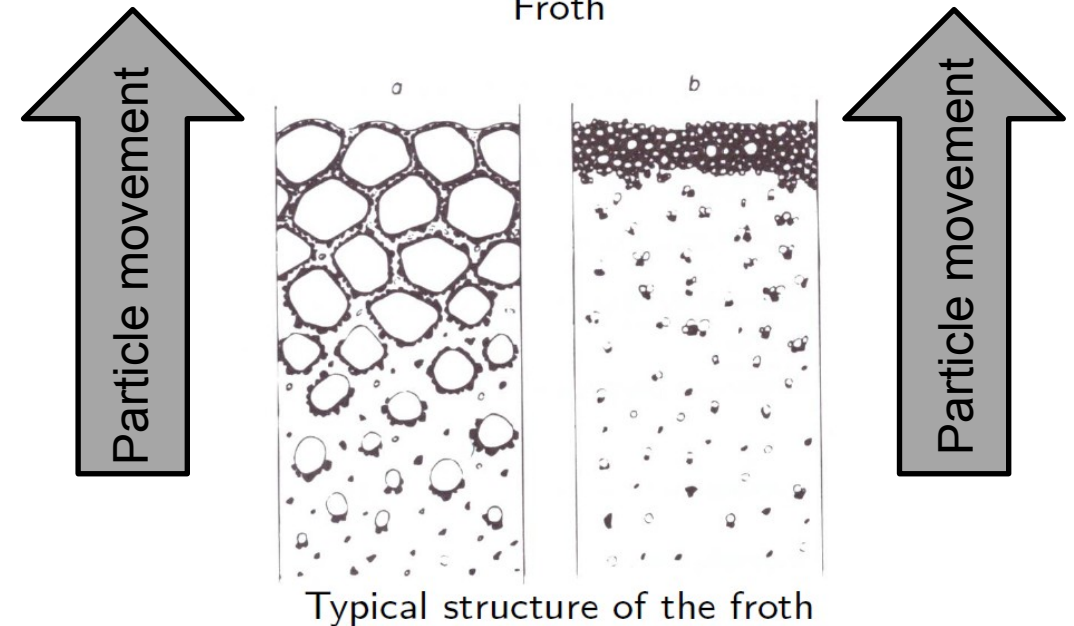


Fig. 2. Pulp and froth recovery model.



Froth



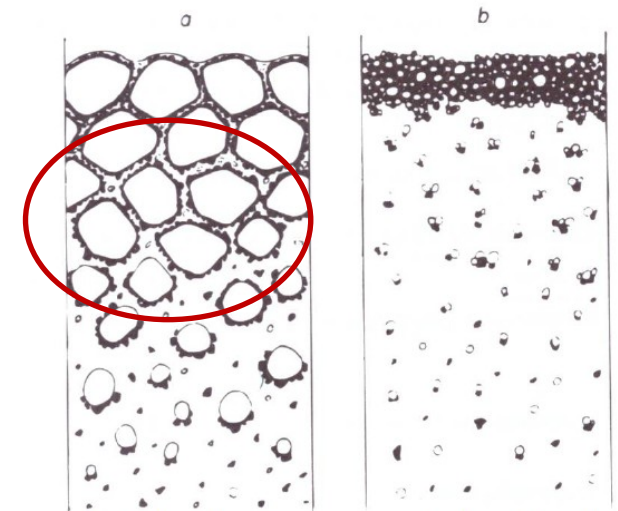
Typical structure of the froth

Wash water addition

- Entrained gangue particles in the froth
- Water addition to the froth, draining down
- Washing out non-attached particles
- Dirty environment – robust solution required



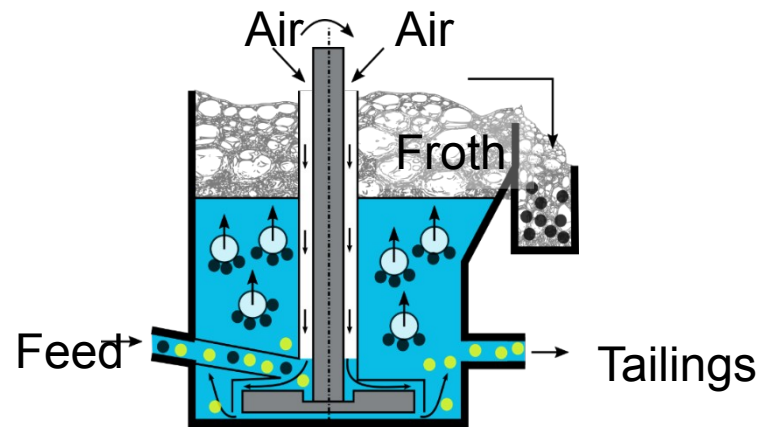
Froth



Typical structure of the froth

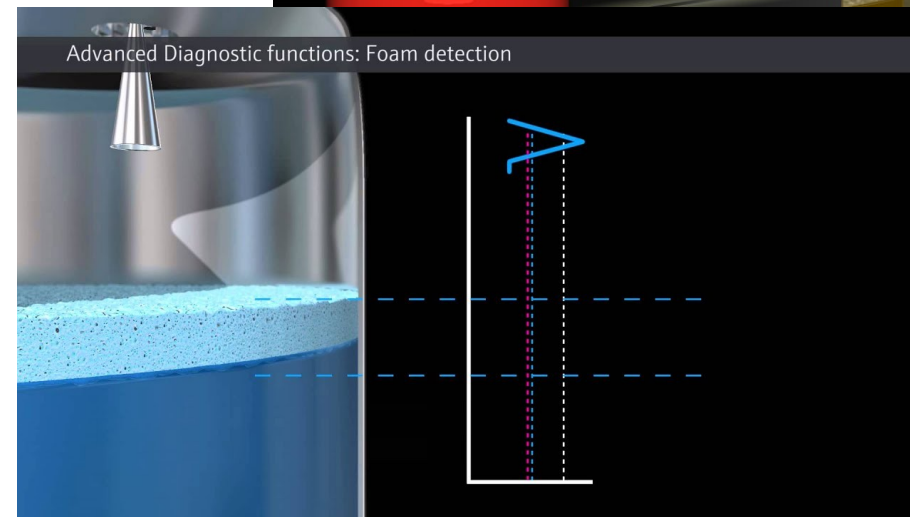
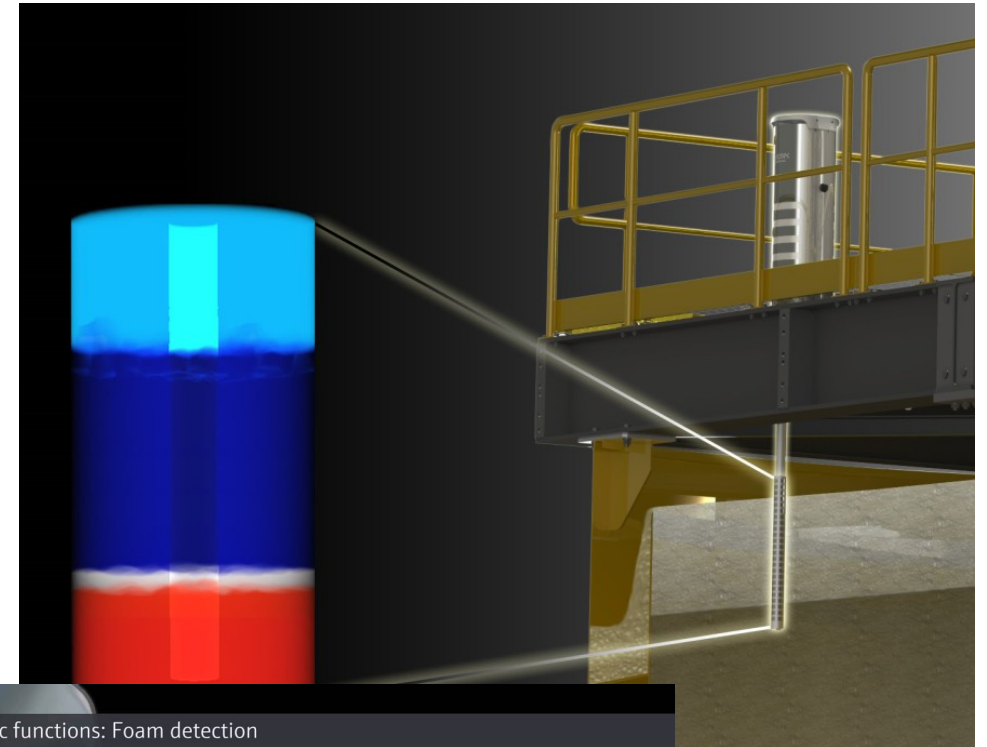
Froth measurement

- Crucial to control/optimize flotation process
- Opaque foam, dirty environment
- Nearly no measurement techniques/devices available



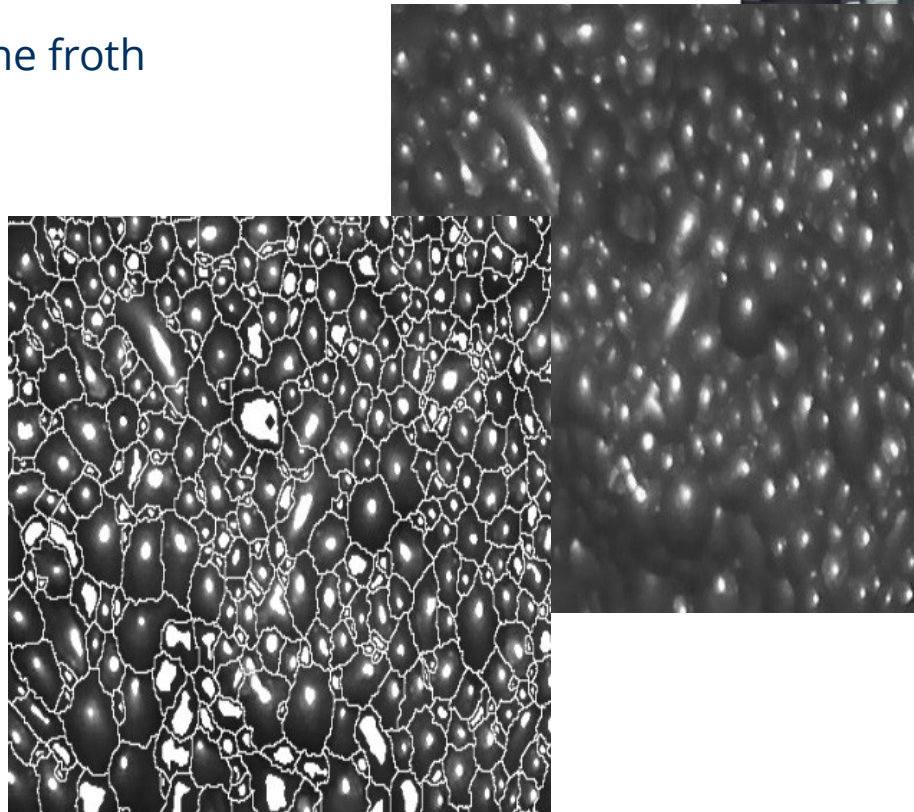
Froth measurement

- Level measurement
- → measurement of level of pulp and froth, froth height
- Electric conductivity,
- Ultrasound time-of-flight
- Radar



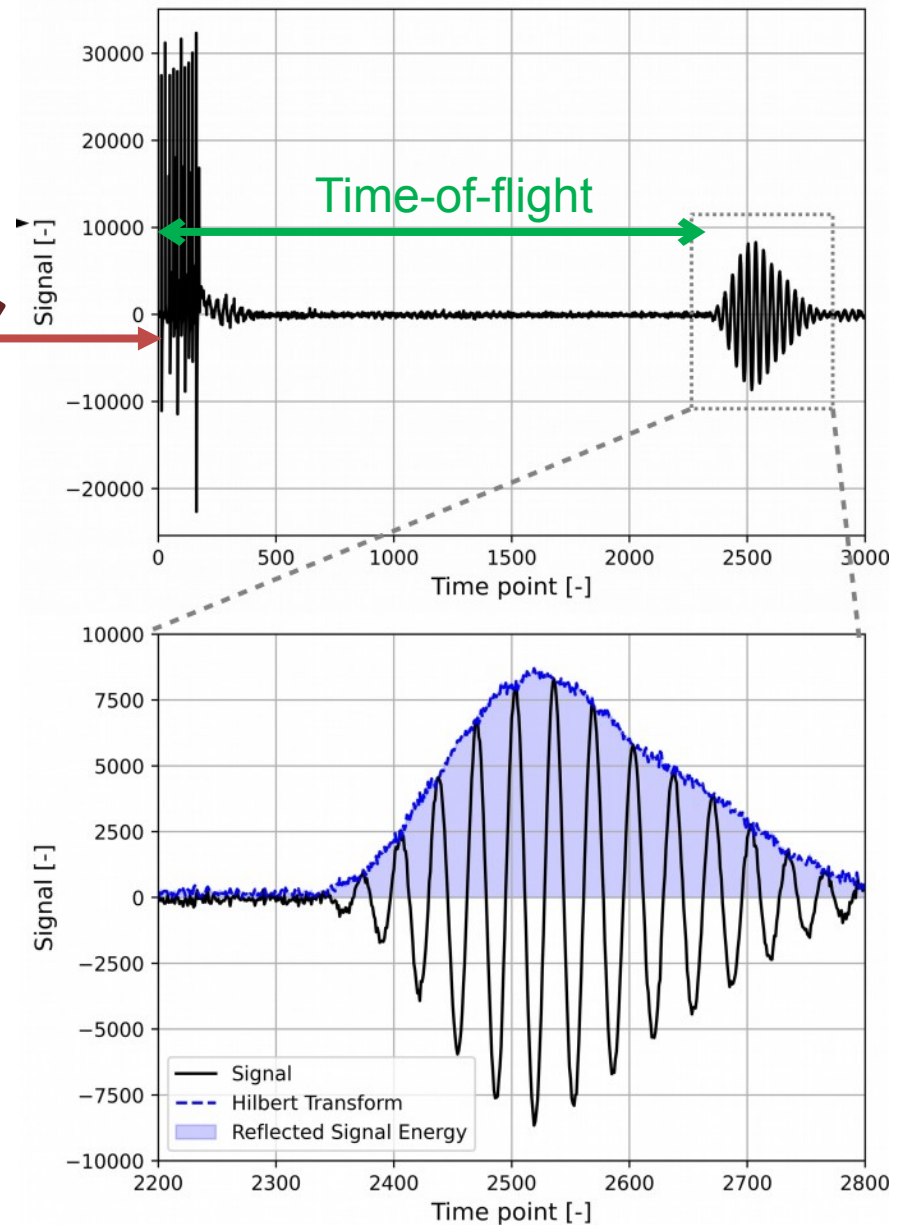
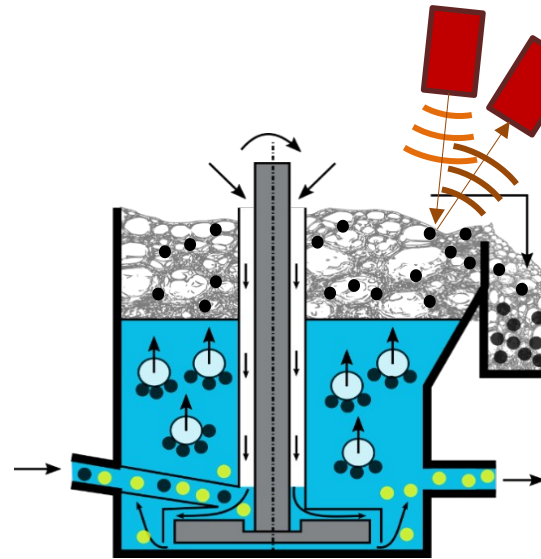
Froth measurement

- Froth imaging
- → measurement of bubble size, froth movement
- → Particle content by color?
- No information about the inside of the froth



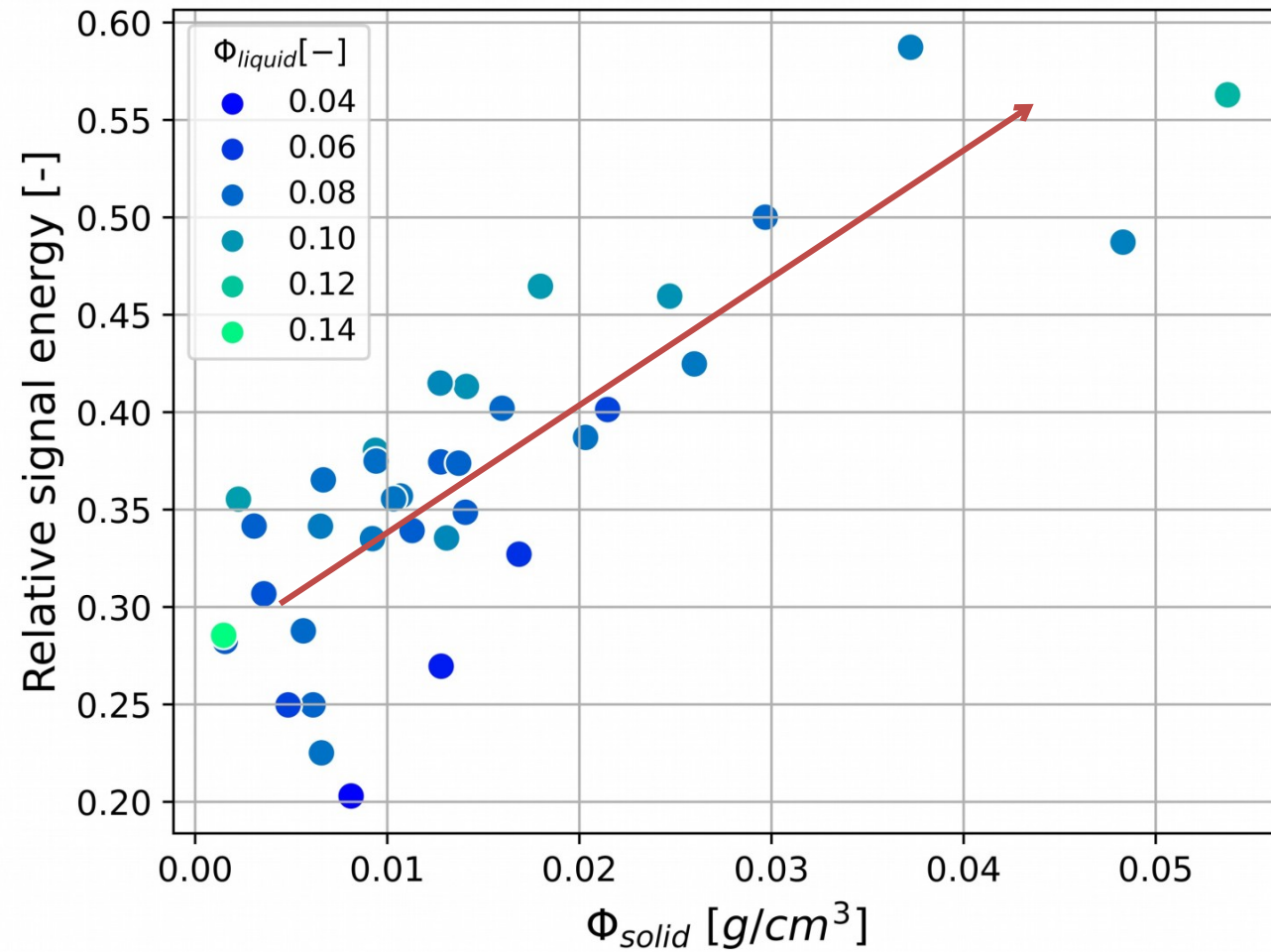
Ultrasound reflectometry

- Ultrasound-Pulse (130 kHz)
- Reflection at the froth surface
- Echo signal recorded
- Echo intensity → Particle fraction
- Time-of-Flight → Froth height



Results

- Echo intensity ~ solid fraction
- Influence of liquid fraction?



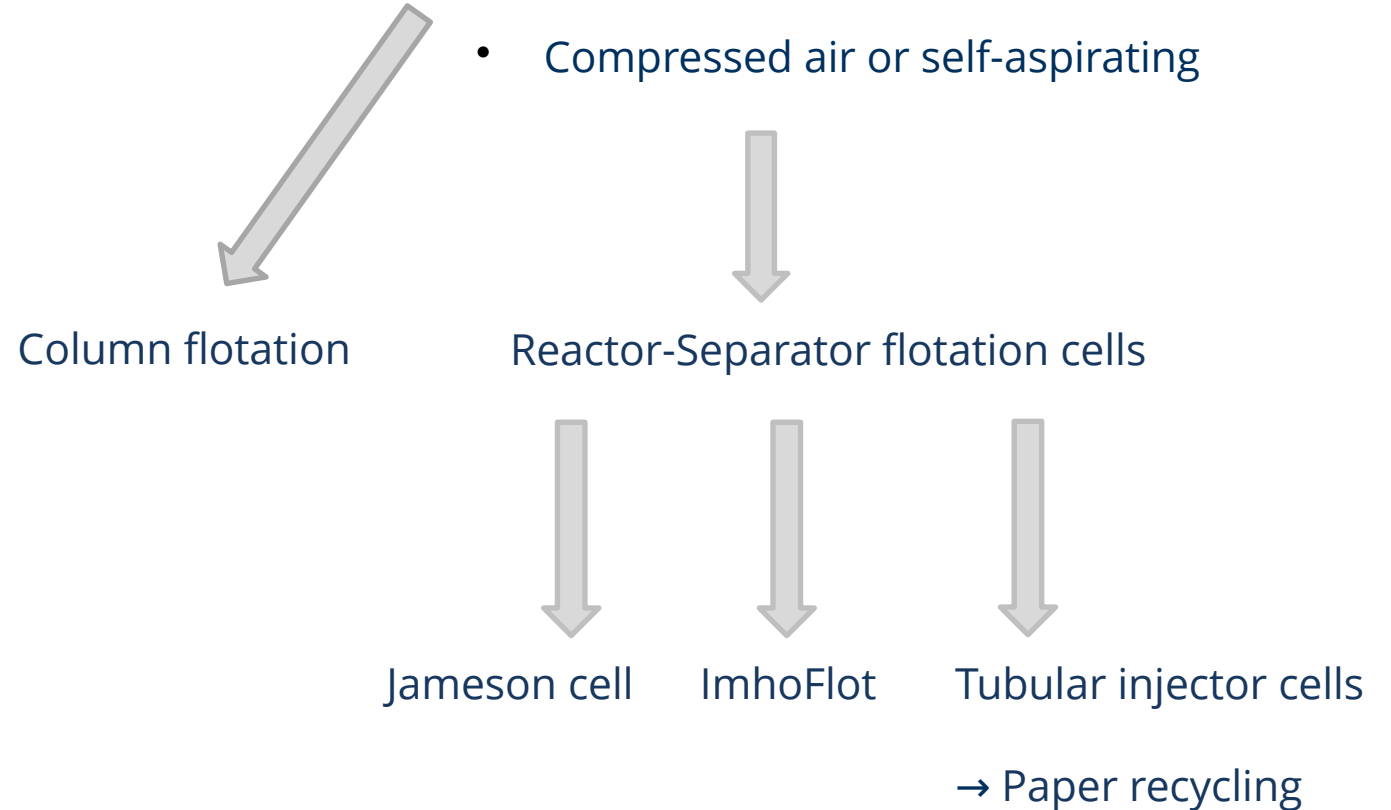
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Different cell designs

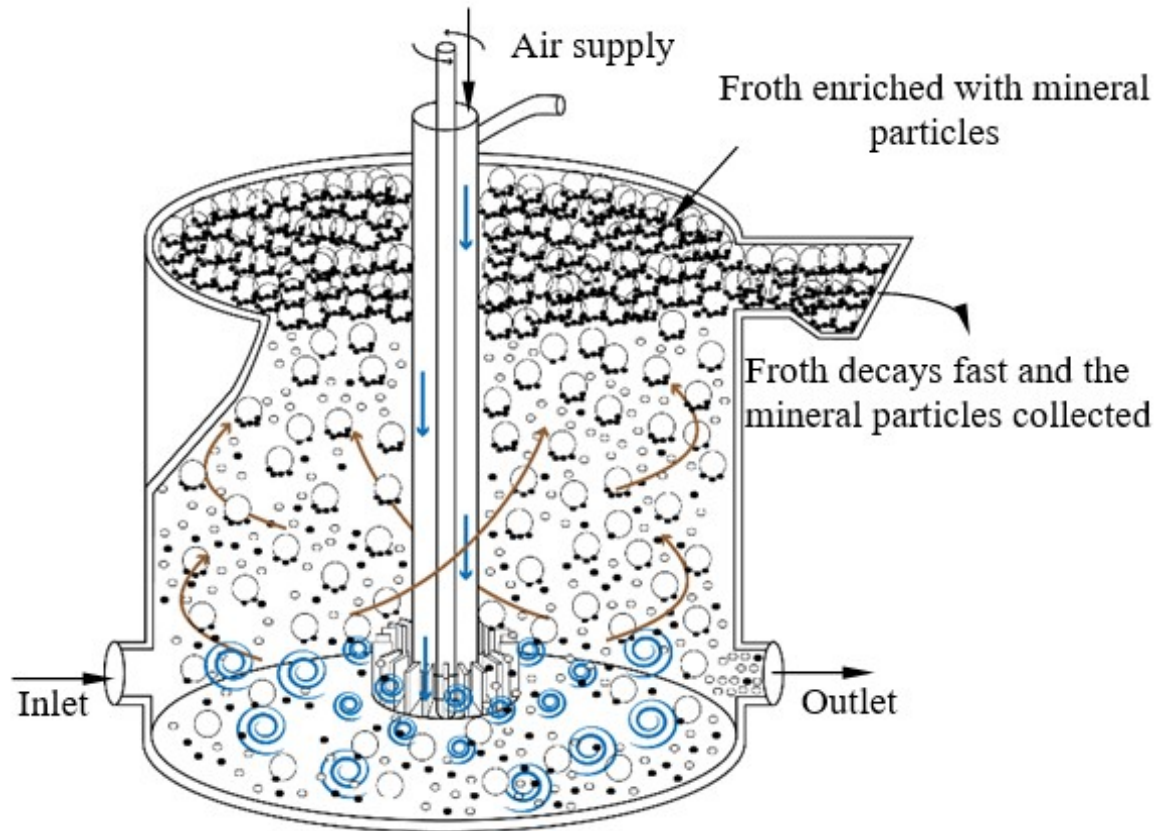
- Mechanical flotation cell
 - Rotor-Stator configuration
 - Compressed air

- Pneumatic flotation cell
 - No moving parts
 - Compressed air or self-aspirating



Mechanical flotation cell

- “Work horse” of froth flotation



Froth zone

→ Concentrated mineral particles

Pulp zone

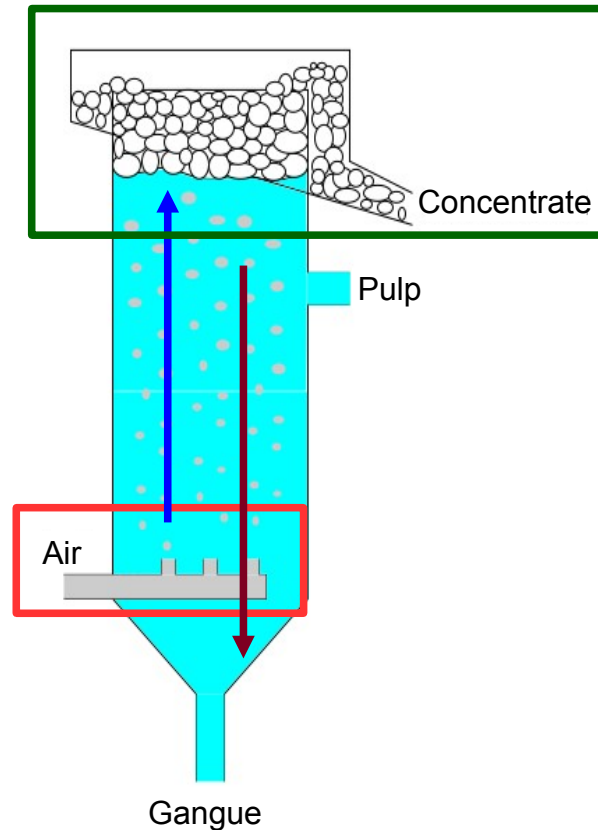
→ Bubble-particle clusters

Mechanical flotation cell

- Different sizes, up to 800 m³



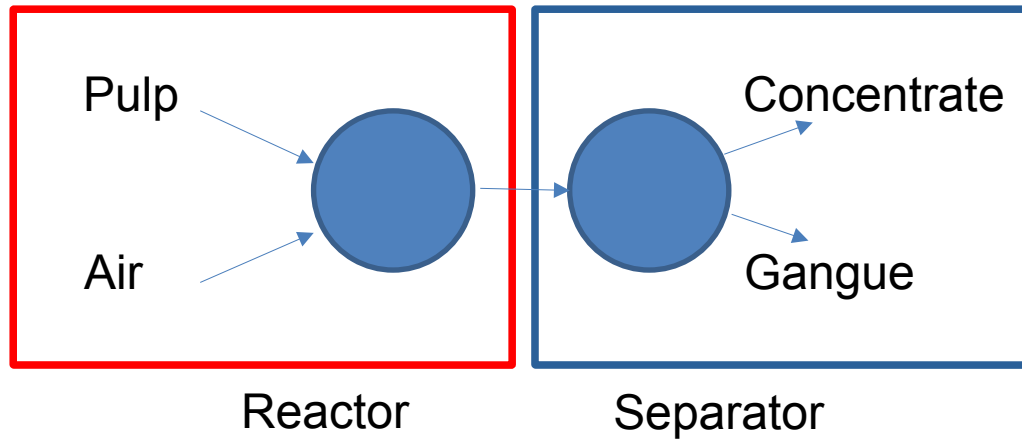
Column flotation



- Low turbulence
→ low recovery rate
- Bubble generator
→ gas flow and bubble size
- Air and pulp in counter-current
→ effective contact
- Deep froth
→ high grade of the extract
→ improved by wash water

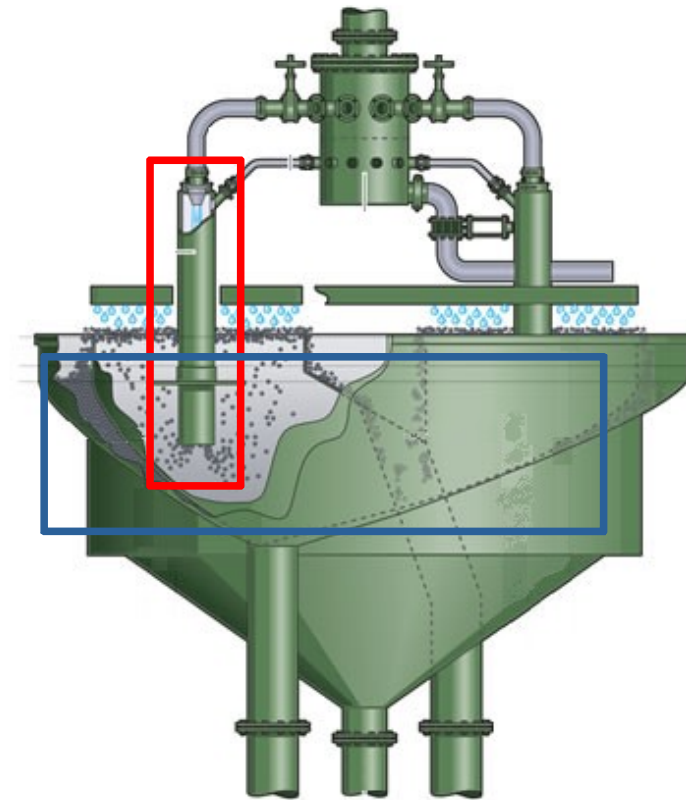
Reactor-separator approach

- Approach for fine particle flotation



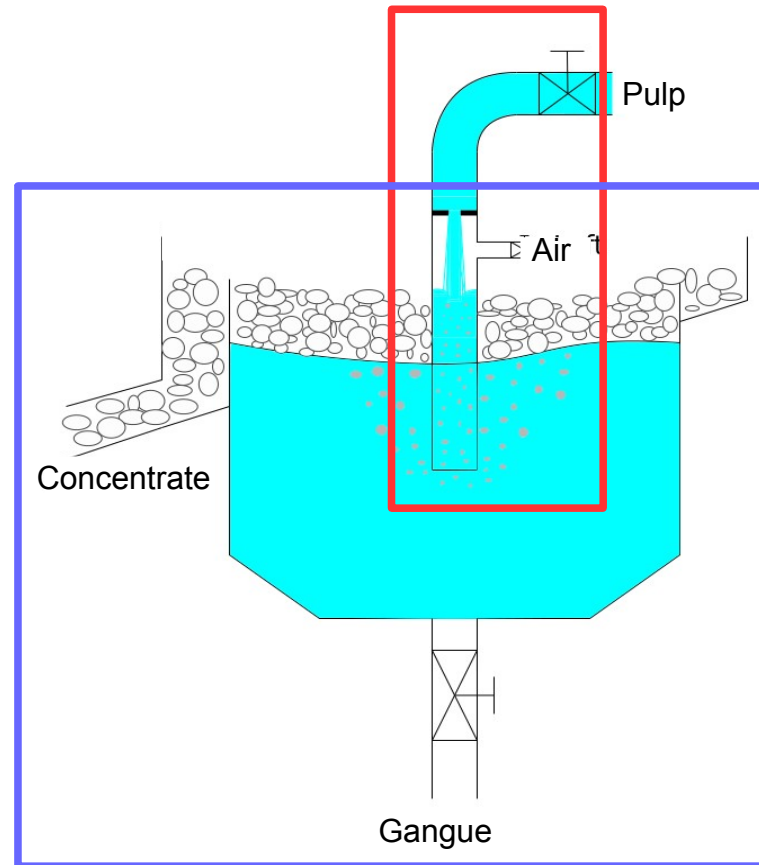
- Decoupled optimization of reactor and separator
- High turbulence, shear in reactor
- Quiescent flow in separator

$$E_{coll} = P_c \times P_a \times (1 - P_d)$$



Quelle: Jameson, G. J,

High-Intensity Flotation Cells: e.g. Jameson Zelle



Downcomer

- Turbulent flow
- Particle-bubble-contact
- (self aspirating)

Tank

- Separation process
- rising of bubble-particle clusters
- Settling of gangue particles
- Typically smaller than mechanical or column flotation cells

Jameson Cell reactor

- Approach for fine particle flotation

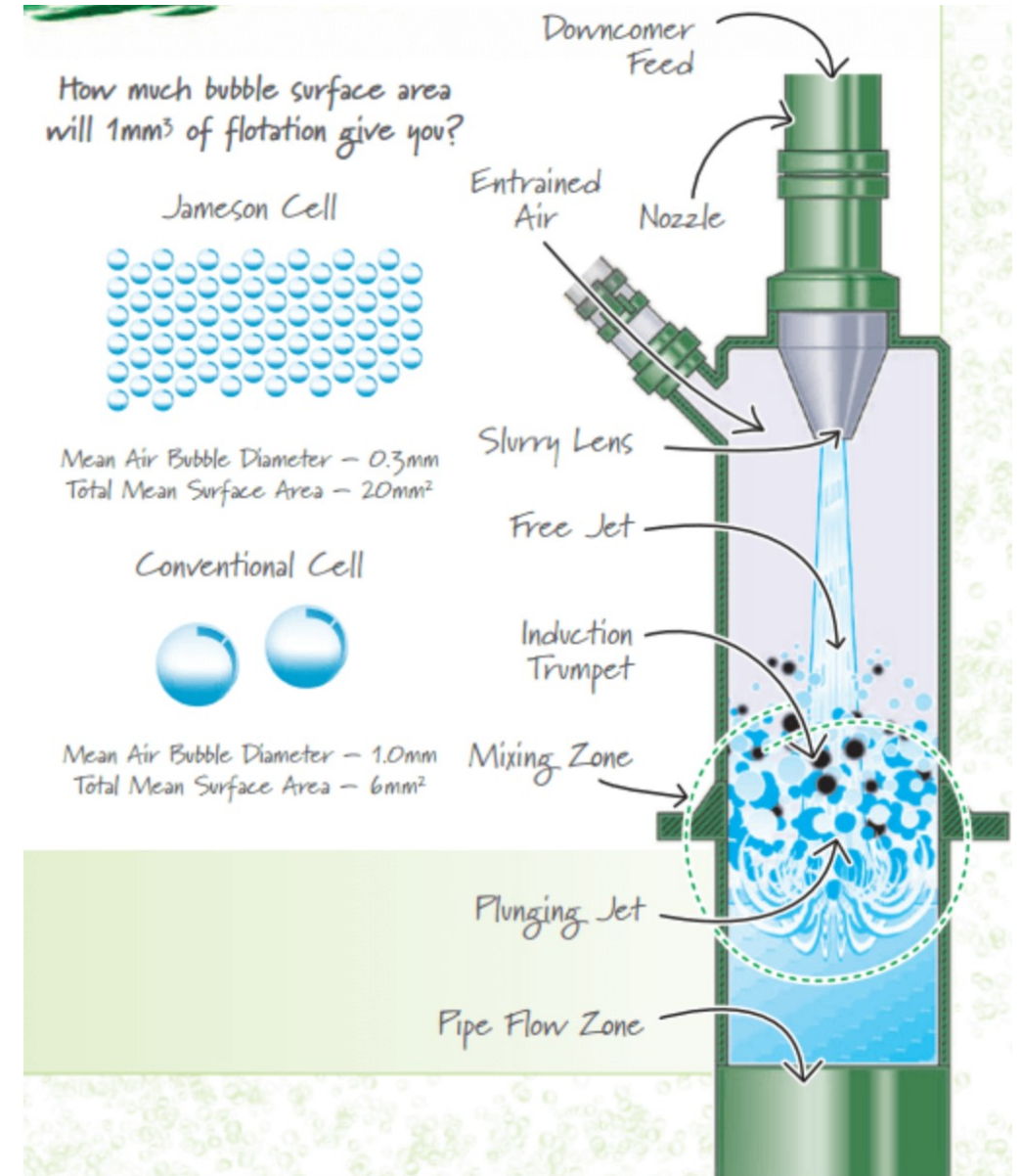
$$\frac{dN_p}{dt} \propto \frac{N_p Q_g}{d_b^2} G^{3/2}$$

Small particle diameter d_p
→ reduced recovery rate

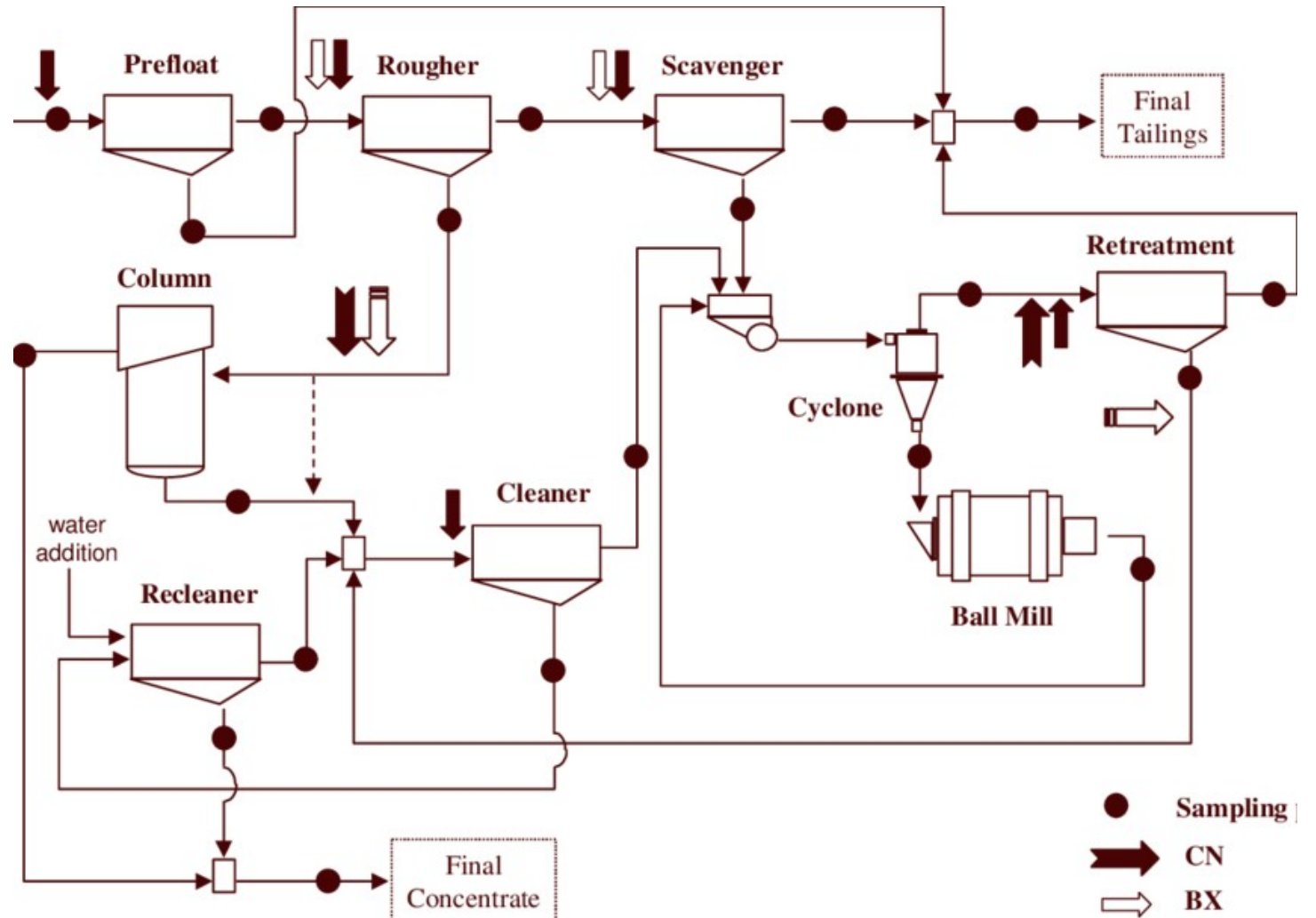
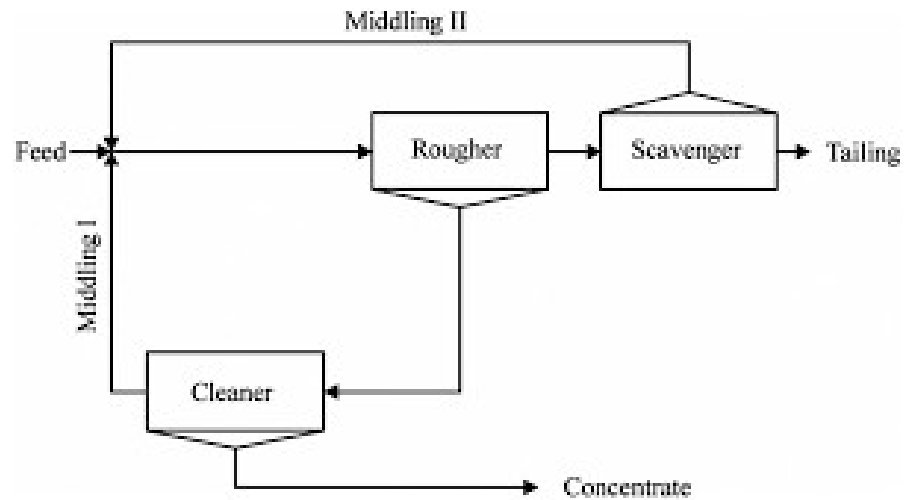
N_p and Q_g defined by the process

→ Increased shear rate G !

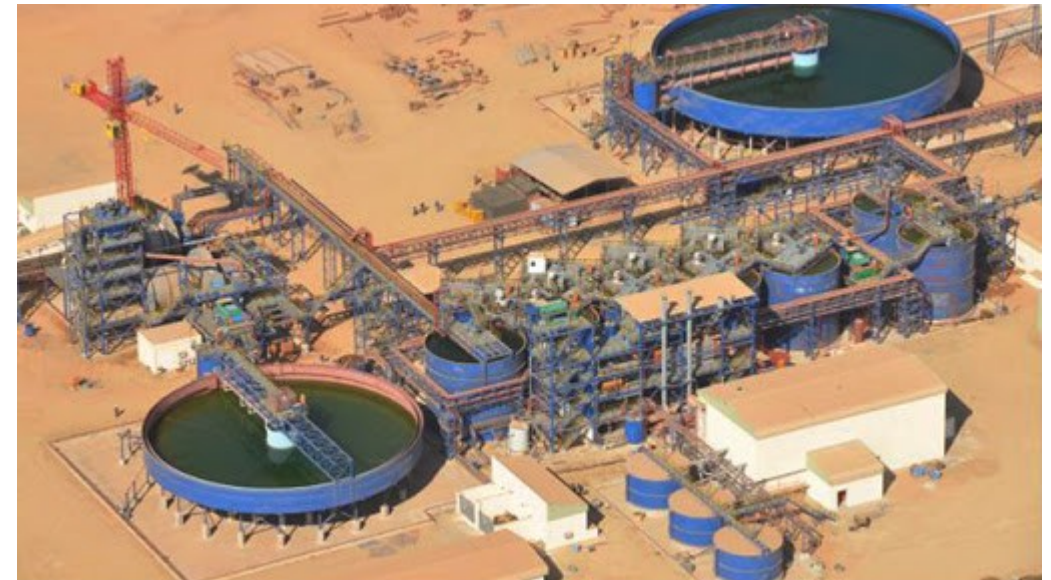
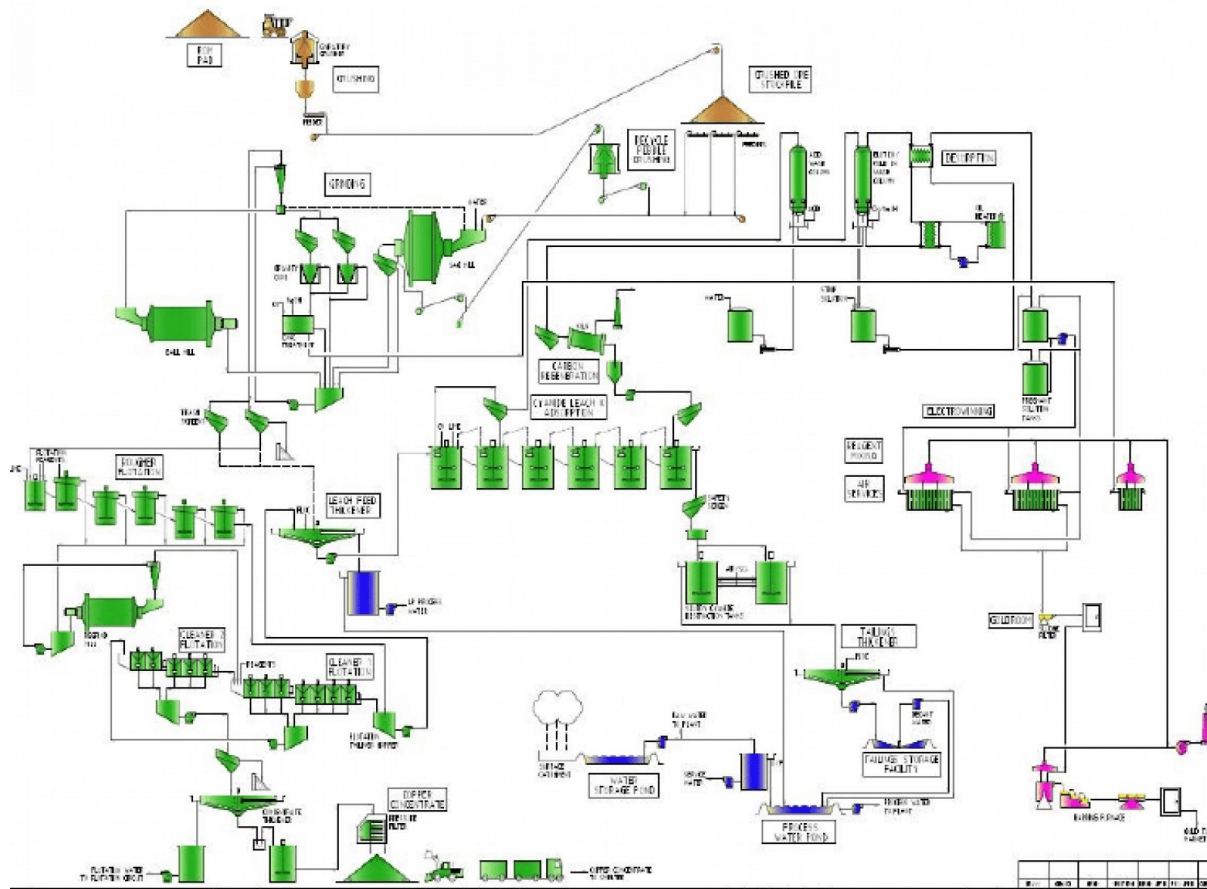
→ Reduced bubble diameter d_b !



Flotation plant design



Flotation plant design

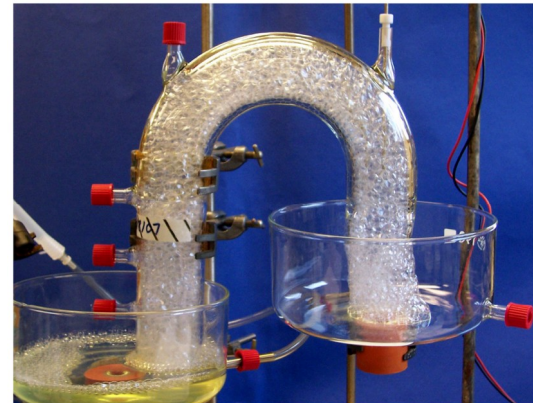
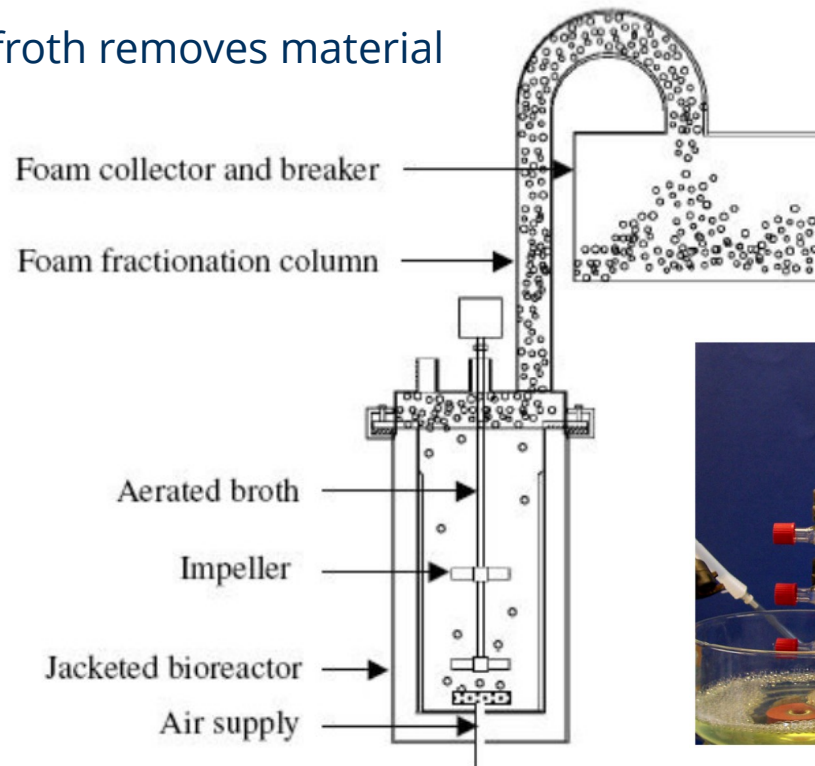


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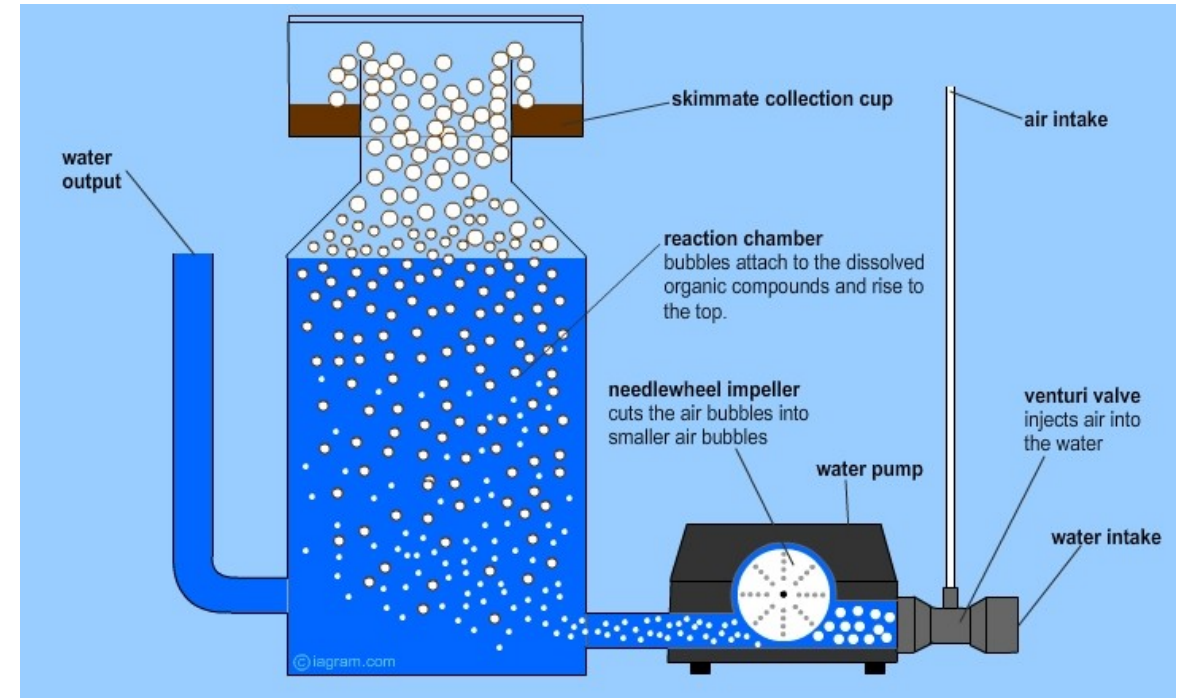
Foam fractionation / Adsorptive bubble separation

- Removal/recovery of hydrophobic material from solution
- Rising bubbles pick up material
- Froth generation at the surface
- Overflowing froth removes material



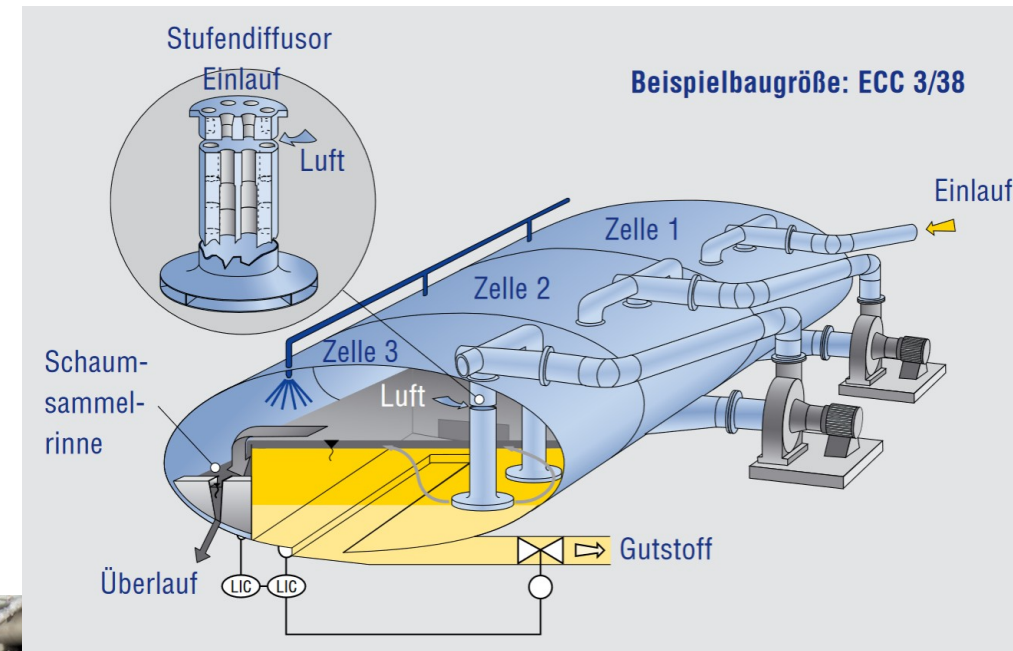
Protein skimmer

- Removal/recovery of hydrophobic bio-substances (proteins, bacteria, biosurfactants)
- Application in biochemical industry researched, but not yet full potential
- Application in fish tanks



De-inking process

- Removal of old ink to produce recycled paper
- Sodium hydroxide (NaOH)
 - swelling of the fibres
 - ink-film breaks
- Surfactant (Fatty acid)
 - hydrophobizes ink droplets
- Sodium silicate
 - coagulation
- Hydrogen peroxide
 - bleaching



Dissolved air flotation (waste water treatment)

- Water, saturated with air at several bar
- Saturated air enters flotation cell,
- Microbubbles form on the surface of hydrophobic particles

