Exercises

Crystallization rate – calculation

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Crystallization - Examples

Example 1: Crystallization rate

At the crystallization of technical sugar solutions, which are in accordance with the diffusion theory of the crystal growth, the following quantities were found:

- Diffusion coefficient $D = 1.7 \cdot 10^{-10}\ m^2/s$
- Diffusion layer thickness $\delta = 43 \cdot 10^{-6}\ m$
- Rate constant of the surface reaction $k_r = 68 \cdot 10^{-6}\ m/s$

Calculate the **rate constant of the diffusion k_D** and the total crystallization constant **K**. Decide **which of the two processes is the control one** and what is the **relative proportion** of diffusion to the total resistance **W**. The resistance is defined as the reciprocal value of the velocity constant.

Rate constant and resitance calculation

The rate constant of diffusion:

$$k_D = \frac{D}{\delta} = \frac{1.7 \cdot 10^{-10} \ [\frac{m^2}{s}]}{43 \cdot 10^{-6} \ [m]} = 3.95 \cdot 10^{-6} \text{ m/s}$$

The rate constant of the surface reaction $k_r >> k_D$, which means that the crystallization process **is controlled by diffusion!**

Rate constant and resitance calculation

The crystallization constant is defined as:

$$1/K = 1/k_r + 1/k_D$$

and the resistance as: $W = W_r + W_D$

Rate constant and resitance calculation

The crystallization constant is defined as:

$$1/K = 1/k_r + 1/k_D$$

Resistance : $W = W_r + W_D$

After fitting into the equation, we get:

$1/K = 3.74 \cdot 10^{-6}$ m/s

and the **total resistance:** $W = 2.68 \cdot 10^5$ s/m

Rate constant and resitance calculation

Total resistance : $W = 2.68 \cdot 10^5$ s/m

Resistance W_r = reciprocal value $1/k_r$

$$W_r = 0.15 \cdot 10^5 \text{ s/m}$$

Diffusion resistance W_D = reciprocal $1/k_D$

$$W_D = 2.53 \cdot 10^5 \text{ s/m}$$

The diffusion resistance W_D is **94%** of the total resistance **W**, which confirms that **the control process is diffusion!!!**

Rate constant and resitance calculation Summary

The rate constant of diffusion:

$$\mathbf{k_D = D / \delta} = 1.7 \cdot 10^{-10}\ m^2/s\ /\ 43 \cdot 10^{-6}\ m = \mathbf{3.95 \cdot 10^{-6}\ m/s}$$

The rate constant of the surface reaction $\mathbf{k_r >> k_D}$, which implies that the crystallization process **is controlled by diffusion**!

The crystallization constant is defined as: $\mathbf{1/K = 1/k_r + 1/k_D}$

After fitting into the equation, we get: $\mathbf{1/K = 3.74 \cdot 10^{-6}\ m/s}$

and the **total resistance**: $\mathbf{W = 2.68 \cdot 10^{5}\ s/m}$

Reciprocal value $\mathbf{1/k_r}$ is: $\mathbf{W_r = 0.15 \cdot 10^{5}\ s/m}$

and reciprocal $\mathbf{1/k_D}$ is: $\mathbf{W_D = 2.53 \cdot 10^{5}\ s/m}$

The diffusion resistance $\mathbf{W_D}$ is **94%** of the total resistance **W**, which confirms that **the control process is diffusion**.

Example 2 : Crystals calculation

Calculate the amount of crystals to achieve the desired target product size

Determine what amount of crystals is required to initiate the crystallisation batch process if the following requirements for the slurry produced are given:

- the final weight of 40 t

- the final crystal content of 55% in the suspension

- the average final crystal size of 1.4 mm.

Calculate the amount of crystals to achieve the desired target product size

The following were used to initiate the crystallization (= inoculation):

a) Suspensions of microcrystals, so-called "slurries" with a particle size of 17 μm (slurries containing 50% of crystals). It is presumed that 25% of added crystals dissolve in the industrial crystallizer.

b) Crystals with a mean size of 0.1 mm.

c) Suspension containing 40% crystals with a mean crystal size of 0.25 mm

Calculate the amount of crystals to achieve the desired target product size

Calculation:

For the calculation, we apply the **volume factor $k_v = 0.75$,** and the density of the slurry $\rho = 1.59$ g / cm^3 for the shape defining factor:

$$V = k_v \cdot L^3$$

Then we get the relationship between the **mass m** (mg) and the **size** of the crystals:

$$m = k_v \cdot \rho \cdot L^3 = 1.19 \cdot L^3$$

Calculate the amount of crystals to achieve the desired target product size

Calculation:

Mass of the average crystal in the resulting product:

$$m_1 \text{ (mg)} = ???$$

Number of crystals in the product:

$$N = ???$$

Calculate the amount of crystals to achieve the desired target product size

Calculation:

Mass of the average crystal in the resulting product:

$$m_1 = 1.19 \cdot 1.43 = 3.27 \text{ mg}$$

Number of crystals in the product:

$$N = 40.10^9 \cdot \ 0.55 / 3.27 = 6.73 \cdot 10^9$$

Calculate the amount of crystals to achieve the desired target product size

Calculation:

Ad a)

Mass of one microcrystal:

$m_1 = 1.19 . 0.0173 = 5.85 . 10^{-6}$ mg

Mass of the slurry:

$m_{sl} = 6.73.10^9 . 5.85.10^{-6} . 100 / 50 . 1.25 = 98 . 10^3$ mg = 98 g

Calculate the amount of crystals to achieve the desired target product size

Calculation:

Ad b)

Mass of one crystal of 0.1 mm

$m_1 = 1.19 \,.\, 0.13 = 1.19 \cdot 10^{-3}$ mg

Mass of crystals:

$m_k = 6.73 \cdot 10^9 \cdot 1.19 \cdot 10^{-3} = 8.01 \cdot 10^6$ mg = **8.01 kg**

Calculate the amount of crystals to achieve the desired target product size

Calculation:

Ad c)

Mass of one crystal (L = 0.25 mm)

$m_1 = 1.19 \cdot 0.253 = 0.0186$ mg

Suspension Weight

$m_s = 6.73.10^9 \cdot 0.0186 \cdot 100/40 = 0.313 \cdot 10^9$ mg = 313 kg

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Mass Transfer & Crystallization

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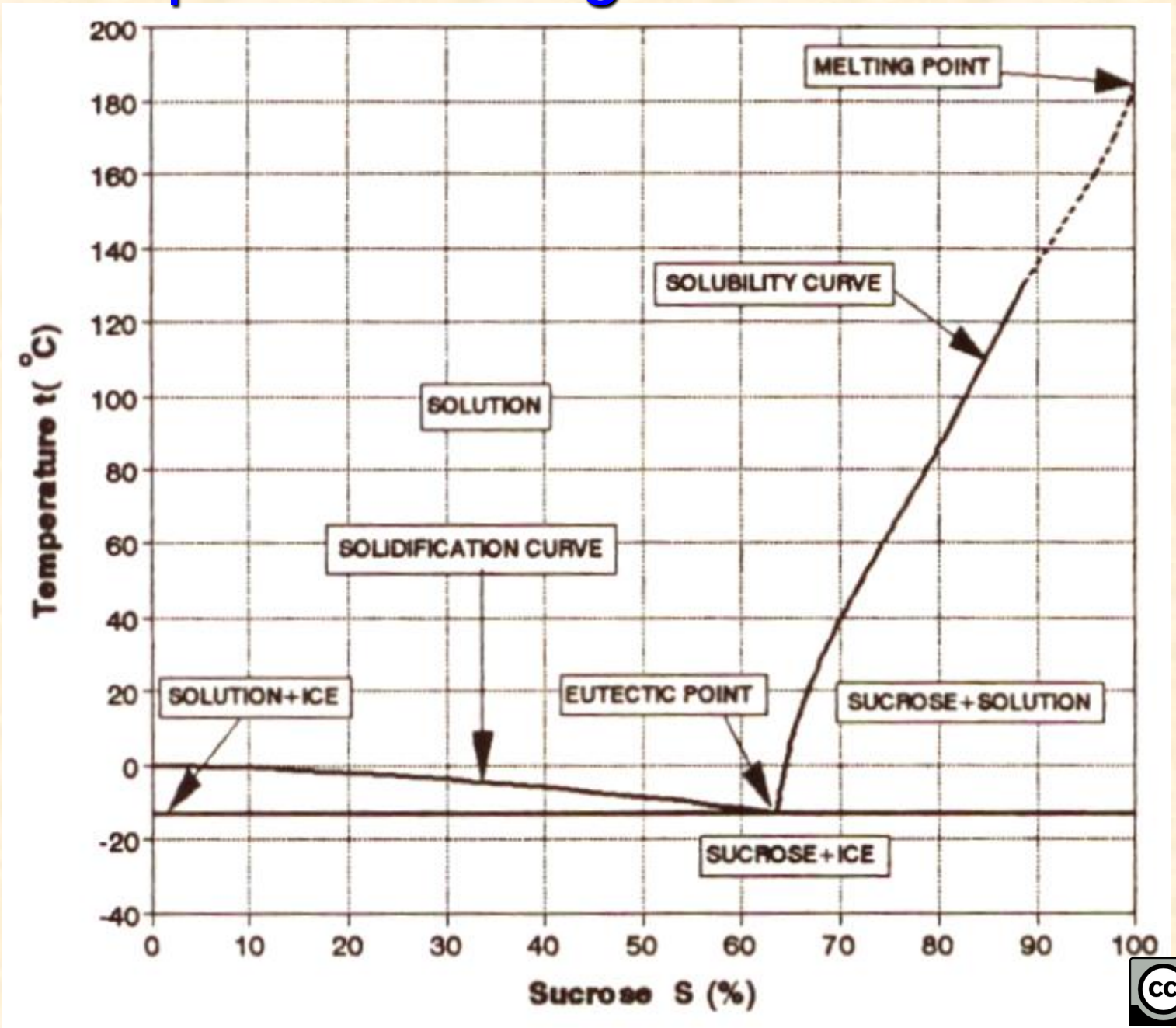
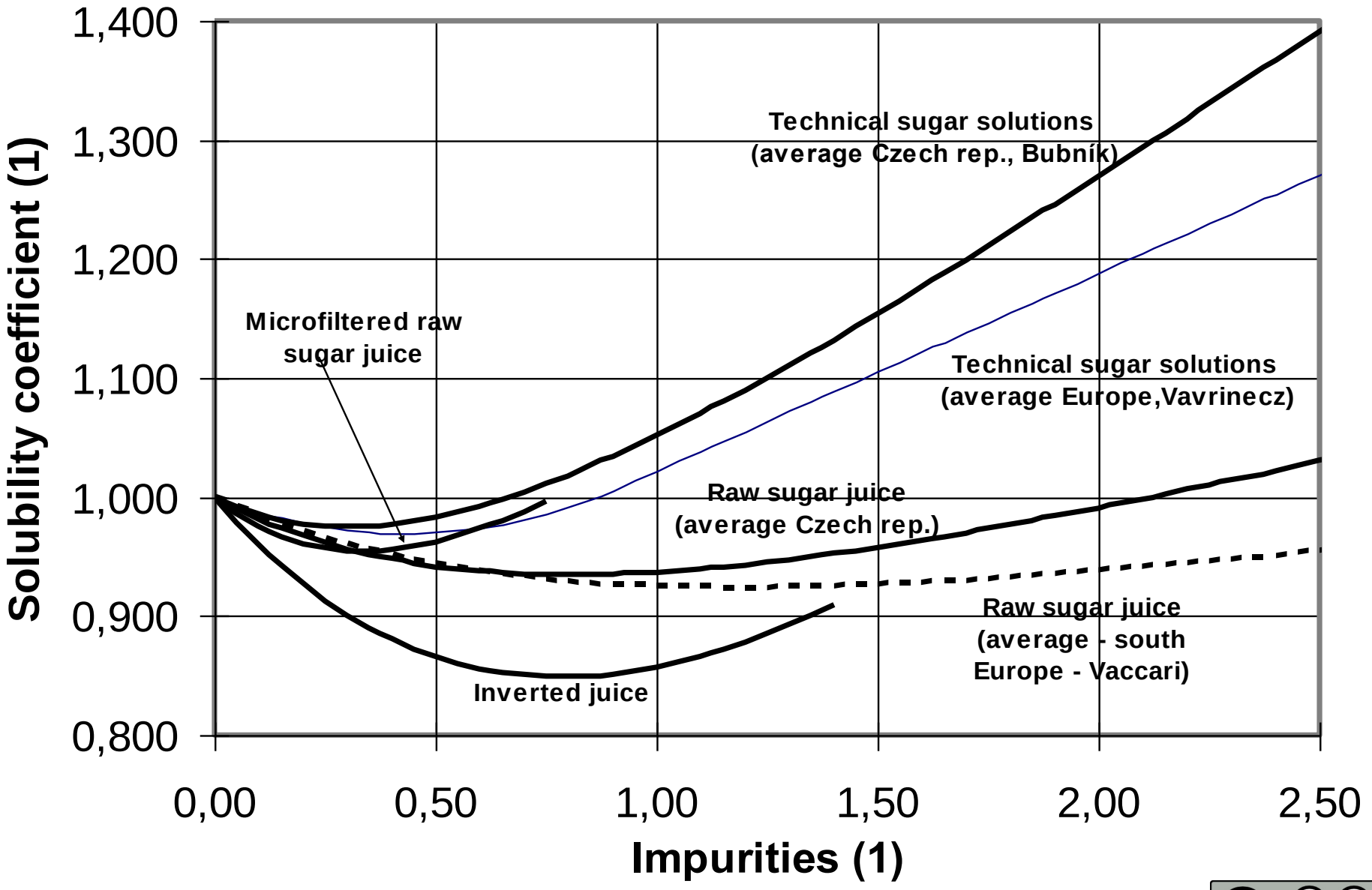
Phase equilibrium diagram sucrose-water



Solubility curves for technical sugar solutions



The thermodynamic driving force of crystallization

crystallization driving force expressed in terms of the **supersaturation**

- defined as: $\Delta c = c - c_{eq}$
- or the relative supersaturation: $s = (c - c_{eq})/c_{eq} = \Delta c/c_{eq}$
- or supersaturation ratio: $S = c/c_{eq} = s + 1$.

Kinetics of Nucleation

Primary nucleation:

Nucleation rate N_N (#/s.m³)

$$\frac{dN}{d\tau} = k_N (c - c_{eq})^n$$

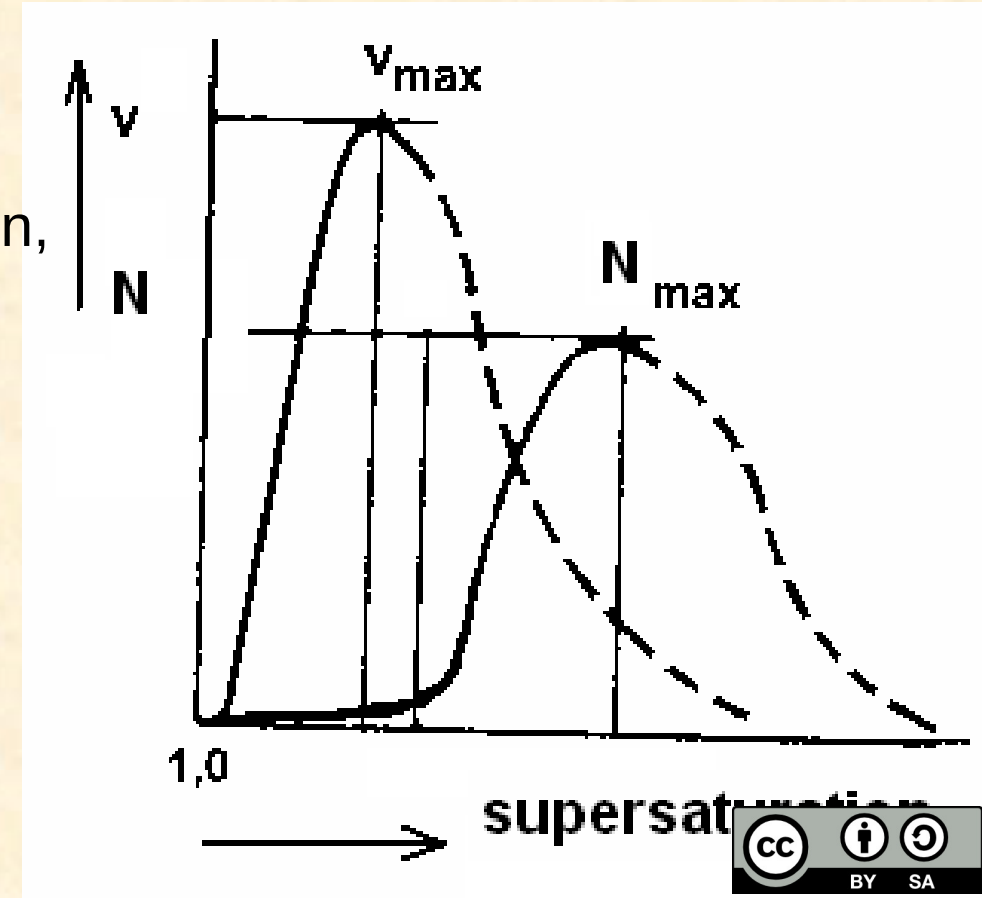
where N = the number of crystals

k_N = the rate constant of nucleation,

n = the nucleation exponent

N_m (kg/s.m³)

$$\frac{dm_N}{d\tau} = k_{Nm} (c - c_{eq})^n$$



Secundary nucleation

Nucleation rate N_N (#/s.m^3)

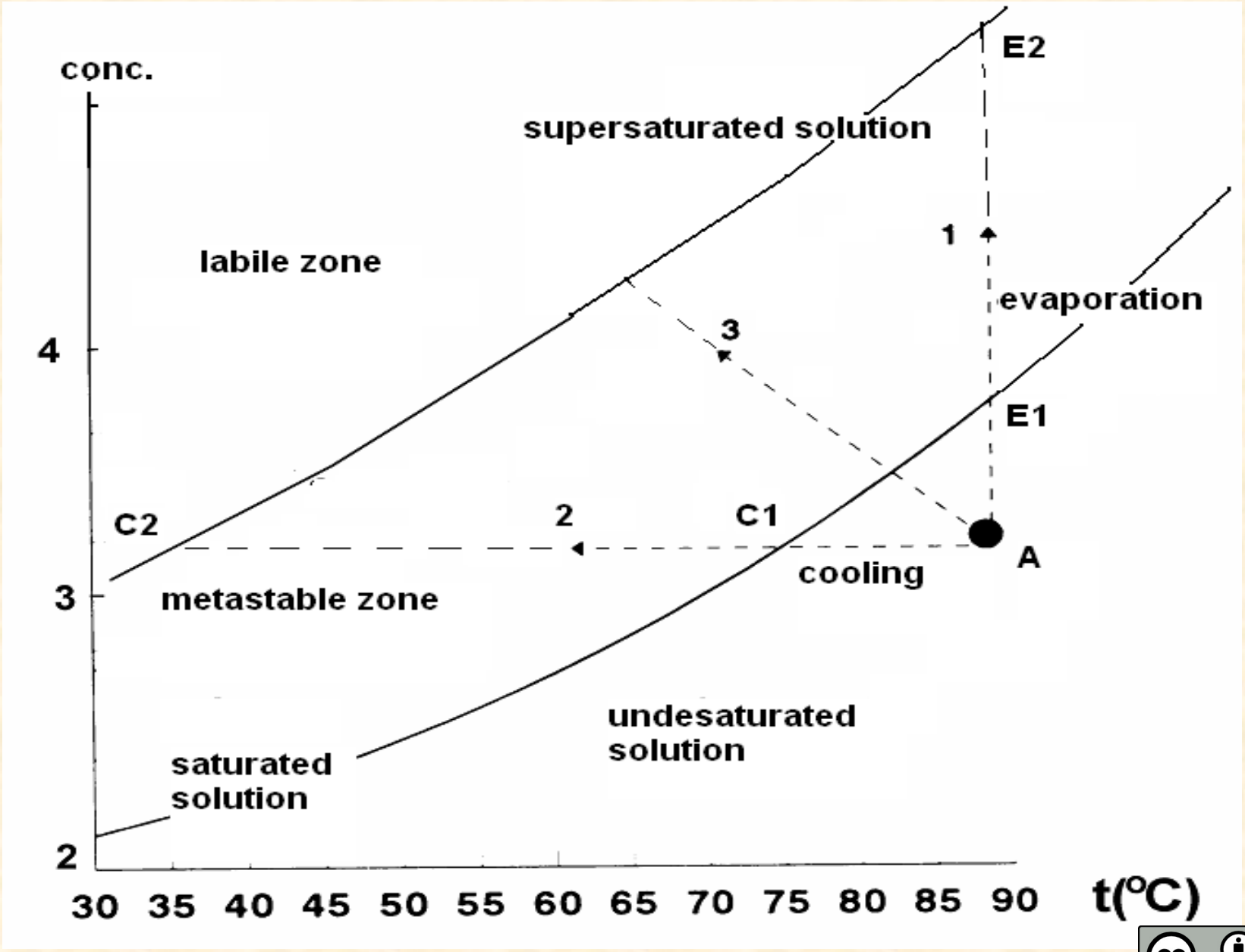
$$\frac{dN}{d\tau} = k_{Ns}.m^c(c - c_{eq})^n$$

where N – number of crystals, k_{Ns} – rate konstant of nucleation, n – nucleation exponent, m – mass of presented crystals, c - coefficient

Effect of Individual Parameters on Secondary nucleation:

…. + Concentration of suspension, crystal abrasion (see photo)

Metastable zone



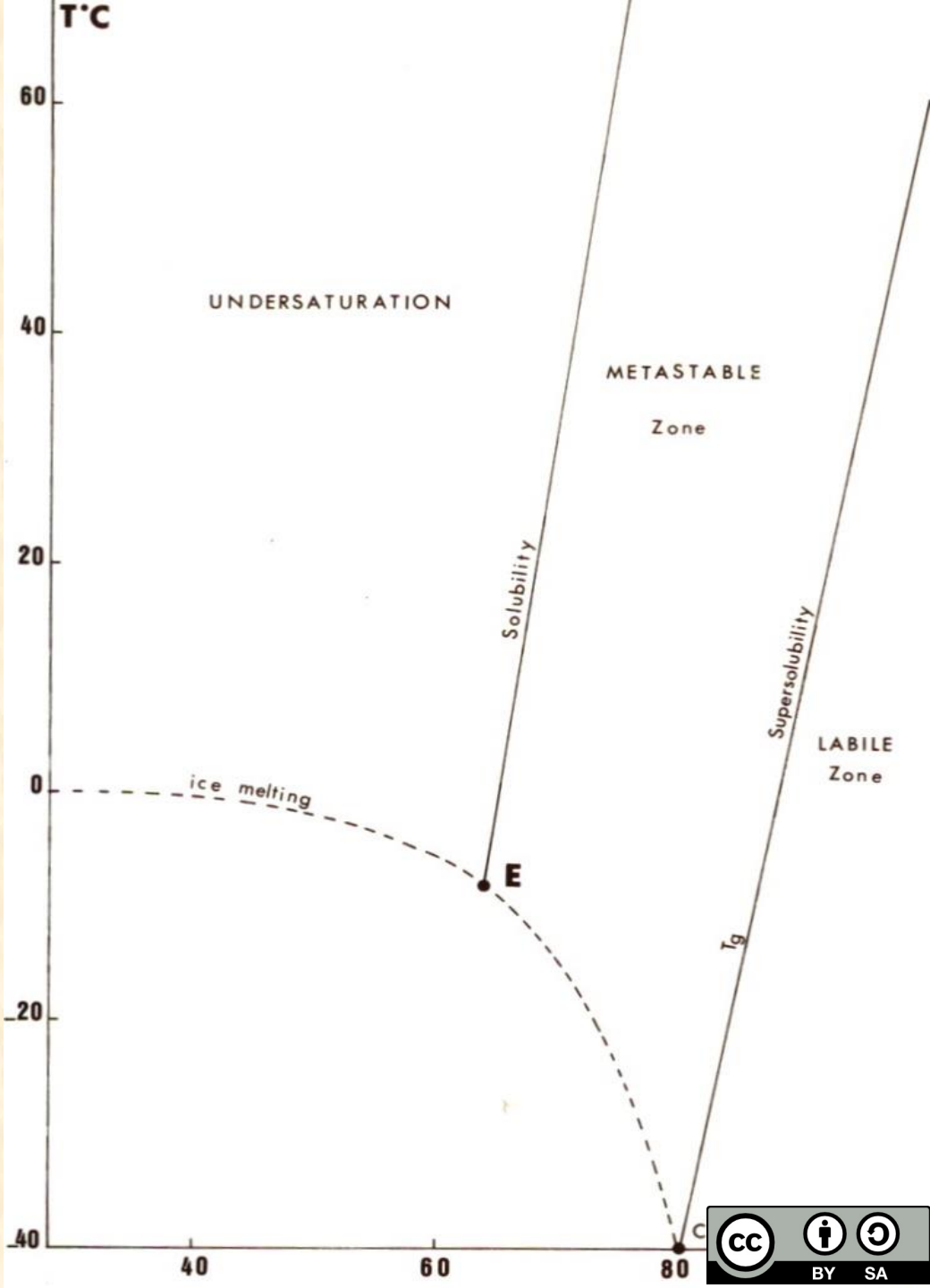
Phase diagram of sucrose-water binary system

showing:

(-------) the ice-melting curve,

(E) the hypothetical eutectic point (-13,9°C) ,

the maximally concentrated amorphous solution with C'_g = 80 % and T'_g = - 40°C



Dependence of ultrasonic rate on temperature in determination of the metastable zone of citric acid

(by Omar and Ulrich)

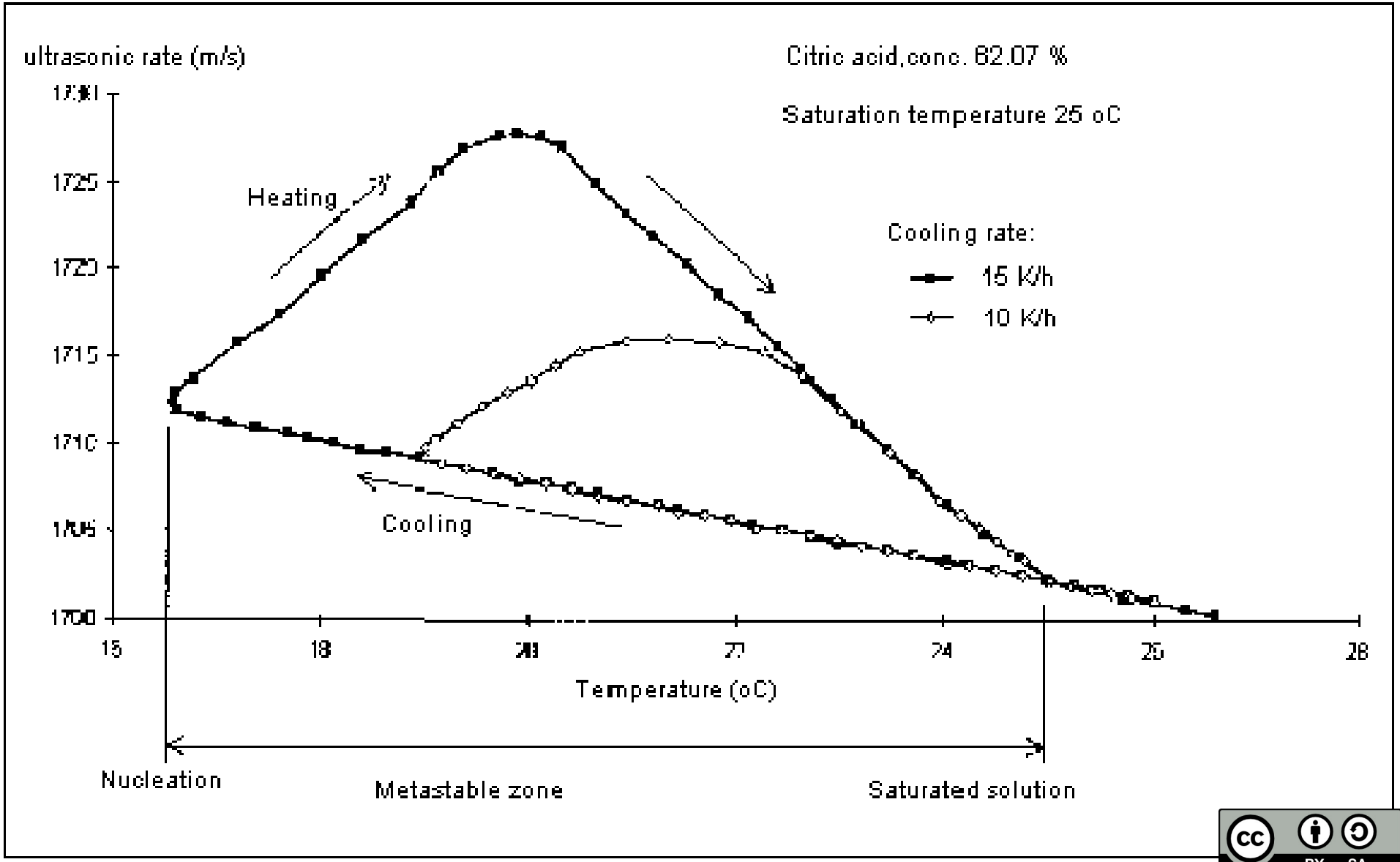
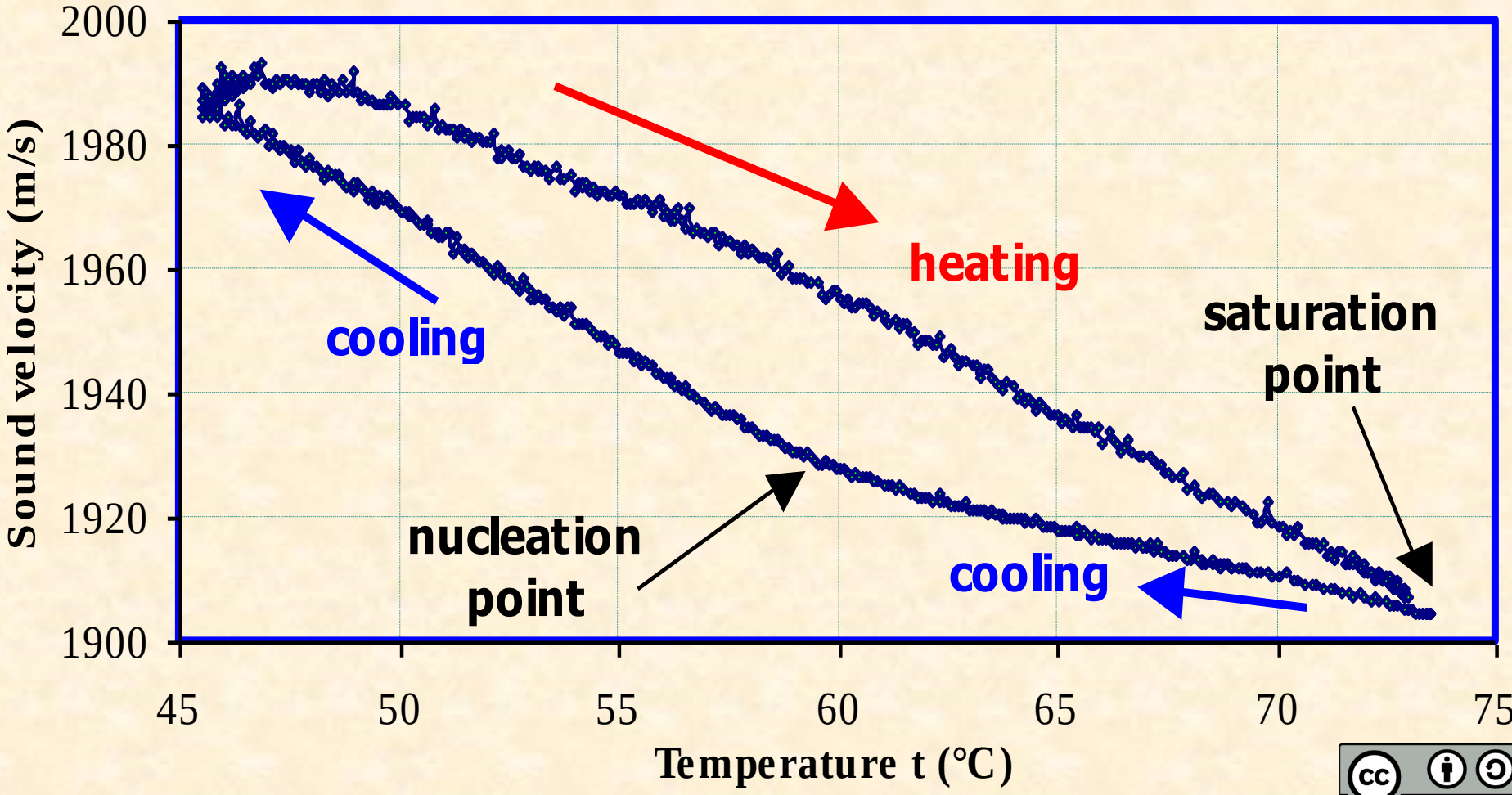


Illustration of the course of the sound velocity

Metastable zone width and solubility determination in one test
(pure sucrose solution: dry subst. 75.62 %, cooling and heating rate 10 °C/h).



The crystal growth rate - Basic concepts

The **rate of growth** can be characterised in several different ways:

❖ **Linear growth rate** is expressed by a change in a characteristic crystal dimension with time: $L_c = dL / d\tau$

❖ The **characteristic dimension** is considered to be a fictitious or actual dimension (crystal length, diameter of a sphere with the same volume etc.)

Crystal shape factors :

❖ Crystal volume is expressed as: $V_c = k_v . L^3$ and its surface: $A_c = k_a . L^2$, then for the **overall linear growth rate** follows: $dV_c / A_c . d\tau$

❖ For chemical engineering applications, the **mass crystal growth** rate is most frequently used: $m_g = dm / d\tau = \rho . dV_c / d\tau$

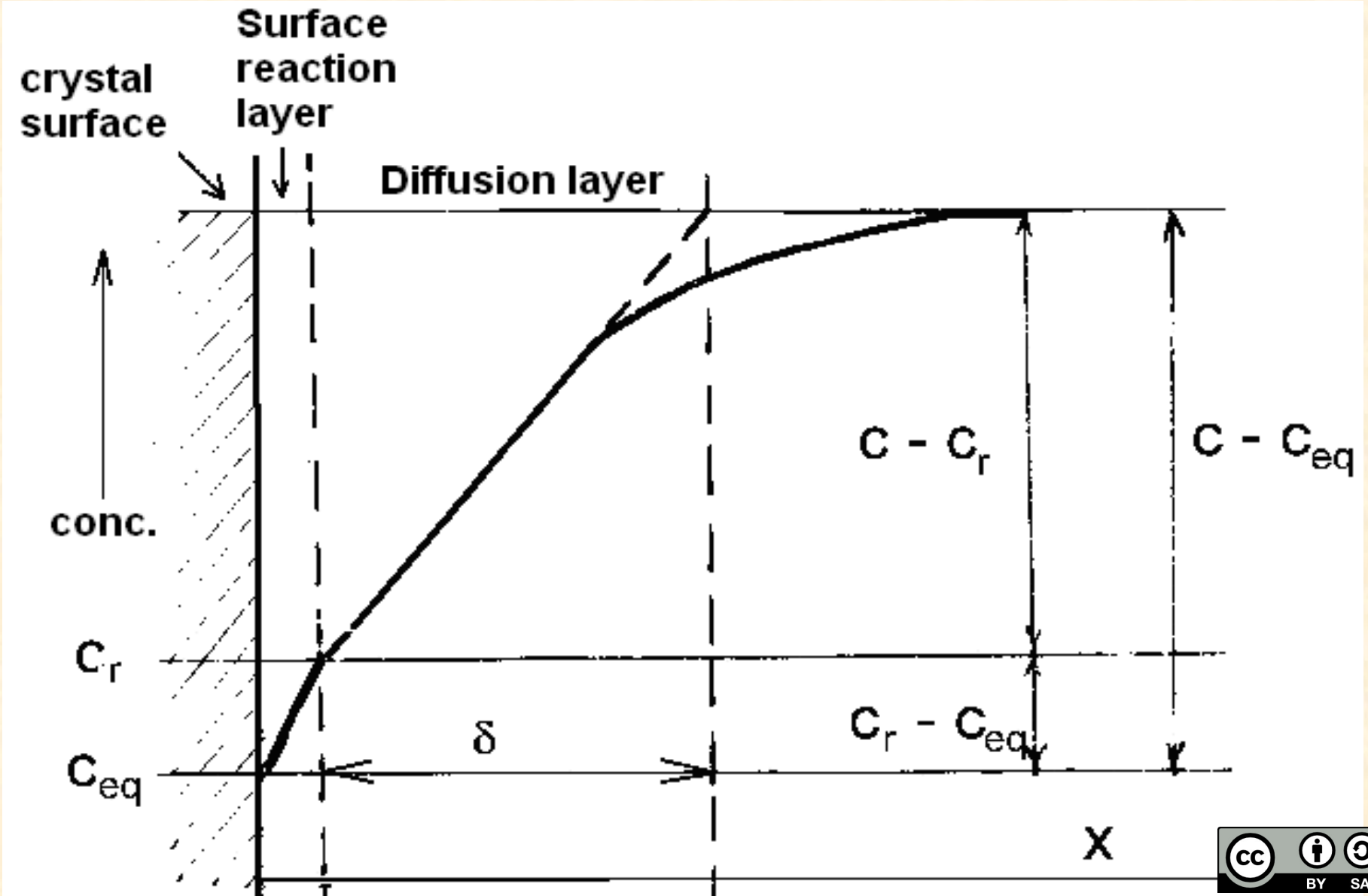
❖ It follows from previous equations that

$$m_g = (3 k_v . \rho / k_a) . A_c . L_c$$

This is the relationship between the mass and the overall linear crystal growth rates.

Diffusion model of the crystal growth

concentration driving force for a two-step process



❖ The last (4th) step may be important only when the removal of heat through conduction and convection is sufficiently slow and is important especially in the **crystal growth from melts**.

❖ **The Diffusion rate** can generally be described by the Fick's first law:

$$\frac{dm}{d\tau} = A\,k_d\,(c - c_r) = A\,\frac{D}{\delta}\,(c - c_r)$$

where $k_d = D/d$.

❖ The **Rate of incorporation** of particles into the crystal lattice **(surface reaction)** is dependent on the difference in concentrations of species within the boundary layer and that in the saturated solution. It can be written to a first approximation that:

$$\frac{dm}{d\tau} = k_r\,(c_r - c_{eq})^r$$

where r is an exponent with a value dependent on the conditions, primary on the supersaturation (limits from 1 to

In case of **steady state**, the velocity of both processes is the same. If $r = 1$, then the difficult-to-measure concentration at the crystal surface c_r is eliminated:

$$v = \frac{dm}{A\,d\tau} = \frac{1}{\frac{1}{k_d} + \frac{1}{k_r}}(c - c_{eq}) = \frac{k_d\ k_r}{k_d + k_r}(c - c_{eq}) = K\ \Delta c$$

If $r = 1 - 2$, then after approximation: $v = K\,\Delta c^g$

where K – crystallization constant, g – exponent of crystallization.

From this equations follows:

If $k_d >> k_r$, then $v = k_r\,\Delta c$ (crystallization proces is controlled by surface reaction);

If $k_r >> k_d$, then $v = k_d\,\Delta c$ (crystallisation proces is controlled by diffusion)

Resistance of Crystallization process

$$W = \frac{1}{K} = \frac{1}{k_d} + \frac{1}{k_r} = W_d + W_r$$

Resistance of Diffusion process

$$W_d = \frac{1}{k_d} = \frac{\partial}{D}$$

Resistance of Surface reaction

$$W_r = \frac{1}{k_r}$$

Example - control process

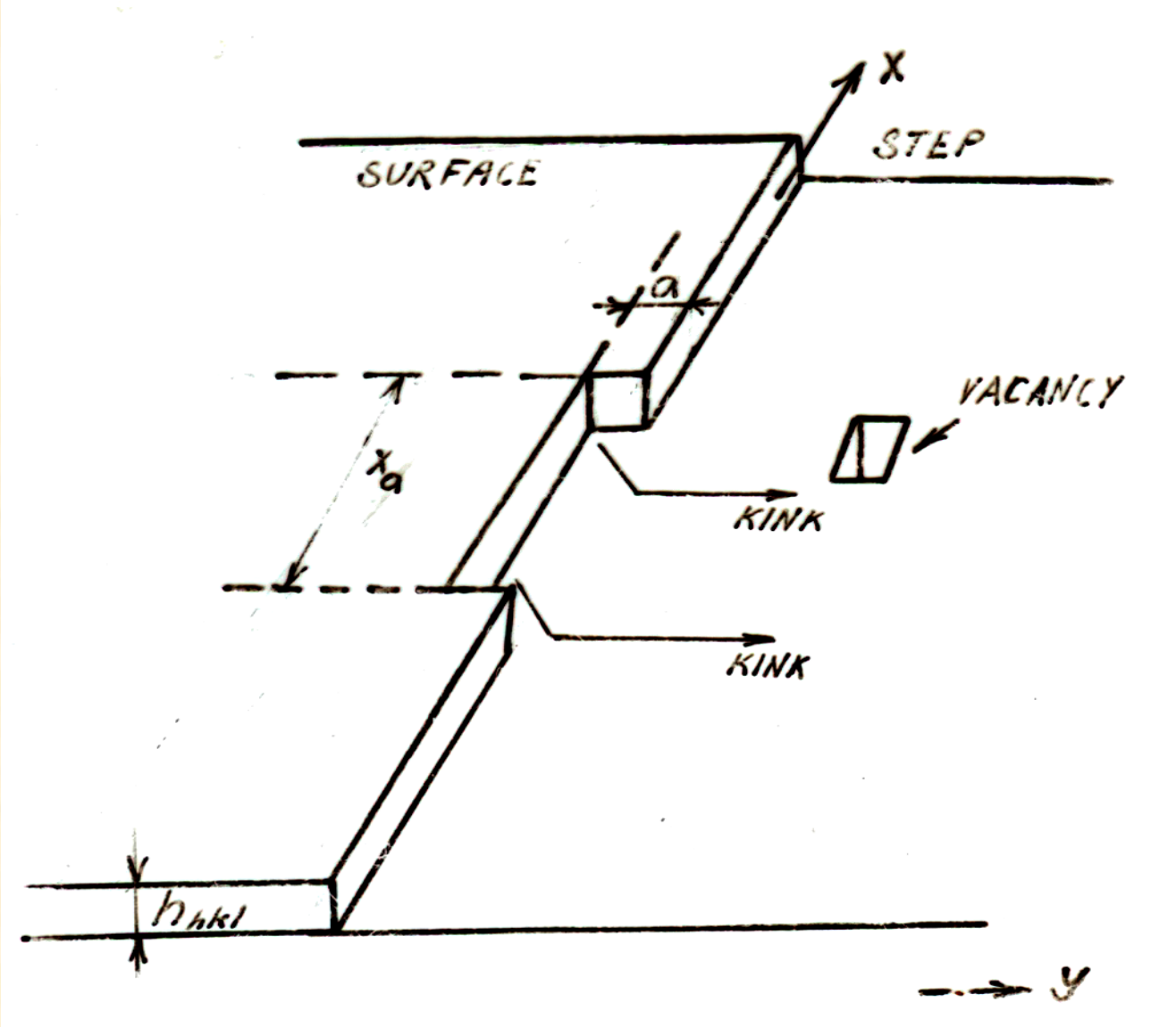
$D = 1{,}7.10^{-10}\, m^2/s$ $\quad \partial = 43.10^{-6}\, m$

$k_R = 67{,}8.10^{-6}\, m/s$

??? k_d , W_d , W_r , W

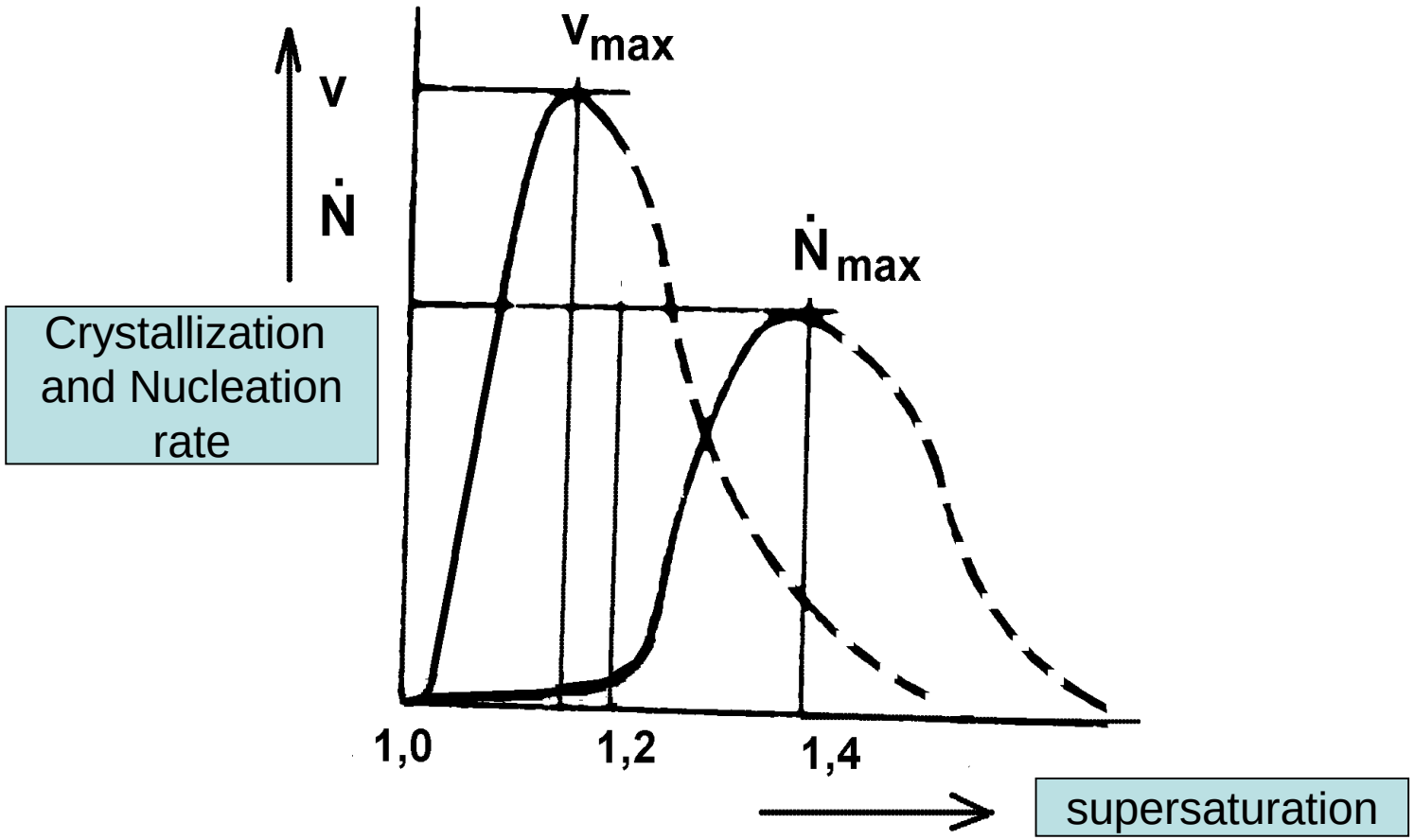
if W = 100 % , that W_d = ? % , W_r = ? %

The incorporation of particles into the crystal lattice **(surface reaction)**



Effect od supersaturation on crystallization and nucleation rate

(example: sucrose)



❑ **Supersaturation** $v = K\,\Delta c^{g}$

❑ **Temperature:** Arrhenius equation $K = K_0\,.\exp(-E/R.T)$

where K – crystallization constant, K_0 - coefficient, E – activation energy, R – gas constant, T – temperature.

❑ **Viscosity**: $v = \dfrac{k}{\eta^{q}}$

where v – crystallization rate, k - coefficient, q - exponent, η – dynamic viscosity

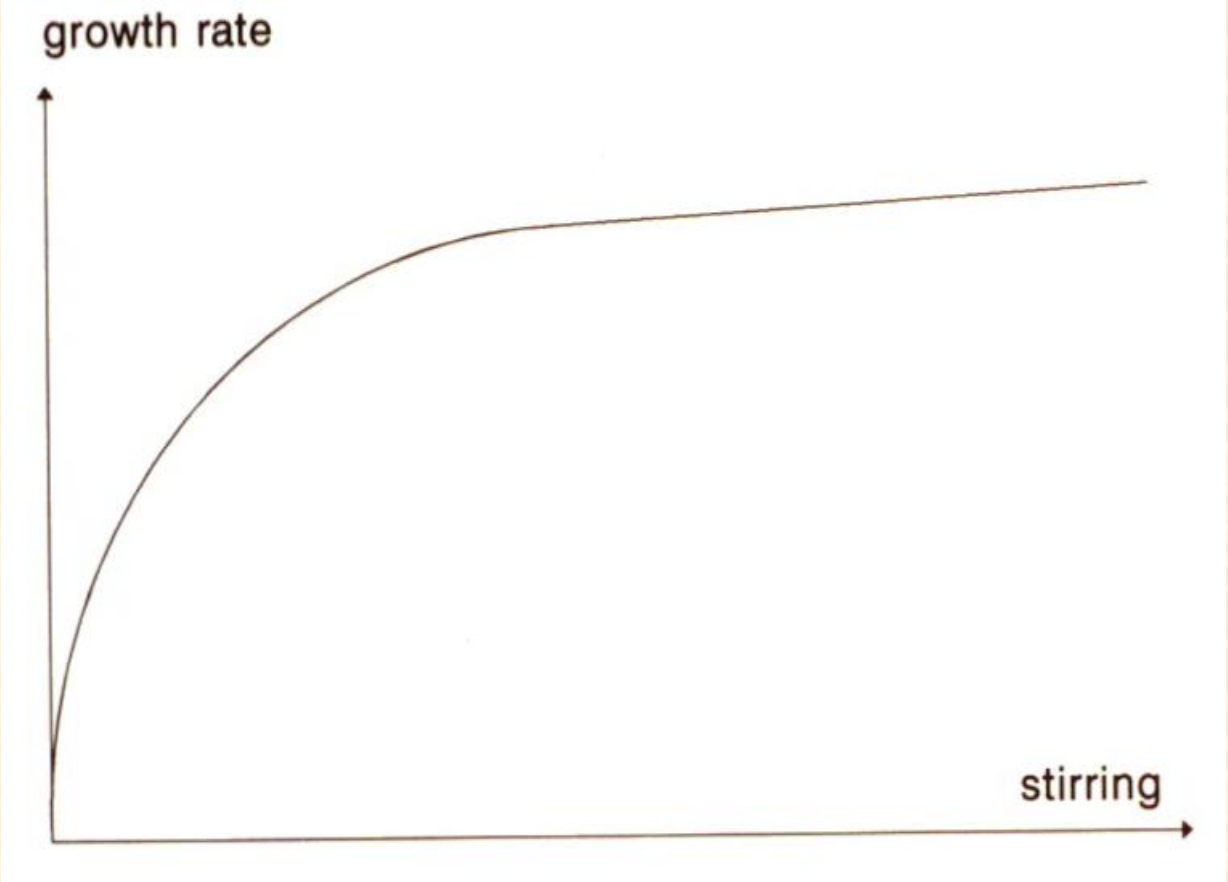
❑ **Hydrodynamic condition:** $Sh = a\,\mathrm{Re}^{0,6}\,Sc^{0,3}$

where *Sh* – Sherwood number, ***Re* – Reynolds number**, *Sc* - Schmidt number

❑ **Intensity of mixing**: $K = k.\,u^{2/3}$

where *K* – crystallization constant, *k* - coefficient, *u* – stirring frequency.

Limit of stirring



❑ **Crystal length (diameter):** $\dot{L} = k_L . L^b$ (Bransom eq.)

❑ **Crystal content:** $\nu = \nu_1 . \varepsilon^2$

where ν – crystallization rate in crystal suspension, ν_1 – crystallization rate at the presence of one crystal, ε - porosity.

Crystallization process - Mass transfer

$$Sh = a + b\,Re^{c}\,Sc^{d}$$ **Froessling equation**

$$Sh = 0{,}29\,Re^{0{,}6}\,Sc^{1/3}$$ (for mixing)

Sherwood Number (mass transport)

$$Sh = \frac{k_d\,L}{\rho_l\,D}$$

Schmidt Number (physical properties)

$$Sc = \frac{\eta}{\rho_l\,D}$$

Reynolds Number

(fluid dynamics)

$$Re = \frac{u\,L\,\rho_l}{\in \eta}$$

$$Re = \frac{u\,L\,\rho_l}{\eta}$$

Mass and energy balance

Mass balance

$$m_o = m_f + m_c + m_g$$

input sol. mother sol. crystals vapour

Energy balance

$$m_o \; c_{p,o} \; t_o + m_r \; h_r + Q = m_f \; c_{p,f} \; t_f + m_c \; h_c + m_g \; h_g + m_c \; c_{p,c} \; t_c + Q_z$$

Input solution | Reaction | Heating | Mother solution | Crystallization heat | Vapour | Crystal | Heat loss

The Dynamics of establishing a steady state

❖ In order for steady state to be attained in the crystallizer **after the beginning** of the experiment, it is usually necessary that it works with constant parameters for the **time equal to six- upto sixteen-times the mean retention time** of the solution.

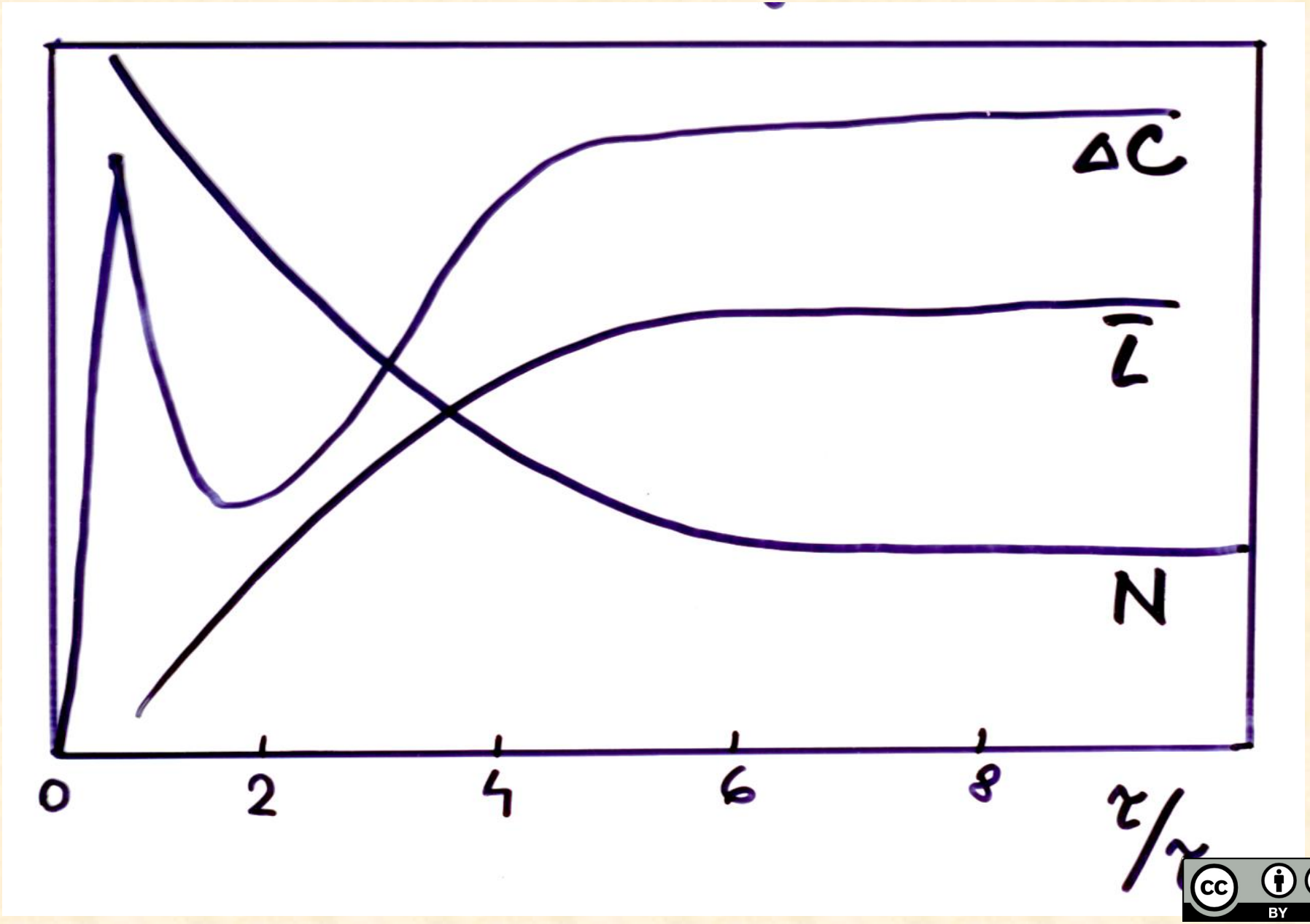
❖ the crystallizer may even work permanently in a **periodically oscillating state**.

❖ The conditions, under which such instability occurs, have not yet been satisfactorily explained, but it can be expected that the crystallizer will attain steady state in most cases.

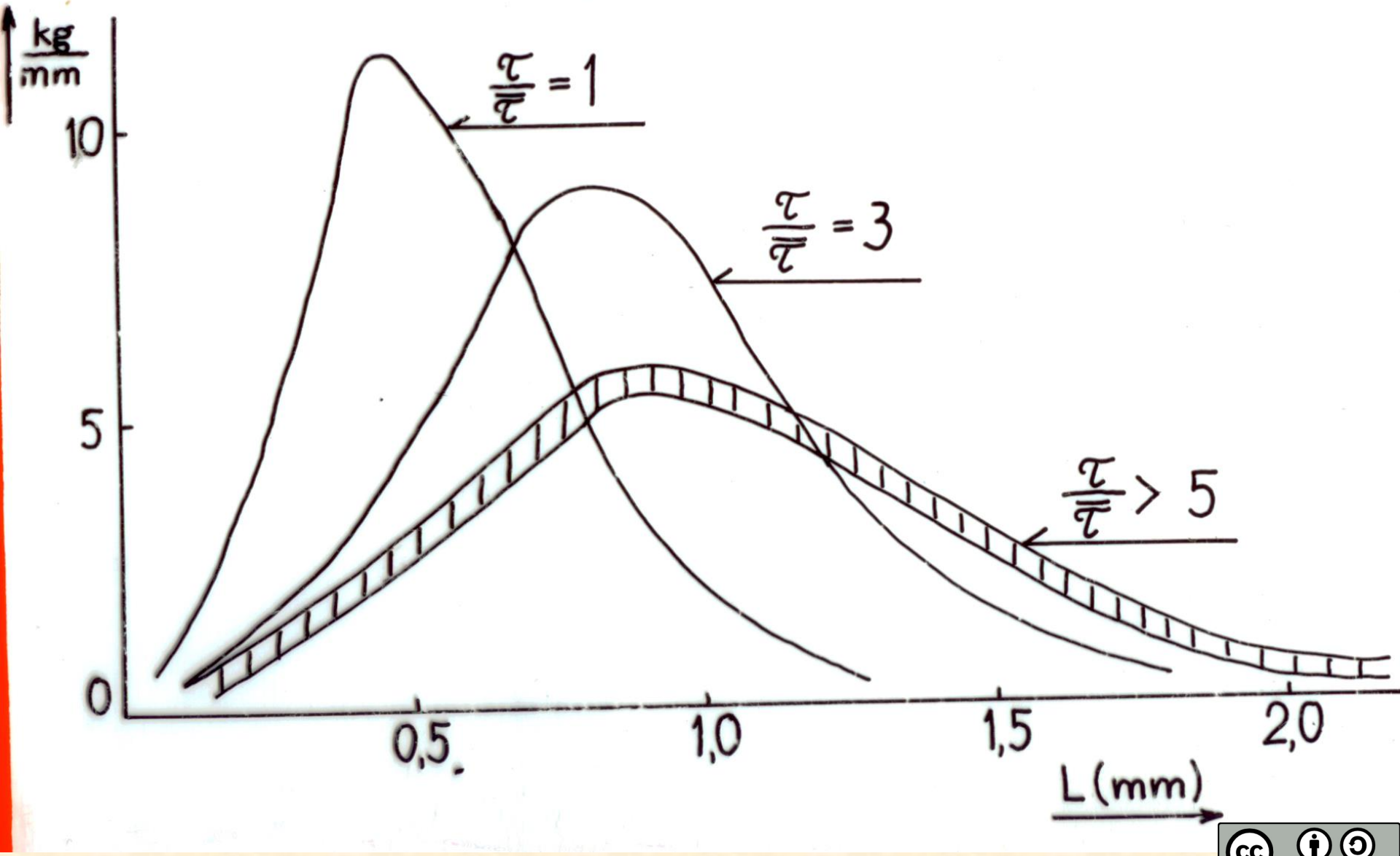
❖ A mathematical model of a **continuous crystallizer** that permits to study the steady-state dynamics is based on **simultaneous solution of the supersaturation balance:**

$$\frac{d(c-c_{eq})}{d\tau} = s - K.A_c(c-c_{eq})^g - k_{Ns}.m^c(c-c_{eq})^n$$

Process parameters during steady state achievement



Crystal size distribution during steady state achievement



Advanced Processes in Food Technology and Biotechnologies

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Crystal Size Distribution

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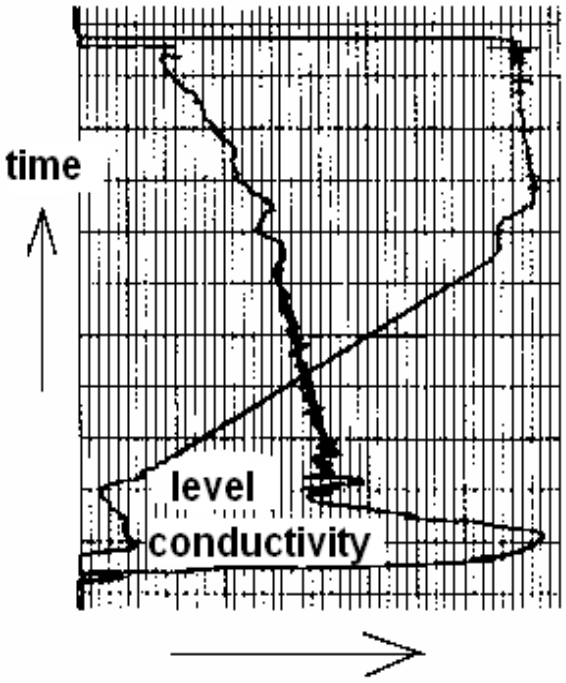
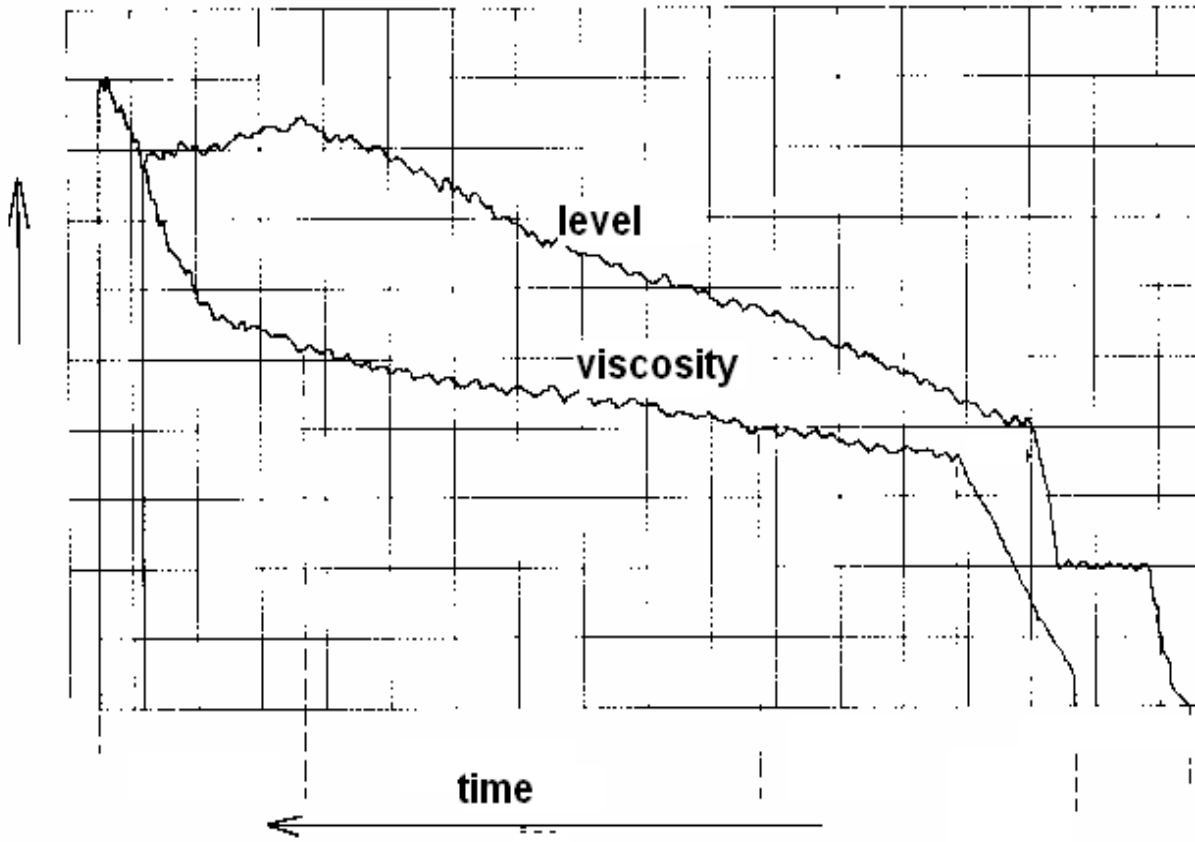
Control of the crystallization process by conductivity and viscosity measurements





Crystal Size Distribution - CSD

CSD: also termed the **sieve spectrum**

- Number distribution
- Mass distribution

Two basic forms of distribution:

- the differential size distribution f(L)

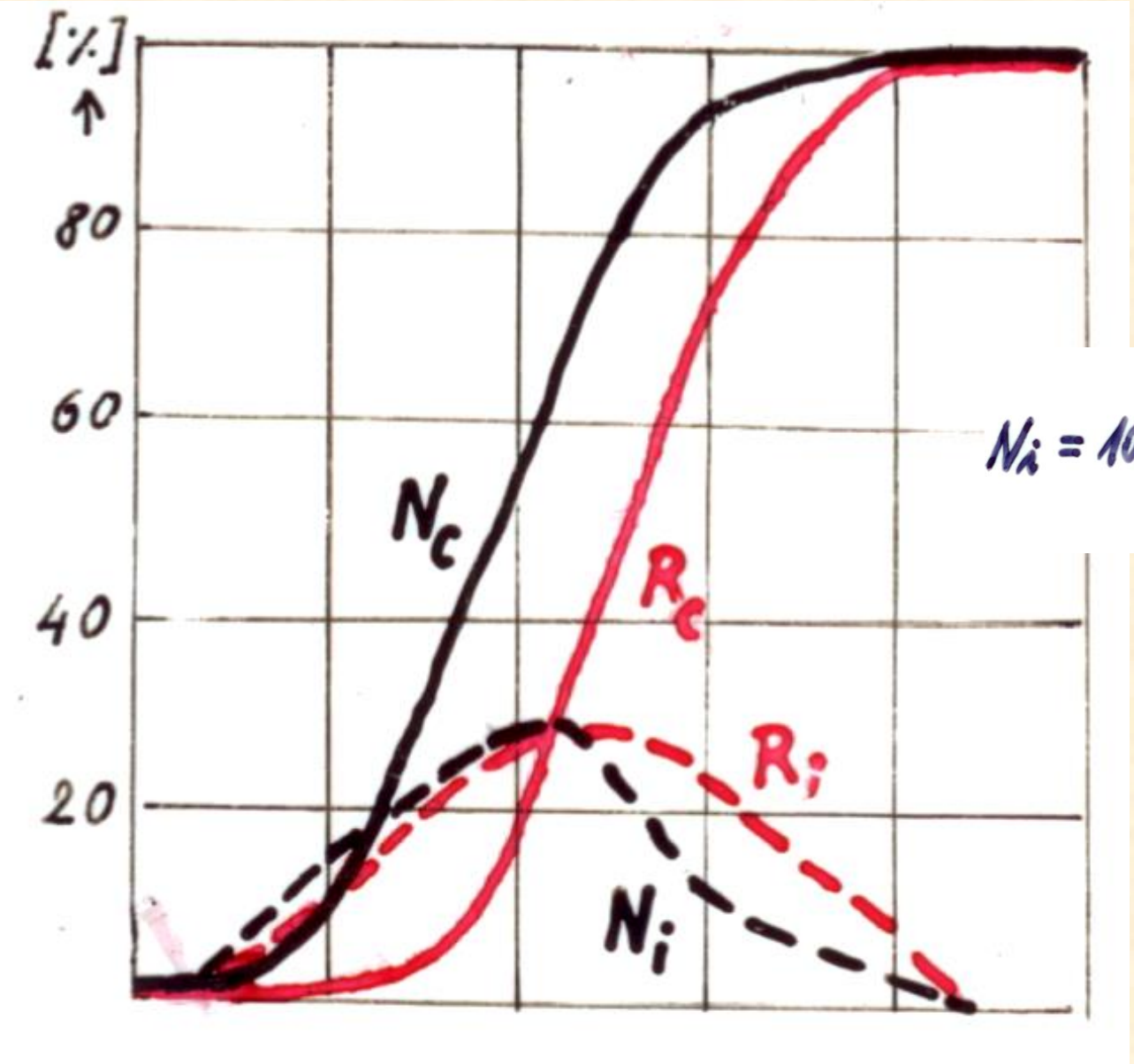
  - fraction: number or mass

- the cumulative distribution F(L)

  - “oversize fraction“

CSD measurement: sieve analysis, image analysis, optical methods, sedimentation, laser device …

Graphical representations of the number (N) and mass (R) in the CSD



$$N_i = 100 \frac{n_i}{\sum n_i} = 100 \frac{R_i / L_i^3}{\sum R_i / L_i^3}$$

Distribution functions

Normal distribution (Gauss, symmetrical around L_{50})

$$f(L) = \frac{1}{\sigma(2\pi)^{1/2}} \exp\left[-\frac{(L - L_{50})^2}{2\sigma^2}\right]$$

Log-Normal distribution

$$f(L) = \frac{1}{(2\pi)^{1/2} \log \sigma} \exp\left[-\frac{\log^2 (L/L_{50})}{2 \log^2 \sigma}\right]$$

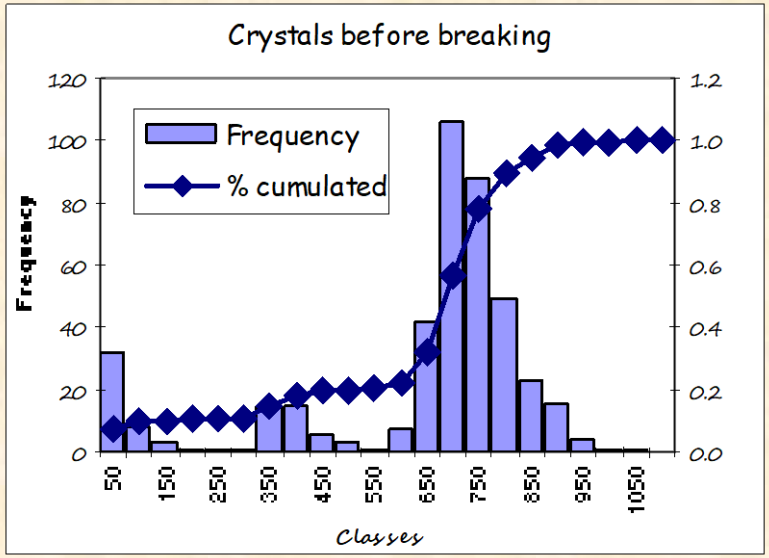
Gamma function

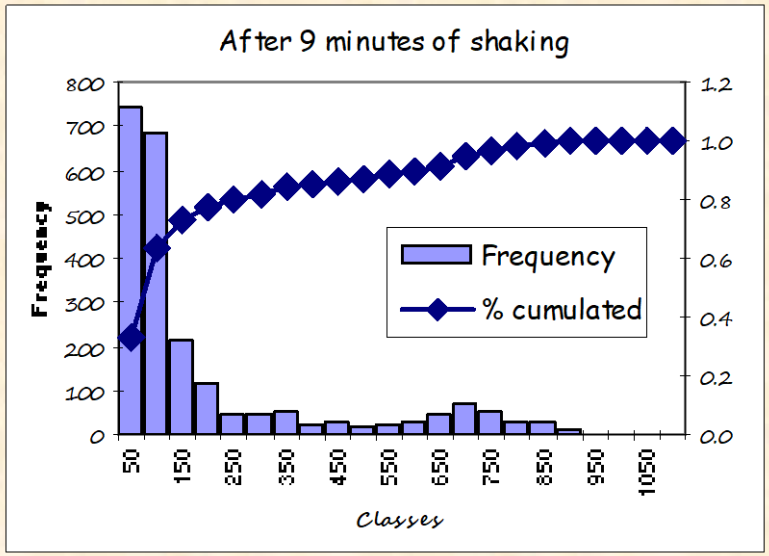
$$f(L) = L^{a'} \exp\left(\frac{a'L}{b}\right) / \Gamma(a' + 1)(b/a')^{a'+1}$$

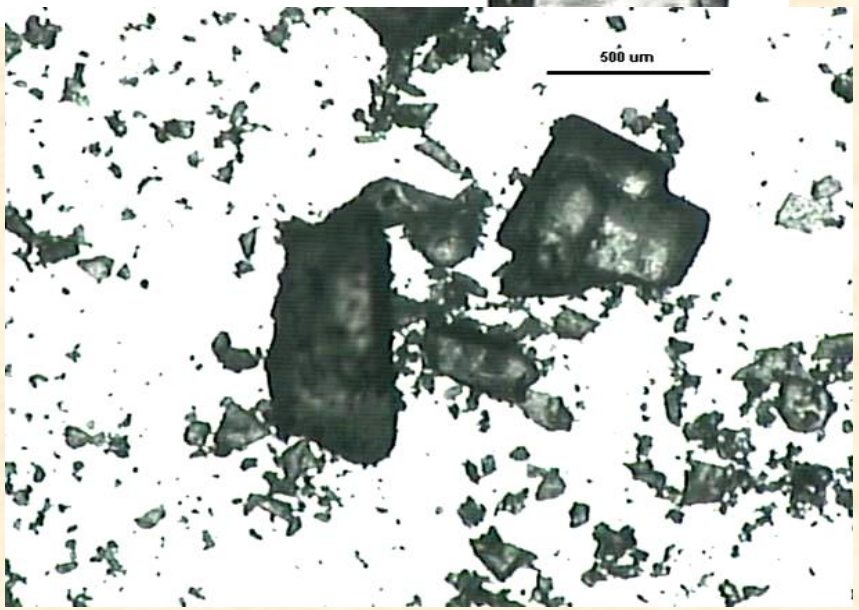
Rosin-Rammler-Sperling (for cummulative distribution)

$$M(L) = 100 \,.\, \exp[-L/L_{\text{mean}})^{\gamma}]$$

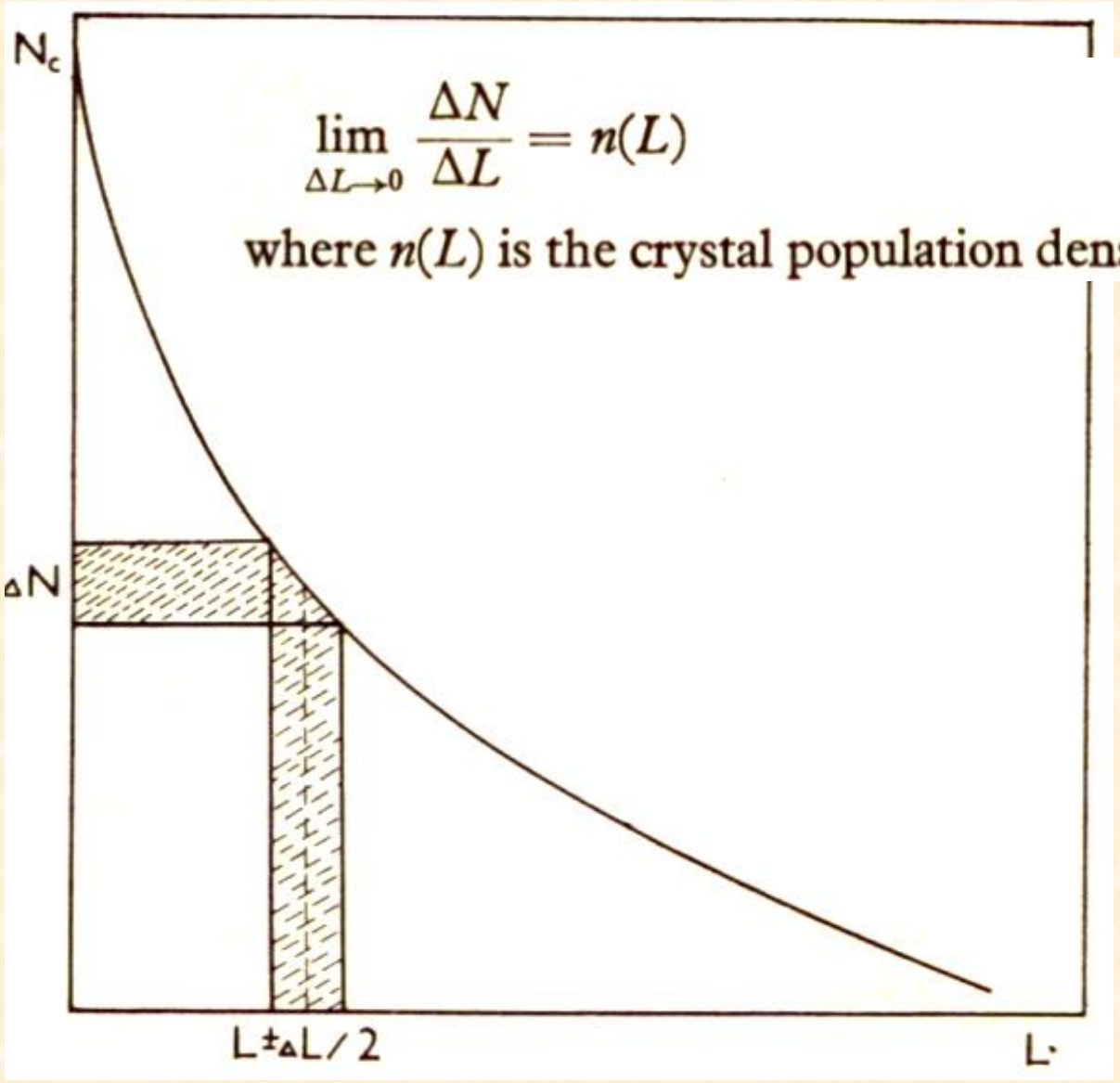
Histograms and pictures of sucrose crystal showing dependence on the period of breaking.







Population Balance



$$\lim_{\Delta L \to 0} \frac{\Delta N}{\Delta L} = n(L)$$

where $n(L)$ is the crystal population density of crystals with size L

Population density n(L) of the crystals can be expressed as a function of their size. Then a complete description of the CSD is obtained (the zeroth to third moment of CSD):

$$N_c = \int_0^\infty n(L)\, \mathrm{d}L\,,$$

$$L_c = \int_0^\infty n(L)\, L\, \mathrm{d}L\,,$$

$$A_c = \beta \int_0^\infty n(L)\, L^2\, \mathrm{d}L\,,$$

$$m_c = \alpha \varrho_c \int_0^\infty n(L)\, L^3\, \mathrm{d}L\,.$$

The population balance of the MSMPR crystallizer: Population Density Balance

At steady state, it holds that

$$\frac{dn}{dt} = 0$$

and the population balance is simplified to the form

$$\frac{dn}{dL} + \frac{n}{\dot{L}\bar{t}_1} = 0$$

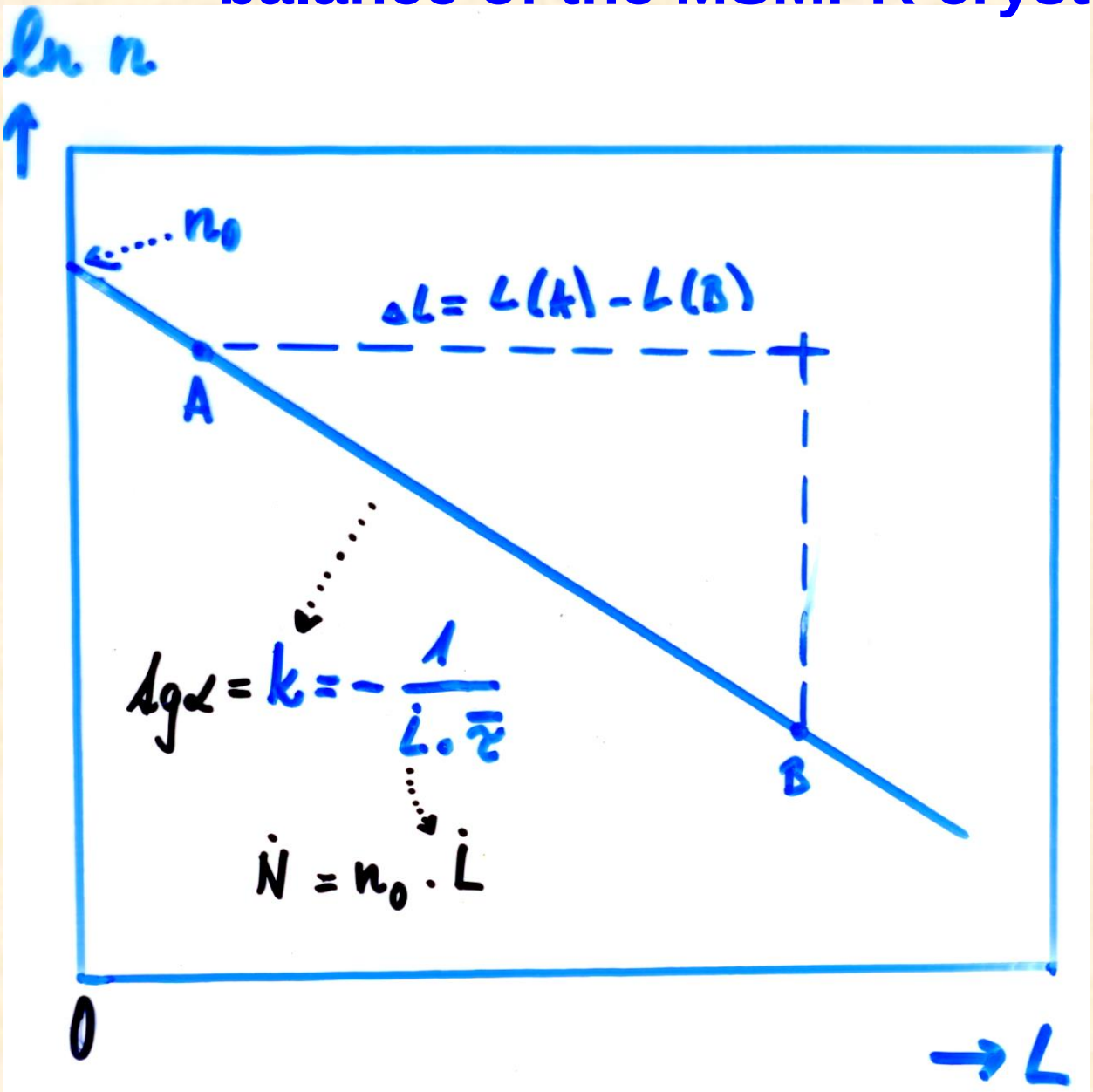
with the solution

$$\int_{n^0}^{n} \frac{dn}{n} = \int_{0}^{L} \frac{dL}{\dot{L}\bar{t}_1}$$

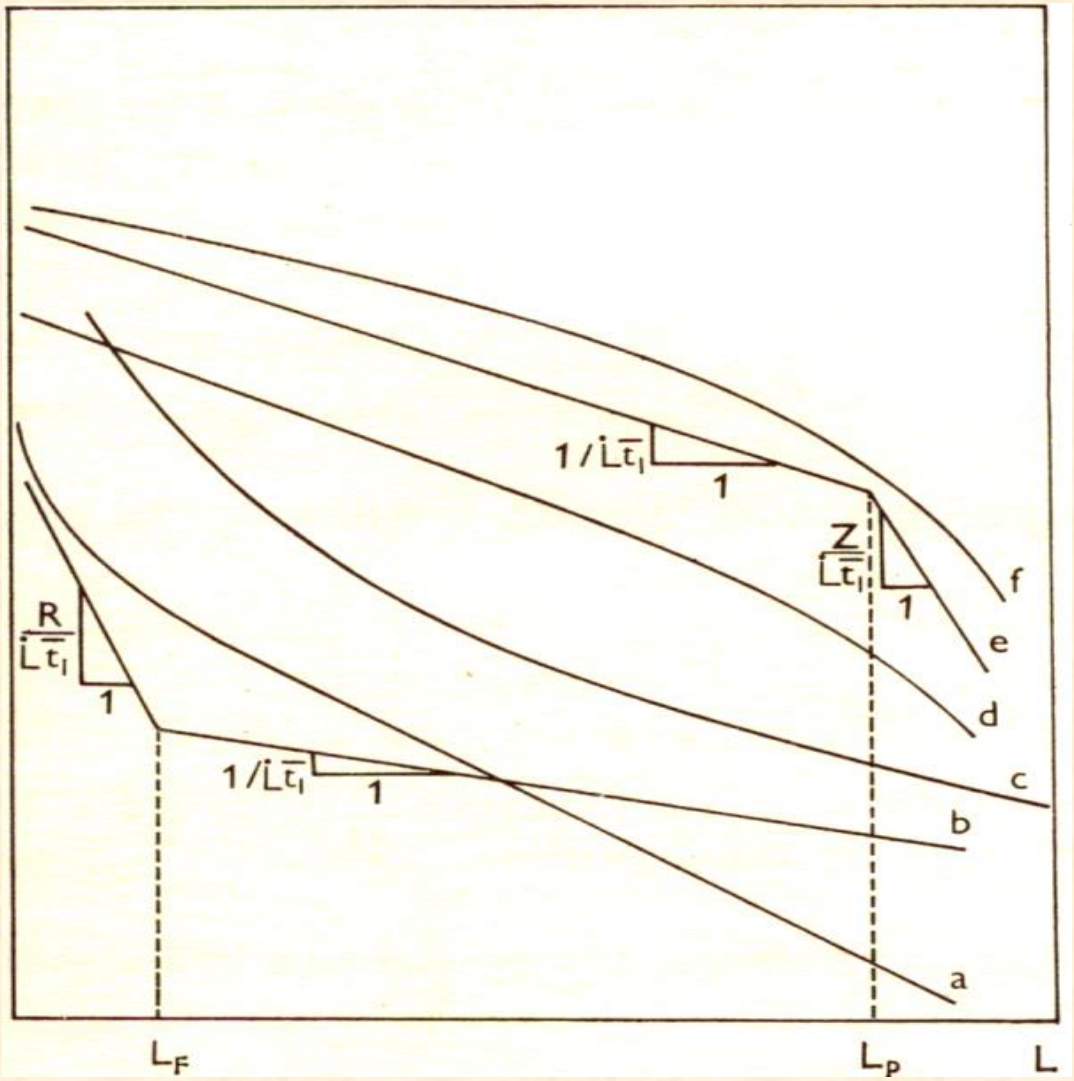
or

$$n = n^0 \exp\left(-L/\dot{L}\bar{t}_1\right).$$

Graphical representation of the population balance of the MSMPR crystallizer

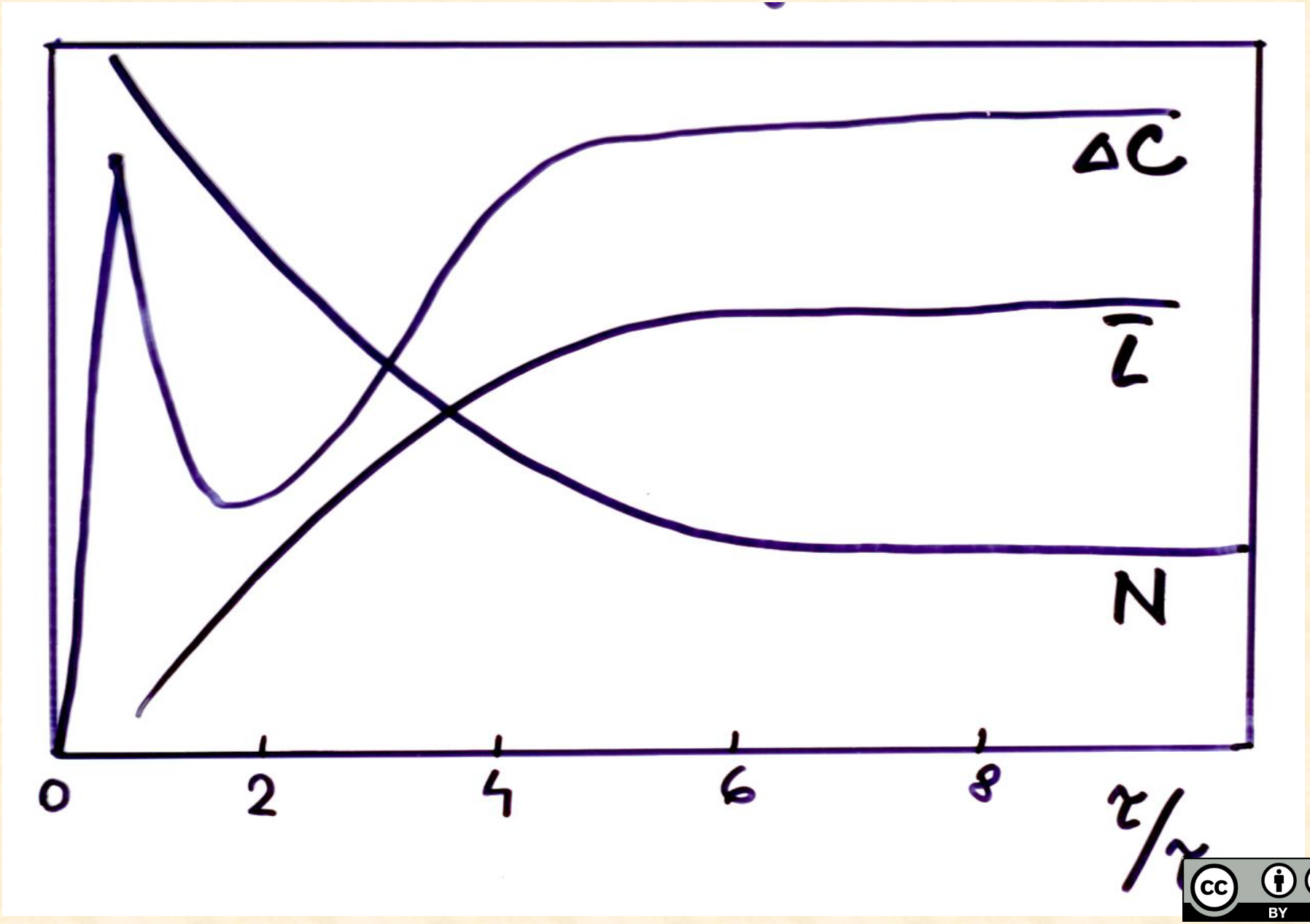


Deviations from an ideal MSMPR crystallizer.

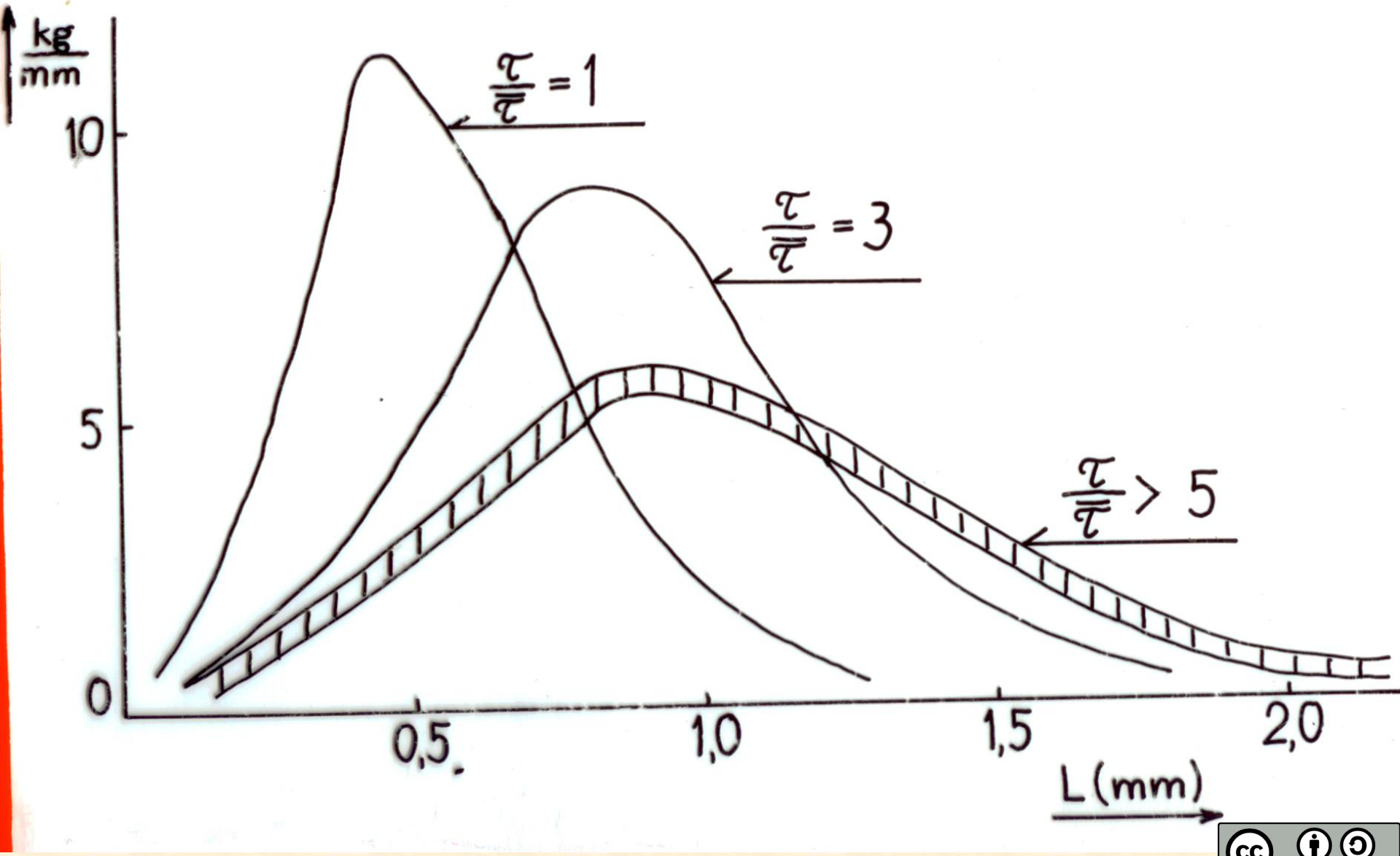


a – unintentional dissolution of small crystals, b – separate dissolution of small crystals, c – deviation from the McCabe ΔL-law, d – internal classification, e – sampling of the classified product, f – splitting of the crystals to particles with comparable sizes.

Process parameters during steady state achievement



Crystal size distribution during steady state achievement



Advanced Processes in Food Technology and Biotechnologies

Exercises
Photocatalytic Process

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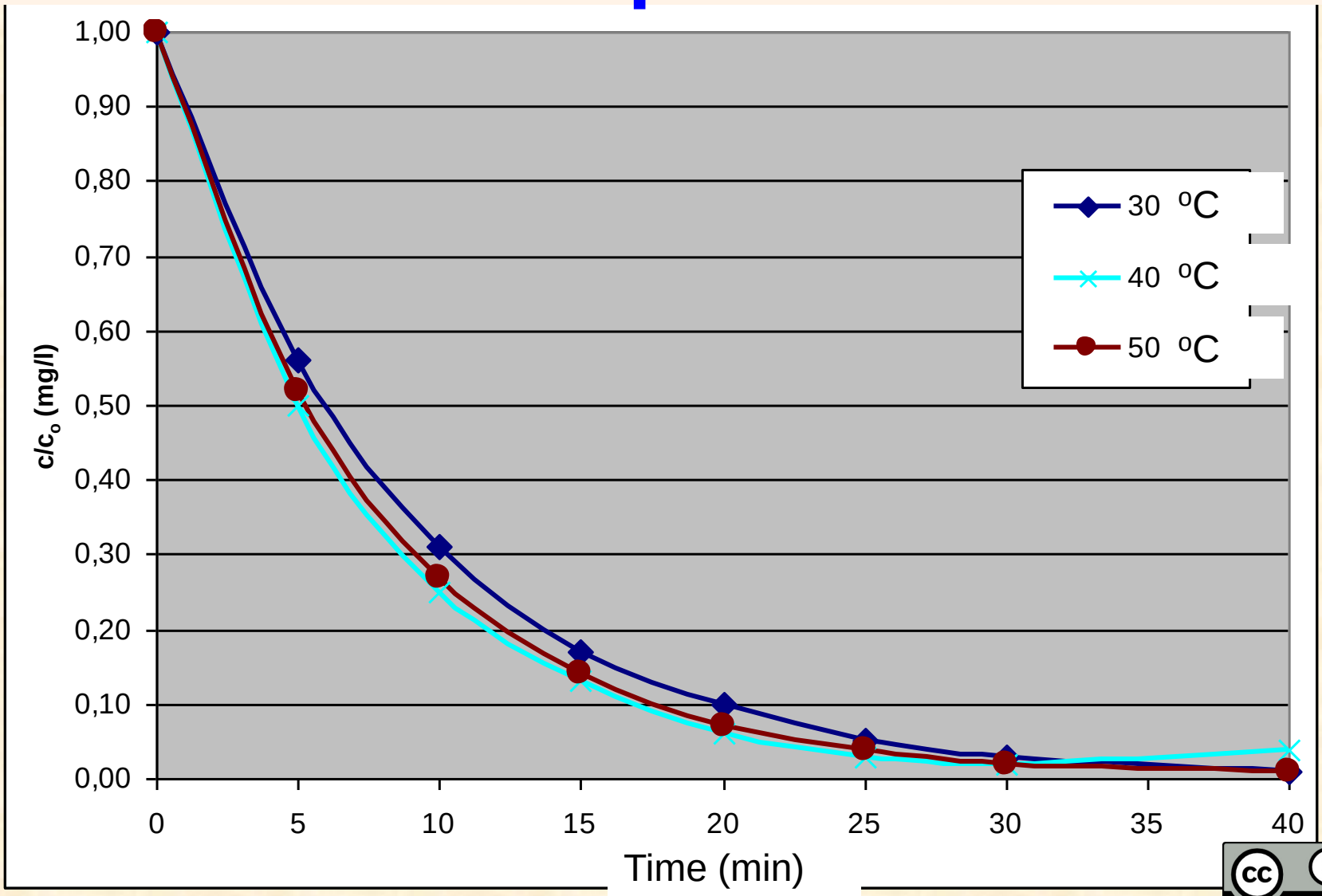
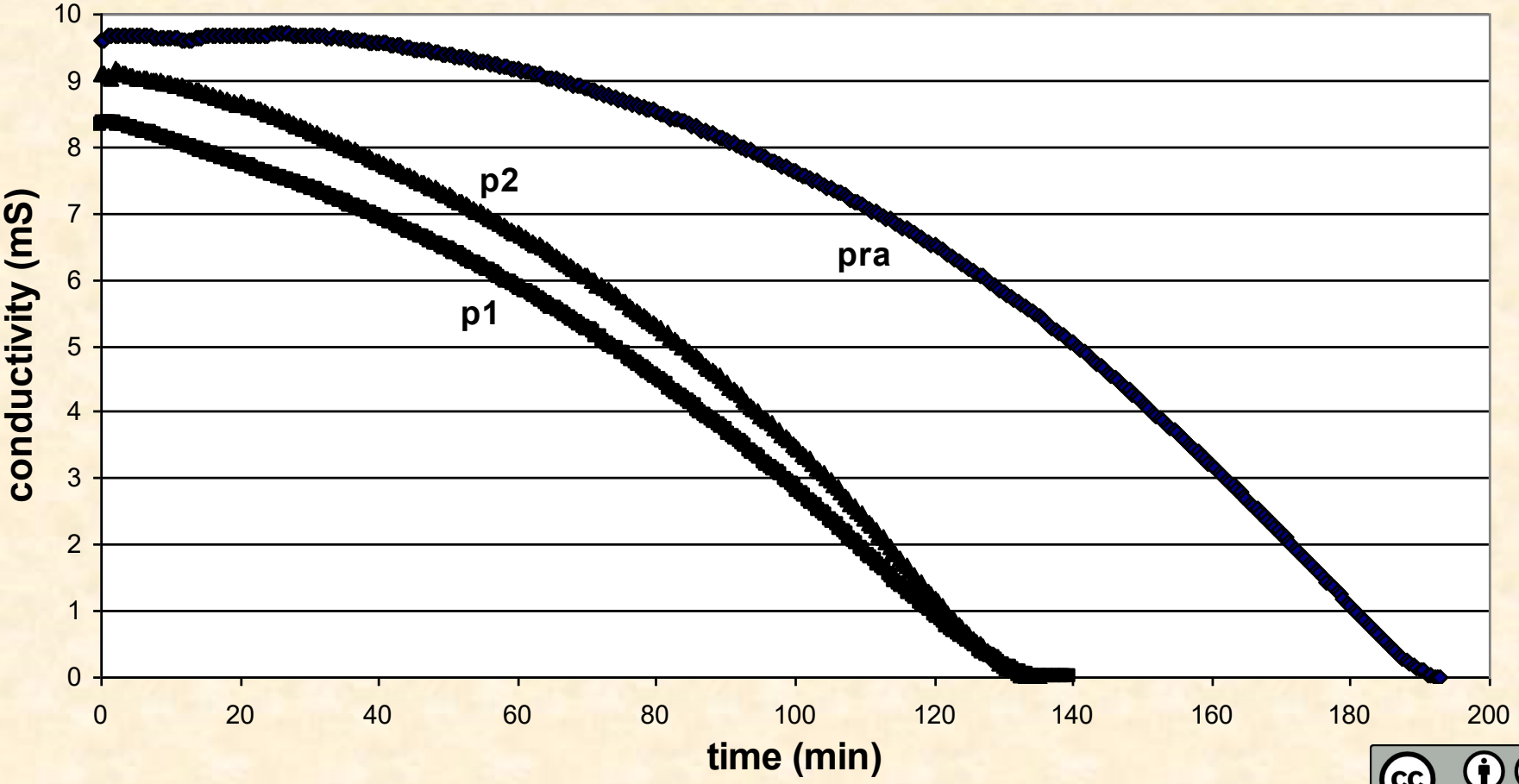
Phenolic substances decomposition



Decomposition of oxalic acid

Legend: p1, p2 – two trials under the same conditions with catalyst,

pra – the same experiment with no catalyst used



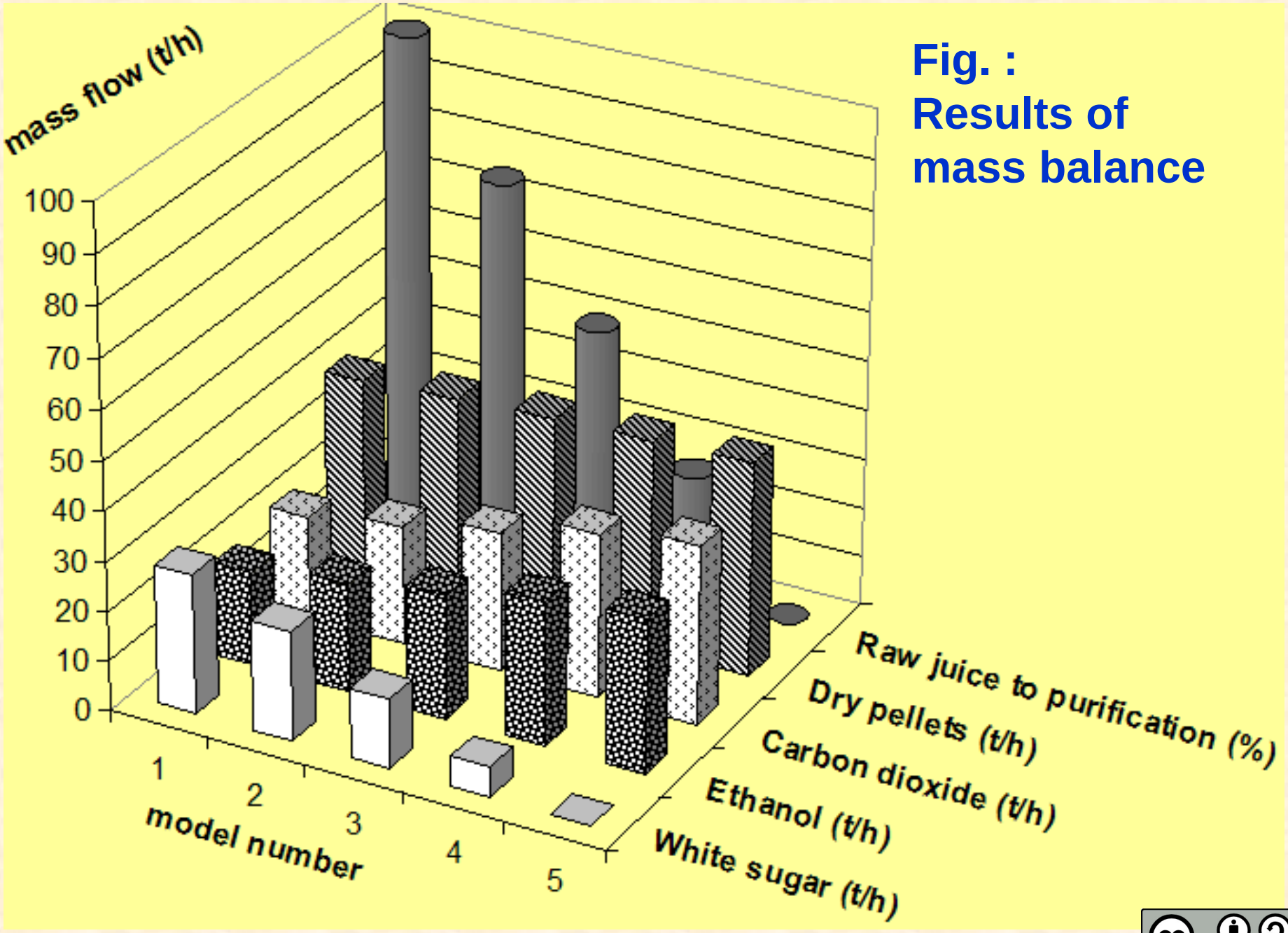


Fig. : Results of mass balance

CONCLUSION

Model 1:

If all raw juice is used for sugar production, we could obtain:
28 t/h of sugar,
19 t/h of ethanol,
40 t/h of feeding pellets
21 t/h of carbon dioxide

Model 5:

Using all raw juice for fermentation yields:

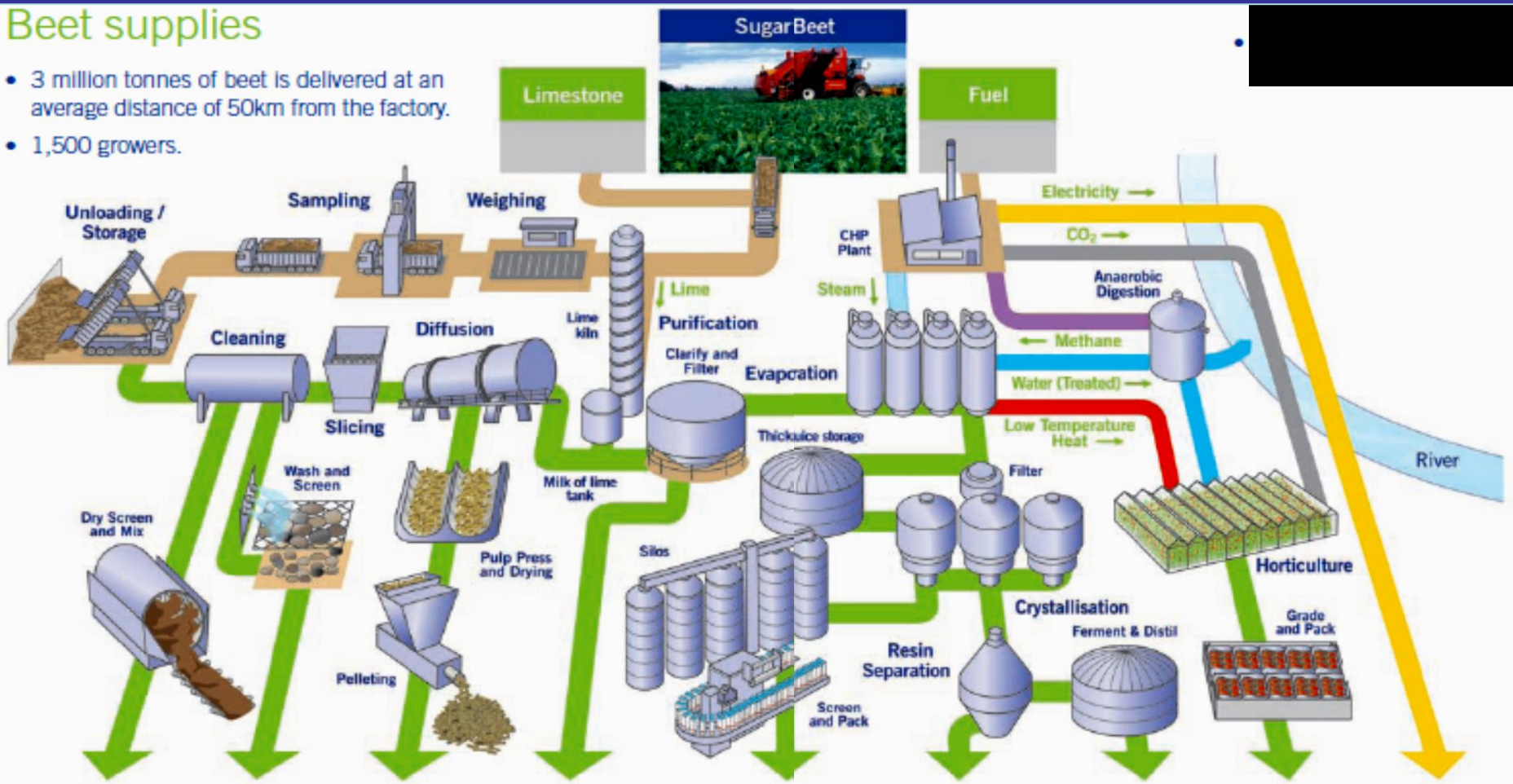
0 t/h of sugar,
31 t/h of ethanol,
43 t/h of feeding pellets
36 t/h of carbon dioxide.

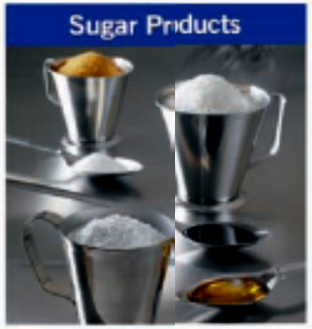
- The shown scheme provides large possibilities to plan a production according to calculations, monitoring the financial profit from the product sales.
- A large amount of produced CO_2 is also a valuable by-product for beverage industry.
- Salt content in dried beet pulp can be reduced by crystallization – it will be potentiality evaluated too

Sugar Beet Refinery Wissington (UK)

Beet supplies

- 3 million tonnes of beet is delivered at an average distance of 50km from the factory.
- 1,500 growers.
- [redacted]





Advanced processes in food technology and biotechnologies

Image analysis - Exercises

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MINISTRY OF EDUCATION, YOUTH AND SPORTS

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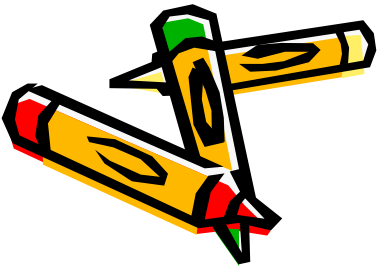
Information sources

http://sch.vscht.cz/vyuka/international-students/erasmus-students/

Databases: ScienceDirect, Scopus, Web of Science



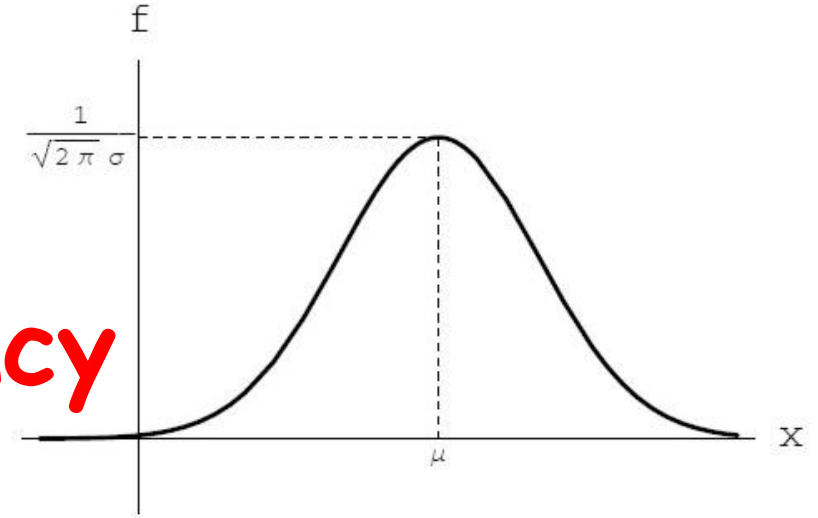
Two distribution models

- Normal distribution function for volume fraction $x_V(A)$
- Log-normal distribution function for particle frequency (B) - by calculating χ^2, where the statistic probable values of frequency (or volume fraction) are computed according to:

$$\chi^2 = \sum_j^k \frac{(n_j - np_j)^2}{np_j},$$

where n_j is the frequency (or volume fraction), n_{pj} is the theoretical (expected) frequency (or volume fraction).

The theory of calculation of expected frequency



The normal probability distribution is defined by the equation:

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} \quad pro \quad -\infty < x < \infty,\ \sigma > 0,\ \mu \in \mathbf{R}.$$

where, η and σ are the mean and standard deviations of the random variable x.

The log-normal probability distribution is defined by the equation:

$$f(x) = \begin{cases} \frac{1}{\sqrt{2\pi}\sigma} \cdot \frac{1}{x} e^{-\frac{1}{2}\left(\frac{\ln x - \mu}{\sigma}\right)^2} & for\ x > 0 \\ 0 & otherwise \end{cases}$$

Calculation of expected frequency - theory

Probability density of random variable with standard normal distribution is a function:

$$\varphi(x) = \frac{1}{\sqrt{2\pi}} e^{-\frac{x^2}{2}} \quad pro \quad -\infty < x < \infty$$

and the form of the distribution function is

$$\Phi(x) = \int_{-\infty}^{x} \frac{1}{\sqrt{2\pi}} e^{-\frac{t^2}{2}}\, dt, \quad x \in \mathbf{R}$$

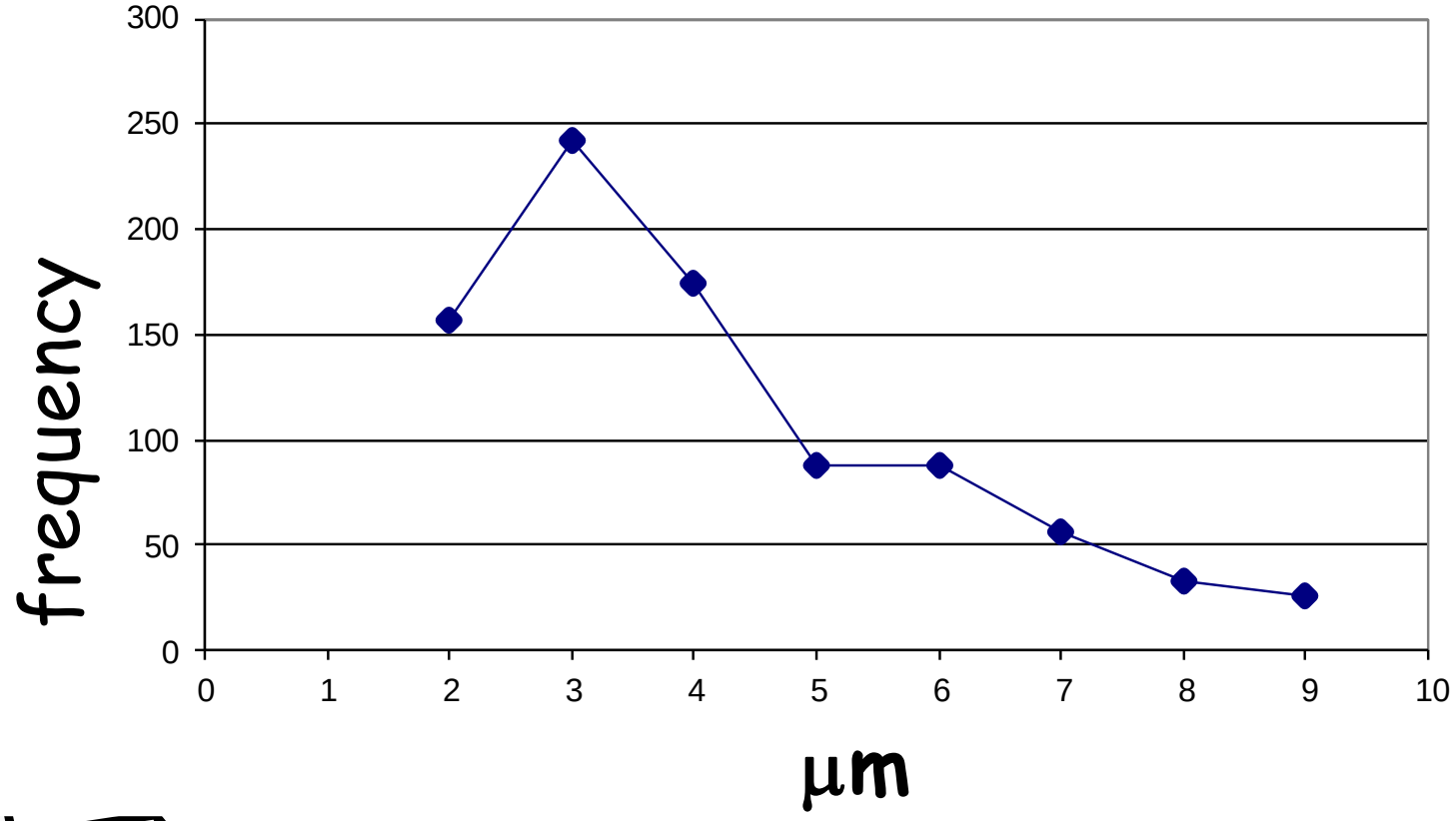
Calculation of expected frequency - theory

The probability of the frequency in given interval is:

$$P: \quad d_{e\,j} \in (d_{e\,j} - \Delta d_e;\ d_{e\,j} + \Delta d_e) = \Phi\left(\frac{de\,j + \Delta de - \bar{d}_e}{s}\right) - \Phi\left(\frac{de\,j - \Delta de - \bar{d}_e}{s}\right)$$

Goodness of fit test for normality: $$\chi^2 = \sum_j^k \frac{(n_j - np_j)^2}{np_j}$$

Example



Example

$$P: d_{e\,j} \in (d_{e\,j} - \Delta d_e;\ d_{e\,j} + \Delta d_e) = \Phi\left(\frac{de\,j + \Delta de - \bar{d}_e}{s}\right) - \Phi\left(\frac{de\,j - \Delta de - \bar{d}_e}{s}\right)$$

Bins	2	3		5	6	7	8	9 …
ln bins	0,693147	1,098612		9438	1,791759	1,94591	2,079442	2,197225 …
de	2,6	3,5	4,	5,5	6,5	7,5	8,5	9,5 …
ln de	0,956495	1,252763	1,5040	,704748	1,871802	2,014903	2,140066	2,251292 …
frequency	157	242	174	88	88	56	33	26 …
%	16,6		18,4	9,3	9,3	5,9	3,5	2,8
1st fraction	-0,9712	,37797	0,082214	0,458214	0,776117	1,051498	1,294401	1,511685 …
2nd fraction	-1,80744	-0,97126	-0,37797	0,082214	0,458214	0,776117	1,051498	1,294401 …
fi1	0,16602	0,35197	0,46812	0,67724	0,7823	0,85314	0,90147	0,93448 …
fi2	0,03515	0,16602	0,35197	0,53188	0,67724	0,7823	0,85314	0,90147 …
P*100	13,087	18,595	11,615	14,536	10,506	7,084	4,833	3,301 …

Goodness of fit test for normality:

$$\chi^2 = \sum_j^k \frac{(n_j - np_j)^2}{np_j}$$

Bins	2	3	4	5	6	7	8	9 …
ln bins	0,693147	1,098612	1,386294	1,609438	1,791759	1,94591	2,079442	2,197225 …
de	2,6	3,5	4,5	5,5	6,5	7,5	8,5	9,5 …
ln de	0,956495	1,252763	1,504077	1,704748	1,871802	2,014903	2,140066	2,251292 …
frequency	157	242	174	88	88	56	33	26 …
%	16,6	25,6	18,4	9,3	9,3	5,9	3,5	2,8
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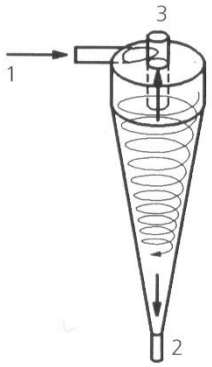
fi2	0,03515	0,16602	0,35197	0,53188	0,67724	0,7823	0,85314	0,90147 …
P*100	13,087	18,595	11,615	14,536	10,506	7,084	4,833	3,301 …

test of normal distribution merged intervals:											
%	16,6	25,6	18,4	9,3	9,3	5,9	6,3	8,5		f	test. chí^2
P*100	13,087	18,595	11,615	14,536	10,506	7,084	8,134	6,549			
chí^2	0,960	2,666	4,001	1,870	0,133	0,187	0,436	0,566	10,820	5	11,071

the distribution is log-normal for significancy 0,05

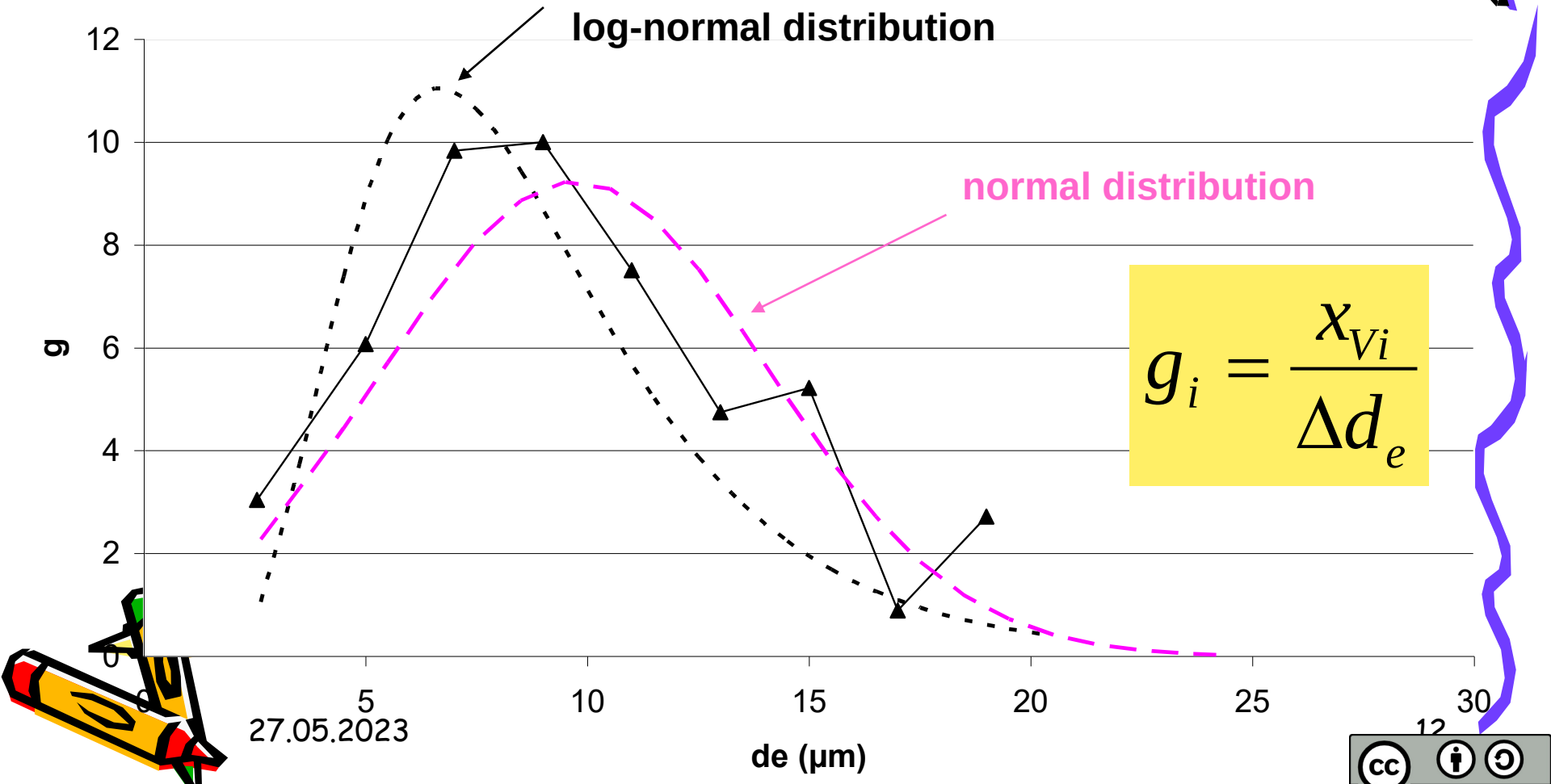


Statistic parameters for distributions A and B, significance α = 0.05

	Distribution A				Distribution B			
Suspension	Mean d_e	Standard deviation d_e (σ)	χ^2	Criterion χ^2	Mean ln d_e	Standard deviation ln d_e (σ)	χ^2	Criterion χ^2
1. sample C	15.3	7.9	14.82	15.50	1.570	0.485	6.72	11.07
1. sample D	9.7	4.3	5.80	16.91	1.506	0.438	7.86	11.07
1. sample E	25.4	17.0	22.84	12.59	1.644	0.525	6.00	5.99
2. sample C	55.9	65.9	161.45	15.50	1.460	0.562	26.52	11.07
2. sample D	20.4	13.1	21.41	14.06	1.376	0.536	32.20	9.48
2. sample E	32.8	26.5	20.76	7.81	1.410	0.560	30.04	11.07

- ✓ **Both hypotheses of A and B distributions are suitable for the suspensions C and D;**
- ✓ **Neither of the two distributions agrees with data of suspension E.**

1st sample of suspension D



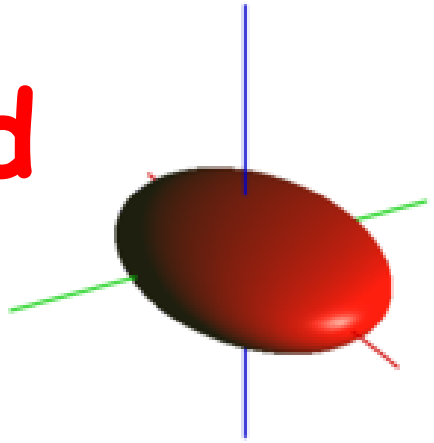
$$g_i = \frac{x_{Vi}}{\Delta d_e}$$

Image analysis of larger objects

Bigger objects (e.g. grains):

- usually lower quantity of objects
- in some cases there is a need to measure 3D

General triaxial ellipsoid



Volume: $V = \frac{4}{3}\pi abc$,

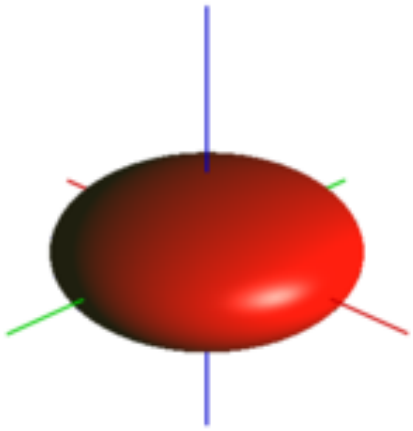
Surface: $S = 2\pi c^2 + \frac{2\pi b}{\sqrt{\left(a^2 - c^2\right)}}\left[c^2 F\left(k,\varphi\right) + \left(a^2 - c^2\right)E\left(k,\varphi\right)\right]$

where a, b, c (a>b>c) are the lengths of half-axes of the ellipsoid,

$$F\left(k,\varphi\right) = \int_0^{\varphi} \frac{d\psi}{\sqrt{\left(1 - k^2 \sin^2\psi\right)}} \qquad k = \frac{a}{b}\sqrt{\frac{b^2 - c^2}{a^2 - c^2}}$$

$$E\left(k,\varphi\right) = \int_0^{\varphi} \sqrt{\left(1 - k^2 \sin\psi\right)}\, d\psi \qquad \varphi = \arccos\frac{b}{a}$$

Oblate spheroid



Volume: $V = \frac{4}{3}\pi a^2 b$

Surface: $S = 2\pi\left(a^2 + \frac{b^2}{2\varepsilon}\ln\left(\frac{1+\varepsilon}{1-\varepsilon}\right)\right)$

$$\varepsilon = \frac{\sqrt{a^2 - b^2}}{a}$$

where a, b are the lengths of half-axes of the spheroid and ε is the eccentricity of the eclipse

Advanced Processes in Food Technology and Biotechnologies

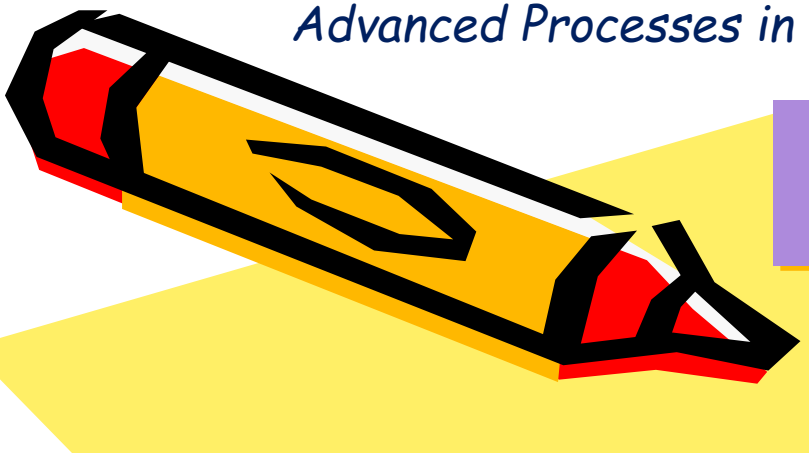


Image analysis

Exercises – Practical applications of image analysis

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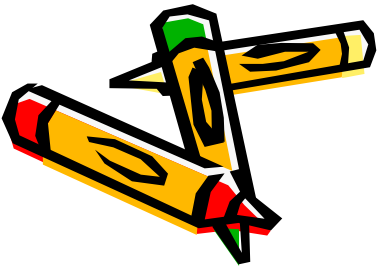
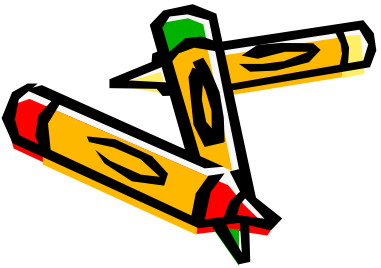


Information sources

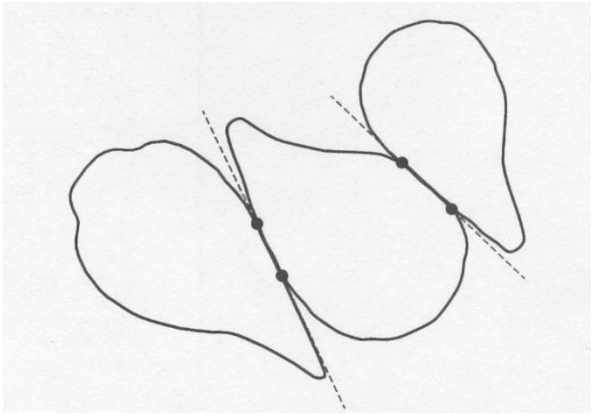
http://sch.vscht.cz/vyuka/international-students/erasmus-students/

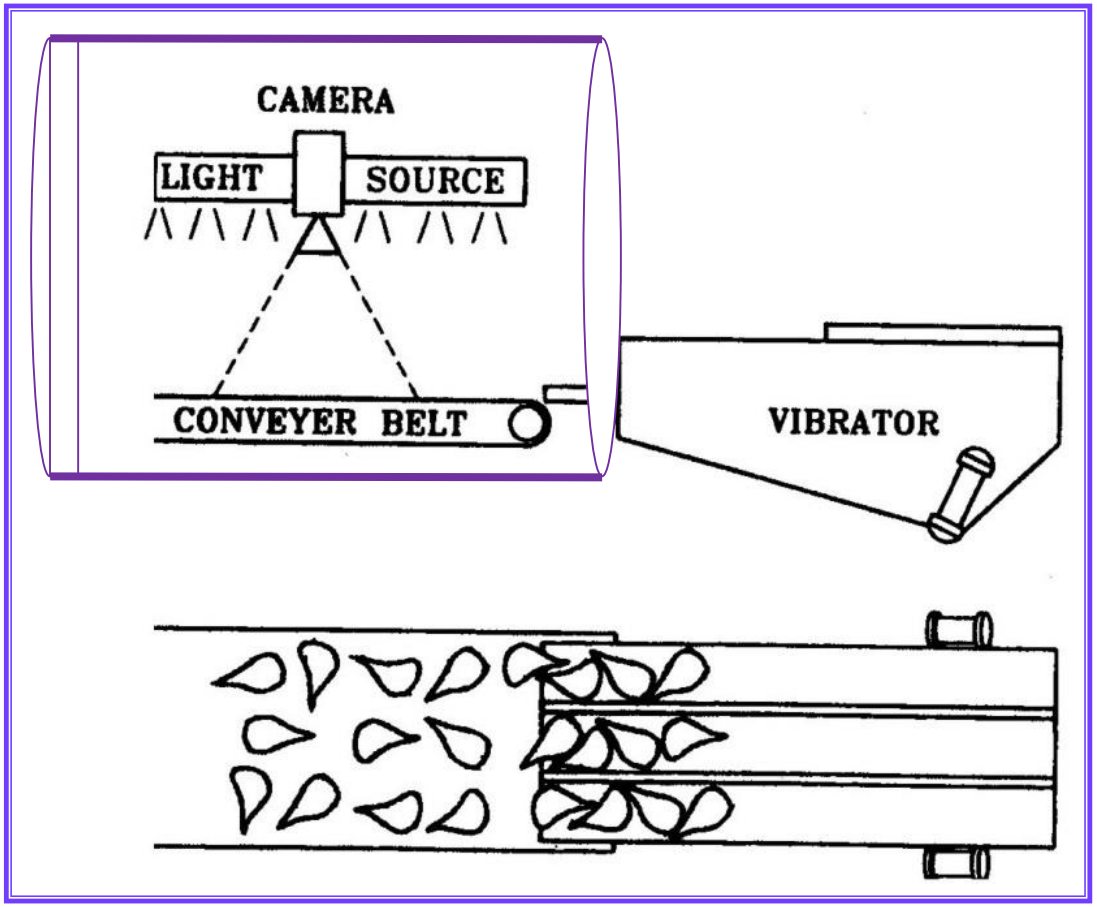
Databases: ScienceDirect, Scopus, Web of Science



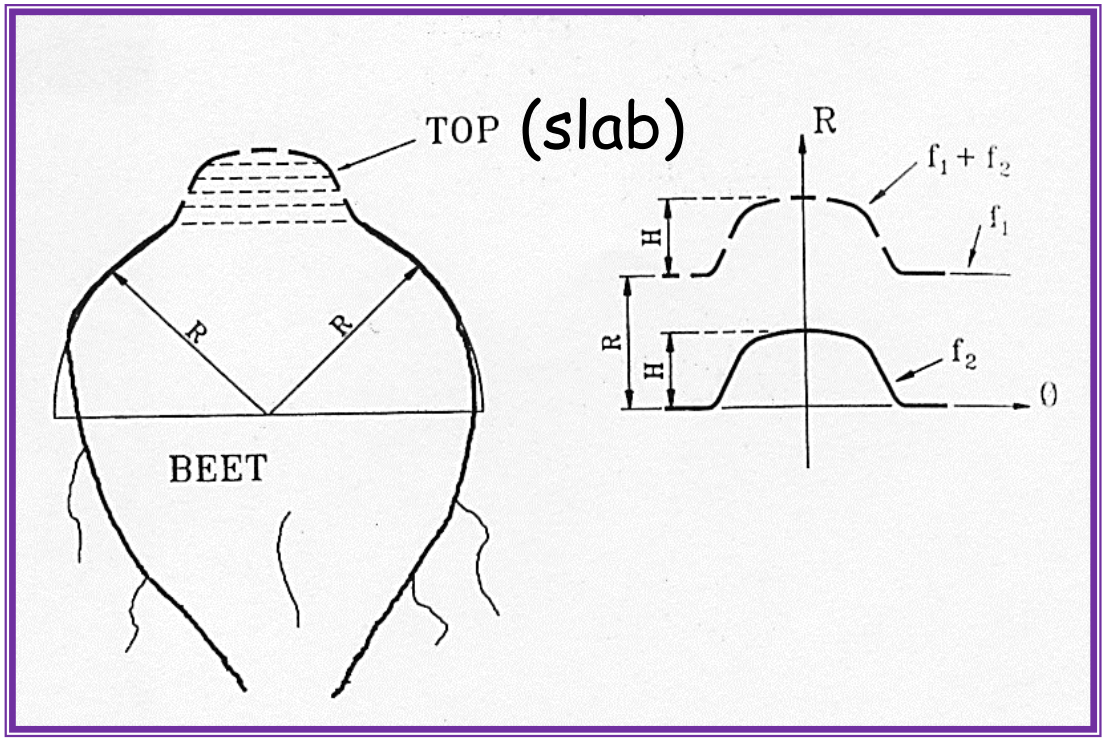
Sugar industry

Assessment of organic impurities





Assessment of organic impurities



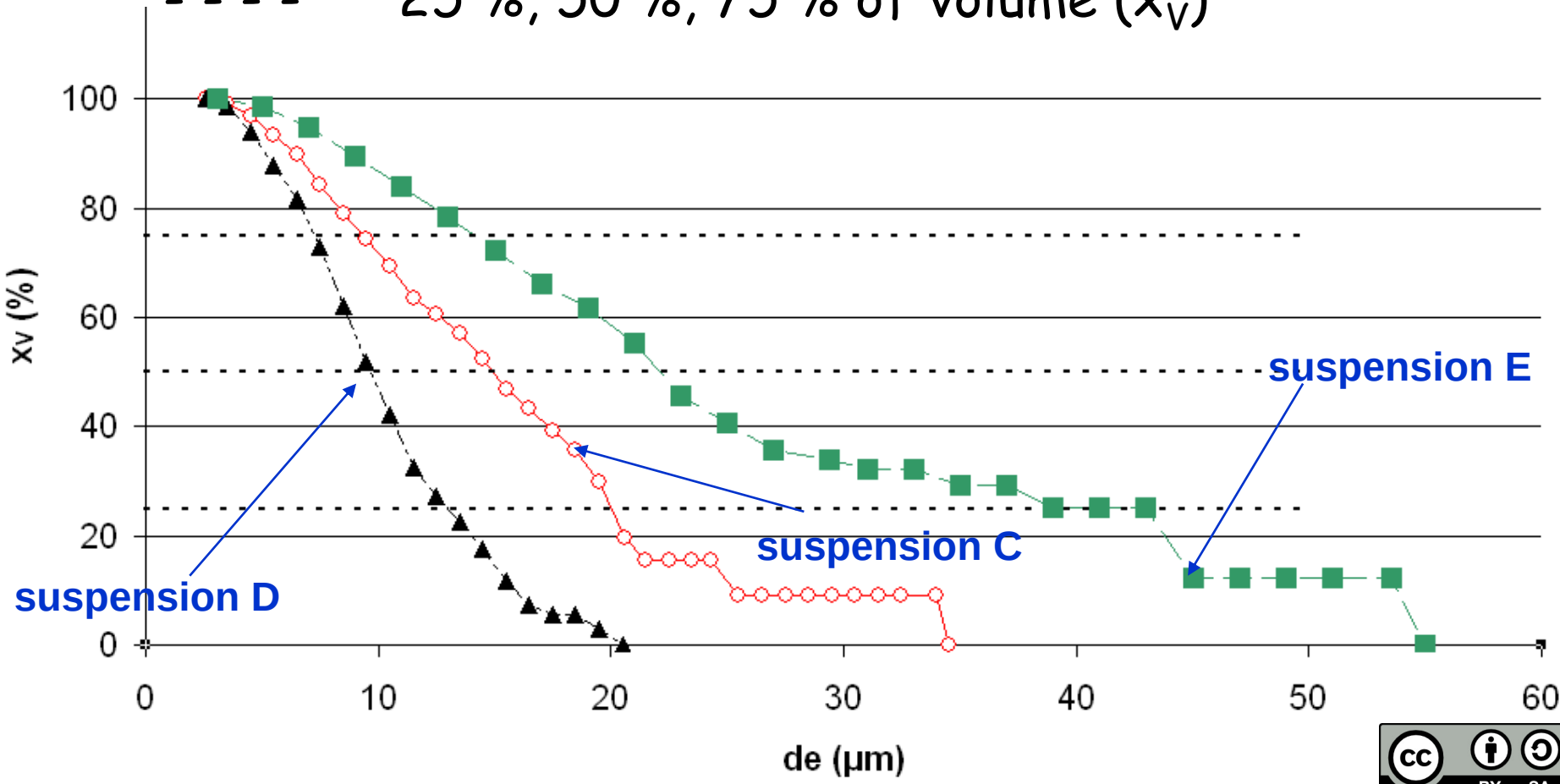
Cumulative distribution curves

—o— the input of suspension C into hydrocyclons,

-···-▲-···- the output of suspension D,

--■-- the output of suspension E,

- - - - 25 %, 50 %, 75 % of volume (x_V)

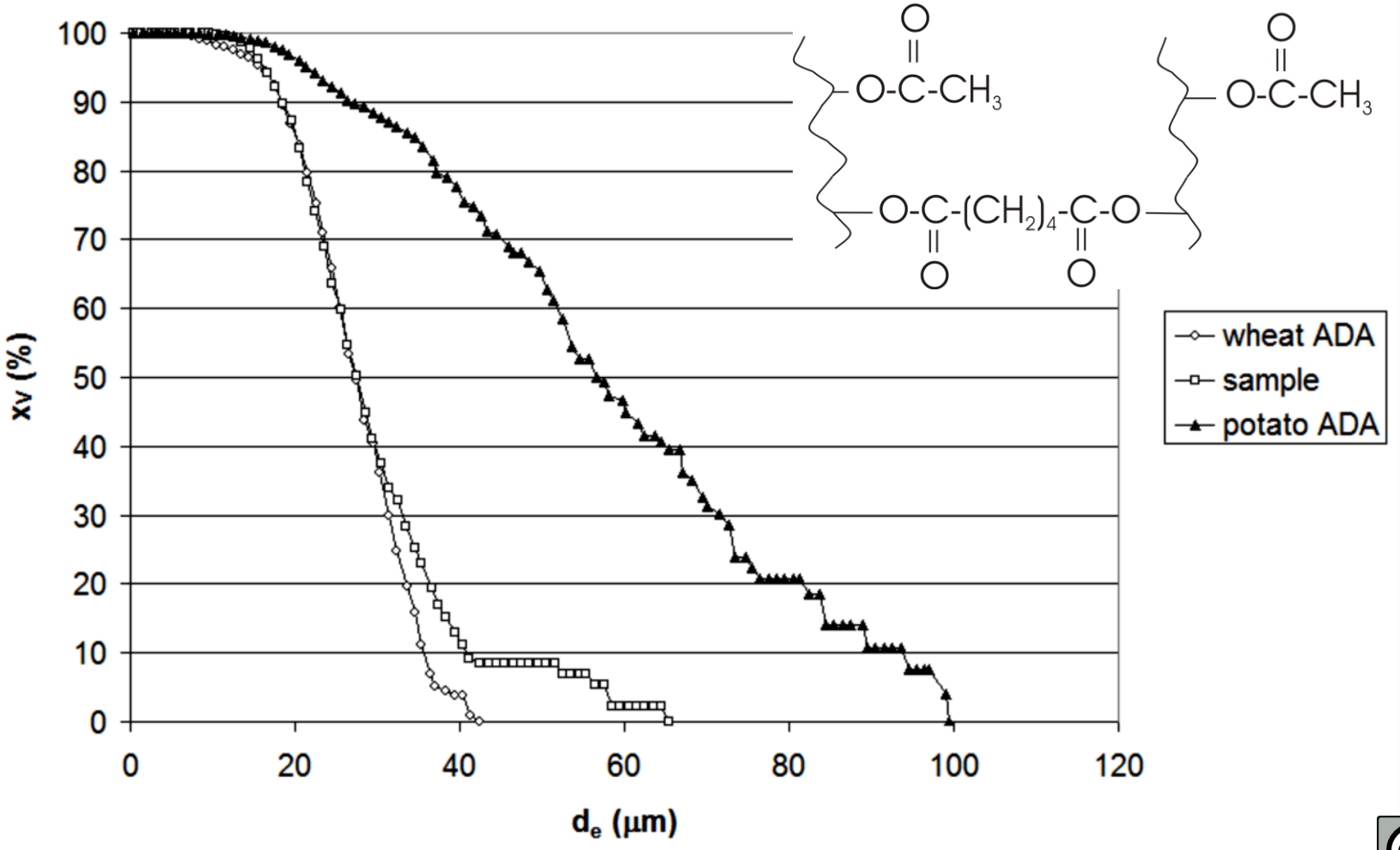


$$R = \frac{d_e^{25} - d_e^{75}}{2.d_e^{50}}$$

medium	sugar factory	Equivalent diameter (µm) for part of particles volume (%)			
		25	50	75	R
1st carbonation mud (mixed with water)	A	78.3	53.9	21.4	52.8
1st carbonation mud (mixed with water)	B	32.5	20.7	14.6	43.2
1st carbonation juice	A	29.9	22.6	16.2	30.3
1st carbonation juice	B	35.7	27.6	18.2	31.7
1st carbonation juice with flocculant	A	106.2	82.2	52.9	32.4
1st carbonation mud after thickening filters	B	29.9	20.6	13.0	41.0
suspension C	A	20.0	14.9	9.4	35.6
suspension D	A	13.0	9.7	7.3	29.4
suspension E	A	43.0	22.1	14.1	65.5

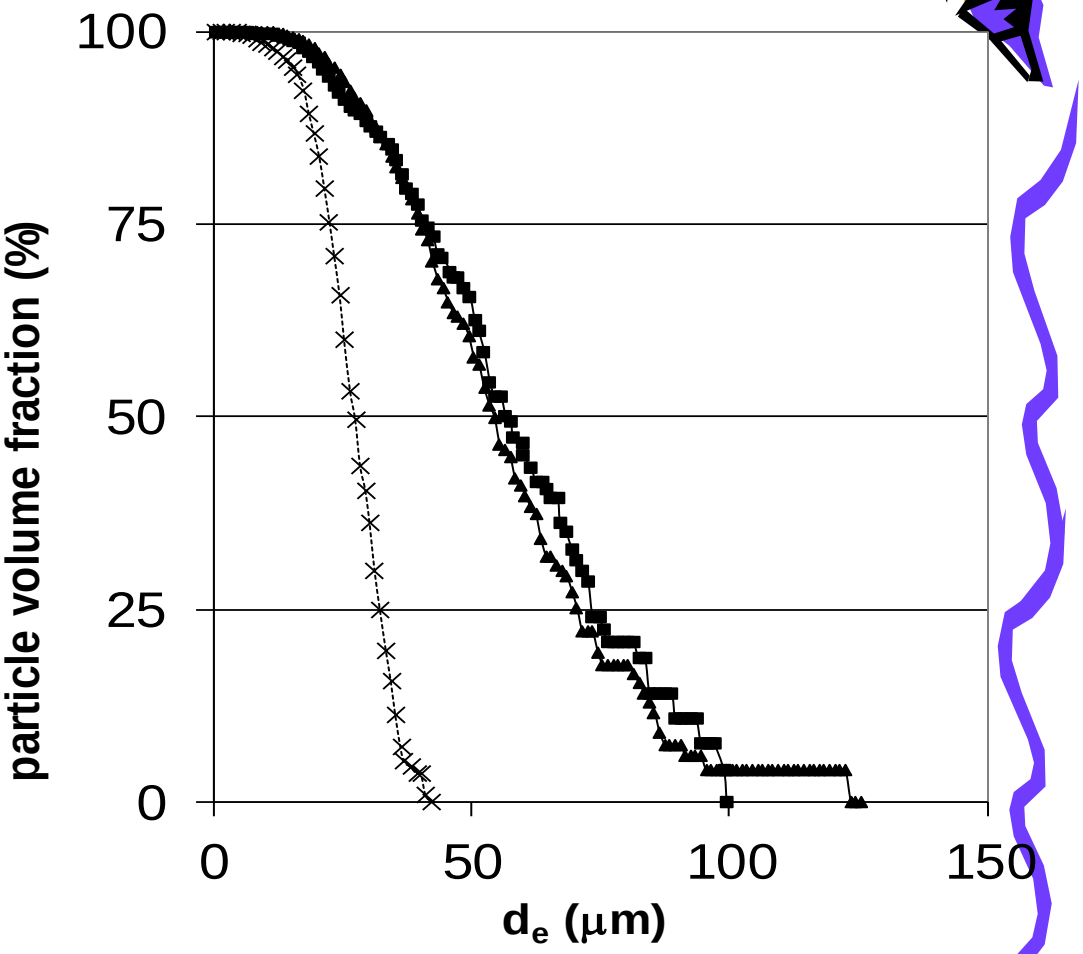
Starch identification

Identification of the starch origin



Identification of the starch origin

The size of starch granules remains largely unchanged during chemical modification, therefore we can compare the modified starch with native or other modified potato and wheat starches. Image analysis was used in such a way as to successfully identify the origin of cationic starch.



Separation and purification techniques

Exercises – Separation efficiency

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Information sources

http://sch.vscht.cz/vyuka/international-students/erasmus-students/

Cheryan M. (1998): Ultrafiltration and Microfiltration Handbook, In: Technomic Pub. Co. (Eds.), Lancaster, Pensylvania, pp. 243.

The efficiency of filtration

- **Permeate and retentate - chemical composition;**
- **Defines which particles were retained and which were transferred to permeate;**
- **Concentration of component in feed, permeate and retentate.**

Concentration factor (ratio)

- **VCR/VCF** **volumetric concentration factor**
- **MCR/MCF** **mass concentration factor**

Definition:

$$VCR = \frac{V_F}{V_R}$$

V_F feed volume

V_R retentate volume

Separation efficiency – Rejection

- Properties of permeate and rententate
- It requires the use of analytical methods
- Concentration of a component in different process streams

$$R = 1 - \frac{ci_{downstream}}{ci_{upstream}}$$

Rejection factor *R*

Expresses the relation between the concentration of a component above and below the membrane:

***ci*$_{downstream}$, *ci*$_{upstream}$ concentration of a component *(i)* below and above the membrane, respectively**

Apparent rejection *R*

$$R = 1 - \frac{c_{iP}}{c_{iF}}$$

***ci*$_{upstream}$ equals to the concentration of a component *i* in the bulk (i.e. in the feed, c_{iF})**

***ci*$_{downstream}$ equals to the concentration in the bulk of permeate (c_{iP})**

Intrinsic rejection

***c*$_{upstream}$ equals to the concentration of a component at the membrane surface – difficult to measure sometimes.**

Separation efficiency – Retention, recovery

Retention factor *r*

Refers to concentration of a component in permeate and retentate

$$r = 1 - \frac{C_{iP}}{C_{iR}}$$

Relative recovery η_i

Expresses the amount of component gained by the process:

$$\eta_i = \frac{m_{i,out}}{m_{i,in}}$$

a ratio of the weight of the component in the useful product $m_{i,out}$ to the total weight of the component entering the process $m_{i,tot}$

Separation and purification techniques

Exercises – Filtration velocity

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Information sources

http://sch.vscht.cz/vyuka/international-students/erasmus-students/

Cheryan M. (1998): Ultrafiltration and Microfiltration Handbook, In: Technomic Pub. Co. (Eds.), Lancaster, Pensylvania, pp. 243.

1. Filtration velocity

- Expressed as a permeatevolumetric flow across 1 m^2 of the membrane surface under given conditions (temperature and pressure)

$$l \cdot h^{-1} \cdot m^{-2}$$

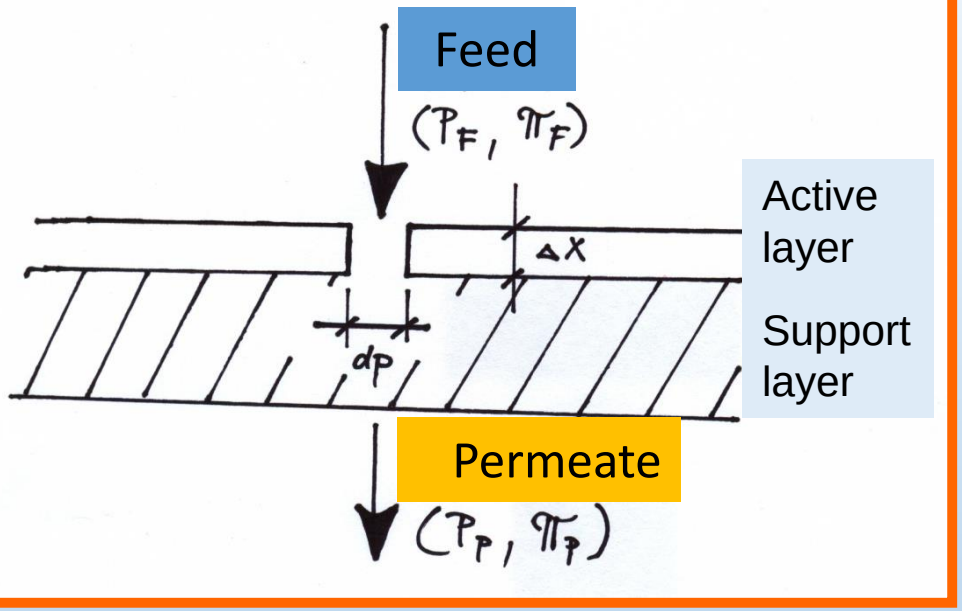
- Affected by permeability and pore density (porosity)
- Low permeability can be compensated by higher membrane area

In general:

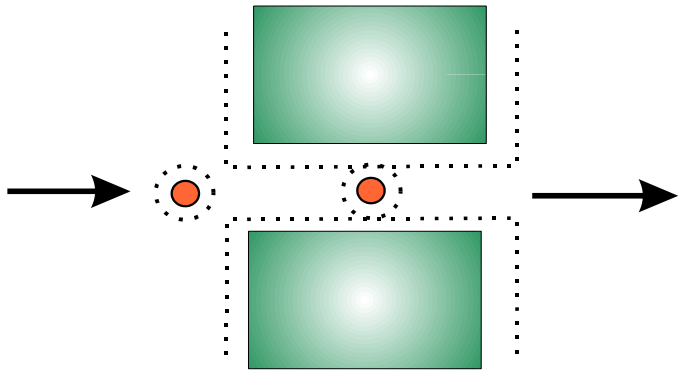
$$mass\_flow = area \cdot \frac{driving\_force}{resistance}$$

Filtration theory:

Pressure-driven processes: driving force = pressure gradient



Cross section of the membrane



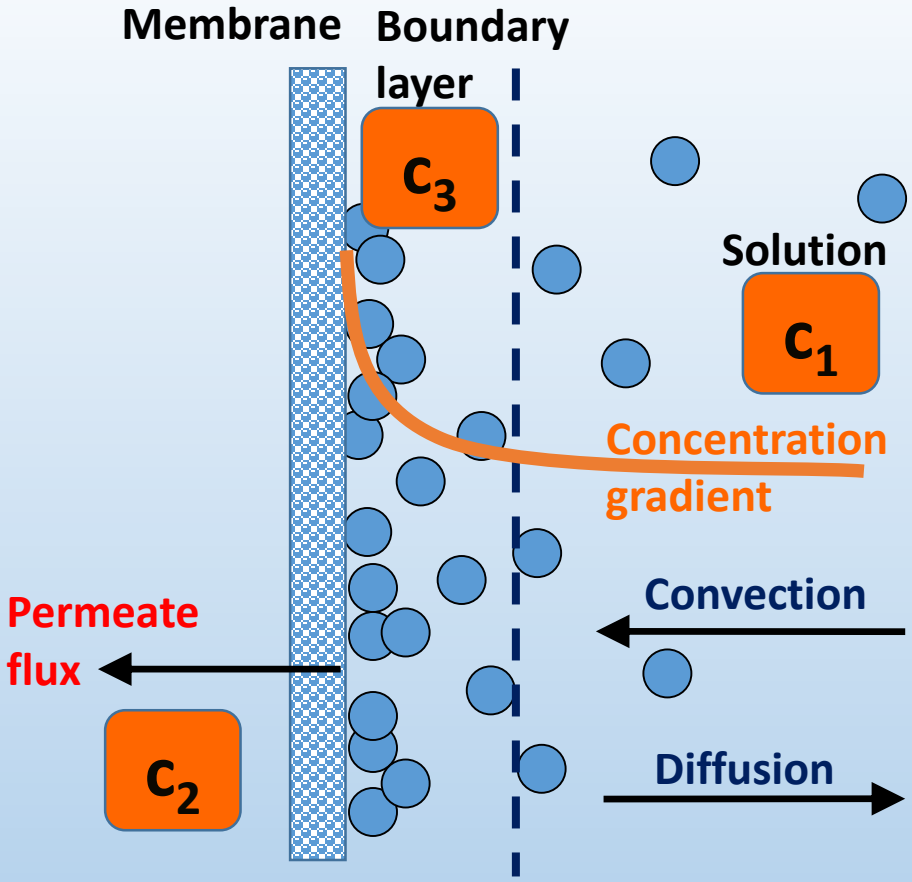
Pressure drop : $P_T = P_F - P_P$

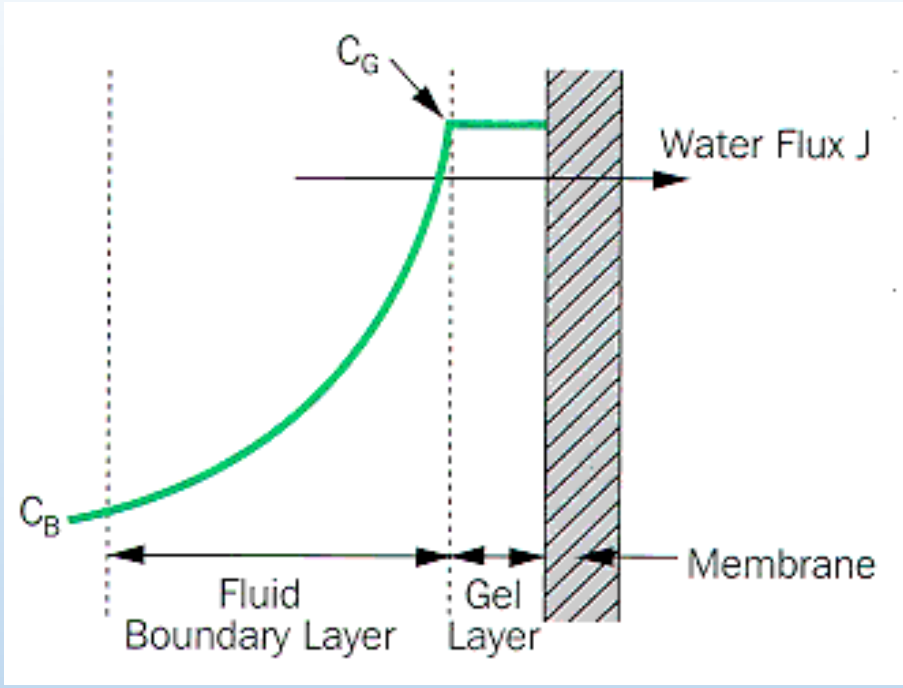
Osmotic pressure within the membrane: $\Delta\pi = \pi_F - \pi_P$

Real driving force: $= P_T - \Delta\pi$

If the osmotic pressure is negligible, the driving force of the process: $= P_T$

Concentration polarization:





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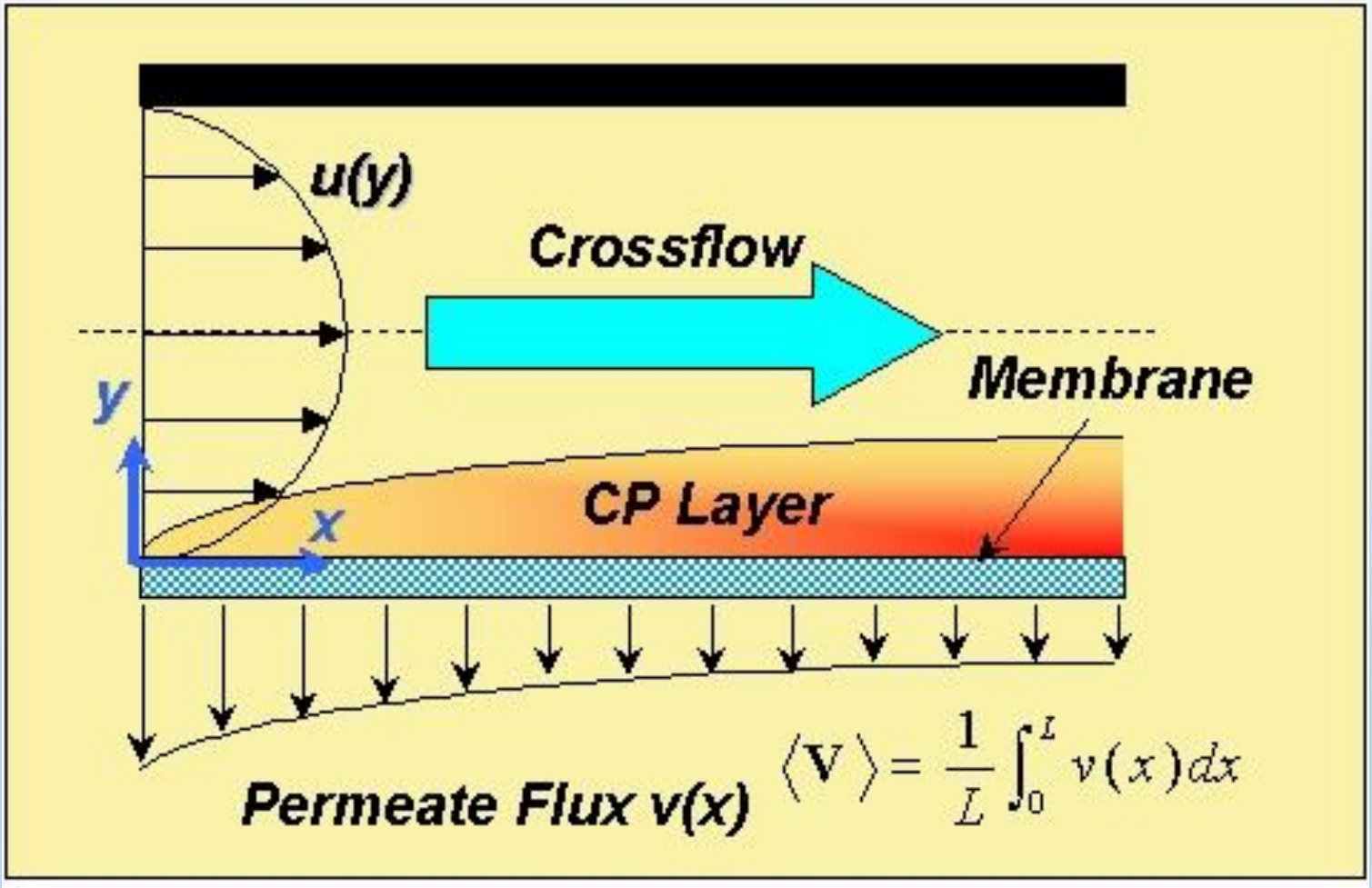
Concentration of components in the boundary layer is higher than in the bulk of solution

- **Formation of a concentration profile – under extreme conditions – gel or precipitate, secondary membrane**
- **Increased membrane resistance**

Concentration polarization:



Pressure-driven membrane processes

Driving force = pressure gradient

Real driving force: ➔ reduced by the pressure drop in polarization layer, secondary membrane or gel layer

- Convective flow J_s

$$Js = J \cdot c_1$$

- Diffusion velocity (neglected concentration gradient c)

$$Js = D \cdot \frac{dc}{dx}$$

- Filtration equation:
  G = specific membrane permeability

$$-G \cdot c_2 + D \cdot \frac{dc}{dx} + G' \cdot c_1 = 0$$

Permeate flow Diffusion Convection

Flux, fouling, membrane cleaning

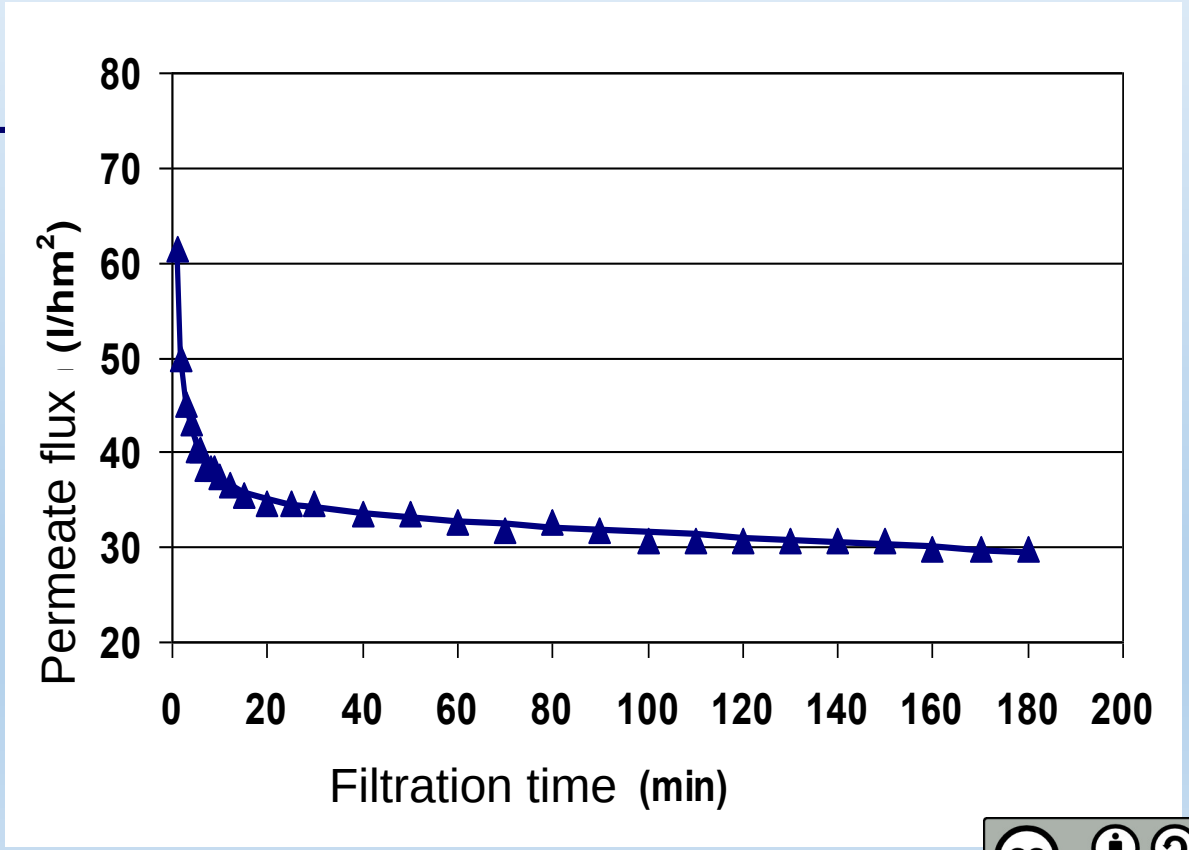
Discharge = permeate flow, flux [$l.h^{-1}.m^{-2}$]

Permeate flow drops during the filtration – problem!

The drop is caused by

- **concentration polarization**
- **silting of membrane pores called**

  fouling effect



Description by mathematical models for permeate flow

Parameters describing membrane permeability

Pure water flux J_v

Importance:

- **To estimate efficiency of membrane cleaning procedure**
- **The ratio of pure water flux before filtration and after the membrane cleaning should be less than 20%**

Definition:

The permeate flow during filtration of pure (demineralised) water at 20 °C and a given pressure expressed per 1 m² of the membrane surface area:

$$Jw = \frac{J_P \cdot k_t}{S}$$

J_W pure water flux ($l.h^{-1}.m^{-2}$)

J_P permeate flow

k_t temperature coefficient (20 °C)

S membrane surface area (m^2)

Separation and purification techniques

Exercises – Calculations

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Exercises and Calculations

Problem 1

The initial permeate flow rate on the ultrafiltration membrane, having a filtration area of 0.5 m^2, was 360 $l/h.m^2$. After 3 hours of the filtration process, the flow rate was measured again as the permeate volume; i.e. the volume of permeate collected during 30 seconds was 300 ml. How much has the flux changed since the beginning of the process if the filtration ran at the constant pressure of 0.2 MPa and temperature 40 °C?

Exercises and Calculations

Problem 2

50 litres of sugar solution was filtered on a nanofiltration membrane at the temperature of 60 °C and pressure of 8 MPa. After 10 hours of filtration, 30 litres of permeate were collected. The concentrations of K^+ ions in the feed and permeate streams were 620 and 30 mg/l, respectively. Calculate the volume concentration factor, retention factor and apparent rejection of potassium ions on the membrane used.

Exercises and Calculations

Problem 3

The pure water flux before filtration, measured at 20 °C and 1 MPa, was 1000 l/h.m^2. After filtration and membrane cleaning, the pure water flux was measured again at the temperature of 25 °C and pressure 2 MPa. Its value was 160 l/h.
The viscosity coefficient at the temperature 25 °C is 0.888 and the membrane area is 0.1 m^2. Calculate the pure water flux drop and estimate if the cleaning procedure was sufficient.

Separation and purification techniques

Exercises – How to prevent membrane fouling?

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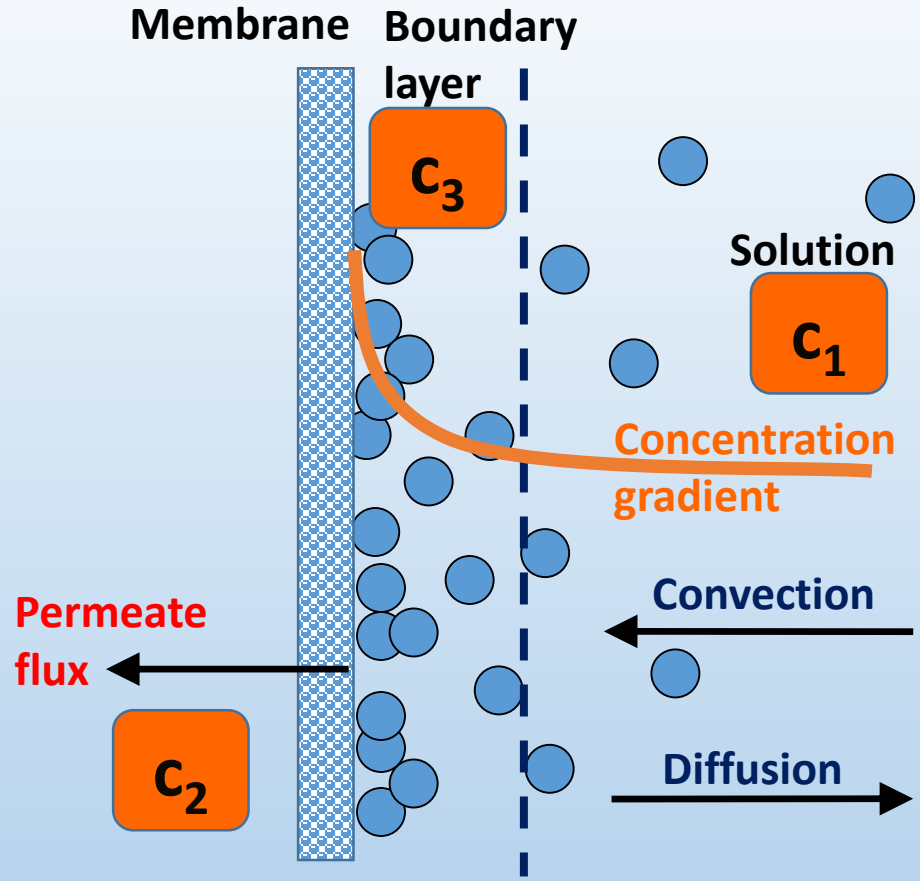
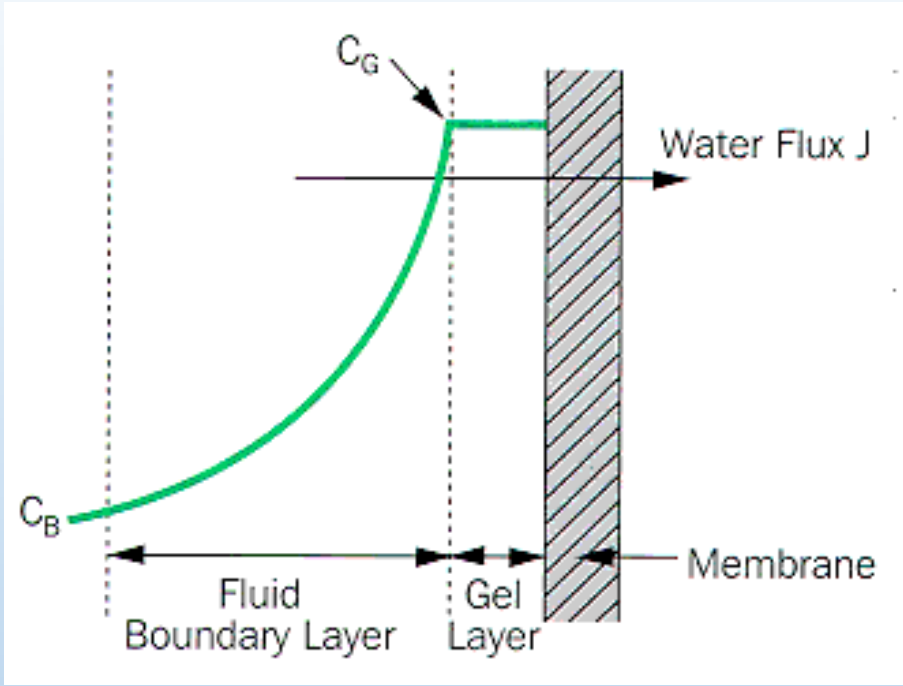
Concentration polarization:





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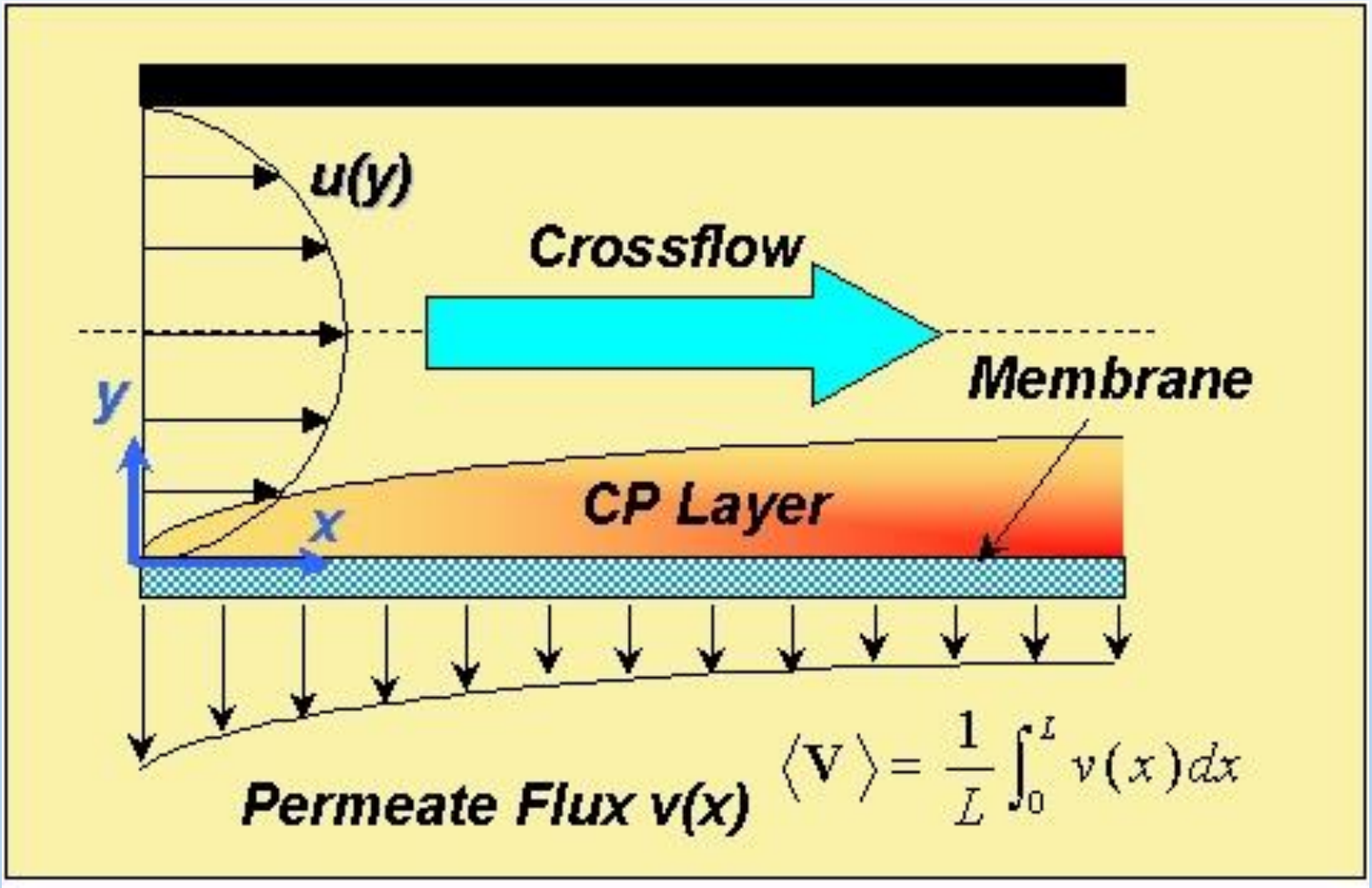
Concentration of components is higher in a boundary layer than in the bulk of solution

- **Formation of a concentration profile – under extreme conditions – gel or precipitate, secondary membrane**
- **Increased membrane resistance**

Concentration polarization:



Factors influencing the fouling effect

Problem

On the basis of your knowledge of filtration kinetics, name all possible factors which can reduce the fouling effect and formation of concentration polarisation layer on the membrane.

In other words: name all possible factors how to increase the velocity of the filtration process.

Factors influencing the fouling effect

a) Membrane properties

- Pore size (permeability)
- Active layer thickness
- Affinity of dissolved components to the membrane

b) Character of medium to be filtered

- Viscosity
- Ionic strength
- pH
- Density
- Concentration
- Reactivity of molecules with the membrane
- Shape and size of separated molecules
- Sample pre-treatment – precipitation, addition of ballast material, pre-filtration (to improve the molecule to pore size ratio)

Factors influencing the fouling effect

c) Conditions during the process operation

- **Driving force – e.g. pressure (increasing during filtration)**

  X irreversible fouling! – limit pressure

  X limit flux! – formation of concentration polarization layer, gel!

- **Temperature**

- **Hydrodynamics (character of the flow along the membrane) – maintain turbulent flow:**

  - **Pulsation, ultrasound, air bubbling**

  - **Back-flushing (asymmetric and composite membranes – high risk of tearing the active layer off)**

Separation and purification techniques

Exercises – factors affecting the separation efficiency in a chromatographic column

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www.sciencedirect.com

https://onlinelibrary-wiley-com.ezproxy.vscht.cz/

Jönsson J.A. (1987): Chromatographic Theory and Basic Principles, Marcel Dekker, New York

Essential theory of chromatographic methods

Distribution of analyte:

Analyte is in equilibrium between the two phases:

$A_{mobile} = A_{stationary}$

Equilibrium constant = partition coefficient $K = c_{A(stat)} / c_{A(mob)}$

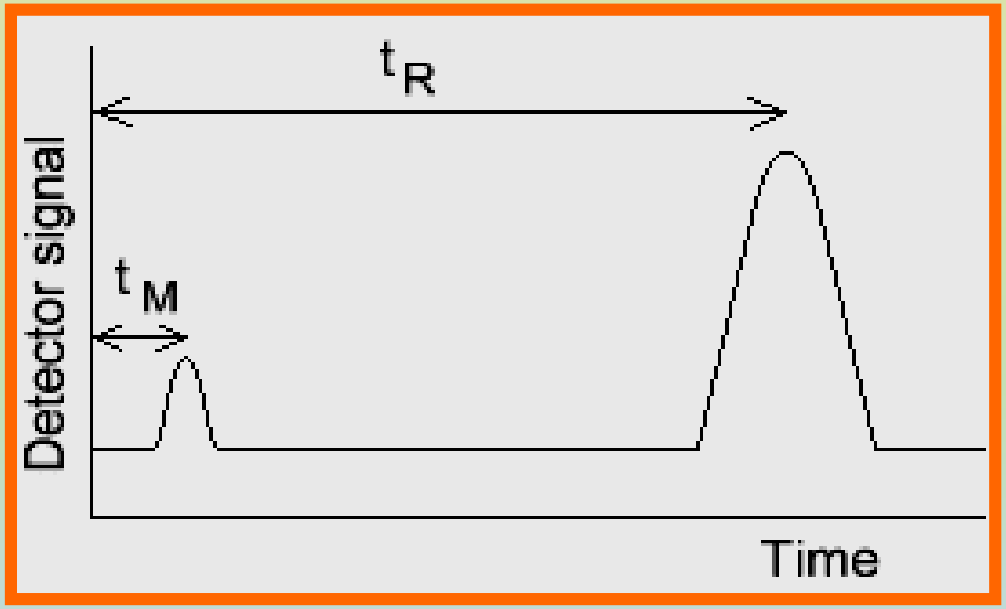
c = analyte molar concentration in a mobile and stationary phase, respectively

- Retention time (t_R)

= a time between sample injection and analyte reaching a detector (max.)

- Dead time (t_M)

= a time of mobile phase passage through the column



Satisfactory separation – different retention times of anal

Retention parameters

Capacity factor k' describes the speed of an analyte through the column

- independent of the system geometry, but expresses the thermodynamical character of sorbent-analyte-eluent.
- Defined as (for the analyte A): $k'_A = t_R - t_M / t_M$

t_R and t_M – easily obtained from a chromatogram - values:

$k' < 1$
$k' > 20$
$1 < k' > 5$

Retention time t_R – reciprocal to the eluent flux

Retention volume V_R – eluent volume that passed through the column during elution of analyte, independent of flux but the column geometry

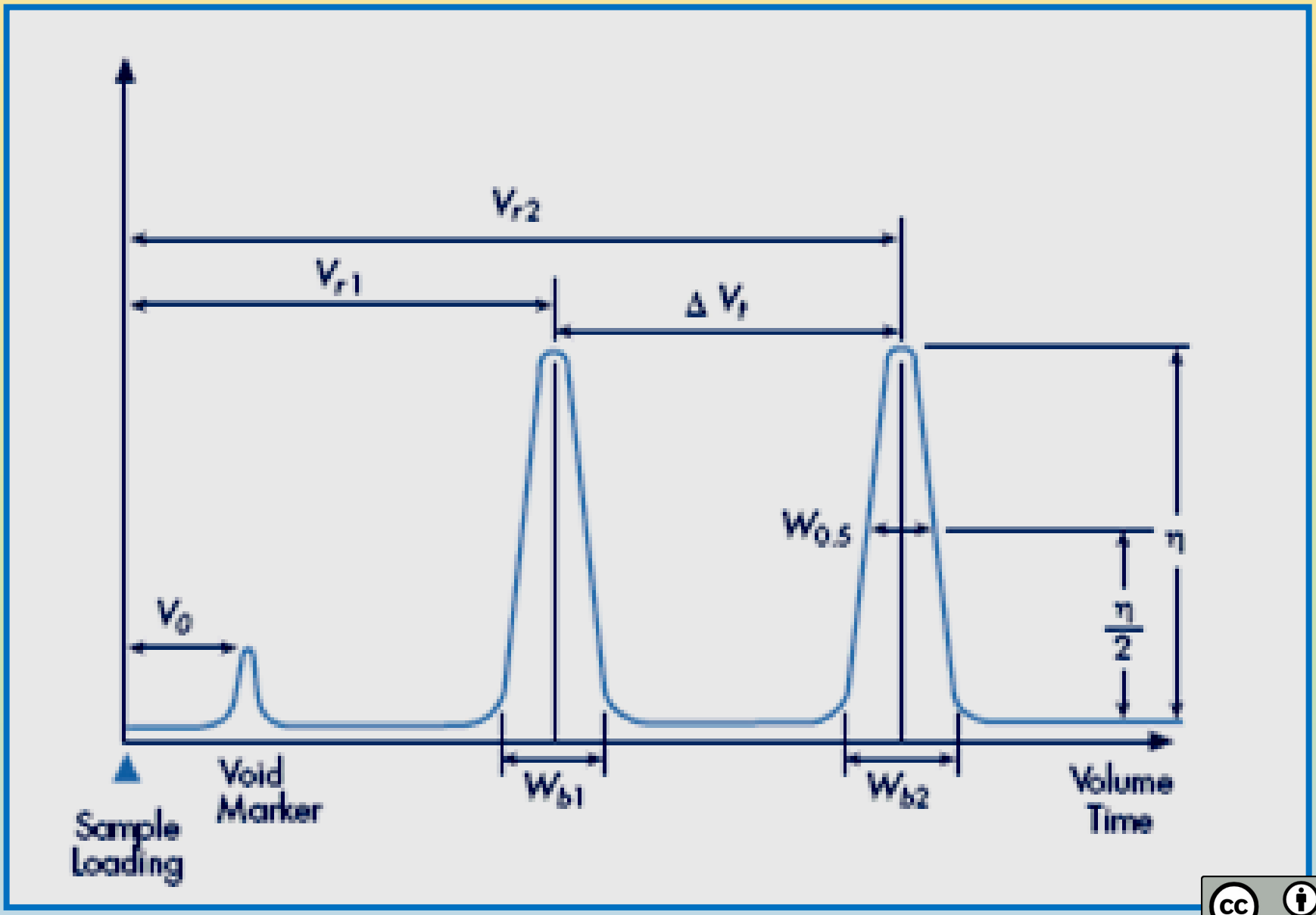
Retention volume:

1. Reduced retention volume – volume of the eluent that passed through the column, while the component was adsorbed on the sorbent
2. Dead volume V_0 – volume of the eluent, that passed through the column, while the component was moving in the mobile phase; equal to the volume of liquid phase in the column, identical for any analyte

Ratio of retention volume to dead volume k – basic and universal retention parameter

$k = V_R/V_o$

Retention volume V_R



Separation efficiency, selectivity and resolution

- Separation efficiency depends on two factors:

1. Selectivity α
   - Expressed by ratio of capacity factors of two peaks (α = selectivity factor)
   - Characteristic of separation capability of sorbent for given component mixture
   - Independent of column efficiency
   - Does not imply the width, but the distance between peak maxima
   - Dependent on component character, eluent composition and properties and binding interactions with sorbent

$$\alpha = \frac{V_{R1} - V_0}{V_{R2} - V_0} = \frac{k'_1}{k'_2}$$

2. Peak width *w*

- Resolution R

Expresses separation power of the whole chromatographic system related to components

Expressed by ratio of peak maxima distance to the mean value of the peak width at the baseline

For symmetric peaks:

if R<1 then we get non-separated peaks
if R=1 then we get just separated peaks
if R>1 then we get separated peaks

$$R = \frac{V_{R2} - V_{R1}}{\frac{1}{2} \cdot (w_1 + w_2)}$$

The theoretical plate model and column efficiency

Optimal separation – sharp, symmetric peaks

Band broadening caused by diffusion – inevitable, BUT efforts to minimize it

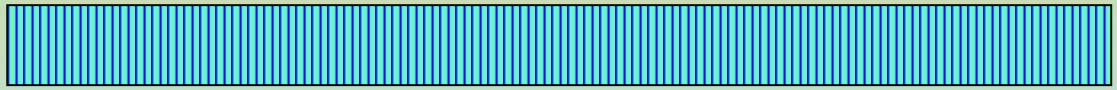
Sometimes it is necessary to determine column efficiency

The theoretical plate model of chromatography

Assumption – a chromatography column divided into large number of separated layers = theoretical plates

Every plate – equilibrium of analyte (mobile phase – stationary phase)

Analyte passes through the column by a transfer of equilibrated mobile phase from one plate into another



L column length

N the number of theoretical plates (the more – the better)

HETP Height equivalent to a theoretical plate (the smaller – the better)

Column length and number of theoretical plates

Theoretical plates do not exist!

$$HETP = L / N$$

- Help to understand the phenomenon
- Determination of the column efficiency; number of theoretical plates for column can be specified according to the character of the chromatographic peak after elution, were $w_{1/2}$ is the peak width at the half-height:

$$N = \frac{5.55 \cdot t_R^{\,2}}{w_{1/2}^{\,2}}$$

- The same column has a different number of theoretical plates for each component of a mixture

Selectivity, resolution and number of plates

↘ Resolution can be related to the number of plates in the column N selectivity factor α retention factor k':

$$R = \frac{\sqrt{N}}{4} \cdot \left(\frac{\alpha - 1}{\alpha} \right) \cdot \left(\frac{1 + k'_B}{k'_B} \right)$$

To obtain high resolution, the three terms must be maximised :

↑ N – ↑ by lengthening the column → increased retention time and increased band broadening - not desirable

↓ HETP – achieved by reducing the size of the stationary phase particles

Capacity factor k' – by changing the temperature (GC) or the composition of the mobile phase (LC); this term – the least effect on the resolution

Selectivity factor α – by changing mobile phase composition, column temperature, composition of stationary phase, using special chemical effects (such as incorporating a species into the stationary phase, which makes complexes with one of the solutes)

Band broadening theory
Van Deemter equation

A more realistic description of the processes inside a column:

takes account of the time taken for the solute to equilibrate between the stationary and mobile phase

UNLIKE the plate model assuming that equilibration is infinitely fast

The resulting band shape of a chromatographic peak is affected:

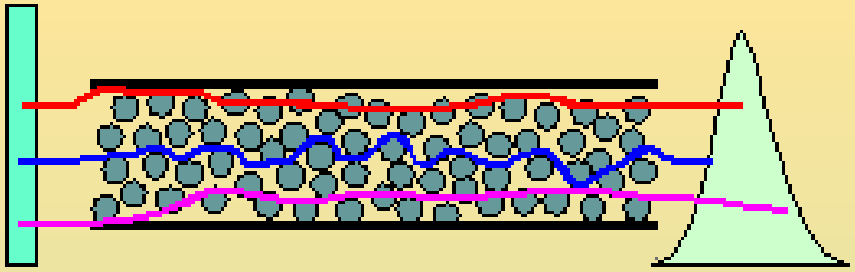
- By rate of elution
- By the different paths available to solute molecules as they travel between particles of stationary phase
- By diffusion
- By mass transport between phases

Considering all this, we obtain Van Deemter equation –the dependence of HETP on the average velocity (*u*) of the mobile phase including factors *A*, *B* a *C,* which contribute to band broadening:

$$HETP = A + B/u + C \cdot u$$

Application: to determine the optimum mobile phase flow

Van Deemter equation



http://hplc.chem.shu.edu/NEW/HPLC_Book/

Factors A, B and C represent:

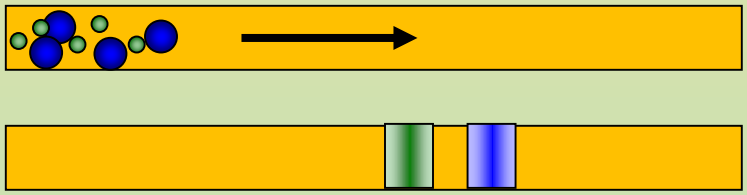
A - Eddy diffusion

Solute molecules take different paths through the stationary phase at random – different paths are of different lengths – band broadening

$$A = 2\lambda d_p$$

d_p is the particle diameter (average), and λ is the constant (almost close to 1) involving size distribution (narrow distribution ↓ λ) both parameters increase pressure

Application of sorbent with small and uniform particles and homogenous filling of column – no dead volume



B - Longitudinal diffusion

The concentration of analyte is lesser at the edges of the band than at the centre- analyte diffuses from the centre to edges

$$B = 2\gamma D_m$$

D_m is the analyte diffusion coefficient in the mobile phase

γ is the factor which is related to the diffusion restriction by column packing

The higher the eluent velocity, the lower the longitudinal diffusion effect (Molecular diffusion in the liquid phase is about five orders of magnitude lower than that that in the gas phase ⇒ for LC almost negligible)

Band broadening theory

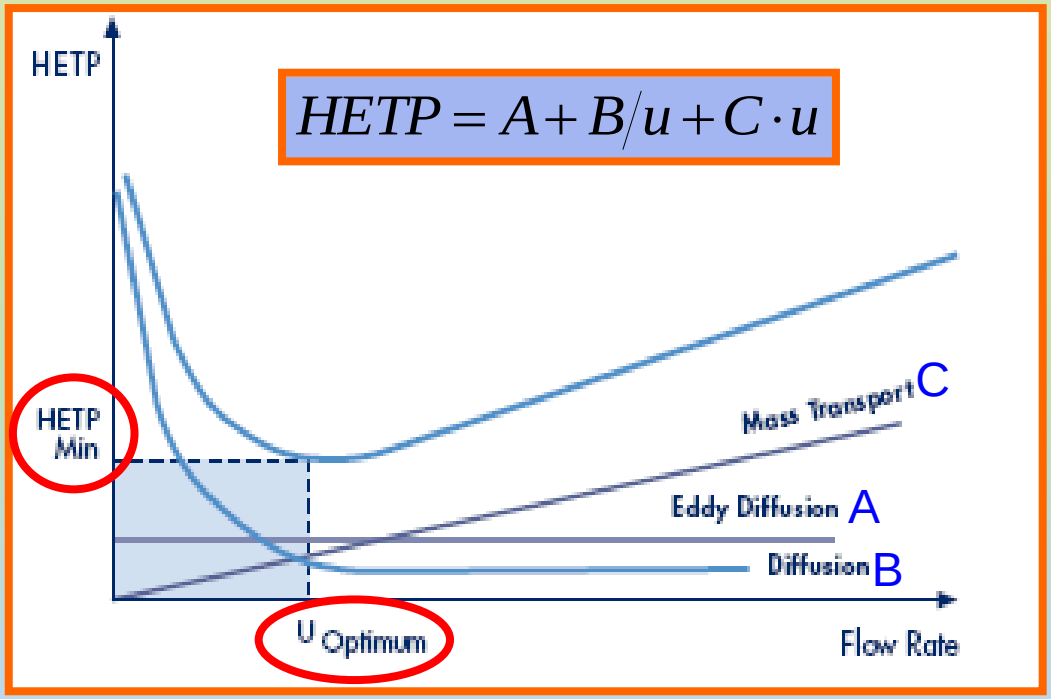
C – Mass transport

Analyte – equilibration between two phases – it takes some time
High mobile phase rate and strong affinity of analyte to sorbent – analyte in the mobile phase will move faster than in the stationary phase.

The most questionable parameter; for the modern types of packing materials it may combine two effects:

- Adsorption kinetics – almost negligible comparing to the diffusion
- Mass transport among particles (by the diffusion)

$$C = \omega d_P^{\,2} / D_m$$



d_p is the particle diameter, D_m is the diffusion coefficient of the analyte in the mobile phase, ω is the coefficient determined by the pore size distribution, shape, and particle size distribution

Different components have different dependencies of HETP on the flow rate on the same column - we can find optimum eluent flow rate where the column efficiency will be the best

Exercises
Supercritical fluid extraction (SFE)

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Information sources

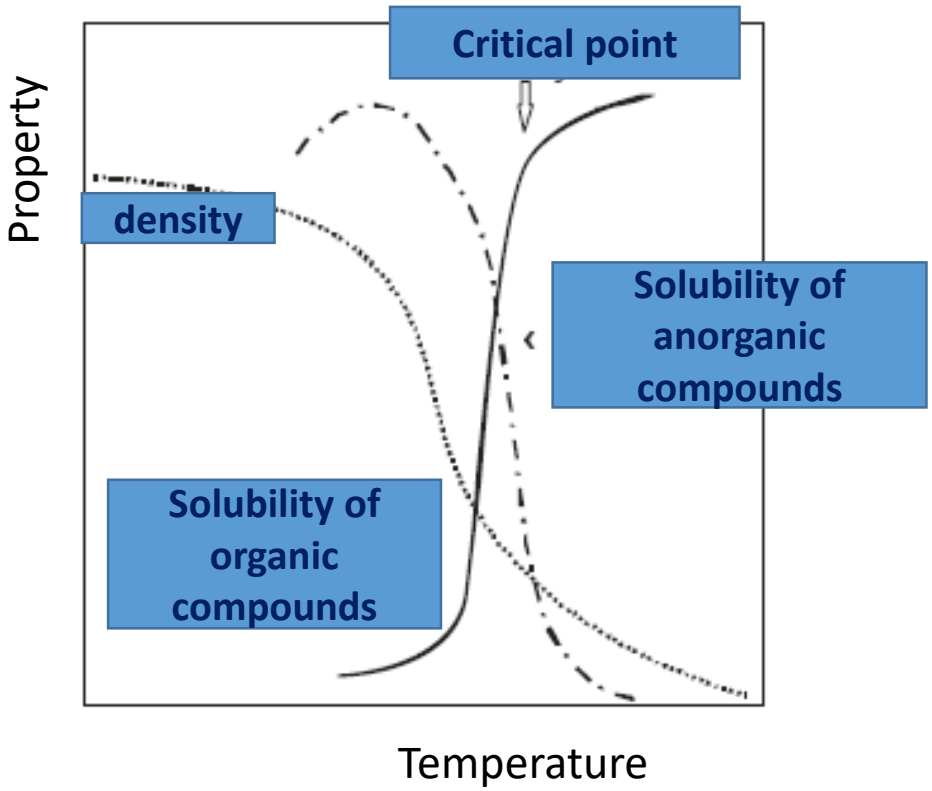
Databases: ScienceDirect, Scopus, Web of Science

http://sch.vscht.cz/vyuka/international-students/erasmus-students/

McHugh M., Krukonis V. (1994): Supercritical Fluid Extraction, In: Brenner H. (Ed.), Butterworth-Heinemann, Massachusetts

Supercritical fluid extraction (SFE)

- An important property is the solubility of material in supercritical liquids
- Solubility of material increases with increasing density (T=constant)
- Near the critical point, the density can steeply decrease with a minimal temperature increase
- The solubility near the critical point often decreases with an increasing temperature and then increases again



Schematic chart of the substance's behaviour near the critical point for selected properties

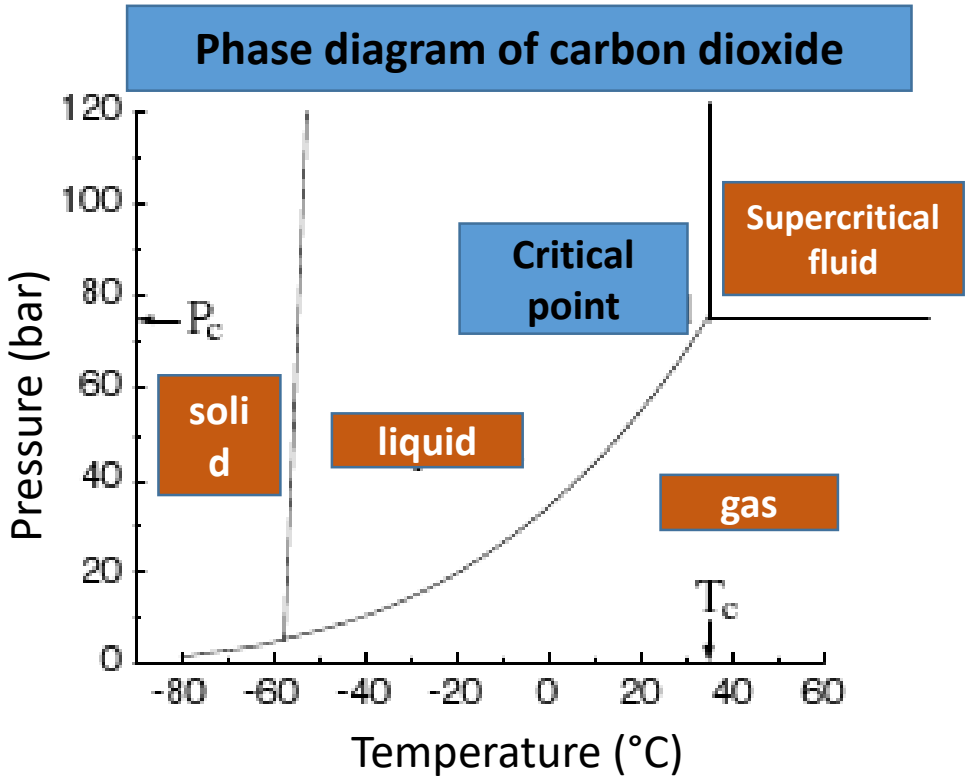
Supercritical fluid extraction (SFE)

➢ Supercritical carbon dioxide

Critical temperature T_c = 35 °C, critical pressure p_c = 75 bar

40 °C:
72 bar → 0.22 g ml^{-1}
400 bar → 0.96 g ml^{-1}

80 °C:
72 bar → 0.14 g ml^{-1}
400 bar → 0.82 g ml^{-1}



Note: The triple point of CO_2 lies at the pressure of 5.2 atm and the temperature of -57 ℃.

At the pressure of 1 atm, CO_2 passes straight from solid to liquid phas (sublimes), at atmospheric pressurem the CO_2 does not exist in liquid phase

EXERCISES
Heat processes I

- **Steam diagram**
- **Heat exchanger calculation**

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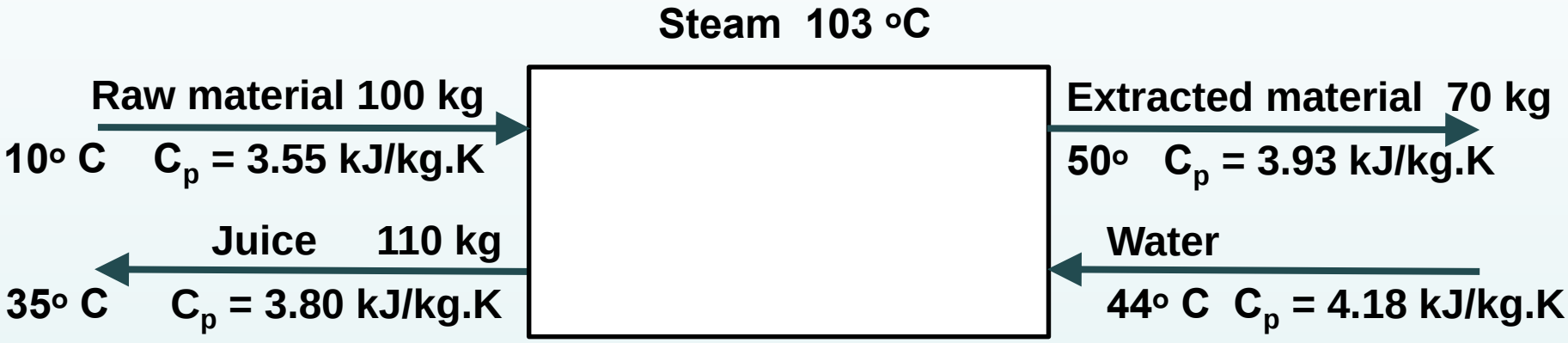
422/2: Properties of water (') and steam (") at the state of saturation – Pressure table (continued)

Pressure	Temperature	Specific volume		Density	Specific enthalpy		Heat of evaporation	Specific entropy	
p in bar	t in °C	v' 10^{-3} m³/kg	v'' in m³/kg	ρ'' in kg/m³	h' in kJ/kg	h'' in kJ/kg	r in kJ/kg	s' in kJ/(kg·K)	s'' in kJ/(kg·K)
21	214.85	1.1809	0.09489	10.54	919.96	2 798.2	1 878.2	2.4700	6.3187
22	217.24	1.1850	0.09065	11.03	930.95	2 799.1	1 868.1	2.4922	6.3015
23	219.55	1.1892	0.08677	11.52	941.60	2 799.8	1 858.2	2.5136	6.2849
24	221.78	1.1932	0.08320	12.02	951.93	2 800.4	1 848.5	2.5343	6.2690
25	223.94	1.1972	0.07991	12.51	961.96	2 800.9	1 839.0	2.5543	6.2536
26	226.04	1.2011	0.07686	13.01	971.72	2 801.4	1 829.6	2.5736	6.2387
27	228.07	1.2050	0.07402	13.51	981.22	2 801.7	1 820.5	2.5924	6.2244
28	230.05	1.2088	0.07139	14.01	990.48	2 802.0	1 811.5	2.6106	6.2104
29	231.97	1.2126	0.06893	14.51	999.53	2 802.2	1 802.6	2.6283	6.1969
30	233.84	1.2163	0.06663	15.01	1 008.4	2 802.3	1 793.9	2.6455	6.1837
31	235.67	1.2200	0.06447	15.51	1 017.0	2 802.3	1 785.4	2.6623	6.1709
32	237.45	1.2237	0.06244	16.02	1 025.4	2 802.3	1 776.9	2.6786	6.1585
33	239.48	1.2274	0.06053	16.52	1 033.7	2 802.3	1 768.6	2.6945	6.1463
34	240.88	1.2310	0.05873	17.03	1 041.8	2 802.1	1 760.3	2.7101	6.1344
35	242.54	1.2345	0.05703	17.54	1 049.8	2 802.0	1 752.2	2.7253	6.1228
36	244.16	1.2381	0.05541	18.05	1 057.6	2 801.7	1 744.2	2.7401	6.1115
37	245.75	1.2416	0.05389	18.56	1 065.2	2 801.4	1 736.2	2.7547	6.1004
38	247.31	1.2451	0.05244	19.07	1 072.7	2 801.1	1 728.4	2.7689	6.0896
39	248.84	1.2486	0.05106	19.58	1 080.1	2 800.8	1 720.6	2.7829	6.0789
40	250.33	1.2521	0.04975	20.10	1 087.4	2 800.3	1 712.9	2.7965	6.0685

STEAM HEATING – EXTRACTION

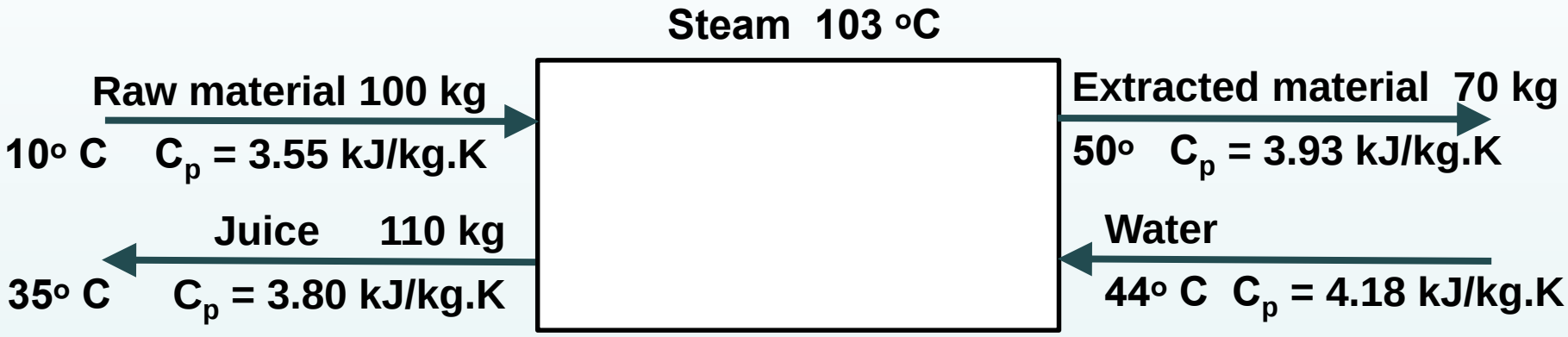


The mass balance:

$$m_W + m_{raw.m.} = m_{ex.mat.} + m_J$$

$$m_W = 70 + 110 - 100 = 80 \text{ kg}$$

STEAM HEATING – EXTRACTION

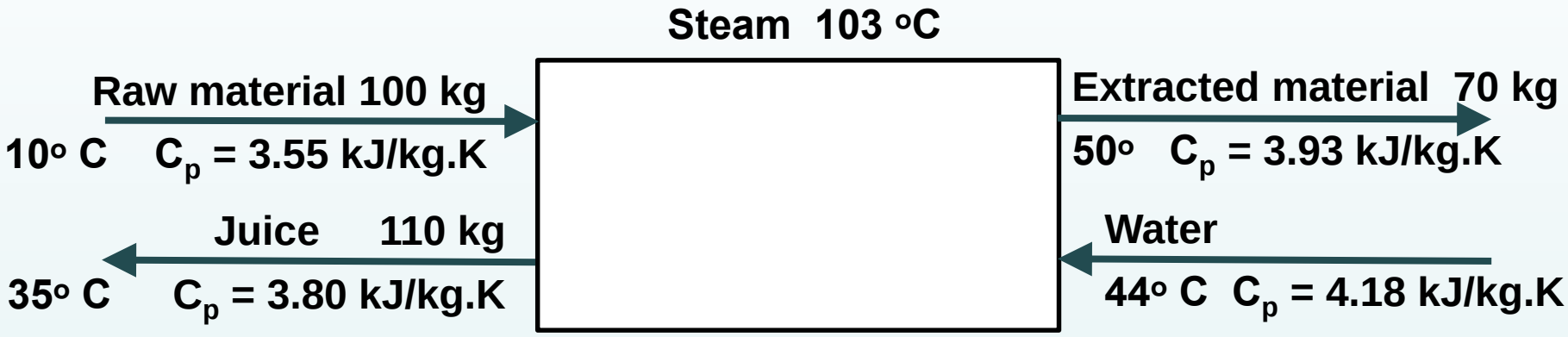


Heat losses 10 %

The enthalpic balance:

$$Q_{raw.mat.} + Q_{water} + Q_{steam} = Q_{juice} + Q_{ex.mat.} + Q_{losses}$$

STEAM HEATING – EXTRACTION



Heat losses 10 %

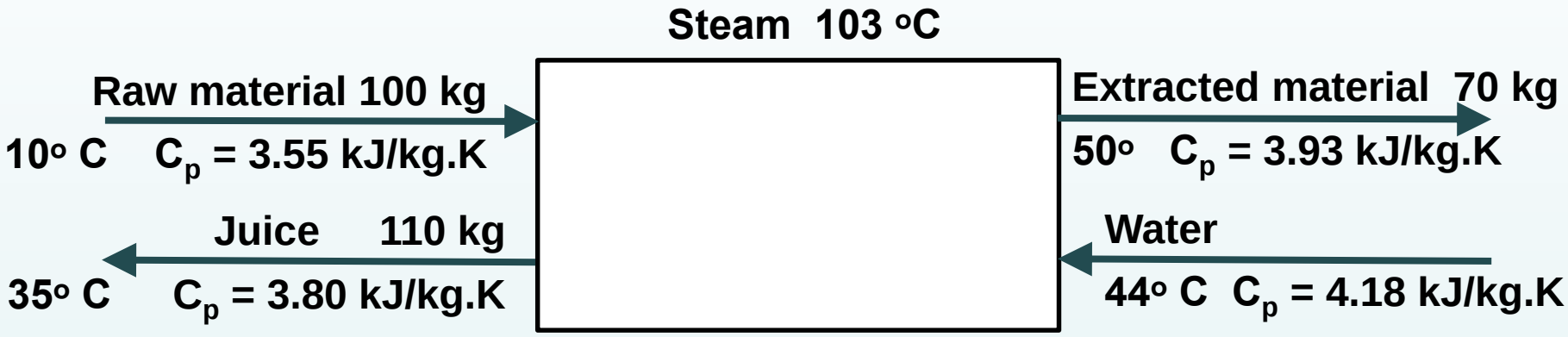
The enthalpic balance:

$$Q_{raw.mat.} + Q_{water} + Q_{steam} = Q_{juice} + Q_{ex.mat.} + Q_{losses}$$

In: $Q_{raw.mat.} + Q_{water} = ???$

Out: $Q_{juice} + Q_{ex.mat.} = ???$

STEAM HEATING – EXTRACTION



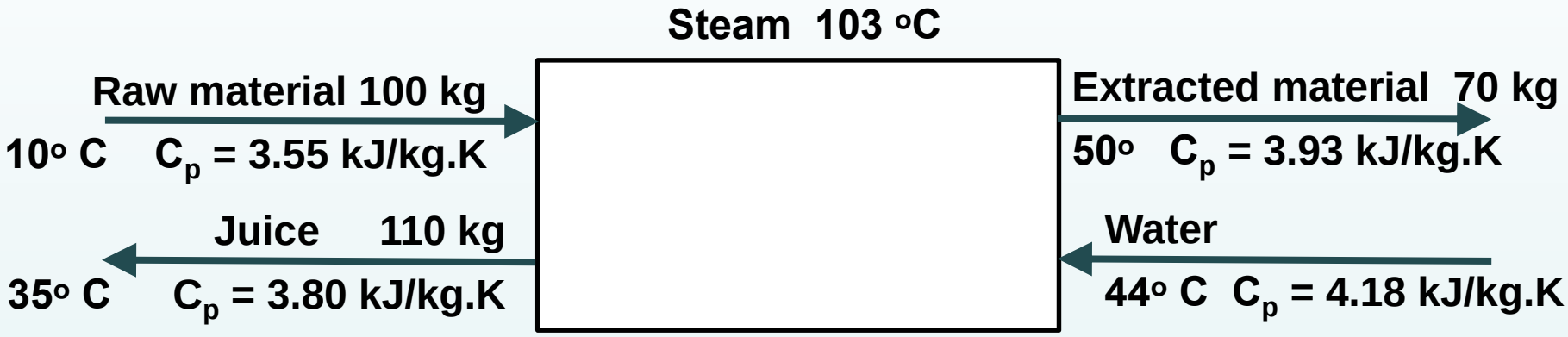
The enthalpic balance:

$$Q_{raw.mat.} + Q_{water} + Q_{steam} = Q_{juice} + Q_{ex.mat.} + Q_{losses}$$

In: $Q_{raw.mat.} + Q_{water} = 100 \cdot 3.55 \cdot 10 + 80 \cdot 4.18 \cdot 44 = 1.83 \cdot 10^4$ kJ

Out: $Q_{juice} + Q_{ex.mat.} = 70 \cdot 3.93 \cdot 50 + 110 \cdot 3.8 \cdot 35 = 2.84 \cdot 10^4$ kJ

STEAM HEATING – EXTRACTION



Heat losses 10 %

Heat consumption:

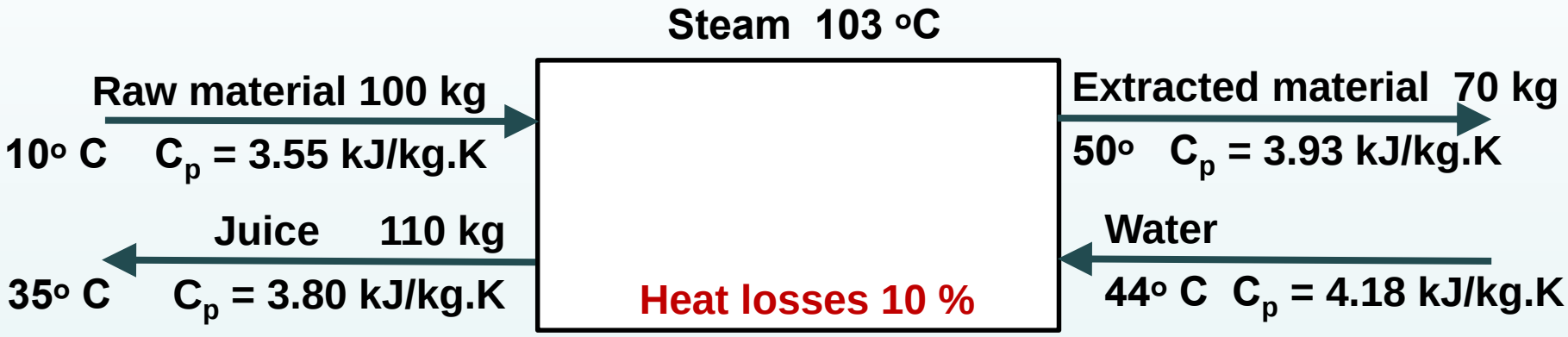
In: $Q_{raw.mat.} + Q_{water} = 1.83 \cdot 10^4$ kJ

Out: $Q_{juice} + Q_{ex.mat.} = 2.84 \cdot 10^4$ kJ

Heat consumption = ("OUT" – "IN") x 1.1 10% losses

$Q^z_{steam} = (2.84-1.83) \cdot 1.1 = 1.12 \cdot 10^4$ kJ

STEAM HEATING – EXTRACTION



Heat of vaporisation:

r_{103} = 2248 kJ/kg

Steam consumption:

$$m_{steam} = \frac{Q^{Z}_{steam}}{r_{103}}$$

$$m_{steam} = \frac{11200}{2248} = 4.9\ kg$$

HEAT EXCHANGER

$$Q = k \cdot a \cdot \Delta t_{l.s.} \quad / \quad Q = k_L \cdot n \cdot L_s \cdot \Delta t_{l.s.}$$

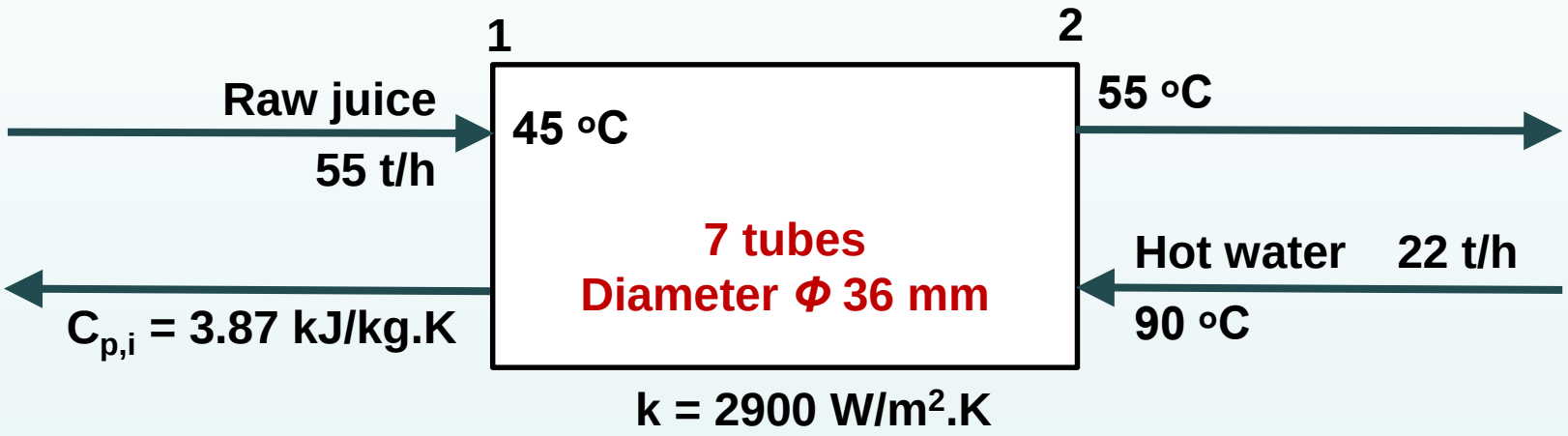
$$Q = m \cdot c_p \cdot \Delta t$$

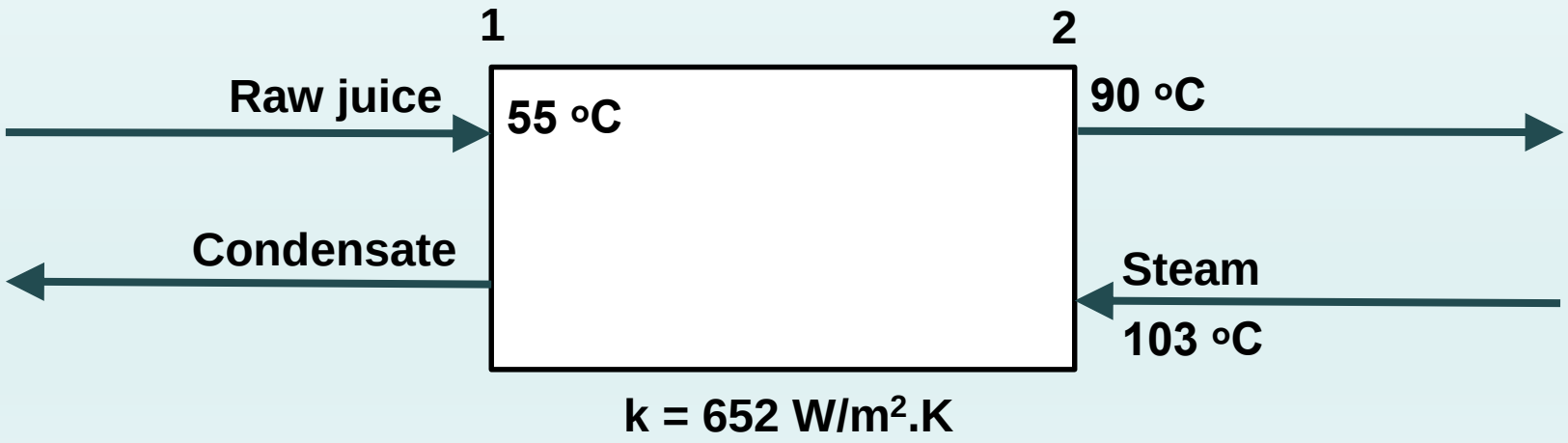
$$\Delta t_{l.s.} = \frac{\Delta t_1 - \Delta t_2}{ln \frac{\Delta t_1}{\Delta t_2}}$$

$$k_L = \pi \cdot d_L \cdot k$$

[W/m.K] [W/m^2.K]

HEAT ECHANGER





Exercises –
Heat processes II

- **Drying**
- **Storage**
- **Air Conditioning**

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MINISTRY OF EDUCATION,
YOUTH AND SPORTS

Zdeněk Bubník

Department of Carbohydrates and Cereals
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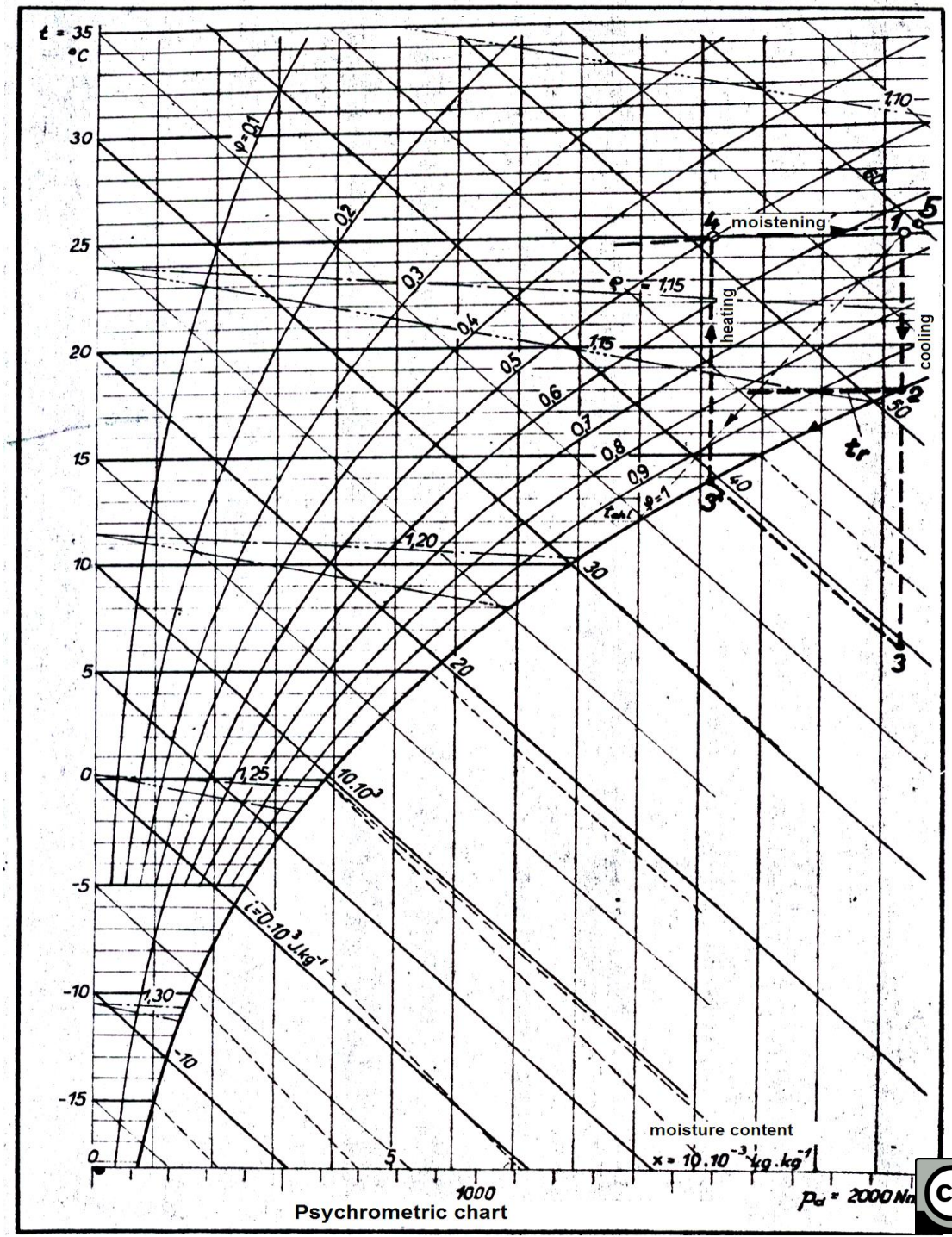
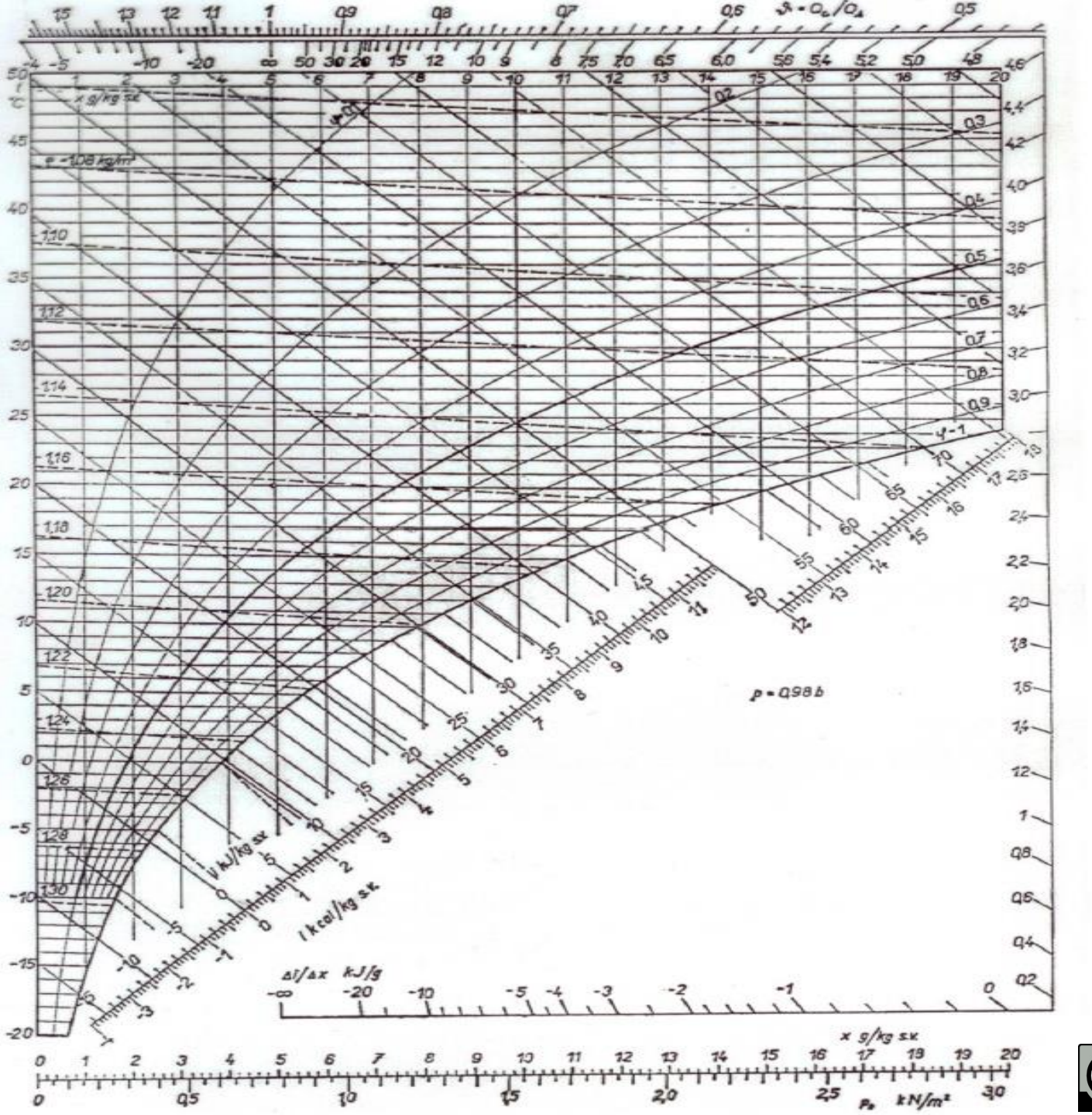
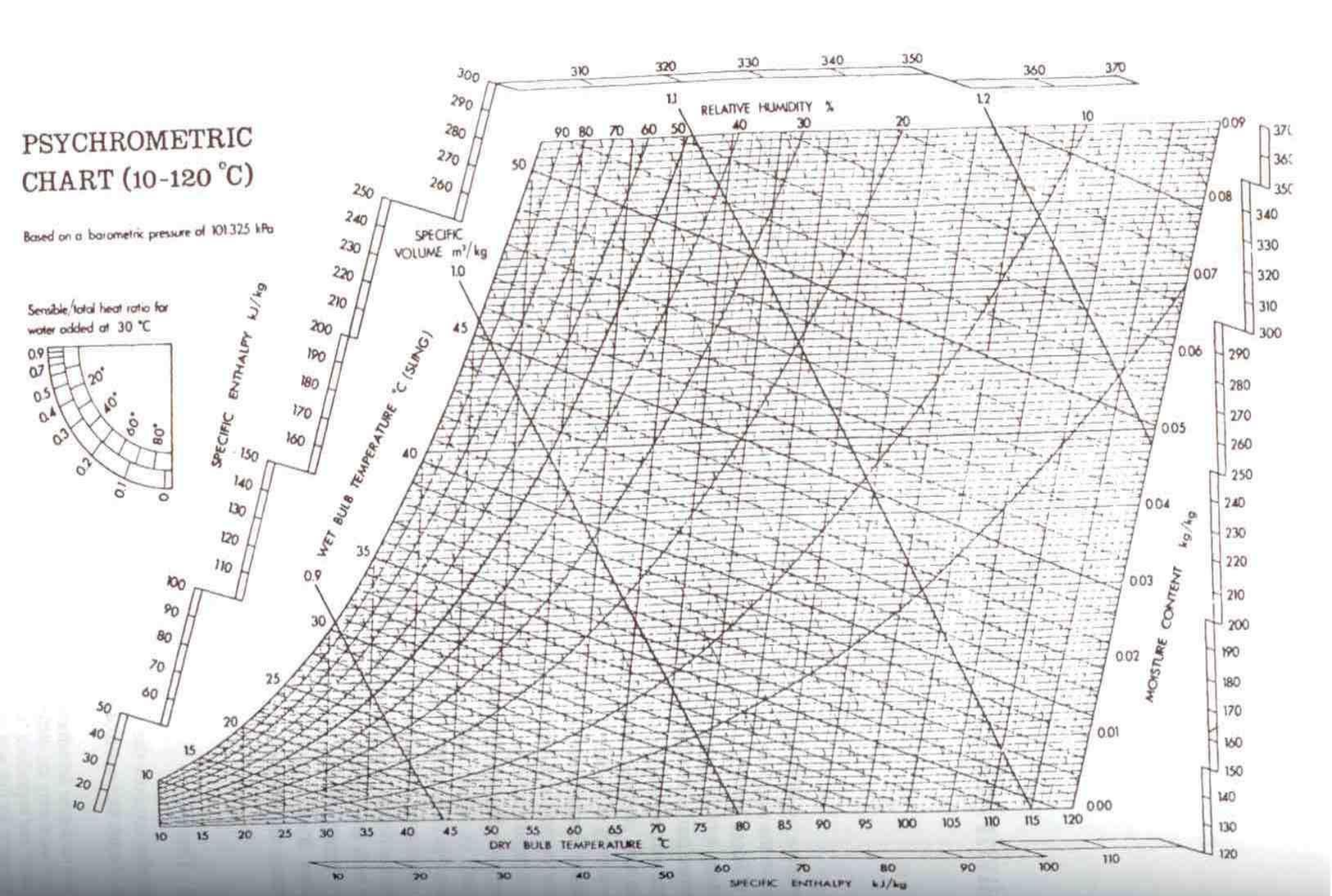
Psychrometric chart (diagram of wet air)




x g/kg s.k.
p = 1,08 kg/m³
1,10
1,12
1,14
1,16
1,18
1,20
1,22
1,24
1,26
1,28
1,30
φ = 0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
0,9
1
p = 0,98 b
i kJ/kg s.k.
i kcal/kg s.k.
Δi/Δx kJ/g
x g/kg s.k.
p_c kN/m²



(Courtesy of Chartered Institution of Building Service Engineers.)

Example:

Production: 750 t of sugar per day

Temperature:	t = 15 °C
Water content:	W = 0.055 %

Storage conditions:

Temperature:	t = 15 °C
Rel. air humidity:	φ = 50 %
Equilibrium humidity:	W_{eq} = 0.027 %

Air-condition:

Temperature:	t = 15 °C
Input Air-Con:	φ_0 = 50 %
Output Air-Con:	φ_1 = 30 %

Questions:

a) How much water must be removed?

b) How much air from air-conditioning will it require?

c) What is the temperature of condensation?

d) How to change the temperature when a new value of φ = 30 % is required?

e) How much water must be removed when the temperature decreases to 10 °C and φ remains constant. The volume of air in the storage hall is 12 000 m^3.

Results:

a) How much water needs to be removed?

$$m_w = 750\ (0.055 - 0.027)/100 = 210\ kg/d$$

Results:

b) How much air from air-conditioning is required?

From the psychrometric chart:

air “output Air-Con“: **3.2 g water / kg air**

air “input Air-Con“: **5.5 g water / kg air**

m_{air} = 210000 / (5.5 – 3.2) = 91304 kg/d

V_{air} = 91304 / 1.18 = 77376 m^3

Results:

c) The temperature of condensation?

5 °C

d) How to change the temperature when a new value of φ = 30 % is required?

23 °C

Results:

e) How much water must be removed when the temperature of air decreases to 10 °C and φ is constant? The volume of the air in the storage hall is 12 000 m³.

From the psychrometric chart:

Air at 15 °C and φ = 50 % : 5.4 g/kg

Air at 10 °C and φ = 50 % : 3.9 g/kg

Results:

e) How much water must be removed when the temperature of air decreases to 10 °C and φ is constant? Volume of the air in the storage hall is 12 000 m^3.

Air at 15 °C and φ = 50 % : 5.4 g/kg

Air at 10 °C and φ = 50 % : 3.9 g/kg

m_{air} = 12000 . 1.20 (density) = 14400 kg air

Results:

e) How much water must be removed when the temperature of air decreases to 10 °C and φ is constant? The volume of the air in the store hall is 12 000 m^3.

Air at 15 °C and φ = 50 % : 5.4 g/kg

Air at 10 °C and φ = 50 % : 3.9 g/kg

m_{air} = 12000 · 1.20 (density) = 14400 kg air

$m_{w\ in}$ = 14400 · 5.4 = 79 kg

$m_{w\ out}$ = 14000 · 3.9 = 56 kg

Removed water: 79 – 56 = 23 kg

Advanced Processes in Food Technology

Trends in Food Engineering

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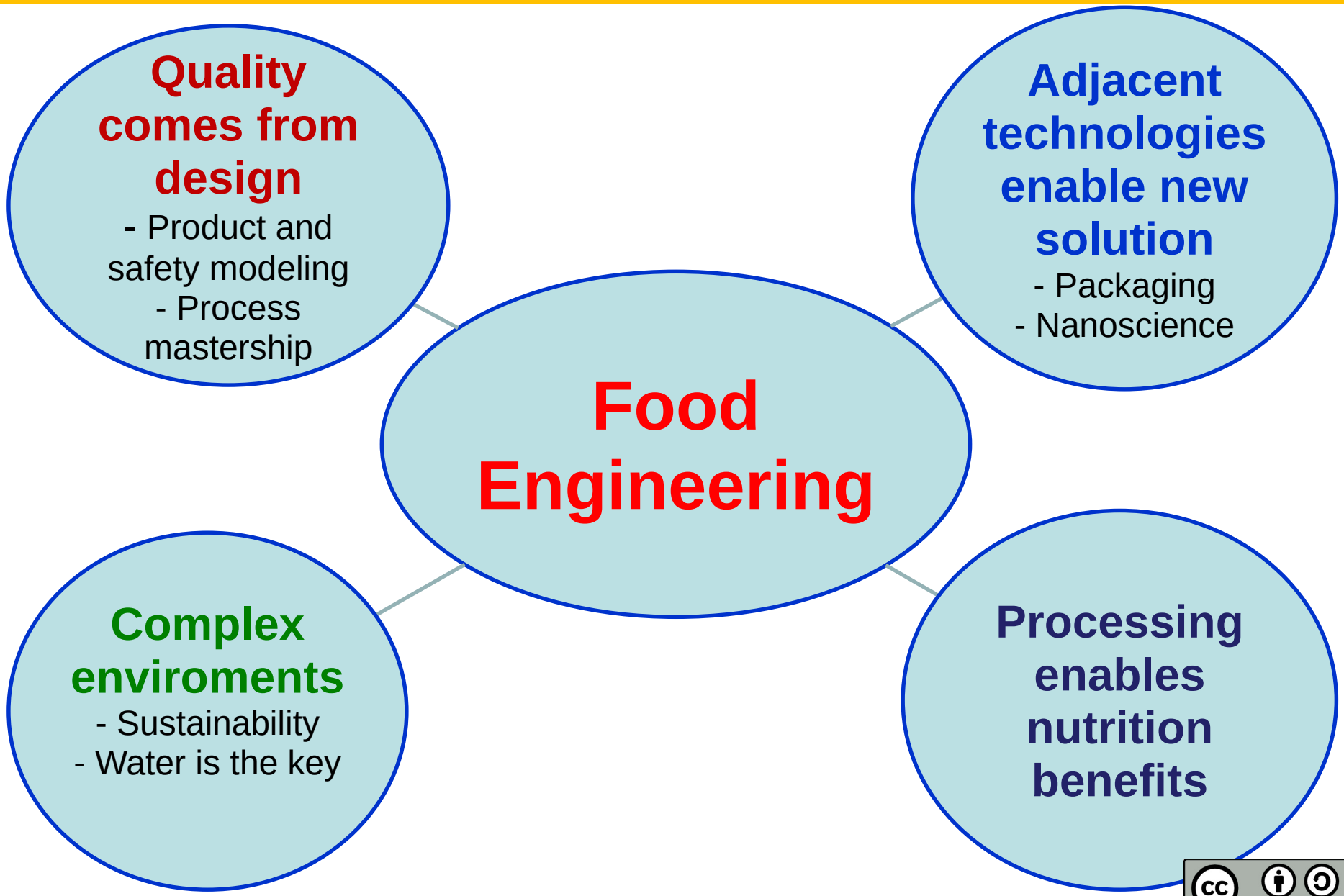
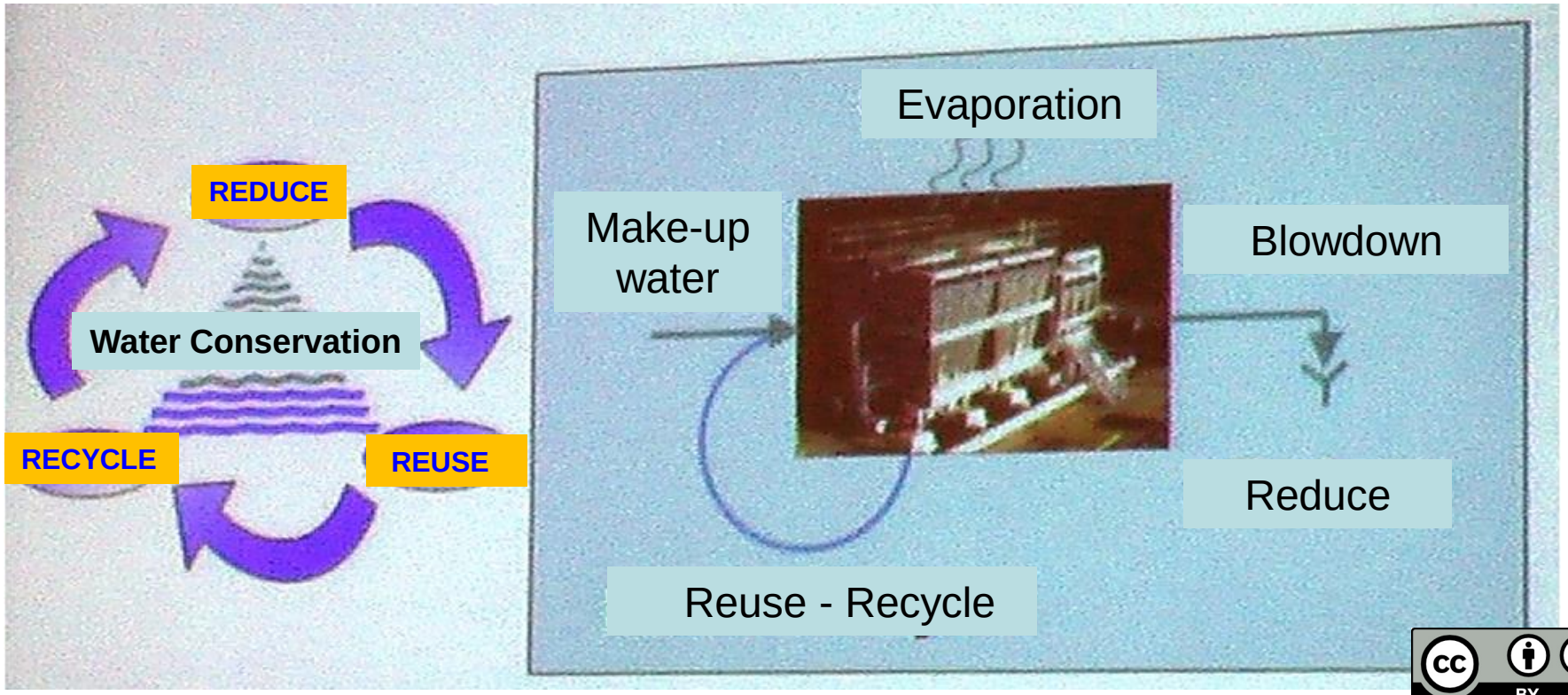
Trends in Food Enginering



Water is the Key – Cycle Optimization

Intensification of processes is necessary to close material loops:

- **Recycling and reuse of cooling water simultaneously reducing blowdowns**
- **Management of “side stream output“ to improve efficiency**



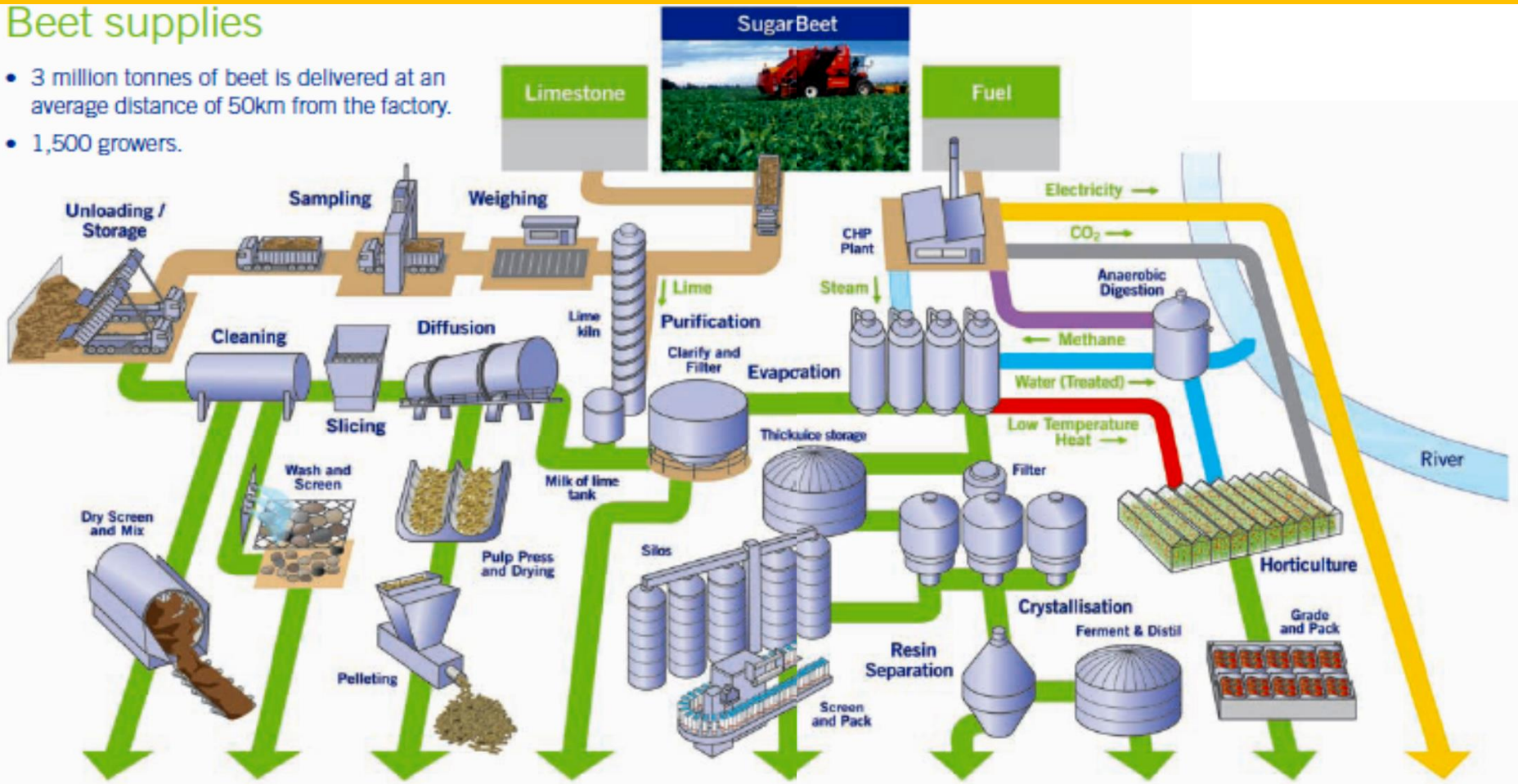
Sustainability Impacts

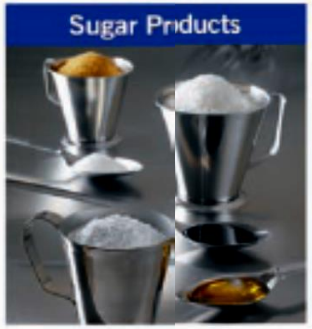
- **Operational Dimensions**
  - Adapting factories to new material flows and management
  - Local sourcing – stamping of miles travelled for imported goods
  - Mandatory generation of clean energy
- **Regulatory Dimensions**
  - Reduction of non-essential inter-market supply
  - New packaging guidelines to control type and amount of used materials
  - Mandatory carbon labelling from retailers
- **Cost Impact**
  - Raw material cost increase through diversion towards biofuels
  - Cost-efficient new technology supporting sustainability
- **Sales Impact**
  - Re-development of products and packaging
  - Reducing packaging input

Sugar Beet Refinery Wissington (UK)

Beet supplies

- 3 million tonnes of beet is delivered at an average distance of 50km from the factory.
- 1,500 growers.

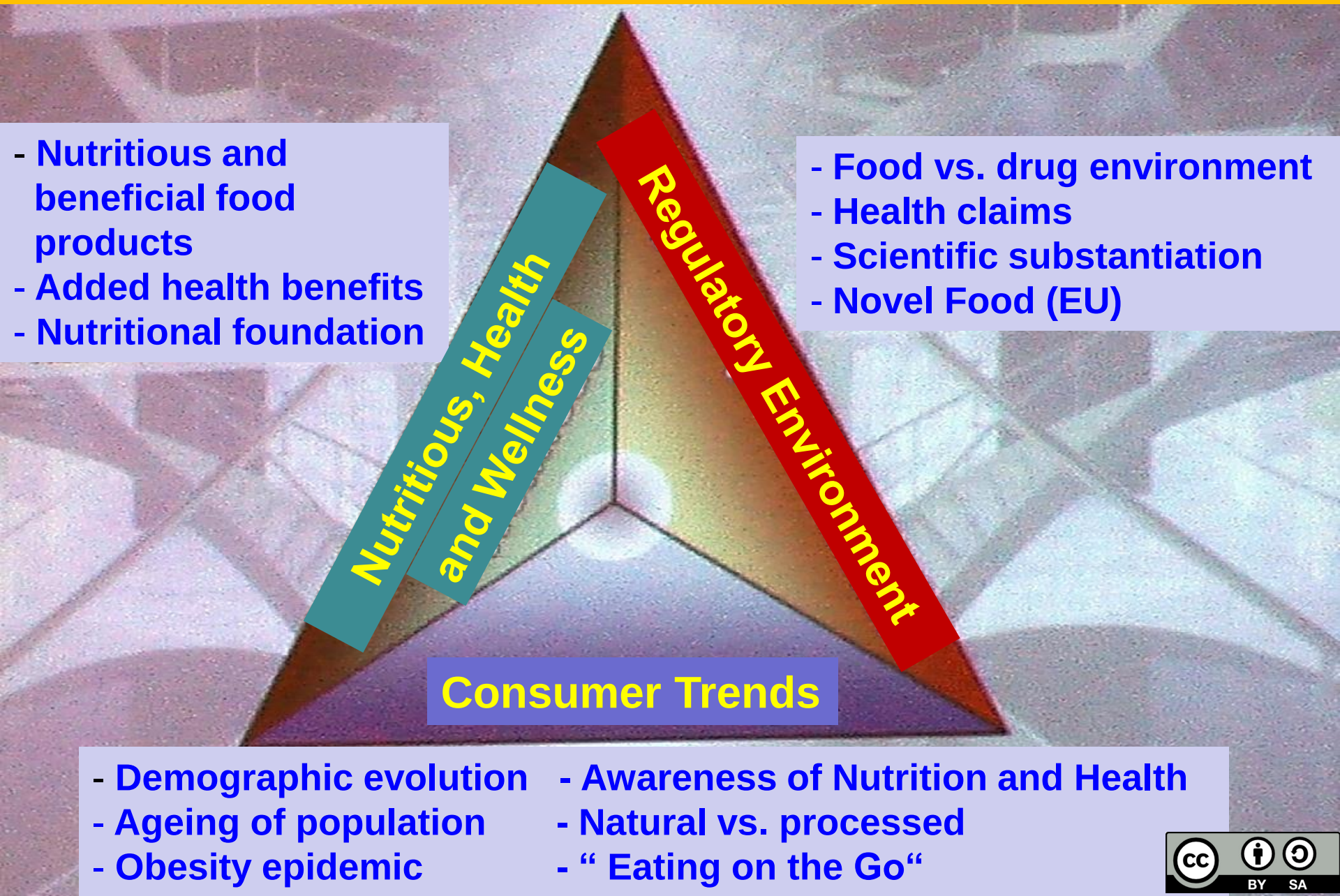




Rational and Emotional Values

- Healthy
- Local
- Social Responsible
- Enviromental Responsible
- Simple Living
- Control

Food Engineering at Interfaces



Food Engineering at Interfaces

- **Food is first about Safety, Nutrition and Emotion.**
- **Value-added foods are built on life science and on the understanding of biology.**
- **Material science plays an increasing role in the structuring of food matrices to enhance nutritional values.**
- **Competitive advantage is increasingly built on efficient use of scientific fields such as physical modeling.**

Food Engineering at Interfaces

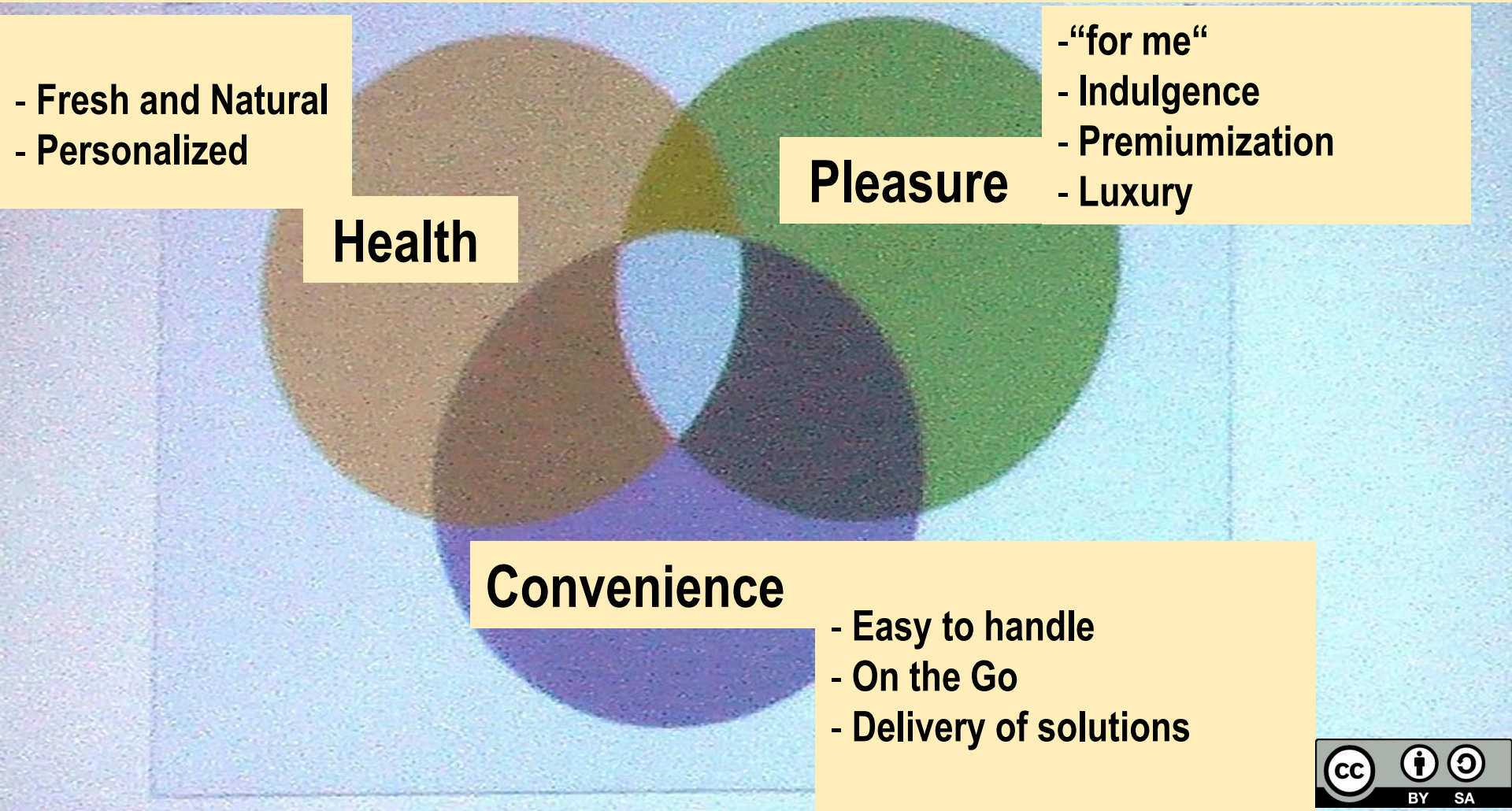
- **Food engineers have to open towards the adjacent fields of science and technology and bring the learning to their field**

- **Food engineers must bridge the science with technology and bring it to commerce**

- **Food engineers are asked to be creative and innovative to provide the means for the food industry going towards nutrition, health and wellness under sustainable conditions**

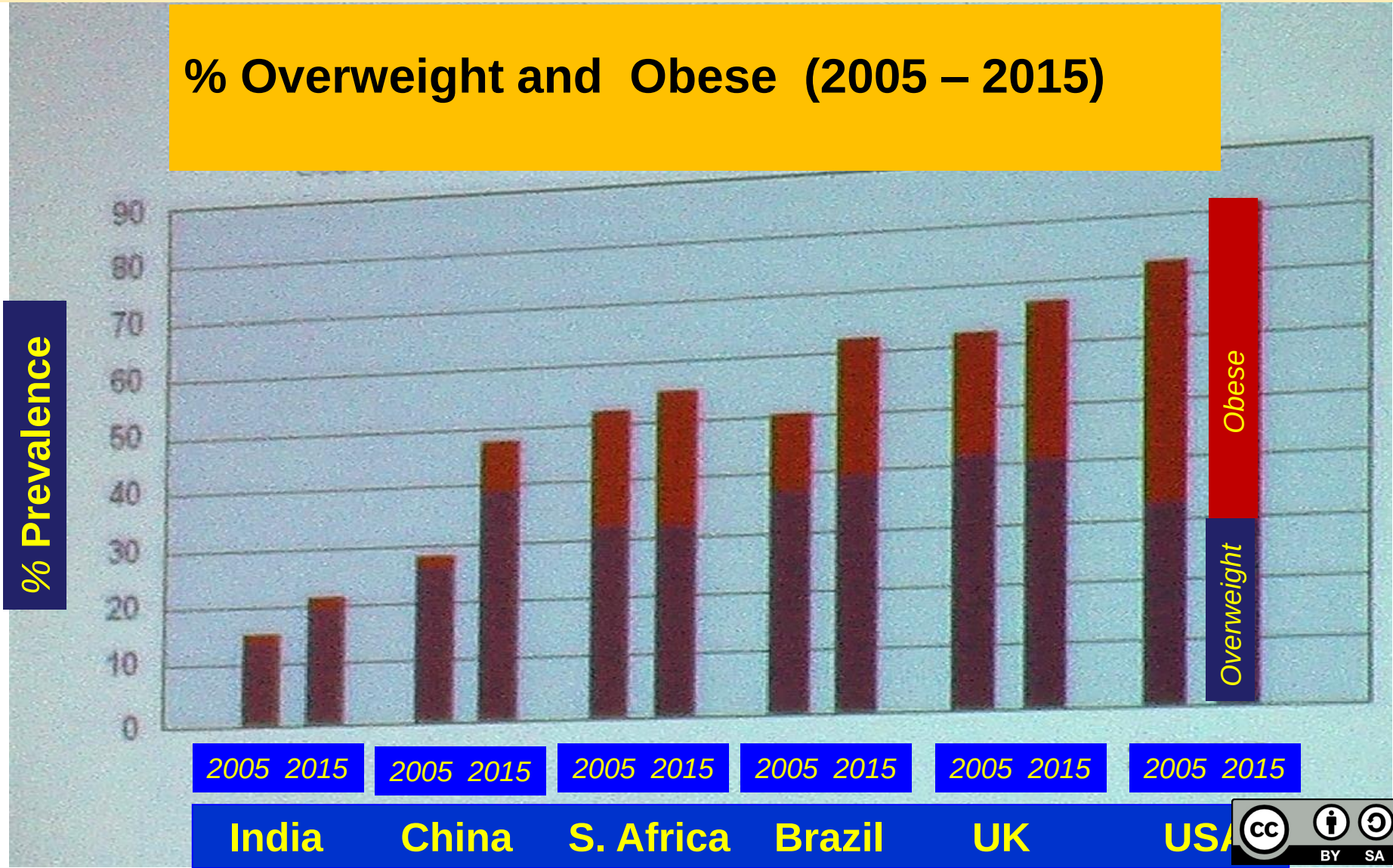
Consumer Benefits Meeting Trends

3 main trends shaping consumer attitudes and behaviours



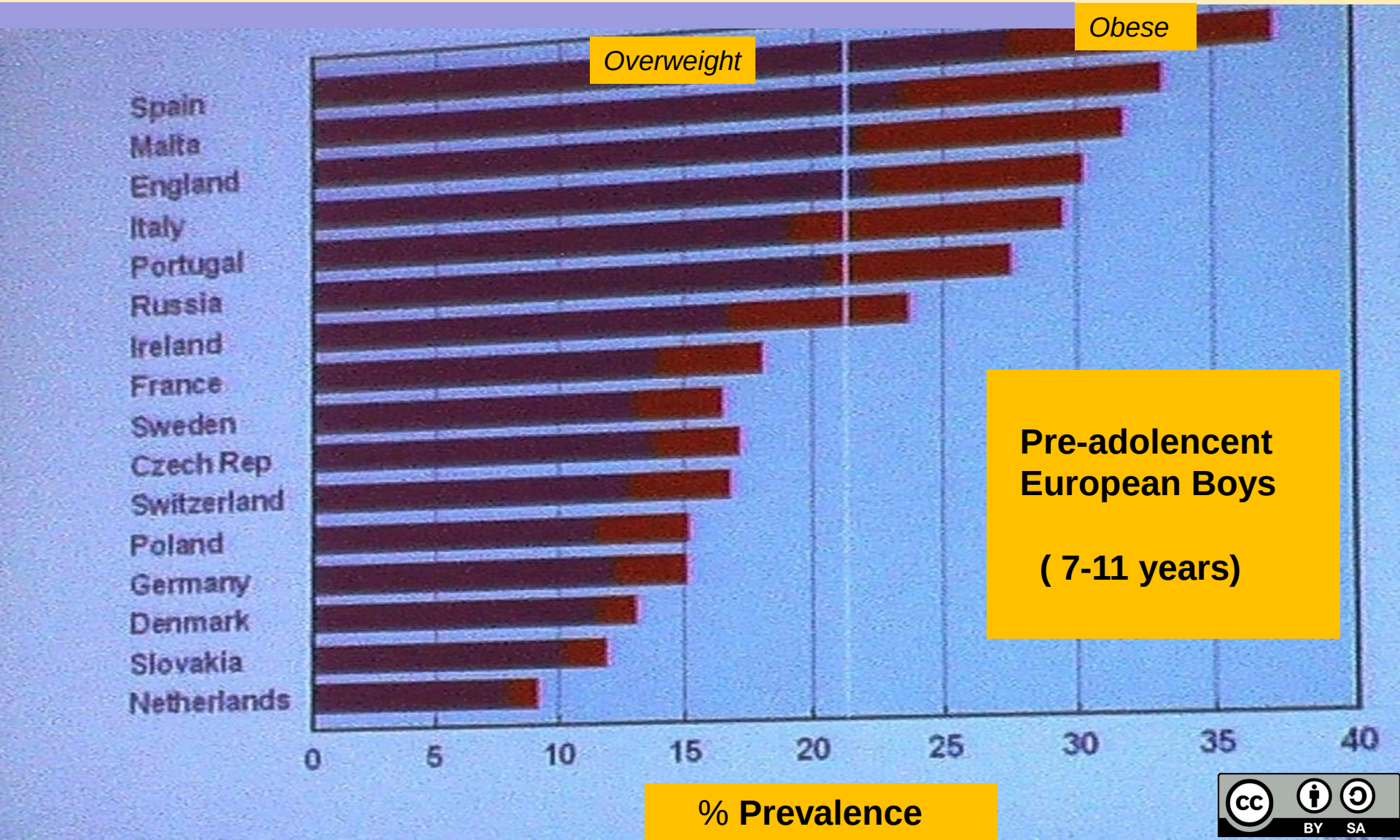
Health Trends:

Obesity is a Growing Problem



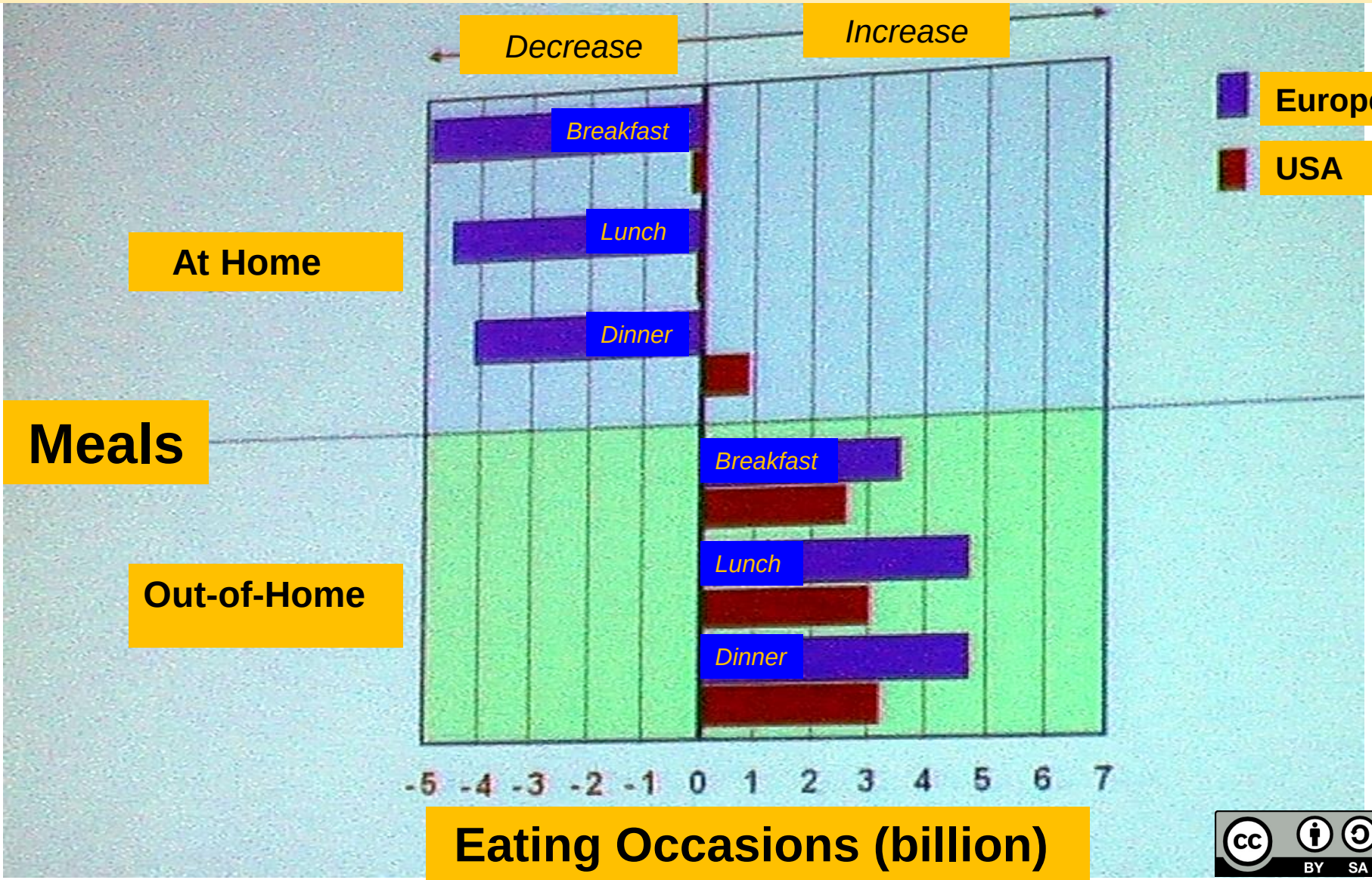
Health Trends:

Obesity - Children are at great risk

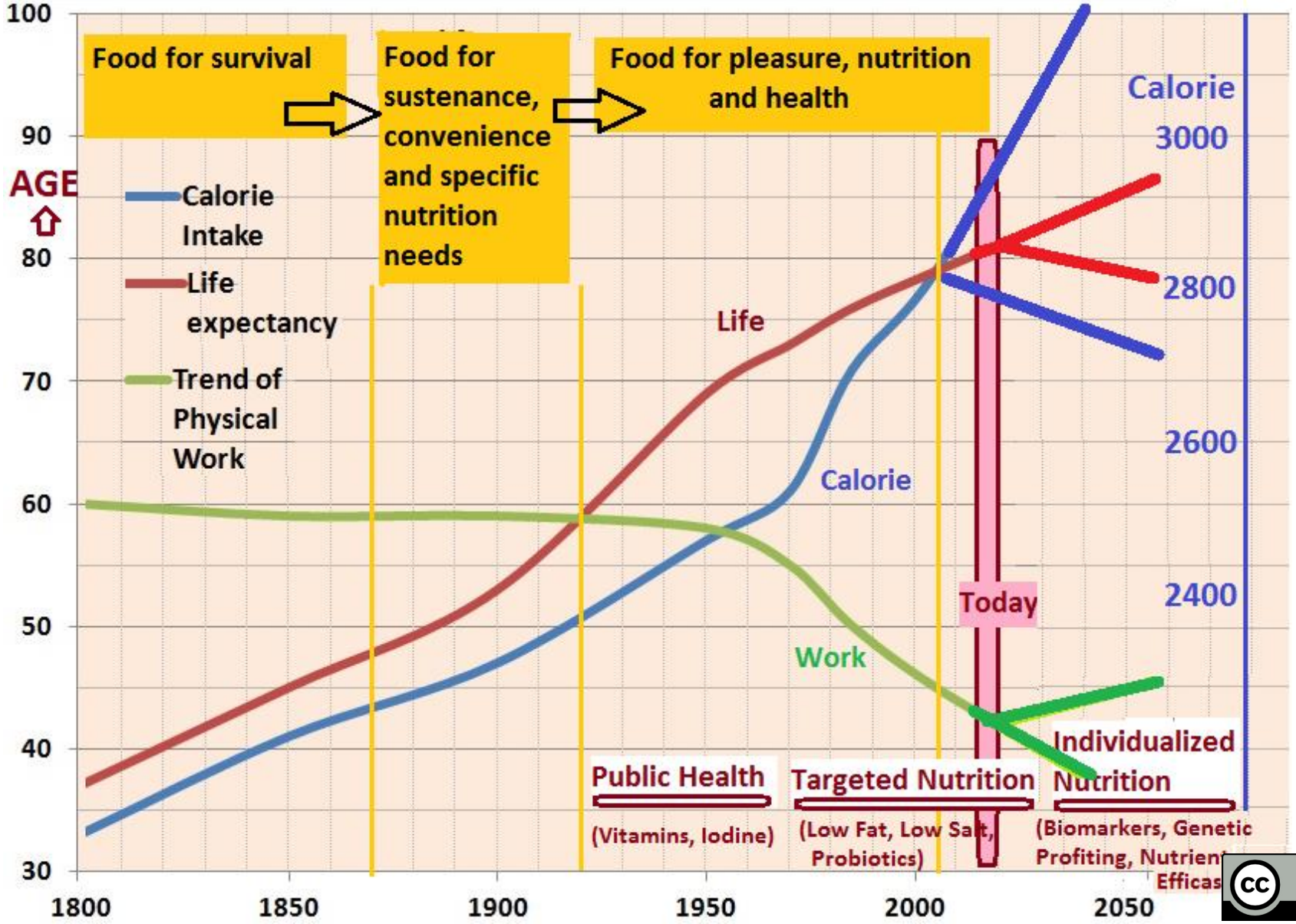


Convenience Trends:

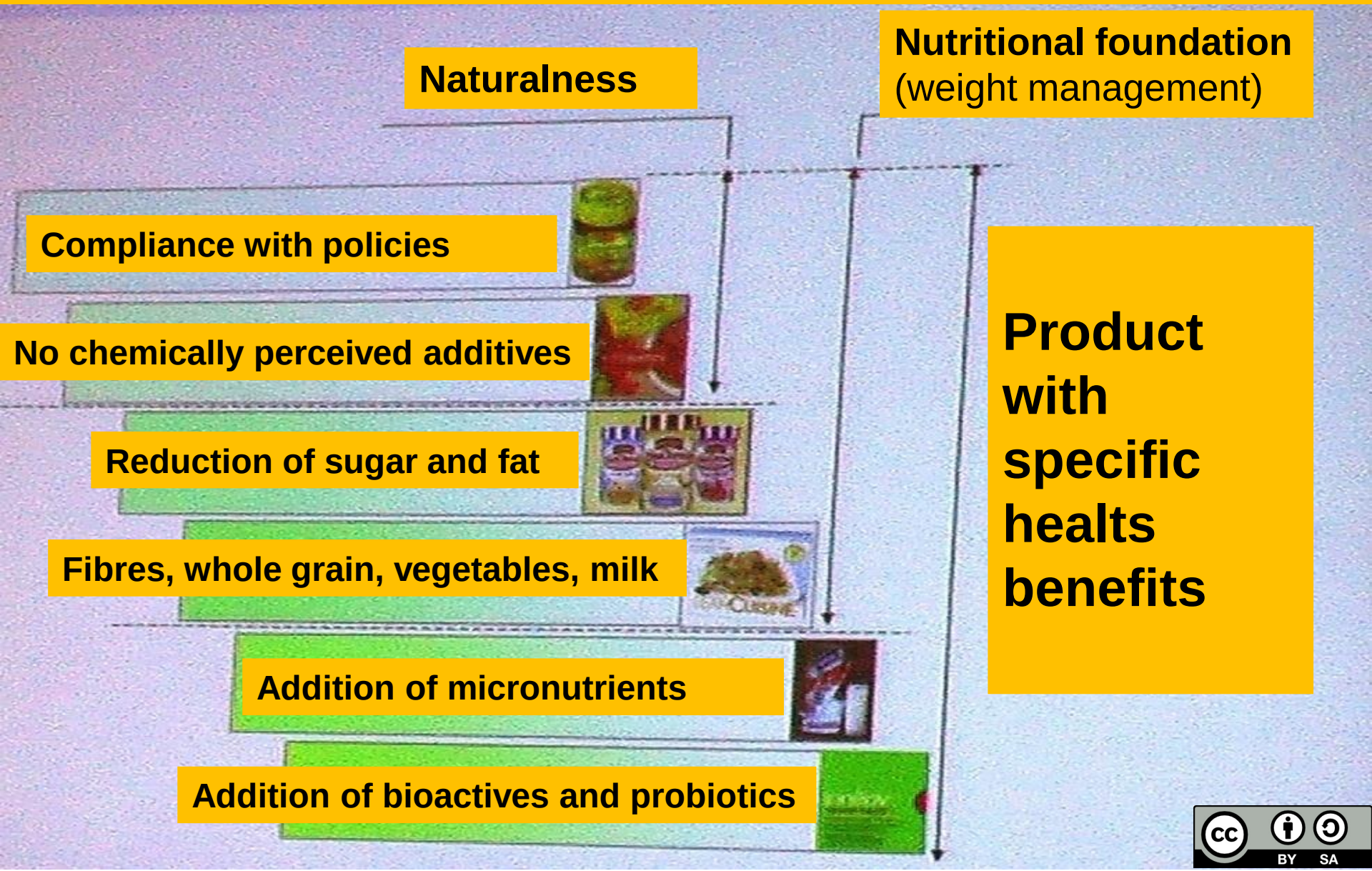
At-Home vs. Out-of-Home Comsuption



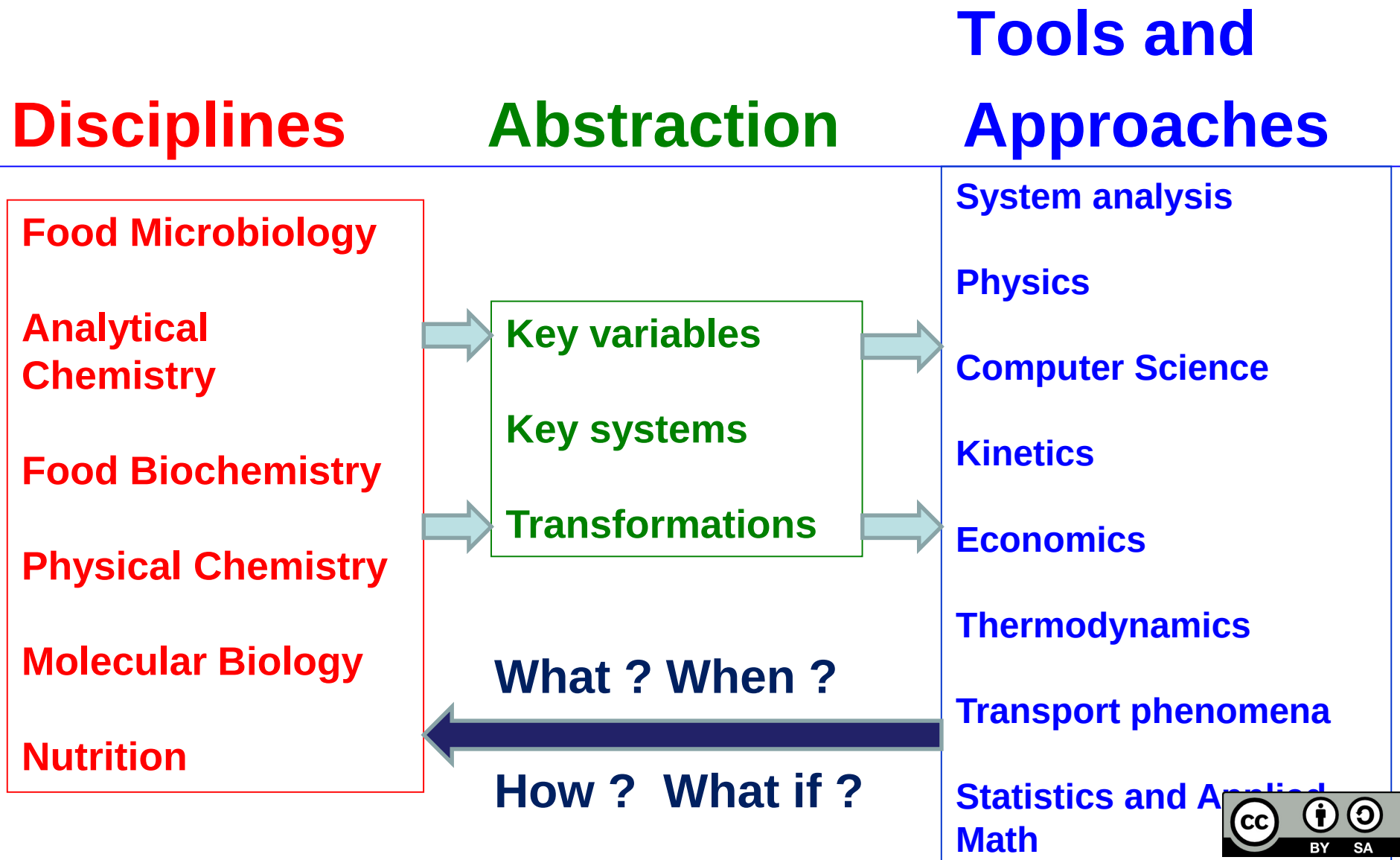
New Nutritional Understanding and Concepts Demand New Scientific Approaches



Food engineering needs to understand the attributes of healthy food products



The Role of Food Engineers and Complex Food Safety Problems



Advanced Processes in Food Technology and Biotechnologies

Mass Transfer

Crystallization - Basic Concept

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INDUSTRIAL CRYSTALLIZATION

Prof. Zdeněk BUBNÍK, PhD
ICT Prague

CONTENT

1. INTRODUCTION

2. THE DRIVING FORCE OF CRYSTALLIZATION

3. NUCLEATION

- Primary nucleation, Secondary nucleation
- The metastable solution zone:
  - The metastable state and supersaturated solution
  - The metastable zone width
- The effect of the individual parameters on nucleation

4. CRYSTAL GROWTH

- Crystal growth rate, crystal shape factors
- The surface diffusion model:
  - Dislocations, growth spiral
- The diffusion layer model
- The effect of the individual parameters on the crystal growth rate
- Measurements of crystal growth rates

5. CRYSTAL SIZE DISTRIBUTION

- Distribution functions
- Crystal population balance
  - Evaluation of the kinetics of nucleation and growth (Fig.)
  - MSMPR crystallizer
- Continuous crystallizer, steady state

6. MODELLING AND DYNAMIC SIMULATION

- Cooling and expansion crystallization
- Optimisation of cooling curve (Fig.)
- Molecular modelling

7. INDUSTRIAL CRYSTALLIZATION PROCESSES

- Isothermal evaporation
- Cooling
- Expansion (combination of evaporation and expansion processes)
- Batch and continuous crystallization
- Crystallization apparatuses
- Control and regulation

INTRODUCTION

- CRYSTALLIZATION is an important **SEPARATION and PURIFICATION TECHNIQUE** used in the food, pharmaceutical, and chemical industries.
- The study of organic crystallization is a multidisciplinary area with chemical engineers, organic solid-state chemists, food and pharmaceutical scientists, and physicists all involved.
- To promote interdisciplinary research and provide for information exchange, international **workshops on Crystal Growth of Organic Materials are organized (BIWIC)**
- The goal of the workshops is to focus on research in emerging areas as well as to provide a forum for the presentations in areas of interest to the food and pharmaceutical industries
- The main topics are: molecular modelling, polymorphism, **crystallization in food and pharmaceutical industry**, industrial crystallization and general topics.

Application of Crystallization Process in Food and Pharmaceutical Industry

- sucrose, fructose, glucose, lactose and other saccharides
- milk fat, chocolate, stearic acid, oleic acid
- amino acids
- sodium gluconate
- protein crystallization
- pharmaceutical powders
- aspartame
- vitamins
- enzymes
- lysozyme

Basic Concepts

❖ **Crystallization** is a process in which a solid phase is precipitated from a gaseous or liquid phase.

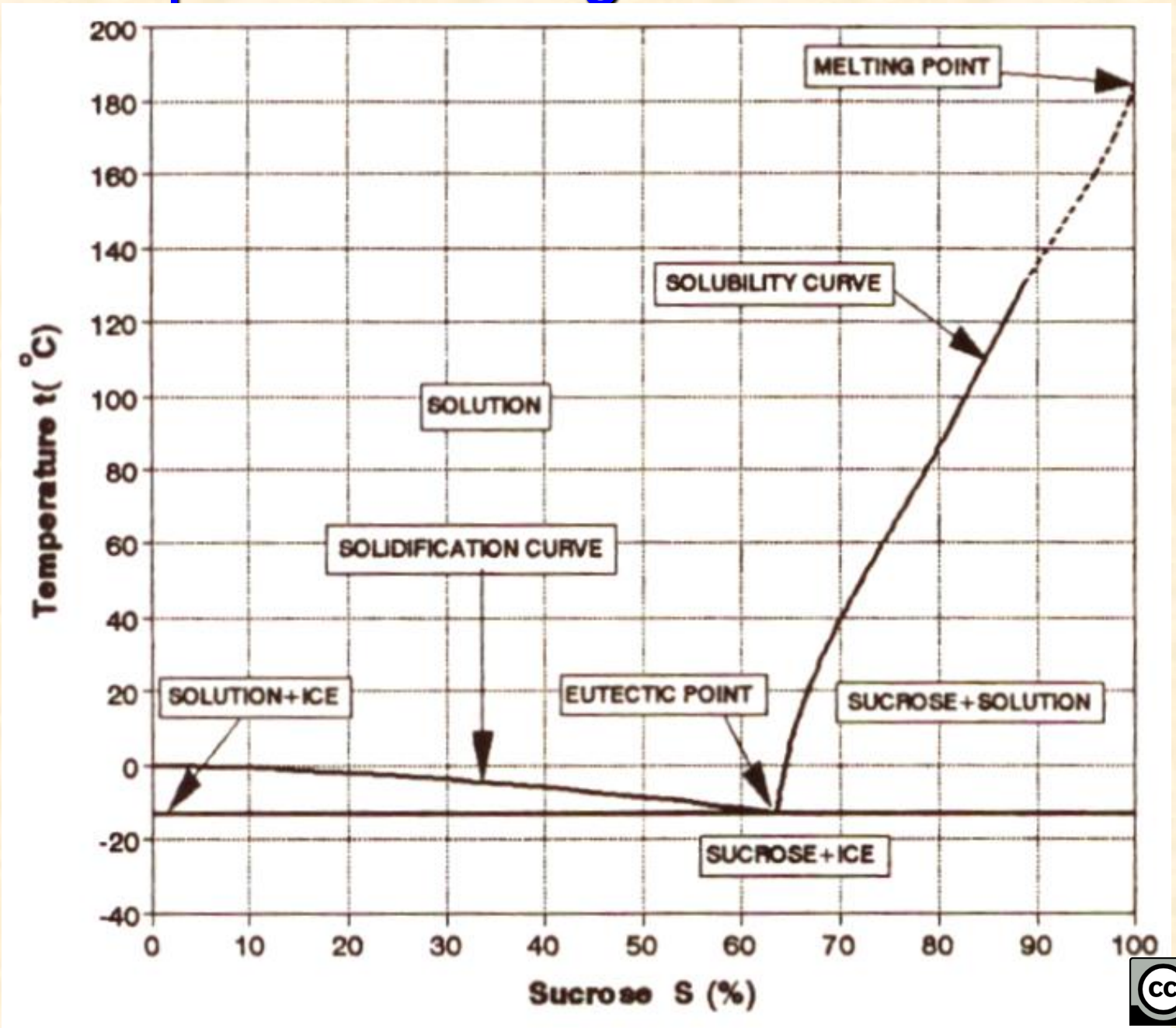
❖ The liquid phase may be either a melt or a solution.

❖ A solid phase is precipitated from a solution if the **chemical potential of the solid phase is less than that of the dissolved component** to be precipitated from the solution.

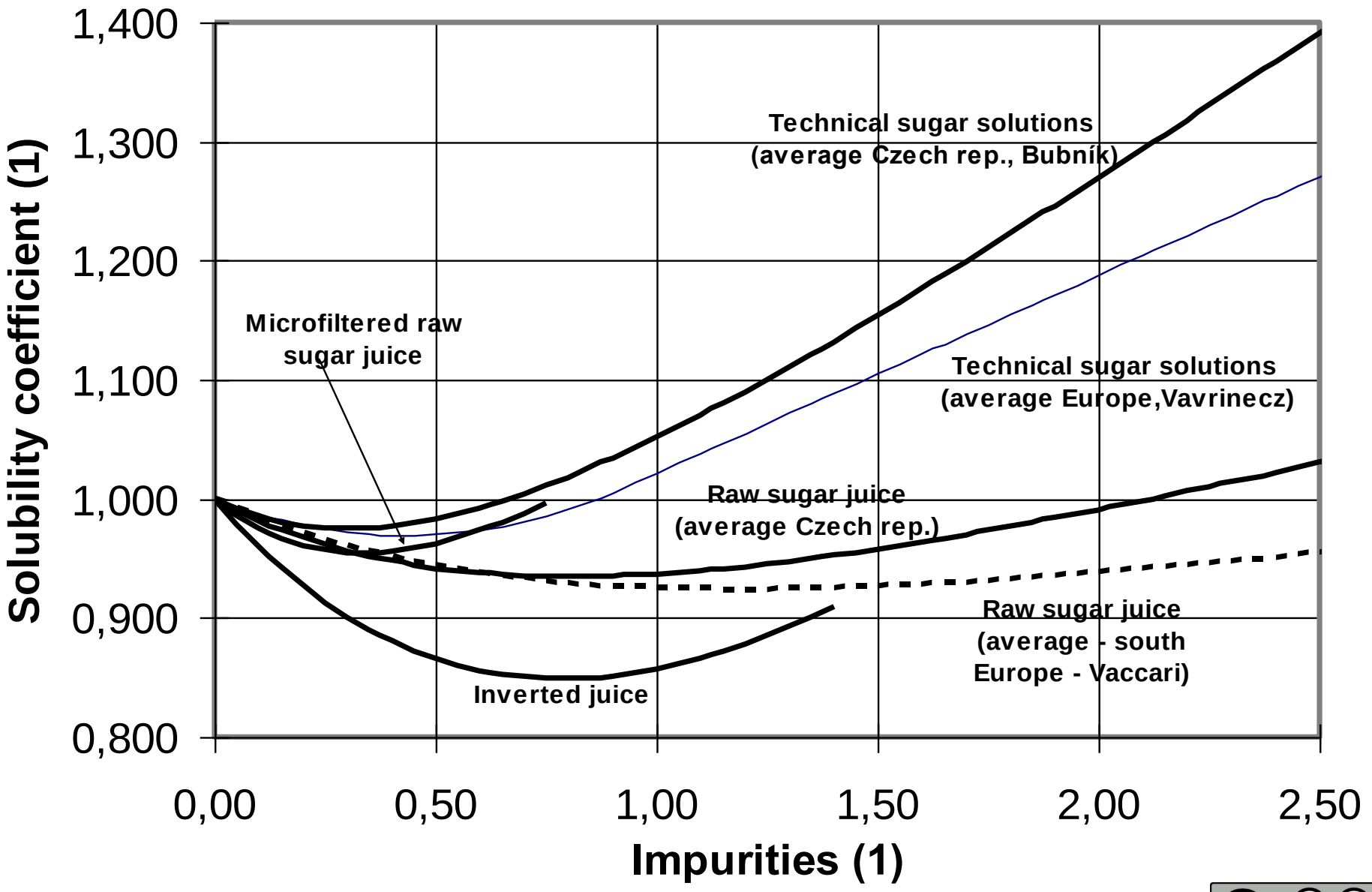
❖ A solution in which the **chemical potential** of the dissolved component **is the same** as that of the corresponding solid phase is in **equilibrium** with this solid phase under the given conditions and termed a **saturated** solution.

❖ This equilibrium state is defined by the concentration of the component in the saturated solution at a given temperature and concentration of the other components, i.e. by the **solubility**.

Phase equilibrium diagram sucrose-water



Solubility Curves for Technical Sugar Solutions



The Thermodynamic Driving Force of Crystallization

- The driving force of crystallization is expressed thermodynamically as the difference in the **chemical potentials** of crystalline substance in the supersaturated solution and in the saturated solution.
- It is common in crystallization studies to introduce the nucleation and crystal growth as functions of the crystallization driving force expressed in terms of the **supersaturation**,
- defined as: $\Delta c = c - c_{eq}$
- or the relative supersaturation: $s = (c - c_{eq})/c_{eq} = \Delta c/c_{eq}$
- or supersaturation ratio: $S = c/c_{eq} = s + 1$.

In order for crystallization to proceed, this equilibrium concentration must be exceeded by some **supersaturation methods:**

a) by ***cooling*** a solution in which the solubility of the given component increases with increasing temperature or by heating a solution in which the solubility of the given component decreases with increasing temperature,

b) by ***evaporating*** the solvent under heating,

c) by ***adiabatic evaporation*** of the solvent, where the removal of the heat of vaporisation of the solvent is reflected in a decrease in the temperature of the solution,

d) by ***adding*** *a* less ***efficient solvent*** that is miscible with the original solvent,

e) by ***salting-out*** through addition of further substances that may, e.g., contain a common ion with the crystallised substance and that decrease its solubility,

f) by ***chemical reaction*** in solution leading to formation of a crystalline substance,

g) in other ways, e.g. *electrochemically.....*

The kinetics of crystallization can then usefully be divided into **two stages:**

1. Formation of crystal nuclei or nucleation

- Primary
- Secondary

2. Crystal growth

Both these stages occur simultaneously in the crystallizer, but they will be considered separately in the study of crystallisation processes.

Nucleation

Primary nucleation: no presence of crystals of producing material

- Homogenous: no presence any particles
- Heterogenous: presence of particles of other material (dust, colloids …)

Secundary nucleation: crystals of producing material are presented in a crystallizator, i.e. “crystallization in suspension"

Kinetics of Nucleation

Primary nucleation:

$$\frac{dN}{d\tau} = k_N (c - c_{eq})^n$$

Nucleation rate N_N (#/s.m^3)

where:

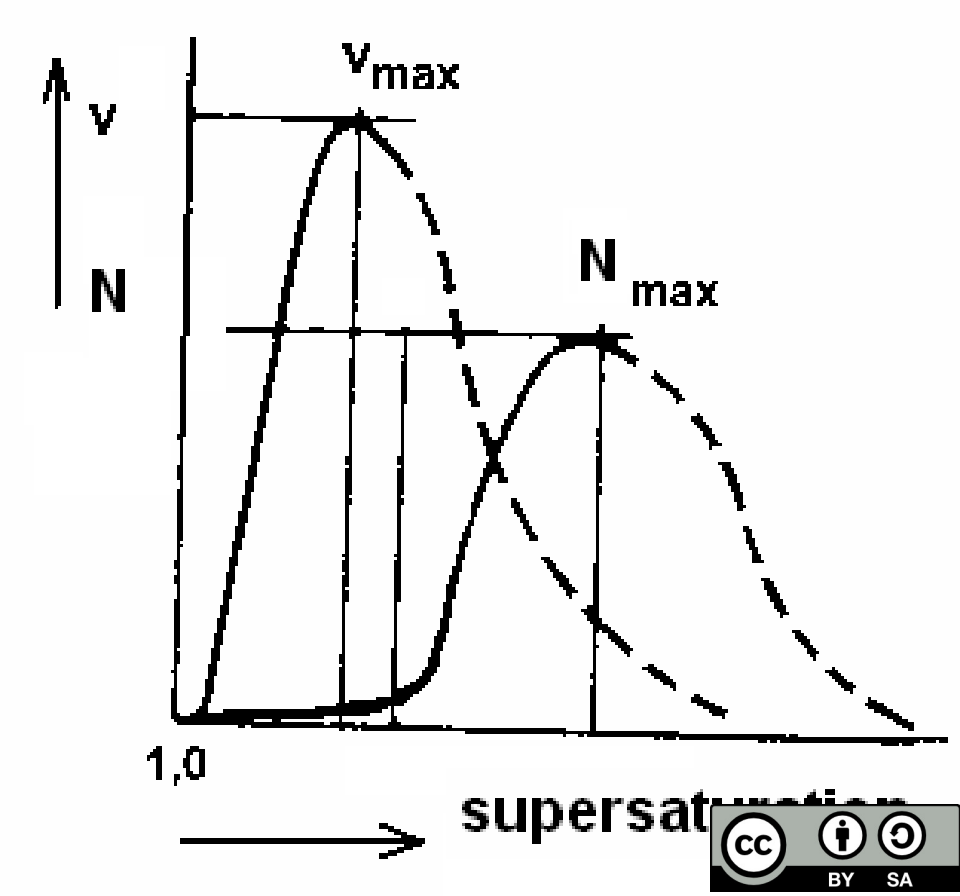
N – number of crystals

k_N – rate constant of nucleation

n – nucleation exponent

N_m (kg/s.m^3)

$$\frac{dm_N}{d\tau} = k_{Nm} (c - c_{eq})^n$$



Effect of Individual Parameters on Primary nucleation:

- **Supersaturation** (see Fig.)
- **Mixing –** nucleation at lower supersaturation
- **Impurities :** soluble – effect on solubility,
  insoluble – dust, colloids (product quality)

Secundary nucleation

$$\frac{dN}{d\tau} = k_{Ns}.m^{c}(c - c_{eq})^{n}$$

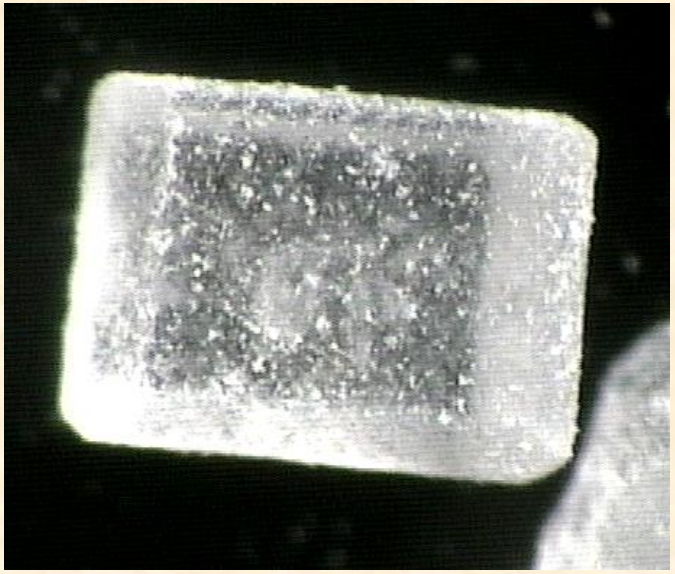
Nucleation rate N_N (#/s.m³)

where N – number of crystals, k_{Ns} – rate constant of nucleation, n – nucleation exponent, m – mass of presented crystals, c - coefficient

Effect of Individual Parameters on Secondary nucleation:

…. + Concentration of suspension, crystal abrasion (see photo)

crystal abrasion

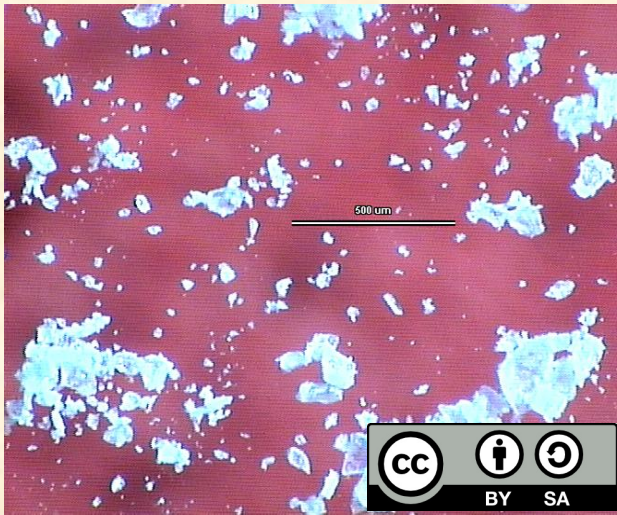


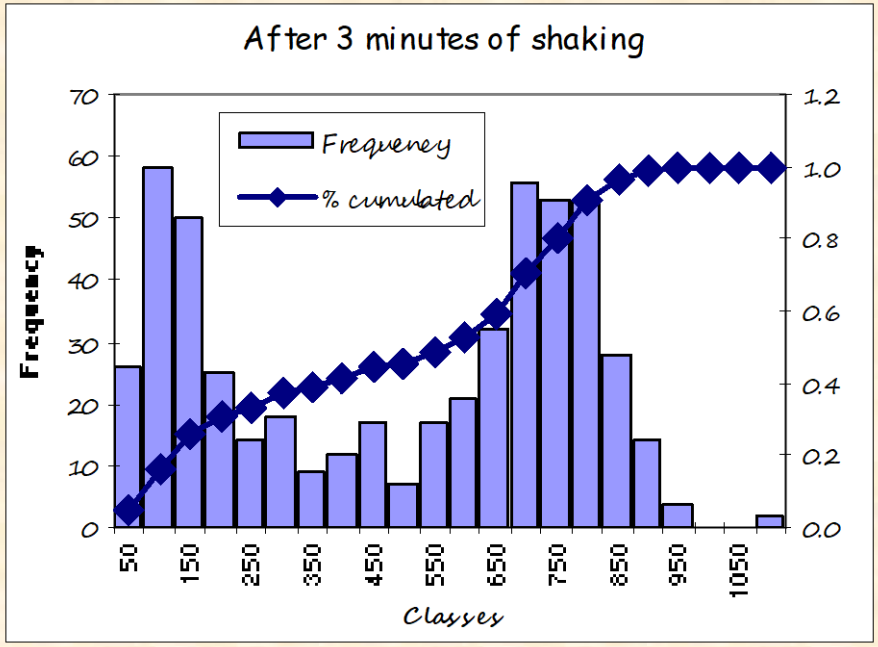
crystal abrasion

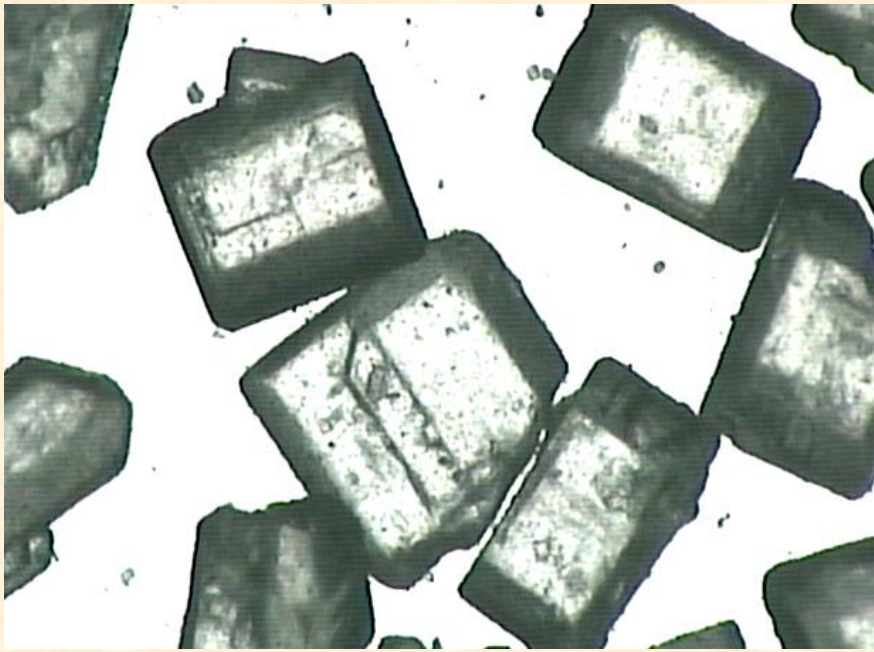
crystal attrition

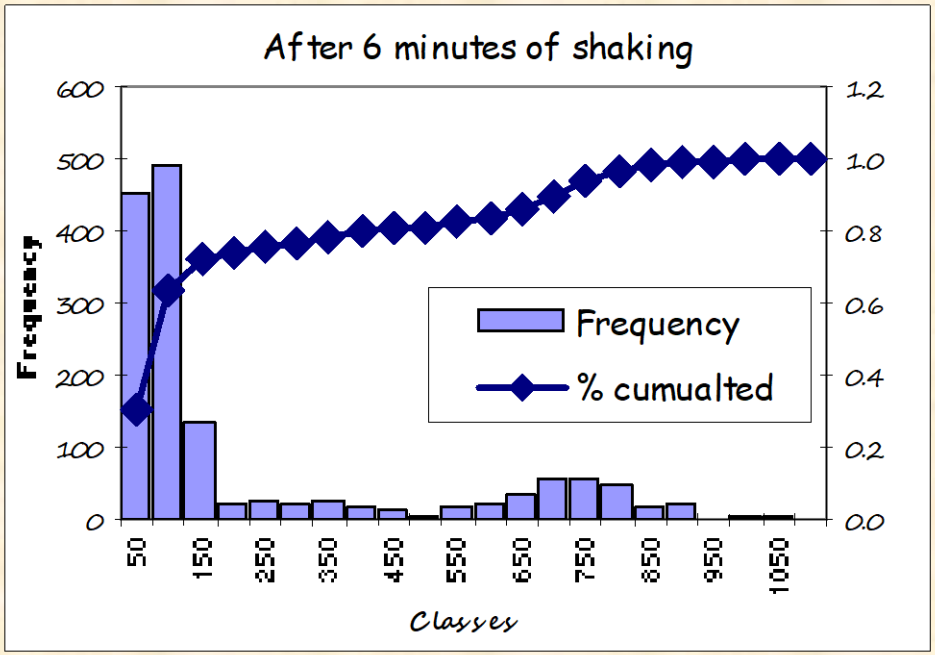
crystal fracture

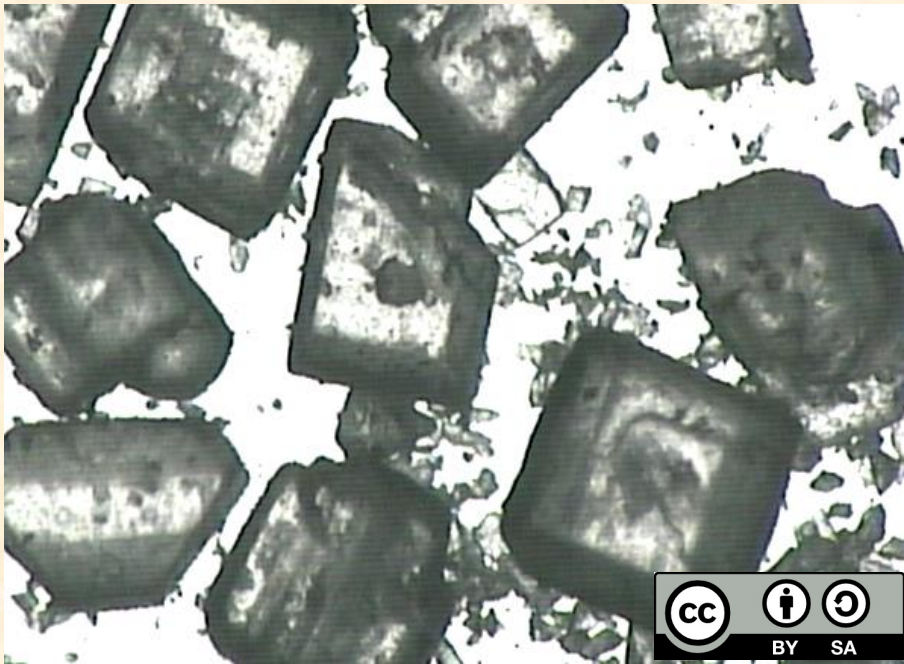
crystal fragmentation




After 3 minutes of shaking
Frequency
% cumulated
Frequency
Classes
70
60
50
40
30
20
10
0
1.2
1.0
0.8
0.6
0.4
0.2
0.0
50
150
250
350
450
550
650
750
850
950
1050




After 6 minutes of shaking
Frequency
% cumualted
Classes
600
500
400
300
200
100
0
1.2
1.0
0.8
0.6
0.4
0.2
0.0
50
150
250
350
450
550
650
750
850
950
1050



NUCLEATION - The Metastable Zone

The Metastable State of a Supersaturated Solution.

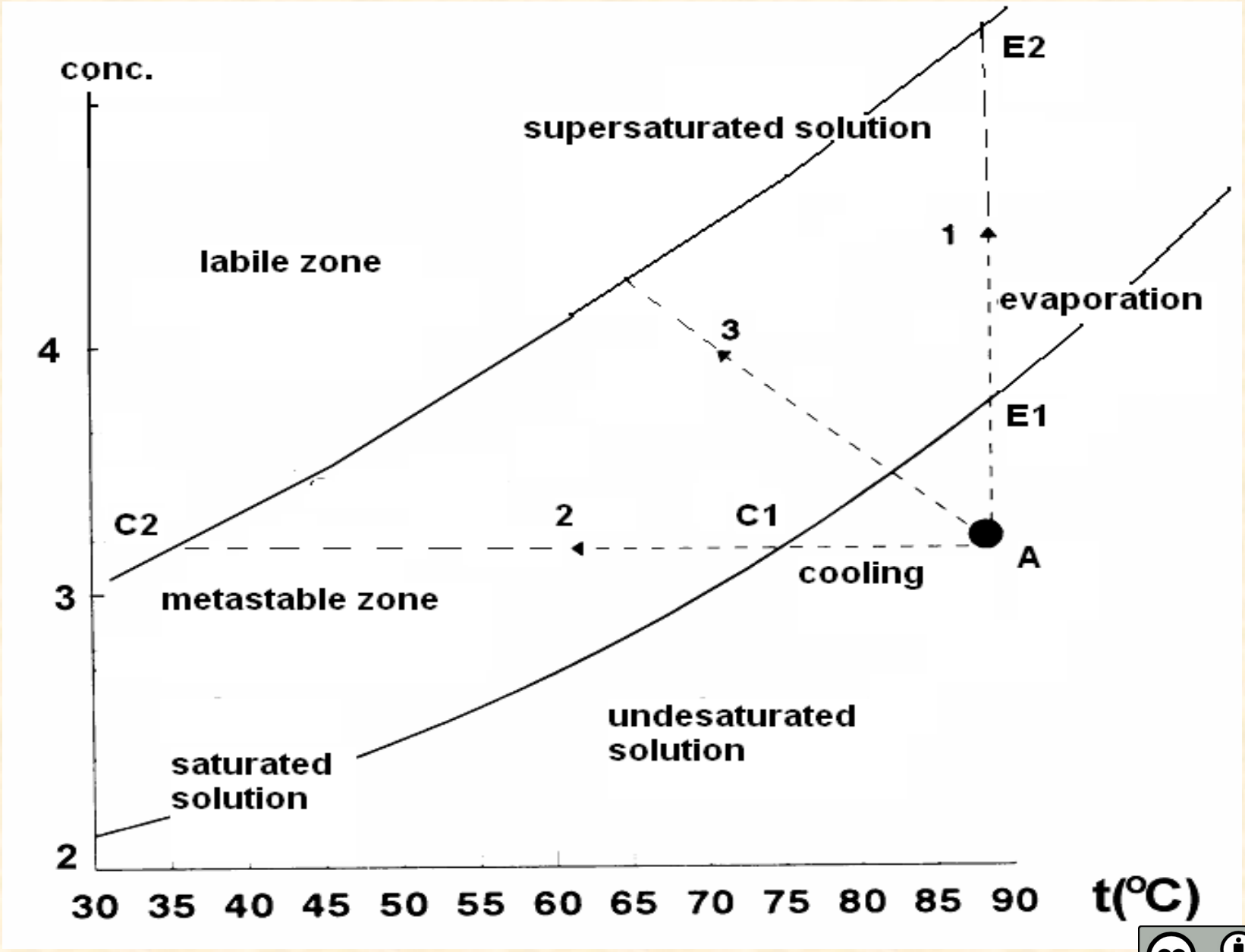
❖ In all described “saturation ways“, a situation can be attained in which the concentration of the solution is somewhat greater than that corresponding to equilibrium = **SUPERSATURATED SOLUTION**.

❖ If the supersaturation is not too great, then the rate of formation of new crystal nuclei is negligible and the state of the solution corresponds to the **metastable zone**: new crystals are formed only in a limited extent and the crystals already present grow.

❖If the supersaturation is further increased, then **the boundary of the metastable zone** is attained. When this boundary is exceeded, the rate of nucleation rapidly increases and the crystallization process becomes uncontrolled.

❖ The metastable zone is limited on one side by the above-mentioned **boundary of the metastable** zone and on the other side by the **solubility curve**

Metastable zone



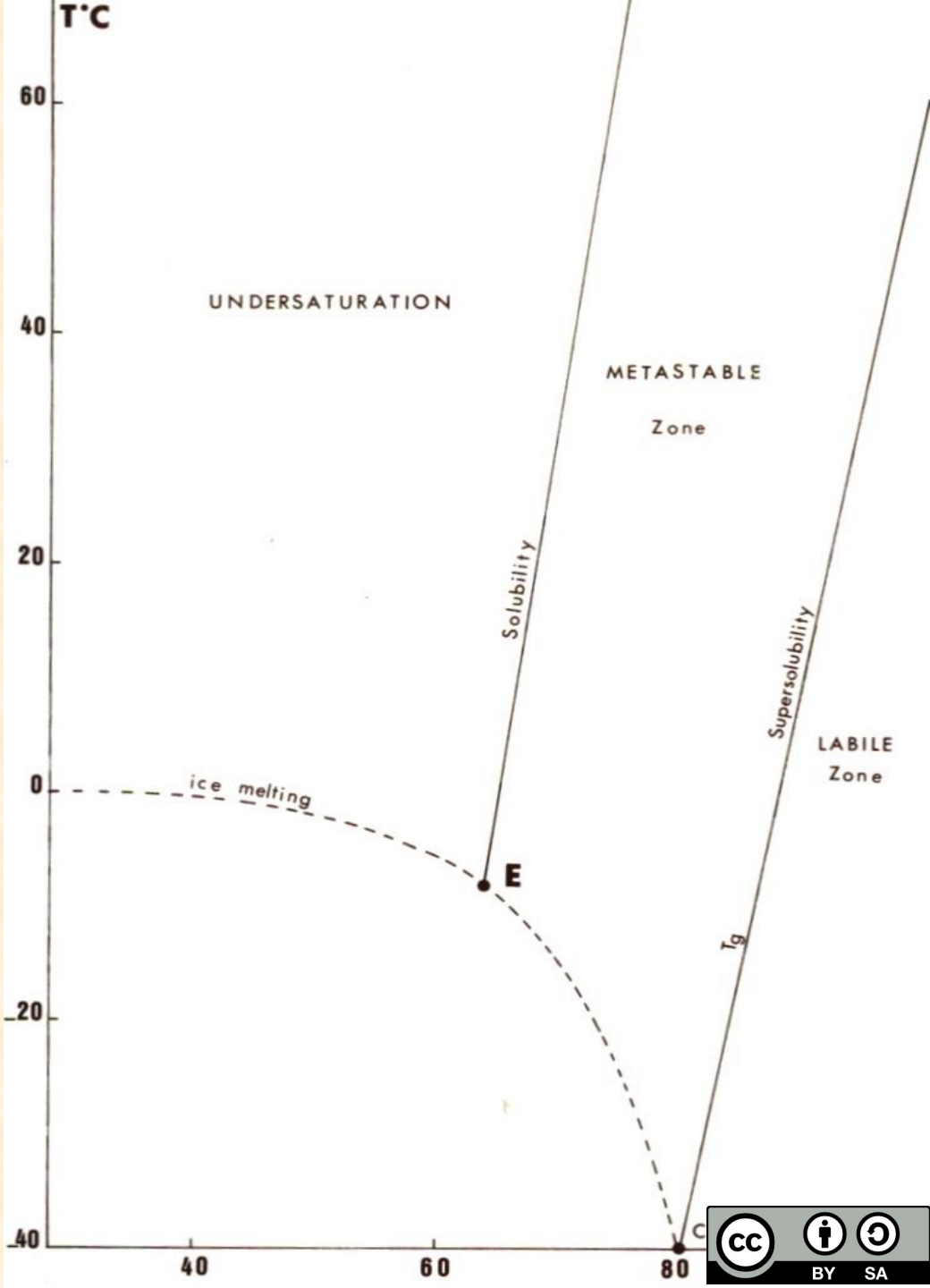
Phase diagram of sucrose-water binary system

showing:

(-------) the ice-melting curve,

(E) the hypothetical eutectic point (-13,9°C) ,

the maximally concentrated amorphous solution with C'_g = 80 % and T'_g = - 40°C



The Dependence of the Ultrasonic Rate on Temperature in Determination of the Metastable Zone of Citric Acid

(by Omar and Ulrich)

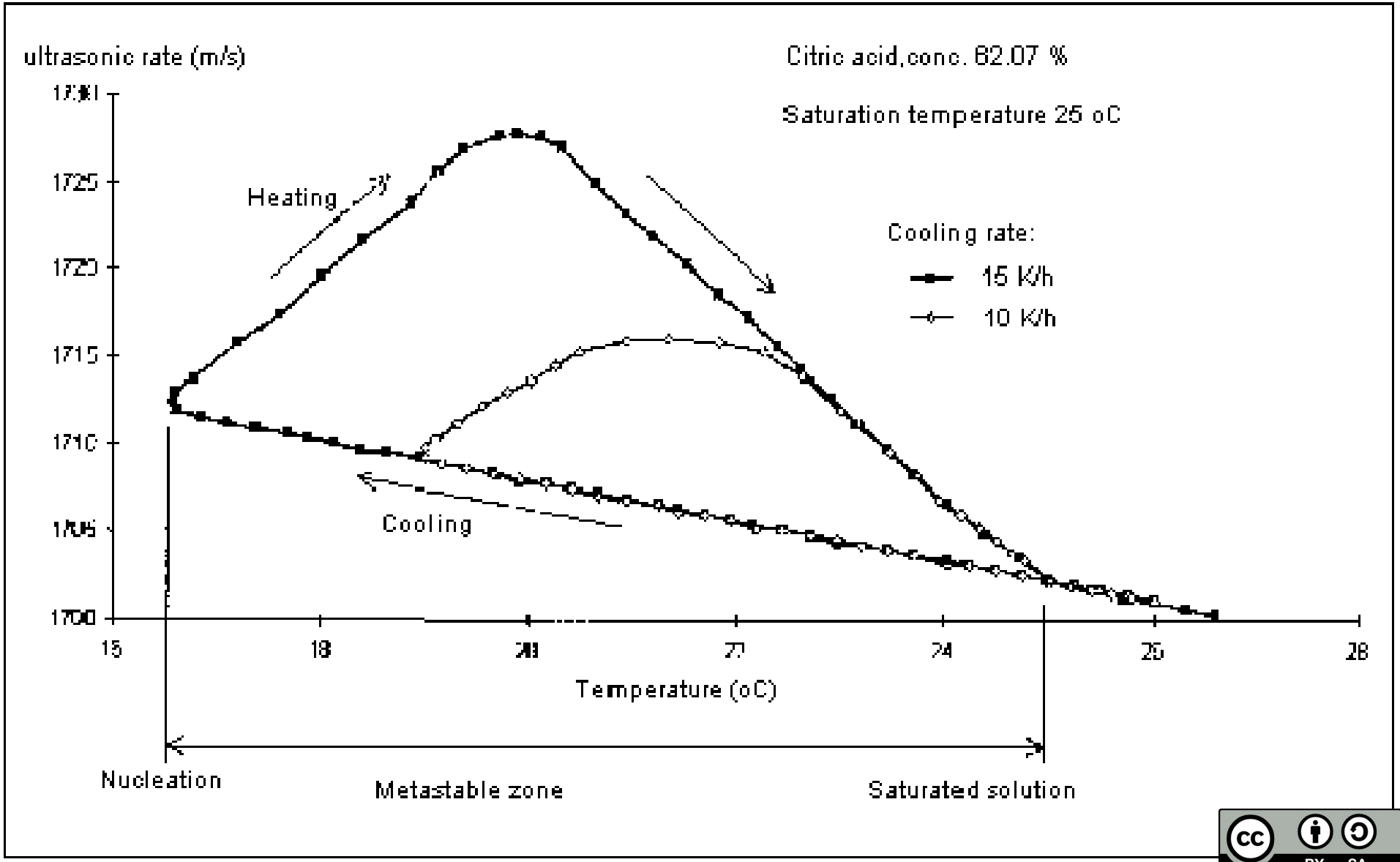
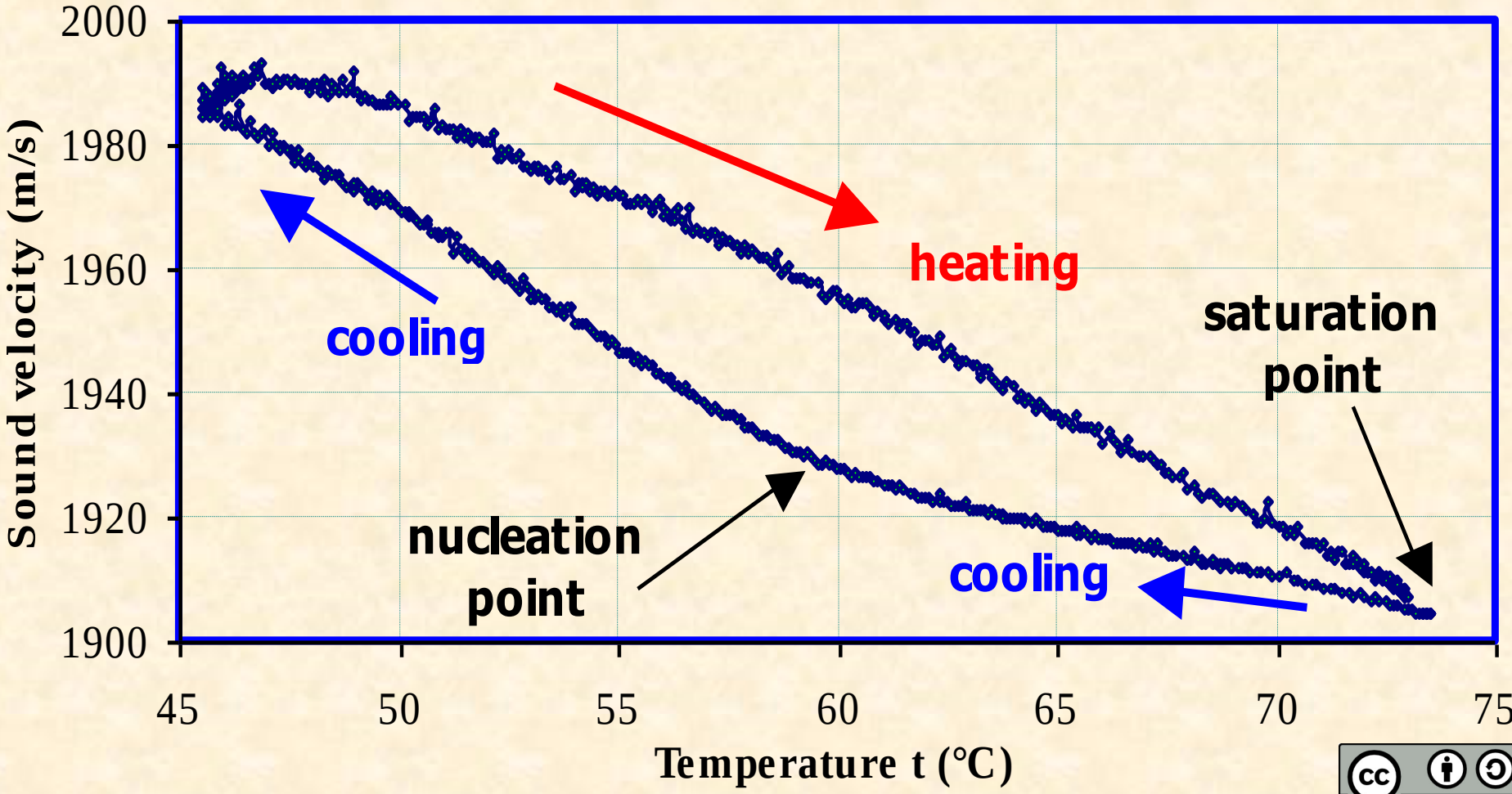


Illustration of the Course of the Sound Velocity

Metastable zone width and solubility determination in one test
(pure sucrose solution: dry subst. 75.62 %, cooling and heating rate 10 °C/h).



Crystal Growth Rate - Basic Concepts

The **rate of growth** can be characterised in several different ways:

❖ **Linear growth rate** is expressed by a change in a characteristic crystal dimension with time: $L_c = dL / d\tau$

❖ The **characteristic dimension** is considered to be a fictitious or actual dimension (crystal length, diameter of a sphere with the same volume, etc.)

Crystal shape factors:

❖ Crystal volume is expressed as: $V_c = k_v . L^3$ and its surface: $A_c = k_a . L^2$, then the **overall linear growth rate** is as follows: $dV_c / A_c . d\tau$

❖ For chemical engineering applications, the **mass crystal growth** rate is most frequently used: $m_g = dm / d\tau = \rho . dV_c / d\tau$

❖ It results from the previous equations:

$$m_g = (3 k_v . \rho / k_a) . A_c . L_c$$

This is the relationship between the mass and the overall linear crystal growth rates.

The Theories of the Crystal Growth
The Diffusion Layer Model

❖ The diffusion theory of the crystal growth is among the oldest theories in this field.

❖ The mathematics involved is relatively simple and satisfactory for use in industrial practice.

❖ The crystallization process can be separated into the following basic steps:

1. **Transfer** of substance to the diffusion layer.

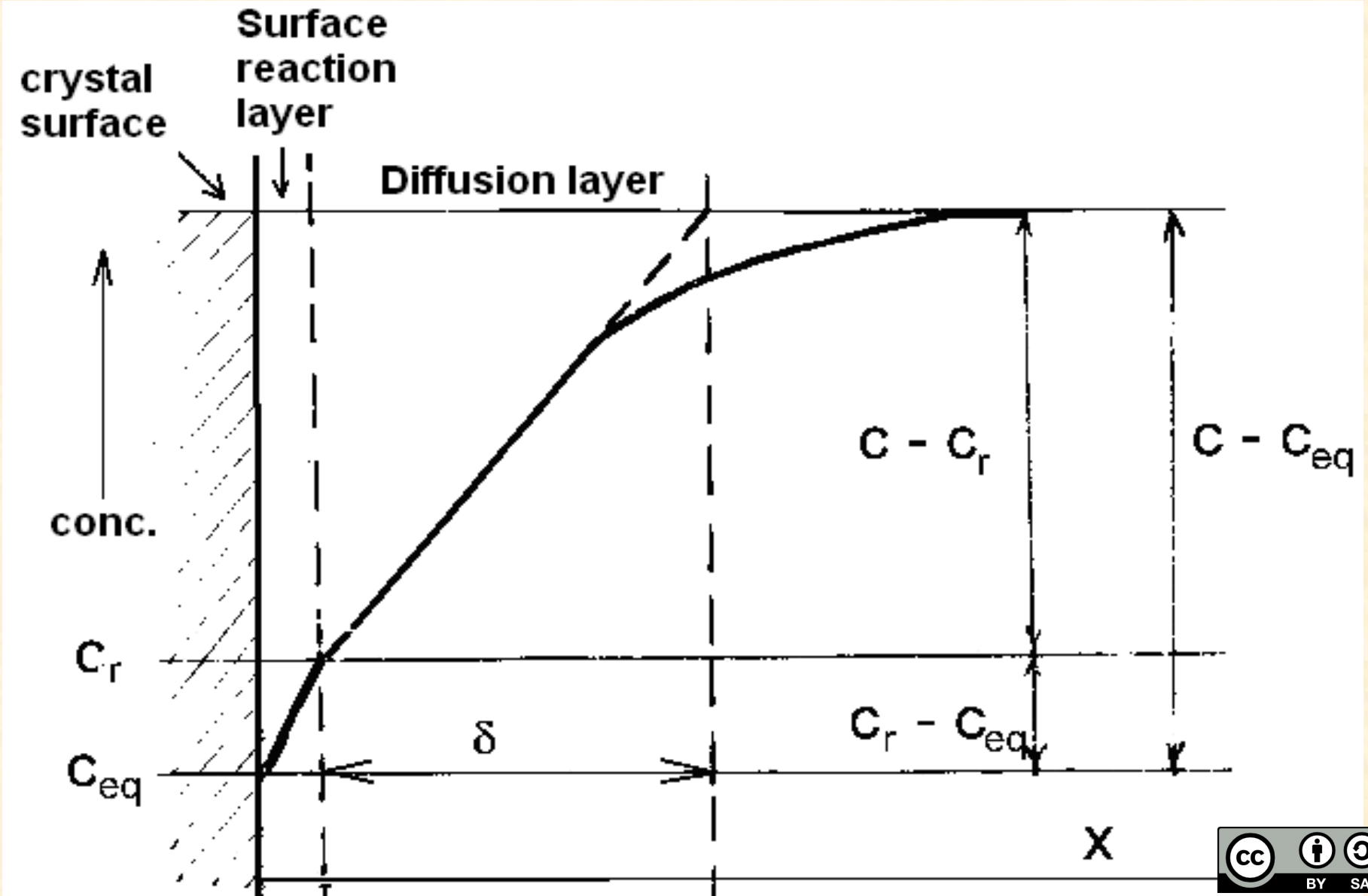
2. **Diffusion** of the substance **through the diffusion layer**.

3. **Incorporation** of particles of the substance **into the crystal lattice** (surface reaction).

4. Removal of heat released during the crystal growth from the crystal into the mother phase.

Diffusion Model of Crystal Growth

concentration driving force for a two-step process



❖ The last (4th) step may be important only when the removal of heat through conduction and convection is sufficiently slow and is important especially in **crystal growth from melts**.

❖ The **diffusion rate** can generally be described by Fick's first law:

$$\frac{dm}{d\tau} = A\,k_d\,(c - c_r) = A\,\frac{D}{\delta}\,(c - c_r)$$

where kd = D/d.

❖ The **rate of incorporation** of particles into the crystal lattice **(surface reaction)** is dependent on the difference in concentrations of species within the boundary layer and that in the saturated solution. It can be written to a first approximation that:

$$\frac{dm}{d\tau} = k_r\,(c_r - c_{eq})^r$$

where r is an exponent with a value dependent on the conditions, primary on the supersaturation (limits from 1 to

In case of **steady state**, the velocity of both processes is the same. If $r = 1$, then the difficult-to-measure concentration at the crystal surface c_r is eliminated:

$$v = \frac{dm}{A\,d\tau} = \frac{1}{\frac{1}{k_d} + \frac{1}{k_r}}(c - c_{eq}) = \frac{k_d\ k_r}{k_d + k_r}(c - c_{eq}) = K\ \Delta c$$

If $r = 1 - 2$, then after approximation: $v = K\,\Delta c^g$

where K – crystallization constant, g – exponent of crystallization.

From this equations follows:

If $k_d >> k_r$, **then** $v = k_r\,\Delta c$ (crystallization proces is controlled by surface reaction);

If $k_r >> k_d$, **then** $v = k_d\,\Delta c$ (crystallisation proces is controlled by diffusion)

Resistance of the crystalization process

$$W = \frac{1}{K} = \frac{1}{k_d} + \frac{1}{k_r} = W_d + W_r$$

Resistance of the diffusion process

$$W_d = \frac{1}{k_d} = \frac{\partial}{D}$$

Resistance of the surface reaction

$$W_r = \frac{1}{k_r}$$

Example - control process

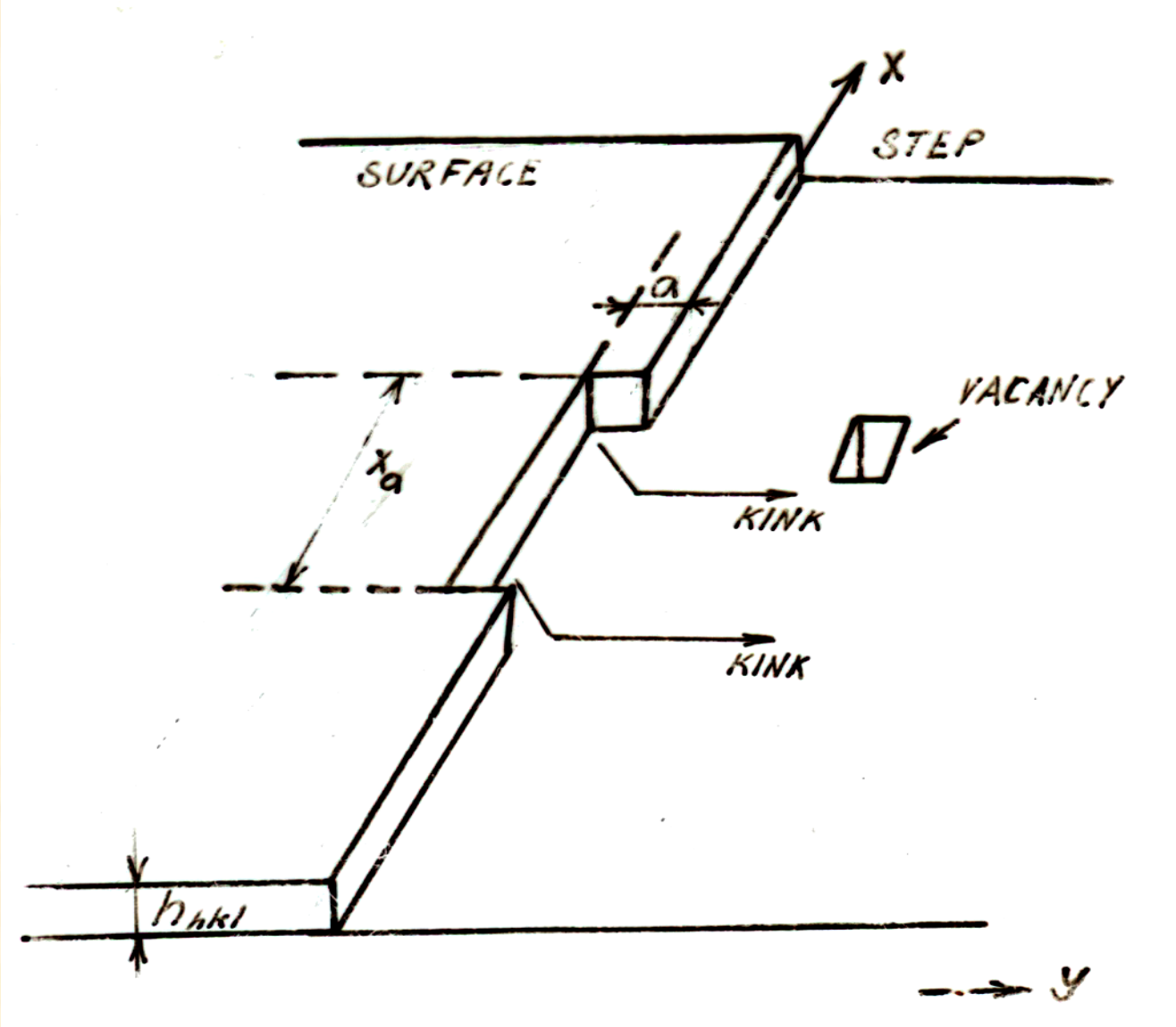
$D = 1{,}7.10^{-10}\, m^2/s$ $\partial = 43.10^{-6}\, m$

$k_R = 67{,}8.10^{-6}\, m/s$

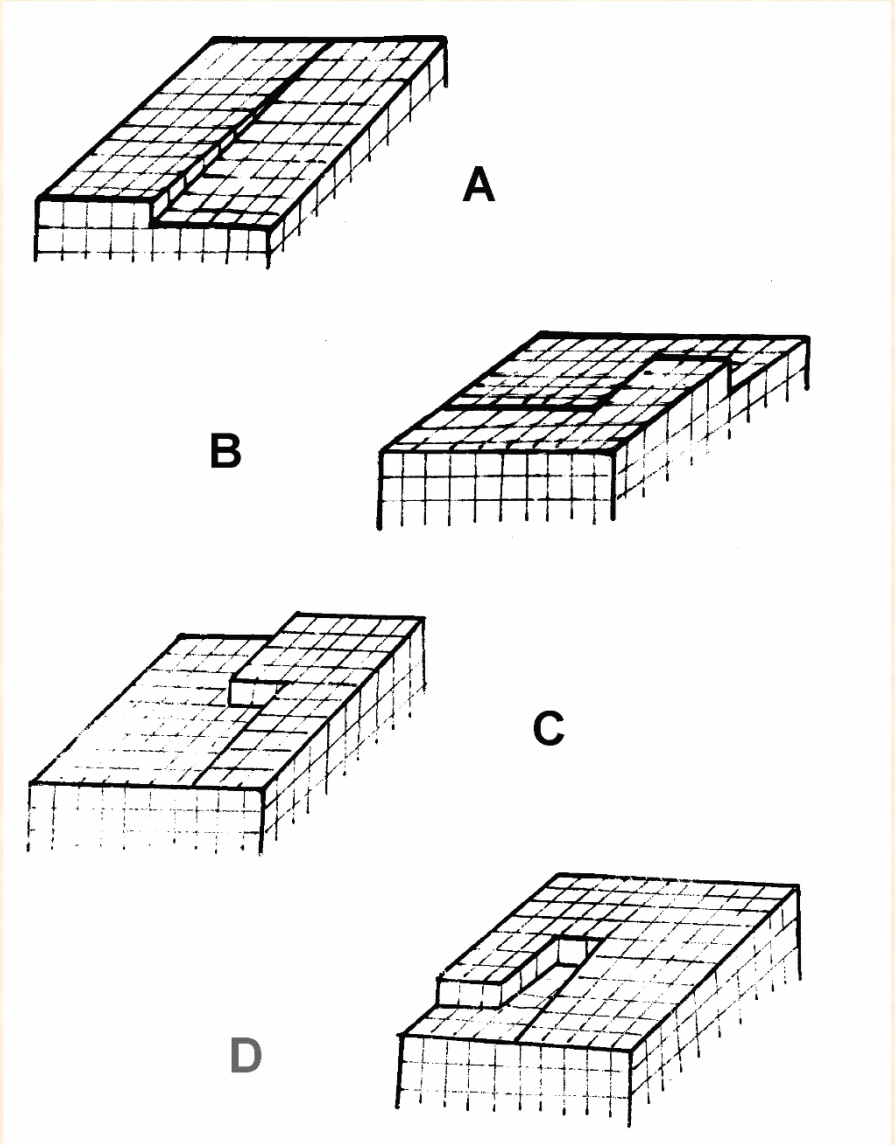
??? k_d, W_d, W_r, W

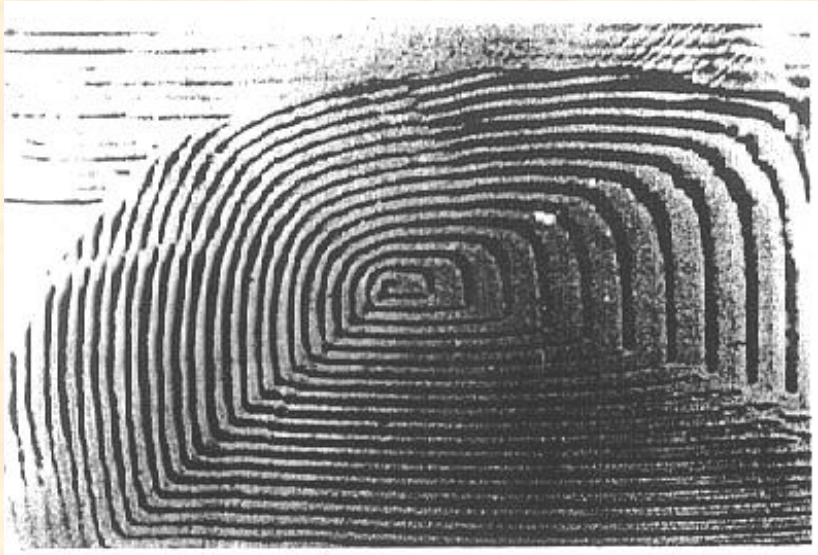
if W = 100 % , that W_d = ? % , W_r = ? %

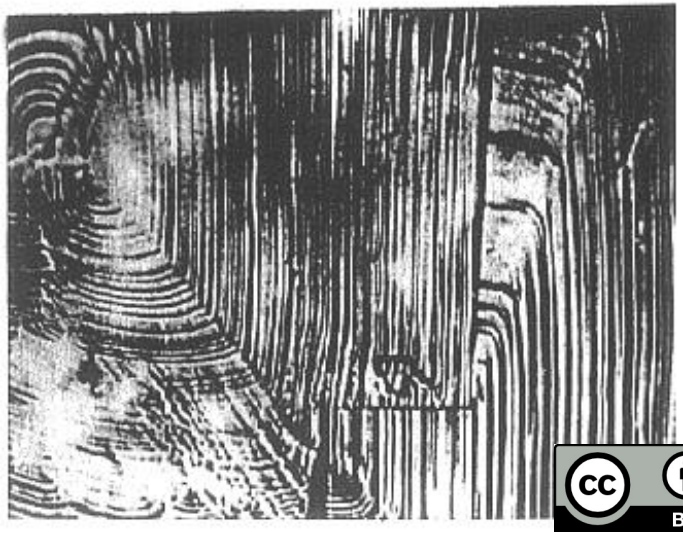
Incorporation of particles into the crystal lattice **(surface reaction)**



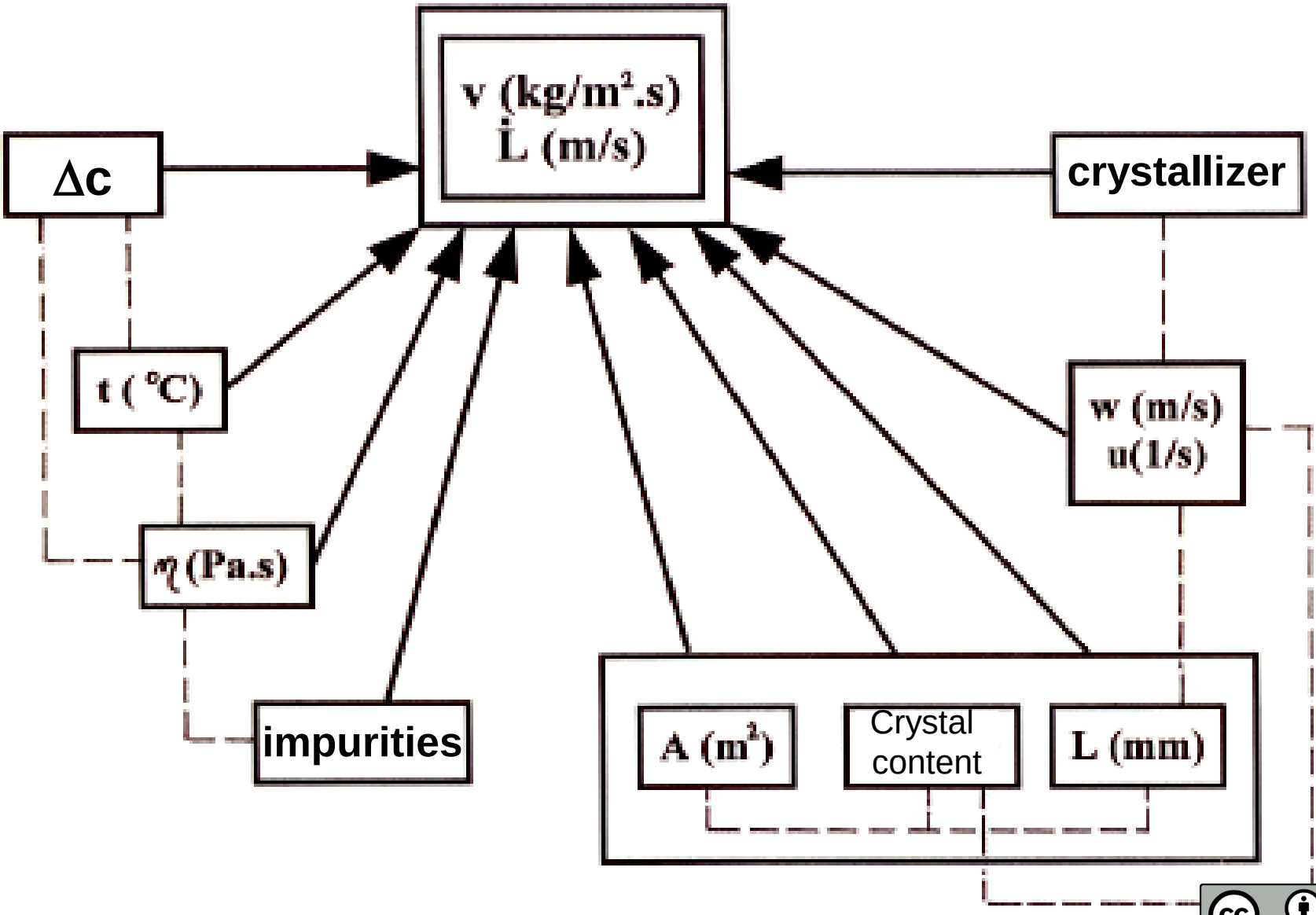
Model and Photograph of the Surface of a Growing Crystal





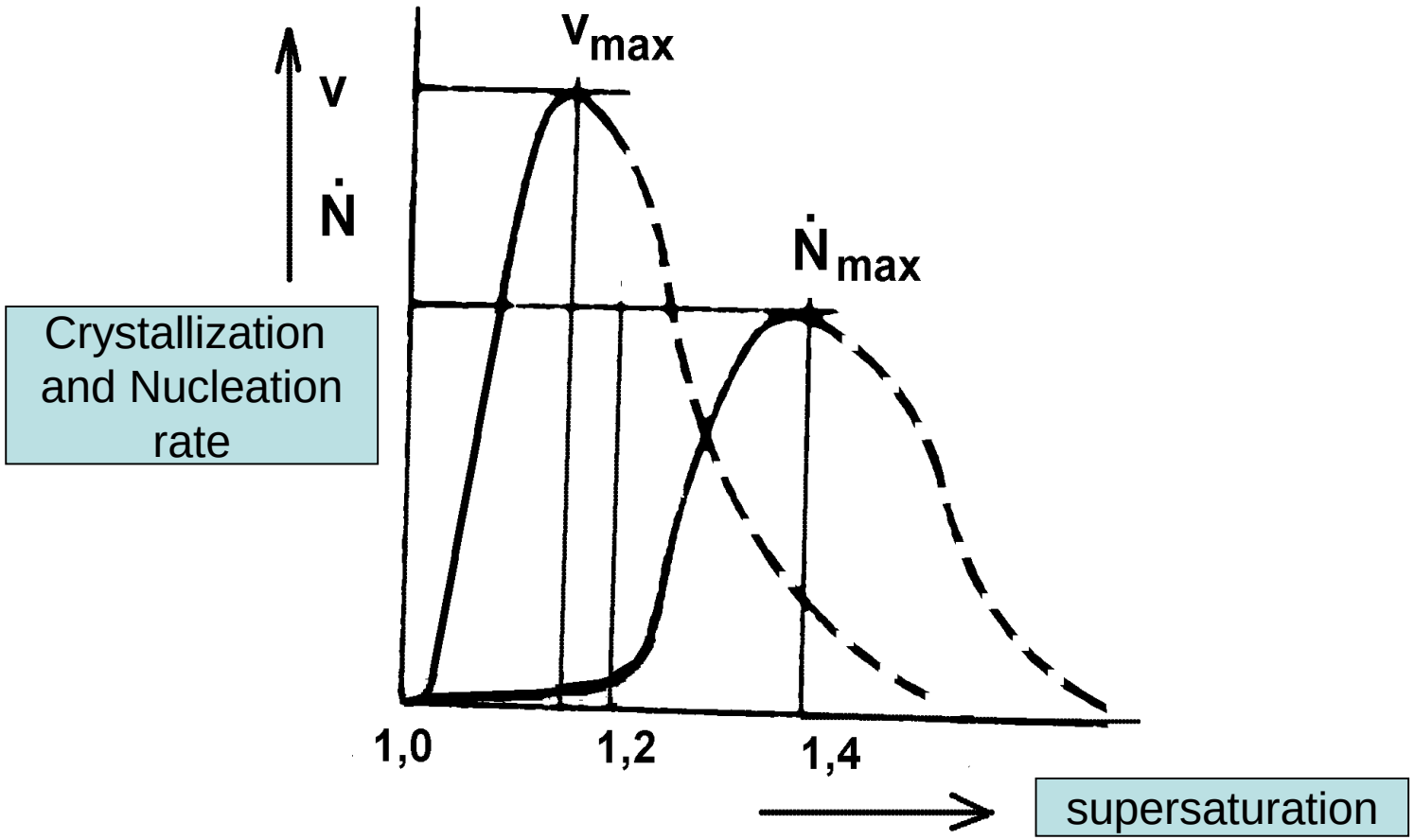


Effect of Individual Parameters on Crystal Growth Rate



Effect of Supersaturation on Crystallization and Nucleation Rates

(example: sucrose)



❑ **Supersaturation** $v = K\,\Delta c^{g}$

❑ **Temperature:** Arrhenius equation $K = K_0\,.\exp(-E/R.T)$

where K – crystallization constant, K_0 - coefficient, E – activation energy, R – gas constant, T – temperature.

❑ **Viscosity**: $v = \dfrac{k}{\eta^{q}}$

where v – crystallization rate, k - coefficient, q - exponent, η – dynamic viscosity

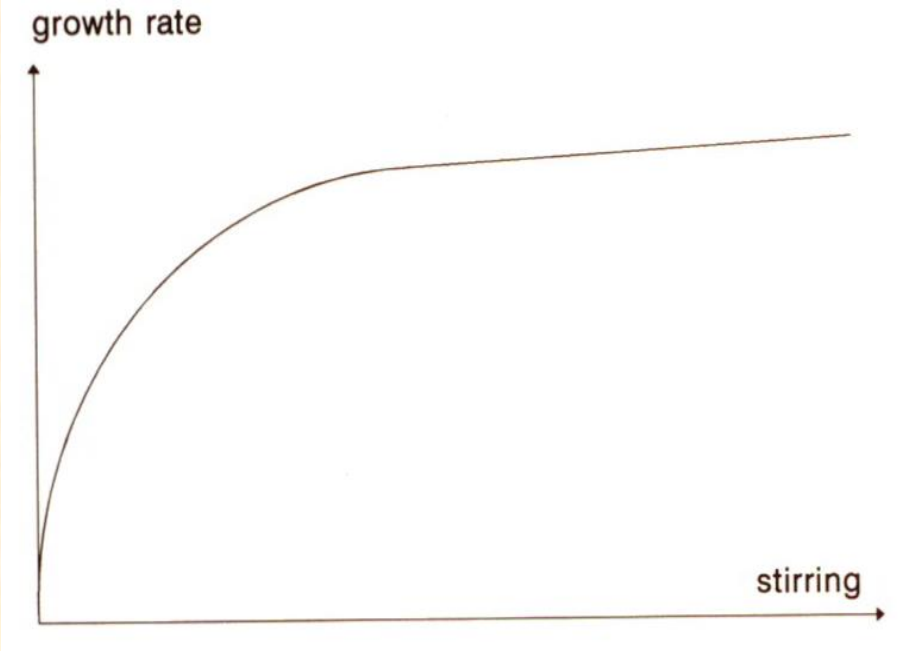
❑ **Hydrodynamic condition:** $Sh = a\,\mathrm{Re}^{0,6}\,Sc^{0,3}$

where Sh – Sherwood number, ***Re*** **– Reynolds number**, Sc - Schmidt number

❑ **Intensity of mixing**: $K = k.\,u^{2/3}$

where K – crystallization constant, k - coefficient, u – stirring frequency.

Limit of stirring



- **Crystal length (diameter):** $\dot{L} = k_L . L^b$ (Bransom eq.)

- **Crystal content:** $\nu = \nu_1 . \varepsilon^2$

where ν – crystallization rate in crystal suspension, ν_1 – crystallization rate at a presence of one crystal, ε - porosity.

Crystallization Process - Mass Transfer

$$Sh = a + b\,Re^{c}\,Sc^{d}$$ **Froessling equation**

$$Sh = 0{,}29\,Re^{0{,}6}\,Sc^{1/3}$$ (for mixing)

Sherwood Number (mass transport)

$$Sh = \frac{k_d\,L}{\rho_l\,D}$$

Schmidt Number (physical properties)

$$Sc = \frac{\eta}{\rho_l\,D}$$

Reynolds Number

(fluid dynamics)

$$Re = \frac{u\,L\,\rho_l}{\in \eta}$$

$$Re = \frac{u\,L\,\rho_l}{\eta}$$

Mass and Energy Balance

Mass balance

$$m_o = m_f + m_c + m_g$$

input sol. mother sol. crystals vapour

Energy balance

$$m_o\ c_{p,o}\ t_o + m_r\ h_r + Q = m_f\ c_{p,f}\ t_f + m_c\ h_c + m_g\ h_g + m_c\ c_{p,c}\ t_c + Q_z$$

Input solution | Reaction | Heating | Mother solution | Crystallization heat | Vapour | Crystal | Heat loss

The Dynamics of Establishing a Steady State

❖ In order for steady state to be attained in the crystallizer **after beginning** the experiment, it is usually necessary that it works with constant parameters for a **time equal to six- to sixteen-times the mean retention time** of the solution.

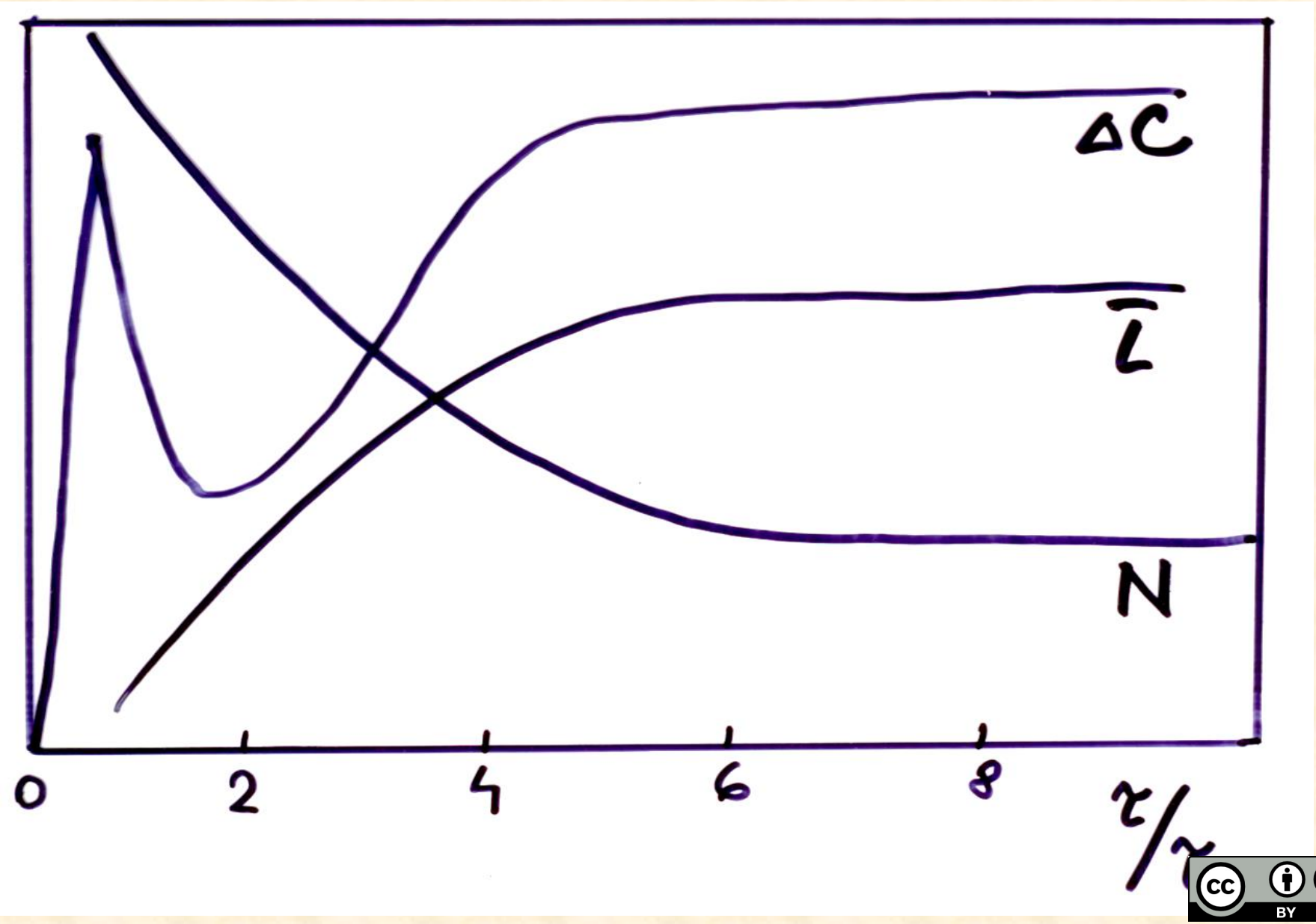
❖ the crystallizer may even work permanently in a **periodically oscillating state**.

❖ The conditions under which such instability occurs have not yet been satisfactorily explained, but it can be expected that the crystallizer will attain steady state in most cases.

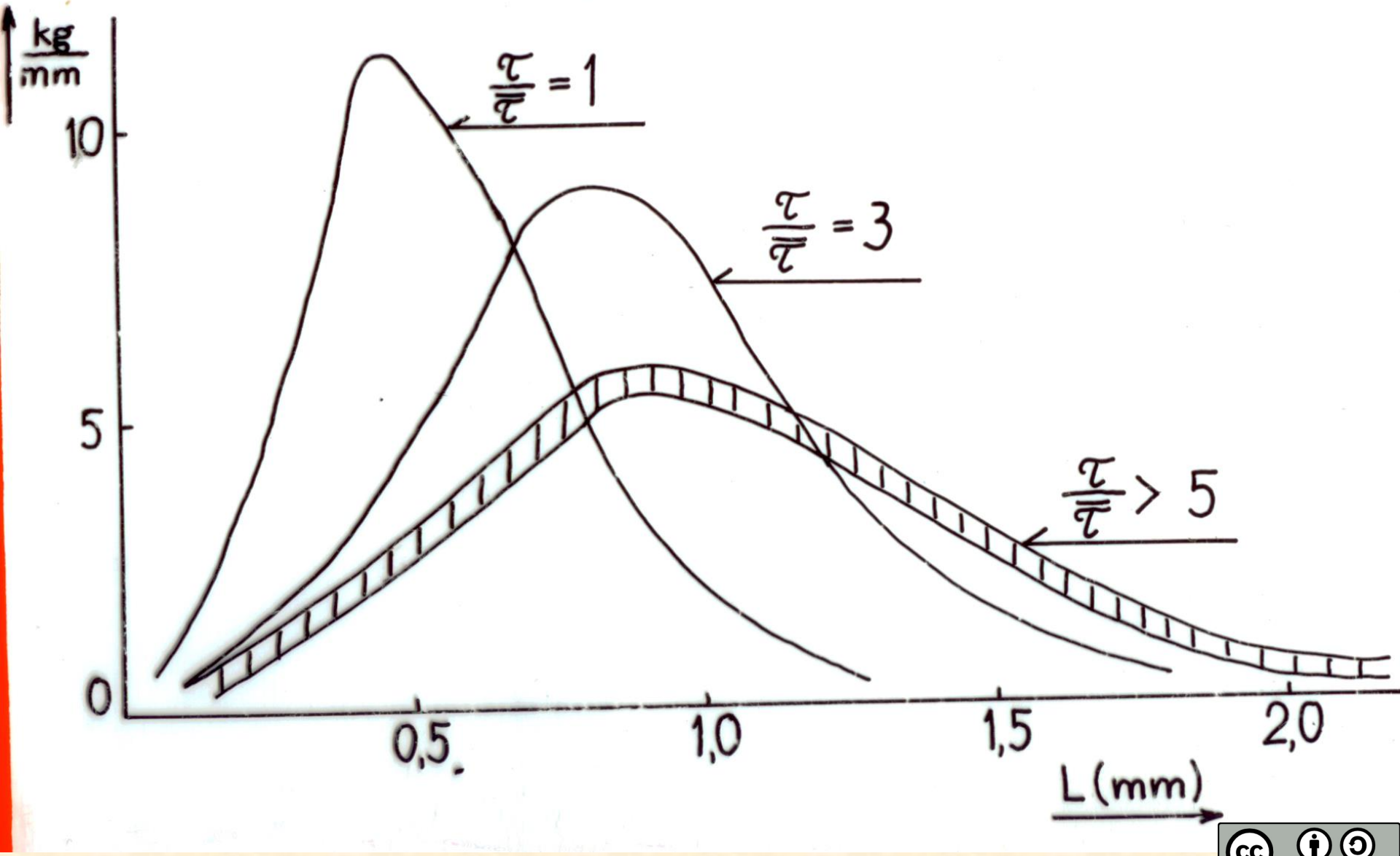
❖ A mathematical model of a **continuous crystallizer** that permits study of the steady-state dynamics is based on **simultaneous solution of the supersaturation balance:**

$$\frac{d(c-c_{eq})}{d\tau} = s - K.A_c(c-c_{eq})^g - k_{Ns}.m^c(c-c_{eq})^n$$

Process Parameters During Steady State Achievement



Crystal Size Distribution During Steady Dtate Achievement



Advanced Processes in Food Technology and Biotechnologies

Industrial Crystallization

Crystal Size Distribution

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INDUSTRIAL CRYSTALLIZATION

Prof. Zdeněk BUBNÍK, PhD
ICT Prague

Crystallization processes

- ***Cooling***
- ***Isothermal evaporating***
- ***Adiabatic evaporation***
- ***Adding a less efficient solvent***
- ***Salting-out effect***
- ***Chemical reaction***

New processes:

- **Crystallization with preference**
- **Supercritical crystallization**
- **Gas-antisolvent effect**

Crystallization with preference

Example: separation of the D- and L-form of a substance from racemic mixture

1) Start: the racemic mixture in metastable state

- **conc. of L-form = conc. of D-form**
- **Nucleation rate = 0**
- **Solubility of D- and L-form ie equal**

2) Addition of crystals of D- or L-form (according to requirement)

- **present crystals grow**
- **new crystals do not appear**

3) After achievement of the required size : separation of the crystals

4) Process is repeated with the other form of crystals … etc.

Supercritical crystallization

- **Example: the different solubility of D- and L-form in supercritical solvent**
- **Typical solvent: liquid CO_2**
- **Advantage: non-toxic, non-flammable, cheap, high purity, easy to remove**
- **Defined dispersity (drugs)**
- **Sprey drying (sorbitol, valine …)**

“Gas-antisolvent“ effect

- Principle: a decrease of the solubility by addition of compressed gas
- Application: if the crystals of a required size distribution are needed (especially for size in nm)
  - polymers
  - catalyzers
  - drugs
  - proteins

Racemic mixture separation (D and L form)

1) Application of a substance with specific chemical reactivity:

D/L + spec. substance …. D/spec. substance + L

2) Chromatographic separation:
Simulated moving bed

3) Crystallization with preference

4) Supercritical crystallization:
Example: different solubility of D- and L-forms in a supercritical solvent

Crystallization processes

- Periodical
- Continuous

- One step
- Multistep (“cascade“)

- With classification
- Small crystal dissolving
- Without stirring/mixing
- Stirred
- Way of nucleation – without, slurry, microcrystalls …

Crystallizers

Criterion:

- **physical and chemical properties of solutions and suspensions (solubility, viscosity, thermal stability, heat transfer)**

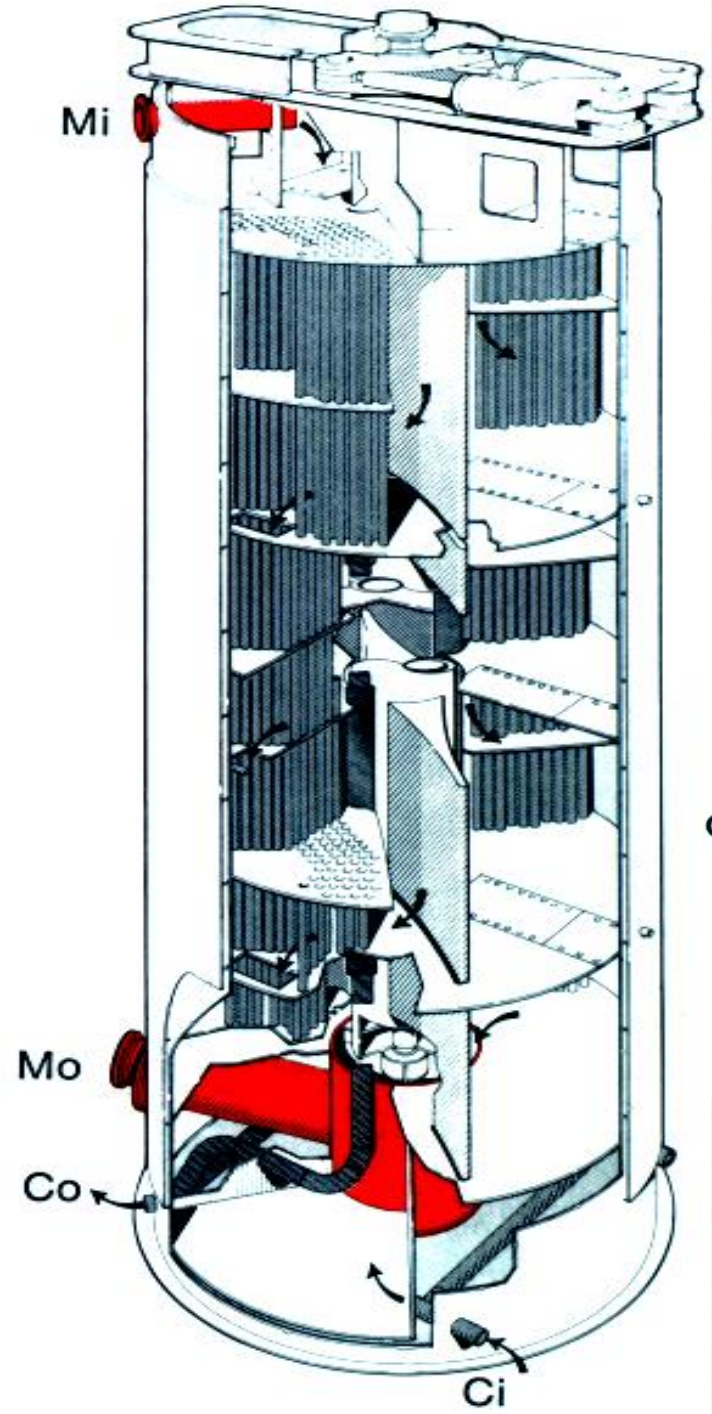
- **product quality requirement (crystal size, distribution, agglomeration)**

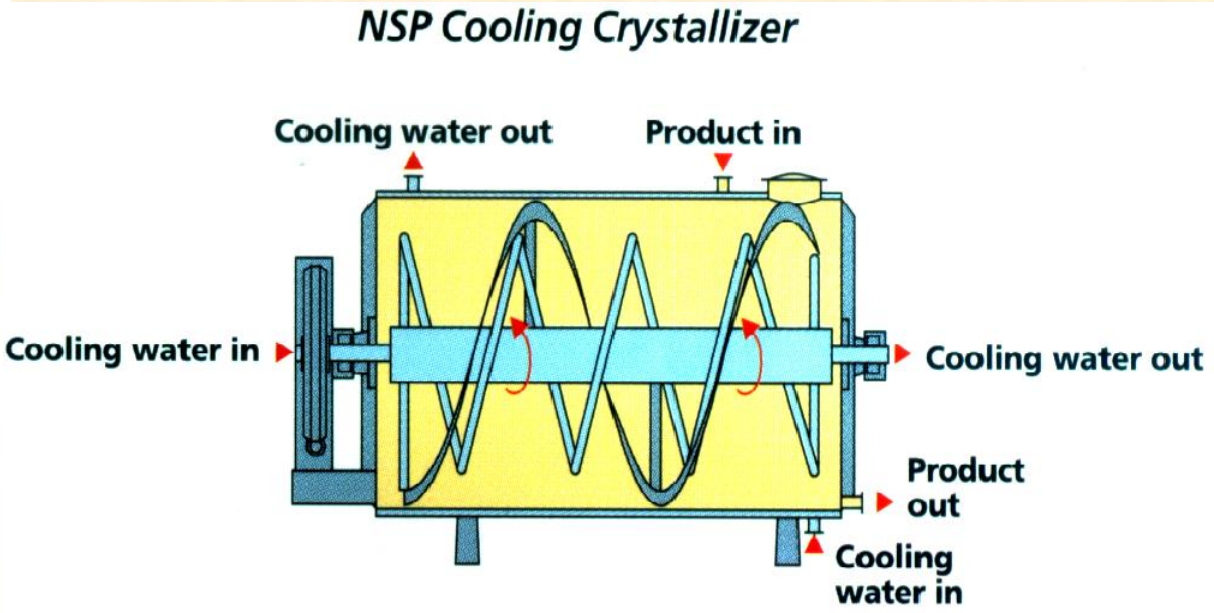
  X

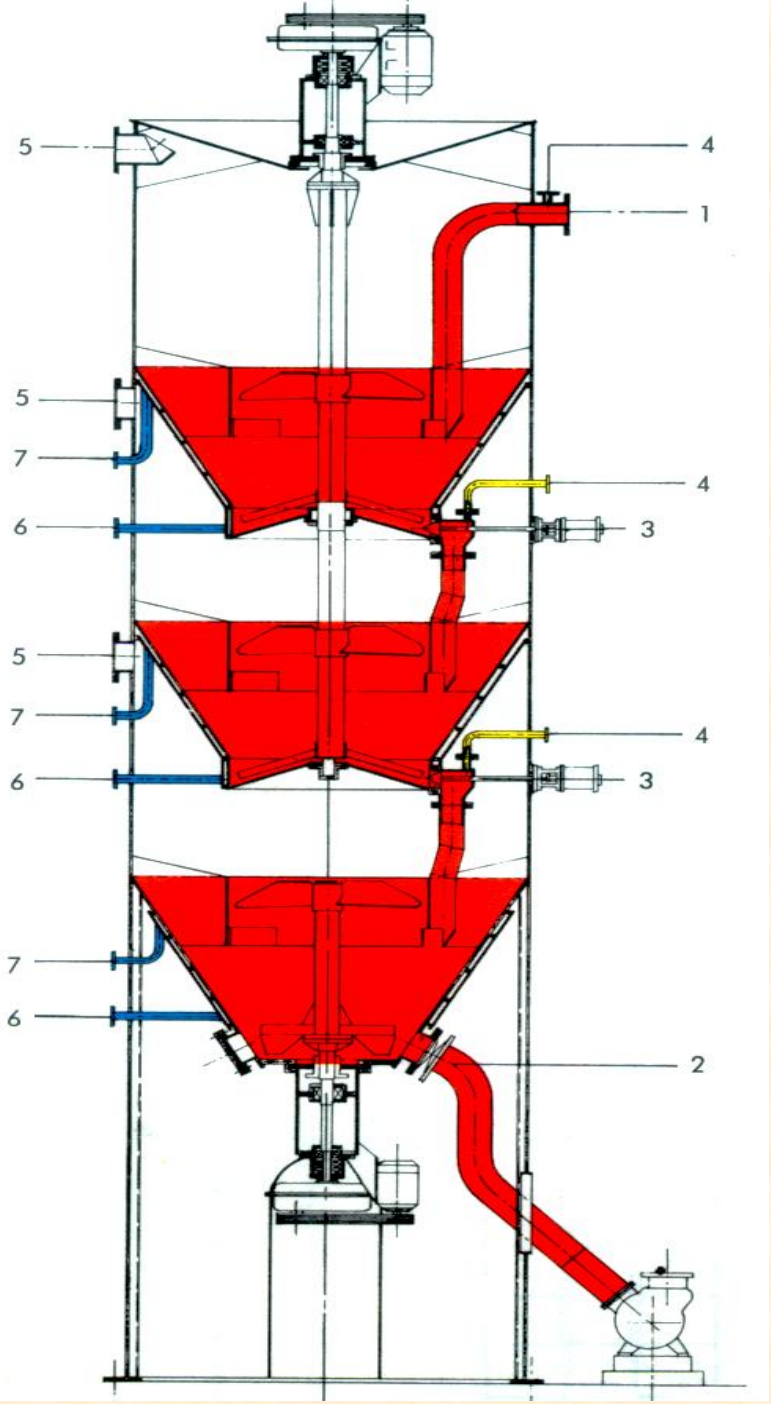
  financial expenses (investment, separation, drying, storage, energy …)

- **capacity (periodic, continuous process)**

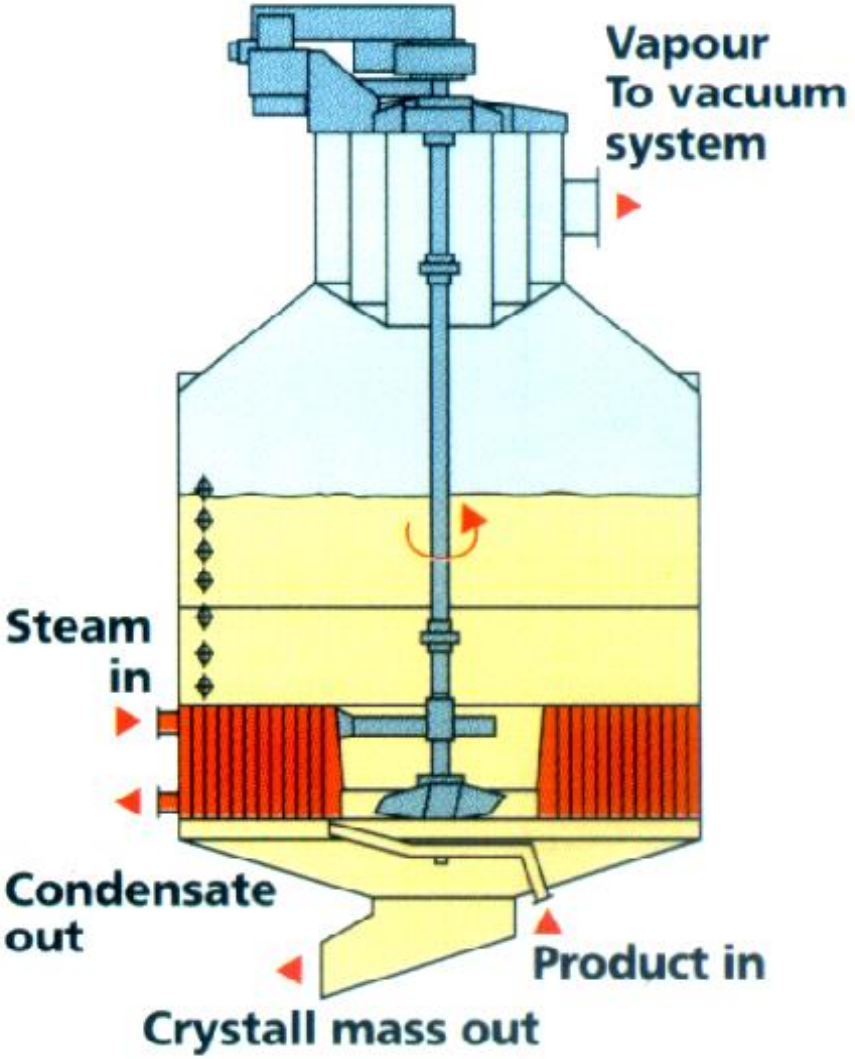
Cooling crystallizers



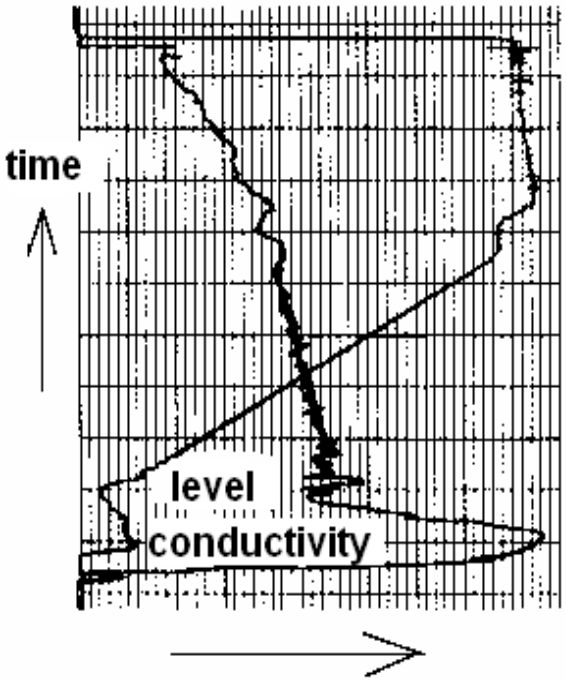


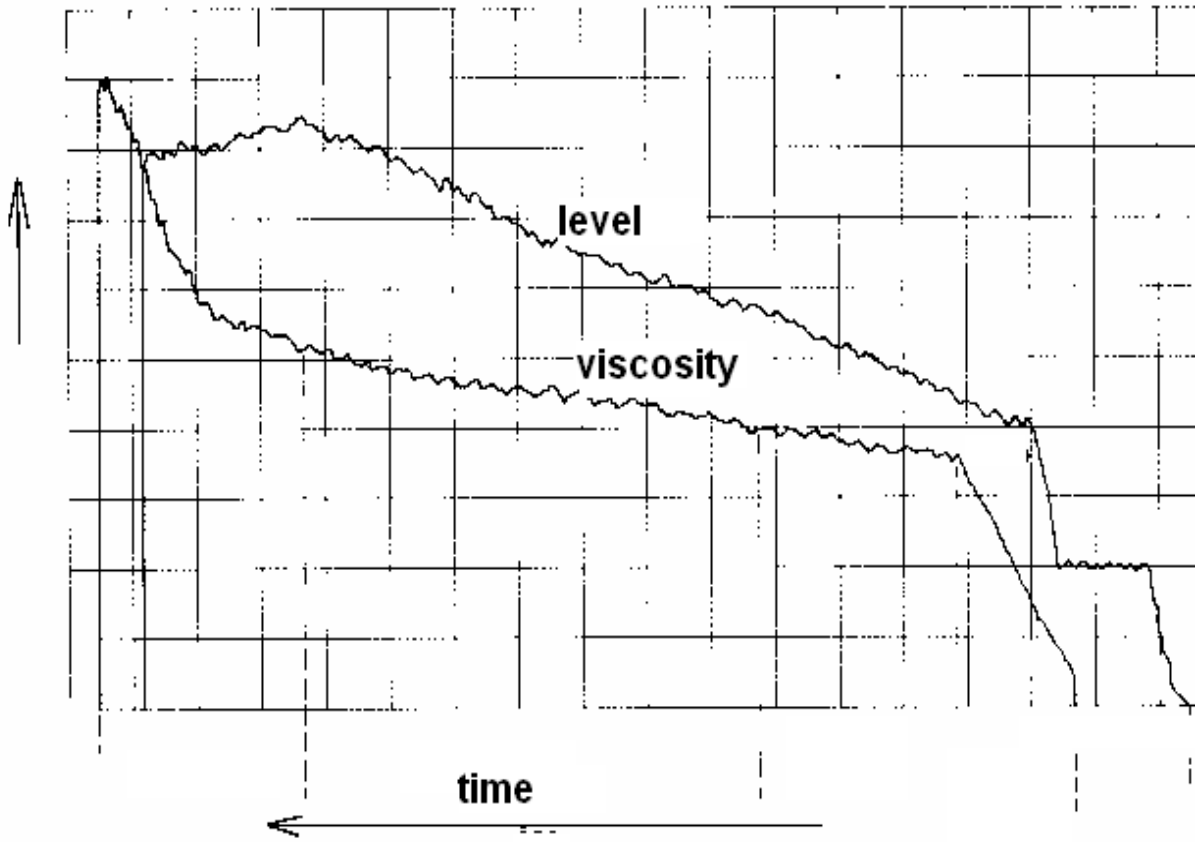


NSP Vacuum pan crystallizer



Control of the crystallization process by conductivity and viscosity measurements





Crystal Size Distribution - CSD

CSD: also termed the **sieve spectrum**

- Number distribution
- Mass distribution

Two basic forms of distribution:

- the differential size distribution f(L)

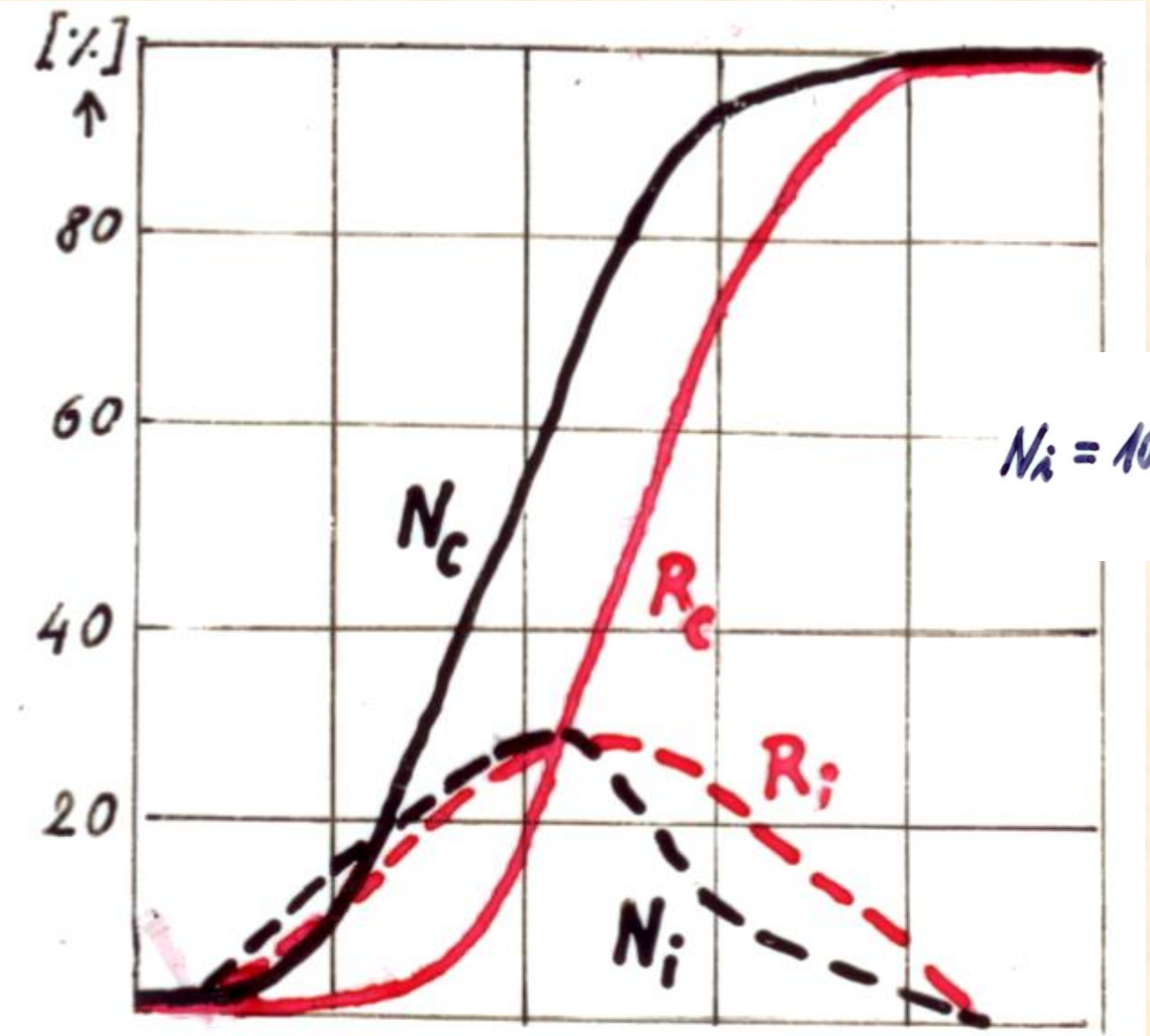
  - fraction: number or mass

- the cumulative distribution F(L)

  - “oversize fraction“

CSD measurement: sieve analysis, image analysis, optical methods, sedimentation, laser device …

Graphical representation of the number (N) and mass (R) CSD



$$N_i = 100 \frac{n_i}{\sum n_i} = 100 \frac{R_i / L_i^3}{\sum R_i / L_i^3}$$

Distribution function

Normal distribution (Gauss, symmetrical around L_{50})

$$f(L) = \frac{1}{\sigma(2\pi)^{1/2}} \exp\left[-\frac{(L - L_{50})^2}{2\sigma^2}\right]$$

Log-Normal distribution

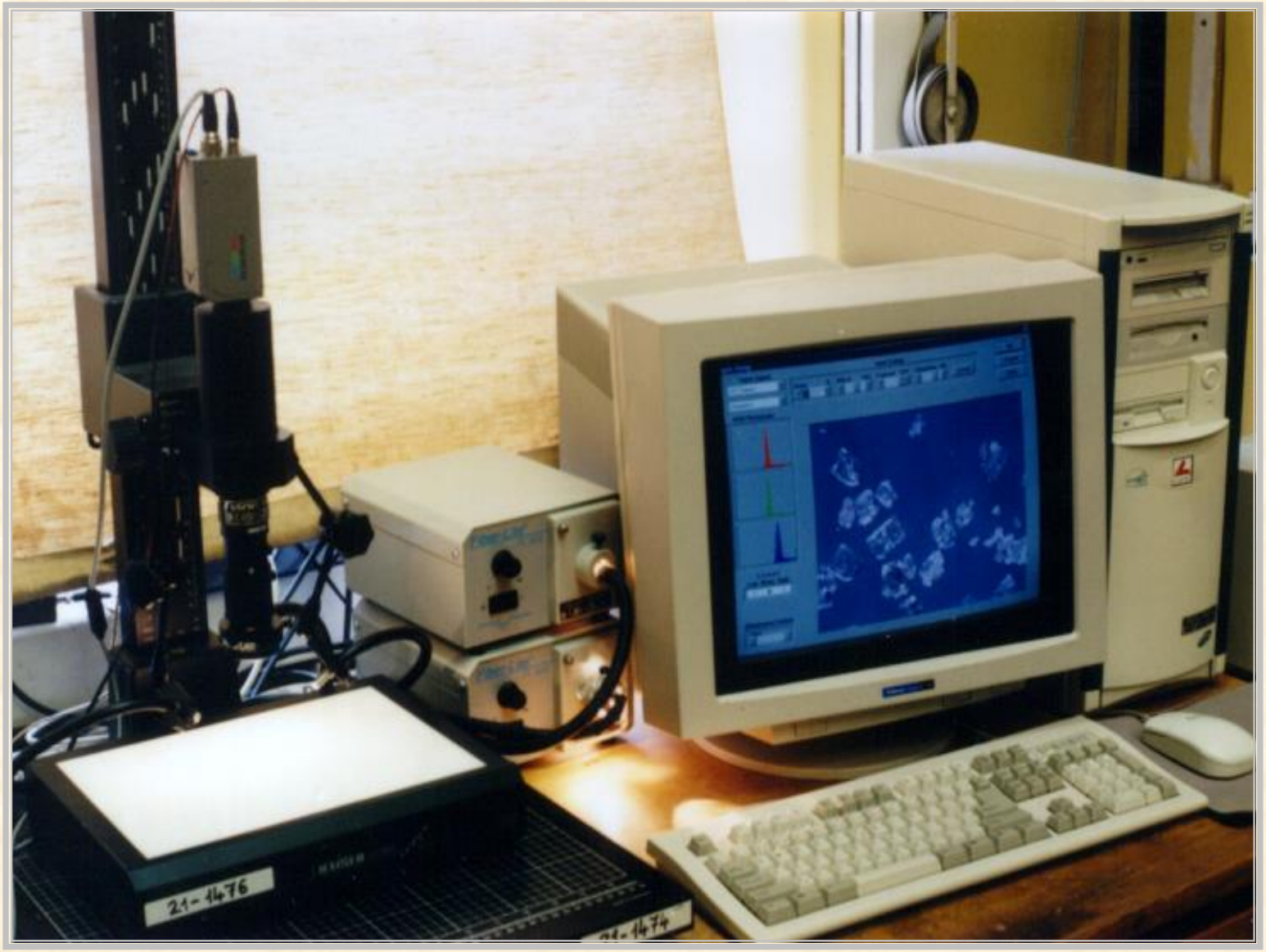
$$f(L) = \frac{1}{(2\pi)^{1/2} \log \sigma} \exp\left[-\frac{\log^2 (L/L_{50})}{2 \log^2 \sigma}\right]$$

Gamma function

$$f(L) = L^{a'} \exp\left(\frac{a'L}{b}\right) / \Gamma(a' + 1)(b/a')^{a'+1}$$

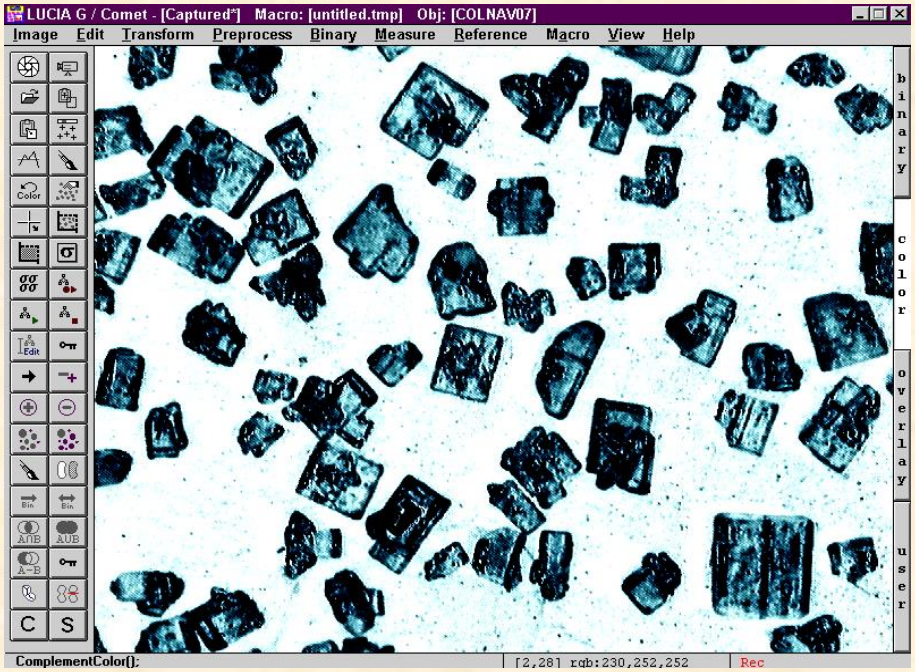
Rosin-Rammler-Sperling (for cummulative distribution)

$$M(L) = 100 \,.\, \exp[-L/L_{\text{mean}})^{\gamma}]$$

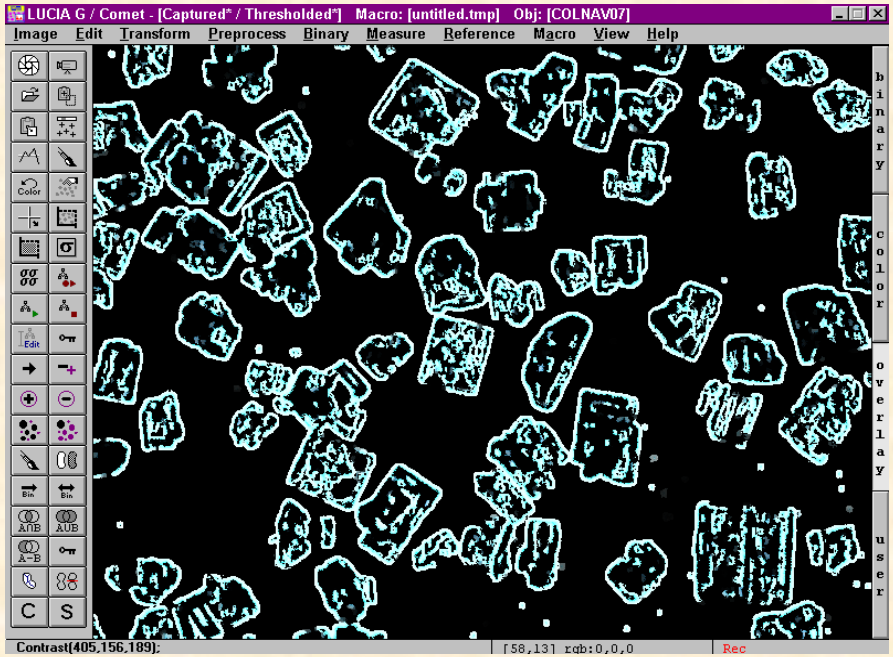


Instrumental set-up of the image analysis system LUCIA (ICT Prague)

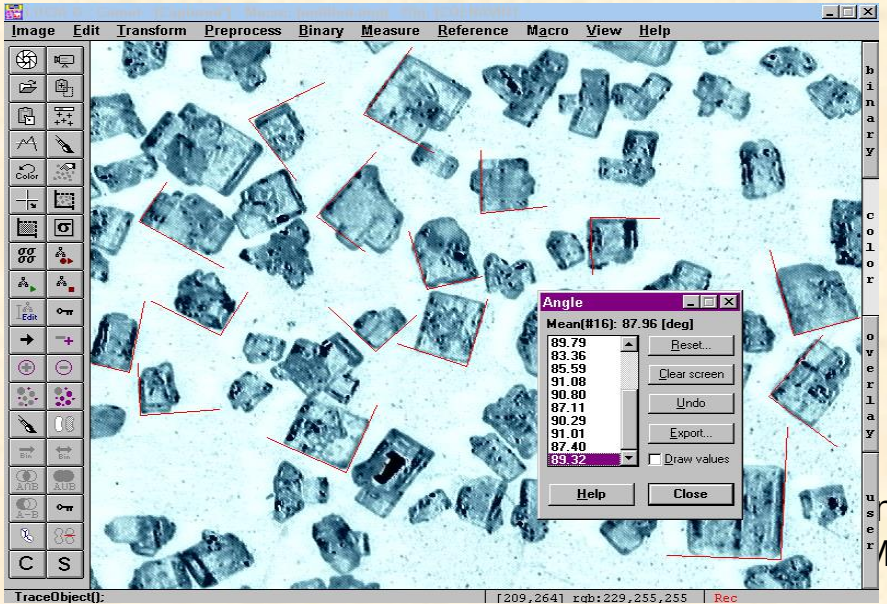
Complementary colors



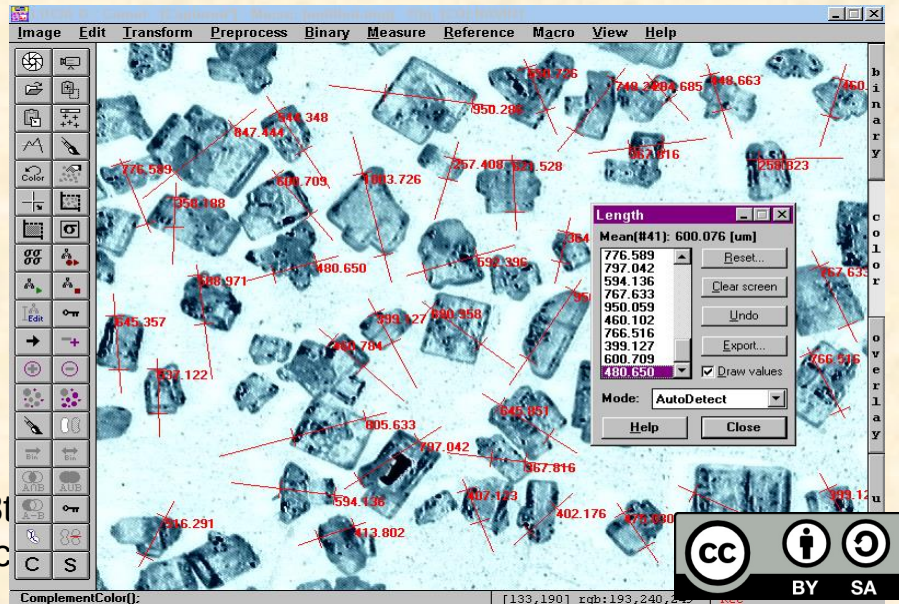
Linear morphology



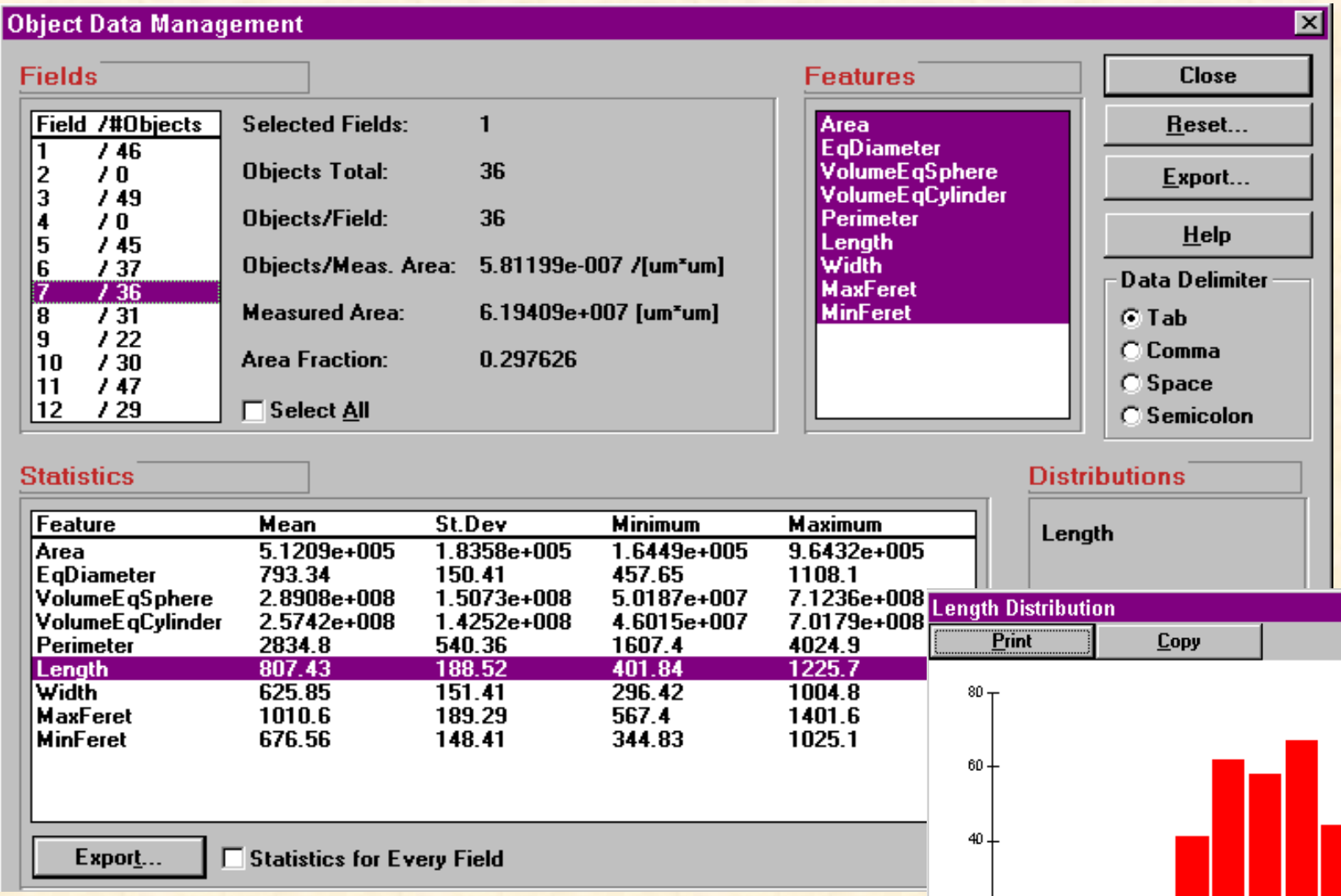
Angle measurement



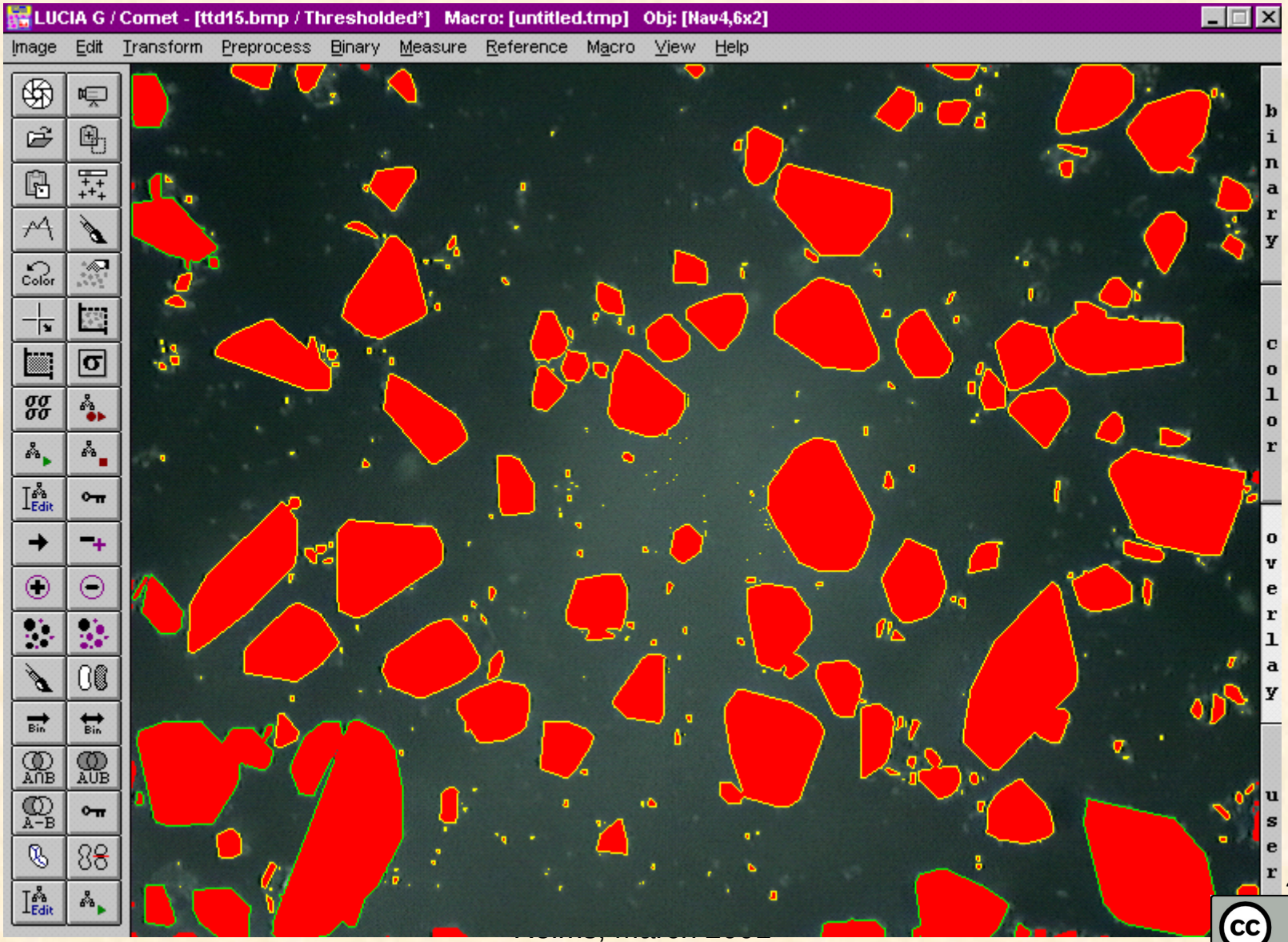
Lenght measurement



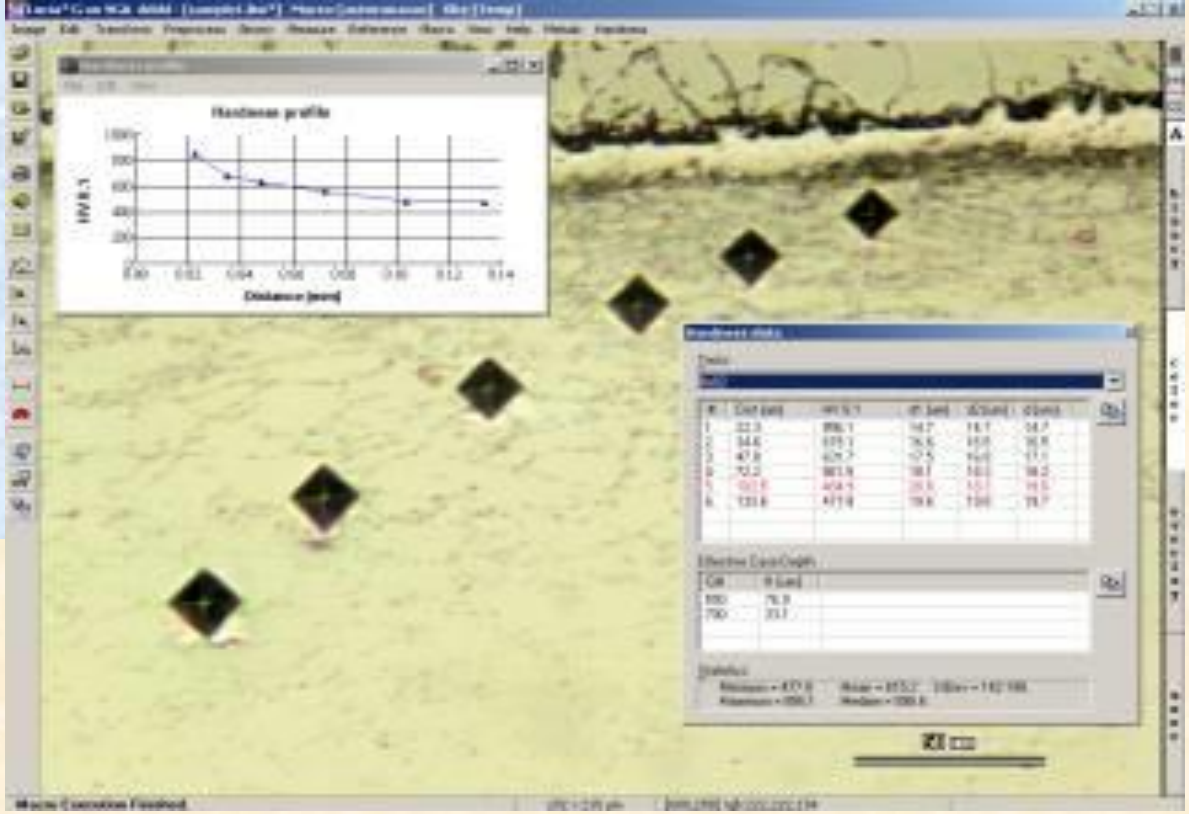
Crystal size distribution: Results of CSD



Refinery T , Sample 15 – Convex Hul

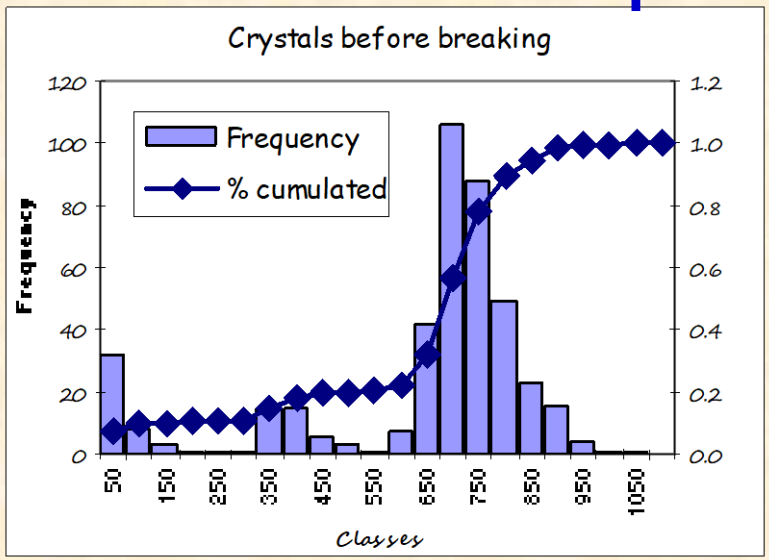


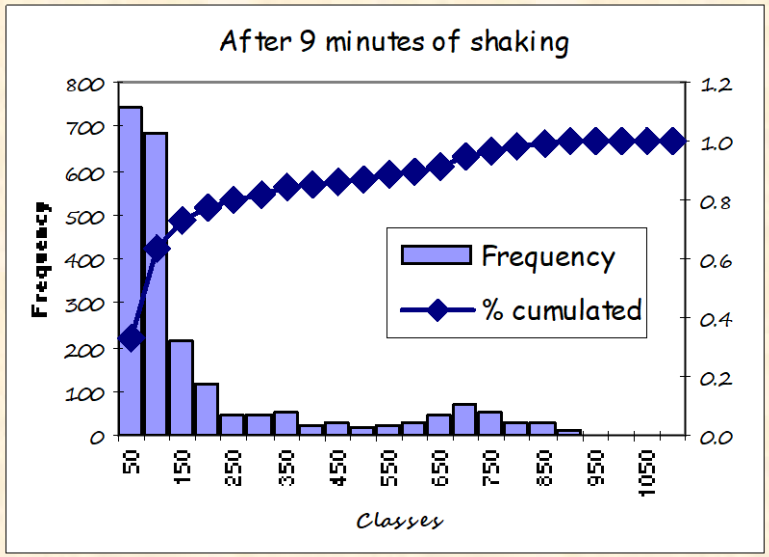
LUCIA Hardness screenshot

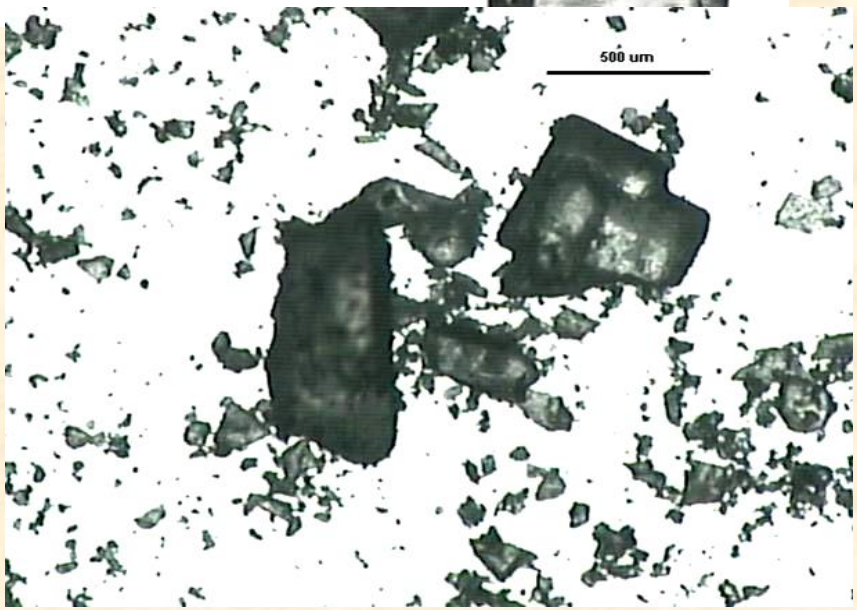


- LUCIA Hardness is a special LUCIA module developed for hardness measurements according to Vickers and Knoop. (Brinell in preparation)
- This module works according to the DIN 50 190 and EN ISO 6507-1 norms
- It is possible to communicate with Mitutoyo and Buehler digital micrometric screws and to determine the indents position automatically
- It is possible to work in many measure modes

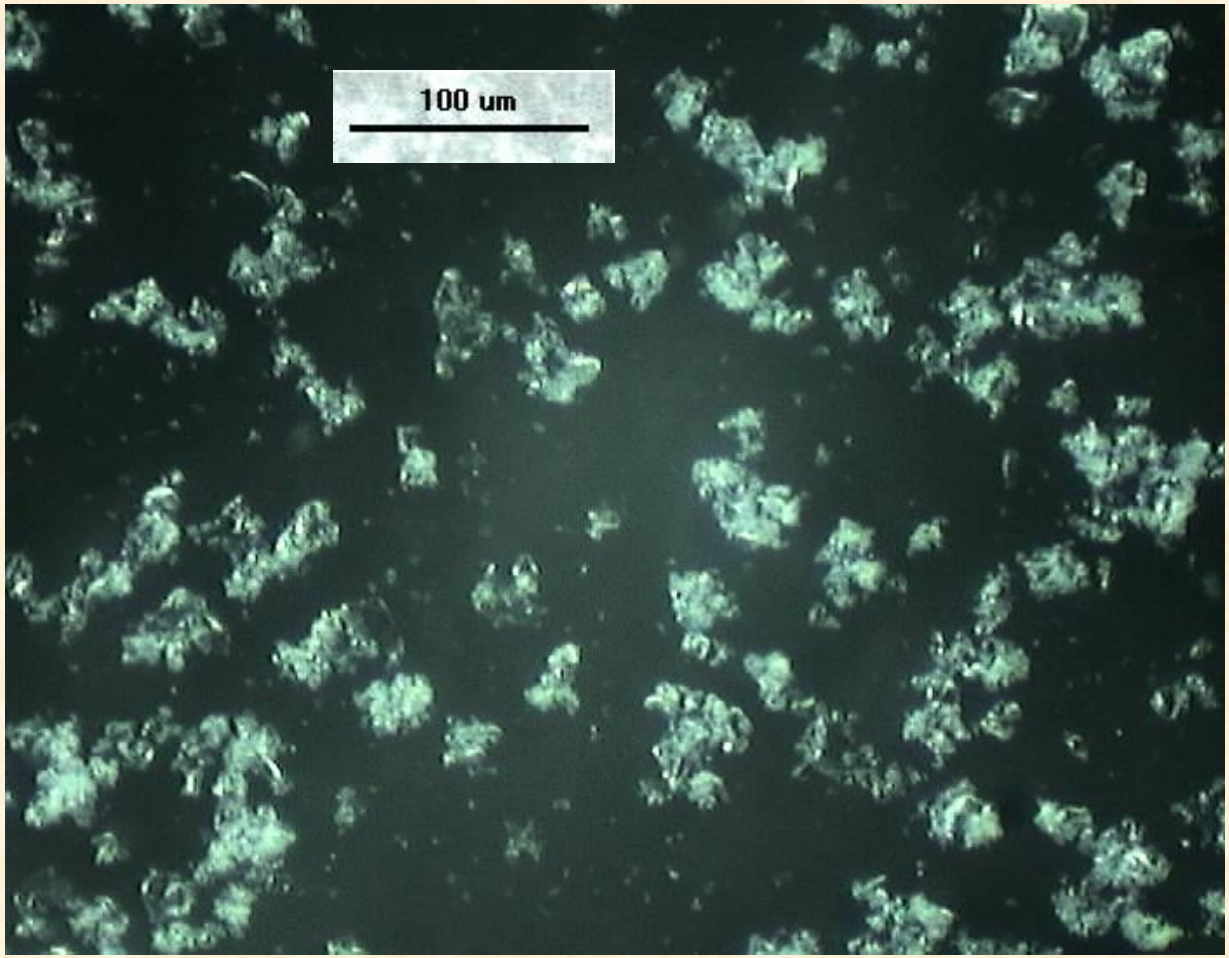
Histograms and pictures of sucrose crystal in dependence on a period of breaking.



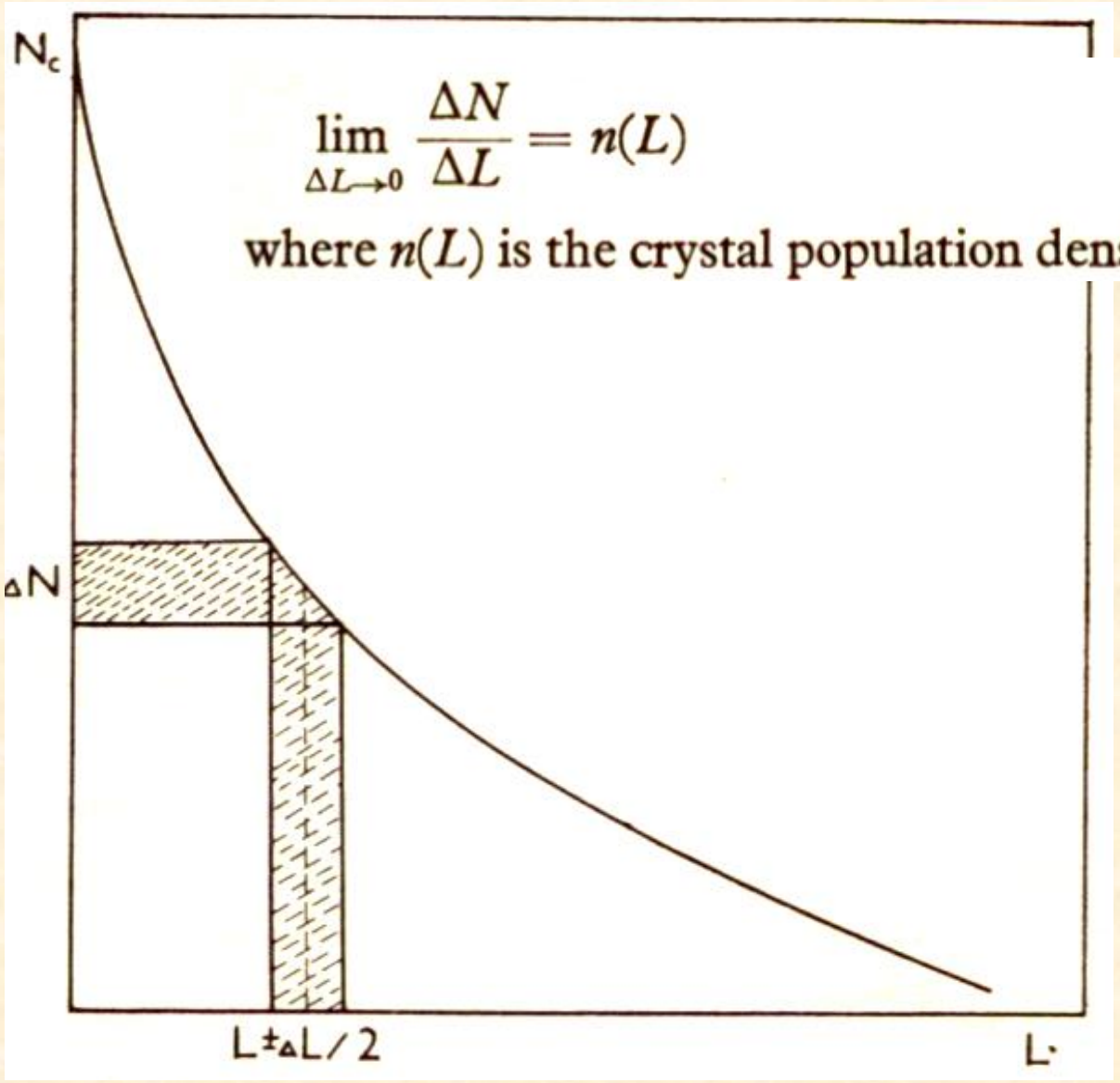




Slurry – suspension of microcrystals



Population Balance



$$\lim_{\Delta L \to 0} \frac{\Delta N}{\Delta L} = n(L)$$

where $n(L)$ is the crystal population density of crystals with size L

Population density ***n(L)*** of the crystals can be expressed as a function of their size, then a complete description of the CSD is obtained (the zeroth to third moment of CSD):

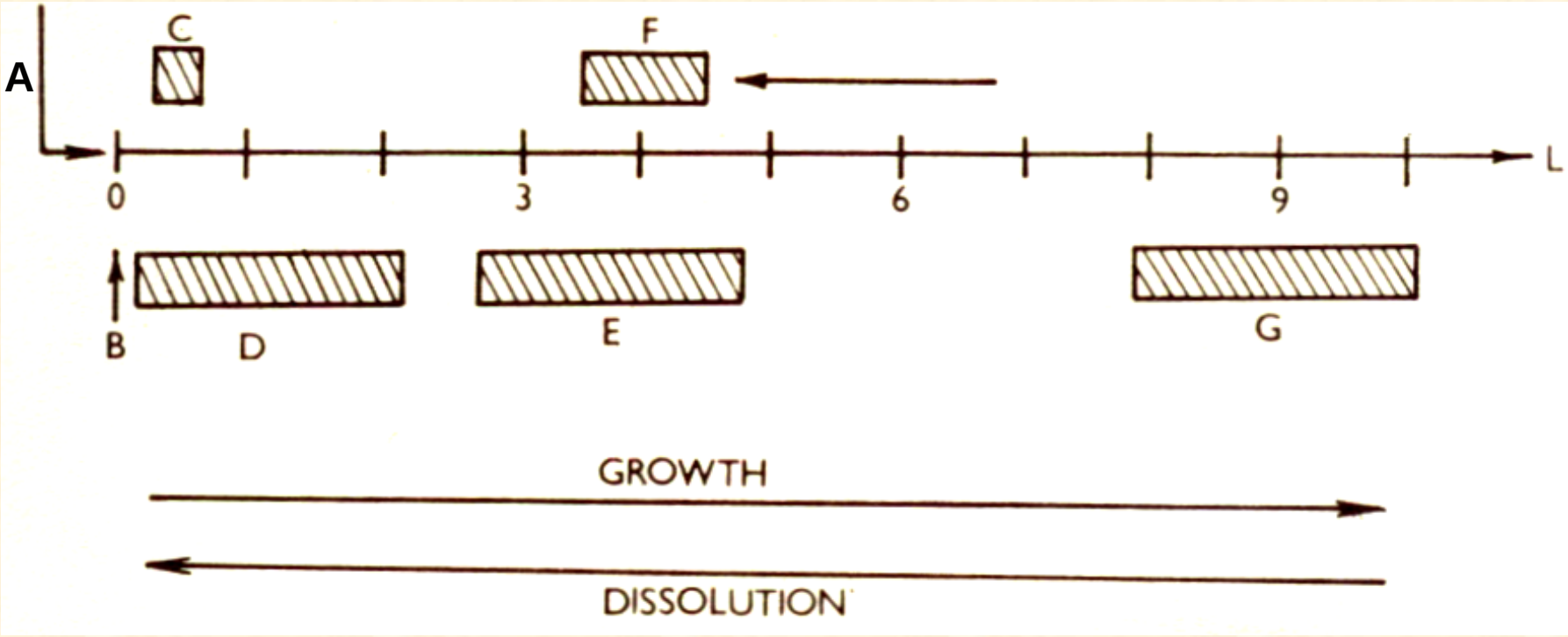
$$N_c = \int_0^\infty n(L)\, \mathrm{d}L\,,$$

$$L_c = \int_0^\infty n(L)\, L\, \mathrm{d}L\,,$$

$$A_c = \beta \int_0^\infty n(L)\, L^2\, \mathrm{d}L\,,$$

$$m_c = \alpha \varrho_c \int_0^\infty n(L)\, L^3\, \mathrm{d}L\,.$$

Processes contributing to the formation of a distribution of crystal sizes



A – primary nucleation, B – secondary nucleation, C – abrasion, D – dissolution of small crystals, E – agglomeration, F – macroabrasion, G – classification.

The population balance of the MSMPR crystallizer

Steady state:

a) perfect mixing of the suspension in the crystallizer (constant crystal population density at all points),
b) steady-state (constant crystal population density at all times),
c) suspension samples correspond to that in the crystallizer,
d) the feed is constant and does not contain any crystals,
e) the suspension volume is constant.

The population balance of the MSMPR crystallizer: Population Density Balance

At steady state, it holds that

$$\frac{dn}{dt} = 0$$

and the population balance is simplified to the form

$$\frac{dn}{dL} + \frac{n}{\dot{L}\bar{t}_1} = 0$$

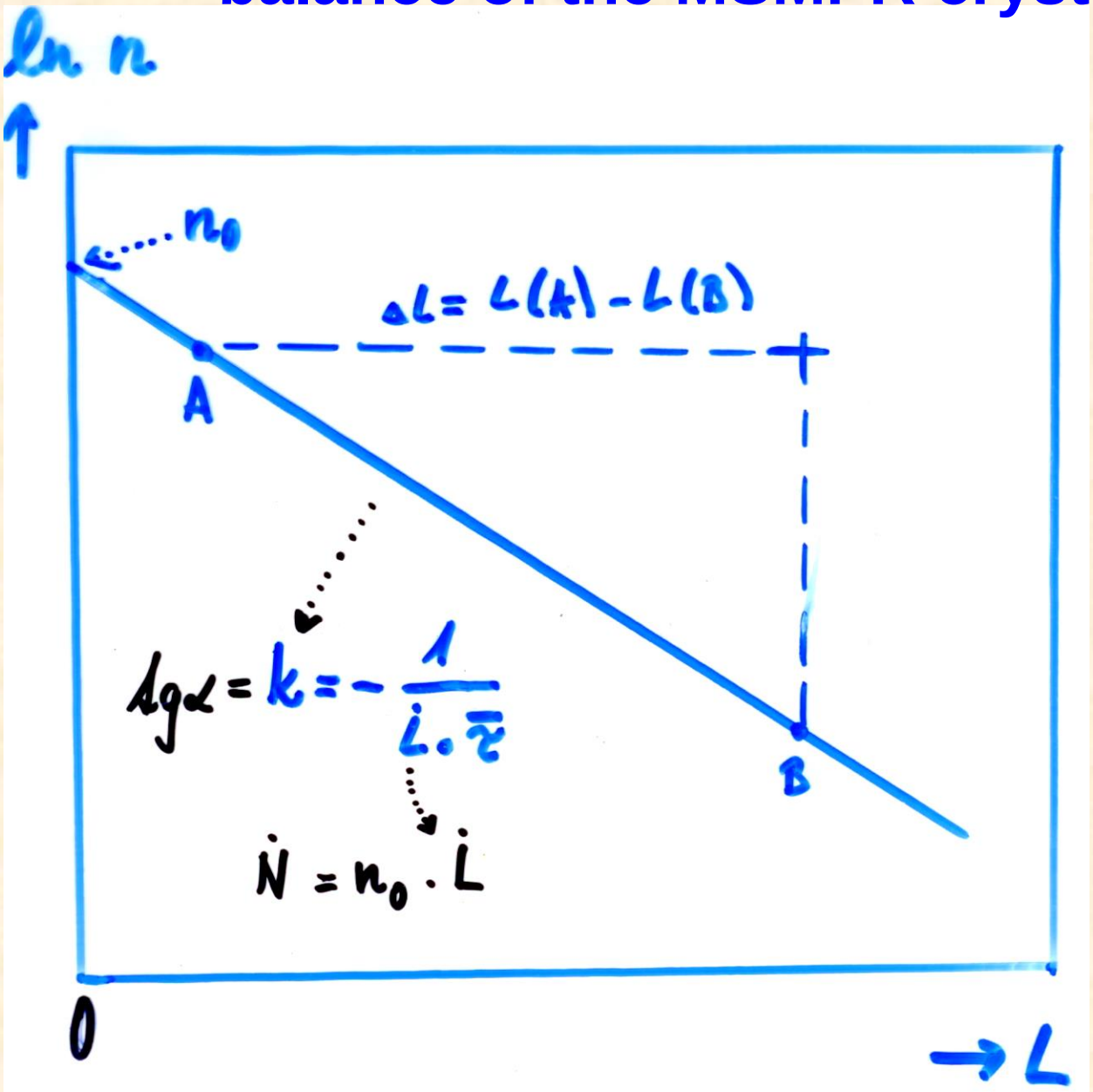
with the solution

$$\int_{n^0}^{n} \frac{dn}{n} = \int_{0}^{L} \frac{dL}{\dot{L}\bar{t}_1}$$

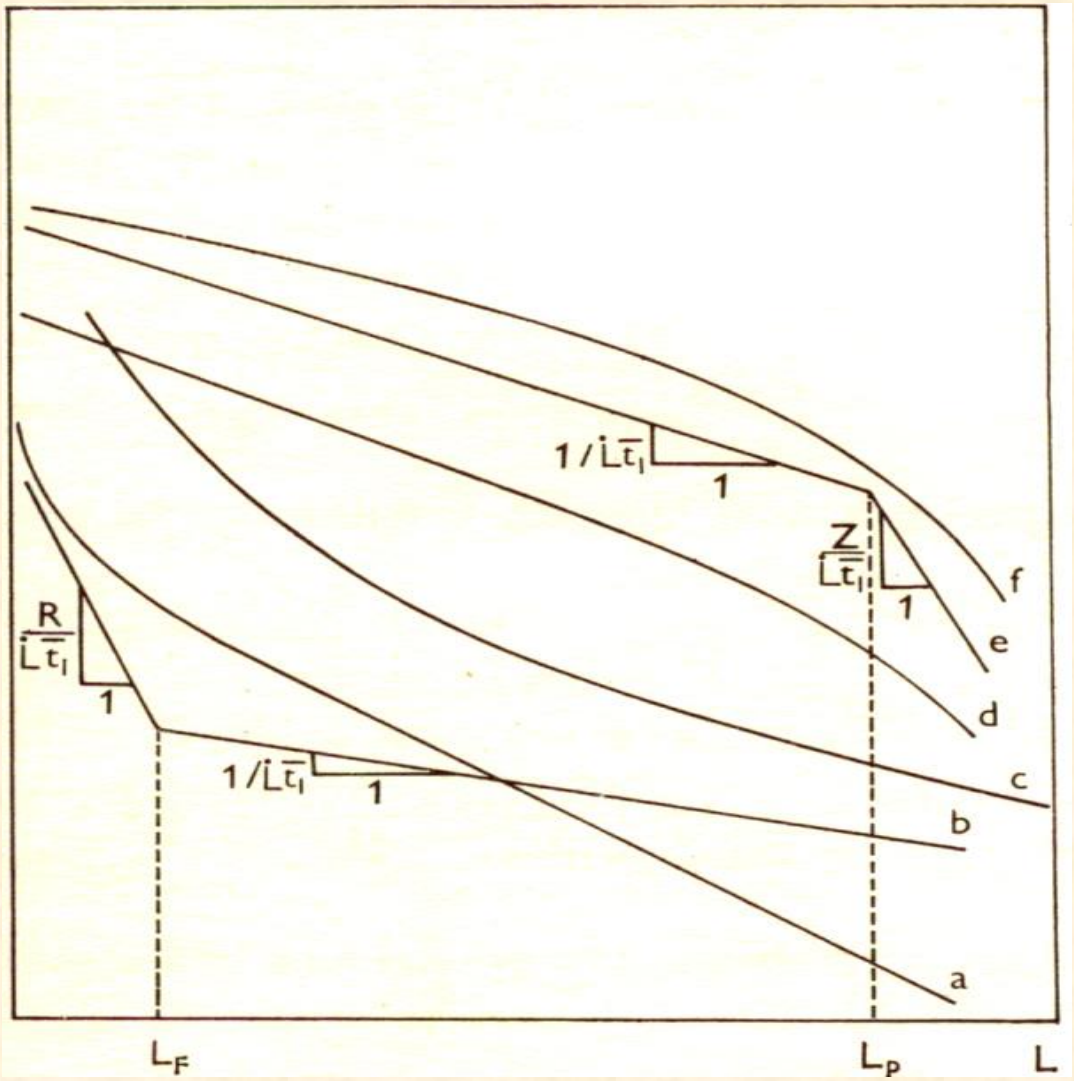
or

$$n = n^0 \exp\left(-L/\dot{L}\bar{t}_1\right).$$

Graphical representation of the population balance of the MSMPR crystallizer

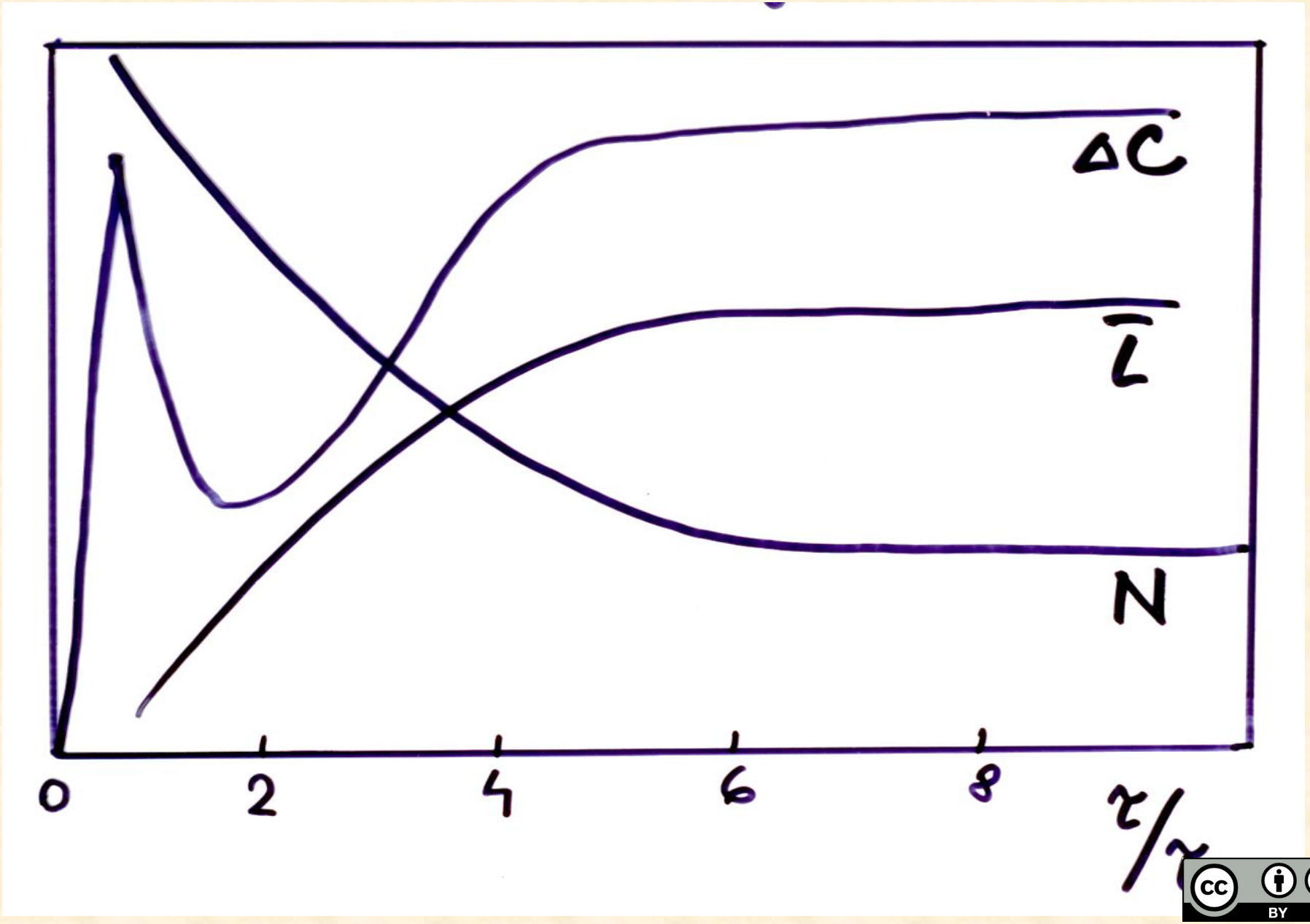


Deviations from an ideal MSMPR crystallizer.

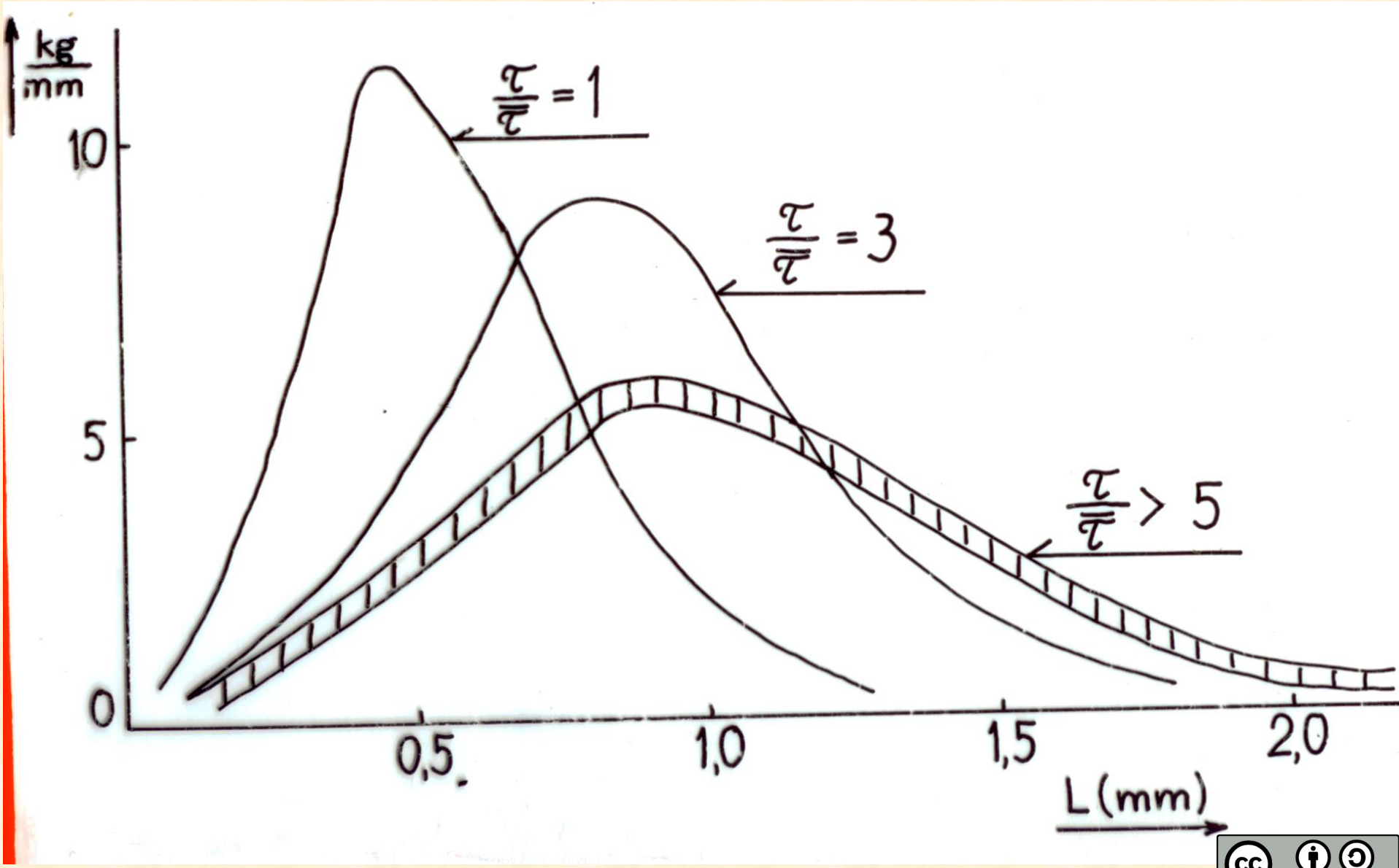


a – unintentional dissolution of small crystals, b – separate dissolution of small crystals, c – deviation from the McCabe ΔL-law, d – internal classification, e – sampling of the classified product, f – splitting of the crystals to particles with comparable sizes.

Process parameters during steady state achievement



Crystal size distribution during steady state achievement



Photocatalytic Process – Application in the Food Industry

Non-Waste Production

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION,
YOUTH AND SPORTS

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Potential of

photocatalytic process

in decomposition of pollutants

from food technologies

Introduction

Photocatalytic processes enable a transformation of light energy into electric or chemical one.

An expansion of the following branches connected with research and application of photocatalytic technologies can be expected:

- Electricity production using photovoltaic cells
- Controlled biomass production using a photosynthetic ability of green plants, algae, etc.
- Photocatalytic transformation of carbon dioxide into substances of high energy content
- **Degradation of pollutants**

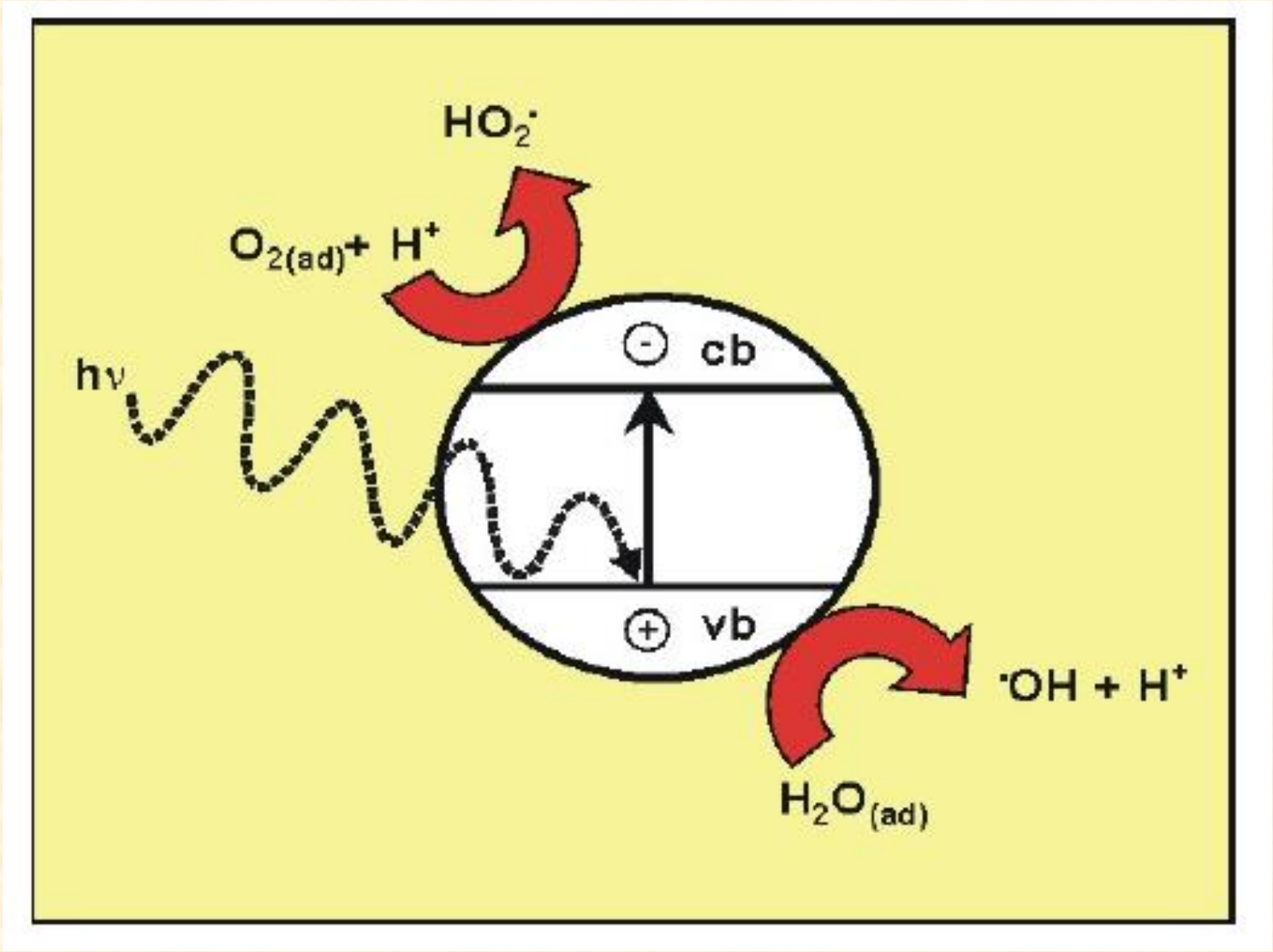
- Light illuminating a semiconductor particle causes electron excitation from a energy lower valence band into a higher conduction band and creates electrically charged centres (also known as the positive holes):

photon + semiconductor = h+ + e-

where **e-** is a mobile electron and **h+** is the positive centre.

- The electrons undergo reduction and the positive centres enter oxidation reactions with reductants.
- Positives centres are strong oxidants. Radicals **OH·**, the strongest known oxidizer, arise in a presence of water.
- Organic compounds on the catalyst surface or near the catalyst are oxidized into carbon dioxide, water and inorganic salts.

Principles of photocatalytic process



Photocatalytic reaction is affected by:

a) **the energy of the illuminating light,**

b) **the ability of the catalyst to absorb light quantum,**

which is given by the size of particles and their chemical and crystallographic structure in nano-scale

- nanocrystalline TiO_2 …

c) **the technical design.**

Advantages of practical applications of photocatalytic processes

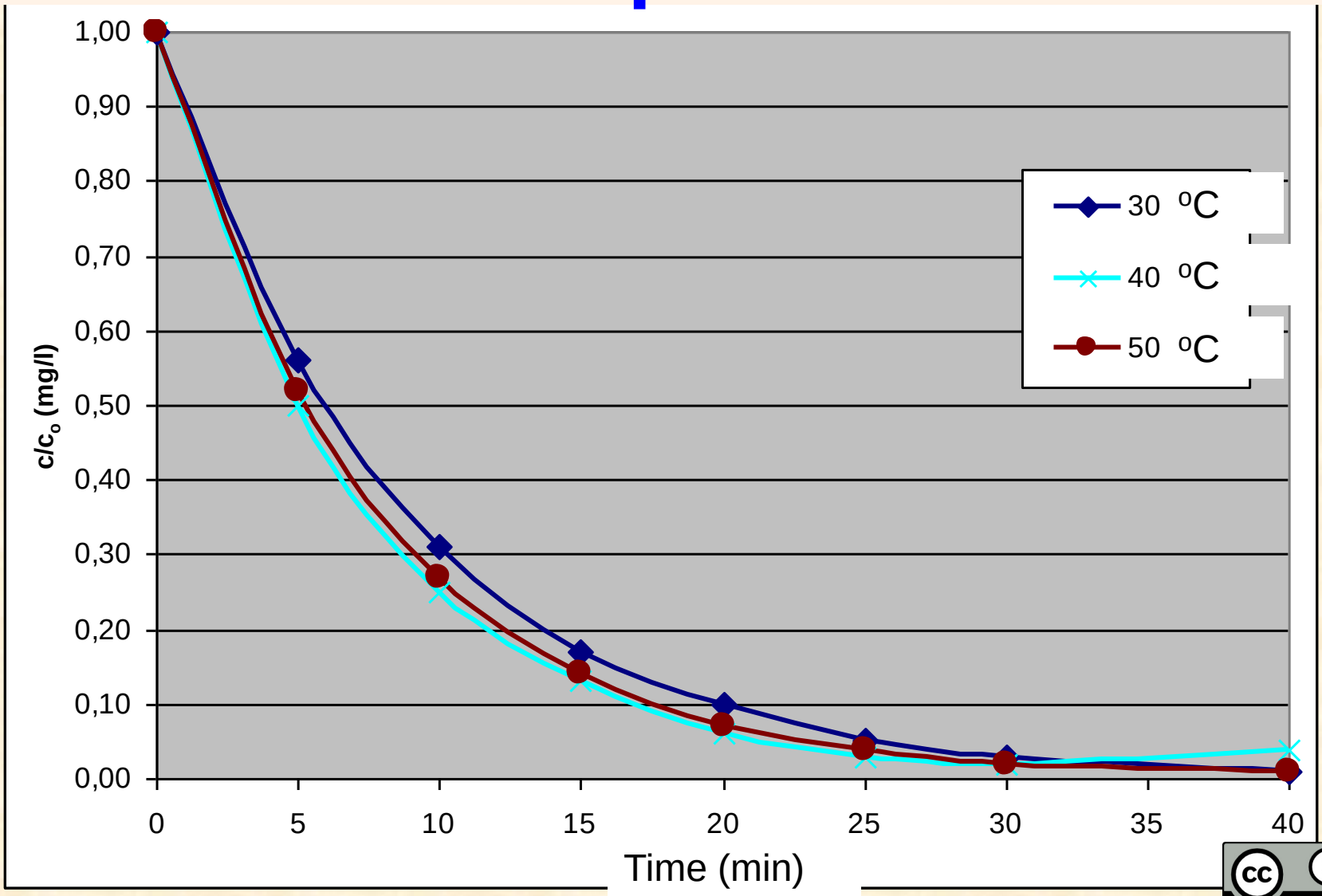
Photocatalysis is a modern technology whose number of applications grows exponentially. It follows the concept of sustainable development and improvement of quality of life in the near future:

- High energy demands tend to use other alternative energy sources like the solar energy, whose application does not increase the amount of carbon dioxide in the atmosphere.
- Photocatalytic oxidation processes use natural resources without chemicals.
- Photocatalytic degradation of organic compounds used in air and water purification does not produce other wastes burdening the environment.
- Connection of photocatalysis with membrane technologies improves the potential of both technologies.

The potential of photocatalysis in agricultural and food technologies:

- New ecological system for treatment of waste water, groundwater and production of drinking water.
- Improved sanitation and hygienics in industrial workplaces, households and application of surfaces with photocatalytic coating.
- Higher air quality, removing of microorganisms, toxic compounds, odours and ethylene in working and storage areas.
- Economical benefits in comparison with conventional techniques.

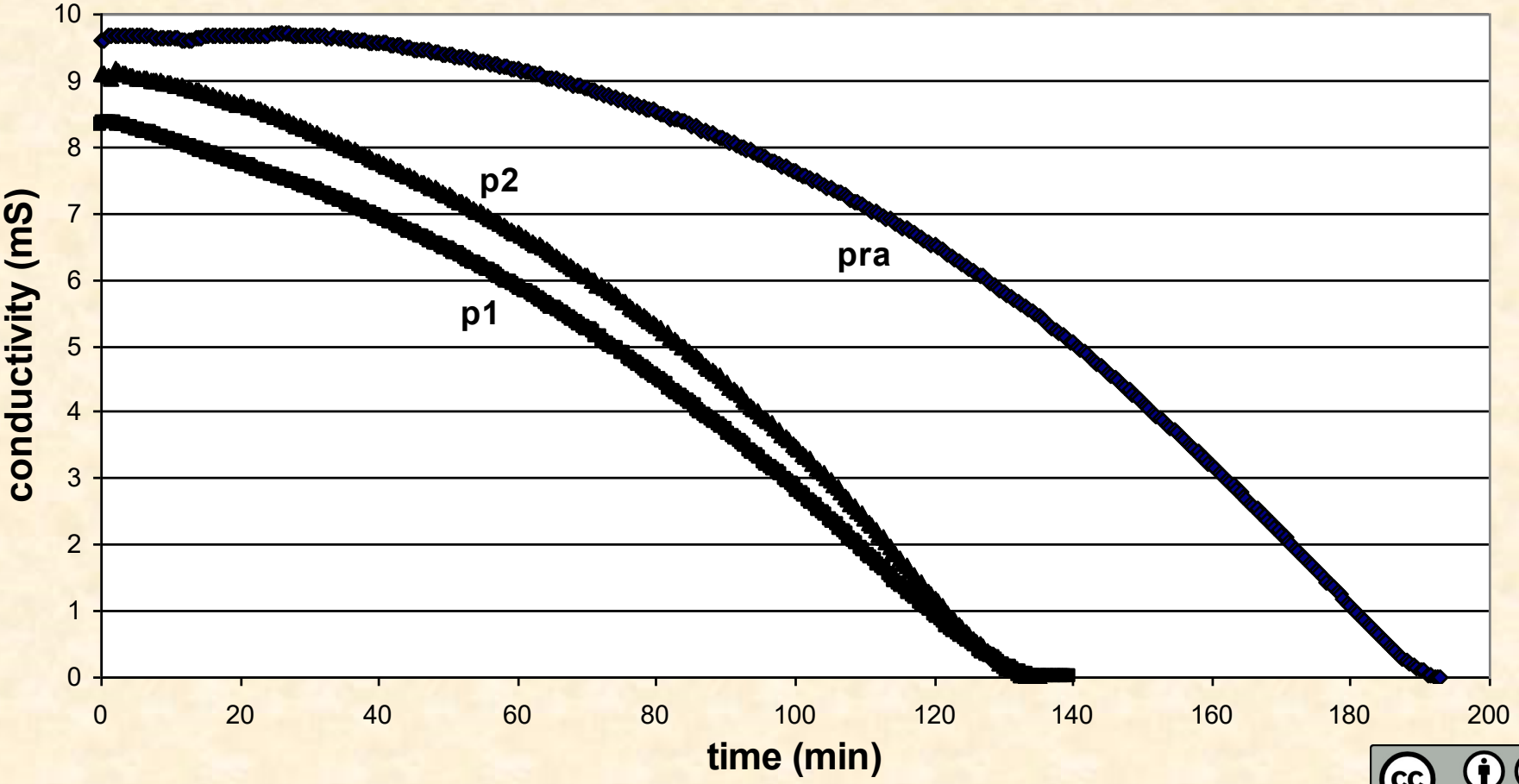
Phenolic substances decomposition



Decomposition of oxalic acid

Legend: p1, p2 – two trials made under the same conditions with catalyst,

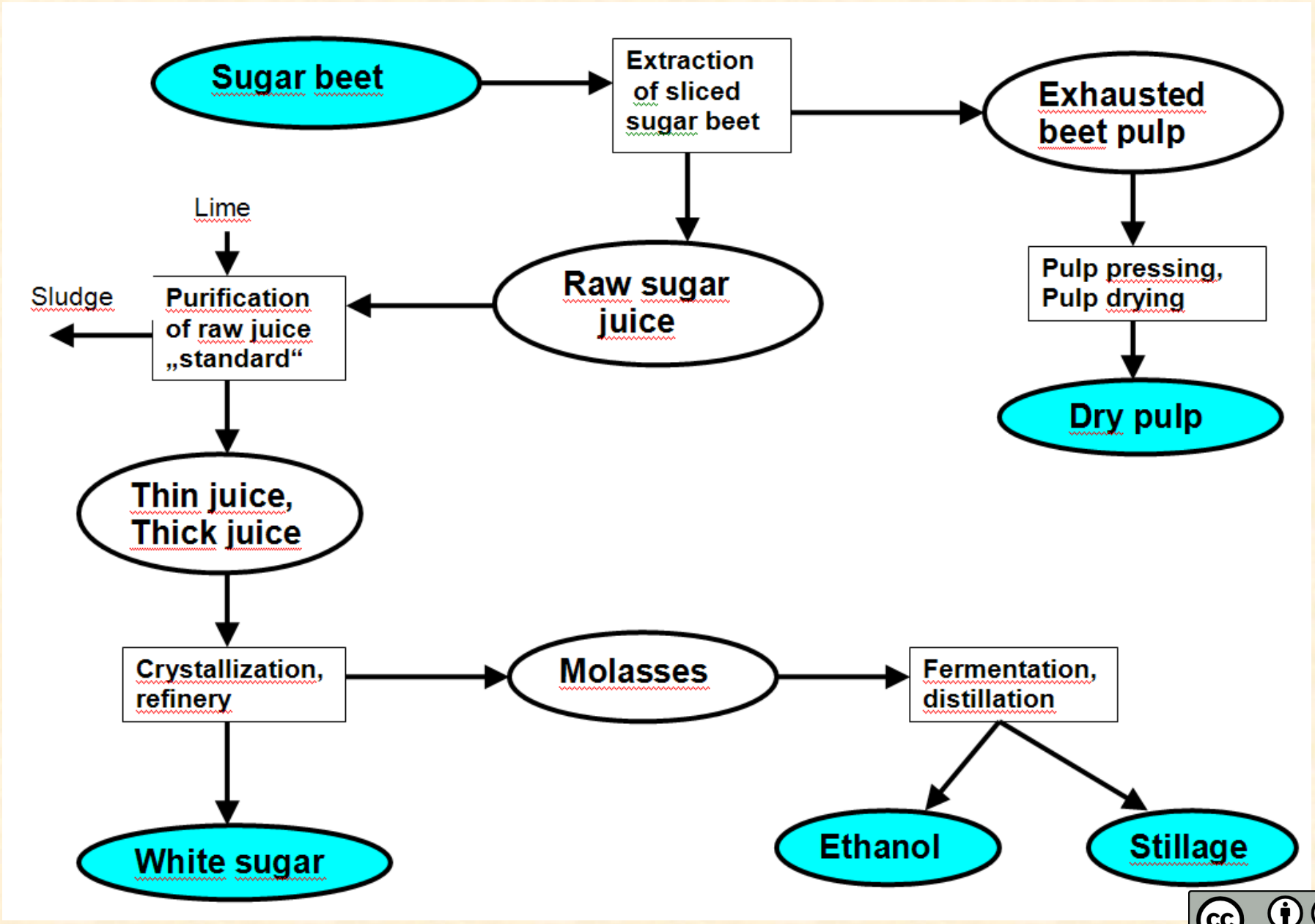
pra – the same experiment with no catalyst used



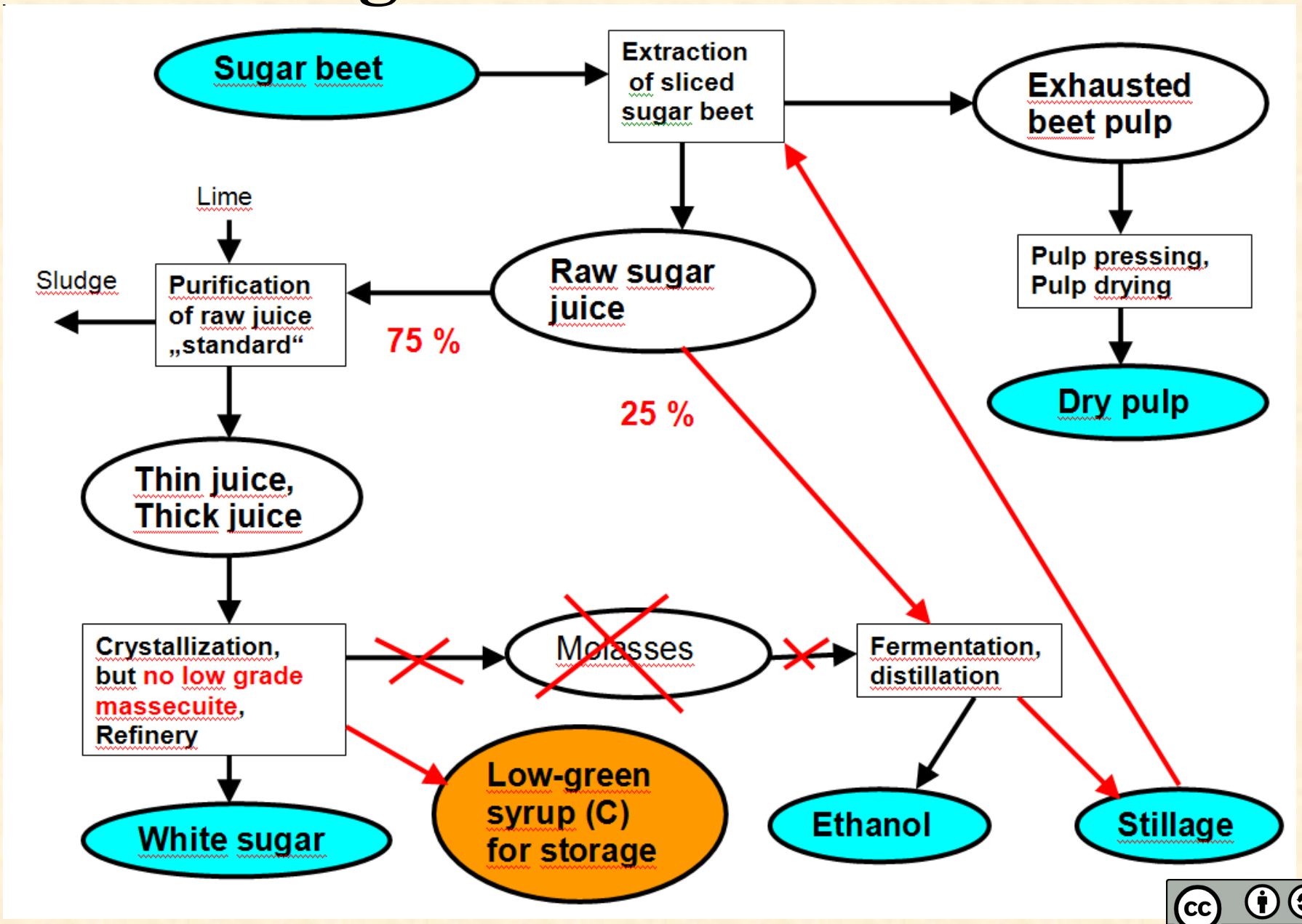
Non-waste production process in a sugar factory.

- Biofuel production.
- Implementation of novel processes.
- Crystallization of stillage

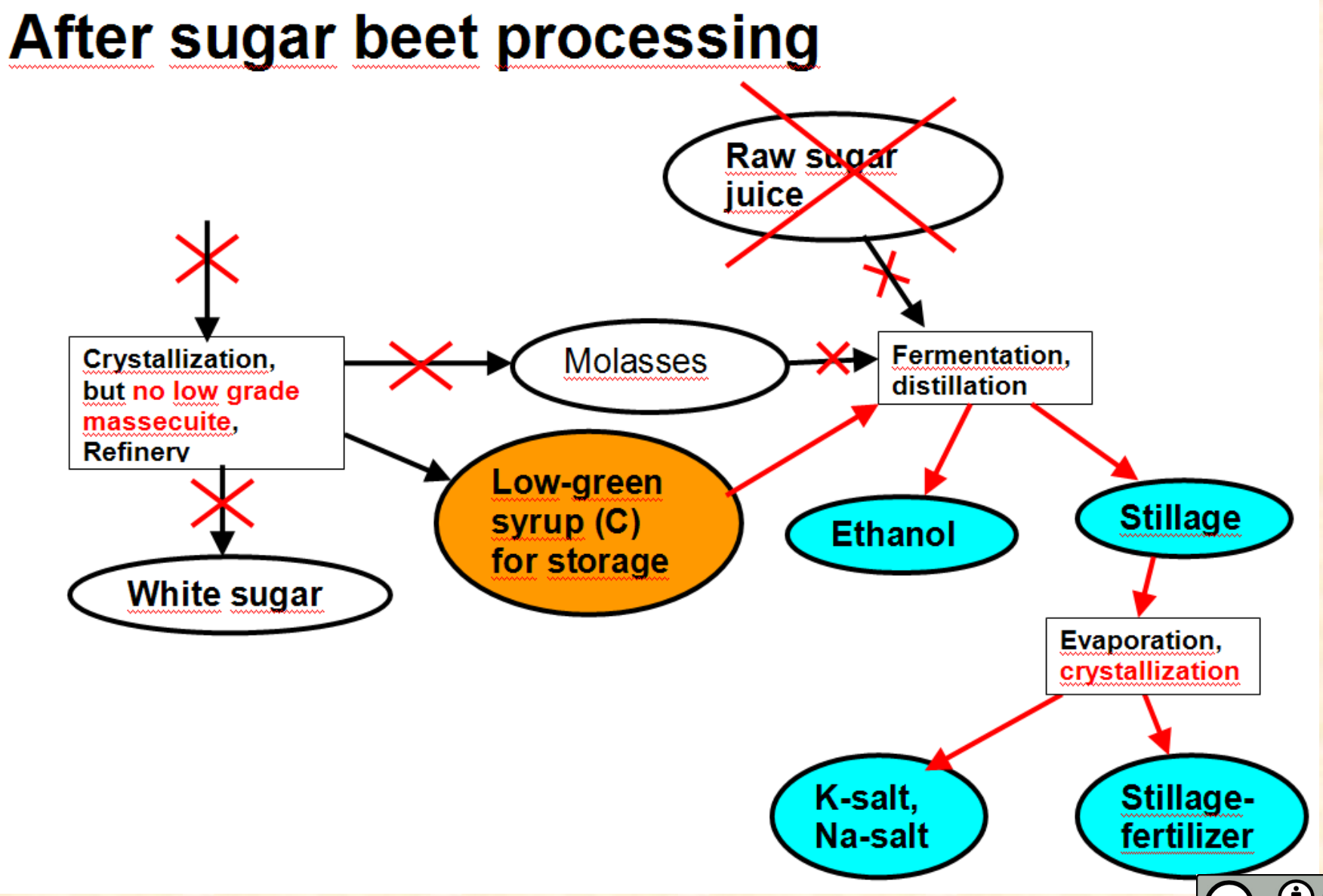
Standard scheme



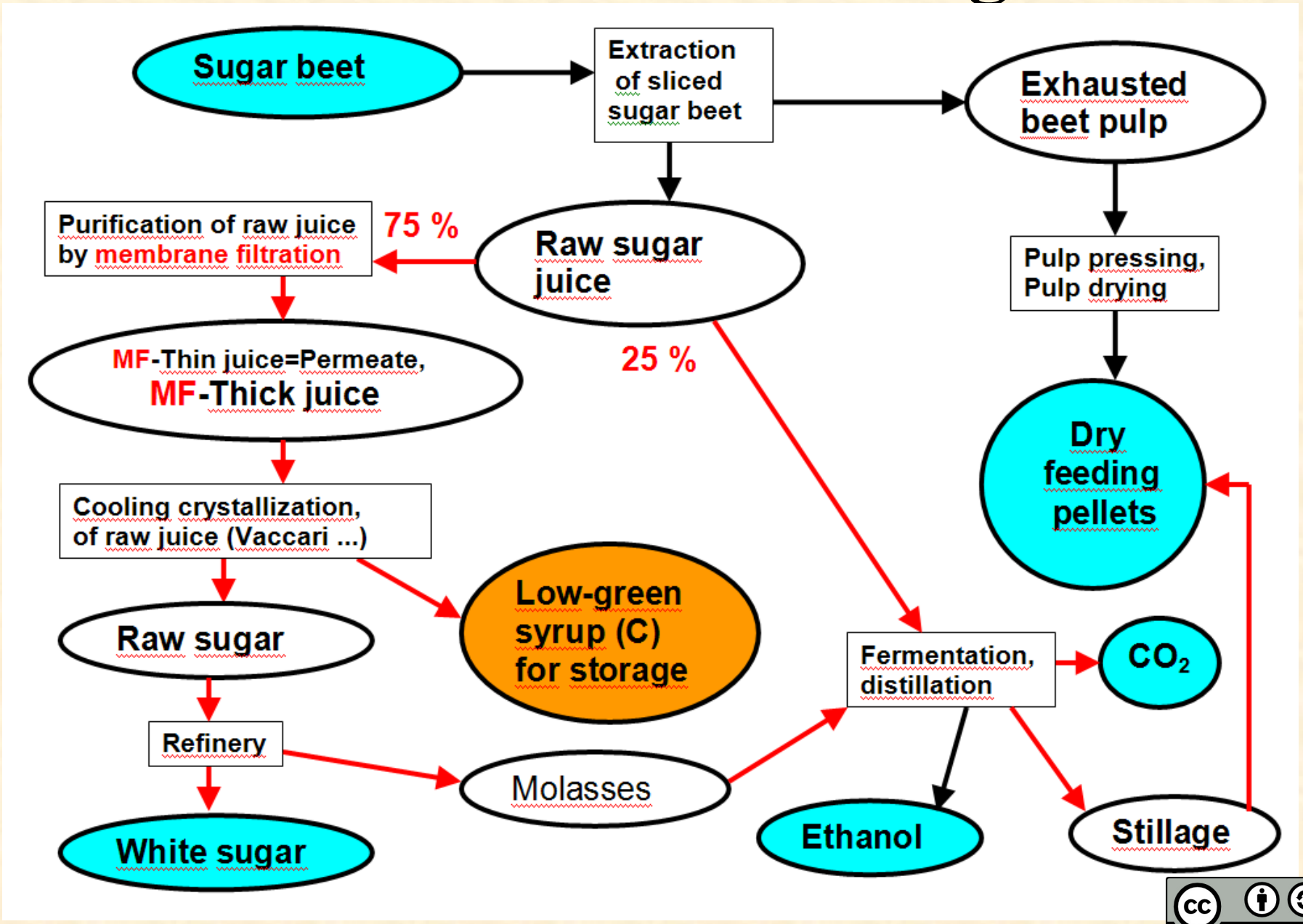
Technological scheme of TTD



TTD scheme –cont.



New scheme of UCT Prague



New scheme of UCT Prague – cont.

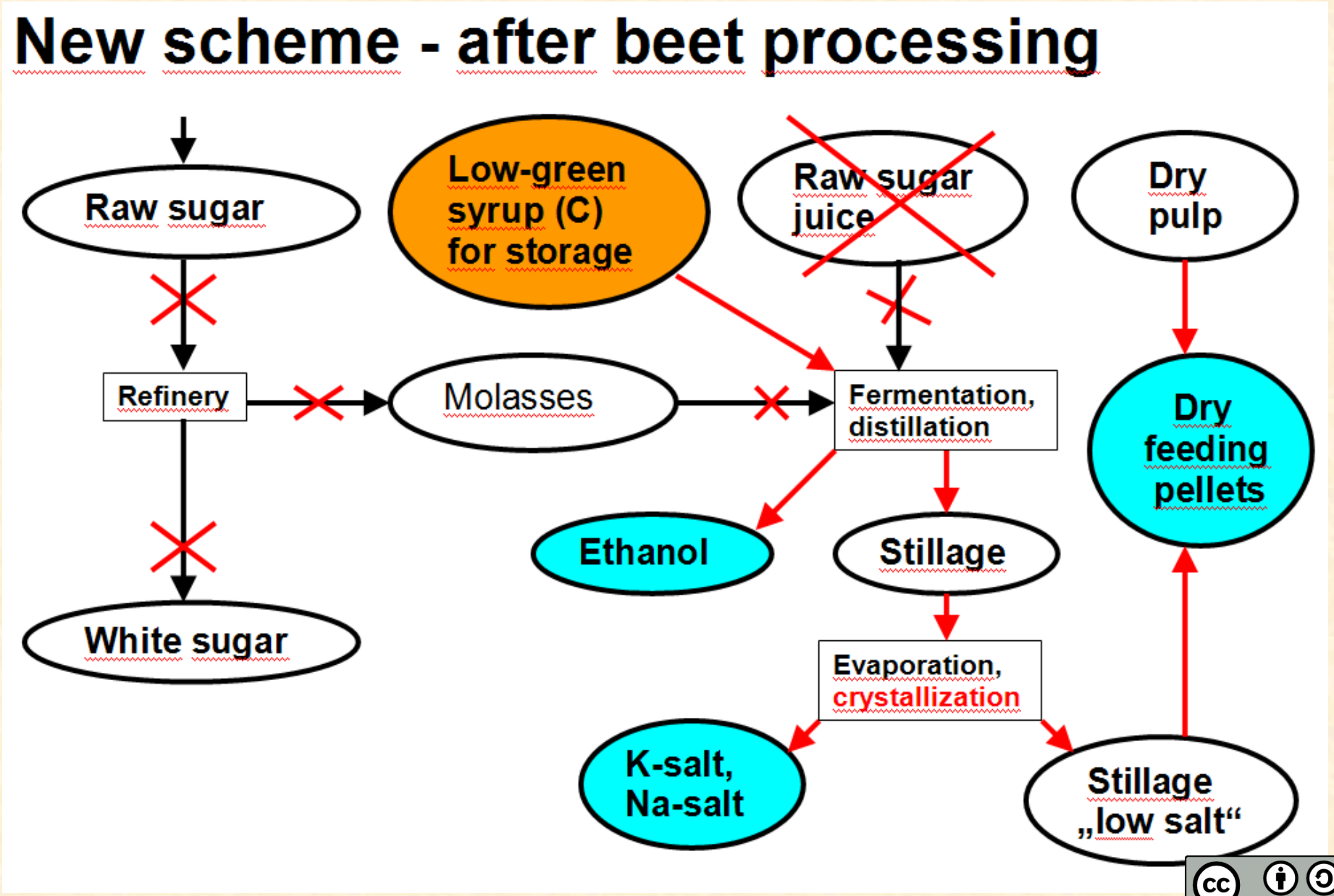
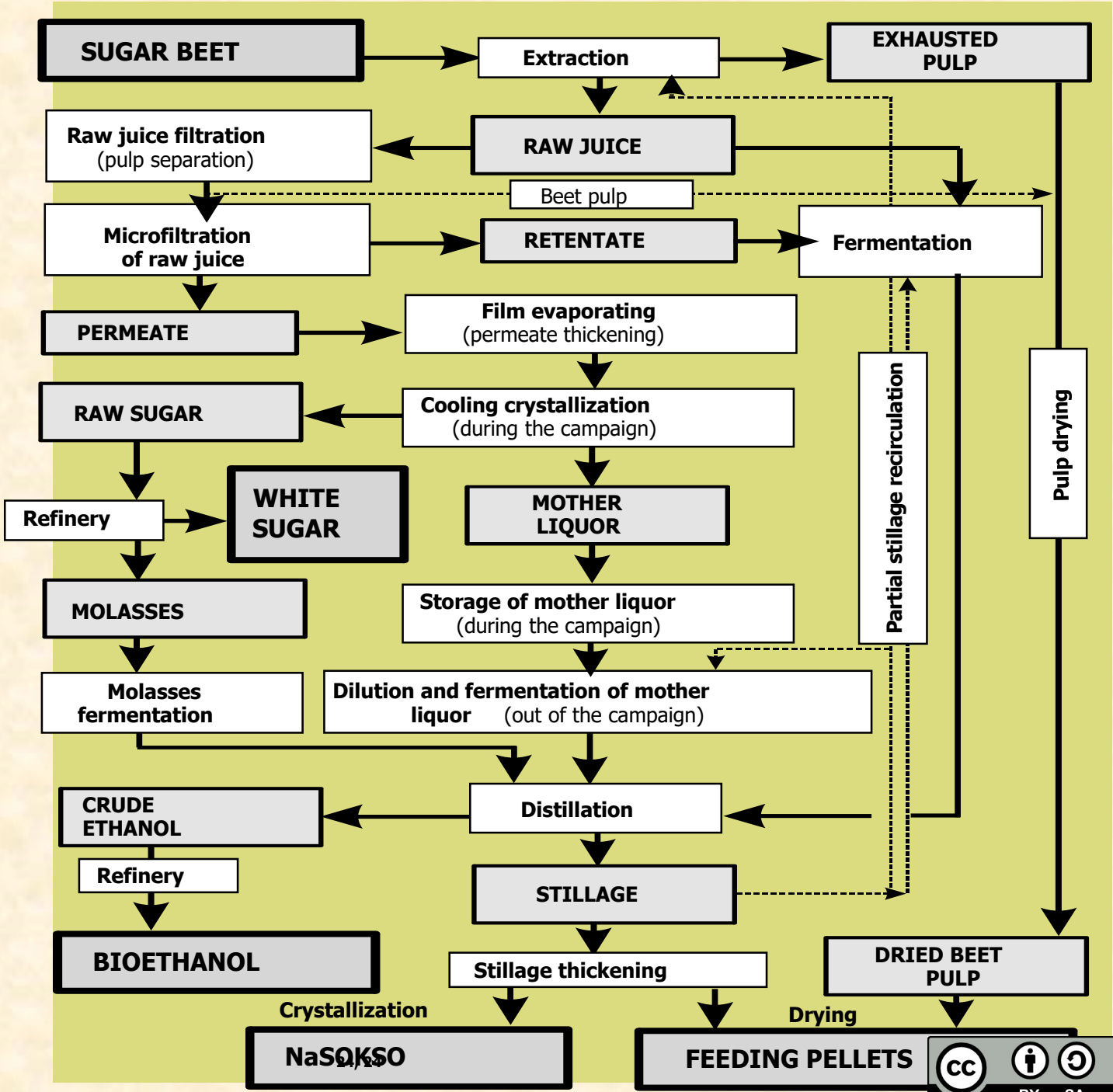
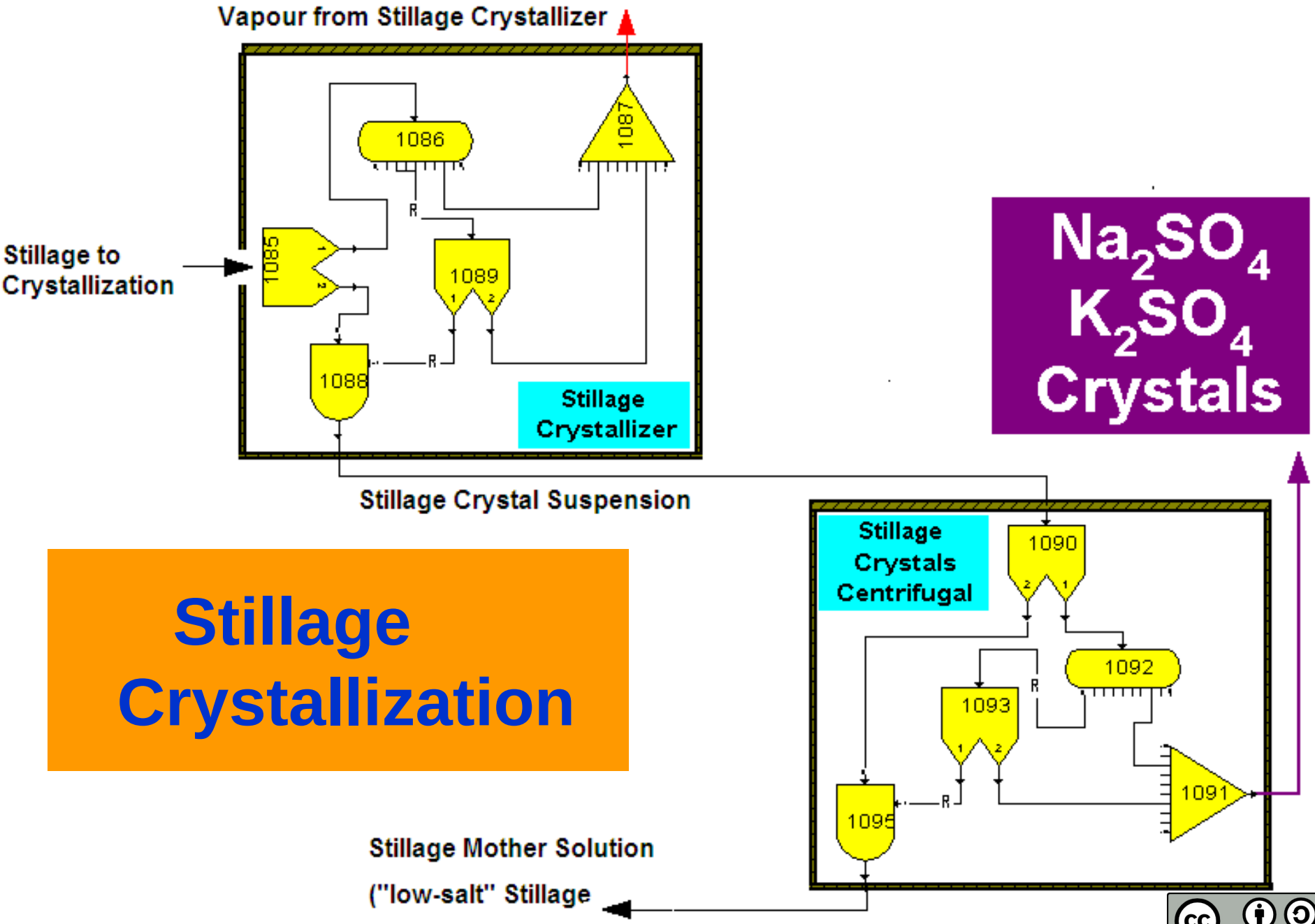


Fig.:

Complete technological scheme that would connect sugar and ethanol production.

UCT Prague





Stillage Crystallization

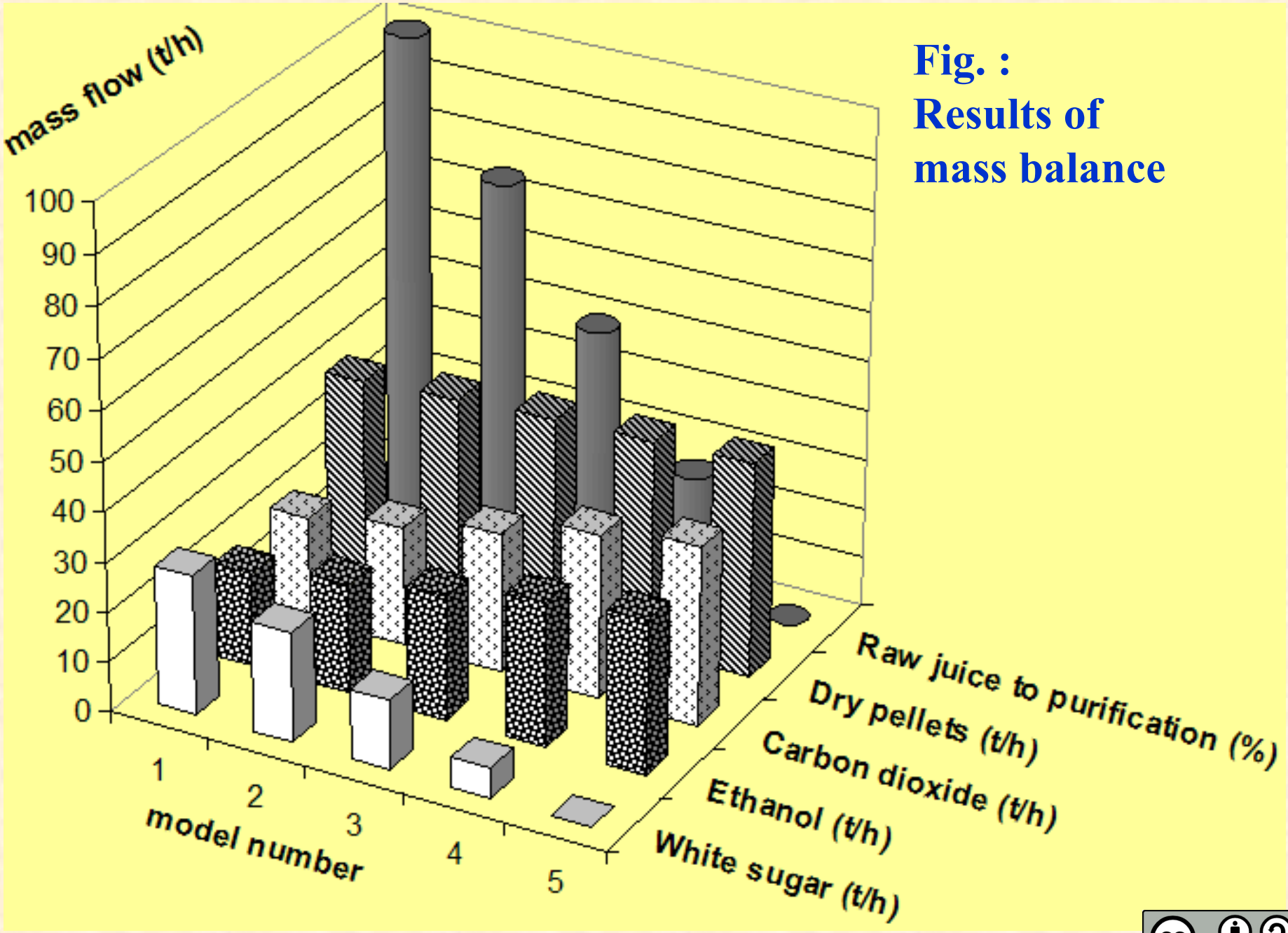


Fig. :
Results of mass balance

CONCLUSION

Model 1:

If all raw juice is used for sugar production, we could obtain:
28 t/h of sugar,
19 t/h of ethanol,
40 t/h of feeding pellets
21 t/h of carbon dioxide

Model 5:

Using all raw juice for fermentation yields:

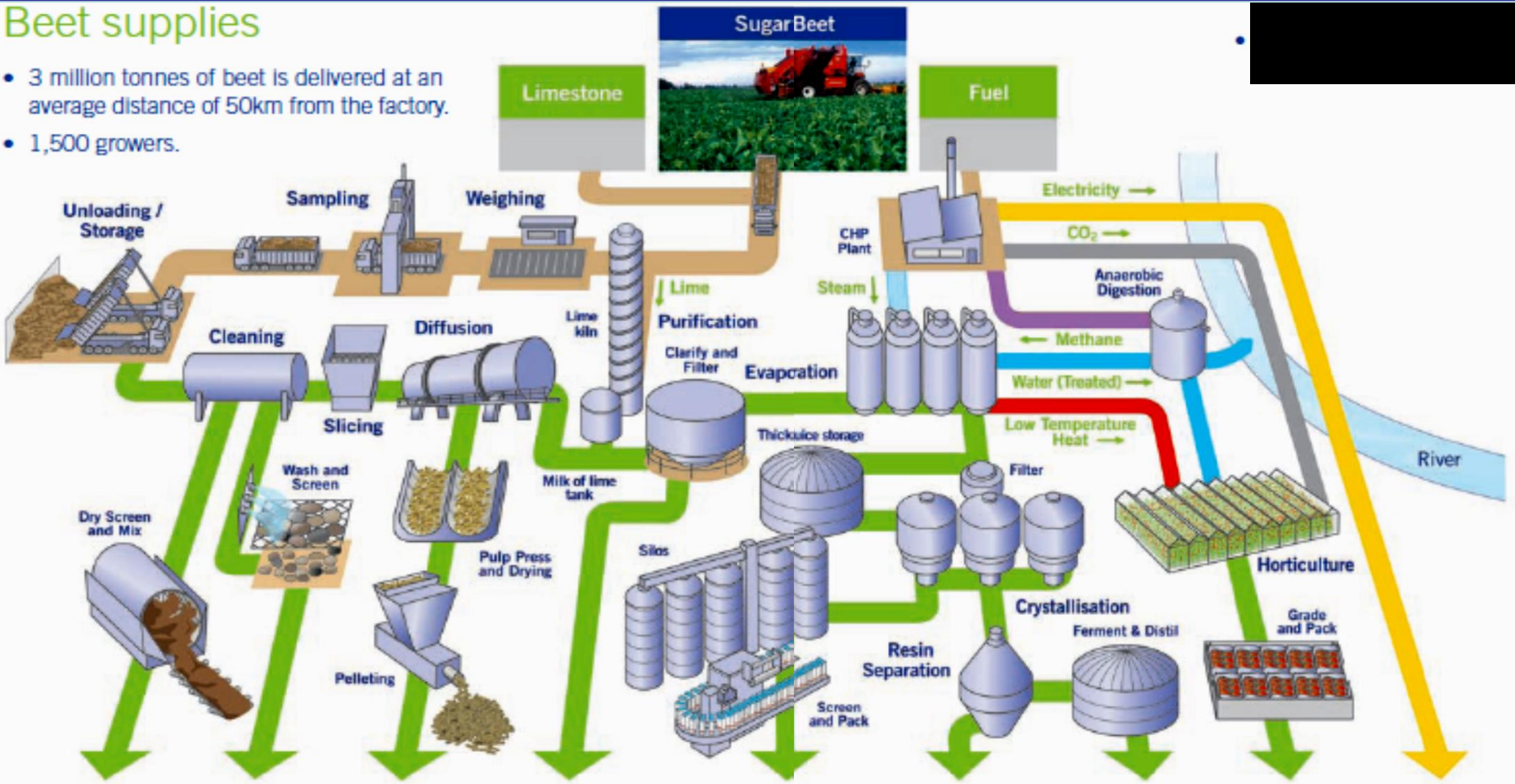
0 t/h of sugar,
31 t/h of ethanol,
43 t/h of feeding pellets
36 t/h of carbon dioxide.

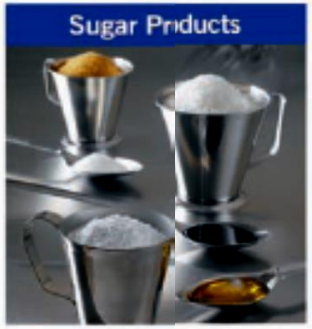
- The shown scheme provides large possibilities to suggest production according to calculations monitoring the financial profit from the product sales.
- A large amount of produced CO_2 is also a valuable by-product for beverage industry.
- Salt content in dried beet pulp can be reduced by crystallization. Also this potentiality will be evaluat

Sugar Beet Refinery Wissington (UK)

Beet supplies

- 3 million tonnes of beet is delivered at an average distance of 50km from the factory.
- 1,500 growers.





Advanced processes in food technology and biotechnologies

Image analysis

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UNIVERSITY OF CHEMISTRY AND TECHNOLOGY PRAGUE

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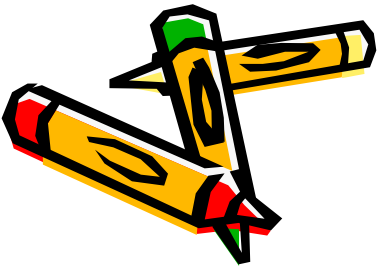
Information sources

http://sch.vscht.cz/vyuka/international-students/erasmus-students/

Databases: ScienceDirect, Scopus, Web of Science



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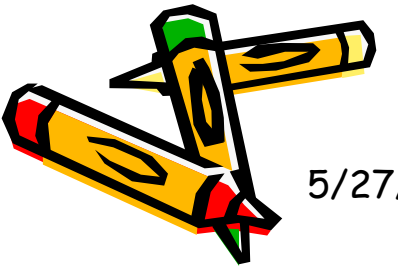
a) Theory of image analysis (IA)

b) Practical applications of image analysis in agriculture and food industry

c) Demonstration in laboratory exercises

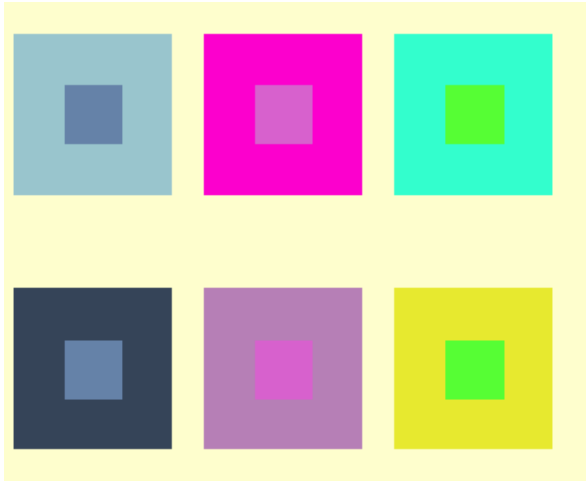


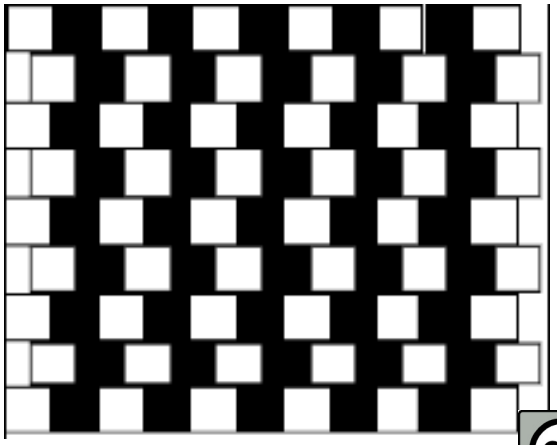
Introduction

- In making physical assessment of agricultural materials and foodstuffs, images are undoubtedly the preferred method in representing concepts to the human brain.
- Many of the quality factors affecting foodstuffs can be determined by visual inspection and image analysis.

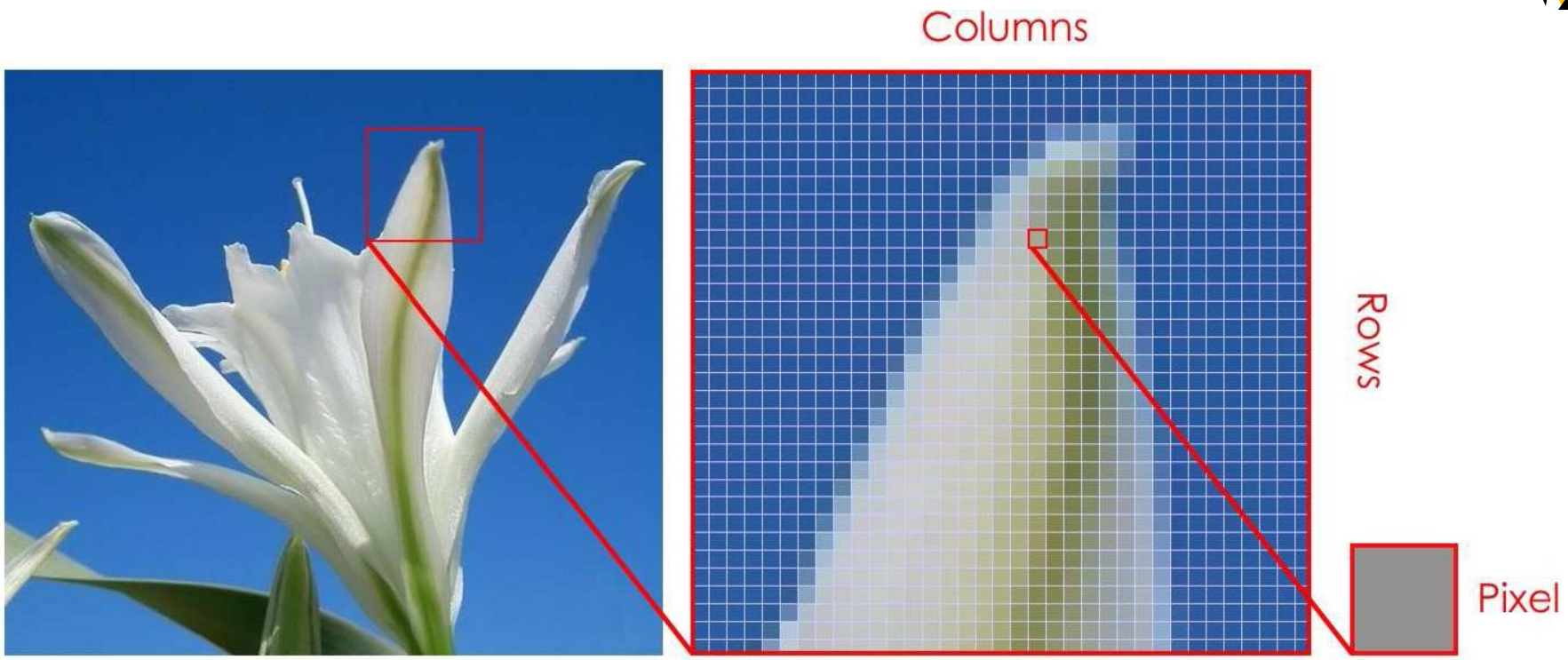
Human x machine vision

- The **machine vision** is more or less exact imitation of the human one.
- Machine vision benefits in cases where human vision is affected by optical illusions. Computer can assess the size and colors of objects in the image completely **objectively**.
- The advantage of the machine vision is also in the ability of **recording of a large number of objects** in the visual field of the camera during short time (a man remembers only a fraction of them) or the possibility to record and **analyze very fast processes**.
- In some cases, we can be disappointed; for example, when we very clearly see or detect the measured parameter of the product (damage, characteristic size...), and the computer is not able to filter out all disturbances. The analysis can be impossible, or at least very difficult to program and therefore becoming expensive or unreliable.





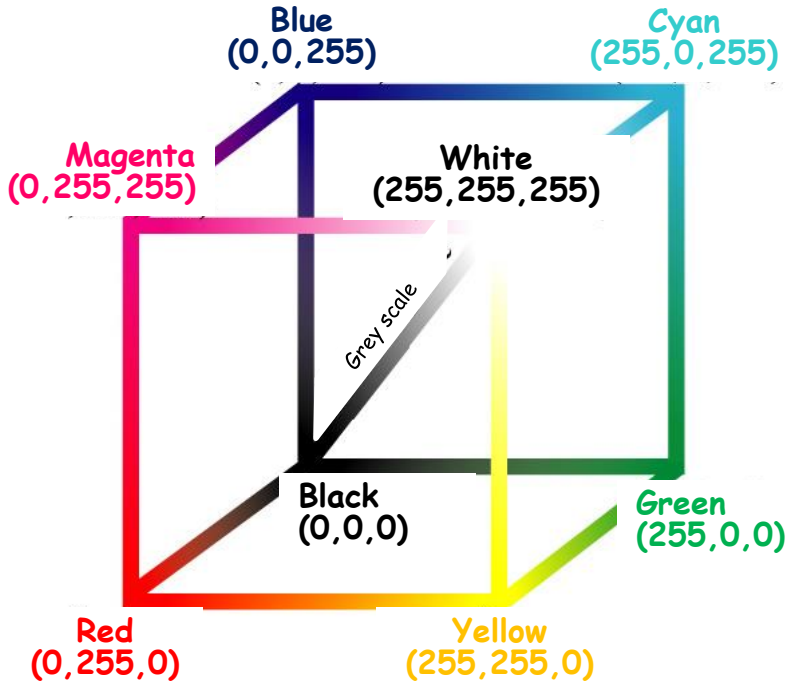
Digital image



Models describing colour in a digital image

RGB model

- *The combination of colours (Red, Green, Blue)* is used to describe all colours in a spectrum. The model might be imagined as a cube of the 3D system.

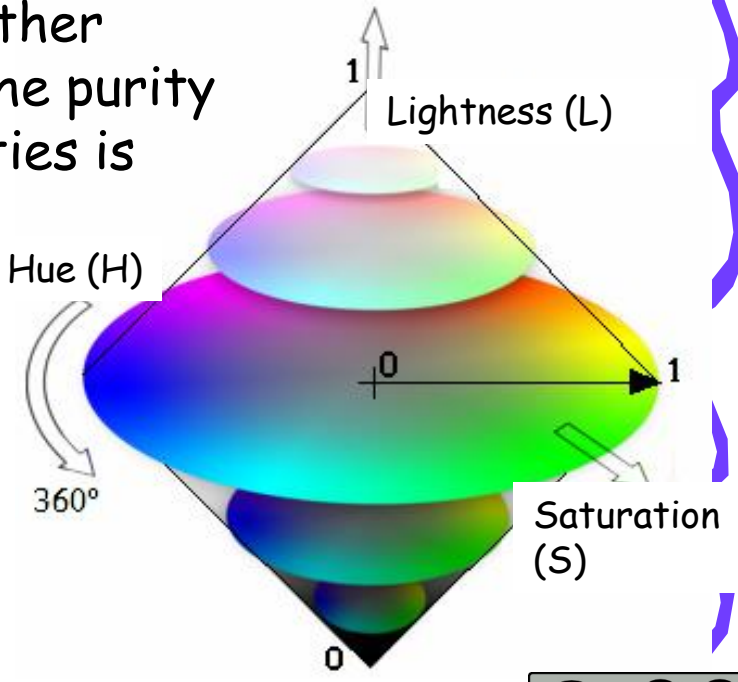


Models describing colour in a digital image

HSL model

Hue, Saturation and Lightness.

- **Hue** corresponds to the dominant wave length of the given colour.
- **Saturation** determines the addition of other colours of the spectrum, it represents the purity of the colour. The colour without impurities is fully saturated.
- **Lightness** describes the quantity of the white light in a given tinge.



27.05.2023

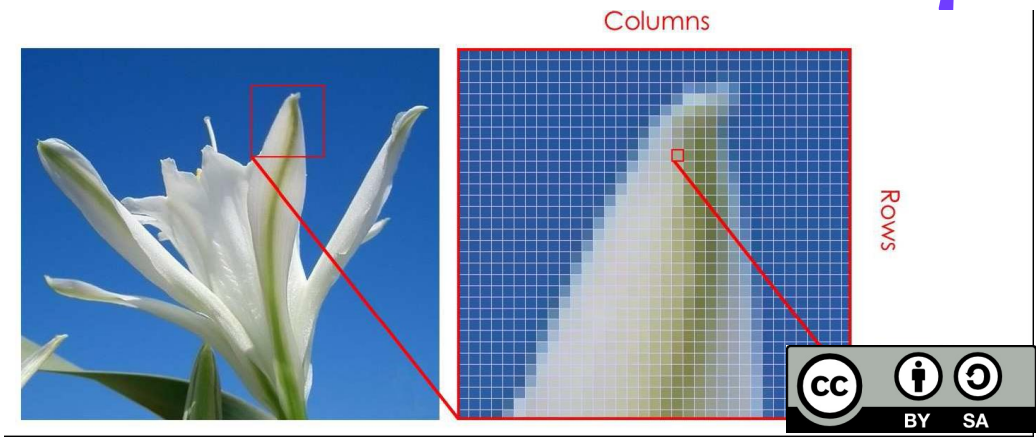
Principle of image analysis

Image analysis systems perform two main operations:

- the first one is obtaining of picture of a measured object
- and the second one is computer evaluation and measurement.

Capture and saving of images

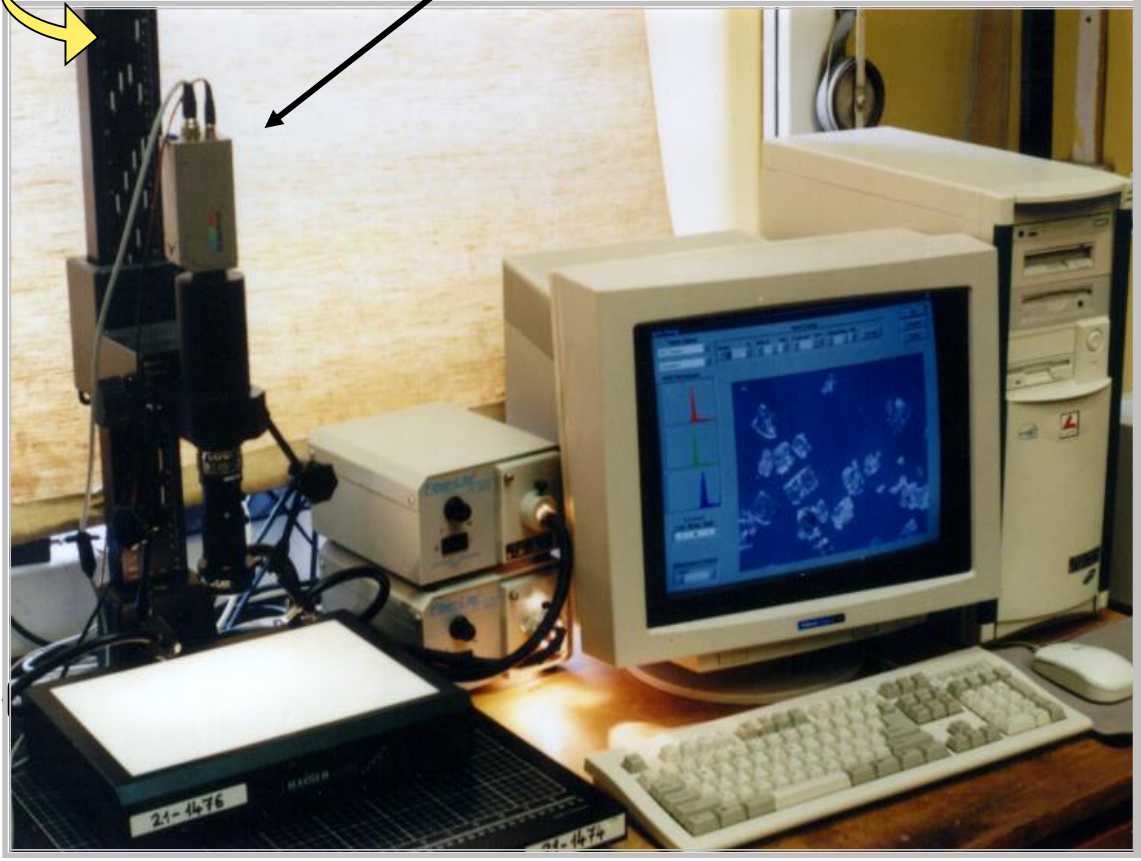
- raster formats jpg, bmp…
- the file contains information of every pixel
- the file size depends on image resolution and colour threshold
- resolution: how many dots are depicted per the length unit, dpi = dots per inch; 1 inch = 2.54 cm



Imaging system LUCIA G

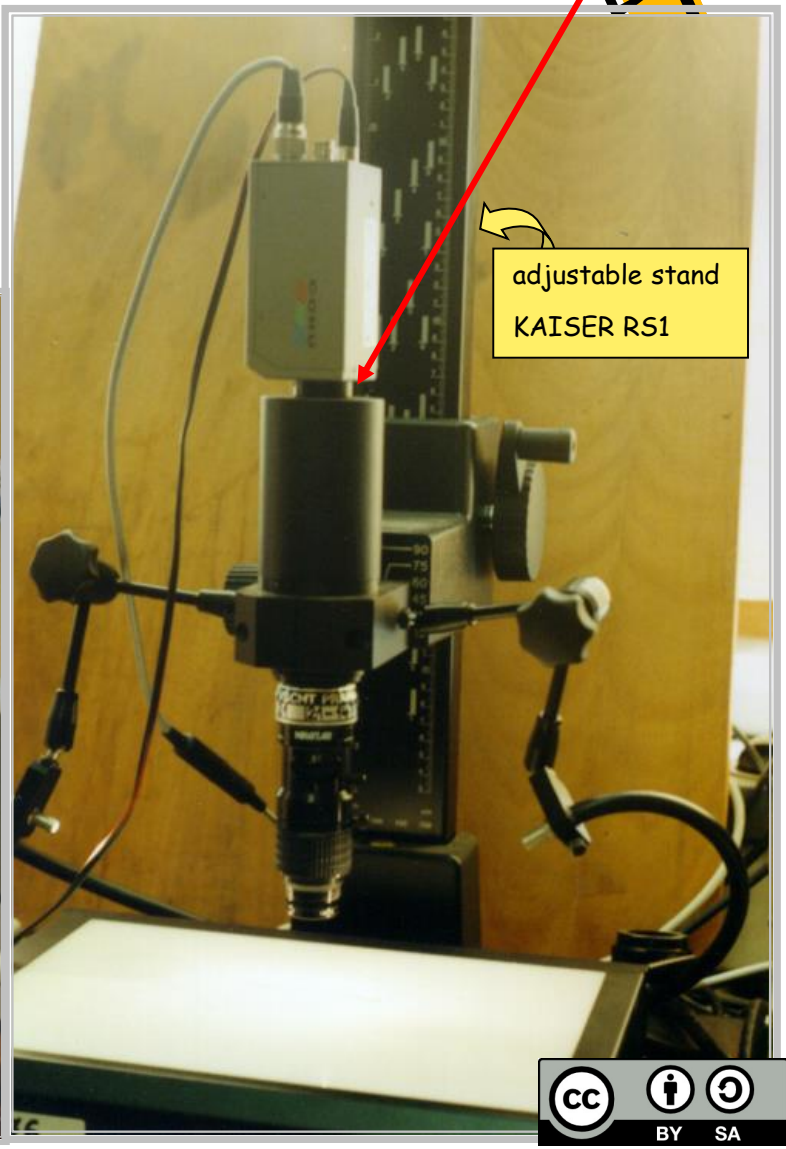
adjustable stand KAISER RS1

camera Cohu 2252 TV CCD



camera Cohu 2252 TV CCD

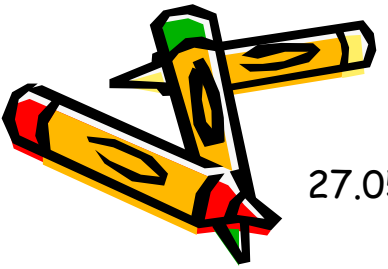
adjustable stand KAISER RS1



Optimal hardware components

- transparent or non-transparent objects/colour

The provision of correct and high-quality illumination, in many vision applications, is absolutely decisive. Traditionally, the two most common illuminates are fluorescent and incandescent bulbs, even though other light sources such as light-emitting diodes (LEDs) and electroluminescent sources are also useful.



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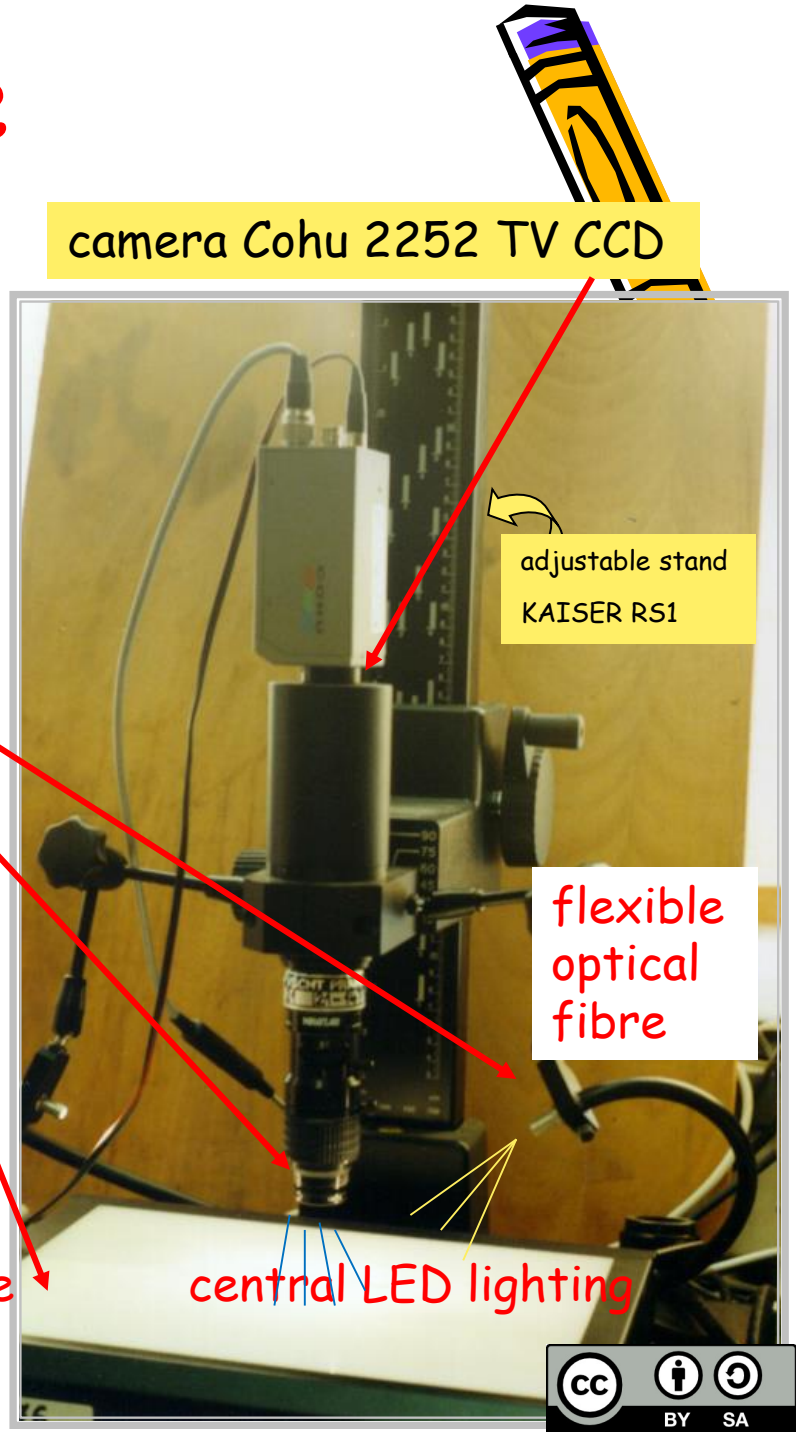


The choice of lighting

- lighting from above:
  - is used for analyses of materials in which we study the surface structure of particles or their colour separation,
- lighting from below:
  - is used for analyses of the shape and size of particles or for frequency (number) determinations,
- lateral lighting:
  - is useful for structure or texture studies – e.g. crystals,
- scanner.

Image analysis system

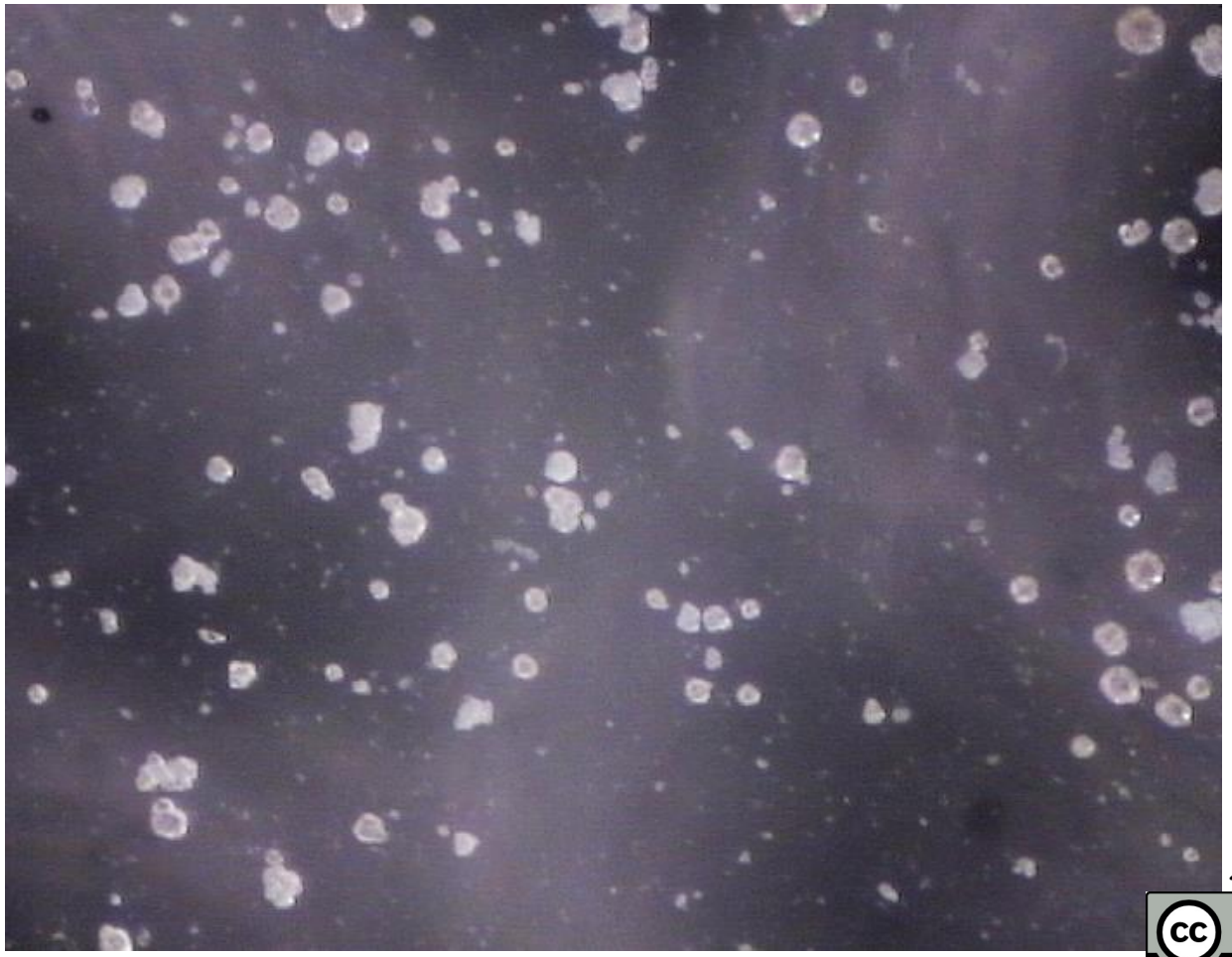
- NIS – ELEMENTS V5.2 imaging system (Laboratory Imaging Ltd., Prague, Czech Republic) with a Imagingsourse digital colour camera (DFK 33UX250, 5 MPix, 2448 x 3038) placed on an adjustable stand

Main tasks in raster image processing

- saving of images and data,
- colour balancing,
- image segmentation and object detection,
- geometrical and morphological operations,
- statistical analysis of the image information,
- frequency analysis,
- texture classification.

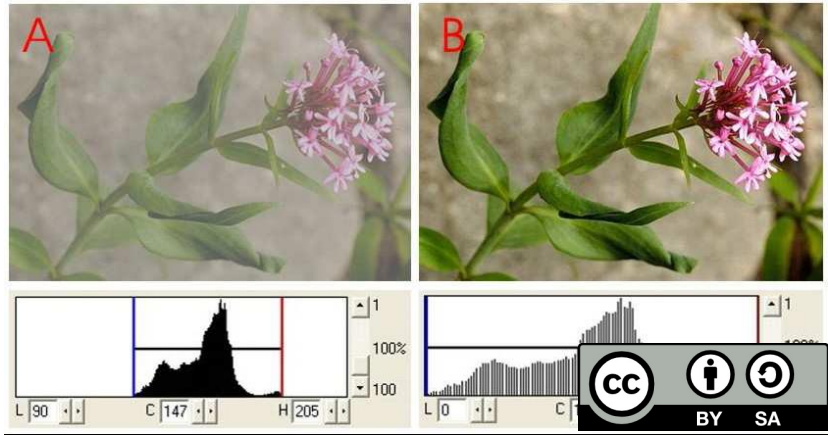
Monitor - microphotography

for **scanned objects** of carbonation mud/live image



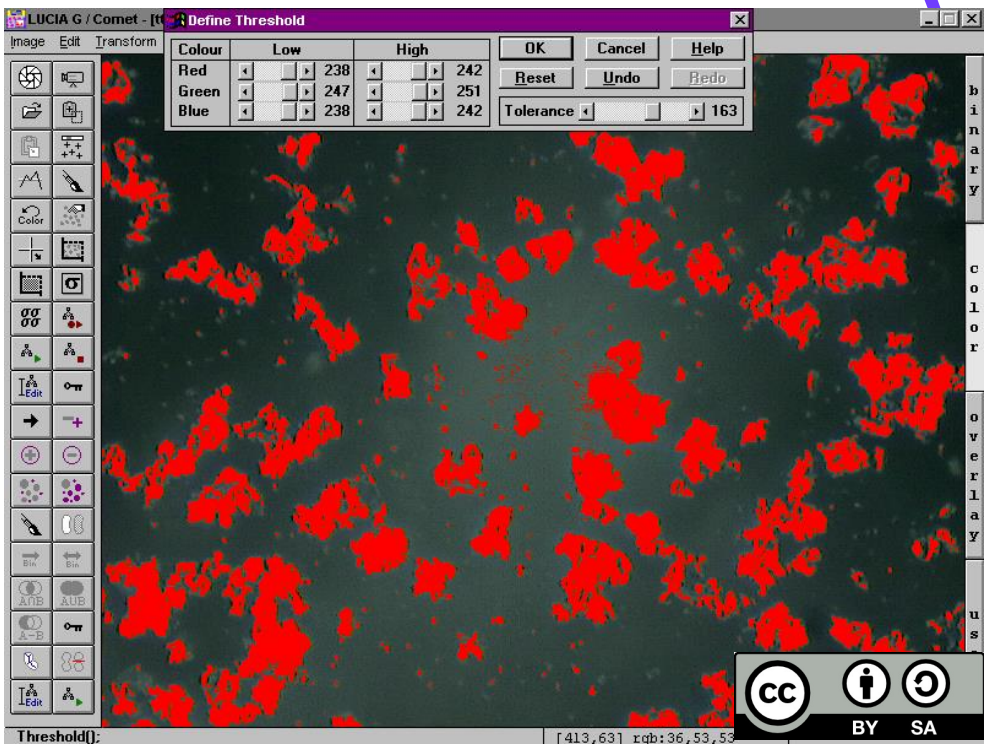
Contrast enhancement

- Sometimes the captured image is not contrasted enough; in other words, the intensity values of the image are restricted to a small range of intensity levels, and thus pixels with different intensity values are not well distinguished from each other



Segmentation, tresholding

- The most important process in the transformation of an image from the pre-elaboration to its measurement (or of one or more parts of it), is *segmentation*. It is a crucial step that allows to reduce images to information, dividing the image into regions and distinguishing the objects of interest.
- In the thresholding-based segmentation the image is partitioned into two classes using a single value, called bi-level tresholding, or in multiple classes using multiply level values, called multilevel tresholding.



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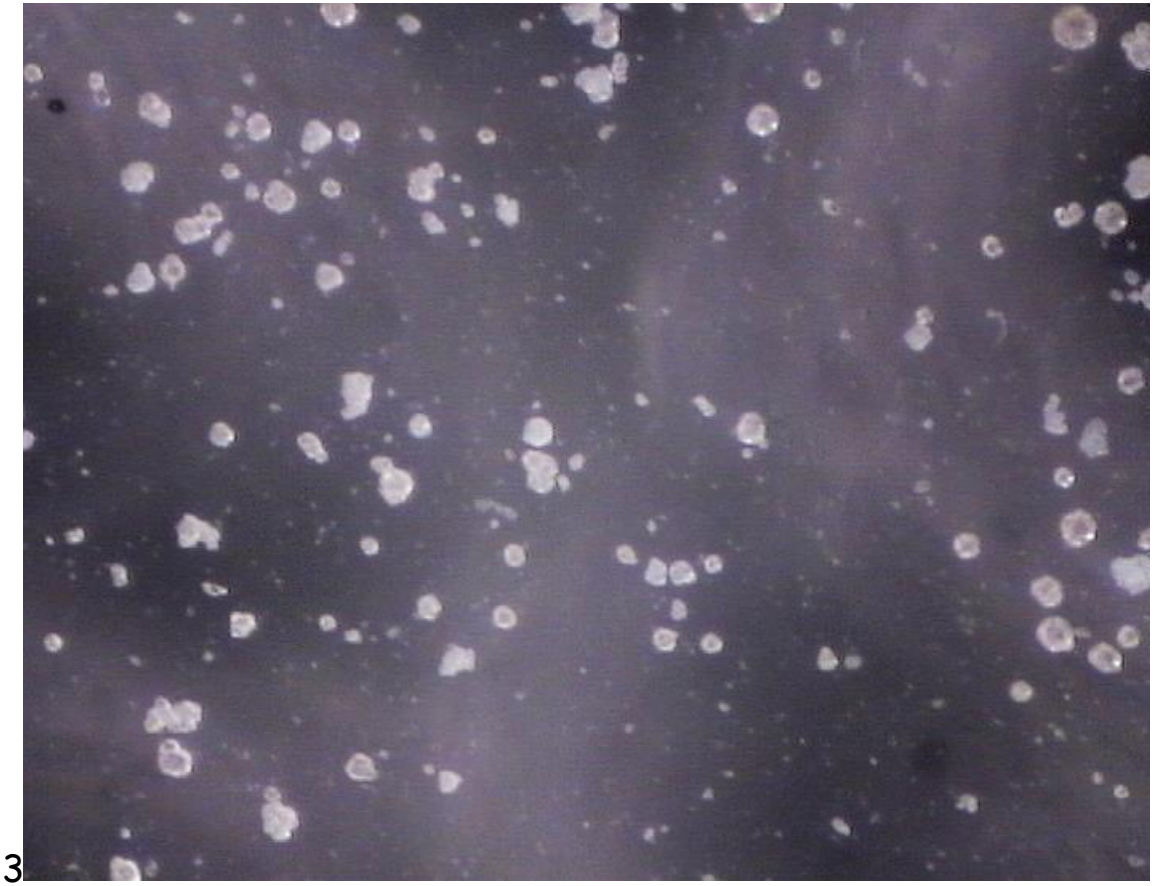
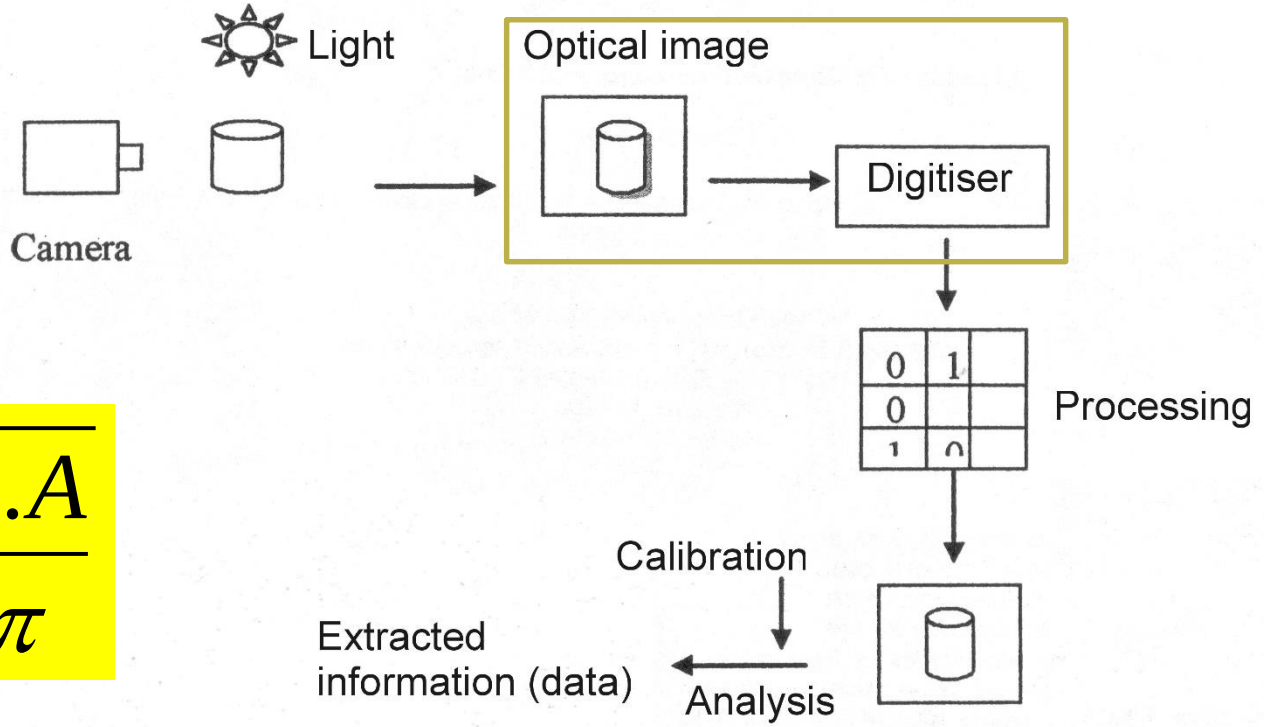
Evaluation of small particles

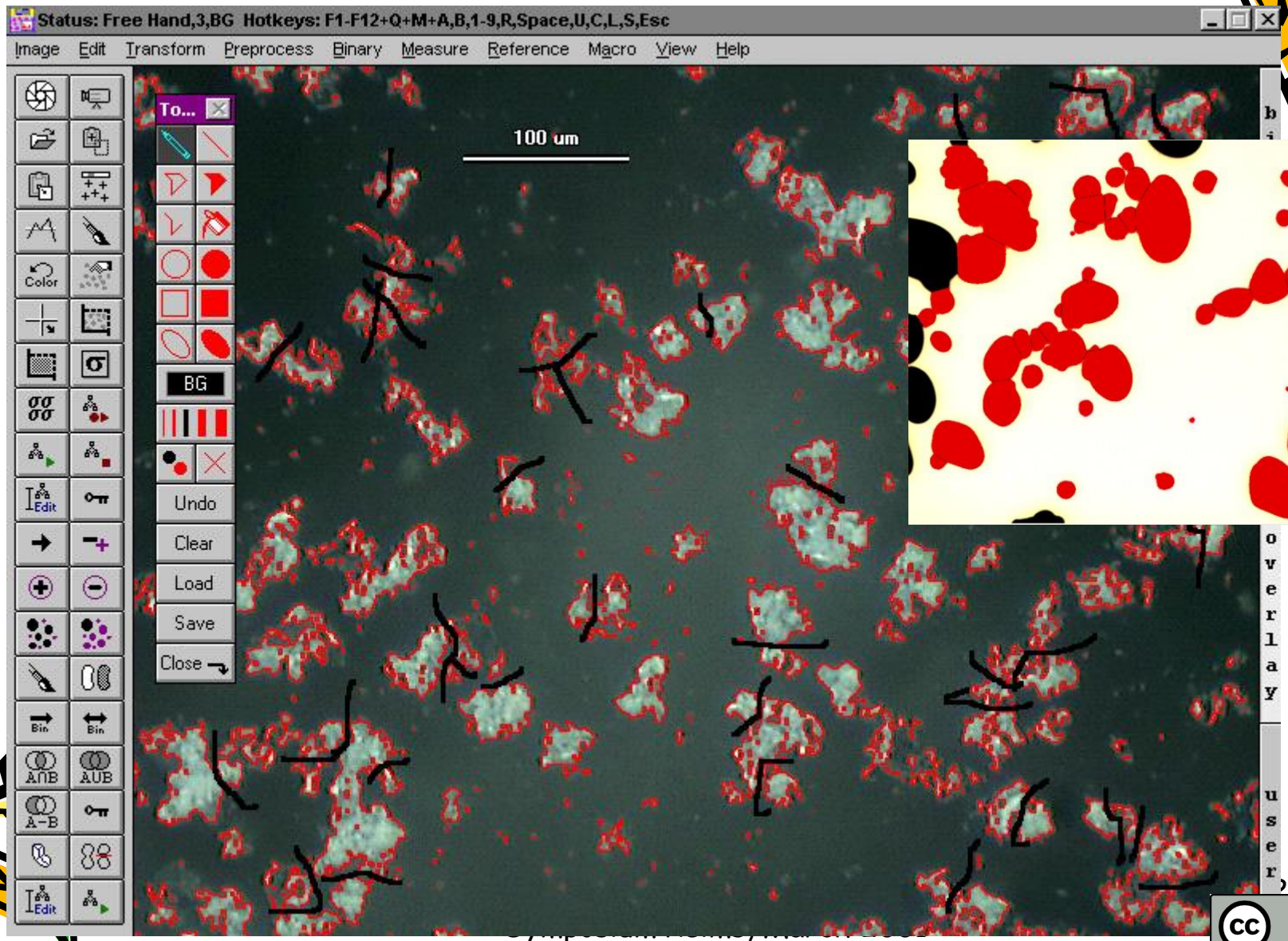


Principles of image analysis in particle size measurement

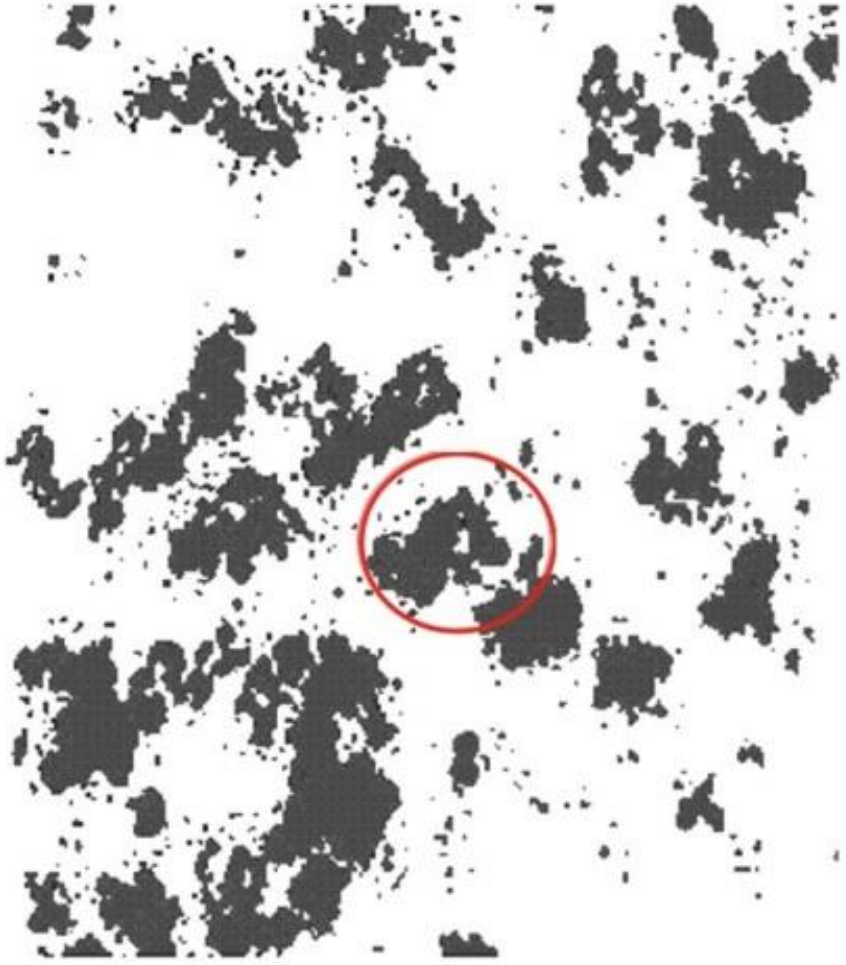


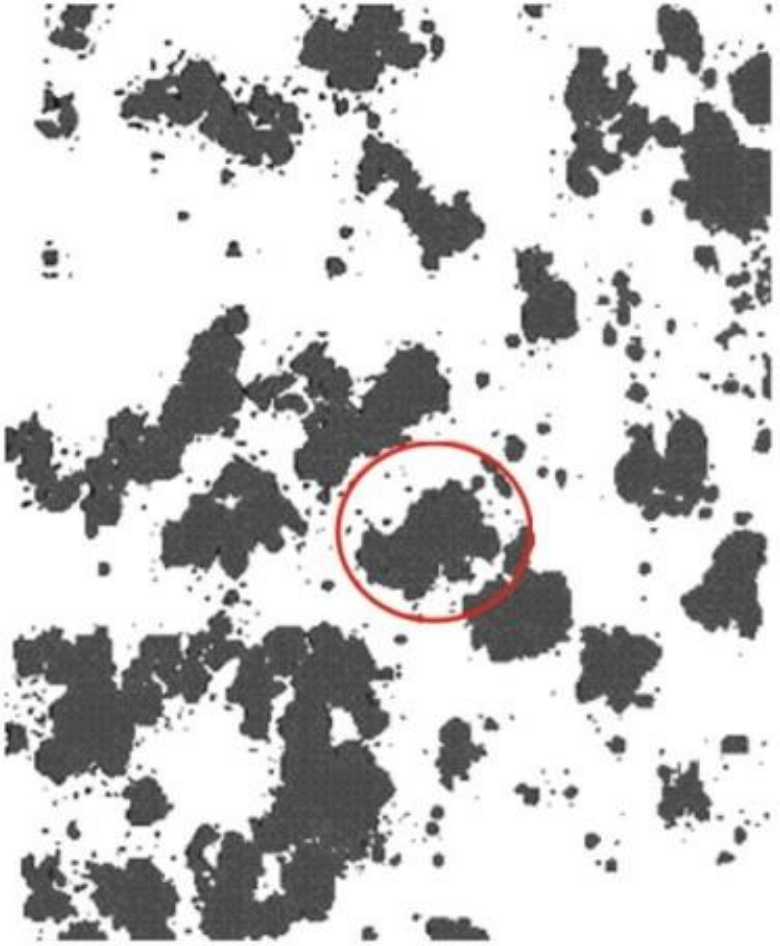
$$d_e \equiv \sqrt{\frac{4.A}{\pi}}$$

Binary edition after contour



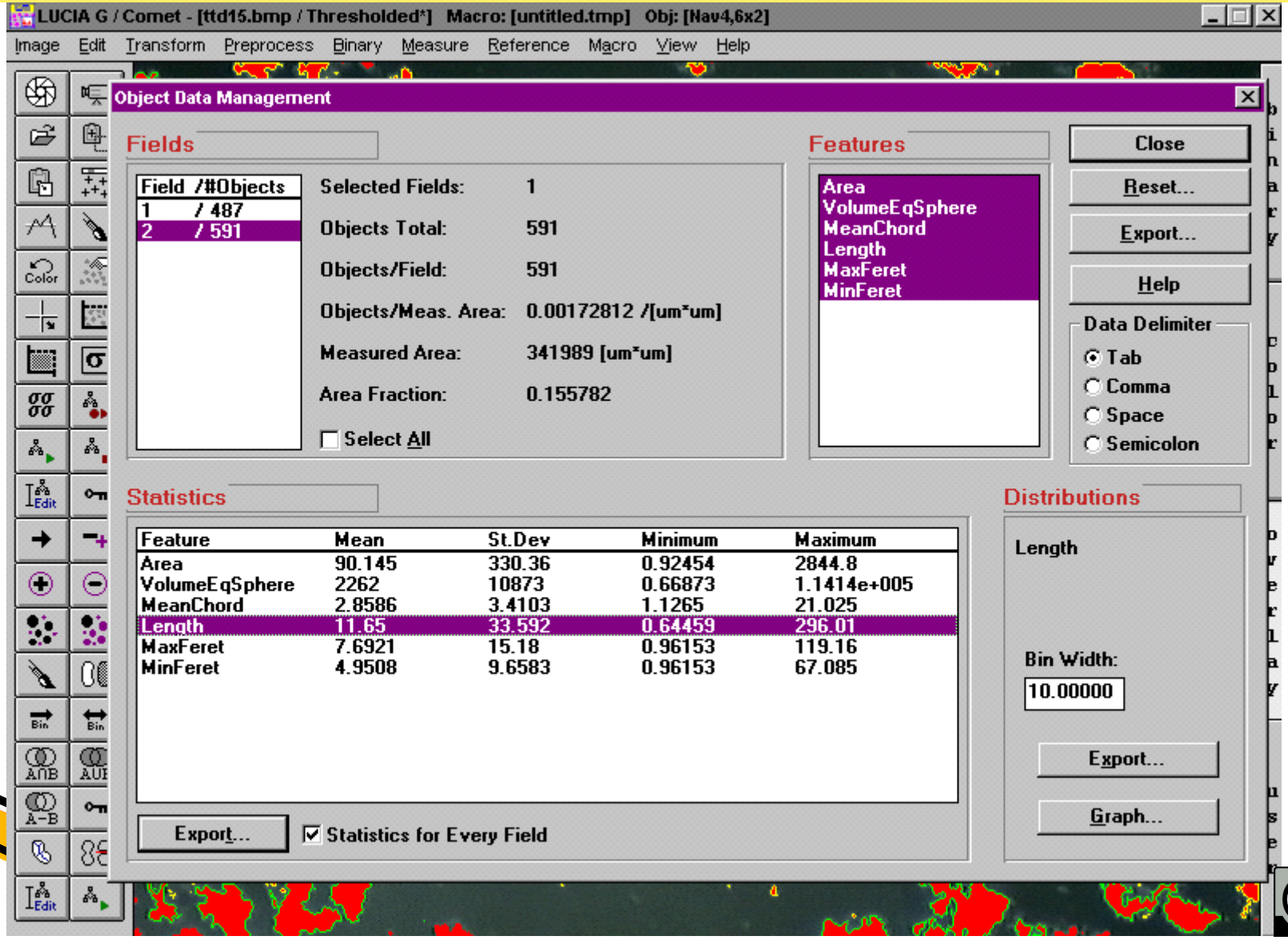
Fill holes



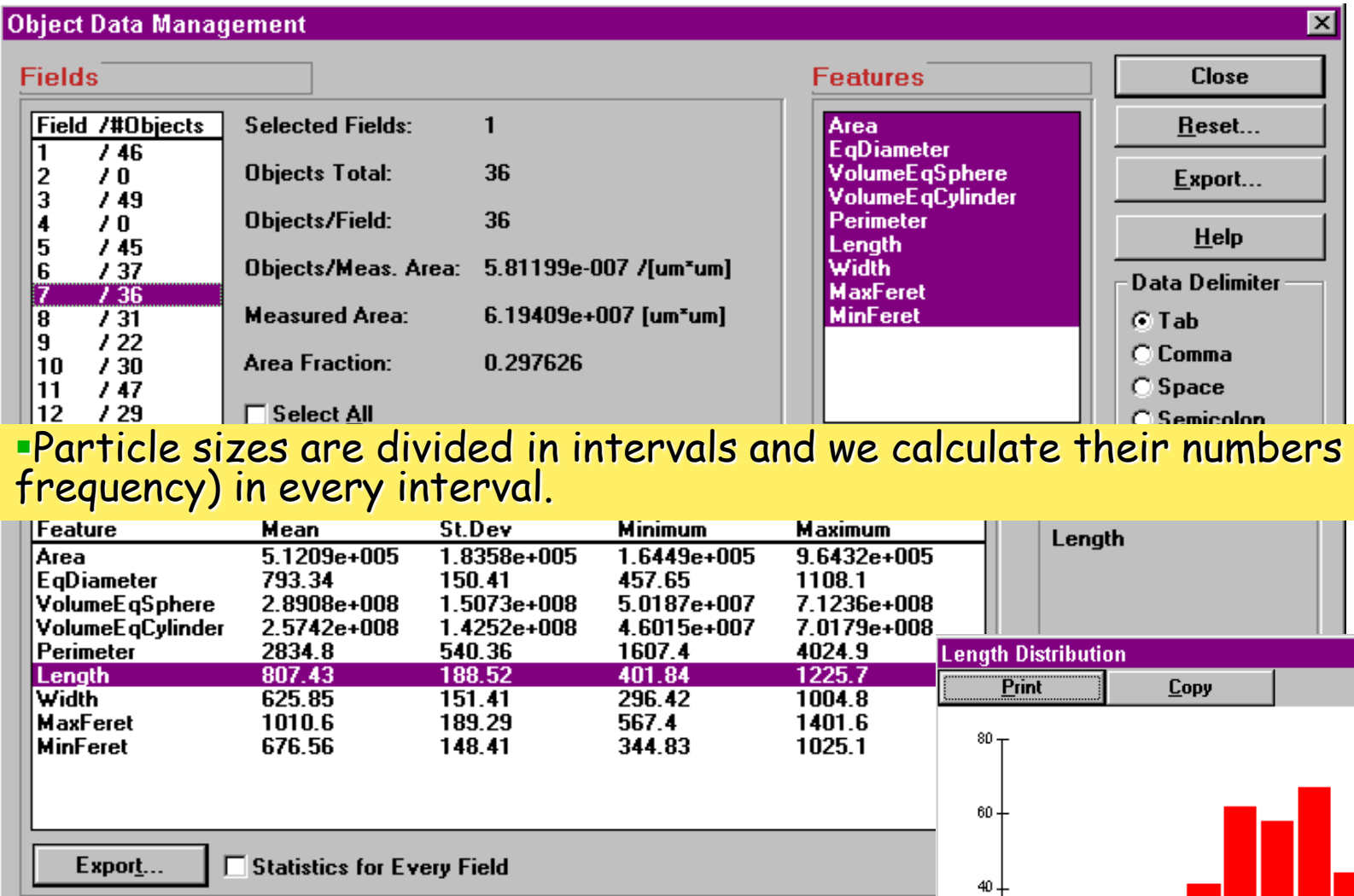


Object Data Management

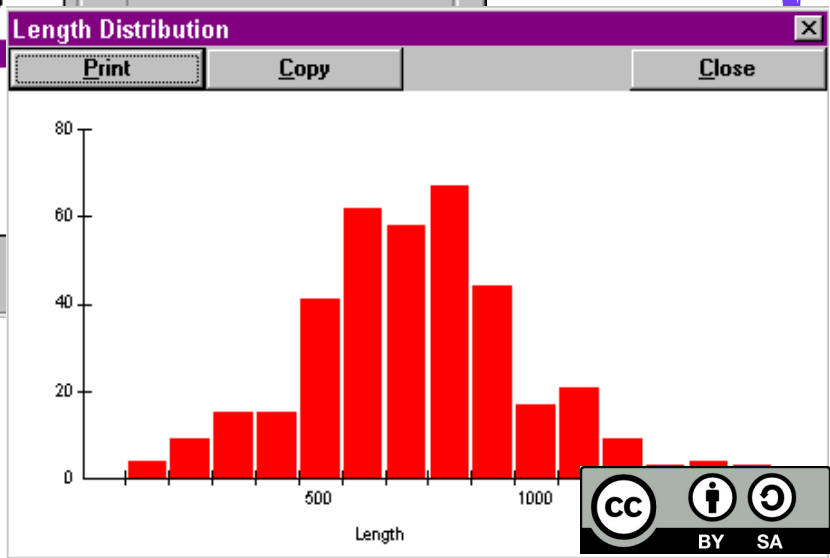
All results are processed and statistically evaluated. The program calculates basic characteristics – mean value, standard deviation, minimal and maximal value.



Crystal size distribution: Results of CSD



- Particle sizes are divided in intervals and we calculate their numbers (i.e. frequency) in every interval.

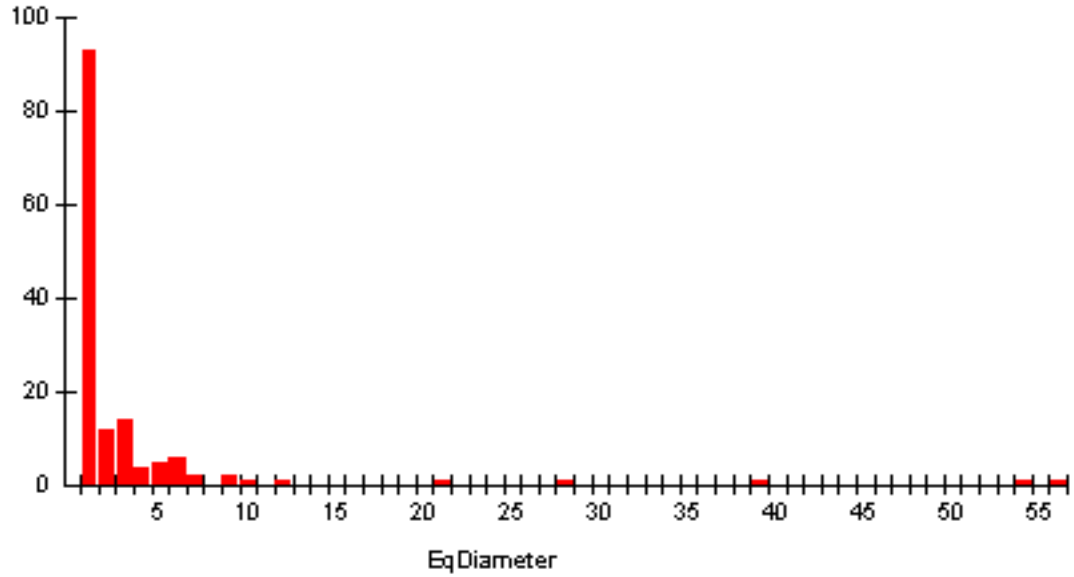


Outputs from the image analysis system

Projected area	(A) measured
Equivalent diameter	$d_e \equiv \sqrt{\frac{4.A}{\pi}}$
Perimeter	(o) measured
Circularity	Cir = 4π . A / o^2

Maxferet	(L) measured
Minferet	(w) measured
Aspect ratio (Elongation)	E = L / w
Eccentricity	$e = \sqrt{1-(w/L)^2}$

Histograms



•Data in these frequency histograms can be used for next statistic evaluation, because simple statistics is usually not sufficient. We obtain histograms to create a wider histogram for every suspension and calculate the total size particle distribution.

•Except this type of histogram, we also created histograms where instead of frequency we evaluated a volume fraction for every size interval. This type of histogram is analogous if we sieve the particles and weight the separate sieve fractions, of course, when solids are homogenous. The volume fraction is equal to the mass fraction then.

A histogram of volume fractions in a sample of suspension from a sugar factory

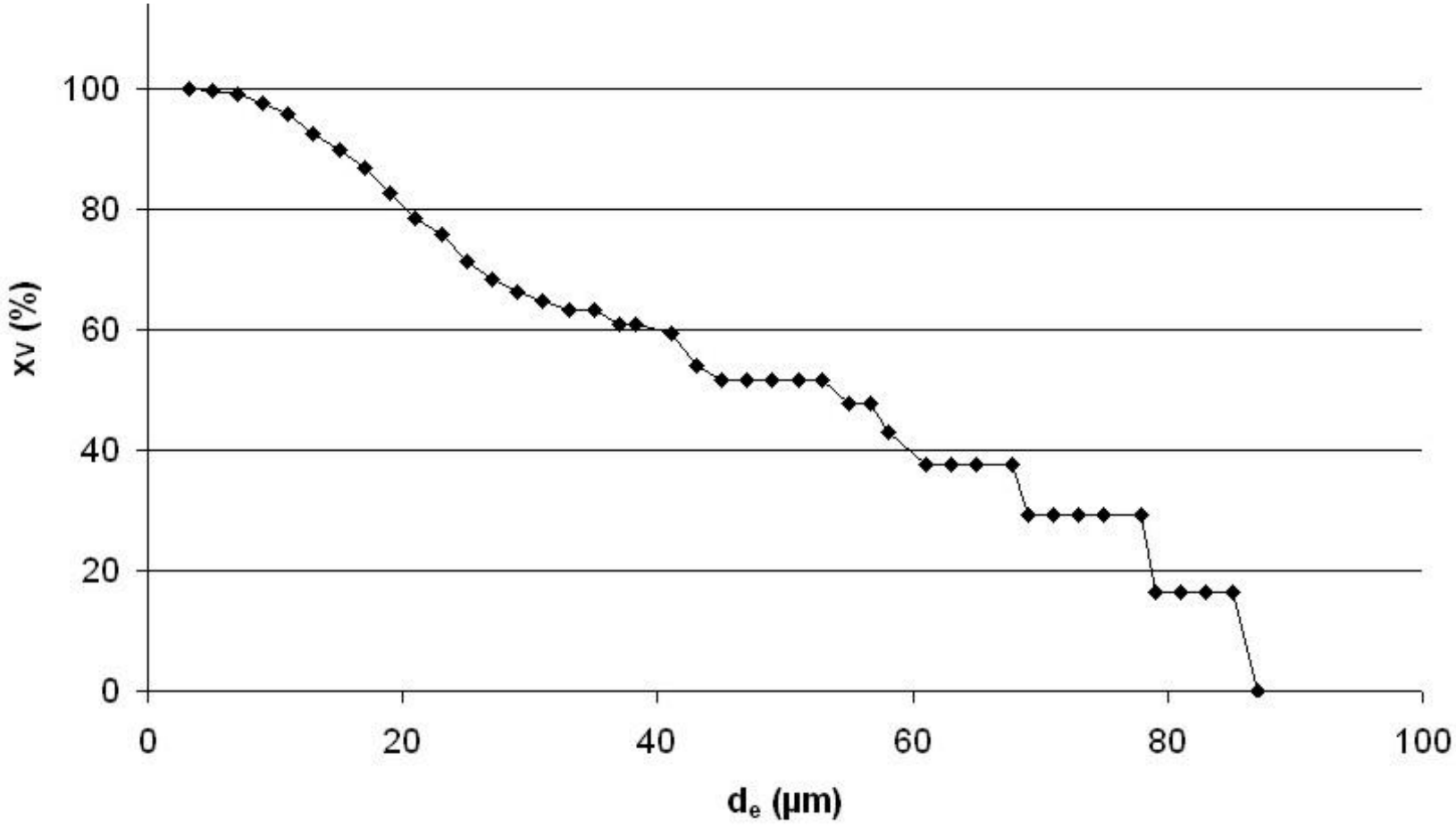
Legend:

—o— carbonation slurry concentrate from filters Diastar,

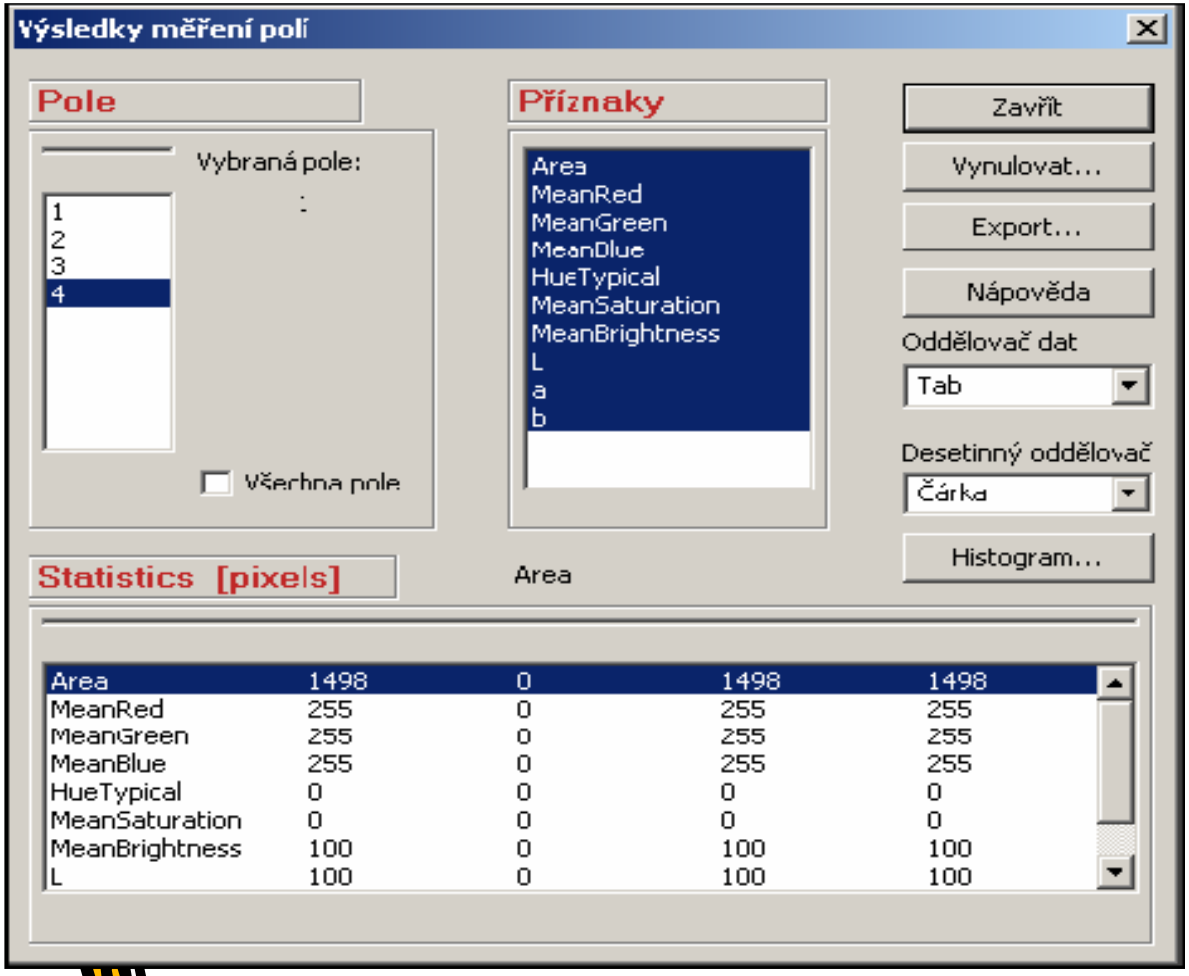
—■— 1st carbonation juice

$$g_i = \frac{x_{Vi}}{\Delta d_e}$$

A cumulative distribution curve for solid carbonation mud (—♦—)



Colour evaluation



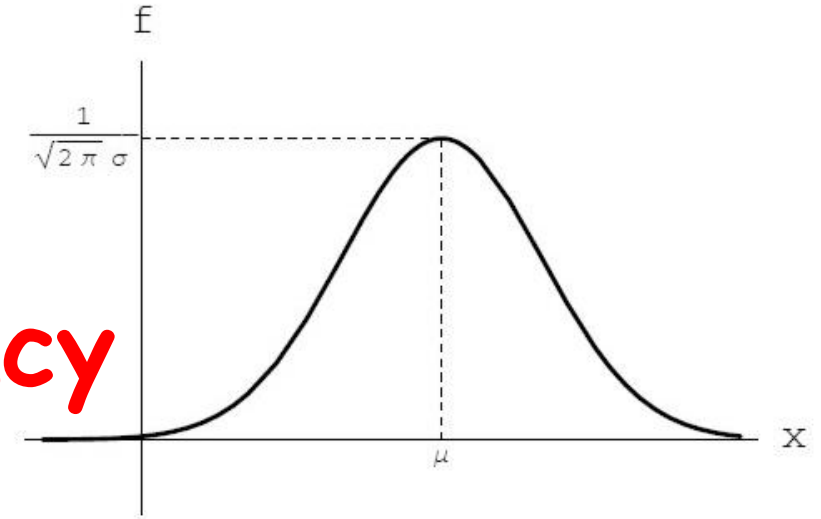
Two distribution models

- Normal distribution function for volume fraction $x_V(A)$
- Log-normal distribution function for particle frequency (B) - by calculating of χ^2, where the statistic probable values of frequency (or volume fraction) are computed according to:

$$\chi^2 = \sum_j^k \frac{(n_j - np_j)^2}{np_j},$$

where n_j is the frequency (or volume fraction), n_{pj} is the theoretical (expected) frequency (or volume fraction).

Theory of calculation of expected frequency



The normal probability distribution is defined by the equation:

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} \quad pro \quad -\infty < x < \infty,\ \sigma > 0,\ \mu \in \mathbf{R}.$$

where, η and σ are the mean and standard deviation of the random variable x.

The log-normal probability distribution is defined by the equation:

$$f(x) = \begin{cases} \frac{1}{\sqrt{2\pi}\sigma} \cdot \frac{1}{x} e^{-\frac{1}{2}\left(\frac{\ln x - \mu}{\sigma}\right)^2} & for\ x > 0 \\ 0 & otherwise \end{cases}$$

Calculation of expected frequency - theory

Probability density of a random variable with standard normal distribution is a function:

$$\varphi(x) = \frac{1}{\sqrt{2\pi}} e^{-\frac{x^2}{2}} \quad pro \quad -\infty < x < \infty$$

and the form of the distribution function is

$$\Phi(x) = \int_{-\infty}^{x} \frac{1}{\sqrt{2\pi}} e^{-\frac{t^2}{2}}\, dt, \quad x \in \mathbf{R}$$

Calculation of expected frequency - theory

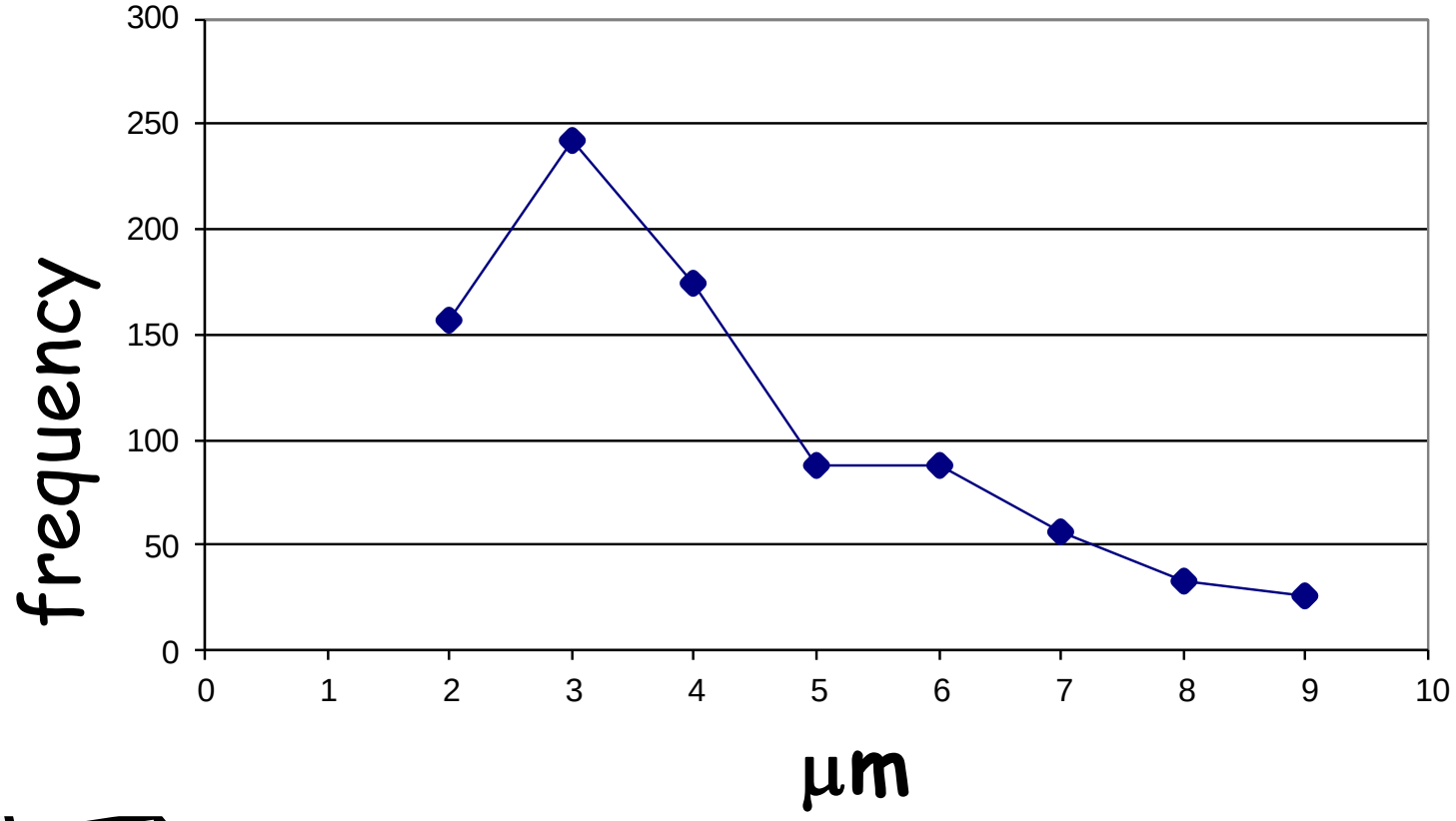
The probability of the frequency in a given interval is:

$$P: \quad d_{e\,j} \in (d_{e\,j} - \Delta d_e;\ d_{e\,j} + \Delta d_e) = \Phi\left(\frac{de\,j + \Delta de - \bar{d}_e}{s}\right) - \Phi\left(\frac{de\,j - \Delta de - \bar{d}_e}{s}\right)$$

Goodness of the fit test for normality:

$$\chi^2 = \sum_j^k \frac{(n_j - np_j)^2}{np_j}$$

Example



Example

$$P: d_{e\,j} \in (d_{e\,j} - \Delta d_e;\ d_{e\,j} + \Delta d_e) = \Phi\left(\frac{de\,j + \Delta de - \bar{d}_e}{s}\right) - \Phi\left(\frac{de\,j - \Delta de - \bar{d}_e}{s}\right)$$

Bins		2	3		5	6	7	8	9	…
ln bins		0,693147	1,098613		9438	1,791759	1,94591	2,079442	2,197225	…
de		2,6	3,5	4,	5,5	6,5	7,5	8,5	9,5	…
ln de		0,956495	1,252763	1,5040	,704748	1,871802	2,014903	2,140066	2,251292	…
frequency		157	242	174	88	88	56	33	26	…
%		16,6		18,4	9,3	9,3	5,9	3,5	2,8	
1st fraction		-0,9712	37797	0,082214	0,458214	0,776117	1,051498	1,294401	1,511685	…
2nd fraction		-1,80744	-0,97126	-0,37797	0,082214	0,458214	0,776117	1,051498	1,294401	…
fi1		0,16602	0,35197	0,46812	0,67724	0,7823	0,85314	0,90147	0,93448	…
fi2		0,03515	0,16602	0,35197	0,53188	0,67724	0,7823	0,85314	0,90147	…
P*100		13,087	18,595	11,615	14,536	10,506	7,084	4,833	3,301	…

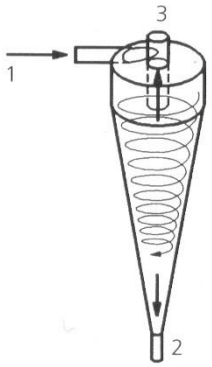
Goodness of the fit test for normality:

$$\chi^2 = \sum_j^k \frac{(n_j - np_j)^2}{np_j}$$

Bins	2	3	4	5	6	7	8	9 …
ln bins	0,693147	1,098612	1,386294	1,609438	1,791759	1,94591	2,079442	2,197225 …
de	2,6	3,5	4,5	5,5	6,5	7,5	8,5	9,5 …
ln de	0,956495	1,252763	1,504077	1,704748	1,871802	2,014903	2,140066	2,251292 …
frequency	157	242	174	88	88	56	33	26 …
%	16,6	25,6	18,4	9,3	9,3	5,9	3,5	2,8
1st fraction	-0,97126	-0,37797	0,082214	0,458214	0,776117	1,051498	1,294401	1,511685 …
2nd fraction	-1,80744	-0,97126	-0,37797	0,082214	0,458214	0,776117	1,051498	1,294401 …
fi1	0,16602	0,35197	0,46812	0,67724	0,7823	0,85314	0,90147	0,93448 …
fi2	0,03515	0,16602	0,35197	0,53188	0,67724	0,7823	0,85314	0,90147 …
P*100	13,087	18,595	11,615	14,536	10,506	7,084	4,833	3,301 …

test of normal distribution merged intervals:											
%	16,6	25,6	18,4	9,3	9,3	5,9	6,3	8,5		f	test. chí^2
P*100	13,087	18,595	11,615	14,536	10,506	7,084	8,134	6,549			
chí^2	0,960	2,666	4,001	1,870	0,133	0,187	0,436	0,566	10,820	5	11,071

the distribution is log-normal for significancy 0,05

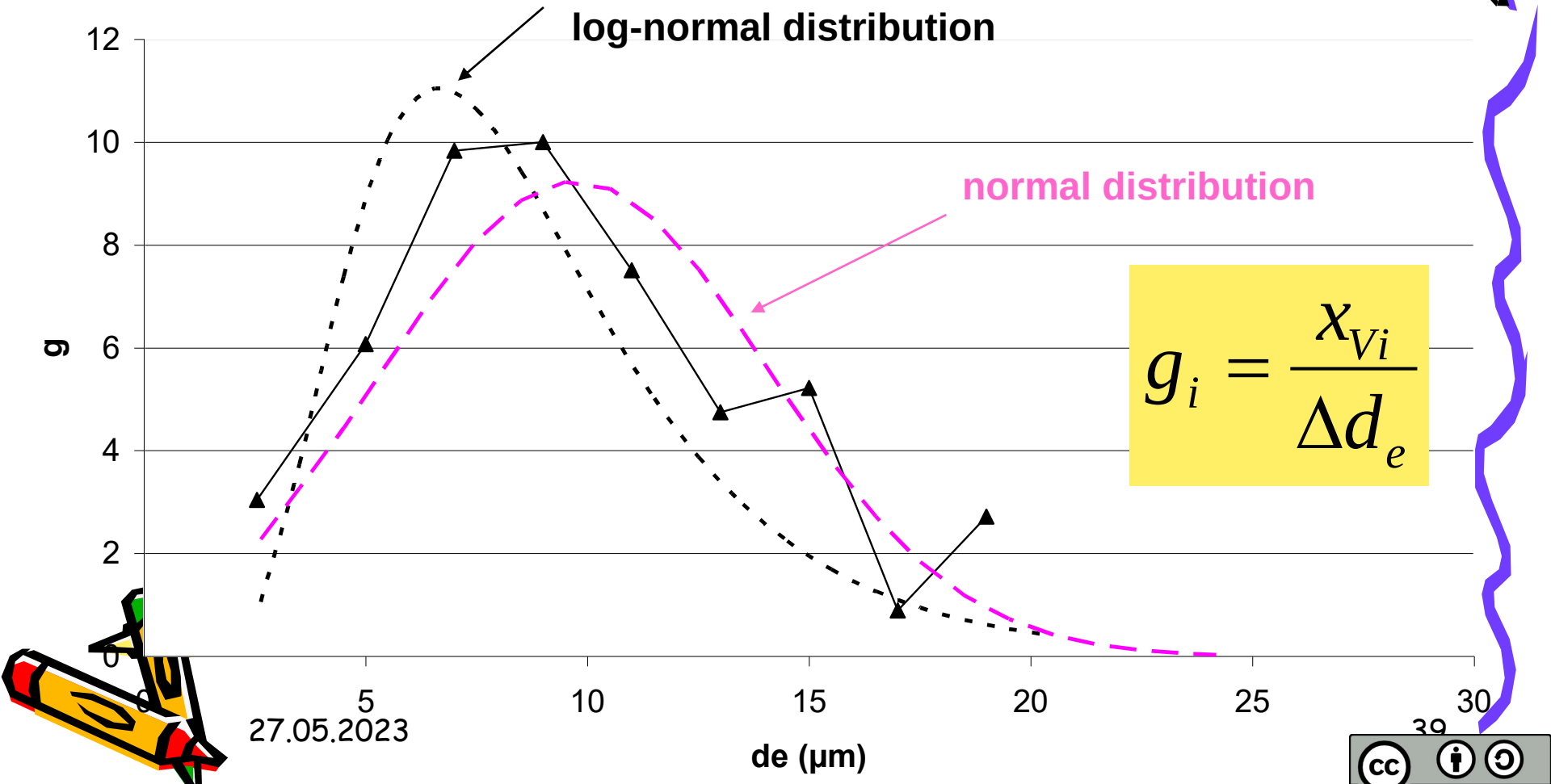


Statistic parameters for distributions A and B, significance α = 0.05

	Distribution A				Distribution B			
Suspension	Mean d_e	Standard deviation d_e (σ)	χ^2	Criterion χ^2	Mean ln d_e	Standard deviation ln d_e (σ)	χ^2	Criterion χ^2
1. sample C	15.3	7.9	14.82	15.50	1.570	0.485	6.72	11.07
1. sample D	9.7	4.3	5.80	16.91	1.506	0.438	7.86	11.07
1. sample E	25.4	17.0	22.84	12.59	1.644	0.525	6.00	5.99
2. sample C	55.9	65.9	161.45	15.50	1.460	0.562	26.52	11.07
2. sample D	20.4	13.1	21.41	14.06	1.376	0.536	32.20	9.48
2. sample E	32.8	26.5	20.76	7.81	1.410	0.560	30.04	11.07

- ✓ **Both hypotheses of A and B distributions are suitable for the suspensions C and D;**
- ✓ **Any of these distributions do not agree with data of the suspension E.**

1st sample of the suspension D



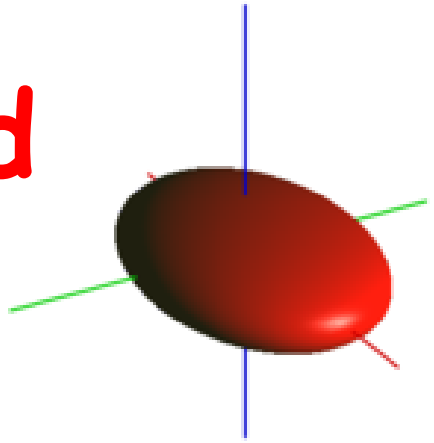
$$g_i = \frac{x_{Vi}}{\Delta d_e}$$

Image analysis of larger objects

Bigger objects (e.g. grains):

- usually lower quantity of objects
- in some cases there is a need to measure 3D

General triaxial ellipsoid



Volume: $V = \frac{4}{3}\pi abc$,

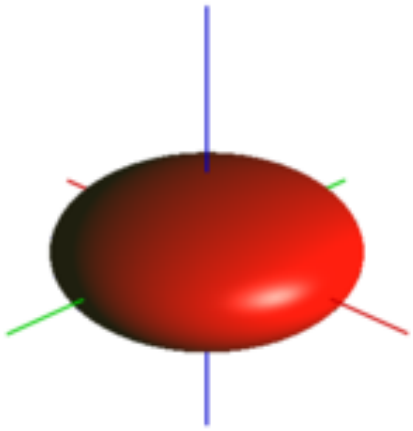
Surface: $S = 2\pi c^2 + \frac{2\pi b}{\sqrt{\left(a^2 - c^2\right)}}\left[c^2 F\left(k,\varphi\right) + \left(a^2 - c^2\right)E\left(k,\varphi\right)\right]$

where a, b, c (a>b>c) are the lengths of half-axes of the ellipsoid,

$$F\left(k,\varphi\right) = \int_0^{\varphi} \frac{d\psi}{\sqrt{\left(1 - k^2 \sin^2\psi\right)}} \qquad k = \frac{a}{b}\sqrt{\frac{b^2 - c^2}{a^2 - c^2}}$$

$$E\left(k,\varphi\right) = \int_0^{\varphi} \sqrt{\left(1 - k^2 \sin\psi\right)}\, d\psi \qquad \varphi = \arccos\frac{b}{a}$$

Oblate spheroid



Volume: $V = \frac{4}{3}\pi a^2 b$

Surface: $S = 2\pi\left(a^2 + \frac{b^2}{2\varepsilon}\ln\left(\frac{1+\varepsilon}{1-\varepsilon}\right)\right)$

$$\varepsilon = \frac{\sqrt{a^2 - b^2}}{a}$$

where a, b are the lengths of half-axes of the spheroid and ε is the eccentricity of the eclipse

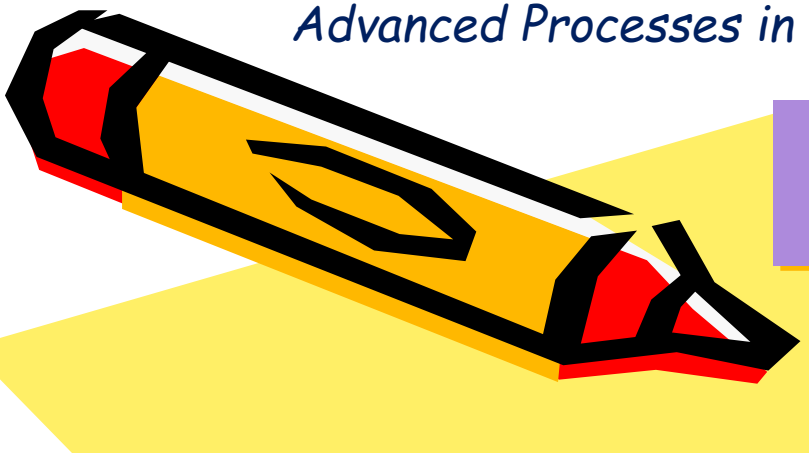


Image analysis

Applications of image analysis in agriculture and food industry

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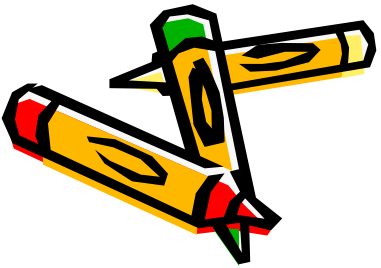
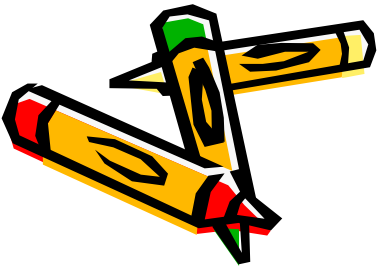


Information sources

http://sch.vscht.cz/vyuka/international-students/erasmus-students/

Databases: ScienceDirect, Scopus, Web of Science



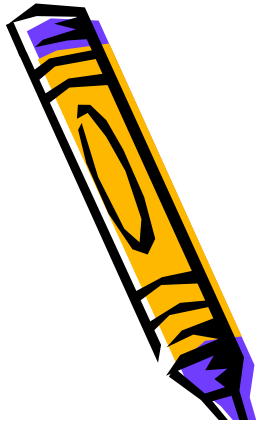
Food industry

- Shape analysis;
- Size measurement;
- Colour measurement;
- Texture analysis;
- Inspection process.

Uses of image analysis in food industry and agriculture

- Evaluation of the quality and grading of food;
- Evaluation of mixing;
- Evaluation of crystallization;
- Separation and aggregation processes;
- Evaluation of food texture and microstructure;
- Varietal classification or morphometric characterisation of grain;
- Evaluation of seedling infection.

Examples of image analysis and machine vision applications in food industry



Agriculture and packaging of food:

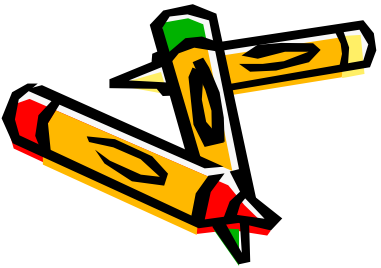
- Quality evaluation of fruit,
- Sorting potatoes,
- Assessing the quality of cereals (wheat, rice, corn...),
- Precise agriculture.

Food industry:

- Quality evaluation of meat;
- Sugar industry (reception of sugar beet, microcrystals as a seed for crystallization, aggregation, dissolving or separation of carbonation mud particles using hydrocyclones or clarifiers, etc.);
- Starch industry (identification of starch origin);
- Assessing the quality of cereal products (bakery products, pasta);
- Assessing the quality of other foods (pizza, cheese, chips, French fries...);
- Application in other parts of the factory (e.g. wastewater treat

Agriculture

- Evaluation of the soil structure.
- Optimisation of sowing.
- The character of vegetation growing on the field
- Prediction of yields, estimation of the effect of weeds on the yield.
- Weed mapping to estimate herbicides dosing.
- Search for potatoes from a previous crop to prevent from the spread of mildew to newly seeded crops (e.g. sugar beet).
- Determination of the Leaf area index (LAI), if LAI = 100% then the maximum seasonal growth.
- Determination of the chlorophyll content in leaves.



Sorting potatoes

- Automated inspection stations for machine vision grading of potatoes on size and shape have been reported.
- Potato-packaging industry – in a successful use of the machine vision system, defects such as greening, cracks, common scab and rhizoctonia must be detected.

Qualitative evaluation of fruit

- **Apples**

- The grading of an apple by using a computer vision begins by acquiring an image and finishes with evaluation of the fruit's quality after the different objects have been characterized by features such as their shape or their colour in order to recognize the defects.
- The shape can be evaluated by Fourier descriptors, with which the fruits are graded with an error rate of 6 % using linear discriminant analysis. To grade bi-colour fruits according to their colour, the blush has to be distinguished from the ground colour.
- Defects can be observed because of their different luminance compared with the surrounding sound tissue.
  - *Grading machines* – a simple camera or a camera and a mirror, 2 cameras; ligting tunel; rolling cylinders.
  - *Evaluation of surface defects* – fungi (mold), damage from insects or birds, mechanical damage, frozen fruit, sunburnt - different brightness.

Qualitative evaluation of fruit

- **Apples**

  Each apple presents two areas – the calyx and the stalk – which are not defects but may represent similar aspects. Consequently, these areas have to be recognized before or after image segmentation.

Qualitative evaluation of fruit

- **Citruses**

✓ Citrus fruits present rounded surfaces that make it difficult to inspect the boundary of each fruit in the images and to perform an accurate measurement of the commercial size. Following detection of a blemish, the next step is identification. It is essential to know whether a blemish only affects the appearance of the fruit, or whether it can progress to the point where it damages the whole piece or contaminates other fruit. As a complement to the citrus inspection line, citrus pre-grading lines are sometimes included. On these lines, the fruits are sorted by colour and then they are transported to de-greening rooms.

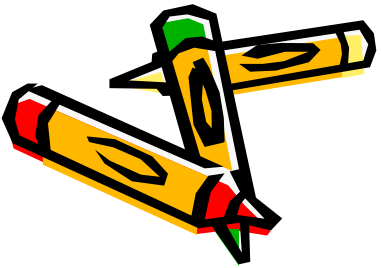
✓ *Lighting*: it is necessary to solve problems connected with higher velocity (flow) through the processing line – shades (dispersed light is used), contact of fruits.

Qualitative evaluation of fruit

- **Strawberries**
- Grading strawberries according to external quality parameters such as size and shape can be easily implemented using common colour cameras.
- Early studies were performed evaluating the feasibility of using colour machine vision and near-infrared imaging to detect bruises on strawberries.
  - Potential faecal contamination (in the field).

Quality assessment of olives

- *Evaluation of surface defects* – such as cracks, splits, stains, skin damage, hail damage, ripped or crushed fruit, presence of stalks, atypical colour, or softness.
- *Sorting* - it is necessary to minimise the contact between olives.

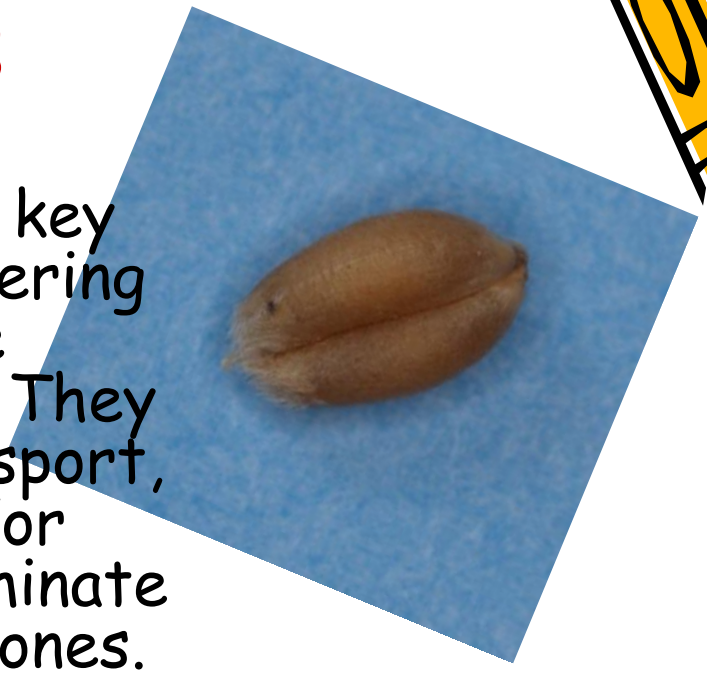


Assessing the quality of seeds

• Cereal quality assessment

- ✓ Substantial work dealing with the use of morphological (size and shape) features for classification of different grain species, classes, varieties, damaged grains and impurities has been reported in the literature. A few investigations with selected clean samples have been carried out using colour features; only limited research has been reported based on the use of textural features (information on the surface properties).
- ✓ Diagnostic of the damage from insects using X-rays or IR light.

Size properties of seeds of different varieties



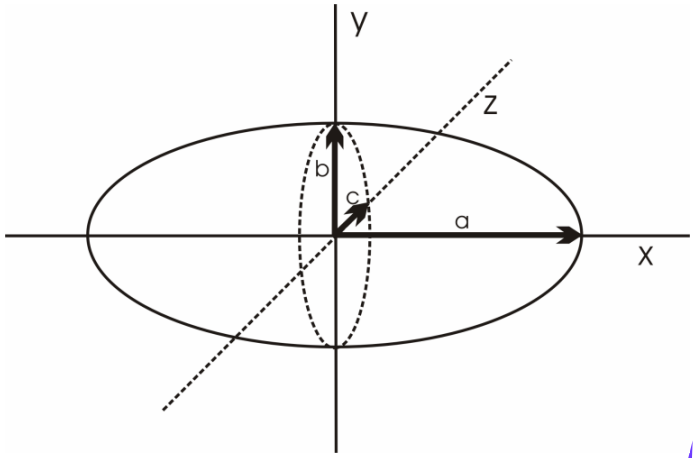
- Physical properties of seeds are key parameters for design of engineering processes and machines, storage structures, and process control. They include heat treatment, air transport, milling, germination or malting. For example, bigger bean seeds germinate faster than smaller and medium ones.
- The size and shape are important in their electrostatic separation from undesirable materials and in the development of sizing and grading machinery.
- The shape of the material is significant for analytical prediction of its drying behaviour.
- Large seeded cultivars of azuki beans exhibit slower water absorption than smaller ones. Cultivars of faba beans and chickpeas require longer cooking times than small seeded cultivars.

Assessing the quality of wheat

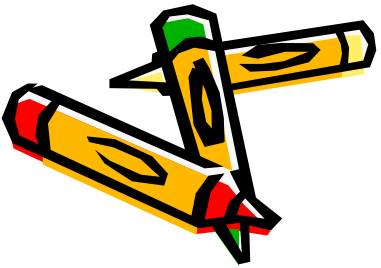
Potential practical application of machine vision technology:

- Automation of rail wagon unloading;
- Optimization of grain cleaning;
- Quality monitoring of exported grains;
- Detection of low-level insect infestation.

Wheat grain



- FIRATLIGIL-DURMUŞ *et al.*[i] used digital image analysis to test the quality parameters of six wheat varieties of *Triticum aestivum* L. and one variety of *Triticum duro-compactum* L. The size data were used for calculation of volume and surface areas of wheat kernels modelled as a general ellipsoid. The calculation of surface area using finite element method (FEM) was based on computer software MAPLE 9.0 and the results were compared with a simplified method. The values of specific surface area, the weight of 1000 kernels, and the surface area of 1000 kernels ranged from 1.08 - 1.22 m^2/kg, 40.09 - 55.00 g, and 477.6 - 620.4 cm^2, respectively.



[i] Firatligil-Durmuş E., Sýkorová A., Šárka E., Bubník Z., Schejbal M., Příhoda J.: Geometric parameters of wheat grains using image analysis and FEM approach. 18th International Congress CHISA 2008, Praha. CD-ROM.

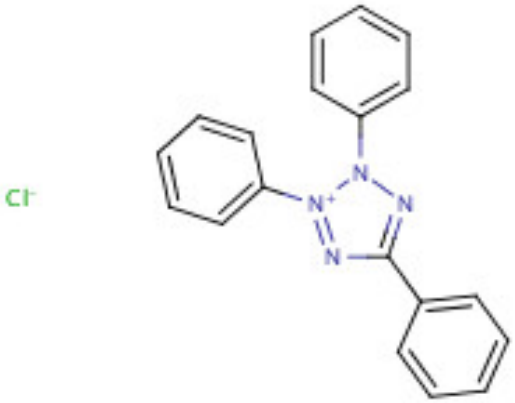
The assessment of the quality of rice

Physical properties:

shape, size, tint and its distribution, damage, impurities.

Assessing the quality of corn

- Machine vision systems have been developed for measuring corn kernel breakage with promising results, and for measuring corn kernel fungal damage.
- Colour, shape, size;
- Contamination of soil and fungi;
- Glassiness, hardness;
- Germination of seeds (dyeing by 2,3,5- trifenyltetrazolium chloride).



Pea seeds quality

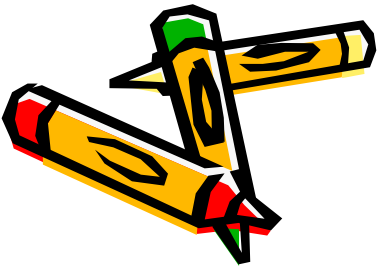
- KADLEC et al.[i] dealt with shape characterization of pea seeds using image analysis to determine the specific surface area of 0.60 m^2/kg for micro-wave drying. Surface area of dried pea seeds was calculated by means of measured equivalent diameter of the seed. Pea seed was considered as ideal sphere, surface of sprout was eliminated.

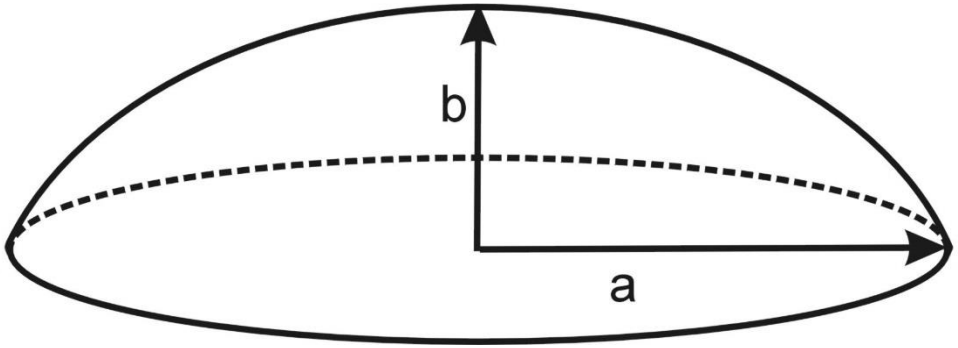
- [i] KADLEC P., SKULINOVÁ M., ŠÁRKA E., FOŘT I.: Microwave and vacuum microwave drying of germinated pea seeds. Proceedings of the 17th International Congress of Chemical and Process Engineering CHISA 2006 (CD ROM), Prague, Czech Republic.

Lentil seeds

- FIRATLIGIL-DURMUŞ *et al.*[i] used image analysis to measure the specific surface area of green and red Turkish lentils (*Lens culinaris* Medik). The results indicated that the performance of two sphere segments approximation method was better than that of the oblate spheroid method to estimate the surface area and volume of lentils. The height (thickness) of lentils was constant and equal for both varieties, and therefore it was possible to simplify geometrical models. When the results of VENORA et al. and BHATTACHARYA et al. were compared with our results, it indicated that Turkish varieties are the same as Sicilian landraces and Canadian in size.
-

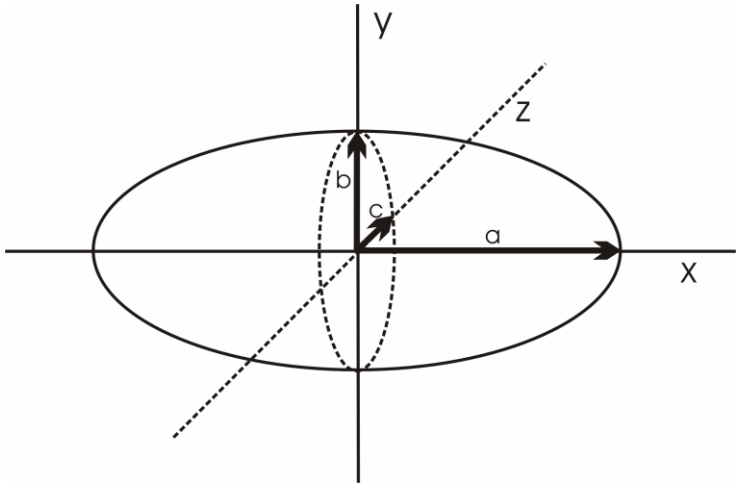
[i] FIRATLIGIL-DURMUŞ E., ŠÁRKA E., BUBNÍK Z.: Image vision technology for characterization of shape and geometrical properties of two varieties of lentils grown in Turkey. Czech J. Food Sci., 26: 109–116 (2008).





Bean seeds

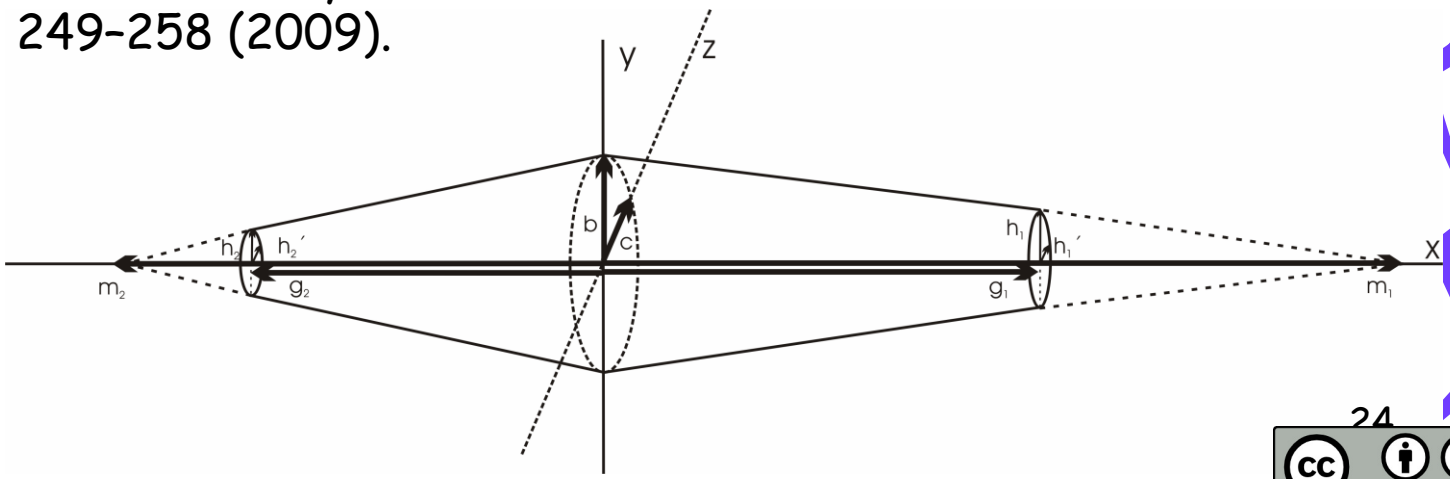
- FIRATLIGIL-DURMUŞ [i] *et al.* measured the seed sizes (projected area, equivalent diameter, length, width, etc.) of bean varieties obtained from the Czech Republic and Turkey using image analysis, and completed data of lentils from both countries. Triaxial ellipsoid approximation method was suitable for most of the bean varieties except white speckled red bean from Turkey. For white speckled red bean from Turkey, the sphere segment approximation method was the best suitable model. The specific surface areas of beans and lentils were determined from 0.58-0.76 m^2/kg and from 1.16-1.20 m^2/kg, respectively.
- [i] Firatligil-Durmuş E., Šárka E., Bubník Z., Schejbal M., Kadlec P.: Size properties of legume seeds of different varieties using image analysis. J. Food Eng., 99: 445-451 (2010)



Barley grain

- Sykorova et al. [i] investigated and determined size variations between the kernels of six barley cultivars grown in the Czech Republic. The geometric model consisting of two cone frustums provided the best approximation of volume for all cultivars.

[i] Sýkorová A., Šárka E., Bubník Z., Schejbal M.: Size distribution of barley kernels. Czech J. Food Sci. 27 (4): 249–258 (2009).



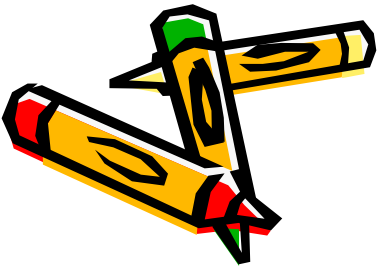
Quality evaluation of meat

Quality evaluation of raw meat

- **Pork, beef, mutton**

Evaluation of colour and marbling; skeletal maturity:

Computer vision technique has been demonstrated as a rapid, alternative, and objective approach for measuring meat colour and marbling. Beef grading systems use lean colour and the degree of cartilage ossification at the tips of the dorsal spine of the sacral, lumbar, and thoracic vertebrae to determine the physiological maturity of beef carcasses. Computer vision system was used to predict beef yields and to enhance yield grading. Research on predicting meat texture (tenderness) is the most challenging of computer vision applications in the meat quality evaluation.



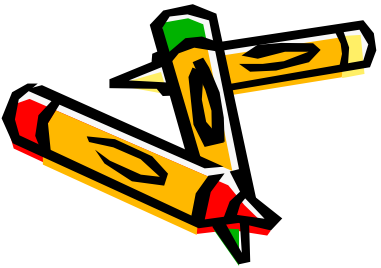
Evaluation of the quality of cooked meat and meat products

- Using computer vision systems, the shrinkage measurement of cooked meats can be implemented automatically. From the segmented pores of cooked meats, the porosity, number of pores, pore size, and size distribution can be measured.

- Colour measurement of cooked products can be influenced by sodium nitrate addition. The feature *image texture* of cooked meats have a good relationship with one of the most important food texture attributes, i.e. tender

Evaluation of quality of poultry

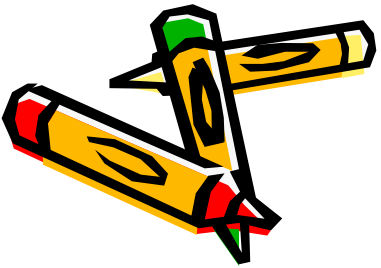
- A technique for recognizing global or systemic defects on poultry carcasses by using colour-imaging system has been reported.
- A colour-image processing system was developed to detect skin tears, feathers, bruising.



Evaluation of quality of poultry

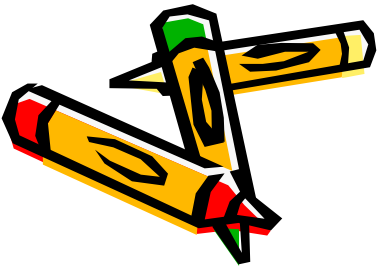
- Multispectral and hyperspectral image systems are used for special applications in quality characterization.
- Hyperspectral system of image analysis is used to detect faecal contamination.

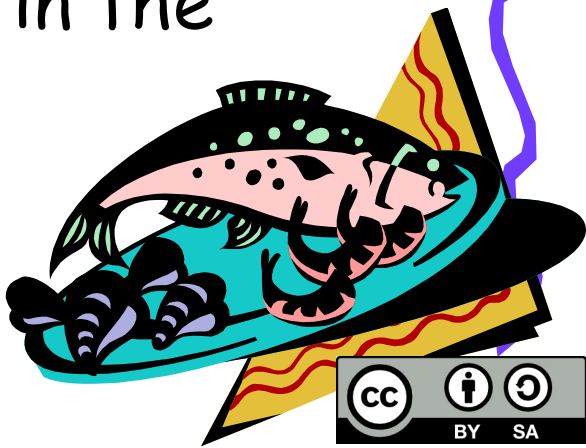
Hyperspectral data are created from more than 100 of colour bands with an interval of 5-10 nm, multispectral data consists of 5 – 10 colour bands with an interval of 70 - 400 nm.



Qualitative assessment of fish and seafood

- Quality attributes of seafood include appearance (size, shape, colour), smell, taste, nutritional aspects, and safety-related properties. Machine vision can potentially evaluate all these attributes (some of them indirectly).
- *Shape* – laying of pieces of fish in the same direction in a can

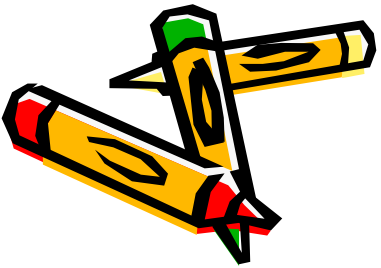




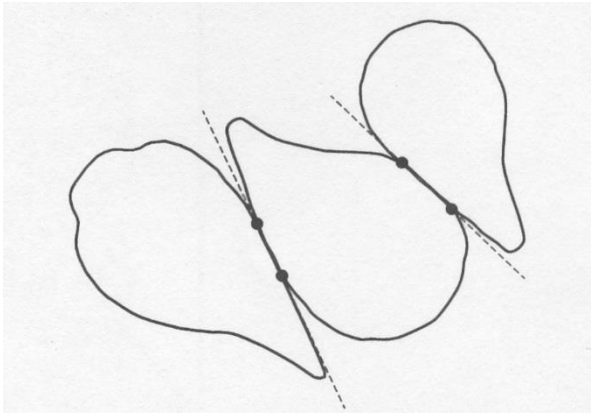
Sugar industry

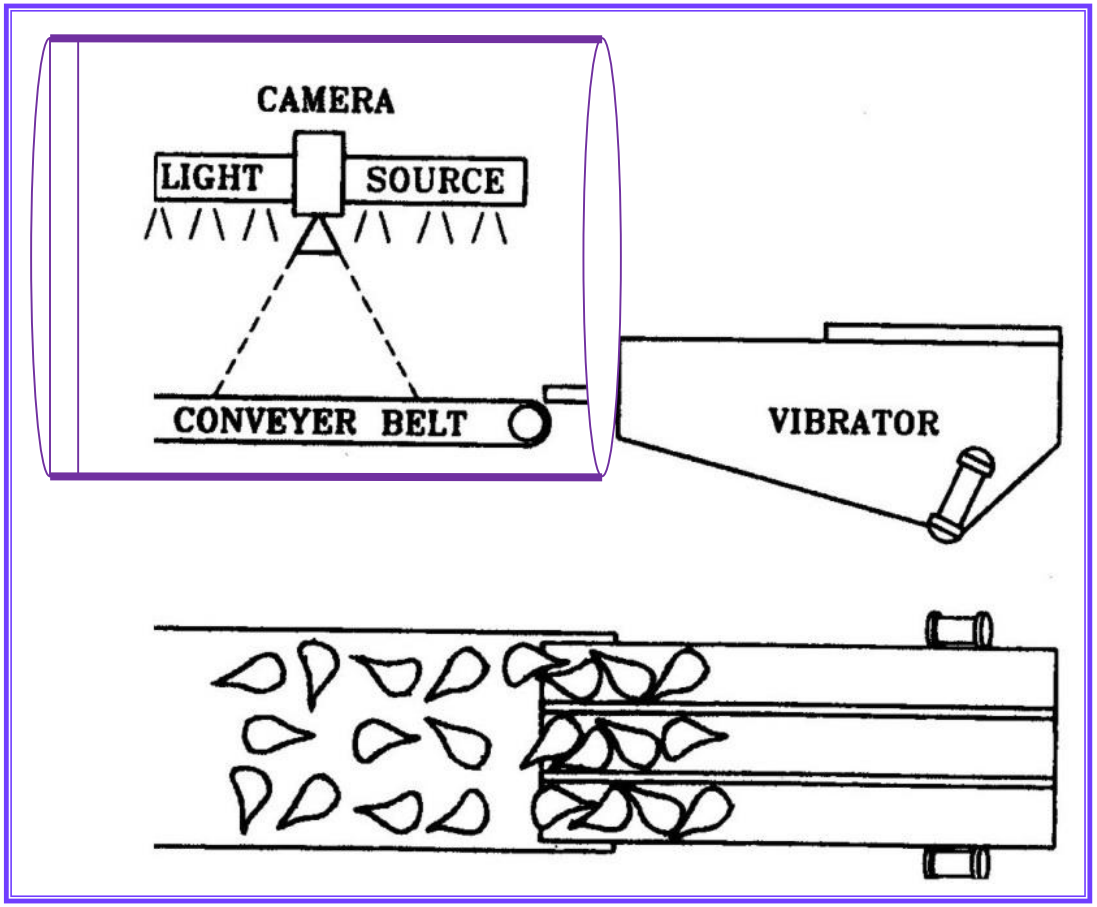
Reception of sugar beet

- Laboratory assessment of organic impurities content and the quality of removing the slabs from the top of the beet root after harvesting.
- Assessment of geometric parameters of beet bulbs.
- Assessment of surface of beet bulbs.
- "Dark" slices on a conveyor belt.

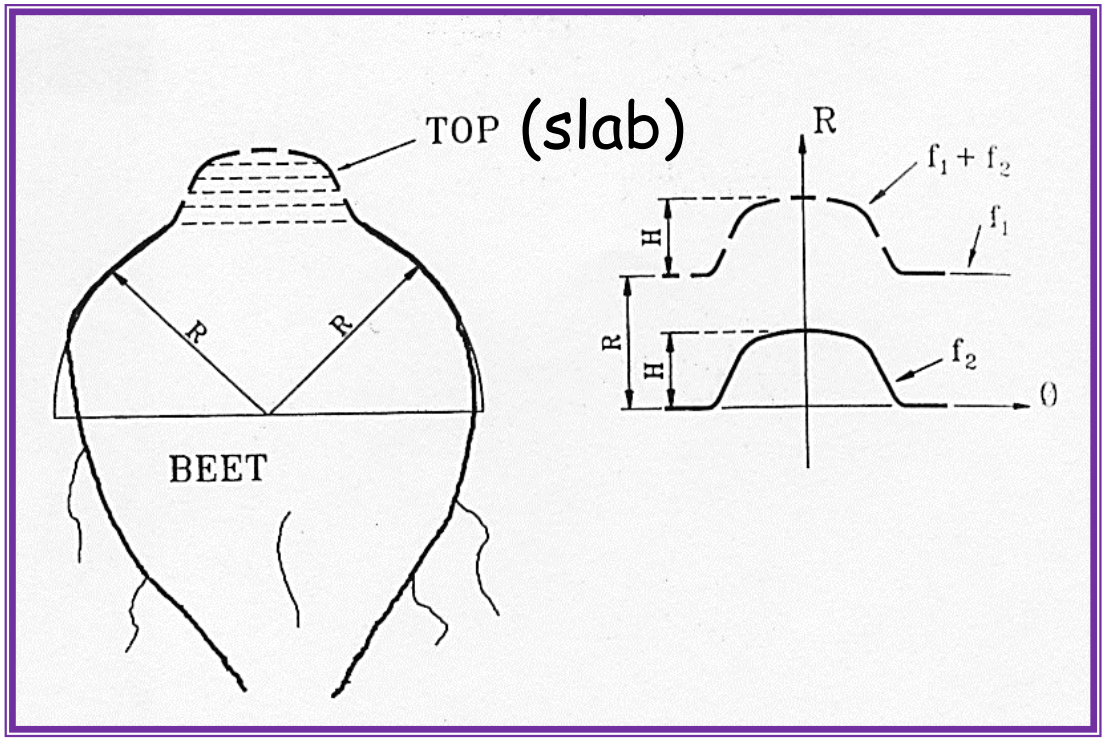


Assessment of organic impurities





Assessment of organic impurities



Sugar crystallization

- Image analysis in sugar technology observes microparticles: sugar microcrystals used as a seed for industrial crystallization or precipitate of prelimed and carbonation juice.
- This method enables to evaluate processes where numbers and sizes of particles vary, such as nucleation, crystal growth, aggregation, dissolving, and separations using hydrocyclones or decanter centrifuges, etc.
- The saturoscopic method together with image analysis have been suggested and tested for the solubility measurement of high viscous solutions with wide metastable zone.

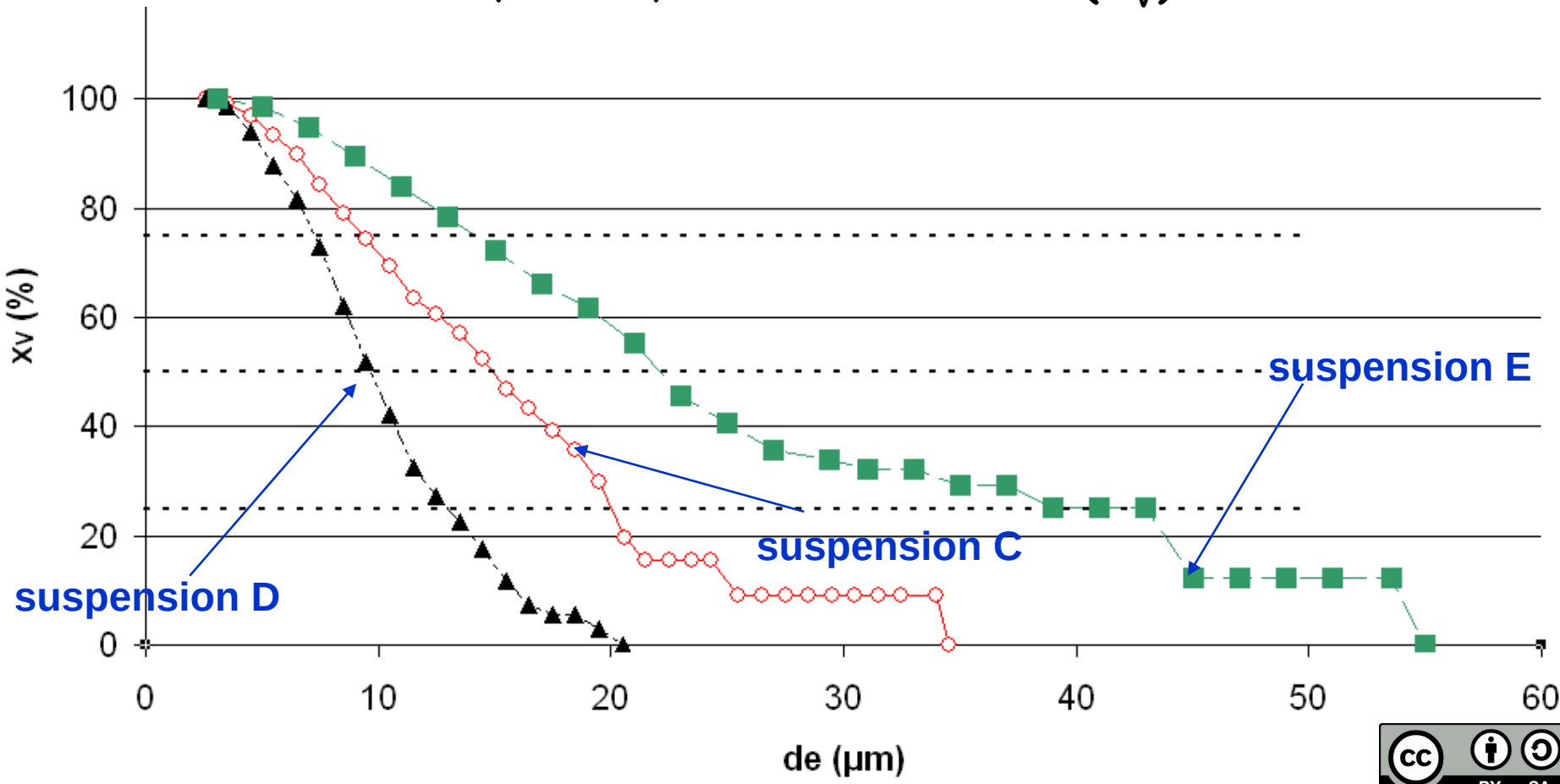
Cumulative distribution curves

—o— the input of suspension C into hydrocyclons,

-···-▲-···- the output of suspension D,

--■-- the output of suspension E,

- - - - 25 %, 50 %, 75 % of volume (x_V)



$$R = \frac{d_e^{25} - d_e^{75}}{2.d_e^{50}}$$

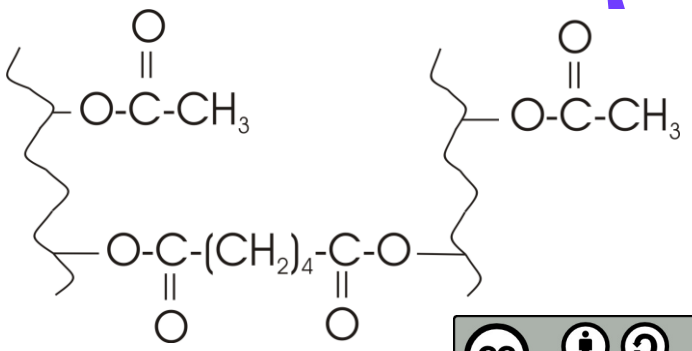
medium	sugar factory	Equivalent diameter (µm) for part of particles volume (%)			
		25	50	75	R
1st carbonation mud (mixed with water)	A	78.3	53.9	21.4	52.8
1st carbonation mud (mixed with water)	B	32.5	20.7	14.6	43.2
1st carbonation juice	A	29.9	22.6	16.2	30.3
1st carbonation juice	B	35.7	27.6	18.2	31.7
1st carbonation juice with flocculant	A	106.2	82.2	52.9	32.4
1st carbonation mud after thickening filters	B	29.9	20.6	13.0	41.0
suspension C	A	20.0	14.9	9.4	35.6
suspension D	A	13.0	9.7	7.3	29.4
suspension E	A	43.0	22.1	14.1	65.5

Starch identification

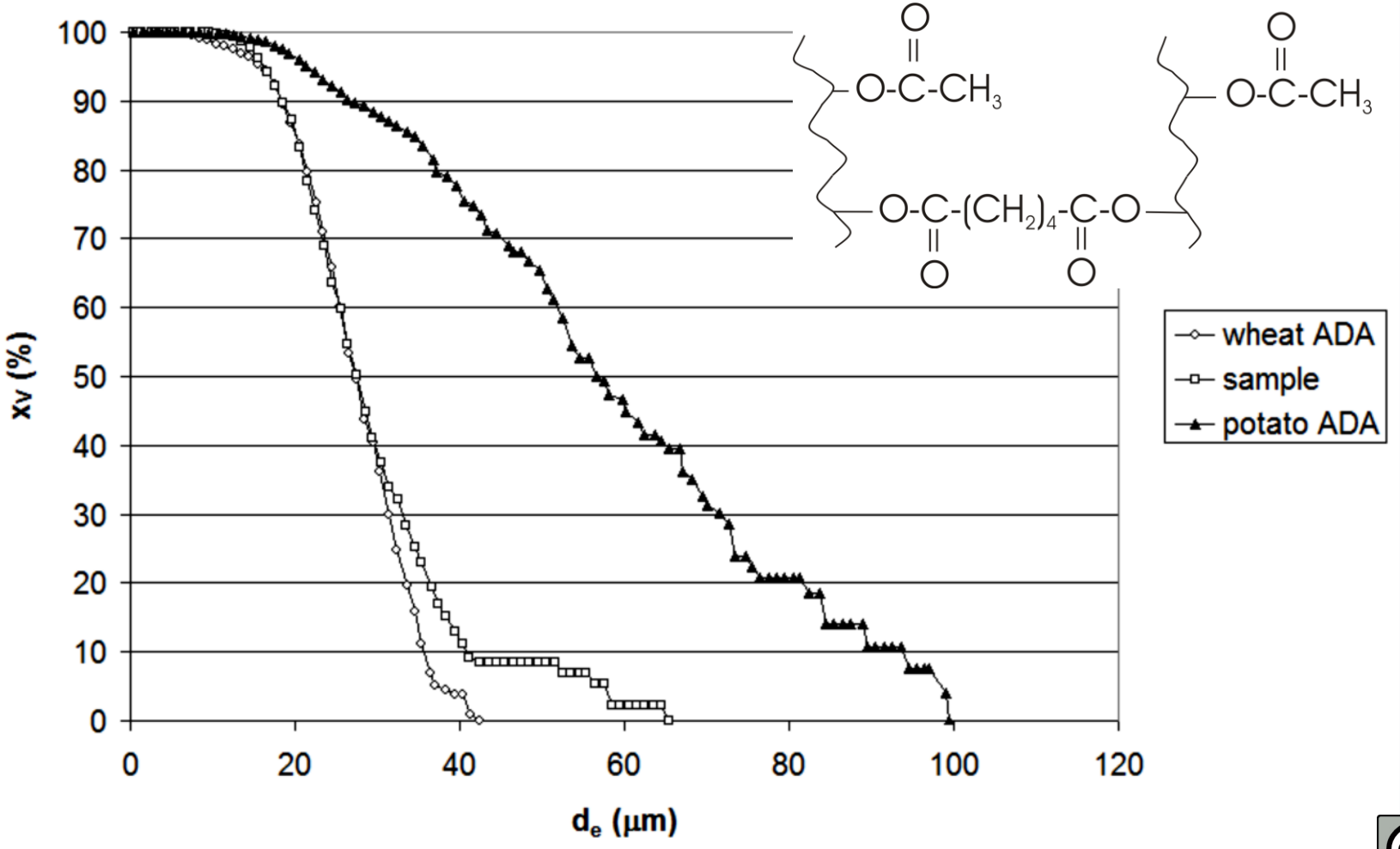
Identification of starch origin

- The origin of starch mixed with other additives can be identified after inking by iodine tincture using image analysis measurement of granule size.
- comes from the size distribution of starch granules.
- Šárka and Bubník [i] measured the particle size of acetylated distarch adipate (ADA) in three suspensions; a commercial mixture containing other additives and potato and wheat commercial ADA starches. From the data, the particle size distribution was calculated and the normality of the size distribution for volume fraction was tested. The starch in the mixture was identified as wheat ADA, Problems can occur when particles in a mixture stick to fat or when the particle colour is very similar to the colour of inked starch.

[i] Šárka E., Bubník Z.: Using image analysis to identify acetylated distarch adipate in a mixture. Starch/Stärke, 61(8), 457 – 462, (2009)

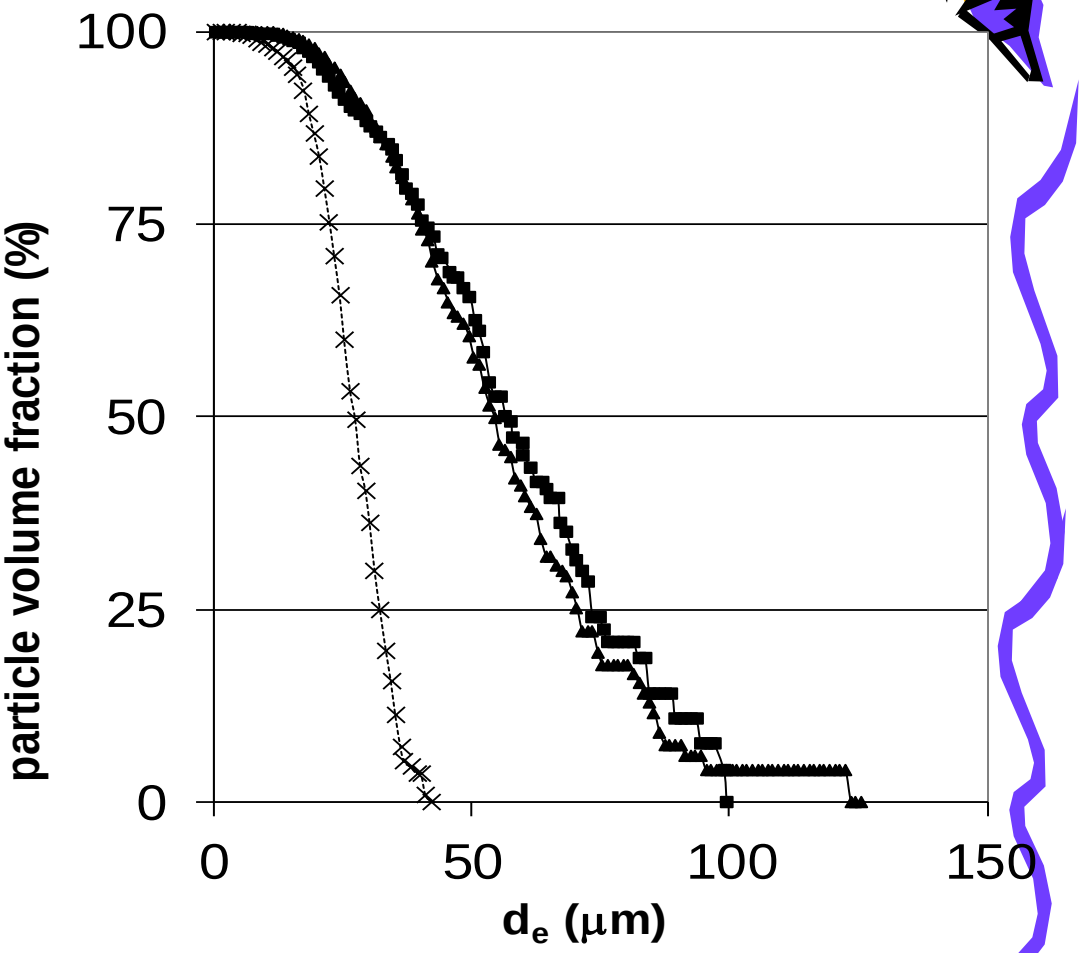


Identification of starch origin



Identification of starch origin

The size of starch granules remains largely unchanged during chemical modification, therefore we can compare the modified starch with native or other modified potato and wheat starches. Image analysis was used in a such way to successfully identify the origin of cationic starch.

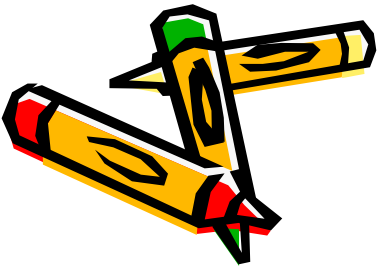


Cereal products

Assessing the quality of cereal products

Baked products

- The physical properties of baked products, such as colour, shape and size are important quality attributes of most baked foods. Texture is a food quality attribute which affects the total experience perceived by the consumer. Computer-vision based textural analysis has advanced significantly over the past 10 years (pores...).
- Colour (caused mainly by Maillard's reaction) is connected with time and temperature, and influenced by water content and additives.



Assessing the quality of pasta

- Image analysis systems for noodle-colour measurement are equipped with flat-bed scanners.
- Assessment of the quality of flour.
- Additives – number of dots (spots).

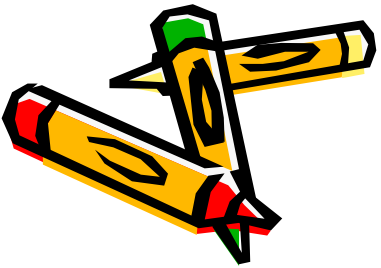
Other food products

Assessing the quality of pizza

- Size, shape;
- Colour (dough, filling);
- Distribution of the filling on the top.

Assessing the quality of cheese

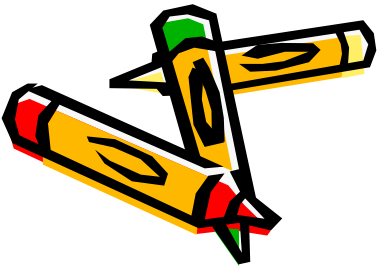
- Melting of cheese is accompanied by visible changes of size and shape, cheese meltability is a natural target for computer-vision based measurement for improved accuracy and consistency. The extent of browning can be evaluated using computer vision technology as well. It is possible to use computer image analysis to quantify the extent of hole formation (hole areas) in cheeses. Calcium lactate crystals in Cheddar cheese as a quality defect might be evaluated using digital photography and image analysis.



- Morphology (for grated cheese as well), integrity of cheese.

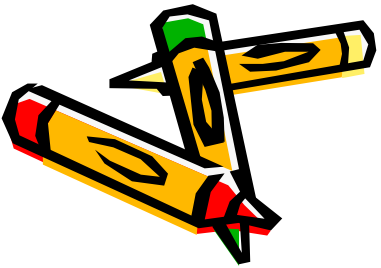
Assessing the quality of chips or French fries

- Colour – connected with Maillard's reaction and the acrylamide formation; grading.
- Texture.



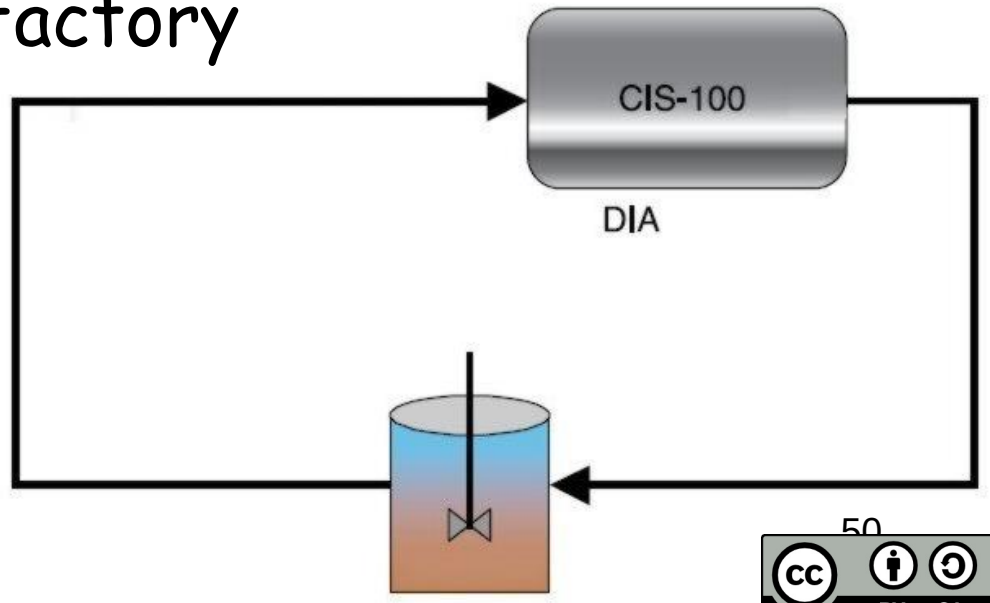
Waste water treatment

- Size of flakes and characteristics of the (activated) sludge.
- Assessment of the ability to settle and the resulting clarity.
- Differentiation of fibres from flakes.
- Physico-chemical properties of microbial granules.
    - Determination of the number of nitrifying bacteria.



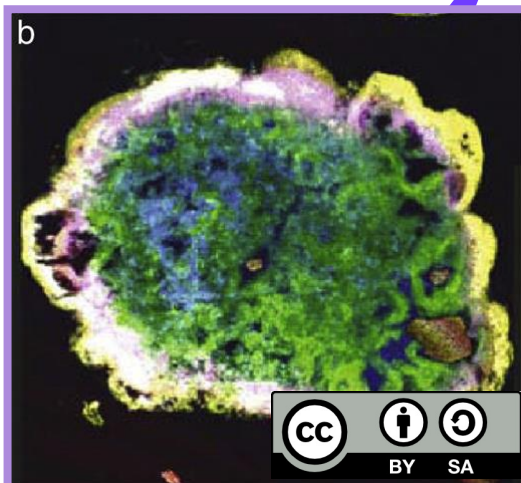
The size and shape of flakes

- Dynamic image analysis: CIS-100 video channel (firm Ankersmid, Belgium).
- The system characterises sizes and shapes of particles from individual scans of moving particles by the use of software. The background is eliminated and the mean value is calculated from a satisfactory number of particles (e.g. 10 000).



Physico-chemical properties of microbial granules

- Microbial granules are important for biological treatment of wastewaters. Unlike conventional flakes, granules are denser, more stable, and sediment better, which provides good separation, higher concentration of biomass and higher resistance to temperature shocks.
- Image analysis can evaluate their morphology, colour, shape, roughness of the surface, abrasiveness and porosity.



Some other applications

- Monitoring the enzymatic degradation of the beet mass.
- Characterization of the particle size of dust during the manufacture of pellets.
- Particle size analysis of feed (pellets).
- Shape factor and surface roughness of granules, e.g. in pharmaceuticals.
- Measurement of aggregates of yeast.
- Measurement of bubble sizes.

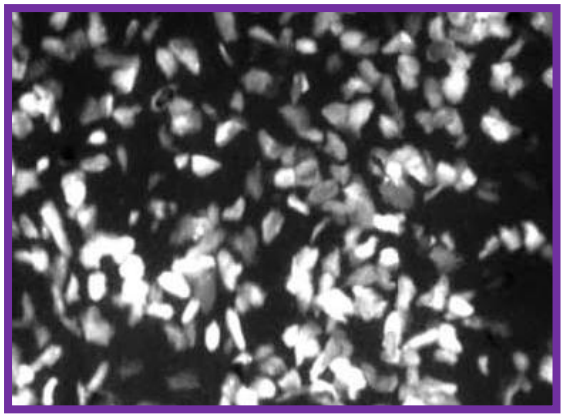
Monitoring of enzymatic degradation of sugar beet pulp

Pectinolytic and cellulolytic enzymes are used in enzymatic degradation.

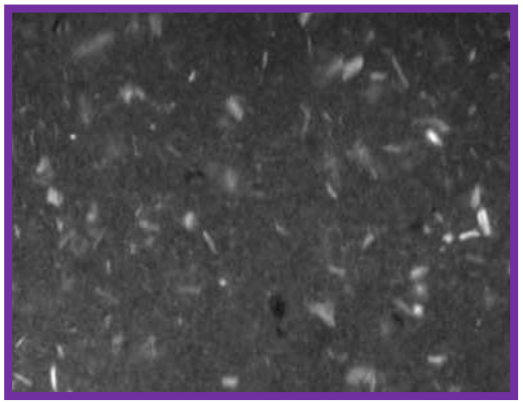
The methods used to characterise overlapping particles are:

→ Image analysis using mathematical morphology to determine particle size distribution;

→ and fractal analysis to test the uniformity of particles.



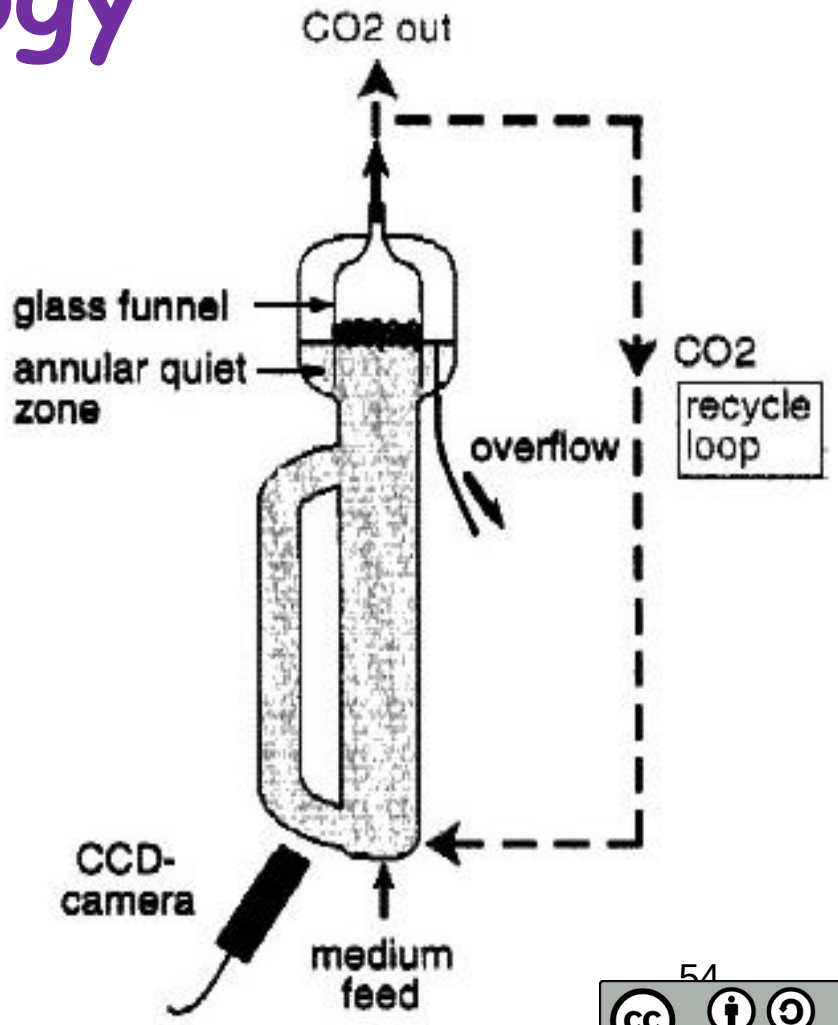
Initial state



After 24 h

Measurement of yeast aggregates in fermentation technology

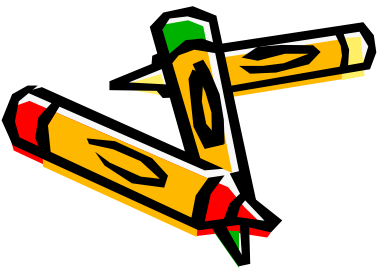
- The effectiveness of ethanol fermentation can be significantly improved by yeast recycling.
- The fermentation ability of yeast depends on the size of yeast aggregates – it is important to monitor this parameter.
- On-line measurement can be carried out by IA based on evaluation of texture.



Conclusions

Image analysis can be recommended as a simple, rapid and efficient method for evaluation of:

- Size properties of seeds or fruits of different varieties;
- Colour of meat or fruit;
- Texture properties of cereal products;
- Particle size distribution in suspensions;
- Changes in particle size during a technological process;
- Evaluation of full-scale separation operations;
- Identification of native or modified starches.



Separation and purification techniques

Introduction into membrane separation processes

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Information sources

http://sch.vscht.cz/vyuka/international-students/erasmus-students/

Cheryan M. (1998): Ultrafiltration and Microfiltration Handbook, In: Technomic Pub. Co. (Eds.), Lancaster, Pensylvania, pp. 243.

Introduction into membrane separation processes

Contents

1. Classification of membrane separation processes

Filtration set-up (dead-end, cross-flow)

Membrane processes according to the mechanism of separation, driving forces, membrane types and shapes

2. Basic terminology

Permeate, retentate, filtrate, up-stream, down-stream process

3. Membranes and their characteristics and properties

Separation properties (permeability, porosity, pore size, cut-off, selectivity)

Membrane description – structure, material, shape, function,

Introduction into membrane separation processes

Contents - continuation

4. Membrane modules

Character of the flow along the membrane
Construction, types, set-up
Laboratory scale, industrial scale operation
Special modules (rotating, vibrating,)
Membrane reactors

1. Classification of membrane separation processes (MSP)

MSP = separation techniques use a semipermeable membrane, which forms a selective barrier

Filtration principle = separation due to the different size of at least two fluid components (gas or liquid).

MEMBRANE:

- Creates a selective barrier
- Is a barrier between two phases
- Hinders mass transport, but enables limited and controlled passage of certain components
- Has liquid, solid or gas character (or combination of all)

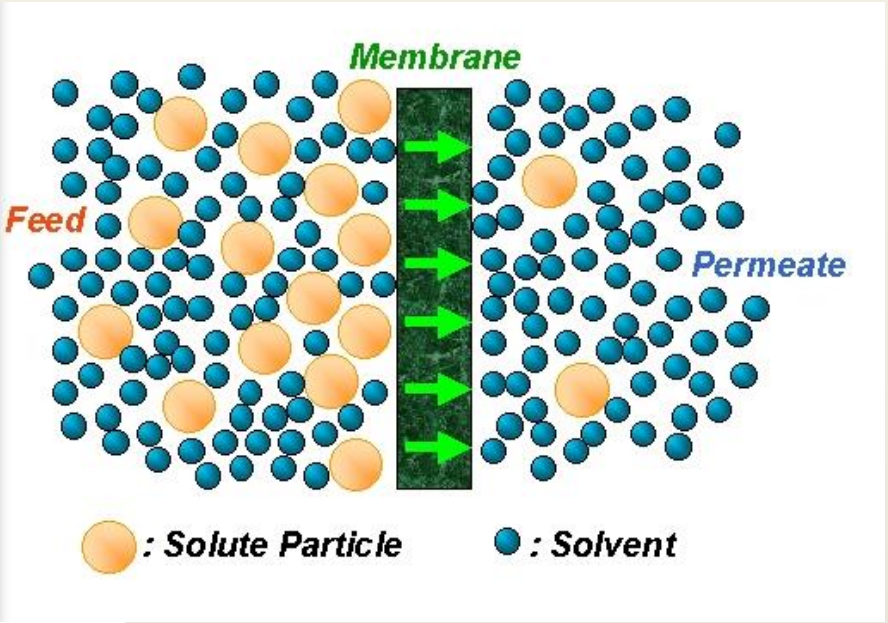
A membrane separates feed into:

- **Retentate (concentrate)**

  = enriched with substances retained by the membrane

- **Permeate (filtrate)**

  = a stream passing through the membrane, devoid of substances retained by the membrane



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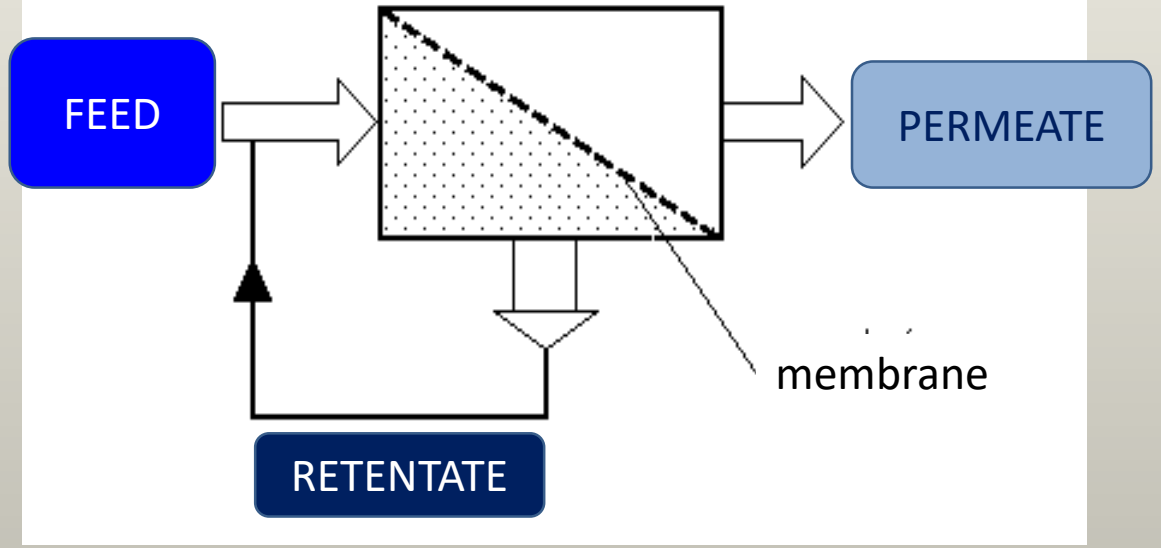


Basic mechanisms of substance separation on a membrane are:

- **Sieving effect** - different particle size of substances in a mixture; effect of membrane pore size (diameter)
- **Different charge** of mixture components and on the membrane surface
- **Different diffusivity** - diffusion coefficients of components
- **Different solubility** of components in the membrane (e.g. oil membranes)

Membrane processes can be described according to:

- **Driving force**
- **Type of the membrane**
- **Properties of separated particles**

Driving force of membrane processes

- **Pressure** (pressure driven separation processes – microfiltration, ultrafiltration, nanofiltration, reverse osmosis, pervaporation)
- **Concentration** (dialysis)
- **Chemical potential** (osmosis)
- **Electric potential** (electrodialysis)

Properties of separated particles:

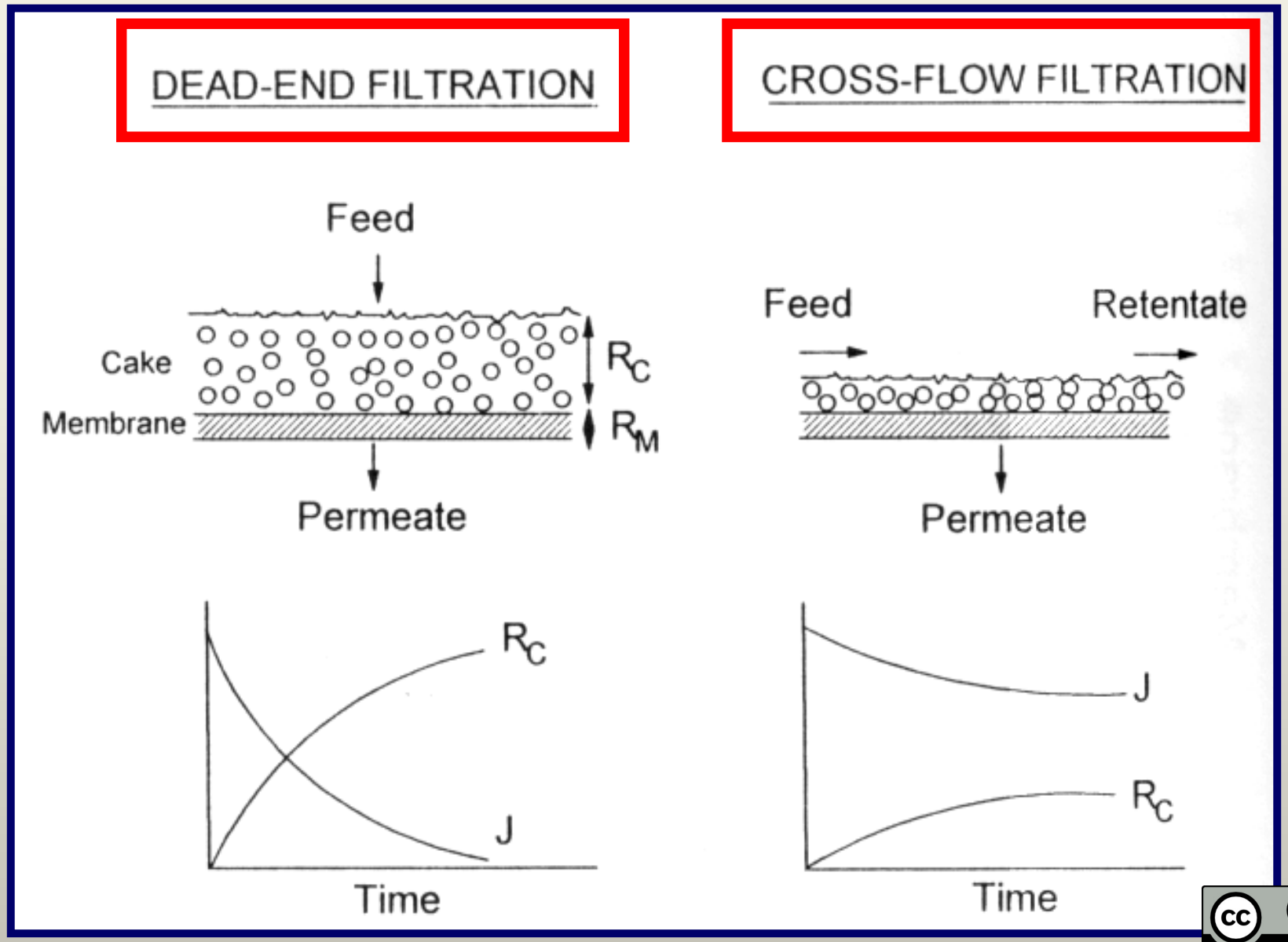
- **Size**
- **Shape**
- **Charge**

Membrane process's characteristics:

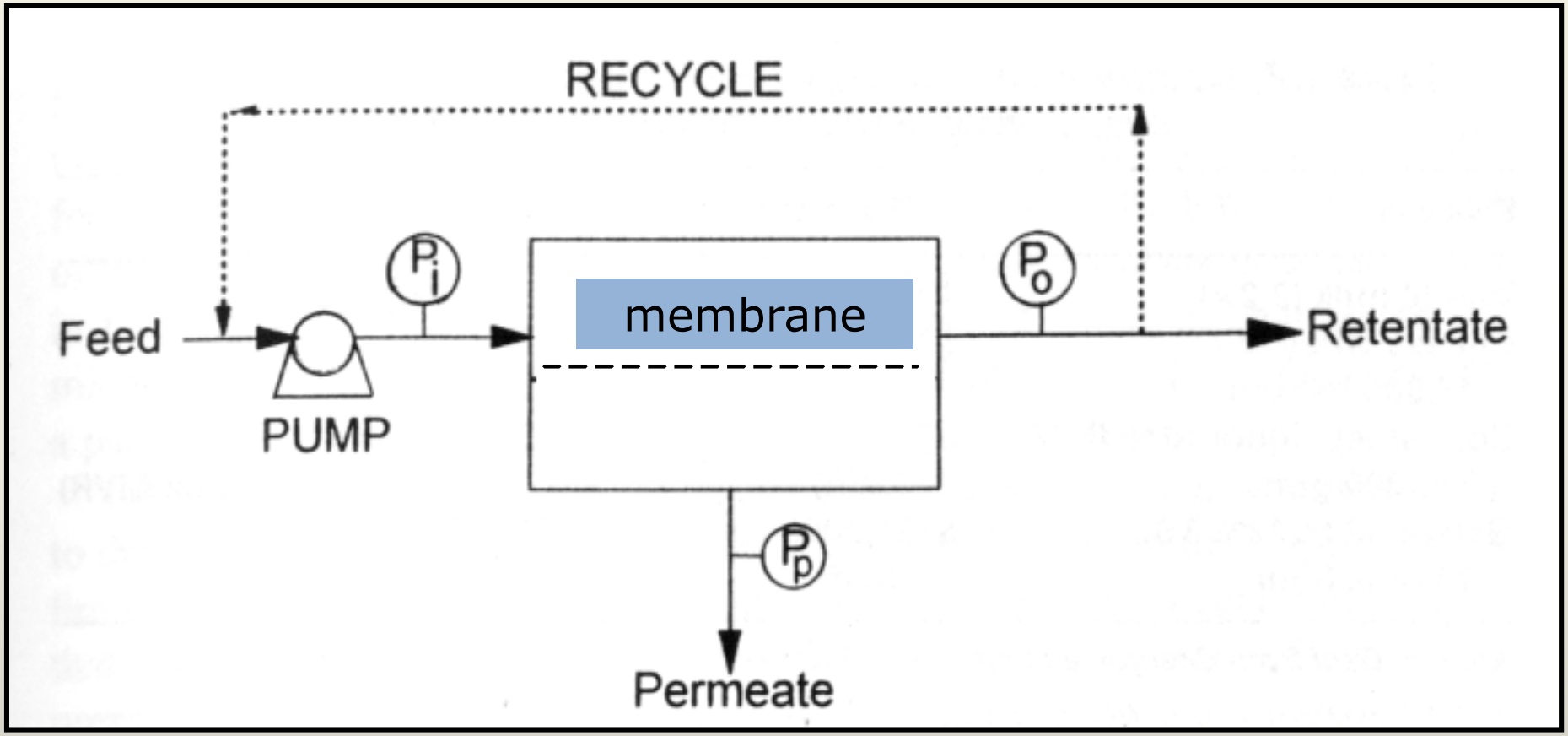
	Driving force	Retentate	Permeate
Osmosis	Chemical potential	Substances dissolved in a solution, water	Water
Dialysis	Concentration gradient	Big molecules, water	Small molecules, water
Microfiltration (MF)	Pressure	Suspended solids (e.g. yeasts), water	Substances dissolved in a solution, water
Ultrafiltration (UF)	Pressure	Big particles, molecules (bacteria), water	Small molecules, water
Nanofiltration (NF)	Pressure	Small molecules, water, bivalent ions, dissociated acids	Monovalent ions, non-dissociated acids, water
Reverse osmosis (RO)	Pressure	Substances, water	water
Electrodialysis (ED)	Potential	Dissolved non-ionogenic substances, water	Ionised substances dissolved in a solution, water
Pervaporation (PV)	Partial pressure	Non-volatile molecules, water	Volatile small molecules,

General set-up of the filtration process

Cheryan M.: Ultrafiltration and Microfiltration Handbook, Technomic Pub. Co., 1998



Filtration apparatus



“Up-stream“ processes
“Down-stream“ processes

2. Membranes

Separation properties of the membrane are given by:
permeability, selectivity and cut-off

A) Permeability

Permeation = a transport of atoms, molecules and ions in permeable media due to the gradient (of concentration, temperature, pressure, electric potential, etc.)

Permeability:

= is a feature that enables a mass transport through the material
= is expressed as an amount of material that passed (diffused) through some other medium at given conditions
= in membrane processes, is equal to amount (volume, mass) of permeate which was transferred across 1 m^2 of the membrane during a unit of time (h)
= influences the speed (kinetics) of the separation process.

A flow through an ideal semipermeable membrane can be expressed as:

$$J = A \cdot (P_T - \pi_F)$$

J is the permeate flow, expresses a velocity of a component passage through the membrane

A is the permeation coefficient (reciprocal to resistance)

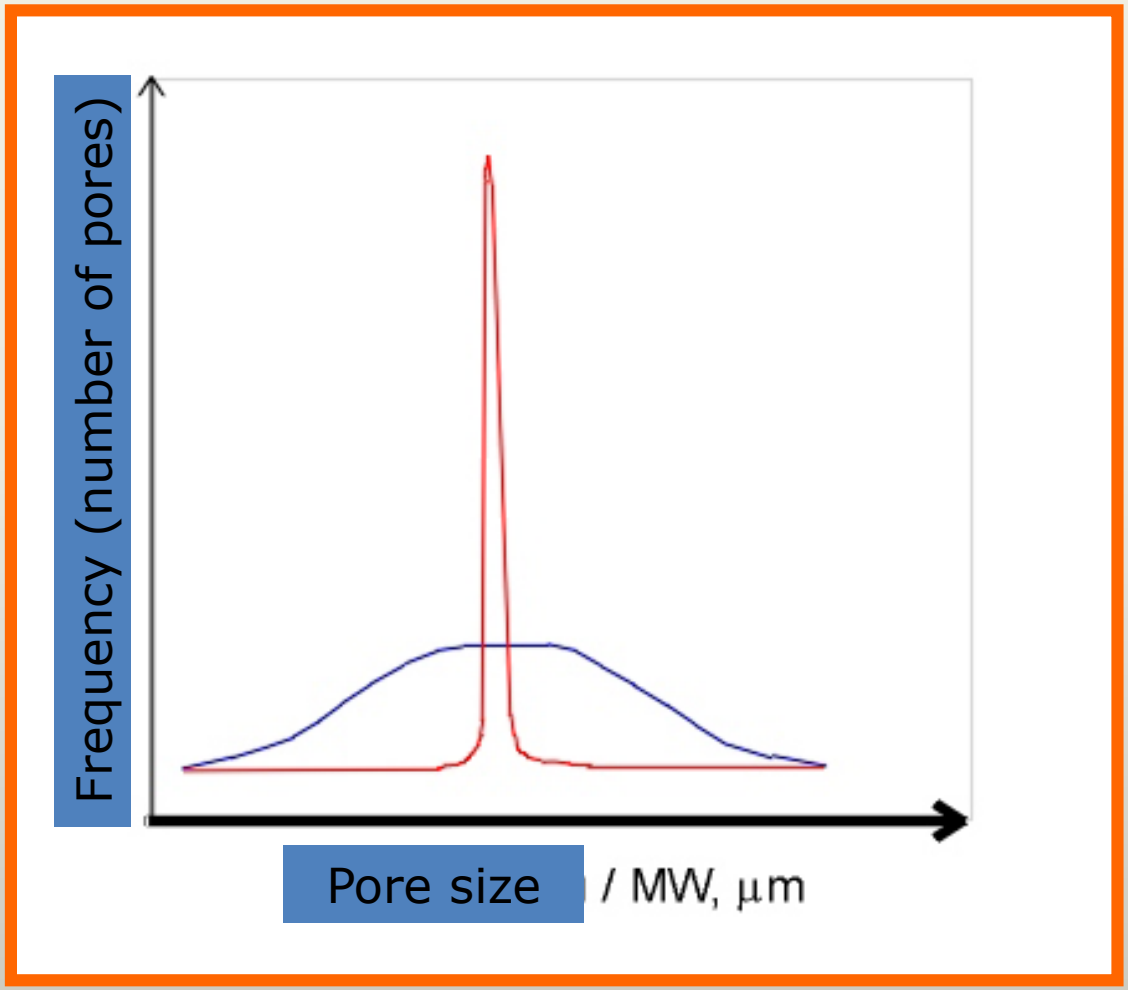
P_T is the trans-membrane pressure

π_F is the osmotic pressure of the solvent.

Membrane permeability depends on **porosity** (a ratio between total pore area and membrane area)

B) Selectivity

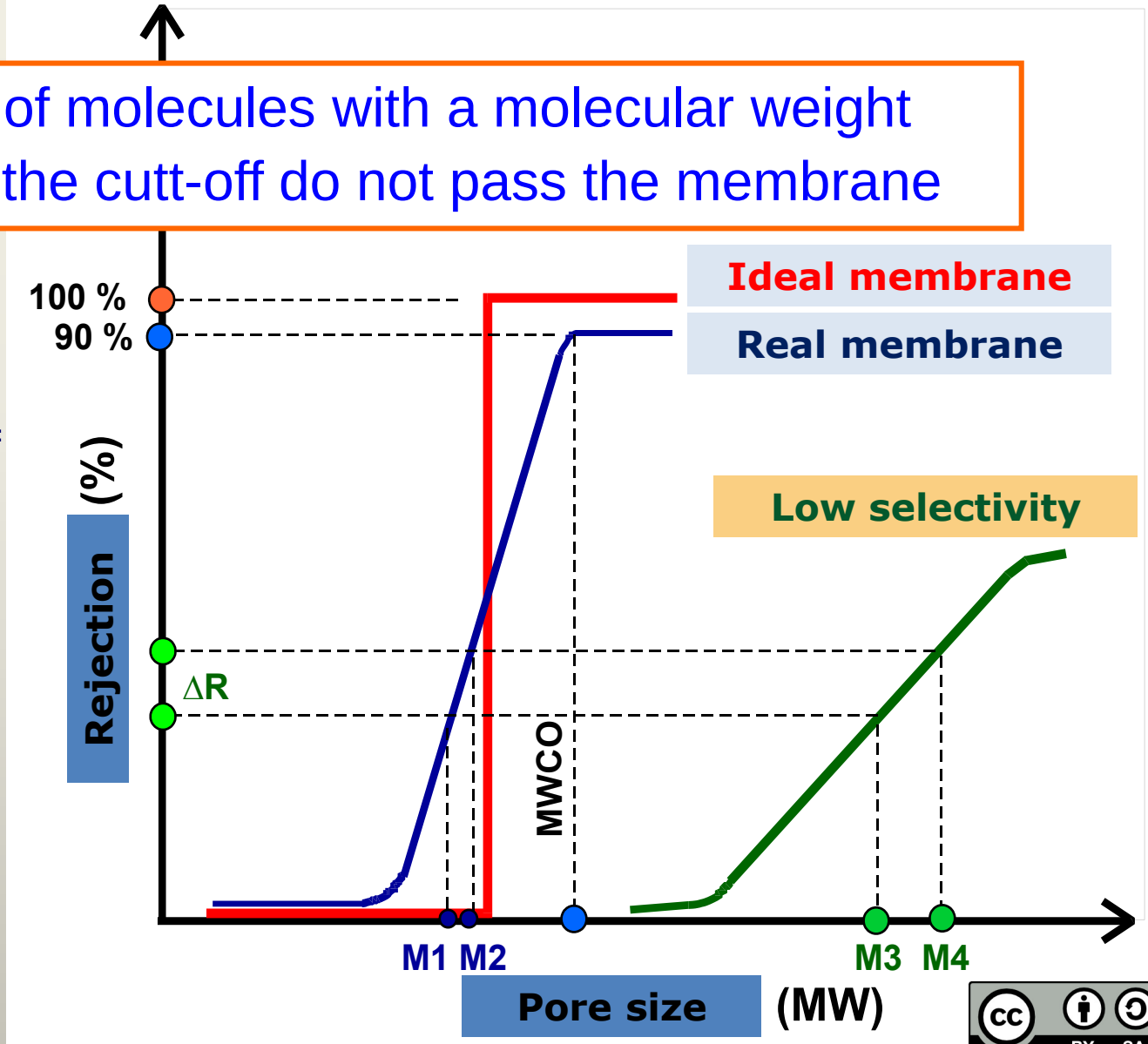
- Selectivity influences separation efficiency and permeate purity.
- It depends on pore size and pore size distribution.
- Good selectivity – uniform pore size, i.e. narrow pore size distribution.



C) Cut-off

Definition: 90 % of molecules with a molecular weight corresponding to the cutt-off do not pass the membrane

- Membrane characterisation
- Given by the size of particles which do not pass the membrane
- If the size is expressed as a molecular weight ⇒ MWCO Cut-off
- Other units: μm, Da



Membrane classification:

Membranes can be divided according to:

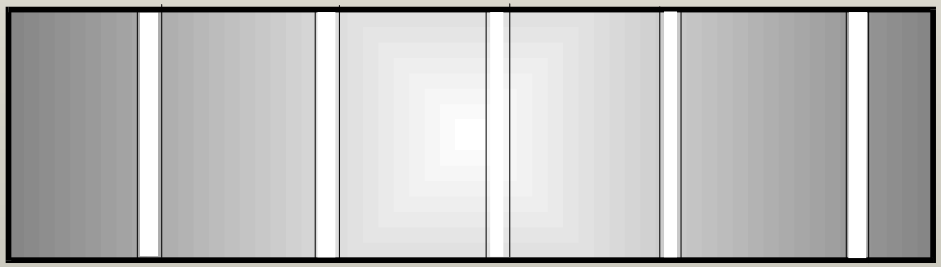
- Membrane origin (natural, synthetic)
- Membrane structure (porous, non-porous, surface morphology)
- Membrane application (gas–gas, gas–liquid, liquid–liquid separations)
- A mechanism of separation (adsorption, diffusion, ion exchange, osmotic pressure, inert membrane)

Membrane structure:

1. Microporous membrane

– isotropic = uniform pore size within the membrane thickness – filtration can be performed on both sides

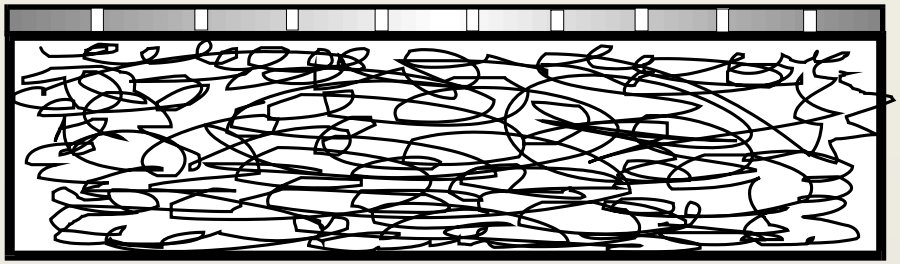
– anisotropic = various pore sizes in membrane layers – particles can penetrate into the membrane; pore blocking, permeate flow reduction, or low retention of components

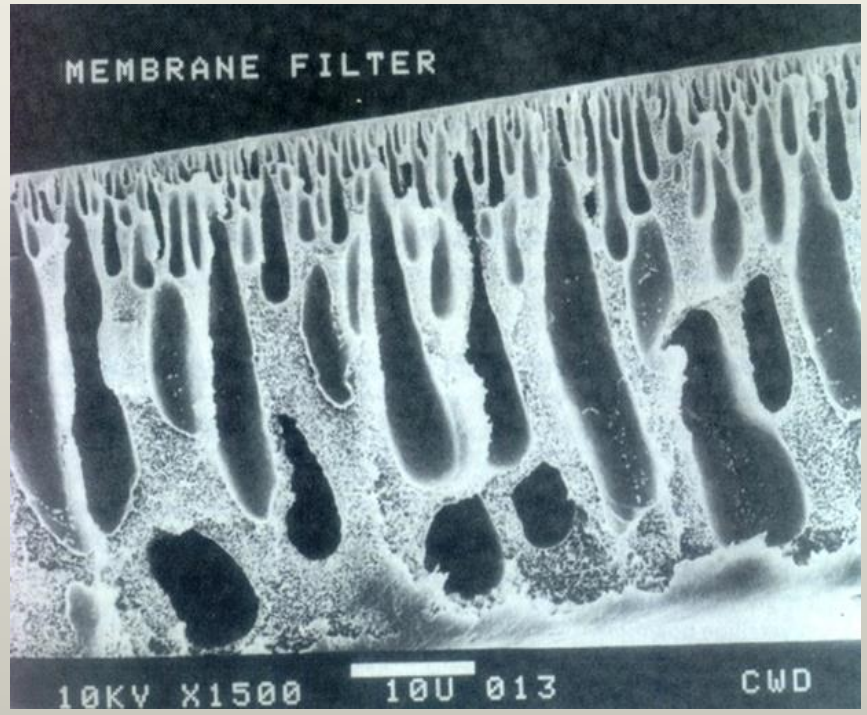


isotropic membrane

2. Asymmetric membrane (with active layer)

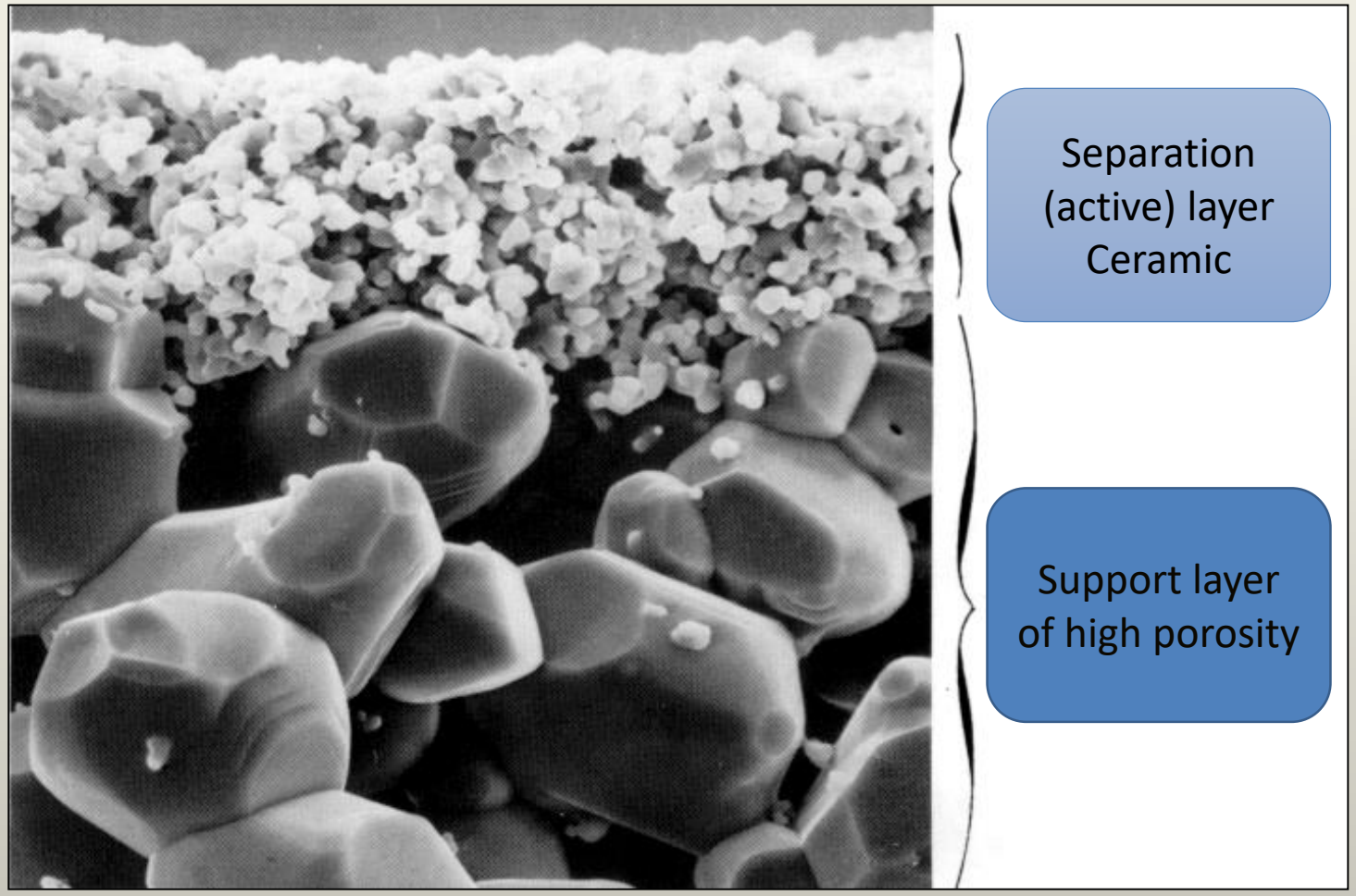
- **A thin active layer is coated on a support layer**
- **A small pore size and small thickness (< 1 μm) of active layer**
- **Performs separation**
- **Molecules do not penetrate into the support; low fouling, filtration kinetics is given by the tangential velocity of medium flow along the membrane**





3. Composite (sandwich) membrane

Several layers – every layer produced by different technique



Membralox ®

Membrane materials

1. Organic

- Cellulose acetate (low costs, low price, wide range of pore sizes, hydrophilic character – reduced fouling)
- Polyamide (low resistance to Cl_2, biofouling)
- Polysulphone (high temperature, pH and chemical Cl_2 resistance)
- Other polymers (nylon, PVDF, PTFE, PP, polycarbonate)

2. Inorganic (= mineral, ceramic)

Called also metallic (stainless steel)

Support layer: ceramic, Al_2O_3, TiO_2

Separation active layer: TiO_2, zirconia, carbon-titanium, carbon-zirconium

Inorganic membranes:

Positives:

+ Inert toward most of chemical solutions (exceptions: HF, H_3PO_4 – Al membranes)
+ High temperature resistance (350 °C) – steam sterilization
+ Wide pH operation range(1 – 13)
+ High pressure resistance (1 MPa)
+ Long lifetime
+ Back-flushing possible

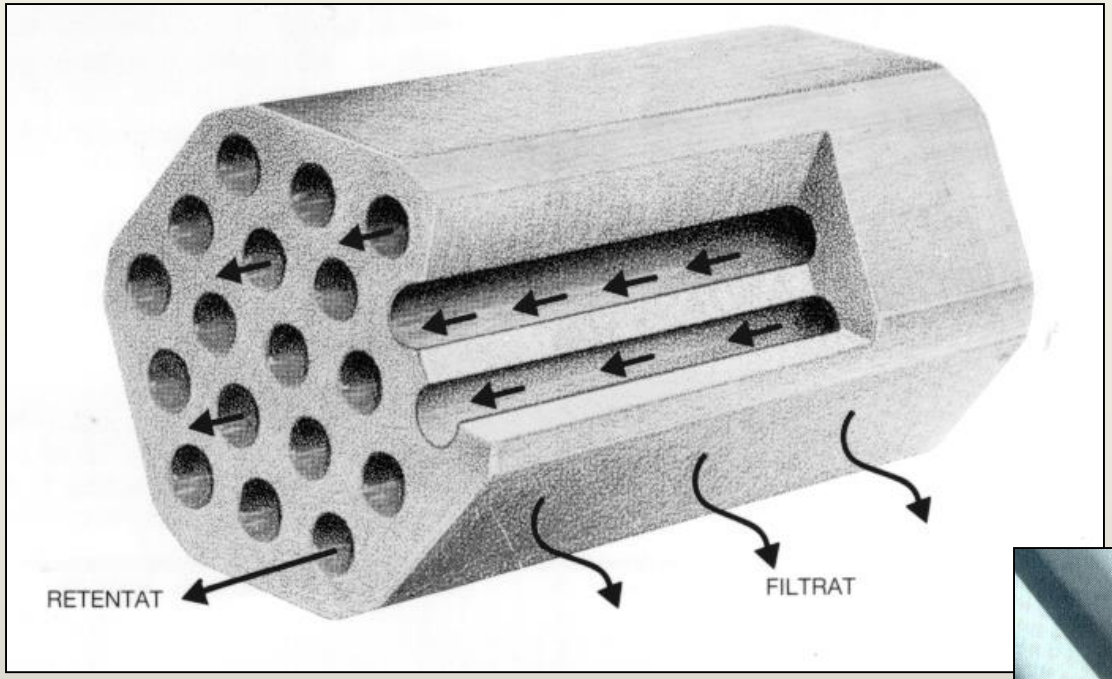
Drawbacks:

- Large pore size (UF, MF, opened NF membranes)
- High pump discharge needed (2 – 6 m/s tangential velocity)
- High producing costs – high prices (high investment

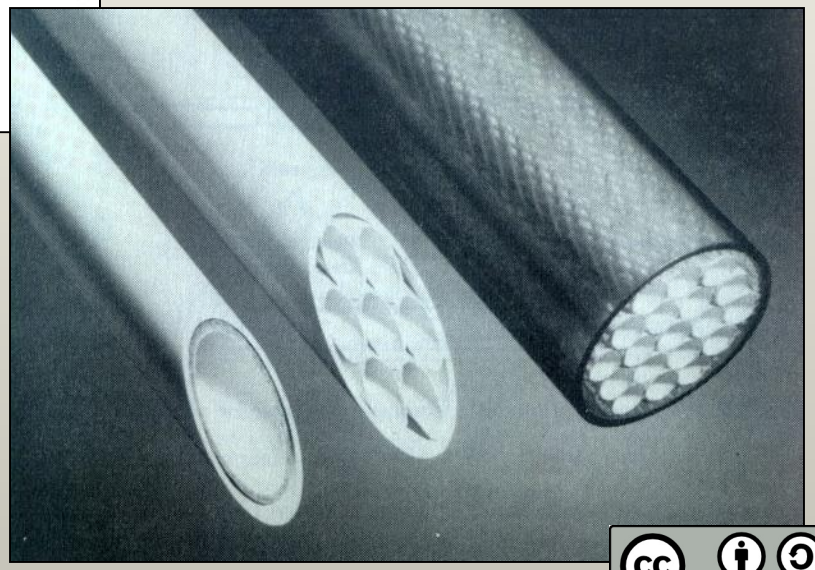
Membrane shapes and arrangements

- Plate, flat, sheet membranes
- Tubular (channel inside > 4 mm)
- Capillary (low diameter)
- Hollow fibres (inner diameter 0.2 – 3 mm)
- Spiral-wound
- Pleated sheet cartridges (dead-end filtration)

Tubular membrane

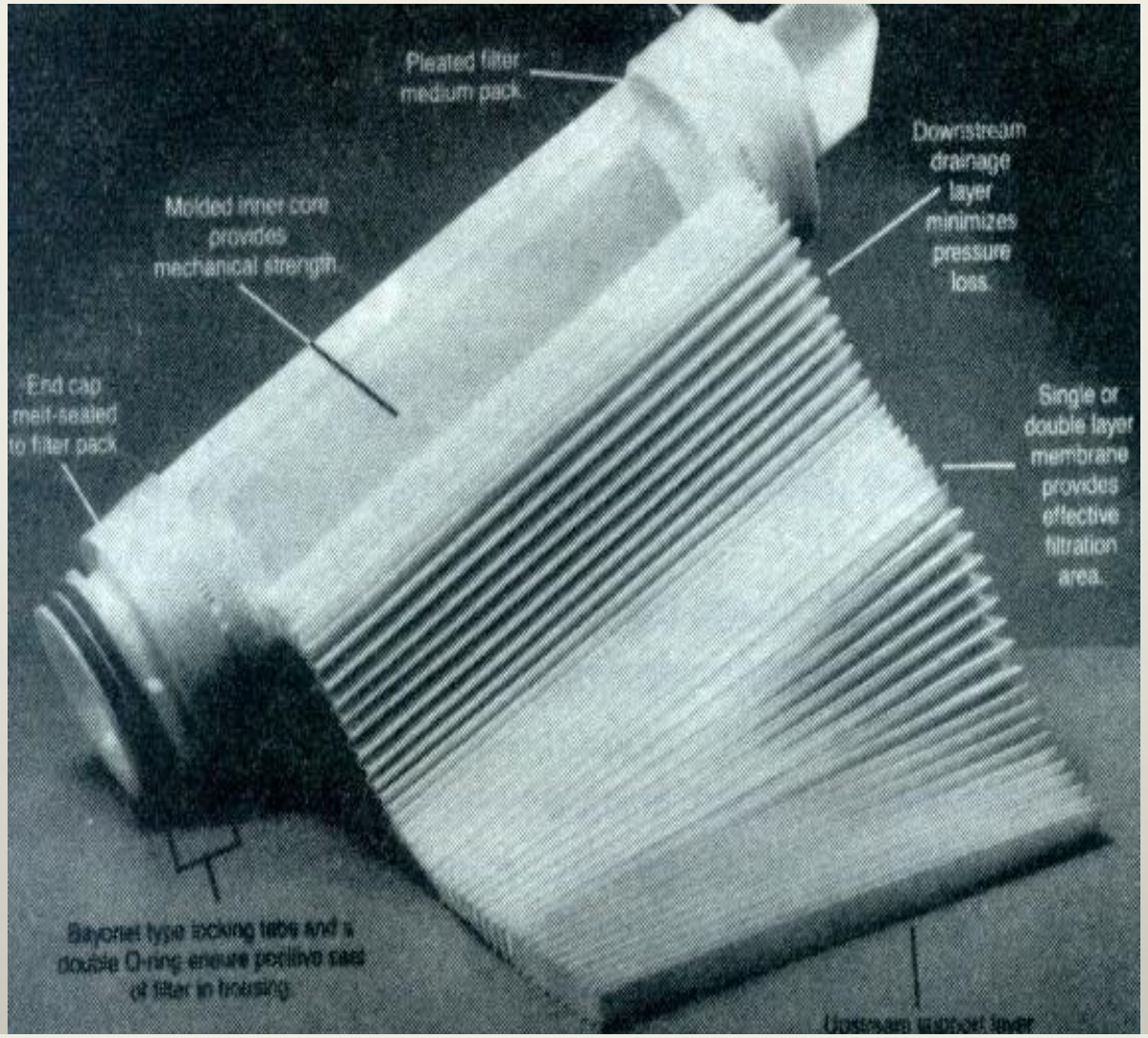


Membralox ®



Cheryan M.: Ultrafiltration and Microfiltration Handbook, Technomic Pub. Co., 1998

Pleated-sheet membrane



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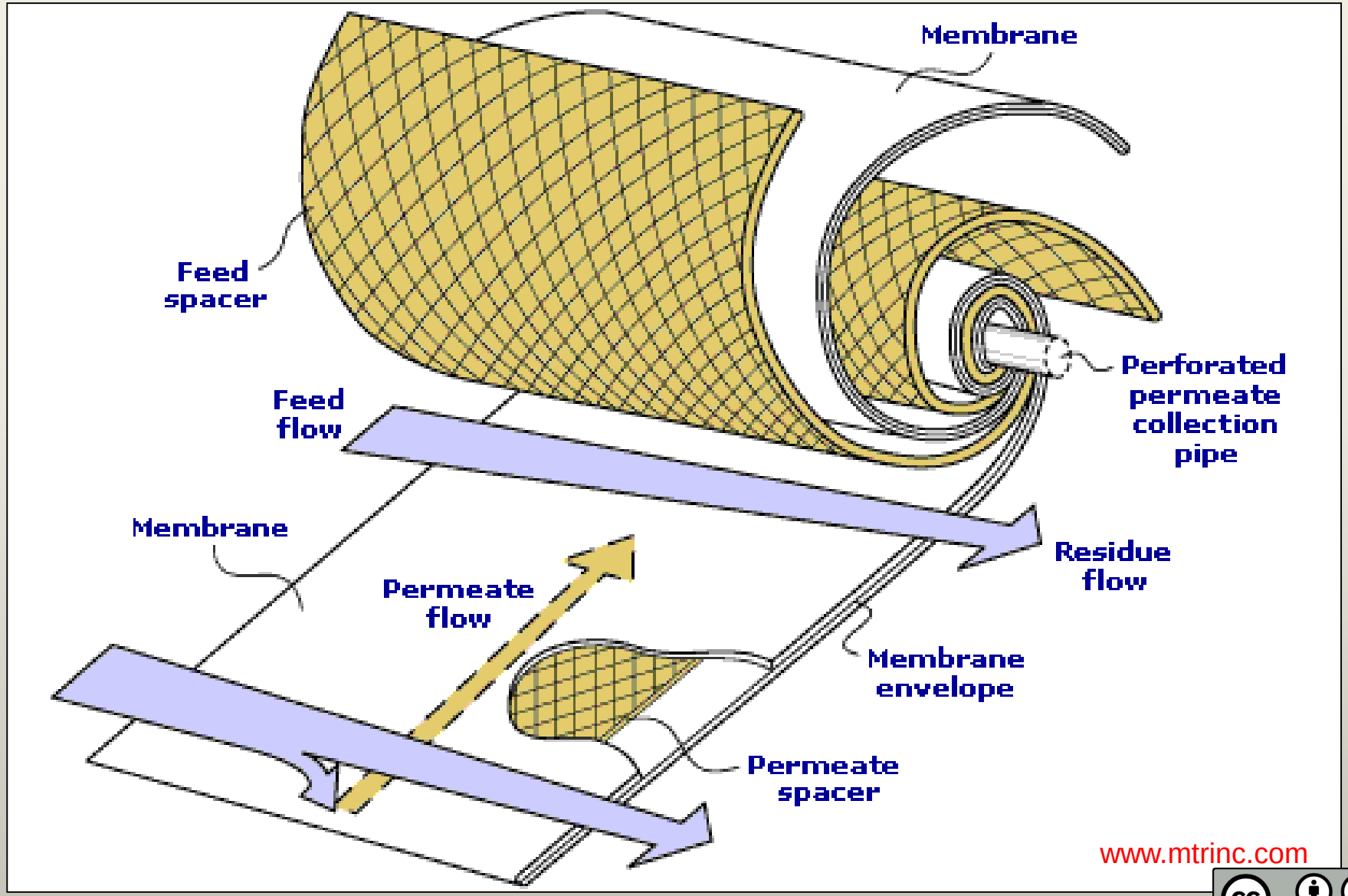
Spiral wound membrane



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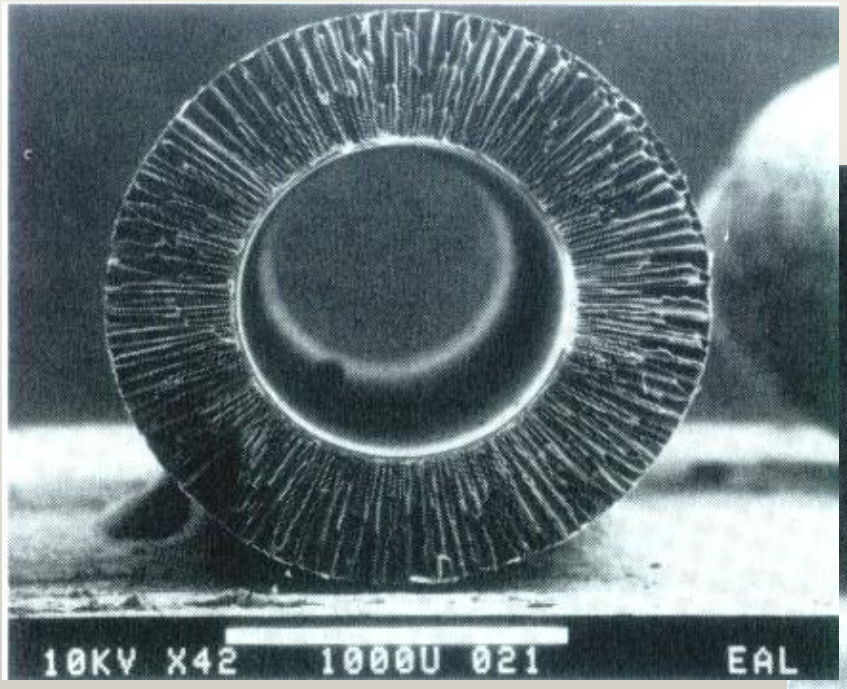
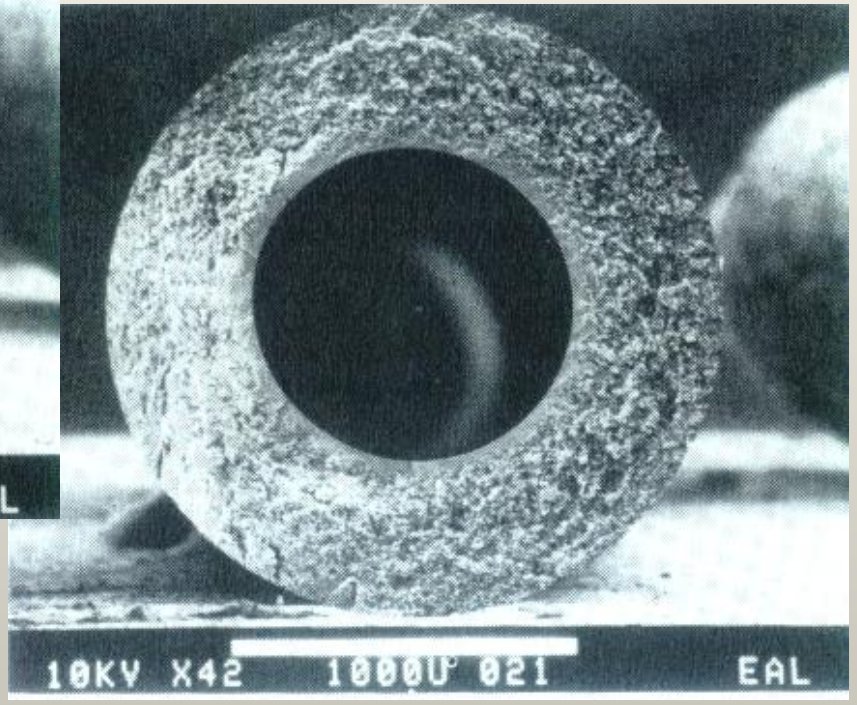
Hollow fibres

Asymmetric structure



Microporous structure



Cheryan M.: Ultrafiltration and Microfiltration Handbook, Technomic Pub. Co., 1998

Biomembranes

Immobilization of enzymes or biological agents (bacteria, yeasts, moulds) on the membrane´s surface

- adsorption, chemical bonds

Liquid membranes

a) **ELM = Emulsion Liquid Membrane**
   – immiscible liquids
b) **ILM = Immobilized Liquid Membrane**

3. Membrane modules

- Rotary membranes: tubular and disk
- Vibrating membranes: disk

Rotary tubular module

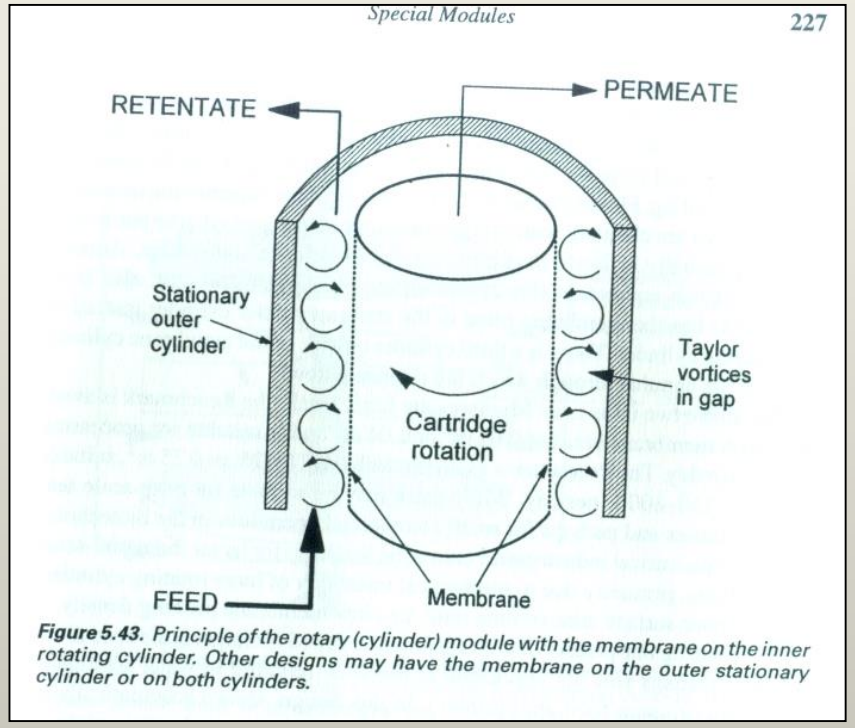
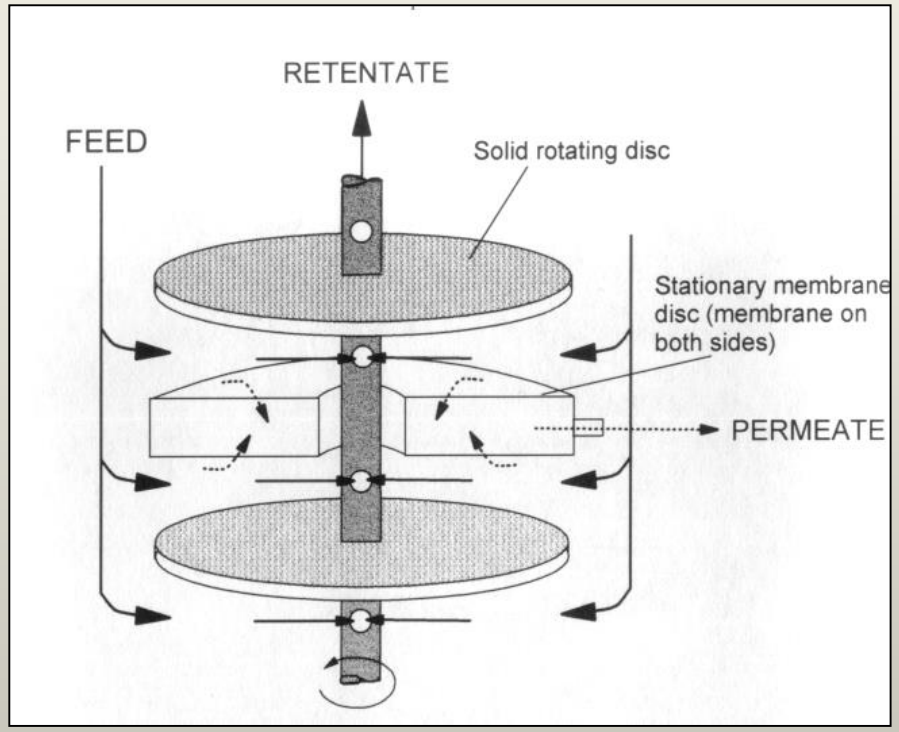


Figure 5.43. Principle of the rotary (cylinder) module with the membrane on the inner rotating cylinder. Other designs may have the membrane on the outer stationary cylinder or on both cylinders.

Rotary disk module

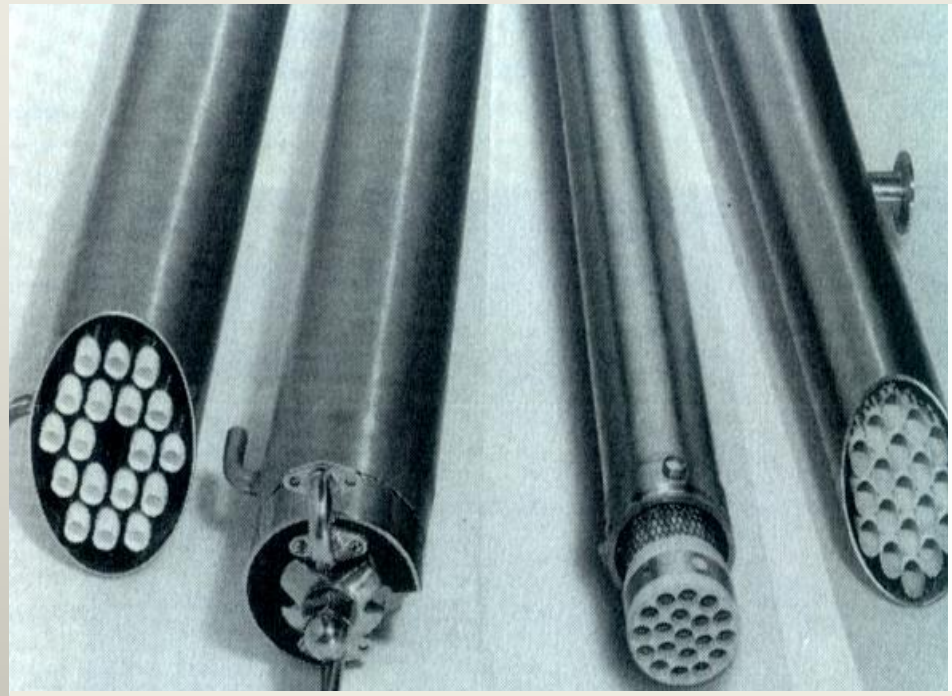


Cheryan M.: Ultrafiltration and Microfiltration Handbook, Technomic Pub. Co., 1998

Filtration area enlargement

Tubular membranes

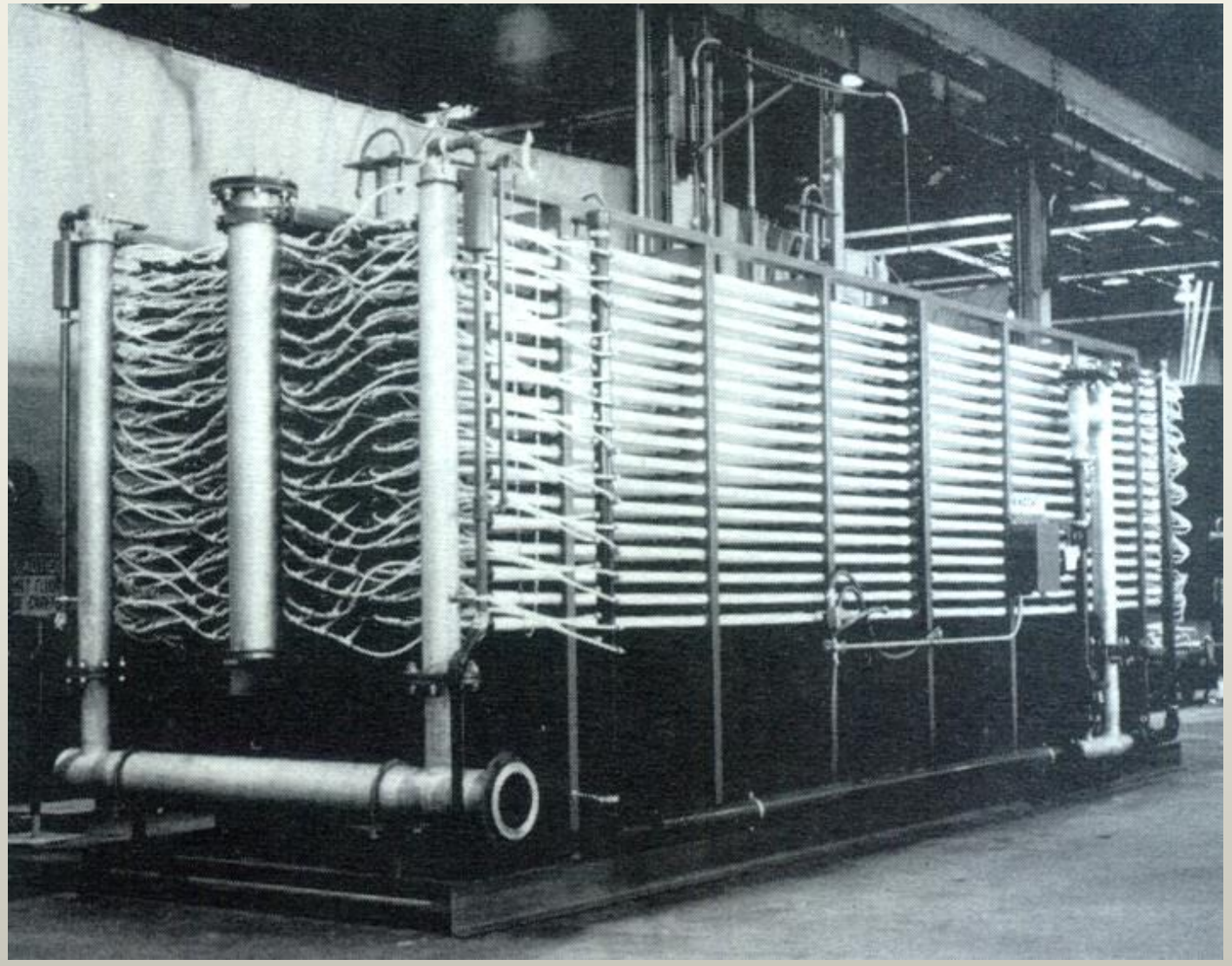
- Integration into cartridges
- Connections of several modules (in parallel, in series, retentate recycling, gradual filtration)



Cheryan M.: Ultrafiltration and Microfiltration Handbook, Technomic Pub. Co., 1998

www.apv.com

Connection of several tubular modules



Cheryan M.: Ultrafiltration and Microfiltration Handbook, Technomic Pub. Co., 1998

Connections of several tubular modules

Air filtration

Two filtration stations – cleaning / operation

www.airproducts.

Filtration area enlargement
Plate modules

www.dayton-knight.com

Membrane reactors

Membrane used:

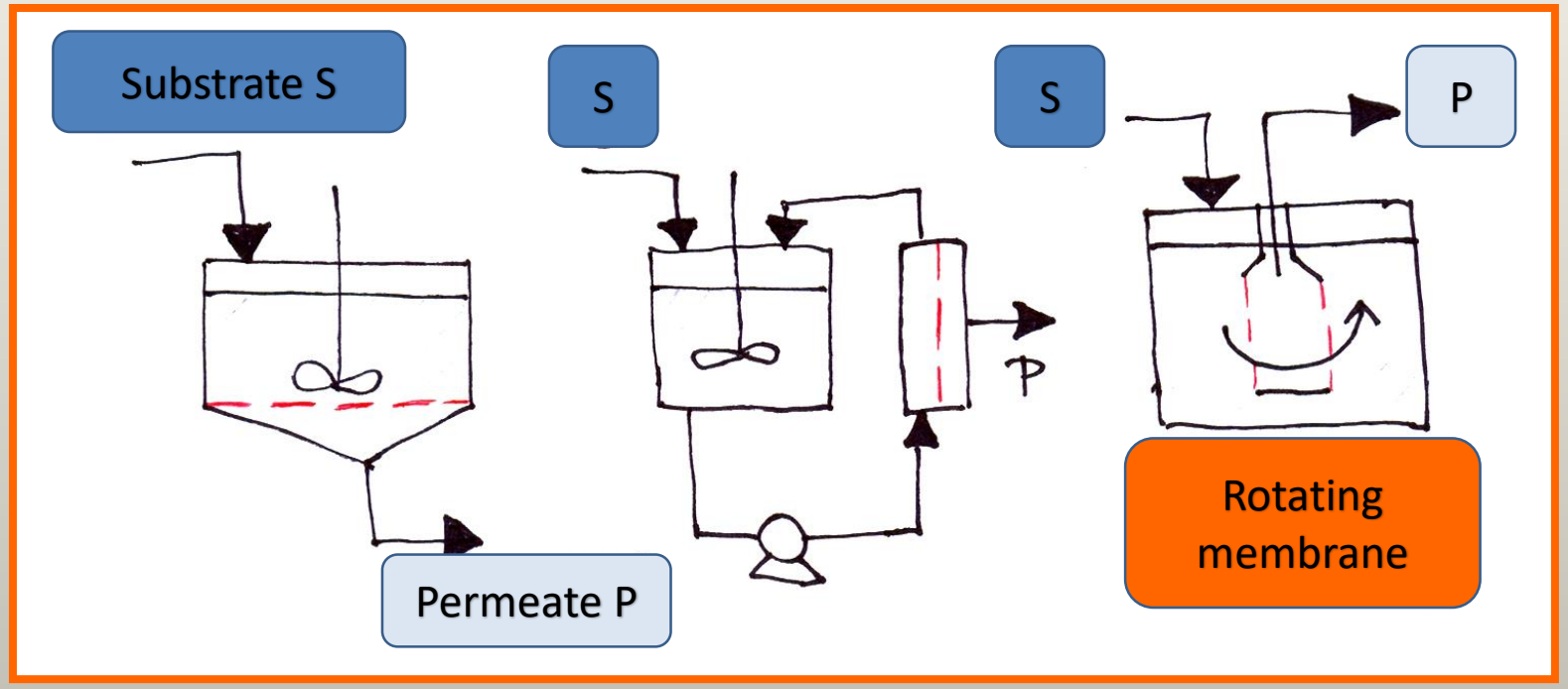
Hollow fibre, flat, rotating cylinder,

Advantages:

- Easier cleaning
- One-step operation (chemical reaction and separation at once)

Placement:

Inside a bioreactor or in external recycling pipes



Separation and purification techniques

Membrane separation processes – Filtration kinetics and separation efficiency

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Information sources

http://sch.vscht.cz/vyuka/international-students/erasmus-students/

Cheryan M. (1998): Ultrafiltration and Microfiltration Handbook, In: Technomic Pub. Co. (Eds.), Lancaster, Pensylvania, pp. 243.

Filtration kinetics and separation efficiency

Contents

1. **Filtration velocity**

Filtration theory, filtration kinetics, driving forces, character of separated particles and molecules (charge, size, shape, affinity, isoelectric point), transport mechanisms, filtration equation

2. **Permeate flux and membrane fouling**

Description of fouling and concentration polarization, factors affecting membrane fouling (membrane properties, solution properties, character of the process), permeate flux enhancement, cleaning and sanitation, pure water flux

3. **Separation efficiency calculations**

Rejection, retention, concentration factor

4. **Exercises**

1. Filtration velocity

- Expressed as a volumetric permeate flow across 1 m^2 of the membrane surface under given conditions (temperature and pressure)

$$l \cdot h^{-1} \cdot m^{-2}$$

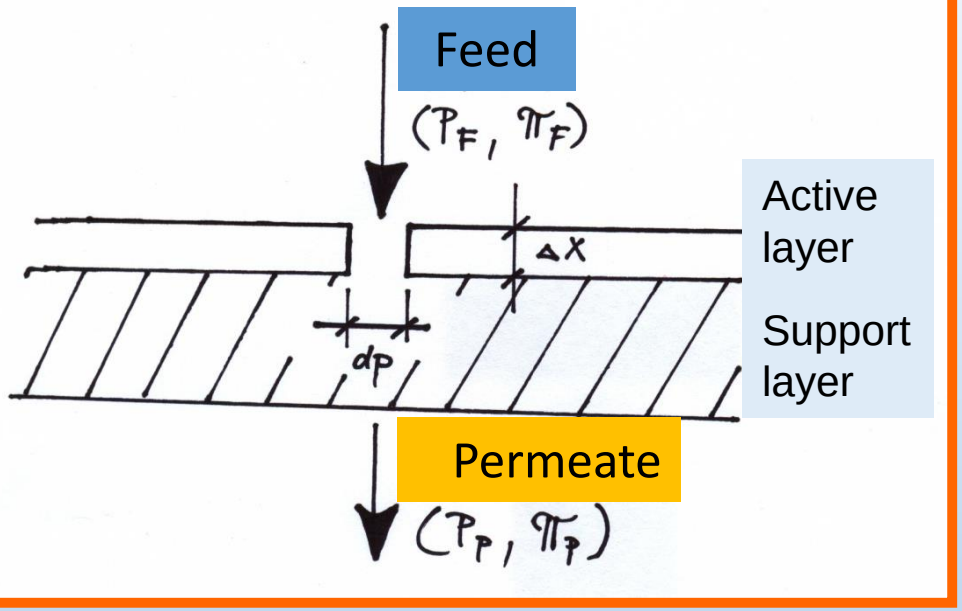
- Affected by permeability and pore density (porosity)
- Low permeability can be compensated by higher membrane area

In general:

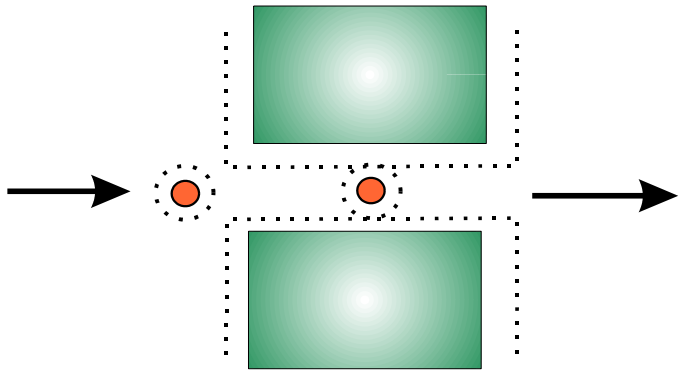
$$mass\_flow = area \cdot \frac{driving\_force}{resistance}$$

Filtration theory:

Pressure-driven processes: driving force = pressure gradient



Cross section of the membrane



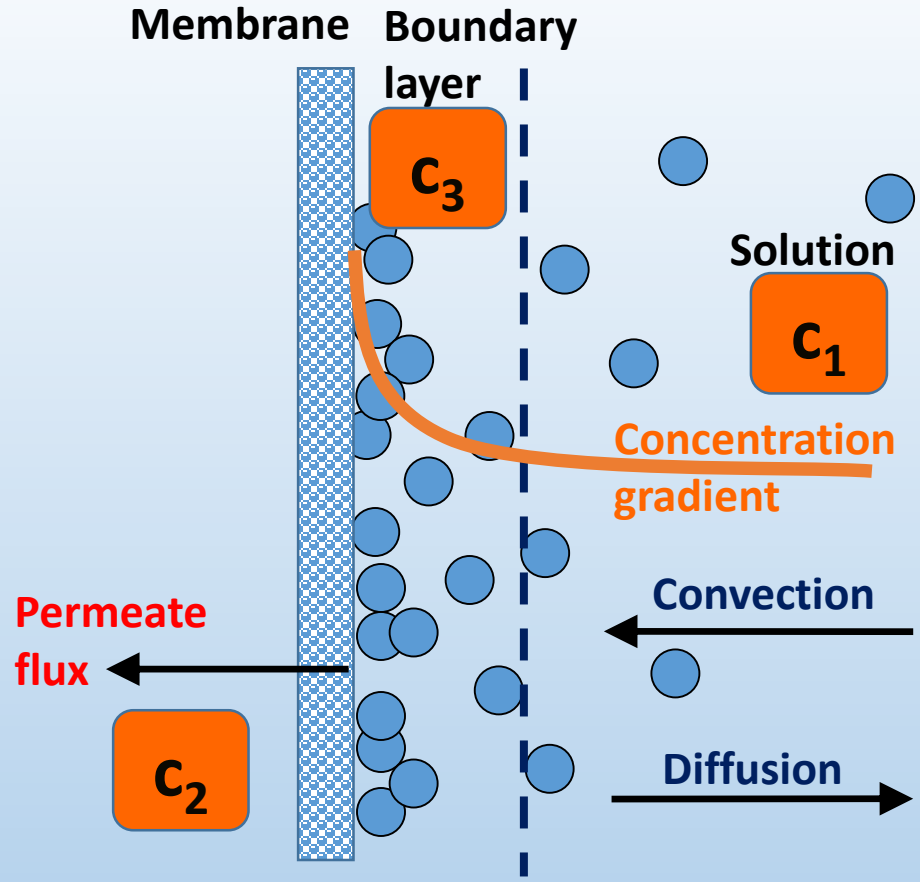
Pressure drop : $P_T = P_F - P_P$

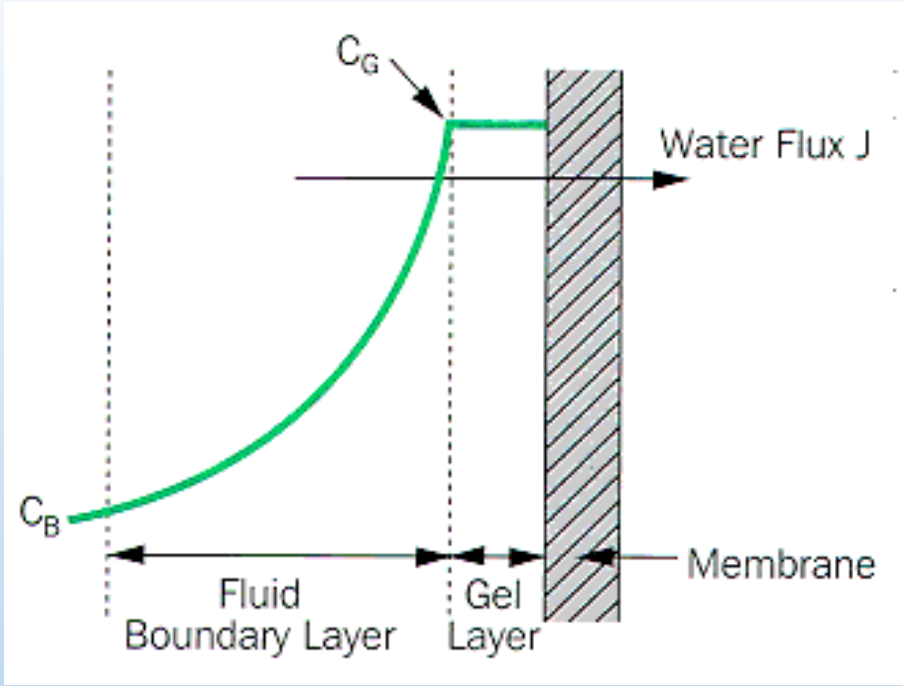
Osmotic pressure within the membrane: $\Delta\pi = \pi_F - \pi_P$

Real driving force: $= P_T - \Delta\pi$

If the osmotic pressure is negligible, the driving force of the process: $= P_T$

Concentration polarization:



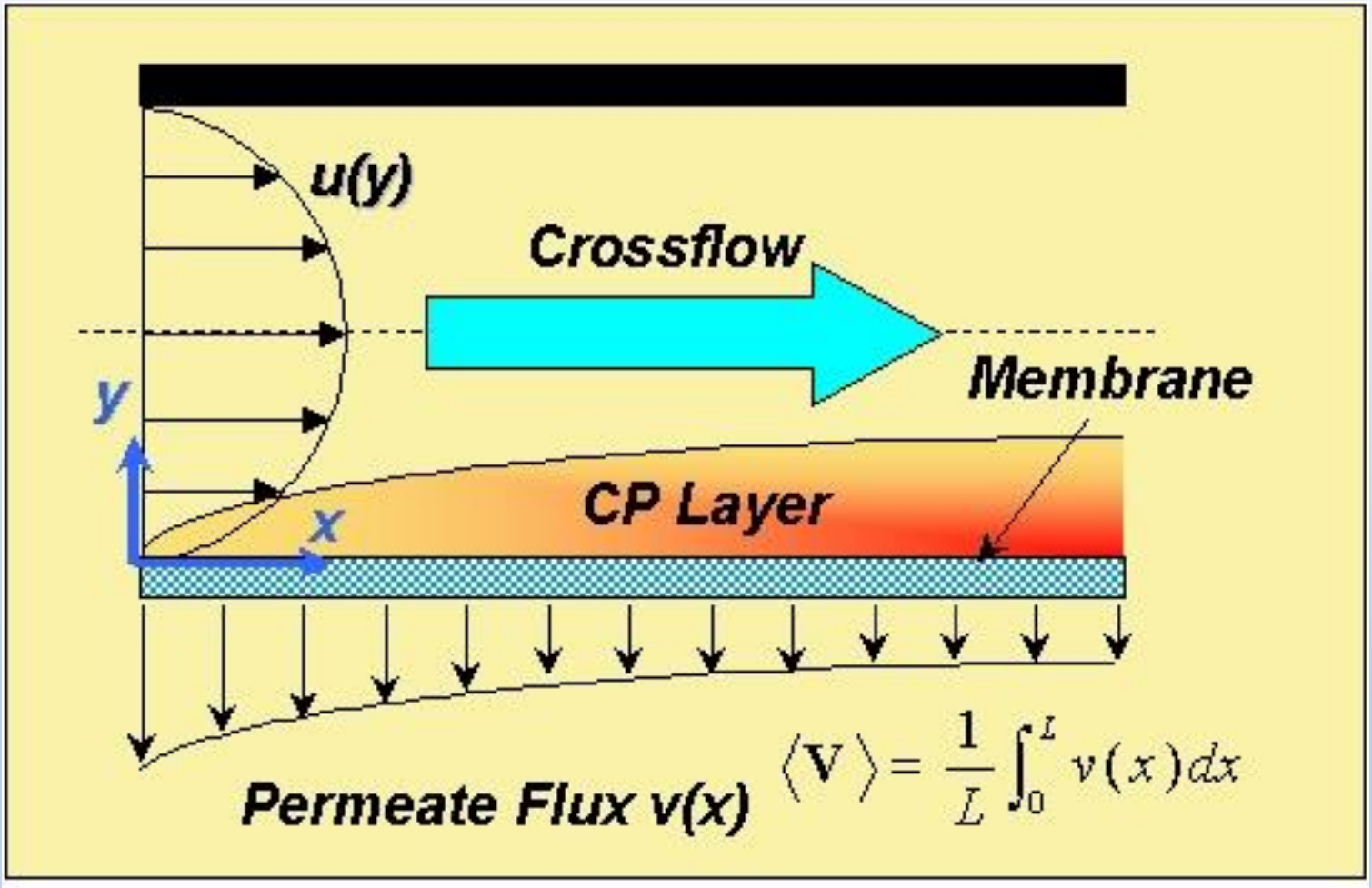


University of Minnesota Duluth; www.d.umn.edu

Higher concentration of components in a boundary layer than in the bulk of solution:

- **Formation of concentration profile – under extreme conditions – gel or precipitate formation, secondary membrane**
- **Increased membrane resistance**

Concentration polarization:



Pressure-driven membrane processes

Driving force = pressure gradient

Real driving force: ➔ reduced by the pressure drop in the polarization layer, secondary membrane or gel layer

- Convective flow J_s

$$Js = J \cdot c_1$$

- Diffusion velocity (neglected concentration gradient c)

$$Js = D \cdot \frac{dc}{dx}$$

- Filtration equation:
  G = specific membrane permeability

$$-G \cdot c_2 + D \cdot \frac{dc}{dx} + G' \cdot c_1 = 0$$

Permeate flow Diffusion Convection

2. Flux, fouling, membrane cleaning

Discharge = permeate flow, flux [$l.h^{-1}.m^{-2}$]

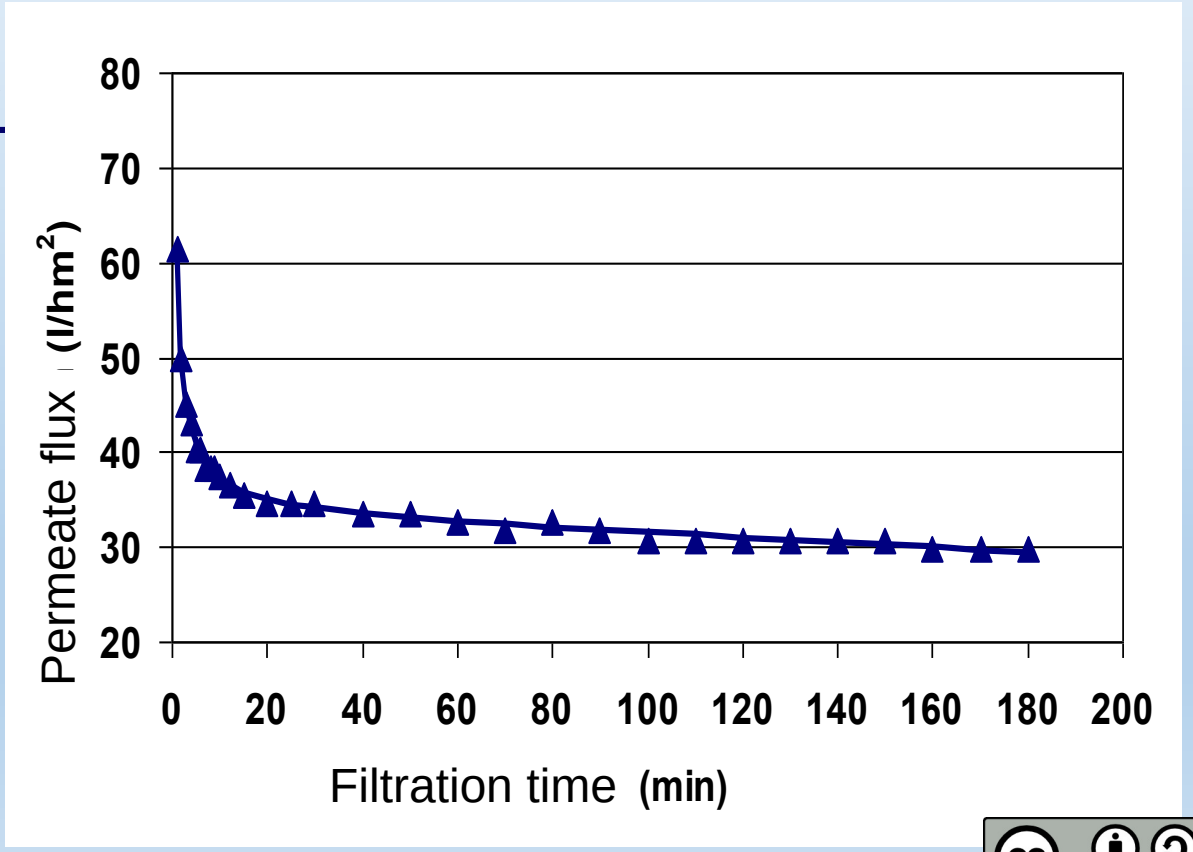
Permeate flow drops within the filtration – problem!

The drop is caused by

- **concentration polarization**
- **silting of membrane pores called**

  fouling effect

Description by mathematical models for permeate flow



Factors influencing the fouling effect

a) Membrane properties

- Pore size (permeability)
- Active layer thickness
- Affinity of dissolved components to the membrane

b) Character of medium to be filtered

- Viscosity
- Ionic strength
- pH
- Density
- Concentration
- Reactivity of molecules with the membrane
- Shape and size of separated molecules
- Sample pre-treatment – precipitation, addition of ballast material, pre-filtration (to improve the molecule to pore size ratio)

Factors influencing the fouling effect

c) Conditions during the process operation

- **Driving force – e.g. pressure (increasing during filtration)**

  X irreversible fouling! – limit pressure

  X limit flux! – formation of concentration polarization layer, gel!

- **Temperature**

- **Hydrodynamics (character of flow along the membrane) – maintain turbulent flow:**

  - **Pulsation, ultrasound, air bubbling**

  - **Back-flushing (asymmetric and composite membranes – high risk of tearing the active layer off)**

Membrane cleaning

- Increases operation costs of the process
- Prolongs dead times
- Back-flushing
- CIP (Cleaning in place): chemicals, detergents, high temperatures
- Steam sterilization (ceramic)
- Chemically: ozone, Cl_2 – corrosive action, NaClO, HNO_3, NaOH – ceramic membranes only
- Mechanically: after the membrane removal, sheet membranes
- Enzymatically

Parameters describing the filtration

Pure water flux J_v

Importance:

- **To estimate efficiency of membrane cleaning procedure**
- **The ratio of pure water flux before filtration and after the membrane cleaning should be less than 20%**

Definition:

Permeate flow during filtration of pure (demineralised) water at 20 °C and a given pressure expressed per 1 m² of the membrane surface area:

$$Jw = \frac{J_P \cdot k_t}{S}$$

J_W the pure water flux ($l.h^{-1}.m^{-2}$)

J_P the permeate flow

k_t the temperature coefficient (20 °C)

S the membrane surface area (m^2)

Filtration efficiency

- Permeate and retentate chemical composition
- Defines which particles were retained and which were transferred to permeate
- Concentration of component in feed, permeate and retentate

Concentration factor (ratio)

- VCR/VCF volumetric concentration factor
- MCR/MCF mass concentration factor

Definition:

$$VCR = \frac{V_F}{V_R}$$

V_F feed volume

V_R retentate volume

Separation efficiency – Rejection

- Properties of permeate and rententate
- It requires the use of analytical methods
- Concentration of a component in different process streams

$$R = 1 - \frac{ci_{downstream}}{ci_{upstream}}$$

Rejection factor *R*

Expresses the relation between the concentration of a component above and below the membrane:

$ci_{downstream}$, $ci_{upstream}$ concentration of a component *(i)* below and above the membrane, respectively

Apparent rejection *R*

$$R = 1 - \frac{c_{iP}}{c_{iF}}$$

$ci_{upstream}$ equals to the concentration of a component *i* in the bulk (i.e. in the feed, c_{iF})

$ci_{downstream}$ equals to the concentration in the bulk of permeate (c_{iP})

Intrinsic rejection

$ci_{upstream}$ equals to the concentration of a component at the membrane surface – difficult to measure sometimes.

Separation efficiency – Retention

Retention factor *r*

Refers to concentration of a component in permeate and retentate

$$r = 1 - \frac{C_{iP}}{C_{iR}}$$

Relative recovery η_i

Expresses the amount of component gained by the process:

$$\eta_i = \frac{m_{i,out}}{m_{i,in}}$$

a ratio of the weight of the component in the useful product $m_{i,out}$ to the total weight of the component entering the process $m_{i,tot}$

4. Exercises and Calculations

Problem 1

The initial permeate flow rate on the ultrafiltration membrane, having a filtration area of 0.5 m^2, was 360 $l/h.m^2$. After 3 hours of the filtration process, the flow rate was measured again as the permeate volume; i.e. the volume of permeate collected during 30 seconds was 300 ml. How much has the flux changed since the beginning of the process if the filtration ran at the constant pressure of 0.2 MPa and temperature 40 °C?

4. Exercises and Calculations

Problem 2

50 litres of sugar solution was filtered on a nanofiltration membrane at the temperature of 60 °C and pressure of 8 MPa. After 10 hours of filtration, 30 litres of permeate were collected. The concentrations of K^+ ions in the feed and permeate streams were 620 and 30 mg/l, respectively. Calculate the volume concentration factor, retention factor and apparent rejection of potassium ions on the membrane used.

4. Exercises and Calculations

Problem 3

The pure water flux before filtration, measured at 20 °C and 1 MPa, was 1000 l/h.m^2. After the filtration and membrane cleaning, the pure water flux was measured again at the temperature of 25 °C and pressure 2 MPa. Its value was 160 l/h.
The viscosity coefficient at the temperature 25 °C is 0.888 and the membrane area is 0.1 m^2. Calculate the pure water flux drop and estimate if the cleaning procedure was sufficient.

Separation and purification techniques

Individual membrane techniques driven by pressure and electric potential gradient

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http://sch.vscht.cz/vyuka/international-students/erasmus-students/

Cheryan M. (1998): Ultrafiltration and Microfiltration Handbook, In: Technomic Pub. Co. (Eds.), Lancaster, Pensylvania, pp. 243.

Introduction into membrane separation processes

Contents

1. Individual membrane processes

Diffusion, diffusion theory, diffusivity, solvation, dialysis, osmosis, pervaporation, gas permeation, membrane distillation

2. Pressure driven membrane processes

Microfiltration, ultrafiltration, nanofiltration, reverse osmosis

3. Membrane separation in electric field

Electrodialysis, membrane electrolysis, electroosmosis, transport depletion, electrophoresis, Donnan dialysis, ion-exchange membranes

Choice of a separation process

Permeate flux ✖ Separation efficiency

- **Define demanded properties of the product**

Define the required purity

90 % industrial enzymes, organic acids,
99 % sugar solutions
99.9 %
99.99 % vaccines

Physical and chemical properties (stability !)

- **Determine the initial properties of raw material**

Composition, chemical and physical properties, raw material properties

- **Choose the process and process set-up**

– Use different physico-chemical properties of products and contaminants
– Remove the highest concentration of pollutants at the beginning
– The most efficient process should be among the first steps
– The most expansive and demanding process should be the la

1. Individual membrane techniques

Terminology:

Diffusion

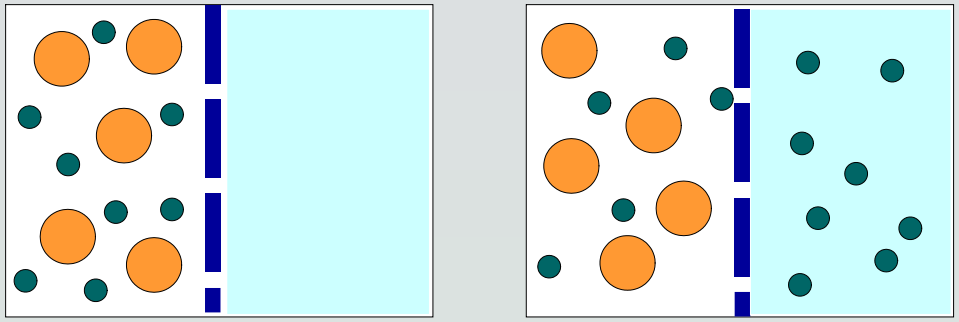
= a movement of molecules in liquid phase in a concentration gradient (from higher concentrated areas to lower concentrated ones)

1st Fick's law

is used to describe a diffusive flow of a liquid (*J*) through the membrane: flux is directly proportional to the concentration gradient (*dC*) and indirectly to the membrane thickness (*dx*), where *D* is the diffusion coefficient (diffusivity):

$$J = -\frac{D \cdot dC}{dx}$$

Dialysis



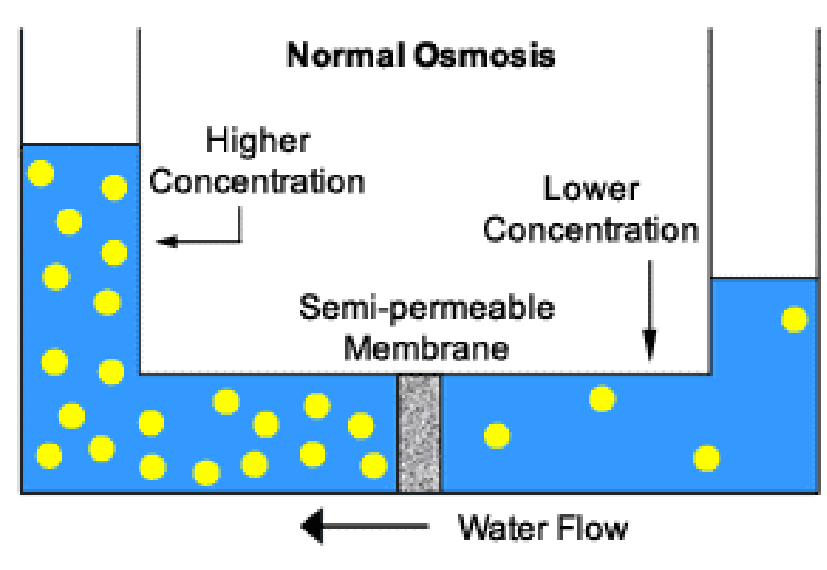
➔ **A transport of small molecules (dissolved in liquid) across the membrane (from hypertonic to hypotonic media); e.g. kidneys**

Driving force: concentration gradient

Osmosis

➔ **A transport of a solvent across the membrane, which retains dissolved molecules (i.e. from hypotonic to hypertonic media)**

Driving force: chemical potential gradient



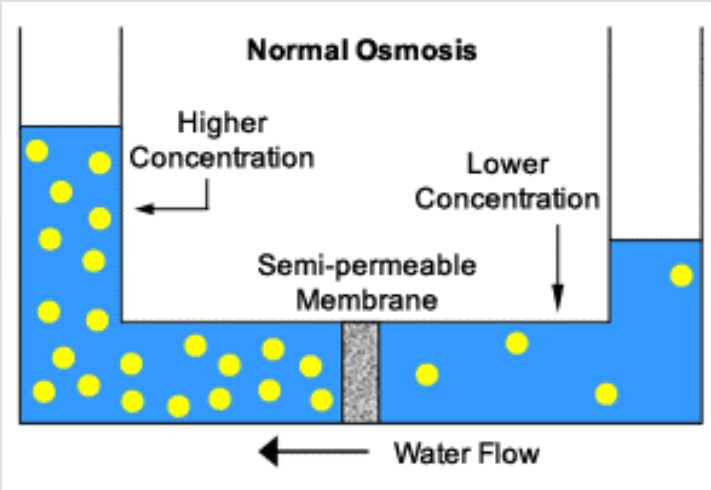
www.visionengineer.com/ env/reverse_osr

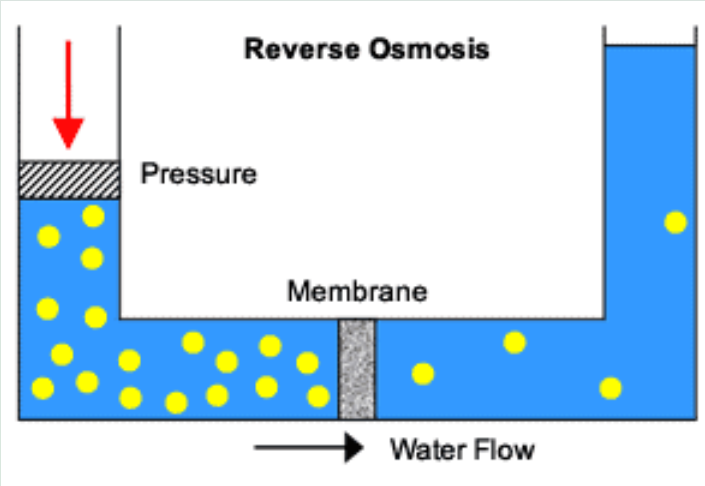
Reverse osmosis (RO)

- A process reversal to osmosis
- Driving force: pressure gradient through the membrane; it must be higher than the osmotic pressure ⇒ high working pressures (3 – 10 MPa)

  $p_{effective} > p_{osmotic}$

- Separation of particles of 10^{-4} μm = **only solvent molecules can permeate through the membrane!**

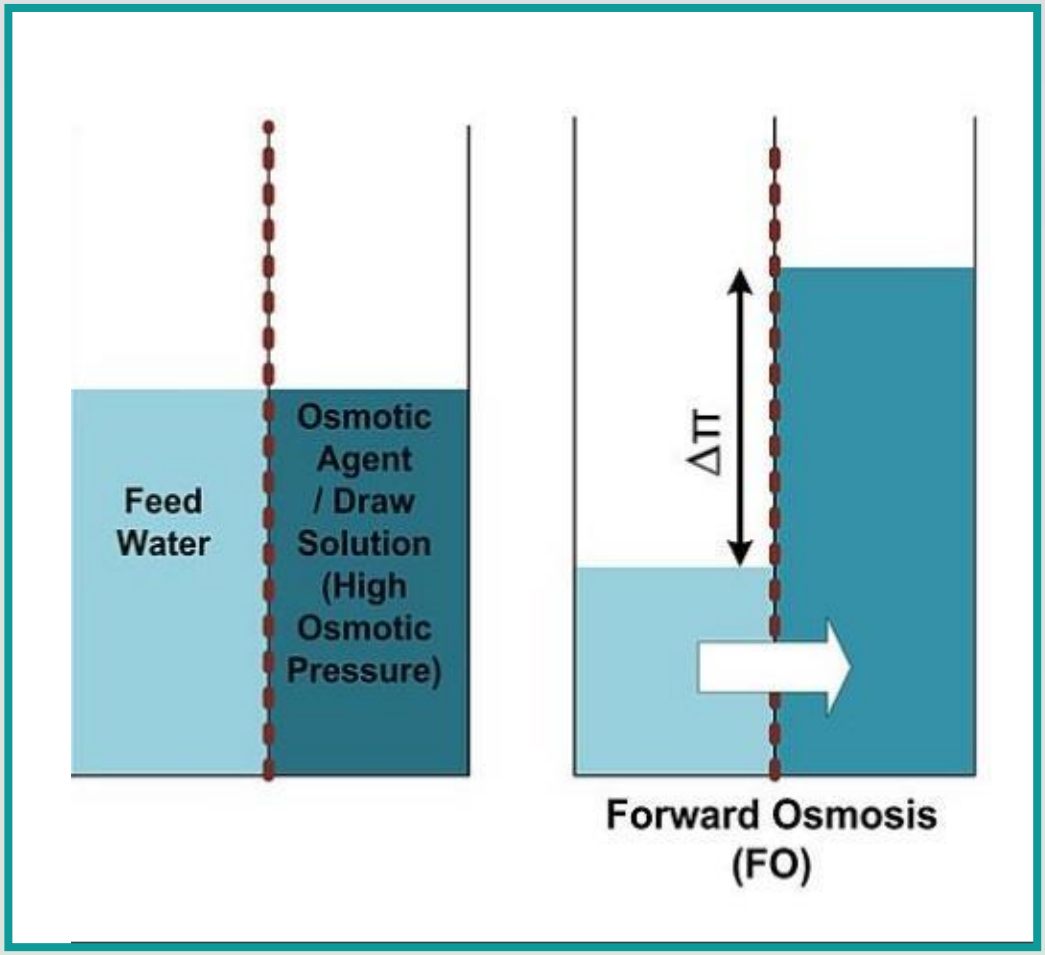




www.visionengineer.com/ env/reverse_os

Osmosis = Forward osmosis (FO)

- Osmosis used in industrial conditions
- Driving force: concentration gradient.
- No membrane fouling
- Desalination – usually as the first step, followed by another separation
- Hydration bags (draw solution solvents = glucose, fructose)



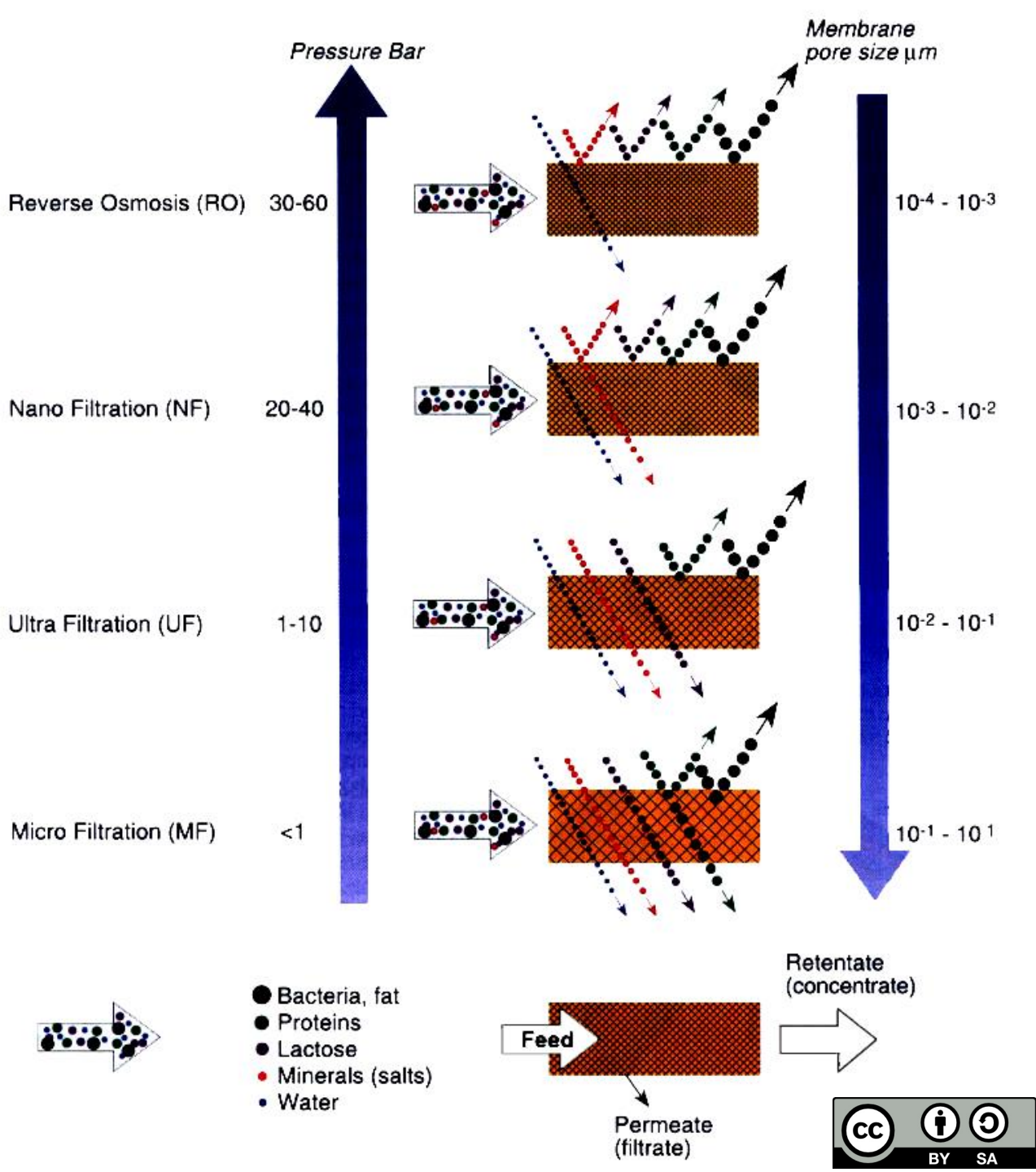
https://en.wikipedia.org/wiki/Forward_osmosis

2. Pressure-driven membrane processes

Microfiltration MF
Ultrafiltration UF
Nanofiltration NF
Reverse osmosis RO

- Conventional filtration - separation of particles bigger than 10 μm.
- BUT: unlike the conventional filtration where only hydrostatic pressure is needed as a driving force (or maximum pressure of 0.1– 0.5 MPa), **membrane filtration requires higher pressure gradients**
- The smaller the pore size, the higher the pressure gradient

Pore sizes and pressures applied in pressure-driven separations



http://fluidsep.in/Dairy.html

Microfiltration (MF)

- Separates particles within the range of 10 – 10^{-1} μm (i.e. bacteria, yeasts, suspended solids, high molecular substances; M>10^6)
- Particles bigger than 5 - 10 μm are better to separate by conventional filtration (dead-end filtration)
- Pressure difference needed: 0.02 do 0.5 MPa = low → low operation cost
- Refining technique; suspended solids are separated from dissolved substances, sieving effect

Ultrafiltration (UF)

Separates particles within the range of 10^{-2} – 10^{-3} μm (i.e. bacteria, viruses, colloids, macromolecular substances, MWCO 5000 – 500 000)

Pressure difference needed: 0.1 do 1 MPa

a technique for mutual concentration and fractionating of molecules or fine colloid suspensions

Sieving effect is the main separation mechanism

Nanofiltration (NF)

- Relatively new membrane process for separation of compounds within a size of $10^{-3} – 10^{-4}$ μm.
- Separation mechanism:
    1. **sieving effect** (large molecules, e.g. sucrose)
    2. **electrostatic forces** between membrane and particles present in solution (ion separation).
- Most of commercially produced NF membranes are negatively charged.
- NF membranes separate dissociated compounds from non dissociated (e.g. organic acids pass the membrane more easy at low pH, but are retained at high pH in a form of their salts, MWCO < 500).
- Membrane cut-off expressed as molecular weight or in Daltons
- Operation pressure 2 - 4 MPa = medium pressure

NF phenomena

- The separation mechanism of NF is not yet totally understood
- Single salt rejection: the higher the salt concentration the lower the salt rejection: NF membranes usually negatively charged – polarization layer is formed (= the effective charge of the membrane is hidden and co-ions can easily pass through the membrane).
- Ion hydration (solvation) affects the separation: e.g. $NaNO_3$ (M= 85 g/mol) retention is lower than the one of NaCl (58 g/mol) because of higher hydration of NaCl molecule in water solution.
- High viscosity caused salt or organic molecules prevents from the back diffusion in the concentration polarization layer and ions accumulate in permeate.

NF phenomena

Donnan effect

– observed at cheese whey NF (at high VCR)

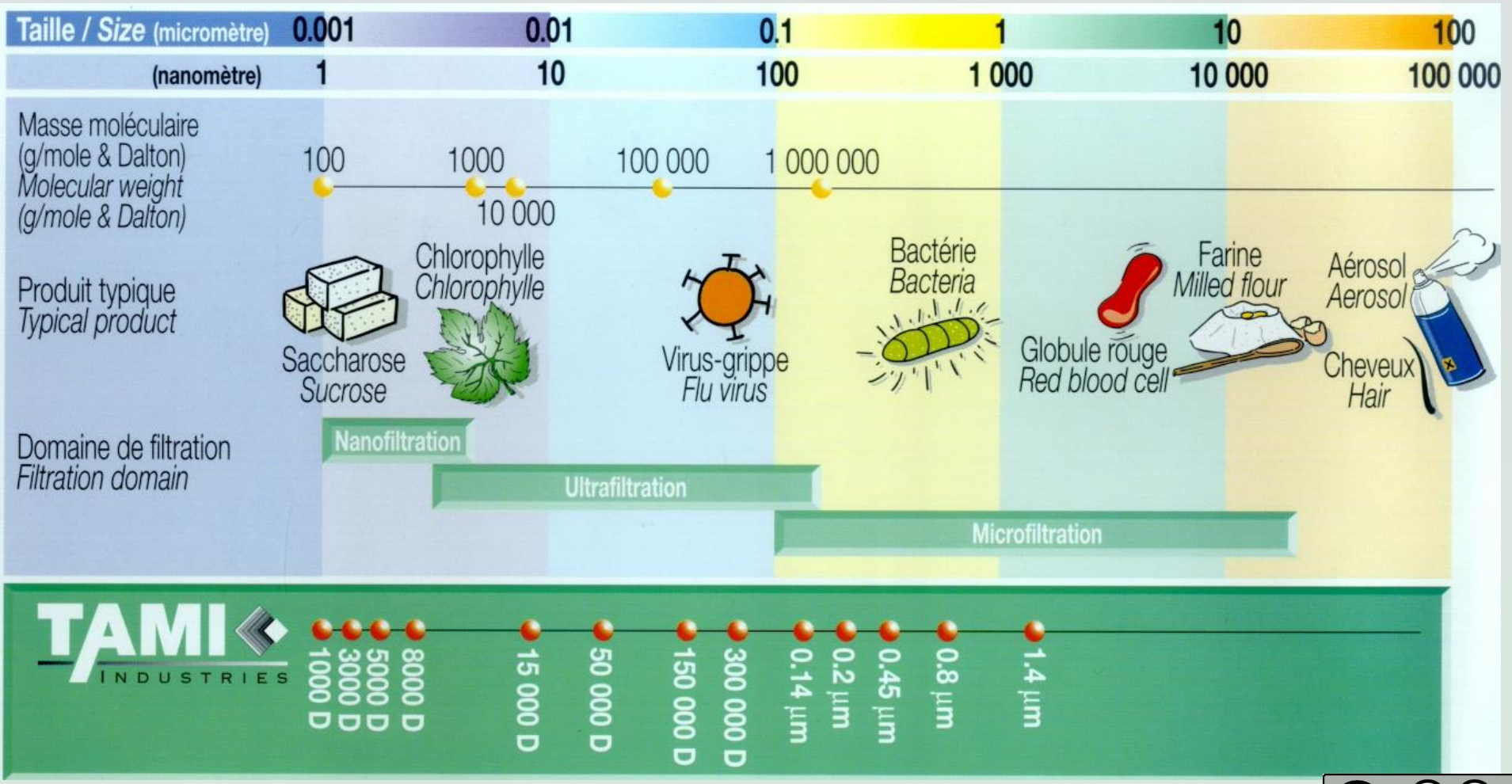
– membrane showed a negative rejection of Cl^- which preferably gathered in permeate

Explanation:

Proteins and other organic compounds are concentrated above the membrane (the gel formation and negatively charged layer occur at the pH 6.2).

This enhances the cation transport through the membrane. Due to the electro-neutrality principle, some anions must pass the membrane too in order to keep the electro-neutrality – only the smallest ones can pass (even against the concentration gradient; *Cuartas-Uribe, 20*

Cut-off of pressure-driven membrane processes



Pervaporation (PV)

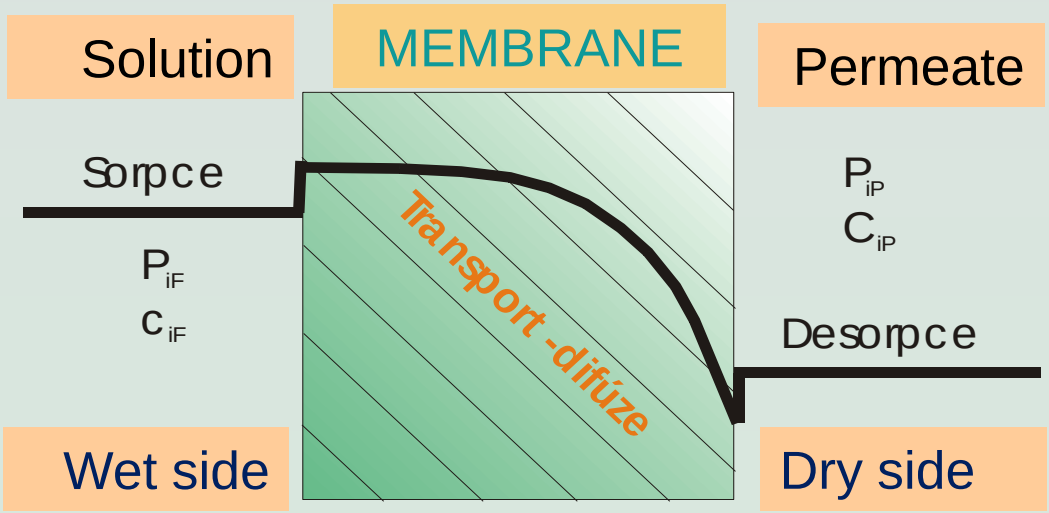
Mixture separation due to the evaporation through the porous membrane = selective barrier between two phases:

➔ Liquid feed – wet side of the membrane – swelling (atmospheric pressure)

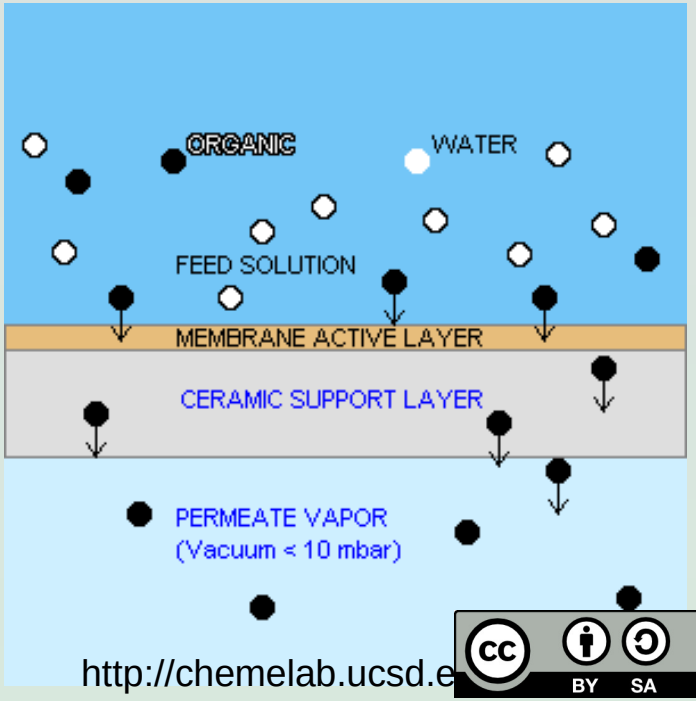
➔ Gas permeate – dry side of the membrane – almost dry (low pressure of vapours)

Principle: a transport from liquid into gas phase – phase change

1. **Adsorption** of molecules from the liquid phase on the membrane
2. **Diffusion** of molecules from in the membrane (limiting process)
3. **Desorption and evaporation** of molecules from the membrane



Driving force: $\Delta\mu_i$ expressed as Δp_i



http://chemelab.ucsd.e

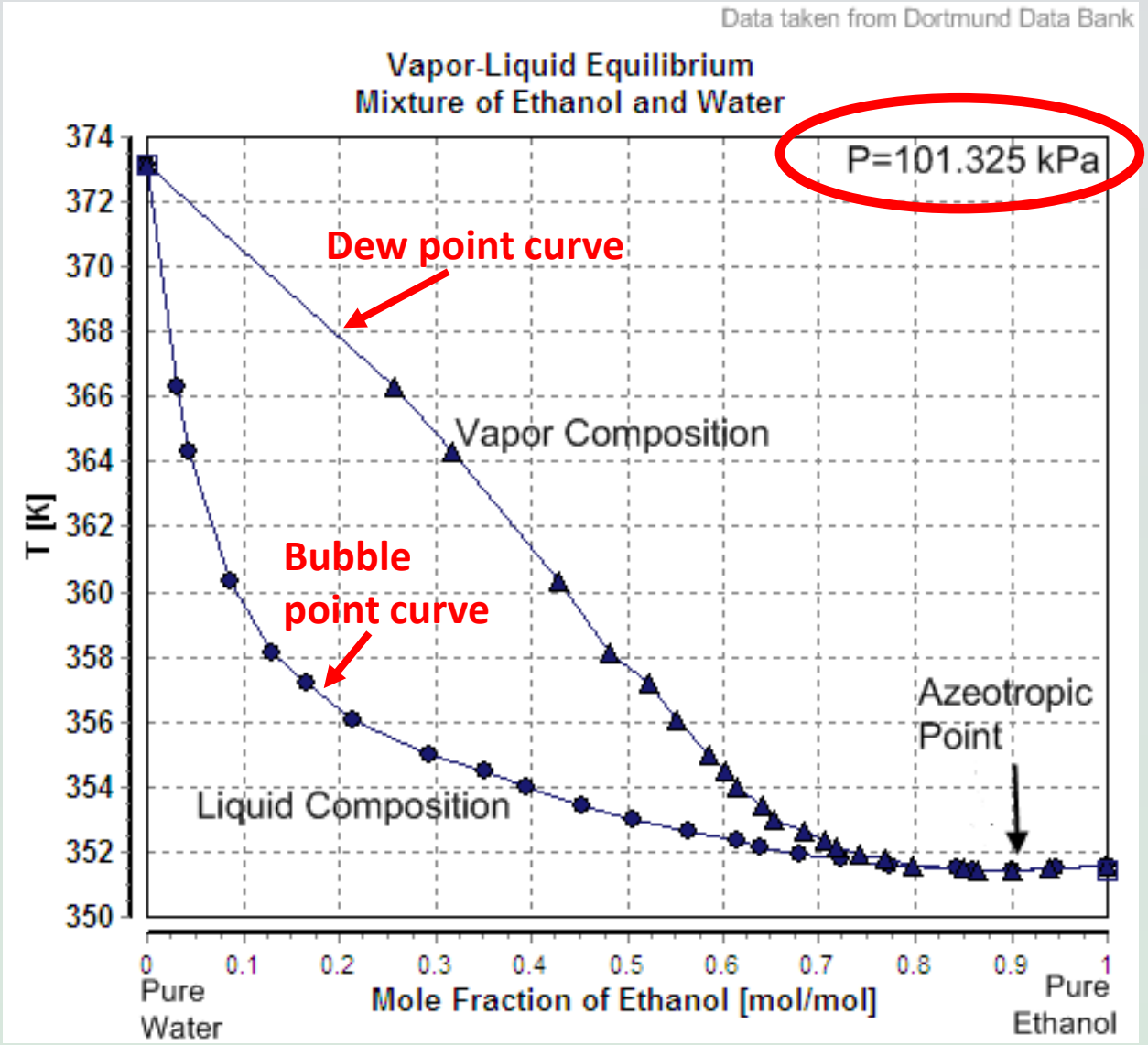
Pervaporation (PV)

- **Driving force: chemical potential difference (expressed as partial pressure), the pressure behind the membrane is lower, which causes evaporation followed by condensation of vapours**
- **Separation mechanisms:** different diffusivity
- Separation of **volatile compounds** (hexane, toluene, ethanol) from liquid mixtures (dehydration of organic solvents), separation of azeotropic mixtures, pollutants and impurities removal, solution concentration

PV membranes:

- Composite membranes (active layer)
- Hydrophobic membranes – separation of organic solvents (polysulfone, polydimethylsiloxane, polyamide)
- Hydrophilic membrane – polar solutions (water, water vapours) – glass, crystalline polymers of hydrophilic nature)

Azeotropic mixture



Ethanol
b.p. 78.4 °C (352 K)

Water
b.p. 100 °C (373 K)

Azeotropic mixture
ethanol – water
(95.6 % EtOH)
b.p. 78.2 °C

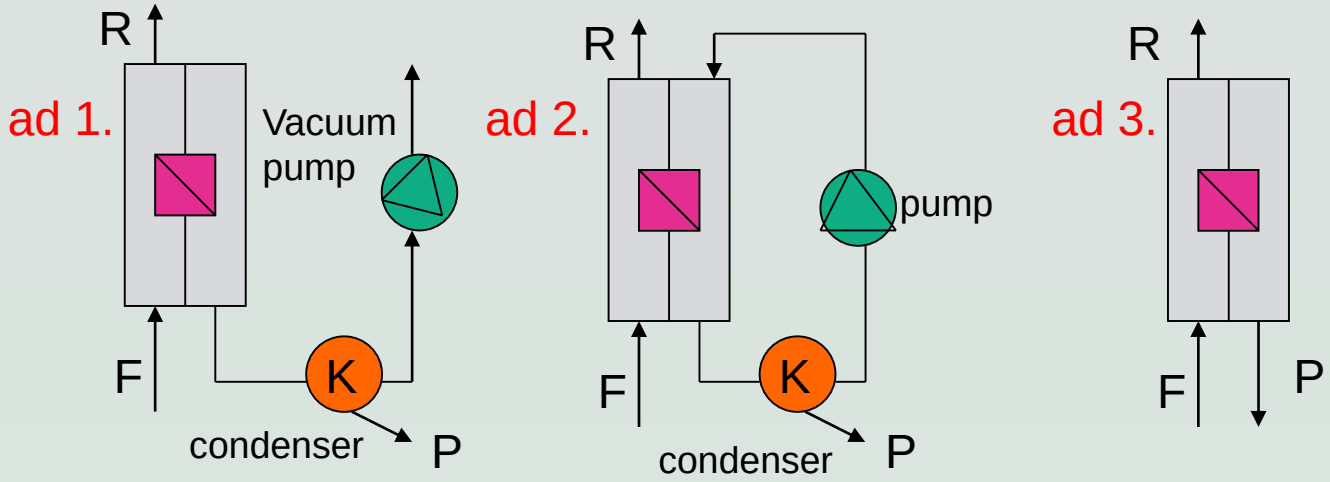
https://commons.wikimedia.org/

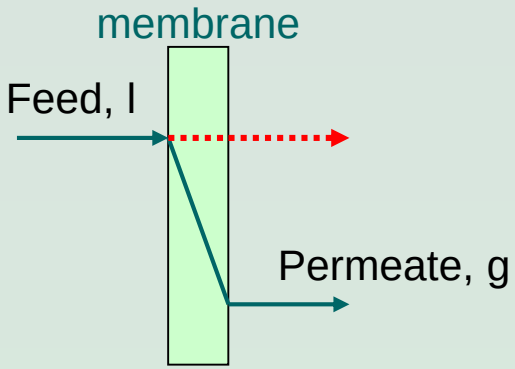
Pervaporation set-up

Modules - membranes: Capillary, hollow fibre, planar, spiral wound, tubular

Minimal p_{iP}:

1. **Permeate side – maintain a vacuum (20 – 30 mbar)**
2. **Permeate side purified by sweeping gas – removal of desorbed compounds)**
3. **Temperature reduction on permeate side – lower p_i of a component *i* (-20 °C, opt. ΔT = 50 °C)**



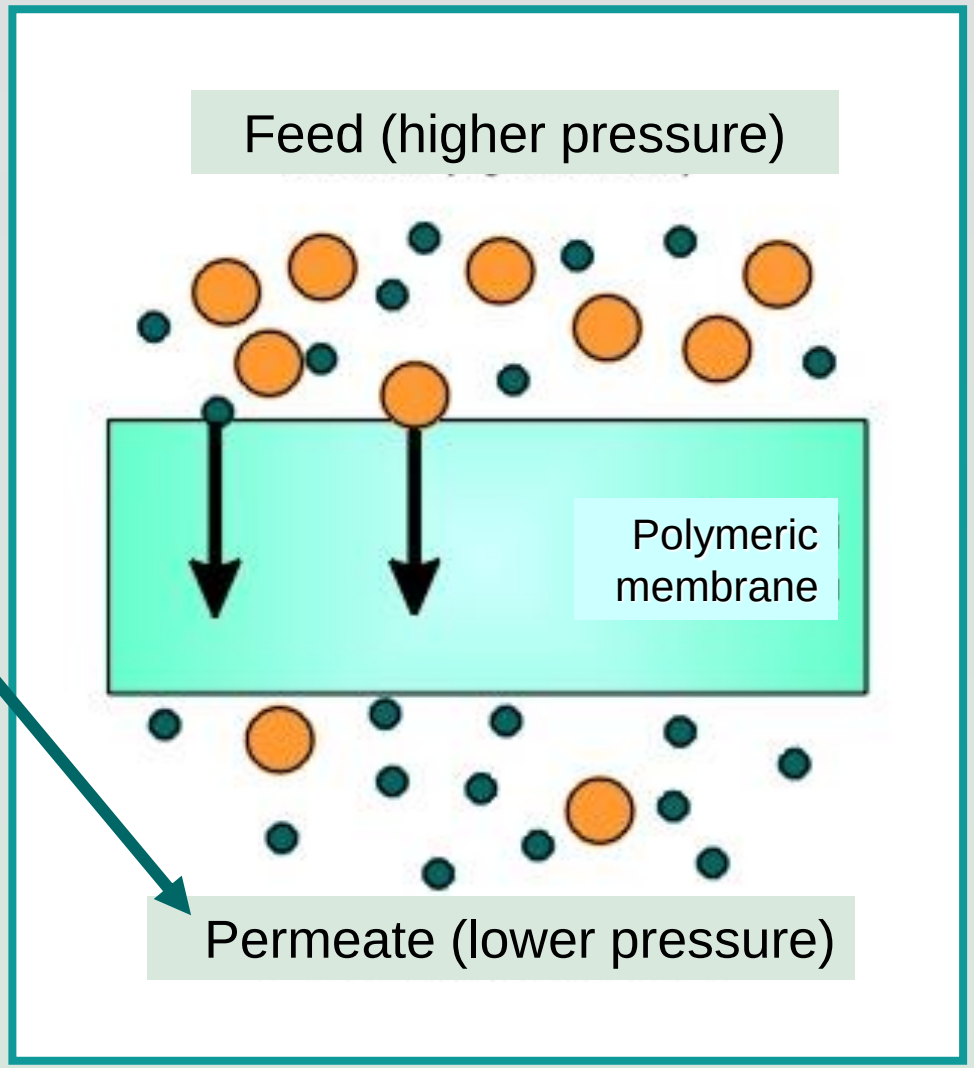


The effect of temperature

- Permeate side - latent heat of vaporization causes cooling
- Isothermic separation ($t_F = t_P$) a flow profile through the membrane is shorter – faster process

Gas permeation

- Similar to pervaporation but uses non-porous membranes
- The same phase on both size of the membrane (gas)
- Concentration gradient is provided by gas removal from the down-stream part of the process (so called sweeping gas is blowing on the permeate side)
- Separation mechanism: different velocity of gas permeation through the membrane (sorption, diffusion, sieving effect, desorption)



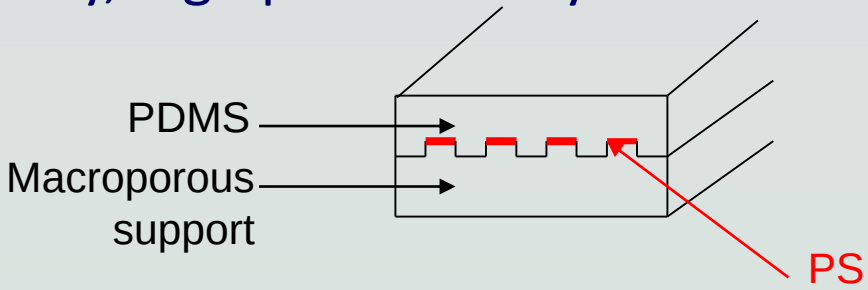
Membranes for gas permeation

Composite structure

Porous PS (polysulphone) coated by thin layer of rubber (PDMS; polydimethylsulphoxan) placed on macroporous support

PDMS – low selectivity, high permeability

PS – reversal



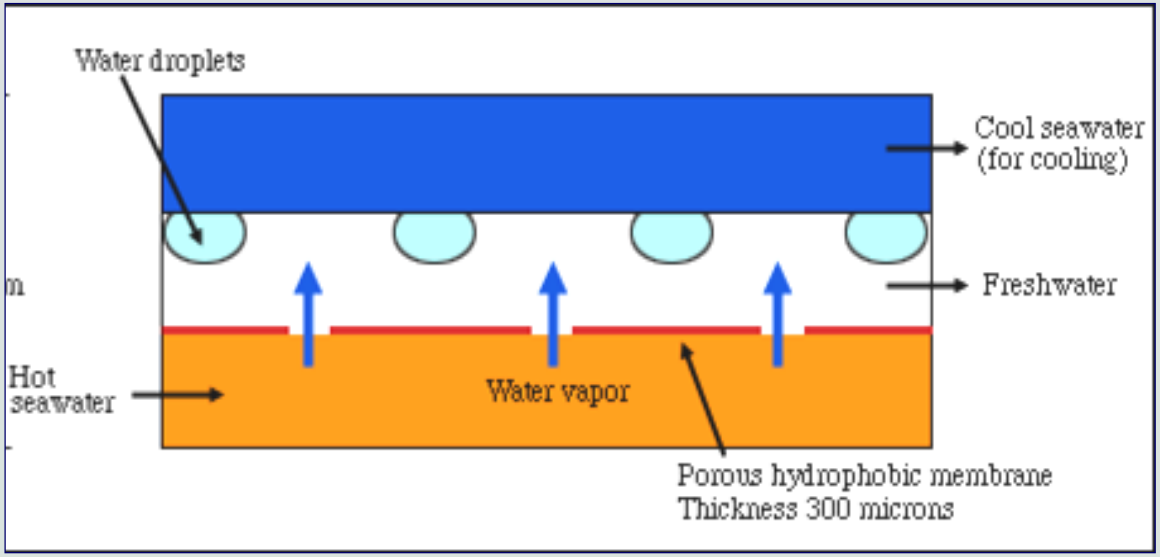
Applications:

- Separation of CO_2, CH_4 from natural gas and biogas)
- H_2S removing from natural gases
- $N_2 – O_2$ separation
- Gas drying (water removing)
- Separation of organic pollutants from air

Membrane distillation (MD)

Uses both distillation and membrane separation – porous hydrophobic membrane (permeable for water vapours but not for liquid water)

Driving force: temperature and pressure gradient



Principle:

➔ One side of the membrane: liquid is heated – evaporation, vapours pass through

➔ Other side: cooling – vapour condensation – water removing

The separation is influenced only by the equilibrium liquid-vapours (the membrane has no effect):

➔Limit – unsuitable for azeotropic mixture separation (azeotropic point = identical composition of gas and liquid phases)

➔Necessary requirement – the membrane must not be sodden – pore blocking, application for hydrophobic solutions

Velocity of permeation is given by Δt – high Δt ensures speed and sele

Membranes for the membrane distillation

- **Hydrophobic (non-polar)**
- **Microporous**
- **Material: PTFE (polytetrafluorethylene = Teflon)**
  PP (polypropylene)

Applications

Separations of

- → **Mixtures EtOH – water (up to 30 - 40 vol. %)**
- → **Water solutions of salts – desalination (e.g. water for heating systems)**
- → **Sea water desalination**

Drawbacks

- → **Low selectivity**
- → **Limited application**

3. Membrane separations in electric field

Principle:

1. Motion of charged particles (dissociation in water) in **electric field** (one of the compounds must be electrolyte)
2. Particle transport through the membrane called **Ion-exchange membranes**

Membrane usually contains only one type of ions

Counter-ion – carries the opposite charge than the one fixed in the membrane

Coion – carries the same charge as the one fixed in the membrane

Driving force: Electric potential gradient

Ion-exchange membranes

- Cation-exchange – motion of cations – sulfo- group $-SO_3^-$, carboxyl group $-COO^-$
- Anion-exchange – motion of anions - tertiary amines $(CH3)_3N^+$
- Bipolar (amfoteric) – contain ionogenic groups of both types; compartment or mosaic structure

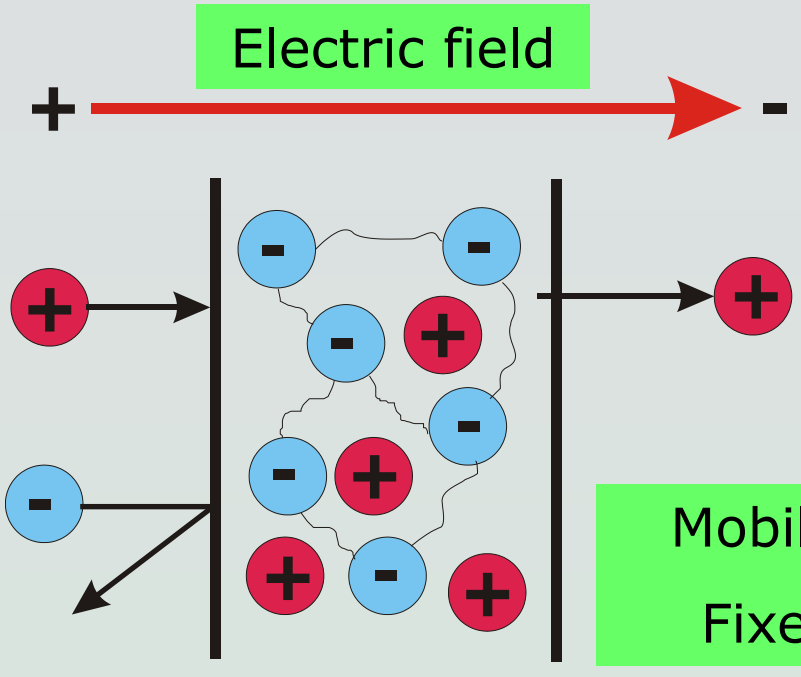
Heterogeneous – older, polymer + ion-exchanger, higher thickness – resistance

Homogeneous – newer, polymer containing ionogenic groups, thin, high capacity $\Rightarrow$ high ion selectivity

Membrane properties:

High ion selectivity (capacity – number of bounded ion groups)
High electrical conductivity
Mechanical properties: cross-linked polymer, swell (in water)
Membrane fouling – membrane poisons (irreversible bound between the molecule and the membrane)

The principle of ion transport



Concentration of ions in the membrane
Donnan equilibrium:

$$c_{FIX} + \bar{c}_- = \bar{c}_+$$

$\bar{c}$ = mobile ions

Non ideal membrane
contains also mobile ions
$\bar{c}_-$ ✖ ideal membrane

Mobile ions

Fixed ions

Electroneutrality principle must be maintained

Coulometric efficiency of the membrane is given by transport numbers: Penetration of co-ions ➔ lower separation effectiveness

$$\bar{t}_+ = 1 - \bar{t}_-$$

Flow $\dot{Q}$ on ion-exchange membranes

Limiting current:

High $\dot{Q}$ (due to high potential)

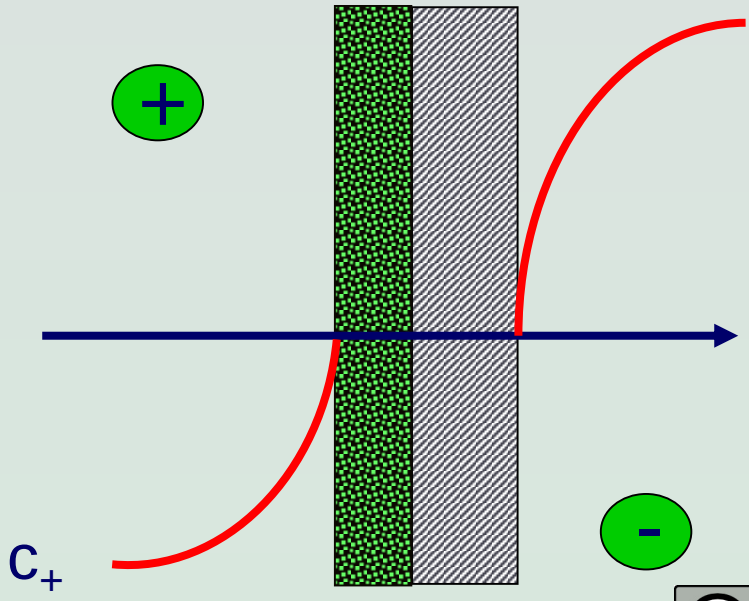
Transport of ions towards the membrane is faster than the diffusion and convective flow: $I > I_{lim} \Rightarrow$ **increased R**

Higher resistance

→ **higher dissipative energy**

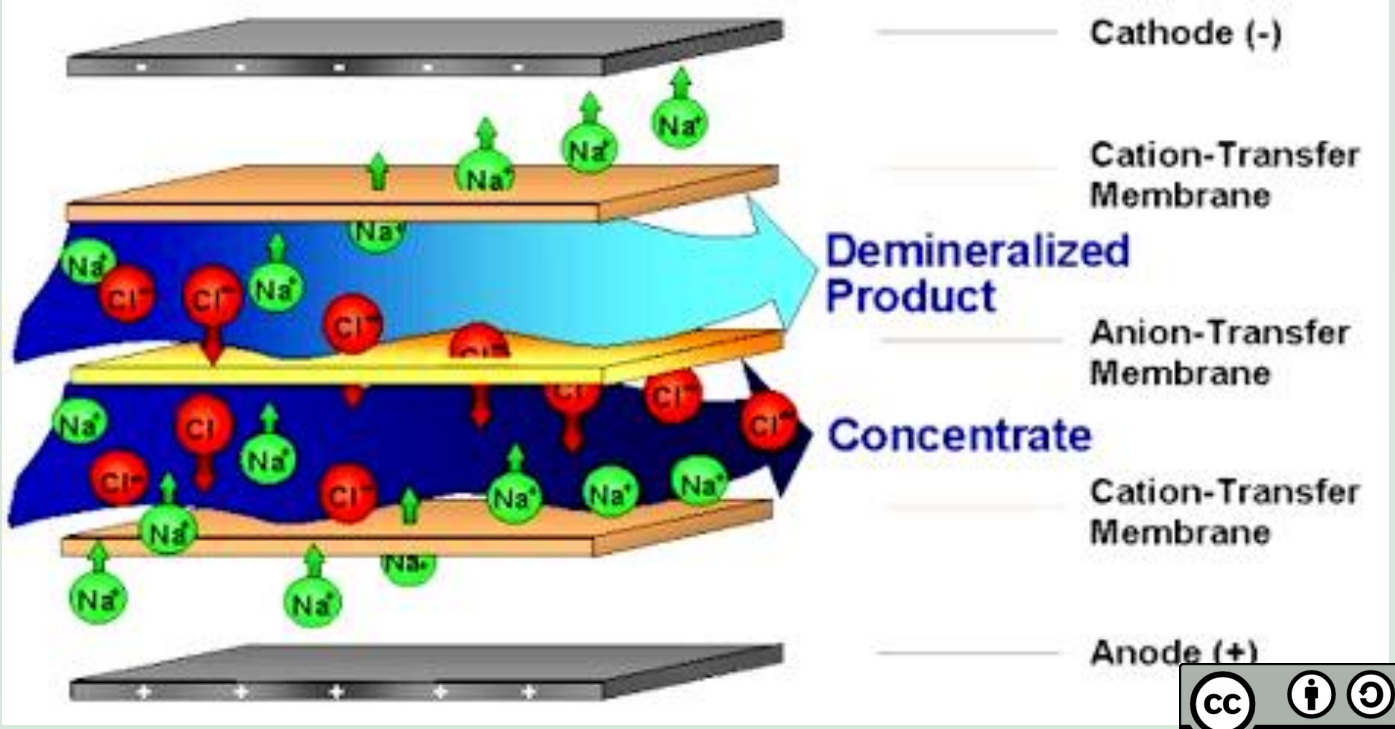
→ **high temperature**

→ **water decomposition (electrolysis)**



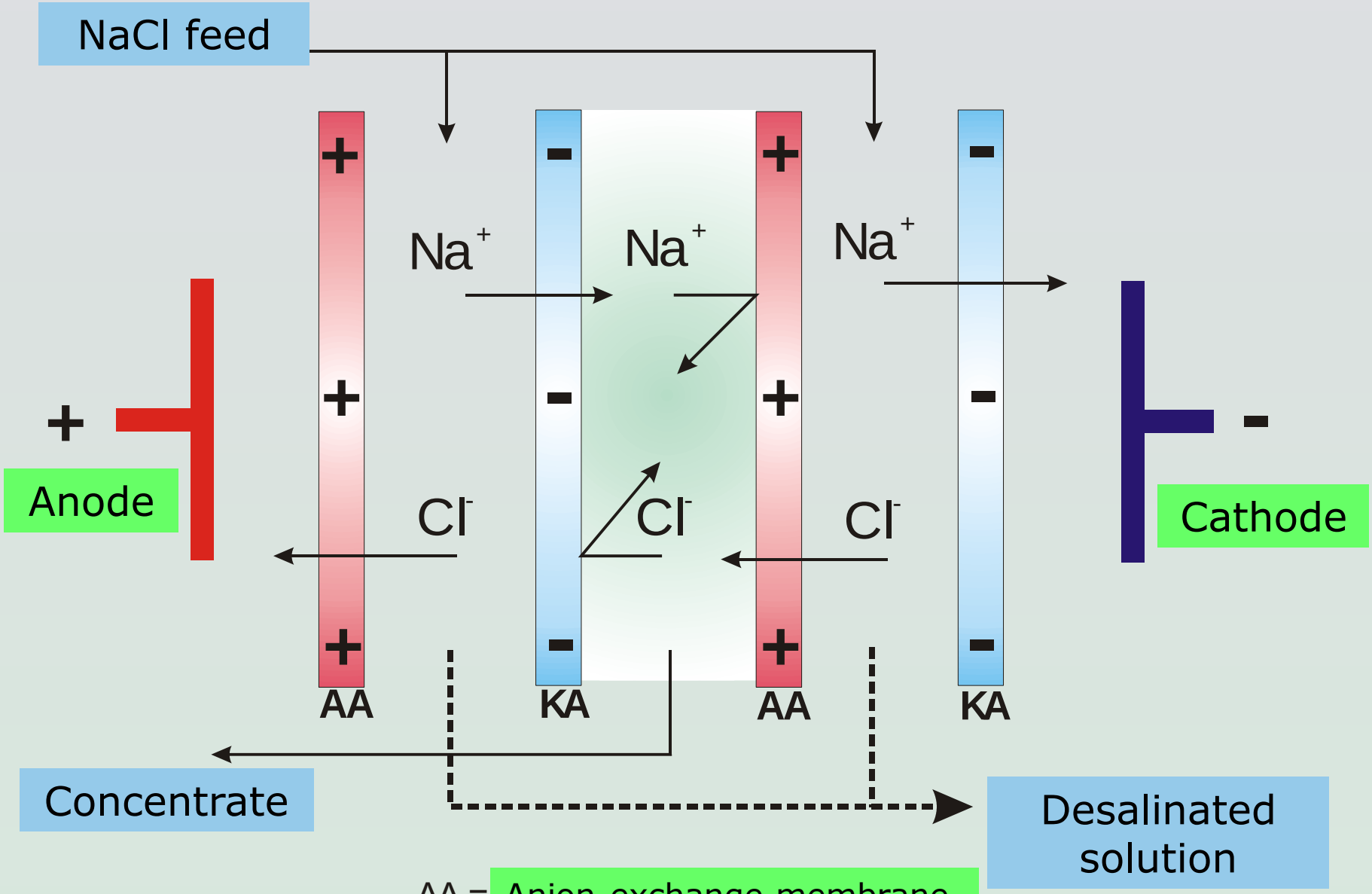
Electrodialysis - Industrial application

- Low-molecular weight charged substances (desalination - potable water, soil desalination - Na_2SO_4, salt production, regeneration of rinsing solution from industry – Ni, sea water desalination)
- Separation of inorganic and organic acids, reducing of acidity of fruit juices and concentrates
- Protein purification (serum, vaccine, enzymes)
- Regeneration of chemical agents



http://w3.bgu.ac.il/ziwr/desalination/images/electrodialysis.gif

Electrodialysis - principle:



Membrane electrolysis (ME)

- → **Electrochemical process using membranes**
- → **Anodic and cathodic compartments divided by membrane**
- → **Redox reactions run directly with electrons from the electrode:**
  - **No redox agents (chemicals) are used**
  - **No waste redox agents are formed**
- → **Reaction kinetics is managed and operated by the electric current**
- → **Usually mild reaction conditions**
- → **Energetically demanding processes run at higher potential**

Applications:

Production of concentrated solutions (e.g. NaOH from NaCl)

- ❑ **Production of organic acids from their salts present in the fermentation broth (lactic acid, acetic acid, citric acid, gluconic acid, etc.)**
- ❑ **Production of inorganic acids from their salts (HCl, HNO_3, H_2SO_4)**

Membrane cell for electrolysis

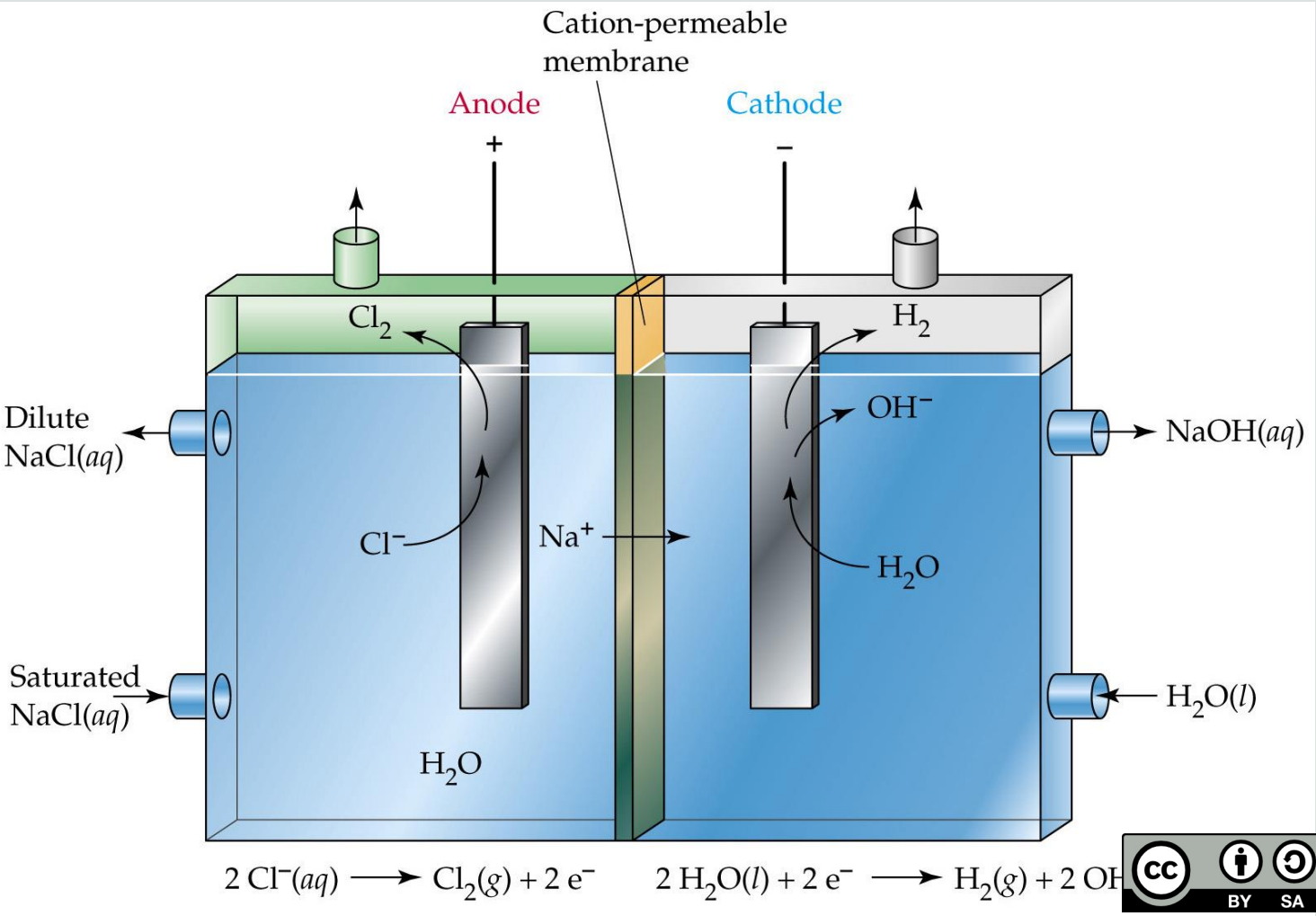
Production of Cl_2,H_2 and NaOH from NaCl:

Anode – Cl ions oxidised to Cl_2

Cathode – water hydrolysis – formation of H_2 a OH^- ions

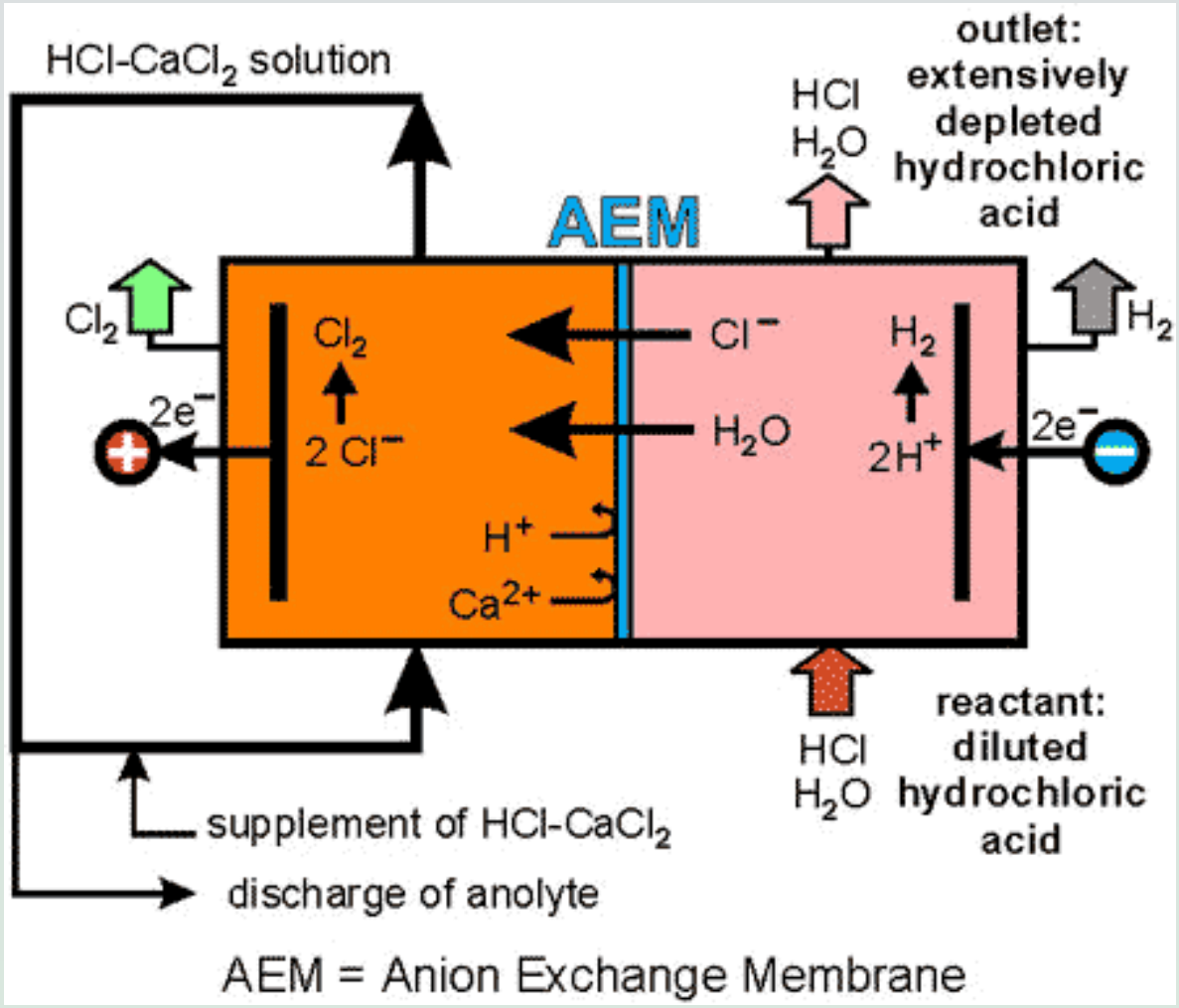
Na^+ passes through the membrane to the cathodic compartment – reaction with OH^-

- **Reactants: NaCl and water**
- **Products: gases Cl_2,H_2, NaOH and depleted NaCl**



http://wps.prenhall.com/wps/media/objects/602/616516/Chapter_18.html

Membrane electrolysis



Cl^- ions come to anodic compartment: high concentration of Cl^- provided by addition of salt - $CaCl_2$.

Cathodic compartment: even low concentration of HCl is sufficient as a source of Cl^- ions

Anion-exchange membranes destroyed by oxidising agents
➔BUT new chlorine resistant membranes are developed recently.

http://www.bci.uni-dortmund.de/tca/web/de/textonly/content/mitarb/akad_oberrat/pics/Fig_4.gif

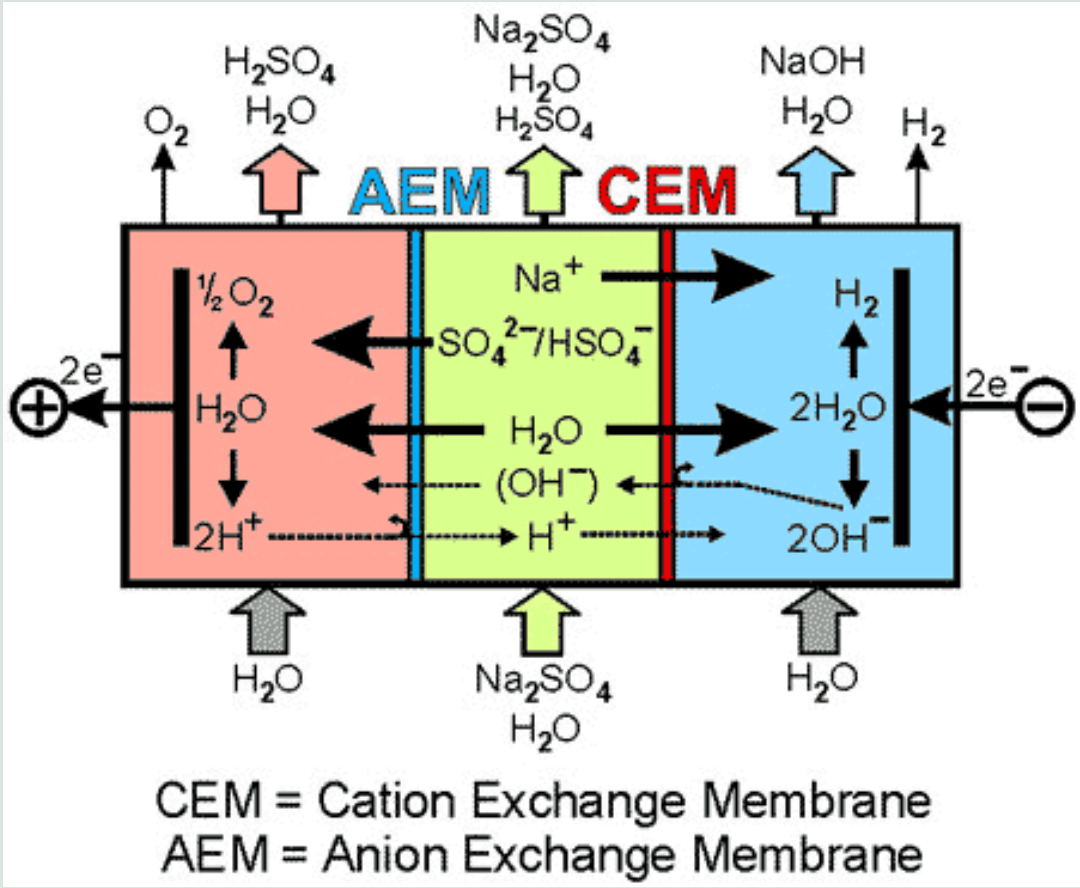
Salt recycling and salt distribution among acids and alkali

Example:

Closed loop of chemical processes:

Sodium sulfate comes to the solution of sulphuric acid and sodium hydroxide

A combination of electrolysis and electrodialysis in anion-exchange membrane



http://www.bci.uni-dortmund.de/tca/web/de/textonly/content/mitarb/akad_oberrat/akad_oberrat.html

Preparative or laboratory scale separations in electric field gradient

Processes using membranes:

- Transport depletion
- Electroosmosis
- Forced-flow electrophoresis

Electrokinetic processes – no membrane:

- Capillary zone electrophoresis
- Electrophoresis
- Isoelectric focusing
- Isotachophoresis

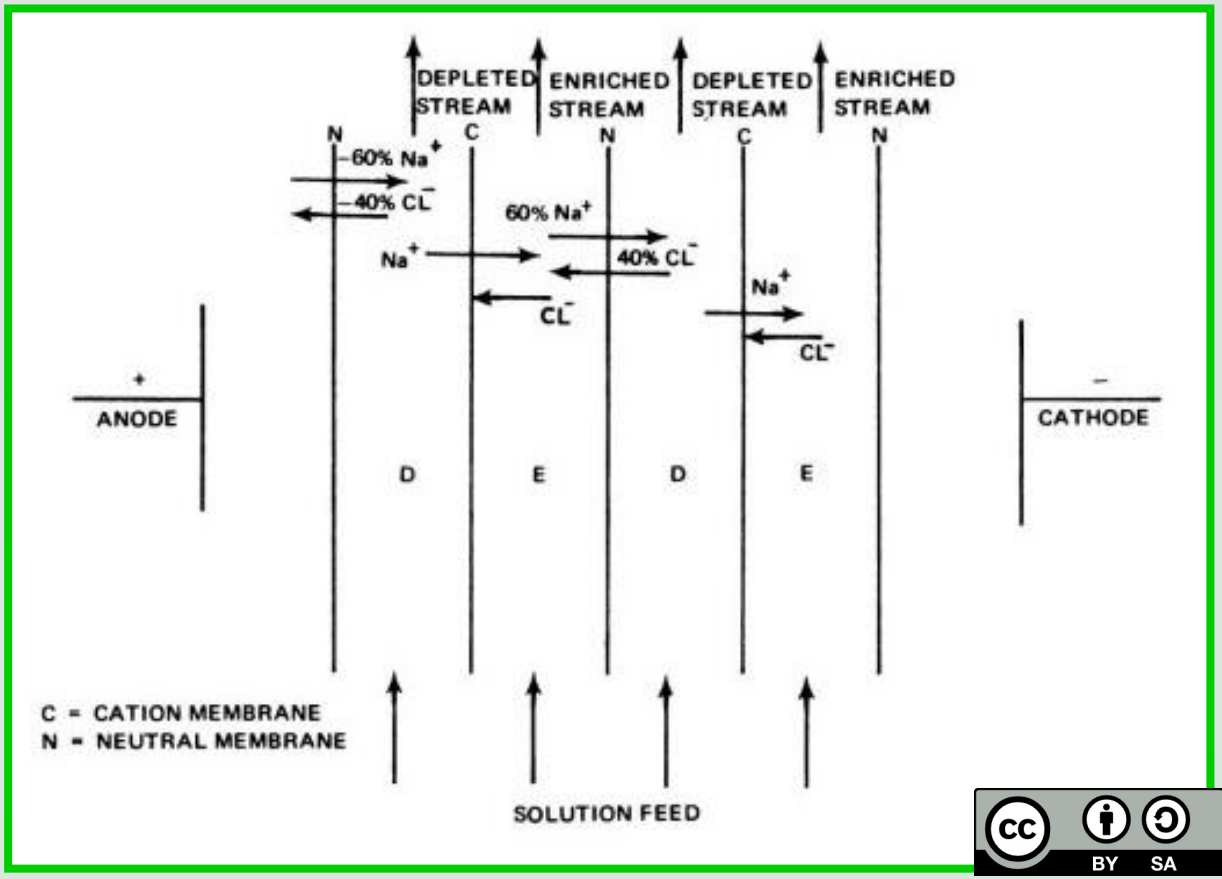
Transport depletion

Principle:

- Electrodialysis with neutral membranes = anion exchange membrane replaced with electroneutral ones
- AE membranes cannot be used ⇒ fouling, low effectiveness

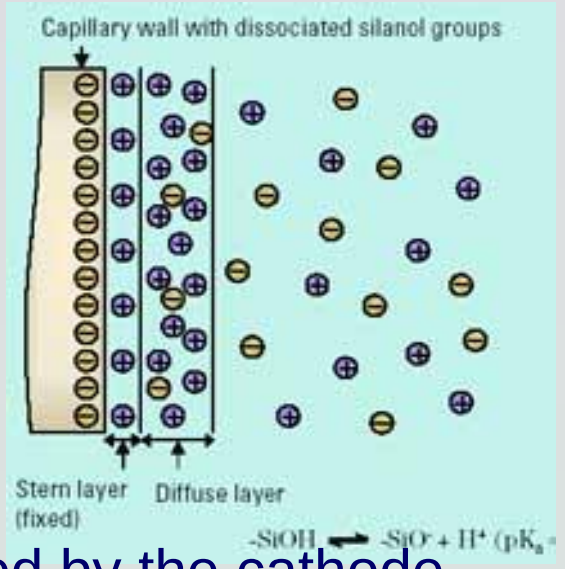
Application:

- Separation of organic substances, colloids



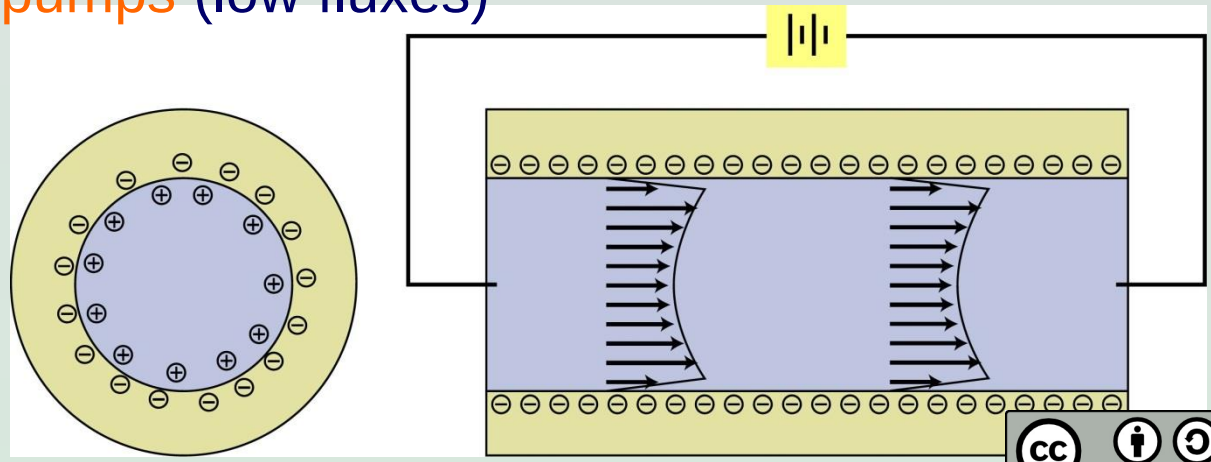
Redman R.: Transport-Depletion Desalination Pilot Plant. Washington D.C.. UNT Digital Library.http://digital.library.unt.edu/ark:/67531/metadc11776/. Accessed October 27, 2011

Electroosmosis



Motion of liquid due to applied potential:

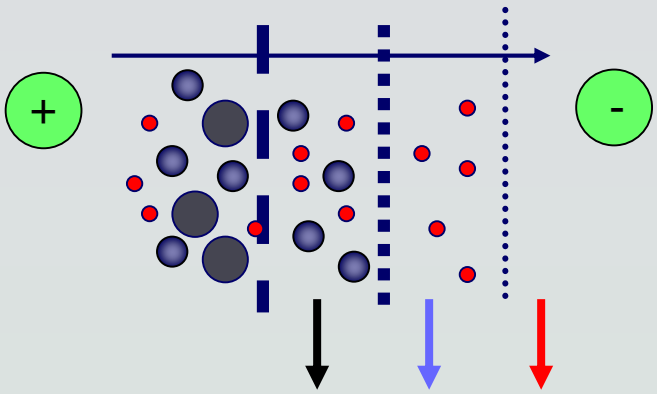
- Cation-exchange membranes – e.g. fused silica, silanol groups (Si-OH), negatively charged (Si-O-).
- Electrical double layer is formed (positively charged)
- Potential over the membrane – cations attracted by the cathode – motion alongside the membrane
- Membrane surface – solvation – molecules of water move as well
- Low pH → the capillary loses its negative charge → the electric double layer is thinner
- Applications – micropumps (low fluxes)



http://www.stanford.edu/~dlaser/electrokinetics_and_eof/electrokinetics_and_eof.htm

Forced-flow electrophoresis

- Several membranes of different cut-off
- Arranged according to cutt-off (sieving effect)
- Usually a three-compartment cell



Zone electrophoresis

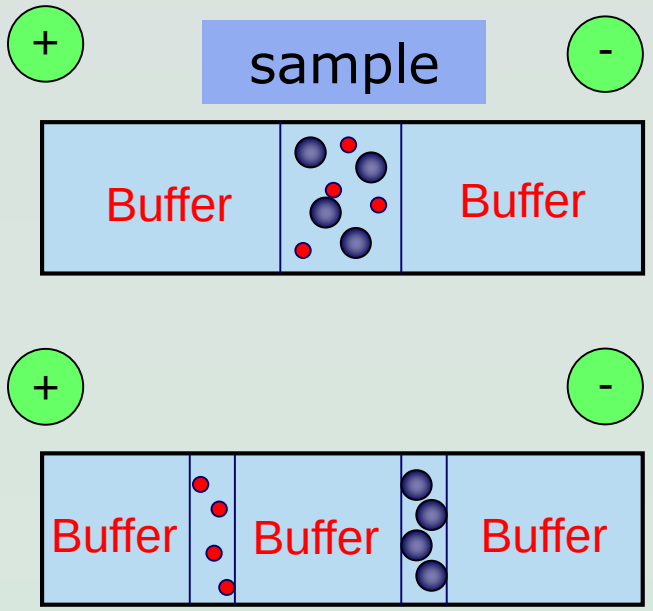
Different ion mobility in electric field

μ_i

Electric field – driving force, increases the speed

Mobility – charge size, molecule size, molecule shape, temperature and concentration

Anticonvective medium: paper, gel (polyacrylamide)

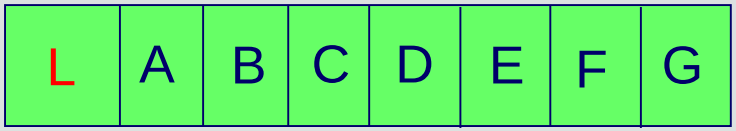


Electrophoresis

Condition of separation: different mobility $\mu_L > \mu_A \ldots > \mu_i > 0$

L – leading electrolyte

Quantitative and qualitative analysis – bend width, distance of the zone

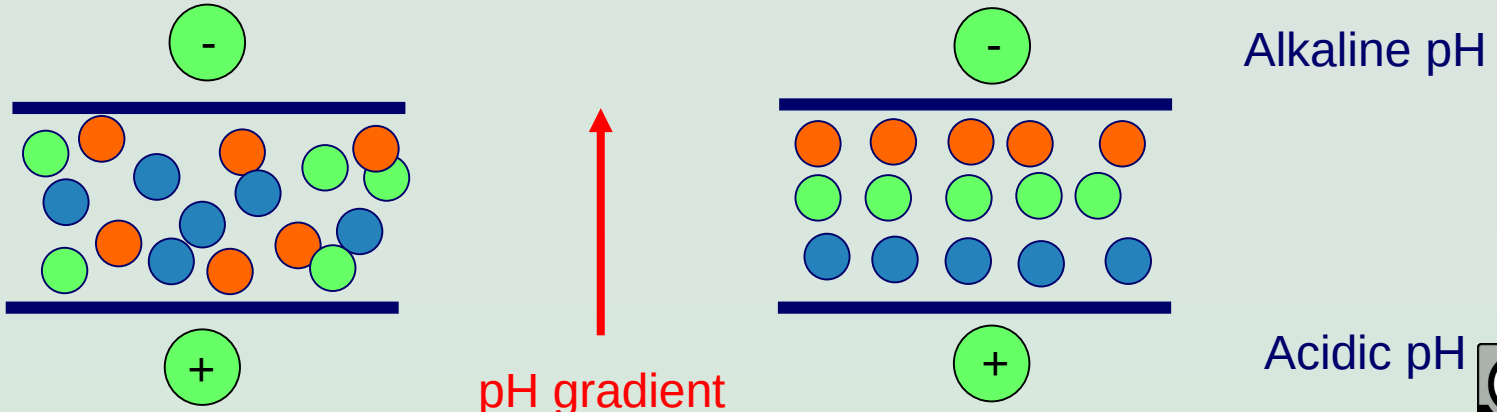


Isoelectric focusation

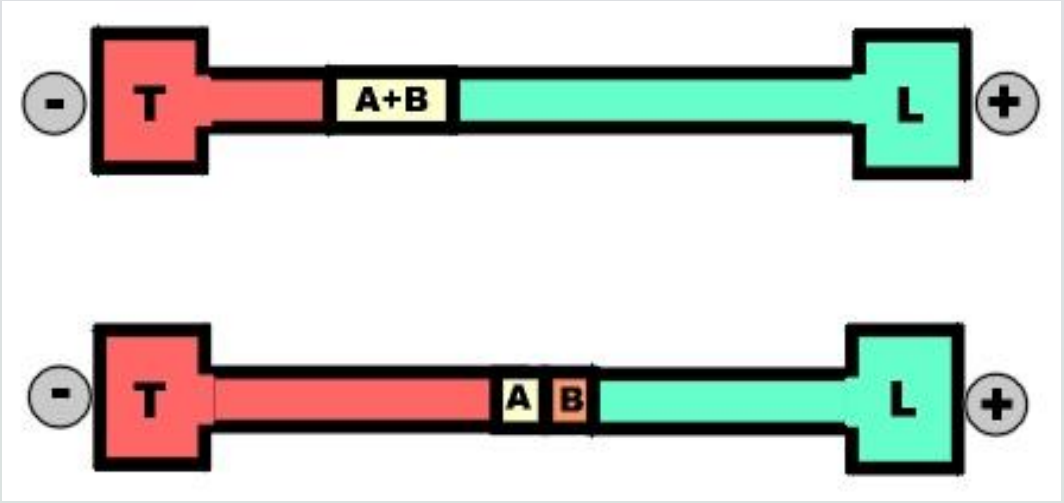
Separation of polyampholytes – gradient of pH and electric field

Sample dispersed in the cell

Separation according to the isoelectric point



Isotachophoresis



→ Similar to capillary electrophoresis

→ Two electrolytes: leading L and terminal T

→ Capillary

→ Quantitative and qualitative analysis

→ Motion of ions in constant electric field

→ **Constant velocity**

Applications:

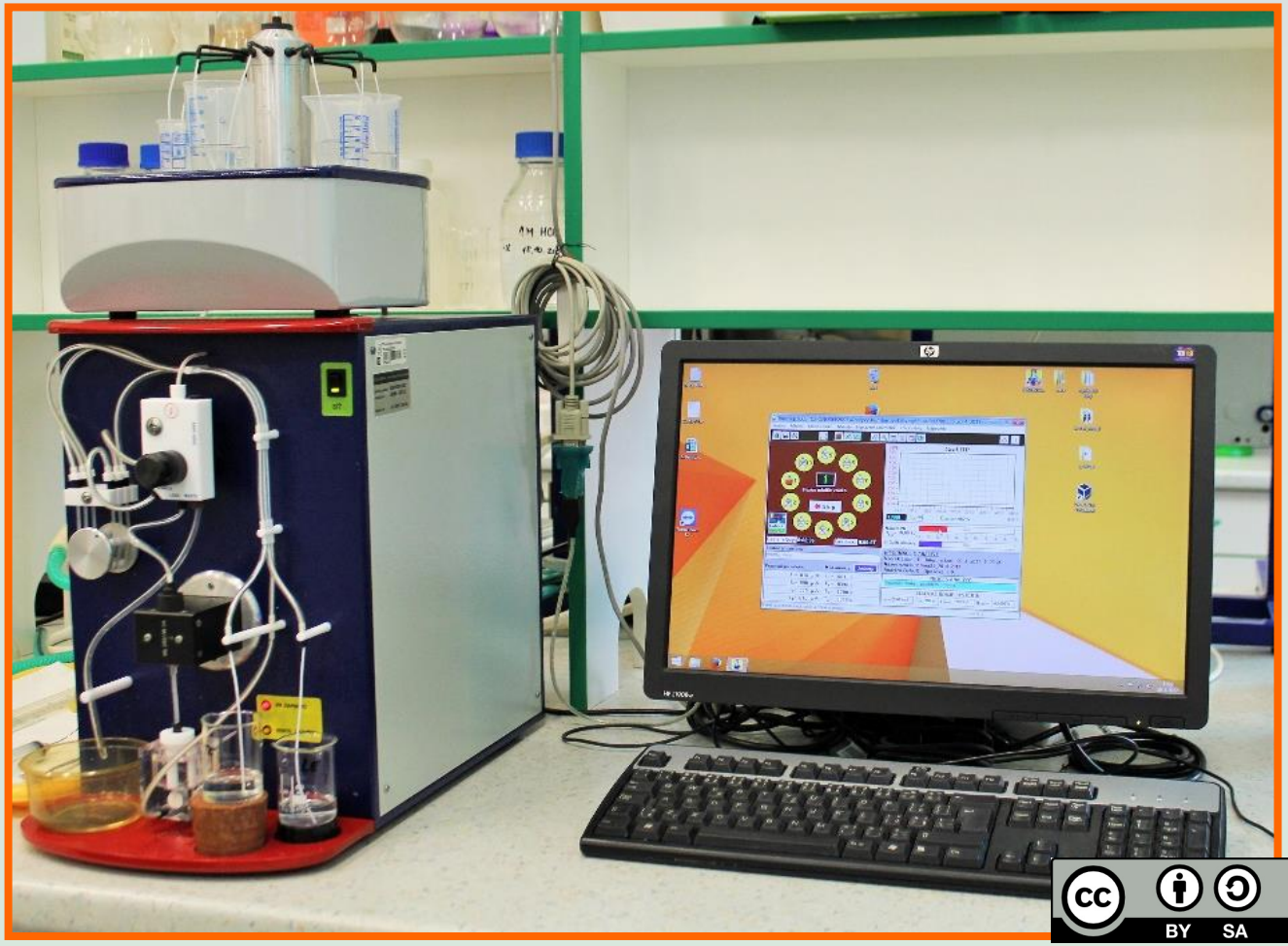
- ❑ Inorganic ions (anions, cations – heavy metals)
- ❑ Organic acids (long-chain fatty acids, amino acids)
- ❑ Amines
- ❑ Others: aspartame, fertilizers, pesticides, preservatives, colorants, medicine, alkaloids…

Izotachophoresis - analysis

Detection:
Electric conductivity, UV, temperature

Izotachophoresis - apparatus

- Simple, compact arrangement
- High versatility for different samples and analytes
- Low operation costs
- Analytical purposes



Separation and purification techniques

Applications of membrane processes in the food industry and biotechnologies

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Information sources

http://sch.vscht.cz/vyuka/international-students/erasmus-students/

Cheryan M. (1998): Ultrafiltration and Microfiltration Handbook, In: Technomic Pub. Co. (Eds.), Lancaster, Pensylvania, pp. 243.

Applications of membrane processes in the food industry and biotechnologies

Contents

1. **Dairy industry**
2. **Meat industry and food preservation**
3. **Production of juices**
4. **Starch industry, bakery and sugar industry**
5. **Beer, wine and beverage industry**
6. **Biotechnologies**

General applications:

- ✓ Removing of high molecular compounds
- ✓ Purification and decolourization
- ✓ Primary purification and concentration before following technological steps
- ✓ Separation of products and valuable substances from wastes or outlets that can be consequently processed
- ✓ Cold sterilization of products
- ✓ Waste water treatment
- ✓ Replacement of conventional filtration techniques using filtration aids (e.g. diatomaceous earth – kieselguhr)

Advantages:

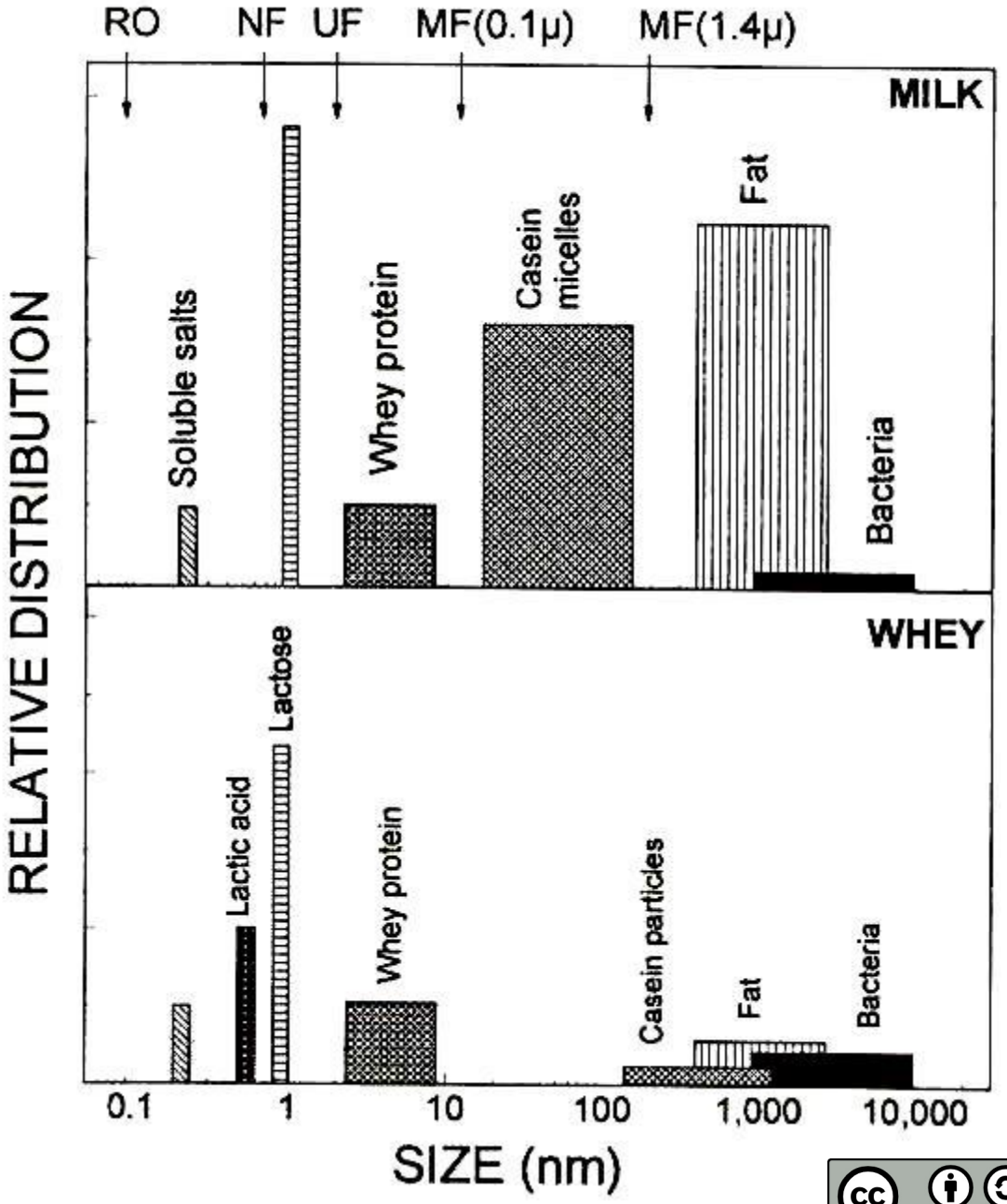
+ No or mild changes of sensory properties
+ The activity of biological active substances is maintained
+ Nutrition values unchanged
+ Reduced operating costs during food production (elimination of heat processes; e.g. distillation, evaporation)

1. Dairy industry

- The largest application potential of membranes among food technologies
- An approximate estimation of a filtration area: 300,000 m^2 worldwide
- UF and RO most common, MF occasionally

Particle and molecule size profile of milk and whey

Cheryan M.: Ultrafiltration and Microfiltration Handbook, Technomic Pub. Co., 1998



Possible application of MF and UF in dairy

- Fat and bacteria removal from milk and whey
- Separation and concentration of high-molecular components of milk and - UF (retentate - proteins, fat and salts bound on proteins)

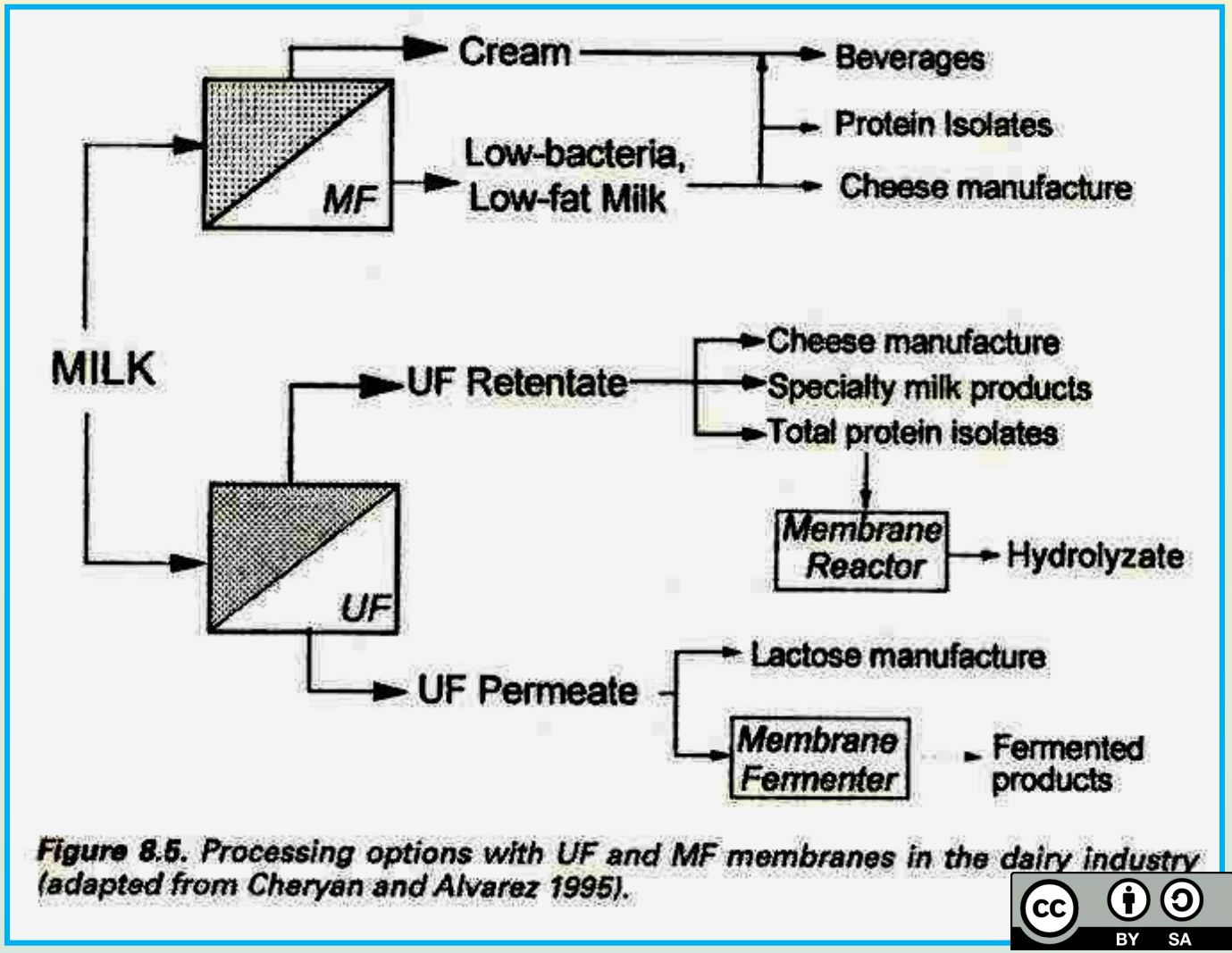
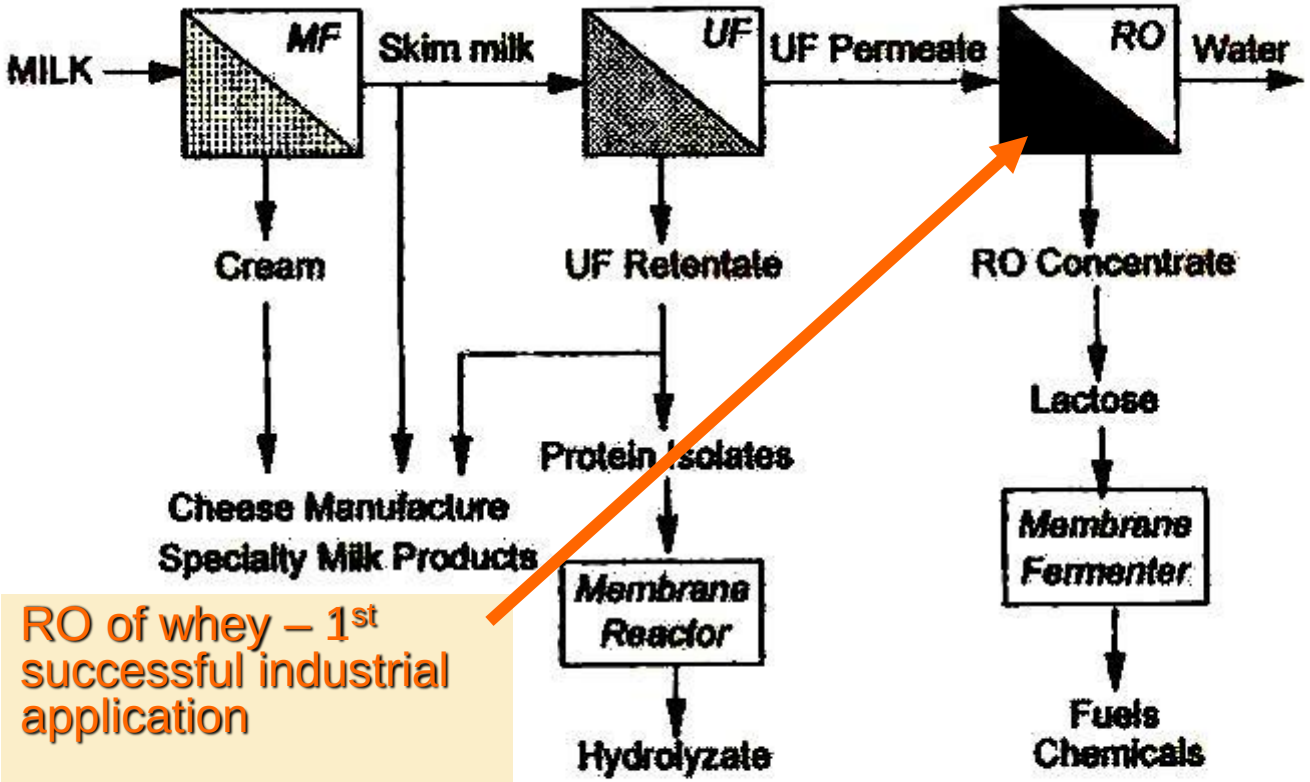


Figure 8.5. Processing options with UF and MF membranes in the dairy industry (adapted from Cheryan and Alvarez 1995).

Cheryan M.: Ultrafiltration and Microfiltration Handbook, Technomic Pub. Co., 1998

Possible application of MF, UF and RO

- Production of whey protein concentrate – defatted whey is concentrated by UF; membrane retains proteins + remaining fat. Lactose, salts and other low molecular components pass into permeate.



RO of whey – 1st successful industrial application

Figure 8.8. Sequential membrane processing in the dairy industry (adapted from Cheryan and Alvarez 1995).

- Concentration of liquid fractions: milk, whey
- WPC = Whey Protein Concentrate; 82-85%
- WPI = Whey Protein Isolate; 90%
- Desalination of whey by NF
- Lactose isolation

Cheryan M.: Ultrafiltration and Microfiltration Ha… Technomic Pub. C…

Possible application of membranes in dairy

Profitable to use UF before milk coagulation and precipitate retentate only
– reduced consumption of milk, lactic culture and rennet.

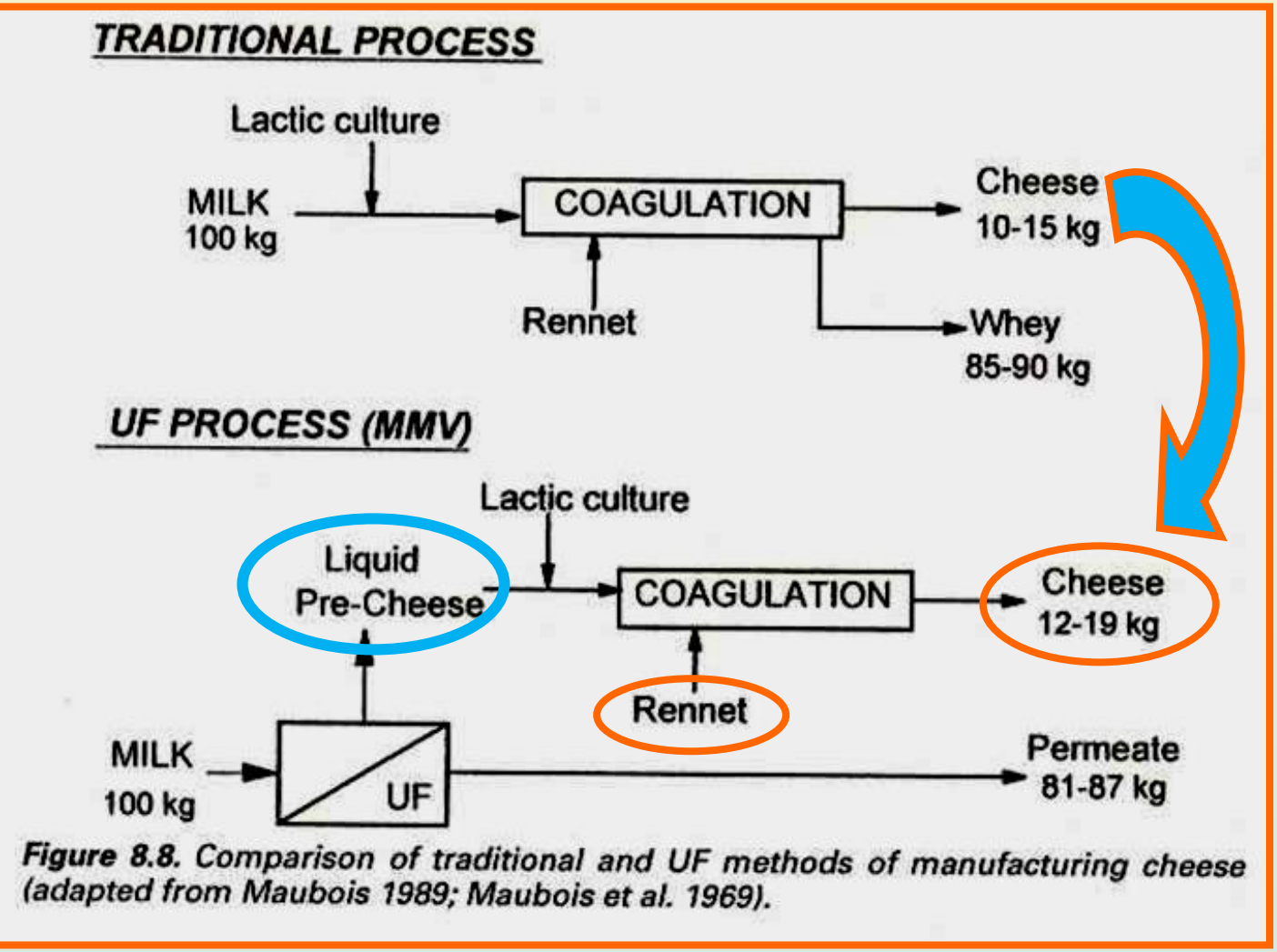


Figure 8.8. Comparison of traditional and UF methods of manufacturing cheese (adapted from Maubois 1989; Maubois et al. 1969).

Drawbacks:

- Higher protein- content – higher milk viscosity – worse addition of rennet and lactic culture – worse cheese texture
- Retentate recirculation – partial homogenization of fat – worse texture of hard cheese

Cheryan M.: Ultrafiltration and Microfiltration Handbook, Technomic Pub. Co., 1998

Other possible application of membranes in dairy

- Filtered milk can be used for production of many other products – condensed milk, dried milk, cheese, cottage, yogurt, ice cream, etc.
- UF - a basic process for cheese production
- Standardization of protein and fat content using UF – stable quality

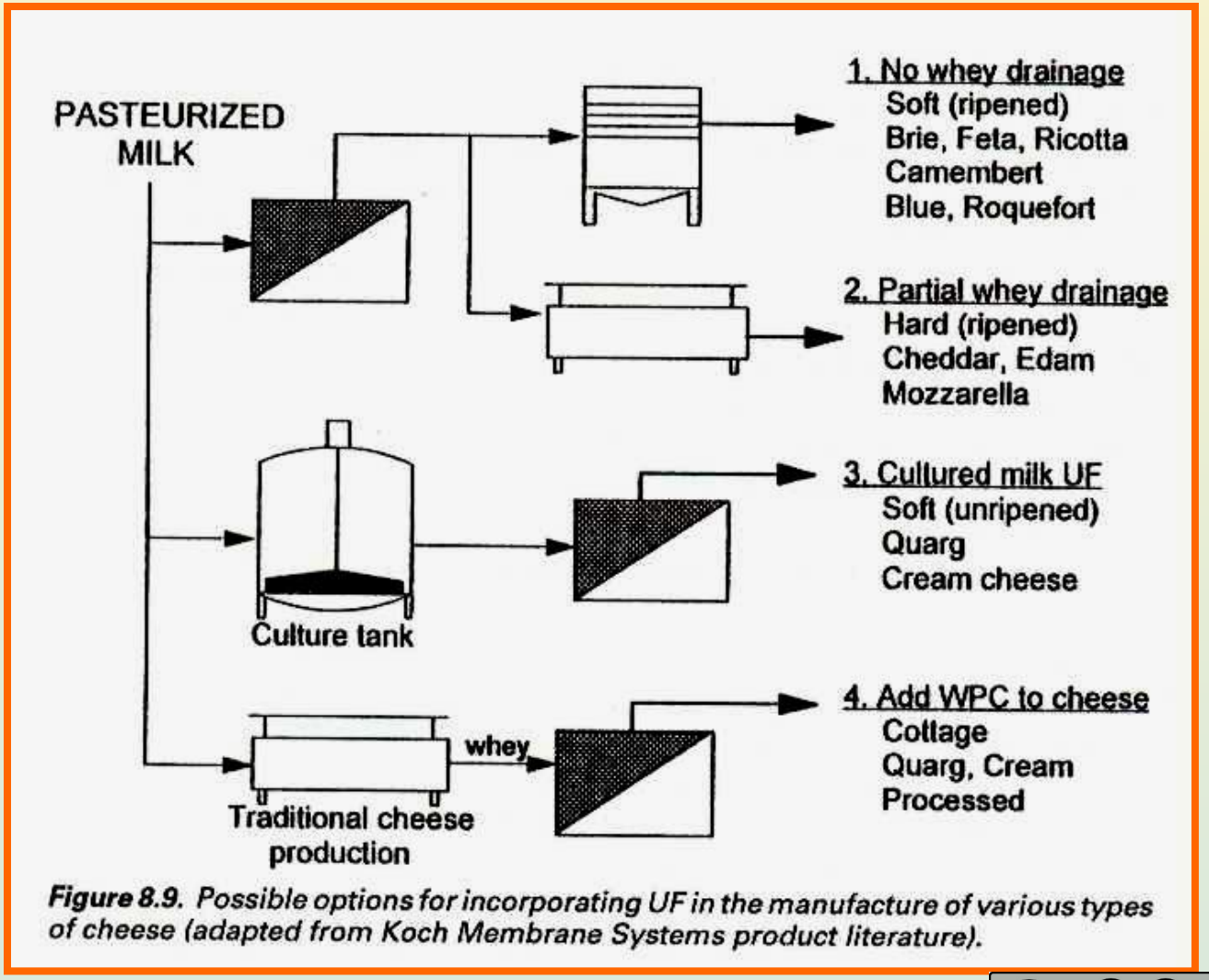


Figure 8.9. Possible options for incorporating UF in the manufacture of various types of cheese (adapted from Koch Membrane Systems product literature).

Cheryan M.: Ultrafiltration and Microfiltration Handbook, Technomic Pu

Beverage industry – fruit and vegetable juices

Manufacture of apple juice by traditional and UF process

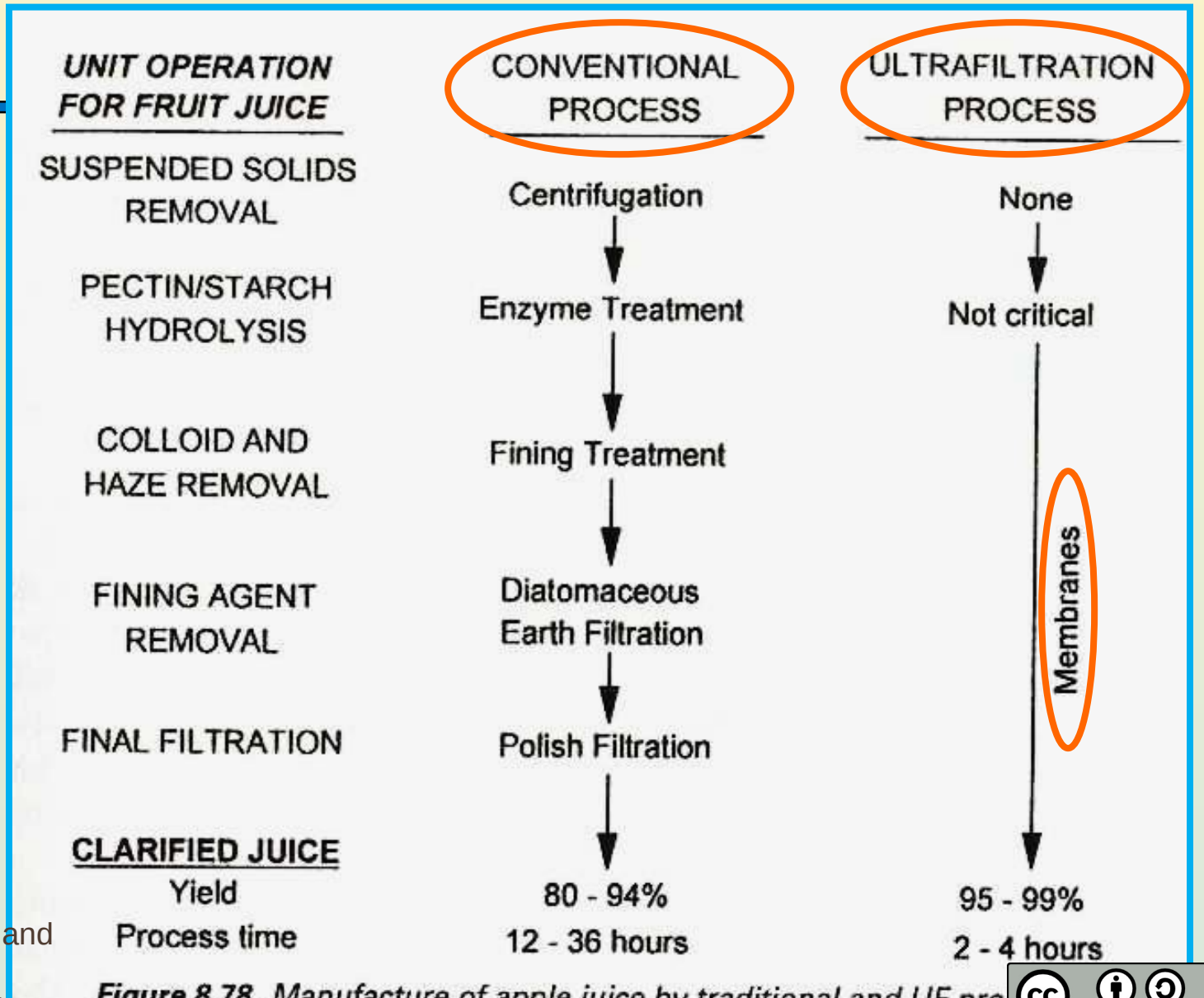


Figure 8.78. Manufacture of apple juice by traditional and UF pro

Cheryan M.: Ultrafiltration and Microfiltration Handbook, Technomic Pub. Co., 1998

Beverage industry – production of fruit and vegetable juices

- **UF:**
- **Cold sterilization and juice fining**
- **Pectinase filtration**
- **Haze removing**

Example: apple juice; ceramic membranes

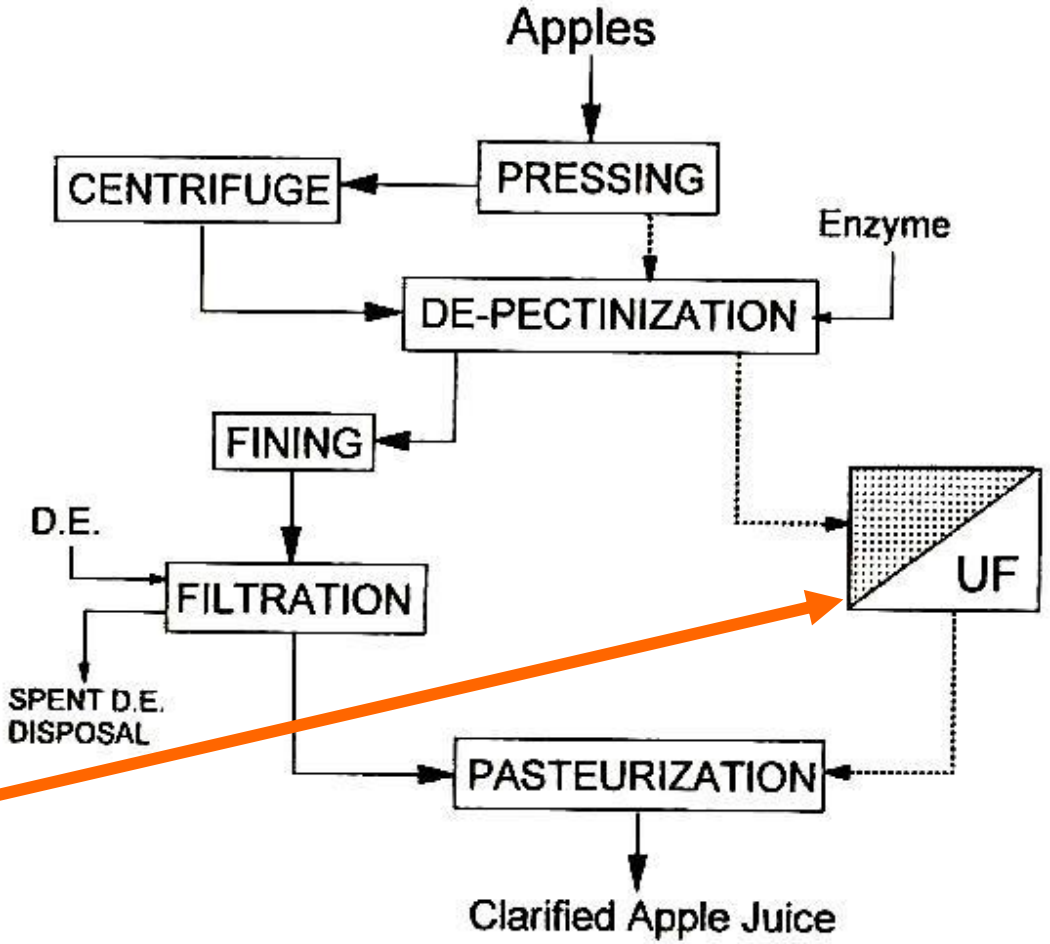


Figure 8.79. *Typical schematic for producing clear fruit juices. Operations on the left side are used in the conventional method. The membrane method is depicted on the right side.*

Cheryan M.: Ultrafiltration and Microfiltration Handbook, Technomic Pub. Co., 1998

Production of fruit juice concentrate

- Combination of UF and RO:
- UF – cold sterilization and juice fining
- RO – concentration before evaporation; permeate from UF can be consequently concentrated by RO
- Concentration of liquid fractions: fruit juices, coffee extract (RO)

Influence of filtration on the juice quality

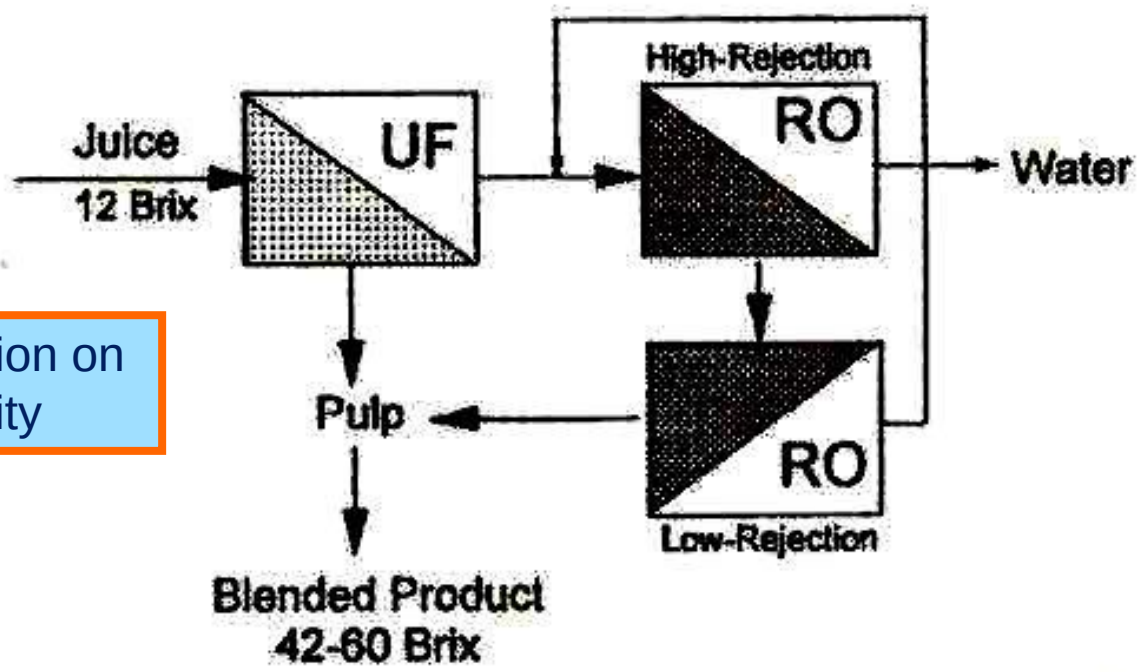


Figure 8.85. Producing high-strength fruit juice concentrates by ultrafiltration and reverse osmosis (adapted from Cheryan and Alvarez 1995).

Cheryan M.: Ultrafiltration and Microfiltration Handbook, Technomic Pub. Co.

Meat processing and food preservation

- UF – animal blood serum concentration
- UF of protective atmosphere for meat product packaging (removing of microorganisms, moisture, solids)
- Removing of oxygen and its replacement by nitrogen (permeation) – increasing of durability of packed meat products
- Purification and isolation of proteins from brines
- Concentration of egg whites and whole eggs
- UF – concentration and desalination of gelatin protein before evaporation

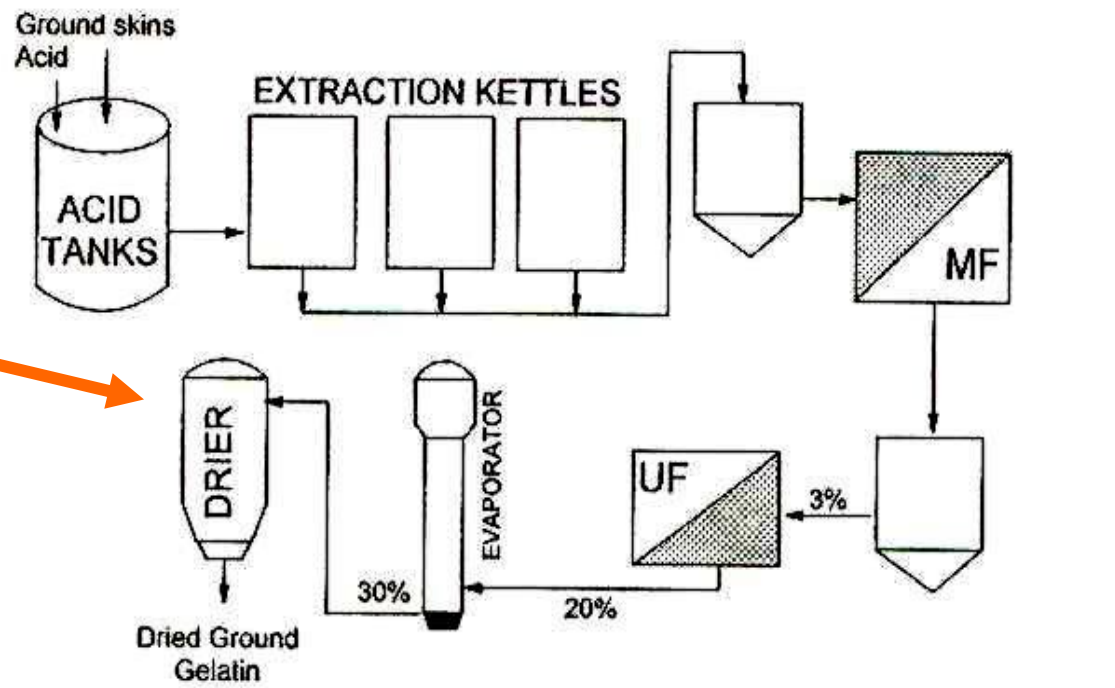
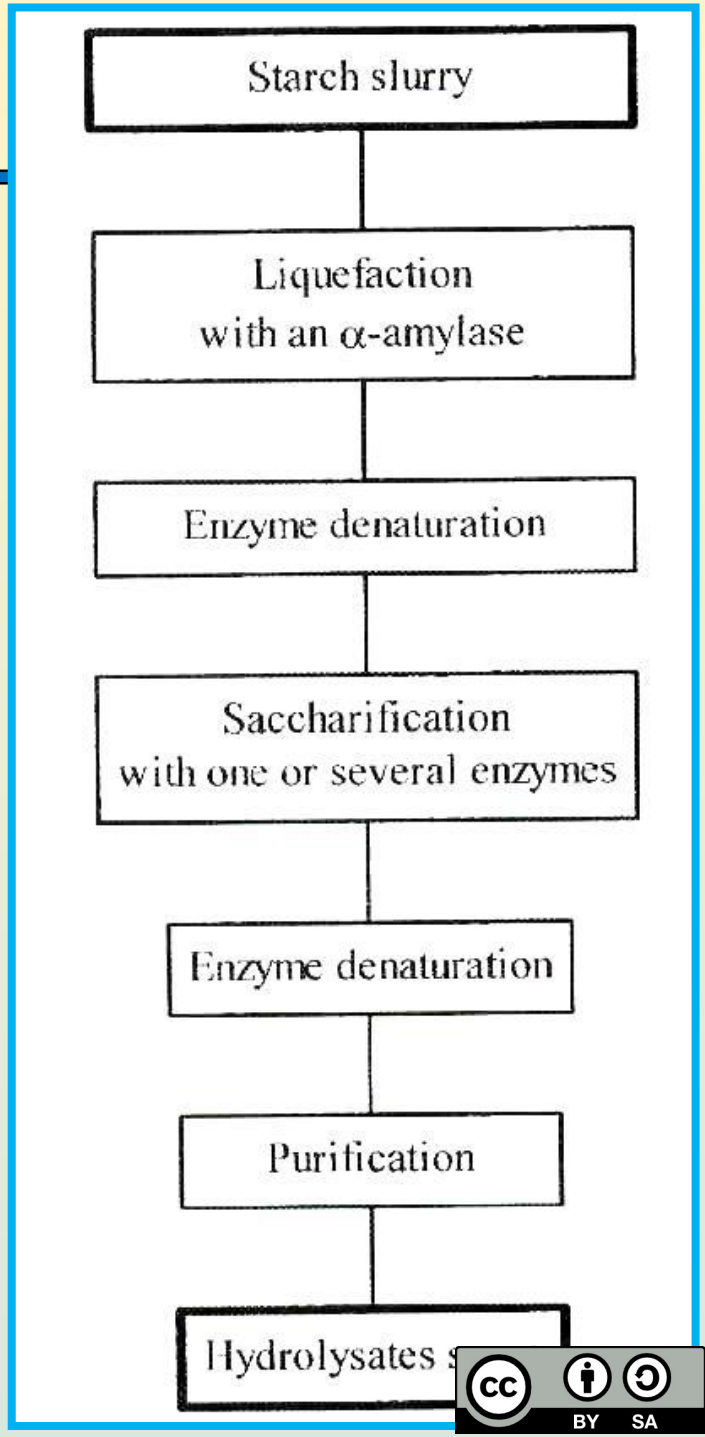


Figure 8.51. Membrane process in gelatin manufacture (adapted from Koch 1984).

Cheryan M.: Ultrafiltration and Microfiltration Handbook, Technomic Pub. Co., 1998

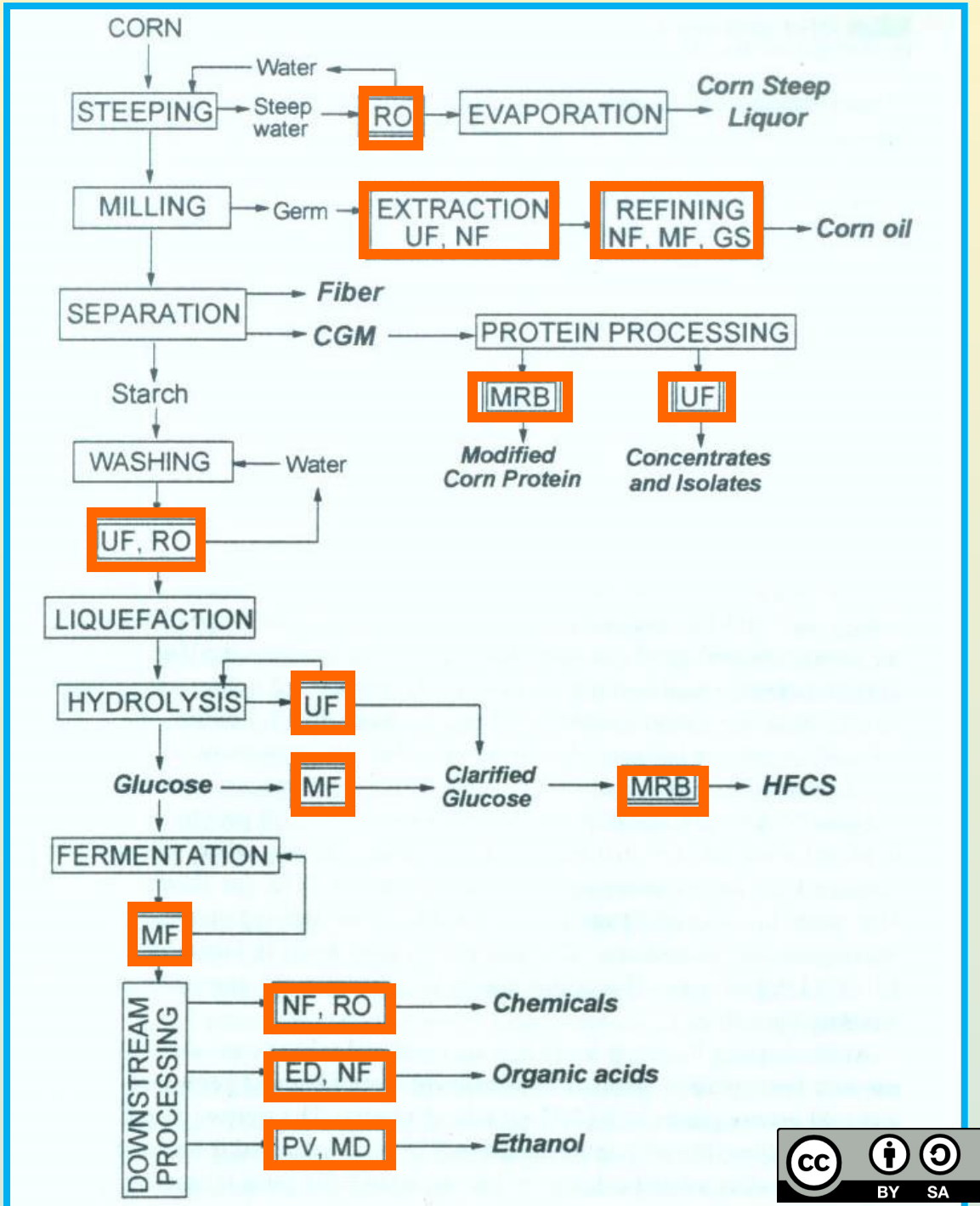
Starch industry

- **Processing of starch syrups (starch hydrolysis to glucose and enzymatic glucose isomerisation to fructose)**
- **UF – separation and concentration of enzymes – reutilization.**
- **Purification of hydrolysates - decolourization, fat removing (corn syrups), separation of proteins, colloids and suspended solids.**
- **Waste water treatment**



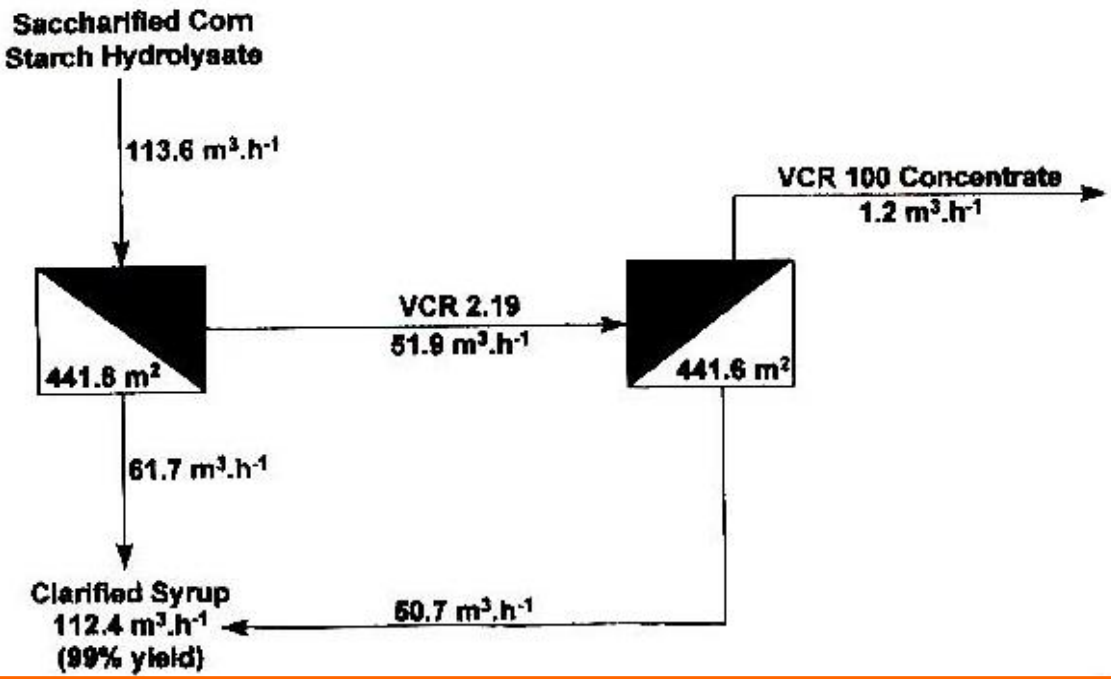
Paolucci-Jeanjean D. et al. (1999): Starch/Stärke 51, No. 1, pp. 25 - 32.

Possible application of membranes in starch syrup clarification



Cheryan M.: Ultrafiltration and Microfiltration Handbook, Technomic Pub. Co., 1998

MF in starch hydrolysate clarification



Parameters:

Starch syrup of 95 DE

filtration area 2 x 442 m^2

Investment costs: 2,08 mil. $

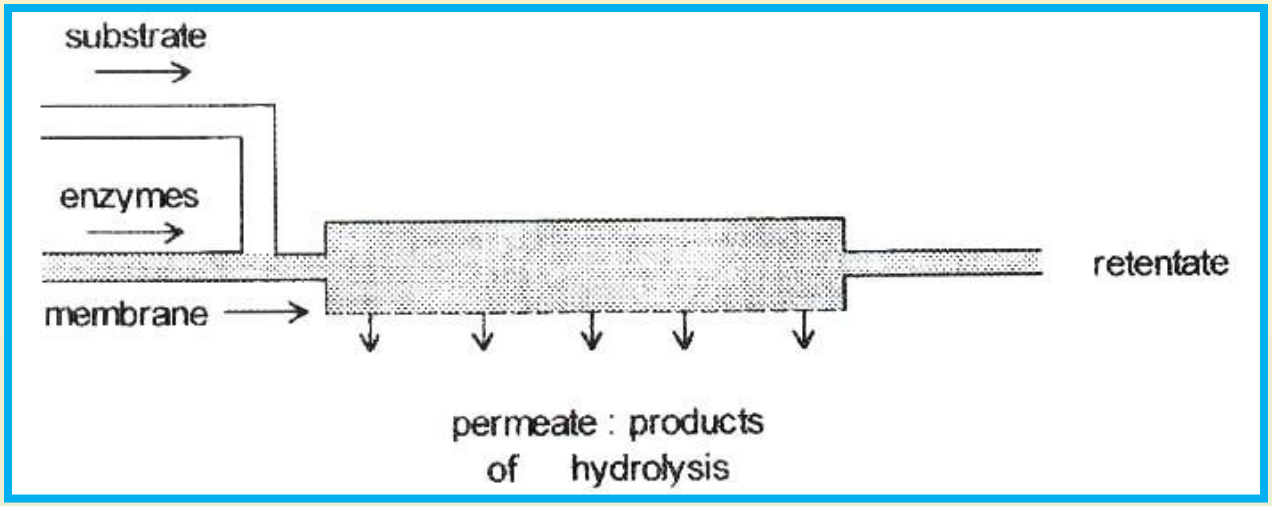
Singh N., Cheryan M. (1998): Journal of food Engineering 38, pp. 57 - 67.

Operating cost comparison

Annual Operating Costs ($) for Microfiltration (MF) and Rotary Vacuum Precoat Filtration (RVPF) for a 113.6 $m^3\ h^{-1}$ (500 gal min^{-1}) Production Line

	MF	*RVPF*
Membrane replacement cost	282 624	0
Diatomaceous earth	0	1 360 779
Disposal cost of diatomaceous earth	0	204 117
Power consumption	186 121	160 355
Labor	25 200	63 000
Cleaning	3533	0
Maintenance	19 930	
Total operating cost	517 408	

Membrane reactors for starch hydrolysis

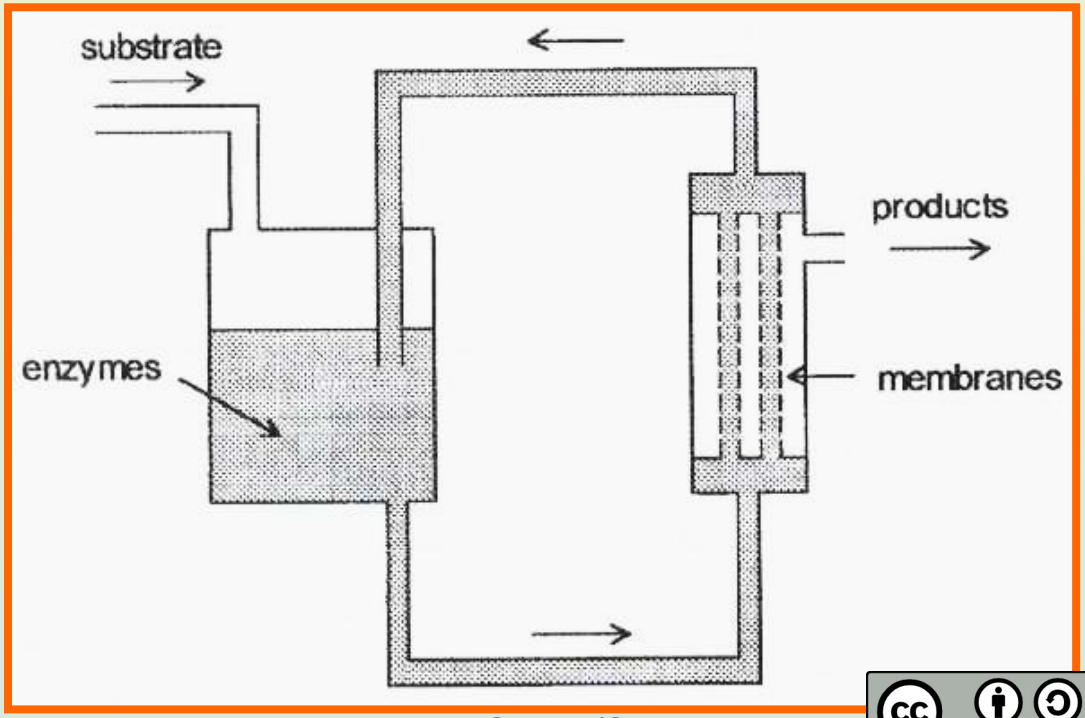


Membrane reactor – production of HFCS (High Fructose Corn Syrups) hollow fibres

α-amylase and glucoamylase added into substrate and filtered

Drawbacks of conventional (batch) technology:

- Low yields
- High volumes of reaction mixtures (high investment costs)
- Product variability (every batch is different)
- Low exploitation of enzyme



Paolucci-Jeanjean D. et al. (1999): Starch/Stärke 51, No. 1

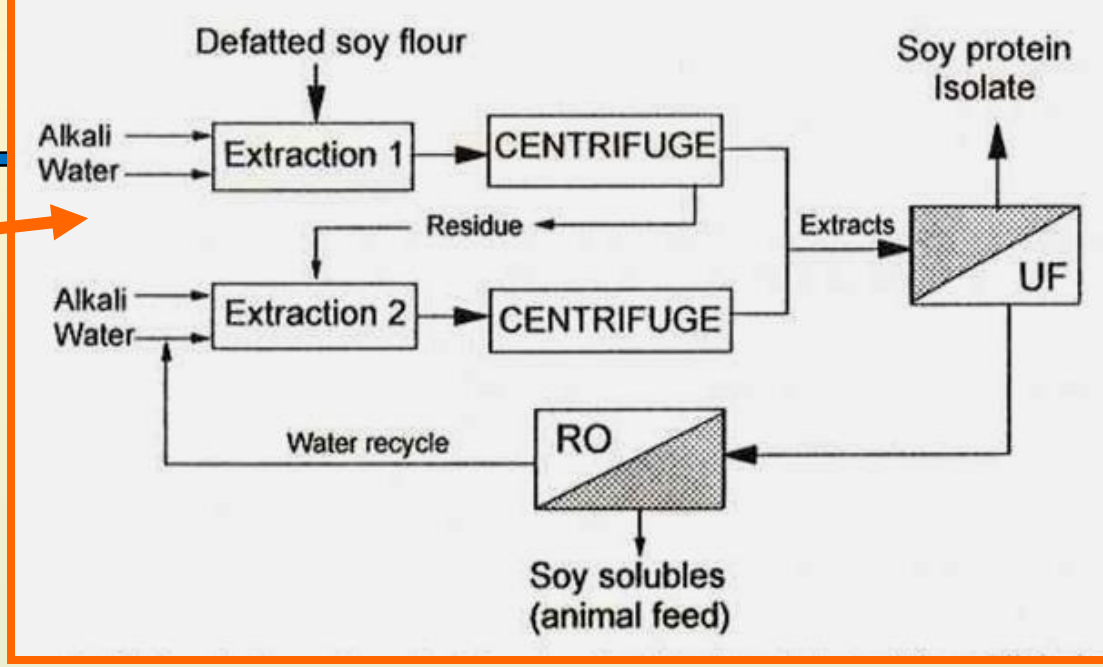
Bakery

- **Isolation and concentration of proteins from soya, oats and wheat**
- **Gluten production:**

  Gluten = a mixture of proteins in a cereal kernel

  Gluten of low quality (contains salts, colorants or aroma from cereals) – undesirable products need to be removed by extraction in alkali solution

  Extract → UF (low molecular compounds pass into permeate).



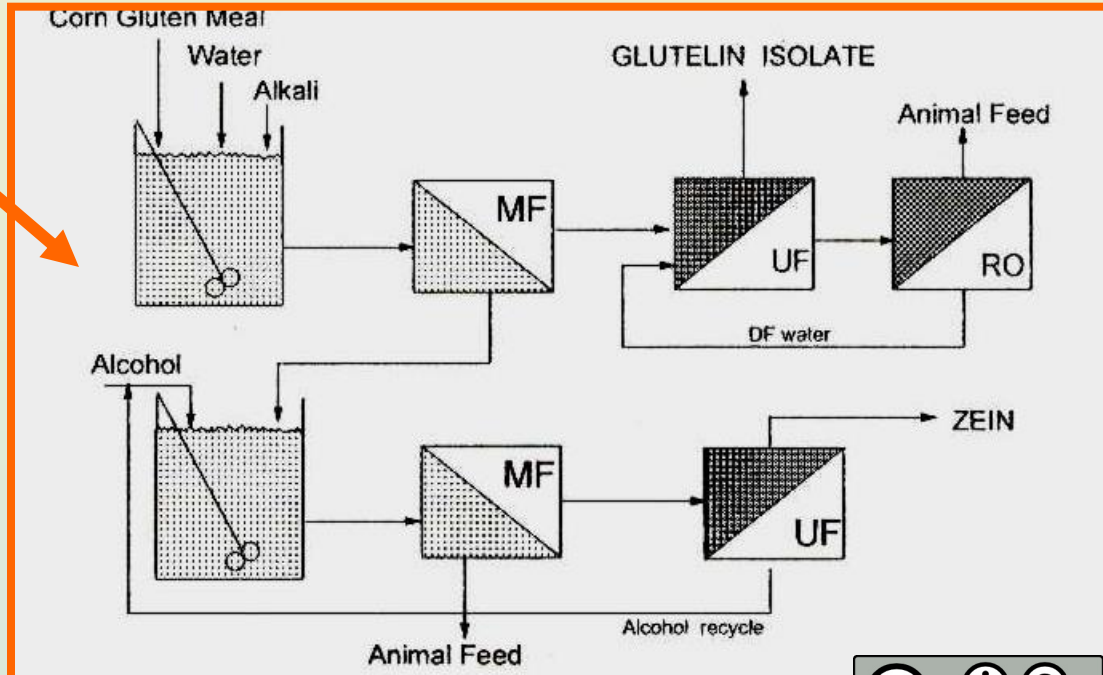


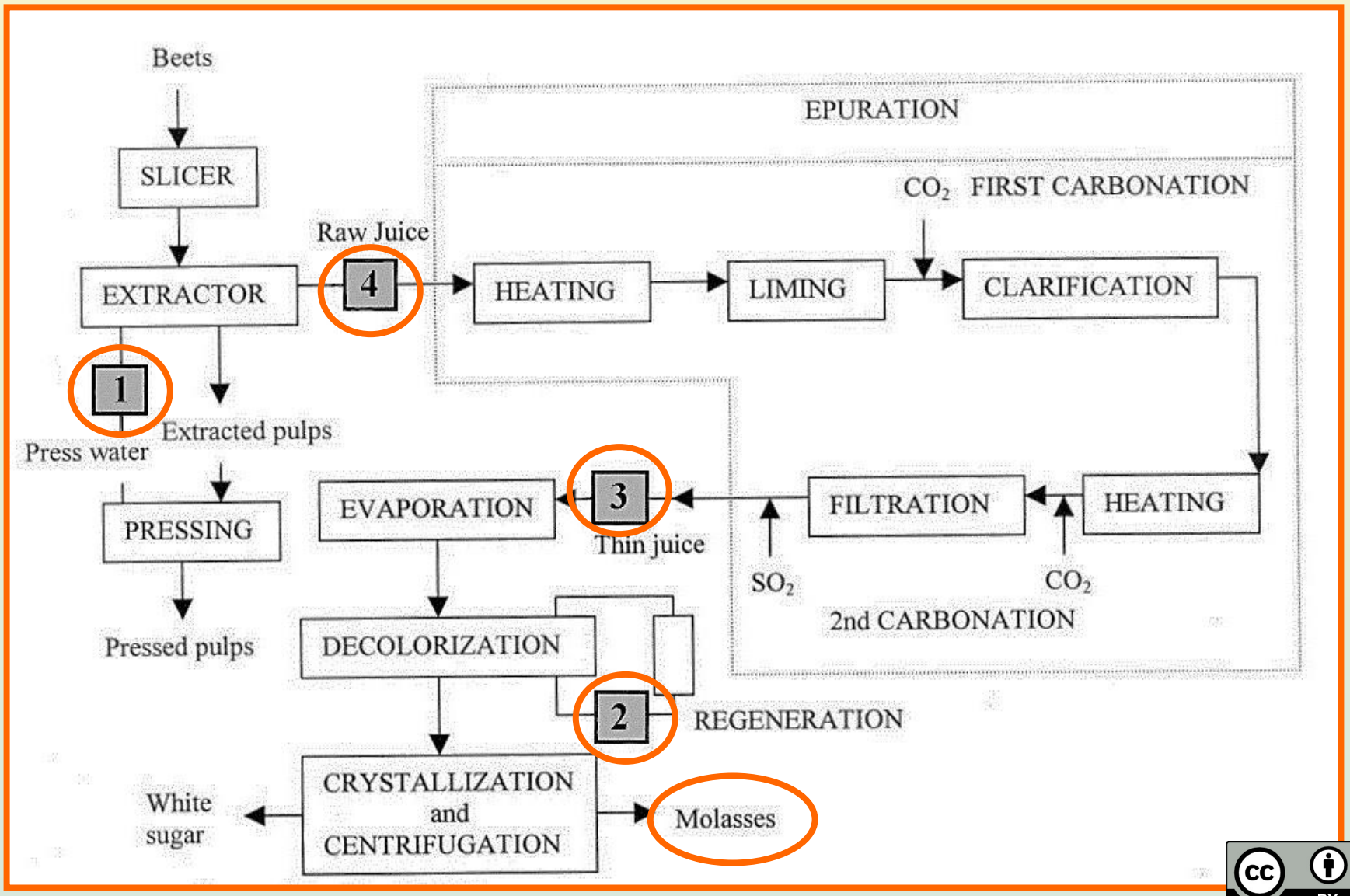
Figure 8.49. Separation of corn proteins by solvent extraction and nology (Cheryan 1992, 1994).

Cheryan M.: Ultrafiltration and Microfiltration Handbook, Technomic Pub. Co., 1998

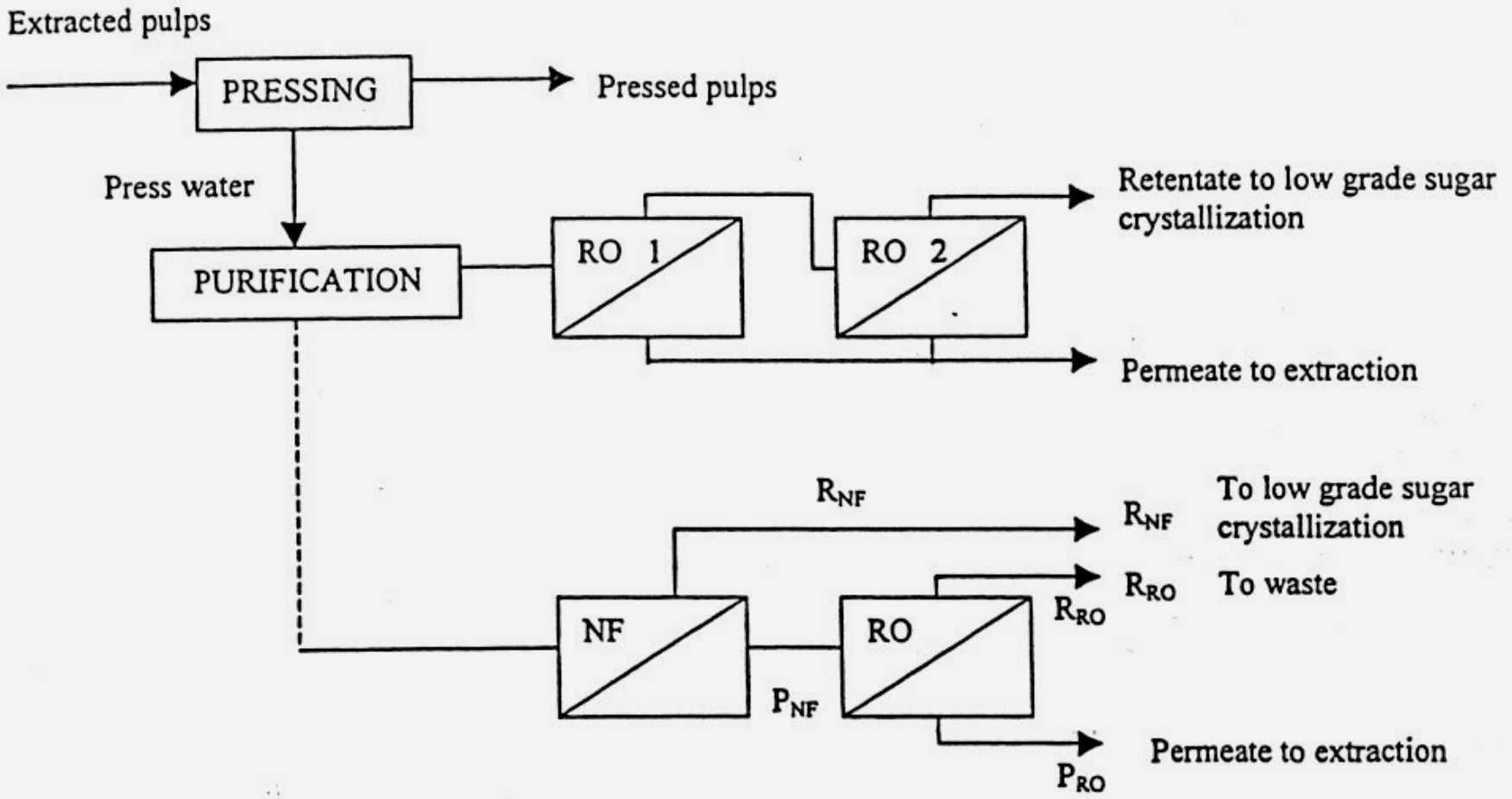
Sugar industry

- **Sugar production = demanding process (technology and energy) – membranes might bring high energy savings**
- **BUT the limitations are: high viscosity, density and osmotic pressure of sugar juices**
- **UF – purification of thin juice (sterility, low colorant content)**
- **RO – concentration of thin juice before evaporation (energy savings)**
- **RO – of water obtained by pressing of extracted sliced beet (so called press water) – sterility, removing of beet tissue, colloids and proteins**

Possible membrane applications in the sugar industry

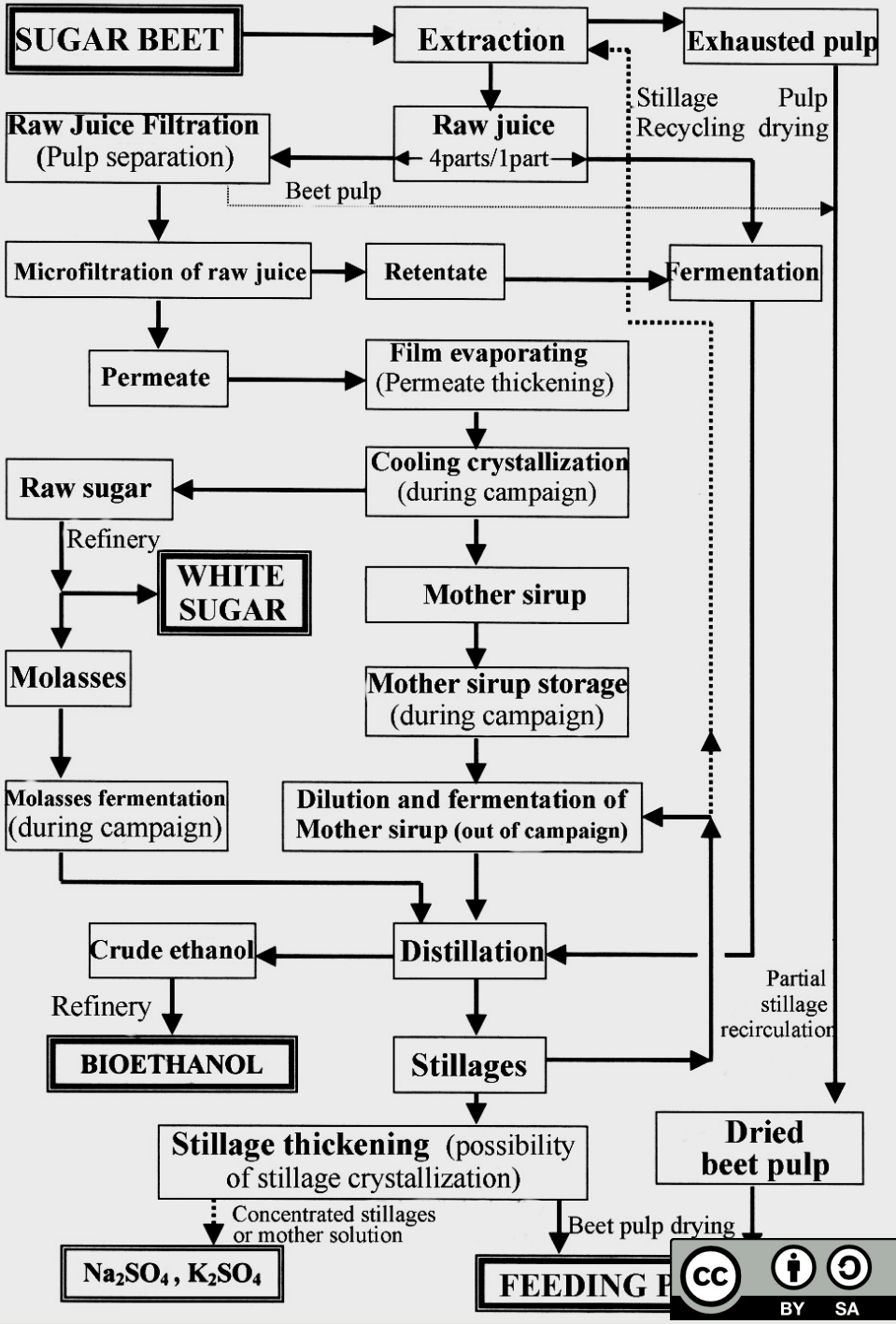


Purification and concentration of press water



The scheme of non-waste technology

Connection of the sugar technology with fermentation

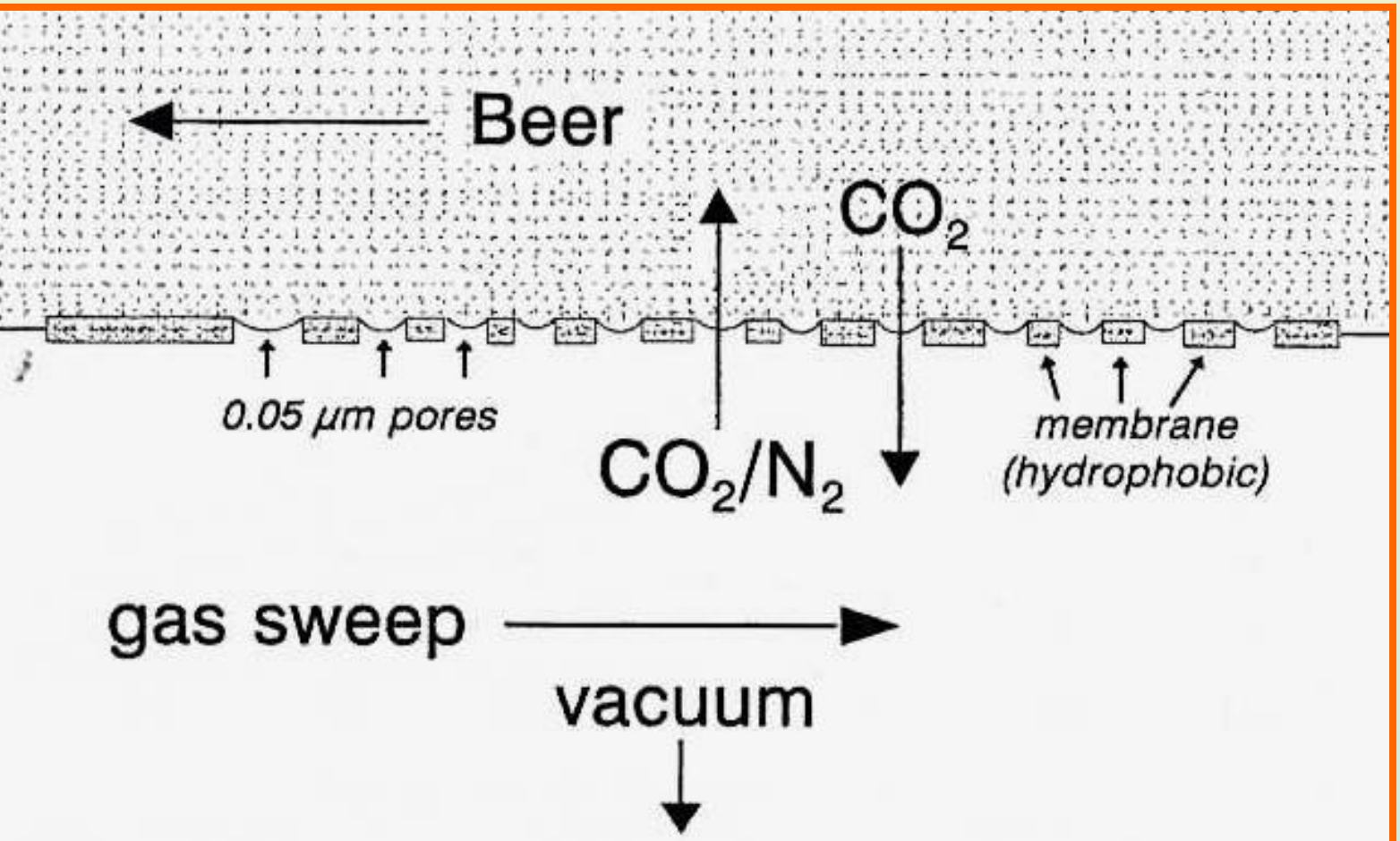


Brewing and wine making technologies

- **UF** – juice fining before fermentation (= removing of colloids, high molecular substances, tannin, suspended solids, polyphenols, and microorganisms)
- Cross-flow **microfiltration** of hopped wort (a supplement to vortex separators)
- **MF** – after fermentation (= yeast separation, replacement of candle filters and filtration using filtration aids, diatomaceous earth)
- **UF** of wine and beer – improving of the product stability (replacement of candle filters and filtration using filtration aids, diatomaceous earth)
- **Pervaporation** - non-alcoholic beer

Removing of CO_2 from beer
Purification, drying and storage of CO_2
Aeration of hopped wort

gas permeation (dense polymeric membranes)



O´Shaughnessy C., McKechnie M. (1996): The Brewer, March 1996, 110.

Membrane applications in wine making

There are several potential benefits of MF and UF in winemaking (Figure 8.86). UF can be used either before the fermentation (i.e., for clarifying

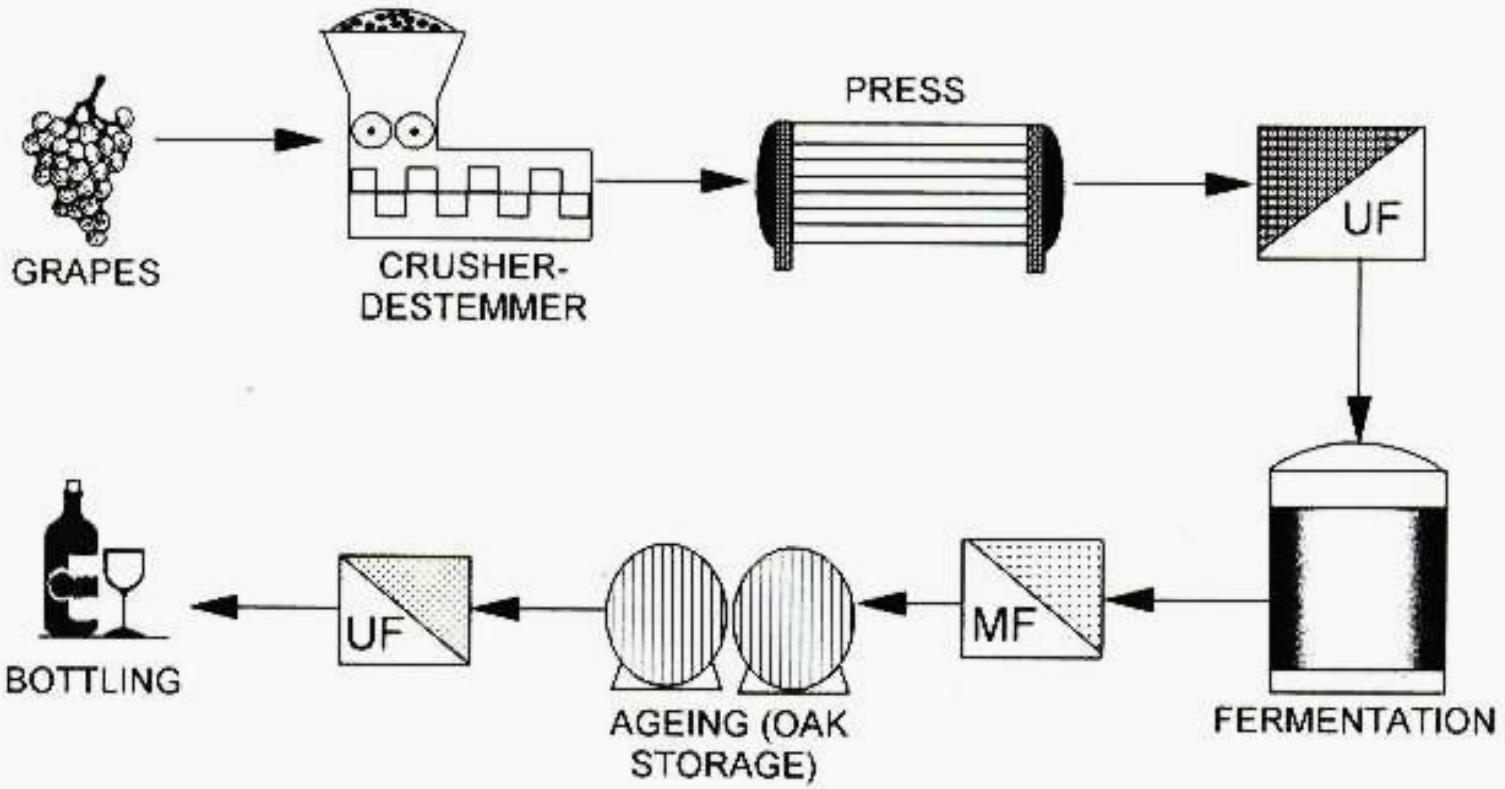
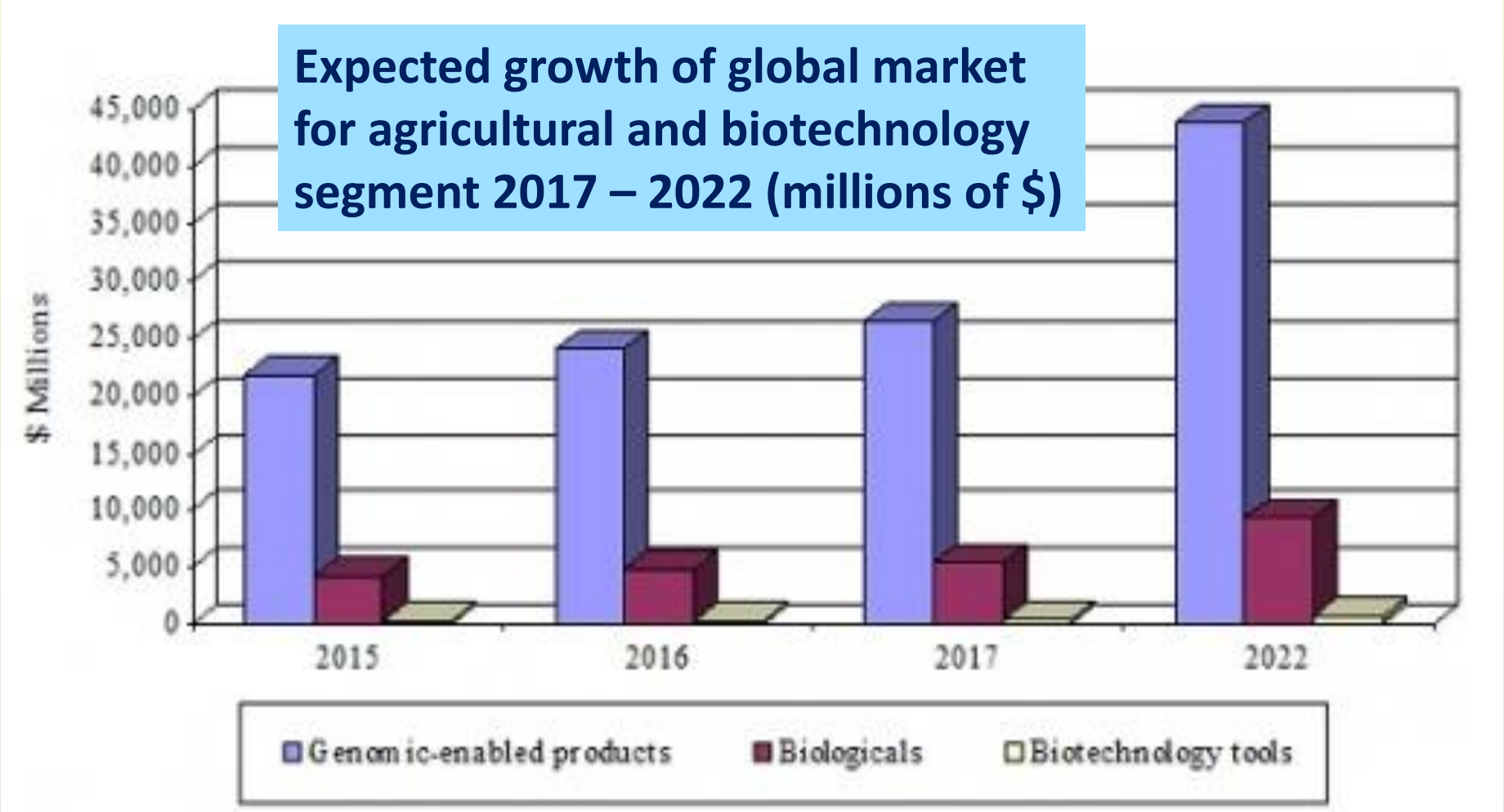


Figure 8.86. *Membrane applications in wine production. The first UF step removes microorganisms, colloids, and high molecular weight materials. The second membrane step (MF) removes yeast. The third membrane step is a final filter: it could also be a sterilizing microfilter.*

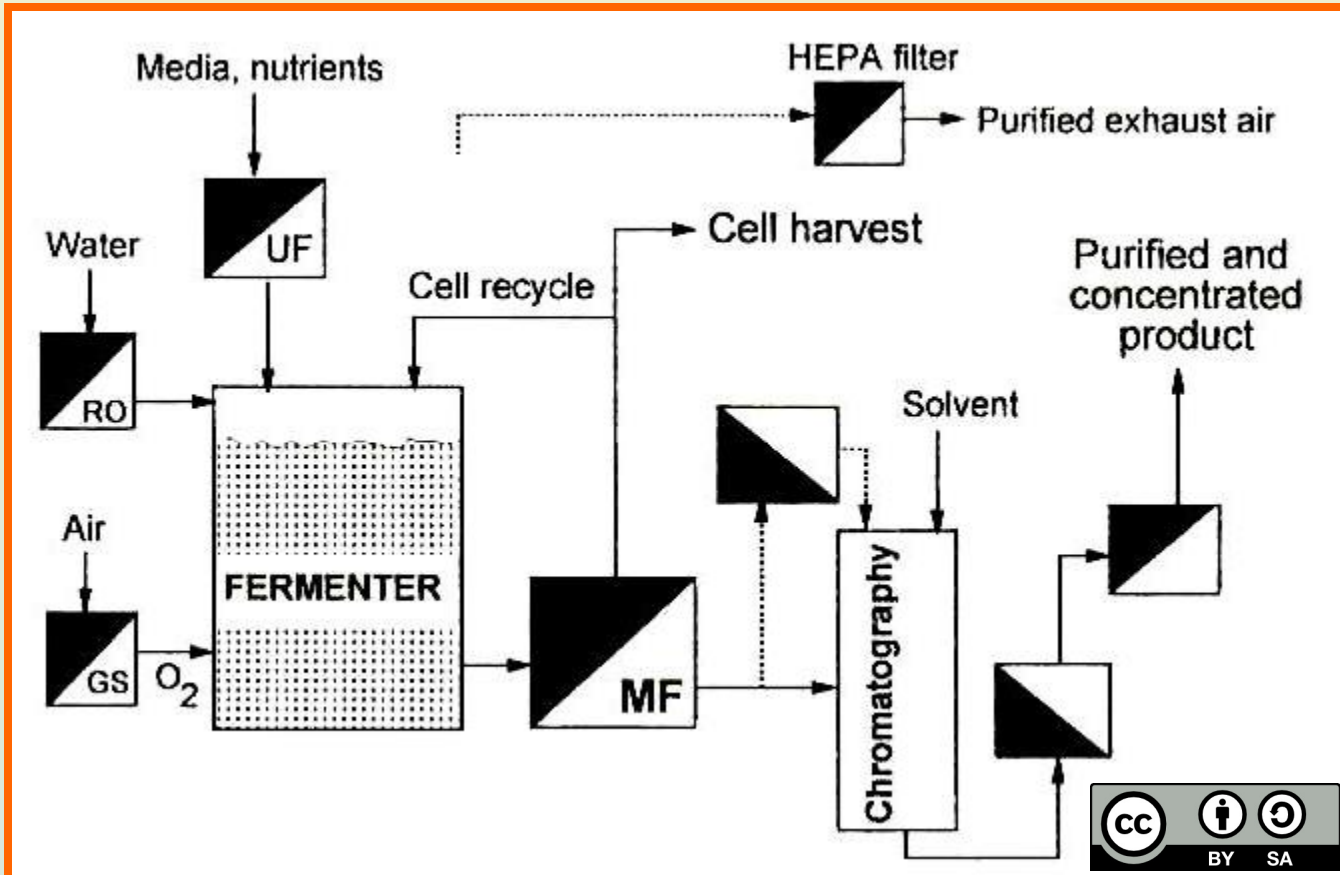
Biotechnologies, medicine and biochemistry

Large potential for membrane processes!



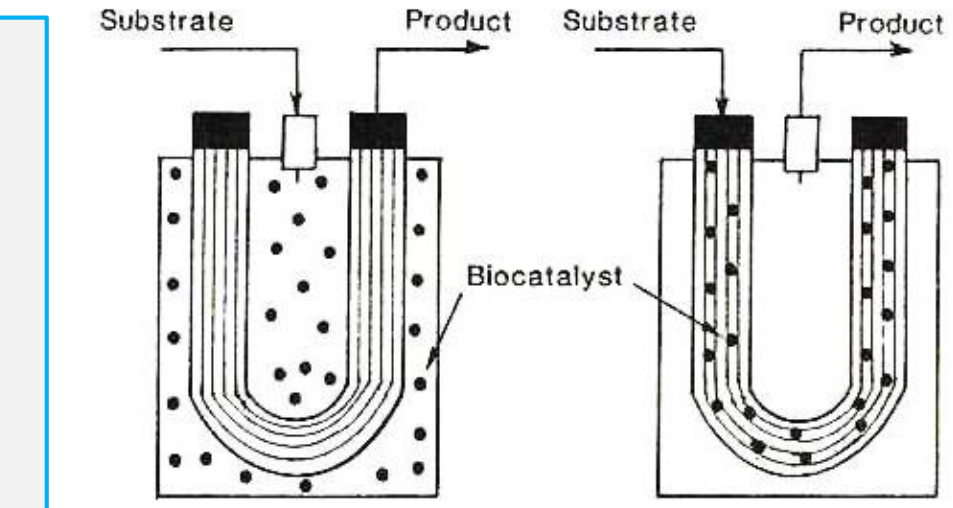
Biotechnologies

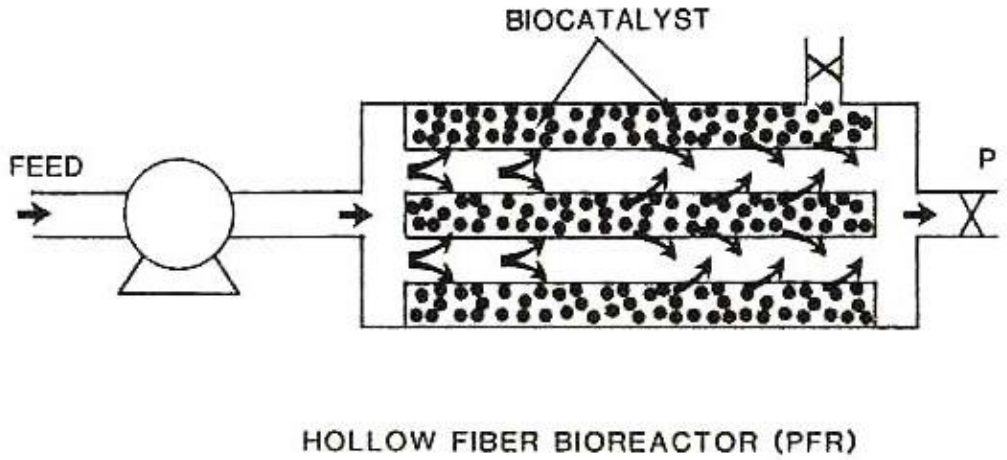
- Bioreactors – enzymatic and microbial conversion (immobilization)
- Tissue culture reactors
- Production of high purity water (so-called ultrapure water)
- Filtration of gases entering the bioreactors (sterility) for cell cultures
- Filtration of exhaust gases from bioprocesses
- Sterilisation of media



Cheryan M.: Ultrafiltration and Microfiltration Handbook, Technomic Pub. Co., 1998

Cell immobilization in a hollow fiber reactor





HOLLOW FIBER BIOREACTOR (PFR)

Figure 8.66. *Schematic of plug flow membrane reactors: Top: hollow fiber beaker reactor; the biocatalyst can be trapped either in the shell side or the tubes; Bottom: tubular type hollow fiber bioreactor. The biocatalyst is loaded into the shell side through the permeate ports. Feed is pumped through the tube under pressure and the product stream removed through the retentate outlet. The reverse (i.e., tube-side loading of biocatalyst) is less common.*

Cheryan M.: Ultrafiltration and Microfiltration Handbook, Technomic Pub. Co., 1998

Biotechnology and pharmaceuticals

Separation of microorganisms and proteins (MF, UF):

- Isolation of cells from fermentation broth

Purification of products after fermentation (MF, UF, NF, RO, membrane electrolysis = removing of organic acids, ED):

- Isolation of metabolites from medium – antibiotics production (Penicillin, Cephalosporin, Streptomycin, Tetracycline; replacement of rotary vacuum filters – improved yields, reduction of processing costs)
- Industrial enzyme production (celullase, peroxidase, protease; concentration of enzymes before downstream processes)
- Purification and concentration of amino acids
- Production and purification of proteins
- Production of organic acids (lactic, butyric, citric and acetic acids)
- Vitamin production, vaccines, monoclonal antibodies and pharmaceuticals
- Removing of viruses in pharmaceutical production
- Concentration and demineralization of blood plasma
- Concentration of peptides

Next membrane applications:

- Sample immobilization in microscopy
- Transfer, immobilization and detection of DNA, RNA and proteins

Separation and purification techniques

Theoretical introduction into chromatographic separation

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Information sources

http://sch.vscht.cz/vyuka/international-students/erasmus-students/

www.sciencedirect.com

https://onlinelibrary-wiley-com.ezproxy.vscht.cz/

Jönsson J.A. (1987): Chromatographic Theory and Basic Principles, Marcel Dekker, New York

Theoretical introduction into chromato-graphic separation

Contents

1. **Theory of chromatographic separations**

Principle of separation, separation efficiency, number of theoretical plates, selectivity, resolution, sorbent capacity, stationary and mobile phase, factors affecting the separation

2. **Individual chromatographic methods**

Adsorption, gel, ion-exchange, affinity chromatography, reverse phase/normal phase chromatography

3. **Sorbents**

Material, composition, porosity, ligand, cross-linking, physical properties

4. **Industrial chromatography – scale-up**

Matrix and column selection, flow rates, sample loading

Theoretical introduction into chromatographic separation methods

Chromatography = a technique that separates compounds (molecules) between two phases (immiscible):

- Mobile phase (eluent) – gas, liquid, supercritical liquid
- Stationary phase (sorbent, matrix)

Terminology: analyte, elution, mobility, chromatogram

Separation principle:

Sample is dissolved in the mobile phase, which passes through the sorbent – reversible interactions of analyte between both phases

Analytes have different solubility in both phases ⇒ different mobility = different retention

The higher the analyte solubility in the stationary phase, the higher the retention in the system

Basic classification of chromatographic methods

- According to mobile phase
  - Liquid (LC)
  - Gas (GC)

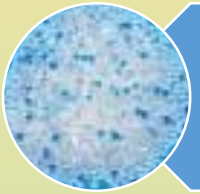
- According to interactions of molecules with sorbent
  - Adsorption
  - Size-exclusion
  - Charge (Ion-exchange chromatography IEC)
  - Specific biological activity (Affinity chromatography)

- According to a scale of application:
  - Analytic
  - Preparative
  - Industrial

Arrangement of the chromatographic process

Basic arrangement similar for all types of applications

Two phases:



SORBENT = STATIONARY PHASE = MATRIX

MOBILE PHASE = ELUENT

Sorbent (small particles, spherical) in a narrow tube - column,

Sample is injected into the mobile phase at the beginning of the column and goes through the column (elution). The average speed of the analyte is proportional to the resident time of sample in the mobile phase.

Arrangement of the chromatographic process

Mobile phase:

- placed in a reservoir, flows through the column
- pump (or hydrostatic pressure difference)

Constant composition during elution – analytes pass through the column due to the different mobility (various speeds) = isocratic elution

Some analytes have strong affinity to sorbent – to release the analyte a composition of the eluent needs to be changed:

- continuously = continuous gradient elution
- in steps = step gradient elution

Detector

Mechanism of retention

Chromatographic separation = dynamic adsorption process

Various analyte – sorbent interactions:

- Hydrophobic (non-specific) – reversed phase chromatography
- Polar (dipole – dipole) –normal phase chromatography
- Ionic (charge) – ion-exchange chromatography (IEC)
- Biospecific – affinity chromatography
- The size of molecules – size-exclusion chromatography (SEC)

All competitive – molecules of analyte vs. mobile phase

- SEC = an exception

The stronger the interaction analyte – sorbent and weaker the interaction eluent – sorbent:

➔ the more is the analyte retained

➔ the longer the retention time is

Essential theory of chromatographic methods

Distribution of analyte:

Analyte is in equilibrium between the two phases:

$A_{mobile} = A_{stationary}$

Equilibrium constant = partition coefficient $K = c_{A(stat)} / c_{A(mob)}$

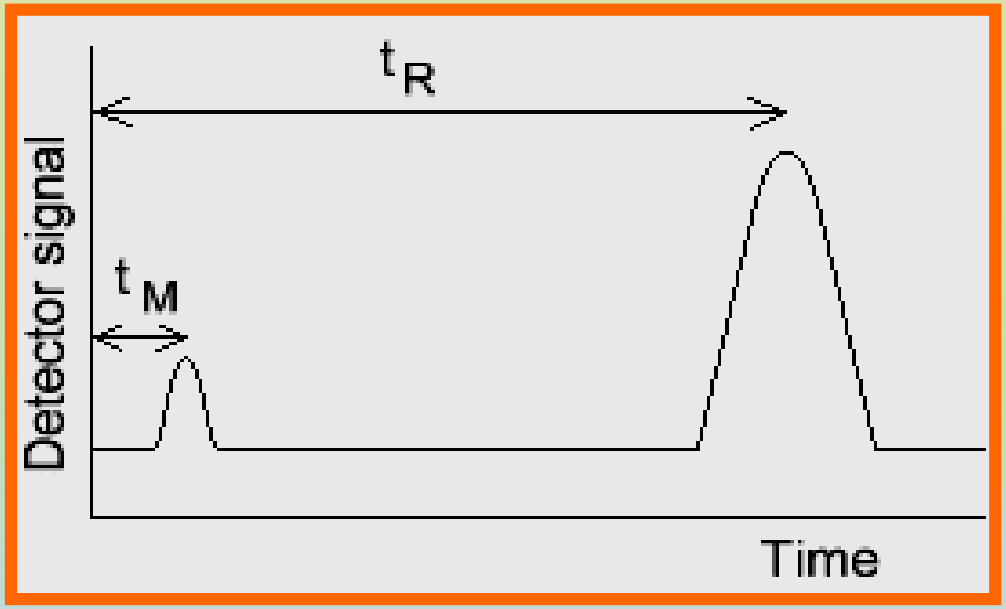
c = analyte molar concentration in mobile and stationary phase, respectively

- Retention time (t_R)

= a time between sample injection and analyte reaching a detector (max.)

- Dead time (t_M)

= a time of mobile phase passage through the column



Satisfactory separation – different retention times of anal

Retention parameters

Capacity factor k' describes the speed of analyte through the column

- independent of the system geometry, but expresses the thermodynamical character of sorbent-analyte-eluent.
- Defined as (for the analyte A): $k'_A = t_R - t_M / t_M$

t_R and t_M – easily obtained from a chromatogram - values:

$k' < 1$
$k' > 20$
$1 < k' > 5$

Retention time t_R – reciprocal to the eluent flux

Retention volume V_R – eluent volume that passed through the column during elution of an analyte, independent of flux but related to the column geometry

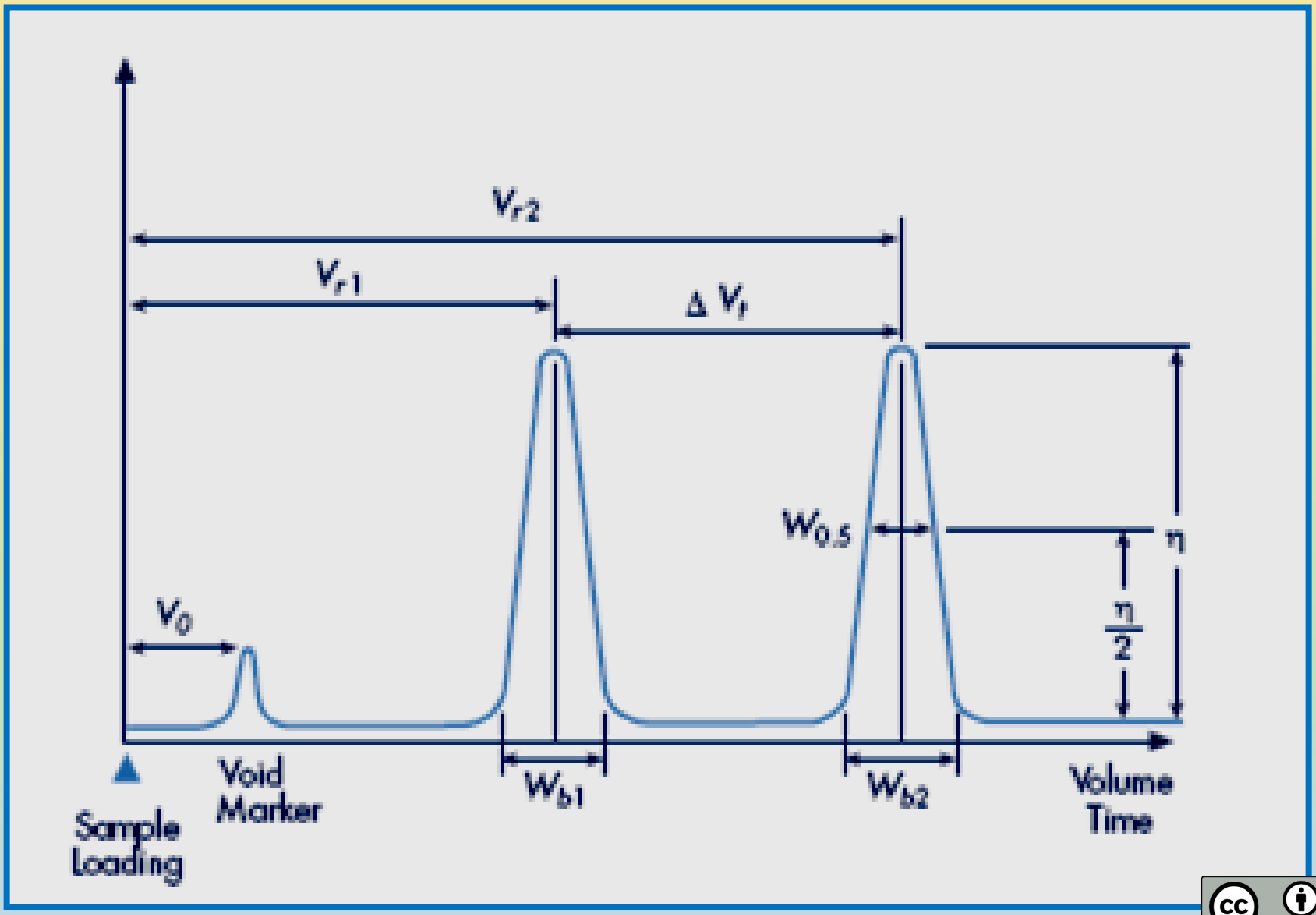
Retention volume:

1. Reduced retention volume – volume of the eluent that passed through the column, while the component was adsorbed on the sorbent
2. Dead volume V_0 – volume of the eluent, that passed through the column, while the component was moving in the mobile phase; equal to the volume of liquid phase in the column, identical for any analyte

Ratio of retention volume to dead volume k – basic and universal retention parameter

$k = V_R/V_o$

Retention volume V_R



Separation efficiency, selectivity and resolution

- Separation efficiency depends on two factors:

1. Selectivity α
   - Expressed by ratio of capacity factors of two peaks (α = selectivity factor)
   - Characteristic of separation capability of sorbent for given component mixture
   - Independent of column efficiency
   - Does not imply the width, but the distance between the peak maxima
   - Dependent on component character, eluent composition and properties and binding interactions with sorbent
2. Peak width *w*

$$\alpha = \frac{V_{R1} - V_0}{V_{R2} - V_0} = \frac{k'_1}{k'_2}$$

- Resolution R

Expresses separation power of the whole chromatographic system related to components

Expressed by the ratio of peak maxima distance to the mean value of the peak width at the baseline

For symmetric peaks:

if R<1 then we get non-separated peaks
if R=1 then we get just separated peaks
if R>1 then we get well separated peaks

$$R = \frac{V_{R2} - V_{R1}}{\frac{1}{2} \cdot (w_1 + w_2)}$$

The theoretical plate model and column efficiency

Optimal separation – sharp, symmetric peaks

Band broadening caused by diffusion – inevitable, BUT effort to minimize

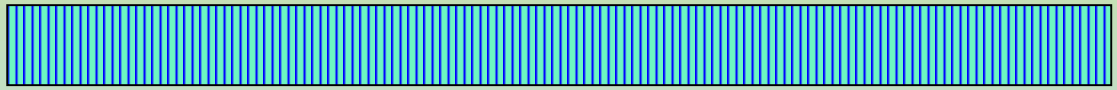
Sometimes it is necessary to determine column efficiency

The theoretical plate model of chromatography

Assumption – chromatography column divided into large number of separated layers = theoretical plates

Every plate – equilibrium of analyte (mobile phase – stationary phase)

Analyte passes through the column due by transfer of equilibrated mobile phase from one plate into another



L column length

N number of theoretical plates (the more – the better)

HETP Height equivalent to a theoretical plate (the smaller – the b

Column length and number of theoretical plates

Theoretical plates do not exist

$$HETP = L / N$$

- Help to understand the phenomenon
- Determination of the column efficiency; number of theoretical plates for column can be specified according to the character of the chromatographic peak after elution, were $w_{1/2}$ is the peak width at the half-height:

$$N = \frac{5.55 \cdot t_R^{\,2}}{w_{1/2}^{\,2}}$$

- The same column has different number of theoretical plates for each component of a mixture

Selectivity, resolution and number of plates

↘ Resolution can be related to the number of plates in the column N selectivity factor α retention factor k':

$$R = \frac{\sqrt{N}}{4} \cdot \left(\frac{\alpha - 1}{\alpha} \right) \cdot \left(\frac{1 + k'_B}{k'_B} \right)$$

To obtain high resolution, the three terms must be maximised :

↑ N – ↑ by lengthening the column → increased retention time and increased band broadening - not desirable

↓ HETP – achieved by reducing the size of the stationary phase particles

Capacity factor k' – by changing the temperature (GC) or the composition of the mobile phase (LC); this term – the least effect on the resolution

Selectivity factor α – by changing mobile phase composition, column temperature, composition of stationary phase, using special chemical effects (such as incorporating a species which makes complexes with one of the solutes into the stationary phase)

Band broadening theory
Van Deemter equation

A more realistic description of the processes inside a column:
takes account of the time taken for the solute to equilibrate between the stationary and mobile phase
UNLIKE the plate model assuming that equilibration is infinitely fast
The resulting band shape of a chromatographic peak is affected:

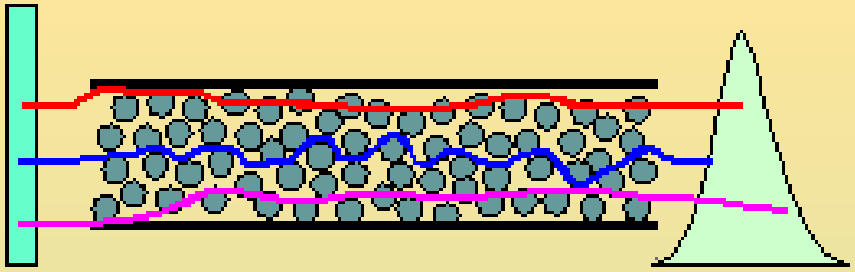
- By the rate of elution
- By the different paths available for solute molecules to travel between particles of stationary phase
- By diffusion
- By mass transport between phases

Considering all this, we obtain Van Deemter equation –the dependence of HETP on the average velocity (*u*) of the mobile phase including factors *A*, *B* a *C,* which contribute to band broadening:

$$HETP = A + B/u + C \cdot u$$

Application: to determine an optimum mobile phase flow

Van Deemter equation



http://hplc.chem.shu.edu/NEW/HPLC_Book/

Factors A, B and C represent:

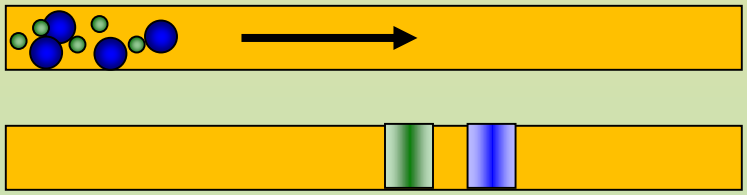
A - Eddy diffusion

Solute molecules take different paths through the stationary phase at random – different paths are of different lengths – band broadening

$$A = 2\lambda d_p$$

d_p is the particle diameter (average), and λ is the constant (almost close to 1) involving size distribution (narrow distribution ↓ λ) both parameters increase pressure

Application of sorbent with small and uniform particles and homogenous filling of column – no dead volume



B - Longitudinal diffusion

The concentration of analyte is less at the edges of the band than at the centre- analyte diffuses from the centre to edges

$$B = 2\gamma D_m$$

D_m is the analyte diffusion coefficient in the mobile phase

g is the factor which is related to the diffusion restriction by column packing

The higher the eluent velocity, the lower the longitudinal diffusion effect (Molecular diffusion in the liquid phase is about five orders of magnitude lower than that in the gas phase ⇒ for LC almost negligible)

Band broadening theory

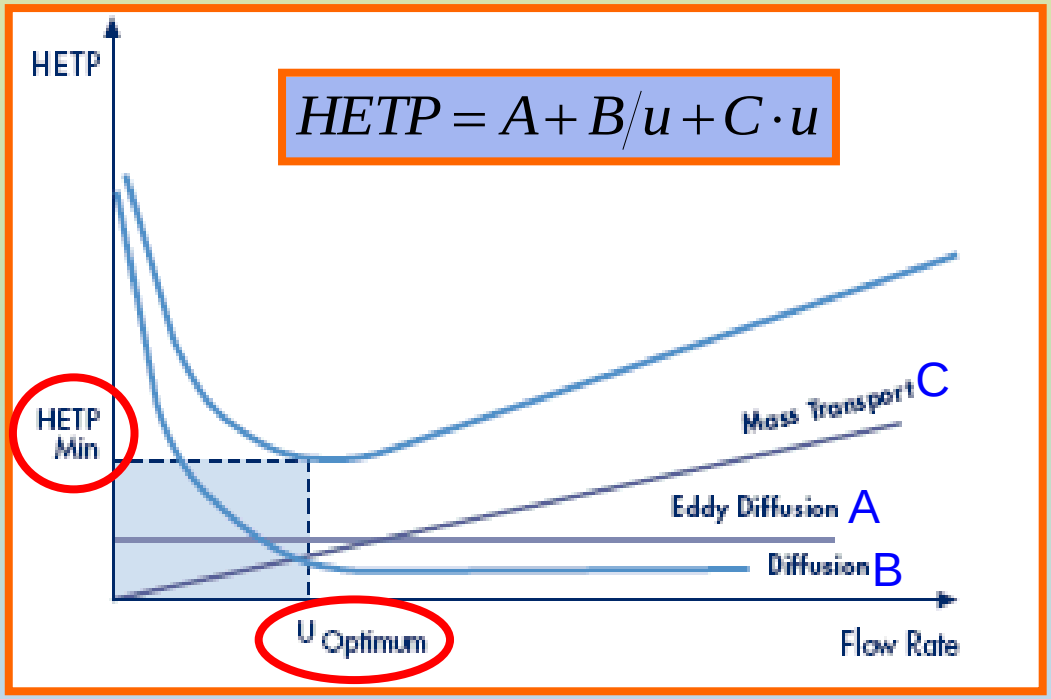
C – Mass transport

Analyte – equilibration between two phases – it takes some time
High mobile phase rate and strong affinity of analyte to sorbent – analyte in the mobile phase will move faster than in the stationary phase.

The most questionable parameter; for the modern types of packing materials it may combine two effects:

- Adsorption kinetics – almost negligible comparing to the diffusion
- Mass transport among particles (by the diffusion)

$$C = \omega d_P^{\,2} / D_m$$



d_p is the particle diameter, D_m is the diffusion coefficient of the analyte in the mobile phase, ω is the coefficient determined by the pore size distribution, shape, and particle size distribution

Different components have different dependencies of HETP on the flow rate on the same column - we can find optimum eluent flow rate where the column efficiency will be the best

Chromatographic techniques

Size-exclusion chromatography (SEC)

A special type of chromatographic separation

- separates compounds on the basis of differences in their molecular sizes (the bigger molecule, the lower retention in the system – they are not able to penetrate the sorbent pores fully)
- Interaction between analyte and sorbent undesirable

Sorbent: insoluble, hygrophilous, porous particles (gel)
Process operation: isocratic (separation according to different various speed of components in the column)
Applications:

- Group separation - the molecules to be separated differ in size to such an extent that it is possible to select a gel in which the larger molecules are totally excluded, the remaining smaller molecules can be eluted much later, e.g. a separation of salts or alcohols from proteins
- Fractionation - separation of molecules with a similar range of sizes. This requires more critical control of conditions and careful selection of a gel matrix

Ion-exchange chromatography (IEC)

- Separation on the basis of charge
- Low energy demands
- Universal application (ion – non-electrolyte, ion –ion)

Molecules are bound by ionic forces to matrix's immobilized groups of opposite charge

Ion-exchange matrices = hydrophilic particles (styrene, DVB, cellulose, agarose, dextran, zeolite, SiO_2) with covalently bonded charged groups:

- Anion exchanger (+ charged) diethylaminoethyl (DEAE) or amines: $R\text{-}NH_2$, $RR'NH$, $RR'R''N$ (N atom - basicity): $R\text{-}NH_2 + H^+ \rightarrow R\text{-}NH_3^+$
- Cation exchanger (– charged) sulfonic $\text{-}SO_3^-$, $\text{-}CH_2SO_3^-$, $\text{-}COO^-$, carboxymethyl (CM)

- pH alters the net number of charges of the component or in the matrix (isoelectric point)
- Increasing salt concentration - desorption (massive number of small counter-ions competing with components for the oppositely charged binding sites on the matrix)

Process operation: isocratic x gradient (industrial applications)

Hydrophobic interaction chromatography (HIC)

Matrix

- uncharged, poorly hydrophilous (gel on the basis of polysaccharides, e.g. agarose)
- with bonded hydrophobic groups (i.e. alkyl chains or phenyl rings)
- high mechanical stability and rigidity
- weak interactions: polar or Van der Waals forces

Applications

Proteins with hydrophobic sites exposed on their surfaces
different affinity of hydrophobic sites to matrix

Increasing of the strength of hydrophobic interactions – raising the ionic strength of the solution (addition of a neutral salt)

Adsorption of the sample to the matrix at high ionic strength

Selective desorption of adsorbed substances altered elution conditions: reducing the ionic strength, raising the pH of eluent, reducing the polarity of the eluent (e.g. by including ethylene glycol), including a detergent

Process operation: gradient (step or continuous)

Reversed phase chromatography

Similar to HIC – increased degree of substitution (hydrophobic content) on the matrix and subsequently stronger sample-matrix interaction (in the case of proteins - the interaction is strong resulting in denaturation)

Applications: small molecules and peptides

Matrix:

non-polar (silica gel modified by non-polar groups, Al_2O_3, synthetic polymers, activated carbon)
high rigidity, macroporous

Eluent:

polar (organic solvents; CH_3OH, alcohols in a mixture with water - isopropanol, nitriles - acetonitrile, ether, water)

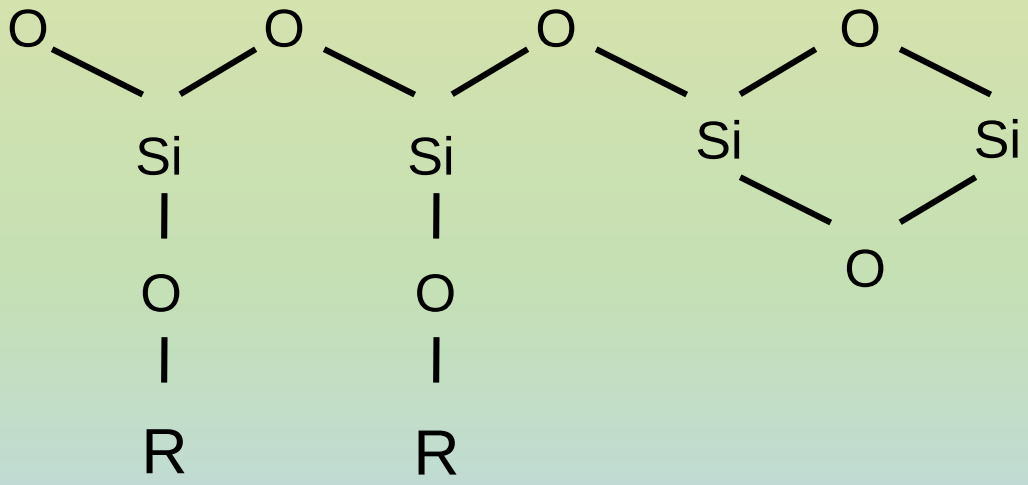
Normal phase chromatography

Sorbent:

polar (silica gel modified by polar groups $SiO_2x\ H_2O$ – strongly acid surface; pH = 3-5, Al_2O_3, $MgSiO_3$)

Eluent:

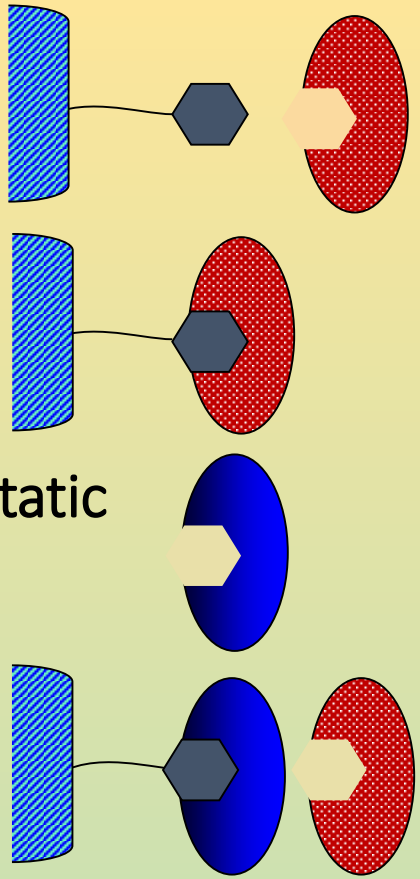
non-polar (hexane, cyclohexane)



R:

– H	polar
– NH_2	polar
– CN	polar
– C18	non-polar
– C	non-polar
– N – C	non-polar
– Si – C	non-polar

Affinity chromatography (AC)



Biospecific bond between the molecule of interest and a specific molecule (called ligand) covalently coupled to a support matrix, ligand - able to bind the sample from the mobile phase

Interactions: Van der Waals, hydrophobic, steric, electrostatic

Matrix: Sepharose, cellulose

Ligand – high affinity to separated molecules
(e.g. colorant, protein, cofactor: NAD, 5-AmP)

Spacer – covalent bond

Affinity matrix – analyte:

- matrices specific to the desired molecule (e.g. for enzyme – ligands: substrate, substrate analogue, inhibitor, or a specific antibody)
- matrices which interact with a group of species (they carry a group-specific or general ligand, e.g. cofactors)

Process operation: adsorption – desorption (elution with a specific co-factor or substrate = competition with the immobilized ligand for the protein, or by altering the pH or ionic strength)

Industrial chromatography – scale-up

Large-scale production starts with laboratory-scale feasibility studies
Laboratory-scale – separation efficiency is an important parameter
However in industrial scale – other factors: as flow rate, sample size, cycle time, etc.

Advantages of industrial application of chromatographic methods:

- Versatile technique
- Simple system
- Mild conditions
- In recoveries approaching 100 % purities !!!
- Operation can be scaled-up without a significant loss in purification

Principles of scaling-up:

- All process volumes scaled-up in direct proportion to the sample volume (i.e. column bed, wash, and elution volumes)
- Column length is held constant (column volume is increased by increasing column diameter or by the number of columns)
- Linear (or superficial) velocity is held constant (volumetric flow rate increases proportionally with sample volume, total separation time remains roughly constant)
- Sample composition is held constant (critical factors are concentration, viscosity, pH and ionic strength)

Matrix selection

Key factors: selectivity and resolution of the stationary phase

- ↘ Smallest possible particle diameter (but it affects pressure, flow rate)
- ↘ Rigidity
- ↘ Narrow particle size distribution (homogenous particles): broad distribution → denser packing → smaller flow paths → reduced column flow rate

Gels

- ↘ Three-dimensional structure, cross linked – mechanical rigidity, elasticity
- ↘ Gel swelling: before filling – the gel needs to be swelled perfectly
- ↘ Inert matrices

Highly compressible gel matrices (Dextrane, cellulose, agarose)

bead deformation and compression → high resistance → pressure drop or limited maximum flow rate → problem in larger columns

High bed heights + non-rigid matrix = no flow

Compensation: a series of shorter columns

Application: fractionation of big molecules

Rigid gel matrices – pressure drop proportional to the bed height, possible high diameters of matrix bed (> 1 m) and height up to 50 cm

Application: desalination

Sample loading

Sample mass and concentration are key factors to determine in initial laboratory studies

➢ **Isocratic techniques (SEC)** – sample loading can have an adverse effect on resolution:

Lab-scale: sample volume= 2 – 3 % of the total column bed volume (V_s)

Large-scale fractionation: sample volume = 5 – 15 % of V_s (for economic reasons, overlapping of eluted peaks, due to excessive loading) compensated by taking fractions and collecting only the central pure portions, the leading and trailing edges are thyen re-chromatographed

Group separation: sample loading can be considerably greater, commonly 25–30 % of V_s

➢ **Desorption techniques (IEC, AC)**

- the sample size relates to the total capacity of the matrix
- sample mass is more important than volume – lab tests: known product concentration through a known volume of matrix
- columns can be used effectively to concentrate dilute samples

Flow rate

A crucial factor in large-scale operations
related to other factors as matrix, column and accessory equipment selection

Matrix:

- Rigid: flow rates grows linearly with pressure
- Semi-rigid: nearly linear behaviour as above, then flatten out to a maximum flow rate - constant as more pressure is applied
- Compressible: maximum flow rate, then decreasing as more pressure is applied (critical pressure!)

Size exclusion chromatography and other fractionation techniques

Resolution usually obtained with flow rate: 1 – 3 $ml/cm^{-2}\ h^{-1}$
Industrial applications need: 10 – 20 $ml/cm^{-2}\ h^{-1}$

In group separation processes:

Resolution is not limiting factor
Flow rates commonly: 50 - 100 $ml/cm^{-2}\ h^{-1}$

IEC a AC:

Flow rates: 20 – 150 $ml/cm^{-2}\ h^{-1}$

Column selection

Materials used

- Stainless steel (great resilience, can be autoclaved or sterilised, reasonable chemical resistance, opaque, corrosive)
- Glass (organic solvents, autoclaved, transparent, fragile)
- Plastic (aqueous solutions, resilient and less expensive, transparent; akrylic, polypropylene)

Other column components:

Bed supports (screens or sintered materials: polyethylene, PTFE or stainless steel and meshes of polyamide, polyester or stainless steel),

'O-ring' seals (variety of materials including ethylene propylene rubber, nitrile rubber, PTFE, etc.)

Column length selection:

SEC (plus other isocratic techniques) – critical parameter (↑length = ↑resolution, problem for compressible gels → series of short columns (the pressure drop across each column is kept low, but total pressure drop across the column 'stack' may be quite high, better packing capability, less plugging – easier cleaning)

IEC, HIC and AC –total column capacity is important, not the lengt

ADVANCED PROCESSES IN FOOD TECHNOLOGY AND BIOTECHNOLOGIES

SEPARATION AND PURIFICATION TECHNIQUES

INDUSTRIAL CHROMATOGRAPHY

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INFORMATION SOURCES

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ASADI M. (2007C): ION EXCHANGE RESIN (483-488). *BEET-SUGAR HANDBOOK*. JOHN WILEY & SONS, INC., HOBOKEN, NEW JERSEY, USA.

ION-EXCHANGE RESINS

ION-EXCHANGE RESINS = ION-EXCHANGERS = *IONEX*

- ✓ Porous-insoluble polymers;
- ✓ Large surface area;
- ✓ Selectively exchange ions (cations and anions) for other ions in a solution;
- ✓ Can operate at high temperatures and different pH ranges.

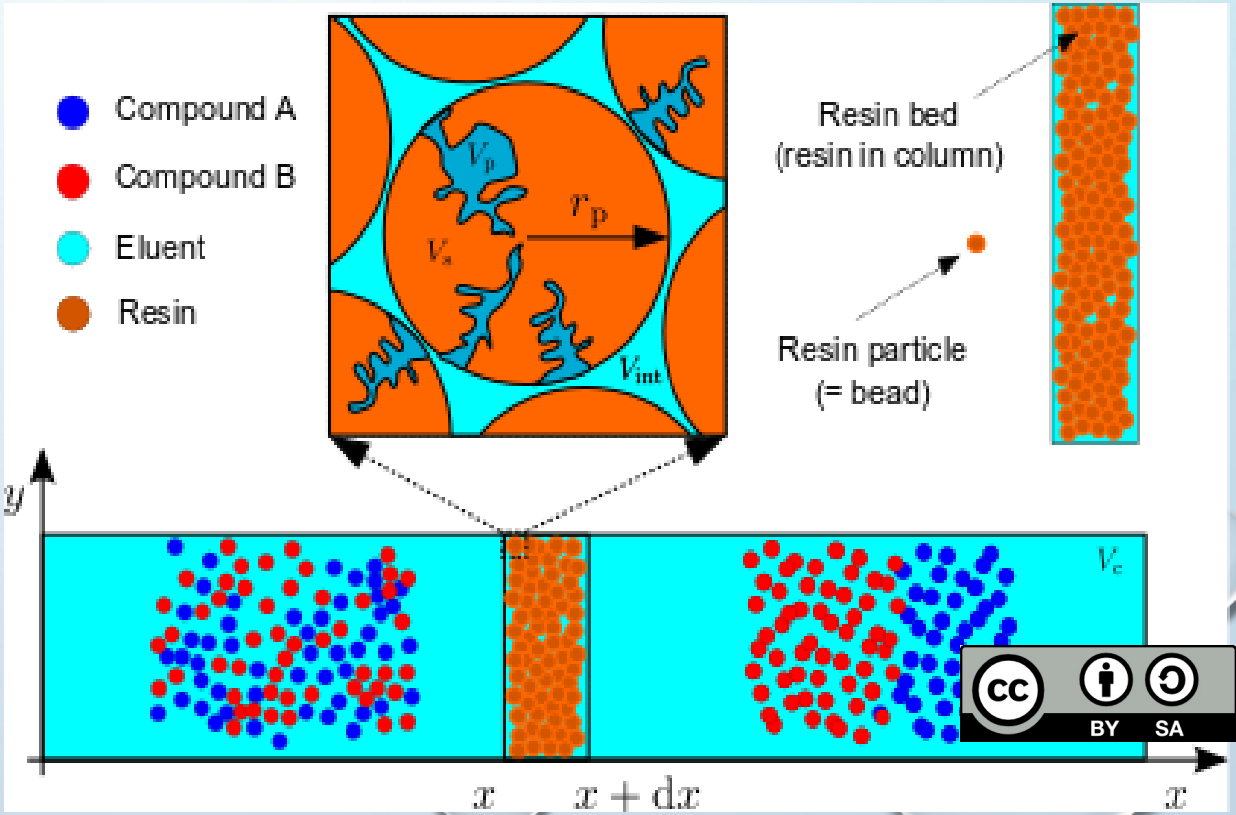
ION-EXCHANGE RESINS

EVERY ION-EXCHANGE RESIN CONSISTS OF:

1. **The support structure** (also **matrix,** skeleton)
   – mostly cross-linked polymer or an inorganic matrix (alumina or zeolite type)
   – small porous or non-porous particles (spherical shapes) or continuous porous matrix (called monolith)
   – sponge-like character – high porosity
   – provides mechanical properties
   – makes the system insoluble

2. **Functional groups**
   – bound to the matrix

Resin bed in a column with a detailed structure of a resin particle and the principle of separation in a column.



BASIC TERMINOLOGY

SELECTIVITY COEFFICIENT (*K*)

- ✓ The measure of a resin's preference for a particular ion.
- ✓ It determines the resin's affinity to the ion (the larger the *K* value, the greater is the affinity).
- ✓ The displacement of ions is based on the selectivity coefficient.

EXCHANGE CAPACITY (CAPACITY)

The ability of the resin to exchange ions expressed in grams per litre of resin (g/L).

COLUMN LOADING

- ✓ Theoretical column capacity
- ✓ Described as hardness removal efficiency:
  The feed hardness minus the hardness of the product after softening, multiplied by the theoretical capacity of the r

TYPES OF ION-EXCHANGE RESINS

Based on their ability to exchange different types of ions:

Anion-exchange resins (*anex*) are able to remove anions from a solution - contain positively charged functional groups (exchangeable group) that have an affinity for anions.

Cation-exchange resins (*catex*) are able to remove cations from a solution - their functional groups are negatively charged.

FUNCTIONAL GROUP

= a group of atoms in a molecule that has specific properties and is responsible for its reactions with other substances.

FUNCTIONAL GROUP IN ION-EXCHANGE RESINS:

- **Acid functional groups** = exchange cations
- **Basic functional groups** = exchange anions

ACID FUNCTIONAL GROUPS

Sulfonic (SO_3H) and carboxyl (COOH) groups

The exchangeable ion of these functional groups can be exchanged for a particular cation present in a solution, e.g.:

H^+ can be exchanged for Ca^{2+} and Mg^{2+} (R marks the matrix of the resin):

$$\mathbf{R\text{-}(SO_3H)^- + Ca^{2+} \leftrightarrow R\text{-}(SO_3Ca) + H^+}$$

$$\mathbf{R\text{-}(SO_3H)^- + Mg^{2+} \leftrightarrow R\text{-}(SO_3Mg) + H^+}$$

The acid functional group can behave as a strong or weak acid

Strong acids can ionise (dissociate) completely, weak acids dissociate only partially - the cation resins can be classified as:

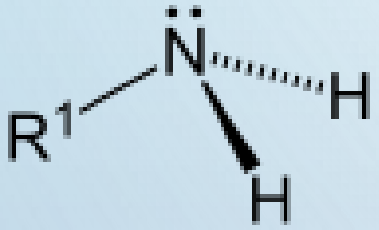
- **Strong-acid cation (SAC) resins** - functional groups are highly dissociated over the entire pH range ($R\text{-}SO_3H$)
- **Weak-acid cation (WAC) resins** – the functional group is only partially dissociated; the dissociation depends on the pH of the solution (R-COOH).

FUNCTIONAL GROUPS WITH BASIC CHARACTER

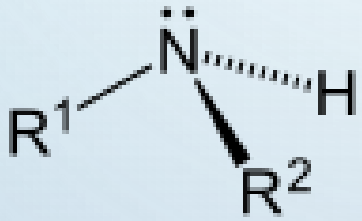
A functional group in anion resins must allow an exchange of anions.

Two different types of base-anion resins can be distinguished:

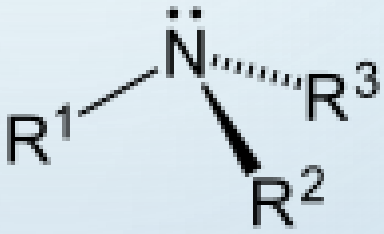
- **Strong-base anion (SBA) resins** - which contain usually quaternary amino groups with the structure NR_4^+
- **Weak-base anion (WBA) resins** - which feature a primary, secondary, and/or tertiary amino group.



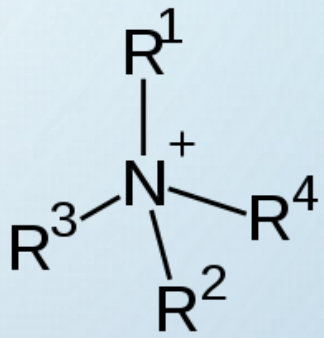
primary



secondary



tertiary



quaternary amines

ION EXCHANGE RESIN OPERATION AND REGENERATION

FOOD INDUSTRY – SPECIAL REQUIREMENTS

Resins used in the **food industry** must be **washed prior their use** to remove all impurities.

After several operation cycles, resins become **exhausted** = the ions originally attached to the matrix are replaced by ions from the solution.

The initial ion-exchange capabilities must be established by the **regeneration process** (chemicals = regenerants introduced). Regenerants contain the same type of ions that was originally attached to the matrix.

RESIN LOSSES AND REPLACEMENT

Regeneration – increases the lifetime and economic feasibility

The lifespan is affected by mechanical, chemical, thermal and radiation shocks, regeneration methods, storage conditions, the t
between cycles, and operating conditions.

SET-UP OF INDUSTRIAL CHROMATOGRAPHIC SYSTEMS

CHROMATOGRAPHY is a **physical method** of separation - the components to be separated are distributed between two phases (**mobile** and **stationary phase)**; the mobile phase moves in a definite direction through the stationary phase.

The chromatographic system - different types of operation:
- **Elution, frontal and displacement** chromatography.

The **ion-exchange chromatography systems** include: tanks with feed and eluent, pumps, valves, chromatography columns filled with resins, a fractionation system and tanks for the output.

TWO TYPES OF POSSIBLE ARRANGEMENT OF ION-EXCHANGE TECHNOLOGY:

Discontinuous (batch) set-up: the feed is dosed discontinuously, with breaks, to the separation system

Continuous system - the feed is dosed all the time, without interruption.

DISCONTINUOUS SYSTEMS
ELUTION CHROMATOGRAPHY

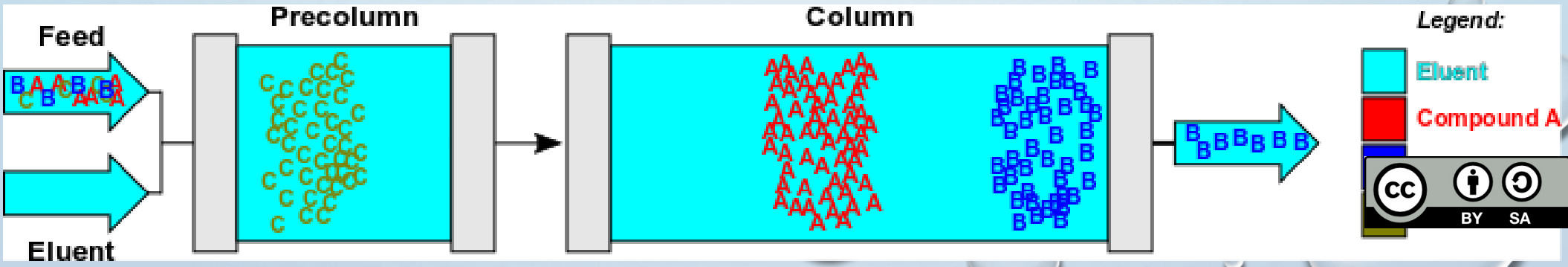
Batch systems = the simplest, also known as first generation systems

Used in preparative chromatography with a sorbent fixed to the column's internal volume.

Components being desorbed from the stationary

ELUTION CHROMATOGRAPHY **-** the feed is periodically injected at the column inlet into the flow of the mobile phase.

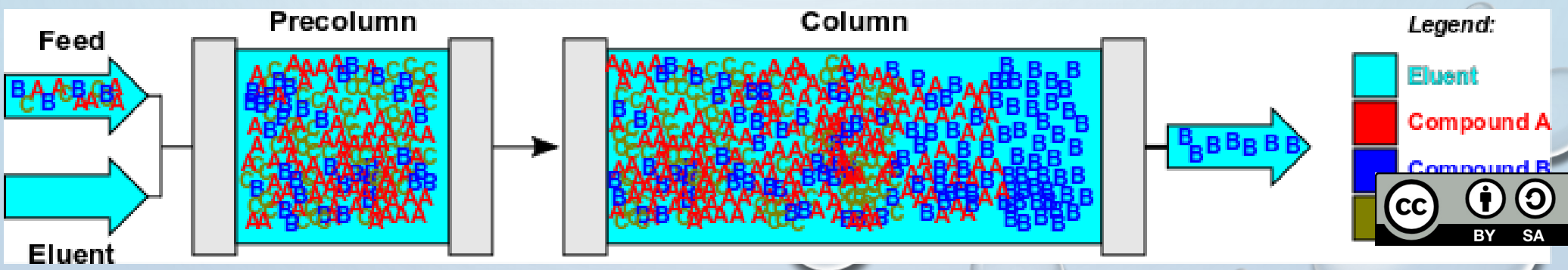
The principle of discontinuous elution chromatography:



DISCONTINUOUS SYSTEMS
FRONTAL CHROMATOGRAPHY

FRONTAL CHROMATOGRAPHY - the feed (sample) is used for the elution as it is continuously applied to the column. The least retained component is then obtained in a pure form until the strongly retained components leave the column too (this is called a **breakthrough** - at this point, the composition of the effluent becomes the same as of the feed).

The principle of discontinuous frontal chromatography:



DISCONTINUOUS SYSTEMS

OPERATION STEPS

1. SERVICE = the solution to be separated is pumped continuously through the resin bed until the resin is nearly exhausted.
2. BACKWASHING = the resin is flushed with a uniform flow of soft water from the bottom of the column bed.
   - to adjust the even distribution of the resin beads within the column (in the previous process, the large particles moved to the bottom of the bed and the smaller ones stayed at the top).
3. REGENERATION = the exhausted resin is treated with a solution to restore its original ion-exchange capacity. Some regeneration processes use a lower concentration of salt every third or fourth cycle to increase its lifetime. The resin is th rinsed with deionised water again.

CONTINUOUS x DISCONTINUOUS SYSTEMS - OVERVIEW

The difference between both systems: the way how the feed is dosed into the system and the product is collected; (i.e. continuity/discontinuity of the feed stream and product withdrawal).

Batch process disadvantages: high eluent consumption, diluted products and low utilisation of the volume of the bed.

➡ lead to the development of a **continuous process.**

First concept - TRUE MOVING BED (TMB)

It assumes a **real counter-current flow of both the sorbent and the liquid**.

- rather against the conventional definition of the stationary phase which should be “stationary” and not moving.
- many technical problems (resin losses and problematic flow inside the column)
- further development of this idea, a theoretical foundation for industrial application of so-called *continuous chromatographic systems*.

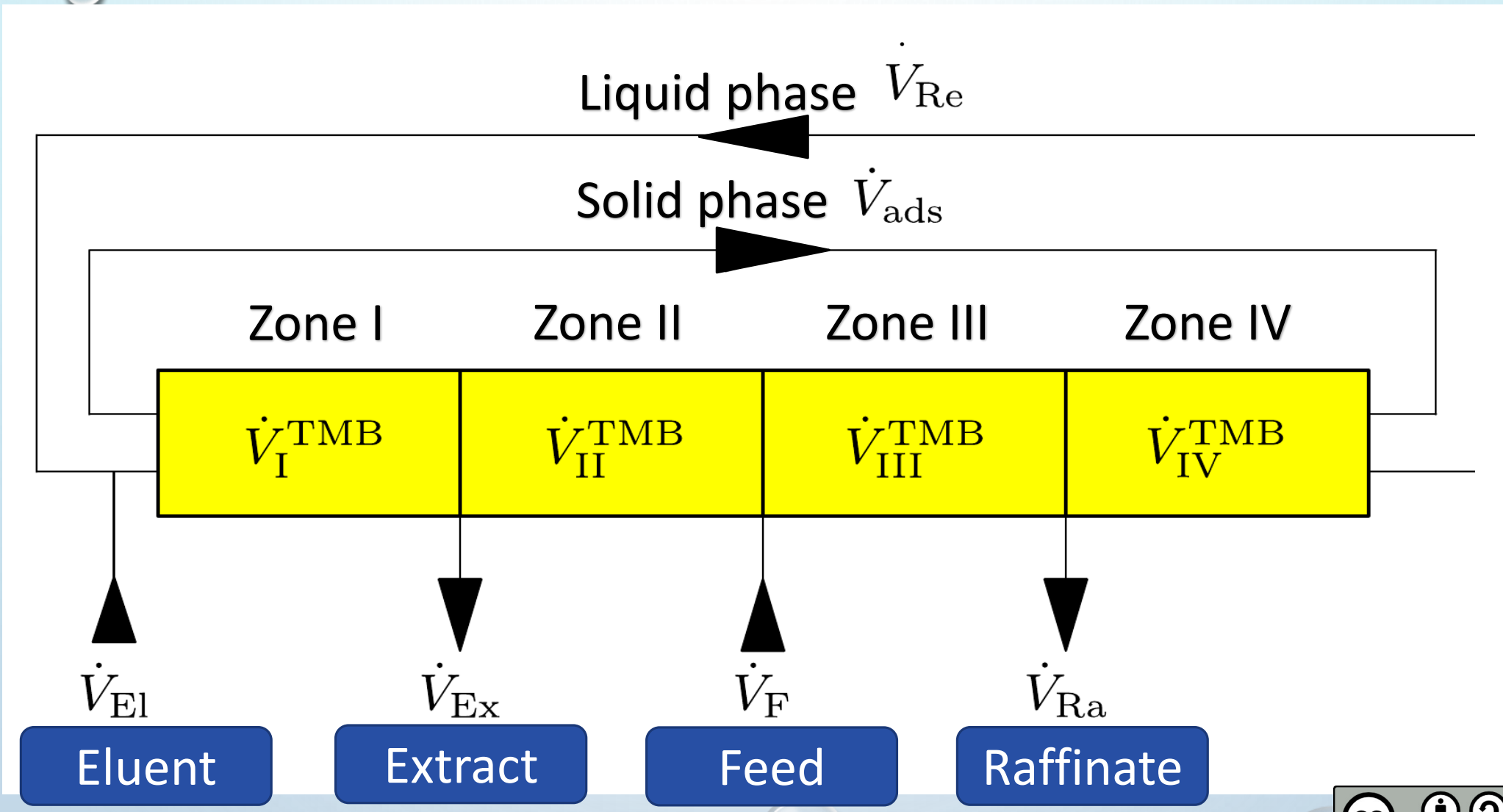
CONTINUOUS SYSTEMS

- Chromatography with column switching
- True moving bed chromatography (TMB)
- Continuous simulated moving bed (SMB) chromatography
- Annular chromatography
- Intermittent simulated moving bed (I-SMB)
- Systems ISEP® and CSEP®
- VariCOL
- ARI system (Amalgamated Research Inc.)
- Finnsugar-Applexion Separation Technology (FAST)

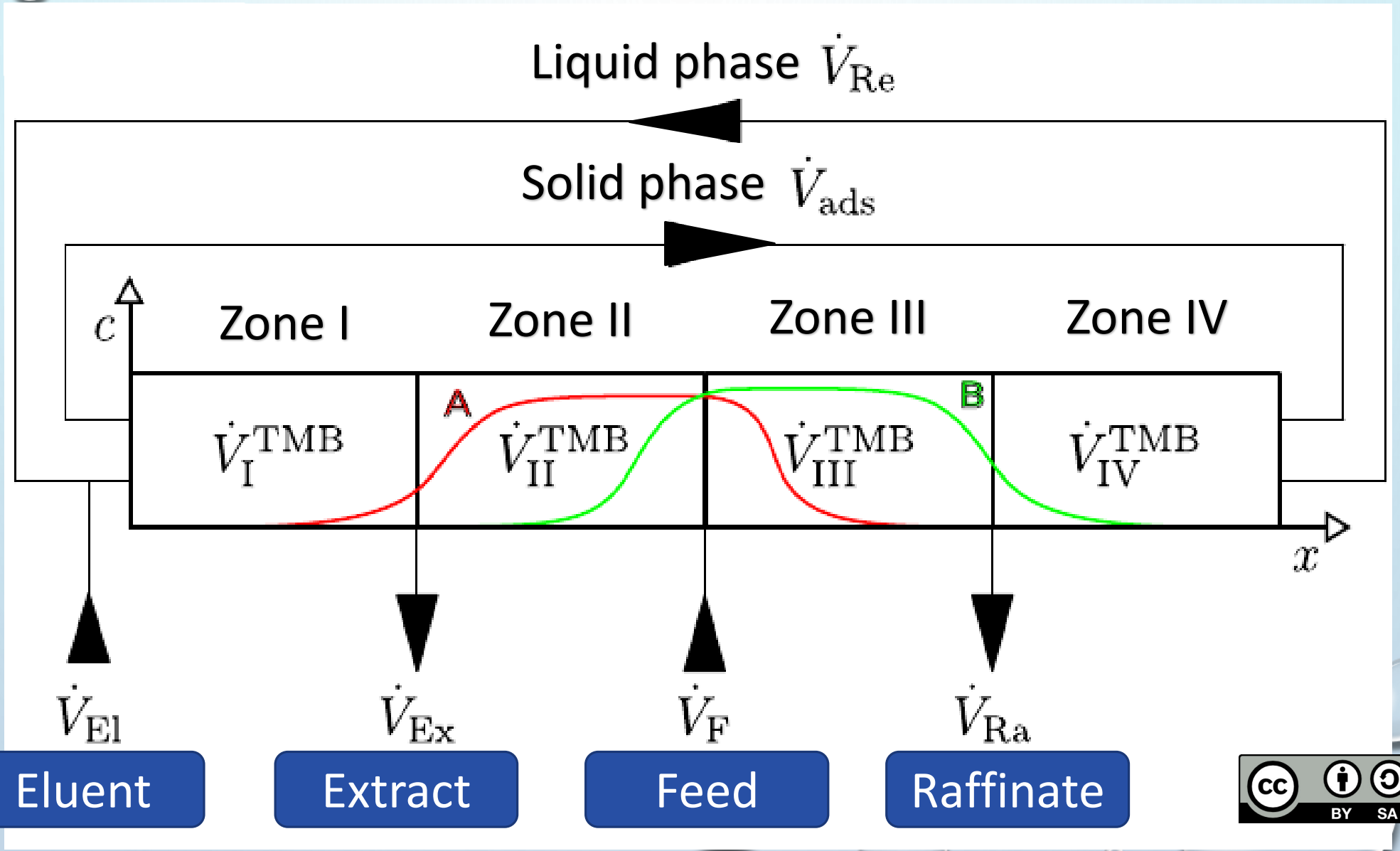
CHROMATOGRAPHY WITH COLUMN SWITCHING

- This arrangement of the chromatographic process uses conventional frontal chromatography and the multi-column system connected in parallel.
- Once a breakthrough is reached at one of the columns, the feed is switched to the next column.
- The previous column can be cleaned with a clean solvent or regenerated.

TMB (TRUE MOVING BED)



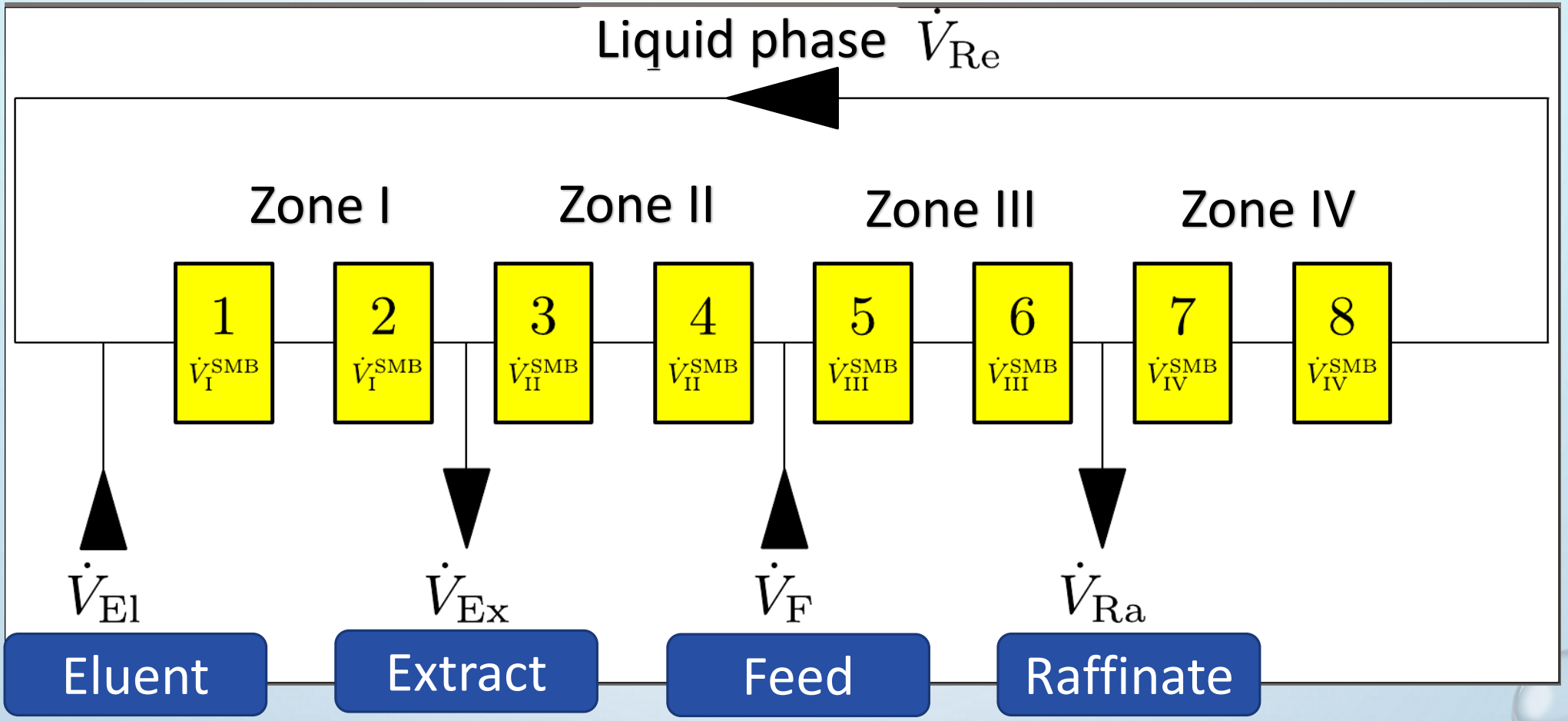
TMB PROFILES



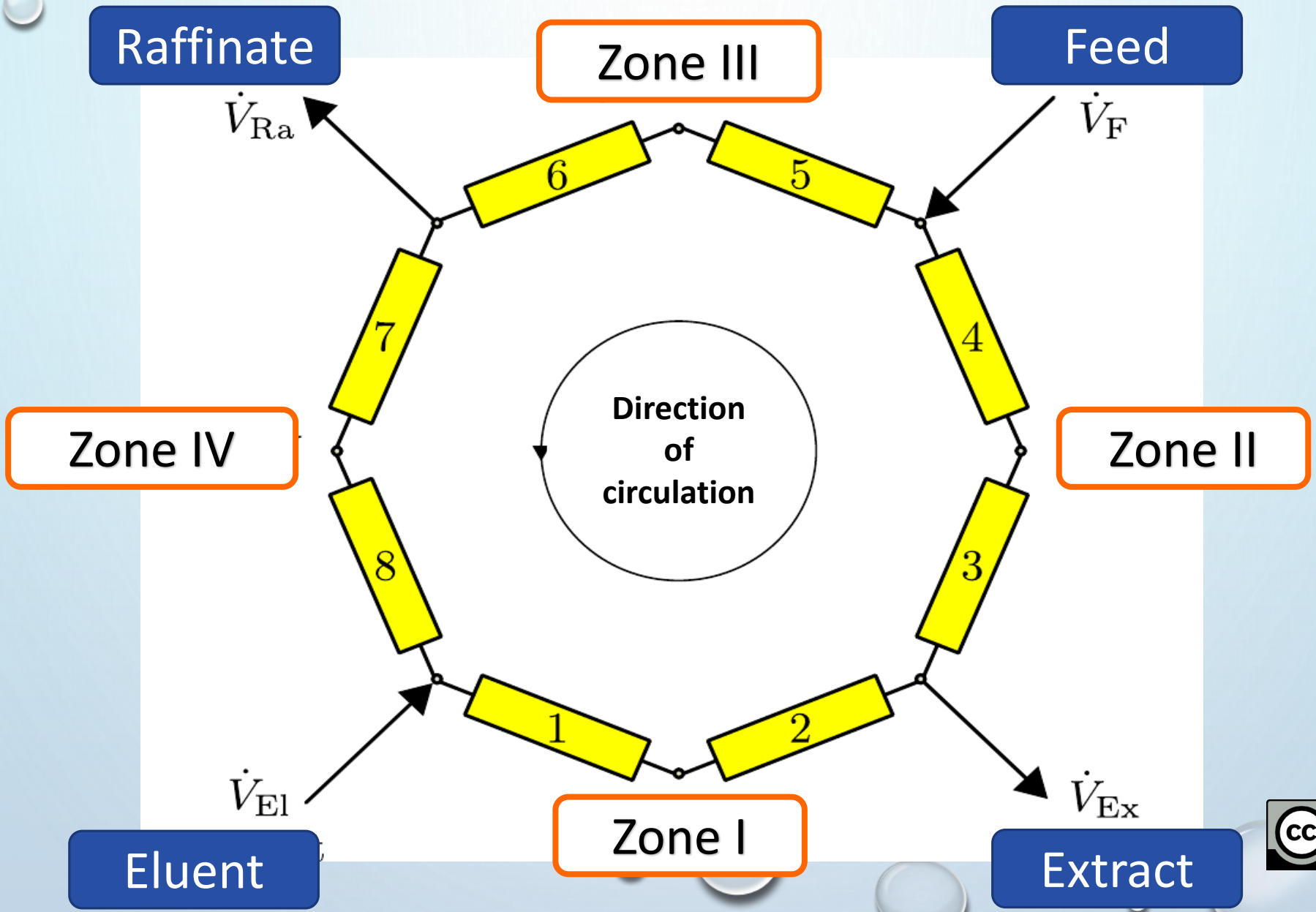
SIMULATED MOVING BED (SMB)

- Developed as an **efficient continuous** separation technique - highly pure products and continuous operation.
- The **counter-current continuous flows** of liquid and matrix are **simulated by changing the position of** inlet and outlet **valves**.
- This happens through a complicated valve-switching system.
- A significant reduction in operating costs - smaller volumes of resins and solvents.
- The chromatographic systems with **all columns serially connected** are generally called simulated moving bed systems.

SIMULATED MOVING BED (SMB)

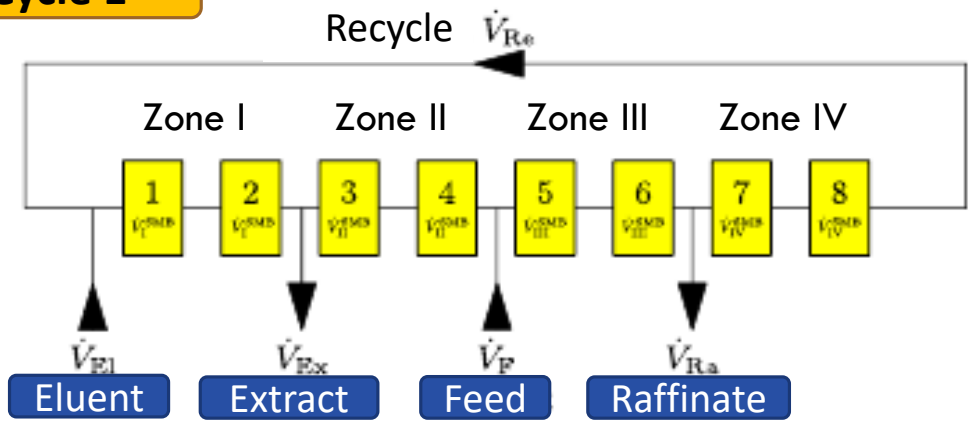


SMB – COLUMN RING FORMATION

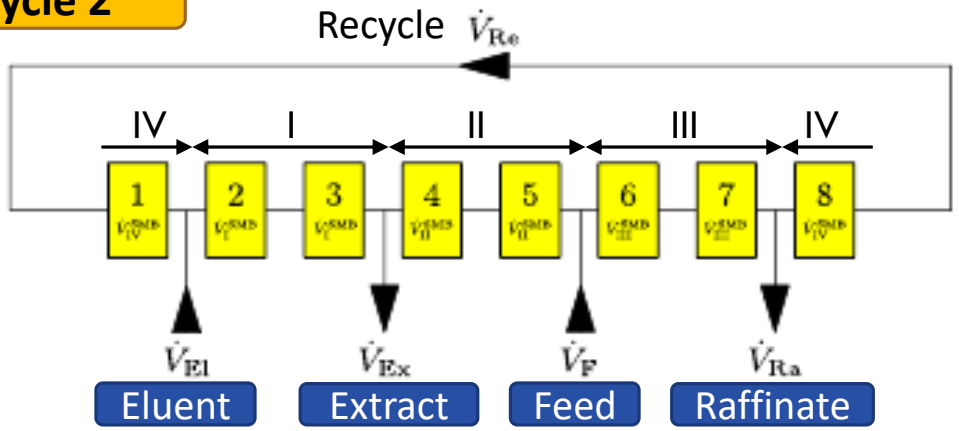


SMB CYCLES

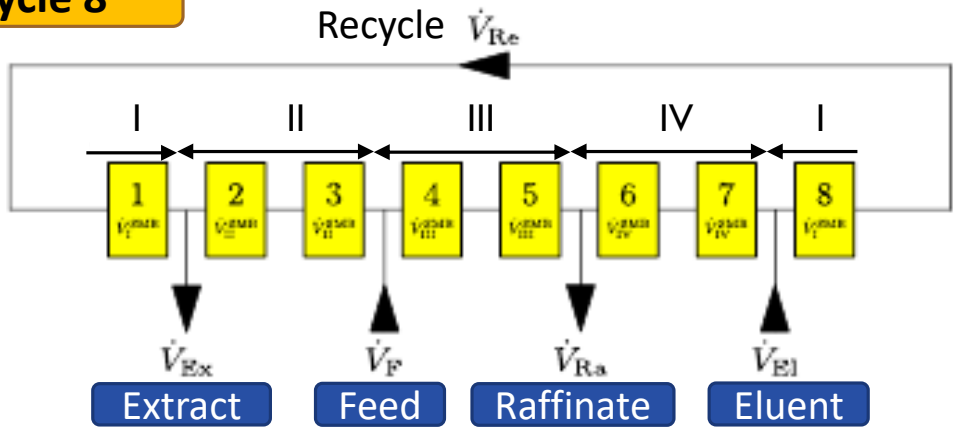
a) Cycle 1



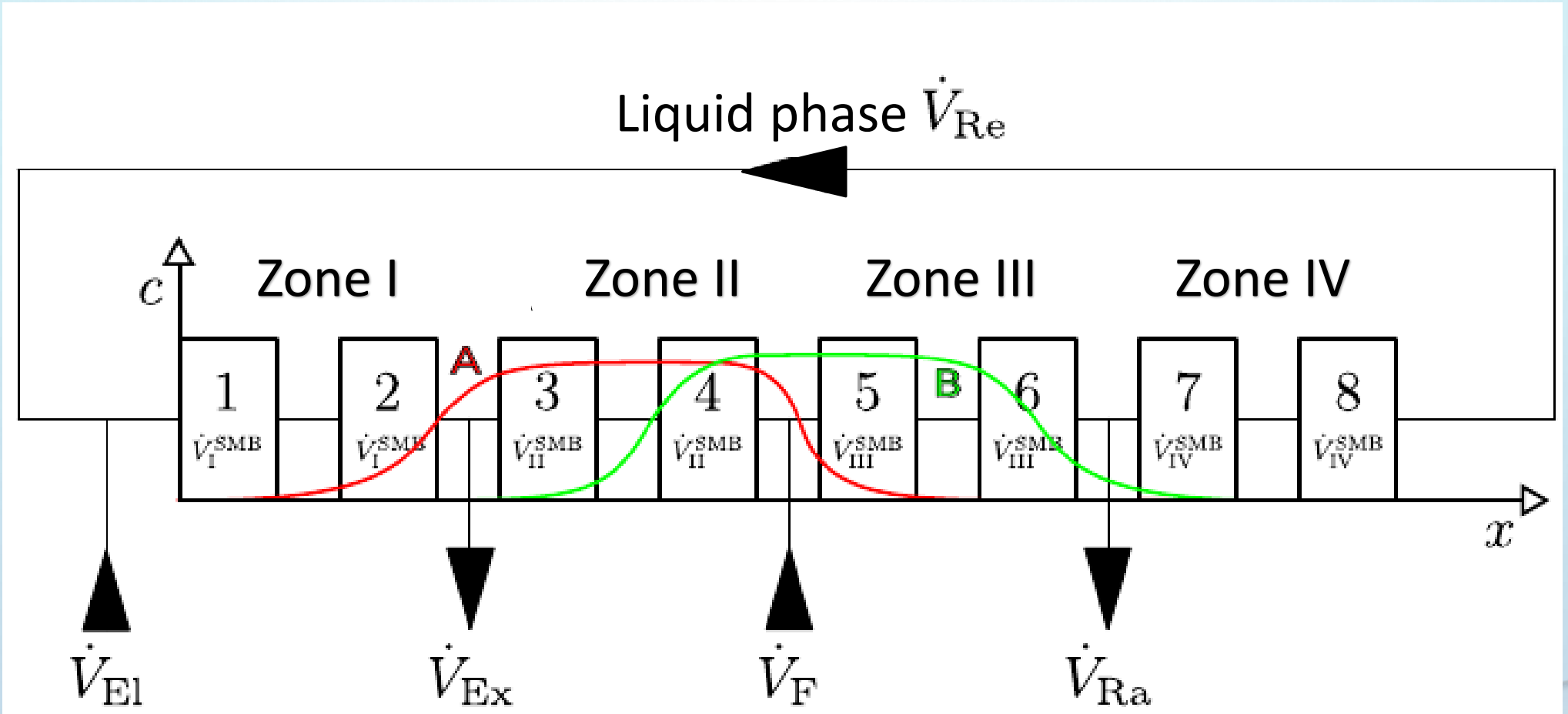
b) Cycle 2



c) Cycle 8



SMB PROFILES



Eluent

Extract

Feed

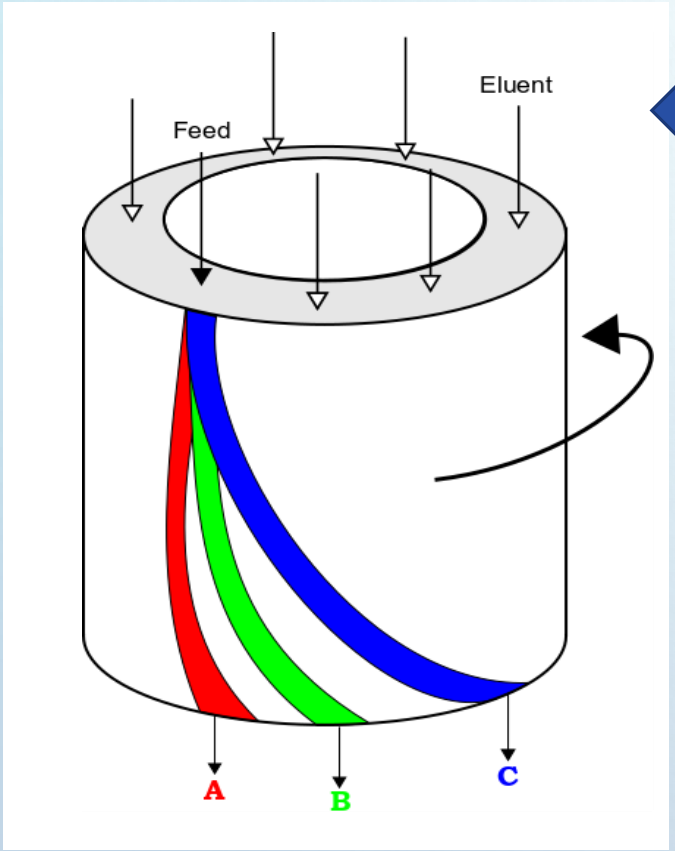
Raffinate

ANNULAR CHROMATOGRAPHY

CONTINUOUS ANNULAR CHROMATOGRAPHY (CAC)

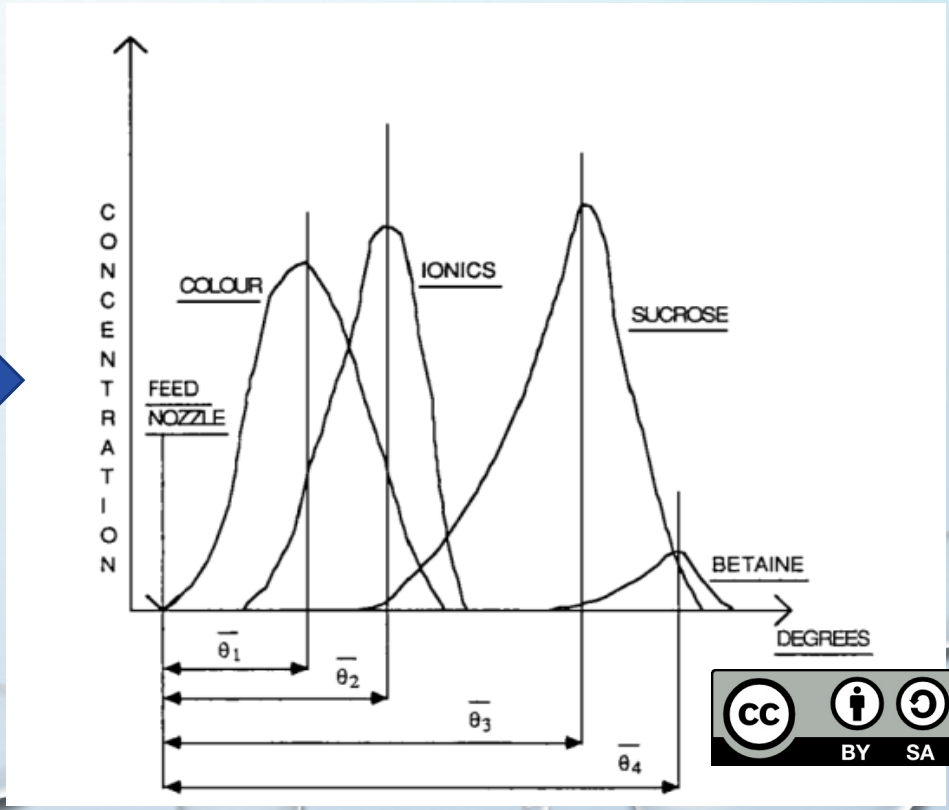
A series of individual columns that slowly rotate past the injection point, the feed is continuously dosed, whilst all columns are continuously flushed with the eluent.

The separation starts along the column axis and the column moves which causes the cross-current flow of the stationary and solid phases.



System set-up

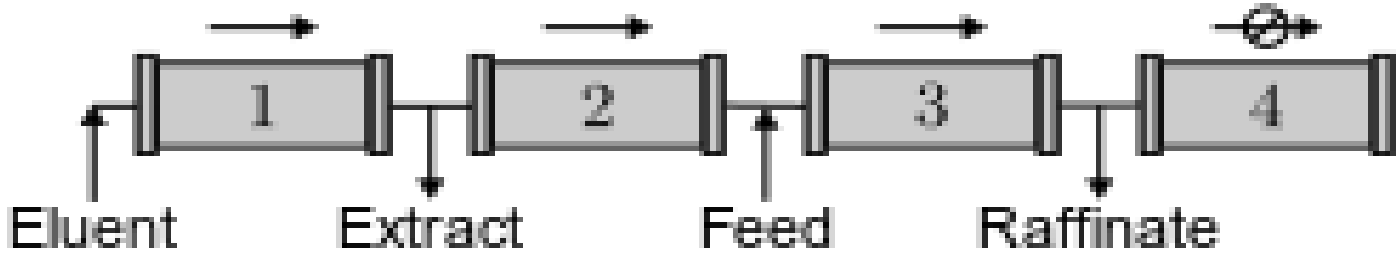
Separation of different fractions from molasses



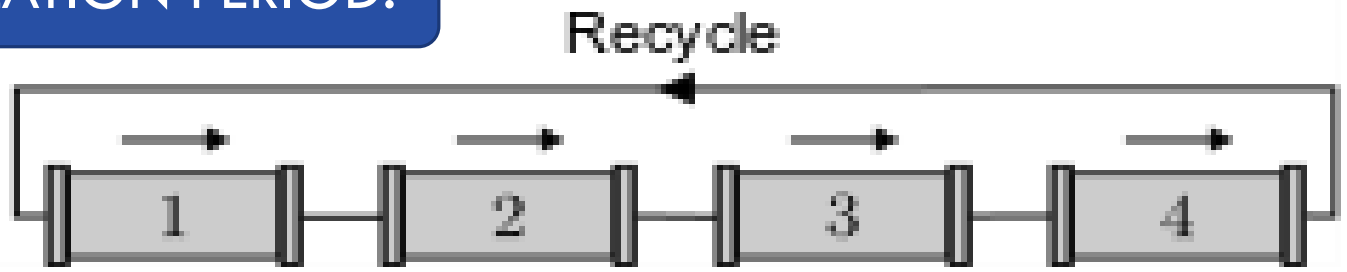
INTERMITTENT SIMULATED MOVING BED (I-SMB)

A modification of a SMB process (higher productivity than conventional SMB).
Invented by Nippon Rensui Corporation and named **Improved SMB**.
Applied in the sugar industry where it is called **intermittent SMB (I-SMB)**.

INJECTION PERIOD:



RECIRCULATION PERIOD:

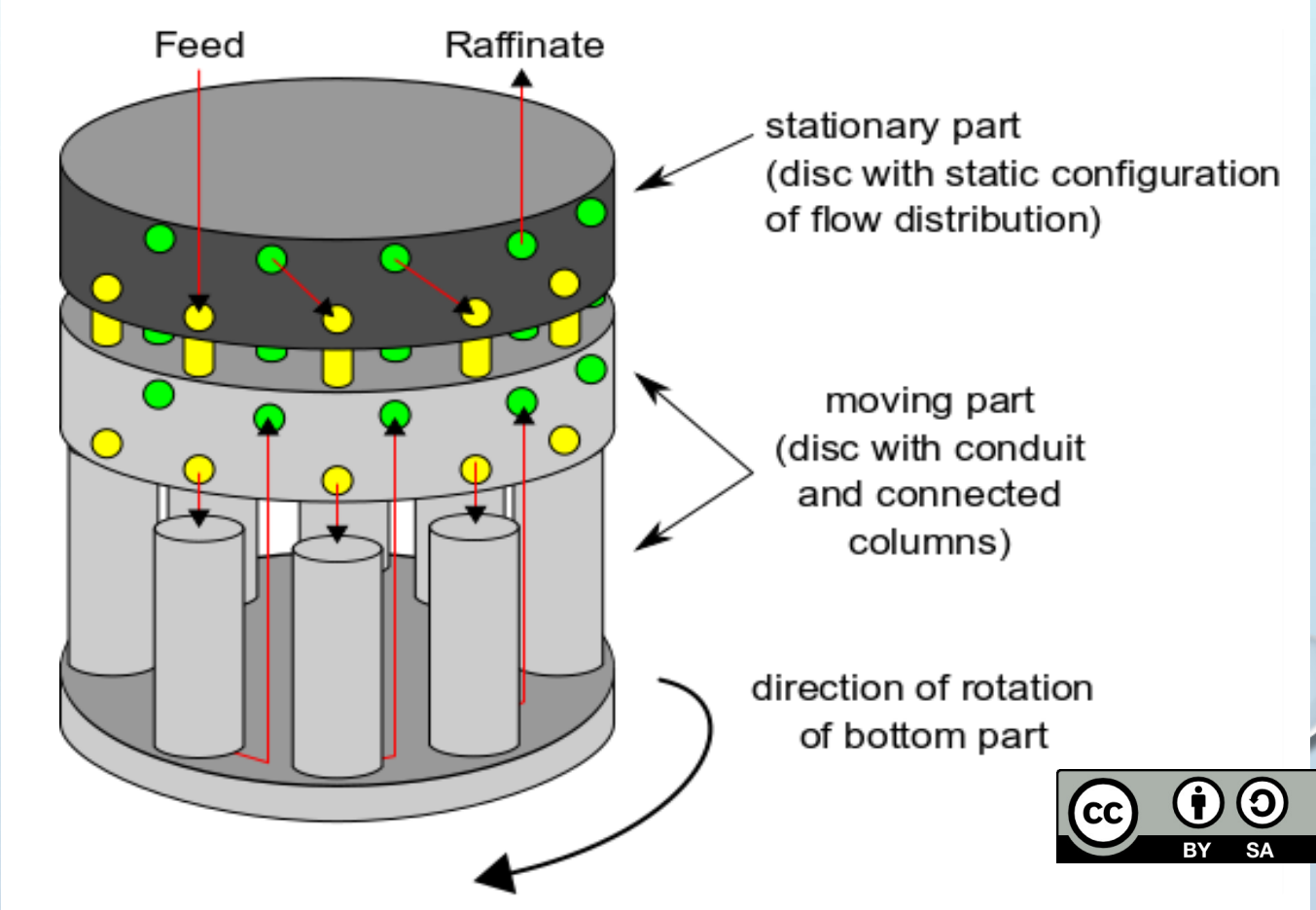


SYSTEM ISEP®

Commercial system **based on annular chromatography** - the annular column is discretized because it has the final number of vertically positioned columns.

Splitting of flows into individual columns is ensured by a multi-way rotary valve, which consists of immovable and movable parts. The input and output current distributor are located on the stator and the columns are located on the rotor.

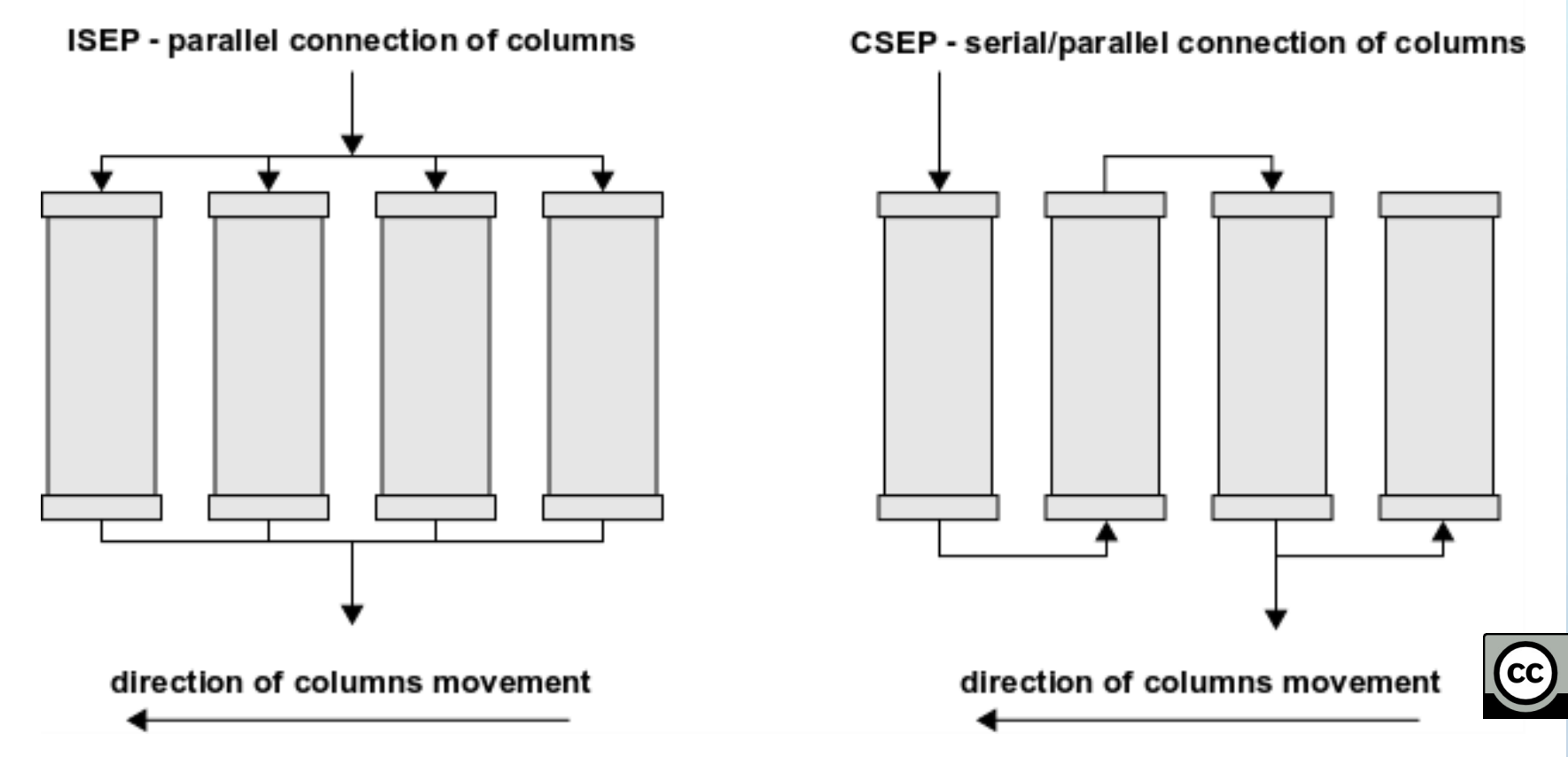
The IonSeparator (ISEP)
= all columns are connected **in parallel**
= identical to the annular chromatograph.



SYSTEM CSEP®

Another commercial system - using the concept of annular chromatography.

The **chromatographic separator (CSEP)** enables both serial and parallel connections of columns via a number of input and output connections, i.e. it can be operated even in the ISEP mode!



VARICOL

TRADITIONAL SMB SYSTEMS (e.g. SMB):

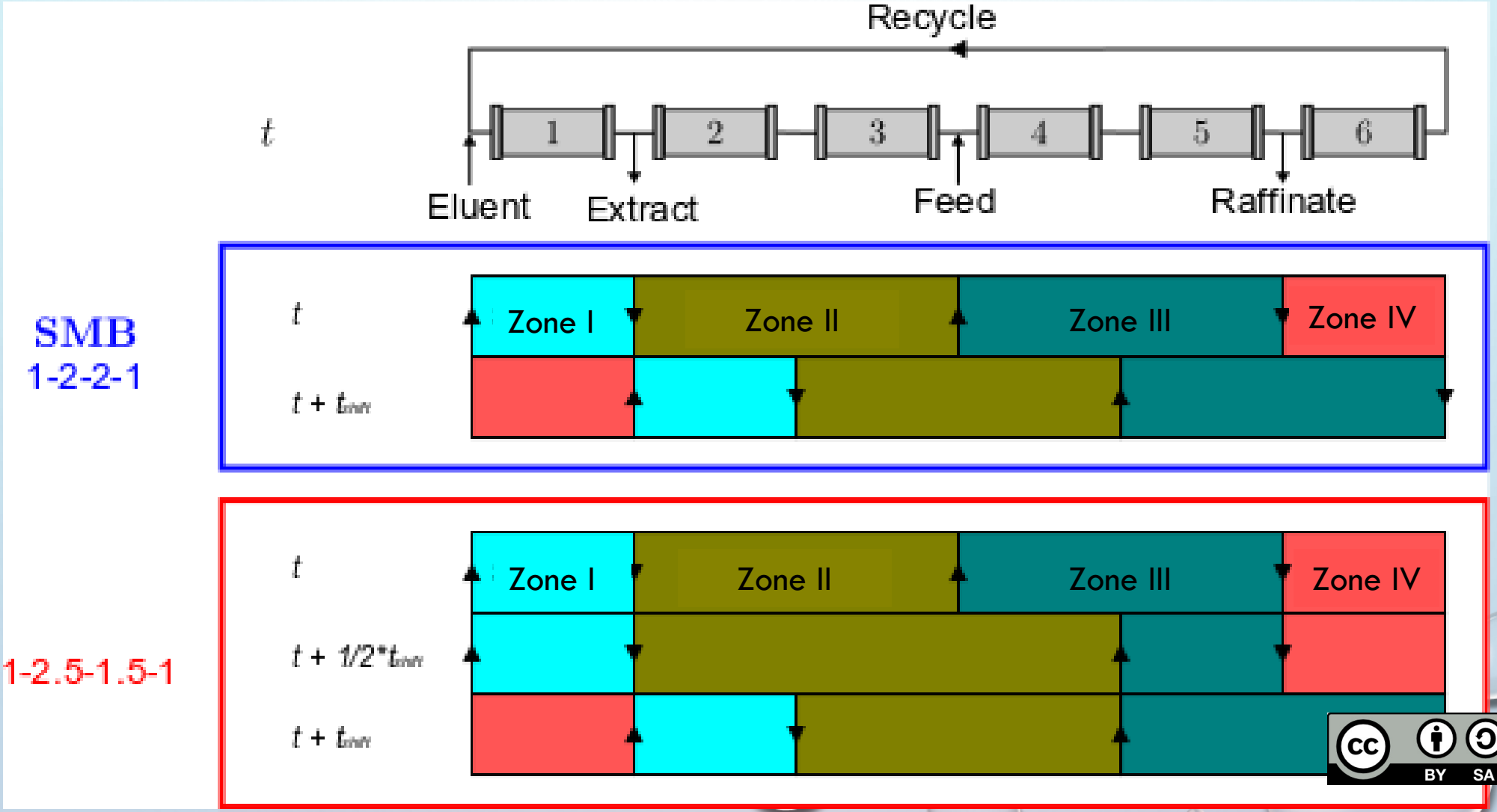
- **Synchronous shift** of inputs and outputs after a constant period (shift period, shift time)
  = SMB has a zone configuration of 1-2-2-1.
- At the end of the period the system always comes to the same state as at the beginning of the period.
- The length of the zone is at least equal to the length of a column.

THE VARICOL PROCESS:

- **Asynchronous shifts** of individual inputs and outputs during one period:
  → The average configuration over one cycle may include non-numeric values.
  → During the cycle, the VariCOL system can have a zone l[illegible] of less than one or even zero.

VARICOL x SMB

Possible zone configuration a) in the SMB system and b) in the VariCOL System.



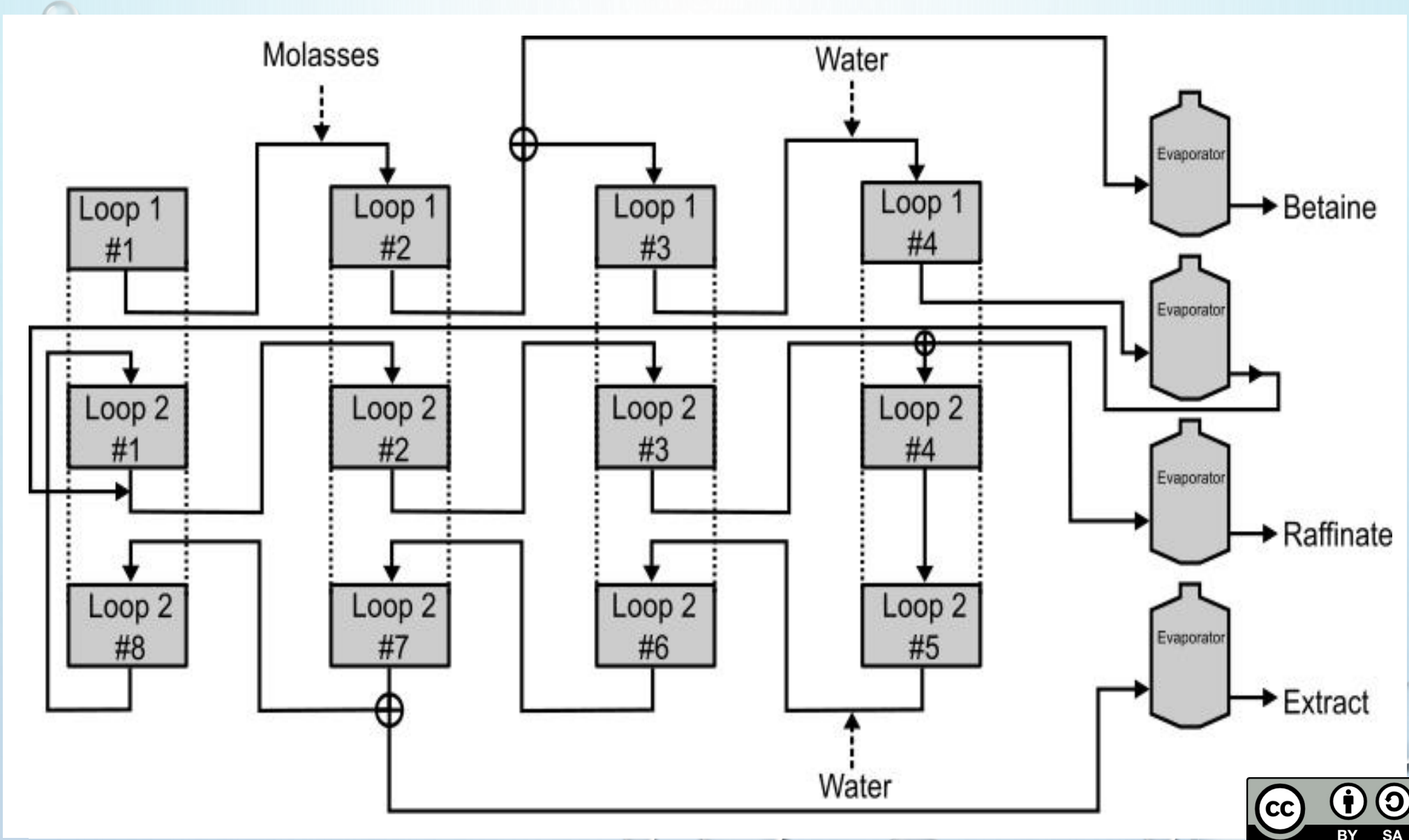
ARI SYSTEM (AMALGAMATED RESEARCH INC.)

Combines ion-exchange with other processes (membranes).
Conventional SMB system - sucrose behaves as a slower acting component (unlike salts and high molecular weight components).
Invert sugar and low molecular mass components move close to sucrose – they are difficult to separate from the sucrose.

ARI SYSTEM:

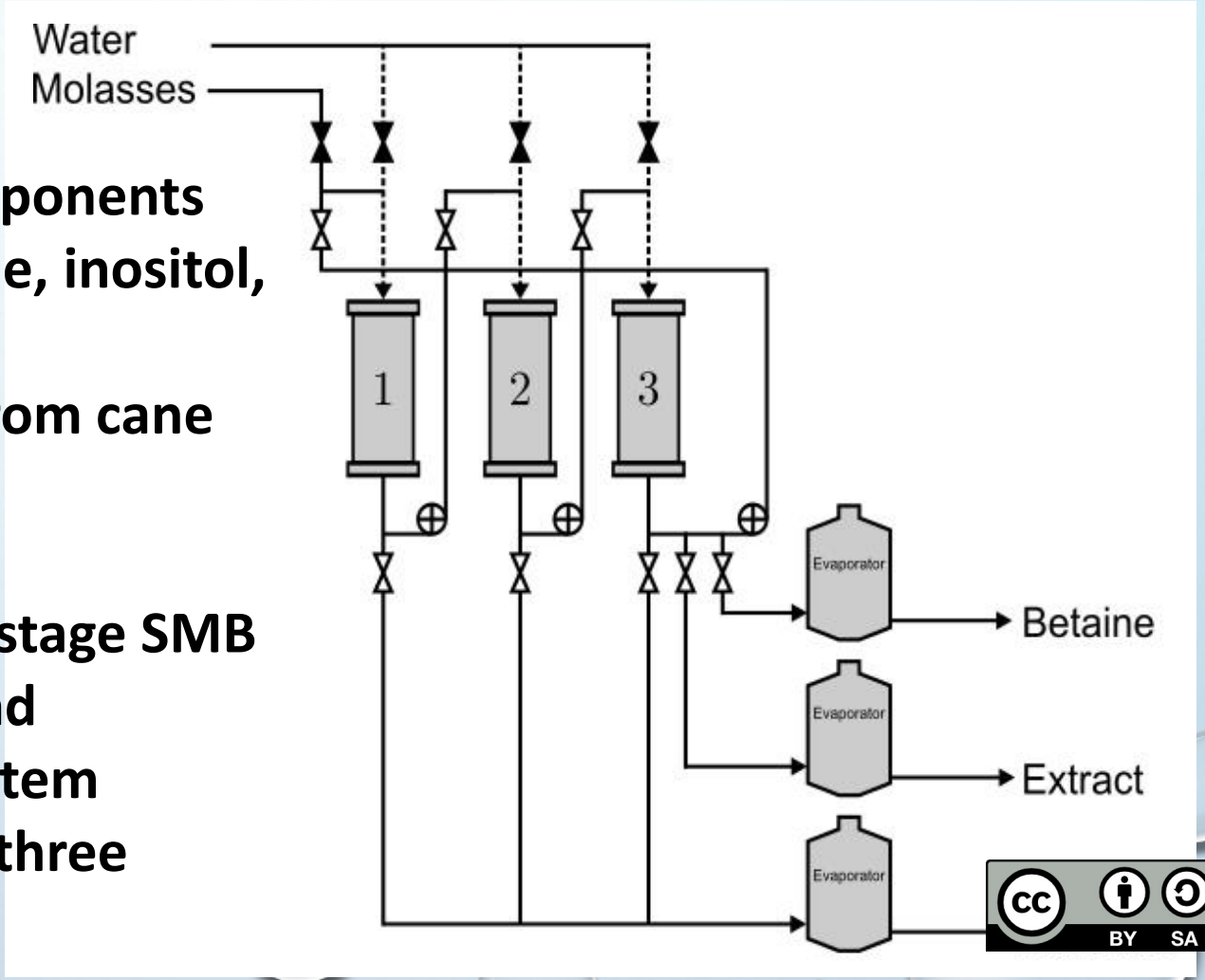
- Loop 1 forces sucrose to behave as an excluded component
  i.e. it moves with the salt fraction.
- Loop 2 works independently from the loop 1.
- The output from the loop 1 (upgrade) enters the loop 2.
- In the loop 2, the sucrose separates from the salts and low molecular mass components.

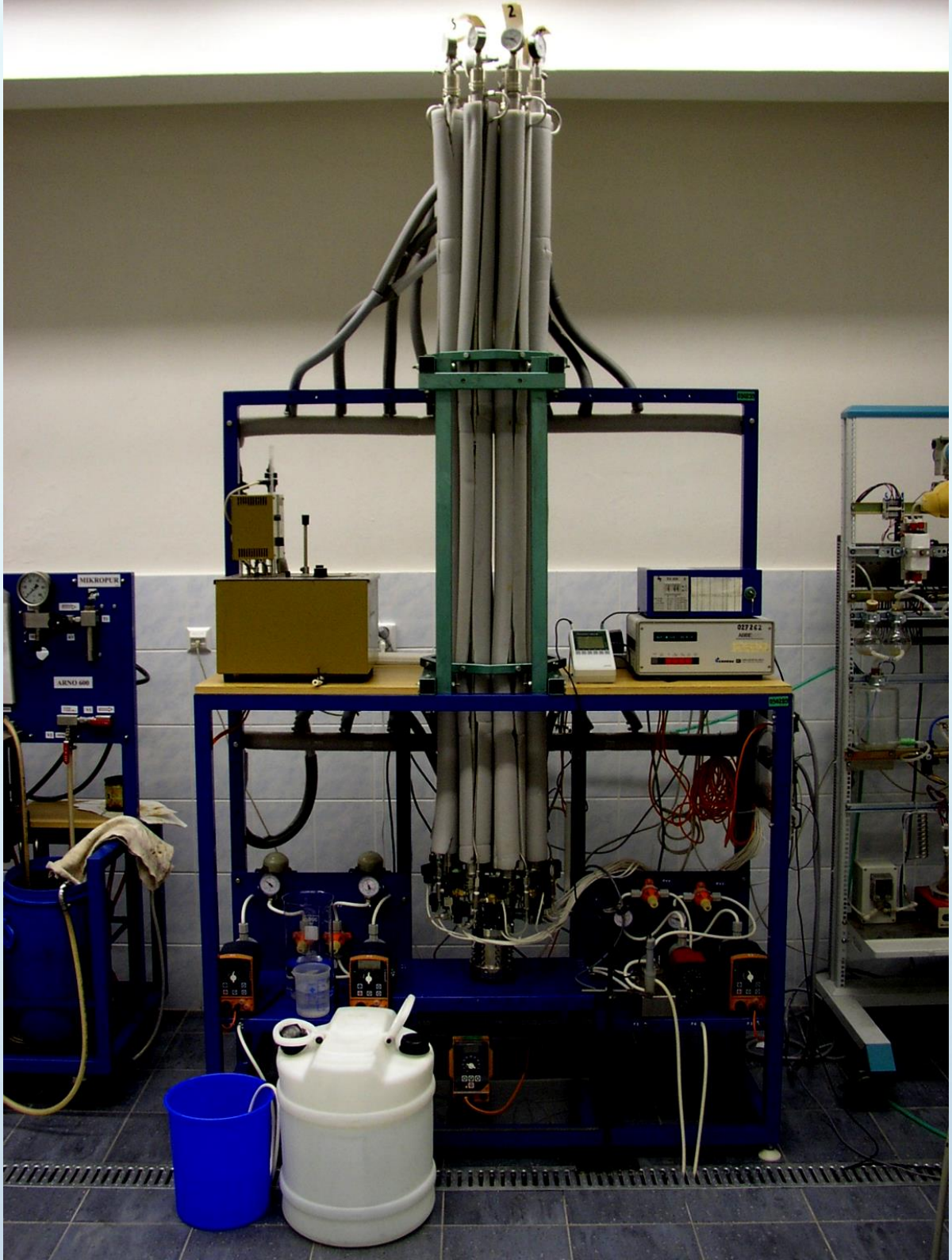
ARI SYSTEM



FAST SYSTEM (FINNSUGAR APPLEXION SEPARATION TECHNOLOGY)

- Separation of multiple components from beet molasses (betaine, inositol, amino acids and sugar);
- Recovery of invert sugars from cane molasses;
- Connects several different technologies, such as multistage SMB process, sequential SMB and sequential multi-profile system
- A single system containing three columns.





www.organo.co.jp

Průměr kolony 3,2 m, výška 15 m

APPLICATIONS

FOOD INDUSTRY, BIOTECHNOLOGIES, PHARMACEUTICALS

- Glucose and fructose separation
- Sugar purification - high purities (xylose, arabinose, trehalose)
- Separation of glucose and xylose from hydrolysed biomass
- Dextran separation
- Beet molasses fractionation to obtain sucrose, glucose and invert
- High purity maltitol
- Separation of vitamin E (α, β, χ, δ tocopherols)
- Protein (enzyme) purification
- Desalination and purification of amino acids (a mixture PRO – LYS, PHE)
- Inositol production
- Separation of lactic and citric acids from fermentation broth
- Separation of saturated fatty acids from unsaturated
- Separation of mono- and triglycerides
- Separation of alpha-pinene from beta-pinene
- Cyclosporin production (high purity)

OTHER APPLICATIONS

SEPARATION OF OPTICAL ISOMERS

- Separation of chiral epoxides
- Isolation of pure enantiomers from racemic mixtures

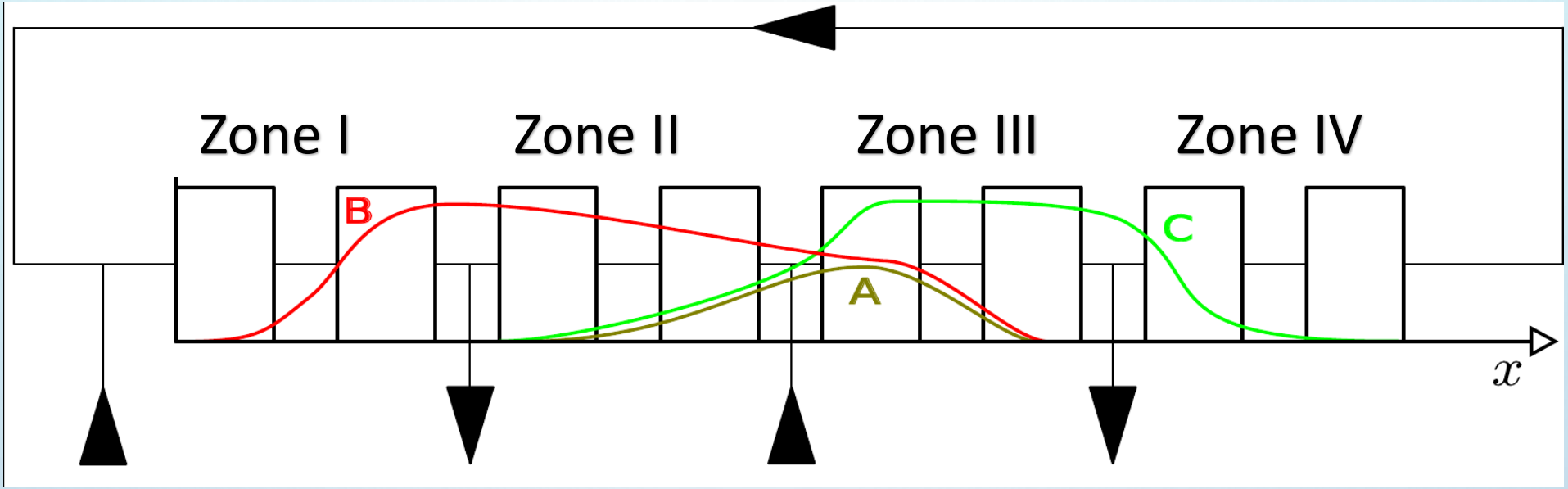
CHEMICAL INDUSTRY

- Separation of olefin and paraffin
- Methanol purification
- Glycerine desalination
- Separation of ethanol from aqueous solutions
- Separation of ethylbenzene
- Separation of toluene and isopropylbenzene (cumene) from mixtures

SMB REACTOR

$$A \leftrightarrows B + C$$

Liquid phase



Eluent | Extract | Feed | Raffinate

Supercritical fluid extraction (SFE)

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Information sources

Databases: ScienceDirect, Scopus, Web of Science

http://sch.vscht.cz/vyuka/international-students/erasmus-students/

McHugh M., Krukonis V. (1994): Supercritical Fluid Extraction, In: Brenner H. (Ed.), Butterworth-Heinemann, Massachusetts

Supercritical fluid extraction (SFE)

Supercritical fluid extraction

(**SFE**, **S**upercritical **F**luid **E**xtraction)

=

extraction using the fluid in supercritical state as an extraction agent; so-called **supercritical fluid** (**SCF**, **S**upercritical **F**luid)

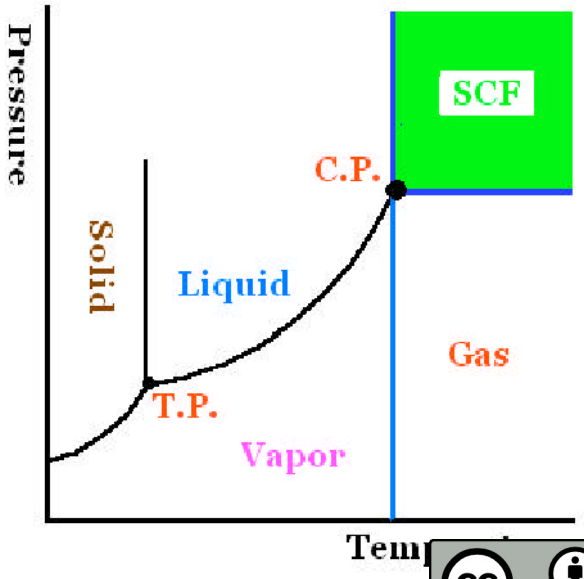
Supercritical fluid extraction (SFE)

Supercritical Fluid (SCF)

=

fluid, which is in the state above its critical point (CP), i.e. above its critical temperature (T_c) and critical pressure (p_c)

- it can be produced by warming a gas or liquid to the temperature higher than its critical temperature T_c by simultaneous compression to the value higher than its critical pressure p_c
- above the critical temperature and pressure - the material is in one condensed state with properties between gas and liquid
- it is used in extraction and also in chromatography as a mobile phase – Supercritical Fluid Chromatography (SFC)



Supercritical fluid extraction (SFE)

Critical values of some substances

Substance	*Critical molecular weight ($g.mol^{-1}$)*	*Critical temperature(K)*	*Critical pressure MPa (atm)*	*Critical density ($g.cm^{-3}$)*
Carbon dioxide (CO2)	44.01	304.1	7.38 (72.8)	0.469
Water (H2O)	18.02	647.3	22.12 (218.3)	0.348
Methane (CH4)	16.04	190.4	4.60 (45.4)	0.162
Ethane (C2H6)	30.07	305.3	4.87 (48.1)	0.203
Propane (C3H8)	44.09	369.8	4.25 (41.9)	0.217
Ethylene (C2H4)	28.05	282.4	5.04 (49.7)	0.215
Propylene (C3H6)	42.08	364.9	4.60 (45.4)	0.232
Methanol	32.04	512.6	8.09 (79.8)	0.272
Ethanol (C2H5OH)	46.07	513.9	6.14 (60.6)	0.276
Acetone (C3H6O)	58.08	508.1	4.70 (46.4)	0.278

Supercritical fluid extraction (SFE)

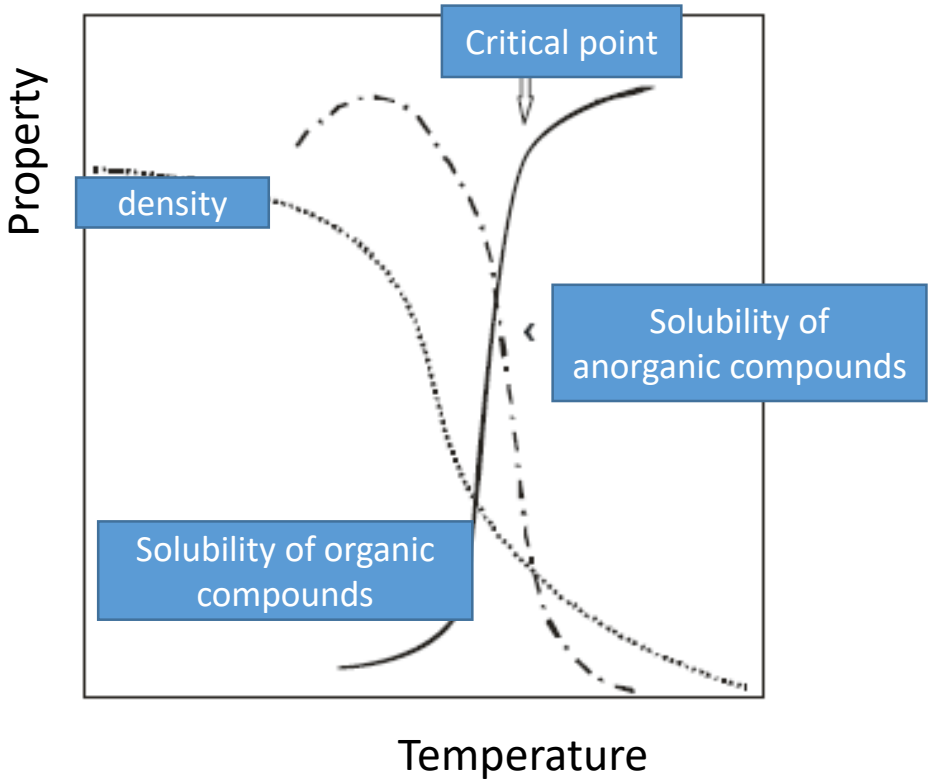
Supercritical fluids – some properties like gases, others like liquids

- are **compressible**, its possible to change their density. The density of SCF is close to density of liquids; the dissolving capability depends on density ⇒ **it is possible to change dissolving propertieby by changes in density**
- **viscosity of SCF** is more than 10 times lower than viscosity of liquids; it can be achieved by fast mass transfer due to the favourable flow characteristic
- **high diffusivity and absence of surface tension** causes easy penetration of SCF into the pores of solid phase, thereby efficent extraction in SFE or fast analysis in SFC

	Density (g ml^{-1})	*Viscosity (Pa s)*	*Diffusivity (cm^2 s^{-1})*
Gas	10^{-3}	$(0{,}5 – 3{,}5).10^{-5}$	0,01 – 1,0
Supercritical Fluid	0,2 – 0,9	$(0{,}2 – 1{,}0).10^{-4}$	$(3{,}3 – 0{,}1).10^{-4}$
Liquid	0,8 – 1,0	$(0{,}3 – 2{,}4).10^{-3}$	(0,5 – 2,0

Supercritical fluid extraction (SFE)

- Important property is the solubility of material in supercritical liquids
- Solubility of material increases with increasing density (T=constant)
- Near the critical point, the density can steeply decrease with minimum of temperature increasing
- Solubility near the critical point often decreases with increasing temperature and then increases again



Schematic chart of substance behaviour near the critical point for selected properties

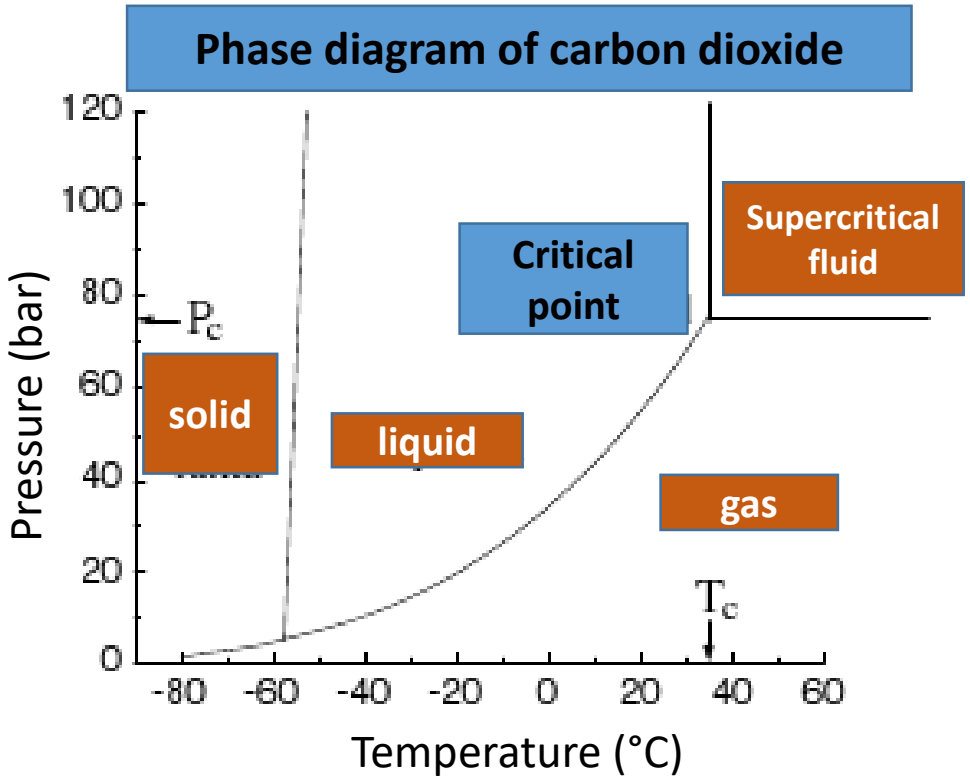
Supercritical fluid extraction (SFE)

Supercritical carbon dioxide

Critical temperature T_c = 35 °C, critical pressure p_c = 75 bar

40 °C:
72 bar → 0.22 g ml^{-1}
400 bar → 0.96 g ml^{-1}

80 °C:
72 bar → 0.14 g ml^{-1}
400 bar → 0.82 g ml^{-1}



Note: The triple point of CO_2 lies at the pressure of 5.2 atm and the temperature of -57 °C.

At the pressure of 1 atm, CO_2 passes straight from solid to liquid pha (sublimes), at atmospheric pressure the CO_2 does not exist in liquid phase

Supercritical fluid extraction (SFE)

- **Advantages of CO_2**
  - **T_c and p_c are relatively low and instrumentally achievable**
  - **nontoxic**
  - **nonflammable**
  - **easy to clean**
  - **compatible with detectors (UV, IR , FID)**

- **Disadvantages CO_2**
  - **nonpolar**
  - **for polar substances: necessary to use modifiers (most often methanol, acetonitrile, water, THF in concentrations of 1 - 20 %, similar to HPLC)**

Supercritical fluid extraction (SFE)

➢ Carbon dioxide in SFE

– Food Industry

- Essential lipids extraction, removing of lipids from nuts, removing of lipids from potato chips – using the carbon dioxide as SCF - the fat content is reduced to the half without loosing taste
- Extraction of hops

- Extraction of caffeine

- Extraction of pesticides and insecticides

Note: Supercritical Fluid Chromatography (SFC) – high cost – only pharmaceuticals, dry cleaning, bio-diesel production, nano- and micro-production, impregnation and dyes

Supercritical fluid extraction (SFE)

➢ Supercritical water

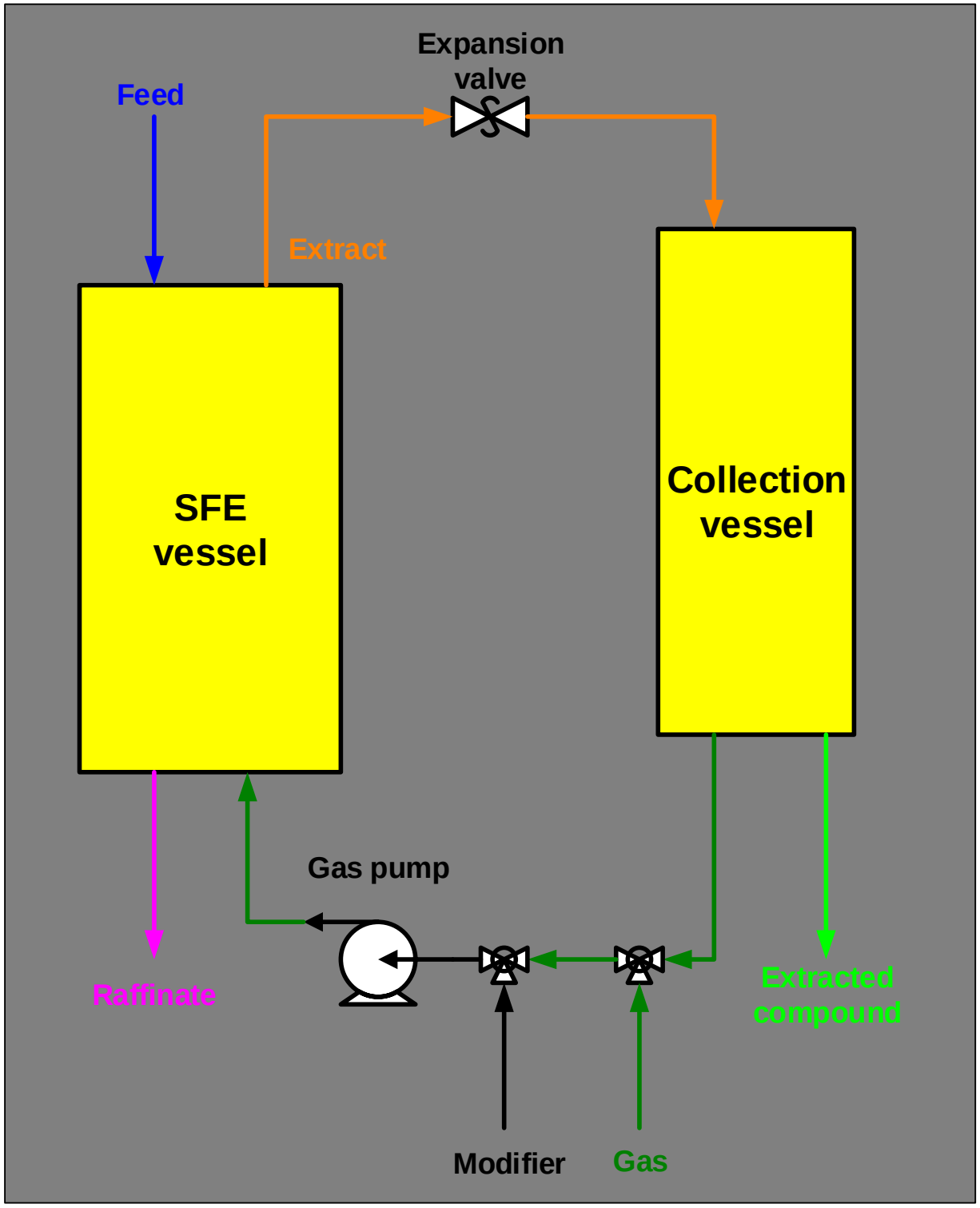
– Conditions for supercritical water are significantly harder:

H_2O : 647.3 K at 22.12 MPa (CO_2 : 304.1 K at 7.38 MPa)

– **Synthesis of inorganic substances** – biggest commercial success in synthesis of silicon crystals for mobile phones

– At supercritical conditions, water is very corrosive for all kinds of steel, a lot of organic substances are not stable in supercritical water, this state can be used by waste disposal – the process is called **supercritical water oxidation** (SWO)

– Above 200 ˚C, the water earns the properties of organic solvents, at about 300 ˚C, it has properties similar to acetone, **substitution of organic solvents by supercritical water** should be environment friendly.

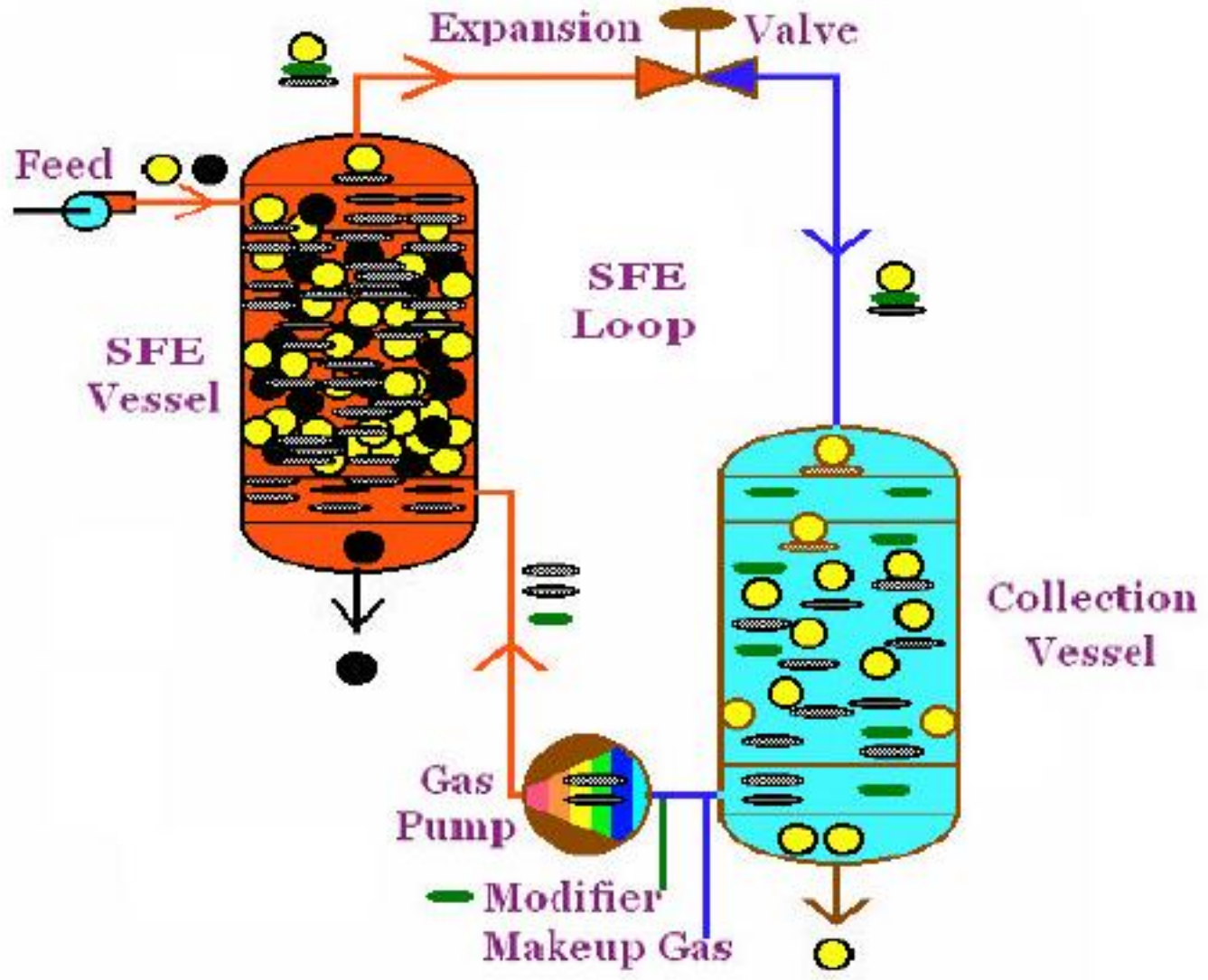


Supercritical fluid extraction (SFE)

Instrumentation

Supercritical fluid extraction (SFE)

Instrumentation



Supercritical fluid extraction (SFE)

Extraction of plant oil, South Korea, 2 x 3800 liters, 550 bars

Supercritical fluid extraction (SFE)

Rice Processing, Taiwan, 3 x 5800 liters, 325 bars

Supercritical fluid extraction (SFE)

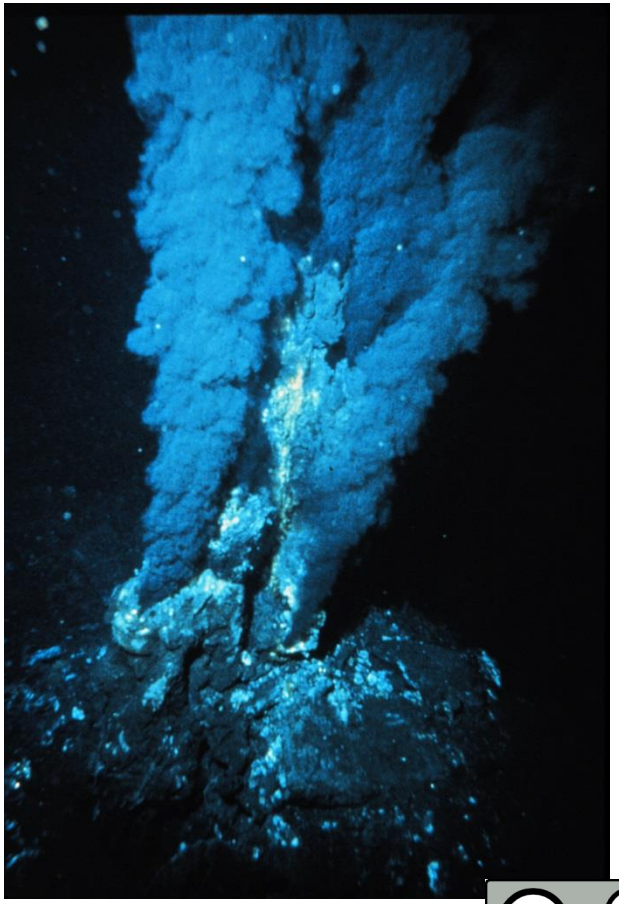
Supercritical CO_2

Very well soluble	**Well soluble**	**Very poorly soluble**
Fragrances	Plant Oils	Sugars
Esencial Oils	Pigments	Starches
Esters, alcohols	Polyphenols	Proteins
Aldehydes, ketons	Waxes	Mineral salts

Supercritical fluid extraction (SFE)

Supercritical fluids in nature

- Sea volcano is a common element of the sea ground, its presence is sometimes expressing by explosion of steam and erosion of reef.
- Some of them are situated in depth (greater then 3 km); big pressure (over than 30 MPa) gained from the weight of water is avoiding the explosion of steam and gases, which are warming the water to more more than 648 K, i.e. the water is in supercritical state.



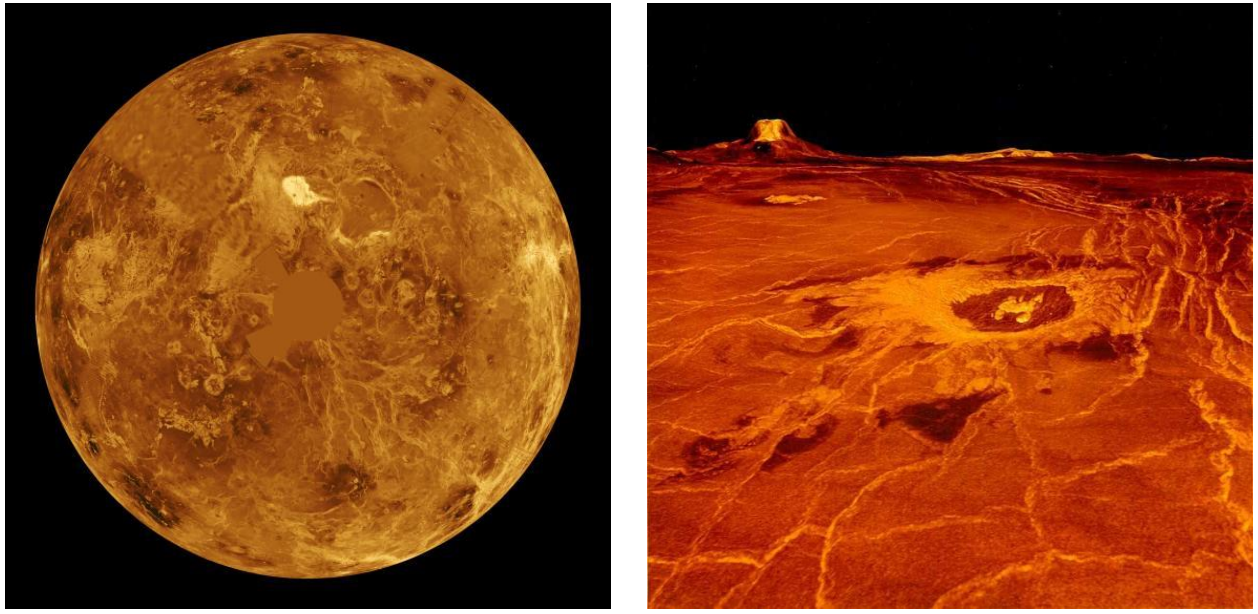
Deep sea volcan

Supercritical fluid extraction (SFE)

Supercritical fluids in nature

Atmosphere of Venus consists of 96.5 % CO_2 and 3.5 % N_2;

The average temperature and pressure on Venus are 735 K and 9.3 MPa, causing the carbon dioxide to be in a supercritical state.



Venus

Heat processes I

- **Steam diagram**
- **Heat exchanger calculation**

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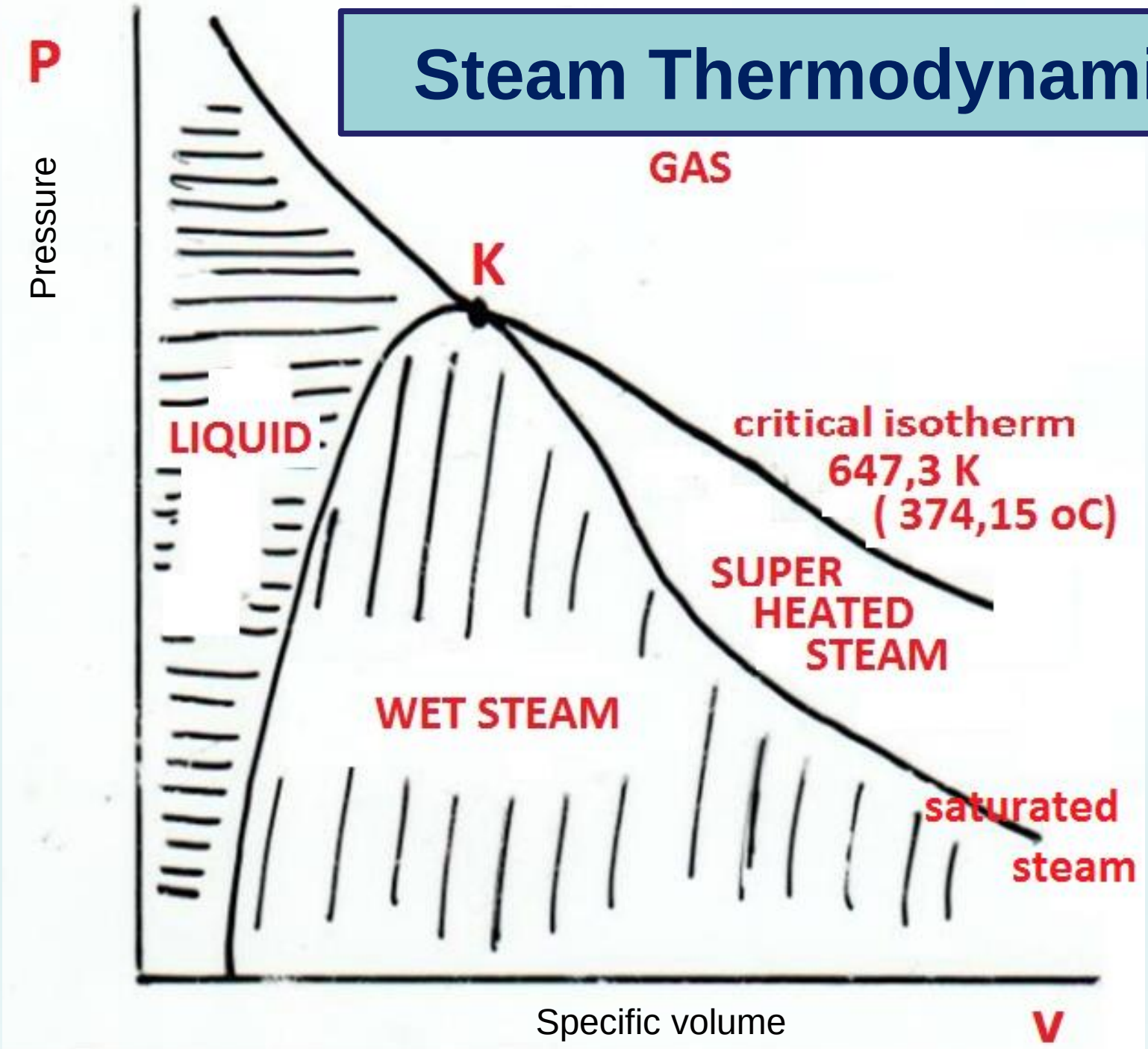
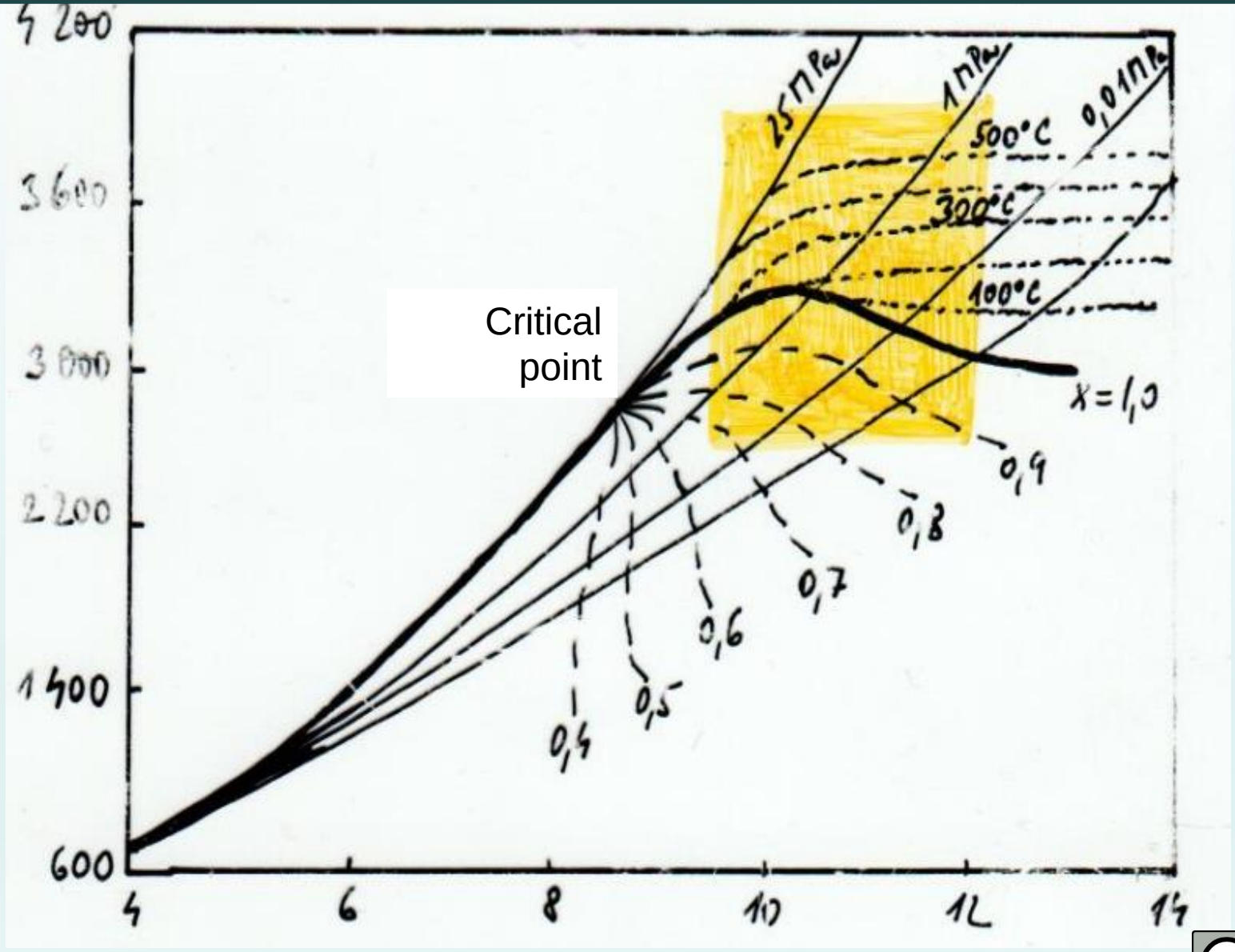
Zdeněk Bubník

Department of Carbohydrates and Cereals
B 42, tel.: 22044 3112
E-mail: zdenek.bubnik@vscht.cz

Steam Thermodynamics



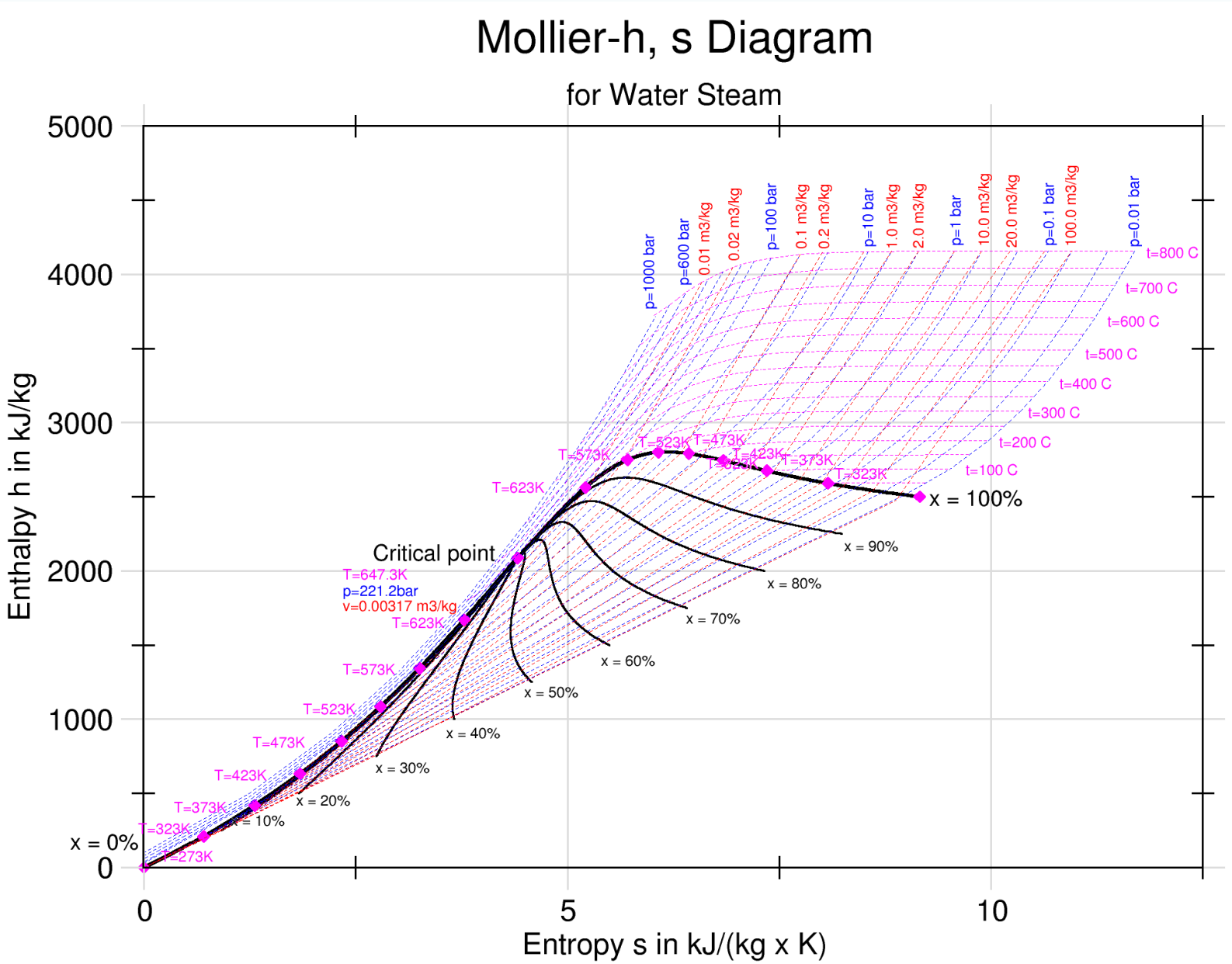
Enthalpy - entropy chart



Enthalpy [kJ/kg]

Entropy s [kJ/kg.K]

Enthalpy–entropy chart



By Markus Schweiss:

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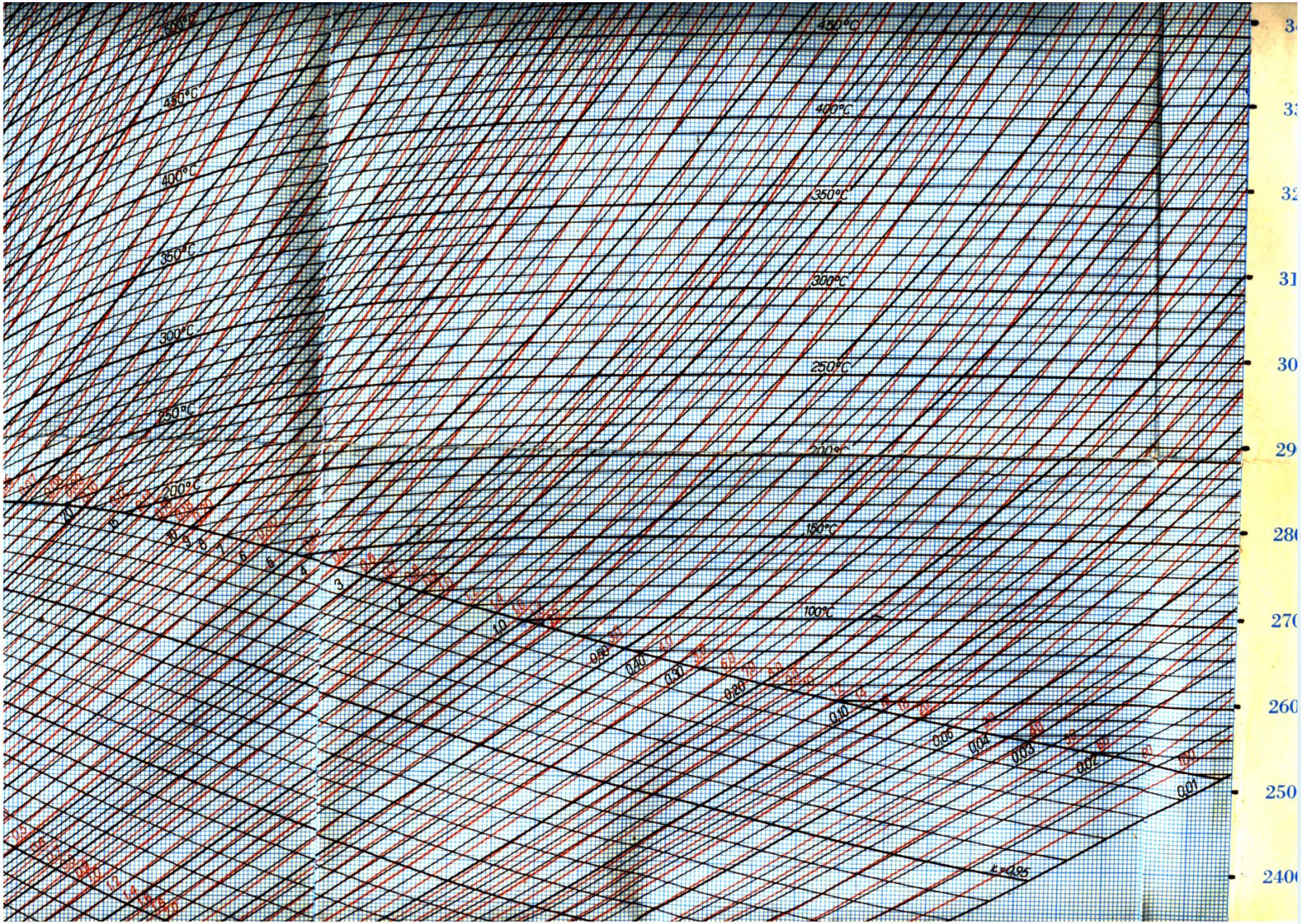
450°C
400°C
350°C
300°C
250°C
200°C
150°C
100°C
k=0,95
3
2
1
0,50
0,40
0,30
0,20
0,10
0,08
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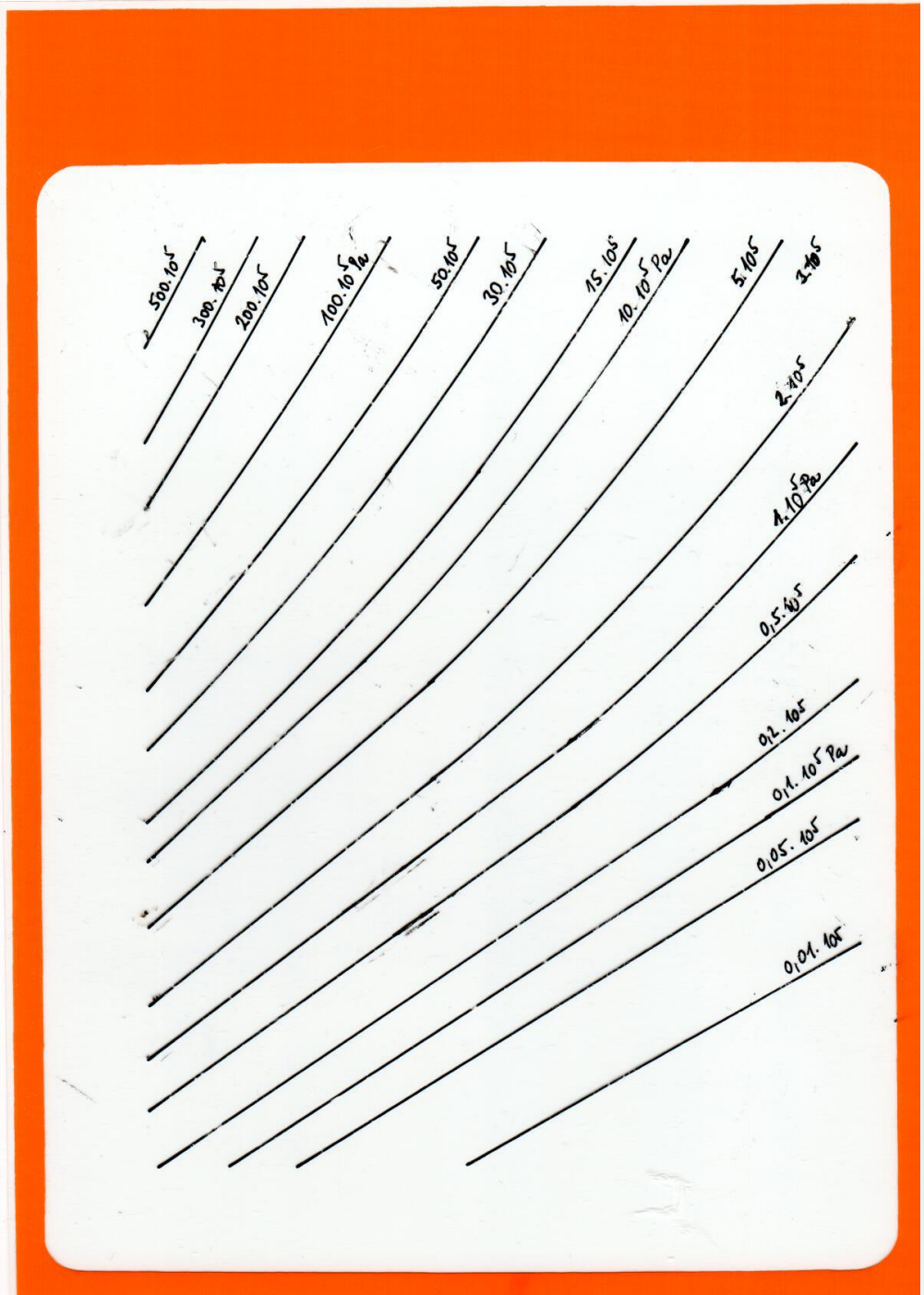
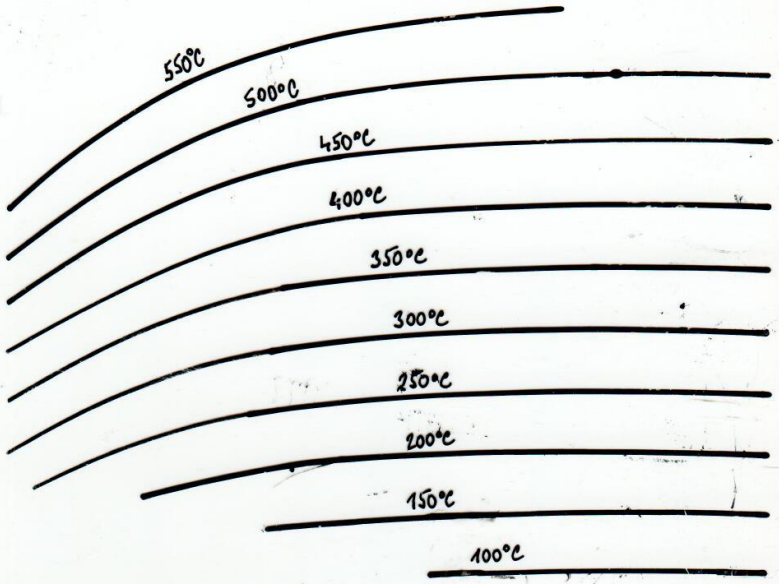
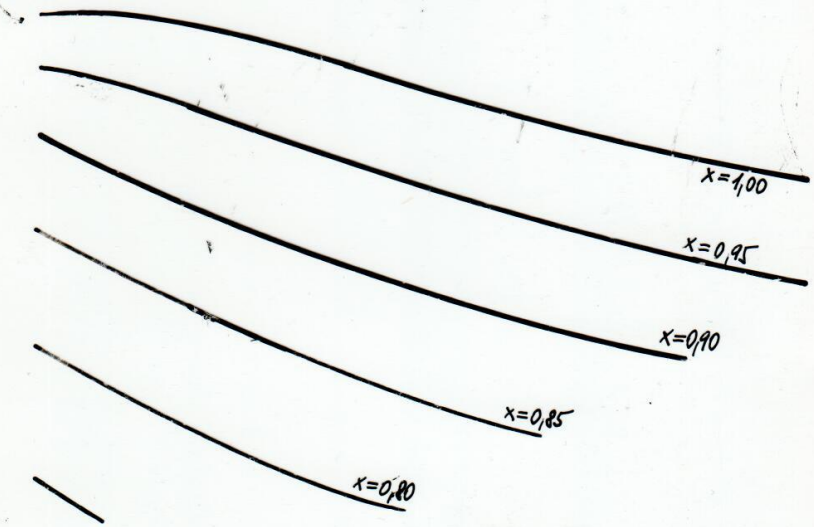
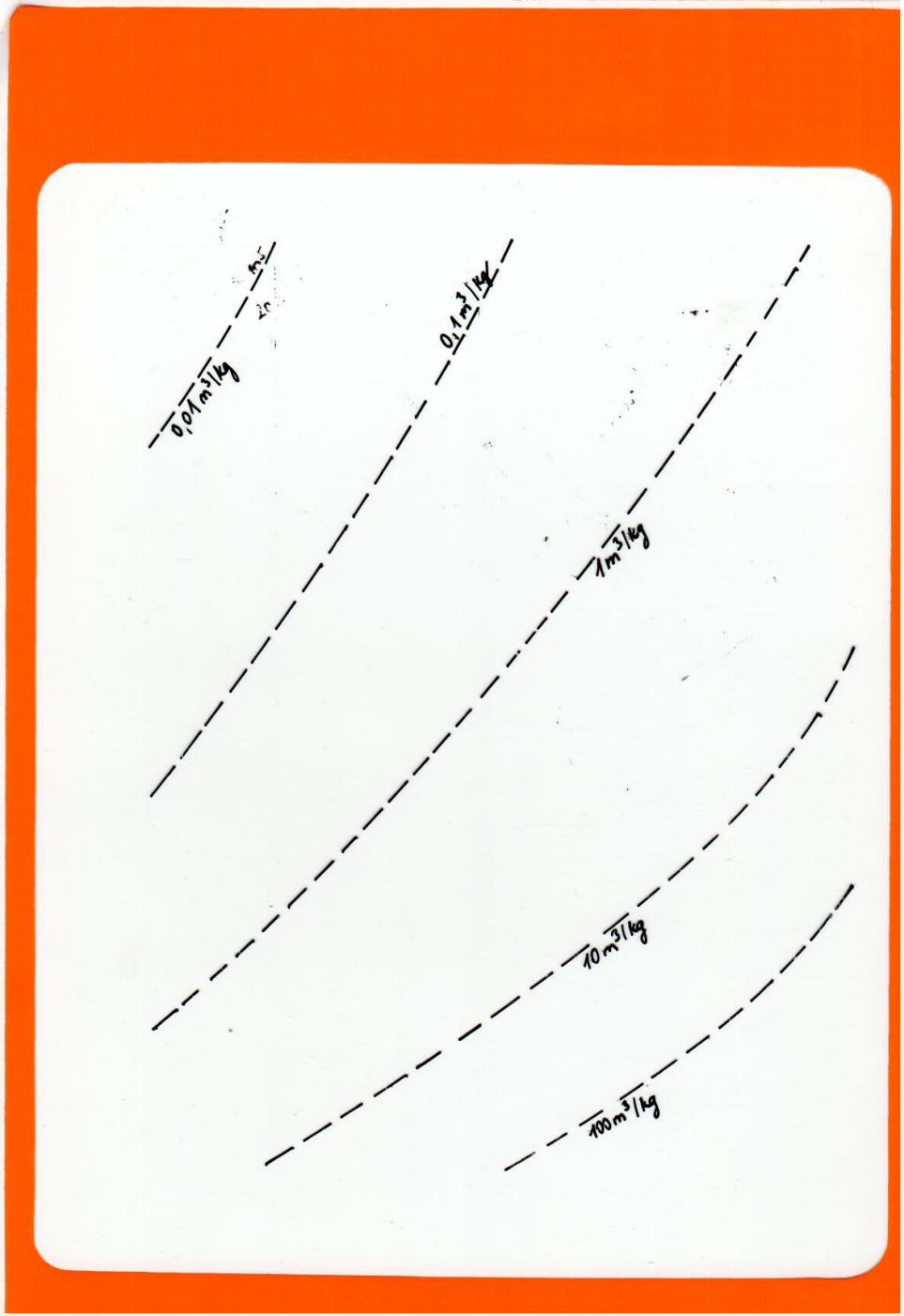
33
32
31
30
29
28
270
260
250
240


500.10⁵
300.10⁵
200.10⁵
100.10⁵ Pa
50.10⁵
30.10⁵
15.10⁵
10.10⁵ Pa
5.10⁵
3.10⁵
2.10⁵
1.10⁵ Pa
0,5.10⁵
0,2.10⁵
0,1.10⁵ Pa
0,05.10⁵
0,01.10⁵







422/2: Properties of water (') and steam (") at the state of saturation – Pressure table (continued)

Pressure	Temperature	Specific volume		Density	Specific enthalpy		Heat of evaporation	Specific entropy	
p in bar	t in °C	v' 10^{-3} m³/kg	v'' in m³/kg	ρ'' in kg/m³	h' in kJ/kg	h'' in kJ/kg	r in kJ/kg	s' in kJ/(kg·K)	s'' in kJ/(kg·K)
21	214.85	1.1809	0.09489	10.54	919.96	2 798.2	1 878.2	2.4700	6.3187
22	217.24	1.1850	0.09065	11.03	930.95	2 799.1	1 868.1	2.4922	6.3015
23	219.55	1.1892	0.08677	11.52	941.60	2 799.8	1 858.2	2.5136	6.2849
24	221.78	1.1932	0.08320	12.02	951.93	2 800.4	1 848.5	2.5343	6.2690
25	223.94	1.1972	0.07991	12.51	961.96	2 800.9	1 839.0	2.5543	6.2536
26	226.04	1.2011	0.07686	13.01	971.72	2 801.4	1 829.6	2.5736	6.2387
27	228.07	1.2050	0.07402	13.51	981.22	2 801.7	1 820.5	2.5924	6.2244
28	230.05	1.2088	0.07139	14.01	990.48	2 802.0	1 811.5	2.6106	6.2104
29	231.97	1.2126	0.06893	14.51	999.53	2 802.2	1 802.6	2.6283	6.1969
30	233.84	1.2163	0.06663	15.01	1 008.4	2 802.3	1 793.9	2.6455	6.1837
31	235.67	1.2200	0.06447	15.51	1 017.0	2 802.3	1 785.4	2.6623	6.1709
32	237.45	1.2237	0.06244	16.02	1 025.4	2 802.3	1 776.9	2.6786	6.1585
33	239.48	1.2274	0.06053	16.52	1 033.7	2 802.3	1 768.6	2.6945	6.1463
34	240.88	1.2310	0.05873	17.03	1 041.8	2 802.1	1 760.3	2.7101	6.1344
35	242.54	1.2345	0.05703	17.54	1 049.8	2 802.0	1 752.2	2.7253	6.1228
36	244.16	1.2381	0.05541	18.05	1 057.6	2 801.7	1 744.2	2.7401	6.1115
37	245.75	1.2416	0.05389	18.56	1 065.2	2 801.4	1 736.2	2.7547	6.1004
38	247.31	1.2451	0.05244	19.07	1 072.7	2 801.1	1 728.4	2.7689	6.0896
39	248.84	1.2486	0.05106	19.58	1 080.1	2 800.8	1 720.6	2.7829	6.0789
40	250.33	1.2521	0.04975	20.10	1 087.4	2 800.3	1 712.9	2.7965	6.0685

What are steam changes – operation?

P = constant (isobaric)

V = constant

T = constant (isothermic)

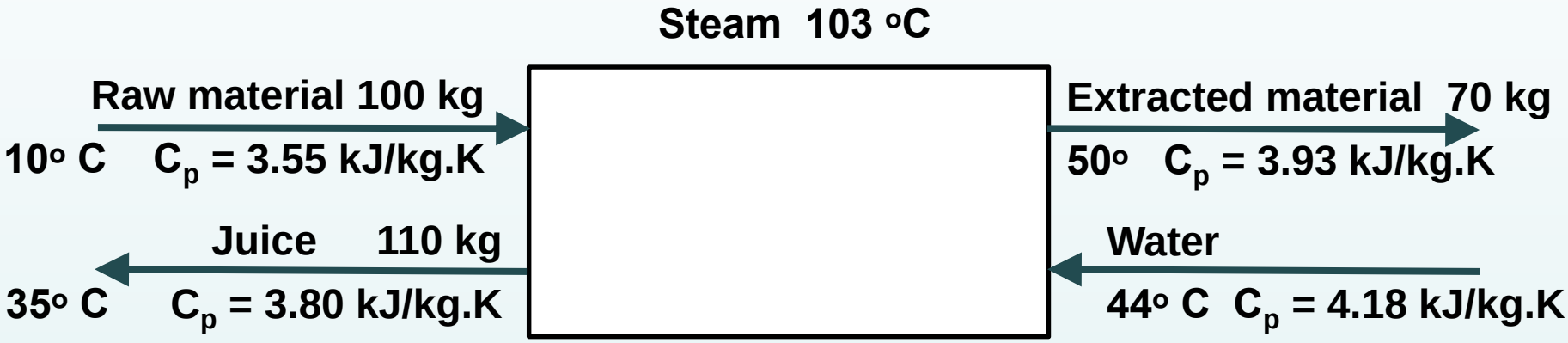
Polytropic

Adiabatic

h = constant (isoenthalpic)

s = constant (isoentropic expansion)

STEAM HEATING – EXTRACTION

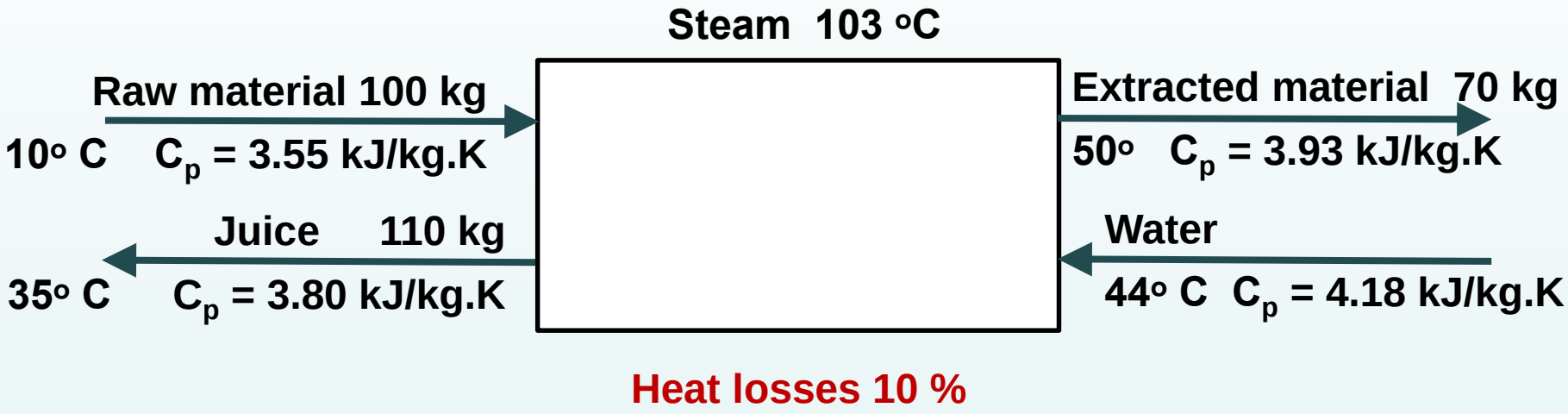


Mass balance:

$$m_W + m_{raw.m.} = m_{ex.mat.} + m_J$$

$$m_W = 70 + 110 - 100 = 80 \text{ kg}$$

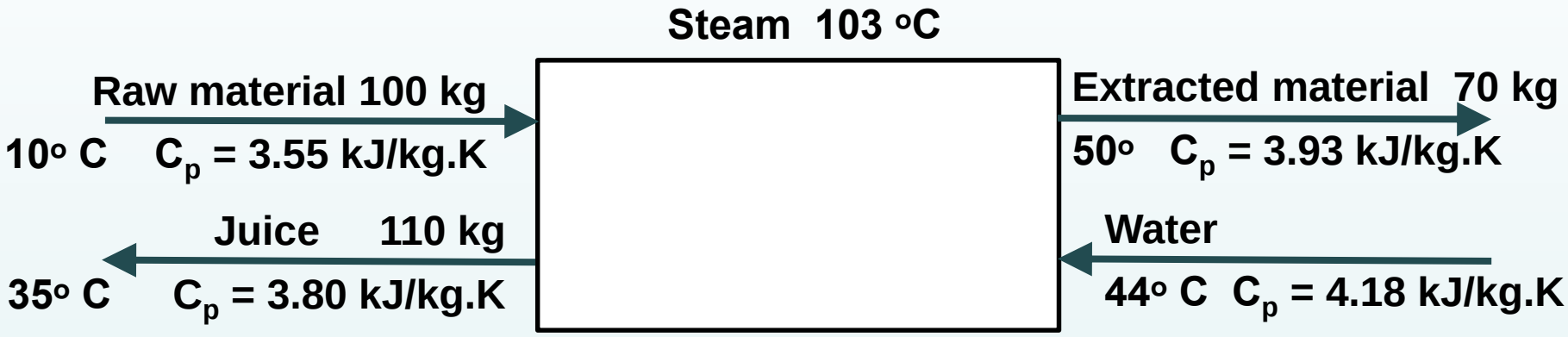
STEAM HEATING – EXTRACTION



Enthalpic balance:

$$Q_{raw.mat.} + Q_{water} + Q_{steam} = Q_{juice} + Q_{ex.mat.} + Q_{losses}$$

STEAM HEATING – EXTRACTION



Heat losses 10 %

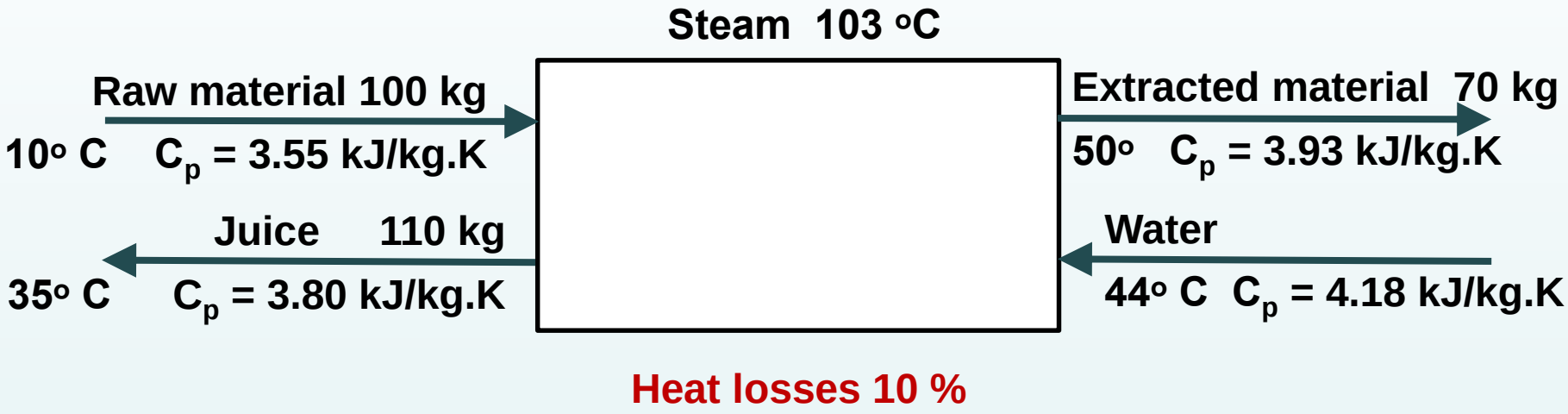
Enthalpic balance:

$$Q_{raw.mat.} + Q_{water} + Q_{steam} = Q_{juice} + Q_{ex.mat.} + Q_{losses}$$

In: $Q_{raw.mat.} + Q_{water} = ???$

Out: $Q_{juice} + Q_{ex.mat.} = ???$

STEAM HEATING – EXTRACTION



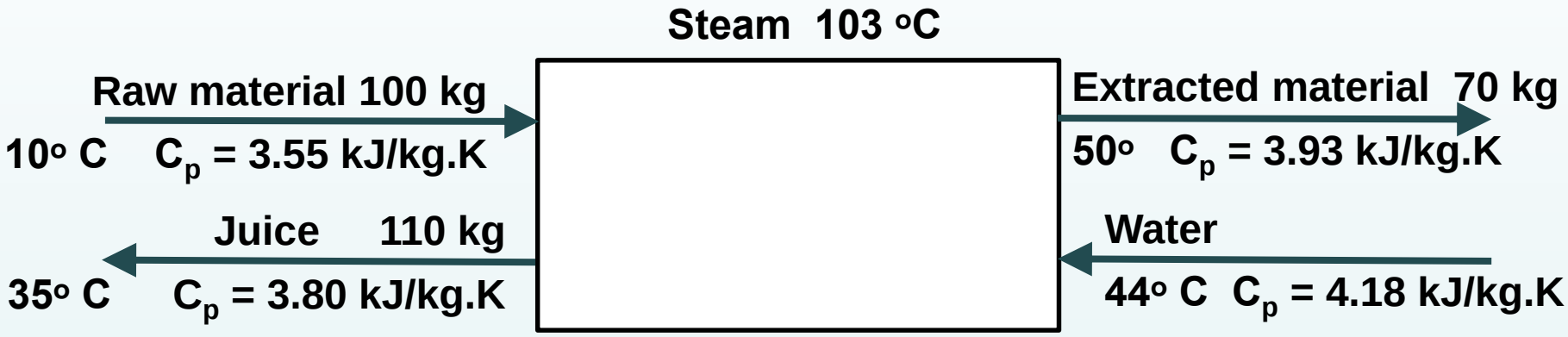
Enthalpic balance:

$$Q_{raw.mat.} + Q_{water} + Q_{steam} = Q_{juice} + Q_{ex.mat.} + Q_{losses}$$

In: $Q_{raw.mat.} + Q_{water} = 100 \cdot 3.55 \cdot 10 + 80 \cdot 4.18 \cdot 44 = 1.83 \cdot 10^4$ kJ

Out: $Q_{juice} + Q_{ex.mat.} = 70 \cdot 3.93 \cdot 50 + 110 \cdot 3.8 \cdot 35 = 2.84 \cdot 10^4$ kJ

STEAM HEATING – EXTRACTION



Heat losses 10 %

Heat consumption:

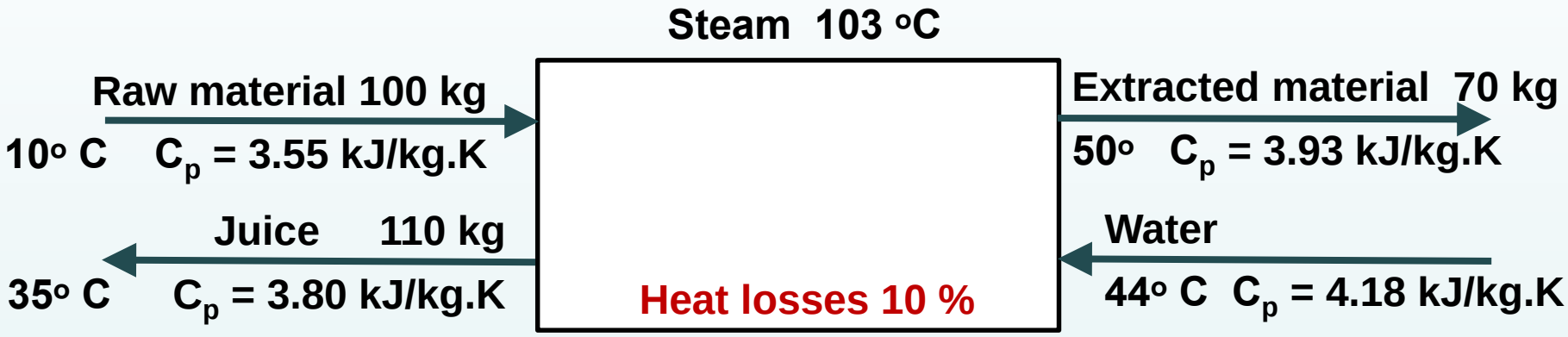
In: $Q_{raw.mat.} + Q_{water} = 1.83 \cdot 10^4$ kJ

Out: $Q_{juice} + Q_{ex.mat.} = 2.84 \cdot 10^4$ kJ

Heat consumption = ("OUT" – "IN") x 1.1 10% losses

$Q^z_{steam} = (2.84-1.83) \cdot 1.1 = 1.12 \cdot 10^4$ kJ

STEAM HEATING – EXTRACTION



Heat of vaporisation:

r_{103} = 2248 kJ/kg

Steam consumption:

$$m_{steam} = \frac{Q^{Z}_{steam}}{r_{103}}$$

$$m_{steam} = \frac{11200}{2248} = 4.9\ kg$$

HEAT EXCHANGER

$$Q = k \cdot a \cdot \Delta t_{l.s.} \quad / \quad Q = k_L \cdot n \cdot L_s \cdot \Delta t_{l.s.}$$

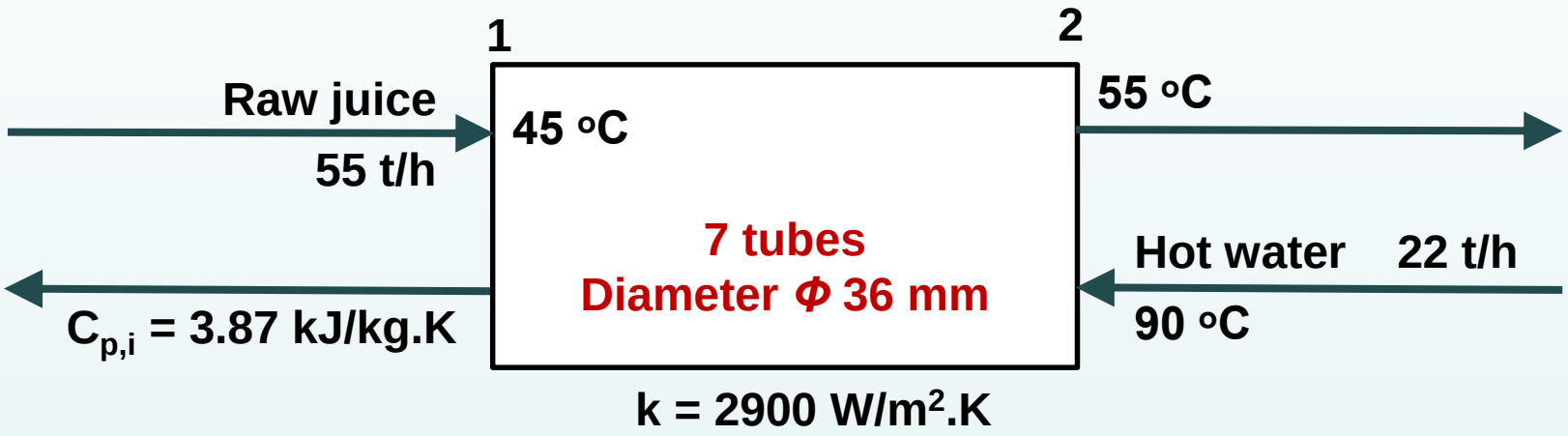
$$Q = m \cdot c_p \cdot \Delta t$$

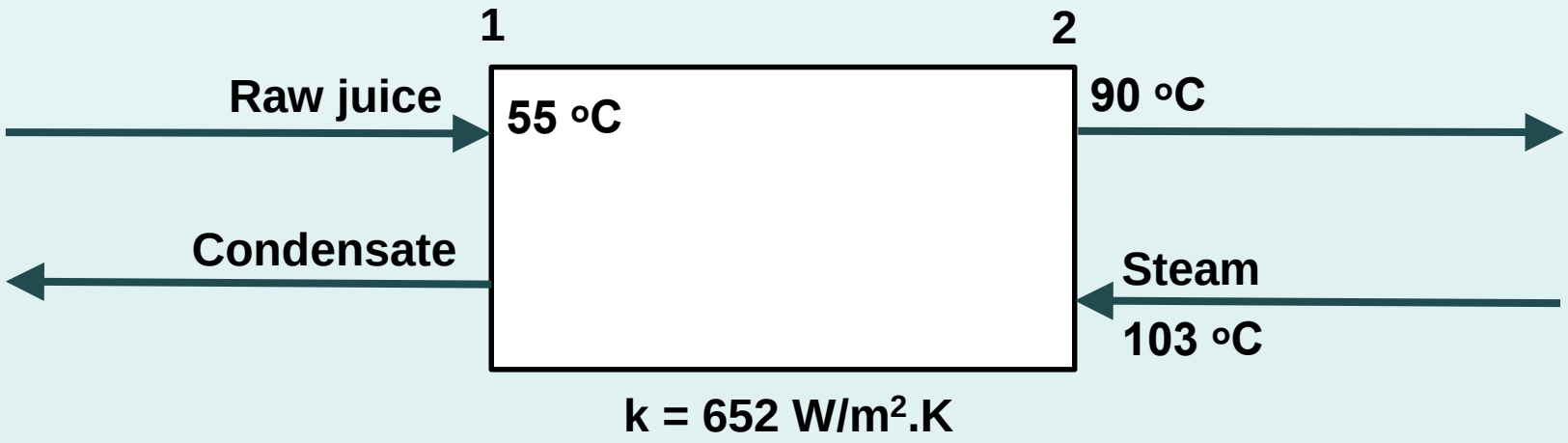
$$\Delta t_{l.s.} = \frac{\Delta t_1 - \Delta t_2}{ln \frac{\Delta t_1}{\Delta t_2}}$$

$$k_L = \pi \cdot d_L \cdot k$$

[W/m.K] [W/m^2.K]

HEAT EXCHANGER





? END

Heat processes II

- **Drying**
- **Store**
- **Air Conditioning**

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YOUTH AND SPORTS

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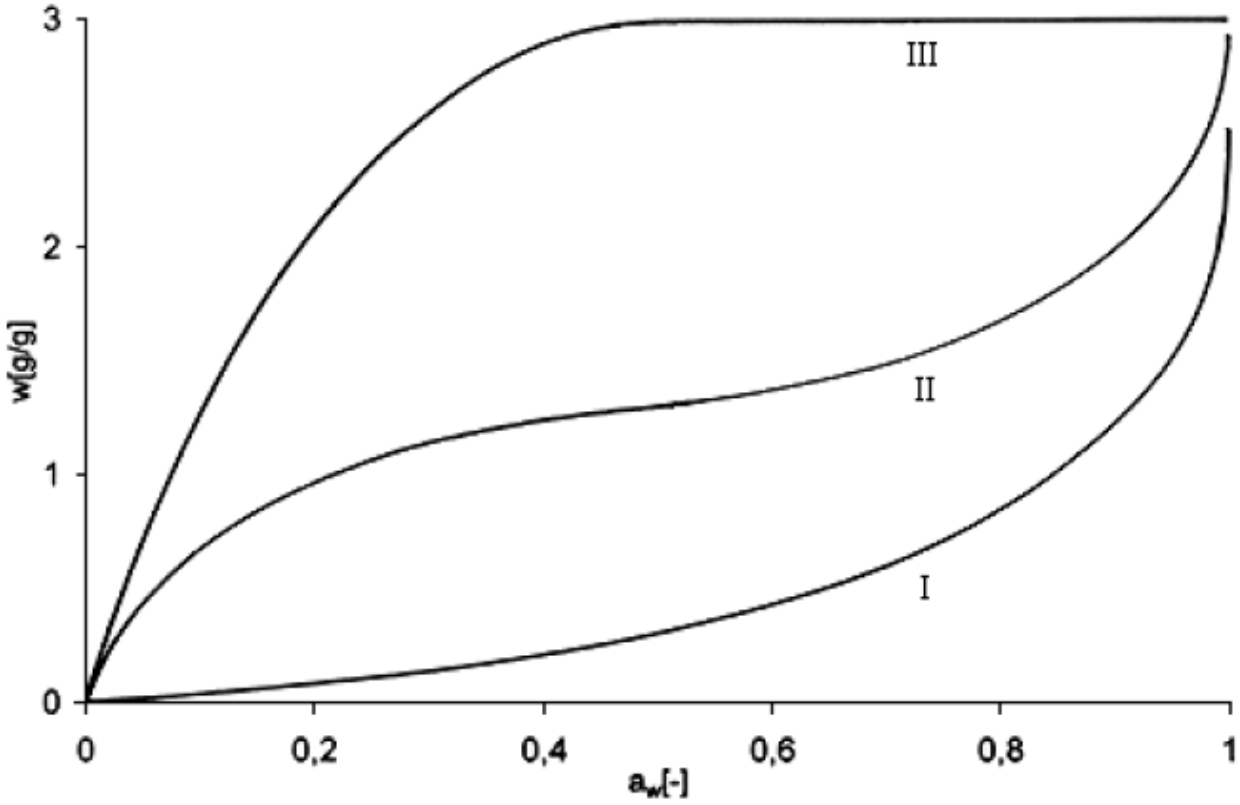
Equilibrium humidity – Sorption isotherms



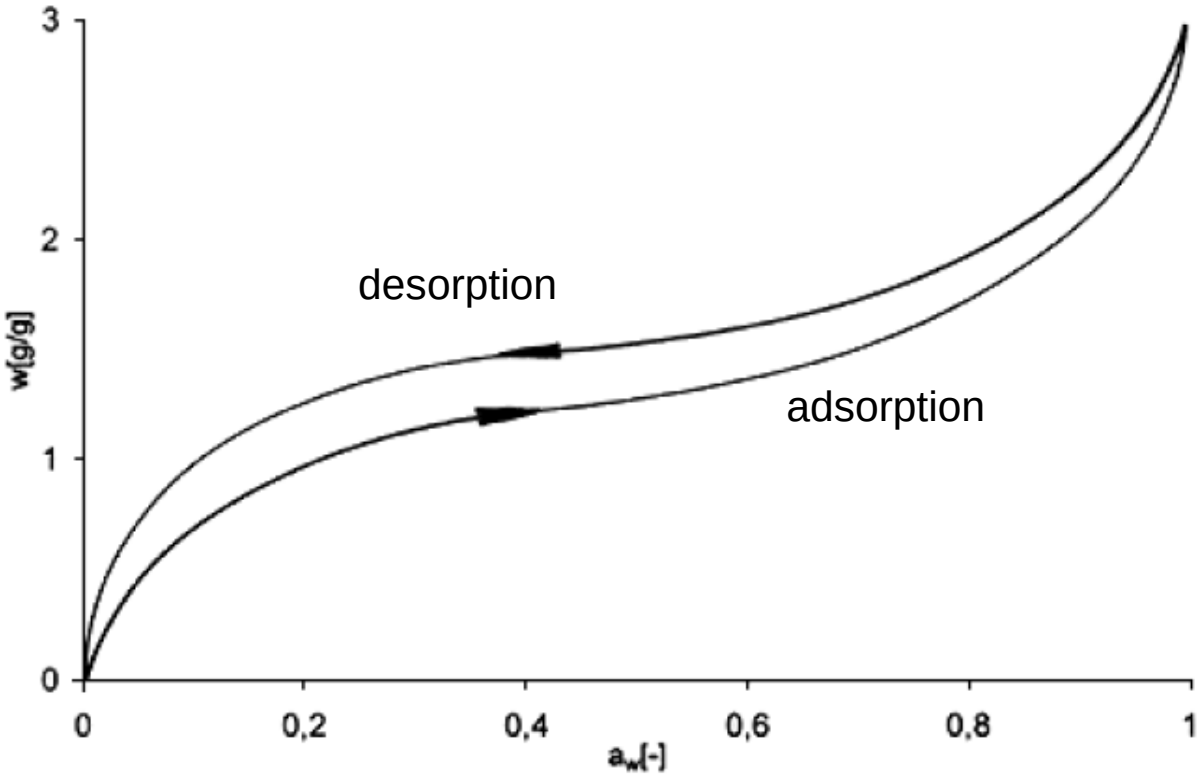
a_w : Water activity = availability of water for MB, enzymatic and chemical activity

…. = RVP Relative Vapour Pressure (P/Pw)

Equilibrium humidity

– Sorption isotherms

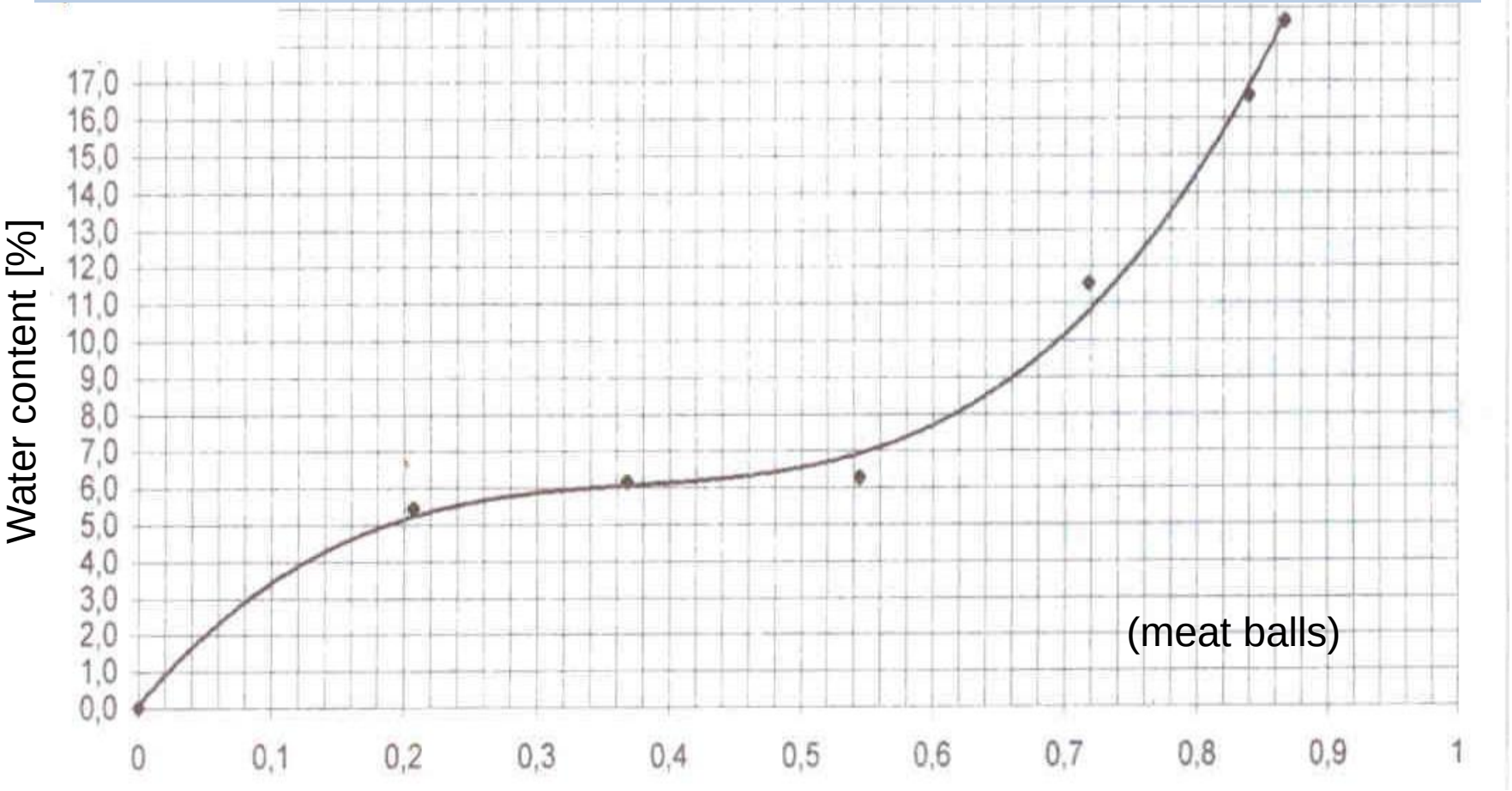
Hysteresis: drying - wetting



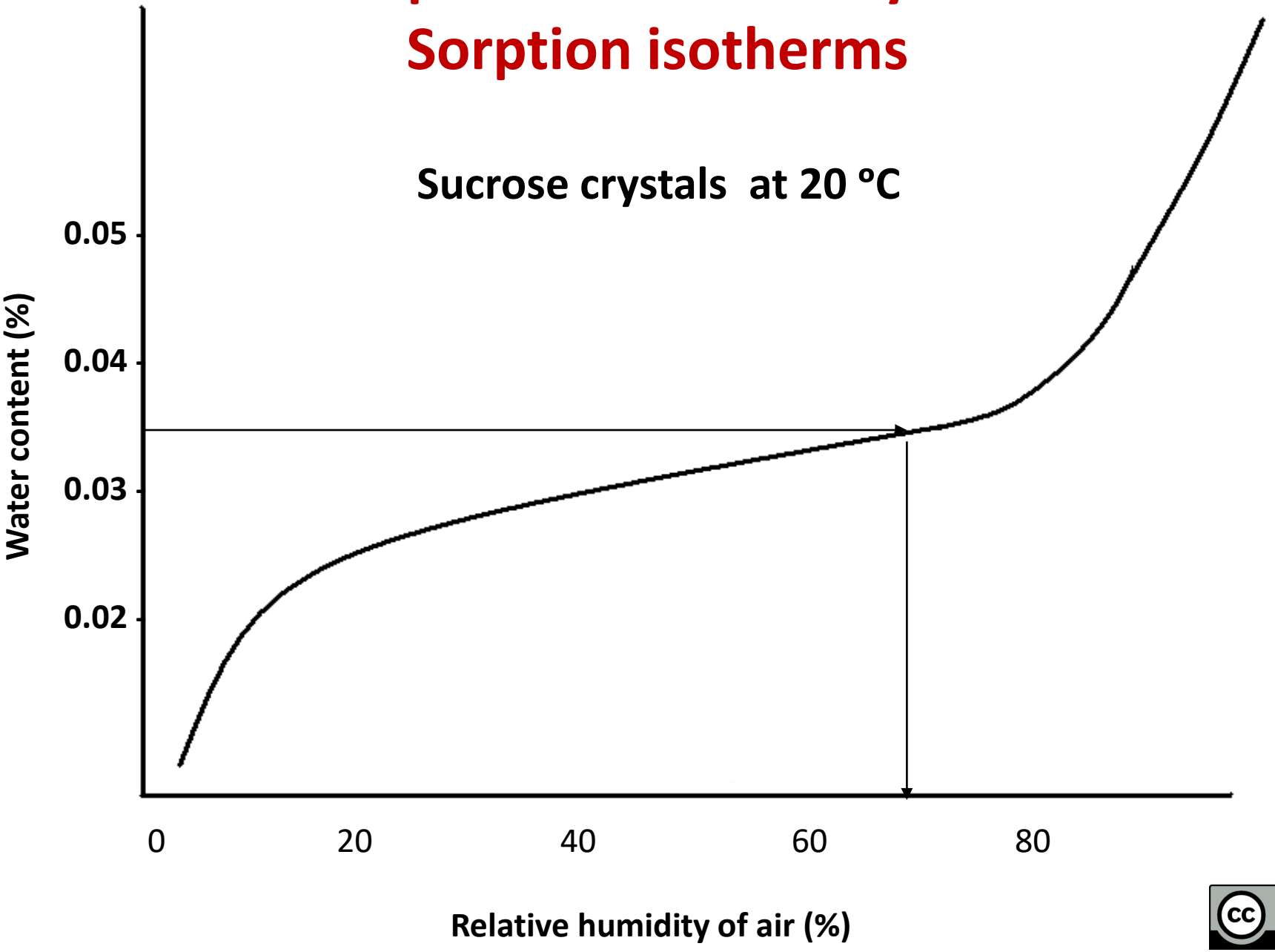
Sorption isotherms

An example of a sorption isotherm of dried meat balls

The isotherm was obtained experimentally by the measurement of water content in a sample of meat ball in atmosphere of different relative humidity



Equilibrium humidity – Sorption isotherms



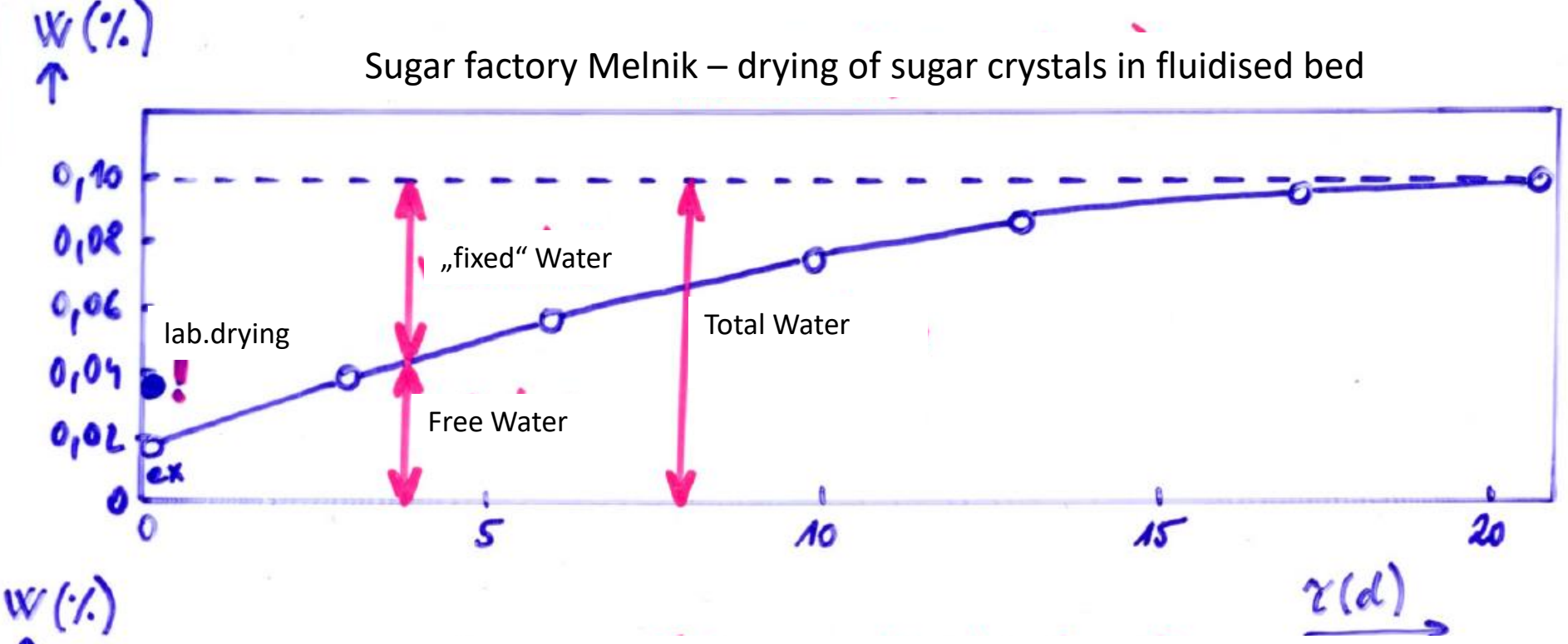
New processes – new problems?

In the case of sugar:

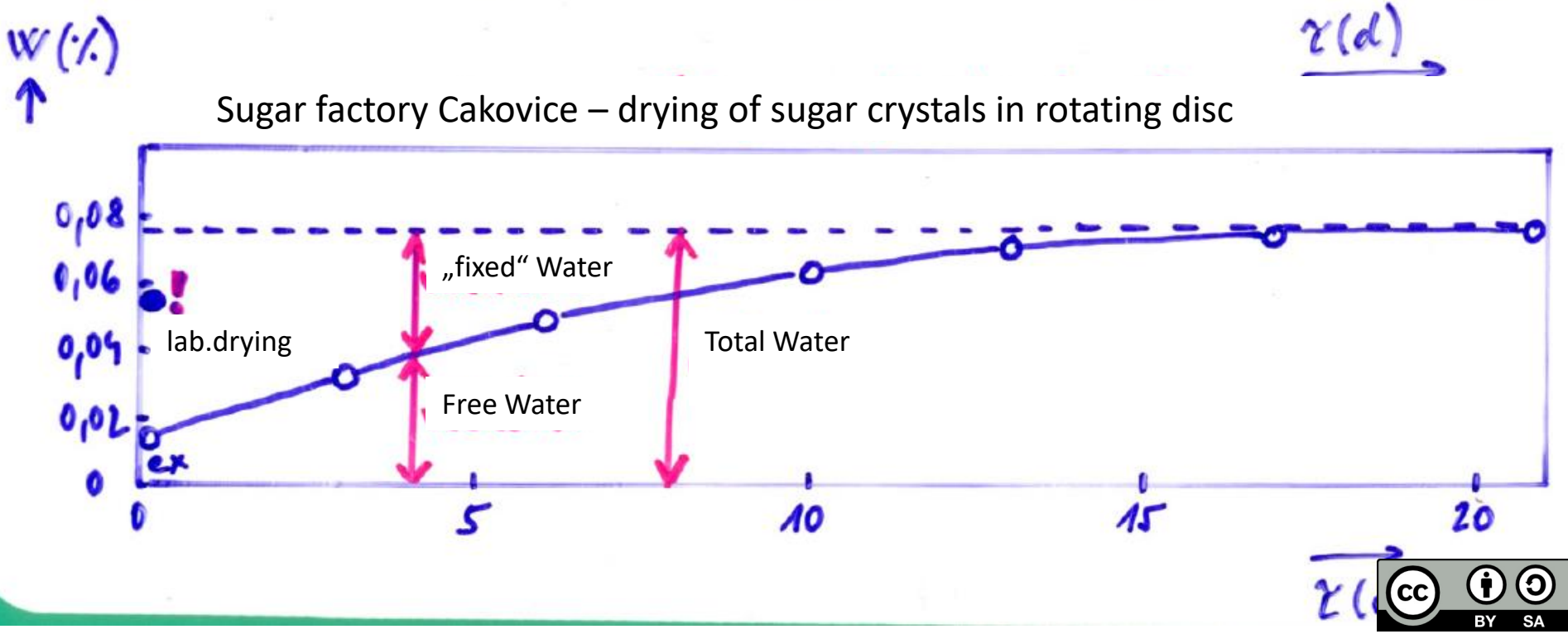
- **Crystallization**
- **Separation**
- **Drying (fluidised bed) – glass transition**
- **Storage (in silos) – recrystallization, free water !!!**
- **New methods of air-condition**

- **Analytical methods: water determination**

Sugar factory Melnik – drying of sugar crystals in fluidised bed



Sugar factory Cakovice – drying of sugar crystals in rotating disc



Kinetics of Nucleation

Primary nucleation:

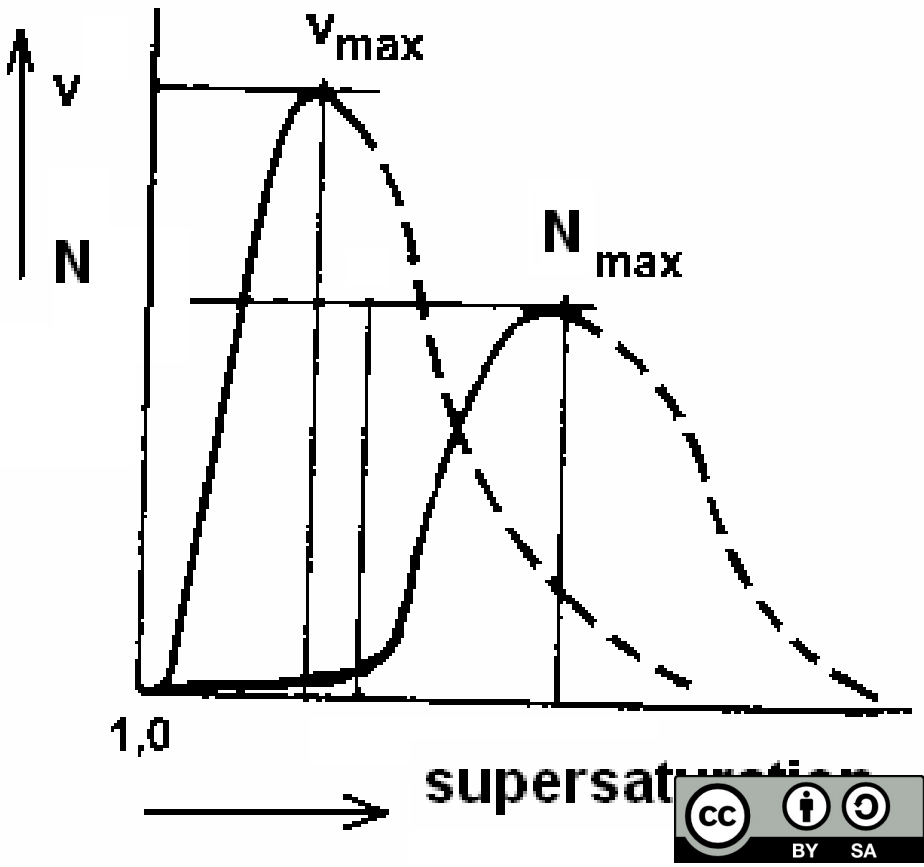
Nucleation rate N_N (#/s.m³)

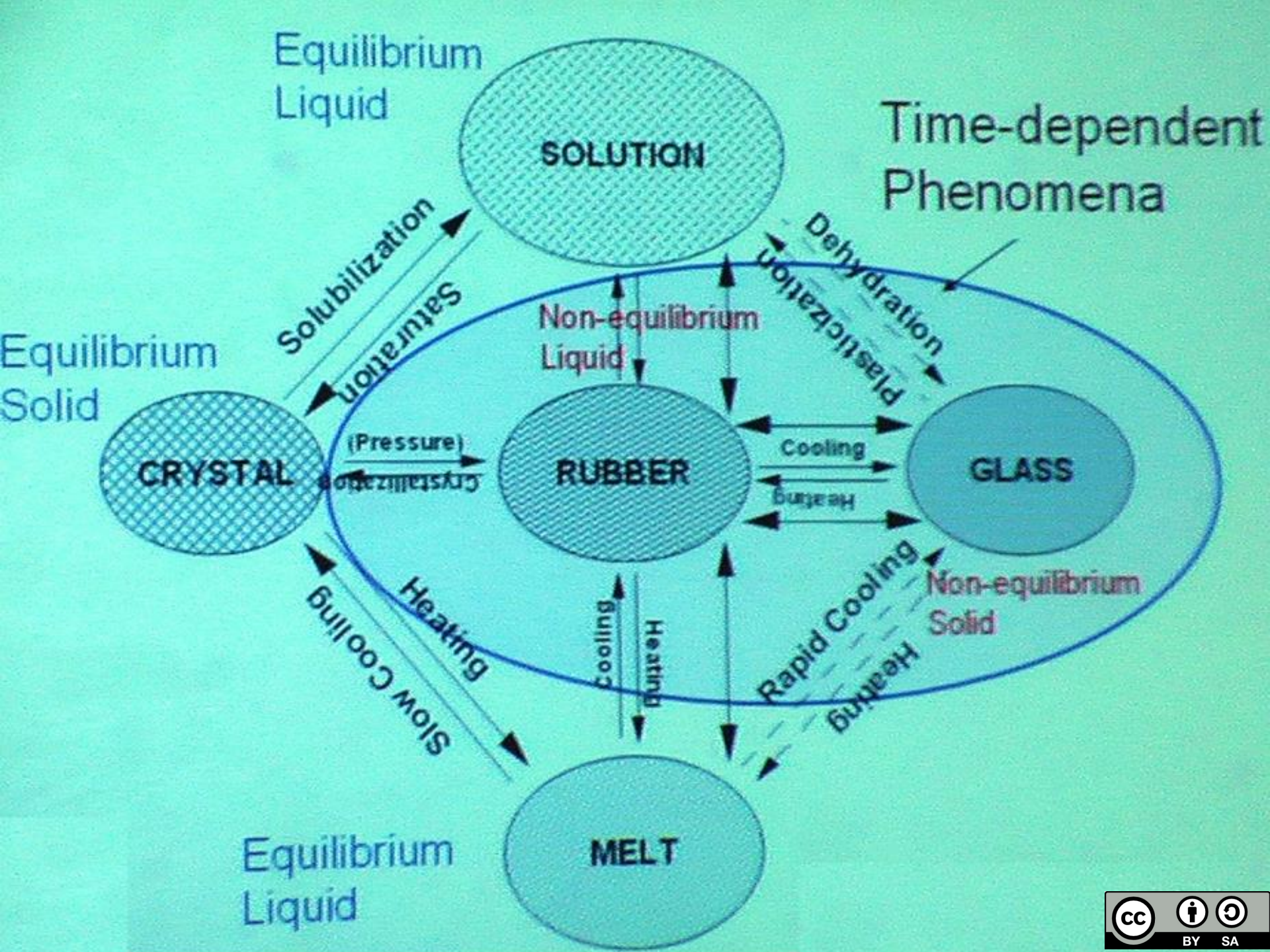
where N – number of crystals,
k_N – rate constant of nucleation,
n – nucleation exponent

$$\frac{dN}{d\tau} = k_N (c - c_{eq})^n$$

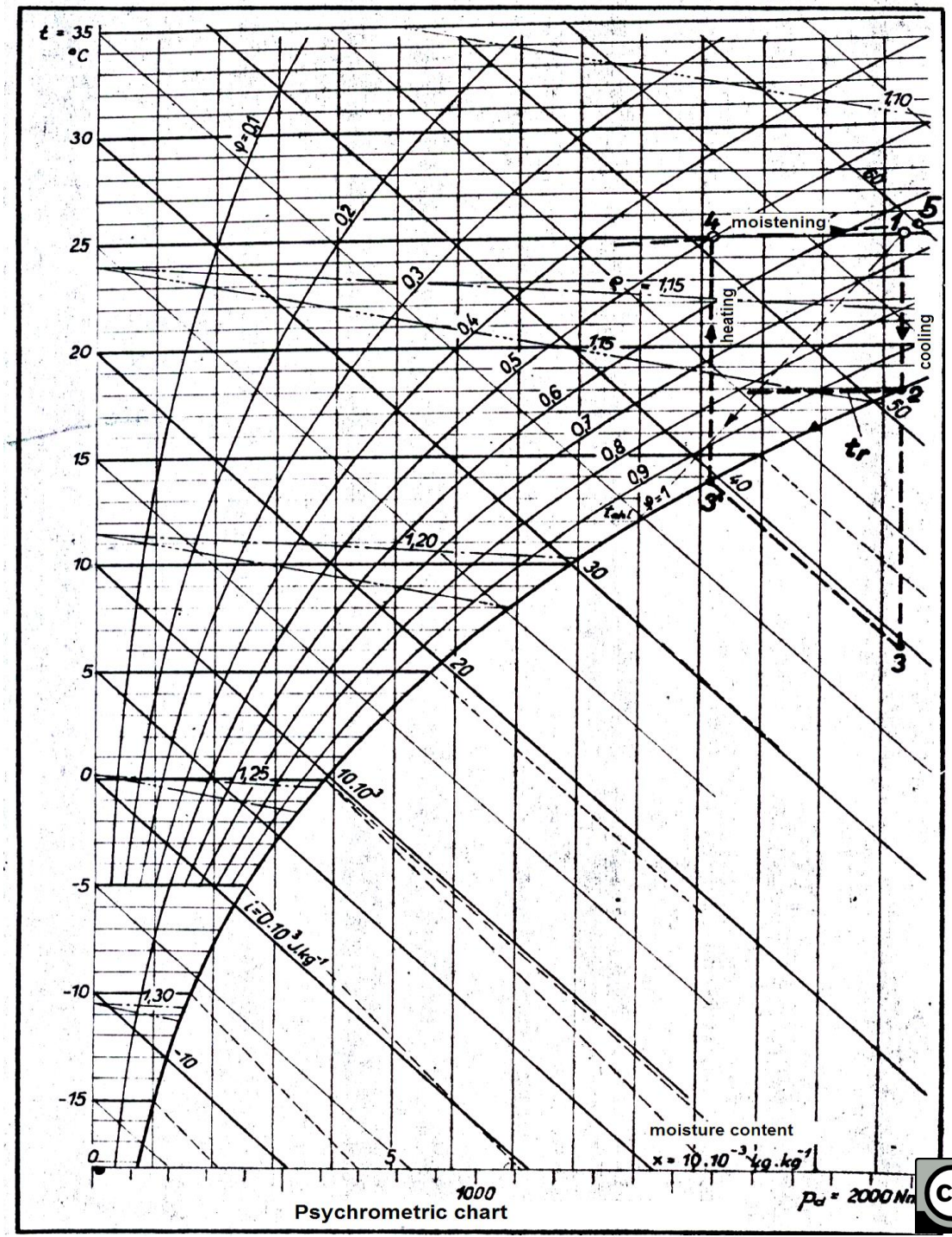
N_m (kg/s.m³)

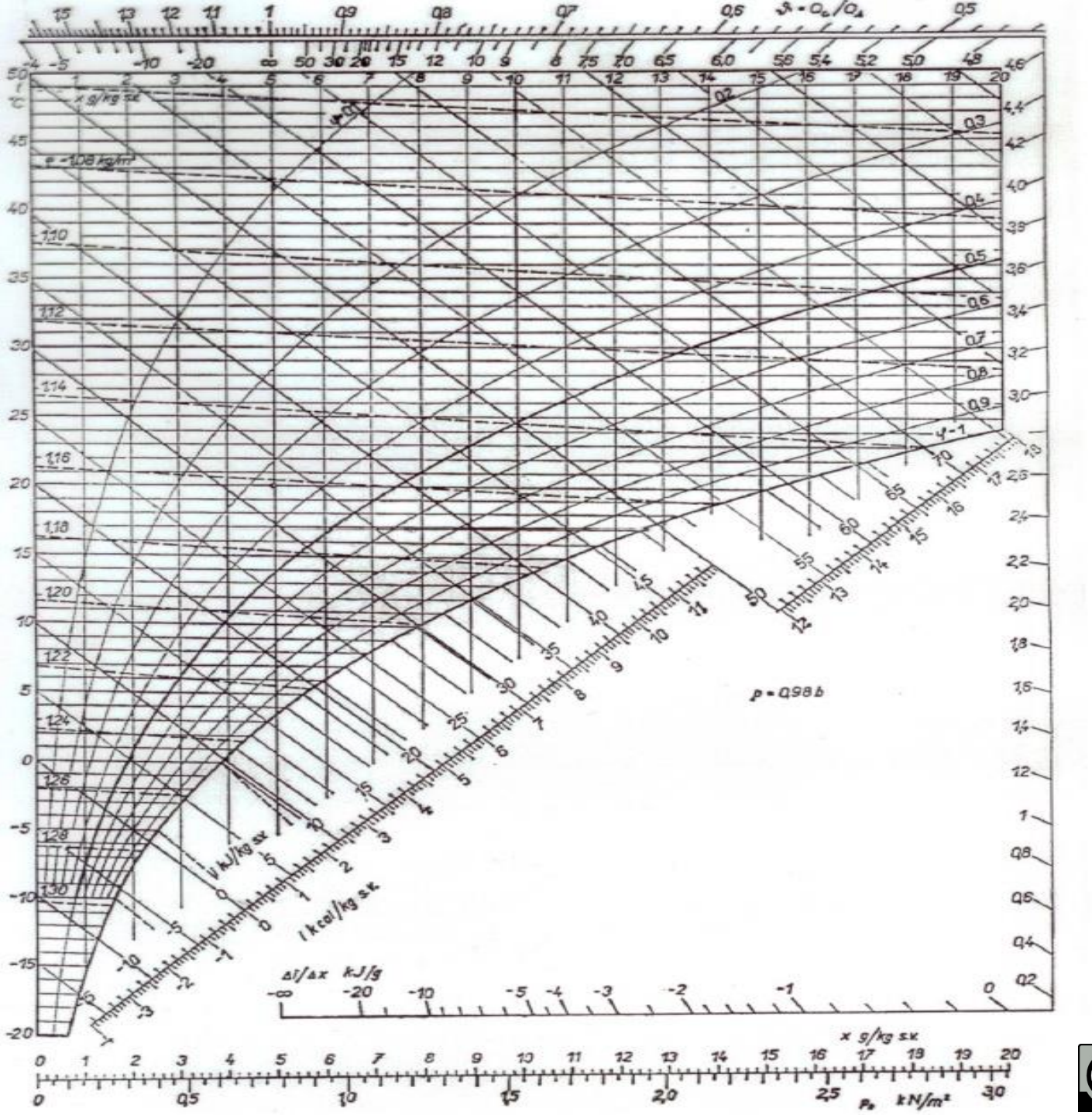
$$\frac{dm_N}{d\tau} = k_{Nm} (c - c_{eq})^n$$

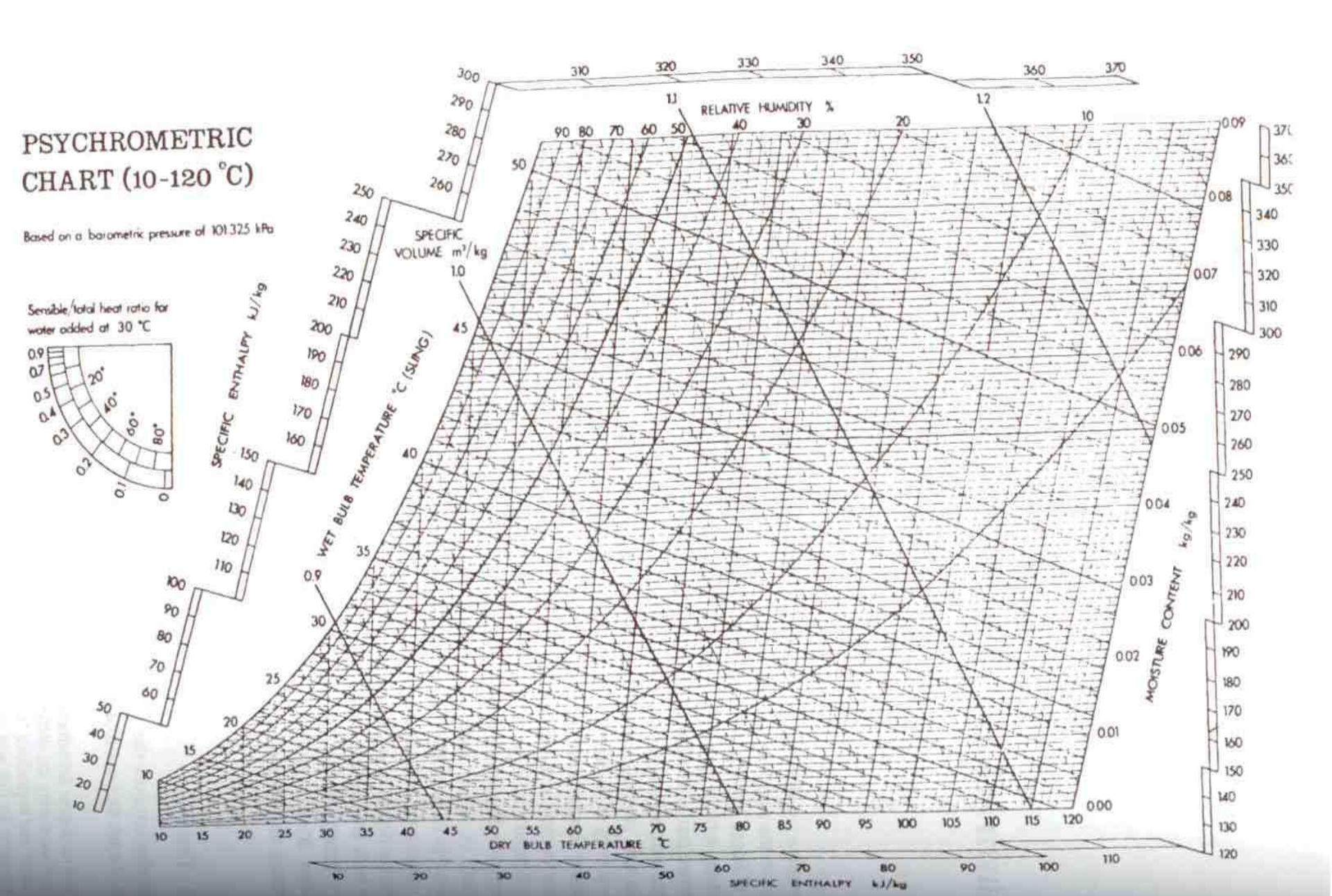



Equilibrium
Liquid
SOLUTION
Time-dependent
Phenomena
Solubilization
Saturation
Dehydration
Plasticization
Equilibrium
Solid
Non-equilibrium
Liquid
CRYSTAL
(Pressure)
Crystallization
RUBBER
Cooling
Heating
GLASS
Heating
Slow Cooling
Cooling
Heating
Rapid Cooling
Heating
Non-equilibrium
Solid
Equilibrium
Liquid
MELT

Psychrometric chart (diagram of wet air)




x g/kg s.k.
p = 1,08 kg/m³
1,10
1,12
1,14
1,16
1,18
1,20
1,22
1,24
1,26
1,28
1,30
φ = 0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
0,9
1
p = 0,98 b
i kJ/kg s.k.
i kcal/kg s.k.
Δi/Δx kJ/g
x g/kg s.k.
p_c kN/m²



(Courtesy of Chartered Institution of Building Service Engineers.)

Example:

Production: 750 t of sugar per day

Temperature:	t = 15 °C
Water content:	W = 0.055 %

Storage conditions:

Temperature:	t = 15 °C
Rel. air humidity :	φ = 50 %
Equilibrium humidity :	W_{eq} = 0.027 %

Air-condition:

Temperature:	t = 15 °C
Input Air-Con:	φ_0 = 50 %
Output Air-Con:	φ_1 = 30 %

Question:

a) How much water must be removed?

b) How much air from air-condition will it require?

c) What is the temperature of condensation?

d) How to change the temperature, when a new value of φ = 30 % is required?

e) How much of water must be removed when the temperature decreases to 10 ^{o}C and φ remains constant? The volume of air in the storage hall is 12 000 m^{3}.

Results:

a) How much water needs to be removed?

$$m_w = 750\ (0.055 - 0.027)/100 = 210\ kg/d$$

Results:

b) How much air from air-condition is required?

From the psychrometric chart:

air “output Air-Con“: 3.2 g water / kg air

air “input Air-Con“: 5.5 g water / kg air

m_{air} = 210000 / (5.5 – 3.2) = 91304 kg/d

V_{air} = 91304 / 1.18 = 77376 m^3

Results:

c) The temperature of condensation?

5 °C

d) How to change the temperature when a new value of φ = 30 % is required?

23 °C

Results:

e) How much water must be removed when the temperature decreases to 10 °C and φ is constant? The volume of air in the storage hall is 12 000 m³.

From the psychrometric chart:

Air at 15 °C and φ = 50 % : 5.4 g/kg

Air at 10 °C and φ = 50 % : 3.9 g/kg

Results - continuation:

e) How much water must be removed when the temperature decreases to 10 °C and φ is constant? The volume of the air in the storage hall is 12 000 m^3.

Air at 15 °C and φ = 50 % : 5.4 g/kg

Air at 10 °C and φ = 50 % : 3.9 g/kg

m_{air} = 12000 . 1.20 (density) = 14400 kg air

Results:

e) How much water must be removed when the temperature of air decreases to 10 °C and φ is constant? The volume of air in the storage hall is 12 000 m^3.

Air at 15 °C and φ = 50 % : 5.4 g/kg

Air at 10 °C and φ = 50 % : 3.9 g/kg

m_{air} = 12000 · 1.20 (density) = 14400 kg air

$m_{w\ in}$ = 14400 · 5.4 = 79 kg

$m_{w\ out}$ = 14000 · 3.9 = 56 kg

Removed water : 79 – 56 = 23 kg

Thank you for your attention!