



**UNIVERSITY OF ROME “LA SAPIENZA”
NANOTECHNOLOGIES ENGINEERING**

MICROPARTICLES CRYSTALLIZERS

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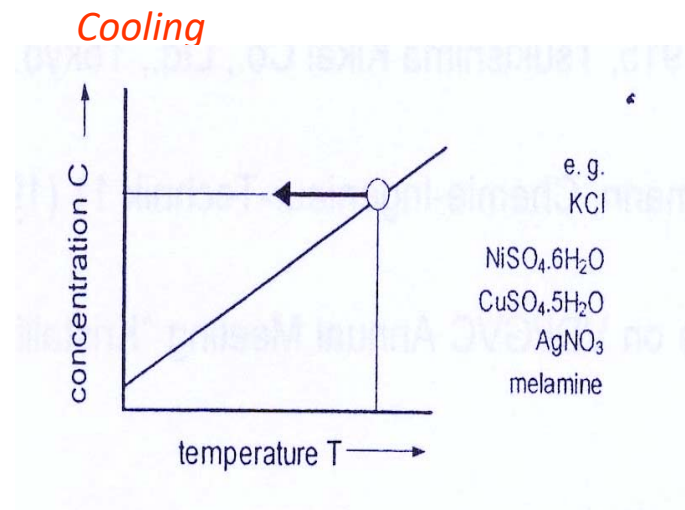
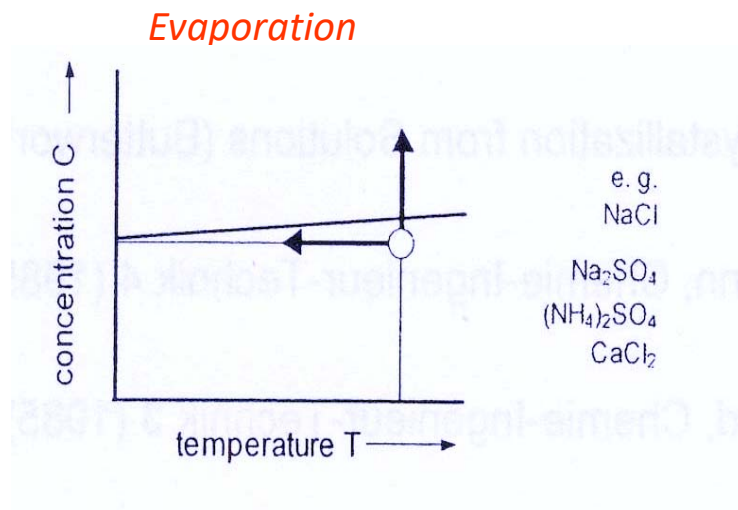
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Crystallization driving force

- A **key parameter** for crystallization is the **supersaturation**. Supersaturation is the temporary increase of concentration of the solute in the solvent, and is produced by evaporation, cooling, chemical reaction, salting out, etc.
- The most common crystallization operations today are those of **evaporative crystallization** and of **vacuum cooling**: in the former, crystallization occurs after some amount of solvent is removed, and this is due to the relatively “flat” solubility of the system at left hand side, in the latter case, the solubility is rather steep (figure at the right end side), and crystallization can be achieved by cooling only.



Types of Crystallizers

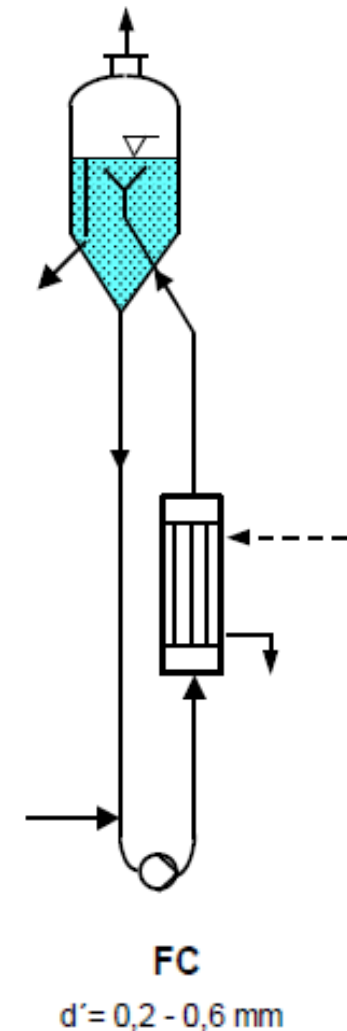
Crystallizers differ mainly in design and the position of the impeller pump.

Most crystallizers need to produce relatively large singular crystals, because this improves crystal purity and handling characteristics, and very often the **crystalline product's marketability**. To achieve a relatively large crystal size, it is important:

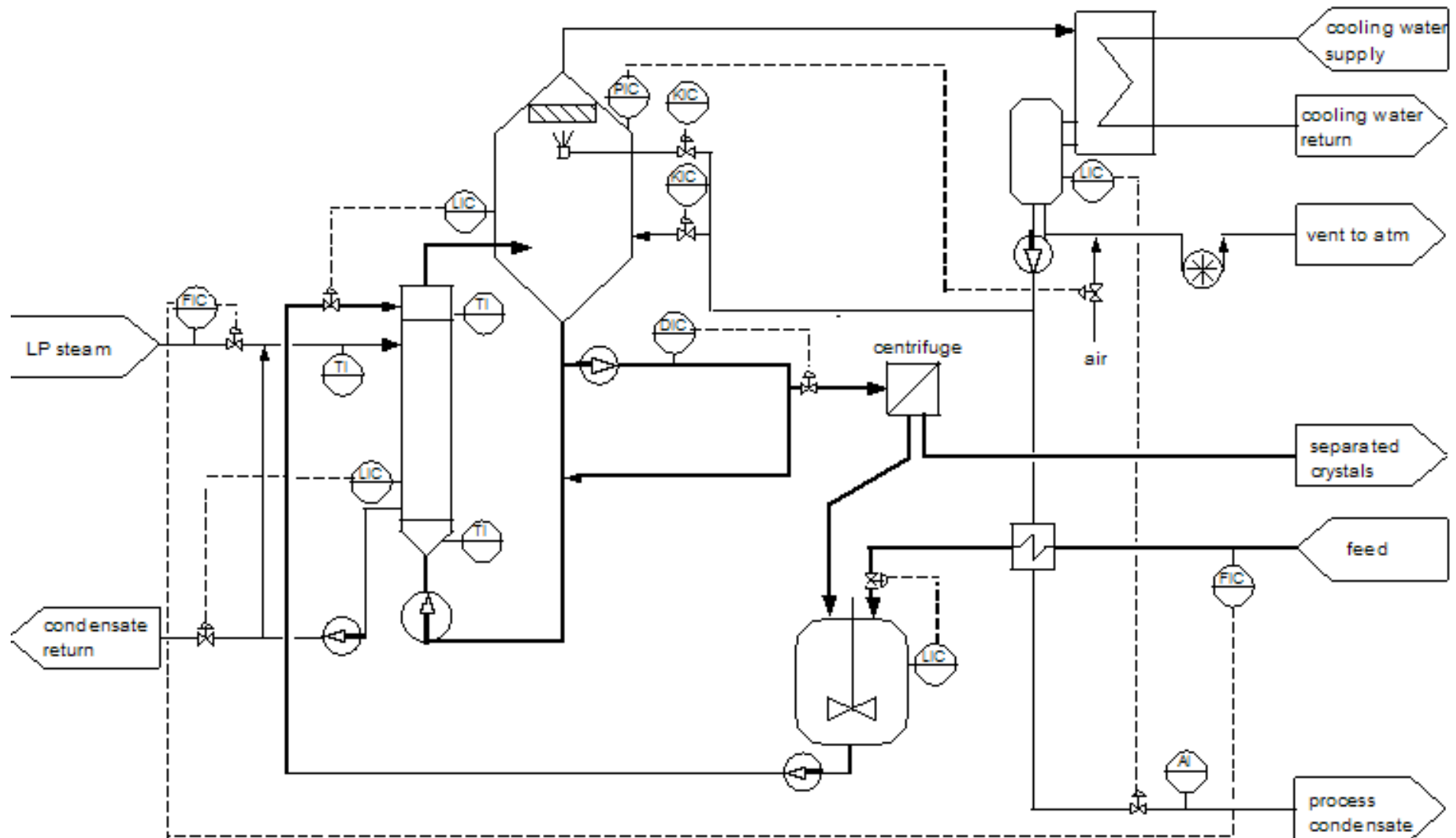
- **To control** the **supersaturation** in the crystallizer so that it does not exceed the metastable region;
- To choose an operating **supersaturation which determines a high growth rate**;
- To adopt a suitable slurry hydrodynamic which **enables** a good **macromixing** and **minimizes secondary nucleation**.

FORCED CIRCULATION CRYSTALLIZER

- The Forced Circulation ("FC") crystallizer is the most common type of crystallizer in the industry. The average FC crystallizer evaporates solvent, thus increasing the supersaturation in the process liquor, and causing crystallization to occur. Most conventional FC units operate under vacuum, or at slight super atmospheric pressure.
- The FC consists of four basic components:
 - the **crystallizer vessel**, which provides most of the volume dictated by the residence time requirements;
 - the **circulating pump**, which provides the mixing energy;
 - the **heat exchanger**, which supplies energy to the crystallizer (a typical evaporative crystallization operation);
 - the **vacuum equipment**, which handles the vapor generated in the crystallizer
- The FC crystallizer is used for general, simple crystallization operations, where large crystal size is not a requirement. The FC design aims to protect the crystal size with regard to reduction to collisions, but has no features to aggressively increase the crystal size.

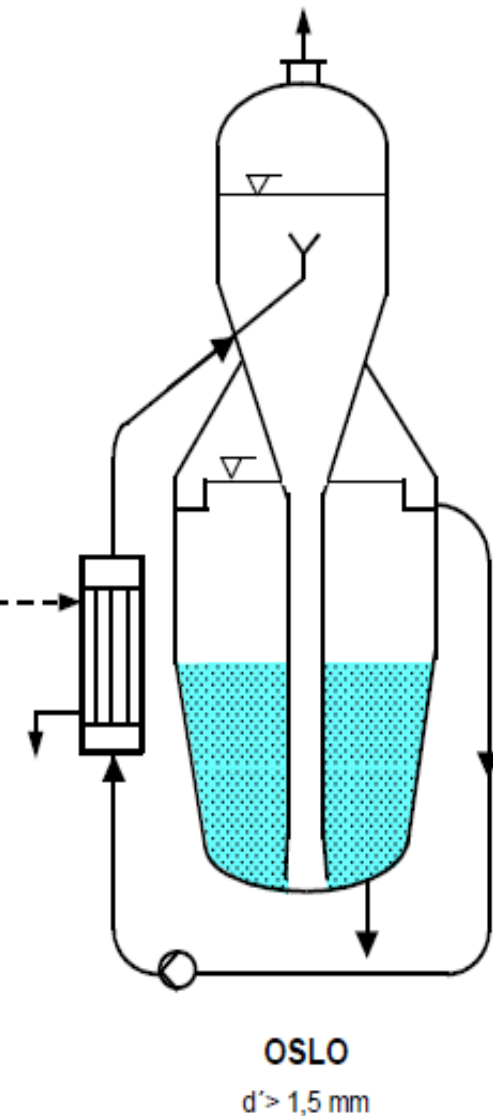


Single effect, steam heated Forced Circulation crystallizer



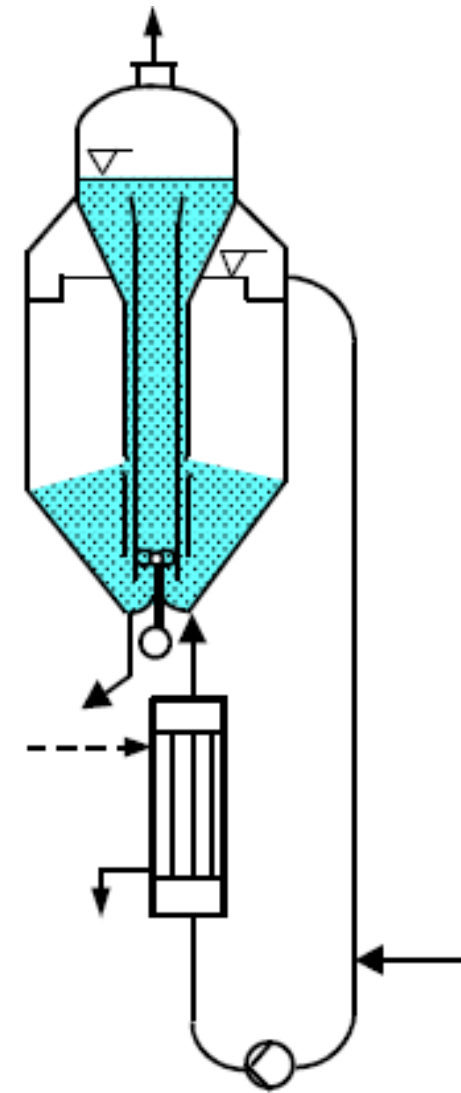
OSLO CRYSTALLIZER

- This crystallizer type originally represented the first major step in modern crystallization technology and equipment design. It was invented by F. Jeremiassen of Krystal A/S, Oslo, Norway, in 1924, and **it took the name of the city in which the design originated**. It is also referred to as "growth-", "fluid-bed-", and "Krystal-" type.
- **The primary advantage** of the OSLO crystallizer until today is **the ability to grow crystals in a fluidised bed**, which is not subject to mechanical circulation methods. A crystal in an OSLO unit will grow unhindered, to the size that its residence time in the fluid bed will allow. The result is that an **OSLO crystallizer will grow the largest crystals**, as compared to other crystallizer types.
- The slurry is removed from the crystallizer's fluidized bed and sent to typical centrifugation sections. **Clear liquor may also be purged from the crystallizer's clarification zone, if necessary.**



TURBULENCE (DTB) CRYSTALLIZER

- The Turbulence ("DTB", for Draft Tube and Baffle) crystallizer is the typical modern type of crystallizer in the industry. This crystallizer has named so because it provides for two discharge streams, one of slurry that contains the product crystals, and another, that is mother liquor (saturated solvent) with a small amount of fines. It promotes crystal growth, and can generate crystals of a larger average size than could be achieved in an FC. Most conventional Turbulence crystallizers operate under vacuum, or at slight super atmospheric pressure.
- The Turbulence (DTB) crystallizer has been studied widely in Crystallization Theory, and can be modelled with accuracy. Its distinct zones of growth and clarified mother liquor make it easy to define in terms of kinetic parameters, and thus, its growth and nucleation rate can be easily calculated. These features make the Turbulence crystallizer very suitable to mathematical description, and thus, subject to good operating control.



Turbulence (DTB)

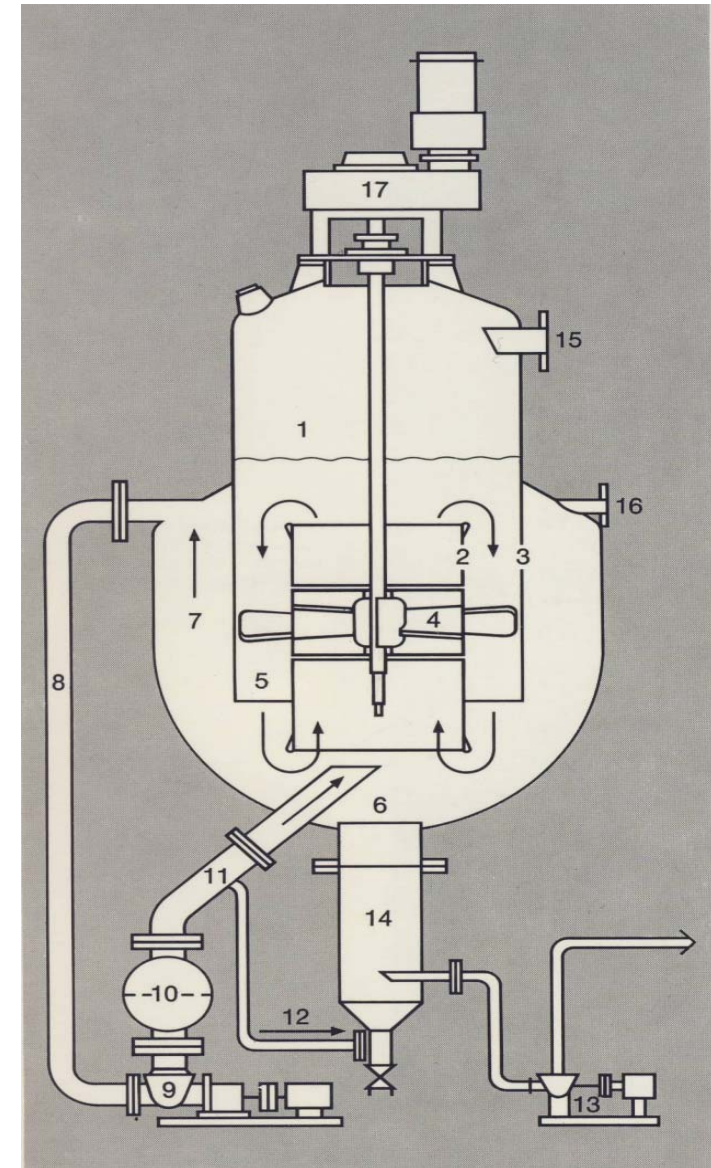
$d' = 0,5 - 1,5 \text{ mm}$

DOUBLE PIPE CRYSTALLIZER

The double pipe (DP) crystallizer is patented by Esher Wyss.

The characteristic is a double impeller which increase the circulation flow around the draft tube, so allowing to reduce the rotation speed of the impeller

- 1 Evaporation zone
- 2 Draft tube
- 7 Classification zone of fines crystals
- 10 Heat exchanger
- 13 Outlet slurry pump
- 14 Elutriation leg



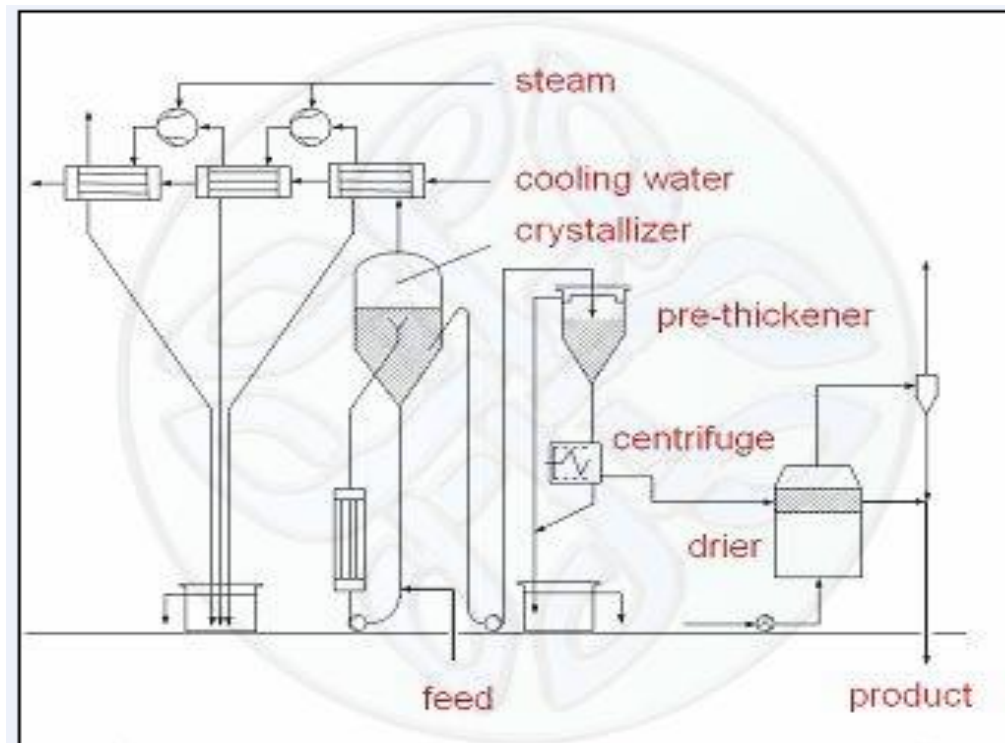
CRYSTALLIZATION DOWN STREAM PROCESSES

The suspension densities are between 15 to 25 wt.-% whereas centrifuges are operated best at 50 to 60 wt.-%. Therefore, the suspension at first is pre-concentrated in pre-thickeners or hydro cyclones.

The clear liquor overflow is recycled. Part of it always has to be taken as purge liquor for bringing out the system impurities.

The underflow is guided to the centrifuge for separation.

The final drying of the product in most of the cases is proceeded in draft-tube or vibrating fluidized-bed dryers.



MODELLING OF CRYSTALLIZERS

Modelling of crystallizers depends on the following characteristics:

- **Operation mode:**
 - Continuous (large capacity crystallizers))
 - Batch (small capacity crystallizers)
- **Fluid dynamics:**
 - Mixed Suspension Mixed Product Removal (MSMPR)
 - Crystal or fluid segregation (CFD analysis is convenient)
- **Driving force:**
 - Evaporation (under vacuum or by heating)
 - Temperature change (cooling crystallizer)
 - Reaction (production of the solute)
 - Non solvent solution (addition of a solvent where the solute is slightly soluble)
- **Seeding:** seeded or unseeded feedstream

MODELLING OF A COOLING MSMPR CRYSTALLIZER

Hypotheses:

- Constancy of liquid composition and characteristics of solid inside the crystallizer and in the outlet stream.
- Crystallization by cooling
- Possibility of presence of crystals in the feed stream

Required balance equations:

- Overall and solute mass balance
- Enthalpy balance
- Crystal population balance

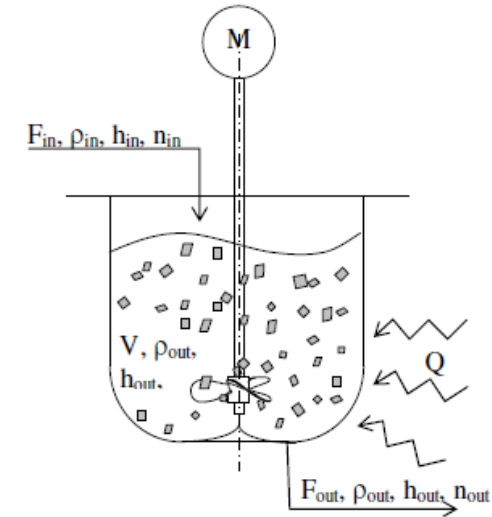
MASS BALANCES

- Overall mass balance:

$$F_{in} = F_{out}$$

- Solute mass balance

$$\frac{F_{in}}{\rho_{in}} c_F = \frac{F_{out}}{\rho_{out}} [(1 - \phi_T) c_L + m_T]$$



where, F_{in} is the mass flow rate of the feed stream, kg/h

F_{out} is the overall mass flow rate of the outlet slurry stream, kg/h

ρ_{in} , ρ_{out} and ρ_c are the density of the feed stream, slurry stream and of the crystals, respectively, kg/m³

c_F and c_L are the solute concentration in the feed stream and in the mother liquor, respectively, kg/m³

ϕ_T is the volumetric hold up of crystals

m_T is the crystal slurry density, kg/m³

ENERGY BALANCE

- The enthalpy balance can be written as follows:

$$H_F - H_S - Q_{cooling} + Q_{crystallization} = 0$$

where

$H_F = c_{pF} (T_F - T_{rif}) F$, is the heat content of the feed stream, kcal/h

$H_S = c_{pS} (T - T_{rif}) S$, is the heat content of the outlet slurry stream, kcal/l

$Q_{cooling}$ is the heat removed by the cooling system, kcal/h

$Q_{crystallization}$ is the heat of crystallization, kcal/l

POPULATION BALANCE

$$-V \frac{d(Gn)}{dL} + \frac{F_{in}}{\rho_F} \cdot n(L)_{in} - \frac{F_{out}}{\rho_S} \cdot n(L) + b(L) - d(L) = 0$$

where

V	volume of the crystallizer
G	linear growth rate, m/s
n(L)	population density of crystal of size L, #/m ⁴ =dN(L)/dL with N the number of crystals per unit volume
b(L)	birth rate density of crystals of size L due to secondary nucleation by catalytic mechanism and collision mechanism, #/m ⁴
d(L)	death rate density of crystals of size L due to breakage, #/m ⁴

POPULATION EQUATION FOR A SIMPLE CASE

In case of the following hypotheses:


- A. No crystals in the feed stream.
- B. Nucleation only by catalytic mechanism, that is $L_{\text{nuclei}} \rightarrow 0$
- C. No crystal breakage

The population balance

$$-V \frac{d(Gn)}{dL} + \frac{F_{in}}{\rho_F} \cdot n(L)_{in} - \frac{F_{out}}{\rho_S} \cdot n(L) + b(L) - d(L) = 0$$

may be simplified as follows:

$$-V \frac{d(Gn)}{dL} - \frac{F_{out}}{\rho_S} \cdot n(L) = 0$$

and rearranging 

$$-\frac{V}{Q_S} \frac{d(Gn)}{dL} - n(L) = 0$$

with Q_S the volumetric flow rate of the slurry

KINETICS DETERMINATION OF KINETICS FROM CSD

From the equation

$$-\frac{V}{Q_s} \frac{d(Gn)}{dL} - n(L) = 0$$

by defining $\tau = V/Q_s$ the crystallizer residence time

and by assuming the growth rate G independent of the crystal size, we obtain:

$$\tau \cdot G \frac{dn}{dL} + n(L) = 0$$

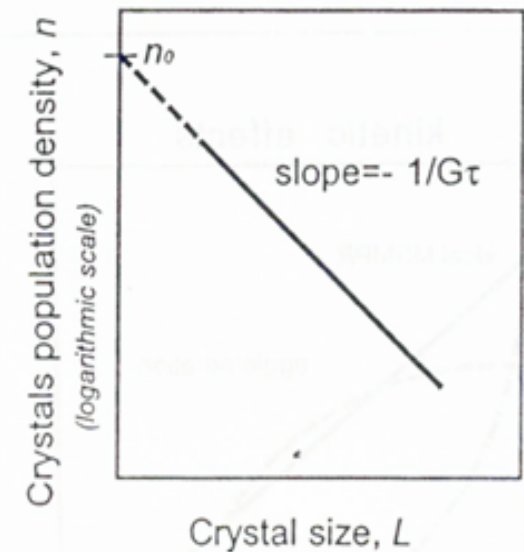
with the boundary limit: for $L=0$ $n(L) = n_0$

by integrating

$$n = n_0 \cdot e^{-\frac{L}{\tau \cdot G}}$$

By plotting $\ln n(L)$ vs L we have a linear relationship with a slope equal to $-1/G\tau$ and intercept equal to n_0

we remind that $n_0 = B_0/G$



$$M_T = \rho_S k_V M_3 = 6 \rho_S k_V n_0 (G \tau)^4$$

$$L_d = \frac{M_4}{M_3} = 3 (G \tau)^3; \quad L_a = 3.67 (G \tau)$$

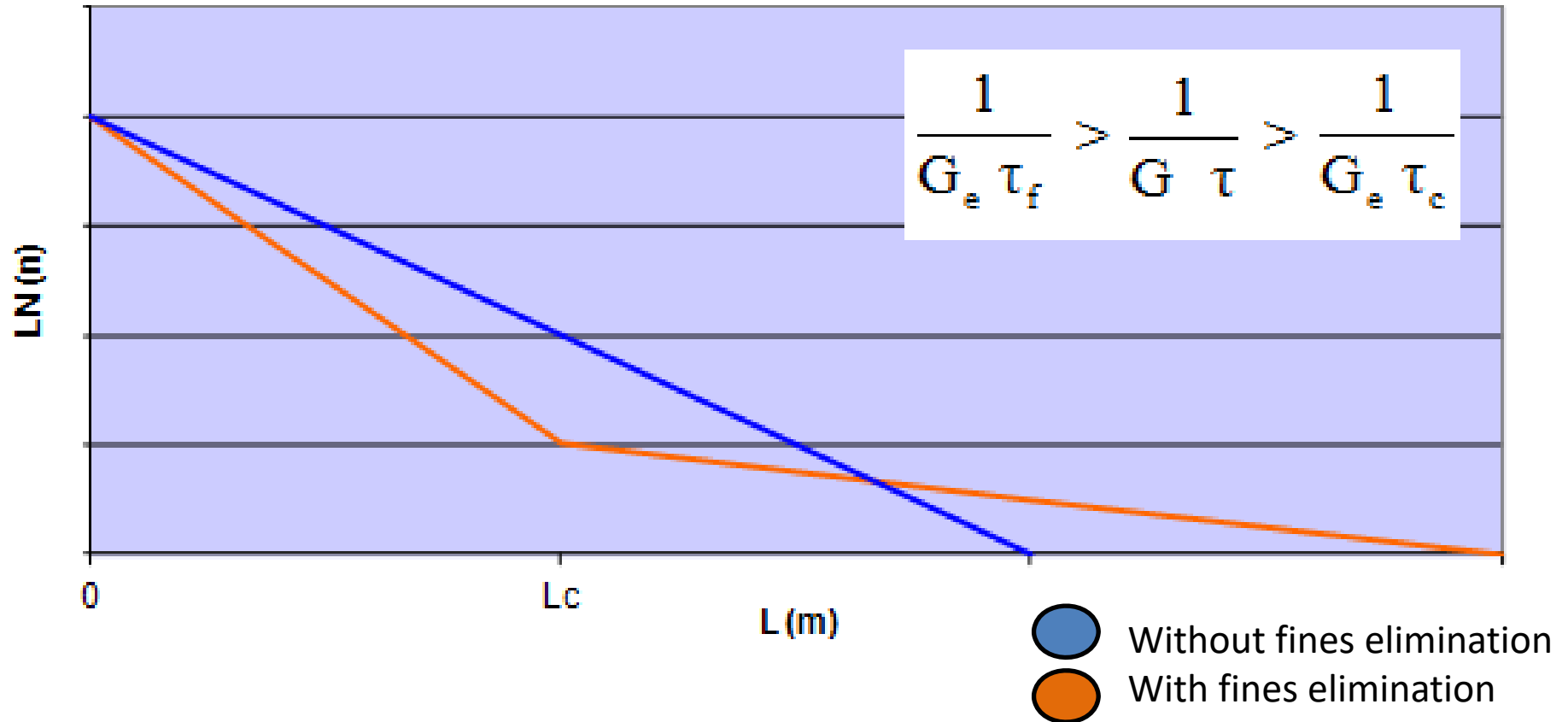
50% della distribuzione granulometrica
cumulativa

dimensione media ponderale

$$h_V = \frac{B_0}{M_3} = \frac{1}{6 G^4 \tau}$$

$$L_a = 3.67 \sqrt[4]{\frac{G}{6 h_V}}$$

WITH FINES ELIMINATION



$$G_e V_c \frac{dn}{dL} + (F_{out} + F_f) n = 0 ; L \leq L_c$$

$$G_e V_c \frac{dn}{dL} + F_{out} n = 0 ; L > L_c$$



$$n = n_0 \text{EXP} \left(- \frac{L}{G_e \tau_f} \right) ; L \leq L_c$$

$$n = n_0 \text{EXP} \left[- \frac{L_f}{G_e \tau_f} - \frac{1}{G_e \tau_c} (L - L_f) \right] ; L > L_c$$